A COMPUTER SIMULATION OF THE TRACE METAL SPECIATION IN SEAWATER

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ABSTRACT

The primary objective of this study was to develop a computer model of the speciation of the components present in seawater. The influence of pH, redox state, dissolved organic matter and adsorption processes on this speciation was to be investigated.

Before any modelling could be done, the components of seawater needed to be found and their concentrations decided upon. An extensive literature search was undertaken to obtain concentrations of both the major and minor components of seawater. The major components were observed to have relatively constant concentrations while the concentrations of trace components were found to be highly variable.

After the collation of component concentration, an extensive database of all the stability constants for the species that result from all possible interactions between the inorganic components of seawater at 25°C was compiled. These stability constants were corrected to an ionic strength of 0.7 mol dm^{-3} using an extended form of the Debye-Hückel equation. Constants for the formation of mixed halide species and hydroxycarbonates were included in the database. The actual speciation calculations were performed using the FORTRAN program MINTEQA2 [All90].

The speciation results showed that the dominant ligands for metal speciation in seawater were chloride, hydroxide, carbonate and to a much smaller extent sulphate. The ligands bromide, fluoride, iodide, iodate, borate, silicate, chromate, phosphate and nitrate were insignificant although bromide was observed in mixed bromochloride species of Ag^{+} and Hg^{2+}. Because chloride association with the major cations was ignored, the major cations were primarily uncomplexed. Hydroxide species dominated the speciation of the trace metals: Fe^{3+}, Al^{3+}, Cr^{3+}, Sn^{2+} and Hg_2^{2+} at a pH of 8.1. Chloride species were important for Cu^{+}, Ag^{+}, Cd^{2+} and Hg^{2+} while carbonate dominated the speciation

patterns of Cu^{2+}, UO_2^{2+} and Pb^{2+}. Dissolved Zn^{2+}, Ni^{2+}, Mn^{2+}, Fe^{2+} and Co^{2+} were found primarily as the uncomplexed aqua ion.

pH affected the speciation patterns of some of the trace metals but not others. The metals that were dominated by chloride species were unaffected by varying pH. Allowing atmospheric carbon dioxide to dissolve, changed the dissolved carbonate concentration. This was especially noticeable at high pH where the concentration of dissolved carbonate increased dramatically. The speciation of the carbonate dominated metals, those present mainly as aqua ions and cadmium(II) were affected significantly at high pH by whether carbon dioxide was allowed to dissolve or not. The redox state of the ocean proved insignificant for the redox state distribution of all trace metals except manganese. The concentration of a trace metal (in the picomolar to micromolar range) was unimportant to its speciation except to those metals that precipitated (iron, manganese and aluminium).

The model developed investigated the influence of dissolved organic matter on trace metal speciation. It was decided to use marine fulvic acid as representative of marine organic matter that complexes trace metals. A literature search was performed to investigate the characteristics of marine fulvic acid. These included elemental composition, spectroscopic behaviour and functional group concentrations. Another important characteristic investigated was experimental reports of the complexation of trace metals by marine organic matter. The correlation between these experimental results and the speciation predicted by the model developed, would lend credence to the model.

In order to model the influence of marine organic matter, a model had to be developed which would represent the complexation of trace metals by these substances. The FORTRAN program RANDOM [Mur81] was used as a basis for modelling organic

complexation. This model is a statistical model which determines how often one might expect functional groups in dissolved organic matter to occur in close proximity to each other to form bi- or tridentate chelating sites. The model thus provides estimates of binding site concentrations as well as a measure of the binding strength of those sites (from the site type identification). Because marine organic matter has different functional group characteristics (most notably a higher nitrogen content when compared to the soil fulvic acids for which RANDOM was originally developed), it was decided to extend the concept of RANDOM to include binding to nitrogen and sulphur-containing binding sites.

RANDOM was rewritten in TURBO-PASCAL. New features included in this version are a user-friendly data input system, the ability to run on a personal computer, the generation of more structures than the original program and the inclusion of nitrogen and sulphur as aliphatic amine and thiol groups. The RANDOM concept was validated for the protonation and binding of copper by Suwannee River fulvic acid. Unfortunately the binding to nitrogen could not be validated as the sample used was low in nitrogen. An attempt was made to extract fulvic acid from seawater but the samples extracted were highly contaminated with calcium and silicon. They also exhibited abnormally high nitrogen concentrations.

Four models of marine fulvic acid were developed: one included binding to nitrogen and sulphur-containing sites, another excluded binding to sulphur-containing sites, the third had no sulphur and a lower nitrogen content while the last contained binding only to oxygen-containing sites. The first model predicted that copper is highly bound by dissolved organic matter in seawater at natural concentration levels which is in agreement with experiment. The binding of copper is predicted to be to nitrogen-containing sites. Sulphur-containing binding sites were responsible for the binding of lead, cadmium, zinc, nickel, silver and to a lesser extent cobalt at natural organic levels.

When sulphur was excluded, only copper and nickel were observed to be bound at natural levels. Solely oxygen-containing ligands were able to bind trace metals only at high organic concentrations. In this case these sites were found to be important for copper(II), nickel(II), cobalt(II), iron(II), iron(III), manganese(II), aluminium(III) and zinc(II). The model thus predicts that the binding to oxygen-containing sites alone is unable to explain observed experimental complexation of trace metals in the marine environment and that binding to nitrogen and sulphur functionalities needs to be considered.

Adsorption processes were modelled by using hydrous ferric oxide as a model suspended solid. At low concentrations of solid particles, lead(II) and chromium(III) are significantly adsorbed. At higher concentrations of solid, adsorption affects the speciation of zinc(II), nickel(II), cobalt(II), manganese(II), tin(II) and copper(II). The anions: silicate, phosphate and chromate are strongly adsorbed. The adsorption of dissolved organic matter onto solid particles was also considered. The adsorption of this matter lowered the adsorption of trace metals by blocking surface binding sites. The adsorption of anions was drastically reduced because of the negative charge generated on the solid surface.

The model was extended to study the chemical processes that occur in the estuarine region of rivers. This involved setting up a generalized model of river freshwater. A literature search was performed to discover the expected concentrations of the components of river water. The components of river water were then mixed conservatively with those of seawater to provide 6 intermediate steps between the extreme ionic strengths. For the river end and the intermediates, thermodynamic databases of stability constants were set up using the same method used in setting up the seawater database. The mixing model took into account the binding of trace metals to

organic matter (represented by fulvic acid) and the effect of adsorption processes (as modelled by hydrous ferric oxide).

It was discovered that trace metals were highly adsorbed by solid particles in solid-rich river waters. On entering the sea these metals were desorbed rapidly (in the ionic strength range 0.1-0.2 mol dm^{-3}). The primary reason for this rapid desorption was the competitive adsorption of the cations, magnesium and calcium (which have high concentrations in seawater), onto solid particles. As the rivers progressed further into the sea, further desorption was brought about by the complexation of trace metals by components present in seawater. This was especially true for cadmium and mercury (which are dominated by chloride species) and copper (bound by organic matter) which showed a significant decrease in their free ion concentrations.

The model, which includes adsorption onto HFO and fulvic acid modelled by nitrogen and sulphur containg amino acids and amines, thus predicts the complexation of trace metals (especially copper) by dissolved organic matter and adsorption of trace metals (especially lead and chromium (III)) by solid particles to be important chemical processes occurring in seawater.

CONTENTS

ABBREVIATIONS

{}	activity
β_i	formation constant of species i
γ_i	activity coefficient of ion i
ΔG_m^θ	standard molar Gibb's free energy
ΔH_m^θ	standard molar enthalpy
τ	surface charge density
Ψ	surface potential
Γ	sorption density
θ	degree of metal loading
σ	surface charge
12BQ	1,2-benzoquinone, RANDOM ligand number 1
a_H	activity of the free hydrogen ion
$\mathring{a}_i$	ionic size parameter of ion i
a(i,j)	stoichiometric coefficient of component j in complex i
A,B	constants characteristic of the solution used in the Debye-Hückel equation
ACAC	acetylacetone, RANDOM ligand number 9
ACPH	2-acetylphenol, RANDOM ligand number 6
ads	adsorption
AET	2-aminoethanethiol, RANDOM ligand number 33
ALA	alanine, RANDOM ligand number 24
ASP	aspartic acid, RANDOM ligand number 21
ASV	anodic stripping voltammetry
BEAL	β-alanine, RANDOM ligand number 25
BENZ	benzoic acid, RANDOM ligand number 7
c	adjustable parameter used in the Debye-Hückel equation
C_i	concentration of species i

calc	calculated
CAT	catechol, RANDOM ligand number 3
CIT	citric acid, RANDOM ligand number 17
-COOH	carboxyl group
coul	coulombic
CYS	cysteine, RANDOM ligand number 30
DAP	2,3-diaminopropanoic acid, RANDOM ligand number 20
DEM	diethylmalonic acid, RANDOM ligand number 13
DHMB	2,3-dihydroxy-2-methylbutanoic acid, RANDOM ligand number 11
DOC	dissolved organic carbon
DOM	dissolved organic matter
DON	dissolved organic nitrogen
DPASV	differential pulse anodic stripping voltammetry
DPP	differential pulse polarography
E^{θ}	standard electrode potential
E_h	potential relative to the hydrogen half cell reaction
EDTA	ethylenediaminetetra-acetic acid
E(J)	liquid junction potential
ETA	ethanolamine, RANDOM ligand number 27
E(S),E(X)	cell potential differences in pH measurements
exp	experimental
F	Faraday constant
FA	fulvic acid
g	(R/F)ln 10
HBQ	3-hydroxy-1,4-benzoquinone, RANDOM ligand number 2
HBT	3-hydroxybutanoic acid, RANDOM ligand number 13
HMP	2-hydroxy-2-methylpropanoic acid, RANDOM ligand number 15
HFO	hydrous ferric oxide

I	ionic strength
int	intrinsic
ISER	isoserine, RANDOM ligand number 23
K	stability constant
K_m	mixing constant
K_s	stabilization constant
K_{sp}	solubility product
L_i	organic binding site concentration
L_T	total ligand concentration
[M]	free metal concentration
$[M]_b$	concentration of bound metal
$[M]_T$	total metal concentration
m_H	free hydrogen ion molality
m_H^θ	sum of the free and complexed hydrogen molalities in seawater
m_{SO4}	free sulphate molality
MAL	malic acid,, RANDOM ligand number 10
MET	2-mercaptoethanol, RANDOM ligand number 34
N_{exp}	experimental formation function
(nci)	"n combination i" = n!/[(n-i)!i!]
$-NH_2$	amine group
NTA	nitrilotriacetic acid
-OH	hydroxyl group
pH(SWS)	pH on the seawater scale
PHEN	phenol, RANDOM ligand number 8
PHTH	phthalic acid, RANDOM ligand number 4
pM	-log[M]
PN	1,2-propylenediamine, RANDOM ligand number 26
PROP	propanoic acid, RANDOM ligand number 16

PUFAs	polyunsaturated fatty acids
Q	quotient of activity coefficients
R	universal gas constant
R_H	Hamilton statistical factor
S	standard buffer solution used during pH measurements on the IUPAC scale
SAL	salicylic acid, RANDOM ligand number 5
SER	serine, RANDOM ligand number 22
-SH	thiol group
SSA	sulfosalicylic acid
SUCC	succinic acid, RANDOM ligand number 12
T	temperature
T_j	analytical total concentration of component j
T_{FA}	total concentration of fulvic acid
T_H	total concentration of protons
TIPP	represents the model component for organic matter adsorbed onto HFO
TMA	thiomalic acid, RANDOM ligand number 31
TLA	thiolactic acid, RANDOM ligand number 32
TPP	tripolyphosphate
Tris	2-amino-2-hydroxy-1,3-propanediol
UCT	University of Cape Town
X	sample whose pH is being measured using the IUPAC scale
X_j	free concentration of component j
Y_j	optimization function for MINTEQA2
z_i	charge on ion i
Z_H	the average number of protons bound to a ligand

CHAPTER ONE

GENERAL INTRODUCTION

1.1 THE OCEAN

The ocean is an inescapable part of the everyday life of this planet. The effect of the sea can be felt in even the remotest desert where the functioning of this great water reservoir can be seen to influence weather patterns. The ocean is directly involved in the major chemical, geological and biological processes that are responsible for the proper functioning of the earth.

D.W. Hood has described it as *an enormous flywheel that controls climate, regulates the amount of carbon dioxide, oxygen and other gases, transports sediments as part of the major geological cycle, acts as a major reservoir of non-renewable resources and provides a significant portion of the food for terrestrial life forms* [Hoo71].

The ocean is, however, not free from the influence of man despite its immense size and power. Scientists first recognized that human activities could pollute the marine environment about forty years ago when concern arose regarding the release of radioactivity into the ocean from nuclear power stations [Gol92]. More recent ecological disasters such as those at Minimata Bay in Japan and Chartung in Taiwan have highlighted the effect of chemical pollution on the sea and ultimately man [Gol92].

It is thus imperative to predict the potential influence of human activity before such activity has a detrimental effect on the marine environment. In order to do this a thorough understanding of marine processes is necessary. These include the relationship between the ocean and the other major resources of this planet: the air, the sediments and igneous rock [Sil67a, Sil67b]. The first attempt at establishing such a geochemical balance was made by Goldschmidt [Gol33] in 1933 to show how the ocean was formed by the reaction of crustal igneous rock with primary magmatic volatiles (including H_2O, CO_2, HCl, H_2S, N_2, B, Br_2 and I_2). Several other investigators have subsequently

proposed similar theories on the geochemical history of seawater [Rub51, Gol54, Hor65, Gar71, Li72].

Most of the 92 naturally occurring elements have been measured or detected in seawater [Bea89]. The interactions of these components with each other need to be studied. Seawater contains numerous cations and ligands which interact to form a whole host of dissolved complexes and precipitates. Amongst the ligands are various inorganic ligands such as chloride, hydroxide, carbonate and sulphate. Furthermore, metals are also bound by a wide range of humic (e.g. fulvic acids) and other organic substances [Reu77, Per78, Man81, Thu85]. All these components interact with the surfaces of suspended solid particles and sediments [Li81, Dav84, Dzo90]. In addition, metals may be assimilated by living organisms [Mur88, Bea89]. Thus each individual component may exist in a variety of physico-chemical forms. A determination of the identities and concentrations of these forms is commonly termed **speciation.**

Metal ions are vital to the proper functioning of oceanic processes. They act either as essential nutrients or as toxins for the biota that inhabit the earth's seas. Bioavailability and biotoxicity depend not only on the total concentration but more significantly on the speciation of the metals present in the ocean [Luo79, Mag79, Whi79, Flo82]. More specifically the availability of metals to marine organisms is usually determined by free metal ion activity [Sun76, And77, And78, Jac78, Sun78].

Copper concentrations in seawater at natural levels have long been known to be very poisonous to algal photosynthesis [Ste70]. It has been shown that the toxicity of a metal to phytoplankton may be significantly lowered by chelation [Sun76, And78, Mor83a]. Indications are that this is the result of a lowering of the concentration of the free metal ion which is thought to be the most toxic species. By increasing cupric ion activity Sunda and Guillard [Sun76] and Anderson and Morel [And78] have demonstrated that

the growth rate of marine organisms may be reduced. The toxicity of Cu^{2+} has been demonstrated not only for microorganisms but also for more complex creatures such as the bilharzia snail, *Biomphalaria glabrata* [OSu89]. Studies have revealed that the important toxic forms are Cu^{2+} and $CuOH^{+}$ whereas copper carbonates are non-toxic [All92]. Thus information about total copper concentration alone cannot be used to predict toxicity. Knowledge of the chemical forms, i.e. speciation, is necessary.

This has also been demonstrated for other metals such as zinc [Mor83b]. The competitive effects of other metals with copper has also been shown to be important [Sun79, Sun81a]. Studies also reveal that metal deficiencies can be induced in organisms by lowering bioavailability through chelation with ligands such as EDTA [Sun76]. As a consequence of these studies techniques have been developed to use the organism as sensors for determining bioavailability [Wan91].

Recently (November 1993) experiments were performed in the Pacific Ocean to see if pumping iron into the sea, could induce phytoplankton growth [Wel94]. Increased growth was observed but not as great as was expected from laboratory experiments. This may be attributed to various factors: biological, physical and chemical. One of the proposals [Morel in Wel94] was that adsorption of essential trace metals onto sinking iron oxides could have occurred and thus limited phytoplankton growth. However, without knowledge of the chemical processes occurring such hypotheses will remain speculation. This is one example where chemical speciation analysis could help provide insight into real problems which are not confined to the domain of the chemist alone.

A thorough knowledge of the metal speciation in the ocean would thus be important for the sake of chemistry itself, for geochemical understanding of the composition of the ocean and for biological reasons [Dyr74, Stu81, Whi81, Buf88, Li91]. The increasing importance of speciation is reflected by the reviews of water, sediment and soil quality

criteria that are being done in the United States [All92]. This is especially true of cadmium(II), lead(II) and copper(II) which are the principal metals for which speciation is important when considering biotoxicity [All92]. No longer is knowledge of the total concentration deemed solely necessary but other factors (pH, chelating ligand concentration i.e. speciation), that may impact on a metal's behaviour with biota, need also to be considered.

A problem arises when the speciation of metal ions in the sea is to be determined experimentally. Although metal speciation can be reliably determined experimentally in single metal - single ligand systems, the multi-component marine environment precludes the determination of reliable experimental speciation data. Several problems complicate matters:

1. The number of species that occur in the ocean is very large which would make the separation and determination of these species formidable.

2. Trace metals are present at very low concentrations. These are typically in the picomolar to nanomolar range. It is only recently that reliable techniques have been developed to provide reliable total concentration data.

3. The concentrations of individual species are by implication even lower. For reliable concentration values to be determined these species need first to be separated. This step is at present beyond the scope of available analytical techniques.

4. Those techniques which have been developed to study equilibrium systems are prone to disturb the system being studied. Even in circumstances which would

permit determinations of individual species concentrations, there would be the risk of disturbing the equilibria being investigated.

5. The interpretation of measurements may be misleading. Anodic stripping voltammetry is often used for speciation analysis. However, problems are encountered when differentiating between labile and inert metal species. At a hanging drop electrode, copper is labile in the presence of nitrilotriacetic acid (NTA) whereas at a mercury film electrode it is relatively inert under the same conditions [Mor89].

Those techniques which have been developed enable some discrimination between metal species. In general they allow the classification into large groups which have similar chemical properties. The problem of individual species remains intractable. The most common techniques include anodic stripping voltammetry, ion exchange chromatography, ultrafiltration, dialysis and bioassay. Although considerable progress has been made experimentally, the state of the art does not yet allow a completely detailed speciation of seawater to be determined [Lun90].

This has led to the use of computer modelling for the study of complicated multiphase, multicomponent systems such as seawater. The real system is replaced by a simplified model system and conclusions are drawn by analogy [Jen79]. Equilibrium modelling by computer simulation provides an attractive approach for estimating the concentrations of a great number of species (dissolved, precipitated, adsorbed) for a range of metal ions, since it is presently capable of providing more detailed speciation patterns than experimental techniques are.

1.2 MODELLING

Chemical modelling of the ocean dates back to the early 1960s. Sillén [Sil61] and Garrels and Thompson [Gar62] published some of the earliest work in the field.

The use of equilibrium modelling is the first approximation that has to be introduced to obtain results. The real situation is far more complex and must include the kinetics of the marine biological, physical and chemical processes which affect speciation. The equilibrium model represents the boundary condition to which the ocean must be progressing, albeit at an extremely slow rate [Stu81].

As a consequence of his belief that the geochemical balance proposed by Goldschmidt [Gol54] required a remarkable acid-base balance which was an unlikely situation, Sillén compared the real air-sea-sediment system with a model system at equilibrium. He proposed that both the pH and main ionic concentrations of seawater were determined by heterogeneous equilibrium with alumino-silicates. This concept could account for the constancy of pH and ocean composition that is observed.

Recent thinking is that the composition of natural waters is governed by the balance between the rate of addition of dissolved components and their rate of removal which results in a steady-state condition. Two such models are those of McDuff and Morel [McD80] and Whitfield and Turner [Whi83]. Whereas this is more likely to be the case than equilibrium control, equilibrium modelling continues to be widely regarded as a useful technique [Mel90]. In view of the complexity of marine systems, equilibrium modelling offers much in the way of simplicity [Mur88].

The model of Garrels and Thompson [Gar62] (first proposed in 1962) was the first to quantitatively describe the speciation of the eight major components in seawater (K, Na, Ca, Mg, Cl^-, HCO_3^-, CO_3^{2-} and SO_4^{2-}).

As the work was performed without the aid of a computer, several assumptions were made. Chloride was assumed not to form ion pairs with the major cations in seawater. Free activity coefficients were calculated from the MacInnes convention and were assumed to be functions of total ionic strength. Activities of charged ion pairs and those of neutral species were set equal to the activities of the bicarbonate anion and carbonic acid respectively.

These assumptions have been questioned by a number of authors. Johnson and Pytkowicz [Joh78, Joh79] have shown that chloride ion pairing does occur in seawater which means that the effective ionic strength is not 0.69 mol dm^{-3} but 0.53 mol dm^{-3}. Furthermore the assumptions regarding the calculation of activity coefficients have also been reviewed [Kes69, Kes75, Pyt79]. It is, nevertheless, important to note that Garrels and Thompson succeeded in setting up a model which has become the basis for subsequent work [Ski65]. This seminal paper has been described as a *Citation Classic*, that is a paper cited far more frequently than other papers in the same field [Tho92].

Like most other models, the work of Garrels and Thompson was based upon the Bjerrum ion association theory of ion pair formation [Bal79] although some models such as that of Whitfield [Whi73] have been based on the Bronsted-Guggenheim hypothesis of specific site interaction [Gug35, Mil92]. The results of both approaches tend to be in agreement with each other. In fact the approaches are complementary and can be very powerful when used together [Whi75a, Whi75b, Mil92].

The extension of speciation calculations to trace element constituents soon followed. This was first performed by Zirino and Yamamoto [Zir72] and Dyrssen and Wedborg [Dyr74]. The formation of precipitates, mixed ligand species as well as chloride ion pairing was ignored. Furthermore the interaction of marine organic matter was not considered.

The advent of high speed computers has led to the development of more comprehensive models [Mor72, Tur81, Mil82, Ahr85, Mot87, Mil90, Mil92]. However, the effect of naturally occurring organic ligands has been ignored except that the treatment of Turner et al. [Tur81] included metal-humic binding constants which were estimated or obtained from the measurements made by Mantoura et al. [Man78]. All these models required the compilation of thermodynamic databases, relevant to the ionic strength (0.7 mol dm^{-3}) of seawater.

Particularly impressive is the work of Motekaitis and Martell [Mot87] whose database has been compiled over the course of two to three decades. Their model consisted of 167 complexes which arose from the interaction of 19 components. They used critical stability constants which were adjusted to 0.7 mol dm^{-3} using an empirical technique based on experimentally observed variations of stability constants with ionic strength for complexes of similar charge type [Smi85, Mar85]. They made no detailed attempt to model naturally occurring marine organic matter, although did investigate the effect of EDTA (ethylenediaminetetra-acetate), NTA (nitrilotriacetate), TPP (tripolyphosphate), citrate and SSA (sulfosalicylate) to model the effect of chelating agents that might be introduced through environmental pollution. These authors ignored the formation of mixed ligand complexes and chloride ion pairs although the influence of precipitation was accounted for.

More recently, Byrne et al. [Byr88] have investigated the influence of pH and temperature on the trace metal speciation in seawater. In many cases stability constants were set equal

CHAPTER TWO

THE MODEL

to constants measured at 0.5 or 1.0 mol dm^{-3}, based on the observation that activity coefficients are relatively constant between these two ionic strengths. Carbonate complexation equilibria were described using formation constants expressed in terms of total carbonate ion concentration [Byr85, Can87]. These authors also list the reaction enthalpies used for temperature correction. No precipitation, mixed ligand species or metal-organic interactions were considered.

Millero and Hawke [Mil92] have investigated the speciation of divalent metals in seawater. Activity coefficients were calculated using the Pitzer equation [Pit73]. Equations representing the dependence of stability constants on ionic strength were developed. Again, no attempt was made to model the effect of marine organic matter. Furthermore this study was limited to divalent metals.

Work was carried out at the University of Cape Town by Karen van der Meulen [VdM90]. The thermodynamic database of Motekaitis and Martell [Mot87] was extended to include other ligands and metals. Certain of the constants were updated. Also considered were redox equilibria and the formation of mixed ligand complexes. The effect of marine organic matter on trace metal speciation was modelled using suitable model ligands such as acetylacetone, propanoic acid and salicylic acid.

It is upon this last study that the present research is based. The need for a more comprehensive fulvic acid model was apparent; this was the result of the particularly high nitrogen content of marine organic matter which was not previously included. The need for the inclusion of adsorption was also evident since it is thought that this is a dominant control mechanism in the ocean [Dzo90]. Although the formation constants for aqueous complexes have been tabulated and critically reviewed [Mar74a, Bae76, Smi75, Smi76, Mar77, Smi82, Smi89], constants for the adsorption of inorganic components onto solid surfaces are scattered through the literature and few critical compilations exist. One

exception is the work of Dzombak and Morel [Dzo90]. These two authors reviewed the literature and compiled a database of thermodynamic constants for adsorption onto hydrous ferric oxide. They use the double layer model of specific site adsorption [Stu76]. Constants are reported at infinite dilution. It was decided to use hydrous ferric oxide as a model for adsorption onto solids as the constants have been critically reviewed and the database is the most extensive available since it covers the interactions of almost all the inorganic components present in natural waters.

Doubts are often cast upon the validity of the chemical modelling approach. However, it is not the aim of a model to represent reality fully as the model could then no longer be classified a model. A model is an analytical technique that provides further insight into the chemical processes of dissolution, precipitation, oxidation, reduction and adsorption [Mor72]. It must be borne in mind that at present equilibrium modelling is capable of providing more information about marine chemical processes than experimental techniques are. Reaction kinetics have not yet been successfully incorporated into speciation to any significant degree [Mot87, Mel90]. Improvements will see the inclusion of such kinetic effects.

It is hoped that the use of a model may answer certain questions which present analytical techniques are incapable of answering. A model may also point the direction in which experimental work should proceed i.e. which species should be sought in a particular determination and which are insignificant. If the model can provide answers to questions and direct research then it has served a valuable purpose.

1.3 OBJECTIVES

> *The ultimate goal of research in support of chemical modelling, as in most scientific research, is the improvement of human life, physically, emotionally and aesthetically through the understanding and prediction of processes and events. More immediate objectives include reliable speciation of trace elements, the objective (of which) is to predict toxicity and bioaccumulation in aquatic organisms and ultimately in man* [Jen79].

It is thus envisaged that an extension of the seawater models developed so far would make a significant contribution to the understanding of marine processes.

The objectives of this study are the following :

1. To construct an equilibrium model of the species relevant to seawater and to obtain reliable estimates of their concentrations.

2. To ascertain the total concentrations of all the relevant components of seawater by reviewing the literature.

3. To assemble a reliable thermodynamic database of the possible complexation, redox and precipitation constants for all the possible species that result from the interactions of the components of seawater.

4. To predict:
    i. speciation of the major metal ions in seawater: Na^+, K^+, Li^+, Ca^{2+}, Mg^{2+} and Sr^{2+}.

ii. the inorganic speciation of all biologically important trace metals such as copper, zinc and iron.

iii. the inorganic speciation of toxic heavy metals such as lead, cadmium and mercury.

5. To develop a model for the naturally occurring organic matter by using fulvic acids as representative of dissolved organic matter. Particular emphasis would be placed on the nitrogen content of these acids.

6. To investigate the effect of the aforementioned organic ligands on the inorganic speciation patterns.

7. To extend the model to include adsorption on to solid particulate matter in the ocean with hydrous ferric oxide as model solid. To observe the resultant effects on the speciation patterns.

8. To investigate the change brought about on speciation by the merging of a freshwater stream with the ocean. To this end, to compile critical thermodynamic databases at intermediate ionic strengths between 0 and 0.7 mol dm^{-3}.

9. Where possible, to correlate results obtained with experimental results reported in the literature.

CHAPTER TWO

THE MODEL

2.1 INTRODUCTION

Most of the seawater speciation models that have been developed are based upon the Bjerrum ion association theory [Bal79, Mil92]. There are two approaches that may be employed to solve the problem of metal speciation within this framework. These are the Gibb's free energy approach and the equilibrium constant approach.

The Gibb's free energy approach, first proposed by Dantzig and his co-workers [Whi58], involves minimizing the free energy function

$$\Delta G_m^{\theta} = -RT\ln K \qquad 2.1$$

for a given set of species, subject to the mass action requirements [Whi58].

The equilibrium constant approach, proposed by Brinkley [Bri47], is probably the most widely used method in the field. The mass balance expressions are substituted into the mass balance conditions. The result is a set of non-linear equations which are solved simultaneously by an iterative procedure. This approach is generally preferable since the published equilibrium constants are both more numerous and generally more reliable than the published free energy values [Nor79].

Various computer programs have been developed to solve the mathematical problems that arise when doing chemical speciation modelling. These include HALTAFALL [Ing67] which was used by Turner et al. [Tur81], COMICS [Per67], PSEUDOPLOT [Elg69] and ECCLES [May76]. The FORTRAN program MINEQL [Wes76] has been widely used for speciation calculations and was used by Motekaitis and Martell [Mot87]. MINEQL was also used by Karen van der Meulen [VdM90] for the study upon which this work is based.

It was decided to use the FORTRAN program MINTEQA2 [All90] for the present speciation calculations since it incorporates all the features of MINEQL but is more powerful and in particular is able to solve adsorption calculations. This ability is of particular importance when one considers Objective 7 of this study. Furthermore, MINTEQA2 is user-friendly and flexible.

Once again, it must be stressed that a model cannot represent reality fully. This is the result of the complexity of the real system. Furthermore for the model to be of any use, it must be a simplification which highlights important processes. If it contained all possible reaction processes it would be too complicated for any meaningful conclusions to be drawn from it. The result would be that little new understanding would be generated and the model would have failed in its primary aim.

2.1.1 THE ASSUMPTION OF NO CHLORIDE ION PAIRING WITH THE MAJOR CATIONS

Before the setting up of the model can be discussed, one of the fundamental assumptions: that of no chloride ion pairing with the major cations needs to be discussed. In the model of this thesis ion pairs that form between chloride ions and the major cations (sodium, lithium, potassium, magnesium, calcium, strontium and barium) have been ignored. The primary reason for this exclusion is that it simplifies the modelling. However, all results should be viewed with this exclusion in mind.

Seawater models that have been developed so far [Gar62, Whi81, Mot87, Byr88], do not include chloride ion pairing. However, because of the high chloride concentration in seawater, it has been concluded that chloride ion pairs with the major cations might be significant [Kes75a]. The constants that have been determined [Kes69, Joh78, Maj82,

Byr84] are small but would still indicate that a significant amount of the major cations would be bound by chloride at high chloride concentrations.

Preliminary calculations with constants for major cation-chloride ion pairing taken from Johnson and Pytkowicz [Joh79b] resulted in a reduction of the overall ionic strength. This has the following implications. Constants used in the model have been corrected to an ionic strength of 0.7 mol dm^{-3}. Including chloride ion pairing would mean that these constants would have to be adjusted to a lower ionic strength. However, the change in the formation constants brought about by lowering the ionic strength to 0.5 mol dm^{-3} is small (cf. the constants in Appendix 1.2). This would have a slight effect on the speciation patterns of trace metals.

More significantly the free concentration of the chloride ion would drop. As a consequence the amount of binding of trace metals to chloride ions would decrease in sympathy. Only those species which form significant chloride species would be affected. Higher order chloride species would also decrease in significance relative to other chloride species. A third and minor effect is that less of the other major anions would be bound by the major cations. The free concentrations of ligands such as sulphate and carbonate would increase and thereby allow for more binding of the trace metals.

Bromide and iodide ion pairing with the major cations was ignored in the model for similar reasons to chloride ion pairing. However, the impact of this exclusion is less significant because of the lower concentrations of these ligands. Note that fluoride ion pairing was included in the model.

As Millero and Schreiber [Mil82] point out the small improvement brought about by including chloride ion pairing, does not make the extra work worthwhile. This is because the uncertainty in the formation constants causes a much greater uncertainty in the

speciation results than the exclusion of chloride ion pairing. Whitfield and Turner [Whi81] also point out that the published constants for chloro-complex formation with trace metals do not take into account chloride ion pair formation with the major cations. Furthermore the models that have been developed for seawater are at an ionic strength of 0.7 mol dm^{-3} with no chloride ion pairing. Thus the exclusion of chloride ion pairing is justified so as to allow comparisons to be made between models. The inclusion of chloride ion pairing will not significantly affect conclusions about which ligands dominate the speciation patterns of different trace metals [Sip80].

2.2 THEORY

The thermodynamic basis of chemical modelling has been dealt with in some detail in the literature [Bri47, Whi58, Jen79]. As the Bjerrum ion association theory (in particular the equilibrium constant approach) has been widely used previously, it will also be here. It is also the approach for which the most reliable data exists and this is of particular relevance if the model is to be reliable.

When any speciation model is set up, a set of procedures needs to be followed. These are represented by the flow chart in Figure 2.1. Firstly, the components which make up the model system need to be specified and their total concentrations determined. Secondly, all the complexes (dissolved, precipitated and adsorbed) that may arise from the interactions of these components need to be determined. Once this has been done, formation constants for these complexes must be found from the literature. In cases for which formation constants have not been reported, these must be determined experimentally or estimates made based on analogous systems. The constants are then corrected to the applicable temperature and ionic strength of the model system. These corrections are performed based on certain thermodynamic principles.

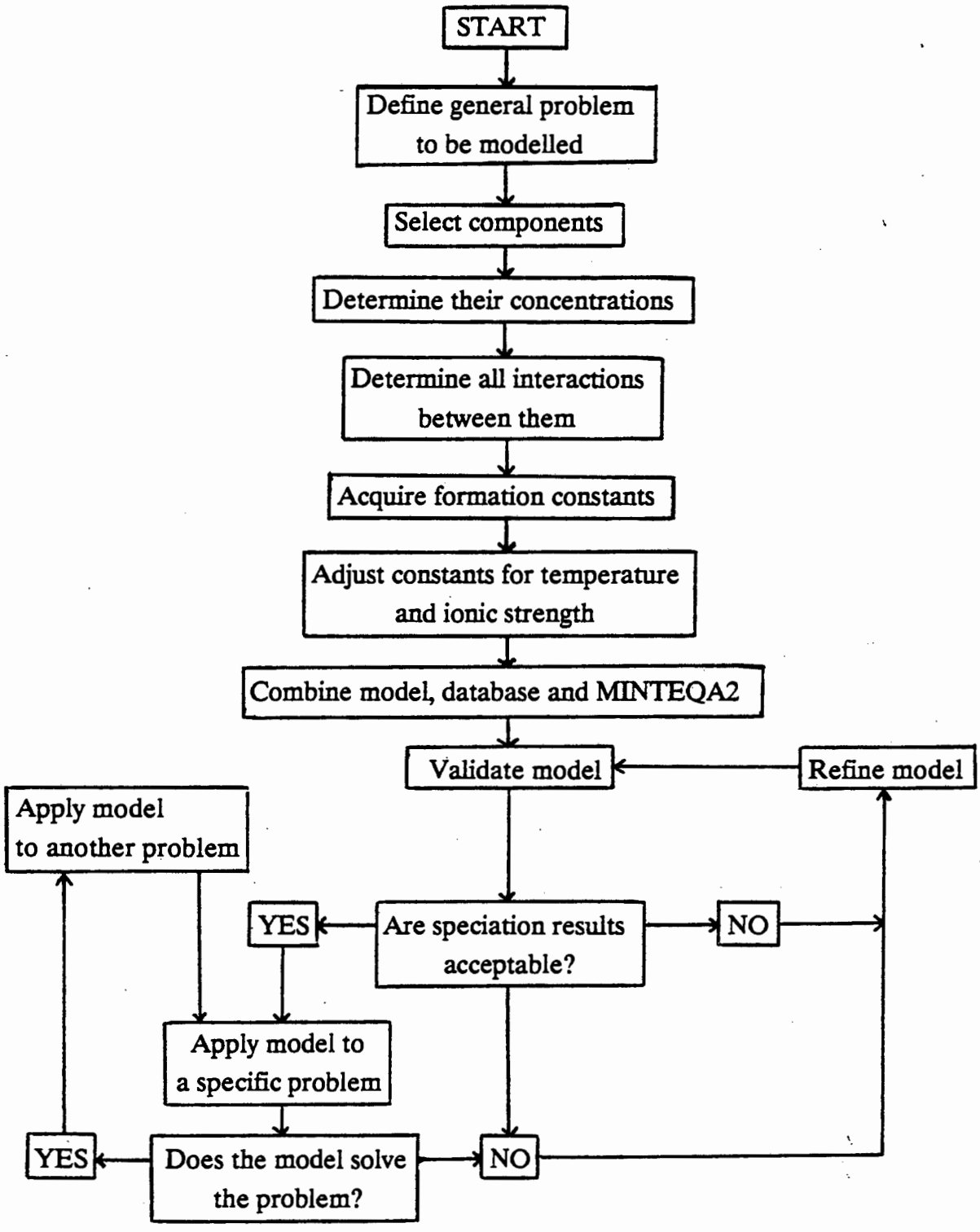


FIGURE 2.1: Flow chart of the procedures employed in chemical speciation modelling

2.2.1 Corrections for Temperature

These corrections are made using the Van't Hoff equation applied to chemical reactions at constant pressure

$$(\partial(\ln K)/\partial T)_p = \Delta H_m^\theta/RT^2 \qquad 2.2$$

where ΔH_m^θ is the standard molar enthalpy of the reaction.

By using the approximation that ΔH is constant over a small temperature range the following equation is obtained

$$\ln(K_2/K_1) = (\Delta H_m^\theta/R)(1/T_1 - 1/T_2) \qquad 2.3$$

This approximation has been found to hold reasonably well over the range of temperature considered in aquatic chemistry [Mor83b]. Where the applicable ΔH data do not exist, estimations are made from metals with analogous properties. In most cases the temperature difference $(T_2 - T_1)$ as well as ΔH is small which causes a small correction to the equilibrium constant. The reported constants are generally a greater source of error than the correction made.

2.2.2. Corrections for ionic strength

Equilibrium constants are often reported at ionic strengths which are somewhat different to that of the relevant model system. This is particularly true of the ionic strength of seawater (0.7 mol dm^{-3}).

Corrections for ionic strength are based upon knowledge of single ion activities. However, single ion activities and single ion activity coefficients cannot be measured experimentally. Estimates of the "real" values can be obtained using non-thermodynamic models, most of which are based on the Debye-Hückel theory of estimating single ion activity coefficients. The Debye-Hückel theory describes single ion activity coefficient behaviour for ions in dilute solutions by considering long range electrostatic interactions between ions of opposite charge. It can be extended to higher ionic strengths through the use of adjustable parameters which account for short range non-electrostatic interactions. The general form of the extended Debye-Hückel equation is

$$\text{Log}\gamma_i = -Az_i^2 I^{1/2} / (1 + B\text{å}_i I^{1/2}) + cI \qquad 2.4$$

where I is the ionic strength of the solution;

γ_i is the activity coefficient of ion, i;

z_i is the charge on ion, i;

A, B are constants characteristic of the solvent that depend on dielectric constant, temperature and density. (A = 0.509; B = 0.328 for water at 25°C (Mar74b));

å_i is an ionic size parameter, estimates which have been given by Kielland (Kie37);

c is an adjustable parameter that accounts for short range non-electrostatic interactions.

The essential difference between models depends on the choice of values for the B, å_i and c parameters.

Linder and Murray {Lin82] report a procedure for correcting formation constants from as few as one or two literature values at different ionic strengths. A computer program LOGK was developed to supply constants at an ionic strength of 0.04 mol dm^{-3} [Mur82].

For a given complexation reaction between a metal, M, and ligand, L,

$$pM^{i+} + qL^{j-} \leftrightarrow (M_pL_q)^{(pi-qj)+} \qquad 2.5$$

the equilibrium constants K_1 and K_2 at ionic strengths I_1 and I_2 are related by

$$K_2 = Q_2K_1/Q_1 \qquad 2.6$$

where Q is the quotient of activity coefficients for the reaction at a given ionic strength.

By combining equations 2.4 and 2.6 it is possible to correct for ionic strength [Lin82]. The assumption is made that the c parameter is the same for each ion in equation 2.5. By supplying values for $å_i$ an overall c for the system can be calculated and used to predict formation constants at different ionic strengths.

The $å_i$ parameters are taken from Kielland [Kie37] who lists this parameter for a variety of ions. Where values are not available the following formulae can be used

for inorganic ions $å_i = 2|z_i| + 2$

for small organic ions $å_i = |z_i| + 4$

If a literature value for the formation constant is available at only one ionic strength, the value of c cannot be determined as discussed above. It is set equal to -0.10 as recommended by Davies for 1:1 electrolytes, instead [Lin82].

In the present study adjustments are carried out using LOGK. The adjustment of solubility products are carried out using an analogous procedure. In this case the program LOGKSP [Voy85] was used.

It should be noted that the reported constants are a greater source of error than the ionic strength adjustment made. This is particularly significant for small ionic strength differences as was revealed by an error analysis conducted by Linder and Murray [Lin82].

2.2.3 Redox Equilibria

It is convenient to define relative electron activity in aqueous solutions by analogy with the former definition of pH, namely

$$pH = - \log\{H^+\} \qquad 2.7$$

The expression for electron activity is

$$pE = - \log\{e^-\} \qquad 2.8$$

where {H+} represents the absolute activity of "free" i.e. hydrated protons in mol dm^{-3} and $\{e^-\}$ represents the activity of the electron relative to the standard hydrogen electrode of unit activity [Tur81].

Equilibrium relationships involving oxidation and reduction reactions may be specified in terms of an equilibrium constant, K^θ, or the standard electrode potential for the reaction, E^θ. The half cell reaction is written as

$$\text{oxidized} + ne^- \leftrightarrow \text{reduced} \qquad 2.9$$

For which E^θ is related to K^θ by the expression

$$E^\theta = 2.303RT\log K^\theta/nF \qquad 2.10$$

where F is the Faraday constant = 96485C;

R the gas constant;

and T the absolute temperature.

Often the redox potential of natural systems is given in terms of E_h, the potential of the system relative to the hydrogen half cell reaction. E_h is related to pE by the expression

$$pE = (F/2.303RT)E_h \qquad 2.11$$

2.2.4 The formation of ternary complexes

It is generally agreed that in a solution containing metal ions and two or more ligands, mixed ligand complexes will be formed [Mar69, Sha69, Bec70]. This is especially true for a multi-ligand system such as seawater which contains numerous ligands in high concentrations [Byr83]. The high halide concentration means that the formation of mixed halide complexes is enhanced.

The stability of these complexes is most often enhanced over their binary counterparts. This has been attributed to statistical effects and has been calculated by Watters [Wat53]. The stability is, however, often greater than that predicted by statistical effects and is the result of electrostatic forces, geometric factors, solvent effects (dipole interactions) and outer versus inner orbital coordination [Mar69]. On the other hand, these effects may result in destabilization.

Consider the reaction between a metal, M and two ligands of equal denticity, A and B

$$i/n\ MA_n + j/n\ MB_n \leftrightarrow MA_iB_j \qquad 2.12$$

where i,j are the stoichiometric coefficients of A and B in the ternary complex and n = i+j.

The formation constant for the ligand species is related to the formation constants of the binary species by

$$\log \beta_{ij} = \log K_m + i/n \log \beta_{n0} + j/n \log \beta_{0n} \qquad 2.13$$

where β_{n0} and β_{0n} are the formation constants for the binary complexes MA_n and MB_n respectively and K_m is the dimensionless mixing constant for reaction 2.12.

K_m is often measured experimentally by comparing the actual mixed complex formation constant with those of the binary species [Mar69]. It arises from both statistical and the non-statistical effects mentioned above.

$$\log K_m = \log K_s + \log (nci) \qquad 2.14$$

where K_s is the stabilization constant and is a measure of the non-statistical contribution while (nci) or "n combination i" is the binomial coefficient, n!/[(n-i)!i!]. This latter term represents the statistical contribution.

Generally it has been found that the values obtained for log K_s are small and lie in the range -0.5 to 1.0 [Mar69]. In this study where mixed ligand species constants were found in the literature, these were converted immediately to the relevant ionic strength using LOGK. Where data did not exist, mixed formation constants were calculated from the binary formation constants and K_m was calculated from the statistical term log (nci) alone, i.e. log K_s was set to zero. This provides a good first approximation.

2.2.5 The thermodynamic basis of the chemical speciation problem

The problem of solving the chemical speciation pattern involves finding the unique solution to a set of non-linear simultaneous equations using an iterative procedure. This is common to all programs used for speciation modelling, although the discussion will be restricted to the program MINTEQA2.

As an illustration, consider a system which has **n** components which react to form **m** complexes. The objective is to calculate the concentrations of all the individual species that make up the equilibrium mixture. To do this, the total or free concentrations of the **n** components need to be known. Analytical techniques are such that in general the total concentrations are known although a few free concentrations may be known. For example free hydrogen concentrations can be determined using a glass electrode while ion-selective electrodes provide data for certain metals and ligands. Initially no precipitation reactions are considered. The concentration, C_i, of each species i can be expressed as a function of the cumulative formation constant β_i and the free concentration of each of its components. It is fixed in an equilibrated system by the Law of Mass Action

$$C_i = \beta_i \prod_{j=1}^{n} X_j^{a(i,j)}, \text{ for } i = 1,m \qquad 2.15$$

where C_i is the concentration of species i;

β_i is the formation constant of i;

X_j is the free concentration of component j;

and a(i,j) is the stoichiometric coefficient of component j in complex i.

To calculate the speciation of the system m equations of the form 2.15 are needed. The problem depends solely on finding the free concentration of each component, X_j. These free concentrations must in turn satisfy the mass balance conditions for all the components. This states that the total concentration of component j is given by the sum of the free concentration of j and that amount of j in each of the complexes. The total concentration can then be calculated by summation and compared with the analytical concentration, T_j by means of a difference function

$$Y_j = \sum_{i=1}^{m} a(i,j)(C_j) - T_j \qquad 2.16$$

The exact solution to the problem is thus the set of free component concentrations such that all the Y_j's = 0. MINTEQA2 thus calculates the concentration of each complex, C_i, based on initial estimates for the free component concentrations, X_j. The total concentration is then calculated. It then makes use of a modified Newton-Raphson procedure [All90] and the difference function Y_j for each component to find improved values for the X_j's. The process is repeated with the new X_j's until all the Y_j's are minimized.

In practice this iterative procedure does not continue until all the Y_j's are zero as this would go on indefinitely. The practice is to minimize until all the difference functions are less than a specified tolerance value. MINTEQA2 uses several special modifications of the Newton-Raphson procedure to find the solution more quickly.

Upon convergence MINTEQA2 then calculates the degree of supersaturation of the potential solid species. Those that exceed their solubility products are allowed to precipitate which changes the free ion concentration. The iteration procedures are

repeated until convergence is again observed. This process continues until no further precipitation or (in the case of over-correction) dissolution occurs.

Where adsorption phenomena are included in the model, these are also subject to mass balance restrictions which depend on the model chosen. MINTEQA2 treats adsorbed species as dissolved species and includes them as such in the iterative convergence procedures.

2.3 ADSORPTION MODELLING

Various models have been proposed to account for adsorption phenomena. These may be divided into two broad classes: non-electrostatic and electrostatic models.

The former class includes the activity K_d, activity Langmuir, activity Freundlich and ion exchange models. These have been in common use for some time and certain conventions as to their use have become accepted [Mor83b].

Electrostatic models take into account the electrostatic influence of charged surfaces in solution. This is particularly relevant in a solution which has many charged species such as seawater. Many colloidal particles carry a substantial surface charge that creates a significant electrostatic potential which extends into the solution. These potentials greatly affect the adsorption of charged ions. The result is that ions of opposite charge are attracted while those of like charge are repelled. This influence is accounted for by including terms in the mass balance equations which modify the activities of sorbate ions approaching the charged surfaces.

The models available have been reviewed by Westall and Hohl [Wes80b]. Three of the most commonly used models are the constant capacitance, diffuse-layer and triple-layer

models. Each of these treats adsorption as a surface complexation reaction and each accounts for the elecrostatic potential at the charged surface. Experiment has shown that such an approach is justified [Dzo90]. The models differ in the types of surface species that are allowed within specific layers extending away from the surface and the parameters of the electrostatic model that each uses.

Because the diffuse-layer model is the model which requires the least number of adjustable parameters, it was chosen for the adsorption calculations carried out in this study. It is also the model for which the most adsorption constants exist.

2.3.1 The diffuse-layer model

This model is based on the original model proposed by Stumm and his co-workers [Stu70b, Hua73, Stu76b]. Its underlying principle is that the sorption of a solute at oxide surfaces may be described as a chemical reaction with specific surface hydroxyl groups. For each reaction the concentration of sorbate, sorbent and surface sites must satisfy a mass law equation.

The free energy of adsorption may be expressed as follows

$$\Delta G^{\theta}_{ads} = \Delta G^{\theta}_{int} + \Delta G^{\theta}_{coul} \qquad 2.17$$

Consequently the equilibrium constant is the product of two terms: an "intrinsic" term corresponding to the chemical free energy of binding to a particular site and a "'variable" coulombic term corresponding to the coulombic free energy of binding caused by the electrostatic charge at the surface. This latter term is calculated from the Gouy-Chapman theory of the electrical double layer by considering one layer of surface charges and a diffuse layer of counter charges in solution.

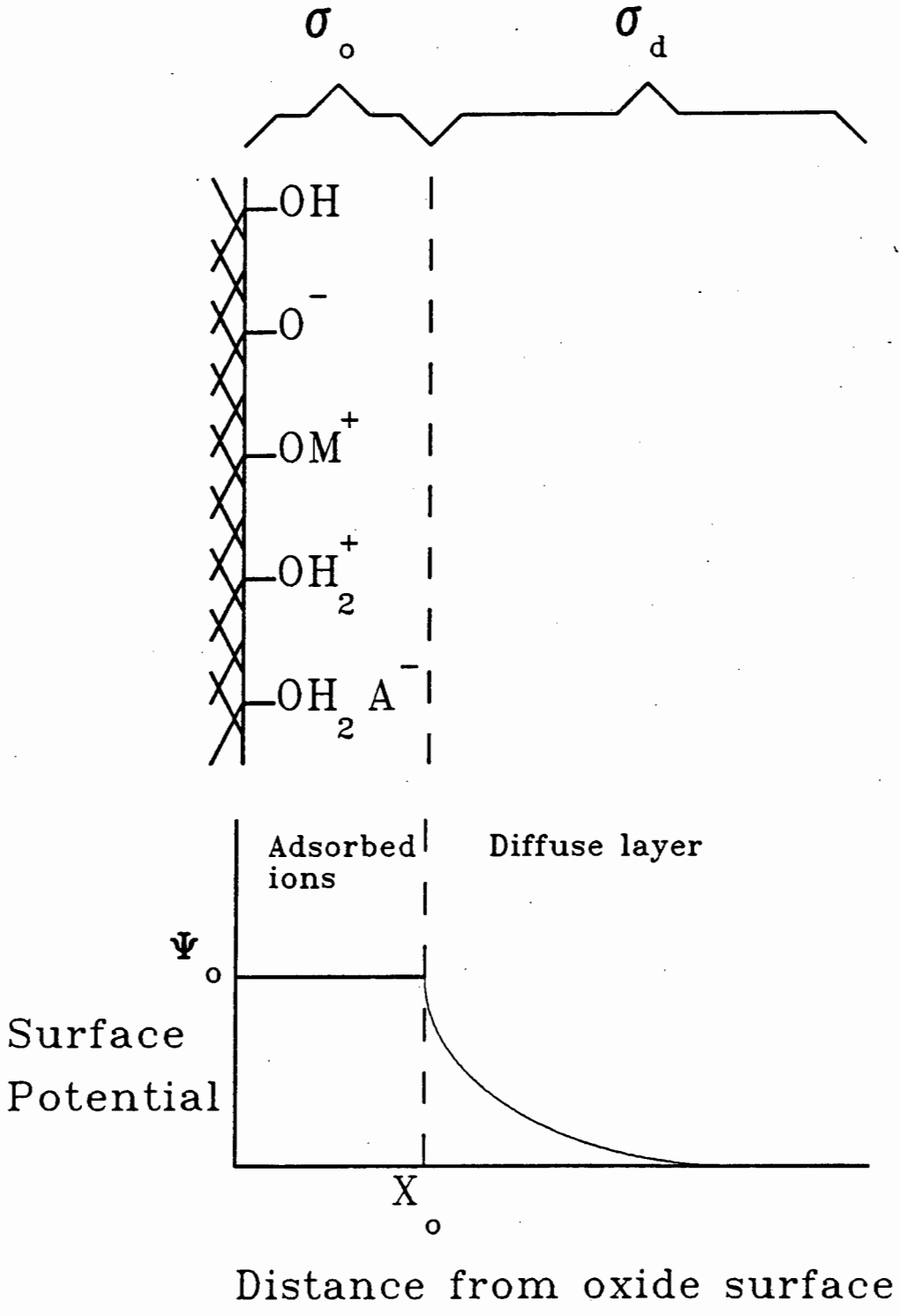


FIGURE 2.2: A representation of the surface of a metal oxide

Above - the surface with various groups bound to it, (M = metal cation, A = anion)

Below - the potential as a function of the distance from the oxide surface

$$\Delta G_{coul} = F\Delta Z\Psi \qquad 2.18$$

where Ψ is the surface potential;

ΔZ is the change in the charge of the surface species due to the adsorption reaction;

F is the Faraday constant.

Surface sites may be represented as SOH groups where the S's are the metals associated with the solid structure and located at the solid-liquid interface. Figure 2.2 is a schematic representation of the surface of such a metal oxide. In the model a charge (σ) associated with the surface is assumed to be balanced by a charge (σ_d) associated with a diffuse layer of counterions such that $\sigma + \sigma_d = 0$. All specifically adsorbed ions contribute to the surface charge (σ). The diffuse-layer model assumes only one plane in which ions are adsorbed on the surface while the triple-layer models has two planes; one for H^+ and OH^- and one for other ions. Figure 2.2 also indicates the relationship between surface charge and potential in the diffuse layer model.

The activities of the ions in solution and particularly near the surface are influenced by the presence of electrostatic potentials which arise from the surface charge. The difference in activity between those ions near the surface and those far away is the result of electrical work in moving the ions across the potential gradient between the charge surface and the bulk solution. The activity change is related to ionic charge (z) and the electrical potential (Ψ) by the following expression

$$\{X_S^z\} = \{X^z\}\,[e^{-\Psi F/RT}]z \qquad 2.19$$

where z is the charge of ion X;

$\{X_S^z\}$ is the activity of ion X near the surface;

$\{X^z\}$ is the activity of ion X in the bulk solution, away from the influence of the charge surface

and $e^{-\Psi F/RT}$ is the Boltzmann factor

The Gouy-Chapman theory relates the total surface charge density (τ) to the surface potential (Ψ) by the expression

$$\tau = 0.1174\ I^{1/2} \sinh (Z\Psi F/2RT) \qquad 2.20$$

where Z is the valency of the symmetrical electrolyte (taken as unity)

and I is the ionic strength.

However surface charge density is also given by

$$\tau = F[\Gamma_H - \Gamma_{OH} + \Sigma(Z_M\Gamma_M) + \Sigma(Z_A\Gamma_A)] \qquad 2.21$$

where F is the Faraday constant;

Z is the valence of a sorbing ion

and Γ is the sorption densities of protons (H), hydroxyl ions (OH), cations (M) and anions (A).

To model the surface reactions, mass action expressions are generated with the Boltzmann factors represented as additional "dummy" components, as proposed by Westall [Wes80a]. The stoichiometries of such factors are included in the definition of the surface reactions. Since the activity coefficients of all surface (adsorbed) species are taken as equal (unity), they cancel out of the expressions for equilibrium constants. Only the free ions in solution contribute Boltzmann factors to the equilibrium constants.

The program MINTEQA2 then uses its iteration procedures to minimize the different concentrations as well as a charge balance equation which balances total surface charge as given by equation 2.20 to that supplied by the excess of charge that complexes to the surface (Equation 2.21).

Adsorption reactions can be classified into the following types: surface acidity (loss/addition of a proton to a reactant site), adsorption of anions and cations via ligand exchange at the hydroxyl sites and lastly the precipitation of cations on the surface. The last case occurs when the sorbate concentration is so high that the sorbing metal replaces one of the metals of the solid lattice of the adsorbing surface.

All of the above reactions except for surface precipitation were included in the model. Surface precipitation reactions were ignored as they require a high cation concentration. This is because the metals which are observed to precipitate onto hydrous ferric oxide (the model solid used) are present in trace concentrations in the ocean and thus surface precipitation can be ignored.

2.4 MODEL CONSTRUCTION

2.4.1 Selection of components

2.4.1.1 Major elements

99.5% of the total dissolved solids in seawater consists of just fourteen components [Cul65]. These are commonly referred to as the major components. They generally form the major conservative species, are present in millimolar concentrations and are well mixed throughout the ocean. The consequence is that they exhibit an almost constant ratio to one another [Cul65].

TABLE 2.1 The major constituents of surface seawater and their total concentrations

Cation	Concentration mol dm^{-3} X 10^3	Anion	Concentration mol dm^{-3} X 10^3
Na^+	479	Cl^-	559
Mg^{2+}	54.5	SO_4^{2-}	28.9
Ca^{2+}	10.5	CO_3^{2-}	2.05
K^+	10.4	Br^-	0.86
Sr^{2+}	0.091	$B(OH)_4^-$	0.425
Li^+	0.026	F^-	0.069
		$SiO_2(OH)_2^{2-}$	0.007
		NO_3^-	0.007

TABLE 2.2 The trace elements of surface seawater and their total concentrations

Trace Element	Concentration mol dm^{-3} X 10^9	Trace Element	Concentration mol dm^{-3} X 10^9
Al^{3+}	55	Pb^{2+}	0.1
Ba^{2+}	33	Cd^{2+}	0.1
UO_2^{2+}	14	Co^2	0.05
Fe^{3+}/Fe^{2+}	8	Hg^{2+}/Hg_2^{2+}	0.01
Mn^{2+}	4	Sn^{2+}	0.01
Ni^{2+}	3.5	Ag^+	0.001
Cu^{2+}/Cu^+	2	PO_4^{3-}	500
Zn^{2+}	2	I^-	100
Cr^{3+}	0.15	IO_3^-	300
CrO_4^{2-}	2		

The concentrations of the major ions were obtained by reviewing the literature [Cul65, Gol65, Bru83b, Ahr85, Bea89] and are listed in Table 2.1. These concentrations are the means of reported values which are in substantial agreement (within 3% of each other) in the case of sodium, potassium, lithium, calcium, magnesium, strontium, sulphate, chloride, bromide, borate and fluoride. The reported carbonate concentration ranges from a minimum for surface waters of 2.05 mmol dm^{-3} to a deep water maximum of 2.3 mmol dm^{-3} [Gol65, Bru83b, Bea89].

In light of the ultimate aim of this work to model man's impact on coastal regions, the surface concentration was taken. The carbonate is assumed to be in equilibrium with atmospheric carbon dioxide which determines a slightly different dissolved carbonate concentration. Consequently the model was run in duplicate; in one case carbon dioxide was allowed to dissolve and in the other not. The reported concentration for silicate ranges from 0.5 to 1000 μmol dm^{-3} but it is not clear whether the values apply to dissolved or total (including particulate) silicates. A total dissolved concentration of 7 μmol dm^{-3} was taken, being the average of values reported for surface waters [Arm65, Sto82, Yea83, Bai85, Orr85]. Nitrate concentrations are weighted on the high side to reflect the fact that they are higher in regions of upwelling near the coasts [Orr81, Yea83, Kre89].

For the most part the pH was fixed at 8.1. This is near the middle of the range for reported ocean pH's. Deviations from this figure are small (less than 0.2) [Sil67, Ahr85]. A pH of 8.1 was also used in previous model studies [Ahr85, Mot87]. In some cases pH was scanned over a limited range.

As pointed out by Sillén and Martell [Sil64] the electron may be treated like any other reactant or product in a chemical reaction. However the redox state of the ocean is difficult to measure [Stu81]. The model was run at pE of 9.1 although this is not

necessarily representative of the ocean. A more detailed discussion follows in sections 2.4.2.7 and 2.5.4.

2.4.1.2 Trace elements

Almost all the 92 naturally occurring elements have been detected in the ocean. As analytical techniques improve it is expected that those that have not as yet been determined, will be discovered [Tur81, Bea89]. Many of these elements are present in trace concentrations (picomolar to nanomolar). Because of their biological importance trace elements have been included into the model. Their concentrations have been listed in Table 2.2.

It should be noted that the concentrations of the trace elements are not conservative in behaviour like those of the major components. The variation has been found to be up to fivefold and depends on local conditions such as adsorption onto solids and the uptake by microorganisms. The low concentrations make analytical determination very difficult which also contributes to the uncertainty [Ahr85].

Because of contamination, the data for iron are unreliable and range from 0.3 to 13 nmol dm^{-3} [Sañ91]. Literature sources do not specify whether dissolved or total iron is reported. A study by Danielsson and Westerlund [Dan83] reports that the total concentration of iron may be higher than previously reported if sufficient time is allowed for digestion and total dissolution. The value chosen was taken from literature [Dan80, Dan83, Dan85a, Sañ91] and is the same as that used in previous model studies [Ahr85]. Manganese data also exhibit great variation since it too can exist in particulate form. The value chosen was slightly higher than the literature mean since most studies report only dissolved Mn^{2+} [Bur83, Bru83c, Bro82, Bru83b, Jic88, Sañ91, Yea91]. In the coastal shelf region values as high as 15 nmol dm^{-3} [Sañ91] and 21 nmol dm^{-3} [Bru83c] have

been reported. The concentrations used for copper, cadmium and zinc are mean values taken from the literature although they are weighted higher to reflect the tendency of these metals to occur in higher concentrations in coastal waters as a result of upwelling [Bru80, Dan80, Spe82, Boy83, Bru83a, Bru83b, Bru83c, Dan83, Yea83, Dan85a, Sañ91, Yea91]. The nickel value is an unweighted mean as the literature values are consistent [Dan80, Boy83, Bru83b, Bru83c, Dan83, Yea83, Dan85a, Jic88, Kre89, Yea91]. Data for mercury, cobalt and silver are scarce so the mean concentrations, weighted somewhat highly, were taken from what literature is available [Dan80, Bru83b, Jic88, Yea91]. Lead concentrations are largely governed by anthropogenic influences [Boy83, Bru83a, Bru83b] so a high value was chosen to reflect the effect of man's pollution. The barium concentration is that given by Bruland [Bru83b] for surface waters. The uranium concentration is quite consistent. The same value was used in previous model studies [Ahr85, Mot87]. Chromium, tin and iodine data pose particular problems since literature values are scarce (in the case of the first two) and all are affected by the redox state of the ocean. Tin was included as tin (II) (concentration from Bruland [Bru83b]) even though tin (IV) species have been reported while chromium was included as chromium (III) and chromate [Cra78]. Concentrations were also included for iodide and iodate to reflect the two redox states possible for iodine [Lis73]. Aluminium data cover a wide range which includes particulate Al, so a mean was used [Sto82, Bru83b, Mea86]. Phosphate too is highly variable and depends on local conditions as it is a nutrient species. A mean was used to reflect a coastal maximum [Boy83, Dan85a, Kre89, Wes91].

2.4.2 Compilation of the database and the acquisition of formation constants and solubility products

The largest source of error when setting up a model is generally due to the reported equilibrium constants. The constants, before ionic strength and temperature adjustments, were taken from the critical compilations of stability constants by Martell and Smith

[Mar74a, Smi75, Smi76, Mar77, Smi82, Smi89]. These constants were rigorously selected by the authors such that the reliability of the constants is high. The constants for the hydrolysis of metal ions were taken from Baes and Mesmer [Bae76]. Use was also made of the JESS thermodynamic database [May91a, May91b] where constants for important interactions were not available in the compilations of Martell and Smith. This was especially true for the interactions of metal ions with the organic ligands used in the model.

In the case of the redox reactions, the equilibrium constants were calculated from standard electrode potentials. These were found in the compilation of Milazzo and Caroli [Mil78] and that of Antelman [Ant82]. The solubility products of certain solids not found in Martell and Smith were taken from Morel [Mor83b] or in the case of aluminosilicates from the paper by Helgeson [Hel69]. Lastly the equilibrium constants for the adsorption of metals onto hydrous ferric oxide were extracted from the critical compilation of Dzombak and Morel [Dzo90].

Initial model runs showed results which were highly unexpected. In some cases these were the result of unreliability or errors in the reported formation constants. This was especially true for the solubility products, in particular the carbonates of magnesium and calcium as well as iron hydroxide. Inaccurate constants were found for iron borates as well as for uranyl hydroxycarbonate. These together with those that determine the redox state and the dissolution of atmospheric carbon dioxide will be discussed in more detail.

2.4.2.1 The stability constants for metal hydroxides

As has been indicated earlier, most of the metal hydroxide formation constants were taken from the compilation of Baes and Mesmer [Bae76]. However, in a few cases the reported constants were associated with large uncertainties. In these cases more recent literature

values were sought and included in the model. These are discussed in more detail in the following section.

2.4.2.1.1 The stability constant for $MgOH^+$

Both the models of Dickson and Whitfield [Dic81] and Millero and Schreiber [Mil82] make use of a log K of 2.21 at 0.0 mol dm^{-3} for the reaction

$$Mg^{2+} + OH^- \leftrightarrow MgOH^+ \qquad 2.22$$

This differs from the value recommended by Baes and Mesmer of 2.56 at 0.0 mol dm^{-3}. The value recommended by Baes and Mesmer [Bae76] is based on the work of Stock and Davis [Sto48] and Hostetler [Hos63] while Dickson and Whitfield [Dic81] and Millero and Schreiber [Mil82] take their constant from the more recent work of McGee and Hostetler [McG75]. These last two authors indicate that the higher formation constant determined in the earlier studies was the result of dissolved impurities such as CO_2 and anomalous electrode responses.

Consequently the constant reported by McGee and Hostetler was used in this model. It was corrected for ionic strength using the correction procedure used by these two authors [McG75]. This gave a log K of -12.23 for the reaction

$$Mg^{2+} + H_2O \leftrightarrow MgOH^+ + H^+ \qquad 2.23$$

at 25 °C and an ionic strength of 0.7 mol dm^{-3}.

2.4.2.1.2 The stability constant for $Al(OH)_3$

Initial calculations indicated that $Al(OH)_3$ is significant in the speciation of aluminium. However, Baes and Mesmer [Bae76] indicate that there is a large uncertainty with respect to the constant for the reaction

$$Al^{3+} + 3H_2O \leftrightarrow Al(OH)_3 + 3H^+ \qquad 2.24$$

They quote the work performed by Nazarenko and Nevskaya [Naz69] who found log K to be -15.6 at 0.1 mol dm^{-3}. This corrects to -15.0 at 0.0 mol dm^{-3}. The most recent compilation by Smith and Martell [Smi89] reports log K to be 25.5 and 24.7 at 0.0 mol dm^{-3} and 0.1 mol dm^{-3} respectively for the reaction

$$Al^{3+} + 3OH^- \leftrightarrow Al(OH)_3 \qquad 2.25$$

These constants are lower than those quoted by Baes and Mesmer when converted into the form of equation 2.24. Log K is -16.5 at 0.0 mol dm^{-3} and -16.7 at 0.1 mol dm^{-3}. These constants were then corrected to 0.7 mol dm^{-3} using Davies' recommendation of c = -0.1, log K = -17.57 and -17.18 respectively. It was decided to use the mean of these values, i.e. -17.37.

Recently Venturini and Berthon [Ven87] measured the formation constants for aluminium hydroxides in 0.15 mol dm^{-3} NaCl. However, these measurements were conducted at a temperature of 37 °C and consequently were not included in the database. Bourcier et al. [Bou93] also found evidence for the species $Al(OH)_3$ which is often ignored. However, they too were not working at 25°C. In this case they measured the hydrolysis constants at very high temperatures (150 to 250°C) and pressures (up to 100 atms).

2.4.2.1.3 The stability constants for copper hydroxides

The hydrolysis constants for copper reported by Baes and Mesmer are associated with large uncertainties. More recently Sylva and Davidson [Syl79] reported log K to be -7.71 in 0.1 mol dm^{-3} KNO_3 for the reaction

$$Cu^{2+} + H_2O \leftrightarrow CuOH^+ + H^+ \qquad 2.26$$

This is in agreement with the value of -7.52 at 0.0 mol dm^{-3} as reported by Sunda and Hanson [Sun79b]. Paulson and Kester [Pau80] report log K to be -8.03 at 0.7 mol dm^{-3} while van den Berg [VdB84a] reports log K as -7.66 at 0.7 mol dm^{-3}. Correcting the results of Sunda and Hanson and that of Sylva and Davidson to an ionic strength of 0.7 mol dm^{-3} one obtains log K to be -7.84 which lies between that reported by van den Berg and that of Paulson and Kester. Log K = -7.84 was consequently used in the model. This differs significantly from log K = -6.50 used by Motekaitis and Martell [Mot87].

The formation constant for $Cu(OH)_2$ has an even greater uncertainty. Paulson and Kester [Pau80] report log K to be -16.70 at an ionic strength of 0.7 mol dm^{-3} for the reaction

$$Cu^{2+} + 2H_2O \leftrightarrow Cu(OH)_2 + 2H^+ \qquad 2.27$$

This differs from the constant reported by van den Berg of log K = -15.91 at 0.7 mol dm^{-3}. However, it is in agreement with the result of Sunda and Hanson [Sun79b] who report log K to be -16.22 at 0.0 mol dm^{-3}. Consequently it was decided to use the result of Paulson and Kester for this stability constant.

2.4.2.1.4 The stability constant for $PbOH^+$

This constant also had a large uncertainty. Sylva and Brown [Syl80] report log K in 0.1 mol dm^{-3} KNO_3 to be -7.86 for the reaction

$$Pb^{2+} + H_2O \leftrightarrow PbOH^+ + H^+ \qquad 2.28$$

These two authors have reworked the data of Olin [Oli60] and found the reported constants to be spurious. Consequently the constant reported by Sylva and Brown [Syl80] was corrected for ionic strength and log K = -7.99 at 0.7 mol dm^{-3} was used in the model.

2.4.2.1.5 The stability constant for $Fe(OH)_2^+$

Smith and Martell [Smi89] report log K for the reaction

$$Fe_3^+ + 2OH^- \leftrightarrow Fe(OH)_2^+ \qquad 2.29$$

to be 21.7 and 22.0 at ionic strengths of 0.5 and 1.0 mol dm^{-3}. These correct to a stability constant of -5.81 at ionic strength of 0.7 mol dm^{-3} for the reaction as written

$$Fe^{3+} + 2H_2O \leftrightarrow Fe(OH)_2^+ + 2H^+ \qquad 2.30$$

This differs from that quoted by Baes and Mesmer [Bae76] who report log K for reaction 2.30 to be -5.67 at 0.0 mol dm^{-3} which corrects to -6.37 at the ionic strength of seawater. Motekaitis and Martell [Mot87], however, used a value of -5.88 for reaction 2.30. Consequently it was decided that the corrected value of -5.81 should be used in the database.

2.4.2.1.6 The solubility product for iron (III) hydroxide

The choice of solubility product for iron (III) with hydroxide depends on the choice of solid iron oxide/hydroxide. Furthermore the reported literature values are distorted by the effects of ageing on the precipitates being measured.

The thermodynamically stable form of iron (III) hydroxide is goethite, FeO(OH), which forms only after several years of ageing [Bae76]. It forms according to the reaction

$$Fe^{3+} + 3H_2O \leftrightarrow FeO(OH) + 3H^+ + H_2O \qquad 2.31$$

Schindler [Sch63] reports log K to be -1.4 in 3 mol dm^{-3} $NaClO_4$. Lindsay calculated a thermodynamic value of -0.02 [Lin79].

Amorphous iron (III) hydroxide forms according to reaction 2.32. The value for log K was measured as -4.9 at 0.0 mol dm^{-3} by Langmuir on freshly precipitated solid [Byr76] while Schindler [Sch63] measured log K to be -2.5 at 0.0 mol dm^{-3} on aged solid.

$$Fe^{3+} + 3H_2O \leftrightarrow Fe(OH)_3(s) + 3H^+ \qquad 2.32$$

This clearly reflects the problem of ageing when measuring constants. Byrne and Kester [Byr76] measured the precipitation of iron (III) hydroxide from seawater and found log K to be -5.67. This corresponds with the value of Langmuir when corrected to infinite dilution (log K = -4.5) whereas Biedermann and Schindler [Bae76] measured the constant after 200 hours of ageing in 3 mol dm^{-3} NaClO4. They found log K to be -3.96 which adjusts to -2.98 at 0.0 mol dm^{-3}.

A decision consequently had to be made as to whether to use amorphous iron (III) hydroxide or α-FeO(OH) to model the solubility of iron. It was decided to use the amorphous iron (III) hydroxide to reflect the very slow kinetics of conversion to goethite. This last step is likely to occur in the sediments. Since the model is of the surface and inputs are balanced by outputs the iron is not likely to have been resident for very long; thus the use of the amorphous form is justified. It also reflects the known information that iron tends to exist as colloidal suspensions of iron oxyhydroxides rather than the more thermodynamically stable pure oxides [Dan80, Mil80, Sym85a].

Martell and Smith report that for the reaction

$$Fe^{3+} + 3OH^- \leftrightarrow Fe(OH)_3(s) \qquad 2.33$$

log K is 38.8 at 0.0 mol dm^{-3} and 38.6 at 3 mol dm^{-3}. The former gives log K to be -3.2 for reaction 2.32. This is in the middle of the range of the data reported by Langmuir and Schindler and would thus reflect some degree of ageing. It was decided to use the constants from Smith and Martell [Smi82]. Log K was found to be -3.80 at 0.7 mol dm^{-3} using the correction recommended by Baes and Mesmer [Bae76].

2.4.2.1.7 The solubility products for other metal oxyhydroxides

To reflect the slow ageing of minerals in the ocean, in general, the solubility product for a metal with hydroxide was chosen as that for the insoluble hydroxide rather than the more thermodynamically stable oxide. Where an active and an inactive form was reported, the solubility product for the active form was used even though this may not be the thermodynamically favoured form in seawater. This was done for magnesium, iron (II) and cobalt (II). Where data for insoluble hydroxides did not exist, the thermodynamically more stable oxides were included as was the case with Ag_2O, HgO, PbO and SnO.

In the case of $Al(OH)_3$ various solubility products are reported. Helgeson [Hel69] reports log K_{sp} to be -8.0 for the crystalline solid and -9.23 for a cryptocrystalline form at an ionic strength of 0.0 mol dm^{-3}. Recently Palmer and Wesolowski [Pal82] investigated the dissolution thermodynamics of gibbsite at various temperatures and ionic strengths. They report log K to be -7.735 at 0.0 mol dm^{-3}, -8.565 at 0.5 mol dm^{-3} and -8.720 at 1.0 mol dm^{-3}. Because of the long equilibration periods involved (20 to 132) days, it would appear that they studied a crystalline solid since their zero ionic strength constants are similar to that reported by Helgeson [Hel69].

It was decided to use the value recommended by Baes and Mesmer [Bae76] as being representative of insoluble aluminium hydroxides (somewhere between the pure crystalline and cryptocrystalline forms). They report log K_{sp} to be -8.5 at infinite dilution which is corrected to -9.58 at an ionic strength of 0.7 mol dm^{-3}.

2.4.2.2 The stability constants for metal chromates

Most of these came from the compilations of Smith and Martell [Smi76, Smi82, Smi89]. However, the stability constants for $KCrO_4^-$ and $NaCrO_4^-$ were taken from Masterton and Berka [Mas66]. They were then corrected to an ionic strength of 0.7 mol dm^{-3} which gave log K's of 0.04 and -0.06 respectively. These constants were calculated from measured osmotic coefficients and consequently have large uncertainties but $NaCrO_4^-$, in particular, cannot be ignored owing to the high sodium concentration in seawater.

2.4.2.3 The stability constants for metal borate complexes

2.4.2.3.1 The stability constants for the formation of major cation-borate ion pairs

Most recently equilibrium constants for the formation of ion pairs between borate and Li^+, Na^+, Mg^{2+}, Ca^{2+} and Sr^{2+} have been reported by Rogers and van den Berg [Rog88]. These constants are relevant to an ionic strength of 0.7 mol dm^{-3}. These authors also reported that the formation constant for $KB(OH)_4$ was too weak to be measured.

Previously borate ion-pair formation constants had been reported, relevant to an ionic strength of 0.7 mol dm^{-3}, by Byrne and Kester [Byr76] for Na^+, Mg^{2+} and Ca^{2+} and by Dyrssen and Hansson [Dyr73] for magnesium.

It was decided to use the constants of Rogers and van den Berg [Rog88] as these are the most recent and include all the major cations. The difference between the constants reported by these two authors and Byrne and Kester [Byr76] are small, with the greatest difference being for $MgB(OH)_4^+$ where log K as reported by Rogers and van den Berg [Rog88] is greater by 0.23.

2.4.2.3.2 The stability constants for iron (III) borates

Preliminary modelling studies performed by Karen van der Meulen [VdM90] revealed that iron (III) was predominantly bound as iron borate species. None of the iron present in the ocean was observed to precipitate. This is at variance with experimental observation that iron exists predominantly as insoluble oxyhydroxides in the marine environment [Dan80, Mil80, Sym85a].

The borate species are formed according to the reaction

$$Fe^{3+} + nB(OH)_4^- \leftrightarrow FeB(OH)_4)_n^{3-n} \qquad 2.34$$

where n = 1,2. The formation constants at 0.7 mol dm^{-3} are quoted by Martell and Smith as 10.85 and 22.4 respectively. A comparison with the original paper by Elrod and Kester [Elr80] shows that the constants, reported by Martell and Smith are incorrect.

Elrod and Kester quote values for log K of -2.0 and -4.7 respectively for the following reactions

$$Fe^{3+} + B(OH)_3 + H_2O \leftrightarrow FeB(OH)_4^{2+} + H^+ \qquad 2.35$$

$$Fe^{3+} + 2B(OH)_3 + 2H_2O \leftrightarrow Fe(B(OH)_4)_2^+ + 2H^+ \qquad 2.36$$

which can be converted to equation 2.34 by combination with the reaction for the protonation of boric acid

$$B(OH)_4^- + H^+ \leftrightarrow B(OH)_3 + H_2O \qquad 2.37$$

Karen van der Meulen used a log K of 8.41 for this reaction but it has subsequently been corrected to 8.85, that included by Smith and Martell [Smi89]. The resultant log K values for the formation of $FeB(OH)_4^{2+}$ and $Fe(B(OH)_4)^{2+}$ are 6.85 and 13.00.

2.4.2.3.3 The stability constants for the interaction of borate and Cu^{2+}, Pb^{2+}, Cd^{2+}, Zn^{2+} and Al^{3+}

Sposito [Spo81] calculated that 97% of the inorganic copper in seawater was bound by borate. Strong borate complexation was also found by Turner and Vukadin (>99%) [Tur83]. Consequently it was decided to investigate the effect of borate on trace metal speciation. The equilibrium constants chosen were those reported by van den Berg [VdB84a] for $MB(OH)_4^+$ and $M(B(OH)_4)_2$ where M = Cu^{2+}, Pb^{2+}, Cd^{2+} and Zn^{2+}. These were measured in 0.7 mol dm^{-3} KNO_3. These results were also in agreement with those of Turner and Vukadin [Tur83] who report that log K for $PbB(OH)_4^+$ is less than 3.5. Van den Berg measured this constant to be 2.20 [VdB84a].

Aluminium borate complexes were excluded on the basis of the measurements of Ohman and Sjoberg [Ohm85]. These measurements were made after Turner and Vukadin [Tur83] concluded that aluminium-borates were significant. However, this conclusion was based on erroneous constants [Shc61, Ohm85].

2.4.2.4 The stability constants for metal phosphate complexes

2.4.2.4.1 The stability constants for major cation phosphates

Although constants for $MHPO_4$ (M = Na, K , Mg and Ca) were readily available [Smi76, Smi82, Smi89], constants for MH_2PO_4 and MPO_4 either had large uncertainties or were not included in the compilations of Martell and Smith. However, in the pH range investigated in this study, it was expected that these species would be significant. Consequently constants were sought elsewhere.

The formation constants for $NaPO_4^{2-}$, NaH_2PO_4, KPO_4^{2-}, KH_2PO_4, $MgH_2PO_4^+$ and $CaH_2PO_4^+$ were taken from Atlas, Culberson and Pytkowicz [Atl76]. The formation constants for $MgPO_4^-$ and $CaPO_4^-$ were taken from Johansson and Wedborg [Joh79a]. All these constants were relevant to an ionic strength of 0.7 mol dm^{-3} and in the case of the magnesium and calcium constants had been corrected for Na^+ pairing. These constants were also used in the study by Millero and Schreiber [Mil82].

2.4.2.4.2 The stability constants for aluminium phosphate complexes

The equilibrium constants chosen for $AlH_2PO_4^{2+}$ and $AlHPO_4^+$ are those recommended by Langmuir [Lan79]. These were estimated from constants for $FeH_2PO_4^{2+}$ and $FeHPO_4^+$. The correlation was based on the fact that a plot of log K's for the formation of complexes between oxygen-donor ligands and aluminium against the log K's for the same ligands with iron (III) is nearly a straight line. The constants were then corrected for ionic strength to give log K to be 17.03 at 0.7 mol dm^{-3} for the reaction

$$Al^{3+} + H^+ + PO_4^{3-} \leftrightarrow AlHPO_4^+ \qquad 2.38$$

and log K of 20.05 for the reaction

$$Al^{3+} + 2H^+ + PO_4^{3-} \leftrightarrow AlH_2PO_4^{2+} \qquad 2.39$$

Jackson and Voyi [Jac88] measured log K for the reaction

$$Al^{3+} + HPO_4^{2-} \leftrightarrow AlHPO_4^+ \qquad 2.40$$

to be 11.4 in 0.15 mol dm^{-3} NaCl at 25 °C. This differs significantly with that predicted by the method of Langmuir [Lan79]. Langmuir calculated log K for reaction 2.40 to be

7.4 at 0.0 mol dm^{-3}. Modelling studies showed, however, that even using the constant of Jackson and Voyi [Jac88], $AlHPO_4^+$ is insignificant over the pH range found in seawater.

2.4.2.5 The stability constants for carbonate species

Significant uncertainty surrounds the constants report for the interactions of metal cations as well as the hydrogen ion with the carbonate anion. The available literature was reviewed in 1983 by Palmer and van Eldik [Pal83]. However, the reported constants do not allow a trend to be observed for the variation of metal carbonate stability constants with ionic strength. Consequently particular attention was paid to carbonate complexes inserted into the model's seawater database.

2.4.2.5.1 The carbonate equilibria

Since it would be interesting to model the average behaviour over a long time scale, it is a good approximation to consider atmospheric carbon dioxide to be in equilibrium with the ocean. Carbon dioxide readily reacts with water according to the reaction

$$2H^+ + CO_3^{2-} \leftrightarrow H_2CO_3^* \leftrightarrow CO_2(g) + H_2O \qquad 2.41$$

where $H_2CO_3^*$ represents the uncharged ion pair H_2CO_3 and aqueous carbon dioxide. Consequently this equilibrium was included in the model.

By splitting the reaction into various steps an equilibrium constant can be found.

$$H^+ + CO_3^{2-} \leftrightarrow HCO_3^- \qquad 2.42$$

has log K of 10.33 at 0.0 mol dm^{-3} [Smi82].

$$H^+ + HCO_3^- \leftrightarrow H_2CO_3^* \qquad 2.43$$

has been measured as log K = 6.35 at 0.0 mol dm^{-3} [Smi82]

Berg and Vanderzee [Ber78] reviewed the constants for the dissolution of atmospheric carbon dioxide and found log K to be -1.47 at 0.0 mol dm^{-3} for the reaction

$$CO_2(g) + H_2O \leftrightarrow H_2CO_3 \qquad 2.44$$

Combining all three steps gives a constant of 18.15 for reaction 2.41. Each step was corrected separately for ionic strength. The corrected constants were calculated to be 9.54 (reaction 2.42), 6.00 (reaction 2.43) and -1.53 (reaction 2.44). The corrected constants for the protonation of carbonate are the same as those reported at I = 0.7 mol dm^{-3} by Dyrssen and Hansson [Dyr73] and are close to those of Harned and Bonner (pK1C = 5.98) [Har45]. This gave an overall constant for reaction 2.41 of log K = 17.07 at 0.7 mol dm^{-3}. This is the form in which it is input to MINTEQA2 along with the partial pressure of carbon dioxide which is $10^{-3.5}$ atmospheres at atmospheric conditions. This gives a value of log Q = 20.57 for the quotient

$$[H_2O]/[H^+]^2[CO_3^{2-}] \qquad 2.45$$

This differs somewhat from the value of 20.80 used in the previous study [VdM90]. This discrepancy arises from the choice of value chosen for the protonation constants. Karen van der Meulen measured the constant for HCO_3^- to be 9.66 at an ionic strength of 0.7 mol dm^{-3} while Pytkowicz and Hawley [Pyt74] recommend a value of 9.68. This differs somewhat from the constants reported by Dyrssen and Hansson [Dyr73] (log K = 9.54), Thurmond and Millero [Thu82] (log K = 9.53) and Byrne and Miller [Byr85] (log K = 9.52) for I = 0.7 mol dm^{-3}. It was decided to use the value reported by Dyrssen and

Hansson as this has also been used in other model studies [Mot87]. However, to observe the sensitivity of the model to the value chosen for this constant the inorganic speciation results (pH = 8.1) were duplicated with log K = 9.68 as recommended by Pytkowicz and Hawley [Pyt74].

2.4.2.5.2 The stability constants for major cation-carbonate complexes

The formation constants for $NaHCO_3$, $NaCO_3^-$, $MgHCO_3^+$, $MgCO_3$, $CaHCO_3^+$ were taken from the seawater model of Pytkowicz and Hawley [Pyt74]. These constants have also been included in more recent models, most notably that of Motekaitis and Martell [Mot87]. The constants for $Mg_2CO_3^{2+}$ and $CaMgCO_3^{2+}$ were also taken from Pytkowicz and Hawley. The constants for potassium carbonate and bicarbonate were set equal to those for sodium.

Smith and Martell [Smi89] report log K to be -2.81 for the reaction

$$Sr^{2+} + CO_3^{2-} \leftrightarrow SrCO_3 \qquad 2.46$$

However, the original paper by Busenburg et al. [Bus84] reports log K to be 2.81 at 0.0 mol dm^{-3}. Consequently this value was corrected to an ionic strength of 0.7 mol dm^{-3} to give a log K of 1.40.

2.4.2.5.3 The stability constant for $UO_2OHCO_3^-$

Initial modelling studies revealed a significant $UO_2OHCO_3^-$ species which was contrary to the expectation that uranyl would exist primarily as $UO_2(CO_3)_3^{4-}$ and to a lesser extent as $UO_2(CO_3)_2^{2-}$ [Ahr85].

The uranyl-carbonate complexes have well established constants but the mixed hydroxycarbonate species are ambiguous and results are misleading [Gre91]. Smith and Martell report that for the reaction

$$UO_2^{2+} + CO_3^{2-} + H_2O \leftrightarrow UO_2OHCO_3^- + H^+ \qquad 2.47$$

log K = 4.1 at 0.1 mol dm^{-3} as was determined by Tsymbal [Tsy69].

However, Grenthe and Lagerman [Gre91] have reworked the data concerning mixed hydroxycarbonate species, including that of Tsymbal. They could not confirm the formation of $UO_2OHCO_3^-$ but discovered other species not included. Since Tsymbal is the only author who reports $UO_2OHCO_3^-$, it was decided to remove it from the database based on the recommendations of Grenthe and Lagerman who do not believe it exists.

2.4.2.5.4 The stability constants for MCO_3 (M = Mn, Fe, Co, Ni)

The formation constants for $MnCO_3$ and $FeCO_3$ are estimated from the technique recommended by Langmuir [Lan79]. Carbonate stability constants are calculated from oxalate stability constants such that log K_{MCO3° = 1.11 x log K_{MC2O4°. The formation constants for MnC_2O_4 and FeC_2O_4 are estimated from the equation developed by Yatsimirskii and Vasil'ev [Lan79] : log K_{assoc} = 2.5 + (0.47 x B) where B is 3.0 for Mn and 4.0 for Fe. This results in log K's for $MnCO_3$ and $FeCO_3$ at an ionic strength of 0.0 mol dm^{-3} of 4.32 and 4.86 respectively. When corrected to I = 0.7 mol dm^{-3} the stability constants are 2.98 and 3.50 respectively. Mention should be made that Bruno et al. [Bru92b] measured the formation constant for FeCO3 to be 5.5 at infinite dilution. This is somewhat higher than the value expected from the method of Langmuir [Lan79]. The latter value was still included in the database as Bruno et al. [Bru92b] measured their

constant from solubility data. Formation constants derived therefrom often have significant errors associated, because of kinetic factors.

The estimation of carbonate constants from oxalate constants was used in the model of Turner et al. [Tur81] for Mn and Fe as well as Ni and Co. It was also used for Mn and Ni in the study by Millero and Hawke [Mil92]. This relationship predicts a stability constants of 5.28 and 5.91 at 0.0 mol dm^{-3} for $CoCO_3$ and $NiCO_3$. When corrected to the ionic strength of seawater these constants become 3.92 and 4.55 respectively.

These constants are somewhat higher than those included in the compilations of Smith and Martell for an ionic strength of 0.7 mol dm^{-3}. These were measured by Zhorov et al. [Zho76] who found log K to be 3.17 for $CoCO_3$ and 3.57 for $NiCO_3$. The constant measured by Zhorov et al. compares favourably with that of Cosovic et al. [Cos82] who determined log K for $CoCO_3$ to be 3.15 ± 0.10 at an ionic strength of 0.56 mol dm^{-3}. Consequently the constants of Zhorov et al. [Zho76] were included in the model.

2.4.2.5.5 The stability constants for copper carbonates

Byrne and Miller [Byr85] determined log K to be 5.73 at an ionic strength of 0.7 mol dm^{-3} for the reaction

$$Cu^{2+} + CO_3^{2-} \leftrightarrow CuCO_3 \qquad 2.48$$

This is lower than the value determined by Symes and Kester [Sym85b] who found log K to be 6.28 at 0.7 mol dm^{-3}. However these authors ignored the formation of $Cu(CO_3)_2^{2-}$ which may account for the large constants reported. Zuelkhe and Kester [Zue83] report the stability constant to be 6.32 in seawater but they too ignore the dicarbonate species.

Bilinski et al. [Bil76] determined log K in 0.1 mol dm^{-3} KNO_3. They found log K to be 6.0 using anodic stripping voltammetry (ASV) and 6.1 using differential pulse polarography (DPP). They, however, did observe $Cu(CO_3)_2^{2-}$. Their results are in agreement with those of Byrne and Miller [Byr85] when converted to an ionic strength of 0.7 mol dm^{-3}. Consequently it was decided to use log K as 5.73.

Byrne and Miller [Byr85] report log K to be 9.3 at the ionic strength of seawater (0.7 mol dm^{-3}) for the reaction

$$Cu^{2+} + CO_3^{2-} \leftrightarrow Cu(CO_3)_2^{2-} \qquad 2.49$$

This agrees with the value found by Bilinski et al. of 9.7 using DPP at an ionic strength of 0.1 mol dm^{-3}. Log K was thus set to 9.3 in the model.

2.4.2.5.6 The stability constant for $ZnCO_3$

Stanley and Byrne [Sta90] measured the stability constant at an ionic strength of 0.68 mol dm^{-3} to be 3.30 for the reaction

$$Zn^2 + CO_3^{2-} \leftrightarrow ZnCO_3 \qquad 2.50$$

Previously this constant had been measured by Bilinski et al. [Bil76] to be approximately 3.9 in 0.1 mol dm^{-3} KNO_3 using DPP. This is in agreement with the result of Stanley and Miller. Zirino and Yamamoto [Zir72] estimated log K to be 5.3 at 0.0 mol dm^{-3}. However, this constant appears to be too large. The constant measured by Stanley and Byrne was thus used in the model.

They also measured log K to be 0.85 at an ionic strength of 0.68 mol dm^{-3} for the reaction

$$Zn^{2+} + HCO_3^- \leftrightarrow ZnHCO_3^+ \qquad 2.51$$

This was used in the model. Ferri et al. [Fer87a] observed the species $Zn(CO_3)_2^{2-}$ and $ZnCO_3(OH)_2^{2-}$. However, no account was made for $ZnCO_3$. As a result these species were ignored.

2.4.2.5.7 The stability constants for lead carbonates

The reported constants for the reaction

$$Pb^{2+} + CO_3^{2-} \leftrightarrow PbCO_3 \qquad 2.52$$

are associated with large uncertainties. Bilinski et al. [Bil76] measured this constant in 0.1 M KNO_3 to be 6.4 using ASV and 6.1 using DPP. Sipos et al. [Sip80] report this constant to be 5.62 in 0.7 mol dm^{-3} $NaClO_4$. Bilinski and Schindler [Bil82] report the stability constant to be 5.40 in 0.3 mol dm^{-3} $NaClO_4$. They determined this value from the solubility of cerrusite for which they calculated $\log K_{sp}$ to be -12.15 in 0.3 mol dm^{-3} $NaClO_4$ for the reaction

$$PbCO_3(s) \leftrightarrow Pb^{2+} + CO_3^{2-} \qquad 2.53$$

The solubility product reported by Bilinski and Schindler appears to be too low. Using stability constants from Smith and Martell, it was calculated that log K_{sp} for cerrusite should be -11.85 at I = 0.3 mol dm^{-3}. Thus reworking the data of Bilinski and Schindler [Bil82] one obtains 5.75 for the formation constant for $PbCO_3$ (reaction 2.52). It should be noted that in the paper by Bilinski et al. [Bil76] a reference is made to this constant

being measured as 5.75. This result agrees with the constants obtained by Bilinski et al. using DPP (0.1 mol dm^{-3}) and by Sipos et al. (0.7 mol dm^{-3}). Correcting these constants to the ionic strength of seawater, one obtains log K to be 5.61 at the ionic strength of seawater which was used in the model.

Bilinski et al. [Bil76] also report log K as 9.1 using DPP and 9.8 using ASV at an ionic strength of 0.1 mol dm^{-3} for the reaction

$$Pb^{2+} + 2CO_3^{2-} \leftrightarrow Pb(CO_3)_2^{2-} \qquad 2.54$$

Baranova [Bar69] determined this constant to be 9.0 at an ionic strength of 1.0 mol dm^{-3} using solubility data while Bilinski and Schindler determined it to be 8.86 in 0.3 mol dm^{-3} $NaClO_4$. Reworking this constant as before one obtains 9.21 for log K. Bilinski et al. [Bil76] report the measurement of this constant by Bilinski and Schindler as 9.15. Lastly Ferri et al. [Fer87b] measured this constant at an ionic strength of 3.0 mol dm^{-3} to be 8.9 ± 0.1 using potentiometric measurements. Combining all these reported constants and using LOGK, the formation constants were corrected to 8.96 at 0.7 mol dm^{-3}. This is the same value used by Byrne et al. [Byr88] in their model and was included in the database as such.

2.4.2.5.8 The stability constant of $CdCO_3$

Bilinski et al. [Bil76] measured this constant to be approximately 3.5 in 0.1 mol dm^{-3} KNO_3 using differential pulse polarography. Gardiner [Gar74] determined this constant to be 4.02 in 0.001 M KNO_3 at 20 °C. This is in agreement with the result of Bilinski et al. However, Zirino and Yamamoto [Zir72] estimated this constant to be 5.1 at infinite dilution. It was decided to correct the constant reported by Bilinski et al. [Bil76] to an

ionic strength of 0.7 mol dm^{-3}. The result was a log K of 3.09 which was included in the database.

2.4.2.5.9 The solubility products of calcium and magnesium carbonates

Initially the insoluble carbonates of magnesium and calcium were included in the model. The model predicted that these would precipitate under seawater conditions. Furthermore, it is expected that the precipitation of calcium carbonate is important in the regulating of pH. This was proposed by McDuff and Morel [McD80].

Ocean waters are nearly everywhere supersaturated with respect to calcium carbonate. Consequently it would be important to investigate this in the model. $CaCO_3$(s) exists as a solid in two different forms which have different solubility products viz. calcite and aragonite. The determination of the solubility products at low ionic strengths has been carried out with good reproducibility by a number of authors [Bac21, Fre29, Mil52, Yan54, Gre65, Lan68, Nak68, Bus82]. Because of the close agreement of values reported in these studies, the thermodynamic solubility products of calcite and aragonite may be taken as -8.50 and -8.30 respectively.

The apparent solubilities of synthetic calcite and aragonite in natural and synthetic seawater have been measured by several investigators (MacIntyre [Mac65], Ingle [Ing73], Berner [Ber75, Ber76], Plath [Pla79] and Morse, Mucci and Millero [Mor80]). In general these are somewhat less (about 20%) than the values calculated from the thermodynamic constants and activity coefficients [Mor80].

Morse et al. propose that this is due to the formation of surface layers of lower solubility than the pure solid on calcite and the slow precipitate inversion on ageing of aragonite [Mor86]. Thus in instead of the thermodynamic solubility products, apparent solubility

products were used to better represent the real system. These were taken from Morse et al. Hence log K_{sp} values of -6.35 and -6.15 were used for calcite and aragonite respectively.

Magnesium is able to precipitate from solution in a variety of forms. In increasing order of solubility these are dolomite, $MgCa(CO_3)_2$; magnesite, $MgCO_3$; nesquehonite, $MgCO_3.H_2O$ and lansfordite, $MgCO_3.5H_2O$. The solubility products of these carbonates are not well-defined. Magnesite solubility products at 0.0 mol dm^{-3} range from -8.20 (Robie and Hemingway) to -7.46 (Halla) [Stu81]. The latter value is that recommended by Smith and Martell and corrects to -6.30 at the ionic strength of seawater. For dolomite, which has an even greater variation of reported values (-16.5 to -19.0 at infinite dilution), the value found by Langmuir [Lan68] was used in the model. This adjusts to -14.58 at the ionic strength of seawater.

2.4.2.6 The stability constants for metal chlorides

Because of the high chloride concentration in seawater it is expected that chlorides will form a significant fraction of the inorganic speciation of trace metals in seawater. Most of these were taken from the compilations by Smith and Martell [Smi76, Smi82, Smi89].

2.4.2.6.1 The stability constant for $FeCl^+$

Smith and Martell do not report a stability constant for $FeCl^+$. Kester et al. [Kes75b] report log K to be 0.79 at infinite dilution. Davison [Dav79] on the other hand estimates log K to be 0.14 at infinite dilution and -0.45 at an ionic strength of 0.7 mol dm^{-3}. This constant was also used in the models of Turner et al. [Tur81] and Byrne et al. [Byr88].

Recently Heinrich and Seward [Hei90] measured the association constant for $FeCl^+$ using a spectrophotometric technique and found log K to be -0.16 at I = 0.0 mol dm^{-3} which is

less than Davison [Dav79]. However, they quote a maximum uncertainty range of -0.30 to 0.13. Davison's constant is at the upper end of this range.

Because the results of Davison [Dav79] lie between the extremes of Kester et al. [Kes75b] and Heinrich and Seward [Hei90], and Davison's constant was used in previous models, log K for $FeCl^+$ was set to -0.45 at the ionic strength of seawater.

2.4.2.7 The redox state of the ocean

To simplify the model an assumption needs to be made about the redox state of the ocean. The redox potential is difficult to measure [Ben73, Stu81] as the redox processes tend not to be at equilibrium. Nevertheless, steady state concentrations tend to be assumed by the individual redox species. Secondly, and more importantly, there is a lack of coupling between the various redox processes. Furthermore they are continuously perturbed by the biological cycle [Mur88]. Consequently the ocean cannot be characterized by a unique pE [Stu81, Mur88].

A simplifying assumption would be to determine a dominant redox couple which would regulate the redox state of the ocean. Unfortunately there is no agreement on this couple.

Sillén [Sil65a, Sil65b] proposed that the oxygen-water couple was the dominant couple and this is generally accepted even though the pE of the ocean may in fact be somewhat less than that predicted. This acceptance is based on the fact that oxygen is abundant in the atmosphere and so could have a strong influence. Oxygen acts as a strong oxidant where the full biologically mediated four electron reduction of oxygen occurs.

The oxygen redox half-cell reaction is

$$¼O_2(aq) + H^+ + e^- \leftrightarrow ½H_2O \qquad 2.55$$

which has a log K of 20.78 at 0.0 mol dm^{-3}. By assuming a constant partial pressure of oxygen of 0.2095 atm this gives a conditional constant of 20.61 for the quotient

$$[H_2O]^{½}/[H^+][e\text{-}] \qquad 2.56$$

This adjusts to 20.39 at 0.7 mol dm^{-3}. Consequently pE is fixed by the relation

$$pE = 20.39 - pH \qquad 2.57$$

This gives a value for the pE of 12.3 at a pH of 8.1.

Breck [Bre72] has challenged Sillén's proposal. Instead he has proposed the two electron reduction of oxygen to hydrogen peroxide as the dominant couple owing to the kinetic difficulty of breaking the oxygen-oxygen bond.

$$O_2 + e^- + 2H^+ \leftrightarrow H_2O_2 \qquad 2.58$$

This has log K = 23.1. By knowing the oxygen partial pressure a conditional constant of 11.21 is calculated for

$$[H_2O_2]^{½}/[H^+][e^-] \qquad 2.59$$

This is converted to 10.99 at the ionic strength of seawater. Unfortunately to be useful a knowledge of the activity of hydrogen peroxide in seawater is necessary. This is

analytically difficult to measure since it is both small and highly variable owing to the ready metal catalysed decomposition of peroxide to oxygen and water in seawater. Breck estimated the peroxide activity of seawater to be 10^{-11} mol dm^{-3} which determines the pE of the ocean according to the relation

$$pE = 16.49 - pH \qquad 2.60$$

At a pH of 8.1 this gives a pE of 8.4. The true redox state of the ocean may lie somewhere between this and that proposed by Sillén. Furthermore, individual redox reactions are not necessarily coupled with each other and deviations from results predicted by a universal pE may occur. Sillén himself recognized this because N_2 is observed as the main form of nitrogen in seawater whereas his calculations predicted that NO_3^- should be the dominant form in seawater [Sil64].

2.4.2.8 Formation constants of mixed ligand species

Dyrssen and Wedborg [Dyr74] have indicated that mixed ligand complexes may be significant for copper, zinc and mercury in seawater. To ascertain the importance of such species mixed halide, hydroxycarbonate and in the case of mercury hydroxyhalide complexes were added to the model. The hydroxyphosphate species added in the previous study [VdM90] were removed because of a lack of data for the $M(HPO_4)_2$ species. These constants were estimated as two to three log units greater than the $MHPO_4$ species. However, the mixed hydroxyphosphate species proved insignificant and thus their exclusion here is justified. The mixed halides were chosen because of the high concentration of halides in seawater while hydroxycarbonates were included because of the high carbonate concentration and high pH.

Where formation constants for hydroxycarbonates existed (uranyl and mercury) the original constants as published by Smith and Martell [Smi76. Smi82, Smi89] were corrected to the relevant ionic strength. For $FeOHCO_3$ the constant reported by Bruno et al. at an ionic strength of 0.0 mol dm^{-3} was corrected to the ionic strength of seawater [Bru92a]. In the case of $PbOHCO_3^-$ and $CuOHCO_3^-$, the formation constants were calculated from log K values for $M(OH)_2$ and $M(CO_3)_2^{2-}$ according to the method discussed earlier. Log K_S was set to zero for both the hydroxycarbonates as well as the mixed halide species included in the model. Mixed halide species were included for Cu^+, Ag^+, Sn^{2+}, Cd^{2+}, Hg^{2+} and Pb^{2+}. The mercury hydroxyhalide constants were corrected directly from those listed by Smith and Martell.

2.4.3 Temperature and ionic strength adjustments

The formation constants used in the model were chosen to be valid for a temperature of 25 °C. This is at the upper end of seawater temperatures but is closer to that found for surface waters. However, the majority of formation constants are published at 25 °C [Smi76, Smi82, Smi89]; so by setting the model up at this temperature the number of adjustments necessary would be kept to a minimum. Other model studies are also performed at this temperature so it would be preferable to keep the temperature the same for comparative purposes.

None of the inorganic species needed correction for temperature. It was only in the cases of formation constants for the species formed between metal ions and the model ligands for fulvic acid that temperature corrections were needed. Here constants were corrected from 20, 30 and 37 °C. The temperature ranges are small, so the assumption of constant ΔH_m^{θ}'s is justified. Note, however, that in many cases ΔH values were not available so those from similar transition metals were used. Nevertheless the change brought about in

log K was always small. The greatest source of error comes not from the correction for temperature but from the reported constants themselves.

Constants were corrected for ionic strength using LOGK. Where conditional values and thermodynamic values were available, the conditional values were chosen as there were no indications of the correction methods used in extrapolating to zero ionic strength to obtain the thermodynamic constants.

2.4.4 The use of MINTEQA2 for modelling

In order to use MINTEQA2 to model the speciation in seawater, the thermodynamic database (relevant to an ionic strength of 0.0 mol dm^{-3}) which came with the package was replaced by the thermodynamic database in Appendix 1. Certain features of MINTEQA2 were not used in this model study. Since modelling would be performed at 25 °C, no corrections for temperature would be required by the program and all the ΔH's were set to zero in the database. Similarly all the Debye-Hückel parameters required by the database were also set to zero as no ionic strength correction would be done by MINTEQA2.

The size of this database necessitated changes to the limits for which MINTEQA2 was designed. Two variables were changed by parameter statement in the subprogram MINTEQA2.INC. NXDIM (the maximum number of components) was set equal to 85 and NYDIM (the maximum number of species formed) was set equal to 1200. Furthermore, the dimension statements for the variables IPTA and IDYDUM in MINTEQA2.INC were changed. Originally these variables had dimension (NXDIM,100) and (100) respectively. This was changed to (NXDIM,250) and (250). The program was then recompiled.

The model was run by 'fooling' MINTEQA2 such that it did not use its own correction procedures to correct for ionic strength. This was done by correcting constants to 0.7 mol dm^{-3} and then substituting them into the MINTEQA2 database. MINTEQA2 was then asked to correct to an ionic strength of 0.0 mol dm^{-3} so that no correction took place. This approach was preferable to correcting all constants to zero ionic strength and then allowing MINTEQA2 to iteratively calculate an ionic strength. Firstly it made running the program much faster; secondly MINTEQA2 uses slightly different correction procedures to LOGK so in the worst case a constant that was corrected from 0.7 mol dm^{-3} to 0.0 mol dm^{-3} and then back again might appear somewhat different. The error is minimized by the approach used since only one set of ionic strength adjustments is made. It should be noted that the constants entered into the MINTEQA2 database for solid species are in fact (- log K_{sp}). H_2O was excluded from the reactants used in the model. The reason for this is that MINTEQA2 corrects the activity of water according to following formula

$$\{H_2O\} = 1 - 0.017 \sum_{i=1}^{n} C_i \qquad 2.61$$

where $\{H_2O\}$ is the activity of water and C_i is the concentration of the individual ions in the liquid. As can be seen, this correction is independent of the ionic strength to which MINTEQA2 is supposed to correct constants. Consequently, the activity of water in the seawater model is not unity when MINTEQA2 models at an ionic strength of 0.0 mol dm^{-3}. To get around this, water was left out as a reactant thereby making the activity unity.

Initial runs using MINTEQA2 revealed that the program was still correcting some formation constants even though the program was being asked to run at an ionic strength of 0.0 mol dm^{-3}. It was discovered that MINTEQA2 contained some formation

constants in a database called ANALYT.DBS which superceded the corresponding constants in the main database. The solution to this problem was to delete all the constants in ANALYT.DBS. A further restriction with MINTEQA2 was that when the program PRODEFA2 was used to create an input file for the model, it included a maximum of 50 adsorption reactions in the input file. Where more reactions were required, these were inserted into the input file by editing it with the VAX editor.

2.5 VALIDATION OF THE MODEL

Before using the model to calculate the speciation of the trace elements, it was necessary to validate it by comparing the computed results with those reported in the literature for experimental determinations. Reported experimental results concern the pH, carbonate concentration and the precipitation (or inhibition thereof) of the major cations.

2.5.1 Validation with respect to pH

2.5.1.1 The measurement of pH in seawater

pH has been defined in terms of hydrogen activity [Sor24, Sor27] as follows:

$$pH = - \log \{H^+\} \qquad 2.62$$

Unfortunately, the practical measurement of pH is not possible with such a definition because of the immeasurability of single ion activities.

Consequently, operational methods are used to measure pH. IUPAC have standardized these approaches [Cov85].

pH is determined from the comparison of the sample solution with a standard buffer of assigned pH(S) in the cell

Reference electrode | KCl (> 3.5 mol dm^{-3}) | X or S | Glass electrode.

The pH(X) of the sample is given by

$$pH(X) = pH(S) + [E(S) - E(X)]/gt - [E(JS) - E(JX)]/gT \qquad 2.63$$

where $g = (R/F)\ln 10$;

R is the universal gas constant;

F is the Faraday constant;

T is the absolute temperature;

E(S) and E(X) are the cell potential differences in the standard and sample solutions respectively

and E(JS) and E(JX) are the liquid junction potentials in the standard and sample solutions.

Operationally pH is defined by setting the term involving liquid junction potentials to zero. The pH(S) of the IUPAC standard buffers are assigned by measurements on cells without liquid junction potentials or alternatively to a single standard buffer.

Unfortunately the conditions in seawater are not the same as those envisaged in the operational definition. Because the sample and the standard buffer solution differ markedly in ionic strength, the residual liquid junction potential is definitely not zero and manifests itself as an error in pH(X).

An alternative pH scale for seawater can be defined in terms of the total hydrogen ion concentration [Bat82] :

$$pH = - \log (m_H{}^T) \qquad 2.64$$

where $m_H{}^T$ is the sum of the free and complexed hydrogen ion molalities in the seawater sample.

This scale was originally proposed by Hansson [Han73]:

$$pH(SWS) = pH_t = pm_H - \log(1+ ß_{HSO4}m_{SO4}) \qquad 2.65$$

where m_H is the free hydrogen ion molality;

m_{SO4} is the free sulphate molality

and $ß_{HSO4}$ is the formation constant for the hydrogen sulphate ion.

The pH(SWS) is based on synthetic seawater containing sulphate and buffered with 2-amino-2-hydroxymethyl-1,3-propanediol (Tris). Because the hydrogen sulphate ion is formed the total hydrogen ion concentration differs from the concentration of the free uncomplexed hydrogen ion. The pH(SWS) of the Tris reference buffer is determined by titration with hydrochloric acid to a final pH of 3. By matching the ionic strength of the standards to that of seawater, the residual liquid junction potential is minimized. If seawater rather than pure water is considered as the solvent, then the minor components (less than 1% of ionic strength) can be considered to have activity coefficients of unity. The pH(SWS) scale is then equivalent to the hydrogen ion activity scale in seawater [Cov88].

Because the saline standards required for seawater measurements using the above scale need to be individually prepared, the use of the standard reference buffers as recommended by IUPAC is still favoured [Cov88]. Covington and Whitfield [Cov88] recommend that the electrode pair should be characterized over the ionic strength and temperature ranges being investigated to assess the impact of the systematic errors associated with the variations in liquid junction potentials and the hydrogen ion activity coefficient.

Covington and Whitfield discuss how systematic errors might arise using the IUPAC scale, pH(X) or the pH(SWS) scale. They recommend that parameters that give a measure of the systematic error such as the difference between the pH assigned to a particular buffer and the pH measured by the electrode pair relative to another selected standard of assigned pH, be reported together with the relevant pH(X) or pH(SWS) values.

Furthermore they discuss the considerable advantages that arise from the use of a cell with a renewable liquid junction such as the Culberson cell. This leads to increased precision and minimizes the need for standardization.

Bates [Bat82] has reported how the various scales for pH of seawater are related. The pH(SWS) is related to the free hydrogen ion molality by

$$pH(SWS) = pm_H - 0.130 \qquad 2.66$$

assuming m_{SO4} to be 0.029 mol kg^{-1} and $ß_{HSO4}$ to be 12. The molality of the free ion is related to the activity of the free ion by

$$pm_H = pa_H - 0.080 \qquad 2.67$$

assuming the activity coefficient of the free hydrogen ion to be 0.83. The IUPAC scale (as developed from the pH_{NBS} scale of the United States National Bureau of Standards) is related to the free ion activity by

$$pH(X) = pa_H - 0.076 \qquad 2.68$$

Where the concentrations are expressed in terms of moles per kilogram of seawater instead of moles per kilogram of water (molality), all values in the above equations are increased by 0.015.

Unfortunately many of the reported pH values for seawater do not include the method of measurement. Estimates of the error in these measurements are also often not reported.

In the results section of this thesis, pH is defined in terms of the free hydrogen activity as in the Linderstrom-Lang-Sorenson definition. This is because speciation calculations have been performed using the computer program, MINTEQA2. This allows individual ion activities to be calculated or specified. Thus where the influence of pH is investigated, pH refers to the Linderstrom-Lang-Sorenson definition and not that recommended by IUPAC or the pH(SWS) scale.

2.5.1.2 Validation procedures with respect to pH performed using MINTEQA2

The pH of seawater is the result of the interactions of the major cations as well as the carbonate and carbon dioxide equilibria [McD80]. Thus if the pH predicted by the model were to agree with experimentally determined results this would validate not only the acid-base equilibria but also the interactions of the major ions which determine their free concentrations.

Unfortunately it was not possible to allow MINTEQA2 to predict a pH. Where carbon dioxide was excluded from dissolving it was hoped that by running the model without a fixed pH, a free hydrogen activity would be predicted by MINTEQA2 and consequently a pH could be determined which could then be compared with experimental observations. However, if carbon dioxide is excluded from dissolving, it was found that there are insufficient constraints to fix a free hydrogen ion concentration as no indication of total dissolved hydrogen was supplied to the model. This would require the model being supplied with an additional parameter such as alkalinity.

If carbon dioxide is allowed to dissolve, an additional parameter is supplied viz. the free hydrogen concentration is related to the free carbonate ion concentration by equation 2.45 while the free carbonate concentration is also constrained by the total carbonate concentration. Thus it was expected that free hydrogen ion concentration could be calculated by MINTEQA2. However, when MINTEQA2 allowed carbon dioxide to dissolve, it removed the constraint on the total concentration of carbonate i.e. total dissolved carbonate concentration in seawater was no longer fixed at 2.05 mmol dm^{-3}.

Consequently it was not possible to validate the model with respect to pH. However, an alternative approach was employed. This involved comparing the total carbonate concentration (at fixed pH) predicted by the model to that observed experimentally.

2.5.2 Considerations on the dissolution of atmospheric carbon dioxide

When the model was run for the first time, it was observed that the model predicted a total carbonate concentration of 1.94 mmol dm^{-3} which differed from the measured carbonate concentration of 2.05 mmol dm^{-3}. This appeared to be somewhat surprising

but is in fact not so. Rearranging the conditional constant 2.45 gives the following relation

$$\log [CO_3^{2-}] = \log [H_2O] + 2\ pH - 20.57 \qquad 2.69$$

Because the pH is fixed and the activity of water is set at unity, the above relation fixes the free carbonate concentration at 42.7 μmol dm^{-3}. This in turn fixes the total concentration of carbonate at 1.94 mmol dm^{-3}. This differs from the analytical concentration of 2.05 mmol dm^{-3}.

The two concentrations are in close agreement though. The small discrepancy can be explained by the fact that when the value of quotient 2.45 is changed slightly to 20.54, MINTEQA2 predicts the analytical carbonate concentration. The difference between calculated and experimental carbonate concentrations can be ascribed to the uncertainty in the equilibrium constant for reaction 2.41. Interestingly if the quotient was set to 20.71 as would be the case if the value recommended by Pytkowicz and Hawley [Pyt74] was used for the stability constant for reaction 2.41, the dissolved concentration of carbonate shows an even greater discrepancy with experimental observations. In this case MINTEQA2 predicts the dissolved carbonate concentration to be 1.81 mmol dm^{-3}.

Furthermore the solubility of carbon dioxide decreases with increasing temperature [Bea89]. The model was run at 25 °C which is slightly higher than that measured experimentally. As a result, if the temperature of seawater were raised to 25 °C as in the model, less carbon dioxide would be expected to dissolve as observed. Lastly there is also an uncertainty in the ocean pH which will affect the free carbonate concentration as predicted by equation 2.45.

It can be seen that the dissolved carbonate concentration as predicted by the model is in reasonable agreement with that measured experimentally. This result represents a plausible validation of the model.

Even though the discrepancy was small it was decided to run the model in duplicate. In one atmospheric carbon dioxide was allowed to equilibrate with the aqueous phase while in the other dissolution of atmospheric carbon dioxide was disallowed. The difference between the two models is evident at high pH's where equilibration increases the dissolved carbonate concentration.

2.5.3 The precipitation of calcium and magnesium carbonates from surface seawater

Initial modelling runs showed that calcite was very close to precipitating out of solution while dolomite and magnesite did in fact precipitate out. The consequence of this is that the dissolved concentration of calcium and magnesium would be different from what is experimentally measured [Cul65, Bru83].

A slight increase in the pH brought about calcite precipitation. This was the result of the increase in free carbonate concentration that arose because of the dissolution of CO_2 [equations 2.41 and 2.45]. Where magnesite was allowed to precipitate this reduced the dissolved magnesium concentration to 13.4 mmol dm^{-3} or 24.6% of the measured value (carbon dioxide allowed to dissolve). Where carbon dioxide was excluded, magnesite precipitation reduced the dissolved magnesium concentration to 52.9 mmol dm^{-3} or 97.1% of the measured concentration. The effect of dolomite precipitation was even more drastic where carbon dioxide was included in the model. The dissolved magnesium concentration decreased to 44.2 mmol dm^{-3} or 81% of the measured concentration while the dissolved calcium concentration dropped considerably to 0.17 mmol dm^{-3} or 1.6 % of the analytical value. If carbon dioxide is excluded the dissolved magnesium

concentration is observed to be 53.6 mmol dm^{-3} (98.3% of the total) and the dissolved calcium concentration to be 9.6 mmol dm^{-3} (91.3% of the total). The model is thus not validated when these minerals are allowed to precipitate as the calculated major ion concentrations are no longer in agreement with the analytical concentrations.

Ahrland [Ahr75] points out that neither magnesite or dolomite are precipitated from surface seawater even though they have been found in sedimentary rock and the ocean is supersaturated with respect to these minerals. The fact that the model predicts their precipitation means that some other factors suppress the precipitation and concomitant decreases in major ion concentration. These anomalies may be explained by kinetic restrictions.

Dolomite precipitation in particular is dominated by kinetic rather than thermodynamic constraints. Machel and Mountjoy [Mac86] observed that despite its high degree of supersaturation, dolomite did not precipitate from seawater. Folk and Land [Fol75] ascribe this to the high degree of Ca-Mg ordering that is required for dolomite formation and that sulphate in high concentrations such as in seawater inhibits precipitation.

Magnesite is also subject to kinetic constraints. The hydration energy of magnesium ions is 20% higher than that of calcium which combined with the low activity of free carbonate ions means that the precipitation of magnesium rich carbonates over calcium rich carbonates is disfavoured. This is because very few carbonate ions have sufficient kinetic energy to penetrate the hydration barrier of magnesium [Fol75].

To reflect the kinetic inhibition of magnesite and dolomite precipitation in the present study, their solubility products were removed from the database.

The solubility products in seawater of calcite (log K_{sp} = -6.35) and aragonite (log K_{sp} = -6.15) would indicate that calcite should precipitate more readily from seawater than aragonite. Several investigators [Kit62, Sim64, Lip73, Ber75a] indicate that the presence of dissolved magnesium suppresses the precipitation of calcite and favours the precipitation of aragonite over calcite. Several other authors indicate that magnesium also suppresses the conversion of aragonite to calcite via dissolution and reprecipitation [Bis68]. Morse [Mor86] reveals that this is the consequence of the solubility of a solid being the result of an equilibrium between the surface composition of the solid and the solution. Two possible hypotheses are :

1) Mg^{2+} acts as a surface poison [Mac86] by being adsorbed as hydrated ions onto the active growth sites [Lip73] and thereby inhibits the spread of monomolecular steps on the crystal surface. It therefore inhibits calcite nucleation and/or growth [Bis68].

2) The incorporation of magnesium into the growing crystal results in a precipitate whose solubility is significantly increased [Win69, Ber75a].

The results of Berner [Ber75a] show that dissolved magnesium severely retards the rate of calcite precipitation. He demonstrates that hypothesis 1 is not quite true since no inhibition occurs at low magnesium concentrations. However the high Mg^{2+}/Ca^{2+} ratio of five to one in seawater means that magnesium may effectively compete with calcium for surface sites. The incorporation of magnesium to form magnesian calcite in the calcite crystal results in increased solubility as was demonstrated by Berner [Ber75a]. He concluded that magnesium was adsorbed on to the surface and subsequently incorporated into the crystal structure which resulted in thermodynamic destabilization and therefore increased solubility. Analysis of precipitates from seawater on pure synthetic calcite seed showed that the precipitate contained 7 to 10% $MgCO_3$. Berner concluded that the

minimum degree of supersaturation required to precipitate calcite from surface seawater is greater than that predicted by thermodynamic solubility products as a result of the increased solubility of magnesian calcite when compared to pure calcite. Aragonite is thus the most stable form of calcium carbonate in seawater. Studies of modern marine sediments reveal only aragonite and high-Mg calcite are found. No low-Mg or pure calcite was found [Bri71].

Aragonite precipitation is not influenced by dissolved magnesium since the latter is neither adsorbed nor taken up in the crystal lattice. Berner, however, showed that an appreciable mass of aragonite seed crystals would be required to initiate precipitation. This is in line with the prediction that aragonite does not precipitate from seawater at normal pH's. It requires the intervention of marine organisms for the precipitation of calcium carbonate in their skeletons [Bea89]. Thus inorganic (that is without the intervention of living organisms) precipitation is not spontaneous in surface seawater because of the inhibition of Mg^{2+} [Mur88].

To reflect the fact that calcite precipitation is kinetically inhibited in seawater, the solubility product for calcite is removed from the database in the present study. Zhong and Mucci [Zho93] have recently measured the kinetics of calcite precipitation in seawater and it is hoped that in the future that this will be one of the examples of kinetically-determined reactions to be included in the model. For the present though, aragonite is used to model calcium carbonate solubility.

2.5.4 Considerations on the redox state of the ocean

The measurement of the redox state of the ocean is difficult since it is likely to reflect the redox level of one couple only [Stu81]. Consequently there is a wide range of reported

pE values (from E_h measurements) and much debate over an acceptable indicator couple [Sill65a, Sil65b, Bre72, Ben73].

The oxygen-water couple fixes the pE at 12.29 according to equation 2.57 while the oxygen-peroxide couple fixes the pE at 8.39 according to equation 2.60. It was decided to scan the pE between 8.4 and 12.3 as these two couples appear to be extremes.

Liss et al. [Lis73] measured the dissolved iodide and iodate concentrations as well as dissolved nitrate and nitrogen concentrations in seawater. They found $[IO_3^-]/[I^-]$ to be 20 which predicted a pE of 10.6 at pH = 8.0. They calculated a pE = 10.5 from the N_2/NO_3^- data.

The model was scanned between pE = 8.4 and pE = 12.3. It was found that the ratio $[IO_3^-]/[I^-] = 20$ at 10.25. The discrepancy with the result of Liss et al. arises because these authors used a constant for the IO_3^-/I^- equilibrium which was not corrected for ionic strength. Furthermore they did not take into account the formation of $MgIO_3^-$. They also calculate a pE at pH = 8.0. At pH = 8.1 they would have found the pE to have been 10.5 as predicted by the iodate/iodide system. However, the concentration ratio used by Liss et al. [Lis73] is for deep water. In surface seawater $[IO_3^-]/[I^-] = 3$ which the model found to occur at pE = 10.10. Nevertheless the results indicate that the pE of the ocean probably lies somewhere between the limits proposed by Sillén and Breck.

A further complication with regard to the redox state of the ocean regards the Cr^{3+}/CrO_4^{2-} equilibrium. The kinetics of the oxidation of chromium (III) to chromium (VI) are notoriously slow. The model calculated the dissolved chromium (III) concentration to be 2.64×10^{-19} mol dm^{-3} at pE = 8.4 and 5.27×10^{-31} mol dm^{-3} at pE = 12.3. These are much lower than the surface chromium (III) concentration measured by Emerson et al. [Eme79]. Similar distributions of CrO_4^{2-} and Cr^{3+} have been found

by Van den Berg et al. [VdB94] although they observed the CrO_4^{2-} concentration to be in the range 3 - 4 nmol dm^{-3}. It was decided to remove the Cr^{3+}/CrO_4^{2-} couple and to enter chromium (III) and chromate as separate components with concentrations of 0.15 nmol dm^{-3} and 2 nmol dm^{-3} respectively. This was to reflect the slow kinetics of oxidation and that both are observable trace components in seawater.

2.6 EXTENSION OF THE MODEL TO INCLUDE ORGANICS

The existence of metal-organic complexes in seawater was postulated as long ago as 1928 [Har28] to explain the apparent supersaturation of ferric ions in seawater. Only recently though have techniques been developed to isolate and characterize metal-organic complexes.

Most models of trace metal speciation in seawater disregard the formation of organic complexes and deal only with inorganic speciation [Gar62, Zir72, Whi73, Whi75b, Mil92]. Others have modelled the influence of organic matter by using single organic molecules which have rigorously known formation constants such as EDTA [Spe58, Duu70, Mal71, Flo76, Gar76, Whi80, Mot87], NTA [Ras77, Whi80, Mot87, Ras88], acetic acid and glycine [Dyr74, Stu75], salicylic acid [Stu70a], and 4-sulphosalicylate [Mot87], pthalic [Stu75], tartaric [Stu75] , glutamic [Stu75] and citric acids [Stu70a, Stu75, Whi80, Mot87]. Strong, non-specific binding agents such as EDTA and NTA tend to overestimate organic complexation [Flo76, Man78, Ras84b] while the rest tend only to complex those metals which bind with their particular donor group which leads to underestimation. An alternative approach is to use the average binding constants which have been determined empirically using natural samples [Man78, Tur81]. Unfortunately this is only valid for the experimental conditions at which the measurements were made and depends on the method of determination used [Buf88].

2.6.1 Marine Organic Matter

There are a whole host of organic molecules in seawater of extreme complexity. Among their properties are the ability to complex metals [Des70, Flo80, Tur85]. 80% of this material has not been characterized.

The low molecular weight organic matter (< 200 g mol^{-1}) consists of free amino acids, fatty acids and carbohydrates. They rarely comprise more than 20% of dissolved organic matter and are unlikely to have a significant effect on metal speciation as a result of their low concentration and rapid recycling by microorganisms [Duu81].

About 80% of marine organic matter consists of high molecular weight, macromolecular compounds which are composed of fulvic acid, humic acid and humin. The distinction between these classes is that proposed by Rashid and King [Ras70]. The humic acid fraction is that fraction that is extracted in alkaline solutions but precipitates in acid solutions whereas fulvic acid does not precipitate on acidification. Humin is the fraction of organic matter that is not extractable in alkaline solutions and is also called kerogen. Fulvic acids interact more strongly with metals than other humic materials [Ste77, Pio84]. Duursma [Duu65] and Ogura [Ogu72] report that only 10-20% (0.1 to 0.2 mg dm^{-3}) of dissolved organic carbon exists as humic material. Ishiwatari indicates the average to be 20% [Ish92]. The concentration of dissolved humic substances is much higher in freshwater than seawater [Ras84a]. Harvey et al. [Har83] found the marine fulvic acid concentration to range from 0.2 to 1.2 mg dm^{-3} with the humic acid concentration being much lower. However, humic substances (fulvic + humic acid) have a higher concentration in sediments than in the overlying water so here the effect of fulvic and humic acids may well be significant. Reported percentages are 60% of total organic matter [Mac78] or 40 - 70% [Nis76]. Some authors report organic matter concentrations of 1 to 2.4 mg dm^{-3} (2 x DOC; based on 50% C) [Ish92]. In the present

work, it was decided to model the effect of marine organic matter using fulvic acids as model compounds as these form the best characterized fraction of marine organic matter.

Marine organic matter differs from that found in rivers and soils. This is the result of their formation in the marine environment and the lack of terrestrial precursors like lignin which result in aromatic compounds [Stu76a]. The contribution of rivers to marine organic matter is small [Duc77]. It is easily distinguishable from terrestrial fulvic acids by several features which will be discussed hereafter such as an increased nitrogen content [Stu78a, Ras84a], lower aromaticity [Stu76a, Pio84] and a higher H/C ratio [Stu78a]. CP/MAS ^{13}C-NMR studies by Gillam and Wilson show that marine organic matter is likely to be derived from marine diatoms and not terrestrial sources [Gil83].

2.6.2 Characterization of marine organic matter

An attempt was made in this study to extract fulvic acid from the sea. It was hoped that the characteristics of this fulvic acid could be used as input for RANDOM. However, the organic matter extracted was not suitable for detailed characterization. The extraction procedure and the results of the tests performed on the extracted marine organic matter are discussed in Appendix 3.

2.6.2.1 Elemental composition

Table 2.6.1 contains information on the elemental composition of marine organic that has been reported in the literature. It should be noted that the samples whose elemental compositions are reported in the literature include both fulvic and humic acids. They were also extracted from seawater as well as marine and estuarine sediments. Note that the procedures used for separating humic and fulvic acid samples are not always the

same. Often no separation was performed. Consequently some of the results in Table 2.6.1 are for combined samples.

The following general observations may be made :

i) the oxygen content is much higher in fulvic acids than in humic acids [Ras84a]. This is accompanied by a lower %C in fulvic acids.

ii) marine samples have a much lower C/N ratio than terrestrial samples [Stu76a, Stu78a, Ras84a, Hed92] which indicates a higher nitrogen content.

iii) marine samples have a higher H/C ratio than terrestrial samples [Stu76a, Stu78a, Hed92] indicating lower aromaticity.

2.6.2.2 Oxygen-containing functional group composition

Severe problems are encountered when determining the functional group composition of humic materials [Dub63]. The methods used are reviewed by Stevenson and Butler [Ste69] and Schnitzer and Khan [Sch72].

Phenolic hydroxyl groups are determined by initially determining total acidity of the sample (by reaction with 0.25 mol dm^{-3} $Ba(OH)_2$ [Bro57, Ras70] followed by titration with 0.1 mol dm^{-3} HCl) and then subtracting the carboxyl content which is determined by the calcium acetate reaction. The applicability of this last reaction, recommended by Wright and Schnitzer [Wri60] and Schnitzer and Gupta [Sch65a] has been questioned [Dub64, Ste72, Per80]. Consequently the results reported in the literature are open to review. Total hydroxyl group concentrations are determined by acetylation with acetic anhydride, liberation of the acetic acid and titration with 0.2 mol dm^{-3} KOH [Cla36, Sch65b]. Alcoholic hydroxyl groups are calculated by subtracting phenolic groups. Carbonyl groups are determined by oximation [Fri59, Sch66]. Functional group data may

Table 2.6.1 The elemental composition of marine fulvic and humic substances

Reference	Elemental composition				
	% C	% O	% N	% S	% H
Ert83 (H/F)					
Range	47.22 - 56.15		4.13 - 5.63		4.77 - 6.18
Mean	53.01		4.91		5.62
Ras84a (H)¶					
Range	52.9 - 54.1	31.4 - 32.4	4.2 - 4.2	1.4 - 2.2	5.5 - 6.7
Mean	53.5	31.9	4.2	1.8	6.1
Stu74 (F)	49.98	36.40	6.40	0.46	6.76
Ish77 (H)	51.10	36.61	7.06		5.23
Fuk94 (H)	49.1	33.5	5.48		6.10
Shi87 (H)	49.8		4.6		5.4
Hat80 (H/F)§					
Range	53.45 - 56.38	31.60 - 36.03	2.57 - 5.09		5.61 - 5.97
Mean	55.28	34.19	4.23		5.80
Nis79 (H)					
Range	48.9 - 59.8		1.1 - 5.6		
Mean	54.5		3.9		
Nis79 (F)					
Range	38.4 - 53.8		2.8 - 4.5		
Mean	47.5		3.8		

Kal88 (H/F)[#]	42.22 - 52.34	33.09 - 44.28	4.90 - 5.64	1.88 -2.34	6.00 - 7.03
Shi91a (H/F)					
Range	50 - 54		4.2 - 5.4		5.0 - 6.7
Mean	52.25		4.8		5.85
Ras70 (H)					
Range	50.2 - 63.6	24.1 - 40.6	3.6 - 5.6		5.5 - 7.3
Mean	56.1	32.9	4.7		6.3
Ras70 (F)					
Range	38.4 - 48.7	41.8 - 54.5	2.8 - 5.2		4.3 - 6.6
Mean	43.8	46.3	4.1		5.8

¶: Estuarine samples ignored;

§: Includes estuarine samples;

#: Marine organic matter was fractionated in this study;

H: Humic acid sample; F: Fulvic acid sample; H/F : Mixed humic and fulvic acid sample.

Table 2.6.2 Functional group analyses

Functionality	Reference	Result
Total acidity	Alb89 (H)	3.85 meq/g
	Alb89 (F)	6.05 meq/g
	Shi87 (H)	3.0 meq/g
	Soh81 (H/F)	
	Range	3.3-4.2 meq/g
	Mean	3.8 meq/g
	Sun91 (H/F)	3.86 meq/g
	Pio84 (H)	
	Range	2.4-5.0 meq/g
	Mean	3.9 meq/g
	Pio84 (F)	
	Range	1.4-6.7 meq/g
	Mean	3.4 meq/g
	Kal88 (H/F)¶	1.7-4.5 meq/g
	Shi91a (H/F)	
	Range	4.2-10.3 meq/g
	Mean	7.6 meq/g
Carboxylate	Ras70 (H)	
	Range	2.0-5.0 meq/g
	Mean	3.2 meq/g
	Ras70 (F)	
	Range	1.0-4.0 meq/g
	Mean	2.1 meq/g
	Soh86 (H/F)	11 - 16 % of all C 4.6-6.7 meq/g§
	Hed92 (F)	15.3 % 6.4 meq/g§
	Soh81 (H/F)	
	Range	2.2-3.1 meq/g
		2.6 meq/g

Phenolic OHs	Ras70 (H) Range Mean Ras70 (F) Range Mean Soh81 (H/F) Range Mean	 0.0-2.5 meq/g 1.4 meq/g 0.0-1.0 meq/g 0.5 meq/g 0.9-1.7 meq/g 1.2 meq/g
Alcoholic OHs	Ras70 (H) Range Mean Soh81 (H/F)	 0.0-3.0 meq/g 1.1 meq/g 1.5-4.0 meq/g 2.9 meq/g
Carbonyl	Ras70 (H) Range Mean Ras70 (F) Range Mean Hed92 (F) Soh81 (H/F)	 3-6 meq/g 4.5 meq/g 3-6 meq/g 4.8 meq/g 3.5 % 1.5 meq/g§ Low
Aromatic carbon	Soh86 (H/F) Hed92 (F)	8-11 % of all C 9 %
Aromatic COOHs	Soh86 (H/F)	negligible
Aromatic protons	Stu74 (F) Har83 (H) Range Mean Har83 (F)	4 % 3-9 % 5.6 % < 2 %

¶: The range is for a fractionated marine organic sample.

§: Calculated using an elemental composition of 50 %C.

H: Humic acid samples; F: Fulvic acid samples;

H/F: Mixed humic and fulvic acid samples.

also be determined indirectly from ^{13}C NMR spectra but here too doubt exists [Stu76a, Mik81, Wil81, Hed92].

The following conclusions may be drawn :

i) Marine humic substances have lower total acidities than those from terrestrial sources [Stu76a, Soh81].

ii) The difference in (i) may be ascribed to the much lower phenolic content of marine humic substances [Stu76a] as well as lower -COOH content.

iii) Alcoholic hydroxyls are more prevalent in marine humics than those from soil [Bur90]. It has been observed in soil samples that alcoholic hydroxyl content is higher in fulvic acids than in humic acids [Mur81].

iv) The carbonyl content of marine humic material is much higher than in terrestrial counterparts [Stu76a] although one report indicates no carbonyl content [Soh81].

v) The average functional group contents in Table 2.6.2 do not account for all the %O present in humic materials. The difference may be ascribed to the presence of oxygen in ether linkages.

Although the above conclusions are for marine sedimentary organic matter, Buffle indicates that $\delta^{13}C$ measurements indicate a similarity in source and composition of marine aquatic fulvic acids and marine sedimentary fulvic acids [Buf88].

The functional group data available are listed in Table 2.6.2.

2.6.2.3 The forms of nitrogen and sulphur

Much of the nitrogen and sulphur content has not been determined. Studies on soil humic substances reveal that 20 to 60% and between 1 and 10% of the nitrogen present exists as amino acid-N and amino sugar-N respectively [Bre55, Bro55, Ste60, Bre68, Tsu78]. Of the rest most is unidentified although small fractions of purine and pyrimidine derivatives have been found. Gagosian and Stuermer [Gag77] concluded that most of the nitrogen in marine humics was not present as hydrolyzable amino acids. Buffle [Buf88] states that 40% of the total nitrogen content is in the form of amino acid derivatives though these are non-hydrolyzable. Fox reports this percentage to be as high as 50 - 70% [Fox83]. Recently Hubberten et al. [Hub94] report that up to 24% of the nitrogen in humic material collected from seawater onto XAD-2 resin and then eluted with methanol to be present as amino acids. They also measured the total amino acid content of seawater to be about 400 nmol dm^{-3}. However, their technique ignores nitrogen which may be in amine groups not associated with amino acids.

The sulphur in soil humic material comprises three fractions [Bie78]. Much (up to 60%) is unidentified; 5 - 35% is C-bonded S and is thought to occur as amino acids [Bie78] and 30 to 80% is in the form of HI-reducible S which exists as phenolic sulphates and sulphated polysaccharides.

2.6.2.4 Macromolecular properties

There is a large range of reported values for molecular weights. This is dependent on the method chosen to measure the molecular weight of the humic material under investigation.

Raspor et al. [Ras84a] found the major fraction of a fulvic acid sample corresponded to a molecular weight of 20000 g mol^{-1}. This was determined using exclusion chromatography with DOC and UV detectors. On the other end of the scale Stuermer and Harvey [Stu74] report that most of a fulvic acid sample that they extracted had a molecular weight < 700 g mol^{-1}. This was determined using gel chromatography. Vapour pressure osmometry measurements by Gillam and Riley [Gil81] indicate the number-average molecular weight to vary from 501 to 792 g mol^{-1}. These authors came to the conclusion that marine fulvic acids had a lower mean molecular weight than fluvial fulvics which in turn had a lower mean molecular weight than fulvic acids extracted from soils. The much lower molecular weight than that found by Raspor et al. [Ras84a] results from the use of gel permeation chromatography where the molecular weight determined depends not only on molecular size but also on molecular shape [Cam72, Buf77].

2.6.2.5 Spectroscopic investigations

2.6.2.5.1 Visible and UV spectroscopy

These were found to be featureless [Ras84a, Stu74] without any maxima or minima. Absorbance increased with decreasing wavelength. A parameter often quoted is the E_4/E_6 ratio (or the ratio of absorbance at 465 and 665 nm). Because the chromophores of humic acids are mainly aromatic compounds [Pow88, Wan90], it has been inferred from E_4/E_6 ratios that marine humic material is less aromatic than soil samples [Stu74]. Ertel and Hedges [Ert83] plotted E_4/E_6 against H/C atomic ratios. They found that as conjugation decreased (an increase in H/C) the E_4/E_6 ratio increased. Surprisingly though the marine humic samples had E_4/E_6 ratios that were lower than expected when compared to their H/C ratios. The E_4/E_6 values measured were 3.68, 4.91, 5.40 and 7.39. The values observed by Kalinowski and Blondeau [Kal88] for a fractionated

sedimentary humic material were 3.40, 3.84, 3.82, 3.46 and 4.37. The unfractionated sample had a value of 4.88.

2.6.2.5.2 IR spectra

Table 2.6.3 which is taken from Murray [Mur81] is a summary of the principal infrared bands and their assignments.

Raspor et al. [Ras84a] found that the C-H stretching band was more pronounced in a deep sea sediment sample of humic material than in samples from estuarine sediments. This would indicate a greater aliphatic content in marine sediments. Hatcher et al. [Hat80] proposed a highly branched unsubstituted aliphatic structure. In general the alkyl C-H stretching absorbance is predominant [Stu78b, Soh81, Ert83].

The carbonyl stretching band was found to be more pronounced with fulvic acid samples than with humic acids which indicated a greater carbonyl and carboxylate concentration in fulvic as opposed to humic acids [Ras84a]. This band was observed to become much narrower and less intense on methylation [Stu78b].

Raspor et al. indicate some degree of quinone functionality (IR band at 1660 cm^{-1}). There is a band nearby at 1640 cm^{-1} and another at 1520 cm^{-1} which may result from amide linkages [Ert83]. Often an absorbance band is observed at 1040 cm^{-1}, indicative of the C-O stretch of carbohydrates [Ert83].

Intense absorption in the 3000 - 3500 cm^{-1} range has been observed which indicates that the heteroatoms which are single bonded to carbon are present primarily as hydroxyl or amino groups.

Table 2.6.3 Principal infrared adsorption band ranges and assignments for humic substances (from Murray [Mur81])

Band§ (cm^{-1})	Assignment	Ref.
3400-3440(s)	Hydrogen-bonded OH, maybe NH	Ste71, Sch72, Adh77, Tan77
2850-2960(w)	Aliphatic CH	Ste71, Sch72, Tan77
2400-2700(w)	Hydrogen-bonded OH of COOH	Sch75
1700-1725(m-s)	C=O of COOH, esters, aldehydes or ketones	Dub63, Sch72, Tan77
1600-1660(m-s)	Aromatic C=C, COO^-, C=O of quinones, H-bonded C=O, C=C conjugated with C=O	Ste71, Sch72, Tan77
1650,1440(w)	Amide of proteins	Ste71
1400-1440(m)	COO^-, OH deformation and C-O stretch of phenolic OH, aliphatic CH	Ste71, Sch72
1230-1250(w)	Phenoxy CO or COO^-	Sch65b, Sch75
1200-1Stu78a(w)	C-O stretch, OH deformation of COOH, aryl esters	Ste71, Sch72
1020-1050(w)	Polysaccharides, silicate impurity	Sch64, Zie64 Kha71, Ste71 Tan77

§: s, strong; m, medium; w, weak.

2.6.2.5.3 Nuclear magnetic resonance spectroscopy studies

Nuclear magnetic resonance spectroscopy is a powerful tool for characterizing marine organic matter which has come into its own recently. However, the quantification of functional groups is difficult because of the overlap of the chemical shifts of various groups [Pio84].

^{1}H NMR studies

Harvey et al. [Har83] found that marine fulvic acids had 4-9% of the H in the arrangement H-C-O-X where X could be H (hydroxyl), C (ether) or O-C (peroxide). Less than 2% of the hydrogen was found to be aromatic. They also estimated there to be 2 to 3 carboxylate groups per molecule.

Marine humic acids have been found to have a greater portion of aromatic protons than marine fulvic acids [Sai81]. This was also observed by Harvey et al. [Har83] who found humic acid to have 3 to 9% hydrogen as aromatic.

Stuermer and Payne [Stu76a] report the ratio of purely aliphatic protons : those next to carbonyls, alcohols, ethers etc : aromatic protons to be 15:10:1 or 58% : 38 % : 4%. Similar observations were made by Harvey et al. [Har83] who found that methyl and methylene protons comprised at least 72% (Mean = 89%) of all protons bound to carbon in marine humic and fulvic acids.

^{13}C NMR studies

Stuermer and Payne [Stu76a] observed an increase in aliphatic ^{13}C signals and a decrease in aromatic signals when compared with terrestrial samples.

Hedges et al. [Hed92] found that most of the carbons in marine humic substances were aliphatic (only 9% is aromatic). About 19% of the carbon is single bonded to oxygen or nitrogen while there is no indication of methoxyl groups. They observed a very low carbonyl percentage (< 5%) but a high -COOH percentage (15-16%) which is at variance with the results of Rashid and King [Ras70]. This a reflection of the fact that NMR data are not always truly quantifiable and there may be a high degree overlap between the signals. Wilson et al. [Wil81] also found contradictory results regarding ketone concentration from ^{13}C-NMR and conventional analytical methods in lake fulvic acid. No ketones were observed using NMR yet conventional analysis indicated their existence.

It has been reported from ^{13}C NMR studies that 50% of the carbon in marine sedimentary fulvic acids is in the form of polysaccharide carbon [Hat80]. These authors report 15% of the carbon to be associated with carboxyl groups. They propose that most of this is in the form of uronic acids associated with polysaccharides. However, Sohn and Hughes [Soh81] report a much lower polysaccharide content which is reported as less than 4% glucose by weight. This result was obtained by the standard colorimetric method of Armstrong and Carr [Arm66]. Kalinowski and Blondeau [Kal88] determined carbohydrate content and found this to be low (5-6%) although one fraction was high (17%). The total uronic acids were also low (1.5% to 2%) with the highest reported concentration being 5%.

2.6.2.6 Conclusions

Marine humic materials have been well characterized with respect to their elemental composition. However some doubt still exists as to the form of nitrogen and sulphur. These compounds have very low aromaticity when compared to their terrestrial counterparts. The total acidity and consequently amount of carboxylate is well known.

There is some discrepancy as to the carbonyl content and this is even more applicable to the alcoholic hydroxyl content. The extent to which polysaccharide structures occur is also subject to some controversy. These structures together with ether linkages may account for the discrepancy between %O and functional group content.

2.6.3 Structures proposed for marine fulvic acids

Harvey et al. proposed a pathway to explain the formation of marine humic acids from marine fulvic acids [Har83]. They proposed that marine fulvic acid is formed from polyunsaturated fatty acids (PUFAs such as triglycerides) which undergo free radical oxidative cross-linking. Humic acid is formed through elimination reactions to give a more aromatic structure. They argue that marine fulvic acids are the precursors of humic acids because the humic acids have similar proton distributions to fulvic acids, except for their slightly higher aromaticity. Their model, though, does not account for the inclusion of nitrogen in marine fulvic acids.

Gagosian and Stuermer [Gag77] propose a hypothetical structure that includes nitrogen. A representation of this structure can be seen in Figure 2.3. The basic building blocks are amino acids, amino sugars, sugars and fatty acids. Their models have molecular weights of 420 - 992 g mol^{-1}. Cross-linking could account for heavier molecular weight molecules. The mechanism for formation is the result of the reaction of sugars and amino acids, through Maillard reactions, rearrangements, cyclizations and decarboxylations, to give compounds known as melanoidins. Marine lipids are then included through ester or amide linkages to give long chain structures.

Hatcher et al. [Hat80] propose that marine fulvic acids are dominated by polysaccharides and polyuronic acids. They propose that these polysaccharides are eliminated by hydrolysis and decomposition to form humic acids.

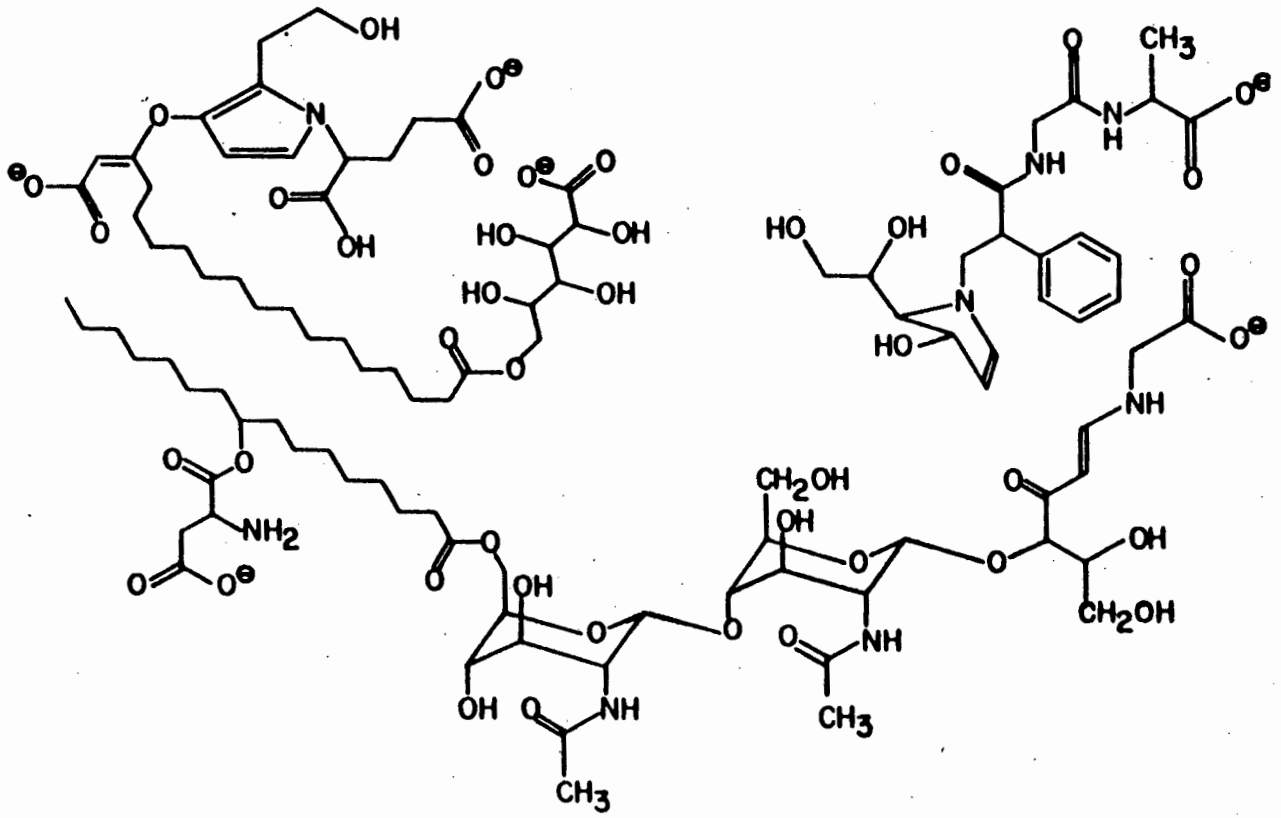


Figure 2.3: The hypothetical structure for marine fulvic acid as proposed by Gagosian and Stuermer [Gag77]

Mention must be made here of the suggestion by Degens [Deg70] that marine organic matter is composed largely of nitrogen-containing compounds. These then form a clathrate-type structure which binds metal ions. This suggestion is important when one considers the results of the model developed in the present work [Chapter Five].

The various pathways of fulvic acid formation are reviewed by Ishiwatari [Ish92]. The true mechanism is probably a combination of the reactions proposed above, for instance melanoidin formation followed by polymerization. This could then be coupled with biopolymer degradation.

2.6.4 Metal-humic equilibria measurements

Mantoura [Man81] has provided a detailed review of the measurement of the metal-complexing capacity of organic material in fresh and seawater. He also compared this to the complexing capacity of NTA and EDTA which he found to be much stronger complexing agents. He reviewed some of the conditional stability constants for metal-organic complexes in soil, lakes and seawater.

Conditional stability constants have been measured using techniques such as differential pulse anodic stripping voltammetry [Dui77, Ras84b, Cap90, Mul91], cathodic stripping voltammetry [VdB84c, Kra86, Apt90, Zha90], chemiluminescence [Sun91], liquid-liquid partition [Mil94], ligand exchange procedures [Mof87], equilibration with MnO_2 [VdB82] and gel filtration techniques [Soh86]. These measurements are easier to perform in freshwater samples where ligand and metal concentrations are higher. In seawater, though, the trace concentrations of many metals makes measurement difficult [Kra86].

Mention must be made here of the so-called 'onion' model proposed by Mackey and Zirino [Mac94] for trace metal organic-complexation. These two authors argue that trace metals are bound together with marine organic matter in pseudo-colloids. The metals bound up in this matter are not in equilibrium with the seawater as there are layers of organic material between some of the metal ions and the aqueous phase. The binding of metal to organic matter can be viewed as the layers of an onion where the layers are concentric rings of organic matter bound together by metal ions. Only the metals ions on the skin of the onion (10-30%) are in true equilibrium. Mackey and Zirino [Mac94] base their theory on the slow release of trace metals from humic material as well as the fact that when natural organic matter binding copper, zinc and lead is titrated with copper, the other two trace metals are not released as might be expected if the binding sites were in equilibrium [Bru89, Cap90, Mac94].

2.6.4.1 Copper-organic interactions

Most studies of metal-organic complexation in seawater have been performed on the speciation of copper. Copper-organic complexation is reported to account for between 50% [Dou86, Mil89] and 98% [VdB84b, Apt90] of dissolved copper. Van den Berg [VdB84b] has reviewed the measurements of the percentage copper bound by organics in seawater. Conditional stability constants have been measured using the above techniques by numerous authors [VdB84b, Soh86, Mof87, Apt90, Sun91]. It has been proposed that the complexation of copper by dissolved organic matter is via oxygen atoms [Pio84]. This is both through the carbonyl and carboxylate groups [Soh86]. This would then explain the greater complexation ability of fulvic acid over humic acid in terms of their respective oxygen contents.

2.6.4.2 Zinc-organic interactions

Conditional stability constants have also been measured to some extent for zinc in seawater [Hir82, Ras84b, VdB87, Bru89, Mul91]. Duincker and Kramer found 60% of zinc to be organically bound [Dui77] although their technique did not differentiate between organically bound zinc and adsorbed zinc. It would appear though that complexation is much less significant than for copper at natural levels of organic material. For zinc the following order of complexation ability was observed: fulvic acid < humic acid < NTA < EDTA [Ras84b]. This indicates that the last two overestimate the effect of organic matter on trace metal speciation. Stanley and Byrne [Sta90] concluded that zinc is bound by zinc-specific sites and not those that bind copper.

2.6.4.3 The interactions of organic matter with cobalt, cadmium, nickel and lead

Studies by Zhang et al. [Zha90] would indicate that cobalt is complexed to a reasonable extent in seawater. (46-100%; Mean = 70%) This complexation is characterized by a high conditional stability constant. The interaction of cadmium and lead with humic materials, on the other hand, appears to be negligible [Ras84b, Pio84] although Capodaglio et al. [Cap90] report 50% Pb complexation. However, anodic stripping voltammetry measurements do not necessarily distinguish between organically bound and adsorbed metal and the percentage reported by Capodaglio et al. is actual DPASV non-labile which includes adsorbed metal. Lead is known to be strongly adsorbed to particulate solids in seawater [Car73, Noz76]. Duincker and Kramer [Dui77] found only 13% of lead to be electroactive to DPASV. However, they do state that this does not imply that 87% percent is bound to organic matter as particulate lead is also non-labile. They found 100% of cadmium to be labile and thus not bound to organic matter. Donat et al [Don94] found that a third to a half of the dissolved nickel was organically associated.

2.6.5 The use of RANDOM to model marine fulvic acids

Although marine fulvic acids have a complex and poorly characterized structure, different samples display similar chemical properties [Mor83b].

Their chemical properties may be described in terms of the concentration of functional groups. This provides a simplification of the overall structure. The model fulvic acid compounds were generated by the computer program RANDOM which is an extension of the original program, RANDOM, developed by Murray [Mur81] at UCT. The new RANDOM (written in Turbo Pascal) also identifies mono, bi- and tridentate bindings sites by randomly assigning functional groups to a carbon backbone and then counting the number of sites. What makes this version different is that it takes into account binding through nitrogen and sulphur atoms. The program requires knowledge of the %C, % aromatic carbon and functional group data for carboxylate, carbonyl, phenolic, aliphatic alcoholic, amino, quinone, methoxy and thiol groups.

In light of the fact that marine organic matter has a much higher nitrogen [Ras84a] and sulphur content than terrestrial fulvic acids, it was decided to extend the original RANDOM program to account for the effect of nitrogen and sulphur donor sites in fulvic acids. This resulted in the new version. The discussion of the workings and listing of this program are to be found in Appendix 2. In chapter three the development of a fulvic acid model for marine organic matter is discussed and the final model shown. The model was then run with the proposed concentrations of model ligands (one for each binding site identified) to observe the effect of organic complexation. Any discrepancy with experimental results would indicate either a lack of specificity (in the case of underprediction) in the RANDOM approach or the presence of other effects such as the adsorption of metals onto organic colloids which may account for a significant fraction of the metal-organic interaction observed in seawater.

2.7 EXTENSION TO INCLUDE ADSORPTION PHENOMENA

The solid-water interface plays an important role in regulating the concentrations of most trace elements in soil and natural water systems. It forms an integral part of the geochemical cycle and can thus not be ignored in a speciation model [Dzo90].

It has been proposed that adsorption forms the dominant control of trace metal distribution in the ocean [Bal81a, Li81, Wan86]. This is via a process called scavenging whereby trace metals which have been transferred to the sea from rivers are adsorbed onto particulate solids [Bea89]. These solids sink to the ocean floor and thereby remove trace metals to the sediments [Bal81a]. Studies have revealed that dissolved trace metal concentrations in the sea are in equilibrium with the surface of sinking particles [Bre79, Bal81a, Hun83]. Evidence for this adsorption process is the ^{226}Ra-^{210}Pb disequilibria observed in the deep sea [Cra73, Bac76, Noz76].

Common hydrous metal oxides, in particular those of iron, aluminium and manganese, are known to sorb a whole host of chemical species. They tend to be the dominant sorbents in natural water systems since adsorption onto their surfaces via metal/proton exchange is strong. Furthermore they form fine colloidal suspensions which coat other suspended particles.

Adsorption phenomena at the solid/solution interface have been studied for more than a century. However, up until recently, they have been important only to the work of soil scientists. The ocean is not a single phase but consists of an aqueous salt solution in which there is a significant amount of suspended and sedimentary particulate solids. It would thus be important to extend the model to the adsorption of trace metals onto these components so as to obtain better understanding of the processes, operating in the ocean.

Adsorption phenomena have been modelled in seawater by Balistrieri and Murray [Bal81b, Bal82a, Bal82b]. They considered adsorption onto goethite (α-FeOOH) and δ-MnO_2 so as to model the processes occurring at ferromanganese nodules. However, the use of these well-aged solids is not particularly relevant to suspended particles. Balistrieri and Murray were also concerned more with the speciation of the major cations. That of the trace metals was not studied in detail.

The ocean contains all the hydrous metal oxides listed above. Iron oxides have been found to be significant in phosphate removal in the ocean [Ber73], so it was decided to see if this effect extended to other trace components. It was decided to use hydrous ferric oxide as a model solid because the adsorption of metals by HFO has been well characterized and reliable adsorption constants exist [Dzo90]. Further improvements to the model would see the inclusion of other solid particles.

2.7.1 Hydrous Ferric Oxide

Iron oxide is found in natural aquatic systems in a number of forms : hematite (α-Fe_2O_3), hydrohaematite (approximately $2Fe_2O_3.H_2O$), goethite (α-FeOOH), lepidocrocite (γ-FEOOH), maghemite (γ-Fe_2O_3), magnetite (Fe_3O_4) and hydrous ferric oxide [Bor65, Sul89].

Hydrous ferric oxide, also known as amorphous ferric oxide and amorphous iron oxyhydroxide, is the solid formed upon the rapid hydrolysis of ferric iron solutions at 20 to 30 °C. The resultant solid is usually amorphous as indicated by X-ray diffraction studies. Natural iron oxides which exhibit similar X-ray diffraction patterns are often called ferrihydrite. HFO resembles a swollen gel since it has a high water content, unlike the other oxides of iron (III).

Its bulk structure is not well defined. Consequently its chemical composition may be represented by the general stoichiometric formula $Fe_2O_3.nH_2O$ where n ranges from 1 to 3. Dzombak and Morel [Dzo90] assume n to be 1 when converting mass-based data to molar units.

On ageing or heating hydrous ferric oxide transforms to more crystalline iron (III) oxide forms. Usually this is the most thermodynamically stable form, goethite (α-FeOOH). This form is commonly found in sediments. Because the model is primarily concerned with the ocean and not sediment porewater, hydrous ferric oxide makes a better choice of model solid than goethite. Its higher surface area also means that it has greater reactivity [Whi86].

The ability of particulate solids to sorb metal ions is strongly dependent on specific surface area i.e. that area of the solid which is exposed to the solution. Unlike the more crystalline forms of iron (III) oxide, HFO has a high surface area although reported values vary, depending on the method of measurement. It was decided to use a surface area of 600 $m^2\ g^{-1}$ as used by Dzombak and Morel [Dzo90] based on the recommendations of Davis and his co-workers [Dav78, Luo83]. This value is higher than that determined by BET measurements (200 to 300 $m^2\ g^{-1}$) but lower than that calculated theoretically (840 $m^2\ g^{-1}$) [Dav77, Dzo90]. The discrepancy is a result of the limitations of the BET method of surface area measurement because the drying step involved may well age the solid and so decrease the surface area. Furthermore an assumption needs to be made about the surface area that is occupied by each adsorbed molecule of N_2 or other adsorbate. Similar surface area measurements have been made for natural ferrihydrite [Car81].

A second factor which determines sorption capability, is the number of active hydroxyl sites which are available to complex metal/ligand ions. These can be classified into two

types : high density, low affinity site which bind metals weakly and low density, high affinity sites which are much stronger. Protons and anions bind equally strongly to the high affinity sites as the low affinity ones. The mean values recommended by Dzombak and Morel of [Dzo90] of 2.25 mmol g^{-1} for weak sites and 56.2 μmol g^{-1} for strong sites were used.

Uehara and Gillman [Ueh81] differentiate between high and low affinity sites on the manner of adsorption. Adsorption of metal ions to low affinity sites is accompanied by proton desorption while this does not occur in the case of high affinity sites. However, in the adsorption reactions listed by Dzombak and Morel [Dzo90], this rule is obeyed by the adsorption of the alkaline earth metals (magnesium, calcium, barium and strontium) only. The adsorption of the heavier metals to the high affinity sites is also characterized by the desorption of a proton as is the case with low affinity sites.

The constants for adsorption were taken from the critical compilation by Dzombak and Morel [Dzo90]. It should be noted that some of these constants are not experimental values but were calculated by linear free energy relationships. Nevertheless they were included in the model for better predictions. The constants were then corrected for ionic strength using the procedure recommended by Dzombak and Morel [Dzo90]. This was because in many cases they had corrected the constants to infinite dilution using this method. There existed a gap in the literature [Dzo90] when a constant for the complexation of magnesium to the high affinity site. Since magnesium is present in high concentrations in seawater, this reaction could not be ignored. This constant was set at log K_{int} = 5.00 at infinite dilution based on trends observed for HFO [Kin76] and goethite [Bou88] in the adsorption of magnesium when compared to that of barium, strontium and calcium. Since trace metal concentrations are low, surface precipitation reactions (most notably for zinc) were ignored.

Electrophoretic measurements on iron oxides in seawater have indicated that these acquire a negative charge from the adsorption of organic matter [Loe75, Hun79, Hun80]. To model this a dummy ligand is added to the database to represent adsorbable organic matter. It is called TIPP and is included so a negative charge can be generated on the surface of solid particles. The constants for adsorption and protonation were those recommended by Morel et al. [Mor90] which are based on the measurements of adsorption of organic matter, made by Tipping [Tip81a, Tip81b, Tip82].

The reactions and equilibrium constants at 0.0 mol dm^{-3} are

$H^+ + L^{2-} \leftrightarrow HL^-$ Log K = 4.40

$2H^+ + L^{2-} \leftrightarrow H_2L$ Log K = 5.10

$=FeOH^\circ + L^{2-} + H^+ \leftrightarrow FeL^- + H_2O$ Log K = 14.10

$=FeOH^\circ + L^{2-} \leftrightarrow FeOHL^{2-}$ Log K = 7.1

where L represents the organic ligand and the adsorption reactions apply to both affinity sites.

These constants, corrected to an ionic strength of 0.7 mol dm^{-3}, are used in the model.

There exists a paucity of data concerning the natural levels of hydrous ferric oxide in seawater. This is the result of two factors : researchers have only recently begun to examine suspended particulate matter and the techniques to identify the oxides present have only recently become available. It would appear that HFO levels in the open ocean are very low. However, close to the shore levels of up to 0.1 mg/l have been measured

[Ing91, Wel91]. Evidence indicates that the iron exists as hydrous ferric oxide rather than the more crystalline goethite as a result of the continuous fluvial input of iron [Pri73, Eme75, Sho80, Shi85]. It was decided to run the model with HFO concentrations varying between 1 $\mu g\ dm^{-3}$ and 1 $g\ dm^{-3}$. This latter end would model the influence of dredging and the interstitial waters of sediments. Moreover the higher concentrations are justified in that HFO is being used as a model for all the solid material in the ocean which has a total content of up to 10 $mg\ dm^{-3}$ in surface water. This value was the same as that used by Morel et al. [Mor90]. Higher values may be expected on the edges of estuaries as has been reported by Fletcher et al. who observed concentrations as high as 50 $mg\ dm^{-3}$ [Fle83].

It should be noted that the use of iron oxides (in particular hydrous ferric oxide) to model adsorption phenomena is justified despite their low concentration because of their high surface area and resulting high surface activity as well as their tendency to coat other particles [Whi86].

CHAPTER THREE

A MODEL FOR MARINE FULVIC ACID

3.1 INTRODUCTION

A model for fulvic acids has already been developed at UCT by Kevin Murray [Mur81]. This model allows the estimation of the concentrations of a variety of metal binding sites that might be expected to occur on an "average" fulvic acid molecule. However, this model was developed for soil fulvic acids where nitrogen and sulphur binding sites are less significant. It was decided in the present work to extend the above model to include sulphur and particularly nitrogen binding sites as these elements are significant in fulvic and humic materials of marine origin.

Other studies have also employed mathematical complexation models to describe the interactions between dissolved organic matter and trace metal cations. These models may be divided into three classes: i) discrete ligand models, ii) continuous distribution models and iii) electrostatic models.

3.1.1 Discrete Ligand Models

Discrete ligand models are also known as multi-site models. An assumption is made that cation binding takes place at a small number of binding sites. Each site has a binding constant associated with it, K_i, and a site concentration, L_i. The mass balance for total metal concentration [Per83, Dzo86, Tur86] is given by

$$[M]_T = [M] + \sum_{i=1}^{m} \frac{K_i[M]L_i}{1 + K_i[M]} \qquad 3.1$$

A formation function for the experimental data may be defined as

$$\bar{N}_{exp} = ([M]_T - [M]) / L_T \qquad 3.2$$

where $[M]_T$ is the total metal concentration, [M] is the free metal concentration and L_T is the total ligand concentration.

3.1 may be rewritten in terms of the formation function

$$N = \sum_{i=1}^{m} \frac{(L_i/L_T)K_i}{1 + K_i[M]} \qquad 3.3$$

The parameters (L_i/L_T) and K_i may thus be used to fit the model. These may be obtained graphically using Scatchard plots or using numerical optimization procedures which minimize the difference between the experimental formation function (equation 3.2) and the calculated one (equation 3.3).

Refinements to the discrete model would see the inclusion of ligand stoichiometry as well as the influence of pH on binding. Cabaniss and Shuman [Cab88a] developed a 5-site binding model for copper-fulvic acid interactions which accounted for pH behaviour in the range (pH = 5 - 9). They found only 1:1 complexes. Higher order binding models were insignificant.

3.1.2 Continuous distribution models

Unlike the discrete ligand models, these models assume a continuum of binding sites which follow some distribution. The formation function is thus given by

$$\bar{N} = \int_0^{\infty} N(K) \frac{K[M]}{1 + K[M]} dK \qquad 3.4$$

Continuous distribution models may be divided into three classes: i) affinity spectra models, ii) normal distribution models and iii) continuous stability function models. The

difference between these models is in the way the distribution of the ligands, N(K), is treated.

With affinity spectra models the formation function (equation 3.4) is changed to

$$\bar{N}([M)] = \int_0^{\infty} N(K) \frac{10^K[M]}{1 + 10^K[M]} dK \qquad 3.5$$

By using a second order approximation of the integral 3.5 the affinity spectrum $\hat{N}(K)$ may be obtained [Dzo86]. By differentiating the formation function a plot of N(K) versus pM (-log[M]) may be obtained. The peaks of this spectrum provide information about the most probable log K controlling complexation (by assuming log K = pM) while integrating the area under the peaks provides the corresponding ligand concentration. Shuman et al. [Shu83] used this approach to model copper interactions with Ogeechee Estuary organic matter.

With the normal distribution models N(K) is assumed to be known. It is assumed to have the shape of a Gaussian distribution function. The parameters needed to fit the model are consequently a mean log K and a standard deviation for the mean binding constant. Variations on this approach include the bimodal Gaussian distribution model developed by Perdue et al. [Per84] for fulvic acid protonation which includes two mean log K's, each with its own standard deviation. Perdue et al. [Per84] introduce this approach because two chemically distinct binding sites (carboxylates and phenols) are observed in humic material.

Continuous stability function models are also called differential equilibrium models. These models describe the average binding constant, K, at any point in a metal-fulvic titration as a continuous function of the degree of metal loading.

A differential binding function is defined as

$$K = \frac{d[ML]}{[M]d[L]} \qquad 3.6$$

The average binding constant is given by

$$\bar{K} = \frac{[M]_b}{[M][L]} \qquad 3.7$$

where $[M]_b$ is the concentration of metal bound to the organic material. The average binding and differential functions are related through

$$K = \frac{d(\bar{K}(1-\theta))}{d\theta} \qquad 3.8$$

where the θ is the degree of metal loading and is equal to $[M]_b/L_T$. Thus the slope of a plot of $\bar{K}(1-\theta)$ versus θ will giver the differential binding function.

3.1.3 Electrostatic models

Electrostatic models try to describe trace metal - humic binding in terms of intrinsic stability constants. Intrinsic stability constants refer to the stability constants for cation-humic interactions in the absence of any electrostatic effects.

Various models have been developed which relate the apparent binding constants to the intrinsic constants. The models differ slightly in approach. What all have in common is that binding is related to the potential on the surface of the humic molecule. Various workers have derived electrostatic interaction factors which account for the influence of

parameters such as the charge on the molecule as well as molecular dimension properties such as the radius of gyration of the molecule.

Most of these models follow the method developed by Tanford [Tan61] for globular proteins and are based on the following assumptions: i) humic substances are assumed to be impermeable spheres; ii) the charge resulting from surface group ionization is spread uniformly across the surface; iii) the charge results from proton dissociation or specific metal ion-binding to the surface and iv) the binding to one site affects other sites only by electrostatic interactions.

Electrostatic models have been developed by Dempsey and O'Melia [Dem83], Tipping et al. [Tip88, Tip90, Tip92], De Wit et al. [DeW90], Bartschat et al. [Bar92] and Falck [Fal89]. Previously [Pre90] an electrostatic model was combined with the RANDOM approach to explain the binding of metal ions by humic substances. However, this model overestimated the influence of metal-humic binding.

3.1.4 Assessment of the various complexation models

The various models all appear to be equally successful in fitting the experimental data used. When the models are used in areas beyond their calibration, discrepancies may occur.

Fish et al. [Fis86] compared discrete ligand models with continuous distribution models. Discrete ligand models were found to be most useful. This is because the binding constants predicted by this approach are easily incorporated into existing speciation packages such as MINEQL or MINTEQA2. When numerical as opposed to graphical methods were used, the accuracy of this approach increased immensely. Fish et al. [Fis86] found the affinity spectrum approach to be highly sensitive to experimental error

but still a useful aid in selecting ligands for the discrete ligand model. Site affinity distribution functions also suffer from conceptual limitations [Alt88]. The normal distribution model required very few parameters to fit experimental data but when these results are extrapolated to situations outside the conditions under which these parameters were determined, erroneous predictions might result. The continuous stability function identified only the weakest and most abundant ligands and was thus of limited use. Because of this Buffle et al. [Buf90a, Buf90b] developed the site occupation density function [SODF] which allows for identification of dominant minor binding sites i.e. those minor sites which dominate binding over a given restricted range of log K or pM.

Turner et al. [Tur86] also examined an electrostatic model, that of Wilson and Kinney [Wil77]. Turner et al. found that unless an arbitrary binding site concentration was chosen, this model was unable to fit the experimental data. Thus a separate binding site determination is necessary before this model can be useful.

Perdue and Lyttle [Per83] compared the discrete ligand approach and continuous (normal) distribution approaches. They found that although the two-component Scatchard equation worked well for two component mixtures, it generated spurious results for more complicated mixtures. This is because it becomes an empirical curve fitting exercise as the number of adjustable parameters increases. Perdue and Lyttle [Per83] found that humic substances would probably be better approximated by continuous models. However, they felt that humic substances are likely to be composed of a set of rigorous discrete complexation models (i.e. a large number of binding sites). Furthermore, the deviation of the simple discrete ligand model from experiment might also be the result of 1:2 metal-ligand complexes which are not included in simple models [Buf77, Per83]. Cabaniss and Shuman [Cab88a], however, found the 2-site model to be less susceptible to changes in experimental conditions than the Gaussian model. They went on to develop a 5-site model which was applicable to a wider pH range.

Dempsey and O'Melia [Dem83] also demonstrated that Scatchard plots are of little use in analysing fulvic acid protonation except that they indicate that such protonation is complex. They concluded that there are many different sites or interactions between sites which make the graphical method of protonation analysis useless.

Thus of the models discussed above, all are equally able to fit the experimental data for which they were designed. Unfortunately they are not universally applicable but depend rather on a set of conditional parameters. This limits their use as predictive tools in situations which are vastly different to those under which they were developed. This is where the RANDOM approach developed by Linder and Murray [Mur81, Lin87] is most useful.

3.2 AIM AND BASIS OF THE RANDOM MODEL

McKnight et al. [McK83] concluded that fulvic acid is the major complexing fraction in dissolved organic material. They compared the binding of copper by Shawsheen River fulvic acid to Shawsheen River DOM. They concluded that fulvic acid may be used to model Cu-DOM interactions if it is assumed that 50% of DOM is important for binding. Consequently it can be seen that knowledge about the interactions of fulvic acids with metals would be important for the understanding of metal-organic interactions in natural systems in general.

It is has been noted that soil fulvic acids from various sources have similar chemical properties which are determined primarily by the chemical properties of their surface phenolic and carboxyl groups [Bur64]. It can thus be postulated that the differences in chemical binding ability that do occur arise from differences in functional group

chemical binding ability that do occur arise from differences in functional group concentrations rather than from different structures [Mur81]. It is on this basis that the model was developed.

The model may also provide insight into the humification process and how "random" this process is. If the binding predicted, correlates well with that observed experimentally, this would indicate that the humification process is "random". However, if the results do not correlate this may indicate some degree of specificity that occurs in the humification process.

The model was developed to provide binding site concentrations from the functional group concentrations given in Table 3.1. This represents the average of the percentage composition and functional group data listed in Tables 2.5.1 and 2.5.2.

3.3 THE GENERATION OF FULVIC ACID STRUCTURES

3.3.1 Procedure

The original program was designed to calculate the average binding site concentrations for 1000 fulvic acid molecules. The new program will generate a variable number of structures. However, certain restrictions needed to be imposed to prevent the problem becoming too complex and consequently unsolvable. A detailed description of the procedures used by the program RANDOM are given in Appendix 2.1. while the TURBO PASCAL listing for this program may be found in Appendix 2.2.

The restrictions used are the same as those imposed on the program by Murray [Mur81]. However, the effect of nitrogen and sulphur binding sites is no longer neglected. Amine ($-NH_2$) and thiol (-SH) groups have been included. The stages followed by the program

show great similarity to those discussed by Murray [Mur81]. These will now be discussed.

3.3.1.1 Generation of the carbon skeleton

1) The aromatic carbons may occur only in single aromatic rings.
2) Each aromatic ring has two, and only two, aliphatic side chains, to create an overall cyclic structure. These chains may be ortho, meta or para with respect to the ring.
3) Branching of the aliphatic chains is limited to methyl groups.
4) All aliphatic carbons are saturated.
5) Carbonyls may not exist as aldehydes, nor may they exist in an α-diketone arrangement.
6) The nitrogen present in the compound is limited to amine groups ($-NH_2$). The sulphur considered for metal binding occurs only as thiol (-SH) groups. The amine and thiol groups are assumed to occur only on the aliphatic chains. This assumption simplifies programming and is made in light of the low aromaticity of marine fulvic acid molecules.
7) Ether linkages are ignored; consequently all oxygen in such functionalities is discarded.
8) The molecular weight of fulvic acid is assumed to be 2000 g mol^{-1}. Varying the molecular weight in the range 700 to 10000 g mol^{-1} did not affect the output of RANDOM significantly.

3.3.1.2 Assignment of functional groups

1) The functional groups considered are carbonyl, carboxyl, phenolic and alcoholic hydroxyl, thiol, amine, quinone and methoxyl. The last two have low incidences

in marine samples. However, as this is a generalized model for fulvic acids that has been developed, they are still included in the program.

2) Firstly the quinone oxygens are assigned to the aromatic rings in ortho or para pairs.

3) The phenolic -OH, methoxyl and aromatic carboxyl are then assigned to the remaining aromatic carbons.

4) The remaining carboxyl, alcoholic hydroxyl, amine and thiol groups are then assigned in that order to the aliphatic chains. No more than two groups may be assigned to a methyl carbon while β-keto acid arrangements are avoided.

5) Note that the carbonyl groups are assigned during the carbon skeleton generation.

The program requires the following data :

1) The fraction of aliphatic carbons that occur in methyl groups.

2) The ratio of ortho, meta and para rings.

3) The fraction of quinone groups that are ortho as opposed to para.

4) The fraction of carboxyl groups that occur on aromatic rings.

5) The percentage carbon in the fulvic acid..

6) The percentage aromatic carbon.

7) The functional group concentrations in meq g^{-1}.

The program then calculates the average number of functional groups that occur per molecule as well as the number of carbons. The number of aromatic carbons is then determined which allows a determination of the number of rings per molecule.

The program has been set up to deal with integral numbers of functional groups and aromatic rings. This makes chemical sense as any individual fulvic acid molecule cannot possess half (or any other fraction) of a functional group. The allocation of functional groups may be explained as follows: let the average number of a particular functional

group be 2.53. A random number is chosen between 0 and 1. If this number is less than 0.53 the number of that functional group is taken to be 2 else it is set equal to 3. Over all the structures generated, this means that the average of the number of functional groups per molecule will be 2.53, provided sufficient structures are generated.

3.3.2 Discussion on the approximations used

The assumption regarding single aromatic rings was made in order to greatly simplify the programming of the structure generation. The decision was also reached on the basis of their occurrence in degradation studies and the lack of data on multiple ring systems [Mur81]. It is expected that binding site concentrations will not be particularly affected by this assumption. The assumption is even less significant for marine fulvic acids which have low aromaticity. The assumption of two aliphatic side chains per aromatic ring reduces branching and simplifies programming. In marine samples this assumption is also insignificant because of the low aromaticity.

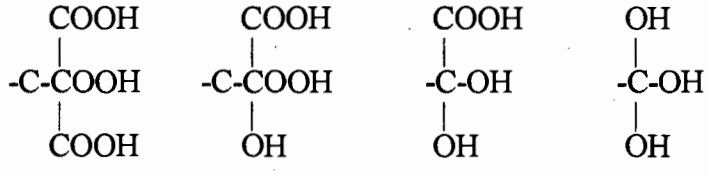
The assumption regarding branching out to methyl groups is included, again, for programming ease. However, its significance is slight since the aliphatic binding sites considered are those (except in the case of acetylacetone) where the functional groups are on adjacent carbons. Thus binding site concentrations are unlikely to be significantly affected by branching to longer chains.

The neglect of double and aromatic bonds is incorporated to simplify programming. Hedges et al. [Hed92] indicate the percentage of unsaturated carbons to be low (10% of aliphatic carbons on subtraction of aromatic carbons). The restriction was also adopted because of the lack of formation constant data for unsaturated model ligands. Some of the unsaturation noted by Hedges et al. [Hed92] may also be the result of keto-enol tautomerism which is accounted for by the inclusion of carbonyl groups.

The ratio ortho : meta : para rings was set to 2:2:1 for the model because this reflects the truly random state. Even in cases of high aromaticity, it has been shown [Mur81] that the effect of this approximation is insignificant. The low aromaticity of marine samples makes it less significant.

α-Diketone arrangements are left out because of their relative instability. They are easily oxidized to two carboxylic acids and may also be "lost" through "benzilic acid" type rearrangements. Because marine fulvic acids are refractory [Buf88] it is assumed that these arrangements would not occur, having already undergone reactions to form more stable compounds. The same applies to β-keto acid arrangements because of their ease of decarboxylation.

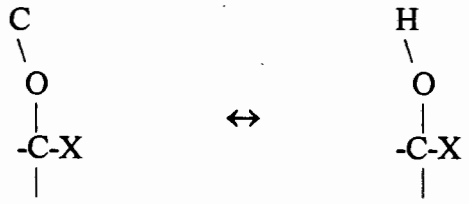
The restriction of only two functional groups per methyl group is for programming ease. It also prevents the unlikely occurrence of tridentate sites on one carbon such as



and the analogous groups with amine and thiol groups. Formation constants for the reactions between the above sites and metal ions are also scarce.

The restriction that ether oxygens are ignored is to simplify programming but is also the result of a lack of data for the complexation of molecules containing ether linkages with metals. Any discrepancy between experiment and the prediction of the model may result from this assumption. The model was also run with the excess oxygen (the difference between the %O predicted by functional group concentrations and that measured experimentally) existing as alcoholic hydroxyls.

This serves as a first approximation for ethers :



where X is -H, -COOH, -OH, $-NH_2$ or -SH.

Certain assumptions were made regarding the forms of nitrogen and sulphur. It was assumed that 80% of nitrogen existed as aliphatic $-NH_2$ and 20% of sulphur existed as aliphatic -SH. These assumptions are empirical but are in line with observations that 5 to 35% of sulphur is bound to carbon [Bie78] for soil humic matter while up to 25% of the nitrogen in marine humic material is in the form of amino acids [Hub94]. The difference between this and the value of 80% used is assumed to occur in purely amine functionalities. A model fulvic acid was also generated, assuming 50% of nitrogen to be present as $-NH_2$. The assumption may be justified if one considers that at 80% nitrogen in NH_2 groups, the amine concentration is 3 meq g^{-1}. By running RANDOM, the output predicts that 0.574 meq g^{-1} of N (or 19.1% of the input) is present in amino acid groups. A further 0.499 meq g^{-1} (16.6%) is present in non-amino acid nitrogen containing groups (PN, ETA and AET). The remaining 63.3% of the amino groups are not counted in binding sites. Of the total DON 15.3% is thus present in amino acid groups which is comparable with the results obtained by Hubberten et al. [Hub94]. The technique of Hubberten et al. [Hub94] may be viewed as a lower bound for amino acid content since they did not analyze for β-alanine (the major amino acid according to RANDOM). The experimental technique they employed may also break down the amino acid groups so that instead of diamo-propanoic acid being observed, one finds alanine or glycine. These amino acids were found to be significant by Hubberten et al. [Hub94].

The model thus provides estimates of binding site concentrations subject to the aforementioned restrictions. Further refinements will see new functional groups and specificity included as more detailed information about the nature of marine fulvic acids is exposed.

3.4 ESTIMATION OF BINDING SITE CONCENTRATIONS

3.4.1 Binding site identification

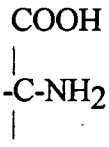
The original RANDOM program incorporated several binding sites. The model ligands for these sites are shown in Figures 3.1 and 3.2 except for citric acid which has been added subsequently. These sites were tri-, bi- and monodentate except for citric acid which is quadradentate. Speciation calculations were not performed with citric acid, however. The sites represented by the model ligands in Figures 3.3 and 3.4 were added in the new program. These sites account for the interaction of aliphatic amine and thiol groups with metals.

The three monodentate sites in RANDOM are aromatic carboxyl, phenolic and aliphatic carboxyl groups (sites 7, 8, 16). They represent the residual carboxylate and phenol not counted in bi- and tridentate sites. It should be noted that residual alcoholic hydroxyl, amine and thiol groups are ignored. Furthermore only ketones in α-arrangements to rings (site 6) and β-diketone arrangements (site 9) are counted. Consequently a large proportion of carbonyl groups are ignored. Discrepancy between the model and experiment may result from this omission.

The tridentate sites chosen are those which form seven-membered rings. This is to simplify programming. A condition, therefore, for their identification is that two of the participating functional groups occur on the same carbon while the remaining functional

group must occur on the adjacent carbon. The tridentate sites included are sites 10, 11, 20, 21, 22, 23, 30 and 31.

It should be noted that the ligands chosen are those where the functional groups occur on carbon backbones of three and four carbons. However, in the case of ethanolamine, 2-aminoethanethiol and 2-mercaptoethanol (sites 27, 33, 34) formation constants for ligands with longer carbon backbones are scarce. Thus the basis for choosing a model ligand is that firstly formation constant data are freely available and then that the carbon chain is as long as possible. 4-carbon chain skeletons are preferred over 3 and 3 over 2. Alanine (site 24) was chosen to represent

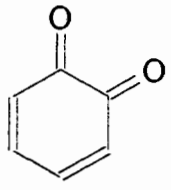


over DL-2-aminobutanoic acid and 2-amino-2-methylpropanoic acid in spite of it having a shorter carbon skeleton because it has been studied more extensively. The difference between the formation constants available for the last two ligands and those published for alanine is small which means that the use of alanine is justified.

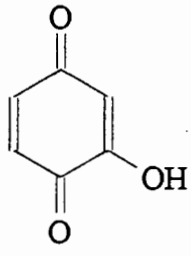
The effects of long range chelation and electrostatic effects [Pre90] are ignored. Also the binding of metals through crown-ether type arrangements is neglected.

3.4.2 Binding site counting

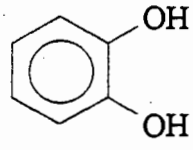
After each structure has been generated, the program searched for and counted the various binding sites. Once this has been done the carbons that incorporate the functional groups are "tagged" so that they may not be incorporated into a another site.



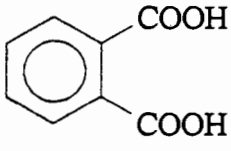
1. 1,2-benzoquinone (12BQ)



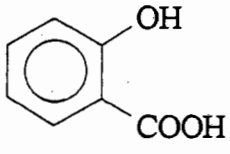
2. 3-hydroxy-1,4-benzoquinone (HBQ)



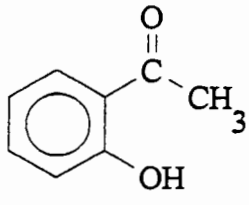
3. catechol (CAT)



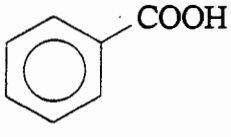
4. phthalic acid (PHTH)



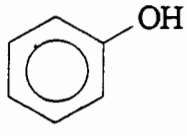
5. salicylic acid (SAL)



6. 2-acetylphenol (ACPH)

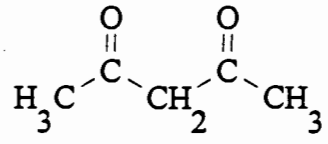


7. benzoic acid (BENZ)

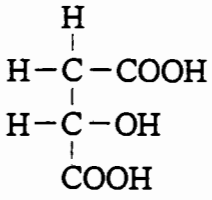


8. phenol (PHEN)

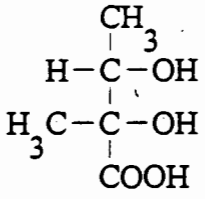
Figure 3.1: The aromatic ligands included in the RANDOM to model fulvic acid metal binding sites



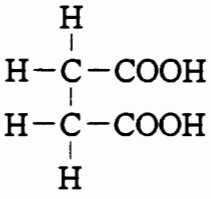
9. acetylacetone (ACAC)



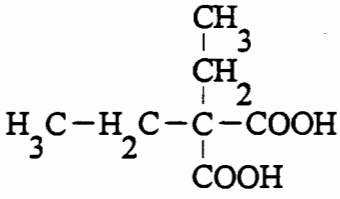
10. malic acid (MAL)



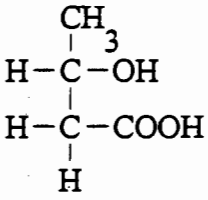
11. 2,3-dihydroxy-2-methylbutanoic acid (DHMB)



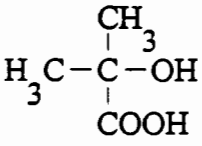
12. succinic acid (SUCC)



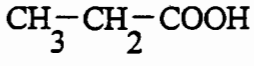
13. diethylmalonic acid (DEM)



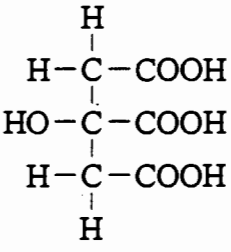
14. 3-hydroxybutanoic acid (HBT)



15. 2-hydroxy-2-methyl propanoic acid (HMP)

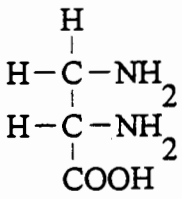


16. propanoic acid (PROP)

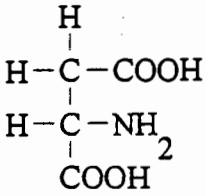


17. citric acid (CIT)

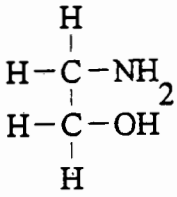
Figure 3.2: The oxygen-containing aliphatic ligands included in the RANDOM to model fulvic acid metal binding sites



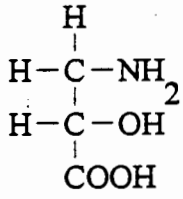
20. 2,3-diamino-propanoic acid (DAP)



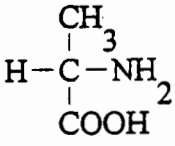
21. aspartic acid (ASP)



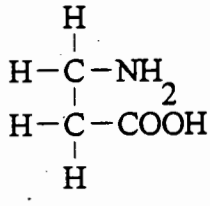
22. serine (SER)



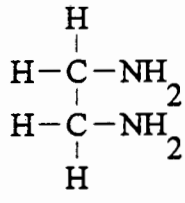
23. isoserine (ISER)



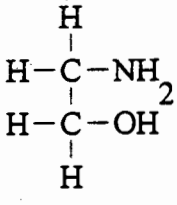
24. alanine (ALA)



25. ß-alanine (BEAL)

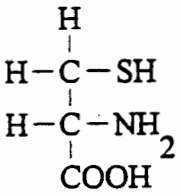


26. 1,2-propylene-diamine (PN)

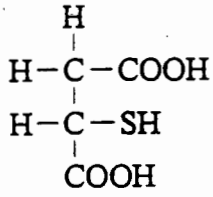


27. ethanolamine (ETA)

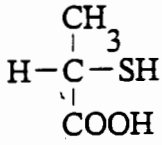
Figure 3.3: The nitrogen-containing aliphatic ligands included in the RANDOM to model fulvic acid metal binding sites



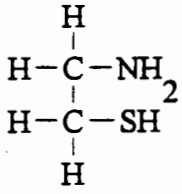
30. cysteine (CYS)



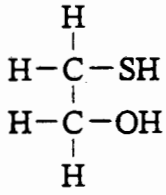
31. thiomalic acid (TMA)



32. thiolactic acid (TLA)



33. 2-aminoethanethiol (AET)



34. 2-mercaptoethanol (MET)

Figure 3.4: The sulphur-containing aliphatic ligands included in the RANDOM to model fulvic acid metal binding sites

This is especially important where two sites share a central carbon. Thus the estimated site concentrations depend on the site counting order. The same situation may even arise where two carbons may be counted as one of two sites. For example consider sites 20 and 21. The first restriction for their identification is that there exist a carbon bound to both a -COOH and an $-NH_2$ group. However, the adjacent carbon may also contain both a -COOH and an $-NH_2$. Obviously the carbons may only be counted as belonging to one site. The solution is to set up the site counting order such that the sites are counted in the order that the site, which binds the most metal under conditions of equal site concentration at the ionic strength, pH and metal concentrations being studied, is counted first. This approach is effective when the difference between metal binding is great but is less so when the sites are similar. Even then though the effect on metal-binding will be small if either site is used.

It should also be noted that tridentate sites must be counted before bidentate sites which include the same functional group arrangements. For example site 20 must be counted before sites 24 and 25 or else site 20's concentration will be zero. Monodentate sites are therefore counted last of all.

The site counting order used in developing the model was: 30 33 20 31 26 21 9 32 22 24 25 27 34 10 13 11 12 15 14 3 5 4 6 8 7 16. Sites 1, 2, 17 and 23 were not searched for. Site 23, isoserine, was not included for two reasons. Firstly the available literature [Mar74a, Smi82, Smi89] includes constants for the interaction of isoserine with only two metal ions, Ni^{2+} and Cu^{2+}. Secondly the formation constant for the interaction of Ni^{2+} and β-alanine is greater than that reported for the interaction of Ni^{2+} and isoserine. However, isoserine (ligand 23) is tridentate and β-alanine (ligand 24) is bidentate. In terms of the procedure used for setting up the site counting order, β-alanine should be counted before isoserine as it binds more metal under seawater conditions. However, if this order is used the resultant concentration of isoserine (as predicted by RANDOM) is

zero as isoserine has the structure of β-alanine with a hydroxyl group in the alpha position. Consequently isoserine was ignored. Sites 1 and 2 were ignored because the concentration of quinones in marine samples is zero while citric acid was ignored because it's incidence is likely to be low (as a quadradentate site) and the original basis of RANDOM was to look for simple binding sites. An early test run of RANDOM (generating 100000 structures) indicated citrate concentration to be 0.00036 mmol g^{-1} i.e only 72 citrate sites could be identified in the 100000 molecules.

Even at a citrate concentration of 500 nmol dm^{-3}, the model calculations of Florence and Batley [Flo76] did not predict any trace metal complexation. Motekaitis and Martell [Mot87], however, used a concentration of 100 nmol dm^{-3} citrate and found 19.7% of copper was so bound. No other trace metals were affected. The concentration used in both these studies is much larger than that predicted by RANDOM for citric acid. The other ligands used in RANDOM also swamp any binding by copper to citrate at the ligand concentrations predicted by RANDOM.

The output of the program is the site concentration in mmol g^{-1}. The model thus proposes that the effect of 1 g dm^{-3} of fulvic acid will be equivalent to all the model ligands expressed in mmol dm^{-3}. Note that the output of the original RANDOM was in meq g^{-1}. The use of meq g^{-1} did not mean that the output had to be divided by the number of dissociable protons on that particular ligand. It merely indicated that the ligand is equivalent to fulvic acid and is in line with the trend to report functional group concentrations as meq g^{-1} in the literature. To prevent this confusion, RANDOM now expresses the ligand concentrations as mmol g^{-1} even though the values are the same as the previous version.

Table 3.1: Functional group composition used by RANDOM to model a typical marine fulvic acid

Elemental composition	
C:	51.25
O:	36.85
H:	6.0
N:	5.2
S:	0.7
Structural Composition(%)	
Aromatic C:	9.0
Functional Groups (meq g^{-1})	
Carboxyl:	3.0
Carbonyl:	5.0
Quinone:	0.0
O-CH_3:	0.0
Phenolic OH:	0.7
Alcoholic OH:	2.0
Aliphatic NH_2:	3.0¶
Aliphatic SH:	0.05§

¶: Assuming 80% of nitrogen is aliphatic NH_2.

§: Assuming 20% of sulphur is aliphatic SH.

Table 3.2: Proposed concentrations§ (mmol g^{-1}) of the model ligands as predicted by RANDOM

No	Ligand	Model				
		N and S included	S excluded	50% N as $-NH_2$	N and S excluded	"Ether" model
30	CYS	0.00050				
33	AET	0.00495				
20	DAP	0.0238	0.0238	0.0088		
31	TMA	0.000325				
26	PN	0.1504	0.1504	0.0558		
21	ASP	0.0223	0.0223	0.0150		
9	ACAC	0.7689	0.7689	0.7786	0.7925	0.7127
32	TLA	0.00245				
22	SER	0.0158	0.0158	0.0105		
24	ALA	0.1310	0.1310	0.0885		
25	BEAL	0.3565	0.3565	0.2444		
27	ETA	0.1932	0.1932	0.1312		
34	MET	0.0040				
10	MAL	0.0135	0.0135	0.0149	0.0176	0.0793
13	DEM	0.1052	0.1052	0.1104	0.1207	0.1202
11	DHMB	0.0077	0.0077	0.0084	0.0096	0.2727
12	SUCC	0.1158	0.1158	0.1316	0.1647	0.1041
15	HMP	0.0977	0.0977	0.1016	0.1094	0.3323
14	HBT	0.1724	0.1724	0.1941	0.2373	0.8059
3	CAT	0.0671	0.0671	0.0671	0.0671	0.0671
5	SAL	0.0564	0.0564	0.0564	0.0564	0.0560
4	PHTH					
6	ACPH	0.0563	0.0563	0.0563	0.0546	0.0577
8	PHEN	0.4531	0.4531	0.4531	0.4531	0.4521
7	BENZ	0.0936	0.0936	0.0936	0.0936	0.0936
16	PROP	1.4860	1.5355	1.6130	1.8600	0.8093

§: Blank spaces indicate that RANDOM did not observe the ligand in question

3.5 RESULTS AND DISCUSSION

3.5.1 The chosen model

Random was run 10 times, generating 100000 structures each time so that 1000000 molecules were generated in total using the functional group data in Table 3.1. The mean binding site concentrations are listed in Table 3.2. These were used to model the effect of marine fulvic acid.

Figure 3.5 is a representation of what RANDOM predicts the structure of marine fulvic acid to be. The cyclic structure simplifies the programming of RANDOM. Linear chains may be generated by breaking this at any point. Site concentrations are not affected significantly. Note that the stereochemistry shown in the figure is not determined by RANDOM, but was chosen arbitrarily.

Figure 3.6 shows the variation of standard deviation of the mean ligand concentration (expressed as a percentage of that mean) plotted against the ligand concentration for the ligands counted in RANDOM. It can be seen that at low concentrations the variation in site concentration is high. This is particularly true for the sulphur ligands.

3.5.2 The effects of parameter uncertainty

Murray [Mur81] investigated the effect of varying the ortho : meta : para ring ratio. He found that this was not significant. This is even less significant, given the aromaticity of marine fulvic acid. In keeping with the concept of a random molecule the ratio of 2:2:1 is also used here.

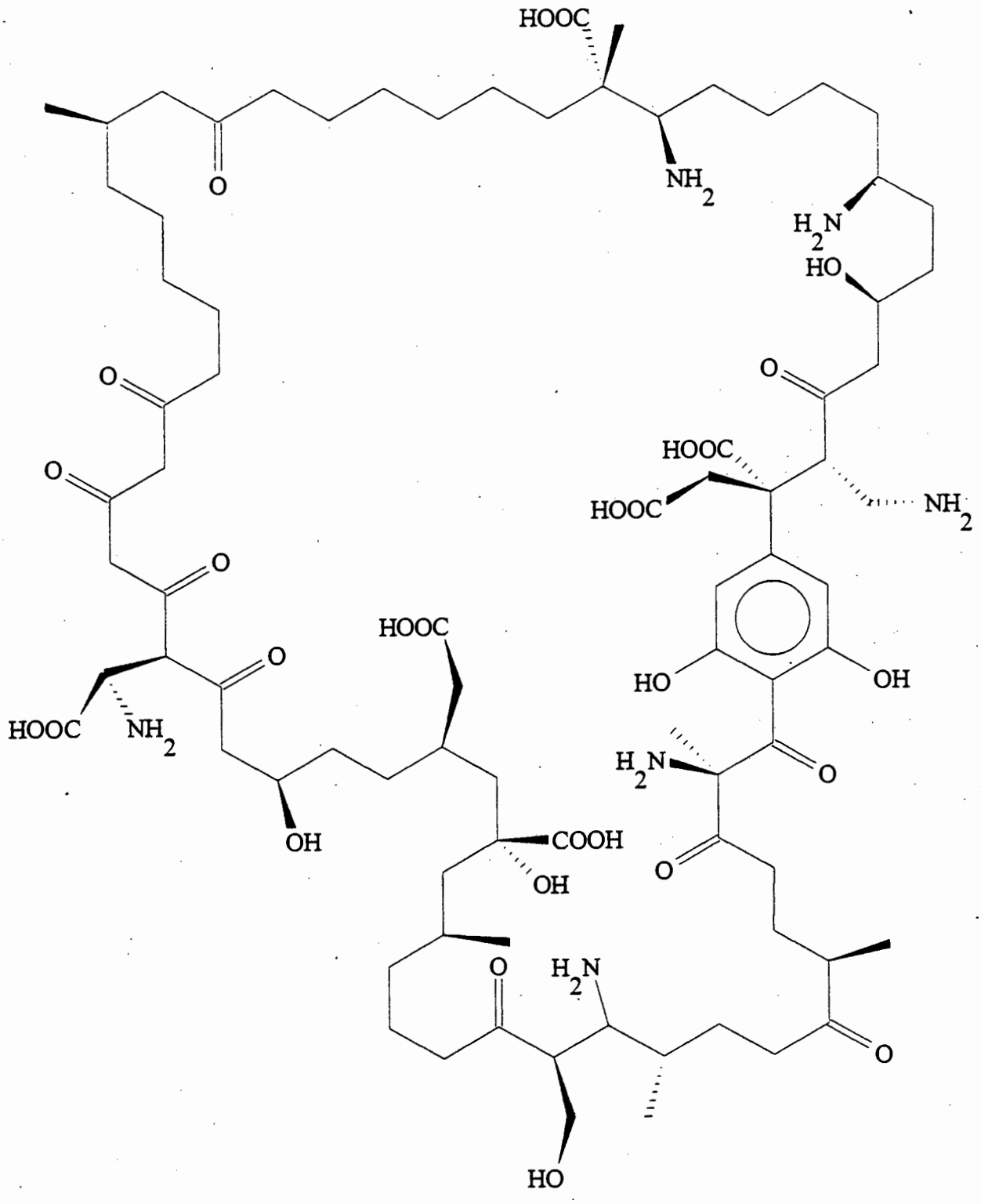


Figure 3.5: A hypothetical structure for marine fulvic acid as predicted by RANDOM.

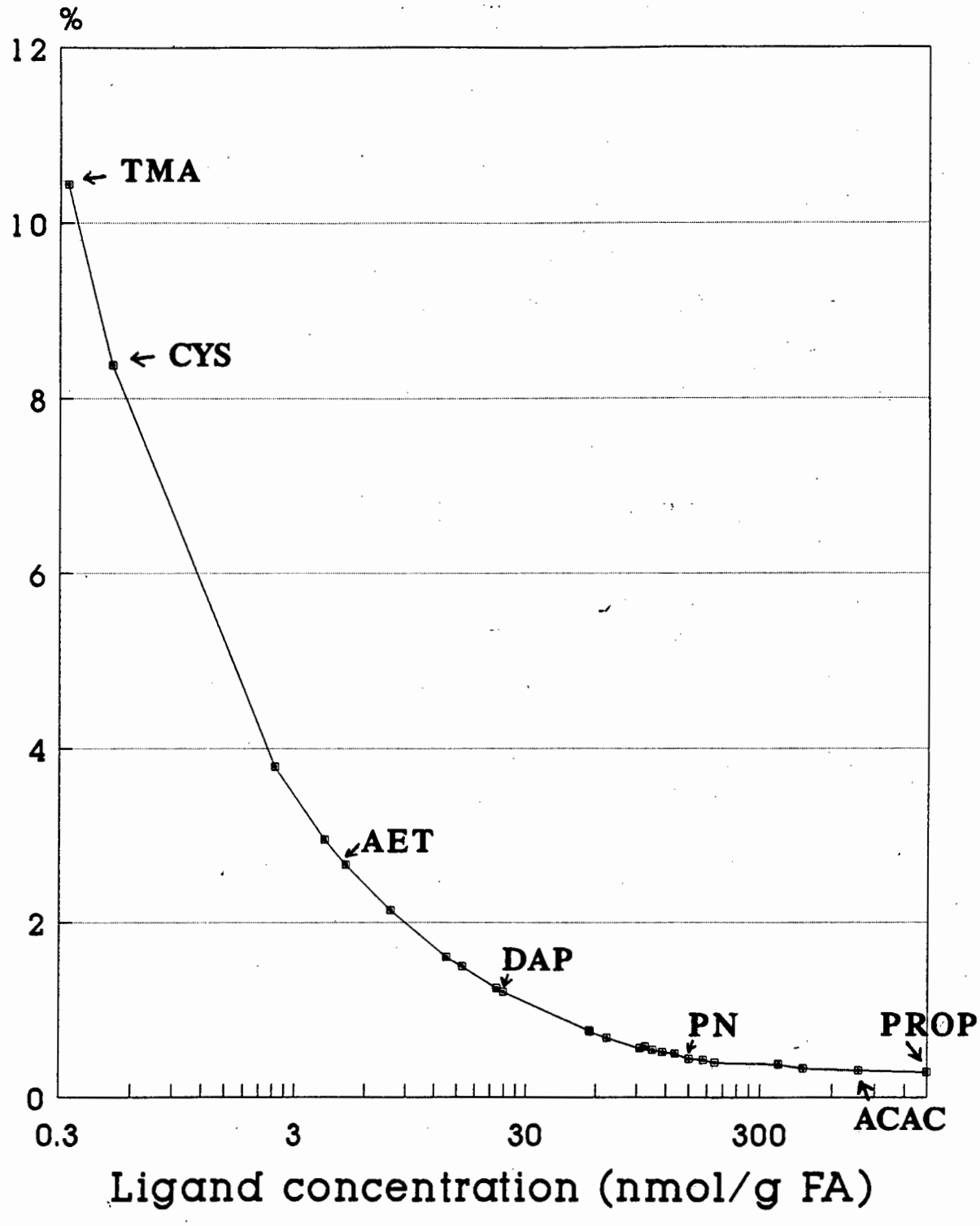


Figure 3.6: The relationship between RANDOM ligand concentration and the standard deviation of that concentration expressed as a percentage of the concentration.

To measure the effect of the fraction of aliphatic carbons that occur in methyl groups this fraction was varied from 0 to 0.4. The results are shown graphically in Figure 3.7. An empirical value of 0.2 was chosen because no evidence to the contrary is available which is the same as that used by Murray [Mur81]. At the functional group concentrations used the effect of this variable is negligible for most ligands except that as the branching increases sites 9 and 16 are seen to increase in concentration.

The percentage aromaticity was also varied from 7.5% to 20.0%. The effect thereof is presented in Figure 3.8. As expected the concentrations of residual aromatic groups (phenol (site 8) and benzoate (site 7)) are seen to increase. This is the result of there being more aromatic carbons which means that the ortho arrangements needed for sites 3 and 5 are less likely to occur. There is also an increase in site 9 concentration (acetylacetone) as a consequence of there being less aliphatic carbons which makes the β-diketo arrangement more likely. The monodentate site 16 (propanoate) decreases in concentration as site 9 is counted before site 16 and any carboxylates on the central carbon are thus ignored. A greater fraction of the carboxylate groups are also to be found in the bi- and tridentate sites, as increased aromaticity means fewer aliphatic carbons and hence a greater probability of the occurrence of bi- and tridentate sites. The model was run with 9% of the carbons being aromatic as determined by Harvey et al. [Har83].

Another factor which was varied was that of the fraction of carboxylate groups that are aromatic. The results are to be found in figure 3.9. As expected aliphatic carboxylate sites decrease while the aromatic sites (5 and 7) increase. The phenolic site 8 decreases since phenolic hydroxyls are now found in site 5 (salicylate). The value chosen for the model was 0.05.

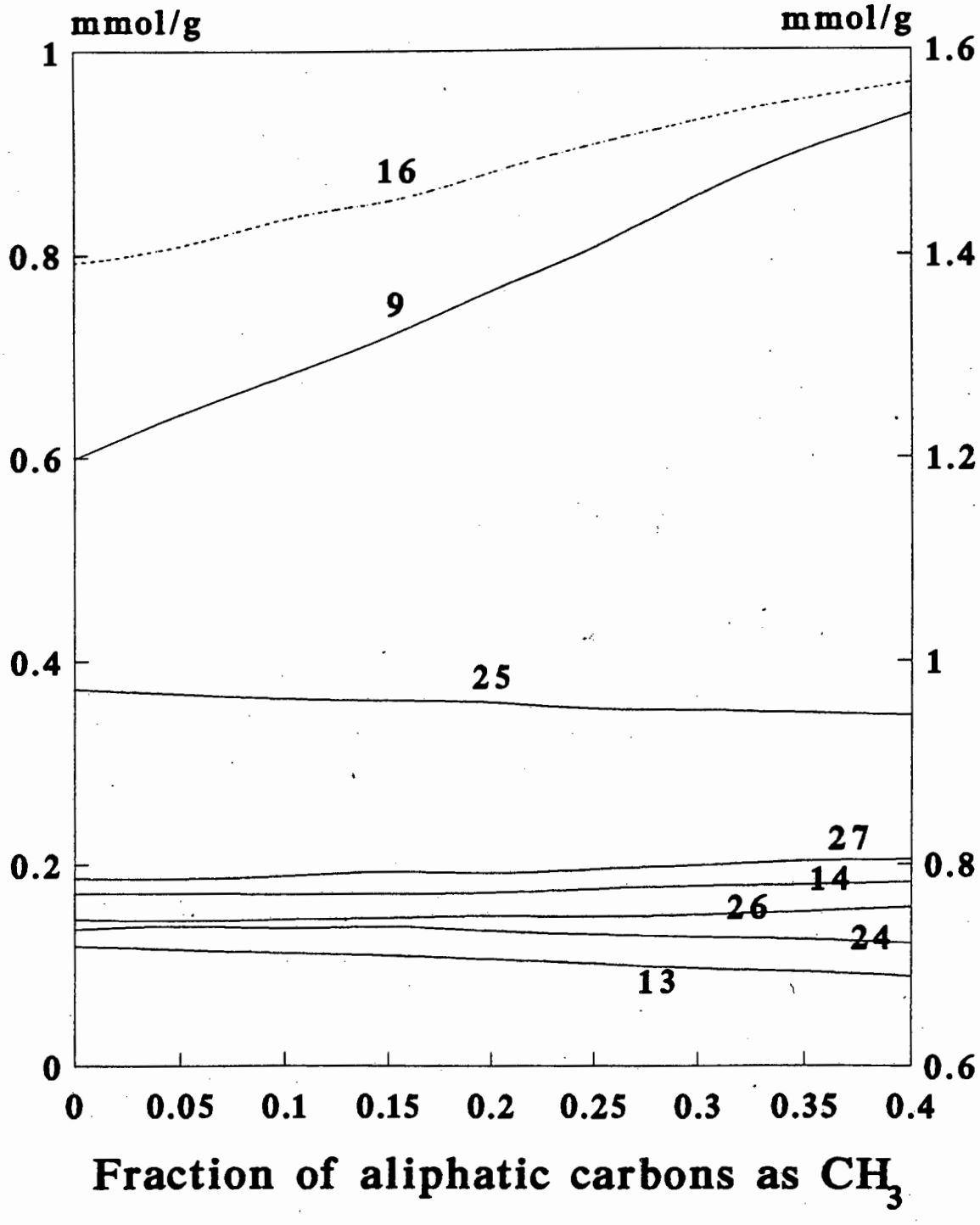


Figure 3.7: The effect of changing the fraction of aliphatic carbons occurring in methyl groups on binding site concentrations of the eight most prevalent aliphatic binding sites. The concentration of propanoic acid (site 16) may be read off the right-hand scale.

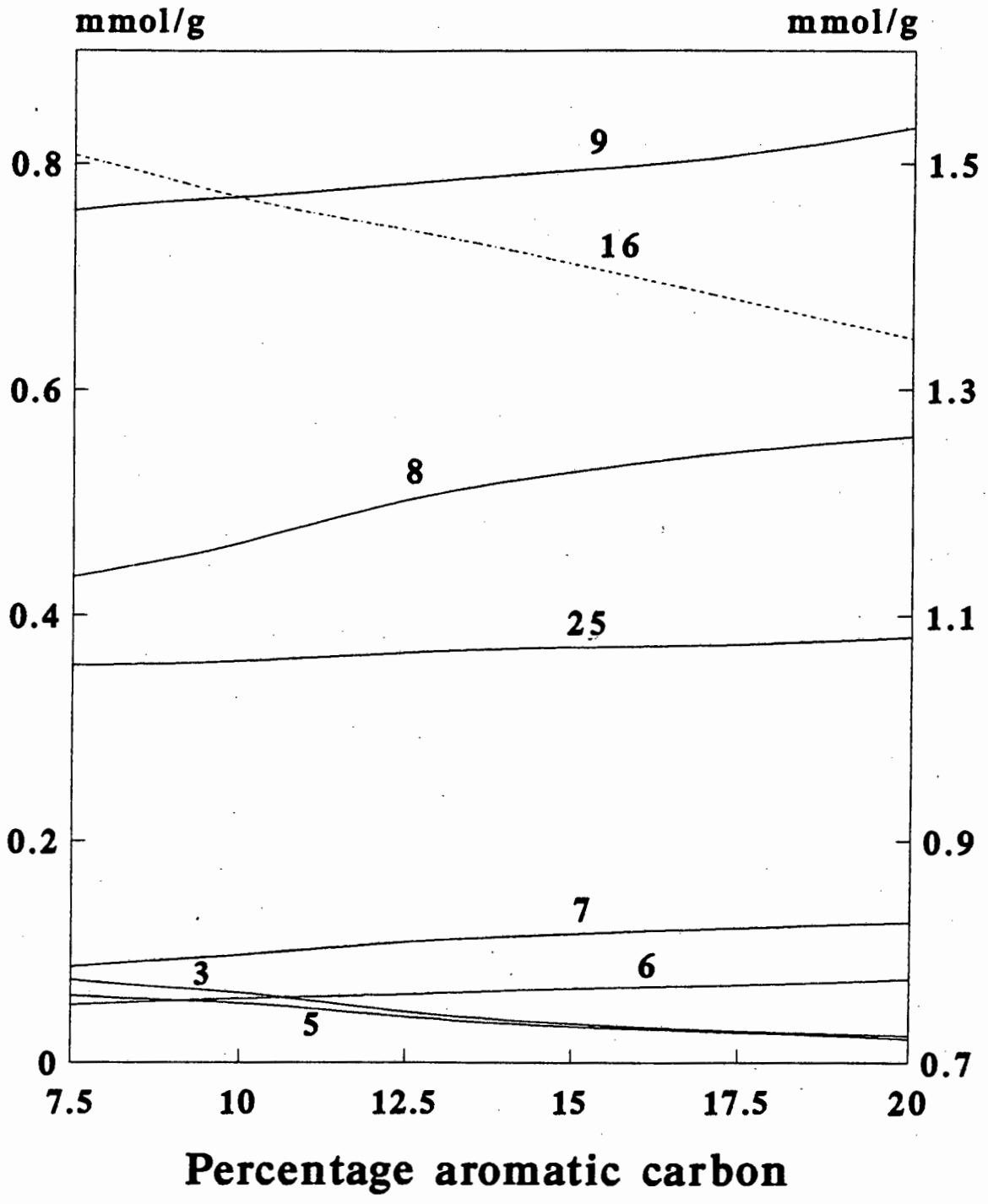


Figure 3.8: The effect of percentage aromatic carbon on the calculated concentrations of aromatic binding sites and the three most common aliphatic sites. The concentration of phthalic acid was 0.0 meq g^{-1} (site 4) throughout. The concentration of propanoic acid (site 16) may be read off the right-hand scale.

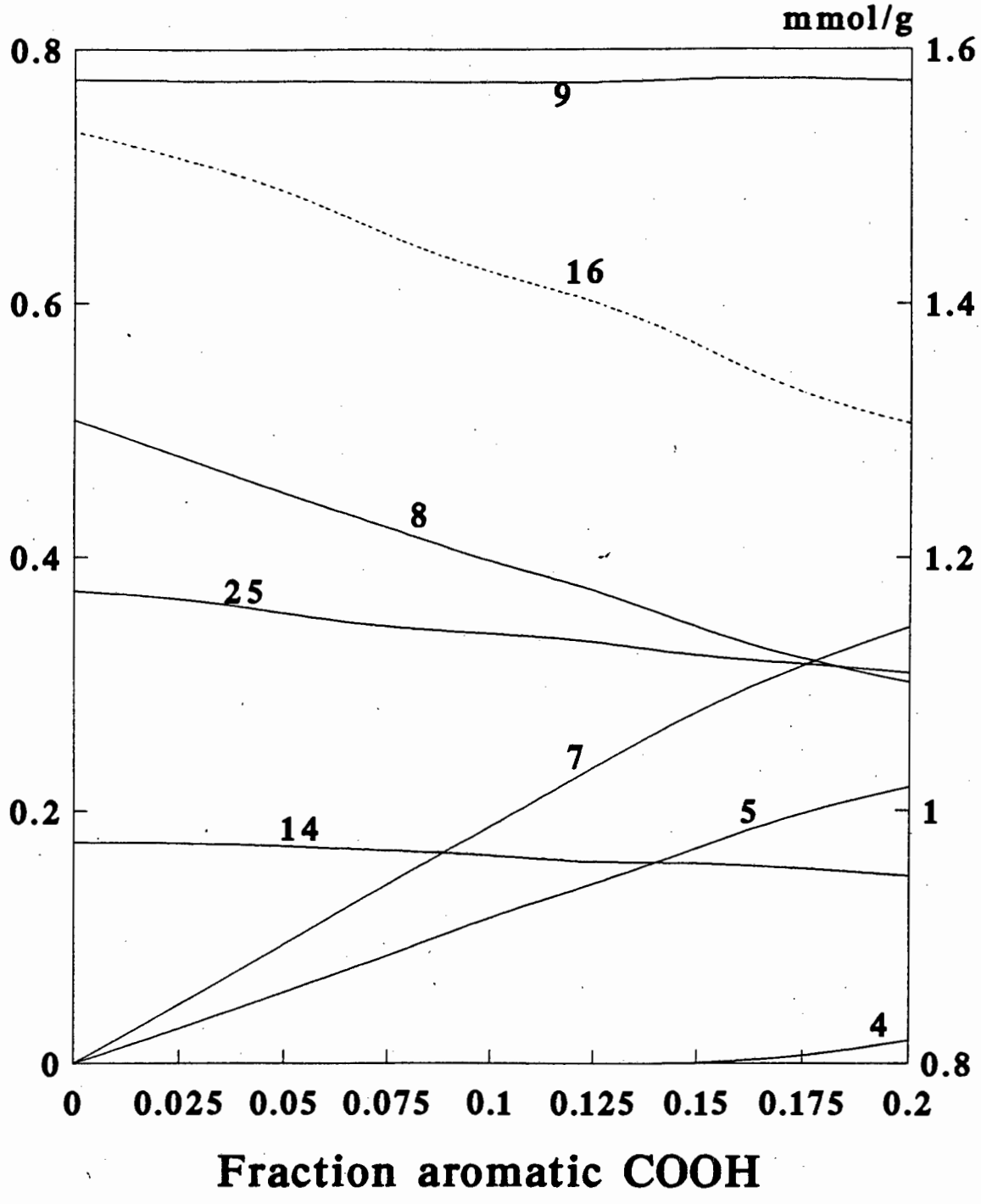


Figure 3.9: The effect of varying the fraction of carboxyl groups that occur on aromatic rings on the calculated concentration of the aromatic sites and the three most prevalent aliphatic sites. The concentration of propanoic acid (site 16) may be read off the right-hand scale.

The chosen fraction of carboxylate groups on aromatic rings was based on the following formulae. The number of mmoles of aromatic sites for carboxylate in 1 g of fulvic acid is given by

$$n_{ar} = 2/3\ (\%C \times \%aroC / 120.11) - [\text{phen OH}] - [\text{quin}] - [OCH_3]$$

where [ ] is the concentration of the relevant functional group in meq g^{-1}. The number of aliphatic sites is given by

$$n_{al} = 2\ \{(\%C \times (100 - \%aroC) / 120.11) - [C{=}O] - [COOH]\} - [SH] - [NH_2] - [\text{alc OH}]$$

For the input data used, n_{ar} = 1.9 and n_{al} = 57.0. On a purely random allocation of carboxylate groups, the fraction that is aliphatic would be expected to be 0.03. The value chosen thus includes a slight bit of specificity.

The elemental percentage of carbon was also varied. The effect of this variation may be seen in figure 3.10. The effect was to increase most binding site concentrations as %C decreased except for the residual monodentate sites (sites 7 (not shown), 8 and 16) which decreased in concentration. The reason for this is that as %C decreases the number of carbons in the fulvic acid decreases, forcing functional groups to be assigned closer together thereby favouring bi- and tridentate sites. The final elemental percentage that was used was 51.25% which is representative of marine humic and fulvic material.

As expected varying the functional group concentrations had most notable effects on the sites that included the particular functional group. Other sites change in sympathy with these variations. Thus by increasing the nitrogen functionality one would expect sites 20, 21, 22, 23, 24, 25, 26 and 27 to increase which does happen. Since these sites are counted before the sites which have aliphatic carboxylate and alcoholic -OH on them, the

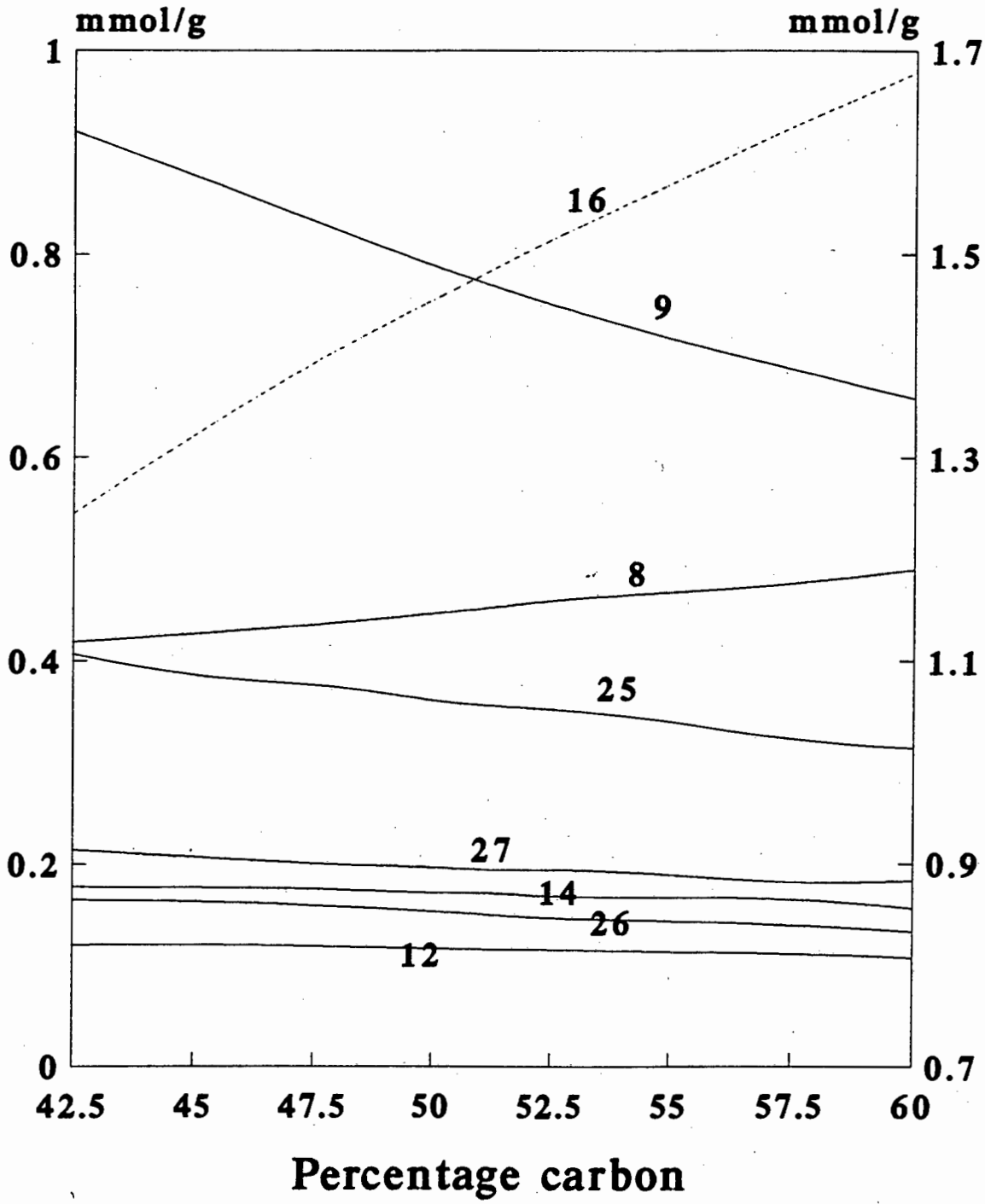


Figure 3.10: The effect of varying the percentage carbon on the calculated concentration of the eight most prevalent sites. The concentration of propanoic acid (site 16) may be read off the right-hand scale.

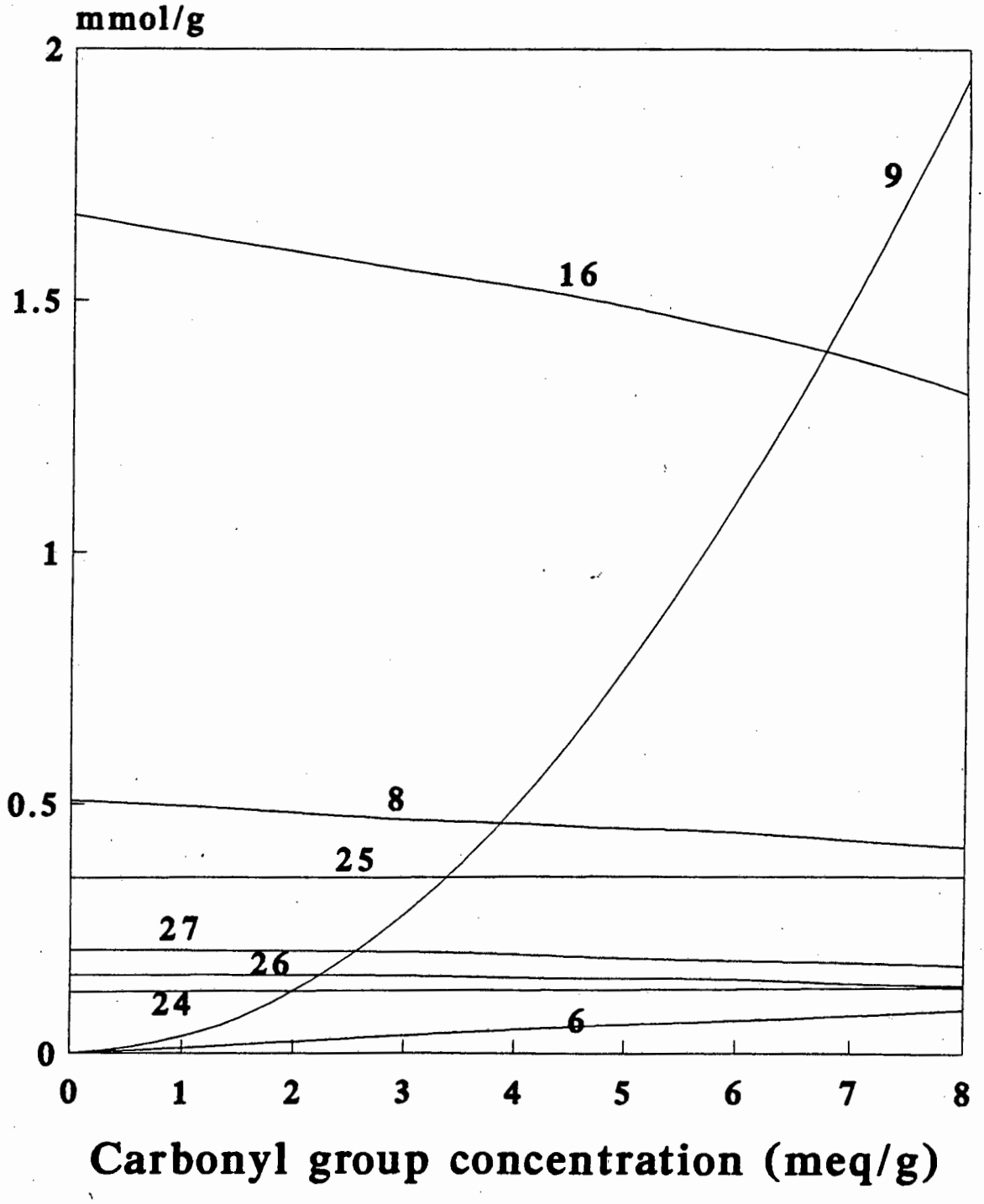


Figure 3.11: The effect of varying carbonyl group concentration on the carbonyl-containing ligands: acetylacetone (site 9) and 2-acetylphenol (site 6) as well as the six most prevalent other ligands.

concentrations of the latter are seen to decrease. The effect of varying the carbonyl concentration is shown in figure 3.11. Noticeable is the sharp increase of site 9. This results from carbonyl groups being forced closer together, thereby into the β-diketo arrangement. It can be observed that for a carbonyl concentration of 5 meq g^{-1}, sites 6 and 9 account for only 1.56 meq g^{-1} or 31.2% of the carbonyl content. The rest of the carbonyls are thus ignored. RANDOM was also run to provide binding site concentrations for the following cases:

1) Sulphur is excluded.
2) 50% of the nitrogen exists as $-NH_2$ (Total nitrogen content is 3.70 meq g^{-1}). Sulphur is again excluded.
3) Nitrogen and sulphur are excluded.
4) All the residual oxygen exists as alcoholic -OH (11.2 meq g^{-1}). This is a model for ether linkages. Nitrogen and sulphur are excluded.

The ligand concentrations for the above models may also be found in Table 3.2.

Any discrepancy between output percentage compositions, molecular weight and H/C ratios are the result of the assumptions made when setting up the model. For instance the %O oxygen is much less than that found experimentally as a result of ether linkages being ignored. Consequently the percentages of the other elements increase while the molecular weight is less than 2000 g mol^{-1}. The same applies to the nitrogen and sulphur which is not accounted for in the amine or thiol groups.

3.6 MODELLING ORGANIC COMPLEXATION IN SEAWATER

The model has provided the first method of estimating binding site concentrations for marine fulvic acids. The site concentrations along with the formation constants for the

relevant metal-ligand equilibria were then input to the overall seawater model to model the effects of marine organic matter. The results thereof are discussed in Chapter Five. Also indicated are the sites that are most important for binding metals which will show that the overall effect of marine fulvic acid may be modelled by relatively few ligands. Many of the RANDOM ligands form weak complexes and are present in concentrations that are so low, that these ligands are insignificant.

As new functional group data come to light, this model may be improved. Furthermore more detailed stucture may be incorporated into the code.

3.7 COMPILATION OF A DATABASE CONTAINING STABILITY CONSTANTS FOR TRACE METAL-MODEL LIGAND INTERACTIONS

The same procedure was followed for setting up a database for the interactions of metal ions with the fulvic acid ligands as was employed when setting up the database for inorganic interactions. Firstly all the possible interactions between the model ligands in Figures 3.1, 3.2, 3.3 and 3.4 and the metal ions present in seawater were listed. Stability constants for these interactions were then obtained and corrected for ionic strength and temperature to give constants relevant to an ionic strength of 0.7 mol dm^{-3} at 25 °C.

Stability constants were obtained for the most part from the critical compilations of Martell and Smith [Mar74a, Smi75, Mar77, Smi82, Smi89]. Where these compilations did not include formation constants, more recent literature values were sought. The corrected constants as well the literature sources for these constants may be found in the database listing in Appendix 1.

In some cases formation constants were not available for the interactions of certain metals with the ligands in figures 3.1 and 3.2. In these cases stability constants for metal ion interactions with ligands with the same functional groups arrangements were used.

Stability constants were not available for the interaction of Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+} and Pb^{2+} with 2,3-dihydroxy-2-methylbutanoic acid. Constants for the interaction of these metals with 2,3-dihydroxypropanoic acid (glyceric acid) were used to fill the gap. Similarly constants were not available for the interaction of Fe^{2+}, Fe^{3+}, Li^{+} and Ag^{+} with 2-hydroxy-2-methylpropanoic acid. These constants were then estimated from those available for interactions with 2-hydroxypropanoic acid (lactic acid) in the case of Li^{+} and hydroxyacetic acid (glycolic acid) for the rest.

The stability constants for the interaction of Li^{+}, Na^{+}, K^{+}, Mn^{2+}, Fe^{2+}, Sn^{2+}, Cr^{3+} and Ag^{+} with propanoic acid were estimated from those reported for acetic acid [Mar77, Smi82, Smi89]. Stability constants were also not available for the interaction of Mn^{2+}, Fe^{2+} and Pb^{2+} with diethylmalonic acid. For these three metals, the reported stability constants for their interaction with malonic acid were used. A ligand with a shorter carbon chain was also used in the case of metal interactions with 1,2-propylenediamine. Stability constants for Mn^{2+}, Fe^{2+}, Co^{2+}, Hg^{2+}, Pb^{2+} and Cr^{3+} were obtained from those reported for their interaction with 1,2-ethylenediamine.

3.8 VALIDATION OF THE RANDOM APPROACH

Before use can be made of a model such as RANDOM in a system like seawater which contains many unquantified interactions, the model needs to be tested in a system which is much simpler and has been quantified. If the model compares well with the quantities measured experimentally, confidence can then be placed in the model predictions in more complicated systems.

In order to test RANDOM, a well analysed fulvic acid is needed. Unfortunately the amount of experimental work performed on marine fulvic acid samples is small. However, detailed analysis has been performed on fulvic acid samples extracted from the Suwannee River in the Georgia, USA. The elemental composition, functional group composition and pH behaviour of these samples have been extensively studied and are collected in a compilation released by the U.S. Geological Survey [USG89]. This material was used to validate RANDOM in a previous study of fulvic acid by Julius Pretorius [Pre90]. However, owing to confusion over what the output of the original RANDOM meant, this validation was not performed properly.

The two characteristics of fulvic acid that were used to test RANDOM in the previous work [Pre90] was used again in the present work viz. the pH behaviour of pure fulvic acid (protonation studies) and the complexation of a metal (namely copper) by this material. Because the purpose of RANDOM is ultimately to provide insight into trace metal behaviour with dissolved organic matter, these two characteristics should provide some insight into the validity of using RANDOM to model fulvic acid.

The functional group and elemental compositions of Suwannee River fulvic acid used in this study as input for RANDOM are listed in Table 3.3. These quantities were the mean of results published in the report of the U.S. Geological Survey [USG89] and elsewhere [Ste83, Thu83, Mac85, Aik87]. Table 3.4 lists the average ligand concentrations that were generated by RANDOM over 100000 fulvic acid structures.

Although Suwannee River fulvic acid is well characterized with respect to percentage carbon and carboxylate groups doubt still exists over the percentage aromatic carbon, and the phenolic hydroxyl concentrations. Consequently models were developed to observe the affect of varying these parameters as well as the fraction of carboxylate groups on aromatic carbons.

Table 3.3: Functional group composition used by RANDOM to model Suwannee River fulvic acid

Elemental composition	
C:	53.5
O:	41.4
H:	4.3
N:	0.7
S:	0.1
Structural Composition(%)	
Aromatic C:	25.0
Functional Groups (meq/g)	
Carboxyl:	6.5
Carbonyl:	2.5
Quinone:	0.0
O-CH3:	0.0
Phenolic OH:	3.5
Alcoholic OH:	2.0
Aliphatic NH2:	0.3§
Aliphatic SH	0.0

Fraction of carboxyl groups on aromatic rings = 0.25

§: Assuming 60% of nitrogen is aliphatic NH2.

Table 3.4: Proposed concentrations of the model ligands as predicted by RANDOM for Suwannee River fulvic acid

No	Ligand	Concentration (meq g^{-1})
30	CYS	0.0000
33	AET	0.0000
20	DAP	0.0000
31	TMA	0.0000
26	PN	0.0000
21	ASP	0.0106
9	ACAC	0.2205
32	TLA	0.0000
22	SER	0.0038
24	ALA	0.0256
25	BEAL	0.0790
27	ETA	0.0232
34	MET	0.0000
10	MAL	0.0673
13	DEM	0.3876
11	DHMB	0.0187
12	SUCC	0.4481
15	2-HMP	0.1785
14	3-HBT	0.3515
3	CAT	0.7623
5	SAL	0.6639
4	PHTH	0.0937
6	ACPH	0.1155
8	PHEN	1.1960
7	BENZ	0.7736
16	PROP	2.3655

3.8.1 Validating the protonation of fulvic acid

3.8.1.1 Theory

RANDOM predicts the concentration of a set of metal and proton binding sites on fulvic acid. If one knows the concentration of binding sites, the number of protons bound to the fulvic acid may be calculated at any pH.

An assumption is made that the binding sites investigated are all the sites which allow protons to bind. With RANDOM this assumption is justified since all proton binding sites are accounted for. RANDOM has three monodentate sites (BENZ, PHEN and PROP) which make up any residual proton binding. The sum of the binding sites times the number of dissociable protons at each sites should thus equal the total acidity.

The average number of protons bound to an individual random ligand at any pH is thus given by the sum of the concentrations of the individual ligand species times the number of bound protons of that species divided by the sum of the concentrations of all of the ligand species [Ros78]. This may be written as follows

$$ {}^{i}Z_H = \frac{\sum_{j=0}^{J} j\beta_{01j}[H^+]^j}{\sum_{j=0}^{J} \beta_{01j}[H^+]^j} \qquad 3.9 $$

where $[H^+]$ is the activity of the hydrogen ion;

β_{01j} is the protonation constant for species HL_j;

i is the ligand number in the RANDOM program;

Expression 3.9 can be derived for each of the RANDOM ligands. To get the total number of protons bound to a particular mass of fulvic acid, one needs to multiply each of the ${}^{i}Z_H$ by the concentration of that ligand in that amount of fulvic acid. It was decided to calculate the number of protons bound per gram of fulvic acid since RANDOM provides ligand concentrations in mmol g^{-1} and calculations are thereby simplified. Consequently the number of protons bound per gram of fulvic acid is given by

$$FA_{Z_H} = \sum_{i=1}^{N} ({}^{i}Z_H \times L_i) \qquad 3.10$$

where L_i is the concentration of ligand i as predicted by RANDOM in mmol g^{-1} of fulvic acid.

A difference from the interpretation used by Julius Pretorius in his validation [Pre90] is that L_i is not divided by the number of dissociable protons. This was the result of an erroneous interpretation of the output of RANDOM which was presented as meq g^{-1}. This led to the contribution of bidentate sites such as salicylate and succinate being underestimated.

Z_H may also be calculated from titration data for fulvic acid such that

$$Z_{Hexp} = \frac{(T_H - [H^+] + K_W/[H^+])}{T_{FA}} \qquad 3.11$$

where T_{FA} is the total number of grams (normally moles) of fulvic acid in the titration

and T_H is the total concentration of dissociable protons present plus the concentration of protons from the mineral acid or base (negative) in the solution at any titration.

Some idea of the usefulness of modelling with RANDOM may be gained, by comparing the experimental Z_H with that predicted by RANDOM.

3.8.1.2 Comparison with experimental protonation data

Experimental pH titration data was taken from Bowles et al. [Bow89]. They dissolved Suwannee River fulvic acid in distilled water and then titrated with NaOH. They measured the response of the pH of the system against the volume of sodium hydroxide added. This data then allowed experimental Z_H values to be calculated according to equation 3.11 provided the total acidity of the fulvic acid sample was known. Appendix 4 contains the miscellaneous TURBO PASCAL programs including ZHBAR which calculates experimental and RANDOM Z_H values.

Noyes and Leenheer used ^{1}H-NMR in dioxane-d_8 to obtained a total acidity value of 10.5 ± 0.9 meq g^{-1}. Figure 3.12 shows the effect of calculating Z_H with varying total acidities. It can be seen that with a total acidity of 9.0 meq g^{-1} Z_H becomes negative and does not level off at 0 protons bound at high pH which means that the total acidity should be higher than 9.0 meq g^{-1}.

Reports of the carboxylate content vary slightly. Thurman and Malcolm [Thu83] report this to be 6.0 or 6.2 meq g^{-1} depending whether titrations or NMR are used to measure this quantity. Noyes and Leenheer [Noy89] report this to be 6.8 meq g^{-1} while the titration data of Bowles et al. [Bow89] would indicate this value to be 6.1 meq g^{-1}.

Because total acidity is likely to be above 9.0 meq g^{-1}, the carboxylate content for RANDOM was set in between the extremes but on the high side at 6.5 meq g^{-1}.

The phenol content of Suwannee River fulvic acid provides a much greater variation. Thurman and Malcolm report values of 1.7, 2.1 and 3.6 meq g^{-1}. The values quoted in the U.S. Geological Survey also vary. Bowles et al. [Bow89] give a value of 1.2 meq g^{-1} but this is based on the number titrated at pH 10 and then doubled. Noyes and Leenheer [Noy89] report 1.4 meq g^{-1} to be reactive to acetylation and Thorn [Tho90] reports 1.5 meq g^{-1} is reactive to methylation. Noyes and Leenheer [Noy89], however, used IR spectrometry to discover that 2.7 meq g^{-1} phenols are unreactive to acetylation. This would give a total phenol content of 4.1 meq g^{-1}. They also calculated total non-carboxylate hydroxyl content to be 4.4 meq g^{-1} and alcoholic hydroxyl content to be 1.5 meq g^{-1} which would give a phenol content of 2.9 meq g^{-1}. It was decided to set the phenol content at 3.5 meq g^{-1} which is the middle of the range estimated by Noyes and Leenheer [Noy89]. It also gives a total acidity [phenol + carboxylate content] of 10.0 meq g^{-1} which is in line with the results in figure 3.12 as a lower total acidity would imply a negative Z_H.

It should be noted that Thorn [Tho89] reports total non-carboxylate hydroxyl content to be 7.0 meq g^{-1} while Thurman and Malcolm [Thu83] report this to be 5.4 or 8.6 meq g^{-1} depending whether liquid or solid state NMR was used. It was decided to set the alcoholic hydroxyl content to 2.0 meq g^{-1} which would give a total non-carboxylate hydroxyl content of 5.5 meq g^{-1} in the middle of the extremes reported [Thu83, Noy89, Tho89].

Various models were developed using RANDOM. The fraction of carboxylate groups on aromatic rings was set at 0.25 and 60% of the total nitrogen was assumed to be present as aliphatic -NH_2. Figure 3.13 shows the effect of a simple model in which all binding is to

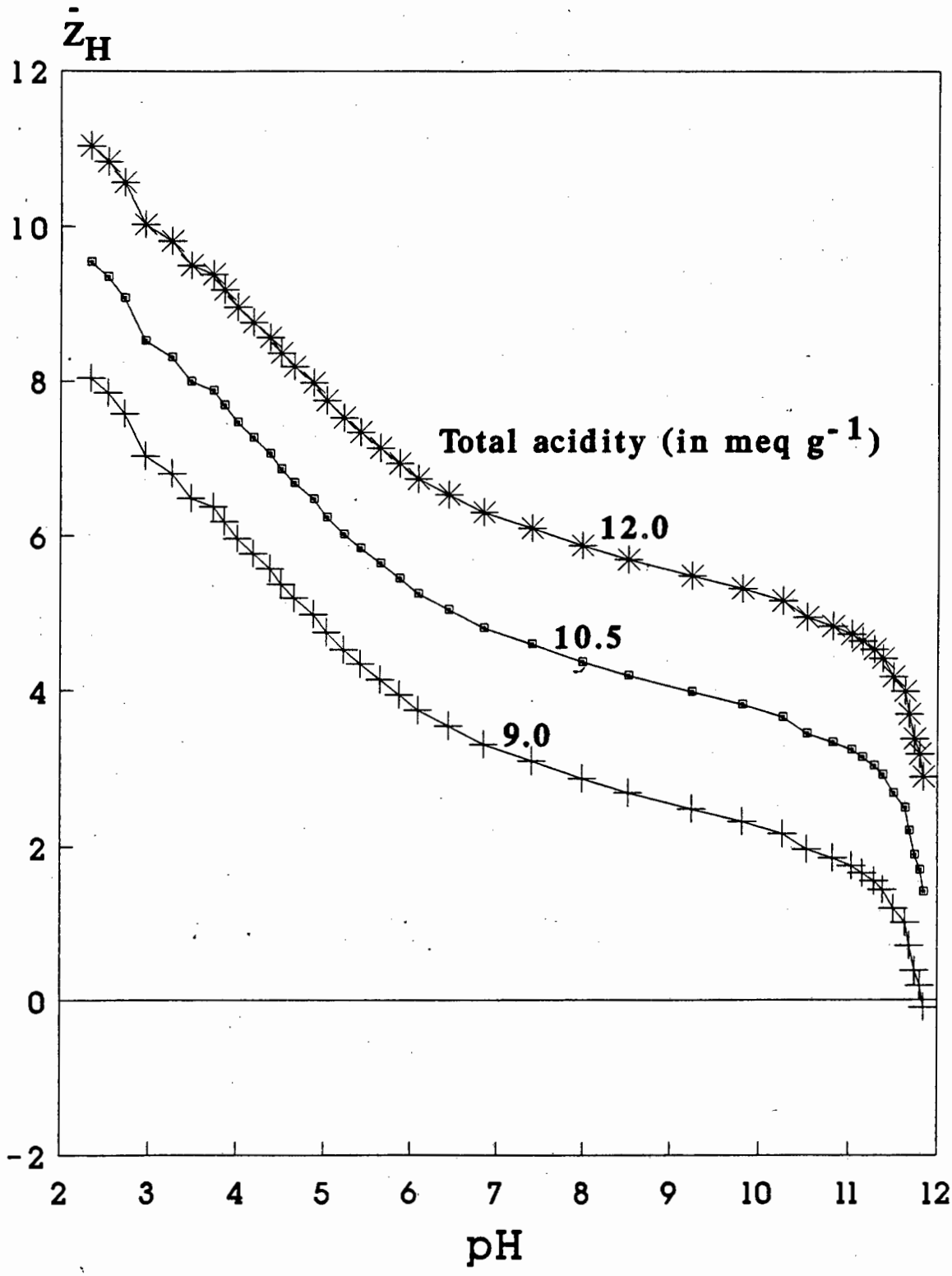


Figure 3.12: The effect on experimental Z_H of varying the total acidity measured for Suwannee River fulvic acid.

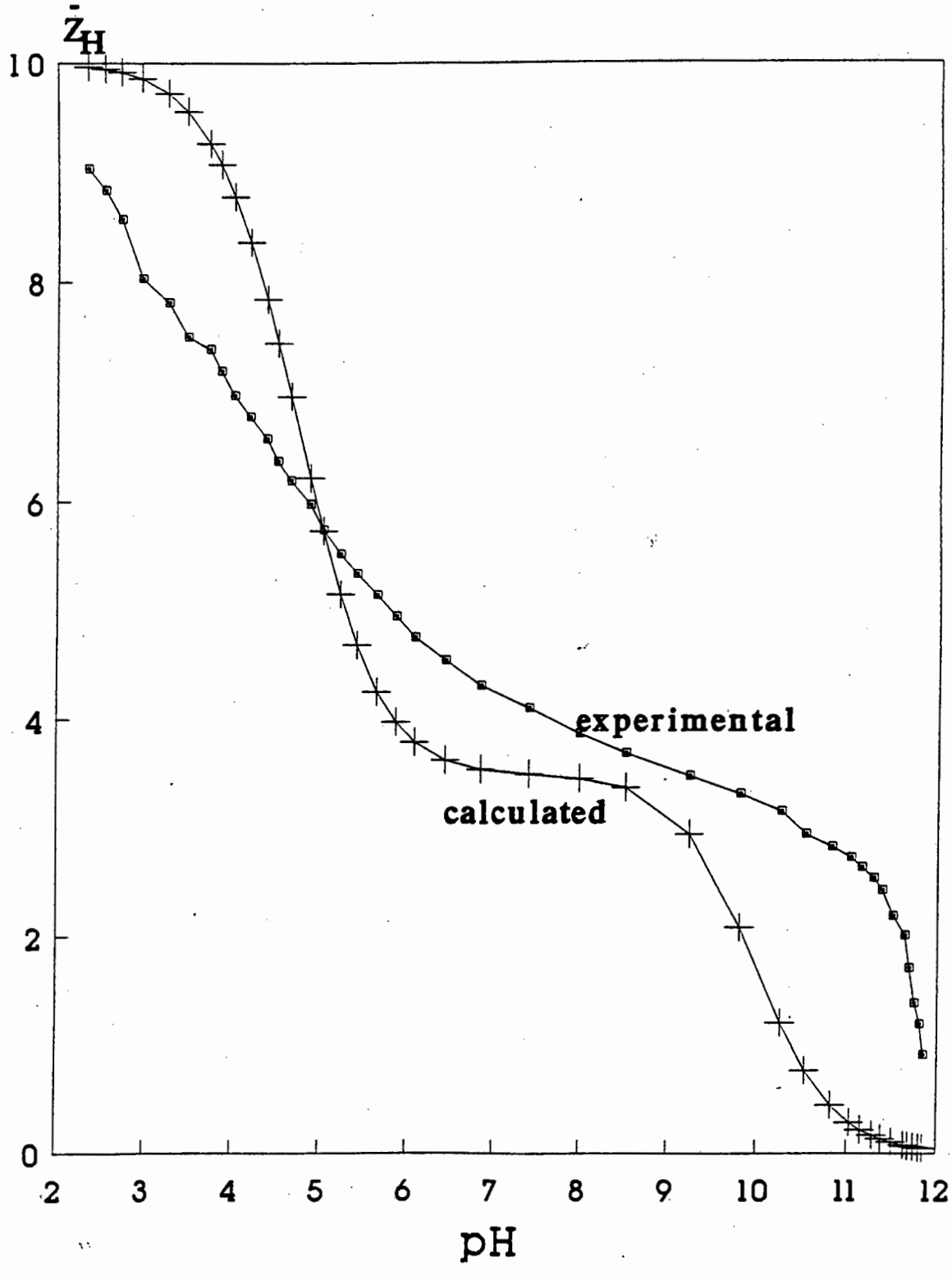


Figure 3.13: A comparison of experimental and calculated Z_H's for Suwannee River fulvic acid. The calculated curve is for the model in which binding to only monodentate sites is allowed.

monodentate sites. Consequently only PHEN, BENZ and PROP were used as ligands in the model. The fit is quite poor. The later models developed showed significant improvement.

Figure 3.14 shows the improvement that is brought about by including all the RANDOM ligands in the model (standard model). The ligand concentrations are as in Table 3.4. Except at low and high pH the experimental and calculated data coincide. The non-coincidence at high pH may be explained by the fact that many of the phenol groups in fulvic acid have been observed to be unreactive to pH titrations [Bow89, Noy89, Tho89]. This results in a large variation in the measured phenol content. RANDOM assumes that the phenols will behave as if they were part of the ligands (PHEN, ACPH, CAT and SAL) but the phenolic hydrogens are obviously more tightly bound than expected. At low pH, the RANDOM fulvic acid does not dissociate. This is because only 3 RANDOM ligands (nitrogen-containing ligands excluded because of their low concentration) have pKas below 3 (DEM = 2.15, PHTH = 2.95 and SAL = 2.97). Consequently RANDOM's prediction does not fit well at low pH because protons are too tightly bound.

However, in the pH range 4.5 to 9.5 the fit is extremely good. This is the pH range that can normally be expected in the aqueous environment and RANDOM is thus validated as far as the protonation of fulvic acids is concerned for natural waters. It should also be noted that Bowles et al. [Bow89] performed their titrations in solutions that had no background electrolyte. At high and low pH ionic strength effects would be expected to have a significant effect. Furthermore electrostatic interactions are likely to be more significant at these pH's because of the higher charge that the fulvic acid would then be carrying.

One of the parameters which was chosen arbitrarily was the fraction (F_{ar}) of carboxylate groups on aromatic rings. This was varied from 0.00 to 0.35 and the results are shown in

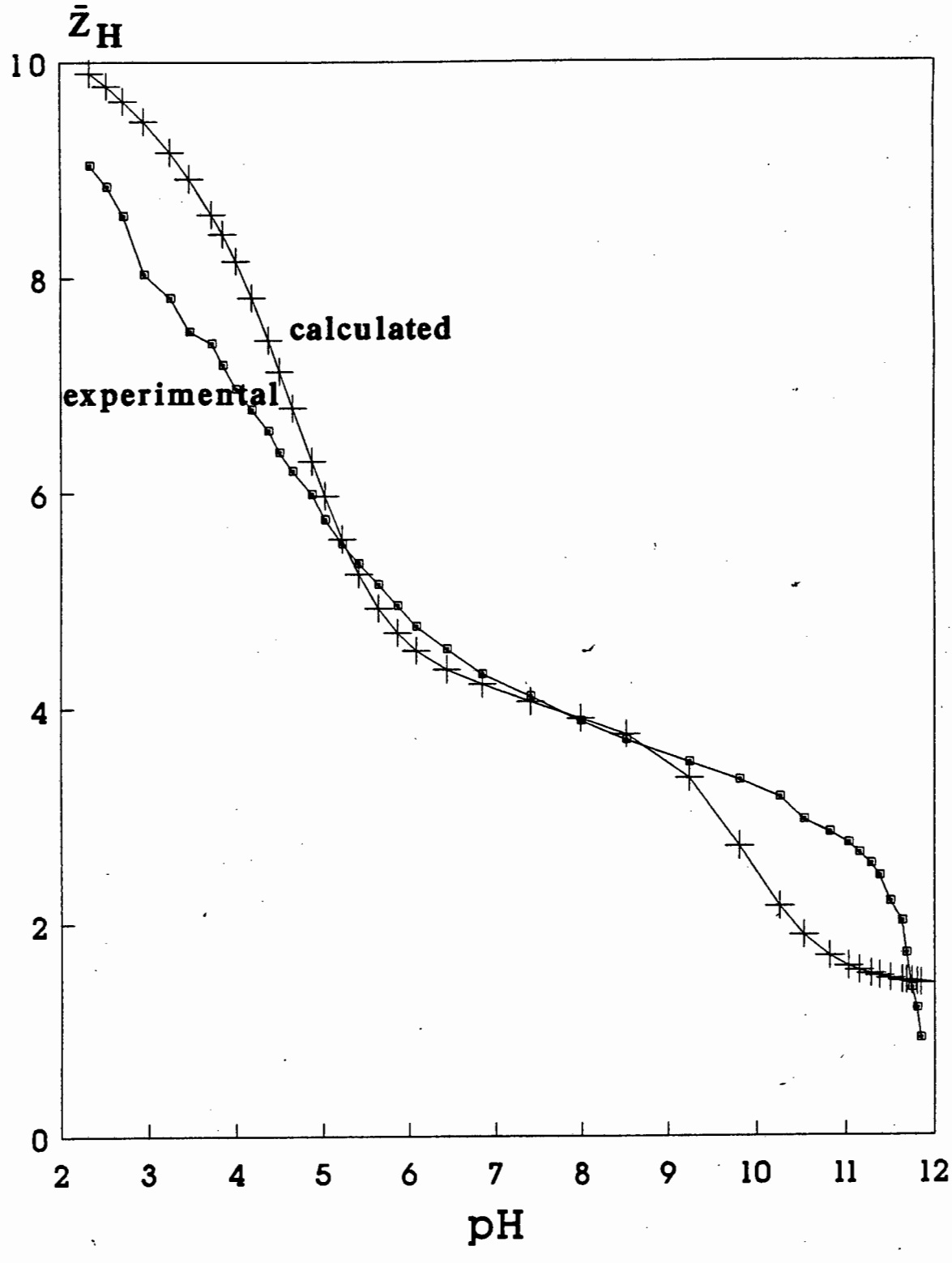


Figure 3.14: A comparison of experimental and calculated Z_H's for Suwannee River fulvic acid. The calculated curve is for the standard model mentioned in the text.

Figure 3.15. When this value was set to 0.4, 6% of the structures generated by RANDOM were incompatible with the input data as there were not sufficient aromatic carbons to accommodate the phenolic and aromatic carboxylate groups. Figure 3.15 indicates that the effect of the fraction of -COOH's on aromatic rings is small except at high pH. At high pH the result may be explained in terms of the higher SAL versus PHEN content. Pure phenol groups have a pKa of 9.98 while that of the salicylic phenols is 13.74. The slight variation at low pH (3.5-5.5) is because of the difference in pKa between phthalic (as well as salicylic) and benzoic acid carboxylate protons. In the previous work [Pre90] which validated RANDOM against the work of Bowles et al. [Bow89] it was observed that the effect of varying the fraction of aromatic carboxylates was very significant. This, however, was the result of erroneously dividing the ligand concentrations by the number of dissociable protons. Consequently as phthalic and salicylic acid concentration increased, the error increases as there was a division by 2 in their concentration but not one for benzoic acid. The error is obvious at low pH where no protons should be dissociated. Consequently Z_H should approach total acidity for all models. This can be seen in Figure 3.15. Pretorius, however, found Z_H decreased as F_{ar} increased because SAL and PHTH's influence was underestimated.

The aromatic content has been observed to be 20.8% [Thu83] and 28% [Tho89]. 25% in the middle of this range was used in the standard model. Figure 3.16 shows the effect of varying aromatic content on the protonation behaviour. The effect is insignificant except at high pH. This again can be explained by the increase in CAT and SAL concentration at low aromaticity because the groups on rings are forced closer together. Z_H at high pH thus increases as aromaticity increases.

Figure 3.17 shows the effect of varying the fraction of nitrogen groups which occur on aliphatic carbons. The effect is again very small because of the very low nitrogen content in Suwannee fulvic acid. Not shown is the effect of changing the ortho:meta:para ratio of

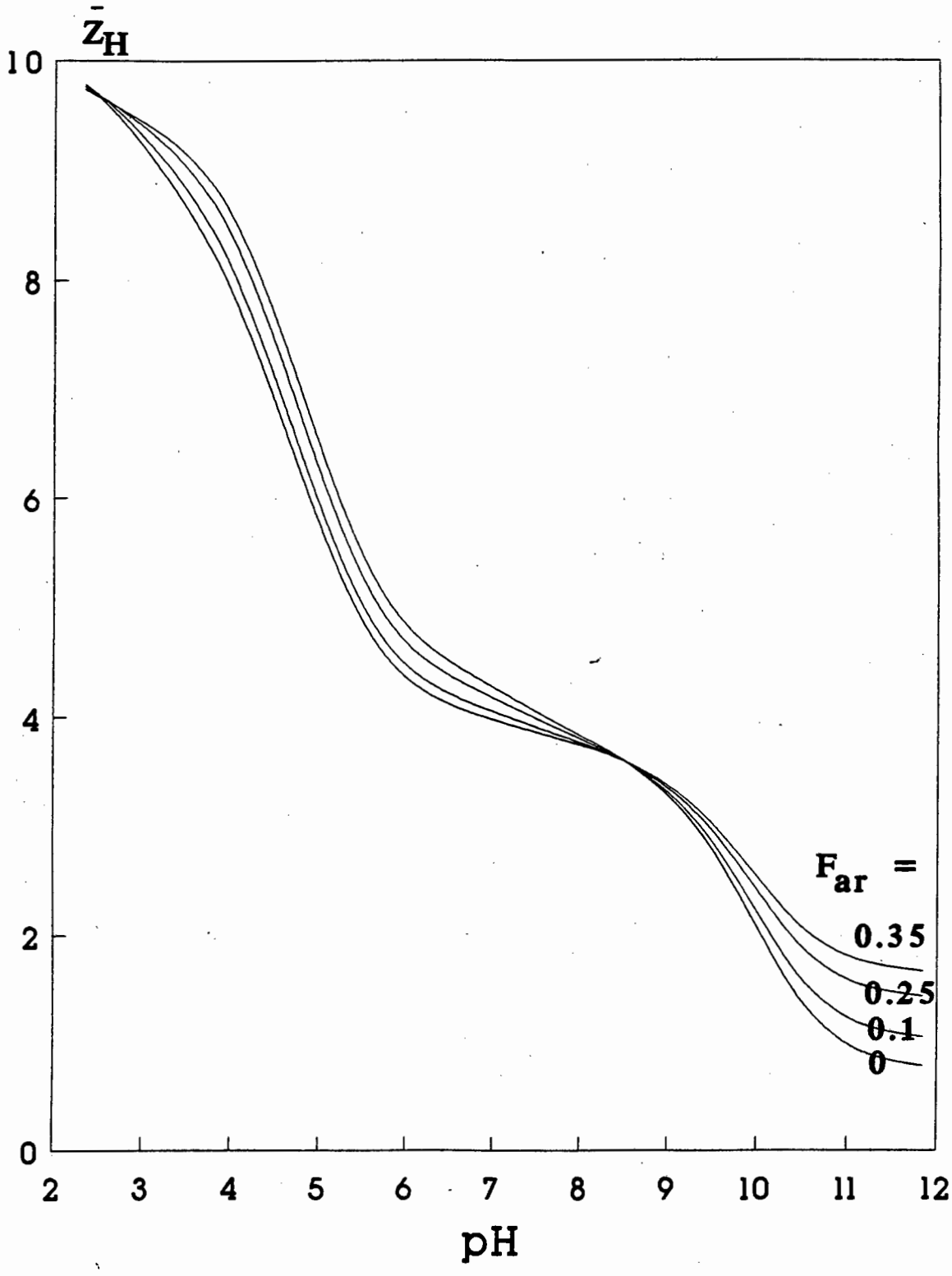


Figure 3.15: The effect on calculated Z_H of varying the fraction of carboxylate groups on aromatic rings for Suwannee River fulvic acid.

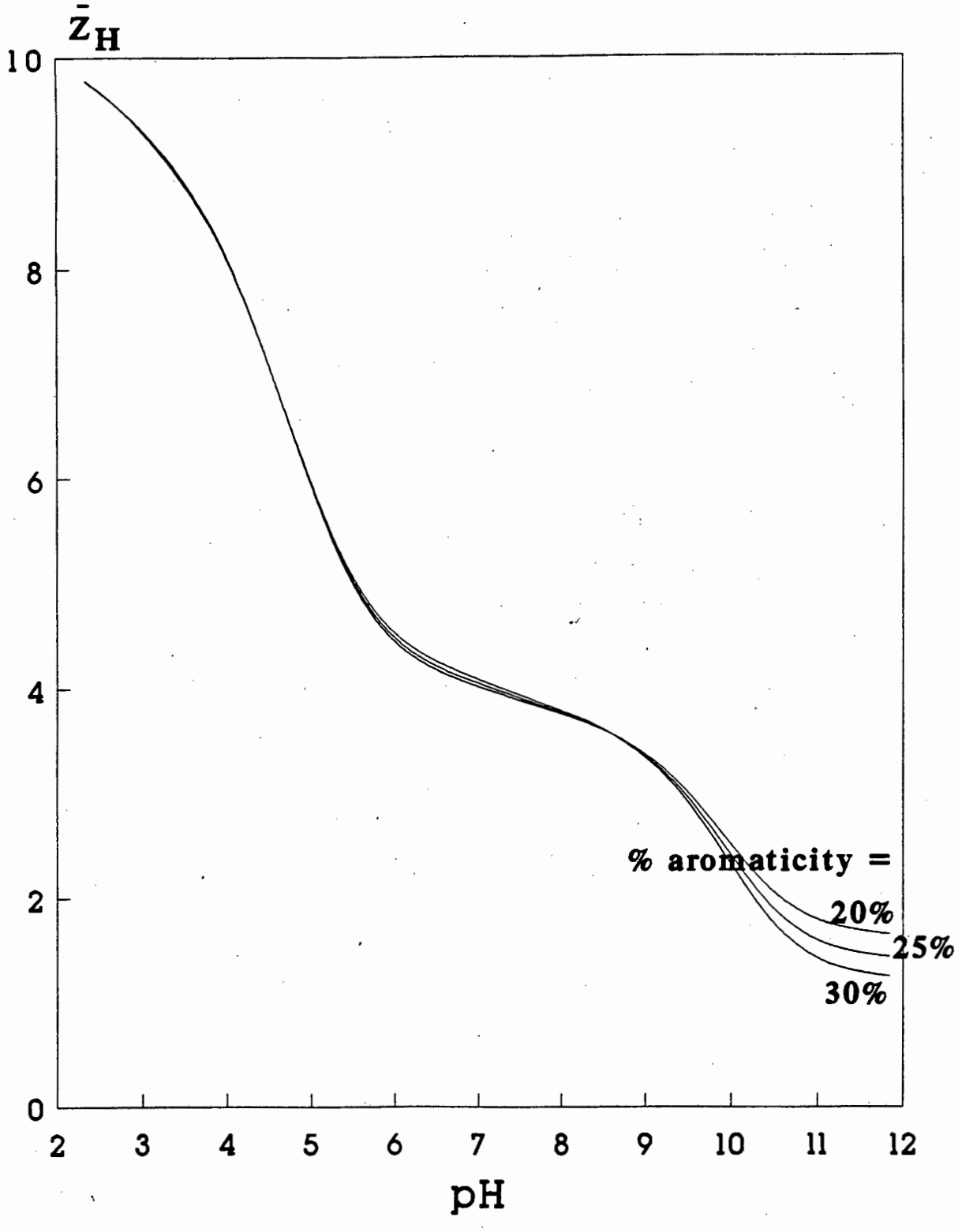


Figure 3.16: The effect on calculated Z_H of varying the percentage aromatic carbon for Suwannee River fulvic acid.

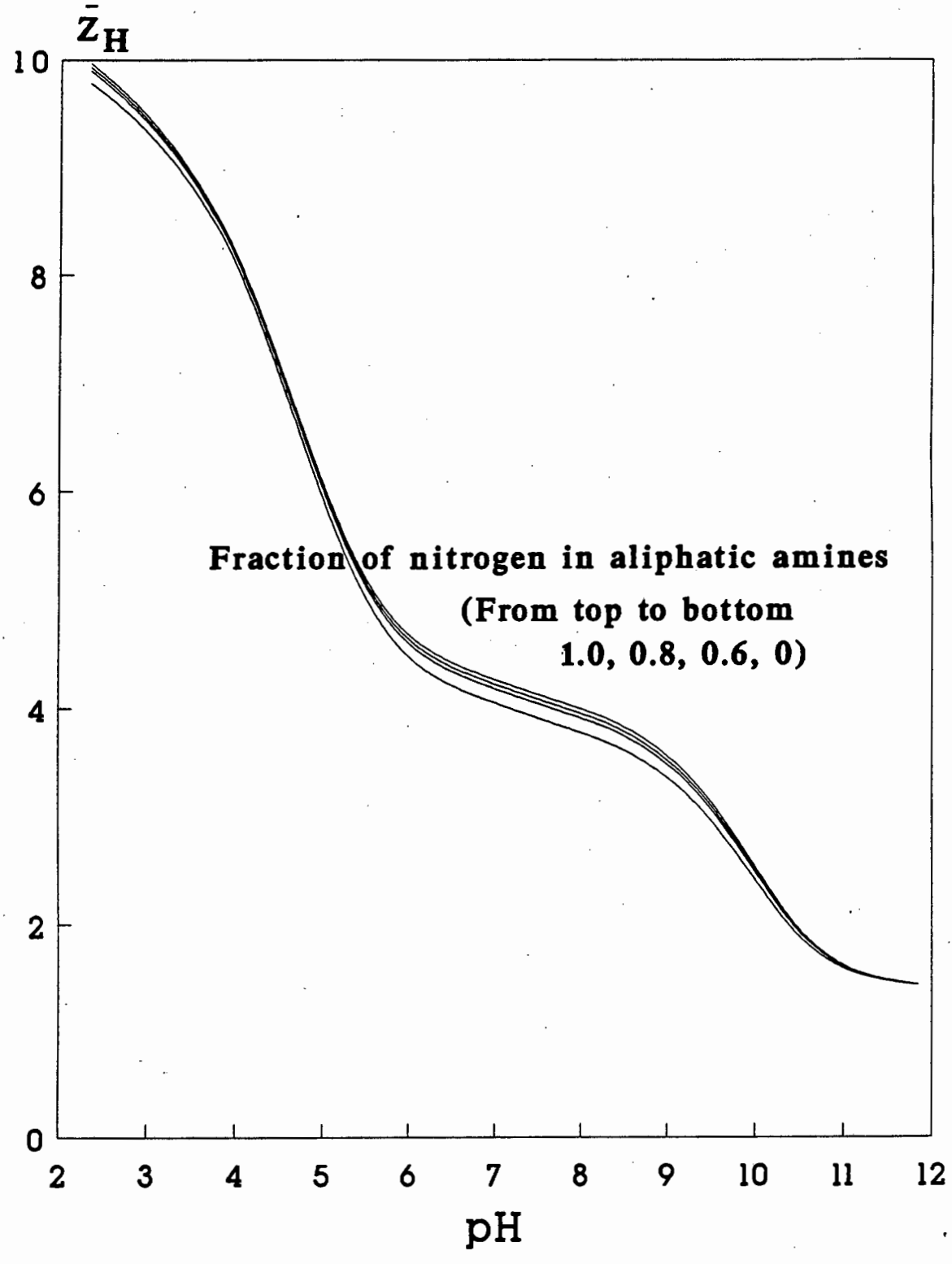


Figure 3.17: The effect on calculated Z_H of varying the fraction of total nitrogen in aliphatic NH_2 groups for Suwannee River fulvic acid.

ring linkages and the fraction of aliphatic carbons in methyl groups. The effect of both is insignificant as was observed by Pretorius in a previous study [Pre90].

Table 3.5 and Table 3.6 give some indication of the effect of the various models. Two statistics are quoted: the root mean square deviation between the experimental and calculated curves and a modified Hamilton R_H statistic

$$R_H = \frac{\sum_{i=1}^{N} ({}^iZ_H^{exp} - {}^iZ_H^{calc})^2}{N \sum_{i=1}^{N} ({}^iZ_H^{exp})^2}$$

The results indicate that the variation between models is small. In the pH range 5.0 to 9.0 the nitrogen models show the best fit. If high pH data points are included increasing the fraction of aromatic -COOH or decreasing aromaticity improves the model but again this effect is not large. What variations that do occur may be explained in terms of variations in the measurements made by Bowles et al. [Bow89], electrostatic effects when the fulvic acids become charged, and ionic strength variations in the original titration. Furthermore at high pH aggregation of the fulvic acids may mean that phenolic protons are not in equilibrium with the solution whereas RANDOM assumes equilibrium. Bowles et al. [Bow89] performed both a continuous titration and a manual titration. In the manual titration the pH was observed to drop steadily between additions (in the pH range 7.0 to 11.5) which would indicate the slow release of protons that are not in equilibrium with solution. At high pH this may explain why the experimental Z_H (calculated from the continuous titration) was higher than that predicted by RANDOM.

In the pH region which is normally experienced in natural waters (4.0 to 9.0) it can be seen that RANDOM accurately predicts the protonation behaviour of Suwannee River fulvic acid.

Table 3.5: RSD values for various models of Suwannee fulvic acid

Low pH	2.0	4.0	4.5	5.0
High pH	12.0	10.0	9.5	9.0
No of Points	40	19	15	11
Model				
Standard	0.799	0.507	0.295	0.156
Monodentate	1.504	0.928	0.699	0.692
$F_{ar} = 0.0$	1.118	0.791	0.535	0.260
$F_{ar} = 0.10$	0.970	0.657	0.411	0.179
$F_{ar} = 0.35$	0.679	0.440	0.324	0.330
%aro = 20	0.731	0.502	0.328	0.265
%aro = 30	0.828	0.501	0.301	0.210
$NH_2 = 1.0$	0.816	0.519	0.303	0.136
$NH_2 = 0.8$	0.806	0.511	0.296	0.141
$NH_2 = 0.0$	0.779	0.504	0.316	0.241

Table 3.6: Hamilton R_H for the models developed

Model				
Standard	0.0239	0.0221	0.0152	0.0099
Monodentate	0.0450	0.0405	0.0360	0.0437
$F_{ar} = 0.0$	0.0335	0.0345	0.0275	0.0165
$F_{ar} = 0.10$	0.0290	0.0287	0.0212	0.0113
$F_{ar} = 0.35$	0.0203	0.0192	0.0167	0.0209
%aro = 20	0.0219	0.0219	0.0169	0.0168
%aro = 30	0.0248	0.0219	0.0155	0.0133
$NH_2 = 1.0$	0.0244	0.0226	0.0156	0.0086
$NH_2 = 0.8$	0.0241	0.0223	0.0153	0.0089
$NH_2 = 0.0$	0.0233	0.0220	0.0163	0.0152

Model codes:

The standard model was developed using the data in Table 3.3. The monodentate model uses only PHEN, BENZ and PROP as ligands. The F_{ar} models show the variation of the fraction of aromatic -COOH's on aromatic rings (Nitrogen content = 0%, % aromaticity = 25%). The %aro models show the variation of changing the percentage of aromatic carbon (Nitrogen content = 0%, F_{ar} = 0.25). The NH_2 models show the variation of changing the fraction of nitrogen as aliphatic NH_2 to the values listed. All other data as in Table 3.3.

3.8.2 Validation of cation binding

In order to validate cation binding, data of metal-fulvic binding for Suwannee River fulvic acid was required. Furthermore this data was needed in a form that contained an experimental measurement that could also be calculated from model predictions.

The trace metal that was chosen to validate cation binding was copper. This is because copper shows the greatest affinity for binding to fulvic acids. Cabaniss and Shuman [Cab88a] measured the binding of copper by Suwannee fulvic acid and it was decided to use their data to validate RANDOM. This is because they measured pCu values (free copper ion activities) which could be generated using MINTEQA2 to allow comparisons.

Consequently the various models developed earlier were tested against the data of Cabaniss and Shuman [Cab88a]. The ligand concentrations for fulvic acid binding sites were input to MINTEQA2 together with the experimental conditions used by Cabanniss and Shuman (i.e. pH, buffer solution component concentrations and total copper concentrations). The database used was the 0.1 mol dm^{-3} database in Appendix 1.2. A problem with the data of Cabaniss and Shuman is that they report copper titration curves for various DOC concentrations and not total fulvic acid concentrations. It was assumed that the fulvic acid used by these authors was 53.5% which allowed fulvic acid concentrations to be calculated. This assumption was also used by Tipping and Hurley [Tip92] when reworking the data of Cabaniss and Shuman [Cab88a].

3.8.2.1 Comparison of experimental and theoretical copper binding to Suwannee River fulvic acid

Figure 3.18 shows the experimental pCu values versus those calculated using RANDOM fulvic acid at a pH of 5.14. Also shown is the free copper concentration in the absence of

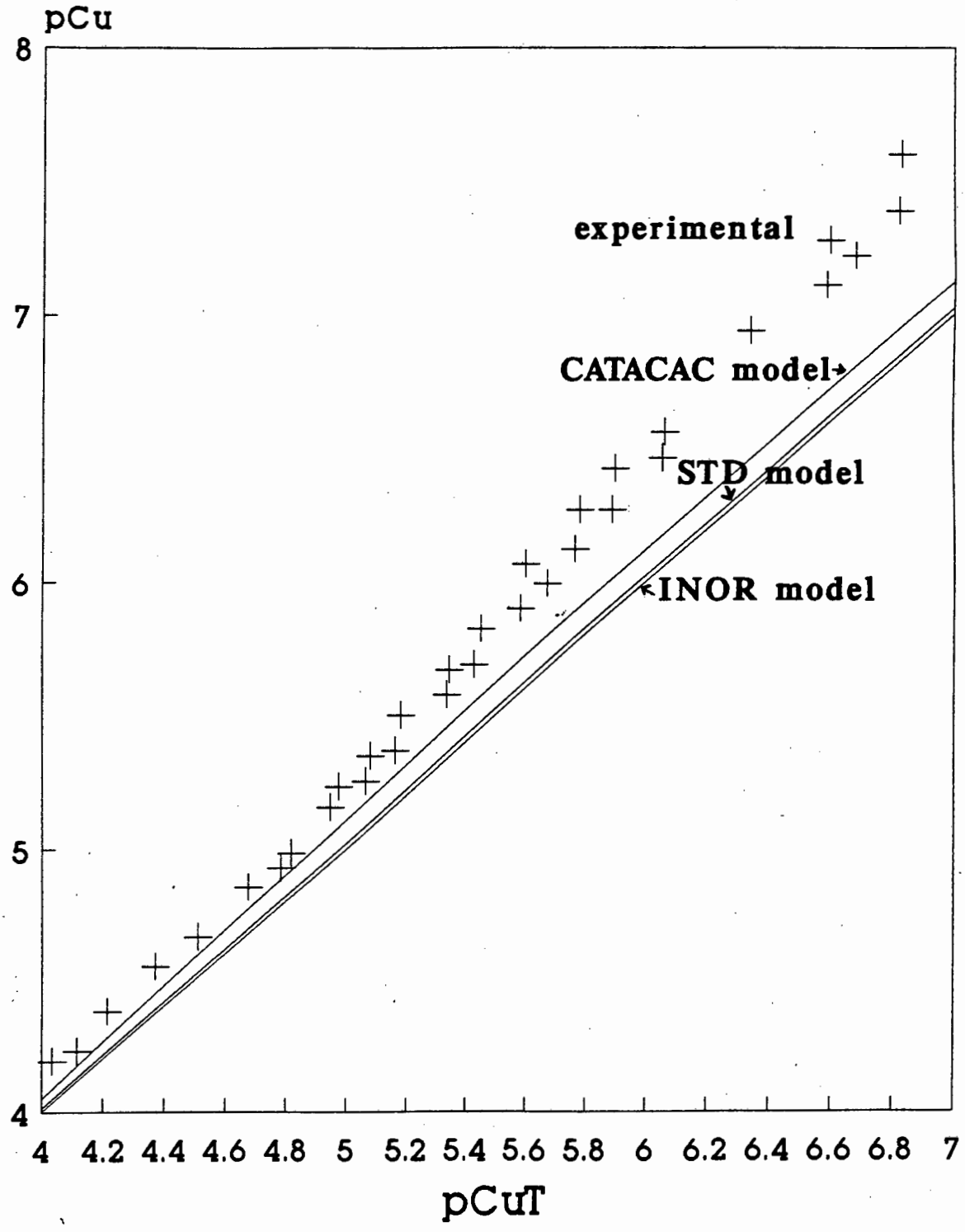


Figure 3.18: A comparison between experimental binding of fulvic acid and the predictions of RANDOM. Conditions: 5 mg dm^{-3} DOC; pH = 5.14; no buffer, I = 0.1 mol dm^{-3}.

fulvic acid. This is indicated by the INOR (or inorganic) model. A further model was developed called the CATACAC (catechol-acetylacetone) model which contained solely catechol and acetylacetone binding sites. In this model all ketone groups are present in ACAC binding sites and all phenols in CAT sites. Using a ketone concentration of 2.7 meq g^{-1} (maximum reported by Thorn [Tho89]) and a phenol concentration of 3.5 meq g^{-1}, one can calculate ACAC and CAT concentrations of 1.35 and 1.75 mmol g^{-1} respectively.

Figure 3.19 shows the variation of pCu with total copper concentration at pH = 7.00. The buffer (1 mmol dm^{-3} phosphate) was also included in the model calculations.

Figure 3.20.1 shows the variation of pCu with total copper concentration at pH = 8.44. The buffer (1 mmol dm^{-3} carbonate) was included in the calculations. Malachite was prevented from precipitating by removing it from the database. The precipitate observed in Figure 3.20.1 causing the straight part of the curves is $Cu(OH)_2$. It can be seen that increased copper complexation is brought about by decreased aromaticity. This is because decreased aromaticity causes an increase in catechol concentration and hence binding. Figure 3.20.2 shows the situation in which all precipitation is disallowed at pH = 8.44. Cabaniss and Shuman [Cab88a] did observe precipitation at high pH. However, they also noted that the precipitate included fulvic acid for which no species was included in the calculation. There is some uncertainty about the solubility product used for $Cu(OH)_2$ in the calculations, so Figure 3.20.2 is probably a more accurate reflection.

Figure 3.21.1 shows the pH dependence of binding by fulvic acid. At low pH RANDOM underestimates binding while overestimating it at high pH. The effect of aromaticity can also be seen at high pH. This is because of the differing catechol concentrations. Some of the discrepancy is the result of Cabaniss and Shuman [Cab88a] having used an unbuffered solution. The comparison of the INORganic curve with the RANDOM and

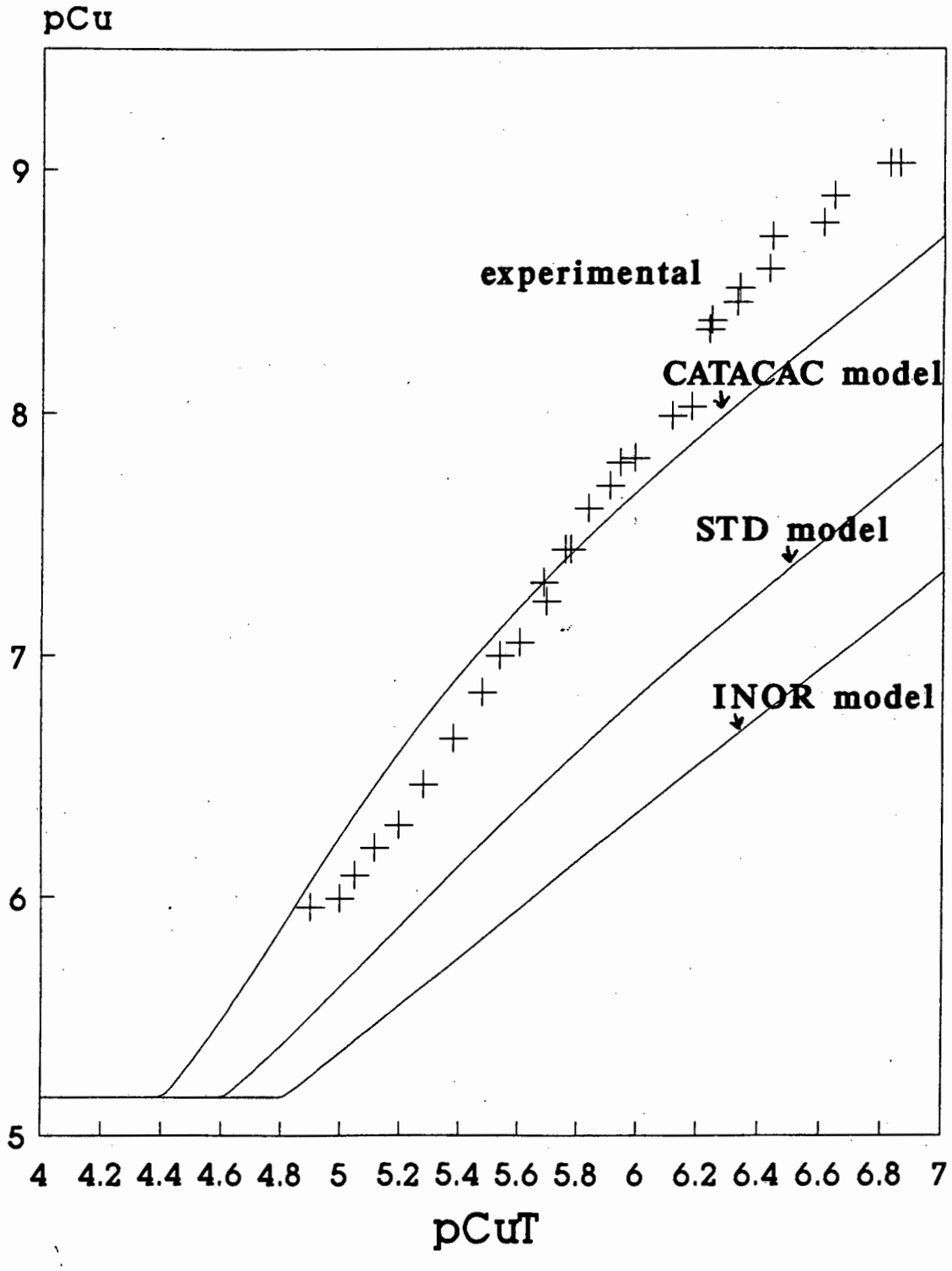


Figure 3.19: A comparison between experimental binding of fulvic acid and the predictions of RANDOM. Conditions: 5 mg dm^{-3} DOC; pH = 7.00; buffer = 0.001 mol dm^{-3} PO_4^{3-}, I = 0.1 mol dm^{-3}.

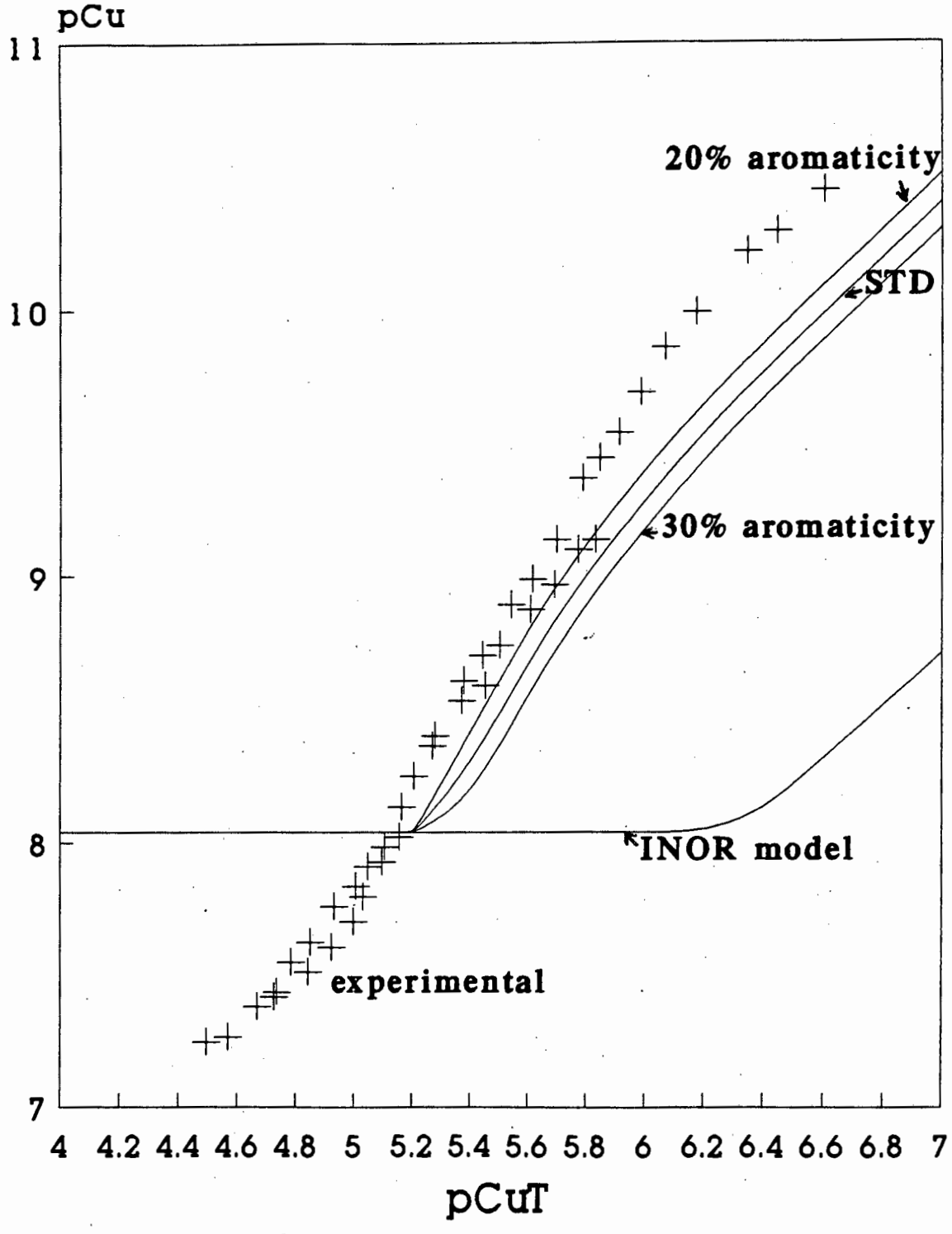


Figure 3.20.1: A comparison between experimental binding of fulvic acid and the predictions of RANDOM. Conditions: 5 mg dm^{-3} DOC; pH = 8.44; buffer = 0.001 mol dm^{-3} CO_3^{2-}, I = 0.1 mol dm^{-3}; $Cu(OH)_2$ precipitation allowed.

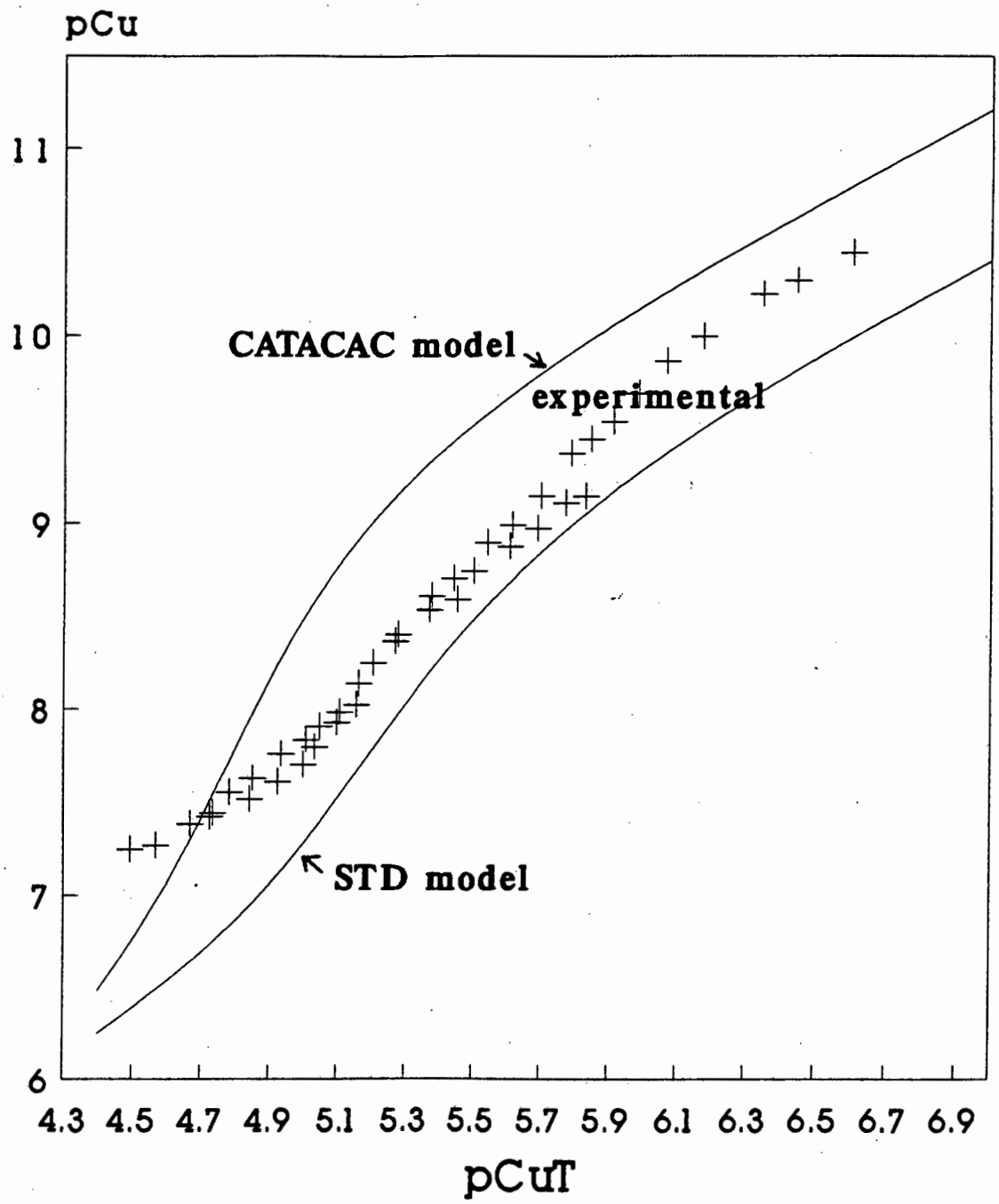


Figure 3.20.2: A comparison between experimental binding of fulvic acid and the predictions of RANDOM. Conditions: 5 mg dm^{-3} DOC; pH = 8.44; buffer = 0.001 mol dm^{-3} CO_3^{2-}, I = 0.1 mol dm^{-3}; precipitation excluded.

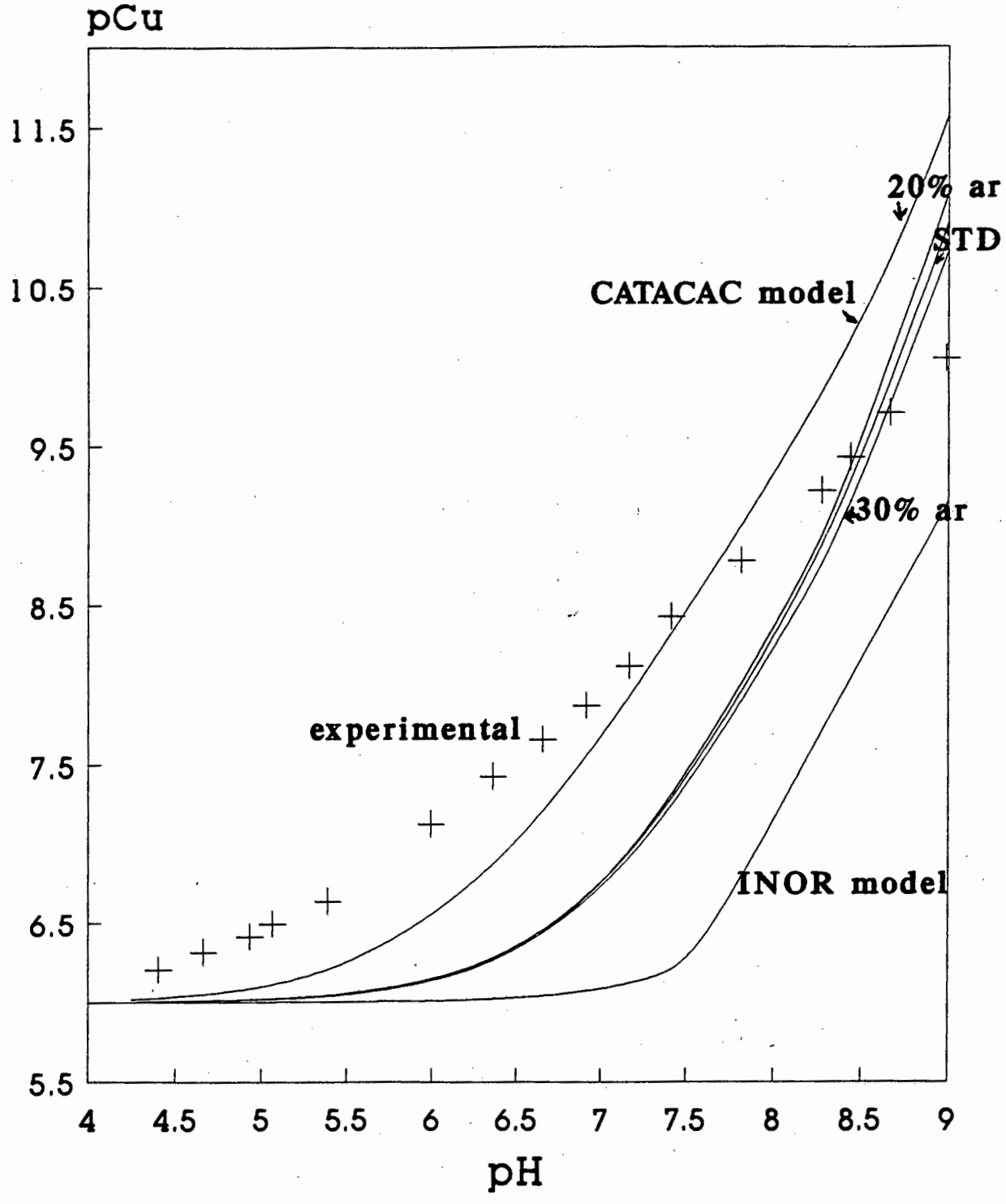


Figure 3.21.1: A comparison between experimental binding of fulvic acid and the predictions of RANDOM as a function of pH. Conditions: 5 mg dm^{-3} DOC; no buffer, I = 0.1 mol dm^{-3}.

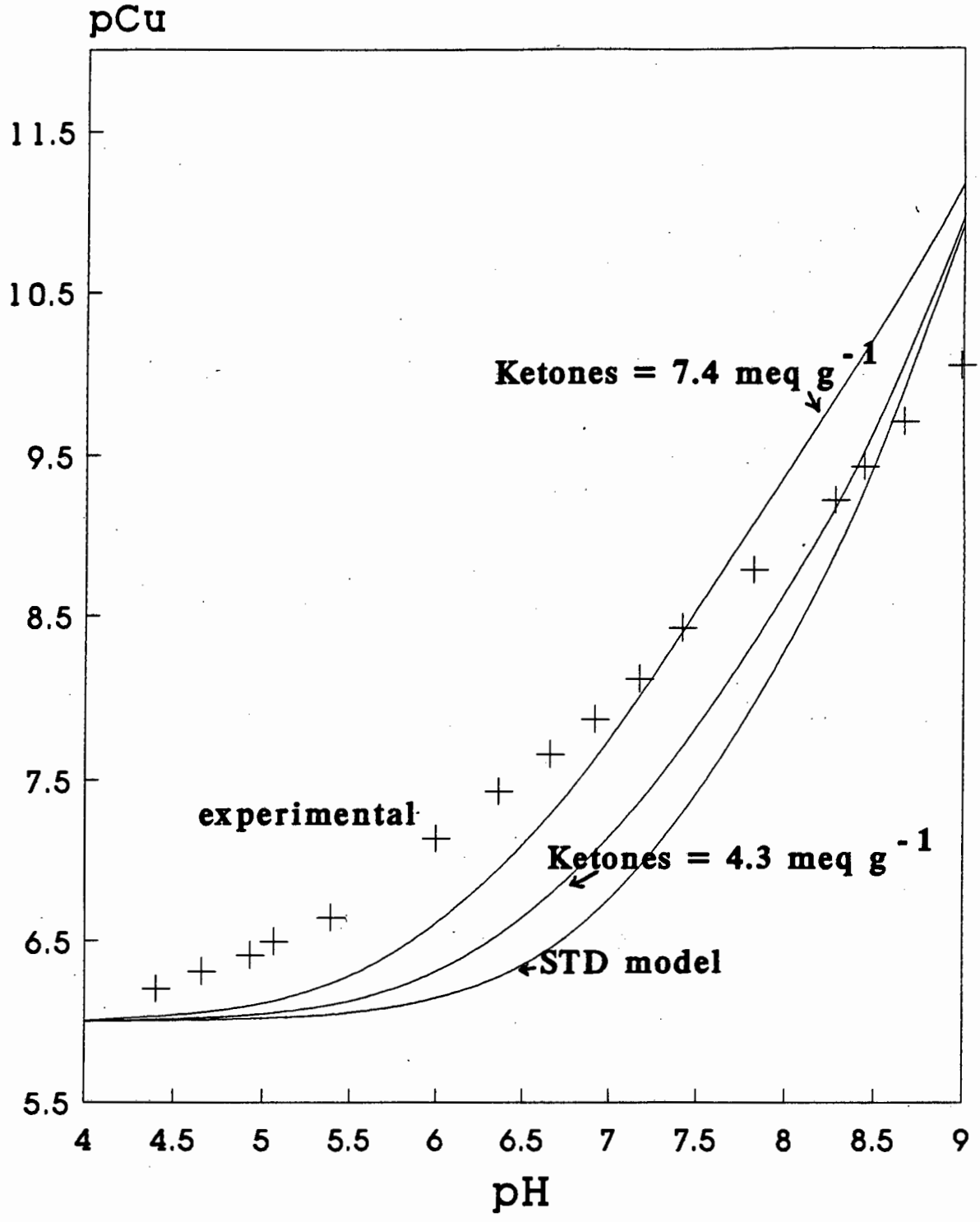


Figure 3.21.2: A comparison between experimental binding of fulvic acid and the predictions of RANDOM as a function of pH. Testing the influence of ketone concentration. Conditions: 5 mg dm^{-3} DOC; no buffer, I = 0.1 mol dm^{-3}.

experimental curves shows that RANDOM is an improvement on totally ignoring fulvic acid binding.

The CATACAC model in all the Figures shown is the best at describing the fulvic acid binding of copper except at high pH in which the binding is overestimated because the catechol concentration is too high. This may indicate some degree of specificity in the formation of fulvic acid samples. A more likely cause for the discrepancy between RANDOM and the experimental data is the variation in the phenol and more importantly ketone concentration. Although the CATACAC model sets an upper limit on the ACAC concentration of 1.35 mmol g^{-1}, a higher ketone concentration will allow a higher ACAC concentration. Furthermore as Figure 3.11 demonstrates the ACAC concentration increases very sharply as the ketone concentration increases.

Thurman and Malcolm [Thu83] report a ketone concentration of 1.7 meq g^{-1}. Thorn [Tho89] reports 6% of the carbon present in fulvic acid as ketone groups which converts to 2.7 meq g^{-1} (This was measured using ^{13}C-NMR). This value was used in the RANDOM calculation. As has been noted earlier with regard to the ketone content of marine fulvic samples, the use of ^{13}C-NMR results in lower concentrations than calculated from conventional analysis. The true ketone content of Suwannee River fulvic acid may well be higher than reported in the U.S. Geological Survey report [USG89]. It should also be noted that in the composition of aqueous fulvic acids reviewed by Buffle [Buf88] the ketone concentration is listed as being in the range of 4.3-7.4 meq g^{-1}. Models were developed using the extremes of this range and their pH dependence is shown in figure 3.21.2. It can be seen that there is a dramatic improvement in fit. This is because the ACAC increased from 0.2205 mmol g^{-1} in the standard model to 0.634 mmol g^{-1} (ketone concentration = 4.3 meq g^{-1}) and 1.991 mmol g^{-1} (ketone concentration = 7.4 meq g^{-1}).

What discrepancies do occur can be explained in terms of the RANDOM ligands used. At high pH binding is primarily to catechol sites. As was shown in the protonation curves, RANDOM overestimates the degree of dissociation of the phenol groups on Suwannee River fulvic acid. Consequently, if these sites are bound by protons, they are less likely to bind cations which explains why RANDOM overestimates binding at high pH. At low pH the underestimate is because there is no binding site in RANDOM which binds cations strongly at low pH as ACAC and CAT (the primary RANDOM binding sites) are still bound by protons at low pH.

It should also be noted that Cabaniss and Shuman determined binding constants for Suwannee River fulvic acid which they then applied to other fulvic acids [Cab88b]. When there model was applied to other fulvic acids, variations of up to 0.50 units were observed. This is comparable with the errors reported when calculating binding using RANDOM. What should be borne in mind is that the errors introduced in the RANDOM approach are more likely the result of errors in the measurement of functional groups concentrations (especially phenols and ketones). RANDOM is a generalized fulvic acid and is easily applied to different fulvic acids. The margin of error is comparable to measuring binding constants for one sample and applying to another.

These results represent a plausible validation of RANDOM with respect to cation binding. Unfortunately the extension to marine samples cannot be shown as no titrations have been performed on marine fulvic acids. In marine samples RANDOM predicts binding to nitrogen-containing sites which are insignificant in Suwannee River fulvic acid. However, as will be shown in the results section, RANDOM predicts percentage binding of metals (in particular copper) which is comparable with that measured experimentally. This too validates the RANDOM approach.

CHAPTER FOUR

INORGANIC SPECIATION

4.1 RESULTS OF THE INORGANIC SPECIATION PATTERN

The aim of modelling the inorganic speciation was to provide information on:

1) The inorganic speciation of the major cations Na^+, K^+, Li^+, Mg^{2+}, Ca^{2+} and Sr^{2+}.
2) The speciation of the inorganic ligands in seawater.
3) The inorganic speciation of the biologically important metals Cu, Fe, Mn, Ni, Zn and Co as well as that of toxic heavy metals Cd, Hg, Pb and Ag. Furthermore the inorganic speciation of Al , Ba and UO_2 was also investigated at the pH of seawater.
4) The effect of varying trace metal concentration on the speciation of these trace metals.
5) The effect of varying pH on the speciation patterns of the trace metals under investigation.
6) The effect of varying pE on trace metal distribution between their various oxidation states.
7) The importance of mixed ligand species to the speciation of Cu^{2+}, Pb^{2+}, UO_2^{2+}, Hg^{2+}, Cd^{2+}, Sn^{2+}, Ag^+ and Cu^+.
8) The effect of the dissolution of atmospheric carbon dioxide on trace metal speciation.

In order to observe the effect of pH the model was first run at the pH of seawater (pH = 8.1) and then the pH was varied from 7.0 to 9.0 at 0.1 intervals. To observe the effects of the redox state of the ocean, the pE was scanned from 8.4 to 12.3.

TABLE 4.1: Computed inorganic speciation of the major cations in seawater

Results are shown as the percentage of the cation appearing in an individual species.

Conditions: temperature, 25 °C; ionic strength, 0.7 mol dm^{-3}; pE, 9.1;

a) atmospheric carbon dioxide assumed to be in equilibrium with the aqueous phase;

b) atmospheric carbon dioxide excluded from equilibrating with the aqueous phase;

c) assumption regarding atmospheric carbon dioxide does not affect the speciation.

Cation		pH	$-\log[M^{n+}]$	Free	SO_4	CO_3 (aq)	CO_3 (s)	Other
Na^+	(c)	7.0	0.33	97.7	2.3			
	(c)	8.1	0.33	97.6	2.3			
	(a)	8.6	0.33	97.3	2.4			
	(b)	8.6	0.33	97.6	2.3			
	(a)	9.0	0.34	96.1	2.5	1.1		
	(b)	9.0	0.33	97.6	2.3			
K^+	(c)	7.0	1.99	97.8	2.2			
	(c)	8.1	1.99	97.8	2.2			
	(a)	8.6	1.99	97.5	2.2			
	(b)	8.6	1.99	97.8	2.2			
	(a)	9.0	2.00	96.3	2.3	1.1		
	(b)	9.0	1.99	97.8	2.2			
Li^+	(c)	7.0	4.59	98.7	1.3			
	(c)	8.1	4.59	98.7	1.3			
	(c)	8.6	4.59	98.7	1.3			
	(c)	9.0	4.59	98.7	1.3			

Mg^{2+}	(a)	7.0	1.31	89.8	10.1			
	(b)	7.0	1.31	89.5	10.1			
	(c)	8.1	1.31	89.0	10.1			
	(a)	8.6	1.34	84.0	9.9	4.0		1.3[v]
	(b)	8.6	1.32	88.5	10.0			
	(a)	9.0	1.45	65.7	8.2	19.9		4.9[v]
	(b)	9.0	1.32	88.5	10.0			
Ca^{2+}	(a)	7.0	2.03	89.4	10.6			
	(b)	7.0	2.03	89.1	10.5			
	(c)	8.1	2.03	88.4	10.5			
	(a)	8.6	2.78	15.8	1.9	1.1	80.7	
	(b)	8.6	2.05	85.3	10.1	1.1	3.0	
	(a)	9.0	3.58	2.5		1.1	95.8	
	(b)	9.0	2.07	81.4	9.6	1.1	8.3	
Sr^{2+}	(a)	7.0	4.11	86.2	13.7			
	(b)	7.0	4.11	85.8	13.7			
	(c)	8.1	4.11	85.8	13.7			
	(a)	8.6	4.56	30.3	5.1		63.9	
	(b)	8.6	4.11	85.8	13.7			
	(a)	9.0	5.36	4.8	0.9		93.9	
	(b)	9.0	4.11	85.9	13.8			
Ba^{2+}	(a)	7.0	7.51	93.8	5.8			
	(b)	7.0	7.51	92.8	5.8			1.1[w]
	(c)	8.1	7.51	92.9	5.8			
	(a)	8.6	7.52	90.9	5.9			2.6[w]
	(b)	8.6	7.51	93.3	5.8			
	(a)	9.0	7.55	86.1	5.9	1.5		8.1[w]
	(b)	9.0	7.51	93.5	5.8			

v: $Mg_2CO_3^{2+}$; w: $BaHCO_3^+$

4.1.1 The inorganic speciation of the major ions

These results are presented in Table 4.1. Immediately noticeable is the fact that at pH = 8.1, these ions exist mainly in the uncomplexed ion form (> 97% for the Group I metals and 85 - 95% for the alkaline earth metals.) At low pH's the most important ligand is sulphate. The speciation of the Group I metals is not affected significantly by pH while that of the alkaline earth metals changes at high pH as a result of carbonate complexation and the precipitation of carbonate solids. This effect is far less significant when carbon dioxide is excluded from equilibrating with the aqueous phase. The speciation of calcium and magnesium at high pH is subject to the restriction that no dolomite or magnesite precipitation is allowed. Although their precipitation is not observed at pH = 8.1 [Cul81], no studies have been performed at higher pH's and their exclusion from precipitation may hence not be justified. Chloride association with these metals was also not considered.

4.1.2 The speciation of the inorganic ligands

The speciation of the inorganic ligands in seawater at pH = 8.1 is tabulated in Table 4.2. The effect of pH on the speciation patterns of SO_4^{2-}, PO_4^{3-}, F^-, IO_3^-, $B(OH)_4^-$, CrO_4^{2-} and $SiO_2(OH)_2^{2-}$ are shown graphically in Figures 4.1.1 to 4.7. The speciation patterns of Cl^-, Br^-, I^- and NO_3^- are constant throughout the pH range investigated (7.0 to 9.0). Figures 4.8.1 and 4.8.2 show the variation in the speciation pattern of carbonate with pH, both when atmospheric carbon dioxide is allowed to dissolve and when carbon dioxide dissolution is excluded.

The speciation results indicate that the halides (except fluoride) are completely uncomplexed. This is the result of the restriction that no association occurs with the major cations. pH significantly affects those ligands which form protonated

TABLE 4.2: Computed inorganic speciation of the inorganic anions in seawater

Results are shown as the percentage of the anion appearing in an individual species.

Conditions: temperature, 25 °C; ionic strength, 0.7 mol dm^{-3}; pH, 8.1;

The assumption regarding atmospheric carbon dioxide does not affect the speciation in any of the cases.

Anion	-log[L^{n-}]	Free	H	H_2	Na	NaH	Mg	MgH	Ca	CaH	Other
Cl^-	0.25	100.0									
Br^-	3.07	100.0									
I^-	7.00	100.0									
IO_3^-	6.60	83.4			7.4		7.4		1.6		
F^-	4.49	46.6			4.4		47.2		1.7		
SO_4^{2-}	1.96	38.2			38.2		19.0		3.8		
CO_3^{2-}	4.35	2.2	60.5		4.4	8.0	12.0	4.8	3.3	1.1	1.0[v] 2.0[w]
NO_3^-	6.54	93.4		5.4							
$B(OH)_4^-$	4.25	13.2	74.1		2.7		8.6		1.4		
$SiO_2(OH)_2^{2-}$	10.98		4.1	94.8							
PO_4^{3-}	10.07		24.1			14.5	6.6	40.5	5.0	4.6	3.9[x]
CrO_4^{2-}	8.85	70.3			28.6						

v: $CaMgCO_3^{2+}$; w: $Mg_2CO_3^{2+}$; x: NaH_2PO_4

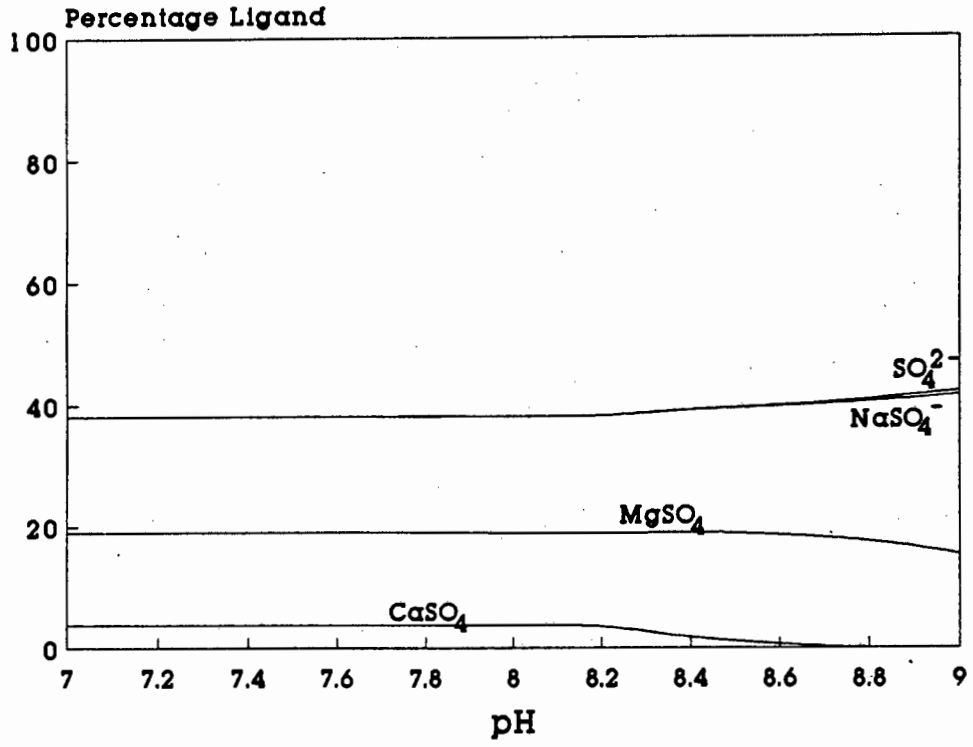


Figure 4.1.1: The speciation of sulphate as a percentage of total ligand versus pH (ionic strength = 0.7 mol dm^{-3}; 25 °C; atmospheric carbon dioxide dissolution included)

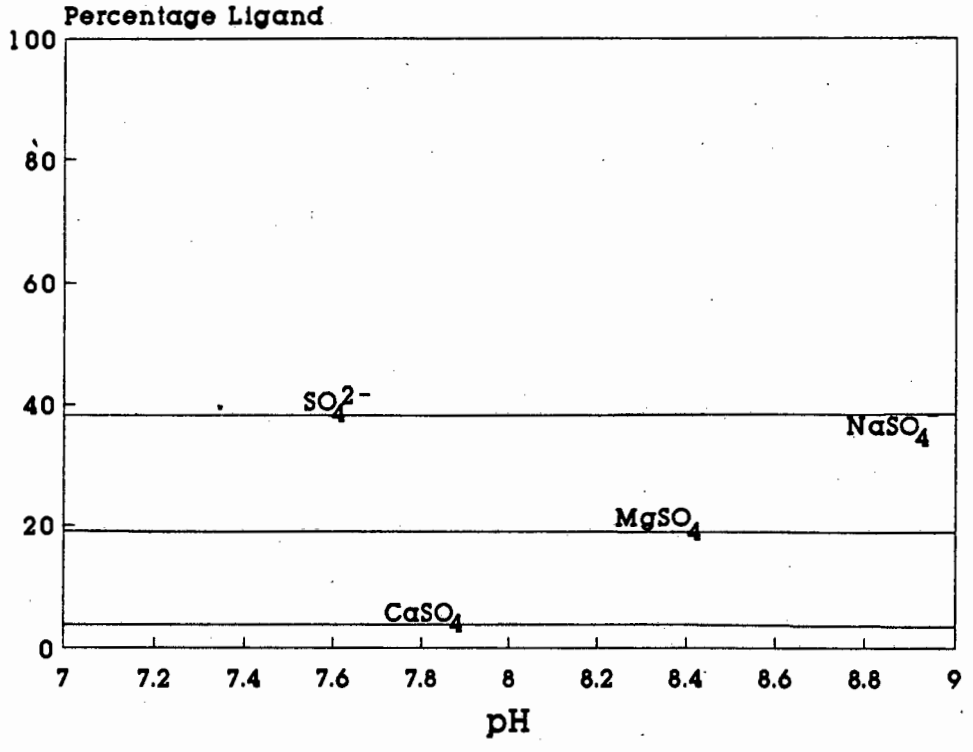


Figure 4.1.2: The speciation of sulphate as a percentage of total ligand versus pH (ionic strength = 0.7 mol dm^{-3}; 25 °C; atmospheric carbon dioxide dissolution excluded)

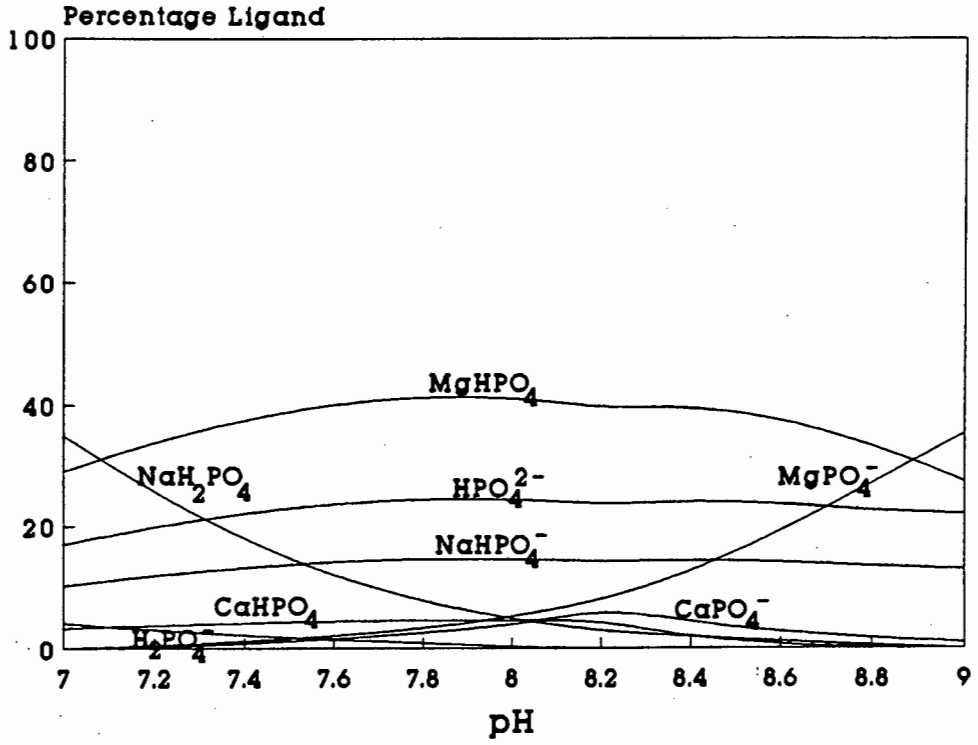


Figure 4.2.1: The speciation of phosphate as a percentage of total ligand versus pH (ionic strength = 0.7 mol dm^{-3}; 25 °C; atmospheric carbon dioxide dissolution included)

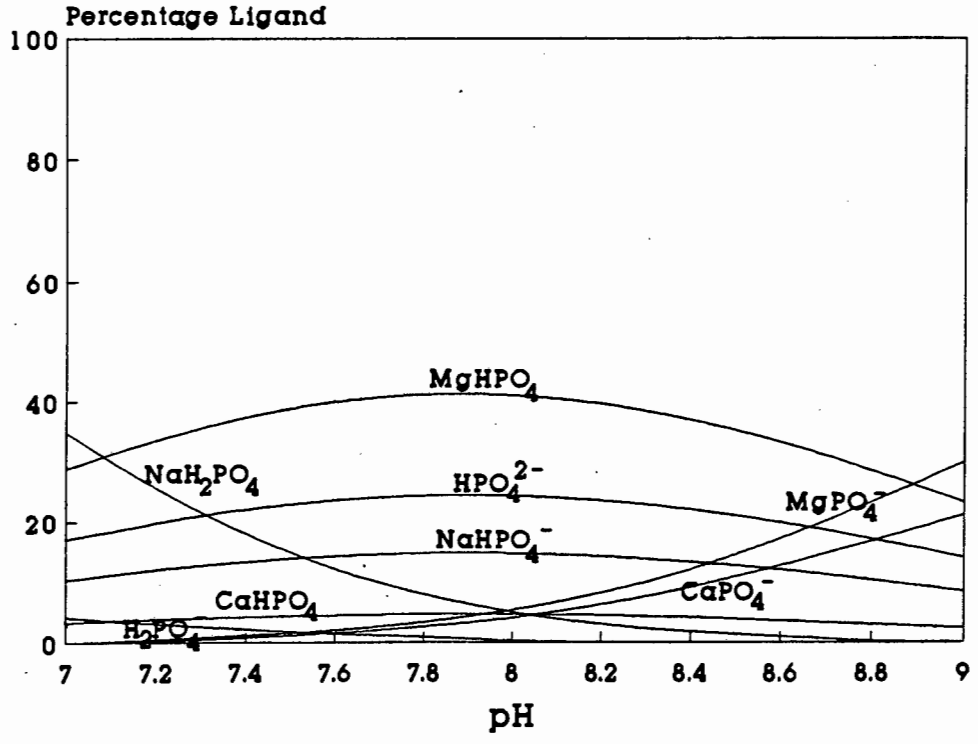


Figure 4.2.2: The speciation of phosphate as a percentage of total ligand versus pH (ionic strength = 0.7 mol dm^{-3}; 25 °C; atmospheric carbon dioxide dissolution excluded)

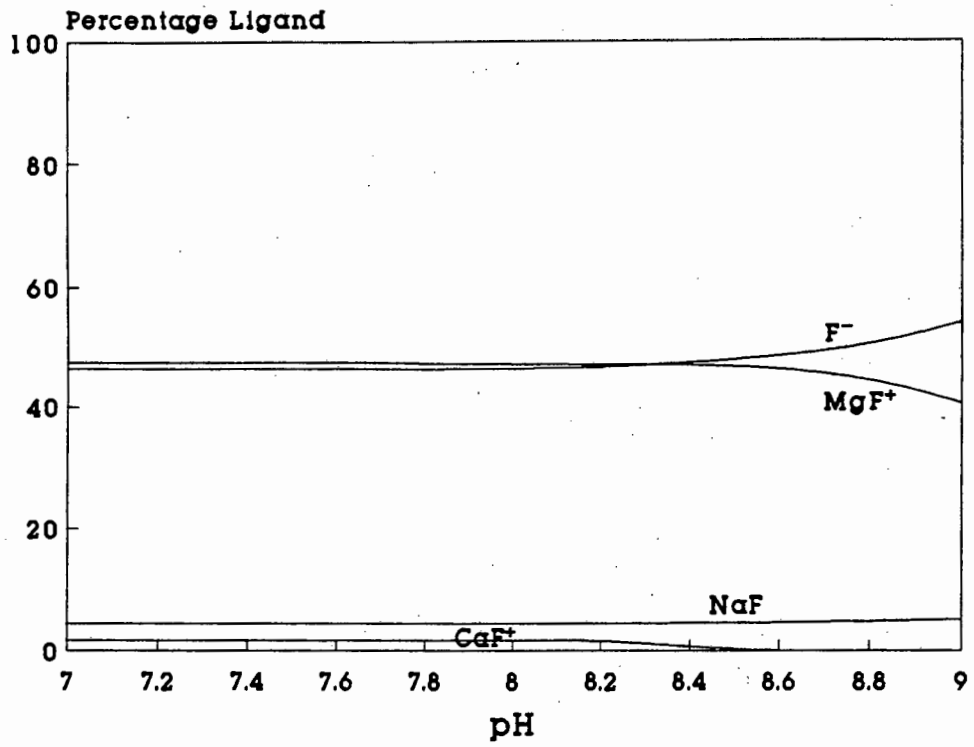


Figure 4.3.1: The speciation of fluoride as a percentage of total ligand versus pH (ionic strength = 0.7 mol dm^{-3}; 25 °C; atmospheric carbon dioxide dissolution included)

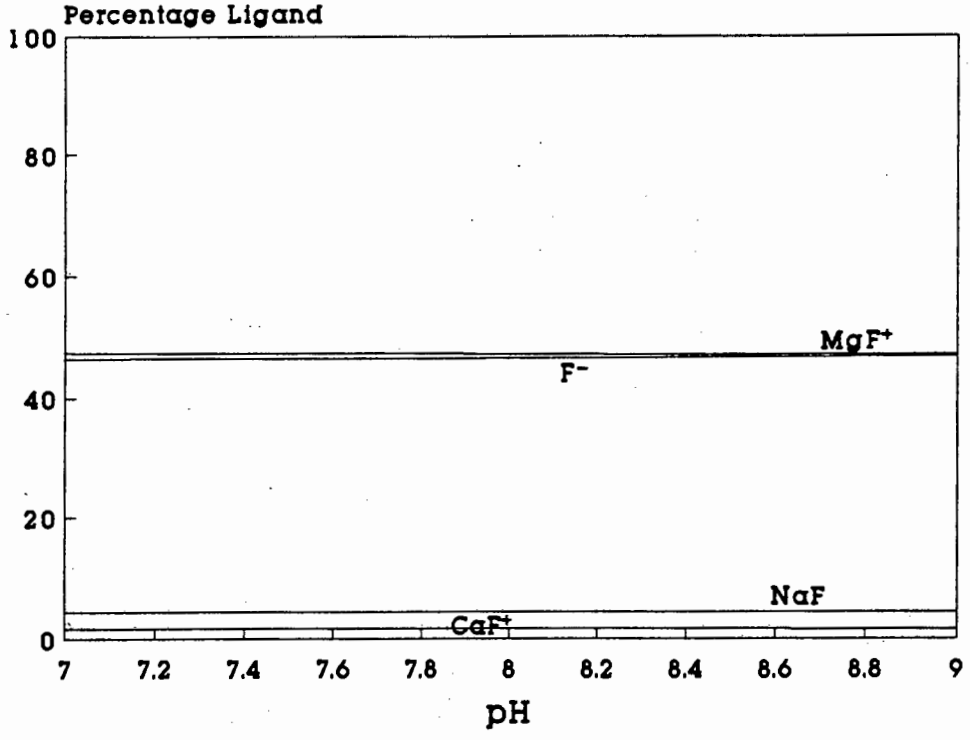


Figure 4.3.2: The speciation of fluoride as a percentage of total ligand versus pH (ionic strength = 0.7 mol dm^{-3}; 25 °C; atmospheric carbon dioxide dissolution excluded)

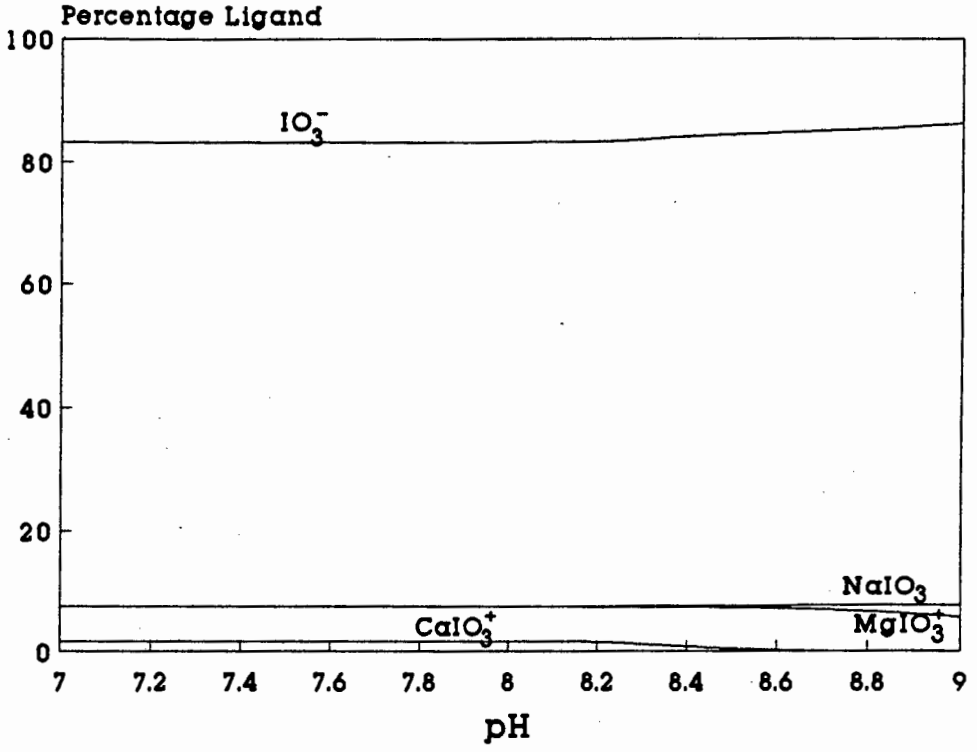


Figure 4.4.1: The speciation of iodate as a percentage of total ligand versus pH (ionic strength = 0.7 mol dm^{-3}; 25 °C; atmospheric carbon dioxide dissolution included)

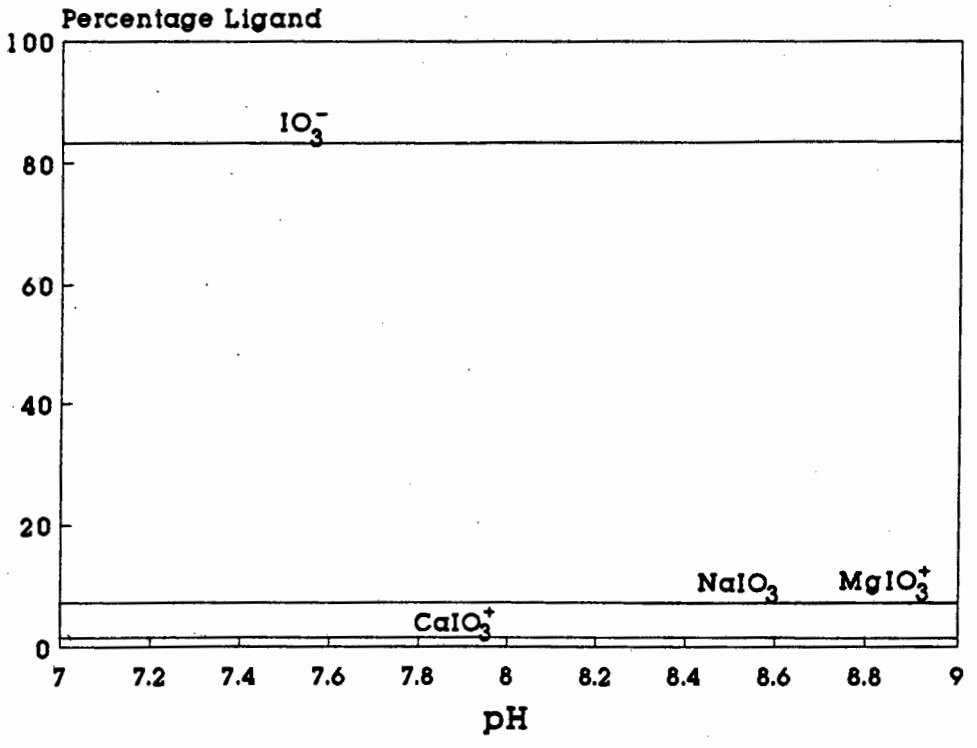


Figure 4.4.2: The speciation of iodate as a percentage of total ligand versus pH (ionic strength = 0.7 mol dm^{-3}; 25 °C; atmospheric carbon dioxide dissolution excluded)

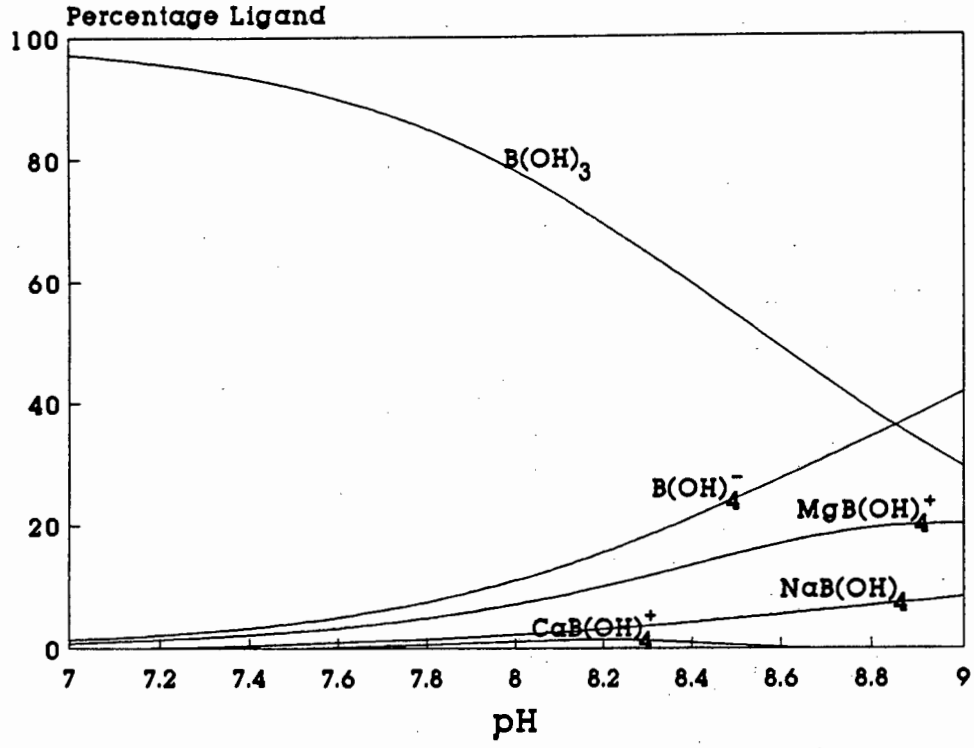


Figure 4.5.1: The speciation of borate as a percentage of total ligand versus pH (ionic strength = 0.7 mol dm^{-3}; 25 °C; atmospheric carbon dioxide dissolution included)

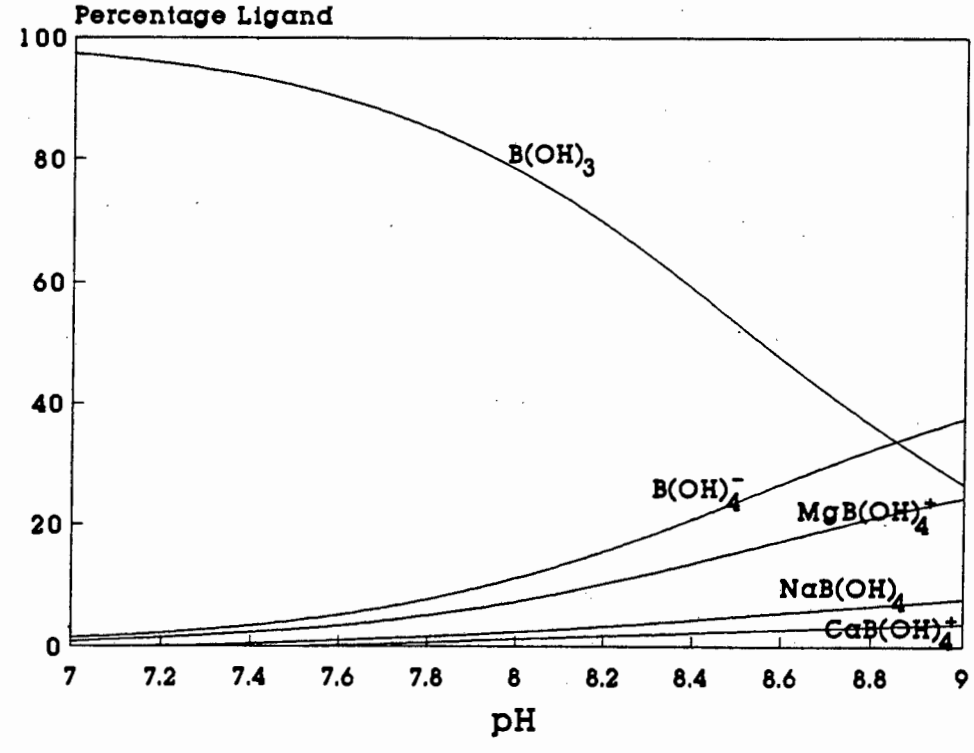


Figure 4.5.2: The speciation of borate as a percentage of total ligand versus pH (ionic strength = 0.7 mol dm^{-3}; 25 °C; atmospheric carbon dioxide dissolution excluded)

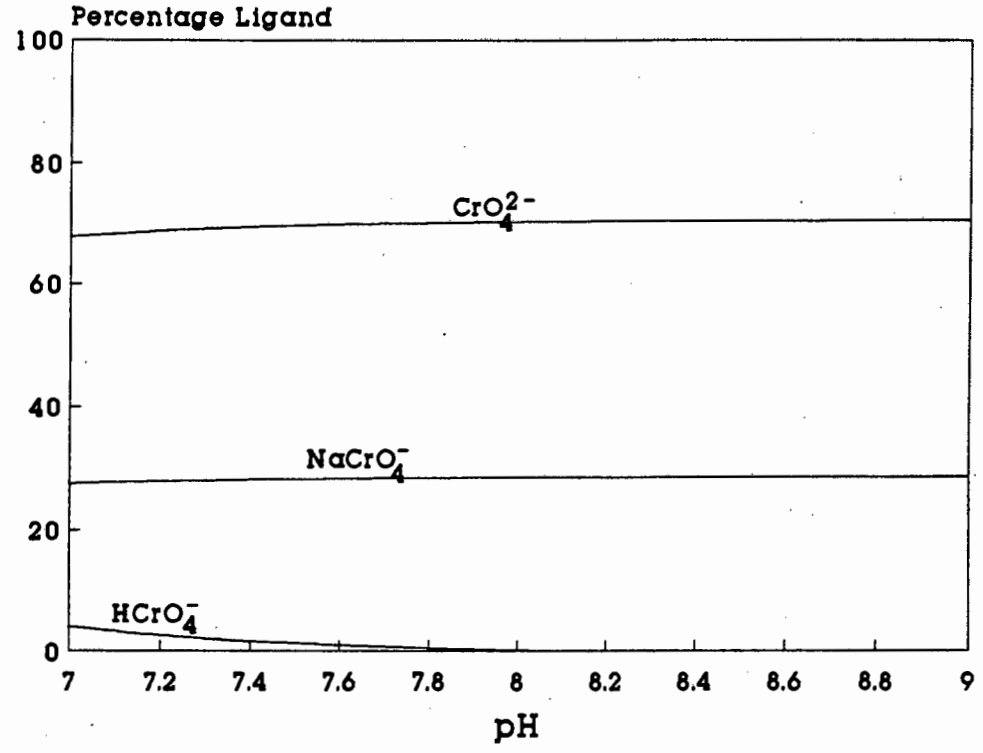


Figure 4.6: The speciation of chromate as a percentage of total ligand versus pH (ionic strength = 0.7 mol dm^{-3}; 25 °C; atmospheric carbon dioxide dissolution does not affect the speciation significantly)

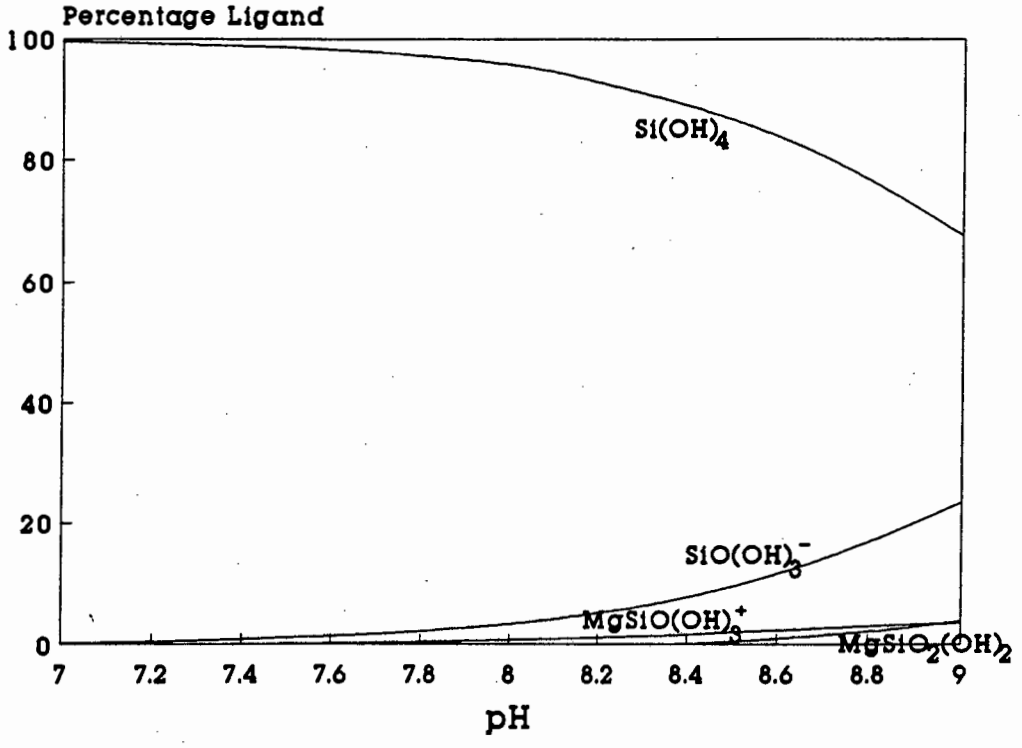


Figure 4.7: The speciation of silicate as a percentage of total ligand versus pH (ionic strength = 0.7 mol dm^{-3}; 25 °C; atmospheric carbon dioxide dissolution does not affect the speciation significantly)

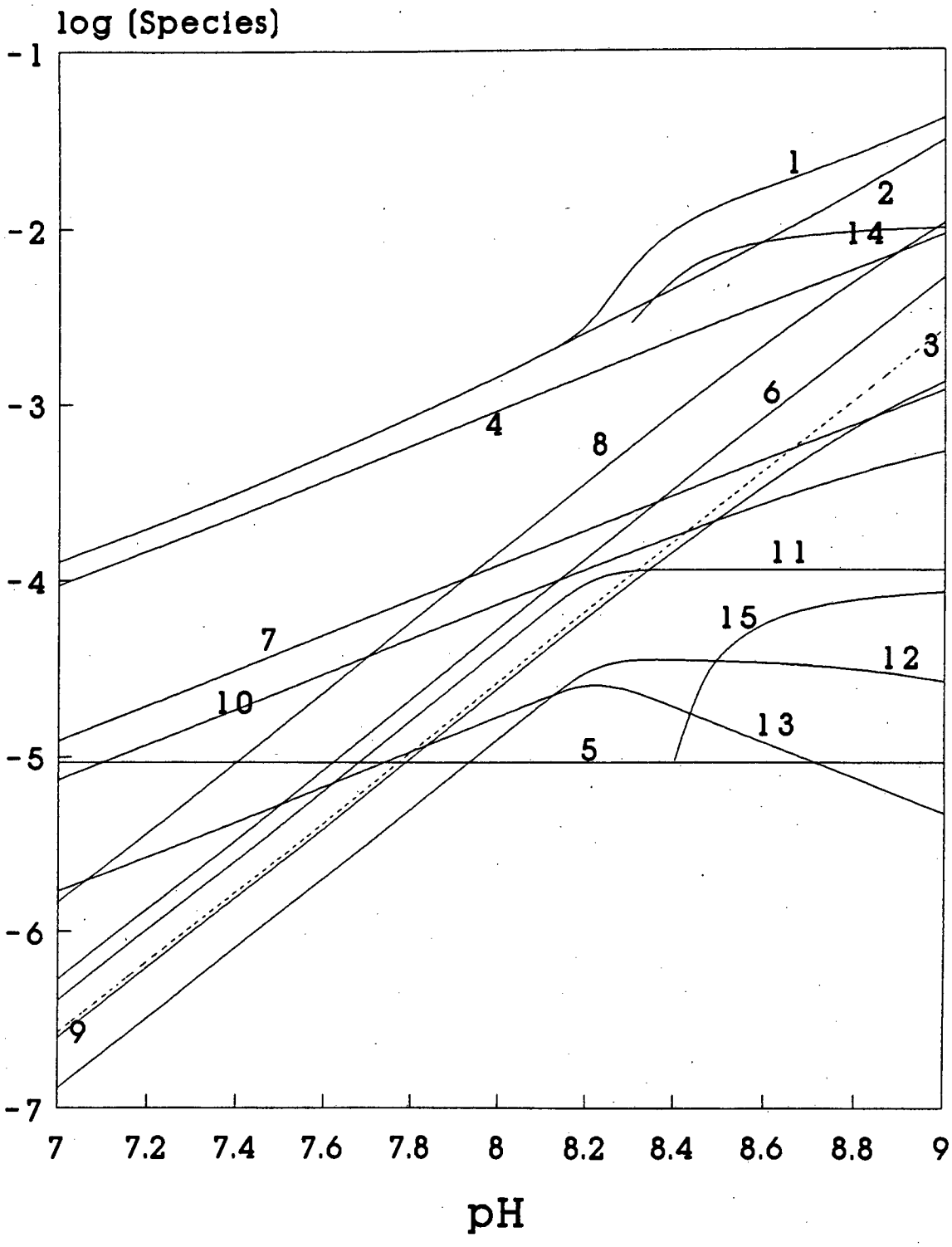


Figure 4.8.1: The speciation of carbonate as a log of species concentration ligand versus pH (ionic strength = 0.7 mol dm^{-3}; 25 °C; atmospheric carbon dioxide dissolution included) [1: total CO_3^{2-}, 2: dissolved CO_3^{2-}, 3: uncomplexed CO_3^{2-}, 4: HCO_3^-, 5: H_2CO_3, 6: $NaCO_3^-$, 7: $NaHCO_3$, 8: $MgCO_3$, 9: $Mg_2CO_3^{2+}$, 10: $MgHCO_3^+$, 11: $CaCO_3$, 12: $CaMgCO_3^{2+}$, 13: $CaHCO_3^+$, 14: aragonite (s), 15: $SrCO_3$ (s)]

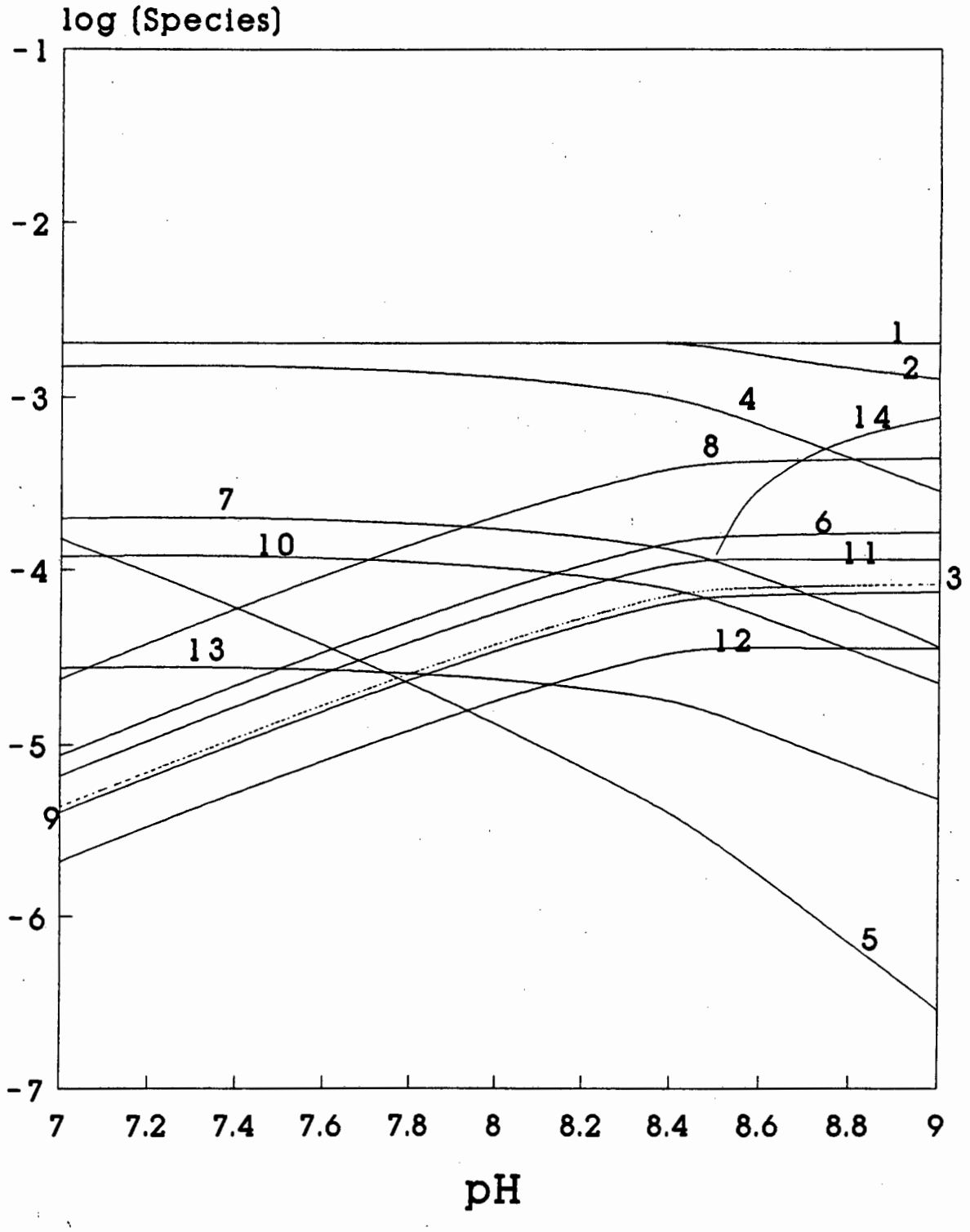


Figure 4.8.2: The speciation of carbonate as a log of species concentration ligand versus pH (ionic strength = 0.7 mol dm^{-3}; 25 °C; atmospheric carbon dioxide dissolution excluded) [1: total CO_3^{2-}, 2: dissolved CO_3^{2-}, 3: uncomplexed CO_3^{2-}, 4: HCO_3^-, 5: H_2CO_3, 6: $NaCO_3^-$, 7: $NaHCO_3$, 8: $MgCO_3$, 9: $Mg_2CO_3^{2+}$, 10: $MgHCO_3^+$, 11: $CaCO_3$, 12: $CaMgCO_3^{2+}$, 13: $CaHCO_3^+$, 14: aragonite (s)]

species in the pH range scanned: borate, carbonate, phosphate and silicate. The primary metals that affect ligand speciation are Na^+, Mg^{2+} and Ca^{2+}. The speciation of F^-, IO_3^-, CrO_4^{2-} and SO_4^{2-} are affected slightly by pH because carbonate binds the major cations more strongly at high pH and they in turn bind the last mentioned ligands less strongly. This effect is especially noticeable when atmospheric carbon dioxide is allowed to dissolve and affects those ligands that are bound strongly by magnesium and calcium the most.

4.1.3 The inorganic speciation of the trace metals

The speciation patterns for the trace metals in seawater at a pH of 8.1 are listed in Table 4.3. The effect of pH on the speciation patterns of the trace metals, considered in this study, is presented graphically in Figures 4.9.1 to 4.25.3. The effect of the dissolution of carbon dioxide may also be noted by comparing the graphs in which carbon dioxide is allowed to dissolve to those in which it is excluded. The following general observations can be made:

1) In the pH range considered, the effect of the ligands: NO_3^-, $B(OH)_4^-$ $SiO_2(OH)_2^{2-}$ (except for Al^{3+}), PO_4^{3-}, IO_3^{2-}, I^-, F^- and Br^- (except for Ag^+ and Hg^{2+}) is minimal. They bind less than 0.1% of any trace metal except for borate which is slightly significant for Cu^{2+} at low pH. At pH = 8.1, it binds 0.4% of the total copper. The primary inorganic binding ligands are Cl^-, CO_3^{2-}, OH^- and to a lesser extent SO_4^{2-}.
2) Ternary species were found to be significant in the model. At pH = 8.1, the mixed halides were important for Ag^+ and Hg^{2+} but not for Cd^{2+}, Sn^{2+}, Pb^{2+} and Cu^+. Mixed hydroxycarbonates were found to be significant for Cu^{2+} and Pb^{2+} at this pH. At lower pH's

hydroxycarbonates were important for UO_2^{2+} while at higher pH's HgOHCl was observed (1.1% at pH = 9.0).

3) Species of the type ML_x where x = 3,4 were important for Cl^- and OH^- complexes.

4) At the pH of seawater (8.1) the trace metals may be classified according to the ligand that binds the most of the metal. The aqua ion is dominant for Zn^{2+}, Ni^{2+}, Co^{2+}, Mn^{2+} and Fe^{2+}. Chloro complexes dominated the speciation of Hg^{2+}, Cd^{2+}, Ag^+ and Cu^+. Carbonato complexes were significant for Cu^{2+}, Pb^{2+} and UO_2^{2+}. Hydroxides were dominant for Fe^{3+}, Al^{3+}, Cr^{3+}, $Sn^{2+}$and Hg_2^{2+}. The manganese classification is dependent on the precipitation of MnO_2 being excluded. The Pb^{2+} speciation also shows chloride complexation to be significant although not as significant as carbonate.

5) Varying the pH affected the speciation of those trace metals which formed strong hydroxides or carbonates at high pH: Sn^{2+}, Cu^{2+}, Zn^{2+}, Ni^{2+}, Fe^{2+}, Mn^{2+}, Pb^{2+}, Co^{2+}, Cr^{3+}, Al^{3+}, Fe^{3+} and UO_2^{2+}. Hg^{2+}, Ag^+ and Cu^+ were not affected significantly by pH while the speciation of Cd^{2+} was affected only in the model in which carbon dioxide dissolution was allowed.

6) The effect of allowing carbon dioxide to dissolve or not was significant for those species affected by pH that formed strong carbonate complexes at high pH. These species were less significant where carbon dioxide was not allowed to dissolve. Thus of the metals listed above Sn^{2+}, Fe^{2+}, Cr^{3+}, Al^{3+} and Fe^{3+} as well as those metals unaffected by pH were not significantly affected by the assumption regarding carbon dioxide.

TABLE 4.3: Computed inorganic speciation of the trace metals in seawater

Results are shown as the percentage of the cation appearing in an individual species.

Conditions: temperature, 25 °C; ionic strength, 0.7 mol dm^{-3}; pH, 8.1; pE = 9.1;

a) atmospheric carbon dioxide assumed to be in equilibrium with the aqueous phase;

b) atmospheric carbon dioxide excluded from equilibrating with the aqueous phase;

c) assumption regarding carbon dioxide does not affect the speciation.

Cation		$-\log[M^{n+}]$	Free	Cl	Cl_2	Cl_3	Cl_4	OH	$(OH)_2$	$(OH)_3$	$(OH)_4$	SO_4	CO_3	$(CO_3)_2$	Other
i) Components for which the aqua ion is the dominant species															
Zn^{2+}	(a)	8.94	56.9	12.7	8.9	4.0	1.6	4.8				5.0	4.8		
	(b)	8.95	56.7	12.6	8.9	3.9	1.6	4.8				5.0	5.1		
Ni^{2+}	(a)	8.71	55.3	30.9								4.1	8.8		
	(b)	8.72	55.1	30.8								4.1	9.2		
Co^{2+}	(a)	10.53	58.4	30.5				1.0				4.4	3.7		1.7^{x}
	(b)	10.54	58.3	30.4				1.0				4.4	3.9		1.8^{x}
Fe^{2+}	(a)	17.16	70.5	14.0				1.4				4.3	9.5		
	(b)	17.16	70.1	13.9				1.4				4.3	10.0		
Mn^{2+}	(a)	w	68.7	24.2								3.8	2.8		
	(b)	w	68.6	24.2								3.8	2.9		

w: Speciation for manganese is for dissolved manganese only. At pE = 9.1 73.0% of the total precipitates as MnO_2. $-\log[Mn^{2+}] = 9.13$

x: $CoHCO_3^+$

ii) Components for which carbonate species are the dominant species															
Cu^{2+}	(a)	10.21	3.1	1.1				5.6					70.4	11.2	6.6^{y}
	(b)	10.23	2.9	1.0				5.3					70.4	11.8	6.6^{y}

UO_2^{2+}	(a)	16.26										1.8	98.2[z]
	(b)	16.33										1.7	98.3[z]
Pb^{2+}	(a)	11.53	3.0	12.6	14.0	6.4		3.8			51.6	4.9	1.7[d]
	(b)	11.54	2.9	12.2	13.6	6.2		3.7			52.6	5.3	1.7[d]

y: $CuOHCO_3^-$; z: $UO_2(CO_3)_3^{4-}$; d: $PbOHCO_3^-$

iii) Components for which chloride species are the dominant species

Cd^{2+}	(c)	11.54	2.9	35.2	43.0	15.2	2.8						
Hg^{2+}	(c	25.37			2.2	11.3	69.0						2.9[e]
													12.2[f]
Ag^+	(c)	16.86			55.9	32.7	7.3						1.5[g]
													1.3[h]
Cu^+	(a)	17.28			90.8	7.9							
	(b)	17.31			90.8	7.9							

e: $HgCl_2Br^-$; f: $HgCl_3Br^{2-}$; g: $AgClBr^-$; h: $AgCl_2Br^{2-}$

iv) Components for which hydroxide species are the dominant species

Al^{3+}	(c)	16.01								1.5	94.0		4.5[i]
Cr^{3+}	(c)	15.75							84.6	13.1	1.6		
Fe^{3+}	(c)	20.50[k]							1.0	0.5	1.2		97.3[j]
		[l]							35.7	18.3	46.0		
Sn^{2+}	(c)	19.71							92.0	8.0			
Hg_2^{2+}	(c)	25.37						99.9					

i: chlorite (s); j: $Fe(OH)_3$ (s)

k: speciation expressed as a percentage of the total concentration; l: speciation expressed as a percentage of the dissolved concentration.

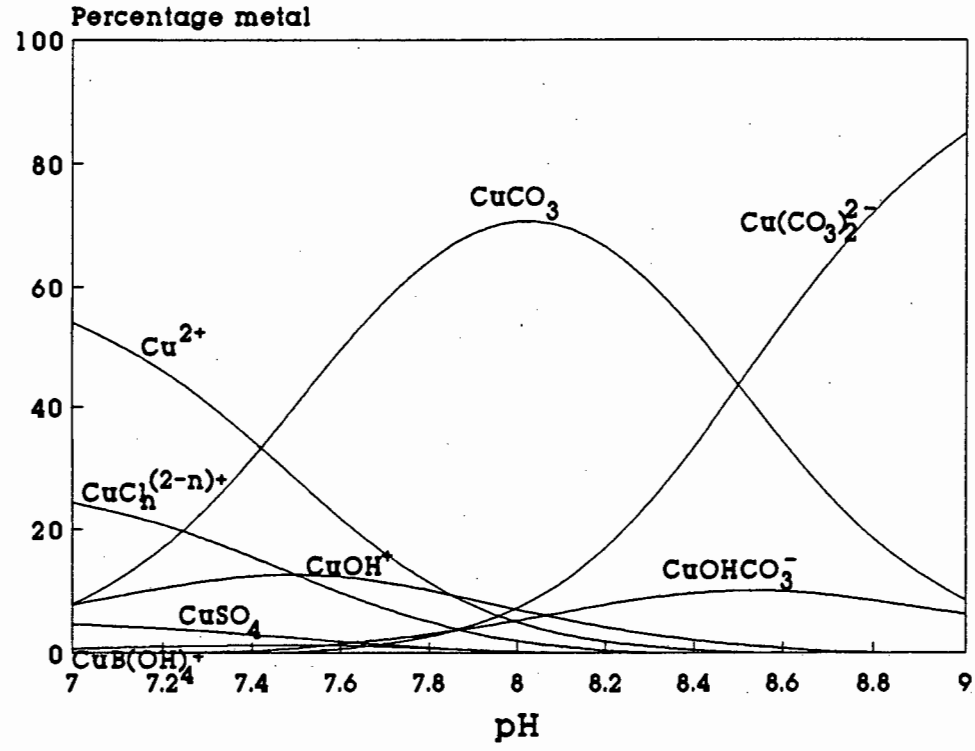


Figure 4.9.1: The inorganic speciation of copper(II) as a percentage of total metal versus pH (ionic strength = 0.7 mol dm^{-3}; 25 °C; atmospheric carbon dioxide dissolution included)

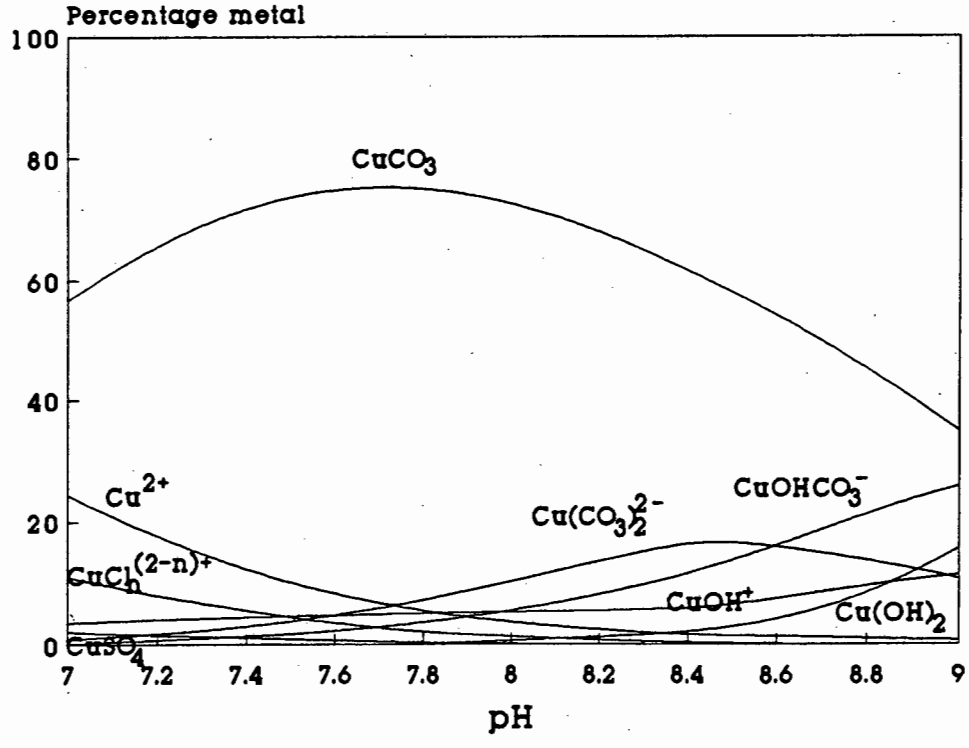


Figure 4.9.2: The inorganic speciation of copper(II) as a percentage of total metal versus pH (ionic strength = 0.7 mol dm^{-3}; 25 °C; atmospheric carbon dioxide dissolution excluded)

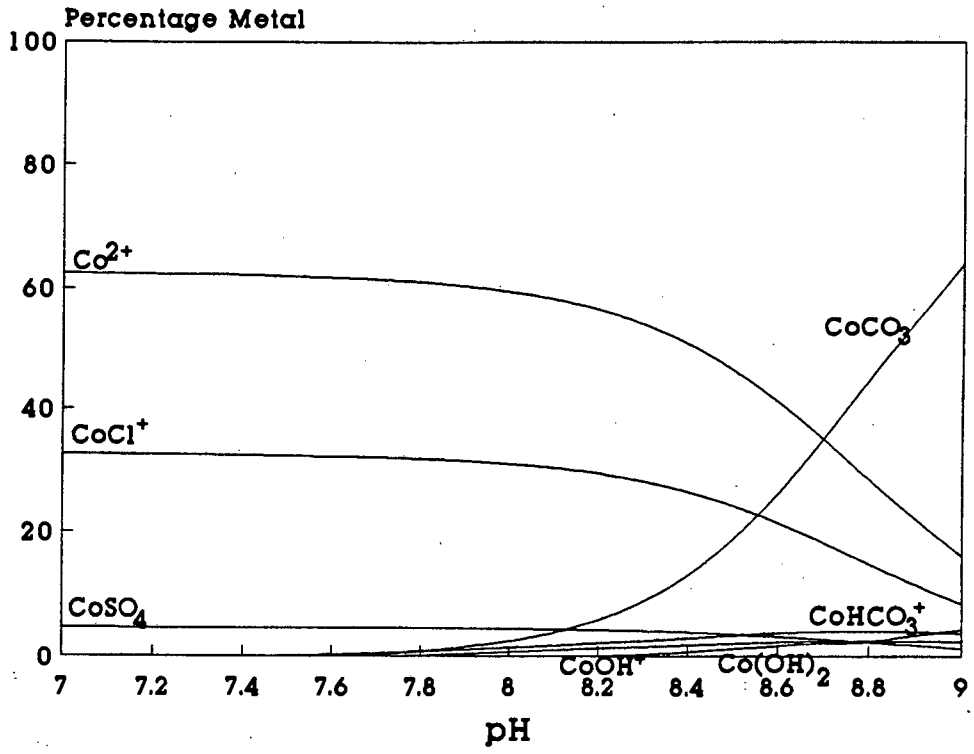


Figure 4.10.1: The inorganic speciation of cobalt(II) as a percentage of total metal versus pH (ionic strength = 0.7 mol dm^{-3}; 25 °C; atmospheric carbon dioxide dissolution included)

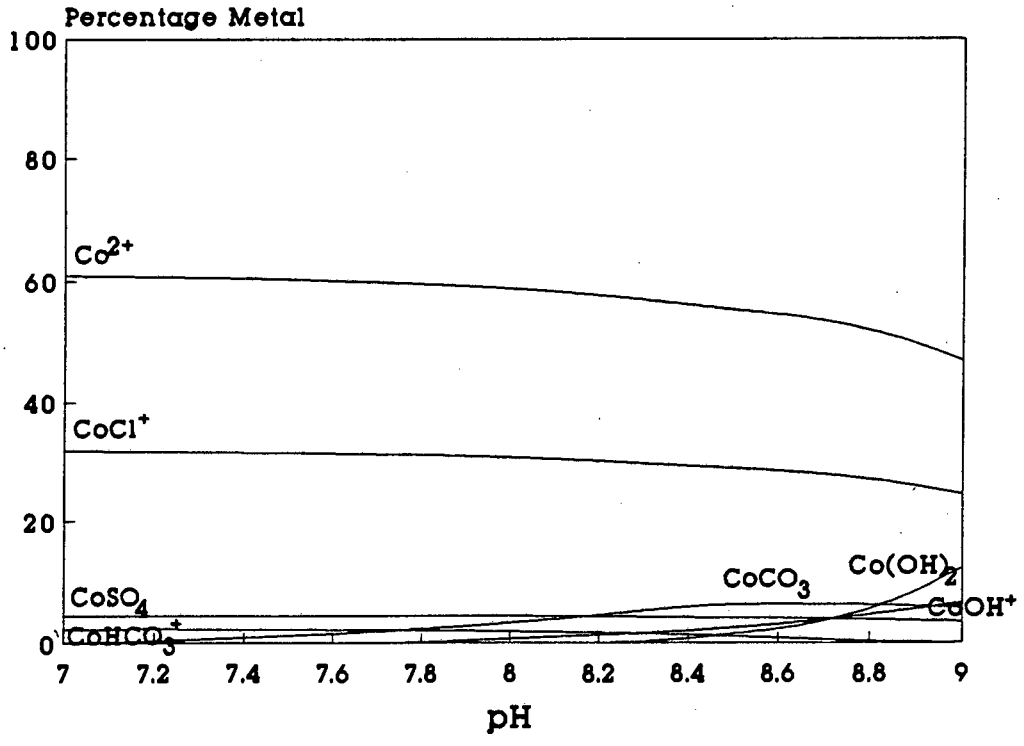


Figure 4.10.2: The inorganic speciation of cobalt(II) as a percentage of total metal versus pH (ionic strength = 0.7 mol dm^{-3}; 25 °C; atmospheric carbon dioxide dissolution excluded)

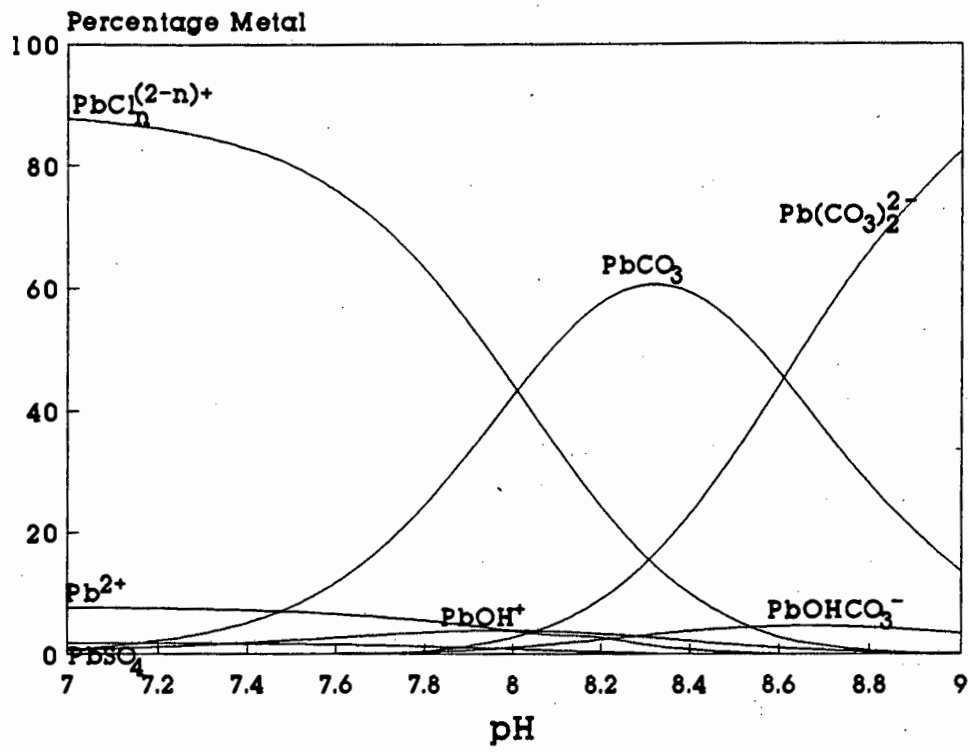


Figure 4.11.1: The inorganic speciation of lead(II) as a percentage of total metal versus pH (ionic strength = 0.7 mol dm^{-3}; 25 °C; atmospheric carbon dioxide dissolution included)

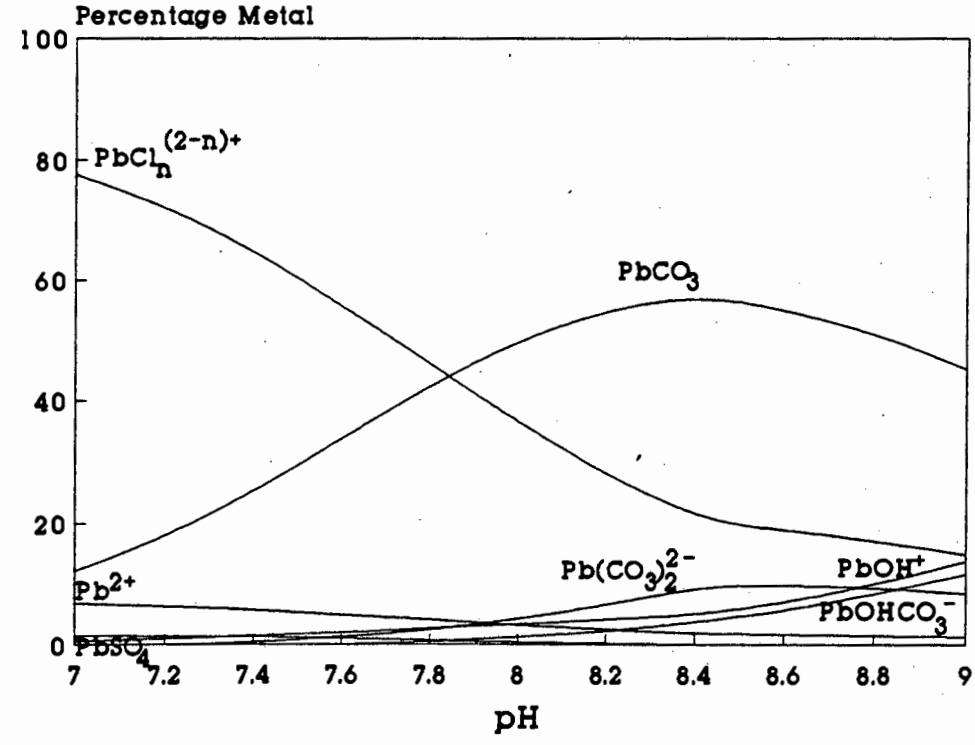


Figure 4.11.2: The inorganic speciation of lead(II) as a percentage of total metal versus pH (ionic strength = 0.7 mol dm^{-3}; 25 °C; atmospheric carbon dioxide dissolution excluded)

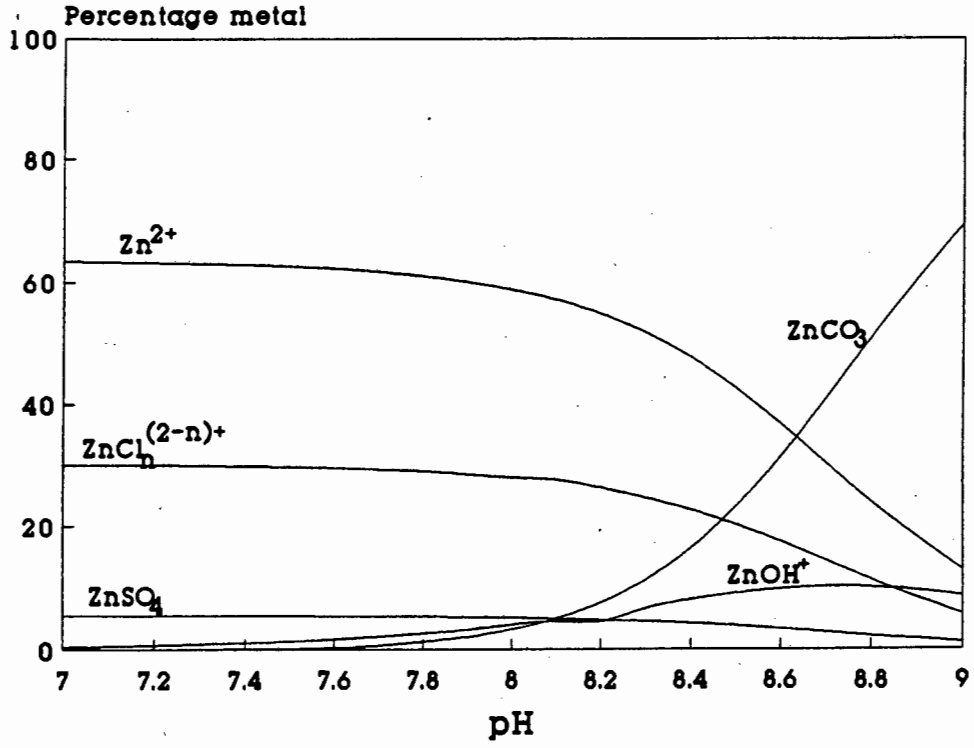


Figure 4.12.1: The inorganic speciation of zinc(II) as a percentage of total metal versus pH (ionic strength = 0.7 mol dm^{-3}; 25 °C; atmospheric carbon dioxide dissolution included)

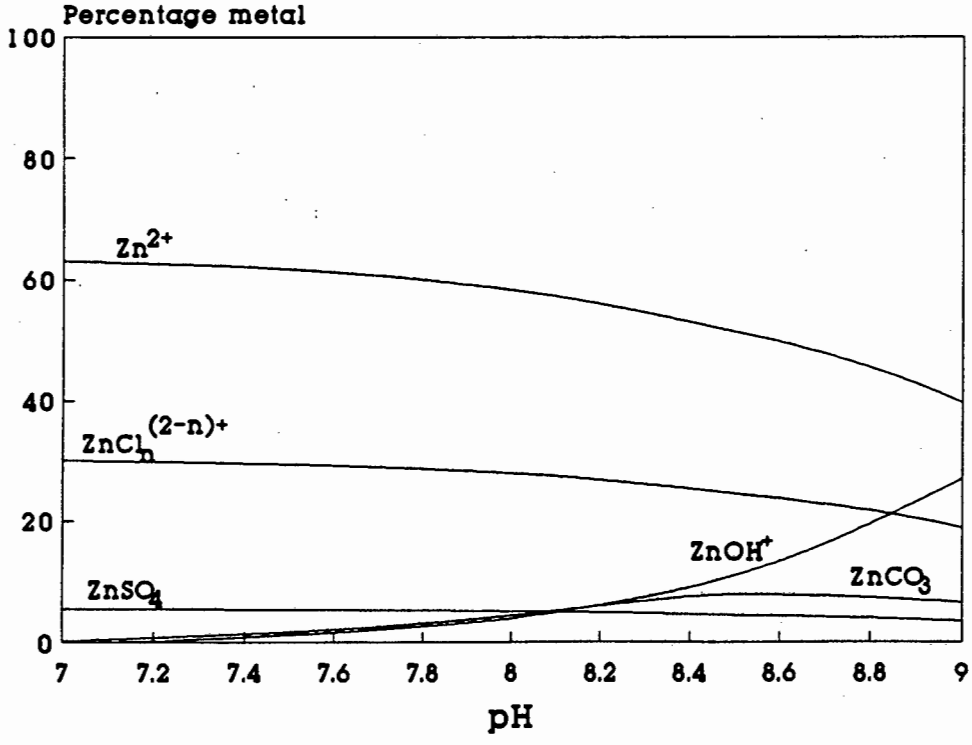


Figure 4.12.2: The inorganic speciation of zinc(II) as a percentage of total metal versus pH (ionic strength = 0.7 mol dm^{-3}; 25 °C; atmospheric carbon dioxide dissolution excluded)

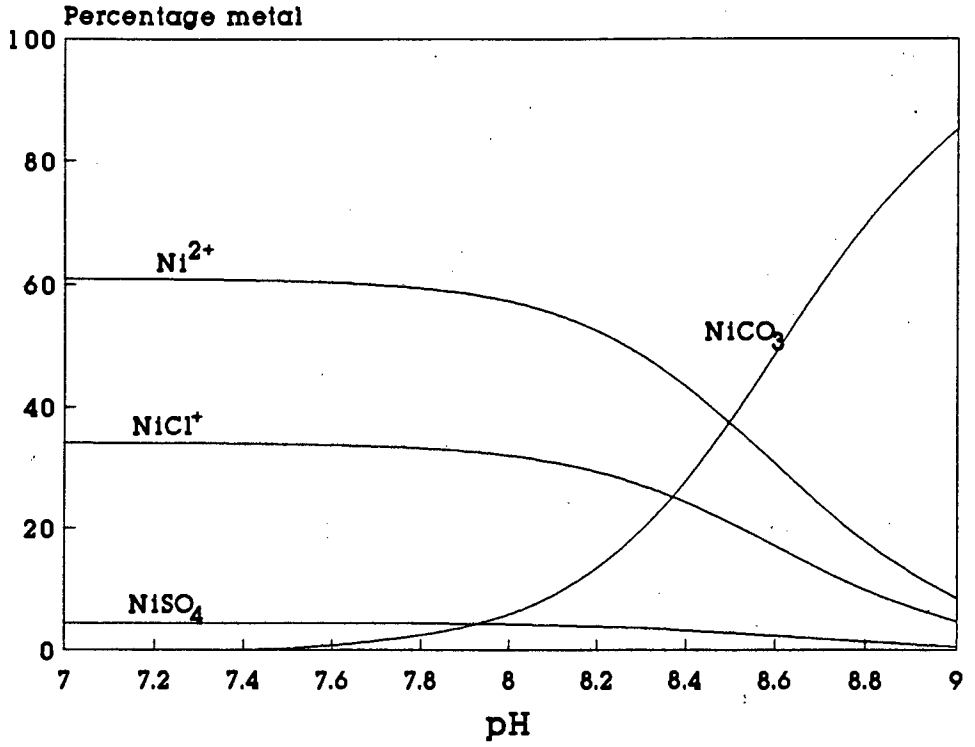


Figure 4.13.1: The inorganic speciation of nickel(II) as a percentage of total metal versus pH (ionic strength = 0.7 mol dm^{-3}; 25 °C; atmospheric carbon dioxide dissolution included)

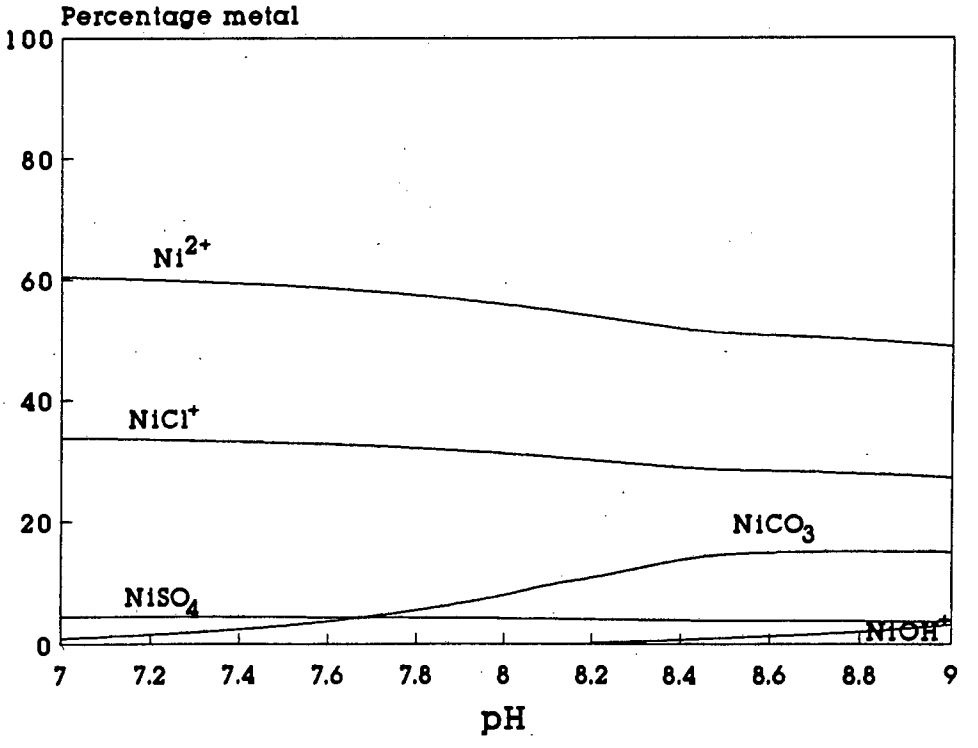


Figure 4.13.2: The inorganic speciation of nickel(II) as a percentage of total metal versus pH (ionic strength = 0.7 mol dm^{-3}; 25 °C; atmospheric carbon dioxide dissolution excluded)

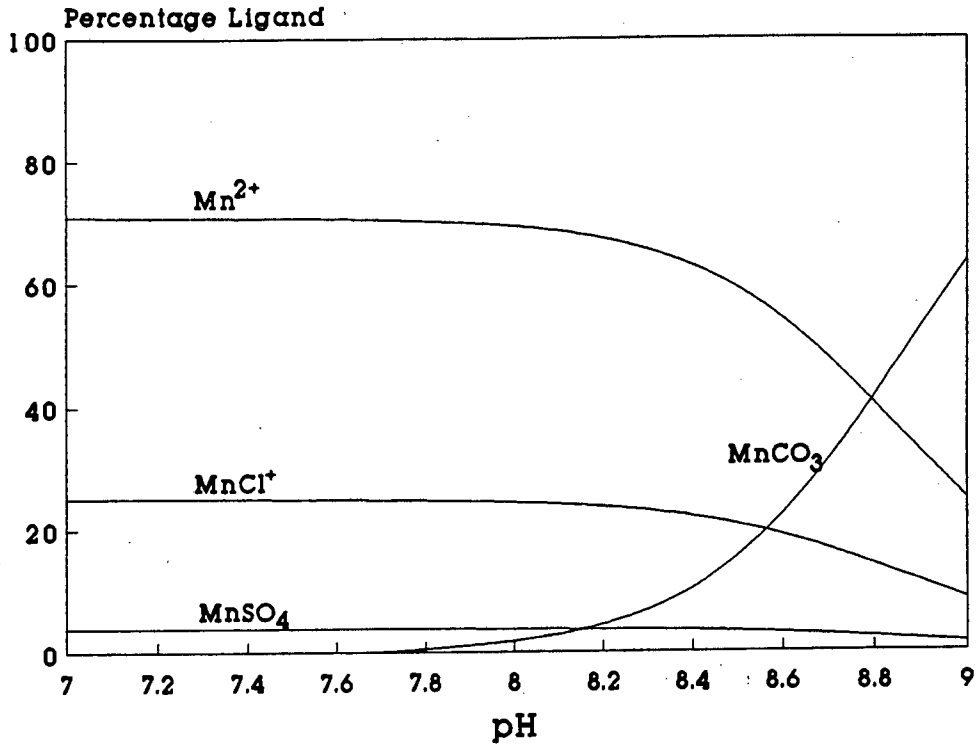


Figure 4.14.1: The inorganic speciation of manganese(II) as a percentage of dissolved metal versus pH (ionic strength = 0.7 mol dm^{-3}; 25 °C; atmospheric carbon dioxide dissolution included)

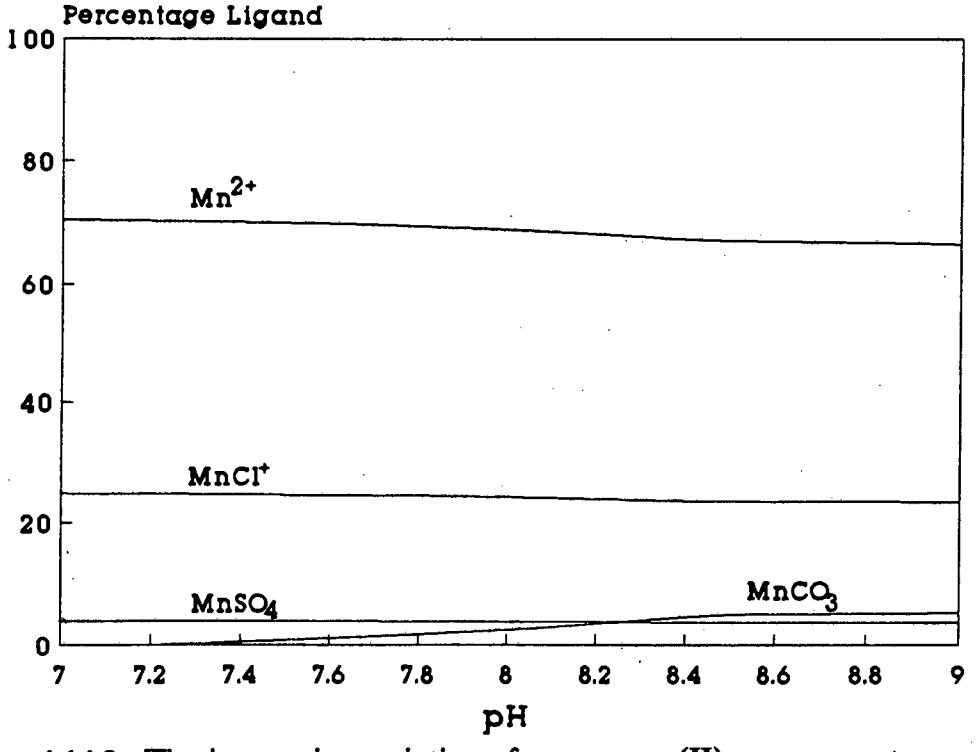


Figure 4.14.2: The inorganic speciation of manganese(II) as a percentage of dissolved metal versus pH (ionic strength = 0.7 mol dm^{-3}; 25 °C; atmospheric carbon dioxide dissolution excluded)

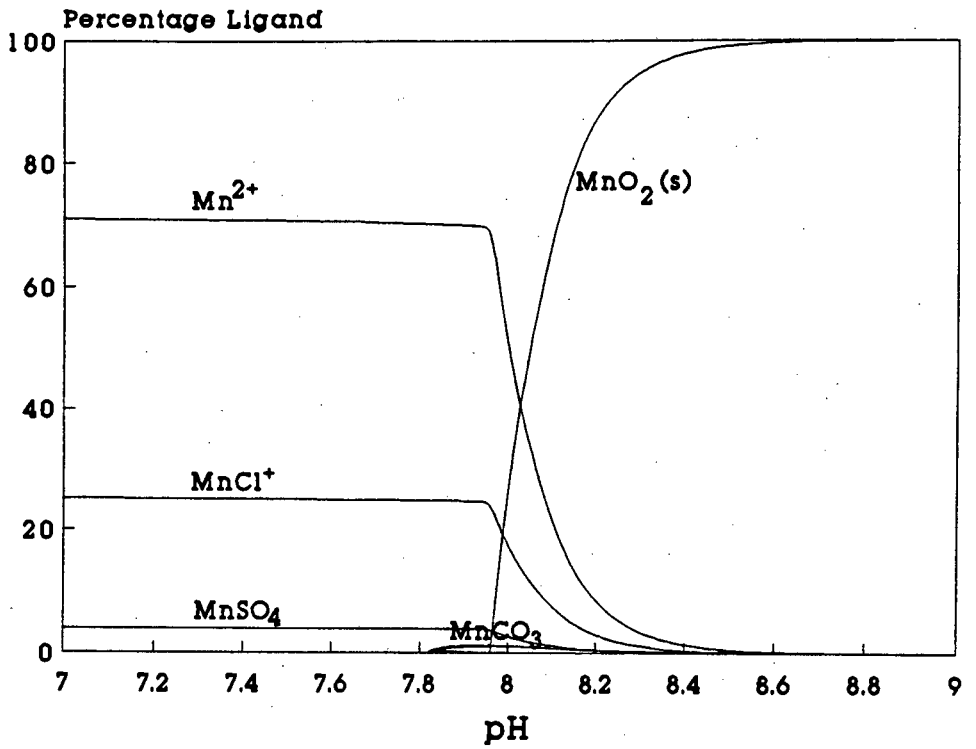


Figure 4.14.3: The inorganic speciation of manganese as a percentage of total metal versus pH (ionic strength = 0.7 mol dm^{-3}; 25 °C; atmospheric carbon dioxide dissolution included)

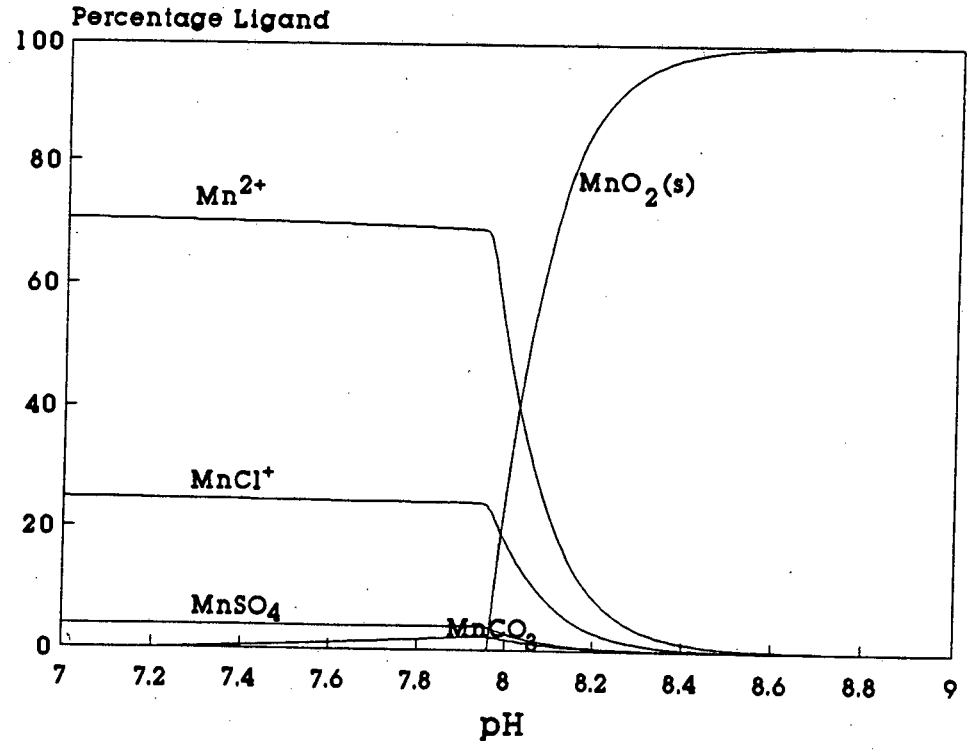


Figure 4.14.4: The inorganic speciation of manganese as a percentage of total metal versus pH (ionic strength = 0.7 mol dm^{-3}; 25 °C; atmospheric carbon dioxide dissolution excluded)

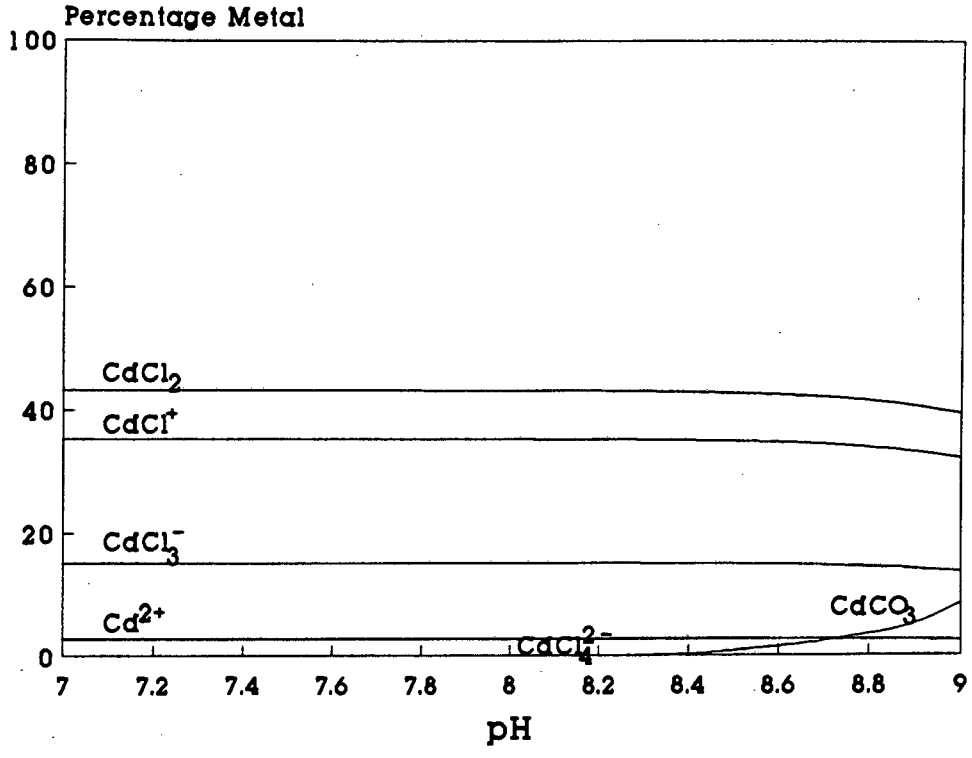


Figure 4.15.1: The inorganic speciation of cadmium(II) as a percentage of total metal versus pH (ionic strength = 0.7 mol dm^{-3}; 25 °C; atmospheric carbon dioxide dissolution included)

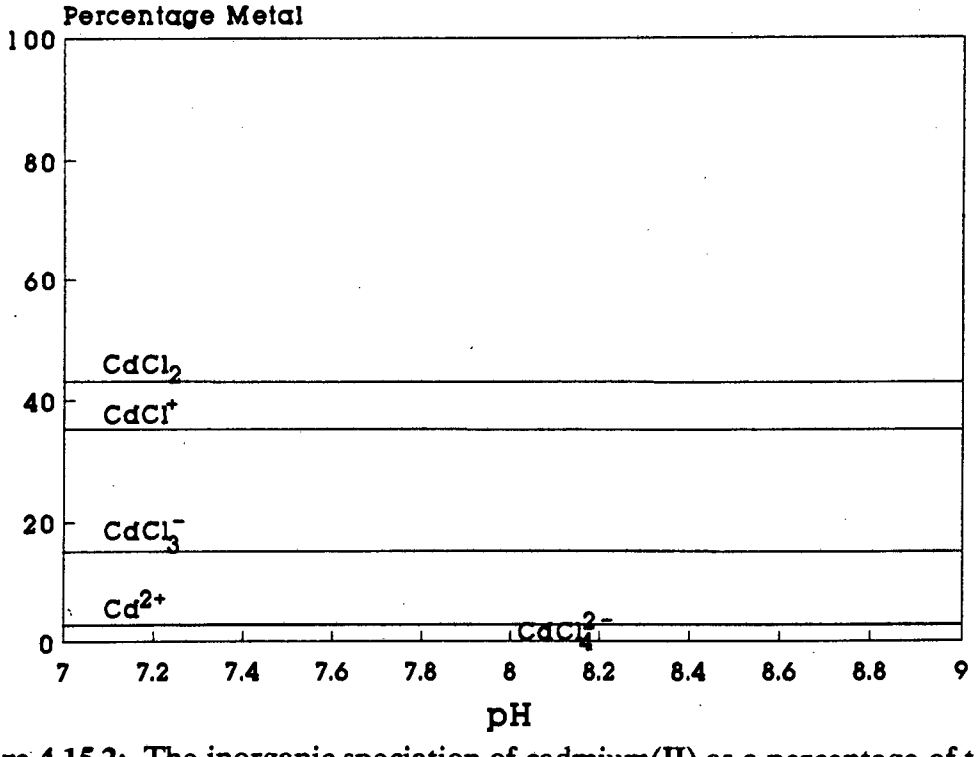


Figure 4.15.2: The inorganic speciation of cadmium(II) as a percentage of total metal versus pH (ionic strength = 0.7 mol dm^{-3}; 25 °C; atmospheric carbon dioxide dissolution excluded)

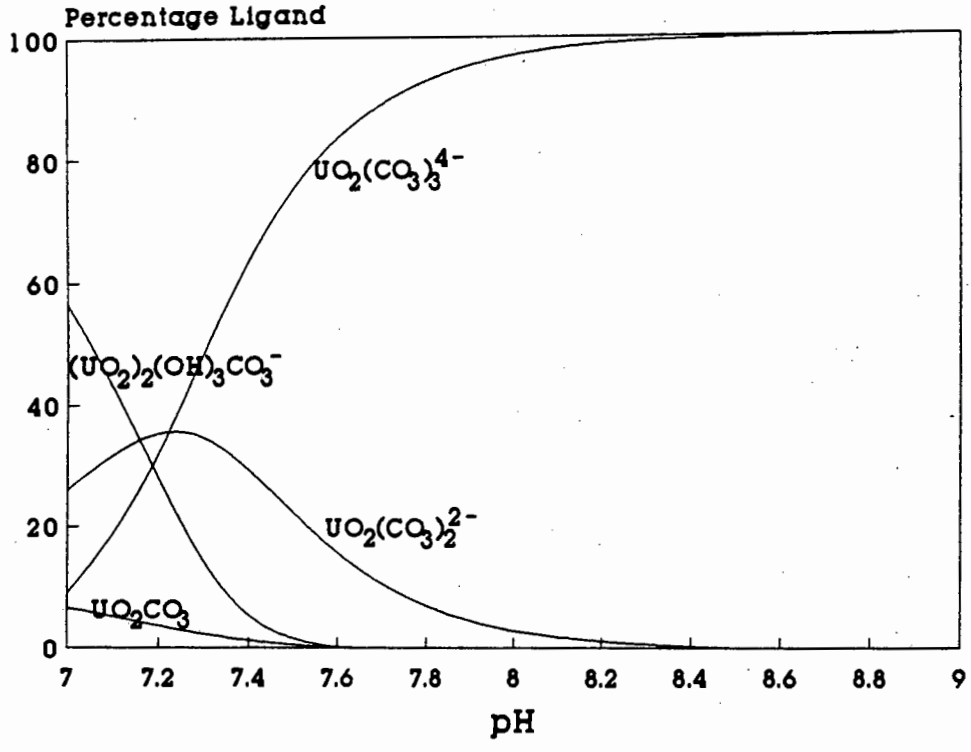


Figure 4.16.1: The inorganic speciation of uranyl as a percentage of total metal versus pH (ionic strength = 0.7 mol dm^{-3}; 25 °C; atmospheric carbon dioxide dissolution included)

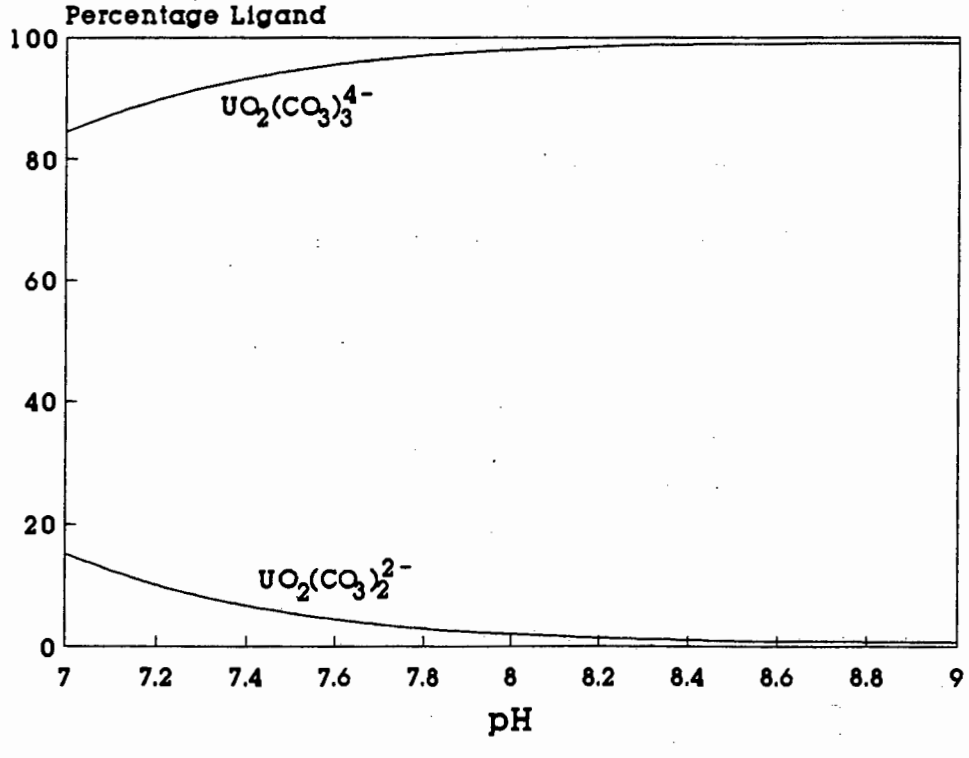


Figure 4.16.2: The inorganic speciation of uranyl as a percentage of total metal versus pH (ionic strength = 0.7 mol dm^{-3}; 25 °C; atmospheric carbon dioxide dissolution excluded)

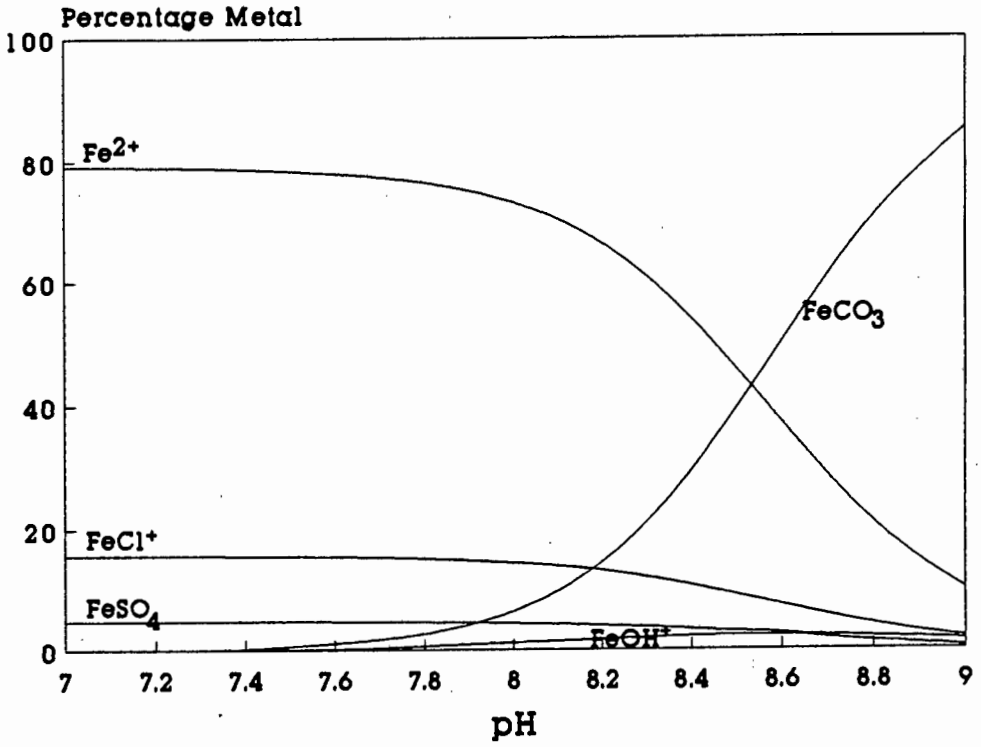


Figure 4.17.1: The inorganic speciation of iron(II) as a percentage of total metal versus pH (ionic strength = 0.7 mol dm^{-3}; 25 °C; atmospheric carbon dioxide dissolution included)

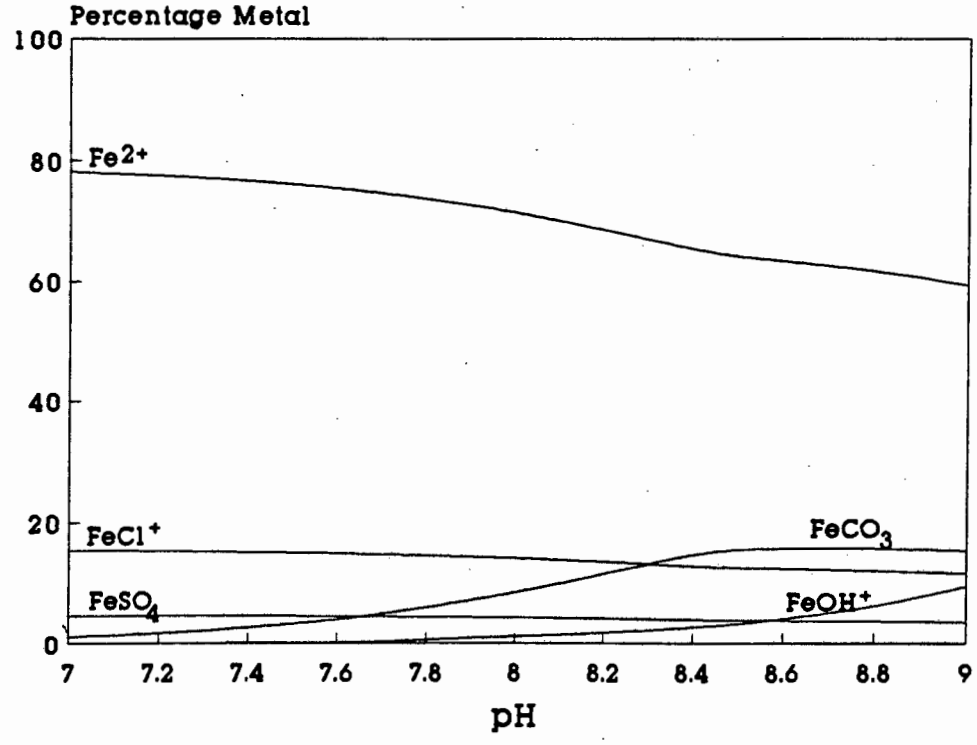


Figure 4.17.2: The inorganic speciation of iron(II) as a percentage of total metal versus pH (ionic strength = 0.7 mol dm^{-3}; 25 °C; atmospheric carbon dioxide dissolution excluded)

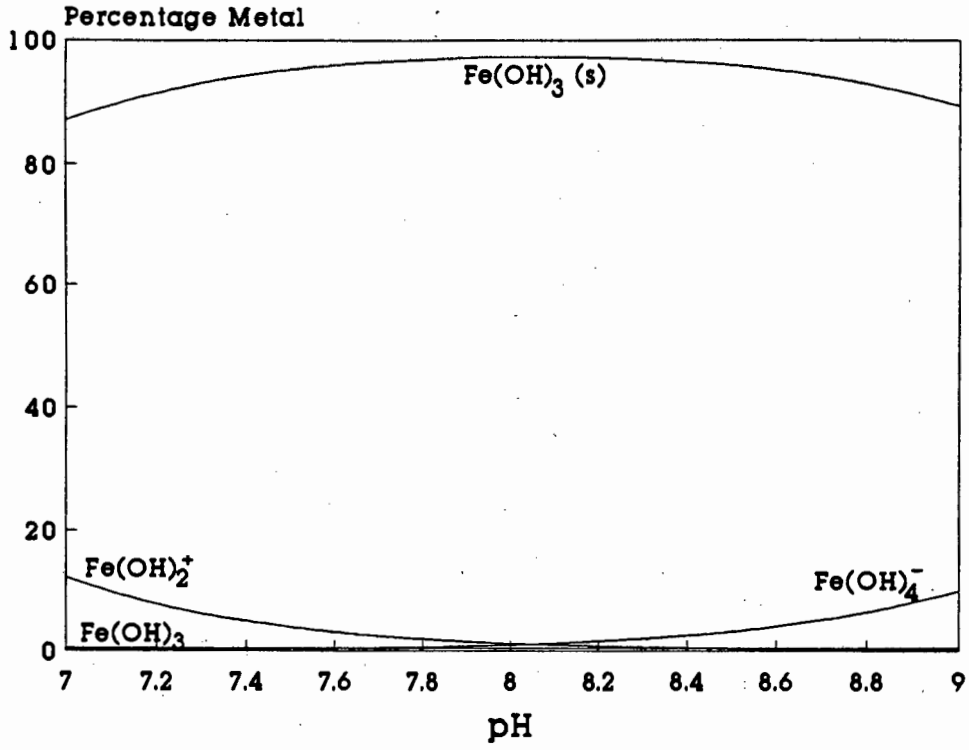


Figure 4.18.1: The inorganic speciation of iron(III) as a percentage of total metal versus pH (ionic strength = 0.7 mol dm^{-3}; 25 °C; atmospheric carbon dioxide dissolution does not affect the speciation)

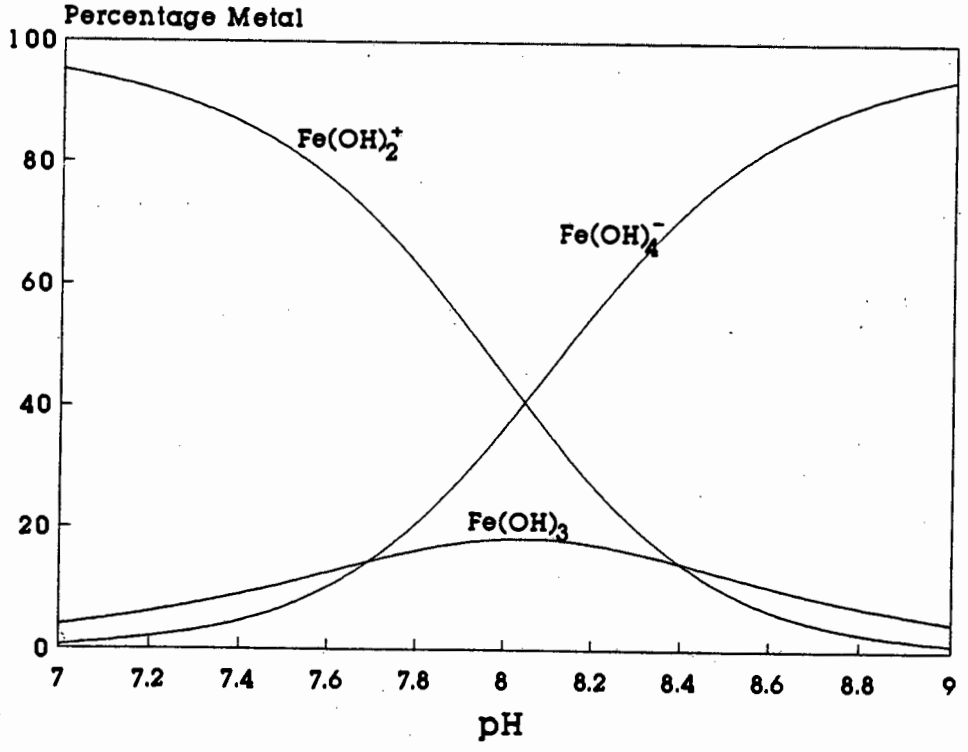


Figure 4.18.2: The inorganic speciation of iron(III) as a percentage of dissolved metal versus pH (ionic strength = 0.7 mol dm^{-3}; 25 °C; atmospheric carbon dioxide dissolution does not affect the speciation)

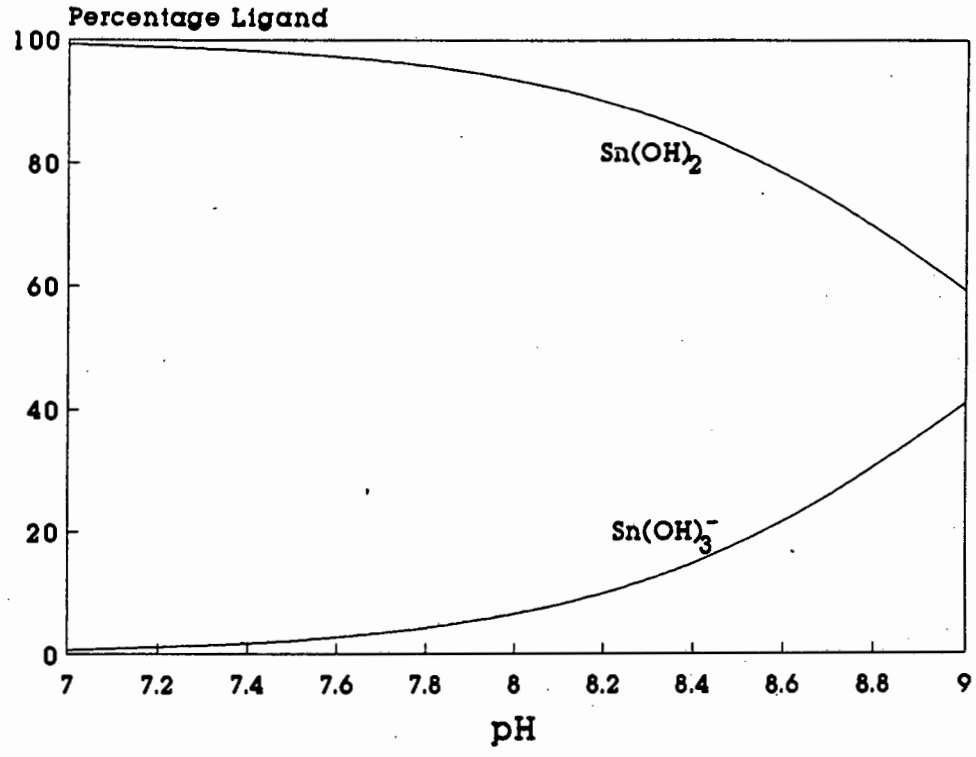


Figure 4.19: The inorganic speciation of tin(II) as a percentage of total metal versus pH (ionic strength = 0.7 mol dm^{-3}; 25 °C; atmospheric carbon dioxide dissolution does not affect the speciation)

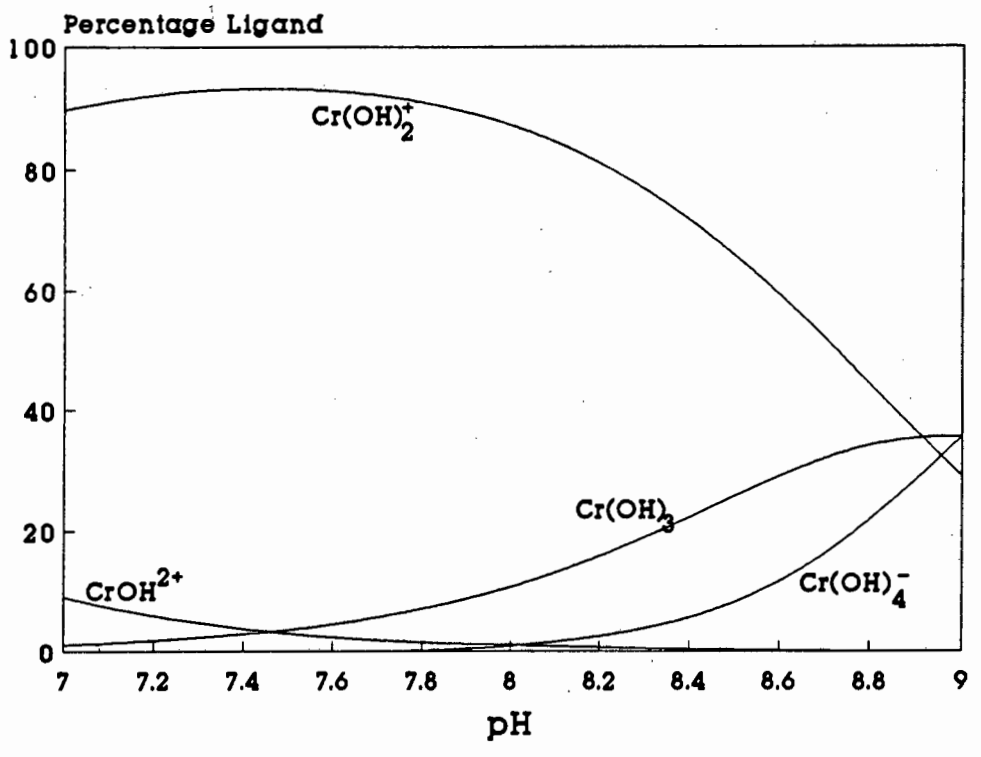


Figure 4.20: The inorganic speciation of chromium(III) as a percentage of total metal versus pH (ionic strength = 0.7 mol dm^{-3}; 25 °C; atmospheric carbon dioxide dissolution does not affect the speciation)

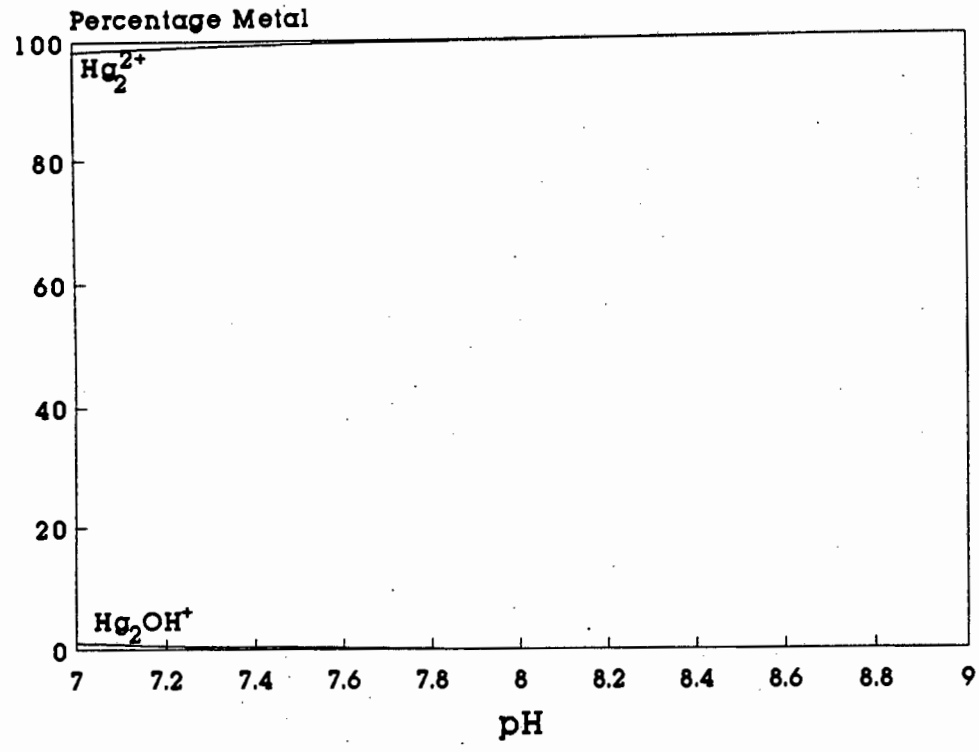


Figure 4.21: The inorganic speciation of mercury(I) as a percentage of total metal versus pH (ionic strength = 0.7 mol dm^{-3}; 25 °C; atmospheric carbon dioxide dissolution does not affect the speciation)

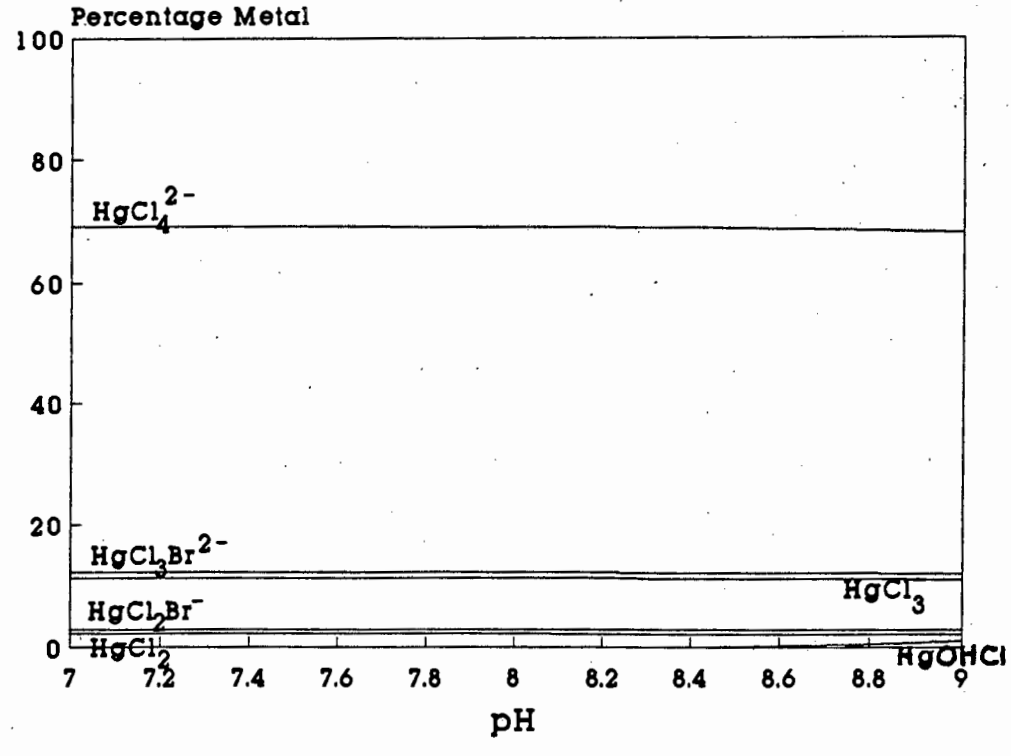


Figure 4.22 The inorganic speciation of mercury(II) as a percentage of total metal versus pH (ionic strength = 0.7 mol dm^{-3}; 25 °C; atmospheric carbon dioxide dissolution does not affect the speciation)

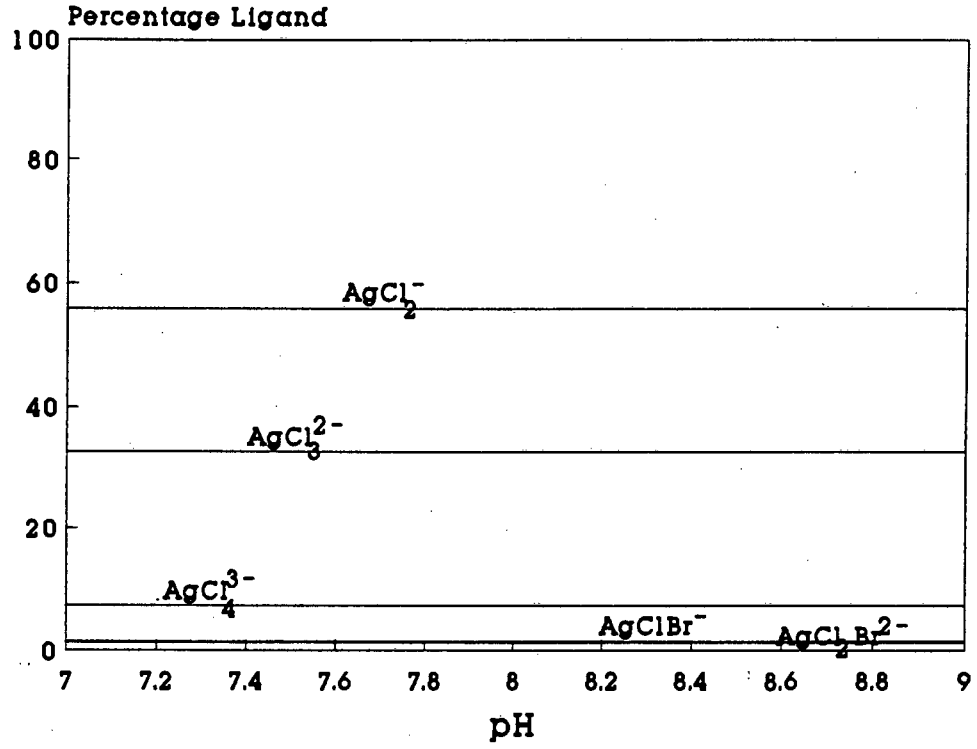


Figure 4.23: The inorganic speciation of silver(I) as a percentage of total metal versus pH (ionic strength = 0.7 mol dm^{-3}; 25 °C; atmospheric carbon dioxide dissolution does not affect the speciation)

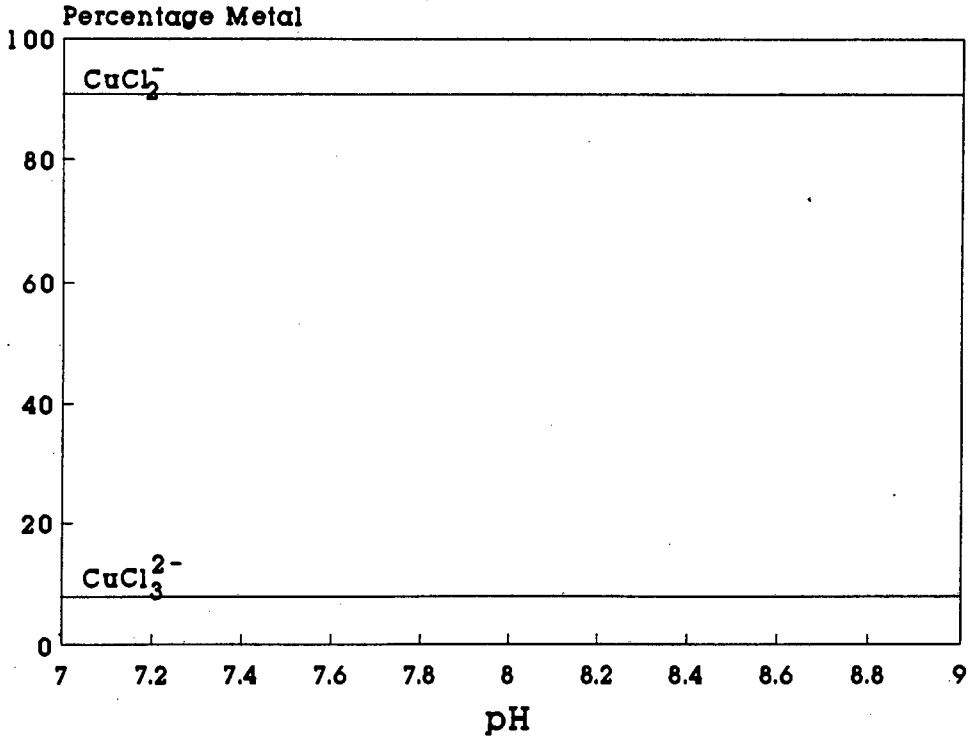


Figure 4.24: The inorganic speciation of copper(I) as a percentage of total metal versus pH (ionic strength = 0.7 mol dm^{-3}; 25 °C; atmospheric carbon dioxide dissolution does not affect the speciation)

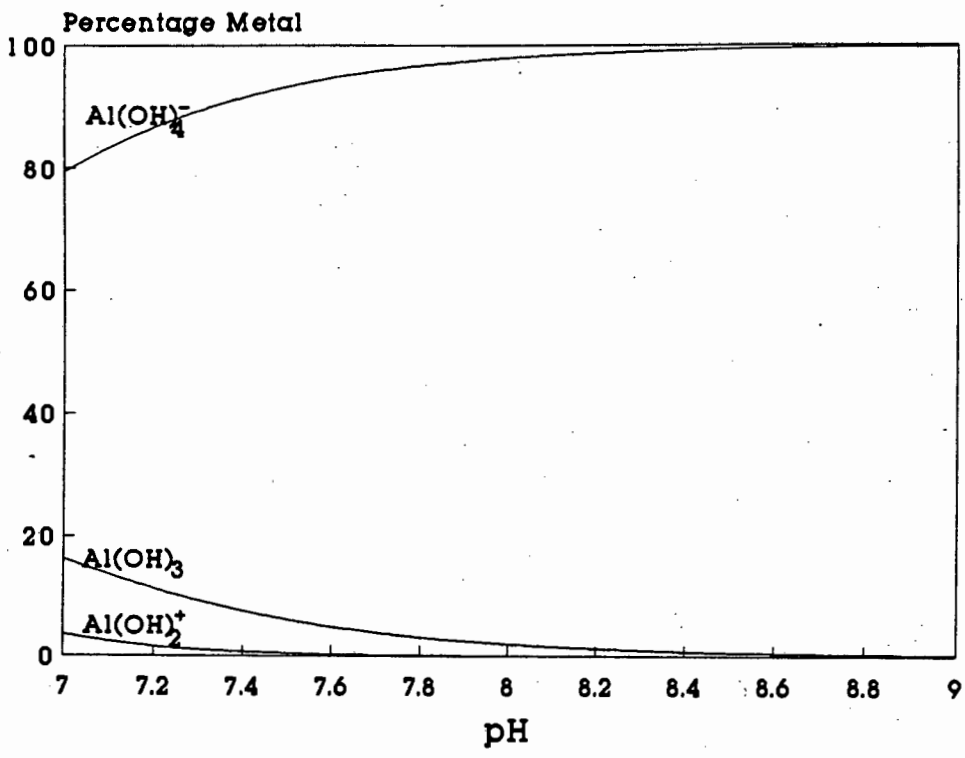


Figure 4.25.1: The inorganic speciation of aluminium(III) as a percentage of dissolved metal versus pH (ionic strength = 0.7 mol dm^{-3}; 25 °C; atmospheric carbon dioxide dissolution does not affect the speciation)

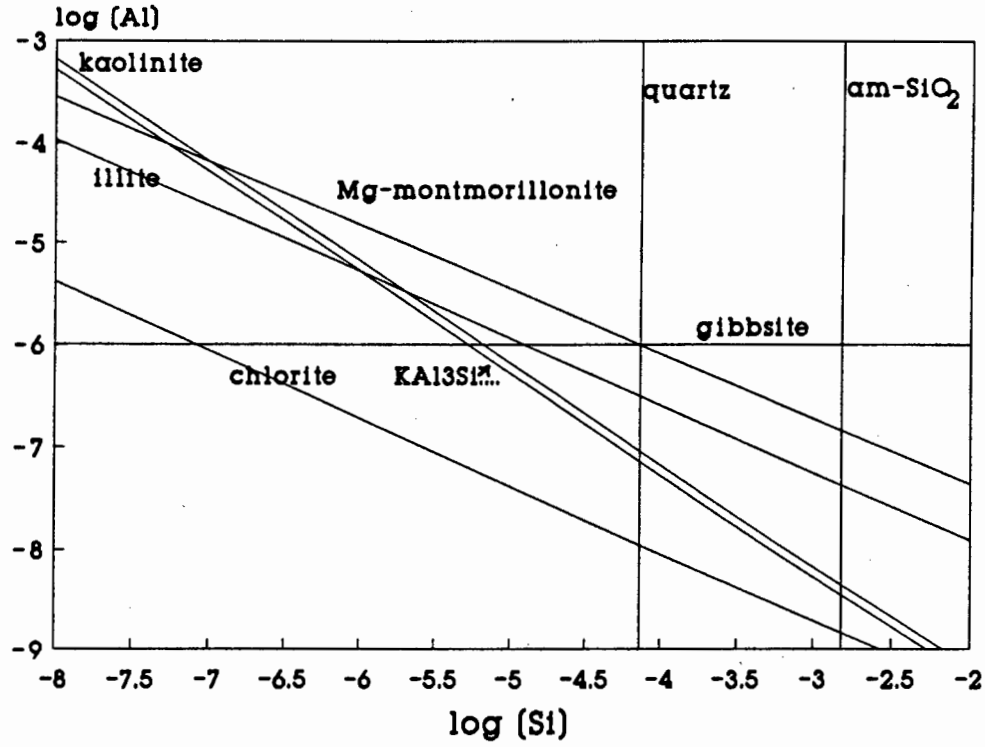


Figure 4.25.2: The effect of dissolved silicate concentration on dissolved aluminium concentration as determined by various aluminosilicates (ionic strength = 0.7 mol dm^{-3}; 25 °C; atmospheric carbon dioxide dissolution does not affect the speciation)

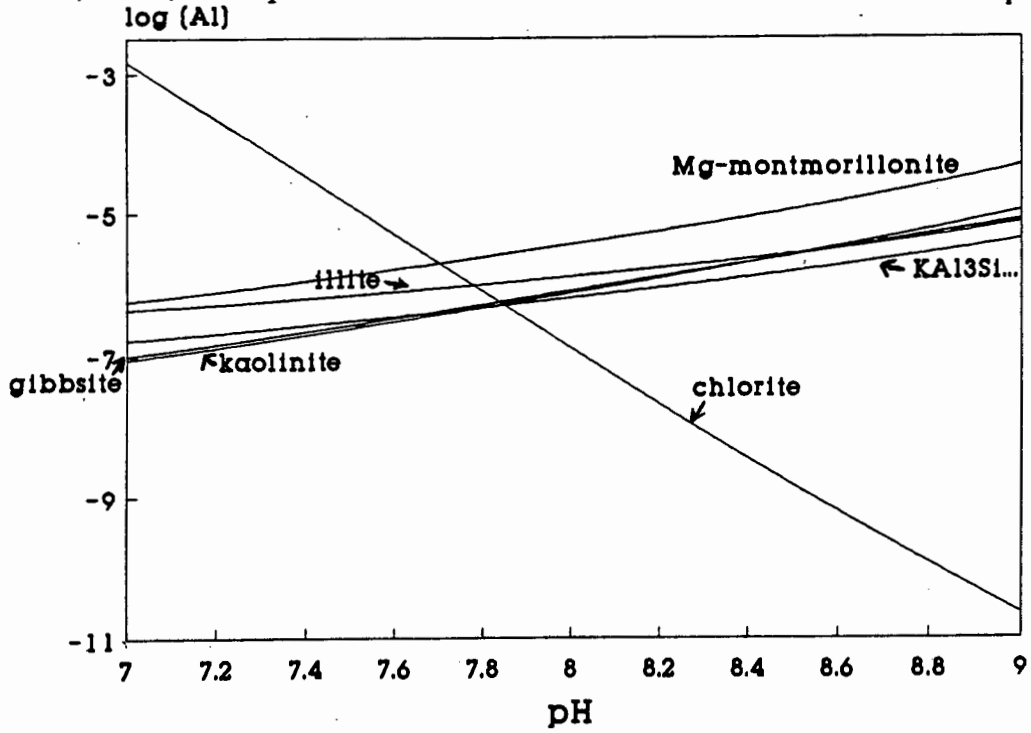


Figure 4.25.3: The effect of pH on dissolved aluminium concentration as determined by various aluminosilicates (ionic strength = 0.7 mol dm^{-3}; 25 °C; atmospheric carbon dioxide dissolution does not affect the speciation; total silicate concentration = 7μmol dm^{-3})

7) The concentration of a trace metal did not affect its percentage speciation pattern in the concentration range 10^{-12} mol dm^{-3} to 10^{-6} mol dm^{-3} provided that the trace metal did not precipitate. The solubility limits for each trace metal and the most likely solid species for each trace metal are given in Table 4.4 (carbon dioxide excluded).

8) The redox state of the ocean in the range, pE = 8.4 to 12.3, was significant only for manganese. For copper, mercury and iron it did not affect the concentration of the major oxidation state significantly. The concentrations of the major oxidation states of various trace components are given in Table 4.5.

4.2 DISCUSSION OF THE INORGANIC SPECIATION PATTERN

4.2.1 Observations on chloride ion pairing

In general chloride ion pairing with the major cations has not been considered in the seawater models that have been developed to date. All are based on the assumption that the halide salts (excluding fluoride) of the alkali and alkaline earth metals are true strong electrolytes and therefore completely dissociated [Joh78].

Kester and Pytkowicz [Kes75a] concluded that chloride ion pairs should be significant under seawater conditions. The chloride ion pairs with the alkali and alkaline earth metals have been measured using several independent methods [Kes69, Joh78, Maj82, Byr84]. These constants are small but would predict significant chloride affinity at high chloride concentrations.

It was decided to perform a preliminary investigation on what the effect of ion pairing on trace metal speciation would be. Constants for chloride ion pairing for the major cations

Table 4.4: The solubility limits of the trace metals in seawater
Conditions: temperature, 25 °C; ionic strength, 0.7 mol dm^{-3}; pH = 8.1; atmospheric carbon dioxide excluded from dissolving.

Cation	Solubility limit (/mol dm^{-3})	Solid species
Fe^{3+}	2.2×10^{-10}	am-$Fe(OH)_3$
Mn^{2+}	1.1×10^{-9}	MnO_2 at pE = 9.1
	9.8×10^{-5}	Rhodochrosite ($MnCO_3$), MnO_2 excluded from precipitating.
Al^{3+}	5.2×10^{-8}	Chlorite ($Mg_5Al_2Si_3O_{10}(OH)_8$)
	1.0×10^{-6}	Gibbsite ($Al(OH)_3$)
Cu^{2+}	1.7×10^{-7}	$Cu(OH)_{1.5}Cl_{0.5}$
	2.3×10^{-7}	Malachite ($Cu_2(OH)_2CO_3$)
Ba^{2+}	3.0×10^{-7}	Barite ($BaSO_4$)
Cd^{2+}	3.1×10^{-7}	$CdCO_3$
Pb^{2+}	6.2×10^{-7}	$Pb_3(OH)_2(CO_3)_2$
	3.9×10^{-6}	Cerrusite ($PbCO_3$)
Sn^{2+}	4.6×10^{-6}	SnO
Cr^{3+}	7.6×10^{-6}	$Cr(OH)_3$
Co^{2+}	1.2×10^{-5}	$CoCO_3$
Ag^{+}	2.8×10^{-5}	Chloroargyrite (AgCl)
Zn^{2+}	7.2×10^{-5}	Smithsonite ($ZnCO_3$)
UO_2^{2+}		did not precipitate
Ni^{2+}		did not precipitate
Hg^{2+}		did not precipitate

Table 4.5: The distribution of trace metals between redox states in the ocean. Conditions: temperature, 25 °C; ionic strength, 0.7 mol dm; pH = 8.1; atmospheric carbon dioxide dissolution does not affect the distribution except in the indicated cases.

Trace component		Concentration at pE = 8.4 (/mol dm^{-3})	Concentration at pE = 12.3 (/mol dm^{-3}
Iodine	IO_3^-	5.141×10^{-17}	4.000×10^{-7}
	I^-	4.000×10^{-7}	1.239×10^{-20}
Chromium	CrO_4^{2-}	2.150×10^{-9}	2.150×10^{-9}
	Cr^{3+}	2.355×10^{-19}	4.699×10^{-31}
Iron	Fe^{3+}	2.174×10^{-10} v	2.174×10^{-10} v
	Fe^{2+}	4.919×10^{-17} w	6.192×10^{-21} w
		4.946×10^{-17} x	6.226×10^{-21} x
Copper	Cu^{2+}	1.999×10^{-9}	2.000×10^{-9}
	Cu^+	9.666×10^{-13} w	1.217×10^{-16} w
		9.156×10^{-13} x	1.153×10^{-16} x
Manganese	Mn^{2+}	4.000×10^{-9}	4.297×10^{-16} w
			4.305×10^{-16} x
	MnO_2	0	4.000×10^{-9}
Mercury	Hg^{2+}	1.000×10^{-11}	1.000×10^{-11}
	Hg_2^{2+}	5.808×10^{-35}	9.634×10^{-43}

v: This is the dissolved concentration, 7.783×10^{-9} mol dm^{-3} exists as am-$Fe(OH)_3$ (s);

w: atmospheric carbon dioxide allowed to dissolve;

x: atmospheric carbon dioxide excluded from dissolving.

were taken from Johnson and Pytkowicz [Joh79b]. Association constants for these were -0.74 (HCl), -0.46 (NaCl), -0.32 (KCl), -0.40 (LiCl), 0.28 ($MgCl^+$), 0.37 ($CaCl^+$), 0.40 ($SrCl^+$) and 0.40 ($BaCl^+$).

13.5% sodium, 17.8% potassium and 15.4% lithium formed chloro ion pairs while the percentages were 43.5%, 48.5%, 49.3% and 51.6 for magnesium, calcium, strontium and barium respectively. The speciation for chloride was 82.9% Cl^-, 11.6% NaCl and 4.2% $MgCl^+$. When ion pairing was excluded the ionic strength predicted by the model was 0.66 mol dm^{-3} but on inclusion of chloride ion pairing this decreased to 0.55 mol dm^{-3}. Johnson and Pytkowicz [Joh79b] proposed an effective ionic strength of 0.53 mol dm^{-3}. It should be noted that this speciation calculation is approximate as the other formation constants in the database are still applicable to an ionic strength of 0.7 mol dm^{-3}.

The effect of chloride ion pairing was ignored so that the ionic strength of seawater could be regarded as 0.7 mol dm^{-3}. If the ion pairing is allowed the ionic strength calculated decreases and the formation constants in the databases would then have to be corrected to the new ionic strength. This procedure would continue until convergence was reached.

The effect of leaving out ion pairing was found to be significant only for those metals which form important chloro species. In general the percentage metal bound by chloride decreases slightly while that of the aqua ion and other ligands increases. The significance of higher order species also decreases while lower order chlorides increase in importance. For example where carbon dioxide is excluded, the speciation of nickel changed to 56.7% Ni^{2+} ($\Delta = +1.4$), 5.0% $NiSO_4$ ($\Delta = +0.9$), 26.3% $NiCl^+$ ($\Delta = -4.5$) and 11.0% $NiCO_3$ ($\Delta = +1.8$). The speciation of mercury changed to 2.9% $HgCl_2$ ($\Delta = +0.7$), 12.5% $HgCl_3^-$ ($\Delta = +1.2$), 63.5% $HgCl_4^{2-}$ ($\Delta = -5.5$), 13.5% $HgCl_3Br^{2-}$ ($\Delta = +1.3$), 3.9% $HgCl_2Br^-$ ($\Delta = +1.0$) and 1.1% $HgCl_2Br_2^{2-}$ ($\Delta = +0.3$). Note that bromide ion pairing was not considered in these preliminary studies. As the free chloride ion concentration

decreased, the free concentrations of other inorganic ligands increased as a result of the complexation of the major cations by chloride. These observations are only approximate as they may also result in part from discrepancies between the ionic strength calculated by the model and that at which the model is set up.

4.2.2 Observations on the formation of mixed ligand complexes

Mixed halide species were found to be significant for those ligands which form strong bromide species. Ag^{+} and Hg^{2+} were observed to form ternary species. For Pb^{2+}, Cd^{2+}, Sn^{2+} and Cu^{+} the differences between log K for MCl_n and log K for MCl_iBr_j where n = i+j were small, unlike $Hg^{2+}$and Ag^{+}. Because the difference in the formation constants of the chloro and mixed bromochloro complexes is not large enough for the first four metals, they do not form mixed halide complexes. The large difference in ligand concentration far outweighs the stabilization brought about by mixed complexes. Bromide is present at the relatively low concentration of 8.6×10^{-4} mol dm^{-3} when compared to chloride (5.59×10^{-1} mol dm^{-3}).

The mixed hydroxycarbonate species were significant in the model because of the high pH and carbonate concentration. In this case the concentrations of the free ligand ($CO_3^{2-} = 4.50 \times 10^{-5}$ mol dm^{-3} and $OH^{-} = 2.19 \times 10^{-6}$ mol dm^{-3}) are much closer together than is the case with bromide and chloride and mixed species are thus statistically favoured. Consequently $PbOHCO_3^{2-}$ and $CuOHCO_3^{2-}$ were observed at the pH of seawater.

4.2.3 The effect of trace metal concentration on speciation

It was observed that the percentage distribution of a trace metal among the various complexes it forms was unaffected by the concentration of that trace metal up until the

point at which the trace metal precipitated, provided that limit was less than 10^{-5} mol dm^{-3}.

The reason for this observation is firstly that the trace metals are not seen to form polynuclear species i.e M_iL_j where $i > 1$. Furthermore the trace metal concentration is much less than that of the major cations. These major cations are conservative, i.e. they have a constant concentration throughout the ocean. The same applies to all the ligands which bind metals strongly (hydroxide, chloride, carbonate and sulphate). Consequently the free ligand concentrations are determined by complexation reactions with the major cations because all the trace metals combined do not bind a significant fraction of any ligand (<0.001%). Because total concentrations are conservative for the ligands and major cations, the free concentrations are also so.

Consider now the reaction between a trace metal M and a ligand L to form a mononuclear species

$$M^{p+} + nL^{q-} \leftrightarrow Ml_n^{(p-q)+}$$

The equilibrium constant is given by

$$K = [ML_n^{(p-q)+}]/[M^{p+}][L^{q-}]^n$$

Since K and $[L^{q-}]$ are constant the ratio $[ML_n]/[M^{p+}]$ is also constant, thus $[ML_n] = k[M^{p+}]$ where k is a constant. The total metal concentration $[M]_T$ is given by the sum of all the metal species:

$$[M]_T = [M^{p+}] + \Sigma\, k_i[M^{p+}] = [M^{p+}]\{1 + \Sigma\, k_i\}$$

for all the k_i's (one for each species). From this it follows that $[MP^+]/[M]_T$ and thus $[ML_n]/[M]_T$ are constant. Consequently it can be seen that the percentage of a metal in a particular species must be constant.

This observation is only valid if no polynuclear species are formed. If this happens $[ML_n]/[MP^+]$ is no longer constant. However, no such species were significant in the model. Furthermore the observation is only valid at trace concentrations because at higher concentrations the metal will have an effect on the free ligand concentration.

If the concentration becomes so large that precipitation of a mineral occurs, the percentage distribution is no longer constant because the dissolved concentration is then fixed while that of the mineral species may increase. Thus as concentration increases the percentage that is dissolved decreases. However, the percentage distribution within the dissolved fraction will remain a constant.

Table 4.4 lists the maximum dissolved concentrations for the trace metals in the model. Also listed is the mineral species which would precipitate out if the concentration rose above the maximum dissolved level. It has been noted though that solubility control (see Table 4.3) is not a dominant control in the ocean except for iron, manganese and aluminium which exist to some degree as solid species at pH = 8.1 [Mur88]. These values are also the maximum levels indicated by inorganic speciation. If organic speciation and adsorption are taken into account the free component concentration decreases even further and so the maximum dissolved concentrations increase.

Hydroxyapatite, in principle, would restrict phosphate concentration to below 150 nmol dm^{-3}. However, it was excluded from the model because of uncertainty in the solubility product and the fact that the influence of Mg^{2+} in the ocean is likely to increase

solubility for reasons analogous to those observed for calcite. No reports of hydroxyapatite precipitation could be found in the literature.

Of interest is the aluminium:silicate relationship. These elements are observed to precipitate as aluminosilicates in the ocean [Kra56, Arm65, Hyd77, Hyd79, Lam84]. However, the degree of precipitation is dependent on the concentrations of silicate and aluminium. Aluminium and silicate concentrations thus exert control on each other. When aluminium concentration is low, silicate concentration may be high and vice versa. Note that silicate is unlikely to precipitate as pure quartz or amorphous SiO_2 as this would require a very low aluminium concentration. It must be borne in mind that the aluminosilicate constants were corrected from thermodynamic constants for pure solids. The true situation in the ocean is far more complex. Figure 4.25.2 shows the variation of dissolved aluminium concentration with dissolved silicate concentration at pH = 8.1 for various aluminosilicate minerals. Figure 4.25.3 shows the variation of dissolved aluminium concentration with pH for a fixed dissolved silicate concentration of 7 μmol dm^{-3}. The maximum dissolved aluminium concentration increases from pH = 7.0 but then decreases again as soon as chlorite starts to precipitate.

Ingri et al. [Ing91] report that the major fraction (65-80% of the total) of silicate is dissolved. This value rose to 99% in deep waters. The model predicts an even higher dissolved silicate concentration (approx. 98%) but this may be explained by the fact that the aluminium concentration was set on the low side. Furthermore the model does not take into account kinetics. In surface waters detrital silicates have not had the time to dissolve yet but by the time they reach deeper waters, they have either settled out completely or dissolved as observed by Ingri et al. [Ing91].

The limitation placed on the barium concentration by barite is very interesting because where barium concentrations have been observed to be high, barite particles have been

found in sediment traps. This was observed in the open ocean [Deh80] and particularly in the Baltic Sea [Bos81]. Bernard et al. [Ber89] found significant concentrations of barite in the Baltic (up to 44% of all particles at some sampling stations). These particles are the result of barium-rich rivers meeting sulphate-rich seawater.

4.2.4 The effect of pH and carbon dioxide dissolution on speciation

These two effects are considered together because the amount of dissolved carbon dioxide is dependent on the pH. At pH = 8.1 the difference between the model where carbon dioxide is included and that in which it is not allowed to dissolve is slight. However, at high pH it becomes significant.

pH was varied to model specific local conditions. In general, the pH does not vary by more than 0.3 from 8.1 [Bea89]. However, the larger variation studied is to measure the effect of larger local pH variations induced by biological action (e.g. in phytoplankton blooms) and the effect of pollution on the ocean. The use of the two carbon dioxide models is to indicate the effect of whether the pH variation is a long term effect (allowing equilibration) or is very localized (carbonate concentration is not determined by atmospheric carbon dioxide or the change in pH is rapid).

As indicated in the results section significant differences occur in the speciation of those components which that form strong hydroxo and carbonate species. Those that form very strong chloro species (Hg^{2+}, Ag^{+} and Cu^{+}) are unaffected. Cd^{2+} is affected when carbon dioxide is allowed to dissolve since $CdCO_3$ is observed at high pH.

Fe^{3+}, Al^{3+}, Cr^{3+}, Sn^{2+} and Hg_2^{2+} are affected by pH because they form strong hydroxide species. The first three have a charge of +3 and consequently a high charge density which means that they have a greater affinity for OH^- which is harder than the

other ligands present in seawater. Because of the strength of the hydroxo species these metals are not affected by the dissolution of carbon dioxide since metal carbonate species have very low concentrations with respect to total metal concentrations.

All the other trace metals are affected by the dissolution of carbon dioxide. This is noticeable at high pH's where MCO_3 complexes are formed. For Cu^{2+} and Pb^{2+} $M(CO_3)_2^{2-}$ species as well as hydroxycarbonates are important. This increase in complexation is brought about by the large increase in dissolved carbonate concentration.

This is because the free carbonate concentration is fixed by the equation

$$10^{20.57} = [H_2O]/[H^+]^2[CO_3^{2-}]$$

Thus

$$\log[CO_3^{2-}] = 2pH - 20.57$$

if the log of the activity of water is set equal to unity. The derivation is discussed earlier in sections 2.4.2.5.1 and 2.5.2.

Figures 4.8.1 and 4.8.2 show the variation of carbonate species concentration with pH for the case when carbon dioxide is allowed to dissolve and when it is not. When carbon dioxide is allowed to dissolve, the log of the free carbonate concentration increases linearly according to the above equation. When carbon dioxide is excluded, the free carbonate concentration increases with pH because the HCO_3^- species decreases in significance as pH increases. This explains why carbonate species are much more significant to the speciation of trace metals when atmospheric carbon dioxide is allowed to dissolve.

The speciation patterns of the alkaline earth metals change as carbonate complexation takes place at high pH. The pattern for magnesium should be viewed with care because of the restriction placed on magnesite and dolomite. Note that Sr^{2+} and Ca^{2+} precipitate at high pH where carbon dioxide dissolves. Ba^{2+} does not precipitate because of its low concentration.

4.2.5 The effect of the redox state of the ocean on the inorganic speciation

Table 4.5 indicates the effect of the couples considered in the model Cu^{2+}/Cu^{+}, Fe^{3+}/Fe^{2+}, Hg^{2+}/Hg_2^{2+}, Mn^{2+}/MnO_2 and IO_3^{-}/I^{-}. As explained in section 2.5.4 the Cr^{3+}/CrO_4^{2-} couple was excluded for kinetic reasons. The results in Table 4.5 show that the Cr^{3+} concentration as predicted by this couple is much lower than that observed experimentally. The pE was scanned between the limits set by the oxygen-water and oxygen-peroxide couples i.e 8.4 and 12.3. This range is expected to cover all marine possibilities except for the few anoxic environments that are very localized e.g Saanich inlet [Eme79, Eme82].

Table 4.5 indicates that the oxidation states: iron (II) and mercury (I) are insignificant in marine environments. Because the redox cycles are continually perturbed by biological intervention [Mur88], these states may be observed in localized environments. For instance iron(III) is often reduced in the sediments and redissolved as iron (II) [Bro82].

The Cu^{+} state is only slightly significant (0.05% of $[Cu]_T$) at pE = 8.4. This value will decrease even further when organic complexation is taken into account as marine organic matter binds Cu^{2+} very strongly.

The IO_3^{-}/I^{-} system has been considered as an indicator of marine pE. Liss et al. [Lis73] observed that the ratio of $[IO_3^{-}]/[I^{-}]$ is 3 in surface waters. The model predicts that this

ratio is observed at pE = 10.13 which is within the limits of the couples proposed by Breck [Bre72] and Sillen [Sil65a, Sil65b].

The only trace metal which is significantly affected by the redox state is manganese which precipitates out as MnO_2. The degree of precipitation depends on pE, pH and the manganese concentration.

For MnO_2 the following equations hold

$$K_{sp} = [H^+]^4[e^-]^2/[Mn^{2+}][H_2O]^2$$

or

$$\log K_{sp} = -41.47 = -4pH - 2pE - \log [Mn^{2+}]$$

At pH = 8.1 this reduces to

$$\log [Mn^{2+}] = 9.07 - 2pE$$

Because the speciation of the dissolved fraction is unaffected by concentration and the aqua ion forms 68.6% of the total speciation

$$[Mn^{2+}] = 0.686\ [Mn]_{diss}$$

Thus the maximum dissolved manganese concentration begins is given by

$$\log [Mn]_{diss} = 9.07 - 2pE + 0.164$$

Precipitation starts to occur when $[Mn]_{diss} = [Mn]_T$. For $[Mn]_T = 4$ nmol dm^{-3} and pH = 8.1, this occurs at pE = 8.82. As the total concentration increases, this pE would be expected to drop.

Murray et al. [Mor83a] found that in the Pacific ocean about 50% of manganese was dissolved. For 4 nmol dm^{-3} manganese, this would indicate an ocean pE of 8.97 which is within the limits set by the O_2/H_2O and O_2/H_2O_2 couples.

The redox state of the ocean is not easily measurable and definable. However, for the trace metals present in seawater it is likely to be significant only for manganese. For the others, one oxidation state is dominant.

An improvement to the model would be the consideration of the kinetics of redox equilibria. As has been indicated, the model does not satisfactorily explain the distribution of chromium between chromium (III) and chromium (VI). Furthermore manganese (II) oxidation is extremely slow at pH < 9 [Mor67] as measured in the laboratory. However, in the sea it is 10^3 - 10^5 times faster because of catalysation reactions which occur on iron oxide surfaces [Sun81b]. At present, though, this is beyond the scope of the model.

4.2.6 Investigation of the sensitivity of the speciation patterns to the formation constants used

As many of the constants used to set up the database were measured at ionic strengths different from that of seawater, these constants had to be corrected for ionic strength which could introduce an error. Furthermore and more significantly the prediction of a formation constant at the ionic strength of seawater was dependent on the accuracy of the original measurement.

In some cases the literature values available for formation constants were in disagreement. This was particularly true of the constants available for metal carbonate equilibria. Consequently the effect of the sensitivity of the speciation patterns to the formation constants for metal carbonates was investigated. Carbon dioxide was excluded from dissolving.

Log K for $CuCO_3$ was changed to 5.39 (Δ = -0.34), $Cu(CO_3)_2^{2-}$ to 8.61 (Δ = -0.69) and $CuOHCO_3^-$ to -3.92 (Δ = -0.35) as recommended by Millero and Hawke [Mil92]. The resultant speciation pattern was 6.0% Cu^{2+} (Δ = +3.1), 6.0% $CuOHCO_3^{2-}$ (Δ = -0.6), 66.1% $CuCO_3$ (Δ = -4.3), 4.9% $Cu(CO_3)_2^{2-}$ (Δ = -6.9), 2.1% $CuCl^+$ (Δ = +1.1), 10.9% $CuOH^+$ (Δ = +5.6) and 1.9 % $Cu(OH)_2$ (Δ = +1.0). As expected the carbonate species decreased in significance although copper (II) is still predominantly bound by carbonate.

The formation constants for lead, likewise, were adjusted. Log K for $PbCO_3$ was changed to 5.26 (Δ = -0.35), $Pb(CO_3)_2^{2-}$ to 8.61 (Δ = -0.35) and $PbOHCO_3^-$ to -4.16 (Δ = -0.18). These new constants were based on the solubility measurements of Bilinksi and Schindler [Bil82]. In this case the speciation pattern changed to 4.3% Pb^{2+} (Δ = +1.4), 34.9% $PbCO_3$ (Δ = -17.7), 3.5% $PbCO_3^{2-}$ (Δ = -1.8), 1.7% $PbOHCO_3^-$ (Δ = 0.0), 18.0% $PbCl^+$ (Δ = +5.8), 20.1% $PbCl_2$ (Δ = +6.5), 0.1% $PbCl_3$ (Δ = +2.9) and 5.5% $PbOH^+$ (Δ = +1.8). Again the significance of the carbonate species decreased but what is significant is that the decrease in the $PbCO_3$ species is 17.7% while it is 4.3% for $CuCO_3$ when the change to the formation constants is comparable. This would indicate that the speciation of lead is far more sensitive to changes in the lead carbonate formation constants.

As a last example the formation constant for $NiCO_3$ was changed to 4.57 (Δ = +1.00) as predicted by Langmuir [Lan79]. The speciation pattern changes to 30.1% Ni^{2+} (Δ=-4.2), 16.8% $NiCl^+$ (Δ = -14.0), 2.2 $NiSO_4$ (Δ = -1.9) and 50.4% $NiCO_3$ (Δ = +41.2). The speciation of nickel is now dominated by carbonate species. This aptly illustrates that

models are only as good as the formation constants used as the formation constant predicted by Langmuir is at variance to that measured by Zhorov et al. [Zho76].

As indicated earlier in section 2.4.2.5.1 Pytkowicz and Hawley [Pyt74] expect the formation constant for HCO_3^- to be 9.68 which differs from the value of 9.54 used in the model. To investigate the response of the model to this important constant, the model was run with the constant from Pytkowicz and Hawley. Carbon dioxide was both allowed to dissolve and excluded from the model.

Where carbon dioxide was not allowed to dissolve, this change fixed the free carbonate concentration at 3.50×10^{-5} mol dm^{-3}. If carbon dioxide is included in the model, the free carbonate concentration becomes 3.09×10^{-5} mol dm^{-3} which fixes the total dissolved carbonate concentration at 1.81×10^{-3} mol dm^{-3}. Consequently the first consequence of the change in the HCO_3^- is a greater discrepancy between the two carbon dioxide models.

As a consequence of the change, the free carbonate concentration is lower in both models. Carbonate species are observed to have decreased significance while dicarbonate species decrease even more sharply. It would be expected that $MHCO_3$ species would increase in significance. However, none of these are observed at the pH of seawater except for $CoHCO_3^+$ which increases from 1.8% to 1.9% (carbon dioxide excluded).

As was the case when the metal carbonate formation constants were changed, lead is affected more significantly than copper. $PbCO_3$ changes to 47.7% (Δ = -4.9), $Pb(CO_3)_2^{2-}$ to 3.7% (Δ = -1.6) and $PbOHCO_3^-$ to 1.5% (Δ = -0.2) while $CuCO_3$ decreases to 70.0% (Δ = -0.4), $Cu(CO_3)_2^{2-}$ to 9.1% (Δ = -2.7) and $CuOHCO_3^-$ to 6.5 (Δ = -0.1). These results are for the case when carbon dioxide is excluded. When carbon

dioxide is included, the change in speciation is greater because of the greater change to the free carbonate concentration.

4.2.7 Comparison with previous model studies and experimental findings

As indicated earlier, previous model studies have been performed to calculate the speciation in seawater. In the main this study is in agreement with those studies.

The inorganic speciation results as predicted by the model are very similar to those of Turner et al. [Tur81]. Some of the discrepancy can be explained because these authors modelled seawater at pH = 8.2. The only differences are the speciation patterns of Mn^{2+} and Ba^{2+}. In the case of manganese Turner et al. did not consider the precipitation of MnO_2. However, the dissolved fraction of manganese has speciation which is very similar to that reported in [Tur81]. In the present model chloride association with the alkaline earth metals was not considered which explains the discrepancy observed between the barium speciations. In all other cases the differences in speciation are less than 10% for an individual species and what differences do occur are the result of different formation constants used.

The model of Motekaitis and Martell [Mot87] also shows remarkable similarities in results. In almost all cases the dominant forms of the trace metal are the same. There is also good correlation between the reported percentages. The differences occur in the Cu^{2+} and Pb^{2+} speciation. This is because they use a constant for $CuOH^+$ of log K = -6.50 which compares with log K = -7.72 used in this model. Consequently in their speciation pattern copper is dominantly bound as hydroxo species. Their much greater $PbCO_3$ constant (log K = 6.20 versus 5.15) accounts for their observation of lead as a predominantly carbonate complex.

Zirino and Yamamoto [Zir72] agree with Motekaitis and Martell that copper is hydroxide dominated but this is the result of the rather high constant that they chose for $Cu(OH)_2$. They also found $Zn(OH)_2$ to be the major species which is at odds with all other speciation calculations (see Table 4.6). This too was the result of an erroneously high formation constant. The choice of the constants used in this model is justified in sections 2.4.2.1.3 and 2.4.2.5.7.

The conclusion of the present study that $CuOHCO_3^-$ is of substantial importance is in agreement with the calculation performed by Byrne and Miller [Byr85]. Symes and Kester [Sym85b] also expect this species although they ignore $Cu(CO_3)_2^{2-}$. Most of the model studies already published agree that the inorganic speciation of copper is dominated by carbonate complexation except for Motekaitis and Martell [Mot87]. Van den Berg [VdB84b] expects copper to be carbonate dominated although hydroxo species are much more significant than in this study as a result of larger formation constants being used for these species.

The model agrees with the results of Byrne et al. [Byr88] and Millero and Hawke [Mil92] except that carbonate complexation is not as strong as that predicted in these models. Consequently, lead is not found to have as high a carbonate domination and iron (II) and nickel (II) form weaker carbonate species than reported.

The result that uranium is present as carbonato complexes is in line with that of Djogic et al. [Djo86]. The activity of the free uranyl ion is expected to remain constant as a result of the buffer action of dissolved carbonate. The total uranium concentration is observed to vary only slightly.

The speciation of cobalt is similar to that reported elsewhere [Tur81, Byr88, Pan91]. All these papers agree that cobalt speciation is dominated by the aqua ion. The percentage

TABLE 4.3: Computed inorganic speciation of the trace metals in seawater

Results are shown as the percentage of the cation appearing in an individual species.

Conditions: temperature, 25 °C; ionic strength, 0.7 mol dm^{-3}; pH, 8.1; pE = 9.1;

a) atmospheric carbon dioxide assumed to be in equilibrium with the aqueous phase;

b) atmospheric carbon dioxide excluded from equilibrating with the aqueous phase;

c) assumption regarding carbon dioxide does not affect the speciation.

Cation		$-\log[M^{n+}]$	Free	Cl	Cl_2	Cl_3	Cl_4	OH	$(OH)_2$	$(OH)_3$	$(OH)_4$	SO_4	CO_3	$(CO_3)_2$	Other
i) Components for which the aqua ion is the dominant species															
Zn^{2+}	(a)	8.94	56.9	12.7	8.9	4.0	1.6	4.8				5.0	4.8		
	(b)	8.95	56.7	12.6	8.9	3.9	1.6	4.8				5.0	5.1		
Ni^{2+}	(a)	8.71	55.3	30.9								4.1	8.8		
	(b)	8.72	55.1	30.8								4.1	9.2		
Co^{2+}	(a)	10.53	58.4	30.5				1.0				4.4	3.7		1.7^{x}
	(b)	10.54	58.3	30.4				1.0				4.4	3.9		1.8^{x}
Fe^{2+}	(a)	17.16	70.5	14.0				1.4				4.3	9.5		
	(b)	17.16	70.1	13.9				1.4				4.3	10.0		
Mn^{2+}	(a)	w	68.7	24.2								3.8	2.8		
	(b)	w	68.6	24.2								3.8	2.9		
ii) Components for which carbonate species are the dominant species															
Cu^{2+}	(a)	10.21	3.1	1.1				5.6					70.4	11.2	6.6^{y}
	(b)	10.23	2.9	1.0				5.3					70.4	11.8	6.6^{y}

w: Speciation for manganese is for dissolved manganese only. At pE = 9.1 73.0% of the total precipitates as MnO_2. $-\log[Mn^{2+}] = 9.13$

x: $CoHCO_3^{+}$

reported in this study (58%) is the same as Turner et al. [Tur81] and close to that reported by Pan and Susak (56%) [Pan91]. The value reported by Byrne et al. [Byr88] is 65%. Pan and Susak [Pan91] believe chloride to be the next most important ligand whereas Byrne et al. [Byr88] believe carbonate and chloride to be equally important. The results of the present work are similar to Turner et al. [Tur81] in that chloride is the next most important ligand (though not as significant as reported by Pan and Susak [Pan91]), followed by carbonate.

The results predicted for mercury and tin should be viewed with care as the present model does not attempt to quantify the σ-bonded carbon interactions that are known to occur in seawater. Thus no methyl-mercury or butyl tin species were modelled. Furthermore only tin(II) was included in the model. Ahrland [Ahr85] expects the speciation of mercury to be dominated by CH_3HgCl with $HgCl_4^{2-}$ second in importance. Thus if the methyl mercury species is ignored, the results are in agreement.

Table 4.6 lists the major species for the trace metals studied in this work, as reported by various other authors. This allows easy comparison between the various models. It can be seen that in most cases there is agreement on the most important ligand.

In general though, the discrepancies between the inorganic speciation as predicted by this model and those of previous studies are slight. Where they do occur they are manifest in different percentage distributions. However, the dominant species for a particular trace metal is normally the same. What differences that do occur, result from the uncertainty in the reported values for formation constants.

CHAPTER FIVE

THE EFFECT OF ORGANIC MATTER ON THE SPECIATION PATTERNS

5.1 LIMITATIONS OF THE RANDOM APPROACH TO MODELLING

Although RANDOM supplies an estimation of the binding site densities for fulvic or humic acids, there are several factors that may result in the predictions made by the model about the complexation of trace metals by organic matter, differing from experimental observations.

Conformational effects of the fulvic acid molecule on metal binding sites are not taken into account by RANDOM. Conformational changes may result from the electrostatic repulsion or attraction of neighbouring groups which could impact on the affinity of particular groups for metal cations. This in turn will affect metal binding by making complexation a function of cation complexation, pH and ionic strength as these all affect electrostatic interactions. Furthermore the molecule may take on conformations that prevent diketones assuming planar arrangements and thereby preventing enolization and consequently reducing complexation [Lin87]. This effect would be most significant where RANDOM predicts strong metal binding to site 9 (represented by acetylacetone). On the other hand fulvic acid may behave as a macrocyclic compound and entrap cations in hydrophilic cavities [Nis76]. The result would be enhanced complexation. This may well be significant in marine fulvic acid which has a high concentration of functional groups. These are distibuted on a long carbon chain (as a result of the low aromaticity) which would supply the necessary flexibility.

The original RANDOM program did not consider the effects of nitrogen and sulphur binding sites on trace metal speciation. The effect of binding to these sites when compared to oxygen-containing ligands is shown in the results section that follows.

TABLE 5.1: Computed speciation of the trace metals in seawater showing the effect of fulvic acid. Results are shown as the percentage of the cation appearing in an individual species. Conditions: temperature, 25 °C; ionic strength, 0.7 mol dm^{-3}; pH, 8.1; pE = 9.1 atmospheric carbon dioxide excluded from equilibrating with the aqueous phase; concentration of fulvic acid = 2 mg dm^{-3}

1) sulphur-containing ligands included, 80% nitrogen exists as NH_2;
2) sulphur-containing ligands excluded, 80% nitrogen exists as NH_2;
3) sulphur-containing ligands excluded, 50% nitrogen exists as NH_2;
4) sulphur-containing and nirogen-containing ligands excluded.

Cation		CYS	$(CYS)_2$	AET	$(AET)_2$	DAP	$(DAP)_2$	PN	$(PN)_2$	ASP	ACAC	$(ACAC)_2$	CAT	$(CAT)_2$	Other
Ag^+	1														6.5% AgMET
Fe^{3+q}	1/2/3/4													1.9	
Ni^{2+}	1			4.2		9.6		6.1							
	2					10.1		6.4							
	3					4.2		2.6							
Cu^{2+}	1/2					1.6	5.8	7.6	83.9						
	3					1.7	5.7	16.9	68.1						
	4										4.9		7.0		
Zn^{2+}	1			5.4											
Cd^{2+}	1	41.7													
Pb^{2+}	1	13.2		1.6											

q: percentage is for dissolved fraction, $Fe(CAT)_2^+$ forms 0.05% of the total.

5.2 RESULTS OF THE EFFECT OF FULVIC ACID ON THE SPECIATION PATTERNS

The effect of fulvic acid binding on trace metal speciation is shown in Tables 5.1 and 5.2. These show the effects of fulvic acid at concentrations of 2mg dm^{-3} and 1000 mg dm^{-3}. The results are shown according to which model for fulvic acid was used namely: [1] sulphur and nitrogen binding included; [2] sulphur binding excluded; [3] nitrogen binding sites of lower concentration (50% N as $-NH_2$) and [4] binding exclusively to oxygen donor sites. Where no data is given in the tables for a particular model, fulvic acid complexation was found to be insignificant. The speciation patterns of the model ligands at a concentration of 2 mg dm^{-3} fulvic acid can be found in Table 5.3. The effect of varying the concentration of fulvic acid on metal speciation for the various models are represented graphically in figures 5.1 to 5.13.

The effect of marine organic matter was modelled in four different ways. The first of these included 80% nitrogen as $-NH_2$ and 20% of sulphur as -SH. The ligands and concentrations for this model fulvic acid are listed in Table 3.2. The second model did not include the effect of sulphur. It was the same as the first except that the sulphur species (CYS, TMA, TLA, AET and MET) were excluded. The third model modelled 50% nitrogen as aliphatic $-NH_2$. The last model excluded sulphur and nitrogen completely. The ligand concentrations for the last three models may also be found in Table 3.2. The fulvic acid concentration was varies from 0.1 mg dm^{-3} to 1000 mg dm^{-3}. McKnight et al. recommend that a fulvic acid concentration of 50% of DOM is reasonable to model dissolved organic matter interactions with trace metals [McK83]. Normal fulvic acid concentration is about 0.5 mg dm^{-3} [Har83] although total dissolved organic matter is about 2 mg dm^{-3} [Rom90], assuming DOM = 2 x DOC]. Thus the most applicable results are those in the range 0.5 to 2 mg dm^{-3}. A higher value of 10 mg dm^{-3} has been observed in localized coastal situations [Rom90]. The dissolved organic carbon

TABLE 5.2: Computed speciation of the trace metals in seawater showing the effect of fulvic acid.
Results are shown as the percentage of the cation appearing in an individual species.
Conditions: temperature, 25 °C; ionic strength, 0.7 mol dm^{-3}; pH, 8.1; pE = 9.1
atmospheric carbon dioxide excluded from equilibrating with the aqueous phase;
concentration of fulvic acid = 1000 mg dm^{-3}
1) sulphur-containing ligands included, 80% nitrogen exists as NH_2;
2) sulphur-containing ligands excluded, 80% nitrogen exists as NH_2;
3) sulphur-containing ligands excluded, 50% nitrogen exists as NH_2;
4) sulphur-containing and nirogen-containing ligands excluded.

Cation		CYS	$(CYS)_2$	AET	$(AET)_2$	DAP	$(DAP)_2$	PN	$(PN)_2$	ASP	ACAC	$(ACAC)_2$	CAT	$(CAT)_2$	Other
Ag^+	1														96.0% AgMET 1.2% $Ag(MET)_2^{2-}$
Fe^{3+q}	1/2/3/4													100	
Al^{3+q}	1/2/3/4													21	
Ni^{2+}	1		5.2	1.5	37.1	3.3	38.8	2.1	11.1						
	2					5.9	69.3	3.7	19.9						
	3					13.2	57.9	8.5	16.8	1.1					
	4										53.6	11.8			
Cu^{2+}	1/2						6.5		93.5						
	3						6.4		93.4						
	4										2.4	75.0	3.3	19.2	
Zn^{2+}	1		2.3	28.4	64.1										
	2					21.9	5.1	23.1	12.9	2.9	4.7		1.7		1.6% $ZnALA^+$
	3					15.1	1.3	16.0	3.3	3.6	8.9		5.6		2.0% $ZnALA^+$
	4										15.9		5.45		

Cation		CYS	$(CYS)_2$	AET	$(AET)_2$	DAP	$(DAP)_2$	PN	$(PN)_2$	ASP	ACAC	$(ACAC)_2$	CAT	$(CAT)_2$	Other
Mn^{2+q}	1/2/3										4.3				
	4										4.4				
Fe^{2+}	1							1.9			16.5				
	2							1.9			16.6				
	3										17.0				
	4										17.6				
Co^{2+}	1	1.0		3.2		30.5	3.7	18.2	1.7	3.1	10.0				
	2					32.0	3.9	19.0	1.8	3.2	10.5				
	3					19.3		11.5		3.5	17.3	1.3			
	4										27.9	2.1			
Cd^{2+}	1	97.1		1.7											
	2							1.6							
Pb^{2+}	1	87.8		10.3											
	2									9.8					1.2% $PbALA^+$
	3									6.8					
Hg^{2+}	1/2								1.5						
Mg^{2+}	1/2/3/4										1.3				
Borate	1/2/3/4														4.2% $B(OH)_2CAT^-$

q: percentage is for dissolved fraction. Fe^{3+} and Al^{3+} are totally in solution. 71.5% of manganese exists as MnO_2 (s).

TABLE 5.3: Computed speciation of the model ligands for fulvic acid in seawater

Results are shown as the percentage of the cation appearing in an individual species.
Conditions: temperature, 25 °C; ionic strength, 0.7 mol dm^{-3}; pH, 8.1;
atmospheric carbon dioxide excluded from equilibrating with the aqueous phase;
concentration of fulvic acid = 2 mg dm^{-3} using the ligand concentrations for model 1.

No	Ligand	-log[L^{n-}]	Free	H	H_2	Na	NaH	Mg	Ca	CaH	Other
30	CYS	11.46		39.1	52.7						4.2% CdCYS, 2.0% NiCYS, 1.3% PbCYS
29	AET	11.07		35.2	61.2						1.5% $NiAET^+$, 1.1% $ZnAET^+$
25	DAP	8.61	5.1	91.4	2.2						
3	TMA	11.02	1.5	98.4							
22	PN	8.43	1.2	88.0	9.4						1.1% $Cu(PN)_2^{2+}$
27	ASP	8.91	2.8	72.9				23.9			
9	ACAC	7.73	1.2	5.6				91.7	1.5		
14	TLA	10.13	1.5	98.5							
26	SER	8.47	10.8	84.2				4.2			
21	ALA	8.18	2.5	93.5				3.9			
24	BEAL	8.16		98.7							
23	ETA	7.98	2.7	97.3							
28	MET	9.36	5.4	94.6							
11	MAL	8.09	30.2			18.2		38.5	12.8		
7	DEM	7.26	26.4			24.6		42.3	5.2		
13	DHMB	7.96	70.6					21.6	7.7		
12	SUCC	6.84	61.7			15.5		19.3	2.9		
2	HMP	6.85	71.8					22.5	5.7		
6	HBT	6.54	83.5					14.0	2.5		
1	CAT	13.16		5.0	67.6						27.4% $B(OH)_2CAT^-$
4	SAL	12.11		83.1			11.2	2.1		2.7	
5	ACPH	8.85	1.3	98.7							
16	PHEN	7.58	2.9	97.1							
15	BENZ	6.76	93.3					5.4	1.3		
17	PROP	5.67	72.6			14.8		10.6	1.7		

CODES USED TO DESCRIBE THE VARIOUS MODELS IN THE FIGURES THAT FOLLOW

1	Nitrogen and sulphur binding included
2	Sulphur binding excluded, 80% of N present as NH_2
3	Sulphur binding excluded, 50% of N present as NH_2
4	Sulphur and nitrogen binding excluded.

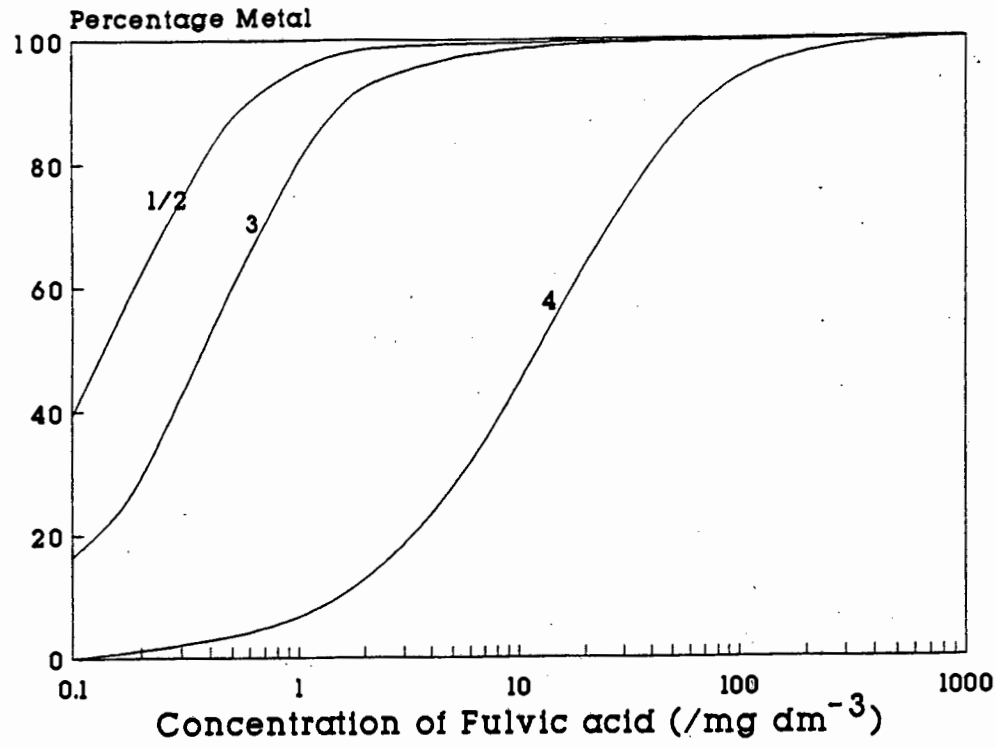


Figure 5.1: The effect of the various fulvic acid models on the organic complexation of copper(II) (ionic strength = 0.7 mol dm^{-3}; 25 °C; atmospheric carbon dioxide dissolution excluded)

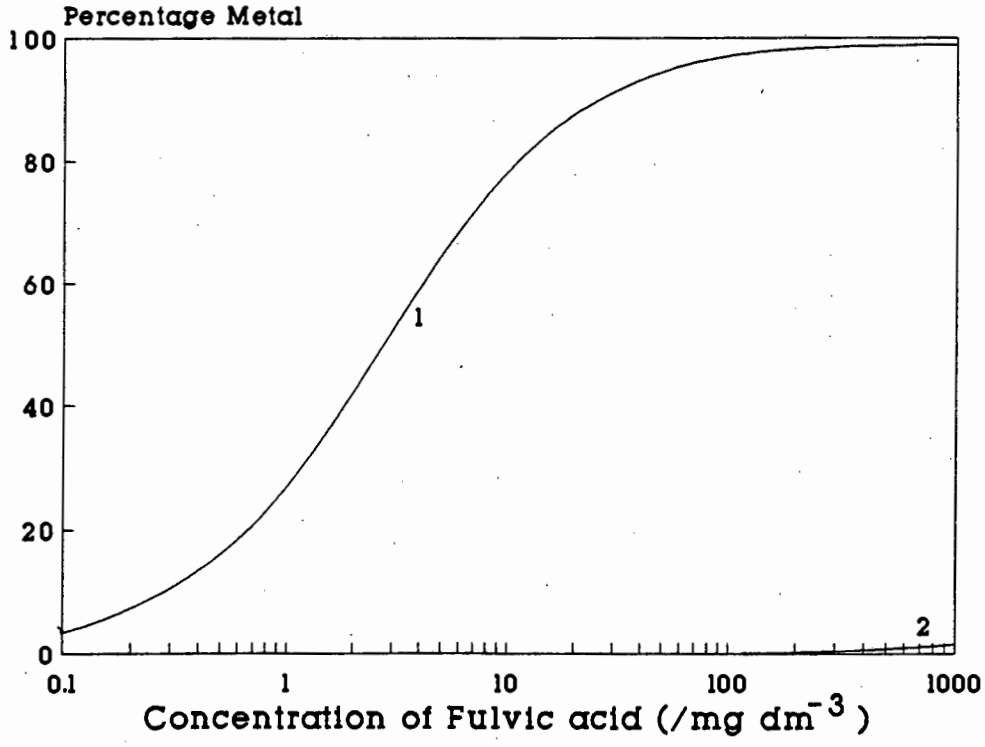


Figure 5.2: The effect of the various fulvic acid models on the organic complexation of cadmium(II) (ionic strength = 0.7 mol dm^{-3}; 25 °C; atmospheric carbon dioxide dissolution excluded)

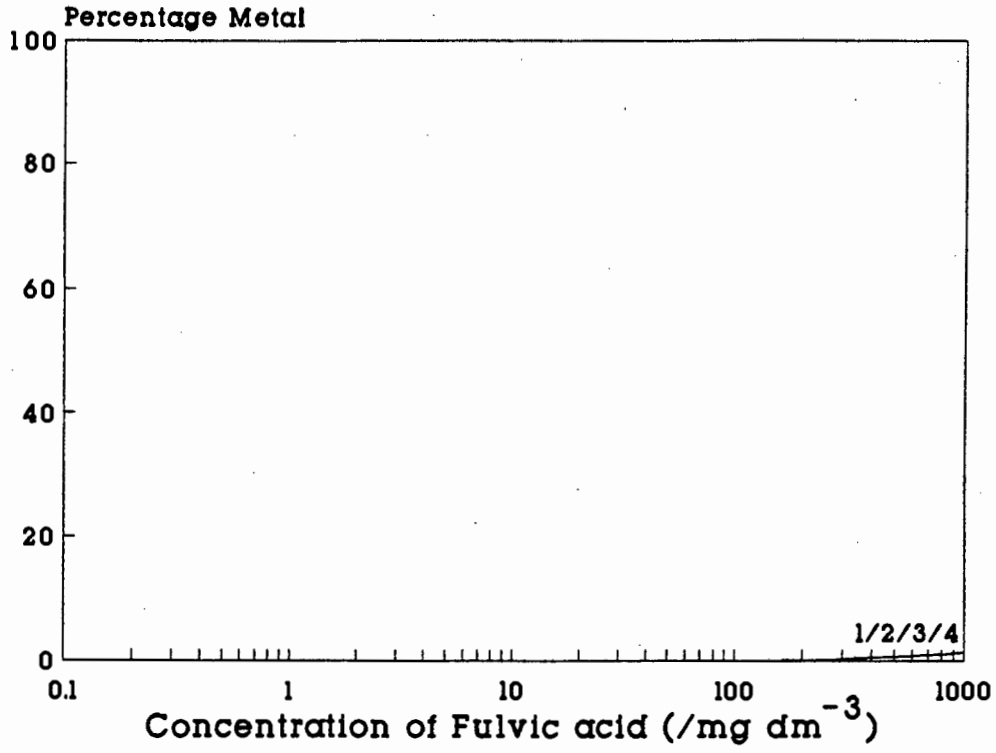


Figure 5.3: The effect of the various fulvic acid models on the organic complexation of magnesium (ionic strength = 0.7 mol dm^{-3}; 25 °C; atmospheric carbon dioxide dissolution excluded)

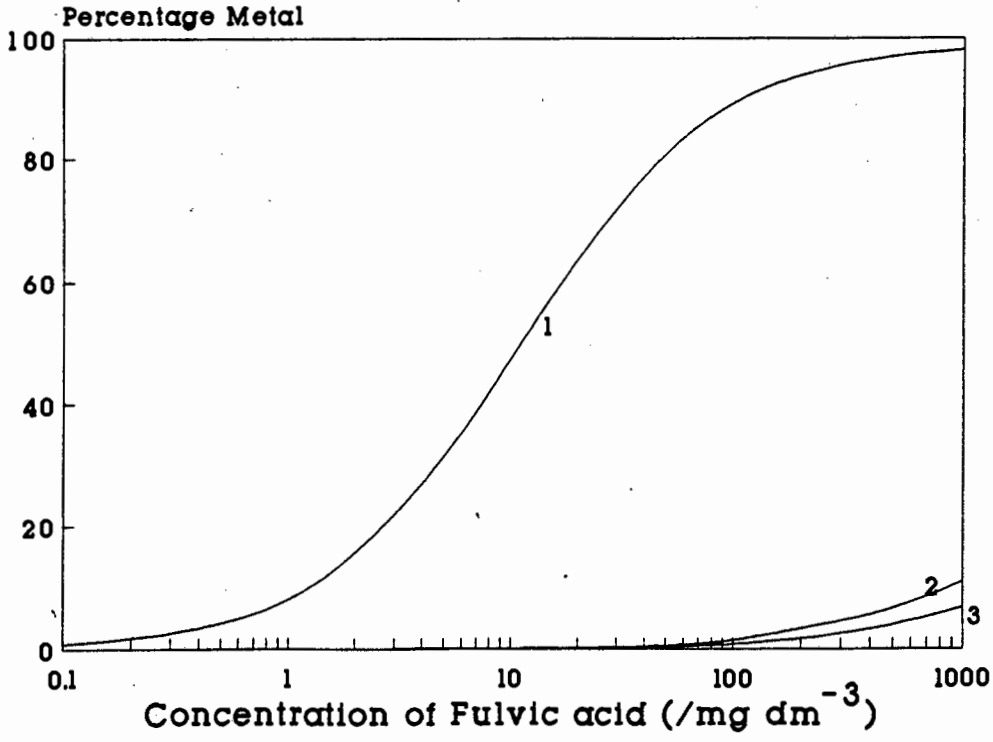


Figure 5.4: The effect of the various fulvic acid models on the organic complexation of lead(II) (ionic strength = 0.7 mol dm^{-3}; 25 °C; atmospheric carbon dioxide dissolution excluded)

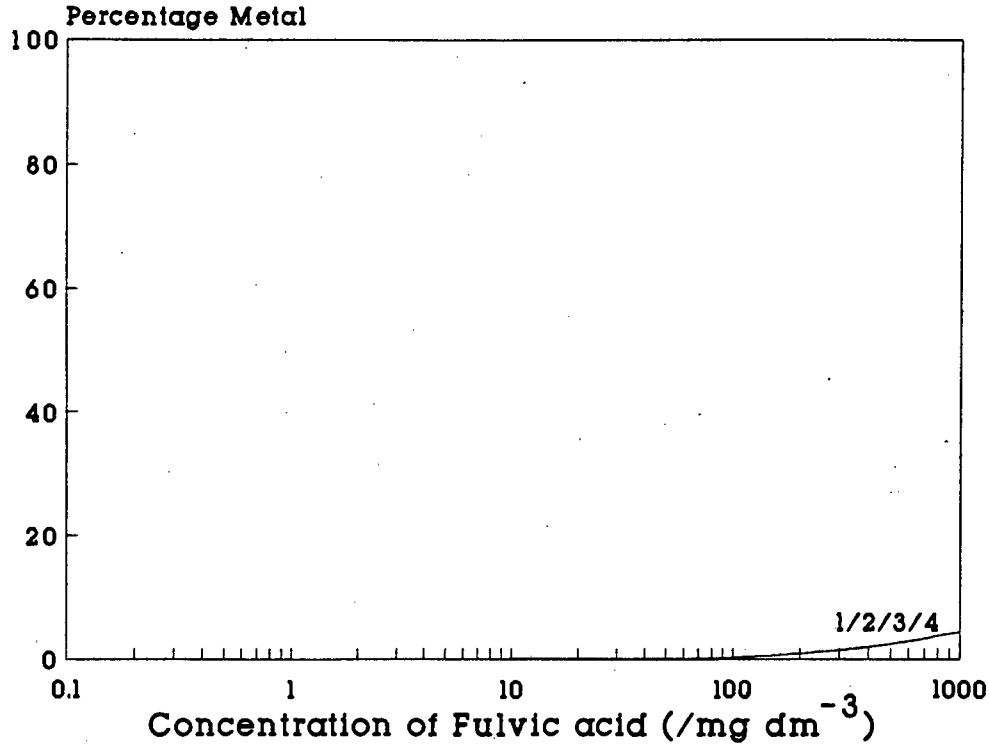


Figure 5.5.1: The effect of the various fulvic acid models on the organic complexation of dissolved manganese(II) (ionic strength = 0.7 mol dm^{-3}; 25 °C; atmospheric carbon dioxide dissolution excluded)

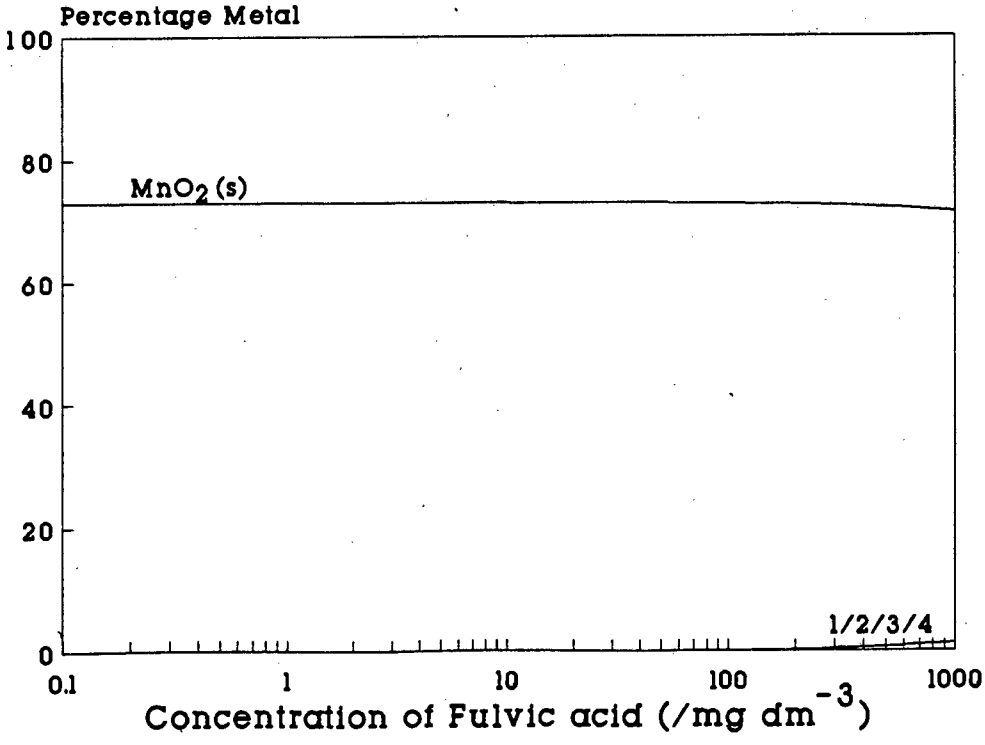


Figure 5.5.2: The effect of the various fulvic acid models on the organic complexation of total manganese (ionic strength = 0.7 mol dm^{-3}; 25 °C; atmospheric carbon dioxide dissolution excluded)

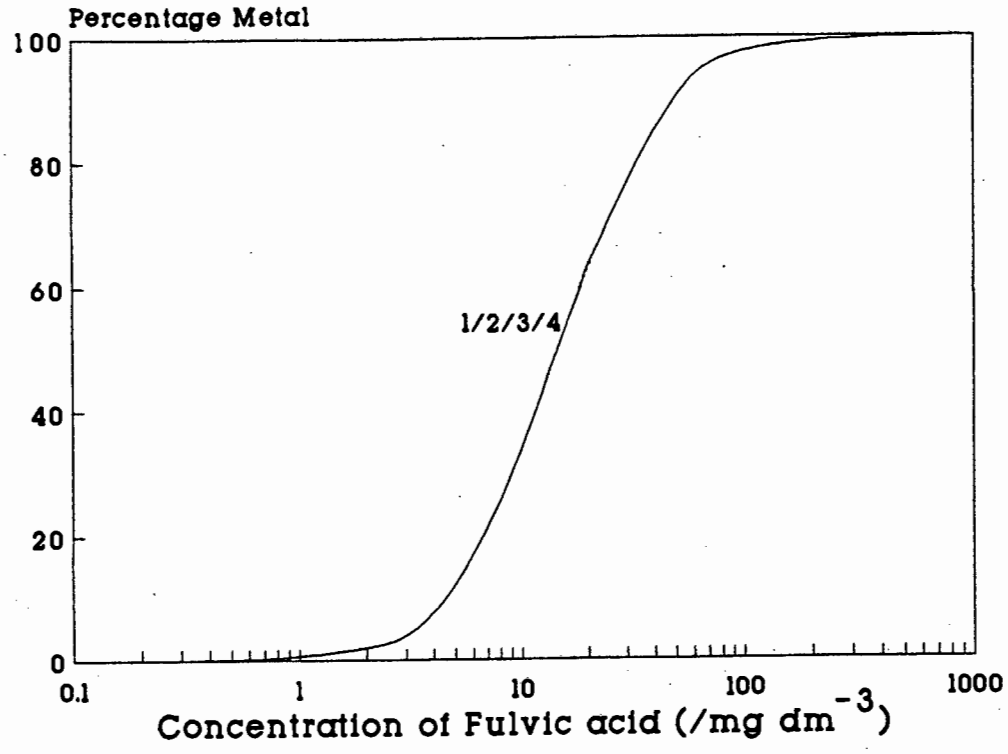


Figure 5.6.1: The effect of the various fulvic acid models on the organic complexation of dissolved iron(III) (ionic strength = 0.7 mol dm^{-3}; 25 °C; atmospheric carbon dioxide dissolution excluded)

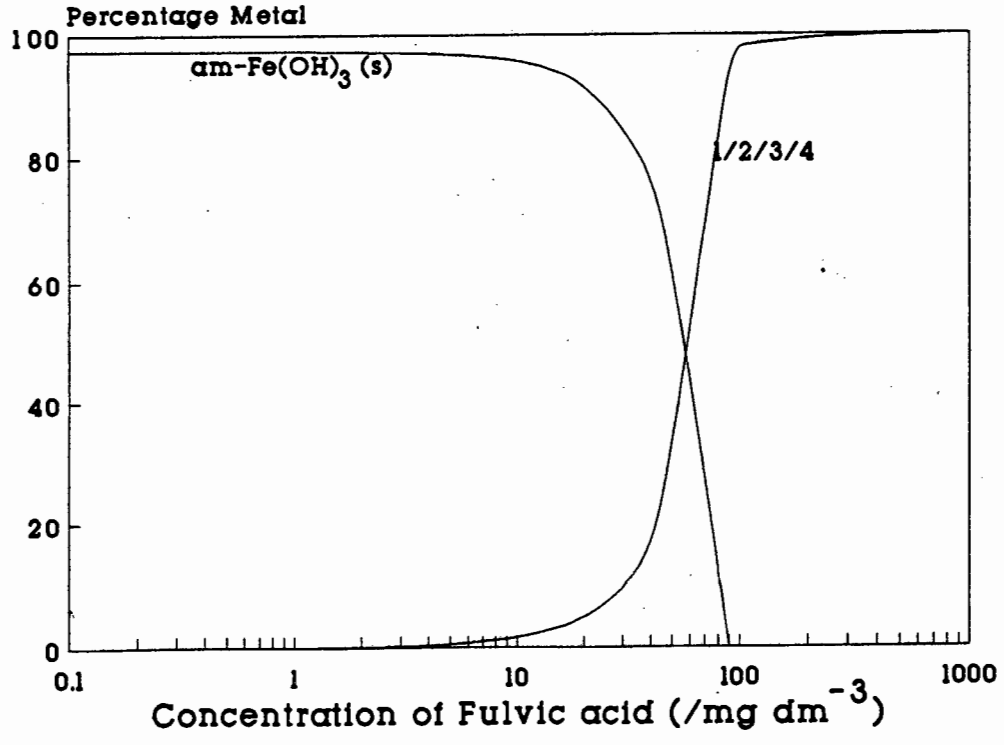


Figure 5.6.2: The effect of the various fulvic acid models on the organic complexation of total iron(III) (ionic strength = 0.7 mol dm^{-3}; 25 °C; atmospheric carbon dioxide dissolution excluded)

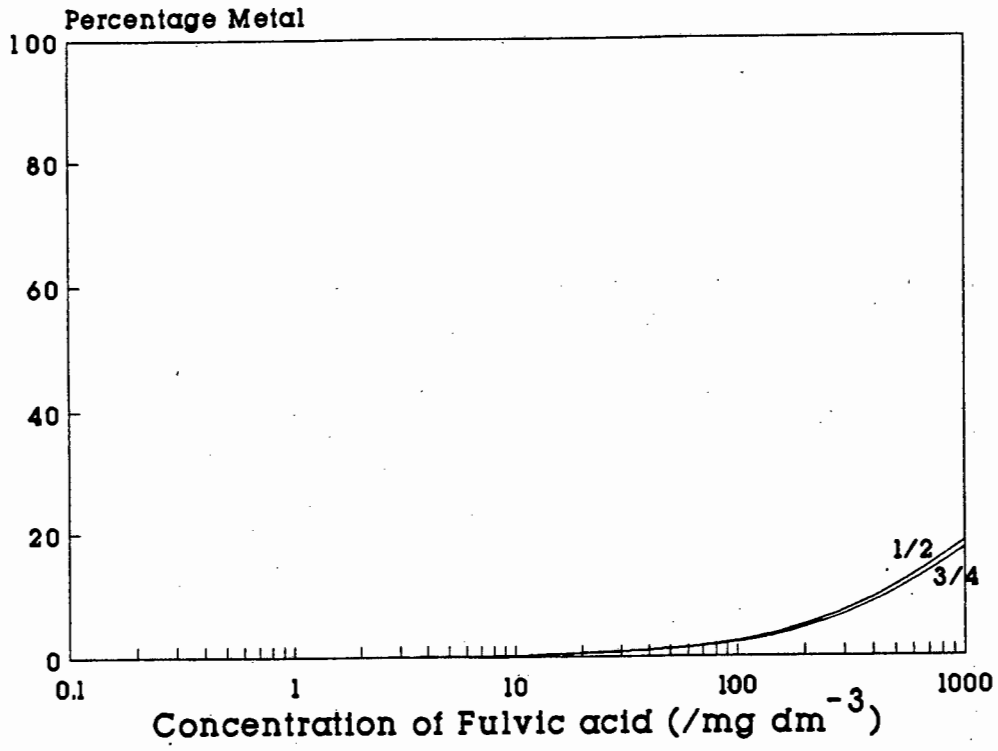


Figure 5.7: The effect of the various fulvic acid models on the organic complexation of iron(II) (ionic strength = 0.7 mol dm^{-3}; 25 °C; atmospheric carbon dioxide dissolution excluded)

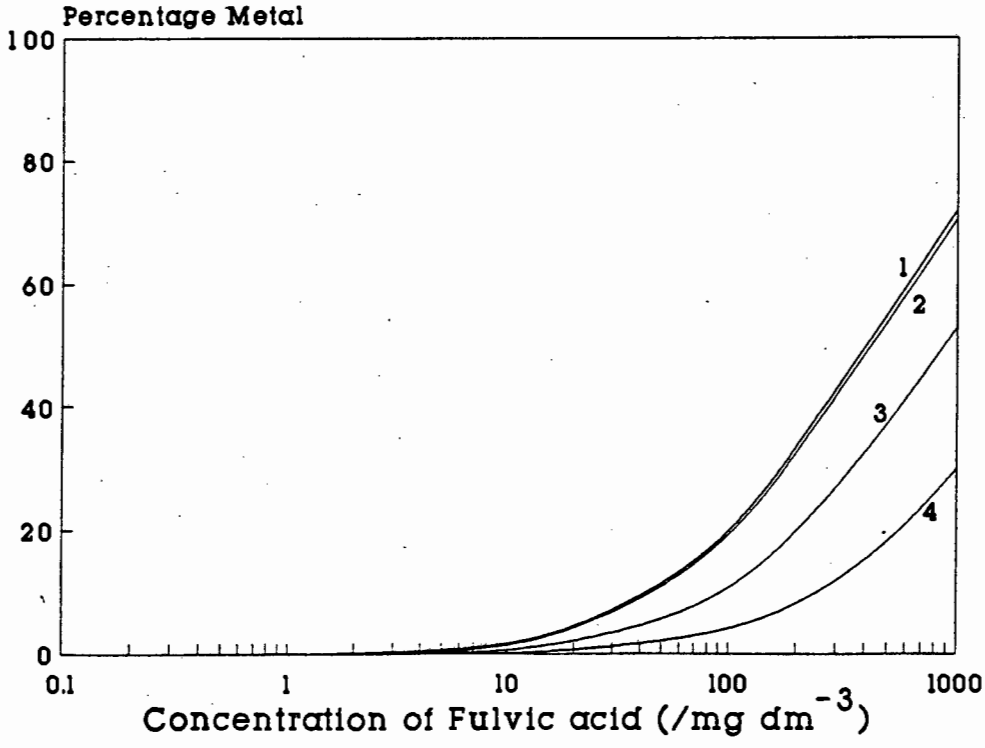


Figure 5.8: The effect of the various fulvic acid models on the organic complexation of cobalt(II) (ionic strength = 0.7 mol dm^{-3}; 25 °C; atmospheric carbon dioxide dissolution excluded)

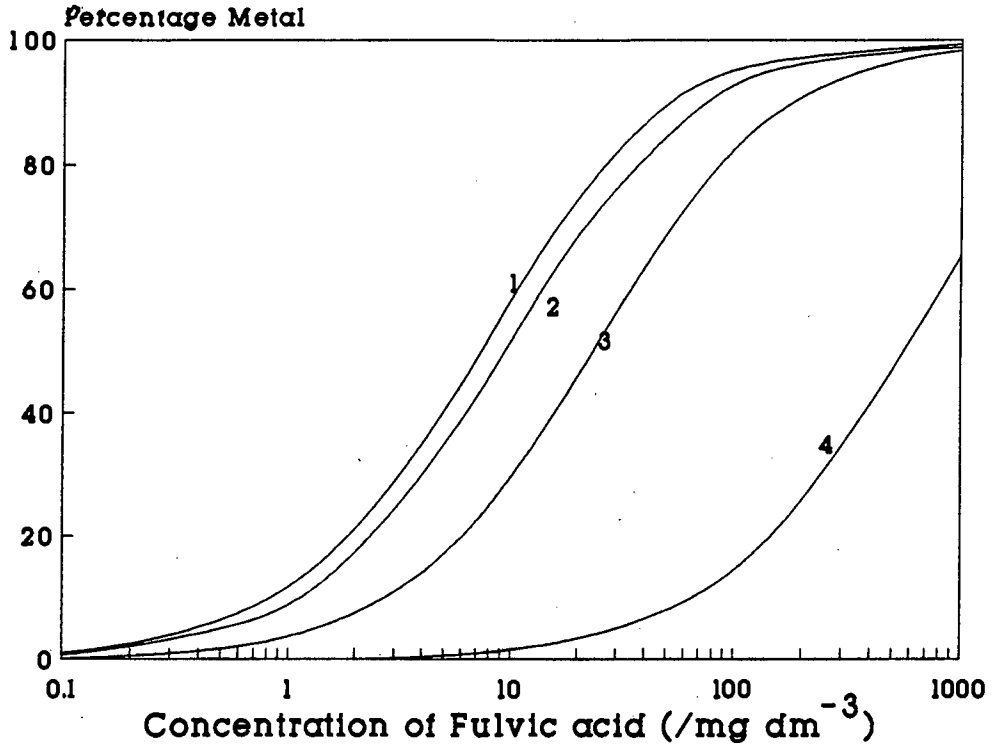


Figure 5.9: The effect of the various fulvic acid models on the organic complexation of nickel(II) (ionic strength = 0.7 mol dm^{-3}; 25 °C; atmospheric carbon dioxide dissolution excluded)

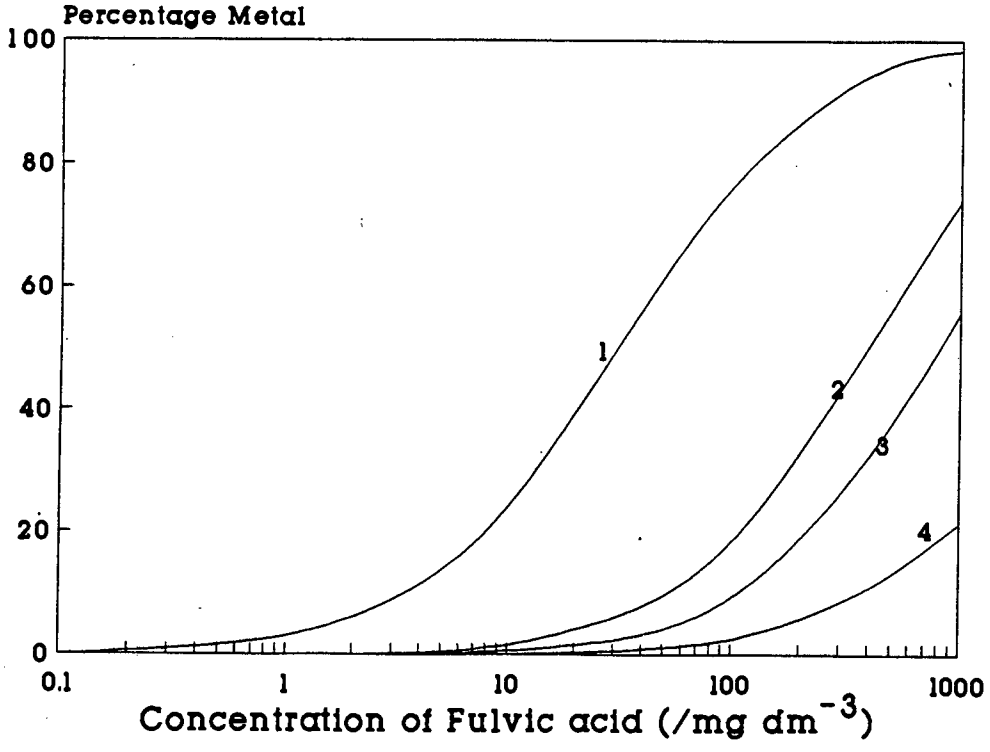


Figure 5.10: The effect of the various fulvic acid models on the organic complexation of zinc(II) (ionic strength = 0.7 mol dm^{-3}; 25 °C; atmospheric carbon dioxide dissolution excluded)

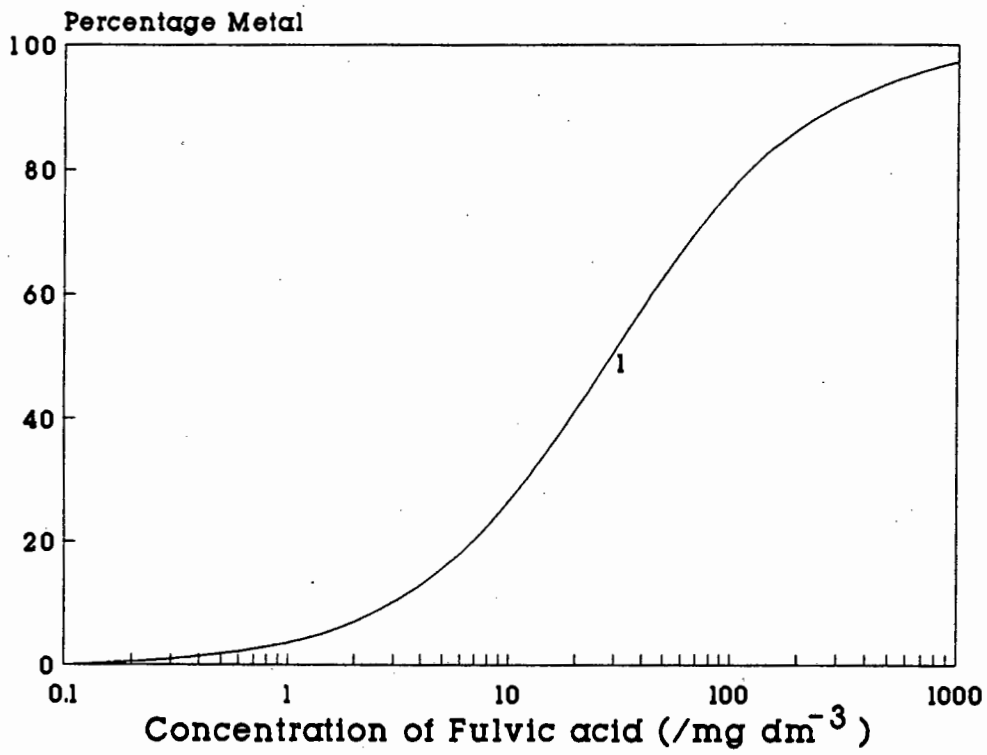


Figure 5.11: The effect of the various fulvic acid models on the organic complexation of silver(I) (ionic strength = 0.7 mol dm^{-3}; 25 °C; atmospheric carbon dioxide dissolution excluded)

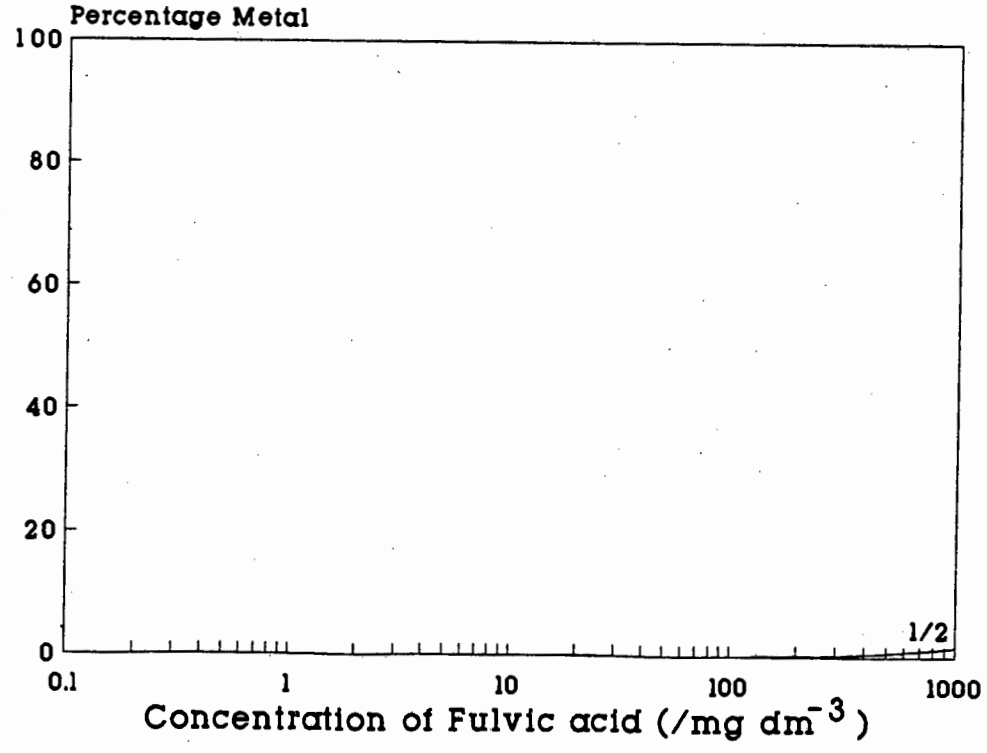


Figure 5.12: The effect of the various fulvic acid models on the organic complexation of mercury(II) (ionic strength = 0.7 mol dm^{-3}; 25 °C; atmospheric carbon dioxide dissolution excluded)

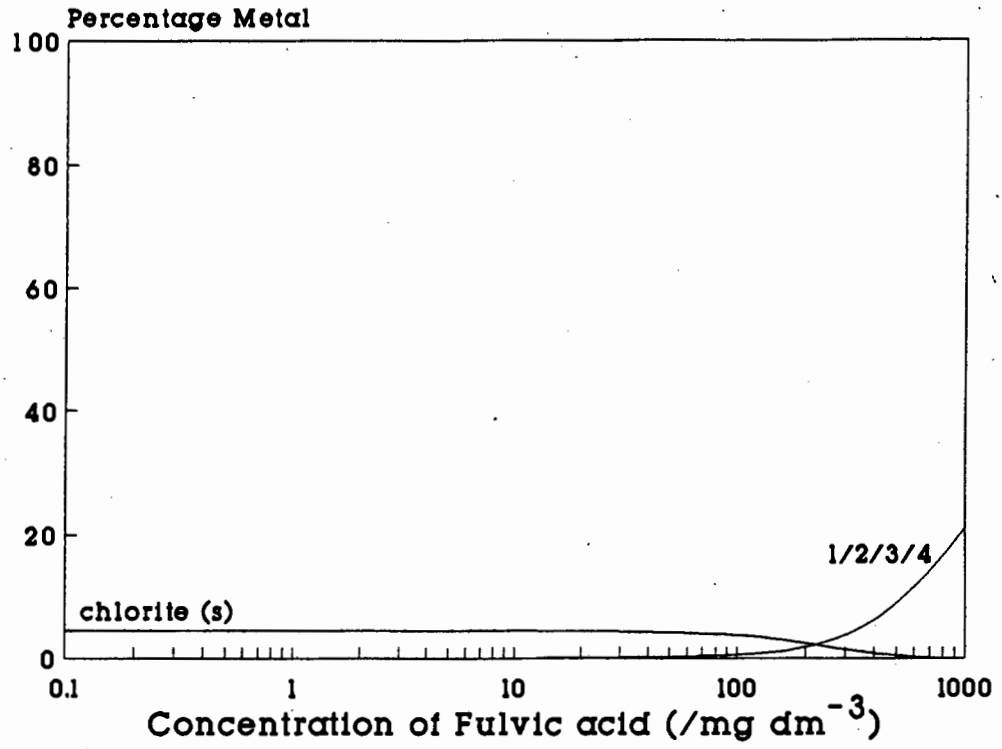


Figure 5.13: The effect of the various fulvic acid models on the organic complexation of aluminium(III) (ionic strength = 0.7 mol dm^{-3}; 25 °C; atmospheric carbon dioxide dissolution excluded)

concentration was observed to vary from 4.65 to 5.75 mg dm^{-3} in the Baltic Sea. The extreme end of the range scanned (1000 mg dm^{-3}) was included to elucidate trends in fulvic acid binding (i.e. what sites are important to which metals) as well as to model specific high organic concentrations which may occur in surface algal blooms [Imb83, Rob91] and in sediments.

The following significant observations can be made about the effect of fulvic acid on the speciation patterns :

1) The speciation patterns of the major cations are unaffected by fulvic acid except at very high concentrations (1000 mg dm^{-3}) where 1.3% magnesium is bound as $MgACAC^{+}$.
2) The speciation patterns of most of the model organic ligands are unaffected by changes in fulvic acid concentration in the range 0.1 to 100 mg dm^{-3}. At high concentrations there is a slight decrease in magnesium-bound species as a result of the complexation of magnesium by acetylacetone. Cysteine, 1,2-propylenediamine and 2,3-diaminopropanoic acid are affected by changes in ligand concentration. This is because these model ligands are bound by trace metals (copper, lead, zinc and nickel) at low fulvic acid concentration. At high fulvic acid concentration they have nearly constant speciation patterns.
3) Zinc, nickel, cadmium, lead and silver form significant species with sulphur-containing ligands. Cobalt is affected to a lesser degree. The significant ligands are cysteine and 2-aminoethanethiol. Silver is bound by 2-mercaptoethanol.
4) Copper and nickel form important complexes with nitrogen-containing ligands at normal concentrations. These ligands bind zinc and cobalt to an intermediate degree. Very weak complexation of cadmium, mercury, lead

and iron(II) by these ligands was observed at high fulvic acid concentrations. The significant ligands are PN = DAP >> ASP > ALA.

5) The only significant species which have solely oxygen-containing functional groups are acetylacetone and catechol. ACAC binds manganese, cobalt, zinc, iron(II) and nickel at high concentrations. It also forms strong complexes at lower concentrations with copper when nitrogen is excluded. Catechol binds copper and to a lesser extent iron(III), aluminium, zinc and borate. At high concentrations, complexation of iron(III) and aluminium by fulvic acid causes these metals to become totally dissolved. Propanoate forms a very weak complex with lead at high concentrations.

6) Manganese, aluminium, iron(II), iron(III) and borate are not affected significantly by which of the four models is used as all give very similar results. This is because binding of these metals is primarily to oxygen-donor sites. What differences do occur result from differences in the concentration of acetylacetone between models. These metals do not form significant complexes with sulphur or nitrogen-containing ligands.

7) Uranyl, tin(II) and chromium(III) form insignificant complexes with marine fulvic matter.

5.3 DISCUSSION OF THE EFFECT OF FULVIC ACID ON SPECIATION

The model predicts that sulphur and nitrogen functionalities are the primary binding sites in marine fulvic acid. The increased nitrogen and sulphur content with respect to terrestrial fulvic acids may explain the increased complexation of trace metals by marine organic matter, observed experimentally. The oxygen-containing functional groups are significant only at fulvic acid concentrations that are greatly in excess of those observed in the marine system. Thus these functional groups alone are unable to account for the

complexation of trace metals by organic matter without the invocation of electrostatic and long range chelation effects.

The most significant result is that even at the very low sulphur concentrations (0.7%) and even lower -SH functionality (20% of all sulphur), sulphur-containing ligands (cysteine and 2-aminoethanethiol) are responsible for significant complexation of zinc, nickel, lead and cadmium. The exclusion of these ligands results in a marked decrease in fulvic acid complexation such that no complexation is observed at natural levels except for nickel which also forms strong complexes with 1,2-propylenediamine and 2,3-diaminopropanoic acid.

What is remarkable about the complexation to cysteine is the very low concentration of this binding site in fulvic acid molecules. In the 1000000 molecules generated by RANDOM to arrive at the concentrations in Table 3.2 , binding site 30 was counted only 1000 times. Thus there is a significant error associated with the concentration used (Figure 3.6). Furthermore owing to the strong complexation of lead and cadmium by cysteine, $M(CYS)_2^{2-}$ complexes predominate when formation constants are measured. The constants for the MCYS species thus have a large associated error. This is especially true of CdCYS which is an approximation. However, at the low ligand concentrations observed in seawater MCYS species are significant. The predictions about binding to sulphur-donor sites must be viewed with care.

The high complexation of silver by 2-mercaptoethanol is surprising since the complexation of silver by other organic ligands is at least 10^6 times less. However, this is the only ligand containing sulphur for which formation constants were available. Even stronger complexation to cysteine and 2-aminoethanethiol may be expected when constants for the complexation of silver(I) to these ligands is included.

The inclusion of nitrogen appears to satisfactorily explain the very high association of copper with marine organic matter that has been observed. Variations in the degree of complexation may result from variations in fulvic acid concentration and nitrogen functional group concentration. Model 3 indicates that the complexation decreases significantly when less nitrogen is present in the metal binding sites. Where 80% nitrogen is present in $-NH_2$ groups, 88.5% of copper is bound by fulvic acid at a concentration of 0.5 mg dm^{-3}. Where 50% nitrogen is found as $-NH_2$, this value decreases to 60.6% which is still significant. If nitrogen is excluded though, this drops sharply to 3.5%.

The complexation of copper also significantly affects the redox distribution between Cu^+ and Cu^{2+}. The complexation of copper(II) results in a much lower free Cu^{2+} concentration which in turn decreases the concentration of copper(I). At a pE = 9.1 and fulvic acid (Model 1 & 2) concentration of 2 mg dm^{-3} the concentration of copper(I) decreases by 106 times and at 1000 mg dm^{-3} it decreases by 2.44×10^7 times when compared to the case in which no fulvic acid is included. Thus copper(I) is even less significant when organic matter is included. However, the sulphur-containing ligands in RANDOM have been observed to reduce Cu^{2+} to Cu^+ [Len64, Mar74a, Smi82, Smi89] which may increase the concentration of copper(I). Furthermore copper(I) complexation to 2-mercaptoethanol in a manner similar to silver(I) might also be observed. However, the formation constant for this reaction has not been measured yet.

The effect of fulvic acid complexation on the redox distribution of iron and manganese is slight except at high fulvic acid concentration where manganese dissolves and the iron(II) concentration decreases because of the significant complexation of iron(III) by catechol.

An interesting observation is that iron(III) is strongly bound by catechol. This results in the dissolution of amorphous iron oxide such that by a fulvic acid concentration of 90 mg

dm^{-3} all the iron(III) is in solution. Binding to the catechol site also provides an insight into the mechanism that may lead to the reduction of iron(III) to iron(II) which has been observed in marine sediments [Mur88]. Thus although in the aqueous phase the concentration of iron(II) decreases as a result of fulvic acid complexation, it is expected to increase in the sediments because anoxic conditions there give rise to a much lower pE. Binding to the catechol site would facilitate the reduction of iron(III) since the catechol ligand could then be oxidized to form ortho-benzoquinone.

A model was also run where all the residual oxygen (i.e. ether linkages etc.) was classified as aliphatic -OH groups. Although this increased the concentration of sites which include -OH groups, the complexation of trace metals by fulvic acid was not increased when compared to model 4. In fact in most cases complexation decreased as a result of the lower acetylacetone concentration. The organic complexation of copper(II) changed to 3.9% CuCAT, 22.5% $Cu(CAT)_2^{2-}$, 2.7% $CuACAC^+$ and 71.0% $Cu(ACAC)_2$. Observable is the decrease in importance of the binding to the acetylacetone ligand. Similar effects were observed for nickel, zinc, cobalt, manganese and iron(II).

As can be seen from Table 5.3 most of the ligands used are strongly protonated at the pH of seawater. Where this is not the case these ligands form strong complexes with magnesium, calcium and sodium (ACAC, MAL, DEM). SUCC, DHMB, HMP, HBT, PROP and BENZ are found in the unprotonated form because of their low formation constants with H^+.. The strong protonation and complexation by major cations observed result in a reduction in the free ligand concentration and thus complexation of trace metals. It is expected that at lower pH complexation will decrease as protonation increases and vice versa although this is complicated by high carbonate complexation (carbon dioxide included) and high hydroxide complexation at high pH which would compete with fulvic acid complexation.

The speciation patterns of CYS, AET, PN and DAP were affected by fulvic acid concentration because at low concentrations these ligands are significantly bound by lead, cadmium and nickel (CYS), nickel and zinc (AET) and copper (DAP and PN). As the fulvic acid concentration increases the fraction bound by trace metals decreases.

Unlike the inorganic speciation case, the assumption that a trace metal's concentration had no effect on its speciation or that of other trace metals is no longer valid. This is because ligand concentrations are no longer greatly in excess of trace metal concentrations and thus their free concentrations could be changed by complexation by trace metals. Changing the concentration of lead, nickel, cadmium, zinc and copper would have an effect on the degree of organic complexation. As an example the copper concentration was varied in the range 1 nmol dm^{-3} to 1000 nmol dm^{-3}. Model 1 was used to model fulvic acid interaction and the concentration of fulvic acid was fixed at 2 mg dm^{-3}. As can be seen from figures 5.14.3, 5.14.4 and 5.14.5 changing the copper concentration affects the speciation pattern of the ligands PN, DAP and CAT. Noticeable is the increase in complexation of these ligands by copper until copper precipitates as $Cu(OH)_{1.5}Cl_{0.5}$. Increasing the copper concentration has an effect on the speciation of nickel as can be seen in figure 5.14.2. As the copper concentration increases the complexation of nickel by PN and DAP decreases. Note, however, that complexation by AET is unaffected as copper does not complex this ligand. At higher fulvic acid concentrations it is to be expected that the copper concentration would affect other trace metals such as zinc and cobalt which are also complexed by PN and DAP. Figure 5.14.1 indicates the change in the copper speciation pattern with concentration. Note that $CuCO_3$ is included as representative of the inorganic speciation of copper. Other inorganic species are excluded for clarity. It can be seen that the binding to PN and DAP decreases in significance as the copper concentration increases while binding to inorganic ligands such as carbonate and organic ligands unaffected by copper concentration such as ACAC increases. The concentration of copper bound in the

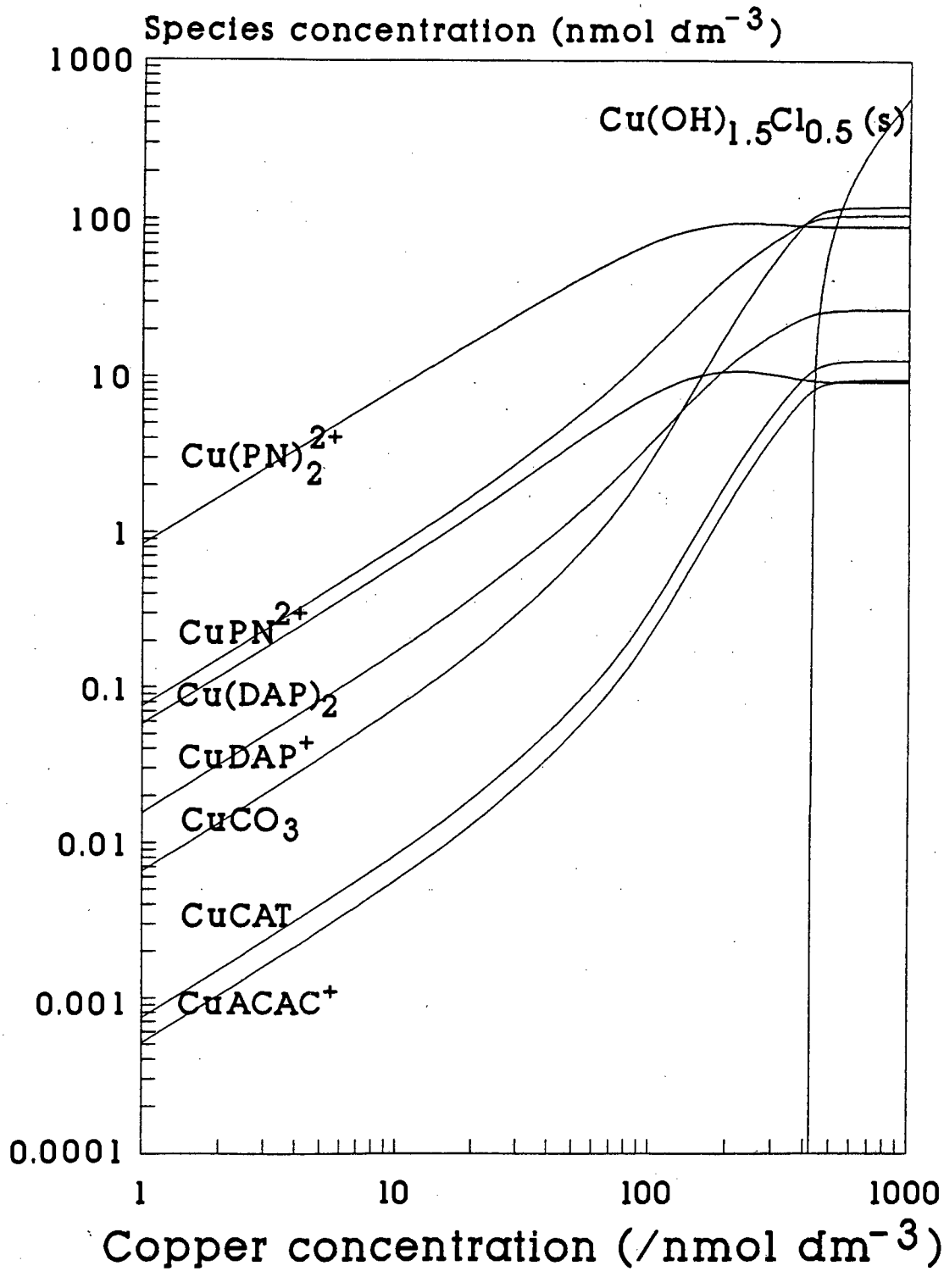


Figure 5.14.1: The effect of total copper concentration on the speciation of copper (II) (ionic strength = 0.7 mol dm^{-3}; 25 °C; atmospheric carbon dioxide dissolution excluded; 2mg dm^{-3} fulvic acid, model 1)

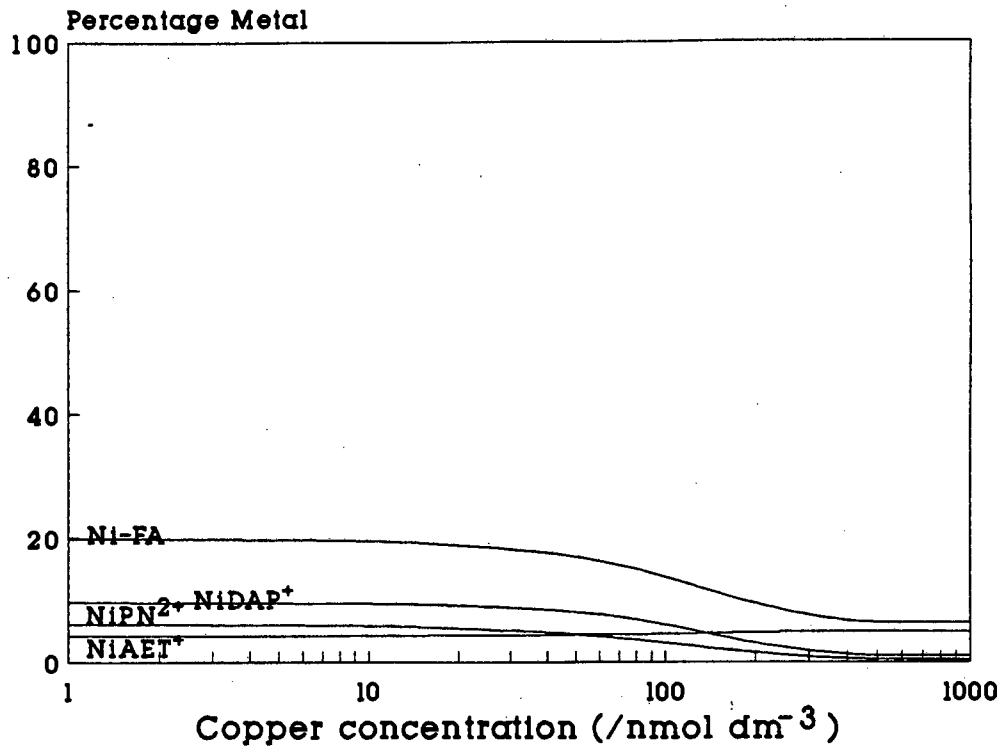


Figure 5.14.2: The effect of total copper concentration on the complexation of nickel(II) by fulvic acid (ionic strength = 0.7 mol dm^{-3}; 25 °C; atmospheric carbon dioxide dissolution excluded; 2 mg dm^{-3} fulvic acid, model 1)

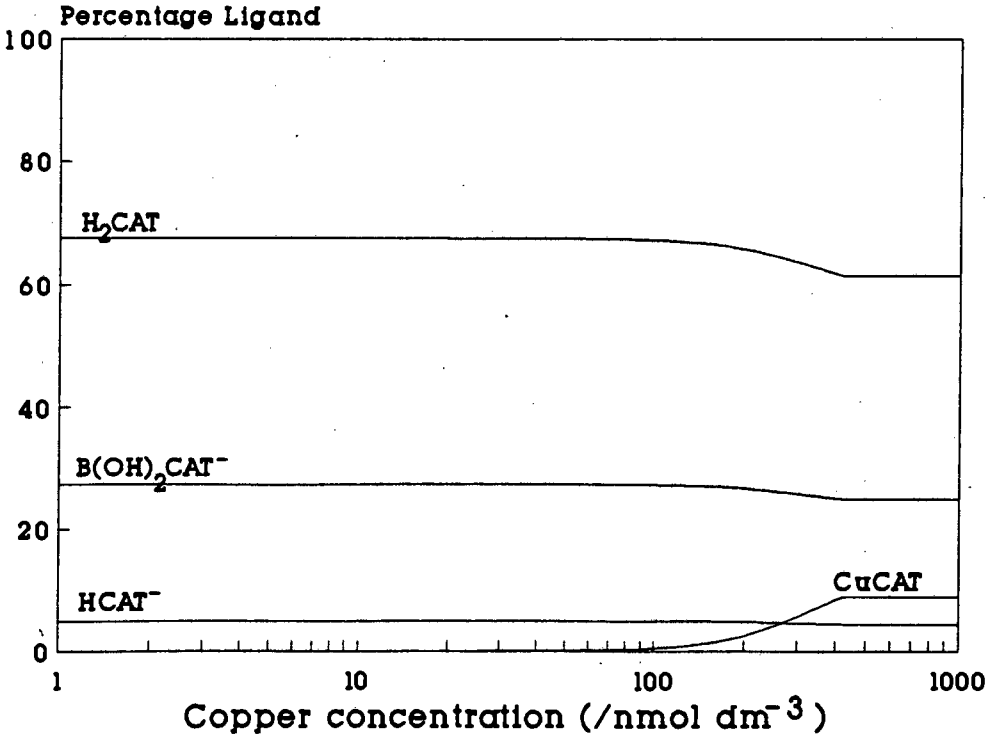


Figure 5.14.3: The effect of total copper concentration on the speciation of catechol (ionic strength = 0.7 mol dm^{-3}; 25 °C; atmospheric carbon dioxide dissolution excluded; 2 mg dm^{-3} fulvic acid, model 1)

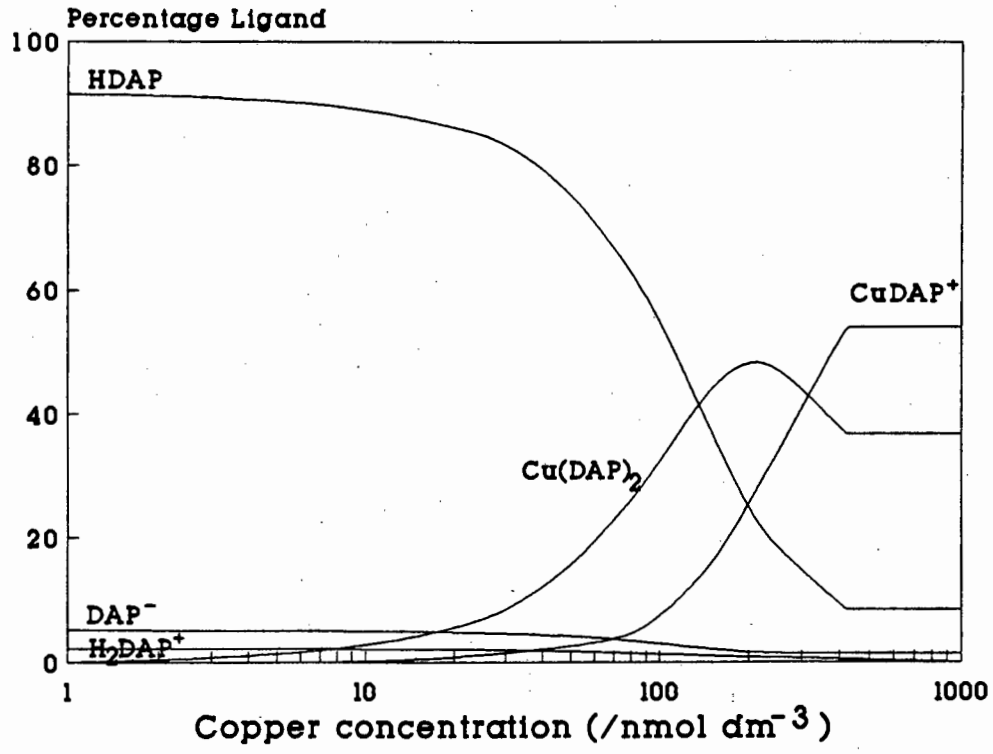


Figure 5.14.4: The effect of total copper concentration on the speciation of 2,3-diaminopropanoic acid (ionic strength = 0.7 mol dm^{-3}; 25 °C; atmospheric carbon dioxide dissolution excluded; 2 mg dm^{-3} fulvic acid, model 1)

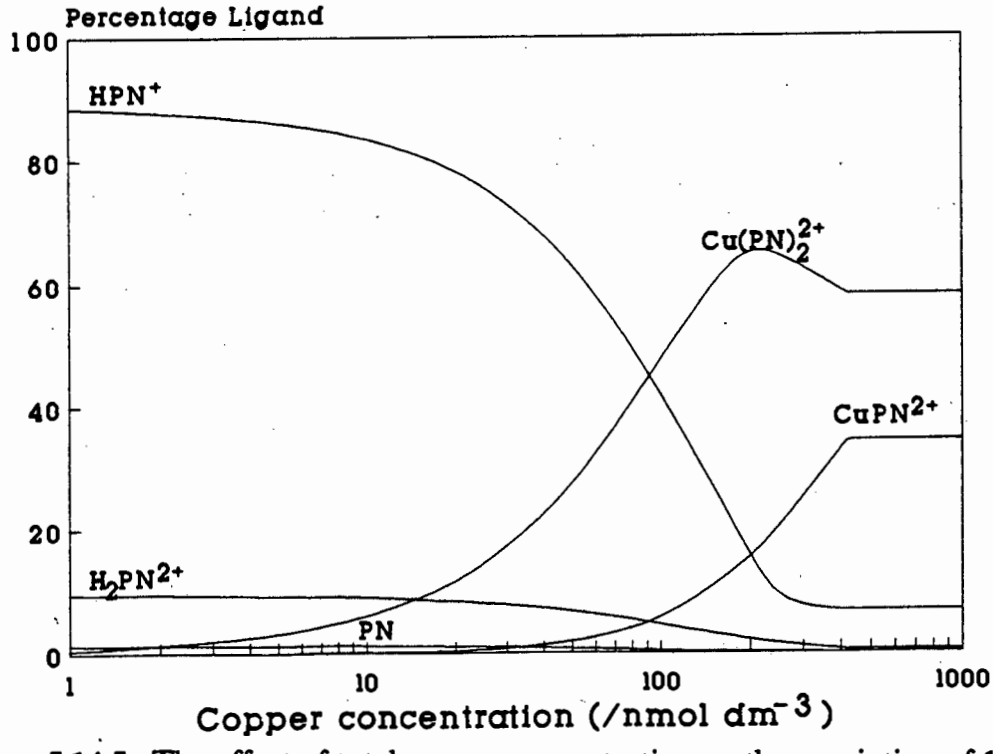


Figure 5.14.5: The effect of total copper concentration on the speciation of 1,2-propylenediamine (ionic strength = 0.7 mol dm^{-3}; 25 °C; atmospheric carbon dioxide dissolution excluded; 2 mg dm^{-3} fulvic acid, model 1)

species $Cu(PN)_2^{2+}$ and $Cu(DAP)_2$ are actually observed to decease at high copper concentration.

The five most significant ligands for each of the trace metals are as follows:

Cu^{2+}	PN > DAP >> ACAC > CAT > ALA
Zn^{2+}	AET > CYS >> PN > DAP > ACAC
Ni^{2+}	AET > DAP > PN > CYS >> ACAC
Co^{2+}	DAP > PN > ACAC > AET > AET
Fe^{3+}	CAT >> ACAC > SAL > MAL > ALA
Fe^{2+}	ACAC > PN > ASP > ALA > SER
Pb^{2+}	CYS > AET >> ASP > ALA > PN > PROP
Cd^{2+}	CYS > AET > PN > MET > ACAC
Mn^{2+}	ACAC >> HMP > ASP > ALA > SER
Hg^{2+}	PN > ACAC >> ALA > ETA > PHEN
Al^{3+}	CAT >> ACAC > SAL > SUCC > MAL
Ag^{+}	MET >> PN > TMA > BEAL > ALA

These results reflect both the complexation ability of the above ligands as well as the influence of their concentration as predicted by RANDOM.

As can be seen the most significant ligands are 2-aminoethanethiol, cysteine, 1,2-propylenediamine and 2,3-diaminopropanoic acid. To a lesser extent acetylacetone, catechol, aspartic acid and alanine may complex trace metals.

These distribution patterns may be explained in terms of the high formation constants for AET, CYS, DAP and PN. The very low concentrations of the cysteine is outweighed by the high stability constants for MCYS complexes (M = Cd, Pb, Zn and Ni). The

complexation by acetylacetone and alanine that is observed results from their presence in relatively high concentrations in the model. Despite relatively high concentrations, solely oxygen-functionality ligands are insignificant because of the low formation constants for the complexation of trace metals by these ligands. The exceptions are acetylacetone and catechol which form much stronger complexes.

Thus the model predicts strong complexation of copper at natural levels by fulvic acid. Where sulphur is included the complexation of nickel, zinc, lead, cadmium and silver is significant. Most other trace metals are not complexed significantly except under conditions of very high organic concentrations. Cobalt(II), iron(III), aluminium and to a lesser extent iron(II) may be complexed in the sediments or under conditions of high biological activity. The complexation of manganese(II) and mercury(II) is low even at high organic matter concentrations while that of chromium(III), tin(II) and uranyl is very insignificant.

5.4 COMPARISON OF THE MODEL RESULTS WITH EXPERIMENTAL FINDINGS

Humic complexation modelling in seawater has been performed by Turner at al. [Tur81]. They found that copper was most likely to be associated with humic material (47%) while the complexation of other trace metals was insignificant (Pb = 2% and all others < 0.1%) . This model agrees that copper complexation is the most significant. Other trace metals, nevertheless, also show some affinity for dissolved organic matter in the marine environment as has been reported experimentally.

The experimental determination of the complexation of trace metals in seawater is difficult. It is complicated by the low concentrations of these species as well as the fact

that the experimental techniques used are non-specific. Consequently the reported metal complexation varies significantly.

However, it is universally agreed that copper forms significant complexes with marine organic matter. The reported percentage ranges from near 50% [Dou86] to nearly 100% [VdB84b, Apt90, Hir94]. These results are in line with the very high copper complexation predicted by the model. In this respect the model agrees with the higher values of 98% found by van den Berg [VdB84b] and 80-92% found by Donat et al. [Don94] rather than the lower values found by Douglas et al. Douglas et al. [Dou86], however, concentrated on interstitial waters in sediments and not the open ocean which may explain their lower results. Previously it has been proposed that copper complexation is through carbonyl [Soh86] and carboxylate [Pio84] oxygen. The model disagrees with this conclusion since these functional groups alone can account for only about 5% of complexation. However, the inclusion of nitrogen to form diamines and amino acid groups significantly increases binding. Note that the amino acid groups still involve complexation through carboxylates. Furthermore macrocyclic effects may involve carbonyls.

The results obtained experimentally by various authors for the complexation of copper organic matter in seawater is listed in Table 5.4 (Also included are the available constants for nickel, cobalt, lead and zinc). Of importance are the pCu values quoted in this table which were reviewed by Hirose [Hir94]. This is the negative of the logarithm of the concentration of the unbound Cu^{2+} ion. Table 5.5 gives the pCu values as predicted by the various models created using RANDOM. Experimentally pCu has been observed to vary form 11.3 to 12.5. When this is compared to the model in which organic matter is excluded, one can see that the pCu value of 10.23 predicted by the model is radically different. If binding is limited to oxygen-containing ligands (CAT and ACAC), the pCu values do not change significantly at natural concentrations of fulvic

Table 5.4: Experimental measures of organic complexation of trace metals in seawater

(Free ion activity, conditional stability constants and ligand concentrations)

(The values in brackets after the reference are the percentage of trace metal associated with organic matter as reported by the authors concerned)

(The definition of ligands 1,2,3 follows that of Hirose [Hir94] i.e. if Log K >= 13, it is ligand 1, 10 < Log K < 13 is ligand 2 and the rest ligand 3)

Sampling Location	pH	pM	L_1(nM)	L_2(nM)	L_3(nM)	LogK_1	LogK_2	LogK_3	Reference
Copper									
Irish Sea	8.2			60-150			10-10.4		VdB82
Western North Pacific	8.1	11.1	7	21		13.8	11.8		Hir82
Adriatic Sea					130-150			7.5	Pla82
Cape San Blas, FL	8.2	11.5		13	80		11.2	9.0	Sun83
Mississippi outflow	8.1	11.3		20	130		11.1	8.9	Sun83
SE Gulf of Mexico	8.2			5	15		>12	9.8	Sun83
Sargasso Sea			2		80	13.7		9.7	Sun83
Irish Sea					64-146			10.0-10.4	VdB84b (98)
South Atlantic	7.7			11	33		12.2	10.2	VdB84c
Tamor Estuary					390			8.6-9.1	Nel85
North Atlantic		12.2-12.7		4-144	2-440		9.8-12	7.4-9.9	Buc86
North Atlantic	8.0-8.3				50-82			7.8-8.2	Kra86
Christiansen Basin	8.0	11.8		50	68		11.7	9.1	Her87 (>99)
Montauk Point	8.2	12.2		20	50		11.7	9.1	Her87 (>99)
Biscayne Bay				5.1	110		12.0	10.5	Mof87 (>99)
Coast of Peru	8.2	11.4		4.5	70		12.3	9.2	Sun87 (98)
Narragansett Bay	8.0	12.5		50	100		12.4	10.0	Sun87
Narragansett Bay	8.0	12.1		20	100		12.0	10.0	Sun87
Northeast Pacific	13.9			1.8	7.6		11.9	9.5-10.6	Coa88
Severn Estuary		11.1-12.8		13-196			11.4-12.8		Apt90 (>99)
North Pacific			1-3		5	13.0		10.0	Coa90
Japan Sea	8.15			1060	5720		9.60	7.57	Mid90
North Carolina Shelf	8.1	12.54	3.3		26	13.2		10.0	Sun91 (>99)
Indian Ocean				4.13			12.6		Don92 (100)

North Sea				16.2			12.4		Don92 (100)
North Pacific	8.15			1540	5100		8.89	7.09	Mid92
North Sea	8.35			13.04			12.99		Cam94
North Sea	8.35			13.74			12.79		Cam94
San Francisco Bay			12		60-80	>13.5		9-9.6	Don94 (80-92)
Japanese Coast	8.15			130	578		9.26	7.40	Mid94
San Francisco Bay			40		119	>13.4		10.7	Mil94
San Francisco Bay				70	100		11.6	9.6	Mil94
Sargasso Sea			0.8			>14.2			Mil94
Central Pacific			2-3		10-15	12.2-13.3		10.2-10.8	Mil94
Nickel									
San Francisco Bay			17-28			> 17			Don94 (35-50)
Liverpool Bay			0.3-6.4			17.7-18.7			Nim89 (30-40)
Menai Strait			5.3			17.7			VdB87b (40)
English Channel			1.8			17.3			VdB87b (50)
Zinc									
South Atlantic					30			7.4	VdB84d
Irish Sea				26	62		8.4	7.5	VdB85
Central North Pacific			1.2			11.0			Bru89
Northeast Pacific	8.2		1.6-2.3			10.2-11.3			Don90
Narragansett Bay					49-104			7.51-7.85	Mul91
Western Atlantic				4-46	32-44	8.16-9.43		7.43-7.73	Mul91
Western North Pacific	8.1	8.7	5	8		10.7	9.3		Hir92
Lead									
North Pacific		12.4			0.2-0.5			9.7	Cap90
Cobalt									
Scheldt Estuary			0.5-1.1			15.7-17.5			Zha90 (Mean=70%)

Table 5.5: Free copper activity (pCu) as predicted by the model

	Fulvic acid concentration (mg dm^{-3})		
Model used	0.5	1.0	2.0
No fulvic acid		10.23	
No nitrogen ligands	10.25	10.26	10.29
Low N concentration (50% as NH_2)	10.68	11.00	11.48
High N concentration (80% as NH_2)	11.19	11.70	12.26

Table 5.6: Random ligand concentrations and mono-species stability constants for Cu at 25 °C and I = 0.7 mol dm^{-3}

Ligand	Log K	Concn at 0.5 mg dm^{-3} FA (nM)		Concn at 2.0 mg dm^{-3} FA (nM)	
		Total	Free	Total	Free
ACAC	8.00	375	4.7	1500	18.6
CAT	13.60	35	$1.7x10^{-5}$	138	$6.9x10^{-5}$
PN	10.87	67	0.9	268	3.7
DAP	10.37	12	0.6	48	2.5

acid (0.5 to 2.0 mg dm^{-3}). The use of nitrogen-containing ligands makes a significant impact. Listed are the effect of the 2 nitrogen models in which 50% and 80% of the total nitrogen is present as aliphatic amine groups ($-NH_2$). In the 80% case the effect on pCu is remarkable with it ranging from 11.19 to 12.26 which coincides with the values reported experimentally. The discrepancies in the reported pCu values may be explained in terms of variations in total copper concentration, variations in organic matter concentration and variations in the functional group content of marine fulvic acids. However, oxygen functionalities are unable to explain copper binding unless macrocyclic or electrostatic effects are invoked, or a very high fulvic acid concentration is used.

Table 5.6 lists the binding constants for the primary binding ligands to copper in RANDOM. Also listed are their total concentrations and their free concentrations. It can be seen that of the four ligands, ACAC's binding constant is not comparable to that observed experimentally. The total ligand concentrations look similar to those found experimentally.

However, the formation constants reported in the literature for marine Cu-organic interactions are conditional constants and do not take into account the protonation of the ligand. Furthermore, the ligand concentrations quoted in the literature are actually apparent complexation capacity which is the concentration of organic matter able to complex a trace metal ion into non-labile complexes [Kra86] which are determined by metal titrations. Thus these values are in effect the moles of added metal which are complexed per litre of sample [Man78] and may bear no relation to an actual binding site concentration. The ligand concentrations calculated by RANDOM do not necessarily reflect what the free ligand concentration might be. This explains why catechol is not as significant as might be expected. It is highly protonated at pH = 8.1 which decreases its free concentration drastically. The formation constants for PN and DAP are comparable to the conditional constants in that they lie in the middle of the reported range for log K.

The free concentrations are lower than literature totals, but this emphasises the point that direct comparisons between a thermodynamic database which includes competing reactions for ligand sites and conditional constants is difficult.

The comparison is further complicated by the fact that the conditional constants may be overestimated because of the slow kinetics of the release of copper from organic interactions [Cam94, Mac94]. The measurement technique may also affect the result obtained (cf. the results obtained by Campos and Van den Berg using different competing ligands [Cam94]). Hirose [Hir94] also indicates that there are likely to be two types of organic ligands in seawater. One, which has low concentration, may be freshly produced by phytoplankton [Hir94]. The other ligand though appears to be longer-living and is likely to be fulvic acid. The pCu overlap between the model and experiment, nevertheless, lends credence to the use of RANDOM for modelling marine metal-organic interactions

Stanley and Byrne [Sta90] used measured conditional stability constants to calculate copper complexation by organic matter in seawater. In all but one case, the complexation was in excess of 90%. These results are similar to that predicted by model. Stanley and Byrne [Sta90] also calculated zinc complexation based on conditional stability constants which were calculated from those for copper using a linear free energy relationship. This exhibited much greater spread and range from 3.8 to 82.2% for zinc-organic complexation with the mean at 32.5%. This is higher than the value predicted by Model 1 (5.5% at 2 mg/l FA). However, 5 of the 15 points calculated by Stanley and Byrne [Sta90] fall within the range 3.8 to 10% which is comparable with the model. Because zinc is strongly bound by a sulphur containing ligand (AET), the model predictions are highly susceptible to the assumptions made. The complexation of zinc can be increased rapidly by increasing sulphur content (as thiols) slightly. Variations in

the observed complexation of zinc could thus be explained by variations in the functional group characteristics of the local fulvic acids.

Stanley and Byrne [Sta90] report that the LFER they use predicts that the logarithms of the stability constants for zinc are less than 8. However, Hirose et al. [Hir82] estimated log K_1 to be 9.3. Van den Berg et al. [VdB87a] found $8.6 < \log K_1 < 10.6$ while the results of Bruland [Bru89] ($\log K_1 = 11.0$)) also indicate that the conditional stability constant for zinc-organic interactions is probably greater than that predicted by the LFER of Stanley and Byrne [Sta90]. This would indicate that binding sites in marine organic matter are moderately zinc specific. Stanley and Byrne [Sta90] calculated their LFER using organic ligands and data from the compilation of Smith and Martell [Smi82]. Sulphur-containing ligands were not included in the LFER as no copper constants are available. These ligands exhibit log K's for zinc in excess of 8 and could explain the specificity observed. In particular log K for $ZnAET^+$ is 10.07 at 0.7 mol dm^{-3} which is in the range measured experimentally by the authors mentioned above.

Florence and Batley [Flo76] predicted that zinc could be strongly bound by cysteine. This is similar to the 2-aminoethanethiol binding predicted by the model since it is also sulphur containing and has a high log K for the interaction with zinc. However, it dominates cysteine because of its higher concentration. The variation in observed results for zinc from 0 to 50% [Flo76, VdB85, Mul91] may result from both conformational effects and thiol content. Muller and Kester [Mul91] also postulate that variations might result from phytoplankton growth cycles as well adsorption reactions in competition to organic complexation.

The model predicts different sites for zinc and lead binding when compared to copper. This is because the speciation of the former sites is dominated by sulphur-containing ligands for which there are no copper formation constants. This may explain the

observation by Mackey and Zirino [Mac94] that zinc and lead are not released from marine humic matter when an excess of copper is added. If the binding sites were the same, zinc and lead would be expected to be released. Mackey and Zirino argue that trace metal binding by marine organic matter is not in equilibrium with the aqueous phase to explain this phenomenon and propose their so-called "onion" model [Mac94].

Cadmium results are conflicting. It is agreed though that in the absence of organic matter cadmium is bound as chloro species which the model predicts. This is confirmed by the results of Baric and Branica [Flo80] who believe cadmium to be found as $CdCl^+$. Piotrowicz et al. [Pio84] report that cadmium interaction with organic matter is dependent on the sample. This may be the result of varying sulphur content as predicted by the model. In the absence of thiol groups no cadmium is bound at natural levels which is what was observed by Duincker and Kramer [Dui77]. Batley and Florence [Flo76] report as much as 75% cadmium is bound in some form to organic matter (colloids and dissolved). This is greater than the complexation predicted by the model and may be the result of conformational effects associated with the organic colloids. The large uncertainties associated with the stability constants for cadmium-organic interactions used in the model must also be borne in mind.

Batley and Florence also found that 10 to 35% of lead was associated with organic colloids and 0 to 20% in molecular organic complexes. Reported complexation of lead by organic material varies from 0 [Pio84] to 50% [Cap90] as determined by varying techniques. These quantities are actually representative of non-labile lead and may be the result of particulate lead and not organically complexed lead [Dui77]. It should be noted that a significant fraction (40 to 80%) of dissolved lead is associated with colloidal inorganic particles [Flo76]. This will be discussed in more detail when adsorption onto particulate solids is considered. Florence and Batley [Flo76] also predicted that cysteine would complex lead strongly in seawater if present in high concentrations. They

concluded though that since the free cysteine concentration is so low [Deg64, Sie66] that this would be insignificant. No allowance was made for the sulphur content of marine fulvic acid.

Cobalt is also expected to form some organic complexes [Zha90]. The degree of complexation is expected to be smaller than for copper though. The model predicts complexation but this is only significant at concentrations greater than natural levels. Thus, the model is unable to explain the complexation observed by Zhang et al. [Zha90] and macrocyclic effects need to be invoked. Note though that Zhang et al. measured non-labile cobalt which may include adsorbed metal. Zhang et al. [Zha90] speculate that complexation of cobalt by organic matter is through porphyrins or metallothioneins. Their conditional stability constants do not obey the Irving-Williams series with respect to copper (See Table 5.4) which casts doubt on their experimental measurements although the possibility of a different binding site to copper can't be ignored. This same observation may be applied to the constants for nickel as well. This illustrates the difficulty of comparing conditional stability constants.

The model predicts that if sulphur-binding is excluded, nickel is the metal second most likely (after copper) to be bound by organic matter. Nickel-organic complexation has been observed by Donat et al. [Don94]] who found 35-50% complexation. However, they also observed that nickel had a much greater formation constant than copper (log $K_{NiL} > 17$). Van den Berg and Nimmo [VdB87b] and Nimmo et al. [Nim89] also found nickel complexation to be in the range 30 to 50% which is slightly higher than the model prediction (approximately 20%). Increasing the fulvic acid concentration to 5 mg dm^{-3} as may be observed in the coastal conditions under which the experimental measurements were made, gives comparable speciation patterns from the model. The constants used in the model are much smaller which is in line with the Irving-Williams series.

The model conflicts with the report by Anderson [And82] that uranium is associated with organic matter in particulates. However, their study was not concerned with the dissolved fraction where the complexation by carbonate far outweighs any contribution that organic ligands can make to the speciation of uranium. The model is in agreement with Djogic et al. [Djo86] on this last point.

Lastly Nakayama et al. found that the complexation of manganese by organics was slight [Nak89] which is in agreement with the model.

In general the agreement between the model and experiment (especially with respect to copper) is good. This increases confidence in the model which allows a more detailed account of speciation patterns than is presently available from experimental techniques. The modelling of trace metal interactions in seawater has been improved when compared to the calculations of Turner et al. [Tur81].

CHAPTER SIX

THE EFFECT OF ADSORPTION ON SPECIATION

6.1 RESULTS OF THE EFFECT OF ADSORPTION ON THE SPECIATION PATTERNS

The results of the effect of the adsorption of the anions and cations, present in seawater, on to hydrous ferric oxide are presented in Tables 6.1 and 6.2. The effect of the concentration of hydrous ferric oxide on trace component speciation is presented graphically in figures 6.2 to 6.13.2. The effect of hydrous ferric oxide concentration on surface charge density may be found in figure 6.1 while figures 6.14.1, 6.14.2, 6.15.1 and 6.15.2 indicate the effect of HFO concentration on adsorption site speciation. The speciation of the adsorption sites may be found in Table 6.3.

In all the adsorption calculations, the dissolution of atmospheric carbon dioxide was excluded while the concentration of dissolved fulvic acid was fixed at 2 mg dm^{-3}. Model 1 from the previous chapter in which sulphur and nitrogen-containing binding sites are included was used to model fulvic acid. The adsorption of the trace components in seawater onto HFO was modelled under two separate conditions. In one no allowance was made for the adsorption of marine organic matter onto particulate matter while in the other this was taken into account by the use of a diprotic acid whose adsorption constants are given in section 2.7.1. It was also assumed that this acid had a proton exchange capacity of 10 meq g^{-1} and had $pK_{a1} = 0.53$ and $pK_{a2} = 3.84$ [Tip81a, Tip81b, Tip82, Mor90]. Because seawater has a dissolved organic matter content of 2 mg dm^{-3}, this gave an acid concentration of 10^{-5} mol dm^{-3}.

The concentration of hydrous ferric oxide was varied from 1 μg dm^{-3} to 1 g dm^{-3}. Symes and Kester [Sym85a] report concentrations of total iron (almost all present as a precipitate) as high as 11 and 55 μg dm^{-3} in the surface and bottom waters of the New York Bight. However, the concentration of iron observed in the open ocean was normally of the order of 0.2 μg dm^{-3}. Price and Calvert [Pri73] measured the particulate

iron in Loch Etive (a Scottish marine loch) to be in the range 10 to 20 μg dm^{-3}. Spencer and Sachs [Spe70] reported a total suspended matter concentration of 0.03 to 0.94 mg dm^{-3} in the Gulf of Maine. Morel et al. [Mor90] used a hydrous ferric oxide concentration of 10 mg dm^{-3} to model particulate matter. In this study too, all the particulate matter is modelled as hydrous ferric oxide, although the concentration of HFO is far smaller (approximately 1-10 μg dm^{-3}). A CSIR report [CSI91] on the situation of waste management and pollution control in South Africa reported that the suspended solid content of effluents from Natal to the sea was in the range 100 to 872 mg dm^{-3} while in the Cape it ranged from 22 to 290 mg dm^{-3}. The range over which HFO concentration was varied thus reflects conditions in the open ocean as well as those near to heavily laden rivers and effluent discharges. The top end of the scale gives some indication of the conditions in the sediments.

The following general results were observed:

1) The speciation of the alkali and alkaline earth metals is largely unaffected by adsorption except at very high solid concentrations (1000 mg dm^{-3}) where slight adsorption occurs.
2) The speciation of anions in the sea is also largely unaffected by adsorption except at high solid concentration. The notable exceptions are phosphate, silicate and chromate.
3) If the adsorption of dissolved organic matter is excluded, a positive surface charge on the solid material results. When the adsorption of organic matter is included, this charge is negative except at very high solid concentrations.
4) The inclusion of organic matter suppresses adsorption in general at low HFO concentrations. This is especially true of anion adsorption.

TABLE 6.1: Computed speciation of the components in seawater showing the effect of hydrous ferric oxide
Results are shown as the percentage of the cation appearing in an individual species.
Conditions: temperature, 25 °C; ionic strength, 0.7 mol dm^{-3}; pH, 8.1; pE = 9.1
atmospheric carbon dioxide excluded from equilibrating with the aqueous phase;
concentration of fulvic acid = 2 mg dm^{-3}, model 1 (sulphur and nitrogen included);
concentration of HFO = 1 mg dm^{-3};
1) adsorption of organic matter onto HFO modelled by the use of model ligand TIPP;
2) adsorption of organic matter onto HFO excluded.

Component		Total adsorbed	Strong site	Weak site
Cr^{3+}	1	88.5	88.5	
	2	98.1	98.1	
Pb^{2+}	1	65.5	63.6	1.9
	2	92.5	92.2	0.3
Zn^{2+}	1	1.5	0.9	0.6
	2	5.9	5.5	0.4
Ni^{2+}	1	0.3	0.2	0.1
	2	1.2	1.1	0.1
Cu^{2+}	1	0.2		0.2
	2	0.3	0.2	0.1
Sn^{2+}	1	0.2		0.2
	2	0.4	0.3	0.1
Co^{2+}	1	0.1		0.1
	2	0.3	0.3	
Cd^{2+}	1	0.0		
	2	0.1	0.1	
Mn^{2+}	1	0.0		
	2[v]	0.3	0.3	
$SiO_2(OH)_2^{2-}$	0.8			0.8
	2	5.1	0.2	4.9
PO_4^{3-}	1	0.1		0.1
	2	26.5	0.4	26.1
CrO_4^{2-}	1	0.0		
	2	2.1	2.0	0.1

v: percentage is for the dissolved fraction, 0.1% of the total is adsorbed

TABLE 6.2: Computed speciation of the components in seawater showing the effect of hydrous ferric oxide
Results are shown as the percentage of the cation appearing in an individual species.
Conditions: temperature, 25 °C; ionic strength, 0.7 mol dm^{-3}; pH, 8.1; pE = 9.1
atmospheric carbon dioxide excluded from equilibrating with the aqueous phase;
concentration of fulvic acid = 2 mg dm^{-3}, model 1 (sulphur and nitrogen included);
concentration of HFO = 1000 mg dm^{-3};
1) adsorption of organic matter onto HFO modelled by the use of model ligand TIPP;
2) adsorption of organic matter onto HFO excluded.

Component		Total adsorbed	Strong site	Weak site
Cr^{3+}	1/2	100.0	100.0	
Pb^{2+}	1/2	100.0	99.7	0.3
Zn^{2+}	1	98.6	91.6	7.0
	2	98.7	91.7	7.0
Ni^{2+}	1	93.6	85.2	8.4
	2			
Cu^{2+}	1	79.3	57.6	21.7
	2	82.8	60.3	22.5
Sn^{2+}	1	80.6	50.9	29.7
	2	80.6	51.0	29.6
Co^{2+}	1	76.4	63.3	13.1
	2	76.4	63.4	1.3
Cd^{2+}	1	39.6	38.4	1.2
	2	39.7	38.5	1.2
Mn^{2+}	1^{v}	79.4	75.0	4.4
	2^{v}	79.4	75.1	4.3
UO_2^{2+}	1/2	0.9	0.7	0.2
Mg^{2+}	1/2	2.2	0.1	2.1
Ca^{2+}	1/2	0.2		0.2
Sr^{2+}	1/2	0.1		0.1
Ba^{2+}	1/2	0.2		0.2

v: manganese is totally dissolved at this concentration of HFO

Component		Total adsorbed	Strong site	Weak site
$SiO_2(OH)_2^{2-}$	1/2	98.6	1.5	97.1
PO_4^{3-}	1/2	99.8	1.3	98.5
CrO_4^{2-}	1	97.0	1.3	95.7
	2	97.1	1.3	95.8
F^-	1	2.8		2.8
	2	2.9	0.1	2.8
SO_4^{2-}	1/2	1.4		1.4
$B(OH)_4^-$	1/2	0.1		0.1

TABLE 6.3: Computed speciation of the adsorption sites on hydrous ferric oxide
Results are shown as the percentage of the cation appearing in an individual species.
Conditions: temperature, 25 °C; ionic strength, 0.7 mol dm^{-3}; pH, 8.1; pE = 9.1
atmospheric carbon dioxide excluded from equilibrating with the aqueous phase;
concentration of fulvic acid = 2 mg dm^{-3}, model 1 (sulphur and nitrogen included).

Species	1 μg dm^{-3}	1 mg dm^{-3}	1 g dm^{-3}
Adsorption of organic matter onto HFO model by the ligand TIPP			
<u>Strong site</u>			
=FeOH			5.1
$=FeO^-$			10.9
$=FeOHMg^{2+}$	80.9	82.5	62.5
$=FeOHCa^{2+}$	14.5	14.7	11.4
$=FeOCrOH^+$	1.9		
$=FeOHTIPP^{2-}$	1.8	2.1	
$=FeOHSO_4^{2-}$			9.4
<u>Weak site</u>			
=FeOH	1.0	1.1	9.4
$=FeO^-$			20.0
$=FeOMg^+$	61.4	61.3	51.8
$=FeTIPP^-$	1.9	1.8	
$=FeOHTIPP^{2-}$	32.4	32.4	
$=FeOHSO_4^{2-}$			17.2
$=FeSiO_3H_4$	2.3	2.3	
Adsorption of organic matter onto HFO excluded			
<u>Strong site</u>			
=FeOH	3.3	4.0	5.2
$=FeO^-$	6.1	7.6	11.1
$=FeOHMg^{2+}$	52.3	59.3	62.3
$=FeOHCa^{2+}$	9.3	10.6	11.4
$=FeOCrOH^+$	11.2		
$=FeOPb^+$	1.9		
$=FeOHSO_4^{2-}$	4.7	6.0	9.6
$=FePO_4^{2-}$	3.2	3.1	
$=FeSiO_3H_4$	7.2	8.2	
<u>Weak site</u>			
=FeOH	7.1	7.3	9.5
$=FeO^-$	13.3	14.1	20.2
$=FeOMg^+$	45.4	45.3	51.7
$=FeOHSO_4^{2-}$	10.2	11.2	17.5
$=FePO_4^{2-}$	7.2	5.6	
$=FeSiO_3H_4$	15.7	15.3	

CODES USED TO DESCRIBE THE VARIOUS MODELS IN THE FIGURES THAT FOLLOW

1	Organic adsortion included
2	Organic adsorption excluded

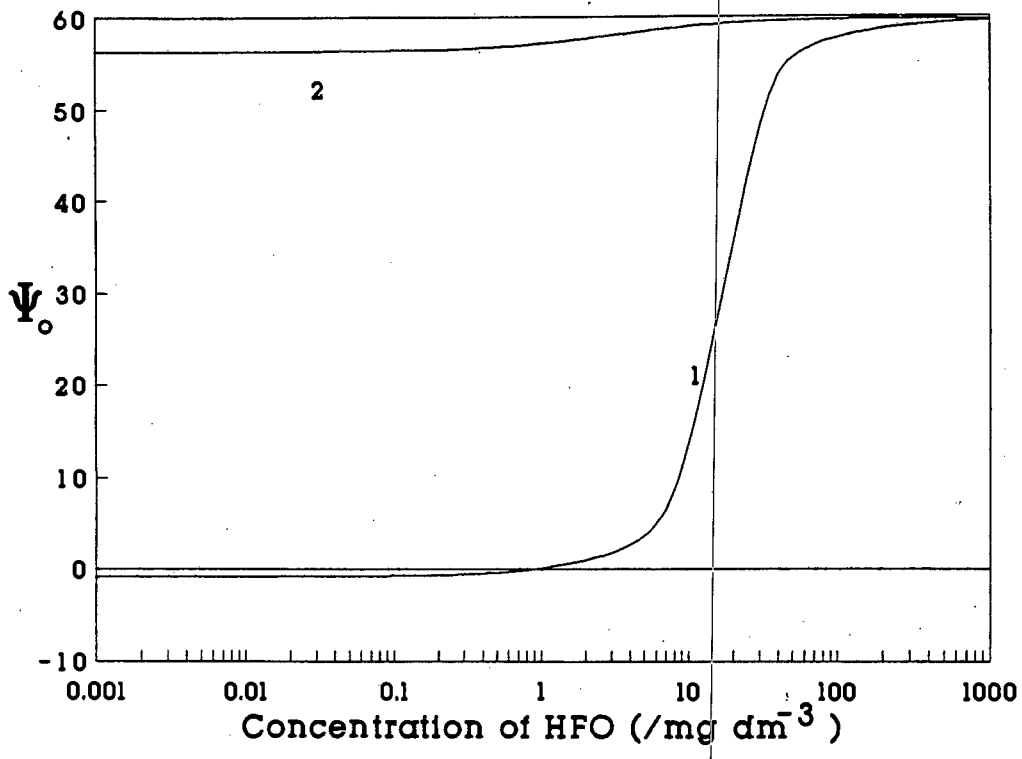


Figure 6.1: The effect of hydrous ferric oxide concentration on the surface charge density (ionic strength = 0.7 mol dm^{-3}; 25 °C; atmospheric carbon dioxide dissolution excluded; 2 mg dm^{-3} FA (N and S binding included))

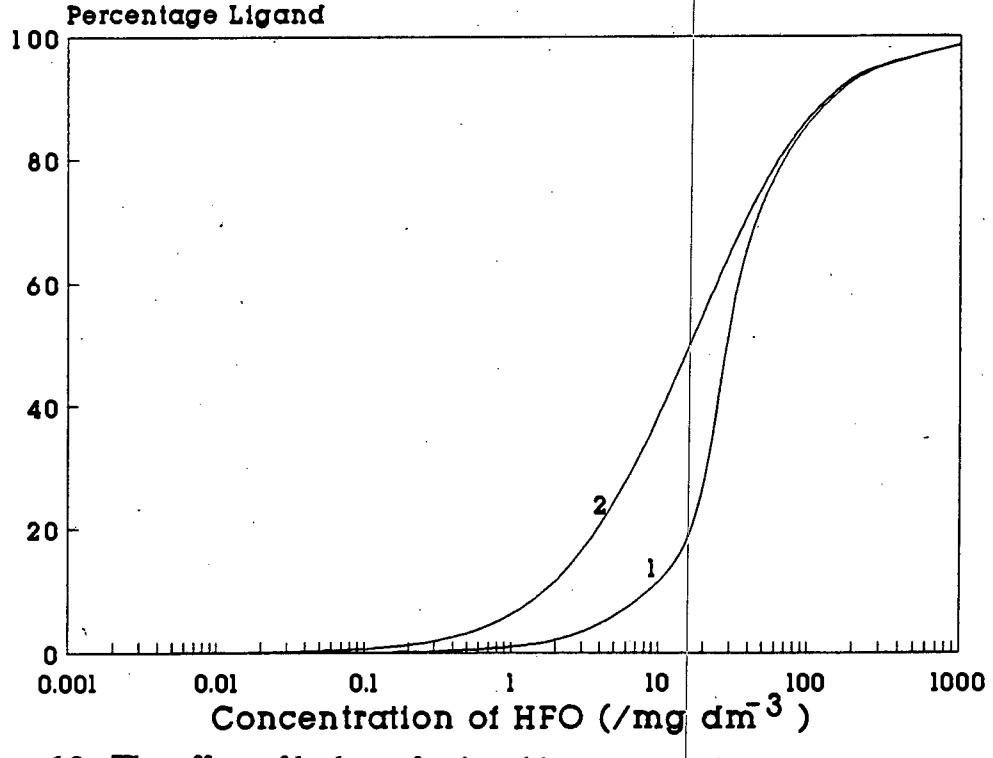


Figure 6.2: The effect of hydrous ferric oxide concentration on the adsorption of silicate (ionic strength = 0.7 mol dm^{-3}; 25 °C; atmospheric carbon dioxide dissolution excluded; 2 mg dm^{-3} FA (N and S binding included))

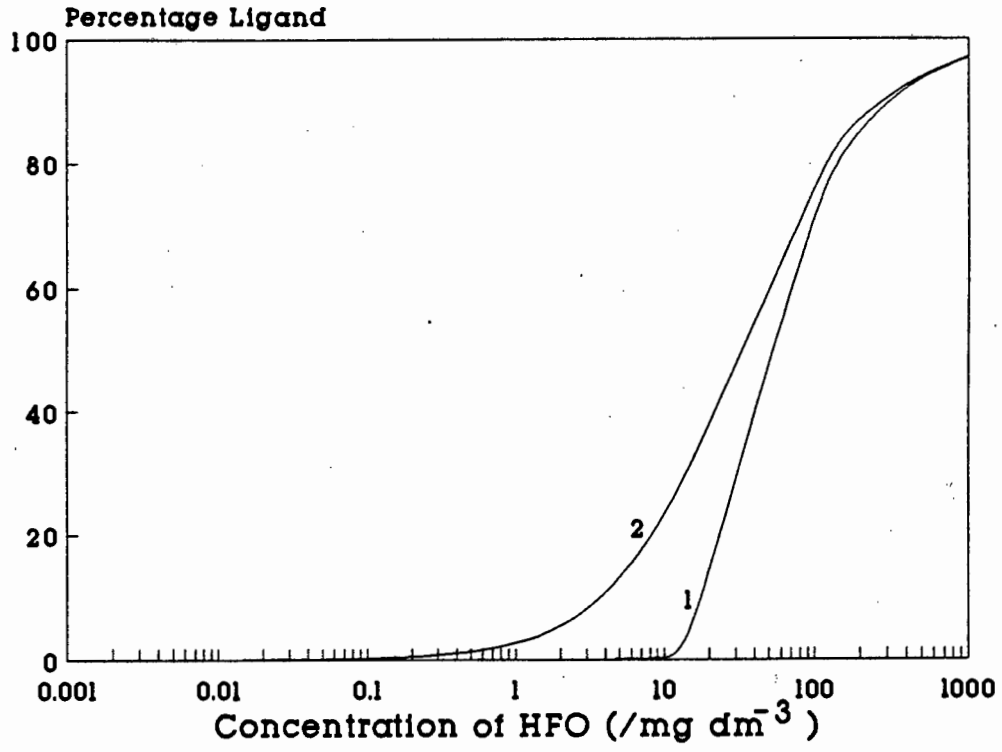


Figure 6.3: The effect of hydrous ferric oxide concentration on the adsorption of chromate (ionic strength = 0.7 mol dm^{-3}; 25 °C; atmospheric carbon dioxide dissolution excluded; 2 mg dm^{-3} FA (N and S binding included))

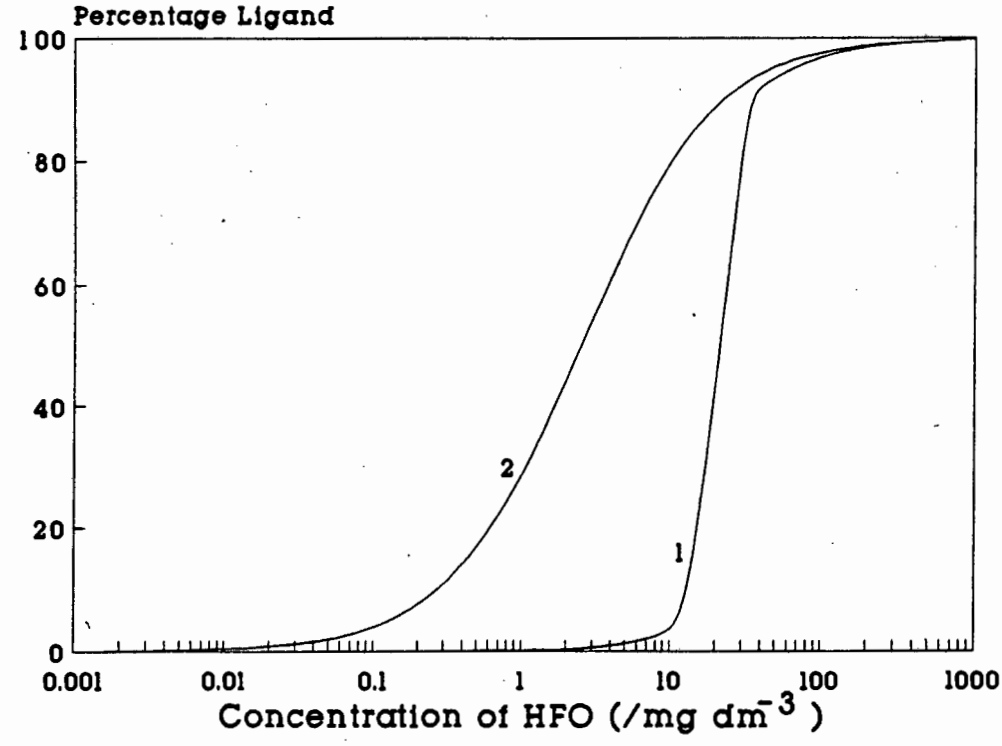


Figure 6.4: The effect of hydrous ferric oxide concentration on the adsorption of phosphate (ionic strength = 0.7 mol dm^{-3}; 25 °C; atmospheric carbon dioxide dissolution excluded; 2 mg dm^{-3} FA (N and S binding included))

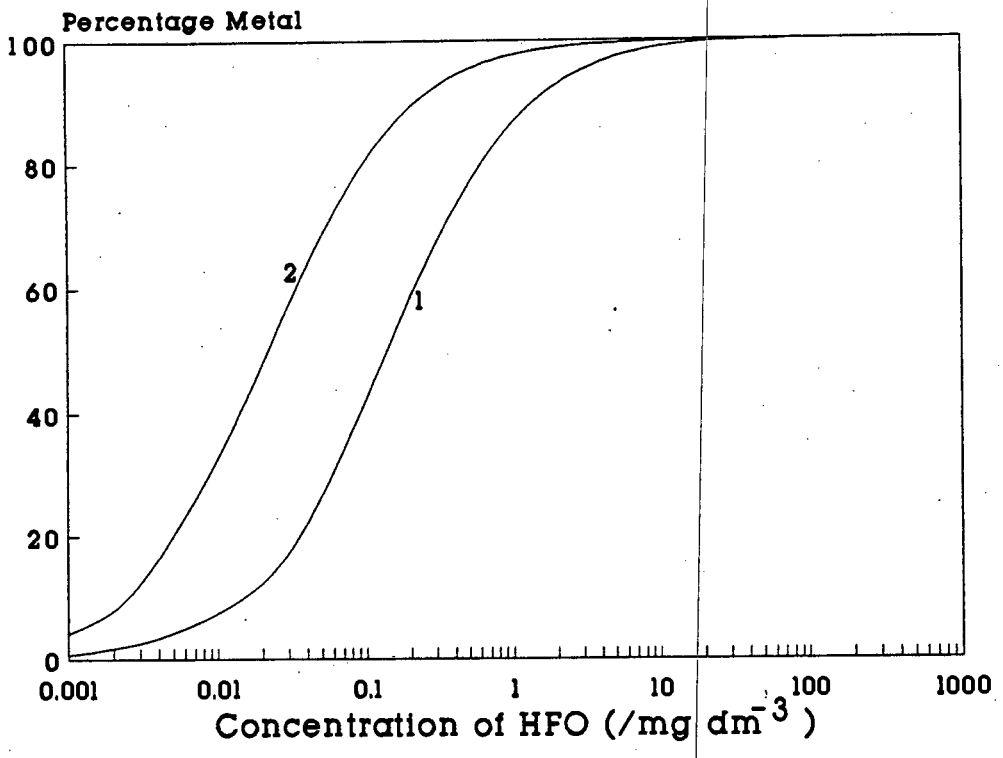


Figure 6.5: The effect of hydrous ferric oxide concentration on the adsorption of chromium(III) (ionic strength = 0.7 mol dm^{-3}; 25 °C; atmospheric carbon dioxide dissolution excluded; 2 mg dm^{-3} FA (N and S binding included))

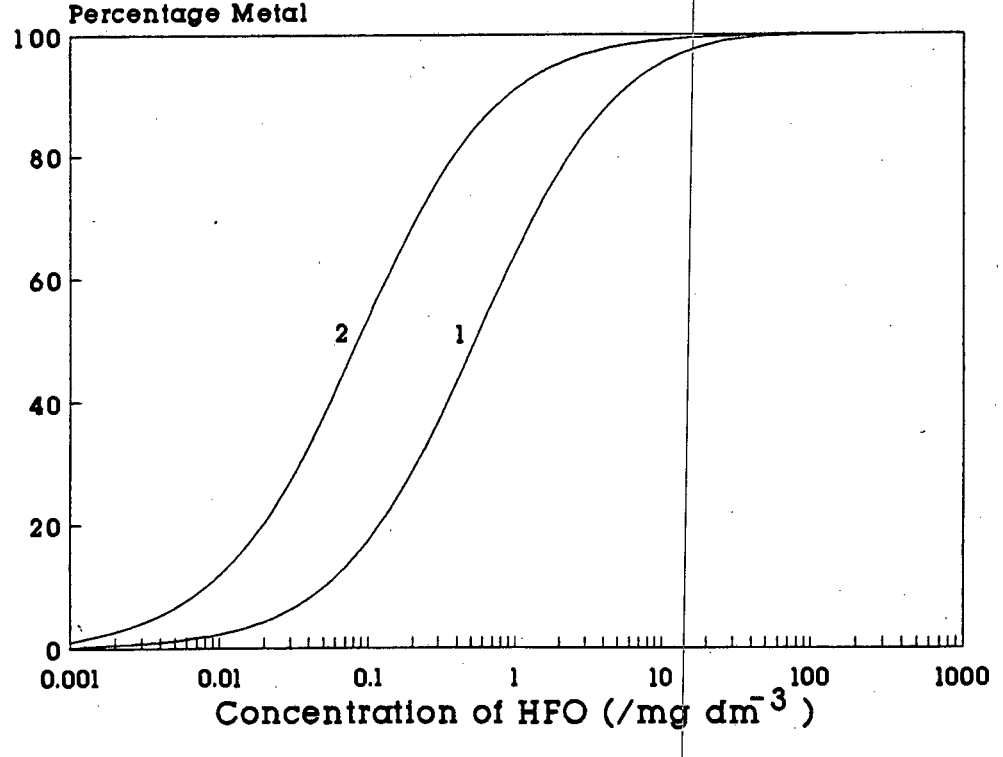


Figure 6.6: The effect of hydrous ferric oxide concentration on the adsorption of lead(II) (ionic strength = 0.7 mol dm^{-3}; 25 °C; atmospheric carbon dioxide dissolution excluded; 2 mg dm^{-3} FA (N and S binding included))

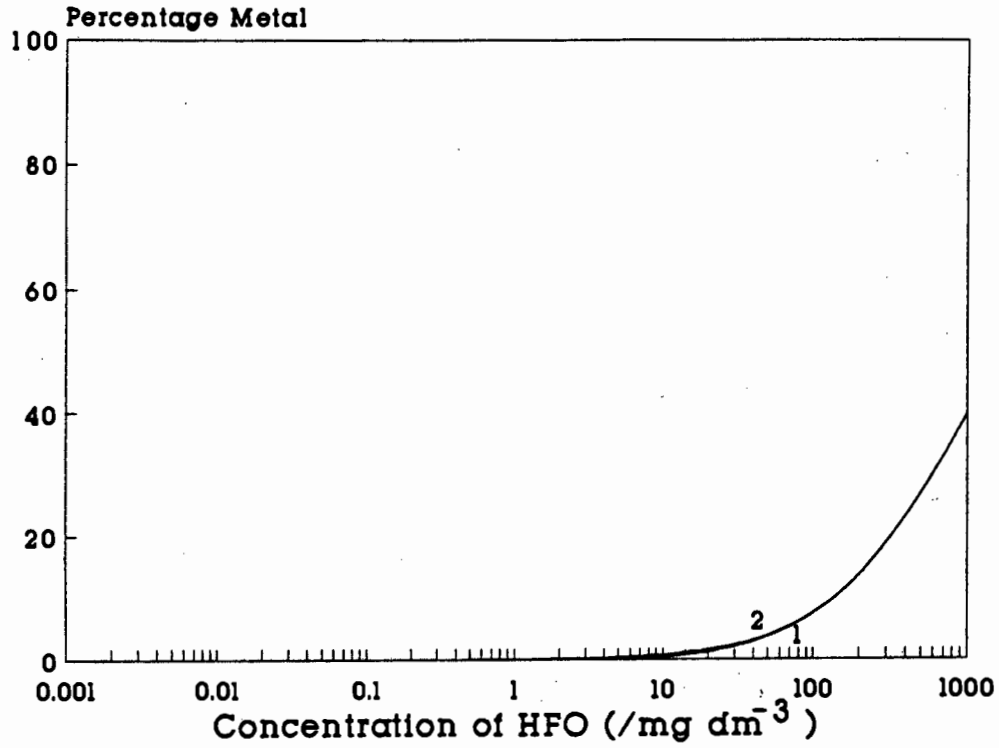


Figure 6.7: The effect of hydrous ferric oxide concentration on the adsorption of cadmium(II) (ionic strength = 0.7 mol dm^{-3}; 25 °C; atmospheric carbon dioxide dissolution excluded; 2 mg dm^{-3} FA (N and S binding included))

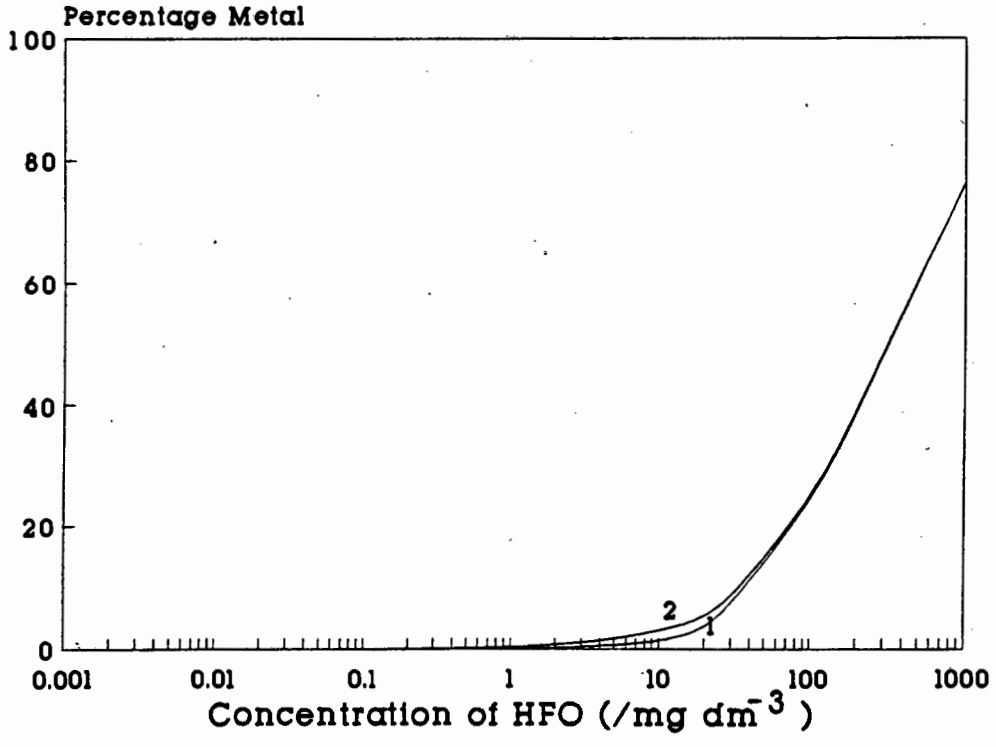


Figure 6.8: The effect of hydrous ferric oxide concentration on the adsorption of cobalt(II) (ionic strength = 0.7 mol dm^{-3}; 25 °C; atmospheric carbon dioxide dissolution excluded; 2 mg dm^{-3} FA (N and S binding included))

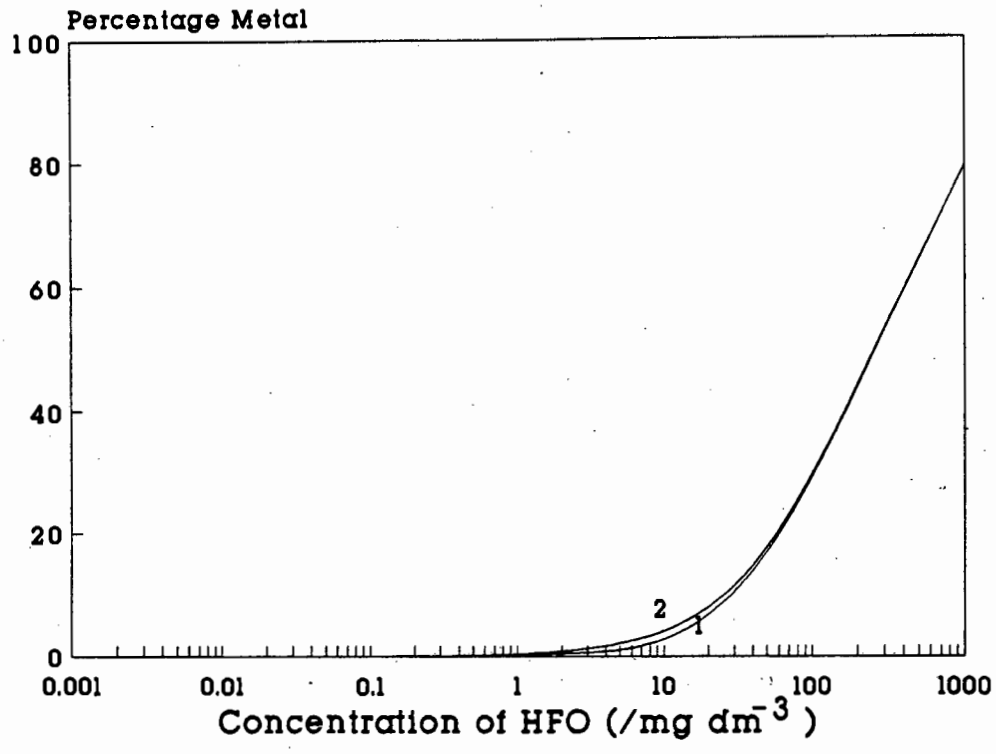


Figure 6.9: The effect of hydrous ferric oxide concentration on the adsorption of copper(II) (ionic strength = 0.7 mol dm^{-3}; 25 °C; atmospheric carbon dioxide dissolution excluded; 2 mg dm^{-3} FA (N and S binding included))

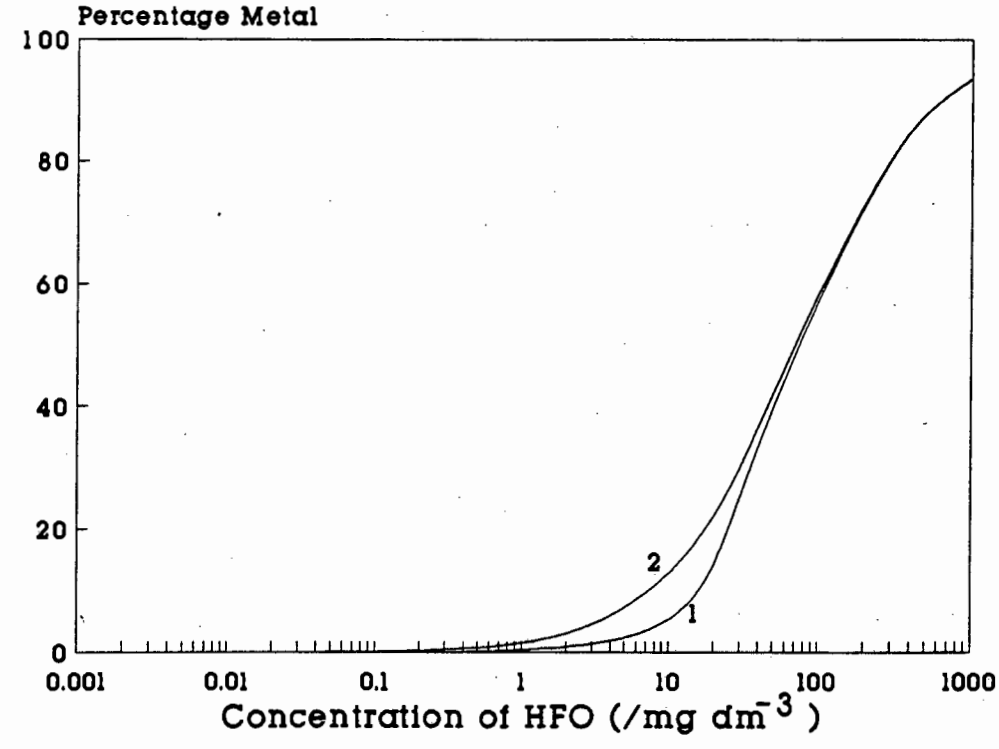


Figure 6.10: The effect of hydrous ferric oxide concentration on the adsorption of nickel(II) (ionic strength = 0.7 mol dm^{-3}; 25 °C; atmospheric carbon dioxide dissolution excluded; 2 mg dm^{-3} FA (N and S binding included))

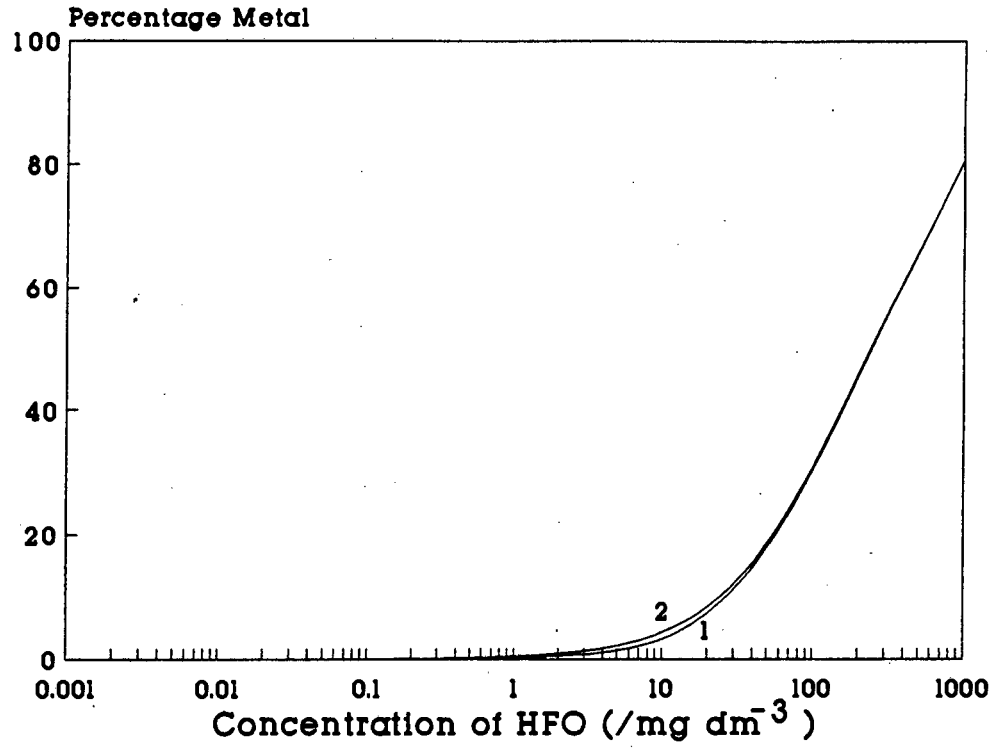


Figure 6.11: The effect of hydrous ferric oxide concentration on the adsorption of tin(II) (ionic strength = 0.7 mol dm^{-3}; 25 °C; atmospheric carbon dioxide dissolution excluded; 2 mg dm^{-3} FA (N and S binding included))

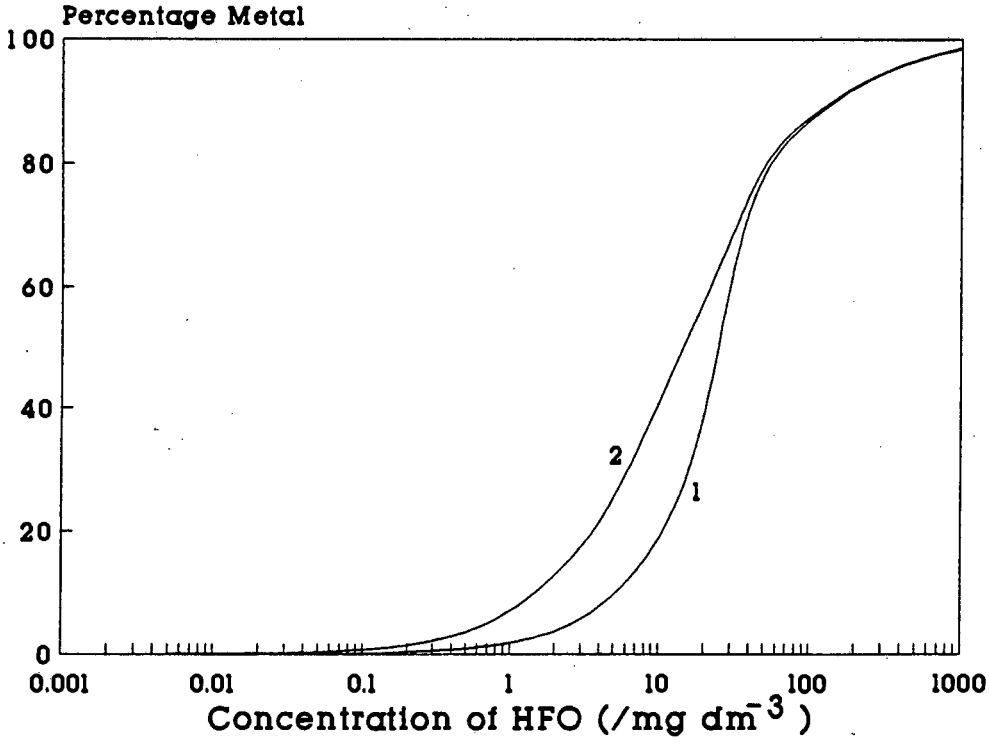


Figure 6.12: The effect of hydrous ferric oxide concentration on the adsorption of zinc(II) (ionic strength = 0.7 mol dm^{-3}; 25 °C; atmospheric carbon dioxide dissolution excluded; 2 mg dm^{-3} FA (N and S binding included))

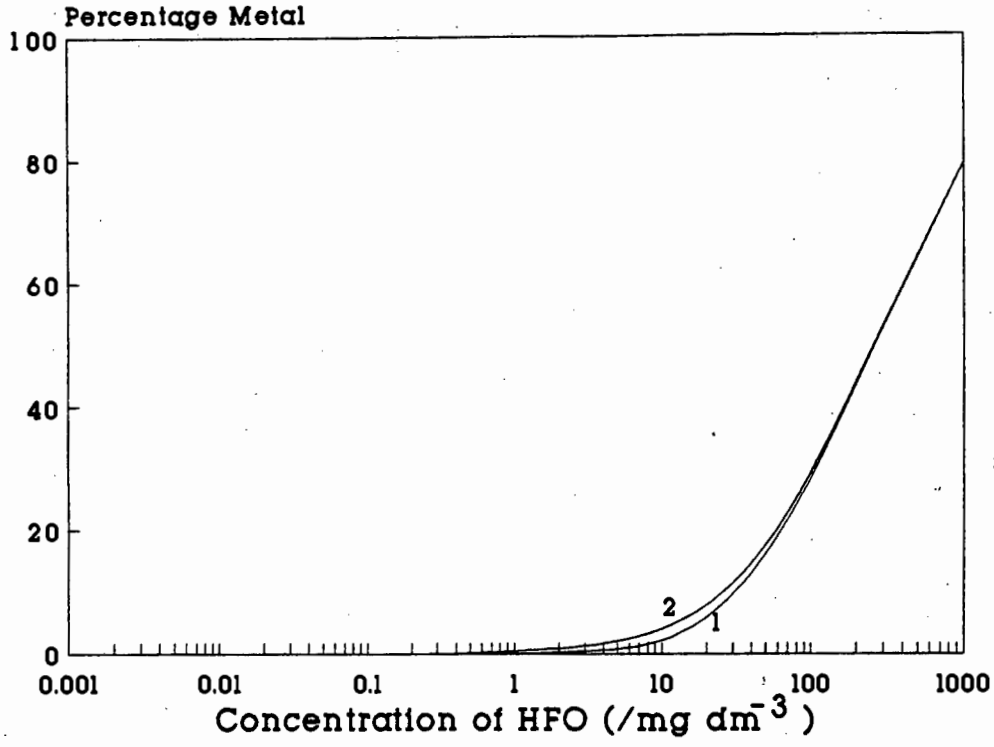


Figure 6.13.1: The effect of hydrous ferric oxide concentration on the adsorption of of dissolved manganese (ionic strength = 0.7 mol dm^{-3}; 25 °C; atmospheric carbon dioxide dissolution excluded; 2 mg dm^{-3} FA (N and S binding included))

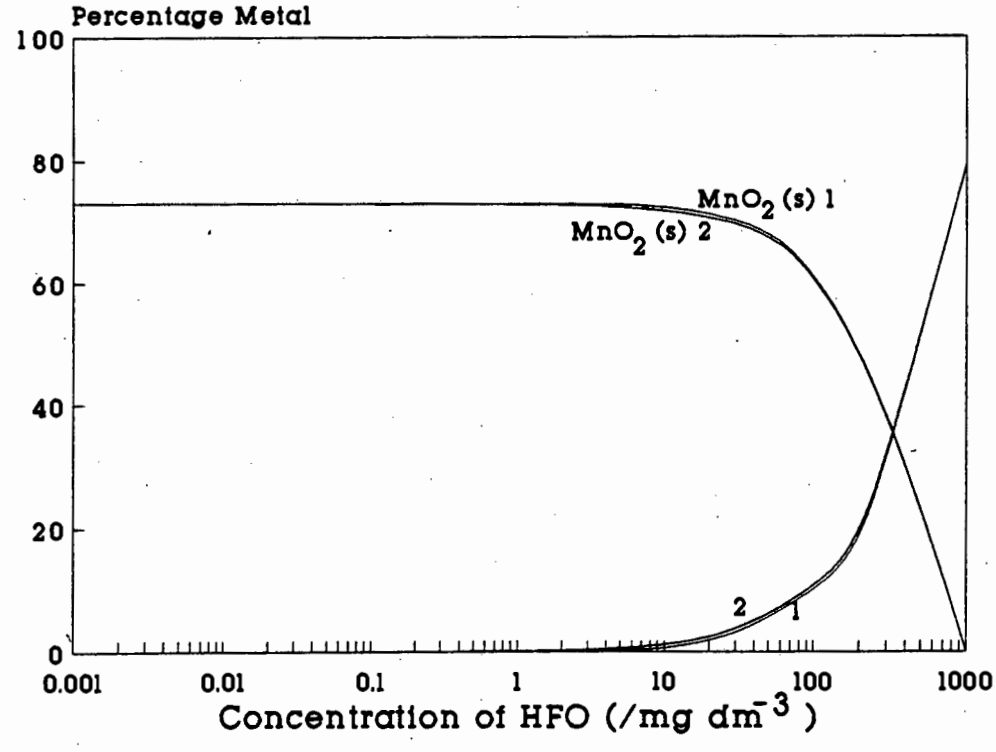


Figure 6.13.2: The effect of hydrous ferric oxide concentration on the adsorption of total manganese (ionic strength = 0.7 mol dm^{-3}; 25 °C; atmospheric carbon dioxide dissolution excluded; 2 mg dm^{-3} FA (N and S binding included))

5) Trace metals are adsorbed on to hydrous ferric oxide to varying degrees. Lead(II) and chromium(III) are strongly adsorbed, even at low concentrations of solid. Zinc(II) and nickel(II) show intermediate adsorption while copper(II), cobalt(II), tin(II), manganese(II) and cadmium(II) are adsorbed only at high solid concentrations. The adsorption of uranyl occurs at very high solid concentrations while that of silver(I) and mercury(II) is very insignificant.

6) Anions are primarily adsorbed on to low affinity (weak) sites while trace metals show a preference for high affinity (strong) sites.

7) The inclusion of the adsorption of organic matter suppresses the adsorption of trace metals on to strong sites while the effect on the adsorption of trace metals onto weak sites is much smaller.

8) As was the case with fulvic acid complexation, the adsorption of trace metals is affected by trace metal concentration. This is especially true of lead(II) and chromium(III).

9) The speciation of both the adsorption sites on HFO is dominated by magnesium in both models. Organic matter is significant to the speciation of the weak sites where organic adsorption is included. Sulphate is significant to the speciation of both sites in both models although its influence is far greater where organic matter is excluded.

6.2 DISCUSSION OF THE EFFECT OF ADSORPTION ON THE SPECIATION PATTERNS

The speciation of the major cations and anions is largely unaffected by adsorption because their adsorption constants are much weaker than those of the trace components which are observed to be adsorbed much more readily. Secondly their concentrations are

greatly in excess of the concentrations of surface sites which means that adsorption is insignificant except at high concentrations of solid material.

The overall positive surface charge that arises when dissolved organic matter is excluded is the result of most of the surface sites being sorbed with magnesium. The sorption of sulphate and phosphate as well as the desorption of protons is not sufficient to supply an overall negative surface charge density. Where organic matter is adsorbed, the solid surface has an overall negative charge until an HFO concentration of 1 mg dm^{-3} where the nett charge is zero. Above this concentration the surface has an overall positive charge. It can be observed that at low concentrations (< 1 mg dm^{-3}) the speciation of the low affinity (weak) site does not vary much which gives rise to a constant negative charge density. Below 1 mg dm^{-3} the adsorption of organic matter is significant. However, by an HFO concentration of 10 mg dm^{-3} all the model organic adsorbent is adsorbed and it can supply no further negative charge to the nett surface charge. Consequently the overall charge becomes positive as magnesium comes to dominate the surface site speciation.

This charge pattern explains why anions are not sorbed at low solid concentrations when organic matter is included. This is the result of the electrostatic repulsion of anions by the negative surface charge. There is a significant difference when this is excluded and silicate and phosphate are seen to be significantly adsorbed at a concentration of 1 mg dm^{-3}. Anions are adsorbed primarily to the weak sites since their adsorption constants for the two sites are the same. Table 6.3 indicates that the free site percentage (=FeOH) for the low affinity sites is much lower where organic matter is allowed to adsorb as a result of the adsorption of TIPP. Consequently the adsorption of anions is greatly reduced for this reason too. Note that at high concentration the speciation patterns are very similar because the speciation of the surface sites is now dominated by magnesium

and sulphate adsorption. The surface site speciation patterns are in fact very similar at high solid concentrations.

The adsorption of organic matter also suppresses the adsorption of trace metals at low concentrations of hydrous ferric oxide. However, this is not because organic matter binds preferentially to the high affinity sites and thereby blocks these sites as might be expected. Table 6.3 indicates that magnesium and calcium bind a much greater percentage of the strong sites at low HFO concentrations where organic matter is included. This increased adsorption of the major cations is to balance to some degree the negative charge created by the adsorption of organic matter to the weak sites. Consequently the free concentration of the strong sites is reduced, thereby inhibiting the adsorption of trace metals which are primarily adsorbed to strong sites. The adsorption of trace metals to weak sites is not significantly affected. Note that increased adsorption that might result from the electrostatic attraction that is caused by the negative surface charge does not occur because of the significant decrease in concentration of available high affinity surface sites.

The strong adsorption of lead can be rationalized in terms of its high adsorption constants. The adsorption of Cr^{3+} is favoured by the high pH of seawater and is affected to a greater extent by pH than the adsorption of other trace metals. This is because the adsorption of divalent trace metals sees the release of one hydrogen ion but two are released per chromium ion adsorbed.

Tin has a high adsorption constant which means that it adsorbs strongly. However, mercury and uranyl also have high adsorption constants and are observed to be adsorbed very weakly. This is because these two metals are strongly bound in seawater by chloro and carbonate species respectively. Consequently their free ion activity is very low which causes adsorption to be low. Copper adsorption is also reduced with respect

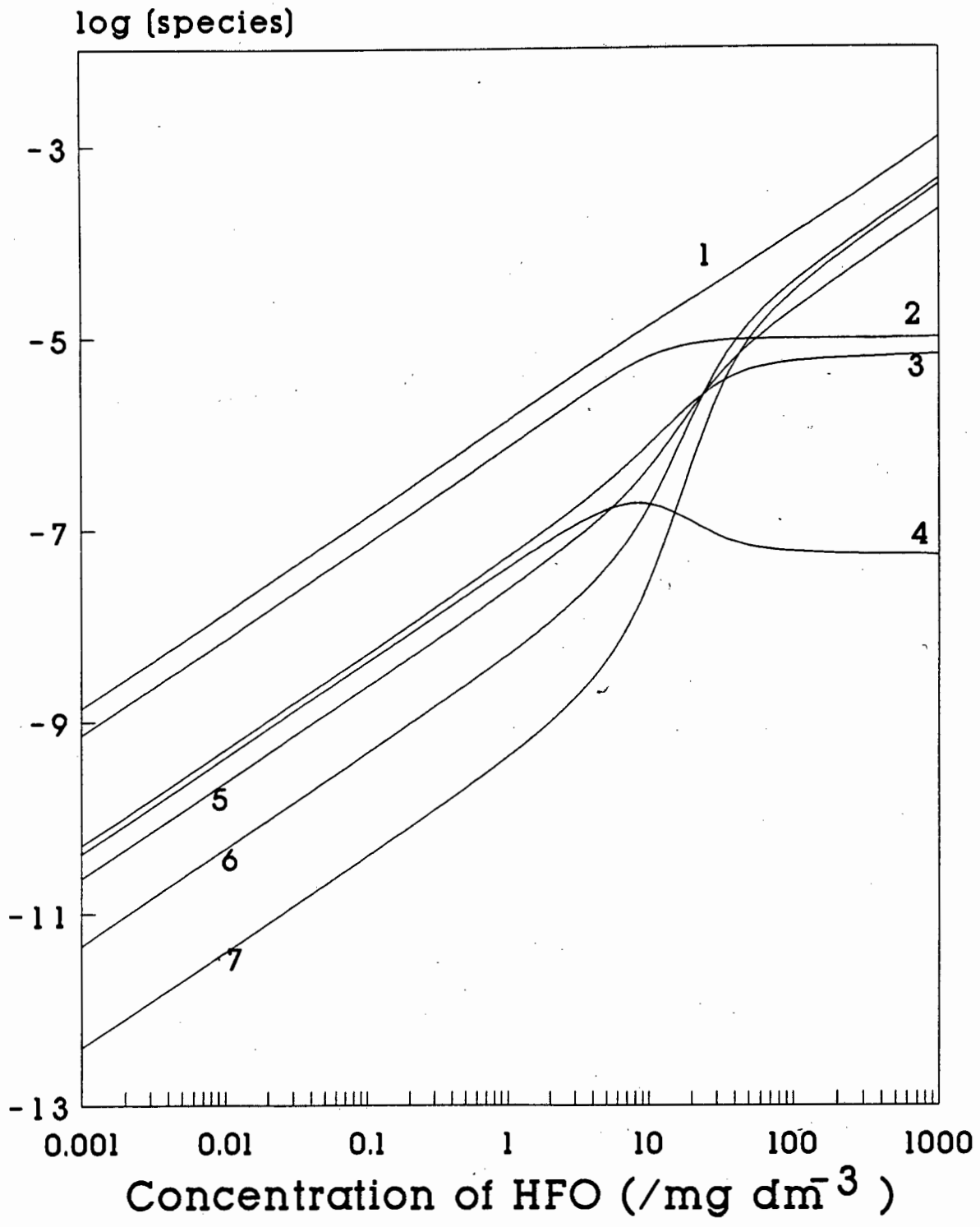


Figure 6.14.1: The effect of hydrous ferric oxide concentration on the speciation of the low affinity site (ionic strength = 0.7 mol dm^{-3}; 25 °C; atmospheric carbon dioxide dissolution excluded; 2mg dm^{-3} fulvic acid (N and S binding included); 10 mg dm^{-3} HFO; organic adsorption included) (1: $=FeOMg^{+}$, 2: $=FeOHTIPP^{2-}$, 3: $=FeSiO_3H_4$, 4: $=FeTIPP^{-}$, 5: =FeOH, 6: FeO^{-} 7: $=FeOHSO_4^{2-}$)

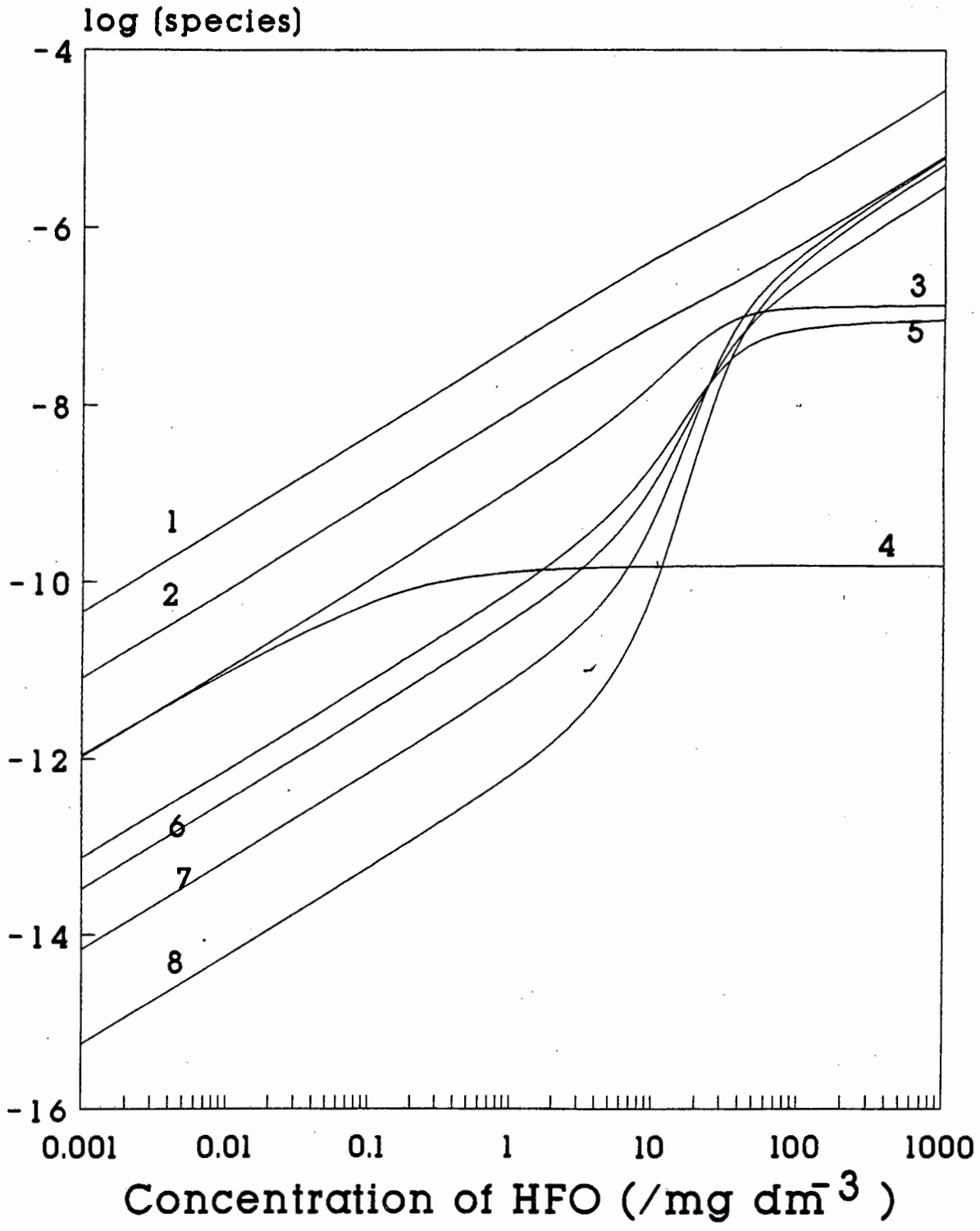


Figure 6.14.2: The effect of hydrous ferric oxide concentration on the speciation of the high affinity site (ionic strength = 0.7 mol dm^{-3}; 25 °C; atmospheric carbon dioxide dissolution excluded; 2mg dm^{-3} fulvic acid (N and S binding included); 10 mg dm^{-3} HFO; organic adsorption included) (1: $=FeOHMg^{2+}$, 2: $=FeOHCa^{2+}$, 3: $=FeOHTIPP^{2-}$, 4: $=FeOCrOH^{+}$, 5: $=FeSiO_3H_4$, 6: =FeOH, 7: $=FeOHSO_4^{2-}$, 8: $=FeO^{-}$)

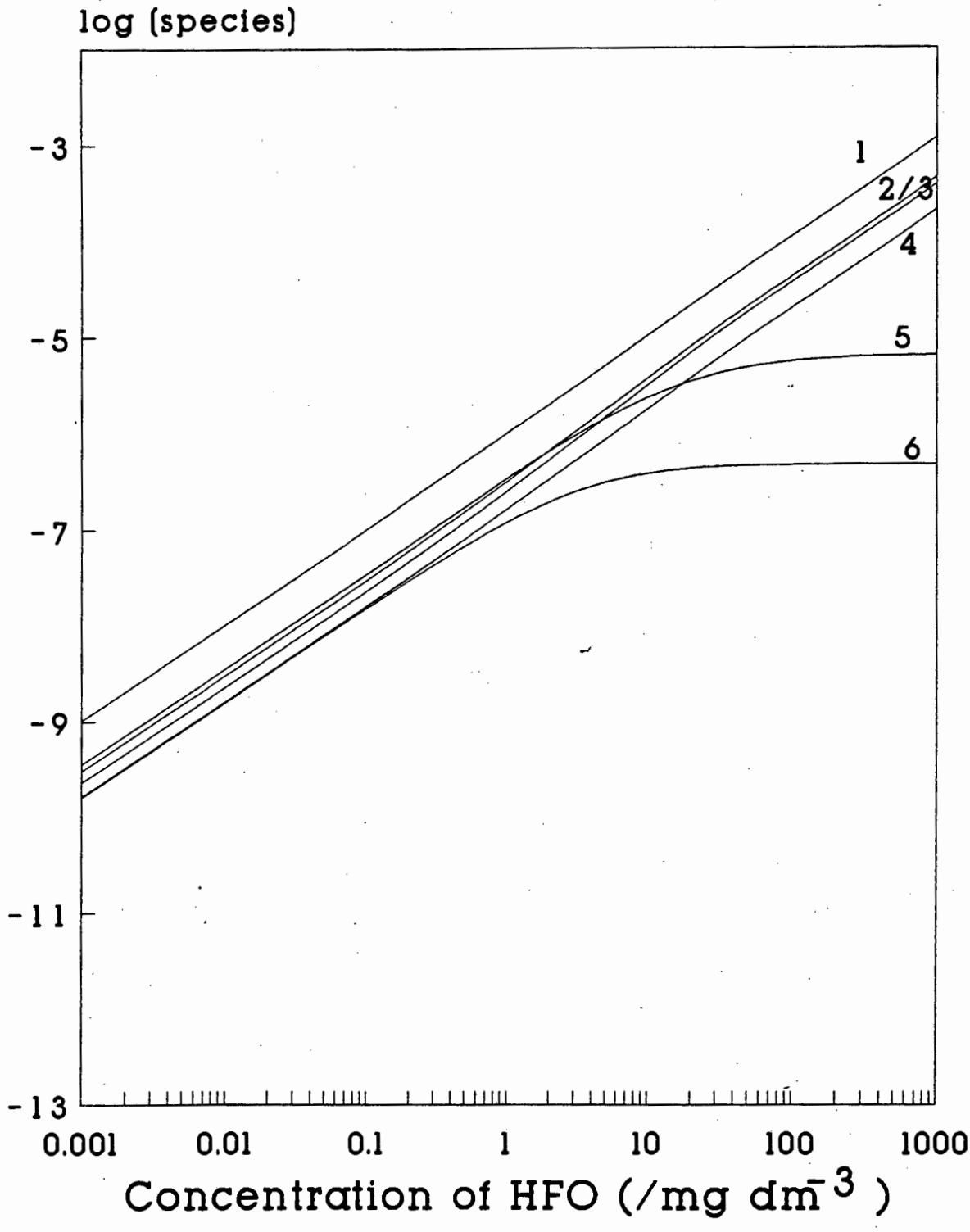


Figure 6.15.1: The effect of hydrous ferric oxide concentration on the speciation of the low affinity site (ionic strength = 0.7 mol dm^{-3}; 25 °C; atmospheric carbon dioxide dissolution excluded; 2mg dm^{-3} fulvic acid (N and S binding included); 10 mg dm^{-3} HFO; organic adsorption excluded) (1: =$FeOMg^+$, 2: =FeO^-, 3: =$FeOHSO_4^{2-}$, 4: =FeOH, 5: =$FeSiO_3H_4$, 6: =$FePO_4^{2-}$)

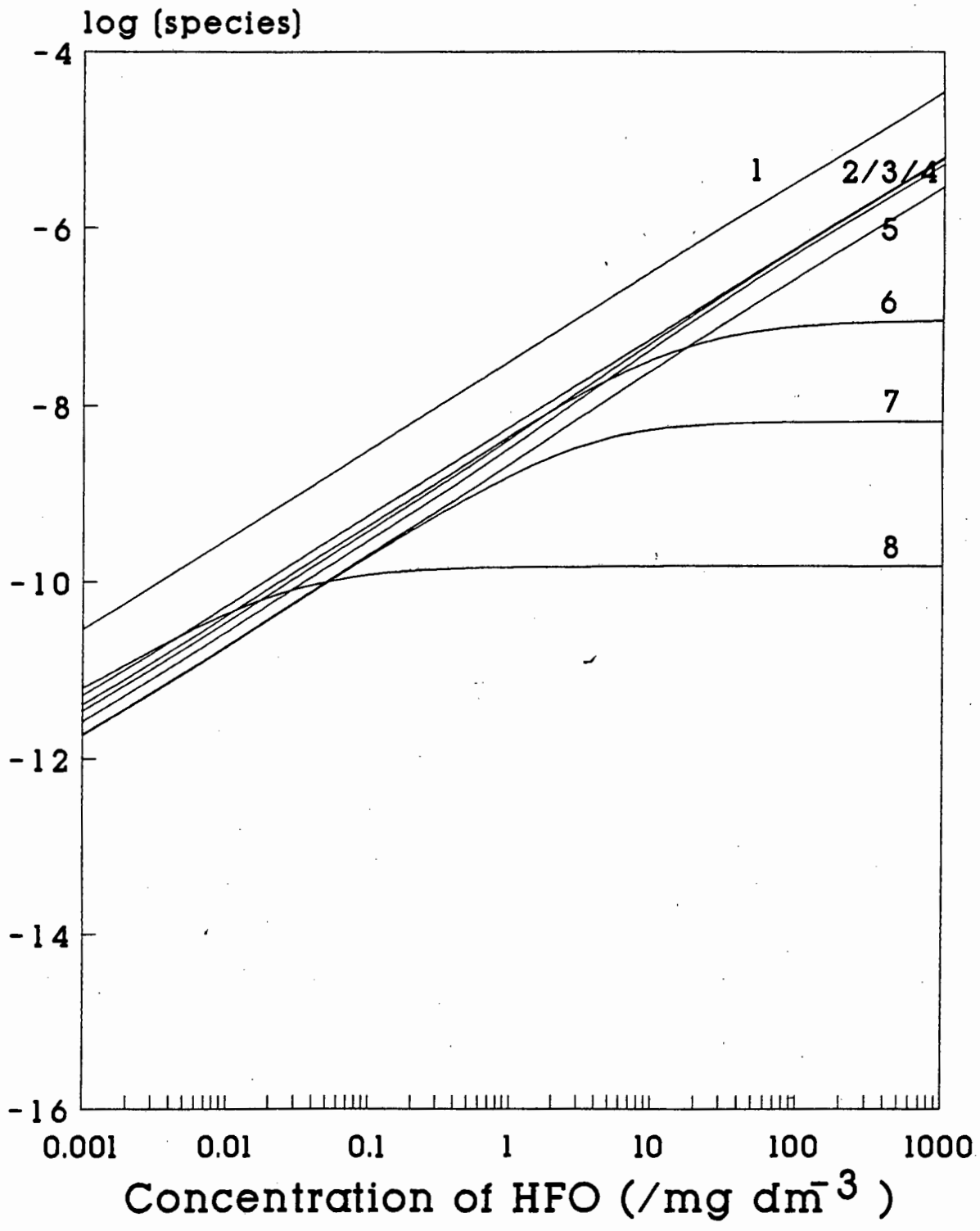


Figure 6.15.2: The effect of hydrous ferric oxide concentration on the speciation of the high affinity site (ionic strength = 0.7 mol dm^{-3}; 25 °C; atmospheric carbon dioxide dissolution excluded; 2mg dm^{-3} fulvic acid (N and S binding included); 10 mg dm^{-3} HFO; organic adsorption excluded) (1: =FeOHMg^{2+}, 2: =FeOHCa^{2+}, 3: =FeO^{-}, 4: =FeOHSO$_4^{2-}$, 5: =FeOH, 6: =FeSiO$_3$H$_4$, 7: =FePO$_4^{2-}$, 8: =FeOCrOH^{+})

to nickel and zinc because of its high organic complexation. Manganese dioxide was observed to dissolve at high solid concentrations because the free manganese concentration decreased as a result of adsorption.

The preference of anions for low affinity sites is because the adsorption constants for anions onto the two types of sites are the same. Consequently adsorption is determined by site density. Cations have larger adsorption constants for the high affinity sites which outweighs the difference in site concentration.

The degree of adsorption of trace metals onto hydrous ferric oxide is of the order: chromium(III) > lead(II) > zinc(II) > nickel(II) > copper(II) = tin(II) > cobalt(II) > manganese(II) > cadmium(II) >> uranyl >> mercury(II) > silver(I).

Figures 6.14.1 to 6.15.2 indicate the speciation of the adsorption sites for the two models. Where organic matter is not included, phosphate is significant to both sites at low concentrations. At higher solid concentrations its contribution levels off as a result of all the phosphate being adsorbed and thus unable to make any further contribution. The same effect can be seen from the contribution of chromium(III) and silicate to the sites in both models. Where organic matter is included, the contribution of organic matter to surface site speciation is also limited by its concentration. Note the curve in the concentration of the deprotonated sites and sulphate bound sites in the model where organic matter is included. At low solid concentrations, these species are insignificant since the surface negative charge is supplied by the adsorption of organic matter. However, at higher solid concentrations these species become much more significant as they are able to balance the positive charge created by the adsorption of magnesium and calcium to a much greater degree than TIPP.

The concentration of lead(II) and chromium(III) affects their speciation patterns because at low solid concentration they bind a significant portion of the high affinity sites. As an example the lead concentration was varied from 0.01 nmol dm^{-3} to 100 μmol dm^{-3} with the concentration of HFO fixed at 10 mg dm^{-3}. Figure 6.16.2 indicates the effect of lead concentration on the adsorption of other trace metals and anions. The anions are largely unaffected by the adsorption of lead because they are preferentially bound by the weak sites to which lead is not significantly adsorbed. The adsorption of lead, however, significantly reduces the free concentration of the high affinity sites, thereby reducing the adsorption of other trace metals. Figures 6.16.3 and 6.16.4 show how lead concentration affects the speciation of the adsorption sites. Note the significant change in the speciation of the strong sites as the adsorption of lead dominates the speciation of this site at high lead concentrations. The speciation of lead too is affected by its concentration as may be seen in figure 6.16.1. Note how the significance of the strong site to lead speciation decreases with increasing lead concentration as all the sites become bound. $PbCO_3$ is included to show the effect of concentration on the inorganic species. The others are left out for clarity. It was observed that they have parallel curves to $PbCO_3$. Lead also binds 1,2-aminoethanethiol and cysteine significantly at high concentrations (35.4% and 97.7% of ligand concentration respectively at 1 μmol dm^{-3}). This in turn affects the speciation of cadmium, zinc and nickel which are significantly bound by these ligands. CdCYS forms 41.7% of cadmium speciation at low lead concentrations but only 1.1% at 1 μmol dm^{-3} lead. $NiAET^+$ changes from 4.0% to 2.9% while $ZnAET^+$ decreases from 4.5% to 3.5%.

The concentrations of phosphate and silicate also affect the adsorption of other components, especially if dissolved organic matter is excluded. If DOM is included, no effect on trace metal speciation was caused by varying silicate concentration. On exclusion of organic matter though, an increase in silicate concentration decreased

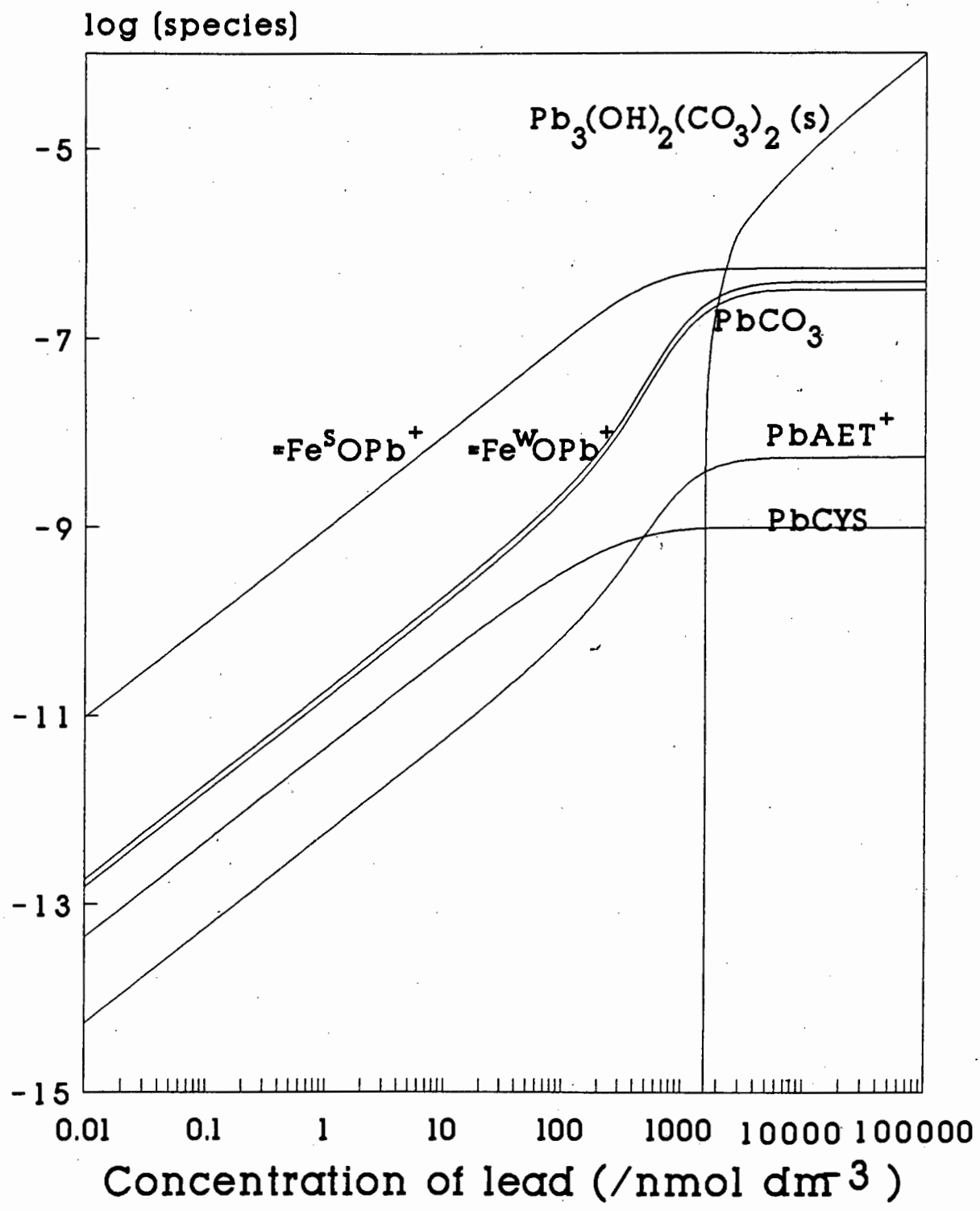


Figure 6.16.1: The effect of lead concentration on the speciation of lead (ionic strength = 0.7 mol dm^{-3}; 25 °C; atmospheric carbon dioxide dissolution excluded; 2mg dm^{-3} fulvic acid (N and S binding included); 10 mg dm^{-3} HFO; organic adsorption allowed)

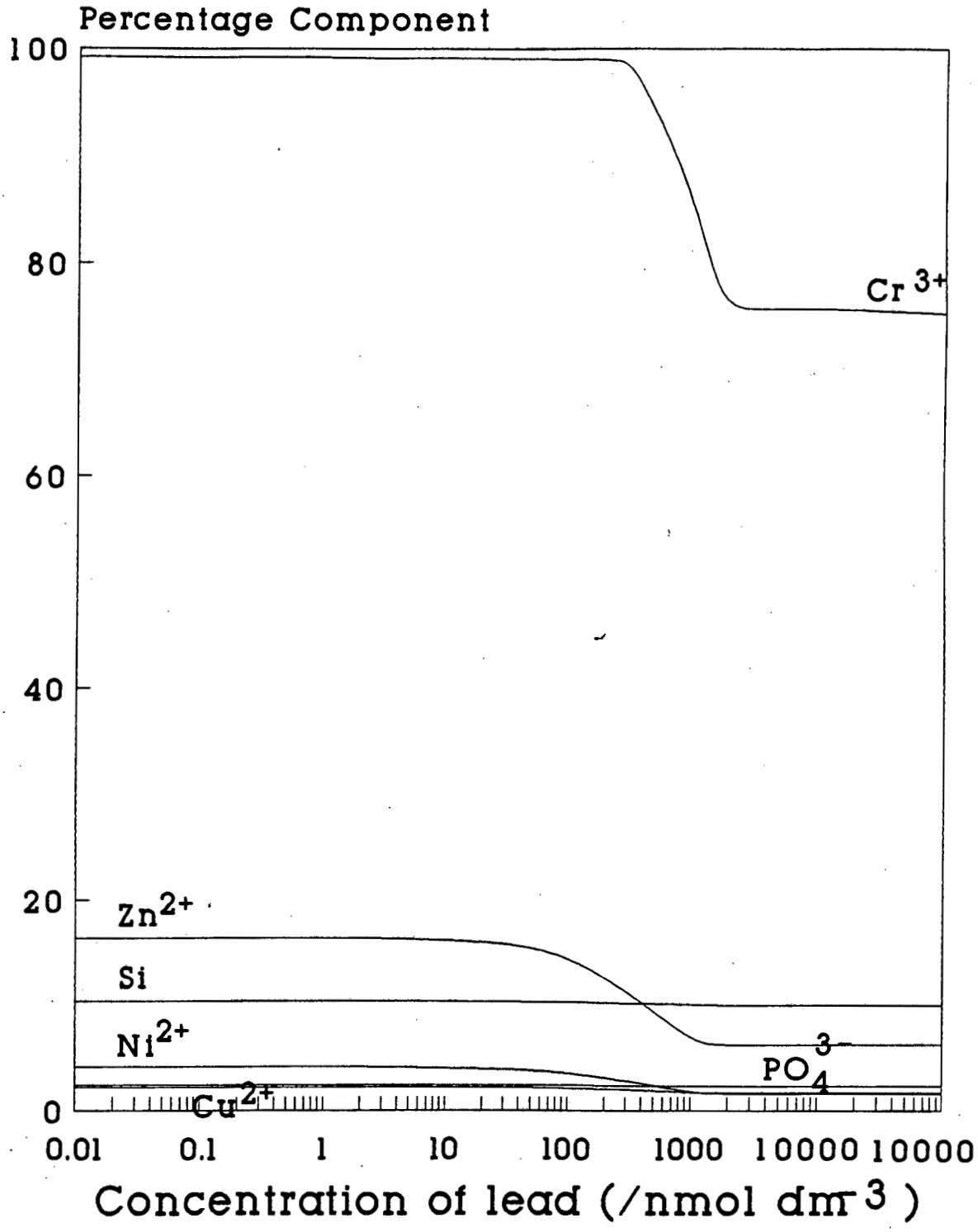


Figure 6.16.2: The effect of lead concentration on the adsorption of selected components (ionic strength = 0.7 mol dm^{-3}; 25 °C; atmospheric carbon dioxide dissolution excluded; 2mg dm^{-3} fulvic acid (N and S binding included); 10 mg dm^{-3} HFO; organic adsorption allowed)

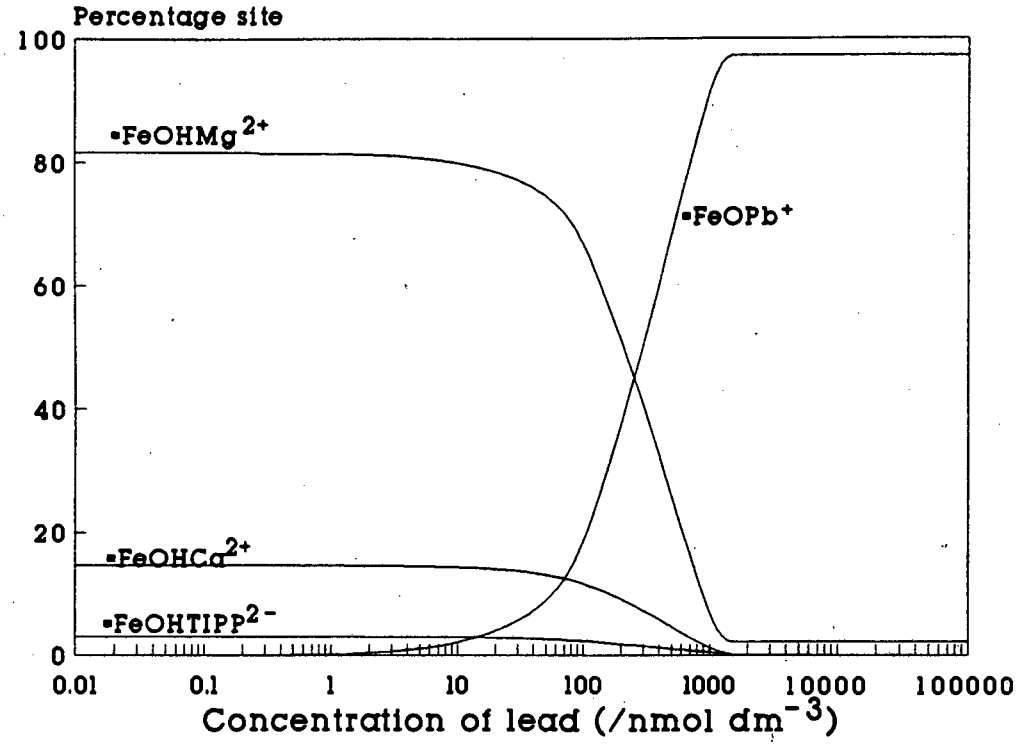


Figure 6.16.3: The effect of lead concentration on the speciation of the high affinity sites (ionic strength = 0.7 mol dm^{-3}; 25 °C; atmospheric carbon dioxide dissolution excluded; 2 mg dm^{-3} FA (N and S binding included); 10 mg dm^{-3} HFO; organic adsorption included)

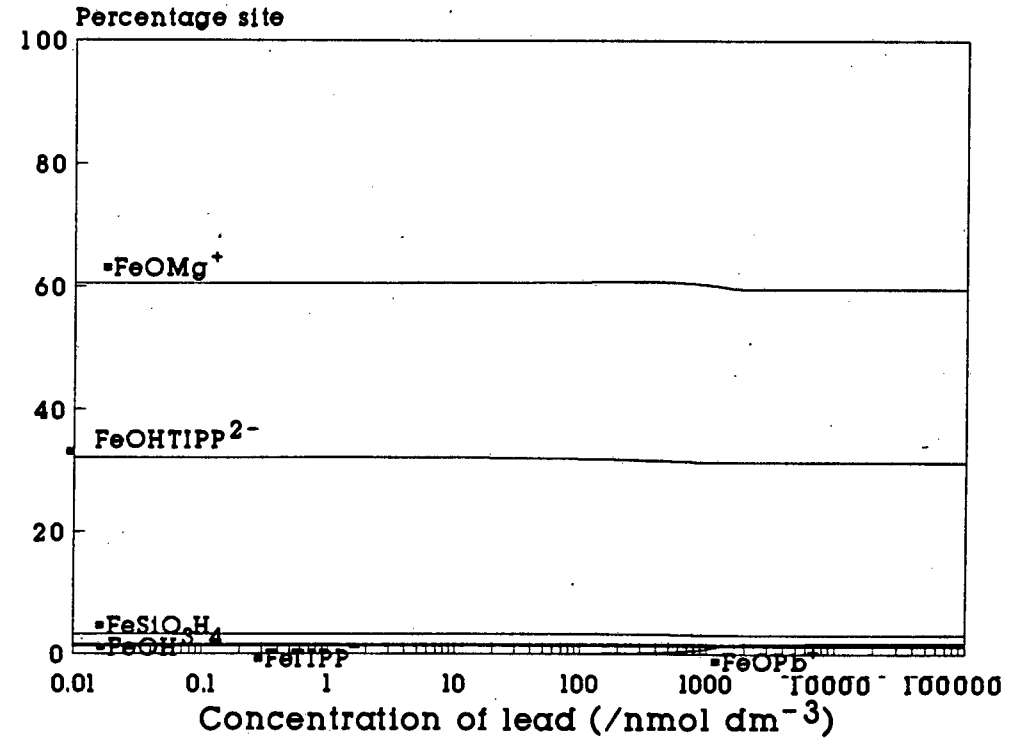


Figure 6.16.4: The effect of lead concentration on the speciation of the low affinity sites (ionic strength = 0.7 mol dm^{-3}; 25 °C; atmospheric carbon dioxide dissolution excluded; 2 mg dm^{-3} FA (N and S binding included); 10 mg dm^{-3} HFO; organic adsorption included)

trace metal adsorption. This is especially noticeable at low concentrations where silicate determines the speciation of the low affinity sites.

The concentration used for the model organic adsorbent, TIPP, also affects the speciation patterns significantly. To observe the effect of this the concentration was varied from 10 nmol dm^{-3} (2 μg dm^{-3} organic matter) to 10 mmol dm^{-3} (2 g dm^{-3}). The concentration of hydrous ferric oxide was kept constant at 10 mg dm^{-3} for these calculations while the concentration of fulvic acid was also fixed at 2 mg dm^{-3}. Fixing the dissolved organic matter (FA) while scanning the adsorbing organic matter (TIPP) may not be accurate, but the experiment was run to elucidate the effect of TIPP concentration without increased complexation resulting from increased fulvic acid concentration. As can be seen from figure 6.17.4 increasing the concentration has the effect of changing the surface charge density from being positive at low organic matter concentration to negative at high concentrations. The reasons for this may be seen in figures 6.17.2 and 6.17.3.

As the TIPP concentration increases, the percentage of low affinity sites bound by it increases thus imparting a nett negative charge. Figure 6.17.1 indicates the effect of TIPP concentration on trace component adsorption. Adsorption is reasonably constant at low concentrations (TIPP < 2 μmol dm^{-3}) because TIPP does not bind any of the adsorption sites significantly in this concentration range. Noticeable is the strong decrease in the adsorption of anions as a result of electrostatic repulsion. The decrease in cation adsorption is because increased TIPP concentration increases the significance of magnesium and calcium adsorption to strong site speciation thereby decreasing the free concentration. This in turn lowers trace metal adsorption. It was observed that trace metal adsorption by the weak sites was not significantly affected by the concentration of organic adsorbant. In fact the percentage bound by weak sites increased slightly through the concentration range investigated because less metal was bound to the strong sites. Most notable was the effect on lead speciation. 98.9% and 0.4% was found to be

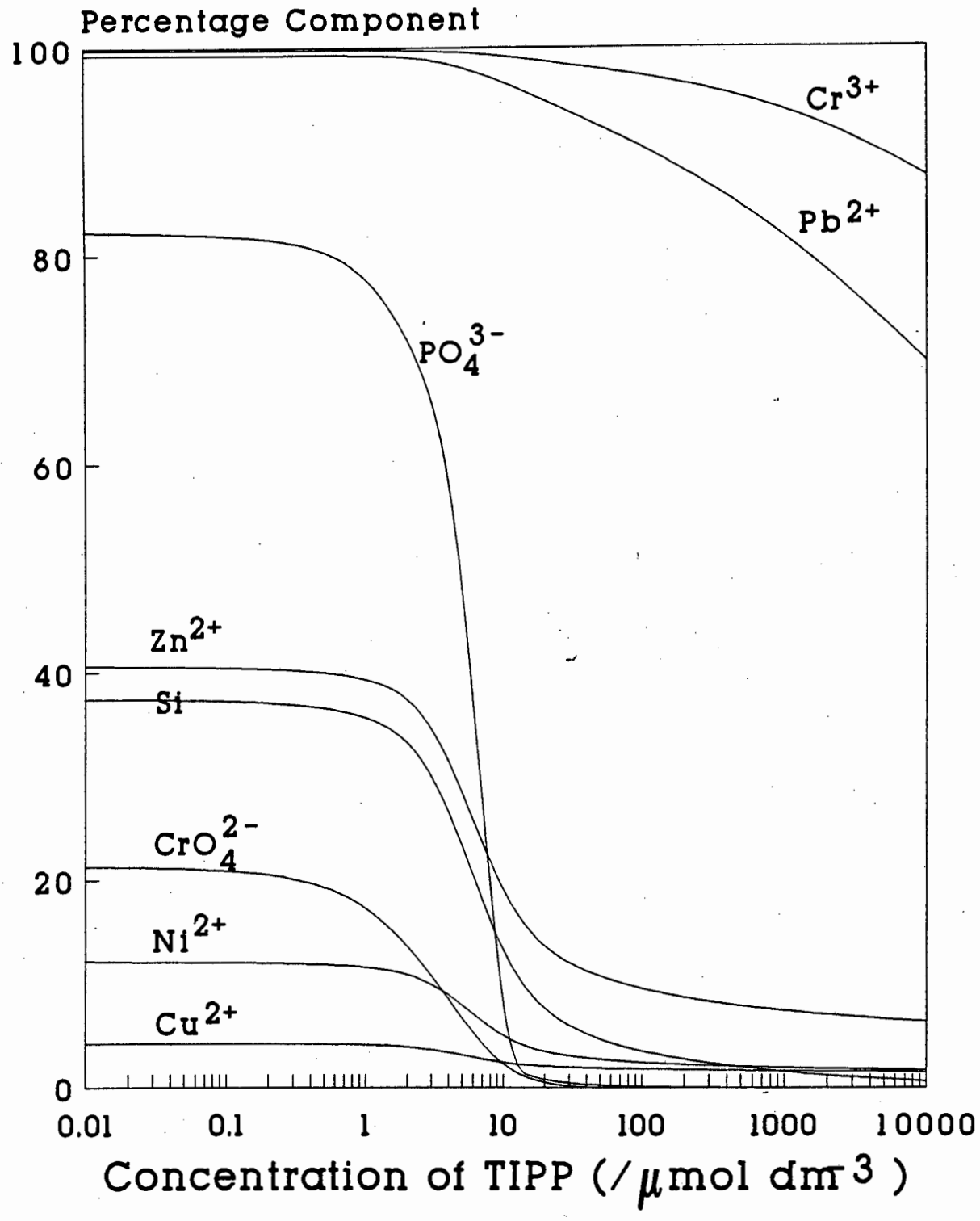


Figure 6.17.1: The effect of the organic adsorbent,TIPP, concentration on the adsorption of selected components (ionic strength = 0.7 mol dm^{-3}; 25 °C; atmospheric carbon dioxide dissolution excluded; 2mg dm^{-3} fulvic acid (N and S binding included); 10 mg dm^{-3} HFO; organic adsorption allowed)

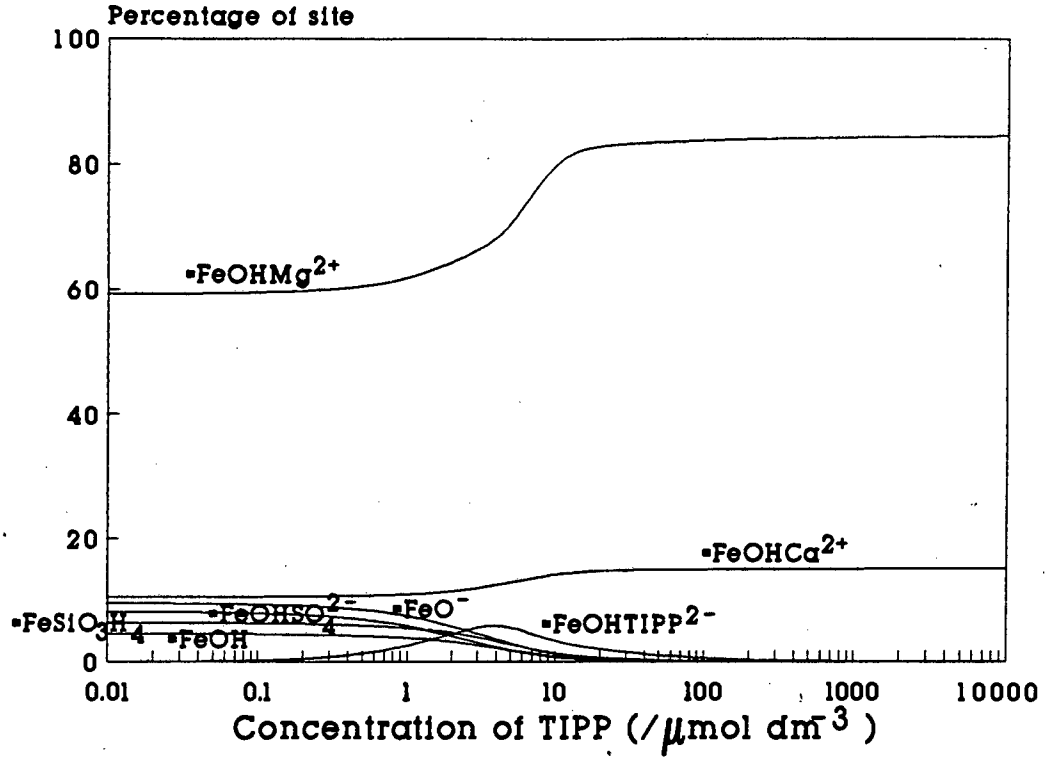


Figure 6.17.2: The effect of TIPP concentration on the speciation of the high affinity sites (ionic strength = 0.7 mol dm^{-3}; 25 °C; atmospheric carbon dioxide dissolution excluded; 2 mg dm^{-3} FA (N and S binding included); 10 mg dm^{-3} HFO)

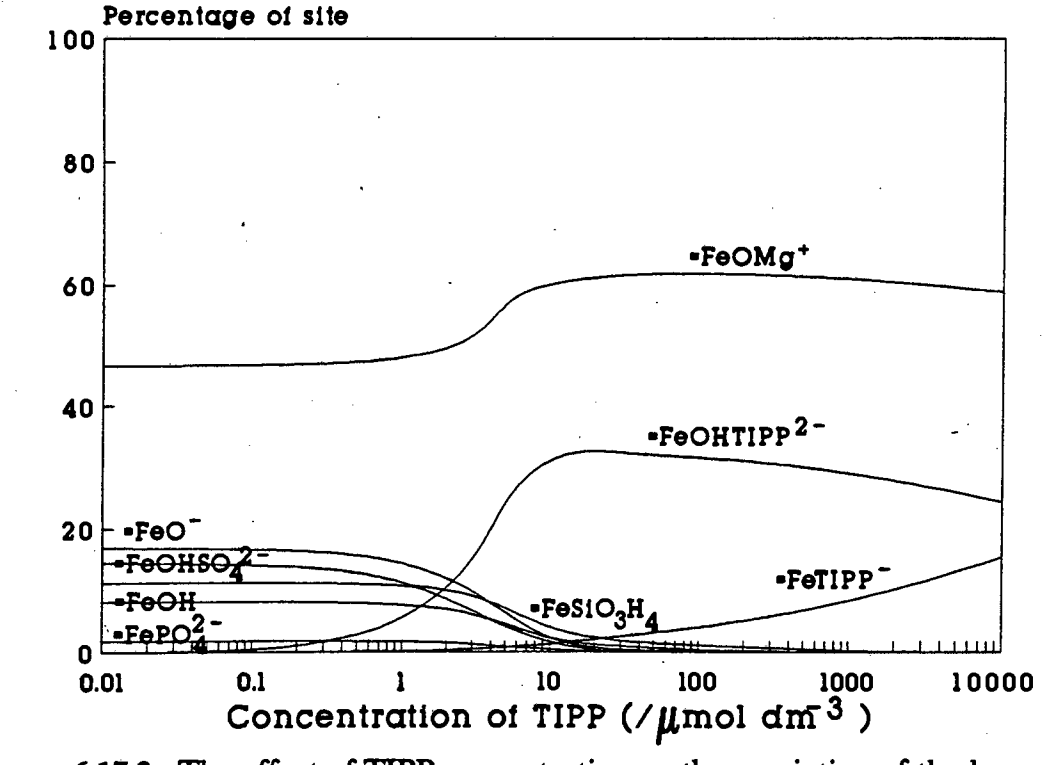


Figure 6.17.3: The effect of TIPP concentration on the speciation of the low affinity sites (ionic strength = 0.7 mol dm^{-3}; 25 °C; atmospheric carbon dioxide dissolution excluded; 2 mg dm^{-3} FA (N and S binding included); 10 mg dm^{-3} HFO)

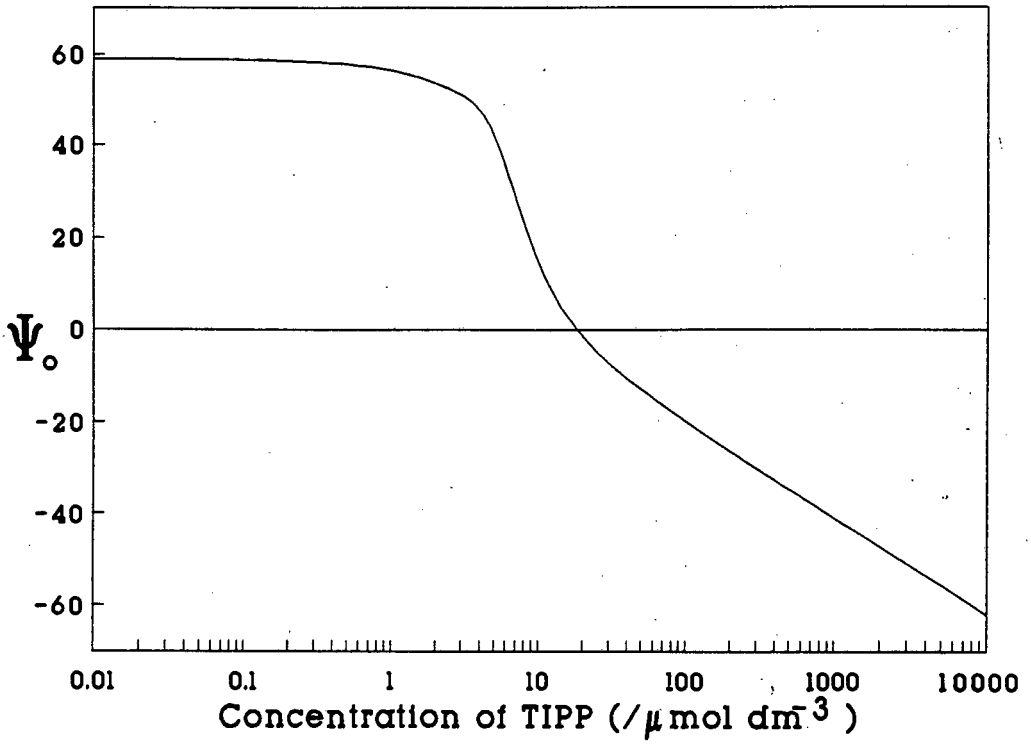


Figure 6.17.4: The effect of TIPP concentration on the surface charge density (ionic strength = 0.7 mol dm^{-3}; 25 °C; atmospheric carbon dioxide dissolution excluded; 2 mg dm^{-3} FA (N and S binding included); 10 mg dm^{-3} HFO)

bound to the strong and weak sites respectively at low concentrations of organic matter ([TIPP] = 10 nmol dm^{-3}). This changed to 52.6% and 16.4% respectively at [TIPP] = 10 mmol dm^{-3}.

Since the choice of the adsorption constant for Mg^{2+} on to the high affinity site was empirical, it was also decided to observe the effect of varying this constant. Lowering it increases trace metal adsorption and the nett negative charge. The effect though was small (< 10% on the adsorption of any trace metal) for a decrease of 0.4 in log K for the adsorption of magnesium to the high affinity sites. The effect on anion speciation was negligible since these bind primarily to the low affinity sites. It should be noted that magnesium adsorption cannot be ignored totally. Magnesium and calcium adsorption suppresses transition metal adsorption, both by lowering free surface site density but also by increasing the positive charge on the surface and thus electrostatic repulsion.

6.3 COMPARISON OF THE MODEL RESULTS WITH EXPERIMENTAL FINDINGS

A significant experimental result that agrees with the prediction of the model is the observation by Batley and Florence [Flo76] that 40 to 80% of dissolved lead is associated with colloidal inorganic particles. This is indicative of the adsorption of lead onto such particles without the mediation of organic matter. The high adsorption of lead predicted by the model is thus heartening.

Further indication of the strong affinity of lead for solid particles is the disequilibrium observed between dissolved ^{226}Ra and ^{210}Pb concentrations in deep water [Cra73, Noz76, Noz86, Kad87]. ^{210}Pb results from the decay of ^{226}Ra. However, in the deep ocean the concentration of ^{210}Pb is 50% depleted with respect to the parent ^{226}Ra. The dissolved concentration of ^{210}Pb is lower than one would expect from simple radioactive

decay and this would indicate significant adsorption [Cra73, Noz86]. Benoit et al. [Ben94] also found that lead was present primarily associated with particulate matter rather than dissolved in a study of six Texas estuaries. This was particularly noticeable at the seawater end.

Bruland and Franks [Bru83c] observed that in surface waters of the Sargasso Sea the percentage of trace metals (Cu, Ni, Zn and Cd) associated with particles was much lower than the dissolved fraction. This is in line with the model findings under conditions of low solid content as would be experienced in the open ocean.

In surface waters less than 10% of copper, nickel and cobalt are associated with suspended solids [Mur88]. This is in line with the finding of the model that these metals are weakly adsorbed at natural solid levels. However, scavenging profiles have been observed for lead, copper [Boy77], nickel [Bre79] and cadmium [Bre79]. This means that these metals are enriched in deep water with respect to the surface and indicates that trace metals are transported by adsorption on to solid particles. Thus some adsorption must occur. The exact degree, though, is determined more by the kinetics and rate of descent of the solid particles which is beyond the scope of the model.

The scavenging of copper is complicated though in that the adsorption of copper onto solid particles is not dominated by inorganic adsorption but rather by the complexation of copper by the organic coating on solid particles. The model agrees with the results of Chester et al [Che88]. Chester et al. found that about 50% of the total copper in suspended material from the Atlantic Ocean was organically associated. Davis also discovered that copper was more likely to bind to adsorbed organic material than surface hydroxyls on alumina [Dav84]. The model indicates that organic complexation far outweighs inorganic adsorption at natural solid levels. This result can be placed in context when the adsorption of zinc is considered. Zinc is observed to be more strongly

adsorbed than copper even though copper has the stronger adsorption constants. This is because the complexation of copper by organic ligands reduces the free copper concentration radically when compared with zinc.

Hirose [Hir90] suggests that the chemical states of metals associated with particulate matter reflects those of the dissolved fraction of the metal. Thus, although the model does not study the interaction of copper with organic matter adsorbed onto solid particles, there will be a significant association of copper with this organic matter. However, because the concentration of particulate organic matter is about 100 times lower than the dissolved level [Sug88, Hir90], the interaction of copper with adsorbed organic matter will be much smaller than the complexation of copper by dissolved organic matter [Hir90].

Berner first observed the removal of phosphate from seawater by iron oxides formed volcanically at the East Pacific Rise [Ber73]. This adsorption of phosphate on to hydrous ferric oxide is also supported by evidence that there is a distinct correlation between phosphate and suspended, non-dendrital iron, found in the Baltic Sea [Ber89]. The high phosphate content of suspended particles also indicates phosphate adsorption [Fil81, Ing91]. The association of phosphorus with iron is the result of the adsorption of phosphate onto iron oxyhydroxides rather than the co-precipitation of apatite [Ber89]. The adsorption of phosphate as predicted by the model is qualitatively in agreement with these results. However, none of these experimental studies quantify phosphate adsorption. Of importance is the affect of natural organic matter which suppresses phosphate (and other anion) adsorption significantly in model predictions.

Silicate has been observed to coprecipitate with natural ferrihydrite [Car81]. This results from the strong adsorption of silicate. It should be noted that the model predicts the same effect in the marine environment. Mackin [Mac89] reports that iron can compete with

aluminium for the removal of silicate from solution. Evidence points towards Fe-Si coprecipitation although the situation is complicated in that Fe-aluminosilicates are actually observed [Mac89].

The use of hydrous ferric oxide over goethite is justified by the observation that the adsorption process suppresses the ordering of natural ferrihydrite and the resultant crystallization [Car81]. This is particularly true of coastal waters where precipitates have not aged. However, in a previous model of the adsorption of seawater components on to goethite it was observed that the surface sites were primarily bound by magnesium and sulphate [Bal82b]. Balistrieri and Murray [Bal82b] did not take into account the adsorption of organic matter. Only one surface site was considered on goethite. The speciation pattern found by these authors is similar to the pattern observed for both sites in this study where organic matter was excluded.

CHAPTER SEVEN

THE MIXING OF A FRESHWATER STREAM AND SEAWATER

7.1 INTRODUCTION

One of the ecological zones most sensitive to the effects of pollution is the estuarine region. Consequently it was decided to develop chemical models for the freshwater end, as well as the various intermediates that occur in estuaries between fresh and seawater. This would represent the various states of mixing of fresh and seawater. The effect of adsorption on the speciation of trace metals under estuarine conditions has been studied by Morel et al. [Mor90]. This study was used as the basis for setting up the present mixing model.

This was accomplished as follows:

1) Firstly seven new databases were set up for the ionic strengths 0.0, 0.1, 0.2, 0.3, 0.4, 0.5 and 0.6 mol dm^{-3}. The correction procedures for literature formation constants were the same as those used in setting up the database for seawater. The databases can be found in Appendix 1.2.

2) Concentrations of the components for a freshwater river system were obtained by reviewing the literature [Whi81, Wat82a, Wat82b, Wat82c, Wat82d, Wat82e, Wat82f, Wat83, DuP85, Tal85, Wat85, Mor90]. The system was developed for South African rivers and an important source of information was the study done by Du Preez [DuP85]. It should be noted that the variations observed in major component concentrations are much greater than the variations observed in seawater. The concentrations of the components of the freshwater stream used in the model are listed in Table 7.1. The concentrations of the trace metals are in some cases higher than normally observed in natural waters but were set to the same values as in the study of Morel et al. [Mor90] for comparative purposes. Various assumptions were then made regarding the mixing system to facilitate modelling.

TABLE 7.1 The constituents used to model freshwater and their total concentrations

Major ion	Concentration μmol dm^{-3}	Trace component	Concentration nmol dm^{-3}
Na^+	325	PO_4^{3-}	800
Mg^{2+}	250	Br^-	250
Ca^{2+}	250	Mn^{2+}	300
K^+	40	Cu^{2+}	100
Cl^-	200	Zn^{2+}	100
F^-	6	Ni^{2+}	100
$SiO_2(OH)_2^{2-}$	250	Cr^{3+}	100
SO_4^{2-}	100	Co^{2+}	10
NO_3^-	10	Pb^{2+}	2
$B(OH)_4^-$	1	Cd^{2+}	1
CO_3^{2-} ¶	610	Hg^{2+}	0.5

pH = 7.0

HFO = 100 mg dm^{-3}

Alkalinity = 500 μmol dm^{-3}

¶: calculated from alkalinity

3) The pH of the river system was set much higher (at 7.0) than that used in a previous model system (pH = 6.0) [Mor90]. This was to accurately reflect the situation that South African rivers are more basic than their American counterparts. Du Preez [DuP85] and the other studies cited by him [Keu74] found the average pH of South African rivers to be about 7.0.

4) The concentration of the trace metals in the freshwater stream was set higher than that observed in rural areas; thus making the model more applicable to urban regions. This would gives some insight into the effect of anthropogenic input and pollution.

5) A solid content of 100 mg dm^{-3} was assumed for the freshwater and 10 mg dm^{-3} for seawater. Hydrous ferric oxide was used to model this solid. An organic ligand was again added to allow the solid particles to have a negative nett surface charge. The organic matter concentrations were 10 mg dm^{-3} in freshwater and 2 mg dm^{-3} in seawater. These concentrations are the same as those used by Morel et al. [Mor91].

6) Furthermore a different fulvic acid model was developed for the freshwater system. This was using the input data for Suwannee River fulvic acid and can be found in Table 3.3. This model has been discussed in detail in Chapter Three. The resulting model ligand concentrations can be found in Table 3.4. Note that the freshwater fulcic acid has a much lower nitrogen content than its marine counterpart. Its aromaticity is also far higher than the marine fulvic acid's. The concentration of fulvic acid used was 10 mg dm^{-3} in freshwater and 2 mg dm^{-3} in seawater.

7) The dissolution of carbon dioxide was excluded from the model as this resulted in a total carbonate concentration which was below that observed in reality in freshwater systems. At a pH of 7.0 and an ionic strength of 0.0 mol dm^{-3}, dissolution of atmospheric carbon dioxide fixed the free carbonate concentration at 22.4 nmol dm^{-3} which in turn determined a total carbonate concentration of

59.0 μmol dm^{-3}. This differs from the concentration observed experimentally (610 μmol dm^{-3} (see section 9)). This indicates that the freshwater system is not in equilibrium with the atmosphere. This is justified because of the lower surface area, extreme turbulence and other carbonate sources (mineral) found in freshwater river systems. Furthermore the influence of biological activity is known to significantly disturb the carbonate/carbon dioxide equilibrium [Mor83b]. The model would thus represent the rapid mixing of the fresh and seawater systems [Mor83b].

8) The mixing of the two systems was assumed to be conservative. That is at ionic strength I the concentration of any given component is given by

$$C(I) = IxC(0.7)/0.7 + (0.7-I)xC(0)/0.7$$

where C(0) and C(0.7) represent the concentrations in fresh and seawater respectively. The effect of this assumption is that all minerals that precipitate are swept along by the current to the regions of higher ionic strength where they may or may not redissolve. This is not always the case [Mor83b]. However, it greatly simplifies the model calculations.

9) The determination of pH in the various mixing stages was far more complicated. pH itself could not be mixed conservatively. Instead the following procedure was employed. Already known was the pH of fresh and seawater, alkalinity in freshwater and carbonate concentration in seawater. The alkalinity in freshwater (0.5 mmol dm^{-3}) was used to calculate the dissolved carbonate concentration (0.61 mmol dm^{-3}). The alkalinity in seawater was calculated from the output at pH = 8.1 and dissolved carbonate concentration of 2.05 mmol dm^{-3}. Total alkalinity in seawater was found to be 2.67 mmol dm^{-3}. Alkalinity and carbonate concentration were then mixed conservatively according to the equation in section 8. The conservative behaviour of alkalinity has been demonstrated by Benoit et al. [Ben94]. The pH of the intermediate stages were chosen as being those pH's which predicted the carbonate concentration to be the same as that

determined by alkalinity. The pH's were 7.63, 8.14, 8.22, 8.22, 8.19, 8.15 for ionic strengths 0.1 to 0.6 mol dm^{-3} respectively. This is depicted graphically in figure 7.1.

10) Aluminium was excluded as it precipitated as a whole host of solid species at the concentration levels found in the literature. This affected the dissolved silicate concentration. However, the effect on the speciation patterns of the other components was negligible. Since the silicate concentration in rivers is highly variable it was decided to model the system with the concentration in Table 7.1 being a dissolved (including adsorbed) silicate concentration. Aluminium was then excluded.

7.2 RESULTS OF THE MIXING MODEL

The results of the mixing of a freshwater and seawater system are presented graphically in figures 7.3 to 7.13. The three curves in the figures represent the logarithms of 1) the total component concentration 2) the dissolved (i.e. not adsorbed or precipitated) concentration and 3) the free aqua ion concentration. Where the gap between the total and dissolved curves narrows, a decrease in percentage adsorption can be inferred except where precipitation (cf. the case of manganese) occurs. A widening of the gap between the dissolved and free ion curves indicates an increase of complexation of the component by dissolved ligands. The percentage of the dissolved fraction that is uncomplexed is seen to decrease. Figure 7.2 indicates the effect of the mixing on the speciation of the hydrous ferric oxide adsorption sites.

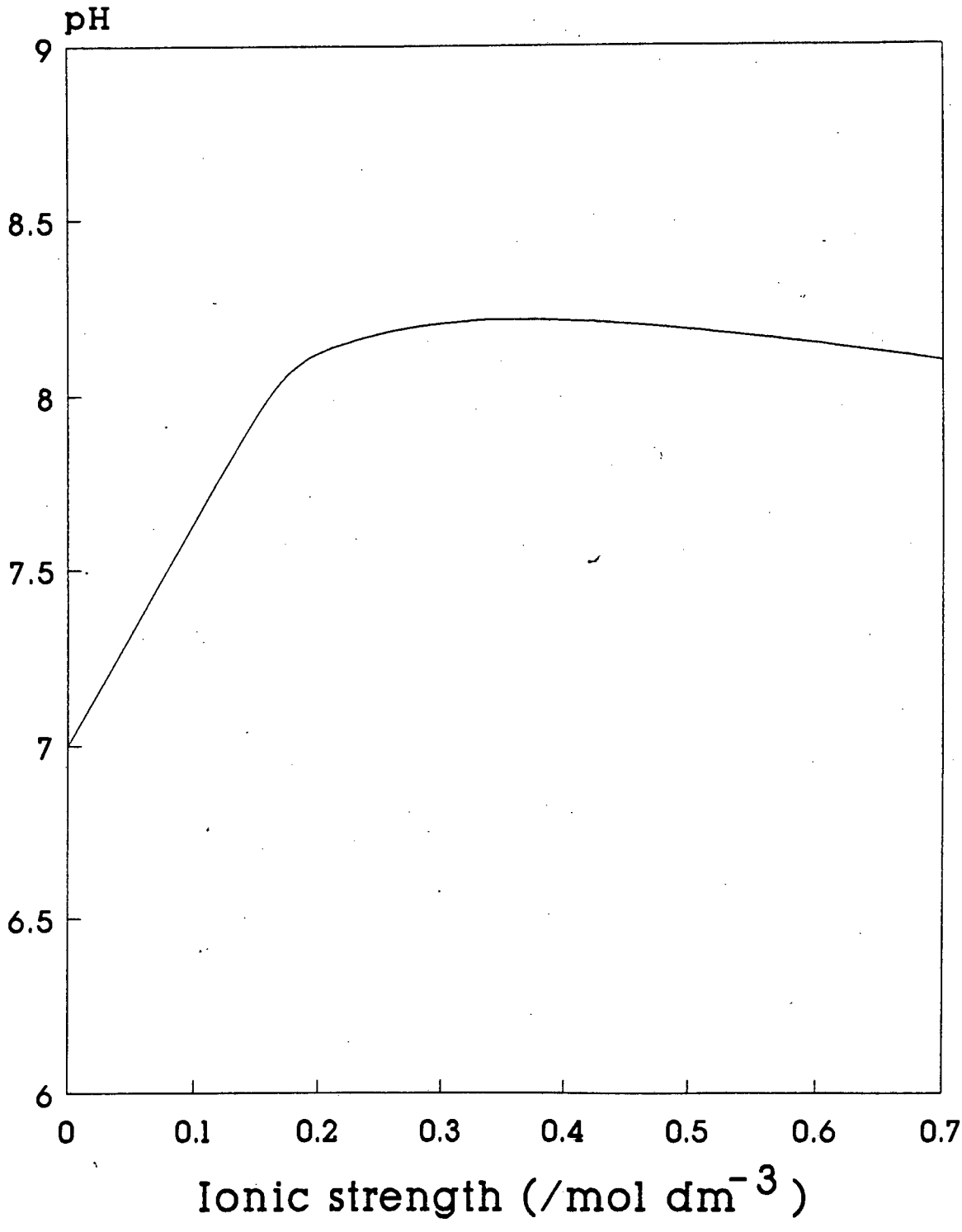


Figure 7.1: The effect of ionic strength on the pH of the solution for the mixing of fresh and seawater.

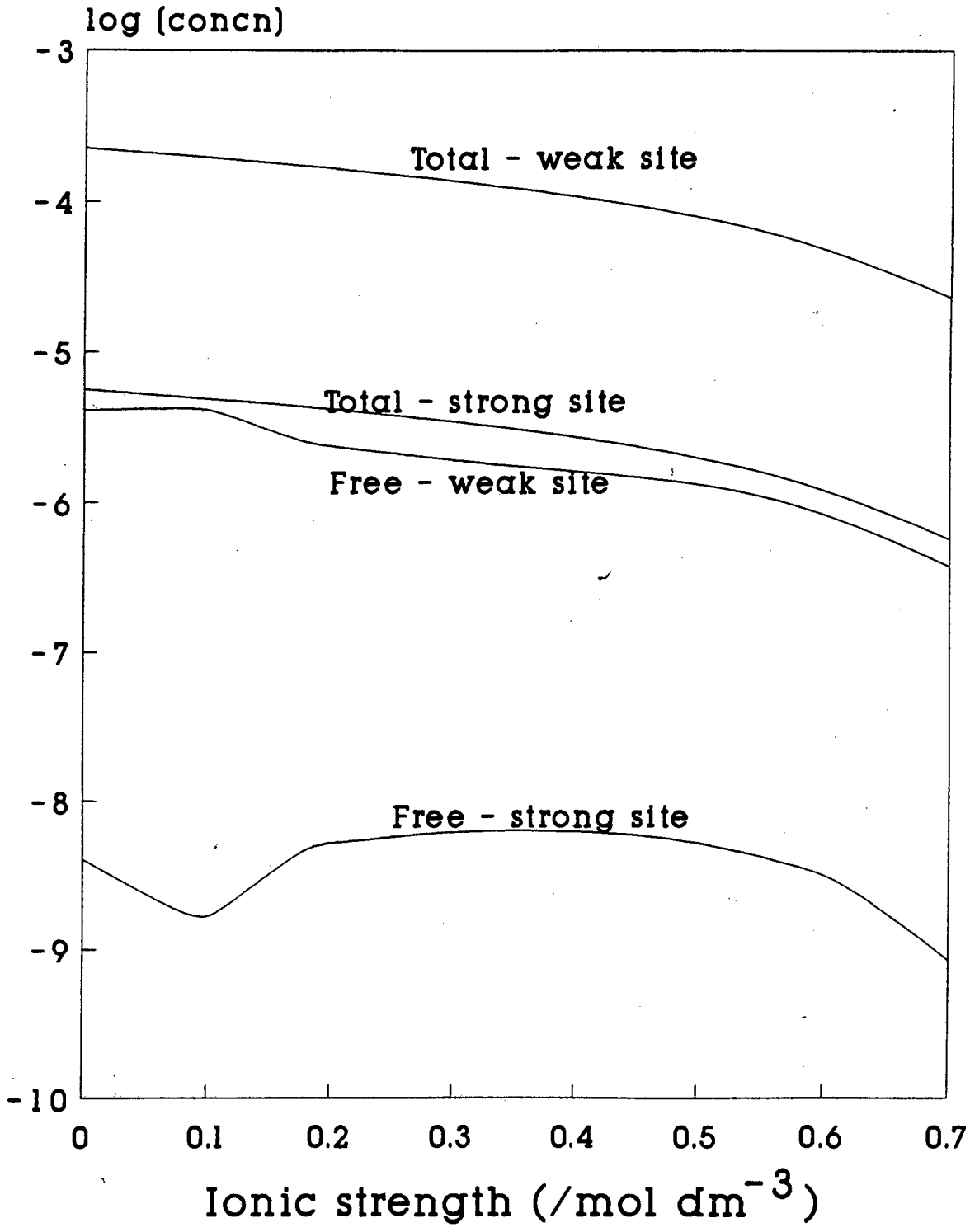


Figure 7.2: The effect of ionic strength on the speciation of the adsorption sites on HFO for the mixing of fresh and seawater.

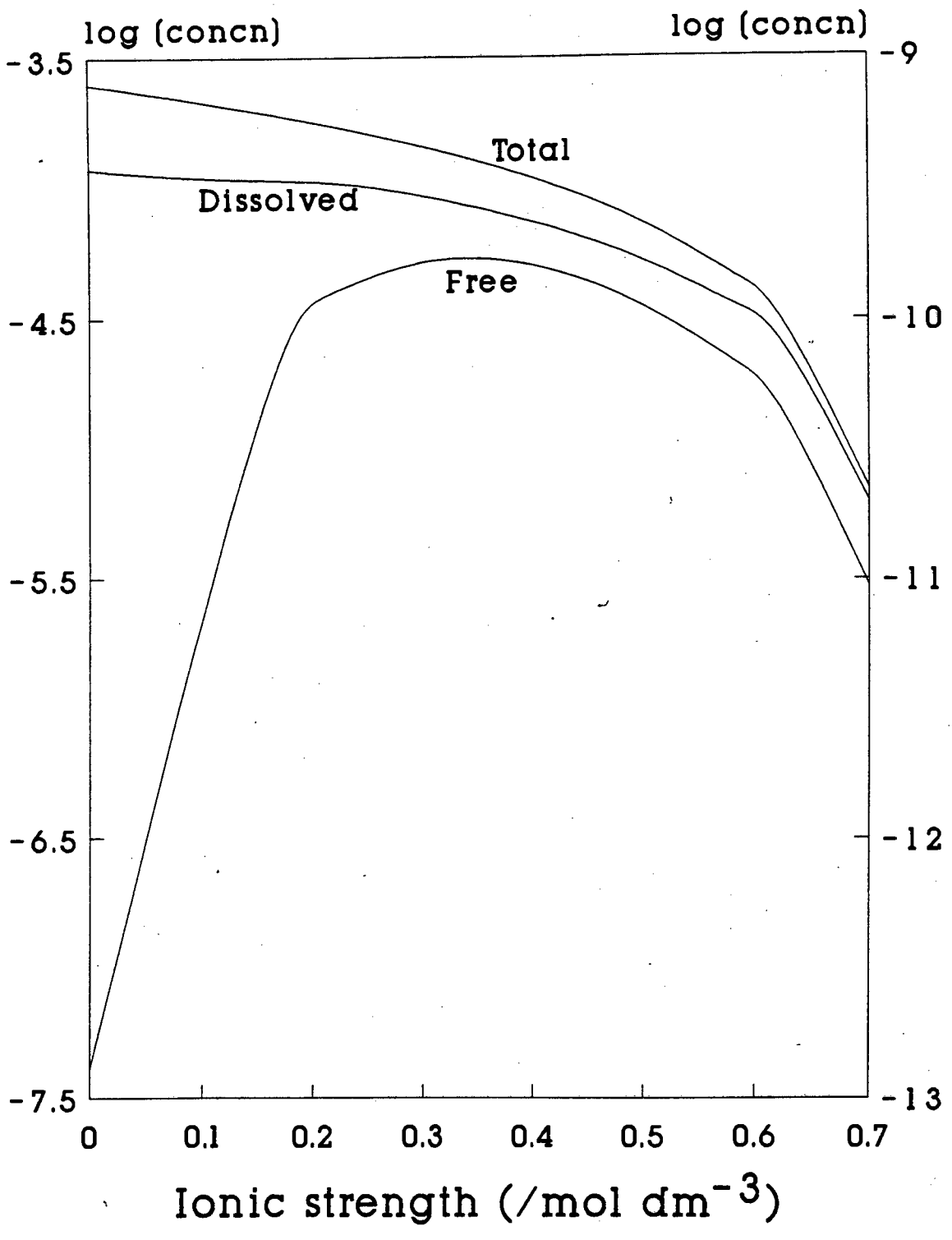


Figure 7.3: The effect of ionic strength on the speciation of silicate for the mixing of fresh and seawater. Free concentration indicated on the righthand scale.

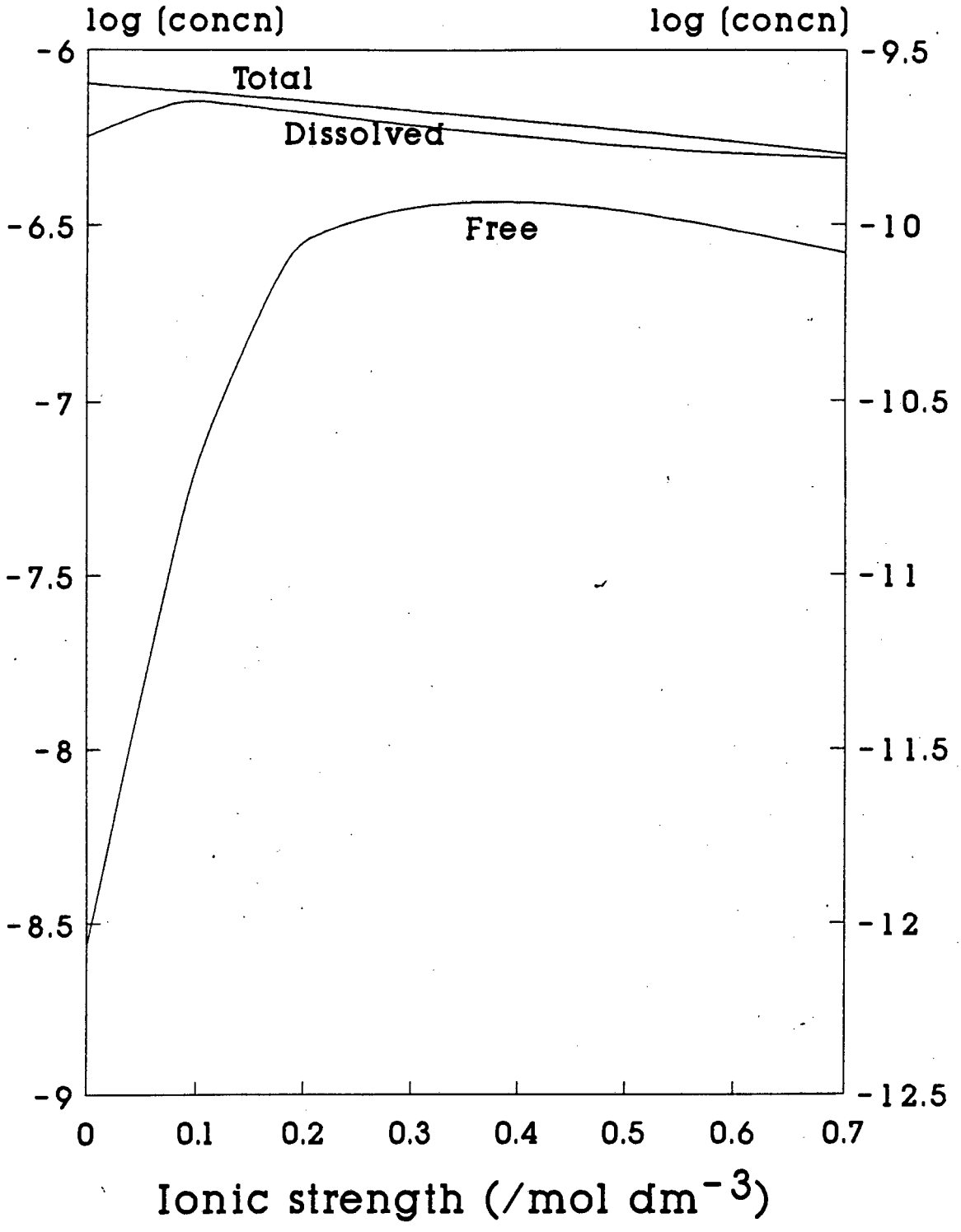


Figure 7.4: The effect of ionic strength on the speciation of phosphate for the mixing of fresh and seawater. Free concentration indicated on the righthand scale.

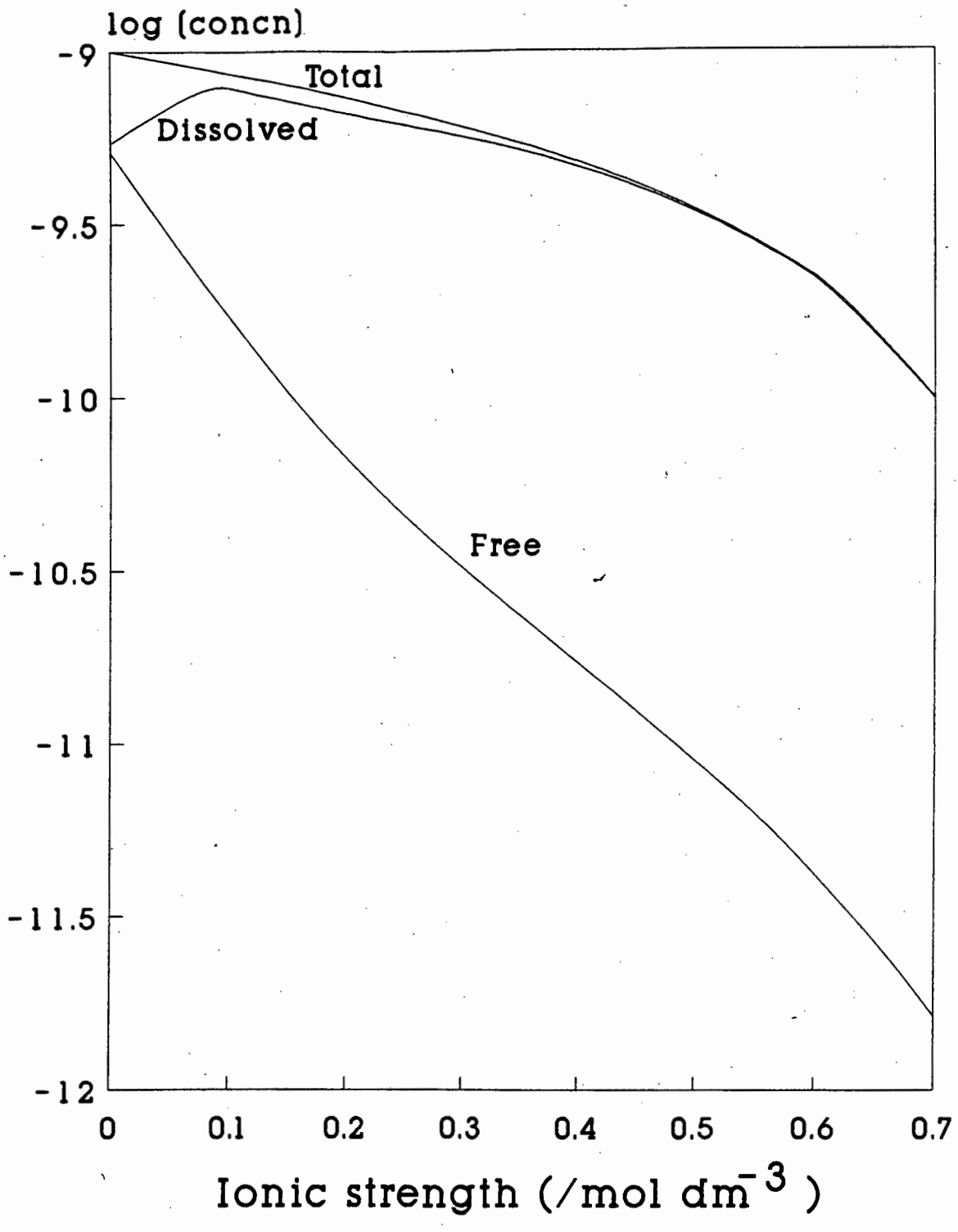


Figure 7.5: The effect of ionic strength on the speciation of cadmium for the mixing of fresh and seawater.

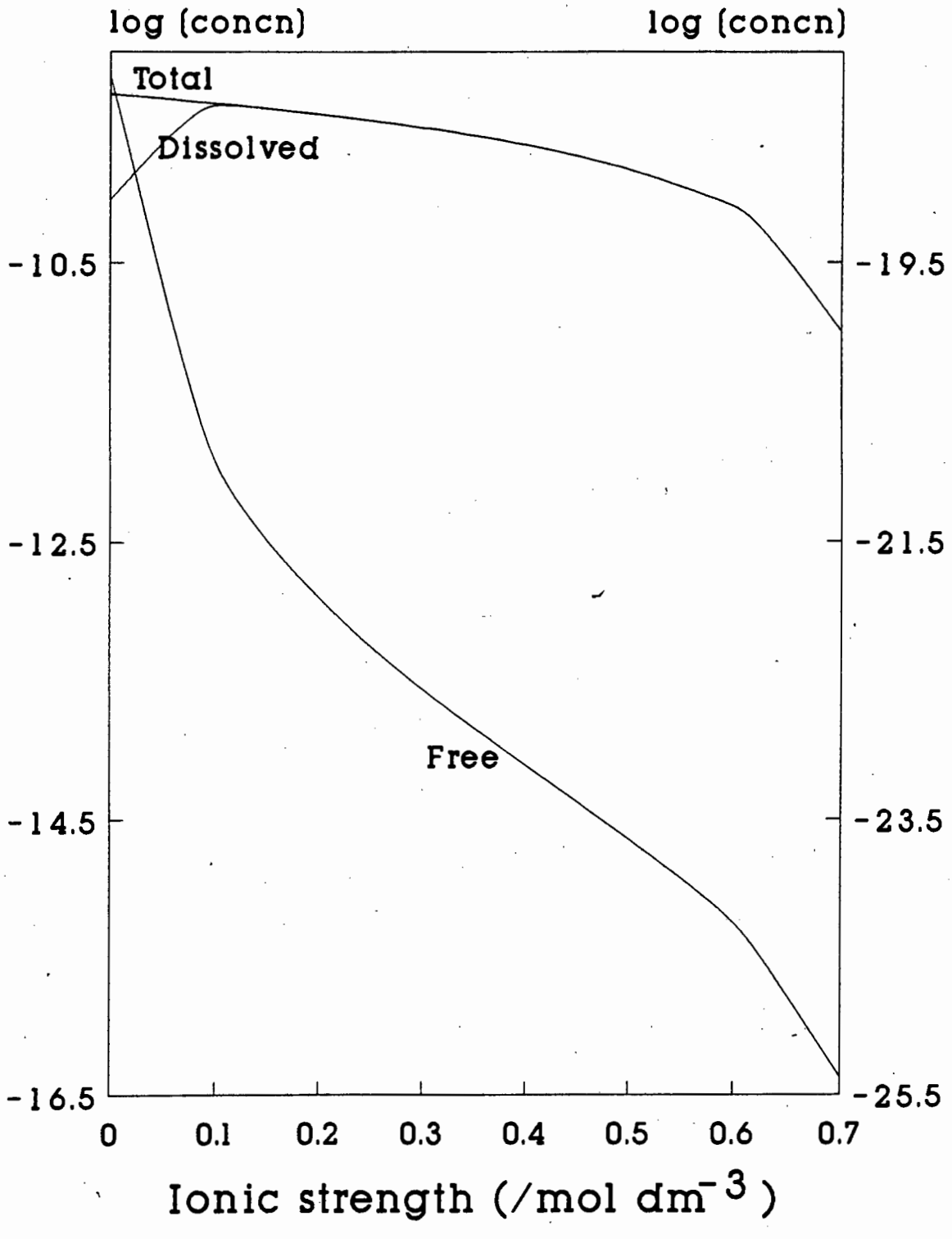


Figure 7.6: The effect of ionic strength on the speciation of mercury(II) for the mixing of fresh and seawater. Free concentration indicated on the righthand scale.

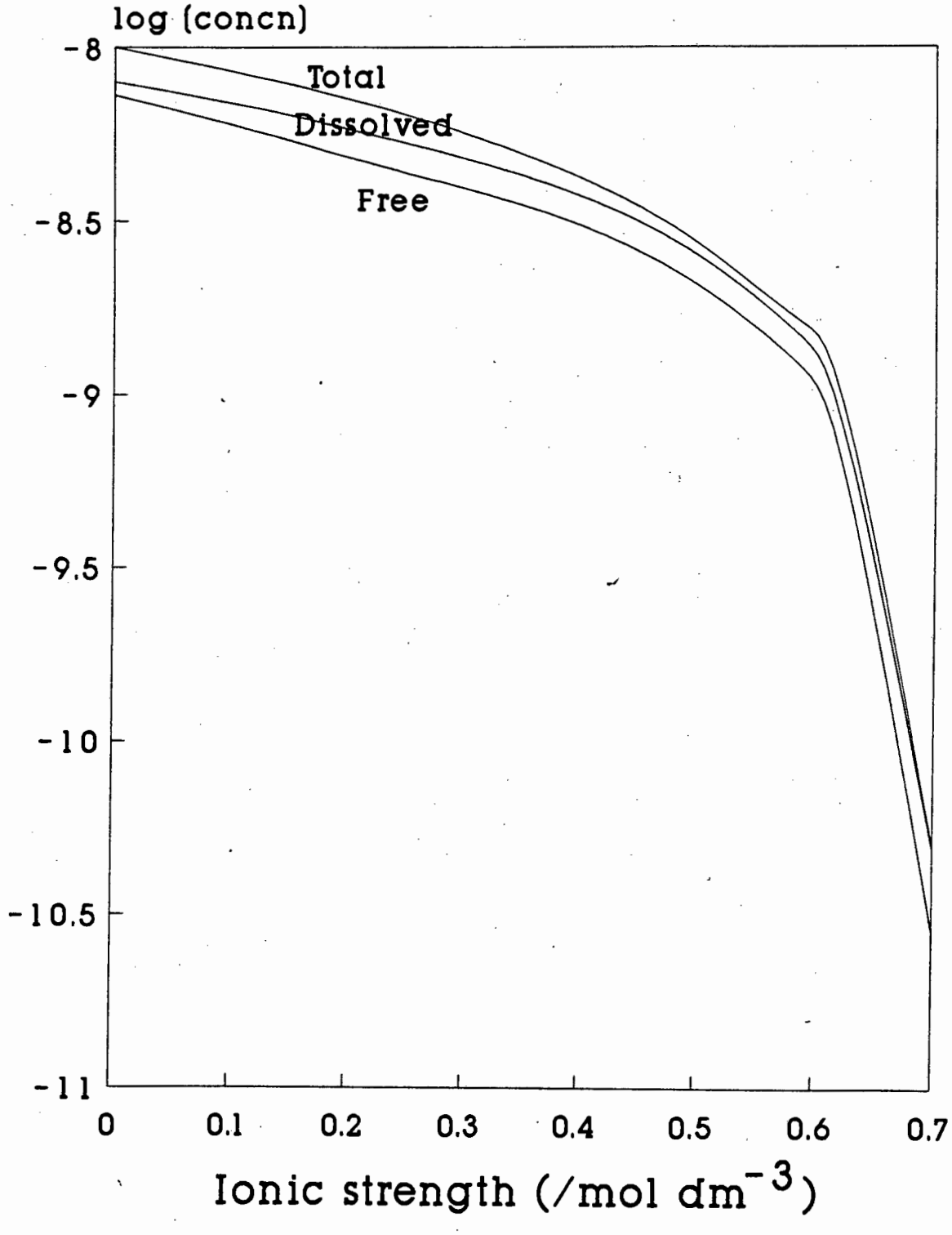


Figure 7.7: The effect of ionic strength on the speciation of cobalt(II) for the mixing of fresh and seawater.

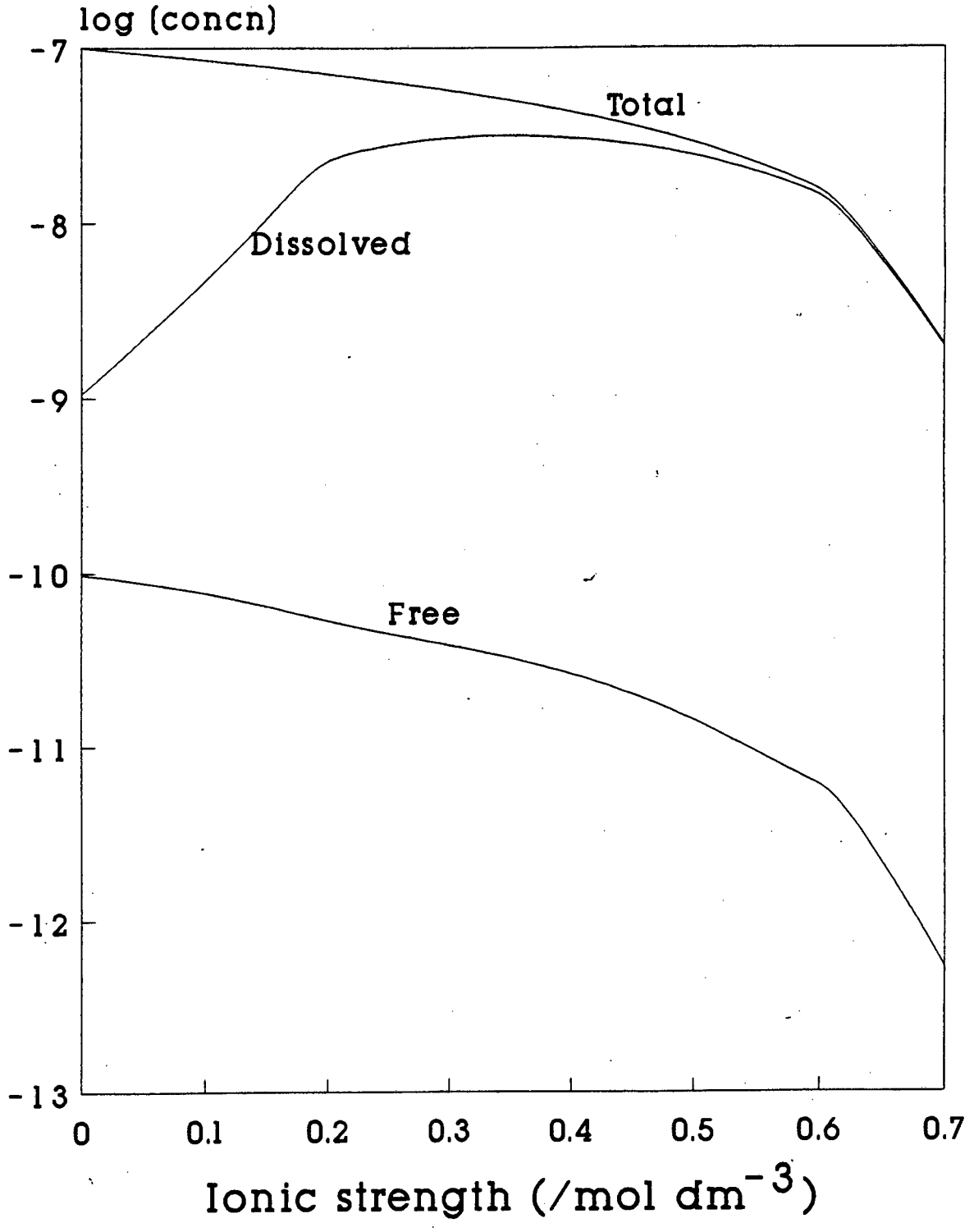


Figure 7.8: The effect of ionic strength on the speciation of copper(II) for the mixing of fresh and seawater.

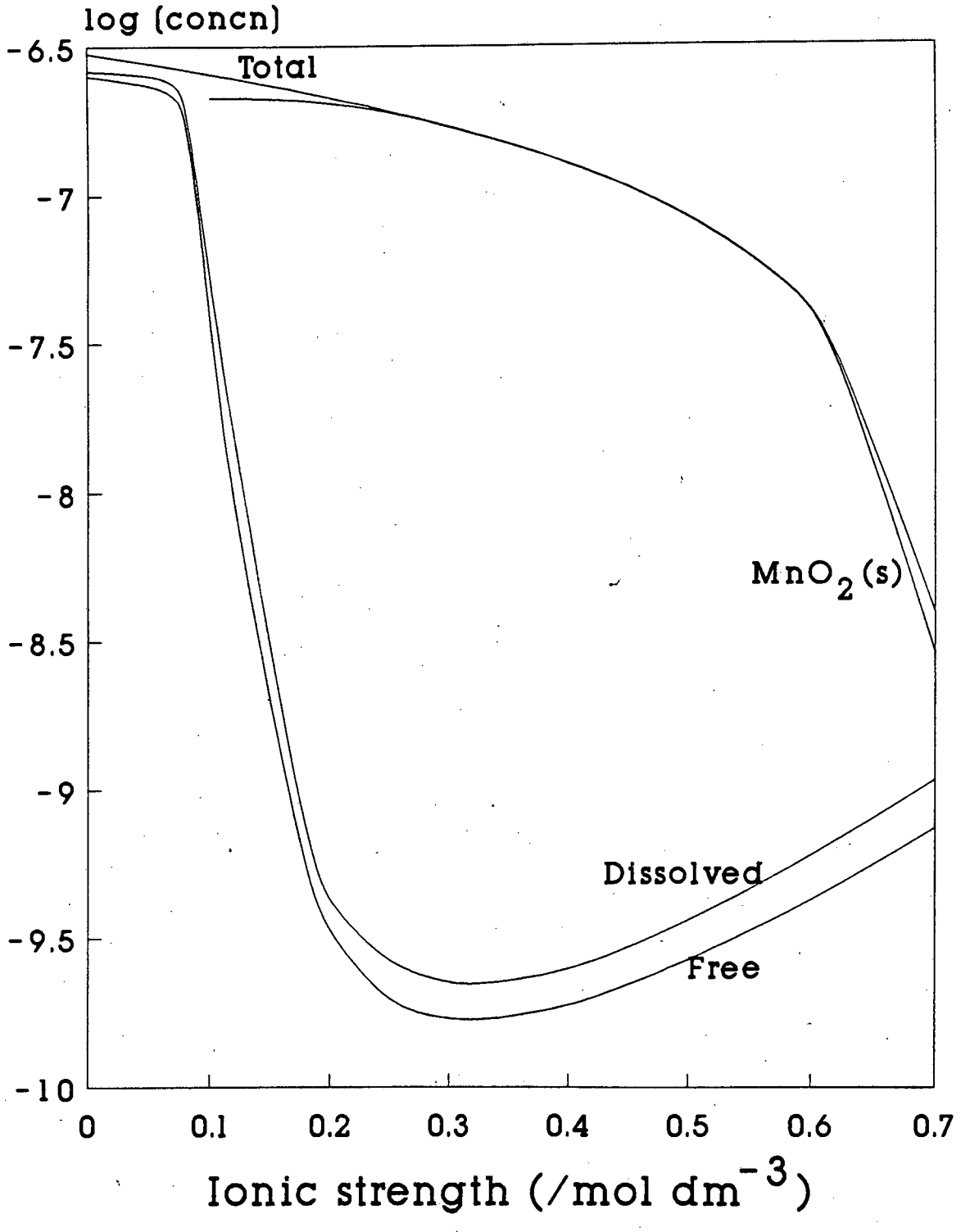


Figure 7.9: The effect of ionic strength on the speciation of manganese for the mixing of fresh and seawater.

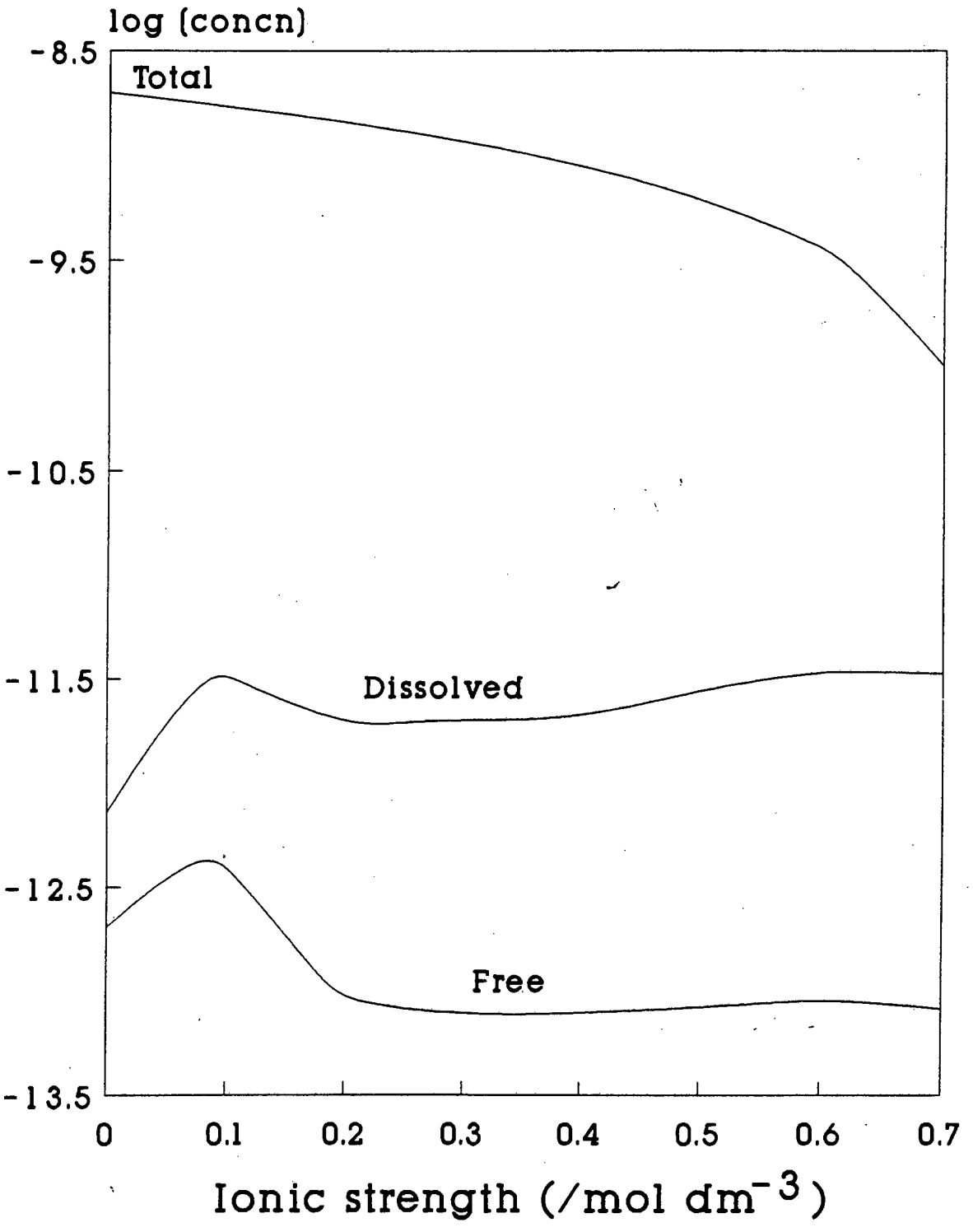


Figure 7.10: The effect of ionic strength on the speciation of lead(II) for the mixing of fresh and seawater.

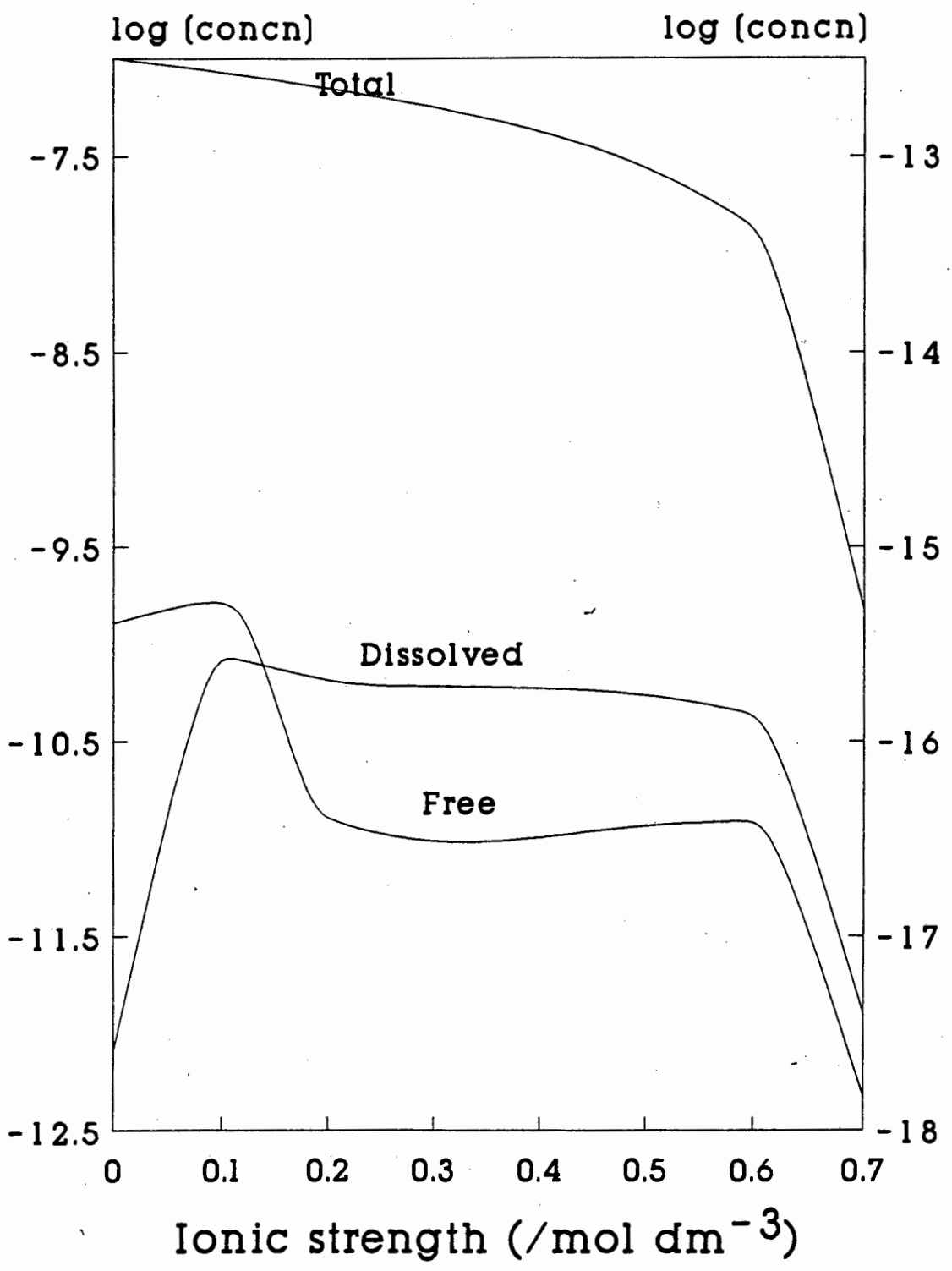


Figure 7.11: The effect of ionic strength on the speciation of chromium(III) for the mixing of fresh and seawater. Free concentration indicated on the righthand scale.

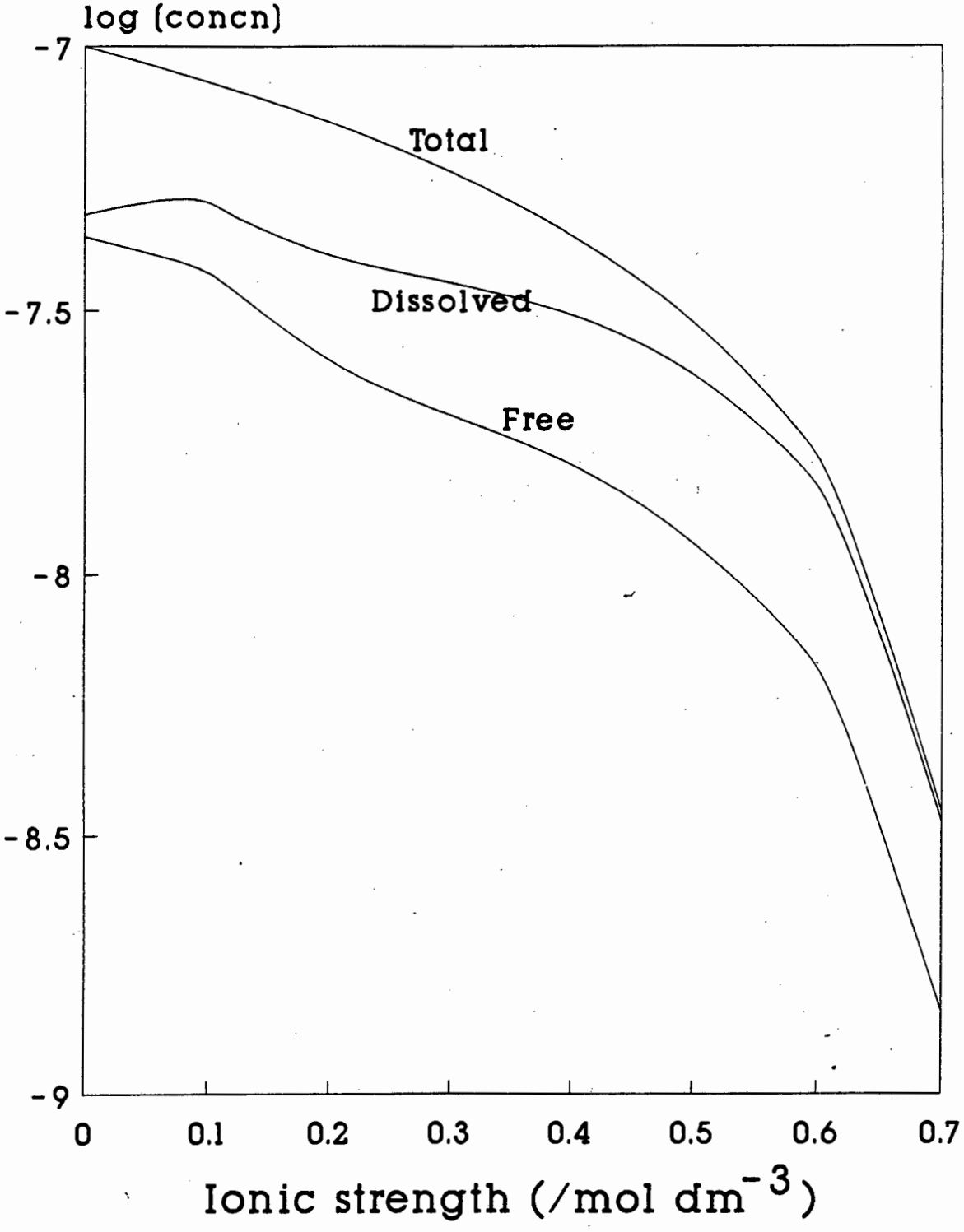


Figure 7.12: The effect of ionic strength on the speciation of nickel(II) for the mixing of fresh and seawater.

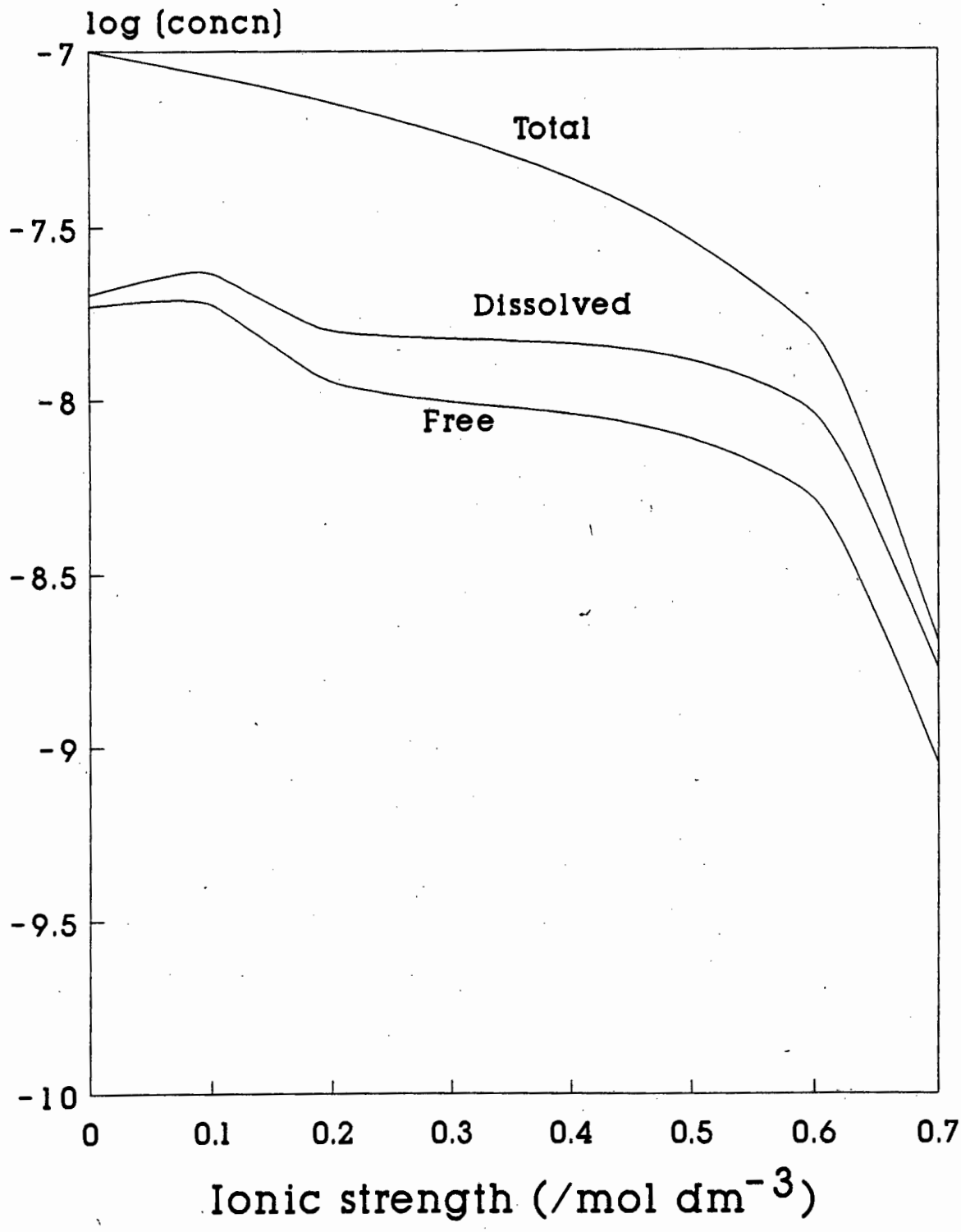


Figure 7.13: The effect of ionic strength on the speciation of zinc(II) for the mixing of fresh and seawater.

The results of the model predictions indicate some interesting effects:

1) The alkali and alkaline earth metals were primarily uncomplexed at all ionic strengths. At higher salinities, sulphate complexation became more significant while in freshwater, a small percentage of Mg and Ca was adsorbed.

2) In freshwater most of the inorganic ligands were uncomplexed. As the ionic strength was increased the complexation by magnesium and calcium increased dramatically for all except chloride and bromide. Phosphate and silicate were strongly adsorbed in freshwater. As ionic strength and concomitantly pH increased these ions were observed to desorb. The increase in pH also brought about a decrease in protonation of these two ions and a resultant increase in free ligand concentration. The increased pH and magnesium concentration had similar effects on the speciation of the model fulvic acid ligands.

3) The trace metals were strongly adsorbed in the freshwater system. A maximum in dissolved concentration was observed in the ionic strength range: 0.05 to 0.15 mol dm^{-3} despite a decrease in total concentration in this range. In the freshwater system most of the residual trace metal concentration that was not adsorbed existed as the free aqua ion. Complexation by acetylacetone and catechol was observed to be significant for copper, nickel, cobalt and mercury. As ionic strength increased, complexation by chloride especially and to a lesser extent hydroxide, sulphate and carbonate increased. Chloride complexation was particularly apparent in the speciation of cadmium and mercury. Copper was complexed by fulvic acid, lead by carbonate and chromium by hydroxide as the ionic strength increased.

4) Manganese precipitated in the range observed as manganese dioxide as the ionic strength increased. Where aluminium was included in preliminary studies, it precipitated as kaolinite at low ionic strengths and as chlorite at higher ionic strengths.

7.3 DISCUSSION OF THE MIXING MODEL

The results observed can be explained as the effect of a number of divergent phenomena occurring simultaneously. Often the result is that conservative behaviour (the percentage speciation pattern is unchanged) is observed. However, the reasons for this behaviour are not that the phenomena occurring in different systems are the same but rather that those that do occur cancel each other out in such a way that no change is observed.

It was observed that the pH of the solution increased as ionic strength increased (Figure 7.1). This was the result of the increase in carbonate concentration and alkalinity as ionic strength increased. However, the pH was observed to have a maximum (8.22) in the ionic strength range 0.3 to 0.4 mol dm^{-3} and then decrease slowly to the pH of seawater. This maximum was somewhat unexpected as the increasing alkalinity should mean an increase in pH. However, there is also the effect of a decrease in ion activity as ionic strength increases. This is reflected in a decrease in the formation constants over the ionic strength range investigated. The primary carbonate species is HCO_3^-. The formation constant for this species is log K = 10.33, 9.74 and 9.54 at ionic strengths 0.0, 0.3 and 0.7 mol dm^{-3} respectively. Thus at constant pH more carbonate is complexed at low ionic strength. Because alkalinity in a system where there are no major cations and carbonate concentration is high is given by

$$[ALK] = 2\,[CO_3^{2-}] + [HCO_3^-] = 2\,[CO_3^{2-}] + 10^K[H^+][CO_3^{2-}]$$

it follows that at constant pH the alkalinity is highest at highest ionic strength as the free ion species is more significant. Consequently the higher alkalinity observed in the seawater endmember does not require as great a pH as might be expected and so the maximum in pH is observed.

The ligand for which the alkaline earth cations have greatest affinity is sulphate. Thus the slight increase in percentage complexation as ionic strength increases is the result of the higher sulphate concentration in the seawater system. Similarly the increase in inorganic ligand complexation by calcium and magnesium is the result of these metals being far more prevalent in seawater.

The speciation patterns of silicate and phosphate may be singled out as being particular in that these anions are strongly adsorbed by hydrous ferric oxide. The decrease in adsorption results from the nett effect of a number of factors. Firstly complexation of the free phosphate ion by calcium and magnesium decreases its free concentration thus decreasing its adsorption. However, this is more than compensated by the decrease in protonation of these ligands. More significant effects are the direct effects of pH and the competitive adsorption of magnesium and calcium on the adsorption process. Firstly an increase in pH has the effect that the adsorption of anions is decreased. This is because the sorption reactions for anions involve the simultaneous adsorption of hydrogen ions. Increasing the pH in freshwater was observed to decrease anion sorption. The higher concentration of calcium and magnesium in seawater means that a greater concentration of these ions is adsorbed as the ionic strength increases (the model approaches seawater). This results in a decrease in the number of available sites available for adsorption and other components are adsorbed less. This effect is much more pronounced for the trace metals. Note that the effect of an increase in the electrostatic attraction of anions caused by the adsorption of these cations is very insignificant.

The most significant result observed for the trace metals is the increase in the dissolved concentration in the estuarine region. This is despite a decrease in the total trace metal concentration.

This result may be rationalized by figure 7.2 which indicates the effect of ionic strength on the speciation of the adsorption sites on hydrous ferric oxide. Firstly the total concentration of each site decreases because of the decrease in solid content as the sea is reached. However, more significant is what happens to the free site concentrations as this determines the adsorption. The free site concentration for the high affinity (strong) adsorption site has a very interesting and very unexpected pattern. The concentration of magnesium changes by 1.5 log units from ionic strength 0.0 to 0.1 mol dm^{-3}. The rapid increase in magnesium concentration far outweighs the decrease in the adsorption constant of magnesium onto the strong site (Δ = -0.34). This together with the increase in calcium concentration decreases the free strong site adsorption. As the ionic strength increases to 0.2 mol dm^{-3} the free strong site concentration increases again, the change in magnesium concentration from 0.1 to 0.2 mol dm^{-3} is now 0.3 log units while the change in the adsorption constant is a decrease of 0.14. Thus a decrease in the free strong site concentration would still be expected. However, the adsorption of magnesium onto the strong site is not affected by pH while its adsorption onto the weak site is favoured by a high pH. The pH changes from 7.63 at 0.1 mol dm^{-3} to 8.14 at 0.2 mol dm^{-3}. Thus the adsorption of magnesium onto the weak sites is favoured. The higher concentration of the weak sites means that the adsorption of magnesium here decreases the nett negative charge on the solid surface significantly. This decrease in surface charge decreases the electrostatic attraction of cations and the adsorption of magnesium (and calcium) onto the strong sites is inhibited. Consequently the free concentration of the strong sites increases while that of the weak sites is observed to decrease.

This decrease in the free site concentration of the high affinity site at an ionic strength of 0.1 mol dm^{-3} affects the speciation of trace metals significantly as they are primarily adsorbed to the strong sites. Rapid desorption of trace metals is observed upon the initial mixing of fresh and seawater. By lowering the pH of the freshwater endmember it was found that the adsorption decreased as the sorption of cations is promoted by pH; thus it

was at first expected that adsorption would increase as pH and concomitantly ionic strength increased. However, this was not the case as a result of competitive magnesium sorption. Because the free site concentration of the strong sites increases from an ionic strength of 0.1 to 0.2 mol dm^{-3} some of the trace metals were actually seen to readsorb (zinc, lead, chromium and nickel) although this effect was small. Further effects such as complexation and ionic strength effects served to decrease adsorption still further as ionic strength increased.

The decrease in adsorption was enhanced by changes in the activity of the free aqua ions of the trace metals. As the ionic strength increased these decreased which resulted in lower adsorption. This effect was modelled by the use of lower adsorption constants for higher ionic strength. Thus the importance of the dissolved aqua ion with respect to the adsorbed species is expected to increase as ionic strength increases.

A further effect that decreased adsorption is the complexation of trace metals in seawater. This results primarily from the increase in ligand concentration in seawater. This effect is most pronounced for mercury and cadmium. These two trace metals are strongly bound by chloride which has a low concentration in freshwater but exists in high concentrations in seawater. With most other trace metals a slight increase in the free ion concentration (as a result of desorption) is observed at an ionic strength of 0.1 mol dm^{-3}. With mercury and cadmium this effect is totally swamped by chloride complexation. Increases in carbonate, sulphate and hydroxide (as a result of increased pH) concentration also resulted in increased complexation of trace metals.

The significant increase in copper complexation at the ionic strength of seawater is caused by the complexation of copper by fulvic acid. The increased nitrogen content in marine fulvic acid imparts a much greater complexing ability to marine fulvic acid. The increase in nitrogen-containing ligands as the seawater was entered increased copper

complexation. Furthermore, the pH increases as mixing occurs. The model ligands are in turn deprotonated which increases their free concentration. This further increases complexation. Overall the free copper ion concentration shows conservative behaviour (this curve is parallel to total concentration). However, this is a nett effect of an increase in free ion concentration as a result of desorption and a decrease in free concentration as a result of complexation. This illustrates that quasi-conservative behaviour may result from competing but opposite phenomena. Cobalt also shows conservative behaviour but this is the result of cobalt being weakly adsorbed and weakly complexed. Consequently the speciation of the free ion is directly determined by the total concentration.

The complexation of some trace metals by acetylacetone in freshwater is caused by the much higher concentration of fulvic acid in freshwater. It is most significant for mercury where 1.8% is bound as $Hg(ACAC)_2$. Because no $HgACAC^+$ is included in the model organic complexation may be even higher. This complexation is swamped by chloride complexation in the sea, however.

The precipitation of manganese with increasing ionic strength was rather the effect of the pH increasing as seawater was approached. Note that the results presented are for a pE = 9.1. The model was unable to account for the variations in redox state that may occur in the estuarine mixing region as there was no data available. The minimum in free manganese concentration corresponds with the maximum in solution pH.

Where aluminium was included it was found that its dissolved concentration was limited by the silicate concentration. In freshwater it precipitates out as kaolinite and as chlorite at I = 0.6 mol dm^{-3}. This precipitation limits the dissolved aluminium concentration to below 100 nmol dm^{-3}. Kaolinite precipitates at low pH and chlorite at high pH which explains the effect observed. If both are excluded aluminium precipitates as gibbsite. The precipitation as aluminosilicates is highly dependant on the silicate concentration.

Consequently lower precipitation is observed in the marine environment where the silicate concentration is lower. Where aluminium precipitation is disallowed for kinetic reasons, its speciation is dominated by hydroxide species, especially $Al(OH)_4^-$.

Lead and chromium show the most significant desorption as these trace metals are strongly adsorbed by hydrous ferric oxide. They are readsorbed slightly at I = 0.2 mol dm^{-3} for reasons discussed earlier. The gap between the free and dissolved concentration curves for these two metals is the result of complexation. Lead is complexed by carbonate in seawater (concentration higher than in freshwater) while chromium is bound in hydroxide species. As the ionic strength increases, pH increases and in so doing increases complexation. Analysis of the curves for chromium indicate that complexation decreases slightly again at the seawater end of mixing. This is the result of the slight decrease of pH from 8.22 to 8.1.

Zinc and nickel have intermediate curves in that they are adsorbed more strongly than cobalt but more weakly than lead. They too show desorption in the estuarine region and some degree of complexation. The free concentration of nickel shows semi-conservative behaviour.

7.4 COMPARISON OF THE MODEL RESULTS WITH EXPERIMENT

Comans and van Dijk discovered that the adsorption of cadmium in estuarine systems was determined by changes in the aquatic environment [Com88]. They concluded that this was the combined result of chloride complexation and the change in ionic strength. Both these effects are observed in the model as they cause a decrease in the free Cd^{2+} ion activity. They found that most of the desorption and mobilization occurred at salinity 6-12‰. or I = 0.12 to 0.24 mol dm^{-3}. This is in very good agreement with the results of the model.

Further studies on a tropical estuary [Win88] indicate that desorption of trace metals in the estuarine region is in fact observed. An increase in dissolved concentration upon initial mixing was observed after which the behaviour was reasonably conservative. The maxima in dissolved cadmium concentration is most notable and has been observed in the Amazon plume [Boy82], the Mississippi outflow [Shi91b] and in southeastern United States estuaries [Win88]. Shiller and Boyle [Shi91b], however, could not find evidence of copper desorption but discovered conservative behaviour instead. The results for nickel also appeared conservative although a slight increase in dissolved nickel concentration with salinity was observed in the field results for the Mississippi plume [Shi91b].

A maximum in dissolved trace metal concentration has been observed for manganese and zinc in the Seine River by Boughriet et al. [Bou92]. They ascribe these maxima to interactions between the dissolved phase and solid particulate matter. Boughriet et al. performed speciation calculations for these two metals and observed chloride complexation with increasing salinity as a percentage of the dissolved fraction. The present work agrees with this conclusion. Laboratory studies by Boughriet et al. [Bou92] showed that manganese could be forced to desorb from natural solids by increasing salinity by adding NaCl. However, no investigation was made into the relative importance of electrostatic and complexation (to Cl^-) effects.

A cadmium maximum has also been observed in the Gironde estuary [Elb87]. This effect was also found in the Rhone although it was much less marked. Elbaz-Poulichet et al. [Elb87] propose that cadmium desorption is the first step to occur after which chloride complexation takes place. This would explain why the maxima does not always occur at the same chlorinity. It would depend on the effects of Mg^{2+} and Ca^{2+} adsorption, pH, solid content, etc. in the estuary.

Lebo discovered that particle-bound phosphorus shows a decrease with increasing salinity in the Delaware estuary [Leb91]. He looked in particular at iron-phosphorus interactions. This result is the same as that observed in the model in that phosphate is observed to desorb from suspended particles as a river enters the sea. He goes further to suggest that particles may serve to buffer the dissolved phosphate concentration in estuarine regions.

Fletcher et al. [Fle83] observed the association of trace metals with particulates in the freshwater and saline regions of the Fraser River estuary in Canada. Spectacular was that 60% of lead was associated with particulates in the freshwater region but this decreased to 15% at the sea. Similar but less spectacular results were observed for copper (30% vs 24%) and cadmium (18% vs 3%). This desorption as well as the high adsorption of lead and the low adsorption of cadmium in seawater, is predicted by the model. The model though does not agree with the conclusion that cobalt is highly associated with particulates (81%) in freshwater. Fletcher et al., nevertheless, also observed desorption of cobalt as the water passed into the sea.

Benoit et al. [Ben94] observed the behaviour of trace metals in six Texas estuaries. They observed that at all salinities filter-retained lead far exceeded lead in the filtrate. The reverse was observed for copper. These results are in line with the model where lead is strongly adsorbed onto particulates while copper is bound by organics and would thus go into solution. At low salinities (0.0 mol dm^{-3}) the model predicts that copper is strongly adsorbed but soon desorbs owing to organic complexation. At higher salinities the model agrees with Benoit et al. [Ben94]. Benoit et al. noted the highest fluctuations are in the freshwater endmembers which are the result of seasonal variations in river discharge and solid load. This would naturally affect comparisons as Benoit et al. measured suspended particulate matter concentrations to be about 40 mg dm^{-3} which is less than that used in the model. This would mean the model over predicts adsorption in freshwater.

Erel and Morgan [Ere91] looked at trace metal enrichment in the ocean. They compared the ratio of trace metal concentration in the ocean to that in the crust. Their results were also normalized with respect to iron by plotting the following function

$$\log ([TM/Fe]_{ocean}/[TM/Fe]_{crust})$$

Note that [TM/Fe] indicates the concentration of the relevant trace metal divided by that of iron in the particular sample (viz. ocean or upper crust).

This was plotted against

$$\log (\beta_{MCl}/\beta_{MOH}) - \log (\beta_{FeCl}/\beta_{FeOH})$$

An analogous plot was made against the carbonate formation constants. From these plots Erel and Morgan [Ere91] were able to observe that cadmium in particular was enriched in seawater. This may be ascribed to its strong Cl^- affinity. Enrichment for copper was also observed. This would be ascribed to organic interactions. Lead shows the opposite behaviour which would be the result of adsorption onto carbonate and hydroxide minerals. Although the model predicts some desorption the lead curve shows that lead is still strongly adsorbed in seawater. Erel and Morgan [Ere91] explain that the complexation of metals by chloride and carbonate (organics in the case of copper) lead to desorption of metals from solid particles. Evidence of this is that in river water and soils, trace metals maintain their constant upper crustal ratio to iron whereas in deep oceans they are strongly enriched.

The results of the model are similar to the results of a previous model system [Mor90]. However, some of the effects observed by Morel et al. are not seen here and result from changes in the pH of the freshwater system. Notable is the different result observed for

lead. They observed an increase in dissolved lead concentration up to the ionic strength of seawater. This may be indicative of different complexation constants used in the two models. In general though there is good agreement between the two models which show rapid desorption followed by quasi-conservative behaviour at higher ionic strengths.

The model thus predicts an increase in dissolved trace metal concentrations in the estuarine regions. What is particularly disturbing is the increase in the free aqua ion concentrations of lead(II), zinc(II) and chromium(III) as the free ion is the most biotoxic species for these metals. Thus what may not be a pollution problem in a freshwater system may well become one in the sensitive estuarine region as a result of remobilization.

CHAPTER EIGHT

CONCLUSION

An important measure of the success of this study would be to see if the original objectives have been met. These can be found in section 1.3. The present work provides a detailed model of the speciation of metals in seawater which takes into account the effect of inorganic ligand complexation, organic ligand complexation and adsorption onto solid particles.

The results obtained are meaningless without the thermodynamic database in Appendix 1. The compilation thereof has been rigorous and all significant interaction between cations and anions in seawater have been included.

The extension of the existing RANDOM model for fulvic acid complexation of trace metals is significant. Not only has the program been rewritten to provide a more user-friendly data input system, but the RANDOM concept of trace metal binding has been extended to include binding to nitrogen and sulphur-containing ligands. This extension is of particular importance in light of the fact that binding to the original RANDOM ligands [Mur81] could not explain the binding of trace metals by organic matter in the marine environment. The RANDOM approach has also been validated for protonation and the binding of copper by Suwannee River fulvic acid using existing experimental measurements [Cab88a, Bow89]. Unfortunately the binding of copper to nitrogen-containing sites in a marine system could not be verified as no experimental data exists.

The three aspects of trace metal speciation which have been studied are the binding by inorganic ligands, organic complexation and adsorption processes.

The model shows that under conditions of thermodynamic equilibrium, the inorganic speciation of trace metals is dominated by the ligands: chloride, hydroxide and carbonate. pH is an important factor in the speciation patterns of those metals which form significant hydroxide and carbonate species. The influence of carbonate species was

found to increase significantly as pH increased if atmospheric carbon dioxide was allowed to dissolve. The model also indicates that atmospheric carbon dioxide appears to be very close to equilibrium with dissolved carbonate in seawater. The redox state of the ocean is insignificant except for manganese and to a much lesser extent copper speciation. Mention must be made of chromium (III) which the model predicts to be very insignificant but which has been observed experimentally [Cra78]. This illustrates that kinetics may well be important in the marine environment. Only three trace metals (iron, manganese and aluminium) have their concentrations controlled by precipitation processes. The results of this study are in good agreement with those of previous studies [Tur81, Mot87, Byr88, Mil92].

Organic complexation of copper is predicted to occur through nitrogen-donor sites. Oxygen-containing binding sites are unable to explain experimentally observed complexation of trace metals by dissolved organic matter in seawater. The results predicted by the model for copper binding are in very good agreement with experiment. Surprising is the prediction of the significance of sulphur-containing binding sites for cadmium, lead, zinc, nickel and silver. This prediction, however, is associated with a large uncertainty as a result of large uncertainties in the concentration of sulphur functionalities in marine fulvic acids as well as large uncertainties in the formation constants used in the model.

Adsorption processes are predicted to significantly affect the speciation patterns of most trace metals. The significant lead adsorption predicted is in line with experiment that lead speciation is controlled by adsorption processes. Organic adsorption is observed to suppress trace metal adsorption in seawater by blocking sites available for adsorption.

The processes occurring during the mixing of freshwater and seawater in the estuarine region of rivers have been successfully investigated. Significant are the desorption of

trace metals from solid particles as they enter the sea. This is the result of ionic strength effects but more importantly the competitive sorption of calcium and magnesium ions. The complexation of trace metals by chlorides, hydroxides and dissolved organic material is also likely to increase as rivers enter the sea.

No model is ever a complete reflection of reality but it can viewed to be successful if it provides further understanding of the processes occurring in the system being studied. The model developed so far provides important insights into complexation by marine organic matter as well as estuarine processes.

As new information comes to light, this needs to be included in the model as modelling is an ongoing process. The kinetics of various reactions need to be included in the model when the algorithms to handle these effects are successfully developed.

Marine fulvic acid needs to be characterized more extensively. It was hoped that the extraction of fulvic acid in this study (Appendix 3) would give some insight into trace metal binding sites. Unfortunately the extracted material was not suitable for detailed characterization. Marine fulvic acid needs to be studied for nitrogen and sulphur functionalities as this study predicts that even at low concentrations, these binding sites may be significant. The validation of the protonation of and binding by marine fulvic acid would also be significant. At present, the model has been validated for river fulvic acid but the extension to marine systems is tenuous as nitrogen-containing binding sites are insignificant in river fulvic acid. As one such exercise, the response of copper in real seawater to ASV and copper in synthetic seawater containing all the major inorganic components as well as the significant binding ligands predicted by RANDOM, could be compared. Electrostatic effects on the binding of trace metals by marine organics need also to be investigated.

Because any model rises or falls on its database, this needs to be constantly reviewed. The interaction of trace metals with inorganic ligands is well studied. However, many of the reported formation constants for the interactions between trace metals and the RANDOM ligands have large uncertainties associated with them. This is particularly true of binding to sulphur-containing ligands. As new formation constants are reported, those included in the database should be reviewed and if necessary updated.

Adsorption onto other solids observed in the marine environment could also added to the model. This is particularly true of those solids that have been observed in the sediments. The competition between various solid phases for the adsorption of trace metals could be modelled. These results could then be correlated with experimental studies performed on various types of marine sediments.

The model developed for fresh and seawater mixing is at present generalized. It is hoped that the model can provide insight into the functioning of real systems. The concentrations used in the model of Chapter 7 could then be changed to those of a real system.

The seawater model developed in this study provides a basis for investigating the impact of chemical pollution on the speciation in a marine system. The variation of parameters (pH, metal concentration, organic matter) can now easily be performed and their impact assessed. The improvements discussed above can only lead to a more versatile and powerful tool for undertsanding the chemisty of the ocean.

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APPENDIX ONE

THE THERMODYNAMIC DATABASE

Appendix 1.1: Stability constants and species definition for reactions at I = 0.7 mol dm^{-3} and 25°C

Note

In the table that follows the columns are as follows: The code refers to the MINTEQA2 code for the particular species; species is the chemical formula or common name, the components required are the MINTEQA2 codes and stoichiometry for the relevant components. The Pts column refers to the number of original data points used corrected to obtain the Log K's in Appendix 1.1 and 1.2. The Refs are the references from which these data points were collected and are listed at the end of this appendix while the method column gives a code for the method of correction used. These were discussed in sections 2.2.1 and 2.2.2: The codes in the method column are

LM: This is the method of correction proposed by Linder and Murray [Lin81] and requires more than 1 original data point.

D: refers to the same method but with c set equal to -0.10 as recommended by Davies. The number in brackets behind the D shows the ionic strength from which the correction was made. Where there are two numbers, the correction was performed separately from 2 ionic strengths and then the mean taken. This was performed, in particular, for I = 0.0 and 0.1 mol dm^{-3} as the LM method doesn't work well in this case.

T: A temperature adjustment was made in this case.

TC: The constants are calculated using the method for ternary complexes in section 2.2.4

BM: The correction method of Baes and Mesmer [Bae76] was used. Note no number of points is given in this case.

Paper: The method of correction in the reference given was used

Formula: In this case the data was fitted to the curve of the species given in the method column at the ionic strength in brackets.

It is hoped that the data presented here will give some measure of the accuracy of the corrected constants i.e. constants corrected from one data point have a larger source of error especially where the ionic strength from which the correction is made is far away from the ionic strength to which the data is corrected.

The Minteqa2 Component Codes

Code	Species	Code	Species
1	e^-	20	Ag^+
30	Al^{3+}	70	Ba^{2+}
90	$B(OH)_4^-$	130	Br^-
140	CO_3^{2-}	150	Ca^{2+}
160	Cd^{2+}	180	Cl^-
190	Co^{2+}	210	CrO_4^{2-}
211	Cr^{3+}	230	Cu^+
231	Cu^{2+}	270	F^-
280	Fe^{2+}	281	Fe^{3+}
330	H^+	360	Hg_2^{2+}
361	Hg^{2+}	380	I^-
381	IO_3^-	410	K^+
440	Li^+	460	Mg^{2+}
470	Mn^{2+}	492	NO_3^-
500	Na^+	540	Ni^{2+}
580	PO_4^{3-}	600	Pb^{2+}
732	SO_4^{2-}	770	$SiO_2(OH)_2^{2-}$
780	Sn^{2+}	800	Sr^{2+}
893	UO_2^{2+}	905	ALA
906	BEAL	910	ACAC
912	ASP	915	ACPH
916	AET	917	BENZ
920	CAT	925	CYS
927	DAP	930	DEM
940	DHMB	945	ETA
950	Zn^{2+}	955	HBT
960	HMP	965	MAL
967	MET	970	PHEN
971	PROP	973	PHTH
975	PN	980	TMA
985	TLA	990	SER
995	SAL	998	SUCC
999	TIPP		

Note: Some of the codes in the list above have been changed from the original codes supplied with MINTEQA2

Code	Species	Components required						Log K	Pts	Method	Refs
Aqueous	*Inorganic Species*										
200900	$AgB(OH)_4$	1.000	20	1.000	90			0.72	2	LM	1
201300	AgBr	1.000	20	1.000	130			4.37	1	AgCl(0)	1
201301	$AgBr_2^-$	1.000	20	2.000	130			7.00	3	LM	1
201302	$AgBr_3^{2-}$	1.000	20	3.000	130			7.97	4	LM	1
201303	$AgBr_4^{3-}$	1.000	20	4.000	130			8.66	2	LM	1
201304	$AgIBr_2^{2-}$	1.000	20	1.000	380	2.000	130	10.32		TC	
201305	AgI_2Br^{2-}	1.000	20	2.000	380	1.000	130	12.20		TC	
201306	$AgI_2Br_2^{3-}$	1.000	20	2.000	380	2.000	130	12.21		TC	
201307	$AgCl_2Br_2^{3-}$	1.000	20	2.000	180	2.000	130	7.47		TC	
201308	$AgClBr_3^{3-}$	1.000	20	1.000	180	3.000	130	8.28		TC	
201309	$AgCl_3Br^{3-}$	1.000	20	3.000	180	1.000	130	6.31		TC	
201310	$AgIBr_3^{3-}$	1.000	20	1.000	380	3.000	130	10.65		TC	
201311	AgI_3Br^{3-}	1.000	20	3.000	380	1.000	130	13.42		TC	
201800	AgCl	1.000	20	1.000	180			2.98	4	LM	1
201801	$AgCl_2^-$	1.000	20	2.000	180			5.11	4	LM	1
201802	$AgCl_3^{2-}$	1.000	20	3.000	180			5.13	2	LM	1
201803	$AgCl_4^{3-}$	1.000	20	4.000	180			4.73	5	LM	1
201804	$AgClBr^-$	1.000	20	1.000	180	1.000	130	6.36		TC	
201805	$AgClBr_2^{2-}$	1.000	20	1.000	180	2.000	130	7.50		TC	
201806	$AgCl_2Br^{2-}$	1.000	20	2.000	180	1.000	130	6.55		TC	
201807	$AgClI^-$	1.000	20	1.000	180	1.000	380	8.16		TC	
201808	$AgClI_2^{2-}$	1.000	20	1.000	180	2.000	380	11.25		TC	
201809	$AgCl_2I^{2-}$	1.000	20	2.000	180	1.000	380	8.43		TC	
202700	AgF	1.000	20	1.000	270			-0.24	3	LM	1
203300	AgOH	1.000	20	-1.000	330			-12.14		BM	2
203301	$Ag(OH)_2^-$	1.000	20	-2.000	330			-23.84		BM	2

203800	AgI	1.000	20	1.000	380			8.01	4	LM	1
203801	AgI_2^-	1.000	20	2.000	380			10.61	4	LM	1
203802	AgI_3^{2-}	1.000	20	3.000	380			13.60	4	LM	1
203803	AgI_4^{3-}	1.000	20	4.000	380			14.20	4	LM	1
203806	$AgIBr^-$	1.000	20	1.000	380	1.000	130	9.11		TC	
203807	$AgCl_2I_2^{3-}$	1.000	20	2.000	180	2.000	380	10.24		TC	
203808	$AgClI_3^{3-}$	1.000	20	1.000	180	3.000	380	12.43		TC	
203809	$AgCl_3I^{3-}$	1.000	20	3.000	180	1.000	380	7.70		TC	
203810	$AgIO_3$	1.000	20	1.000	381			0.22	2	LM	1
203811	$Ag(IO_3)_2^-$	1.000	20	2.000	381			1.60	1	D(0)	1
204920	$AgNO_3$	1.000	20	1.000	492			-0.45	2	LM	1
207320	$AgSO_4^-$	1.000	20	1.000	732			0.47	3	LM	1
207321	$Ag(SO_4)_2^{3-}$	1.000	20	2.000	732			0.23	1	D(2)	1
207322	$Ag(SO_4)_3^{5-}$	1.000	20	3.000	732			0.42	1	D(2)	1
301400	$Al_2(OH)_2CO_3^{2+}$	2.000	30	1.000	140	-2.000	330	1.62	1	D(0.5)	1
301401	$Al_3(OH)_3CO_3^{4+}$	3.000	30	1.000	140	-3.000	330	-0.69	1	D(0.5)	1
302700	AlF^{2+}	1.000	30	1.000	270			6.10	4	LM	1
302701	AlF_2^+	1.000	30	2.000	270			10.97	3	LM	1
302702	AlF_3	1.000	30	3.000	270			14.89	3	LM	1
302703	AlF_4^-	1.000	30	4.000	270			18.06	3	LM	1
302704	AlF_5^{2-}	1.000	30	5.000	270			19.39	1	D(0.5)	1
302705	AlF_6^{6-}	1.000	30	6.000	270			19.82	1	D(0.5)	1
303300	$AlOH^{2+}$	1.000	30	-1.000	330			-5.52	13	LM	1,2,67
303301	$Al(OH)_2^+$	1.000	30	-2.000	330			-11.02	3	LM	1
303302	$Al(OH)_3$	1.000	30	-3.000	330			-17.37	2	D(0;0.1)	1
303303	$Al(OH)_4^-$	1.000	30	-4.000	330			-23.68		BM	2
303304	$Al_2(OH)_2^{4+}$	2.000	30	-2.000	330			-7.94	3	LM	1
303305	$Al_3(OH)_4^{5+}$	3.000	30	-4.000	330			-13.47		BM	2
304920	$AlNO_3^{2+}$	1.000	30	1.000	492			-0.50	1	D(0)	3

305800	$AlHPO_4^+$	1.000	30	1.000	580	1.000	330	17.03	1	D(0)	4
305801	$AlH_2PO_4^{2+}$	1.000	30	1.000	580	2.000	330	20.05	1	D(0)	4
307320	$AlSO_4^+$	1.000	30	1.000	732			2.45	4	LM	1
700900	$BaB(OH)_4^+$	1.000	70	1.000	90			0.48	1	$SrB(OH)_4$(0)	5,6
701400	$BaCO_3$	1.000	70	1.000	140			0.81	1	D(0)	1
701401	$BaHCO_3^+$	1.000	70	1.000	140	1.000	330	10.42	1	D(0)	1
702320	$BaSO_4$	1.000	70	1.000	732			0.75	2	LM	1
702321	$Ba(SO_4)_2^{2-}$	1.000	70	2.000	732			1.51	1	D(1)	1
702700	BaF^+	1.000	70	1.000	270			-0.19	1	CaF^+(1)	1
703300	$BaOH^+$	1.000	70	-1.000	330			-13.78	1	D(0)	5,7
703810	$BaIO_3^+$	1.000	70	1.000	381			0.46	1	D(0)	1
704920	$BaNO_3^+$	1.000	70	1.000	492			0.20	6	LM	1
704921	$Ba(NO_3)_2$	1.000	70	2.000	492			0.03	6	LM	1
902700	$B(OH)_3F^-$	1.000	90	1.000	330	1.000	270	8.52	1	D(1)	1
902701	$B(OH)_2F_2^-$	1.000	90	2.000	330	2.000	270	16.09	1	D(1)	1
902702	$B(OH)F_3^-$	1.000	90	3.000	330	3.000	270	22.25	1	D(1)	1
902703	BF_4^-	1.000	90	4.000	330	4.000	270	28.02	1	D(1)	1
1500900	$CaB(OH)_4^+$	1.000	150	1.000	90			1.06	2	LM	5,6,8
1501400	$CaHCO_3^+$	1.000	150	1.000	140	1.000	330	9.83	2	LM	1
1501401	$CaCO_3$	1.000	150	1.000	140			2.21	2	LM	1
1501402	$CaMgCO_3^{2+}$	1.000	150	1.000	460	1.000	140	3.02	1	D(0.7)	9
1502700	CaF^+	1.000	150	1.000	270			0.60	2	LM	1
1503300	$CaOH^+$	1.000	150	-1.000	330			-13.08	4	LM	1
1503810	$CaIO_3^+$	1.000	150	1.000	381			0.32	1	D(0)	1
1504920	$CaNO_3^+$	1.000	150	1.000	492			0.01	6	LM	1
1504921	$Ca(NO_3)_2$	1.000	150	2.000	492			-0.38	6	LM	1
1505800	$CaPO_4^-$	1.000	150	1.000	580			4.50	2	LM	1,5,10
1505801	$CaHPO_4$	1.000	150	1.000	580	1.000	330	12.56	2	LM	1,5,10

1505802	$CaH_2PO_4^+$	1.000	150	1.000	580	2.000 330	17.88	2	LM	5,11
1507320	$CaSO_4$	1.000	150	1.000	732		1.03	5	LM	1
1507700	$CaSiO_2(OH)_2$	1.000	150	1.000	770		3.14	1	D(1)	1
1507701	$CaSiO(OH)_3^+$	1.000	150	1.000	770	1.000 330	12.94	1	D(1)	1
1507702	$Ca(SiO(OH)_3)_2$	1.000	150	2.000	770	2.000 330	27.99	1	D(1)	1
1600900	$CdB(OH)_4^+$	1.000	160	1.000	90		1.42	1	D(0.7)	12
1600901	$Cd(B(OH)_4)_2$	1.000	160	2.000	90		2.70	1	D(0.7)	12
1601300	$CdBr^+$	1.000	160	1.000	130		1.54	6	LM	1
1601301	$CdBr_2$	1.000	160	2.000	130		2.08	6	LM	1
1601302	$CdBr_3^-$	1.000	160	3.000	130		2.32	6	LM	1
1601303	$CdBr_4^{2-}$	1.000	160	4.000	130		2.53	4	LM	1
1601304	CdI_2Br^-	1.000	160	2.000	380	1.000 130	4.20		TC	
1601305	$CdI_2Br_2^{2-}$	1.000	160	2.000	380	2.000 130	4.79		TC	
1601306	$CdIBr_3^{2-}$	1.000	160	1.000	380	3.000 130	3.87		TC	
1601307	$CdCl_2Br_2^{2-}$	1.000	160	2.000	180	2.000 130	2.54		TC	
1601308	$CdClBr_3^{2-}$	1.000	160	1.000	180	3.000 130	2.75		TC	
1601309	$CdCl_3Br^{2-}$	1.000	160	3.000	180	1.000 130	1.98		TC	
1601400	$CdCO_3$	1.000	160	1.000	140		3.09	1	D(0.1)	13
1601800	$CdCl^+$	1.000	160	1.000	180		1.34	7	LM	1
1601801	$CdCl_2$	1.000	160	2.000	180		1.68	6	LM	1
1601802	$CdCl_3^-$	1.000	160	3.000	180		1.48	5	LM	1
1601803	$CdCl_4^{2-}$	1.000	160	4.000	180		1.00	2	LM	1
1601804	$CdClBr$	1.000	160	1.000	180	1.000 130	2.18		TC	
1601805	$CdClBr_2^-$	1.000	160	1.000	180	2.000 130	2.52		TC	
1601806	$CdCl_2Br^-$	1.000	160	2.000	180	1.000 130	2.24		TC	
1601807	$CdClI$	1.000	160	1.000	180	1.000 380	2.73		TC	
1601808	$CdClI_2^-$	1.000	160	1.000	180	2.000 380	3.92		TC	
1601809	$CdCl_2I^-$	1.000	160	2.000	180	1.000 380	2.94		TC	

1602700	CdF^+	1.000	160	1.000	270		0.54	9	LM	14
1602701	CdF_2	1.000	160	2.000	270		0.54	2	LM	1
1603300	$CdOH^+$	1.000	160	-1.000	330		-10.42		BM	2
1603301	$Cd(OH)_2$	1.000	160	-2.000	330		-20.75		BM	2
1603302	$Cd(OH)_3^-$	1.000	160	-3.000	330		-32.21		BM	2
1603303	$Cd(OH)_4^{2-}$	1.000	160	-4.000	330		-46.79		BM	2
1603304	Cd_2OH^{3+}	2.000	160	-1.000	330		-9.00		BM	2
1603305	$Cd_4(OH)_4^{4+}$	4.000	160	-4.000	330		-31.96		BM	2
1603800	CdI^+	1.000	160	1.000	380		1.86	5	LM	1
1603801	CdI_2	1.000	160	2.000	380		3.18	4	LM	1
1603802	CdI_3^-	1.000	160	3.000	380		4.42	4	LM	1
1603803	CdI_4^{2-}	1.000	160	4.000	380		5.50	4	LM	1
1603804	$CdIBr$	1.000	160	1.000	380	1.000 130	2.93		TC	
1603805	$CdIBr_2^-$	1.000	160	1.000	380	2.000 130	3.50		TC	
1603806	CdI_3Br^{2-}	1.000	160	3.000	380	1.000 130	5.36		TC	
1603807	$CdCl_2I_2^{2-}$	1.000	160	2.000	180	2.000 380	4.03		TC	
1603808	$CdClI_3^{2-}$	1.000	160	1.000	180	3.000 380	4.98		TC	
1603809	$CdCl_3I^{2-}$	1.000	160	3.000	180	1.000 380	2.73		TC	
1603810	$CdIO_3^+$	1.000	160	1.000	381		0.54	2	LM	1
1603811	$Cd(IO_3)_2$	1.000	160	2.000	381		1.55	1	D(0)	1
1604920	$CdNO_3^+$	1.000	160	1.000	492		-0.10	6	LM	1
1604921	$Cd(NO_3)_2$	1.000	160	2.000	492		-0.80	5	LM	1
1605800	$CdHPO_4$	1.000	160	1.000	330	1.000 580	14.17	3	D(3)	1
1605801	$CdH_2PO_4^+$	1.000	160	2.000	330	1.000 580	18.39	3	D(3)	1
1607320	$CdSO_4$	1.000	160	1.000	732		1.00	6	LM	1
1607321	$Cd(SO_4)_2^{2-}$	1.000	160	2.000	732		1.83	4	LM	1
1901300	$CoBr^+$	1.000	190	1.000	130		-0.13	2	LM	1
1901400	$CoCO_3$	1.000	190	1.000	140		3.17	1	D(0.5)	15,16

1901401	$CoHCO_3^+$	1.000	190	1.000	140	1.000	330	10.93	1	D(0.7) 1
1901800	$CoCl^+$	1.000	190	1.000	180			-0.03	4	LM 1
1902700	CoF^+	1.000	190	1.000	270			0.62	1	ZnF^+(1) 17
1903300	$CoOH^+$	1.000	190	-1.000	330			-9.85	5	LM 1,2
1903301	$Co(OH)_2$	1.000	190	-2.000	330			-18.58		BM 2
1903302	$Co(OH)_3^-$	1.000	190	-3.000	330			-31.62		BM 2
1903303	$Co(OH)_4^{2-}$	1.000	190	-4.000	330			-45.83		BM 2
1903304	Co_2OH^{3+}	2.000	190	-1.000	330			-10.73		BM 2
1903305	$Co_4(OH)_4^{4+}$	4.000	190	-4.000	330			-29.60		BM 2
1904920	$CoNO_3^+$	1.000	190	1.000	492			-0.43	5	LM 1
1904921	$Co(NO_3)_2$	1.000	190	2.000	492			-0.36	5	LM 1
1905800	$CoHPO_4$	1.000	190	1.000	580	1.000	330	12.89	1	D(0.1) 1
1907320	$CoSO_4$	1.000	190	1.000	732			0.83	3	LM 1
2111800	$CrCl^{2+}$	1.000	211	1.000	180			-0.50	1	$FeCl^{2+}$(1) 1
2112700	CrF^{2+}	1.000	211	1.000	270			4.25	2	LM 1
2112701	CrF_2^+	1.000	211	2.000	270			7.55	1	AlF_2^+(0.5) 1
2112702	CrF_3	1.000	211	3.000	270			10.09	1	AlF_3(0.5) 1
2113300	$CrOH^{2+}$	1.000	211	-1.000	330			-4.34	2	LM 1
2113301	$Cr(OH)_2^+$	1.000	211	-2.000	330			-10.35		BM 2
2113302	$Cr(OH)_3$	1.000	211	-3.000	330			-19.26		BM 2
2113303	$Cr(OH)_4^-$	1.000	211	-4.000	330			-28.26		BM 2
2113304	$Cr_2(OH)_2^{4+}$	2.000	211	-2.000	330			-4.96		BM 2
2113305	$Cr_3(OH)_4^{2+}$	3.000	211	-4.000	330			-7.89		BM 2
2113810	$Cr(IO3)_2^+$	1.000	211	2.000	381			2.08	1	D(0.5) 1
2115800	$CrH_2PO_4^{2+}$	1.000	211	1.000	580	2.000	330	20.13	1	D(0.2) 1
2301300	$CuBr_2^-$	1.000	230	2.000	130			5.59	2	LM 1
2301301	$CuBr_3^{2-}$	1.000	230	3.000	130			6.41	1	D(5) 1
2301307	$CuIBr^-$	1.000	230	1.000	380	1.000	130	7.14		TC

2301308	$CuIBr_2^{2-}$	1.000	230	1.000	380	2.000	130	7.88		TC	
2301309	CuI_2Br^{2-}	1.000	230	2.000	380	1.000	130	8.87		TC	
2301800	$CuCl$	1.000	230	1.000	180			2.48	1	AgCl(5)	1
2301801	$CuCl_2^-$	1.000	230	2.000	180			5.03	2	LM	1
2301802	$CuCl_3^{2-}$	1.000	230	3.000	180			4.22	2	LM	1
2301803	$Cu_2Cl_4^{2-}$	2.000	230	4.000	180			11.31	1	D(5)	1
2301804	$CuCl_4^{3-}$	1.000	230	4.000	180			2.63	1	D(5)	1
2301804	$CuClBr^-$	1.000	230	1.000	180	1.000	130	5.61		TC	
2301805	$CuClBr_2^{2-}$	1.000	230	1.000	180	2.000	130	6.16		TC	
2301806	$CuCl_2Br^{2-}$	1.000	230	2.000	180	1.000	130	5.43		TC	
2301807	$CuClI^-$	1.000	230	1.000	180	1.000	380	6.86		TC	
2301808	$CuClI_2^{2-}$	1.000	230	1.000	180	2.000	380	8.14		TC	
2301809	$CuCl_2I^{2-}$	1.000	230	2.000	180	1.000	380	6.42		TC	
2303800	CuI_2^-	1.000	230	2.000	380			8.08	1	D(5)	1
2303801	CuI_3^{2-}	1.000	230	3.000	380			9.39	1	D(5)	1
2303802	CuI_4^{3-}	1.000	230	4.000	380			7.96	1	D(5)	1
2303807	$CuClI_3^{3-}$	1.000	230	3.000	380	1.000	180	7.23		TC	
2303808	$CuCl_2I_2^{3-}$	1.000	230	2.000	380	2.000	180	6.07		TC	
2303809	$CuCl_3I^{3-}$	1.000	230	1.000	380	3.000	180	4.56		TC	
2310900	$CuB(OH)_4^+$	1.000	231	1.000	90			3.43	1	D(0.7)	12
2310901	$Cu(B(OH)_4)_2$	1.000	231	2.000	90			6.13	1	D(0.7)	12
2311300	$CuBr^+$	1.000	231	1.000	130			-0.51	3	LM	1
2311400	$CuCO_3$	1.000	231	1.000	140			5.73	3	LM	13,18
2311401	$Cu(CO_3)_2^{2-}$	1.000	231	2.000	140			9.30	3	LM	13,18
2311402	$CuHCO_3^+$	1.000	231	1.000	140	1.000	330	10.57	2	LM	1,18
2311403	$CuOHCO_3^-$	1.000	231	1.000	140	-1.000	330	-3.40		TC	
2311800	$CuCl^+$	1.000	231	1.000	180			-0.20	9	LM	1
2311801	$CuCl_2$	1.000	231	2.000	180			-0.50	3	LM	1

2312700	CuF^+	1.000	231	1.000	270		0.82	1	ZnF^+(1) 17
2313300	$CuOH^+$	1.000	231	-1.000	330		-7.84	2	LM 19,20
2313301	$Cu(OH)_2$	1.000	231	-2.000	330		-16.70	2	LM 20,21
2313302	$Cu(OH)_3^-$	1.000	231	-3.000	330		-28.03		BM 2
2313303	$Cu(OH)_4^{2-}$	1.000	231	-4.000	330		-38.78		BM 2
2313304	$Cu_2(OH)_2^{2+}$	2.000	231	-2.000	330		-11.17		BM 2
2313810	$CuIO_3^+$	1.000	231	1.000	381		0.11	1	D(0) 1
2314920	$CuNO_3^+$	1.000	231	1.000	492		-0.09	6	LM 1
2314921	$Cu(NO_3)_2$	1.000	231	2.000	492		-0.56	4	LM 1
2315800	$CuHPO_4$	1.000	231	1.000	580	1.000 330	13.91	1	D(0.1) 1
2315811	$CuH_2PO_4^+$	1.000	231	1.000	580	2.000 330	18.76	1	D(0) 22
2317320	$CuSO_4$	1.000	231	1.000	732		0.90	5	LM 1
2801400	$FeCO_3$	1.000	280	1.000	140		3.50	1	D(0) 4
2801401	$FeHCO_3^+$	1.000	280	1.000	140	1.000 330	10.07	1	D(0) 1
2801800	$FeCl^+$	1.000	280	1.000	180		-0.45	2	LM 23
2802700	FeF^+	1.000	280	1.000	270		0.82	1	ZnF^+(1) 17
2803300	$FeOH^+$	1.000	280	-1.000	330		-9.79		BM 2
2803301	$Fe(OH)_2$	1.000	280	-2.000	330		-21.00		BM 2
2803302	$Fe(OH)_3^-$	1.000	280	-3.000	330		-32.12		BM 2
2803303	$Fe(OH)_4^{2-}$	1.000	280	-4.000	330		-45.31		BM 2
2805800	$FeH_2PO_4^+$	1.000	280	1.000	580	2.000 330	19.77	1	D(0) 1
2805801	$FeHPO_4$	1.000	280	1.000	580	1.000 330	13.46	1	D(0) 1
2807320	$FeSO_4$	1.000	280	1.000	732		0.74	1	$CdSO_4$(0) 1
2810900	$FeB(OH)_4^{2+}$	1.000	281	1.000	90		6.85	1	D(0.7) 24
2810901	$Fe(B(OH)_4)_2^+$	1.000	281	2.000	90		13.00	1	D(0.7) 24
2811300	$FeBr^{2+}$	1.000	281	1.000	130		-0.14	5	LM 1
2811301	$FeBr_2^+$	1.000	281	2.000	130		-0.36	1	$FeCl^{2+}$(1) 1
2811400	$FeOHCO_3$	1.000	281	1.000	140	-1.000 330	-5.56	1	D(0) 66

2811401	$Fe(CO_3)_2^-$	1.000	281	2.000	140		5.11	1	D(0) 66
2811800	$FeCl^{2+}$	1.000	281	1.000	180		0.63	6	LM 1
2811801	$FeCl_2^+$	1.000	281	2.000	180		0.82	3	LM 1,25
2811802	$FeCl_3$	1.000	281	3.000	180		-0.67	1	D(1) 1
2811803	$FeClBr^+$	1.000	281	1.000	180	1.000 130	0.53		TC
2812100	$FeCrO_4^+$	1.000	281	1.000	210		5.89	1	D(0.4) 1
2812700	FeF^{2+}	1.000	281	1.000	270		5.17	3	LM 1
2812701	FeF_2^+	1.000	281	2.000	270		8.98	1	AlF_2^+(0.5) 1
2812702	FeF_3	1.000	281	3.000	270		11.79	1	AlF_3(0.5) 1
2813300	$FeOH^{2+}$	1.000	281	-1.000	330		-2.74	8	LM 1,2
2813301	$Fe(OH)_2^+$	1.000	281	-2.000	330		-5.81	3	LM 1,2
2813302	$Fe(OH)_4^-$	1.000	281	-4.000	330		-21.90		BM 2
2813303	$Fe_2(OH)_2^{4+}$	2.000	281	-2.000	330		-2.67	7	LM 1,2
2813304	$Fe_3(OH)_4^{5+}$	3.000	281	-4.000	330		-5.83		BM 2
2813305	$Fe(OH)_3$	1.000	281	-3.000	330		-14.20		BM 2
2814920	$FeNO_3^{2+}$	1.000	281	1.000	492		-0.23	2	LM 1
2815800	$FeHPO_4^+$	1.000	281	1.000	580	1.000 330	19.47	1	D(0.5) 1
2815802	$FeH_2PO_4^{2+}$	1.000	281	1.000	580	2.000 330	21.10	1	D(0.5) 1
2817320	$FeSO_4^+$	1.000	281	1.000	732		2.13	4	LM 1
2817321	$Fe(SO_4)_2^-$	1.000	281	2.000	732		2.83	2	LM 1
2817322	$FeHSO_4^{2+}$	1.000	281	1.000	732	1.000 330	1.48	1	D(3) 1
2817700	$FeSiO(OH)_3^{2+}$	1.000	281	1.000	770	1.000 330	21.30	1	D(0.1) 1
3300020	OH^-	-1.000	330				-13.76	5	LM 1
3300900	$B(OH)_3$	1.000	90	1.000	330		8.85	7	LM 1,2
3300901	$B_2O(OH)_5^-$	2.000	90	1.000	330		8.69		BM 2
3300902	$B_3O_3(OH)_4^-$	3.000	90	2.000	330		19.85		BM 2
3300903	$B_4O_5(OH)_4^{2-}$	4.000	90	2.000	330		20.32		BM 2
3301400	HCO_3^-	1.000	140	1.000	330		9.54	5	LM 1,26

3301401	H_2CO_3	1.000	140	2.000	330		15.54	7	LM	1,26
3302100	$HCrO_4^-$	1.000	210	1.000	330		5.77	5	LM	1
3302101	H_2CrO_4	2.000	330	1.000	210		5.17	3	LM	1
3302102	$Cr2O_7^{2-}$	2.000	210	2.000	33		13.43	5	LM	1
3302700	HF	1.000	270	1.000	330		2.94	9	LM	1
3302701	HF_2^-	2.000	270	1.000	330		3.52	6	LM	1
3302702	SiF_6^{2-}	1.000	770	6.000	270	6.000 330	51.78	2	LM	27,28
3302703	$Si(OH)_2F_2$	1.000	770	2.000	270	4.000 330	32.02	1	D(1)	28
3303810	HIO_3	1.000	330	1.000	381		0.52	1	D(0)	1
3305800	HPO_4^{2-}	1.000	580	1.000	330		11.25	3	LM	1
3305801	$H_2PO_4^-$	1.000	580	2.000	330		17.64	5	LM	1
3305802	H_3PO_4	1.000	580	3.000	330		19.43	5	LM	1
3307320	HSO_4^-	1.000	732	1.000	330		1.22	6	LM	1
3307700	$SiO(OH)_3^-$	1.000	770	1.000	330		12.54	4	LM	1
3307701	$Si(OH)_4$	1.000	770	2.000	330		22.00	3	LM	1
3603300	Hg_2OH^+	1.000	360	-1.000	330		-5.06	1	D(0.5)	1
3603301	$(Hg_2)_2OH^{3+}$	2.000	360	-1.000	330		-2.34	1	D(3)	1
3603302	$(Hg_2)_5(OH)_4^{6+}$	5.000	360	-4.000	330		-7.38	1	D(3)	1
3604920	$Hg_2NO_3^+$	1.000	360	1.000	492		0.03	2	LM	1
3607320	Hg_2SO_4	1.000	360	1.000	732		1.22	1	$CdSO_4$(0.5)	1
3607321	$Hg_2(SO_4)_2$	1.000	360	2.000	732		3.37	1	$Cd(SO_4)_2^{2-}$(0.5)	1
3611300	$HgBr^+$	1.000	361	1.000	130		9.00	2	LM	1
3611301	$HgBr_2$	1.000	361	2.000	130		17.12	2	LM	1
3611302	$HgBr_3^-$	1.000	361	3.000	130		19.45	2	LM	1
3611303	HgBr42-	1.000	361	4.000	130		21.04	2	LM	1
3611304	HgOHBr	1.000	361	1.000	130	-1.000 330	5.61	2	LM	1
3611305	HgI_2Br^-	1.000	361	2.000	380	1.000 130	25.33		TC	
3611306	$HgCl_2Br^-$	1.000	361	2.000	180	1.000 130	16.41		TC	

3611307	$HgCl2Br_2^{2-}$	1.000	361	2.000	180	2.000	130	18.91	TC
3611308	$HgClBr_3^{2-}$	1.000	361	1.000	180	3.000	130	20.19	TC
3611309	$HgCl_3Br^{2-}$	1.000	361	3.000	180	1.000	130	17.28	TC
3611310	$HgI_2Br_2^{2-}$	1.000	361	2.000	380	2.000	130	26.19	TC
3611311	$HgIBr_3^{2-}$	1.000	361	1.000	380	3.000	130	23.83	TC
3611312	HgI_3Br^{2-}	1.000	361	3.000	380	1.000	130	28.20	TC
3611400	$HgCO_3$	1.000	361	1.000	140			10.92	2 LM 1
3611401	$HgHCO_3^+$	1.000	361	1.000	140	1.000	330	14.91	2 LM 1
3611402	$Hg(CO_3)_2^{2-}$	1.000	361	2.000	140			14.41	1 D(0.5) 1
3611403	$HgOHCO_3^-$	1.000	361	1.000	140	-1.000	330	4.33	2 LM 1
3611800	$HgCl^+$	1.000	361	1.000	180			6.72	5 LM 1
3611801	$HgCl_2$	1.000	361	2.000	180			13.21	5 LM 1
3611802	$HgCl_3^-$	1.000	361	3.000	180			14.18	5 LM 1
3611803	$HgCl_4^{2-}$	1.000	361	4.000	180			15.22	2 LM 1
3611804	HgOHCl	1.000	361	1.000	180	-1.000	330	3.68	2 LM 1
3611805	HgClBr	1.000	361	1.000	180	1.000	130	15.47	TC
3611806	$HgClBr_2^-$	1.000	361	1.000	180	2.000	130	18.17	TC
3611807	HgClI	1.000	361	1.000	180	1.000	380	18.79	TC
3611808	$HgClI_2^-$	1.000	361	1.000	180	2.000	380	23.58	TC
3611809	$HgCl_2I^-$	1.000	361	2.000	180	1.000	380	19.11	TC
3612700	HgF^+	1.000	361	1.000	270			1.02	2 LM 1
3613300	$HgOH^+$	1.000	361	-1.000	330			-3.68	BM 2
3613301	$Hg(OH)_2$	1.000	361	-2.000	330			-6.35	BM 2
3613302	$Hg(OH)_3^-$	1.000	361	-3.000	330			-21.12	BM 2
3613303	Hg_2OH^{3+}	2.000	361	-1.000	330			-2.86	BM 2
3613304	$Hg_3(OH)_3^{3+}$	3.000	361	-3.000	330			-6.45	2 LM 1
3613800	HgI^+	1.000	361	1.000	380			12.83	1 D(0.5) 1
3613801	HgI_2	1.000	361	2.000	380			23.77	1 D(0.5) 1

3613802	HgI_3^-	1.000	361	3.000	380		27.56	1	D(0.5)	1
3613803	HgI_4^{2-}	1.000	361	4.000	380		29.78	1	D(0.5)	1
3613804	HgOHI	1.000	361	1.000	380	-1.000 330	8.80	1	D(0.5)	1
3613805	HgIBr	1.000	361	1.000	380	1.000 130	20.75		TC	
3613806	$HgIBr_2^-$	1.000	361	1.000	380	2.000 130	22.63		TC	
3613807	$HgCl_2I_2^{2-}$	1.000	361	2.000	180	2.000 380	23.28		TC	
3613808	$HgClI_3^{2-}$	1.000	361	1.000	180	3.000 380	26.74		TC	
3613809	$HgCl_3I^{2-}$	1.000	361	3.000	180	1.000 380	19.46		TC	
3614920	$HgNO_3^+$	1.000	361	1.000	492		0.11	1	$MnNO_3^+$(3)	1
3614921	$Hg(NO_3)_2$	1.000	361	2.000	492		-0.06	1	$Cu(NO_3)_2$(3)	1
3615800	$HgPO_4^-$	1.000	361	1.000	580		10.00	1	D(3)	1
3615801	$HgHPO_4$	1.000	361	1.000	580	1.000 330	20.29	1	D(3)	1
3617320	$HgSO_4$	1.000	361	1.000	732		1.26	1	$CdSO_4$(0.5)	1
3617321	$Hg(SO_4)_2^{2-}$	1.000	361	2.000	732		2.23	1	$Cd(SO_4)_2^{2-}$(0.5)	1
4101400	KCO_3^-	1.000	410	1.000	140		0.63		= $NaCO_3^-$	
4101401	$KHCO_3$	1.000	410	1.000	140	1.000 330	8.99		= $NaHCO_3$	
4102100	$KCrO_4$	1.000	410	1.000	210		0.04	1	D(0.2)	29
4102700	KF	1.000	410	1.000	270		-1.34	1	NaF(1)	1
4103300	KOH	1.000	410	-1.000	330		-14.60		BM	2
4103810	KIO_3	1.000	410	1.000	381		-0.63	1	D(0)	1
4104920	KNO_3	1.000	410	1.000	492		-0.45	4	LM	1
4105800	KPO_4^{2-}	1.000	410	1.000	580		0.42	1		30
4105801	$KHPO_4^-$	1.000	410	1.000	580	1.000 330	11.16	1		30

The potassium phosphate constants were set relative to sodium: -0.1 for KPO_4^{2-} and -0.2 for $KHPO_4^{2-}$ based on evidence in reference 30.

4107320	KSO_4^-	1.000	410	1.000	732		0.30	4	LM	1
4400900	$LiB(OH)_4$	1.000	440	1.000	90		-0.05	1	D(0.7)	8
4402700	LiF	1.000	440	1.000	270		-0.15	1	NaF(0)	1

4403300	$LiOH$	1.000	440	-1.000	330		-13.72		BM	2
4407320	$LiSO_4^-$	1.000	440	1.000	732		0.07	1	D(0)	1
4600900	$MgB(OH)_4^+$	1.000	460	1.000	90		1.13	2	LM	6,8
4601400	$MgCO_3$	1.000	460	1.000	140		2.05	2	LM	1
4601401	$MgHCO_3^+$	1.000	460	1.000	140	1.000 330	9.75	2	LM	5
4601402	$Mg_2CO_3^{2+}$	2.000	460	1.000	140		2.59	1	D(0.7)	1,9
4602700	MgF^+	1.000	460	1.000	270		1.32	2	LM	31,32
4603300	$MgOH^+$	1.000	460	-1.000	330		-12.23	1	Paper	33
4603301	$Mg_4(OH)_4^{4+}$	4.000	460	-4.000	330		-39.09		BM	2
4603810	$MgIO_3^+$	1.000	460	1.000	381		0.26	1	D(0)	1
4605800	$MgH_2PO_4^+$	1.000	460	1.000	580	2.000 330	18.01	1	$CaH_2PO_4^+$(0.7)	11
4605801	$MgHPO_4$	1.000	460	1.000	580	1.000 330	12.79	4	LM	1,5
4605802	$MgPO_4^-$	1.000	460	1.000	580		3.90	1	$CaPO_4^-$(0.7)	10
4607320	$MgSO_4$	1.000	460	1.000	732		1.01	4	LM	1,5
4607700	$MgSiO_2(OH)_2$	1.000	460	1.000	770		4.21	1	D(1)	1
4607701	$MgSiO(OH)_3^+$	1.000	460	1.000	770	1.000 330	13.18	1	D(1)	1
4607702	$Mg(SiO(OH)_3)_2$	1.000	460	2.000	770	2.000 330	28.90	1	D(1)	1
4701300	$MnBr^+$	1.000	470	1.000	130		-0.40	1	$PbBr^+$(1)	1
4701400	$MnHCO_3^+$	1.000	470	1.000	140	1.000 330	10.17	2	LM	1
4701401	$MnCO_3$	1.000	470	1.000	140		2.98	1	D(0)	4
4701800	$MnCl^+$	1.000	470	1.000	180		-0.20	1	$CuCl^+$(1)	1
4702700	MnF^+	1.000	470	1.000	270		0.82	1	ZnF^+(1)	17
4703300	$MnOH^+$	1.000	470	-1.000	330		-10.86	5	LM	1,2
4703301	$Mn(OH)_4^{2-}$	1.000	470	-4.000	330		-47.61		BM	2
4703302	$Mn(OH)_2$	1.000	470	-2.000	330		-22.60		BM	
4703303	$Mn(OH)_3^-$	1.000	470	-3.000	330		-34.92		BM	
4703304	Mn_2OH^{3+}	2.000	470	-1.000	330		-10.09		BM	
4703305	$Mn_2(OH)_3^+$	2.000	470	-3.000	330		-24.83		BM	

4704920	$MnNO_3^+$	1.000	470	1.000	492		-0.40	6	LM	
4704921	$Mn(NO_3)_2$	1.000	470	2.000	492		-0.50	6	LM	1
4705800	$MnHPO_4$	1.000	470	1.000	580	1.000 330	12.81		Set = $NiHPO_4^{2+}$	
4707320	$MnSO_4$	1.000	470	1.000	732		0.70	6	LM	1
5000900	$NaB(OH)_4$	1.000	500	1.000	90		-0.36	2	LM	6,8
5001400	$NaCO_3^-$	1.000	500	1.000	140		0.63	2	LM	1
5001401	$NaHCO_3$	1.000	500	1.000	140	1.000 330	8.99	2	LM	
5002100	$NaCrO_4$	1.000	210	1.000	500		-0.06	1	D(0.2)	29
5002700	NaF	1.000	500	1.000	270		-0.69	7	LM	34,35
5003300	NaOH	1.000	500	-1.000	330		-14.32		BM	1
5003810	$NaIO_3$	1.000	500	1.000	381		-0.72	1	D(0)	1
5004920	$NaNO_3$	1.000	500	1.000	492		-0.91	1	D(0)	1
5005800	$NaHPO_4^-$	1.000	500	1.000	580	1.000 330	11.36	2	LM	1,11
5005801	$NaPO_4^{2-}$	1.000	500	1.000	580		0.52	1	D(0.7)	11
5005802	NaH_2PO_4	1.000	500	1.000	580	2.000 330	18.89	1	D(0.7)	11
5007320	$NaSO_4^-$	1.000	500	1.000	732		0.33	4	LM	1
5401300	$NiBr^+$	1.000	540	1.000	130		-0.05	1	$PbBr^+$(1)	36
5401400	$NiCO_3$	1.000	540	1.000	140		3.57	1	D(0.7)	1,16
5401401	$NiHCO_3^+$	1.000	540	1.000	140	3.000 33	10.93	1	D(0.7)	1
5401800	$NiCl^+$	1.000	540	1.000	180		0.00	1	$CuCl^+$(1)	1
5402700	NiF^+	1.000	540	1.000	270		0.52	1	ZnF^+(1)	14
5403300	$NiOH^+$	1.000	540	-1.000	330		-10.19		BM	2
5403301	$Ni(OH)_2$	1.000	540	-2.000	330		-19.40		BM	2
5403302	$Ni(OH)_3^-$	1.000	540	-3.000	330		-30.12		BM	2
5403303	Ni_2OH^{3+}	2.000	540	-1.000	330		-10.23		BM	2
5403304	$Ni_4(OH)_4^{4+}$	4.000	540	-4.000	330		-26.99		BM	2
5404920	$NiNO_3^+$	1.000	540	1.000	492		-0.17	5	LM	1
5404921	$Ni(NO_3)_2$	1.000	540	2.000	492		-0.97	6	LM	1

5405800	$NiH_2PO_4^+$	1.000	540	1.000	580	2.000	330	17.96	1	D(0.1) 1
5405801	$NiHPO_4$	1.000	540	1.000	580	1.000	330	12.81	1	D(0.1)
5407320	$NiSO_4$	1.000	540	1.000	732			0.83	3	LM 1
5407321	$Ni(SO_4)_2^{2-}$	1.000	540	2.000	732			1.65	1	$Cd(SO_4)_2^{2-}$(1) 1
6000900	$PbB(OH)_4^+$	1.000	600	1.000	90			2.20	1	D(0.7) 12
6000901	$Pb(B(OH)_4)_2$	1.000	600	2.000	90			4.41	1	D(0.7) 12
6001300	$PbBr^+$	1.000	600	1.000	130			1.10	6	LM 1
6001301	$PbBr_2$	1.000	600	2.000	130			1.60	2	LM 1
6001302	$PbBr_3^-$	1.000	600	3.000	130			2.08	6	LM 1
6001303	$PbBr_4^{2-}$	1.000	600	4.000	130			1.70	4	LM 1
6001304	$PbI_2Br_2^{2-}$	1.000	600	2.000	380	2.000	130	3.55		TC
6001305	$PbIBr_3^{2-}$	1.000	600	1.000	380	3.000	130	2.84		TC
6001306	PbI_3Br^{2-}	1.000	600	3.000	380	1.000	130	3.91		TC
6001307	$PbCl_2Br_2^{2-}$	1.000	600	2.000	180	2.000	130	1.82		TC
6001308	$PbClBr_3^{2-}$	1.000	600	1.000	180	3.000	130	1.97		TC
6001309	$PbCl_3Br^{2-}$	1.000	600	3.000	180	1.000	130	1.31		TC
6001400	$Pb(CO_3)_2^{2-}$	1.000	600	2.000	140			8.96	3	LM 13,39
6001401	$PbCO_3$	1.000	600	1.000	140			5.61	3	LM 13,37,38
6001402	$PbOHCO_3^-$	1.000	600	1.000	140	-1.000	330	-3.98		TC
6001800	$PbCl^+$	1.000	600	1.000	180			0.88	8	LM 1
6001801	$PbCl_2$	1.000	600	2.000	180			1.18	8	LM 1
6001802	$PbCl_3^-$	1.000	600	3.000	180			1.09	8	LM 1
6001803	$PbCl_4^{2-}$	1.000	600	4.000	180			0.38	4	LM 1
6001804	PbClBr	1.000	600	1.000	180	1.000	130	1.69		TC
6001805	$PbClBr_2^-$	1.000	600	1.000	180	2.000	130	2.23		TC
6001806	PbCl2Br-	1.000	600	2.000	180	1.000	130	1.90		TC
6001807	PbClI	1.000	600	1.000	180	1.000	380	1.52		TC
6001808	$PbClI_2^-$	1.000	600	1.000	180	2.000	380	2.89		TC

6001809	$PbCl_2I^-$	1.000	600	2.000	180	1.000	380	2.23		TC	
6002700	PbF^+	1.000	600	1.000	270			1.46	1	ZnF^+(1)	40
6002701	PbF_2	1.000	600	2.000	270			2.58	2	LM	1
6003300	$PbOH^+$	1.000	600	-1.000	330			-7.99	2	LM	41
6003301	$Pb(OH)_2$	1.000	600	-2.000	330			-17.52	2	LM	1,2
6003302	$Pb(OH)_3^-$	1.000	600	-3.000	330			-28.26	2	LM	1,2
6003303	Pb_2OH^{3+}	2.000	600	-1.000	330			-6.17		BM	2
6003304	$Pb_3(OH)_4^{2+}$	3.000	600	-4.000	330			-24.09	2	LM	41
6003305	$Pb_4(OH)_4^{4+}$	4.000	600	-4.000	330			-20.02	1	$Cd_4(OH)_4^{4+}$(0.1)	41
6003306	$Pb_6(OH)_8^{4+}$	6.000	600	-8.000	330			-43.12	2	LM	41
6003800	PbI^+	1.000	600	1.000	380			1.25	5	LM	1,40
6003801	PbI_2	1.000	600	2.000	380			2.24	1	D(1)	40
6003802	PbI_3^-	1.000	600	3.000	380			3.07	3	LM	1,40
6003803	PbI_4^{2-}	1.000	600	4.000	380			3.84	4	LM	1
6003804	$PbIBr$	1.000	600	1.000	380	1.000	130	2.22		TC	
6003805	$PbIBr_2^-$	1.000	600	1.000	380	2.000	130	2.89		TC	
6003806	PbI_2Br^-	1.000	600	2.000	380	1.000	130	3.22		TC	
6003807	$PbCl_2I_2^{2-}$	1.000	600	2.000	180	2.000	380	2.89		TC	
6003808	$PbClI_3^{2-}$	1.000	600	1.000	180	3.000	380	3.58		TC	
6003809	$PbCl_3I^{2-}$	1.000	600	3.000	180	1.000	380	1.85		TC	
6004920	$PbNO_3^+$	1.000	600	1.000	492			0.39	5	LM	1
6004921	$Pb(NO_3)_2$	1.000	600	2.000	492			0.38	5	LM	1
6005800	$PbH_2PO_4^+$	1.000	600	1.000	580	2.000	330	18.45	1	D(0)	1
6005801	$PbHPO_4$	1.000	600	1.000	580	1.000	330	12.85	1	D(0)	1
6007320	$PbSO_4$	1.000	600	1.000	732			1.30	3	LM	1
6007321	$Pb(SO_4)_2^{2-}$	1.000	600	2.000	732			2.92	1	$Cd(SO_4)_2^{2-}$(3)	1
7801300	$SnBr^+$	1.000	780	1.000	130			0.70	4	LM	1
7801301	$SnBr_2$	1.000	780	2.000	130			0.85	4	LM	1

7801302	$SnBr_3^-$	1.000	780	3.000	130		0.73	2	LM 1
7801303	$SnBr_4^{2-}$	1.000	780	4.000	130		-0.77	2	LM 1
7801304	SnIBr	1.000	780	1.000	380	1.000 130	1.16		TC
7801305	$SnIBr_2^-$	1.000	780	1.000	380	2.000 130	1.48		TC
7801306	SnI_2Br^-	1.000	780	2.000	380	1.000 130	1.75		TC
7801307	$SnI_2Br_2^{2-}$	1.000	780	2.000	380	2.000 130	1.10		TC
7801308	$SnIBr_3^{2-}$	1.000	780	3.000	130	1.000 380	0.38		TC
7801309	SnI_3Br^{2-}	1.000	780	1.000	130	3.000 380	1.47		TC
7801800	$SnCl^+$	1.000	780	1.000	180		1.04	6	LM 1
7801801	$SnCl_2$	1.000	780	2.000	180		1.44	7	LM 1
7801802	$SnCl_3^-$	1.000	780	3.000	180		1.15	4	LM 1
7801804	SnClBr	1.000	780	1.000	180	1.000 130	1.45		TC
7801805	$SnClBr_2^-$	1.000	780	1.000	180	2.000 130	1.35		TC
7801806	$SnCl_2Br^-$	1.000	780	2.000	180	1.000 130	1.49		TC
7801807	SnClI	1.000	780	1.000	180	1.000 380	1.46		TC
7801808	$SnClI_2^-$	1.000	780	1.000	180	2.000 380	1.89		TC
7801809	$SnCl_2I^-$	1.000	780	2.000	180	1.000 380	1.76		TC
7802700	SnF^+	1.000	780	1.000	270		4.10	1	ZnF^+(1) 1
7802701	SnF_2	1.000	780	2.000	270		6.70	1	D(1) 1
7802702	SnF_3^-	1.000	780	3.000	270		9.49	1	D(1)
7803300	$SnOH^+$	1.000	780	-1.000	330		-3.82		BM 2
7803301	$Sn(OH)_3^-$	1.000	780	-3.000	330		-16.69		BM 2
7803302	$Sn_3(OH)_4^{2+}$	3.000	780	-4.000	330		-7.50		BM 2
7803303	$Sn_2(OH)_2^{2+}$	2.000	780	-2.000	330		-5.03		BM 2
7803304	$Sn(OH)_2$	1.000	780	-2.000	330		-7.53		BM 2
7803800	SnI^+	1.000	780	1.000	380		0.58	1	D(4) 1
7803801	SnI_2	1.000	780	2.000	380		0.87	1	D(4) 1
7803802	SnI_3^-	1.000	780	3.000	380		1.54	1	D(4) 1

7803803	SnI_4^{2-}	1.000	780	4.000	380		1.42	1	D(4) 1
7804920	$SnNO_3^+$	1.000	780	1.000	492		0.47	1	$MnNO_3^+$(1) 1
8000900	$SrB(OH)_4^+$	1.000	800	1.000	90		0.54	2	LM 6,8
8001400	$SrCO_3$	1.000	800	1.000	140		1.40	1	D(0) 60
8001401	$SrHCO_3^+$	1.000	800	1.000	140	1.000 330	10.11	1	D(0) 1
8002700	SrF^+	1.000	800	1.000	270		0.15	1	CaF^+(1) 1
8003300	$SrOH^+$	1.000	800	-1.000	330		-13.59	2	LM 1,42
8003810	$SrIO_3^+$	1.000	800	1.000	381		0.36	1	D(0) 1
8004920	$SrNO_3^+$	1.000	800	1.000	492		0.10	6	LM 1
8004921	$Sr(NO_3)_2$	1.000	800	2.000	492		-0.24	5	LM 1
8007320	$SrSO_4$	1.000	800	1.000	732		1.16	3	LM 1
8931300	UO_2Br^+	1.000	893	1.000	130		-0.85	1	$PbBr^+$(0) 1
8931400	UO_2CO_3	1.000	893	1.000	140		8.24	3	LM 1
8931401	$UO_2(CO_3)_2^{2-}$	1.000	893	2.000	140		15.40	3	LM 1
8931402	$UO_2(CO_3)_3^{4-}$	1.000	893	3.000	140		21.51	2	LM 1
8931405	$(UO_2)_2(OH)_3CO_3^-$	2.000	893	1.000	140	-3.000 330	-1.44	1	D(0.1) 1
8931406	$(UO_2)_3(CO_3)_6^{6-}$	3.000	893	6.000	140		53.69	2	LM 1
8931800	UO_2Cl^+	1.000	893	1.000	180		-0.28	2	LM 1
8932700	UO_2F^+	1.000	893	1.000	270		4.56	1	ZnF^+(1) 1
8932701	UO_2F_2	1.000	893	2.000	270		7.99	1	D(1) 1
8932702	$UO_2F_3^-$	1.000	893	3.000	270		10.54	1	D(1) 1
8932703	$UO_2F_4^{2-}$	1.000	893	4.000	270		11.96	1	D(1) 1
8933300	UO_2OH^+	1.000	893	-1.000	330		-6.10	4	LM 1,2
8933301	$(UO_2)_2(OH)_2^{2+}$	2.000	893	-2.000	330		-5.92		BM 2
8933302	$(UO_2)_3(OH)_5^+$	3.000	893	-5.000	330		-16.33		BM 2
8933810	$UO_2(IO_3)_2$	1.000	893	2.000	381		2.56	1	D(0.2) 1
8933811	$UO_2(IO_3)_3^-$	1.000	893	3.000	381		3.55	1	D(0.2) 1
8934920	$UO_2NO_3^+$	1.000	893	1.000	492		-0.59	1	$MnNO_3^+$(2) 1

8935800	$UO_2H_2PO_4^+$	1.000	893	1.000	580	2.000 330	20.72	1	D(0) 1
8935801	$UO_2(H_2PO_4)_2$	1.000	893	2.000	580	4.000 330	39.88	2	LM 1
8935802	$UO_2H_7(PO_4)_3$	1.000	893	3.000	580	7.000 330	60.49	2	LM 1
8935803	$UO_2H_3PO_4^{2+}$	1.000	893	1.000	580	3.000 330	20.80	1	D(0) 1
8937320	UO_2SO_4	1.000	893	1.000	732		1.79	3	LM 1
8937321	$UO_2(SO_4)_2^{2-}$	1.000	893	2.000	732		2.56	3	LM 1
8937700	$UO_2SiO(OH)_3^+$	1.000	893	1.000	770	1.000 330	19.93	1	D(0.2) 1
9500900	$ZnB(OH)_4^+$	1.000	950	1.000	90		0.90	1	D(0.7) 12
9500901	$Zn(B(OH)_4)_2$	1.000	950	2.000	90		3.32	1	D(0.7) 12
9501300	$ZnBr^+$	1.000	950	1.000	130		-0.71	1	D(3) 1
9501400	$ZnHCO_3^+$	1.000	950	1.000	140	1.000 330	10.69	2	LM 43
9501401	$ZnCO_3$	1.000	950	1.000	140		3.30	2	LM 13,43
9501800	$ZnCl^+$	1.000	950	1.000	180		-0.40	1	$CuCl^+$(1) 43
9501801	$ZnCl_2$	1.000	950	2.000	180		-0.30	3	LM 1
9501802	$ZnCl_3^-$	1.000	950	3.000	180		-0.40	4	LM 1
9501803	$ZnCl_4^{2-}$	1.000	950	4.000	180		-0.55	4	LM 1
9502700	ZnF^+	1.000	950	1.000	270		0.56	9	LM 14
9503300	$ZnOH^+$	1.000	950	-1.000	330		-9.17	3	LM 1,2
9503301	$Zn(OH)_2$	1.000	950	-2.000	330		-19.37	1	D(3) 1
9503302	$Zn(OH)_3^-$	1.000	950	-3.000	330		-28.43		BM 2
9503303	$Zn(OH)_4^{2-}$	1.000	950	-4.000	330		-37.65		BM 2
9503304	Zn_2OH^{3+}	2.000	950	-1.000	330		-8.95		BM 2
9503800	ZnI^+	1.000	950	1.000	380		-1.55	1	D(3) 1
9504920	$ZnNO_3^+$	1.000	950	1.000	492		-0.19	6	LM 1
9504921	$Zn(NO_3)_2$	1.000	950	2.000	492		-0.50	4	LM 1
9505800	$ZnHPO_4$	1.000	950	1.000	580	1.000 330	13.11	1	D(0.1) 1
9505801	$ZnH_2PO_4^+$	1.000	950	1.000	580	2.000 330	18.66	1	D(0) 1
9507320	$ZnSO_4$	1.000	950	1.000	732		0.90	6	LM 1

9507321	$Zn(SO_4)_2^{2-}$	1.000	950	2.000	732		1.70	4	LM	1
Protonation Constants for the Model Organic Adsorbent										
9993300	HTIPP_	1.000	999	1.000	330		3.84	1	D(0)	44
9993301	H_2TIPP	1.000	999	2.000	330		4.37	1	D(0)	44
Fulvic Acid Interactions										
209050	AgALA	1.000	20	1.000	905		3.28	1	D(0)	1
209051	$Ag(ALA)_2^-$	1.000	20	2.000	905		6.92	1	D(0;0.1)	1
209060	$AgHBEAL^+$	1.000	20	1.000	906	1.000 330	9.39	1	D(3)	1
209061	$AgOHBEAL^-$	1.000	20	1.000	906	-1.000 330	-6.19	1	D(3)	1
209062	AgBEAL	1.000	20	1.000	906		3.35	2	LM	1
209063	$Ag(BEAL)_2^-$	1.000	20	2.000	906		7.11	2	LM	1
209170	AgBENZ	1.000	20	1.000	917		0.53	3	LM	1
209171	$Ag(BENZ)_2^-$	1.000	20	2.000	917		0.51	1	D(1)	1
209450	$AgETA^+$	1.000	20	1.000	945		3.11	2	LM	1
209451	$Ag(ETA)_2^+$	1.000	20	2.000	945		6.66	2	LM	1
209600	AgHMP	1.000	020	1.000	960		0.23	1	D(3)	1
209601	$Ag(HMP)_2^-$	1.000	020	2.000	960		0.06	1	D(3)	1
						HMP log K's based on glycolic acid				
209670	AgMET	1.000	20	1.000	967		13.06	1	D(0.1)	1
209671	$Ag(MET)_2^-$	1.000	20	2.000	967		17.82	1	D(0.1)	1
209672	Ag_2MET^+	2.000	020	1.000	967		19.07	1	D(0.1)	1
209700	AgPHEN	1.000	20	1.000	970		0.25	2	LM	1
209710	AgPROP	1.000	020	1.000	971		0.35	1	D(0)	1
209711	$Ag(PROP)_2^-$	1.000	020	2.000	971		0.23	1	D(0)	1
						PROP log K's based on propanoic acid				
209750	$AgPN^+$	1.000	20	1.000	975		5.35	1	D(3)	1

209751	$AgHPN^{2+}$	1.000	20	1.000	975	1.000	330	12.46	1	D(3)	1
209752	$AgH_2(PN)_2^{3+}$	1.000	20	2.000	975	2.000	330	25.23	1	D(3)	1
209753	AgOHPN	1.000	20	1.000	975	-1.000	330	-4.09	1	D(3)	1
209754	Ag_2PN^{2+}	2.000	20	1.000	975			7.23	1	D(3)	1
209755	$Ag_2(PN)_2^{2+}$	2.000	20	2.000	975			12.85	1	D(3)	1
209800	$AgTMA^{2-}$	1.000	20	1.000	980			7.56	1	D(0.1)	1
309100	$AlACAC^{2+}$	1.000	30	1.000	910			8.01	1	D(0.1)T	1
309101	$Al(ACAC)_2^{+}$	1.000	30	2.000	910			15.49	1	D(0.1)T	1
309120	$AlHASP^{2+}$	1.000	30	1.000	912	1.000	330	11.68	1	D(0.5)	1
309121	Al(OH)HASP	1.000	30	1.000	912			7.80	1	D(0.5)	1
309170	$AlOHBENZ^{+}$	1.000	30	1.000	917	-1.000	330	-1.70	1	D(0.5)	1
309200	$AlCat^{+}$	1.000	30	1.000	920			15.87	2	LM	1
309201	$Al(Cat)_2^{-}$	1.000	30	2.000	920			29.07	2	LM	1
309204	$AlH(Cat)_2$	1.000	30	2.000	920	1.000	330	35.11	1	D(0.1)	1
309650	$AlMal^{+}$	1.000	030	1.000	965			3.37	1	D(1)T	45
309651	AlOHMal	1.000	030	1.000	965	-1.000	330	0.64	1	D(0.1)	46
309710	$AlPROP^{2+}$	1.000	30	1.000	971			1.69	1	D(1)	1
309730	$AlPHTH^{+}$	1.000	30	1.000	973			3.12	1	D(0.5)	1
309731	$Al(PHTH)_2^{-}$	1.000	30	2.000	973			6.23	1	D(0.5)	1
309950	$AlSAL^{+}$	1.000	30	1.000	995			12.80	1	D(0.5)	1
309951	$Al(SAL)_2^{-}$	1.000	30	2.000	995			23.37	1	D(0.5)	1
309952	$AlOH(SAL)_2^{2-}$	1.000	30	2.000	995	-1.000	330	14.08	1	D(0.5)	1
309980	$AlSUCC^{+}$	1.000	30	1.000	998			3.13	1	D(0.5)	1
309980	AlOHSUCC	1.000	30	1.000	998	-1.000	330	-0.65	1	D(0.5)	1
309981	$AlHSUCC^{2+}$	1.000	30	1.000	998	1.000	330	6.50	1	D(0.5)	1
708650	BaMal	1.000	70	1.000	965			1.14	2	LM	1
708651	$BaHMal^{+}$	1.000	70	1.000	965	1.000	330	4.91	1	D(0.1)	1
709050	$BaALA^{+}$	1.000	70	1.000	905			0.12	1	D(0)	1

709100	$BaACAC^+$	1.000	70	1.000	910			1.47	1	D(0.1)	1
709120	BaASP	1.000	70	1.000	912			0.66	1	D(0.1)	1
709160	$BaAET^+$	1.000	70	1.000	916			1.14	1	D(0.1)	1
709300	BaDEM	1.000	70	1.000	930			1.12	1	D(0)	1
709400	$BaDHMB^+$	1.000	070	1.000	940			0.66	1	D(0.2)	1
						DHMB log K's based on glyceric acid					
709550	$BaHBT^+$	1.000	070	1.000	955			0.30	1	D(0.2)	1
709600	$BaHMP^+$	1.000	70	1.000	960			0.38	1	D(1)	1
709601	$Ba(HMP)_2$	1.000	70	2.000	960			0.53	1	D(1)	1
709710	$BaPROP^+$	1.000	70	1.000	971			0.20	1	D(0.2)	1
709730	BaPHTH	1.000	70	1.000	973			1.04	1	D(0)	1
709950	$BaHSAL^+$	1.000	70	1.000	995	1.000	330	12.76	1	D(0)	1
709980	BaSUCC	1.000	70	1.000	998			0.65	1	D(0)	1
909200	$B(OH)_2Cat^-$	1.000	90	1.000	920	2.000	330	26.18	1	D(0.1)	1
909201	$B(Cat)_2^-$	1.000	90	2.000	920	4.000	330	48.90	1	D(0.1)	1
909950	$B(OH)_2SAL^-$	1.000	90	1.000	995	2.000	330	23.41	1	D(0.1)	1
909951	$B(SAL)_2^{2-}$	1.000	90	2.000	995	4.000	330	41.74	1	D(0.1)	1
1509050	$CaALA^+$	1.000	150	1.000	905			0.67	1	D(0)	1
1509060	$CaBEAL^+$	1.000	150	1.000	906			1.60	1	D(0.15)T	47
1509100	$CaACAC^+$	1.000	150	1.000	910			2.13	1	D(0.1)	1
1509120	CaASP	1.000	150	1.000	912			1.17	1	D(0.1)	1
1509160	$CaAET^+$	1.000	150	1.000	916			2.02	1	D(0.1)	1
1509170	$CaBENZ^+$	1.000	150	1.000	917			0.16	1	D(1)T	1
1509300	CaDEM	1.000	150	1.000	930			1.33	1	D(0)	1
1509400	$CaDHMB^+$	1.000	150	1.000	940			1.07	1	D(0.2)	1
						DHMB log K's based on glyceric acid					
1509550	$CaHBT^+$	1.000	150	1.000	955			0.50	1	D(0.2)	1
1509600	$CaHMP^+$	1.000	150	1.000	960			0.93	1	D(1)	1

1509601	$Ca(HMP)_2$	1.000	150	2.000	960		1.43	1	D(1)	1
1509650	CaMal	1.000	150	1.000	965		1.66	1	D(3)	1,46
1509651	$CaHMal^+$	1.000	150	1.000	965	1.000 330	5.50	1	D(0;0.1)	1,46
1509710	$CaPROP^+$	1.000	150	1.000	971		0.39	1	D(0.2)	1
1509730	CaPHTH	1.000	150	1.000	973		1.20	1	D(0;0.1)	1
1509731	$CaHPHTH^+$	1.000	150	1.000	973	1.000 330	5.14	1	D(0;0.1)	1
1509900	$CaSER^+$	1.000	150	1.000	990		0.87	2	LM	1
1509950	CaSAL	1.000	150	1.000	995		3.85	1	D(0.25)	48
1509951	$CaHSAL^+$	1.000	150	1.000	995	1.000 330	13.72	1	D(0.25)	48
1509980	CaSUCC	1.000	150	1.000	998		0.71	1	D(0;0.1)	1
1509981	$CaHSUCC^+$	1.000	150	1.000	998	1.000 330	5.44	1	D(0.1)	1
1609050	$CdALA^+$	1.000	160	1.000	905		3.82	1	D(1)	1
1609051	$Cd(ALA)_2$	1.000	160	2.000	905		7.12	1	D(1)	1
1609100	$CdACAC^+$	1.000	160	1.000	910		3.43	3	LM	1
1609101	$Cd(ACAC)_2$	1.000	160	2.000	910		6.09	3	LM	1
1609120	CdASP	1.000	160	1.000	912		3.93	1	D(3)	1
1609121	$Cd(ASP)_2^{2-}$	1.000	160	2.000	912		7.13	1	D(3)	1
1609160	$CdAET^+$	1.000	160	1.000	916		10.74	1	D(0.1)	1
1609161	$Cd(AET)_2$	1.000	160	2.000	916		16.78	1	D(0.1)	1
1609170	$CdBENZ^+$	1.000	160	1.000	917		1.08	2	LM	1
1609171	$Cd(BENZ)_2$	1.000	160	2.000	917		1.66	1	D(1)	1
1609200	CdCAT	1.000	160	1.000	920		7.84	1	D(0.1)T	1
1609250	CdCYS	1.000	160	1.000	925		12.86	1	PbCYS(3)	1
1609251	$Cd(CYS)_2^{2-}$	1.000	160	2.000	925		19.50	1	D(3)	1
1609300	CdDEM	1.000	160	1.000	930		2.06	1	D(0.1)	1
1609400	$CdDHMB^+$	1.000	160	1.000	940		1.39	1	D(0.1)	1
1609401	$Cd(DHMB)_2$	1.000	160	2.000	940		2.78	1	D(0.1)	1
1609450	$CdETA^{2+}$	1.000	160	1.000	945		2.55	1	D(2)	1

1609451	$Cd(ETA)_2^{2+}$	1.000	160	2.000	945		4.59	1	D(2) 1
1609550	$CdHBT^+$	1.000	160	1.000	955		1.22	1	D(2) 1
1609551	$Cd(HBT)_2$	1.000	160	2.000	955		2.06	1	D(2) 1
1609600	$CdHMP^+$	1.000	160	1.000	960		1.26	1	D(1) 1
1609601	$Cd(HMP)_2$	1.000	160	2.000	960		2.18	1	D(1) 1
1609650	CdMAL	1.000	160	1.000	965		1.88	1	D(0.1) 46
1609651	$CdHMAL^+$	1.000	160	1.000	965	1.000 330	5.57	1	D(0.1) 46
1609670	$CdMET^+$	1.000	160	1.000	967		5.87	1	D(0.1) 1
1609671	$Cd(MET)_2$	1.000	160	2.000	967		12.09	1	D(0.1) 1
1609710	$CdPROP^+$	1.000	160	1.000	971		1.18	2	LM 1
1609711	$Cd(PROP)^2$	1.000	160	2.000	971		1.88	2	LM 1
1609730	CdPHTH	1.000	160	1.000	973		1.96	2	LM 1
1609731	$Cd(PHTH)_2^{2-}$	1.000	160	2.000	973		2.92	1	D(1) 1
1609732	$CdHPHTH^+$	1.000	160	1.000	973	1.000 330	5.19	1	D(1) 1
1609733	$CdH(PHTH)_2^-$	1.000	160	2.000	973	1.000 330	6.53	1	D(1) 1
1609750	$CdPN^{2+}$	1.000	160	1.000	975		5.49	1	D(0.65)T 1
1609751	$Cd(PN)_2^{2+}$	1.000	160	2.000	975		10.11	1	D(0.65)T 1
1609800	$CdTMA^-$	1.000	160	1.000	980		9.66	1	D(0.2) 49
1609801	$Cd(TMA)_2^{4-}$	1.000	160	2.000	980		13.28	1	D(0.2) 49
1609900	$CdSER^+$	1.000	160	1.000	990		3.75	1	$ZnSER^+$(3) 1
1609901	$Cd(SER)_2$	1.000	160	2.000	990		6.98	1	$Zn(SER)_2$(3) 1
1609980	CdSUCC	1.000	160	1.000	998		1.63	2	LMT 1
1609981	$Cd(SUCC)_2^{2-}$	1.000	160	2.000	998		2.83	1	D(1)T 1
1609982	$CdHSUCC^+$	1.000	160	1.000	998	1.000 330	6.10	1	D(1)T 1
1909050	$CoALA^+$	1.000	190	1.000	905		4.13	1	D(0;0.1) 1
1909051	$Co(ALA)_2$	1.000	190	2.000	905		7.53	1	D(0;0.1) 1
1909060	$CoBEAL^+$	1.000	190	1.000	906		3.06	2	LM 1
1909061	$Co(BEAL)_2$	1.000	190	2.000	906		5.98	1	D(0.2) 1

1909100	$CoACAC^{+}$	1.000 190	1.000 910		4.85	1	D(0;0.1)	1
1909101	$Co(ACAC)_2$	1.000 190	2.000 910		8.74	1	D(0;0.1)	1
1909120	CoASP	1.000 190	1.000 912		5.52	1	D(0.1)	1
1909121	$Co(ASP)_2^{2-}$	1.000 190	2.000 912		9.86	1	D(0.1)	1
1909150	$CoACPH^{+}$	1.000 190	1.000 915		4.01	1	D(0.1)	1
1909151	$Co(ACPH)_2$	1.000 190	2.000 915		6.77	1	D(0.1)	1
1909160	$CoAET^{+}$	1.000 190	1.000 916		7.69	1	D(1)	1
1909161	$Co(AET)_2$	1.000 190	2.000 916		14.72	1	D(1)	1
1909170	$CoBENZ^{+}$	1.000 190	1.000 917		0.51	1	D(1)T	1
1909200	CoCAT	1.000 190	1.000 920		8.40	2	LM	1
1909201	$Co(CAT)_2^{2-}$	1.000 190	2.000 920		14.83	2	LM	1
1909250	CoCYS	1.000 190	1.000 925		7.57	1	D(0.1)	1
1909251	$Co(CYS)_2^{2-}$	1.000 190	2.000 925		13.83	1	D(0.1)	1
1909270	$CoDAP^{+}$	1.000 190	1.000 927		6.22	2	LM	1
1909271	$Co(DAP)_2$	1.000 190	2.000 927		11.21	2	LM	1
1909272	$CoHDAP^{2+}$	1.000 190	1.000 927	1.000 330	12.43	1	D(0.1)	1
1909273	$CoH(DAP)_2^{+}$	1.000 190	2.000 927	1.000 330	17.90	1	D(0.1)	1
1909300	CoDEM	1.000 190	1.000 930		1.82	1	D(0.1)	1
1909400	$CoDHMB^{+}$	1.000 190	1.000 940		1.40	1	D(0.1)	1
1909401	$Co(DHMB)_2$	1.000 190	2.000 940		2.55	1	D(0.1)	1
1909450	$CoETA^{2+}$	1.000 190	1.000 945		2.25	3	LM	1
1909451	$Co(ETA)_2^{2+}$	1.000 190	2.000 945		3.89	3	LM	1
1909550	$CoHBT^{+}$	1.000 190	1.000 955		0.82	1	D(2)	1
1909551	$Co(HBT)_2$	1.000 190	2.000 955		1.05	1	D(2)	1
1909600	$CoHMP^{+}$	1.000 190	1.000 960		1.46	1	D(1)	1
1909601	$Co(HMP)_2$	1.000 190	2.000 960		2.44	1	D(1)	1
1909650	CoMal	1.000 190	1.000 965		2.46	1	D(0.1)T	1
1909651	$CoHMal^{+}$	1.000 190	1.000 965	1.000 330	5.92	1	D(0.1)T	1

1909710	$CoPROP^{+}$	1.000 190	1.000 917		0.73	2	LM	1
1909711	$Co(PROP)_2$	1.000 190	2.000 917		0.53	1	D(2)	1
1909730	CoPHTH	1.000 190	1.000 973		1.40	5	LM	1
1909731	$CoHPHTH^{+}$	1.000 190	1.000 973	1.000 330	5.95	1	D(0.5)	1
1909750	$CoPN^{2+}$	1.000 190	1.000 975		5.81	2	LM	1
1909751	$Co(PN)_2^{2+}$	1.000 190	2.000 975		10.50	2	LM	1
				PN log K's based on ethylenediamine				
1909800	$CoTMA^{-}$	1.000 190	1.000 980		6.12	1	D(0.1)	1
1909801	$Co(TMA)_2^{4-}$	1.000 190	2.000 980		10.81	1	D(0.1)	1
1909901	$CoSER^{+}$	1.000 190	1.000 990		4.24	2	LM	1
1909902	$Co(SER)_2$	1.000 190	2.000 990		7.70	2	LM	1
1909950	CoSAL	1.000 190	1.000 995		6.43	1	D(0.15)T	1
1909951	$Co(SAL)_2^{2-}$	1.000 190	2.000 995		11.12	1	D(0.15)T	1
1909980	CoSUCC	1.000 190	1.000 998		1.03	1	D(0)	1
1909981	$CoHSUCC^{+}$	1.000 190	1.000 330	1.000 998	5.89	1	D(0.1)T	1
2119170	$CrPROP^{2+}$	1.000 211	1.000 917		4.67	1	D(0.3)	1
2119171	$Cr(PROP)_2^{+}$	1.000 211	2.000 917		6.94	1	D(0.3)	1
2119750	$Cr(PN)_2^{2+}$	1.000 211	2.000 975		12.99	1	D(1)	1
				PN log K's based on ethylenediamine				
2319050	$CuALA^{+}$	1.000 231	1.000 905		8.04	5	LM	1
2319051	$Cu(ALA)_2$	1.000 231	2.000 905		14.83	5	LM	1
2319052	$CuHALA^{2+}$	1.000 231	1.000 905	1.000 330	10.61	1	D(1)	1
2319060	$CuBEAL^{+}$	1.000 231	1.000 906		6.85	1	D(0.1)	1
2319061	$Cu(BEAL)_2$	1.000 231	2.000 906		12.27	1	D(0.1)	1
2319100	$CuACAC^{+}$	1.000 231	1.000 910		8.00	3	LM	1
2319101	$Cu(ACAC)_2$	1.000 231	2.000 910		14.51	3	LM	1
2319120	CuASP	1.000 231	1.000 912		8.66	4	LM	1
2319121	$CuHASP^{+}$	1.000 231	1.000 912	1.000 330	12.45	1	D(0.1)	1

2319122	$Cu(ASP)_2^{2-}$	1.000	231	2.000	912		15.60	4	LM	1
2319123	$CuH(ASP)_2^{-}$	1.000	231	2.000	912	1.000 330	19.45	1	D(0.1)	1
2319124	$Cu_2(ASP)^{2+}$	2.000	231	1.000	912		10.23	1	D(0.1)	1
2319125	$Cu_2(ASP)_2$	2.000	231	2.000	912		18.77	1	D(0.1)	1
2319150	$CuACPH^{+}$	1.000	231	1.000	915		6.30	1	D(0.1)	1
2319151	$Cu(ACPH)_2$	1.000	231	2.000	915		11.47	1	D(0.1)	1
2319170	$CuBENZ^{+}$	1.000	231	1.000	917		1.59	1	D(0.1)	1
2319200	CuCAT	1.000	231	1.000	920		13.60	5	LM	1,50,51
2319201	$Cu(CAT)_2^{2-}$	1.000	231	2.000	920		24.82	3	LM	1,50,51
2319270	$CuDAP^{+}$	1.000	231	1.000	927		10.37	1	D(0.1)	1
2319271	$Cu(DAP)_2$	1.000	231	2.000	927		19.55	1	D(0.1)	1
2319272	$CuHDAP^{2+}$	1.000	231	1.000	927	1.000 330	15.57	1	D(0.1)	1
2319273	$CuH(DAP)_2^{+}$	1.000	231	2.000	927	1.000 330	25.15	1	D(0.1)	1
2319274	$CuH_2(DAP)_2^{2+}$	1.000	231	2.000	927	2.000 330	30.09	1	D(0.1)	1
2319300	CuDEM	1.000	231	1.000	930		4.53	1	D(0.1)	1
2319301	$Cu(DEM)_2^{2-}$	1.000	231	2.000	930		7.35	1	D(0.1)	1
2319400	$CuDHMB^{+}$	1.000	231	1.000	940		2.43	1	D(0.1)	1
2319401	$Cu(DHMB)_2$	1.000	231	2.000	940		4.02	1	D(0.1)	1
2319450	$CuETA^{2+}$	1.000	231	1.000	945		4.65	4	LM	1
2319451	$Cu(ETA)_2^{2+}$	1.000	231	2.000	945		8.64	2	LM	1
2319550	$CuHBT^{+}$	1.000	231	1.000	955		1.87	1	D(2)	1
2319551	$Cu(HBT)_2$	1.000	231	2.000	955		2.83	1	D(2)	1
2319600	$CuHMP^{+}$	1.000	231	1.000	960		2.71	2	LM	1
2319601	$Cu(HMP)_2$	1.000	231	2.000	960		4.35	2	LM	1
2319650	CuMAL	1.000	231	1.000	965		3.25	2	LM	1,46
2319651	$Cu(MAL)_2^{2-}$	1.000	231	2.000	965		8.42	1	D(1)	1
2319652	$CuHMAL^{+}$	1.000	231	1.000	965	1.000 330	4.39	2	LM	1,46
2319653	$Cu_2OH(MAL)_2^{-}$	2.000	231	2.000	965	-1.000 330	4.57	2	LM	1

2319654	$Cu_2(OH)_2(MAL)_2^{2-}$	2.000	231	2.000	965	-2.000 330	0.32	2	LM	1
2319710	$CuPROP^+$	1.000	231	1.000	971		1.70	5	LM	1
2319711	$Cu(PROP)_2$	1.000	231	2.000	971		2.63	4	LM	1
2319730	CuPHTH	1.000	231	1.000	973		2.73	5	LM	1
2319731	$Cu(PHTH)_2^{2-}$	1.000	231	2.000	973		5.09	1	D(0.1)	1
2319732	$CuHPHTH^+$	1.000	231	1.000	973	1.000 330	5.90	2	LM	1
2319750	$CuPN^{2+}$	1.000	231	1.000	975		10.87	3	LM	1
2319751	$Cu(PN)_2^{2+}$	1.000	231	2.000	975		20.34	3	LM	1
2319900	$CuHSER^{2+}$	1.000	231	1.000	990	1.000 330	12.60	1	D(0.1)	1
2319901	$CuSER^+$	1.000	231	1.000	990		7.92	3	LM	1
2319902	$Cu(SER)_2$	1.000	231	2.000	990		14.57	3	LM	1
2319903	$CuOH(SER)_2^-$	1.000	231	2.000	990	-1.000 330	4.49	2	LM	1
2319951	CuSAL	1.000	231	1.000	995		9.93	3	LM	52,53,54
2319952	$CuHSAL^+$	1.000	231	1.000	330	1.000 995	13.72	1	D(0.25)	52
2319952	$Cu(SAL)_2$	1.000	231	2.000	995		17.74	3	LM	52,53,54
2319980	CuSUCC	1.000	231	1.000	998		2.12	1	D(0)	1
2319981	$CuHSUCC^+$	1.000	231	1.000	998	1.000 330	6.75	1	D(0.1)	1
2809050	$FeALA^+$	1.000	280	1.000	905		3.51	1	D(1)	1
2809051	$Fe(ALA)_2$	1.000	280	2.000	905		5.66	Fit wrt Mn,Co & Ni data		
2809100	$FeACAC^+$	1.000	280	1.000	910		4.50	1	D(0)T	1
2809101	$Fe(ACAC)_2$	1.000	280	2.000	910		7.90	1	D(0)T	1
2809120	FeASP	1.000	280	1.000	912		4.40	1	D(1)	1
2809200	FeCAT	1.000	280	1.000	920		7.96	2	LM	1
2809201	$Fe(CAT)_2^{2-}$	1.000	280	2.000	920		13.56	1	D(1)	1
2809250	FeCYS	1.000	280	1.000	925		5.87	Fit wrt Mn,Co & Ni data		
2809300	FeDEM	1.000	280	1.000	930		1.65	1	D(0.1)	1
						DEM log K's based on malonic acid				
2809450	$FeETA^{2+}$	1.000	280	1.000	945		1.57	Fit wrt Mn,Co & Ni data		

2809600	$FeHMP^{+}$	1.000	280	1.000	960		1.34	1	D(1)	1
						HMP log K's based on glycolic acid				
2809650	FeMAL	1.000	280	1.000	965		2.20	1	D(0.1)T	1
2809710	$FePROP^{+}$	1.000	280	1.000	971		0.74	2	LM	1
						PROP log K's based on acetic acid				
2809750	$FePN^{2+}$	1.000	280	1.000	975		4.27	1	D(1.4)	1
2809751	$Fe(PN)_2^{2+}$	1.000	280	2.000	975		7.52	1	D(1.4)	1
						PN log K's based on ethylenediamine				
2809900	$FeSER^{+}$	1.000	280	1.000	990		3.57	3	LM	1
2809901	$Fe(SER)_2$	1.000	280	2.000	990		6.42	2	LM	1
2809950	FeSAL	1.000	280	1.000	995		6.26	1	D(0.15)T	1
2809951	$Fe(SAL)_2^{2-}$	1.000	280	2.000	995		10.92	1	D(0.15)T	1
2809980	FeSUCC	1.000	280	2.000	998		1.15	1	D(0.15)T	1
2819050	$FeALA^{2+}$	1.000	281	1.000	905		10.24	1	D(0.1)	1
2819100	$FeACAC^{2+}$	1.000	281	1.000	910		9.21	1	D(0.1)T	1
2819101	$Fe(ACAC)_2^{+}$	1.000	281	2.000	910		17.79	1	D(0.1)T	1
2819120	$FeASP^{+}$	1.000	281	1.000	912		11.33	1	D(1)	1
2819150	$FeACPH^{2+}$	1.000	281	1.000	915		10.38	3	LM	1
2819200	$FeCAT^{+}$	1.000	281	1.000	920		20.63	2	LM	1
2819201	$Fe(CAT)_2^{-}$	1.000	281	2.000	920		35.44	1	D(0.1)	1
2819300	$FeDEM^{+}$	1.000	281	1.000	930		7.80	1	D(0.5)	1
2819600	$FeHMP^{2+}$	1.000	281	1.000	960		2.90	1	D(1)	1
						HMP log K's based on glycolic acid				
2819650	$FeMAL^{+}$	1.000	281	1.000	965		6.62	1	D(0.1)T	1
2819651	$Fe_2(OH)_2(MAL)_2$	2.000	281	2.000	965	-2.000 330	11.78	1	D(0.1)T	1
2819700	$FePHEN^{2+}$	1.000	281	1.000	970		7.87	3	LM	1
2819710	$FePROP^{2+}$	1.000	281	1.000	971		3.27	1	D(1)T	1
2819711	$Fe(PROP)_2^{+}$	1.000	281	2.000	971		6.00	1	D(3)	1

					PROP log K's based on acetic acid			
2819800	$FeHTMA^{+}$	1.000 281	1.000 980	1.000 330	17.75	1	D(1)	1
2819900	$FeSER^{2+}$	1.000 281	1.000 990		9.20	1	D(1)	1
2819950	$FeSAL^{+}$	1.000 281	1.000 995		16.07	4	LM	1
2819951	$FeHSAL^{2+}$	1.000 281	1.000 995	1.000 330	17.47	1	D(0.1)	1
2819952	$Fe(SAL)_2^{-}$	1.000 281	2.000 995		27.49	1	D(3)	1
2819980	$FeSUCC^{+}$	1.000 281	1.000 998		6.81	1	D(0.5)	1
3309050	HALA	1.000 330	1.000 905		9.67	6	LM	1,55
3309051	H_2ALA^{+}	2.000 330	1.000 905		11.98	6	LM	1,55
3309060	HBEAL	1.000 330	1.000 906		10.11	5	LM	1
3309061	H_2BEAL^{+}	2.000 330	1.000 906		13.72	6	LM	1
3309100	HACAC	1.000 330	1.000 910		8.76	2	LM	1,56
3309120	$HASP^{-}$	1.000 330	1.000 912		9.52	6	LM	1
3309121	H_2ASP	2.000 330	1.000 912		13.16	6	LM	1
3309122	H_3ASP^{+}	3.000 330	1.000 912		15.06	6	LM	1
3309150	HACPH	1.000 330	1.000 915		9.99	2	LM	1
3309160	HAET	1.000 330	1.000 916		10.71	3	LM	1
3309161	H_2AET^{+}	2.000 330	1.000 916		19.05	4	LM	1
3309170	HBENZ	1.000 330	1.000 917		3.97	4	LM	1
3309200	$HCAT^{-}$	1.000 920	1.000 330		13.09	2	LM	1
3309201	H_2CAT	1.000 920	2.000 330		22.32	3	LM	1
3309250	$HCYS^{-}$	1.000 330	1.000 925		10.15	5	LM	1
3309251	H_2CYS	2.000 330	1.000 925		18.38	5	LM	1
3309252	H_3CYS^{+}	3.000 330	1.000 925		20.26	5	LM	1
3309270	HDAP	1.000 330	1.000 927		9.35	2	LM	1
3309271	H_2DAP^{+}	2.000 330	1.000 927		15.83	2	LM	1
3309272	H_3DAP^{2+}	3.000 330	1.000 927		17.32	1	D(0.1)	1
3309300	$HDEM^{-}$	1.000 330	1.000 930		6.64	3	LM	1

3309301	H_2DEM	2.000	330	1.000	930	8.64	3	LM	1
3309400	HDHMB	1.000	330	1.000	940	3.48	2	LM	1
3309450	$HETA^+$	1.000	330	1.000	945	9.66	2	LM	1
3309550	H(HBT)	1.000	330	1.000	955	4.32	5	LM	1
3309600	H(HMP)	1.000	330	1.000	960	3.75	4	LM	1
3309650	$HMAL^-$	1.000	330	1.000	965	4.47	5	LM	1
3309651	H_2MAL	2.000	330	1.000	965	7.61	5	LM	1
3309670	HMET	1.000	330	1.000	967	9.34	4	LM	1
3309700	HPHEN	1.000	330	1.000	970	9.62	4	LM	1
3309710	HPROP	1.000	330	1.000	971	4.65	6	LM	1
3309730	$HPHTH^-$	1.000	330	1.000	973	4.69	4	LM	1
3309731	H_2PHTH	1.000	330	1.000	973	7.34	6	LM	1
3309750	HPN^+	1.000	330	1.000	975	9.95	3	LM	1
3309751	H_2PN^{2+}	2.000	330	1.000	975	17.08	3	LM	1
3309800	$HTMA^{2-}$	1.000	330	1.000	980	9.93	2	LM	1
3309801	H_2TMA^-	2.000	330	1.000	980	14.36	2	LM	1
3309802	H_3TMA	3.000	330	1.000	980	17.28	2	LM	1
3309850	$HTLA^-$	1.000	330	1.000	985	9.91	2	LM	1
3309851	H_2TLA	2.000	330	1.000	985	13.26	3	LM	1
3309900	HSER	1.000	330	1.000	990	8.99	6	LM	1
3309901	H_2SER^+	2.000	330	1.000	990	11.17	6	LM	1
3309950	$HSAL^-$	1.000	330	1.000	995	13.18	4	LM	1
3309951	$H_{2S}AL$	2.000	330	1.000	995	15.96	5	LM	1
3309980	$HSUCC^-$	1.000	330	1.000	998	5.09	6	LM	1
3309981	H_2SUCC	2.000	330	1.000	998	9.03	6	LM	1
3619050	$HgALA^+$	1.000	361	1.000	905	10.21	1	D(0.1)T	1
3619051	$Hg(ALA)_2$	1.000	361	2.000	905	19.09	1	D(0.1)T	1

ALA log K's based on glycine

3619100	$Hg(ACAC)_2$	1.000	361	2.000	910	21.58	1	D(0.5)T 1
3619250	HgCYS	1.000	361	1.000	925	13.92	1	D(0.1) 1
3619270	$HgDAP^+$	1.000	361	1.000	927	8.14	1	D(0.1) 1
3619271	$Hg(DAP)_2$	1.000	361	2.000	927	15.58	1	D(0.1) 1
3619272	$HgHDAP^{2+}$	1.000	361	1.000	927	1.000 330 14.14	1	D(0.1) 1
3619273	$HgH(DAP)_2^+$	1.000	361	2.000	927	1.000 330 21.73	1	D(0.1) 1
3619450	$HgETA^{2+}$	1.000	361	1.000	945	8.51	2	LM 1
3619451	$Hg(ETA)_2^{2+}$	1.000	361	2.000	945	17.33	2	LM 1
3619550	$HgHBT^+$	1.000	361	1.000	955	4.23	1	D(3) 1
3619551	$Hg(HBT)_2$	1.000	361	2.000	955	8.20	1	D(3) 1
3619700	$HgPHEN^+$	1.000	361	1.000	970	8.26	1	D(1) 57
3619701	$HgPHEN_2$	1.000	361	2.000	970	15.77	1	D(1) 57
3619710	$HgPROP^+$	1.000	361	1.000	971	3.85	6	LM 1
3619711	$Hg(PROP)_2$	1.000	361	2.000	971	8.64	1	D(3) 1
3619750	$Hg(PN)_2^{2+}$	1.000	361	2.000	975	24.01	2	LM 1
3619751	$HgPN^{2+}$	1.000	361	1.000	975	14.32	1	D(0.1) 1
						PN log K's based on ethylenediamine		
3619800	$HgTMA^-$	1.000	361	1.000	980	9.31	1	D(0.1) 1
3619801	$Hg(TMA)_2^{4-}$	1.000	361	2.000	980	17.68	1	D(0.1) 1
4109300	$KDEM^-$	1.000	410	1.000	930	0.31	1	D(0) 1
4109650	$KMAL^-$	1.000	410	1.000	965	-0.23	1	D(0) 1
4109710	KPROP	1.000	410	1.000	971	-0.53	1	D(0.1) 1
						PROP log K's based on acetic acid		
4109730	$KPHTH^-$	1.000	410	1.000	973	0.07	1	D(0) 1
4109950	KHSAL	1.000	410	1.000	330	1.000 995 12.64	1	D(0.25) 48
4109980	$KSUCC^-$	1.000	410	1.000	998	-0.20	1	D(0) 1
4409300	$LiDEM^-$	1.000	440	1.000	930	0.37	1	D(0) 1
4409600	LiHMP	1.000	440	1.000	960	-0.38	1	D(0) 1

					HMP log K's based on lactic acid			
4409710	LiPROP	1.000 440	1.000 971		-0.18	1	D(0.1)	1
					PROP log K's based on acetic acid			
4409730	$LiPHTH^-$	1.000 440	1.000 973		0.34	1	D(0)	1
4409980	$LiSUCC^-$	1.000 440	1.000 998		0.17	1	D(0)	1
4609050	$MgALA^+$	1.000 460	1.000 905		1.50	1	D(0)	1
4609100	$MgACAC^+$	1.000 460	1.000 910		3.19	1	D(0)	1
4609101	$Mg(ACAC)_2$	1.000 460	2.000 910		5.55	1	D(0)	1
4609120	MgASP	1.000 460	1.000 912		2.25	1	D(0.1)	1
4609160	$MgAET^+$	1.000 460	1.000 916		2.18	1	D(0.1)	1
4609170	$MgBENZ^+$	1.000 460	1.000 917		0.08	1	D(1)T	1
4609300	MgDEM	1.000 460	1.000 930		1.52	1	D(0)	1
4609400	MgDHMB	1.000 460	1.000 940		0.80	1	D(0.2)	1
					DHMB log K's based on glyceric acid			
4609550	$MgHBT^+$	1.000 460	1.000 955		0.54	1	D(0.2)	1
4609600	$MgHMP^+$	1.000 460	1.000 960		0.81	1	D(1)	1
4609601	$Mg(HMP)_2$	1.000 460	2.000 960		1.47	1	D(1)	1
4609650	MgMAL	1.000 460	1.000 965		1.42	3	LM	1,46
4609651	$MgHMAL^+$	1.000 460	1.000 965	1.000 330	5.25	1	D(0.1)	1,46
4609710	$MgPROP^+$	1.000 460	1.000 971		0.48	1	D(0.2)	1
4609750	$MgPN^{2+}$	1.000 460	1.000 975		0.27	1	D(1.4)T	1
					PN log K's based on ethylenediamine			
4609900	$MgSER^+$	1.000 460	1.000 990		0.90	1	D(3)	1
4609950	MgSAL	1.000 460	1.000 995		4.80	1	D(0.15)T	1
4609980	MgSUCC	1.000 460	1.000 998		0.81	2	LM	1
4609981	$MgHSUCC^+$	1.000 460	1.000 998	1.000 330	5.55	1	D(0.2)	1
4709050	$MnALA^+$	1.000 470	1.000 905		2.38	1	D(0;0.1)	1
4709051	$Mn(ALA)_2$	1.000 470	2.000 905		3.86	1	D(0.15)	1

4709100	$MnACAC^{+}$	1.000	470	1.000	910		3.84	3	LM 1
4709101	$Mn(ACAC)_2$	1.000	470	2.000	910		6.71	3	LM 1
4709120	MnASP	1.000	470	1.000	912		3.27	1	D(0.1) 1
4709200	MnCAT	1.000	470	1.000	920		7.51	2	LM 1
4709201	$Mn(CAT)_2^{2-}$	1.000	470	2.000	920		12.87	2	LM 1
4709250	MnCYS	1.000	470	1.000	925		4.27	1	D(0.1) 1
4709300	MnDEM	1.000	470	1.000	930		1.50	1	D(0.1) 1
						DEM log K's based on malonic acid			
4709450	$MnETA^{2+}$	1.000	470	3.000	945		0.87	1	D(0.1) 1
4709600	$MnHMP^{+}$	1.000	470	1.000	960		0.91	1	D(1) 1
4709601	$Mn(HMP)_2$	1.000	470	2.000	960		1.49	1	D(1) 1
4709650	MnMAL	1.000	470	1.000	965		1.92	1	D(0.1) 46
4709710	$MnPROP^{+}$	1.000	470	1.000	971		0.72	2	LM 1
						PROP log K's based on acetic acid			
4709730	MnPHTH	1.000	470	1.000	973		1.52	1	D(0) 1
4709750	$MnPN^{2+}$	1.000	470	1.000	975		2.76	2	LM 1
4709751	$Mn(PN)_2^{2+}$	1.000	470	2.000	975		4.85	2	LM 1
						PN log K's based on ethylenediamine			
4709900	$MnSER^{+}$	1.000	470	1.000	990		2.47	2	LM 1
4709901	$Mn(SER)_2$	1.000	470	2.000	990		3.96	2	LM 1
4709950	MnSAL	1.000	470	1.000	995		5.61	1	D(0.15)T 1
4709951	$Mn(SAL)_2^{2-}$	1.000	470	2.000	995		9.52	1	D(0.15)T 1
4709980	MnSUCC	1.000	470	1.000	998		0.97	1	D(0) 1
4709981	$MnHSUCC^{+}$	1.000	470	1.000	998	1.000 330	5.72	1	D(0) 1
5009300	$NaDEM^{-}$	1.000	500	1.000	930		0.30	1	D(0) 1
5009650	$NaMAL^{-}$	1.000	500	1.000	965		0.11	1	D(0) 1
5009710	NaPROP	1.000	500	1.000	971		-0.36	1	D(0.1) 1
						PROP log K's based on acetic acid			

5009730	$NaPHTH^-$	1.000 500	1.000 973		0.21	1	D(0)	1
5009950	NaHSAL	1.000 500	1.000 330	1.000 995	12.64	1	D(0.25)	48
5009980	$NaSUCC^-$	1.000 500	1.000 998		-0.27	1	D(0)	1
5409050	$NiALA^+$	1.000 540	1.000 905		5.33	4	LM	1
5409051	$Ni(ALA)_2$	1.000 540	2.000 905		9.78	4	LM	1
5409060	$NiBEAL^+$	1.000 540	1.000 906		4.45	4	LM	1
5409061	$Ni(BEAL)_2$	1.000 540	2.000 906		7.80	3	LM	1
5409100	$NiACAC^+$	1.000 540	1.000 910		5.47	1	D(0;0.1)	1
5409101	$Ni(ACAC)_2$	1.000 540	2.000 910		9.82	1	D(0;0.1)	1
5409120	$NiHASP^+$	1.000 540	1.000 912	1.000 330	11.04	1	D(0.1)	1
5409121	NiASP	1.000 540	1.000 912		6.90	2	LM	1
5409122	$Ni(ASP)_2^{2-}$	1.000 540	2.000 912		12.31	2	LM	1
5409150	$NiACPH^+$	1.000 540	1.000 915		4.17	1	D(0.1)	1
5409151	$Ni(ACPH)_2$	1.000 540	2.000 915		6.93	1	D(0.1)	1
5409160	$NiAET^+$	1.000 540	1.000 916		10.06	1	D(1)	1
5409161	$Ni(AET)_2$	1.000 540	2.000 916		19.82	1	D(1)	1
5409171	$NiBENZ^+$	1.000 540	1.000 917		0.73	1	D(0.1)	1
5409200	NiCAT	1.000 540	1.000 920		8.71	2	LM	1
5409201	$Ni(CAT)_2^{2-}$	1.000 540	2.000 920		14.03	1	D(0.1)	1
5409250	NiCYS	1.000 540	1.000 925		9.57	2	LM	1
5409251	$Ni(CYS)_2^{2-}$	1.000 540	2.000 925		19.70	1	D(0.1)	1
5409252	$NiHCYS^+$	1.000 540	1.000 925	1.000 330	14.56	1	D(0.1)	1
5409270	$NiDAP^+$	1.000 540	1.000 927		7.96	1	D(0.1)	1
5409271	$Ni(DAP)_2$	1.000 540	2.000 927		14.94	1	D(0.1)	1
5409272	$NiHDAP^{2+}$	1.000 540	1.000 927	1.000 330	13.46	1	D(0.1)	1
5409273	$NiH(DAP)_2^+$	1.000 540	2.000 927	1.000 330	20.95	1	D(0.1)	1
5409274	$NiH_2(DAP)_2^{2+}$	1.000 540	2.000 927	2.000 330	26.42	1	D(0.1)	1
5409300	NiDEM	1.000 540	1.000 930		1.94	1	D(0.1)	1

5409400	$NiDHMB^{+}$	1.000	540	1.000	940		1.62	1	D(0.1) 1
5409401	$Ni(DHMB)_2$	1.000	540	2.000	940		2.77	1	D(0.1) 1
5409450	$NiETA^{2+}$	1.000	540	1.000	945		3.12	3	LM 1
5409451	$Ni(ETA)_2^{2+}$	1.000	540	2.000	945		5.66	3	LM 1
5409550	$NiHBT^{+}$	1.000	540	1.000	955		0.99	1	D(2) 1
5409551	$Ni(HBT)_2$	1.000	540	2.000	955		1.28	1	D(2) 1
5409600	$NiHMP^{+}$	1.000	540	1.000	960		1.68	1	D(1) 1
5409601	$Ni(HMP)_2$	1.000	540	2.000	960		2.81	1	D(1) 1
5409650	NiMAL	1.000	540	1.000	965		2.77	1	D(0.1) 46
5409651	$NiHMAL^{+}$	1.000	540	1.000	965	1.000 330	6.11	1	D(0.1) 46
5409671	$Ni_2(MET)_2^{2+}$	2.000	540	2.000	967		10.7	1	D(0.5) 1
5409710	$NiPROP^{+}$	1.000	540	1.000	971		0.78	2	LM 1
5409711	$Ni(PROP)_2$	1.000	540	2.000	971		0.73	1	D(2) 1
5409730	$NiHPHTH^{+}$	1.000	540	1.000	973	1.000 330	5.37	1	D(0.5) 1
5409731	NiPHTH	1.000	540	1.000	973		1.59	5	LM 1
5409750	$NiPN^{2+}$	1.000	540	1.000	975		7.58	3	LM 1
5409751	$Ni(PN)_2^{2+}$	1.000	540	2.000	975		14.03	3	LM 1
5409800	$NiTMA^{-}$	1.000	540	1.000	980		7.08	1	D(0.1) 1
5409801	$Ni(TMA)_2^{4-}$	1.000	540	2.000	987		13.53	1	D(0.1) 1
5409802	NiHTMA	1.000	540	1.000	980	1.000 330	11.53	1	D(0.1) 1
5409850	NiTLA	1.000	540	1.000	985		5.99	1	D(0.5) 1
5409851	$Ni(TLA)_2^{2-}$	1.000	540	2.000	985		13.10	1	D(0.5) 1
5409900	$NiSER^{+}$	1.000	540	1.000	990		5.28	2	LM 1
5409901	$Ni(SER)_2$	1.000	540	2.000	990		9.79	2	LM 1
5409950	NiSAL	1.000	540	1.000	995		6.66	1	D(0.15)T 1
5409951	$Ni(SAL)_2^{2-}$	1.000	540	2.000	995		11.42	1	D(0.15)T 1
5409980	NiSUCC	1.000	540	1.000	998		1.09	1	D(0;0.1) 1
5409981	$NiHSUCC^{+}$	1.000	540	1.000	998	1.000 330	5.82	1	D(0) 1

6009050	$PbALA^{+}$	1.000	600	1.000	905		5.17	1	D(3) 1
6009051	$Pb(ALA)_2$	1.000	600	2.000	905		8.00	1	D(3) 1
6009052	$PbHALA^{2+}$	1.000	600	1.000	905	1.000 330	11.27	1	D(3) 1
6009100	$PbACAC^{+}$	1.000	600	1.000	910		4.31	1	D(0.1) 1
6009101	$Pb(ACAC)_2$	1.000	600	2.000	910		6.93	1	D(0.1) 1
6009120	PbASP	1.000	600	1.000	912		6.80	1	D(3) 1
6009121	$Pb(ASP)_2^{2-}$	1.000	600	2.000	912		9.30	1	D(3) 1
6009160	$PbAET^{+}$	1.000	600	1.000	916		10.89	1	D(0.15) 1
6009170	$PbBENZ^{+}$	1.000	600	1.000	917		1.85	2	LM 1
6009171	$Pb(BENZ)_2$	1.000	600	2.000	917		2.91	1	D(1) 1
6009250	PbCYS	1.000	600	1.000	925		12.19	4	LM 1
6009251	$PbHCYS^{+}$	1.000	600	1.000	925	1.000 330	16.76	1	D(3) 1
6009252	$Pb(CYS)_2^{2-}$	1.000	600	2.000	925		18.50	1	D(3) 1
6009253	$PbH(CYS)_2^{-}$	1.000	600	2.000	925	1.000 330	26.59	1	D(3) 1
6009254	$PbOH(CYS)_2^{3-}$	1.000	600	2.000	925	-1.000 330	7.28	1	D(3) 1
6009300	PbDEM	1.000	600	1.000	930		1.79	1	D(0.1) 1
						DEM log K's based on malonic acid			
6009400	$PbDHMB^{+}$	1.000	600	1.000	940		2.57	1	D(2) 1
6009401	$Pb(DHMB)_2$	1.000	600	2.000	940		3.75	1	D(2) 1
						DHMB log K's based on glyceric acid			
6009450	$PbETA^{2+}$	1.000	600	1.000	945		4.08	1	D(0.1) 1
6009550	$PbHBT^{+}$	1.000	600	1.000	955		2.17	1	D(2) 1
6009551	$Pb(HBT)_2$	1.000	600	2.000	955		3.19	1	D(2) 1
6009600	$PbHMP^{+}$	1.000	600	1.000	960		2.03	2	LM 1
6009601	$Pb(HMP)_2$	1.000	600	2.000	960		3.25	2	LM 1
6009650	$PbHMAL^{+}$	1.000	600	1.000	965	1.000 330	6.95	1	D(1) 1
6009651	PbH_2MAL_2	1.000	600	2.000	965	2.000 330	12.67	1	D(1) 1
6009653	PbMAL	1.000	600	1.000	965		1.94	1	D(1) 46

6009670	$PbMET^{+}$	1.000	600	1.000	967		6.44	1	D(0.1) 1
6009671	Pb_2MET^{3+}	2.000	600	1.000	967		9.11	2	LM 1
6009710	$PbPROP^{+}$	1.000	600	1.000	971		2.19	1	D(2) 1
6009711	$Pb(PROP)_2$	1.000	600	2.000	971		3.21	1	D(2) 1
6009730	PbPHTH	1.000	600	1.000	973		2.85	1	D(1) 1
6009731	$Pb(PHTH)_2^{2-}$	1.000	600	2.000	973		4.03	1	D(1) 1
6009732	$PbHPHTH^{+}$	1.000	600	1.000	973	1.000 330	5.86	1	D(1) 1
6009733	$PbH(PHTH)_2^{-}$	1.000	600	2.000	973	1.000 330	7.81	1	D(1) 1
6009750	$Pb(PN)_2^{2+}$	1.000	600	2.000	975		9.03	1	D(0.1) 1
6009751	$PbPN^{2+}$	1.000	600	1.000	975		5.05	1	D(0.2) 1
		PN log K's based on ethylenediamine (only for mono species)							
6009900	$PbSER^{+}$	1.000	600	1.000	990		4.65	1	$ZnSER^{+}$(3) 1
6009901	$Pb(SER)_2$	1.000	600	2.000	990		7.39	1	$Zn(SER)_2$(3) 1
6009980	PbSUCC	1.000	600	1.000	998		2.59	3	LM 1
6009981	$PbHSUCC^{+}$	1.000	600	1.000	998	1.000 330	6.95	2	LM 1
6009982	$Pb(SUCC)_2^{2-}$	1.000	600	2.000	998		3.99	2	LM 1
6009984	$PbH_2(SUCC)_2$	1.000	600	2.000	998	2.000 330	12.93	2	LM 1
6009985	$PbH(SUCC)_2^{-}$	1.000	600	2.000	998	1.000 330	8.82	2	LM 1
7809710	$SnPROP^{+}$	1.000	780	1.000	971		3.40	1	D(3) 1
7809711	$Sn(PROP)_2$	1.000	780	2.000	971		5.84	1	D(3) 1
		PROP log K's based on acetic acid							
8009050	$SrALA^{+}$	1.000	800	1.000	905		0.09	1	D(0) 1
8009100	$SrACAC^{+}$	1.000	800	1.000	910		1.52	1	D(0.1) 1
8009120	SrASP	1.000	800	1.000	912		1.00	1	D(0.1) 1
8009160	$SrAET^{+}$	1.000	800	1.000	916		1.32	1	D(0.1) 1
8009300	SrDEM	1.000	800	1.000	930		1.12		Set = BaDEM
8009400	$SrDHMB^{+}$	1.000	800	1.000	940		0.75	1	D(0.2) 1
		DHMB log K's based on glyceric acid							

8009550	$SrHBT^+$	1.000	800	1.000	955		0.34	1	D(0.2)	1
8009600	$SrHMP^+$	1.000	800	1.000	960		0.57	1	D(1)	1
8009601	$Sr(HMP)_2$	1.000	800	2.000	960		0.75	1	D(1)	1
8009650	SrMAL	1.000	800	1.000	965		1.27	2	LM	1
8009651	$SrHMAL^+$	1.000	800	1.000	965	1.000 330	5.04	1	D(0.1)	1
8009710	$SrPROP^+$	1.000	800	1.000	971		0.29	1	D(0.2)	1
8009980	SrSUCC	1.000	800	1.000	998		0.76	1	D(0.2)	1
8009981	$SrHSUCC^+$	1.000	800	1.000	998	1.000 330	5.43	1	D(0.2)	1
8939050	UO_2ALA^+	1.000	893	1.000	905		7.14	1	D(0.1)	55
8939051	$UO_2(ALA)_2$	1.000	893	2.000	905		14.70	1	D(0.1)	55
8939060	UO_2HBEAL^{2+}	1.000	893	1.000	906	1.000 330	12.01	1	D(1)	58
8939061	$UO_2H_2(BEAL)_2$	1.000	893	2.000	906	1.000 330	23.60	1	D(1)	58
8939100	UO_2ACAC^+	1.000	893	1.000	910		7.02	1	D(0;0.1)	1
8939101	$UO_2(ACAC)_2$	1.000	893	2.000	910		13.18	1	D(0;0.1)	1
8939102	$UO_2H(ACAC)_2$	1.000	893	2.000	910	1.000 330	17.67	1	D(0;0.1)	1
8939120	UO_2ASP	1.000	893	1.000	912		3.52	1	D(0.7)	1
8939121	UO_2HASP^+	1.000	893	1.000	912	1.000 330	11.97	2	LM	1,59
8939122	$UO_2H_2(ASP)_2$	1.000	893	2.000	912	2.000 330	23.19	2	LM	1,59
8939200	UO_2CAT	1.000	893	1.000	920		15.33	1	D(0.1)T	1
8939201	UO_2HCAT^+	1.000	893	1.000	330	1.000 920	19.20	1	D(0.1)T	1
8939202	$UO_2H(CAT)_2^-$	1.000	893	1.000	330	2.000 920	33.49	1	D(0.1)T	1
8939250	UO_2HCYS^+	1.000	893	1.000	925	1.000 330	15.80	1	D(0.1)	55
8939251	$UO_2H_2(CYS)_2$	1.000	893	2.000	925	2.000 330	31.88	1	D(0.1)	55
8939300	UO_2DEM	1.000	893	1.000	930		6.80	1	D(0.5)	1
8939301	$UO_2(DEM)_2^{2-}$	1.000	893	2.000	930		11.01	1	D(0.5)	1
8939550	UO_2HBT^+	1.000	893	1.000	955		2.39	1	D(1)	1
8939551	$UO_2(HBT)_2$	1.000	893	2.000	955		4.36	1	D(1)	1
8939600	UO_2HMP^+	1.000	893	1.000	960		3.19	1	D(1)T	1

8939601	$UO_2(HMP)_2$	1.000	893	2.000	960		5.14	1	D(1)T 1
8939650	UO_2OHMAL^-	1.000	893	1.000	965	-1.000 330	2.08	1	D(1) 1
8939651	$(UO_2)_2(OH)_2(MAL)_2^{2-}$	2.000	893	2.000	965	-2.000 330	7.42	2	LM 1
8939700	UO_2PHEN^+	1.000	893	1.000	970		5.63	1	D(0.1)T 1
8939710	UO_2PROP^+	1.000	893	1.000	971		2.33	1	D(1)T 1
8939711	UO_2PROP_2	1.000	893	2.000	971		4.36	1	D(1)T 1
8939730	UO_2PHTH	1.000	893	1.000	973		4.43	1	D(1) 1
8939900	UO_2HSER^{2+}	1.000	893	1.000	990	1.000 330	9.88	1	D(0.5) 1
8939901	UO_2SER^+	1.000	893	1.000	990		8.47	1	D(0.1) 55
8939902	$UO_2(SER)_2$	1.000	893	2.000	990		14.39	1	D(0.1) 55
8939950	UO_2HSAL^+	1.000	893	1.000	995	1.000 330	15.19	1	D(0.1)T 1
8939951	UO_2SAL	1.000	893	1.000	995		11.70	1	D(0.1)T 1
8939952	$UO_2(SAL)_2^{2-}$	1.000	893	2.000	995		20.46	1	D(0.1)T 1
8939980	UO_2SUCC	1.000	893	1.000	998		3.78	2	LM 1
8939981	UO_2HSUCC^+	1.000	893	1.000	998	1.000 330	7.27	2	LM 1
8939982	$UO_2H(SUCC)_2$	1.000	893	2.000	998	1.000 330	11.14	1	D(1) 1
9509050	ZNOHALA	1.000	950	1.000	905	1.000 330	-3.64	1	D(0.5) 1
9509051	$ZnALA^+$	1.000	950	1.000	905		4.55	4	LM 1
9509052	$Zn(ALA)_2$	1.000	950	2.000	905		8.53	4	LM 1
9509060	$ZnBEAL^+$	1.000	950	1.000	906		3.88	1	D(0.5) 1
9509061	$Zn(BEAL)_2$	1.000	950	2.000	906		7.17	1	D(0.5) 1
9509100	$ZnACAC^+$	1.000	950	1.000	910		4.57	3	LM 1
9509101	$Zn(ACAC)_2$	1.000	950	2.000	910		8.08	2	LM 1
9509120	ZnASP	1.000	950	1.000	912		5.54	1	D(0.1) 1
9509121	$Zn(ASP)_2^{2-}$	1.000	950	2.000	912		9.96	1	D(0.5) 1
9509122	$ZnHASP^+$	1.000	950	1.000	912	1.000 330	10.58	1	D(0.1) 1
9509160	$ZnAET^+$	1.000	950	1.000	916		10.07	2	LM 1
9509161	$Zn(AET)_2$	1.000	950	2.000	916		18.78	2	LM 1

9509170	$ZnBENZ^{+}$	1.000	950	1.000	917			0.73	1	D(0.1)	1
9509200	ZnCAT	1.000	950	1.000	920			9.55	2	LM	1
9509201	$Zn(CAT)_2^{2-}$	1.000	950	2.000	920			17.36	2	LM	1
9509250	ZnCYS	1.000	950	1.000	925			8.74	1	D(0.1)	1
9509251	$Zn(CYS)_2^{2-}$	1.000	950	2.000	925			18.06	2	LM	1
9509252	$ZnHCYS^{+}$	1.000	950	1.000	925	1.000	330	14.46	2	LM	1
9509253	$ZnH(CYS)_2^{-}$	1.000	950	2.000	925	1.000	330	24.19	2	LM	1
9509254	$ZnH_2(CYS)_2$	1.000	950	2.000	925	2.000	330	29.72	2	LM	1
9509270	$ZnDAP^{+}$	1.000	950	1.000	927			6.12	1	D(0.1)	1
9509271	$Zn(DAP)_2$	1.000	950	2.000	927			11.39	1	D(0.1)	1
9509272	$ZnHDAP^{2+}$	1.000	950	1.000	927	1.000	330	12.59	1	D(0.1)	1
9509273	$ZnH(DAP)_2^{+}$	1.000	950	2.000	927	1.000	330	18.25	1	D(0.1)	1
9509274	$ZnH_2(DAP)_2^{2+}$	1.000	950	2.000	927	2.000	330	24.63	1	D(0.1)	1
9509300	ZnDEM	1.000	950	1.000	930			2.01	1	D(0.1)	1
9509450	$ZnETA^{2+}$	1.000	950	1.000	945			2.53	3	LM	1
9509452	$Zn(ETA)_2^{2+}$	1.000	950	2.000	945			4.83	2	LM	1
9509550	$ZnHBT^{+}$	1.000	950	1.000	955			0.98	1	D(2)	1
9509551	$Zn(HBT)_2$	1.000	950	2.000	955			1.64	1	D(2)	1
9509600	$ZnHMP^{+}$	1.000	950	1.000	960			1.71	1	D(1)	1
9509601	$Zn(HMP)_2$	1.000	950	2.000	960			3.00	1	D(1)	1
9509650	ZnMAL	1.000	950	1.000	965			2.53	1	D(0.1)	46
9509651	$ZnHMAL^{+}$	1.000	950	1.000	965	1.000	330	5.94	1	D(0.1)	46
9509710	$ZnPROP^{+}$	1.000	950	1.000	971			0.81	2	LM	1
9509711	$Zn(PROP)_2$	1.000	950	2.000	971			1.27	2	LM	1
9509730	ZnPHTH	1.000	950	1.000	973			1.69	1	D(0)	1
9509731	$Zn(PHTH)_2^{2-}$	1.000	950	2.000	973			3.06	1	D(0)	1
9509750	$ZnPN^{2+}$	1.000	950	1.000	975			5.96	3	LM	1
9509751	$Zn(PN)_2^{2+}$	1.000	950	2.000	975			11.43	3	LM	1

9509800	$ZnTMA^-$	1.000	950	1.000	980			7.62	2	LM	1
9509801	$Zn(TMA)_2^{4-}$	1.000	950	2.000	980			14.21	1	D(0.1)	1
9509802	$ZnOHTMA^{2-}$	1.000	950	1.000	980	-1.000	330	-0.46	2	LM	1
9509803	ZnHTMA	1.000	950	1.000	980	1.000	330	9.87	1	D(0.1)	1
9509850	ZnTLA	1.000	950	1.000	985			6.79	1	D(0.5)	1
9509851	$Zn(TLA)_2^{2-}$	1.000	950	2.000	985			14.30	1	D(0.5)	1
9509901	$ZnSER^+$	1.000	950	1.000	990			4.50	2	LM	1
9509902	$Zn(SER)_2$	1.000	950	2.000	990			8.40	2	LM	1
9509950	ZnSAL	1.000	950	1.000	995			6.56	1	D(0.15)T	1
9509980	ZnSUCC	1.000	950	1.000	998			1.45	2	LM	1
9509981	$Zn(SUCC)_2^{2-}$	1.000	950	2.000	998			2.05	2	LM	1
9509982	$ZnHSUCC^+$	1.000	950	1.000	998	1.000	330	5.86	1	D(0.1)T	1
Solid Species											
2002000	Ag_2O	2.000	20	-2.000	330			-12.97	5	LM	1,2
2003000	Gibbsite	1.000	30	-3.000	33			-9.58		BM	2
2007000	$Ba(OH)_2$	1.000	70	-2.000	33			-24.86	1	D(0.2)	1
2015001	$Ca(OH)_2$	-2.000	330	1.000	150			-23.20		BM	2
2016000	$Cd(OH)_2$	-2.000	330	1.000	160			-14.06		BM	2
2019000	$Co(OH)_2$	1.000	190	-2.000	330			-13.60		BM	2
2021100	$Cr(OH)_3$	1.000	211	-3.000	330			-13.26		BM	2
2023000	Cu_2O	2.000	230	-2.000	330			1.32		BM	2
2023100	$Cu(OH)_2$	-2.000	330	1.000	231			-9.04	3	LM	1
2028000	$Fe(OH)_2$	1.000	280	-2.000	33			-13.26		BM	2
2028100	$am\text{-}Fe(OH)_3$	-3.000	330	1.000	281			-3.80		BM	1,2
2028101	$Fe(OH)_2NO_3$	1.000	281	1.000	492	-2.000	330	-2.13	1	D(1)	1
2036100	HgO	1.000	361	-2.000	330			-2.74		BM	2
2046000	Brucite	1.000	460	-2.000	330			-17.31		BM	2

2047000	$Mn(OH)_2$	-2.000	330	1.000	470			-15.60		BM	2
2047001	MnO_2	-4.000	330	1.000	470	-2.000	1	-41.47	1	D(0)	61
2054000	$Ni(OH)_2$	1.000	540	-2.000	33			-13.40		BM	2
2060000	Litharge	1.000	600	-2.000	330			-13.21		BM	2
2078000	SnO	1.000	780	-2.000	330			-2.16		BM	2
2089300	$UO_2(OH)_2$	1.000	893	-2.000	330			-5.93		BM	2
2095000	$Zn(OH)_2$	-2.000	330	1.000	950			-12.74		BM	2
4002000	AgBr	1.000	20	1.000	130			11.93	4	LM	1
4023000	CuBr	1.000	230	1.000	130			8.04	2	LM	1
4023100	$Cu(OH)_{1.5}Br_{0.5}$	1.000	231	0.500	130	-1.500	330	-3.95	1	D(0)	1
4036000	Hg_2Br_2	1.000	360	2.000	130			21.10	1	D(0)	1
4036100	$HgBr_2$	1.000	361	2.000	130			18.87	1	D(0.5)	1
4060000	$PbBr_2$	1.000	600	2.000	130			4.66	1	D(0)	1
4102000	Chloroargyrite	1.000	20	1.000	180			9.66	5	LM	1
4123000	CuCl	1.000	230	1.000	180			6.47	2	LM	1
4123100	$Cu(OH)_{1.5}Cl_{0.5}$	1.000	231	0.500	180	-1.500	330	-3.71	2	LM	1
4136000	Hg_2Cl_2	1.000	360	2.000	180			16.83	2	LM	1
4160000	$PbCl_2$	1.000	600	2.000	180			3.99	2	LM	1
4195000	$Zn(OH)_{1.5}Cl_{0.5}$	1.000	950	0.500	180	-1.500	330	-8.12	1	D(0)	1
4203000	$AlOHF_2$	1.000	30	2.000	270	-1.000	330	7.20	1	D(0)	1
4207000	BaF_2	1.000	70	2.000	270			4.98	1	D(0)	1
4215000	Fluorite	1.000	150	2.000	270			9.63	1	D(0)	1
4244000	LiF	1.000	440	1.000	270			2.53	1	D(0)	1
4246000	MgF_2	1.000	460	2.000	270			7.37	1	D(0)	1
4260000	PbF_2	1.000	600	2.000	270			6.30	2	LM	1
4278000	SrF_2	1.000	800	2.000	270			7.64	1	D(0)	1
4302000	AgI	1.000	20	1.000	380			15.77	2	LM	1
4336000	Hg_2I_2	1.000	360	2.000	380			27.49	2	LM	1

4336100	HgI_2	1.000	361	2.000	380		27.92	1	D(0.5) 1
4360000	PbI_2	1.000	600	2.000	380		7.24	2	LM 1
4378000	SnI_2	1.000	780	2.000	380		4.49	1	D(4) 1
4402000	$AgIO_3$	1.000	20	1.000	381		7.10	2	LM 1
4407000	$Ba(IO_3)_2$	1.000	70	2.000	381		7.68	1	D(0) 1
4415000	$Ca(IO_3)_2$	2.000	150	2.000	381		5.00	5	LM 1
4416000	$Cd(IO_3)_2$	1.000	160	2.000	381		7.03	2	LM 1
4419000	$Co(IO_3)_2$	1.000	190	2.000	381		4.73	6	LM 1
4421100	$Cr(IO_3)_3$	1.000	211	3.000	381		5.28	1	D(0.5) 1
4423100	$Cu(IO_3)_2$	1.000	231	2.000	381		6.09	6	LM 1
4423101	$Cu(OH)_{1.5}(IO3)_{0.5}$	1.000	231	0.500	381	-1.500 330	-3.94	1	D(0) 1
4436000	$Hg_2(IO_3)_2$	1.000	360	2.000	381		16.89	1	D(0) 1
4441000	KIO_3	1.000	381	1.000	410		1.35	1	D(0) 1
4454000	$Ni(IO_3)_2$	1.000	540	2.000	381		4.15	2	LM 1
4460000	$Pb(IO_3)_2$	1.000	600	2.000	381		11.55	1	D(0) 1
4480000	$Sr(IO_3)_2$	1.000	800	2.000	381		5.34	5	LM 1
4489300	$UO_2(IO_3)_2$	1.000	893	2.000	381		6.89	1	D(0.2) 1
4495000	$Zn(IO_3)_2$	1.000	950	2.000	381		4.38	7	LM 1
5002000	Ag_2CO_3	2.000	20	1.000	140		10.03	1	D(0) 1
5007000	$BaCO_3$	1.000	70	1.000	140		7.35	1	D(0) 1
5015000	Aragonite	1.000	150	1.000	140		6.15	2	LM 1
5016000	$CdCO_3$	1.000	160	1.000	140		12.40	1	D(0) 1
5019000	$CoCO_3$	1.000	190	1.000	140		9.52	1	D(0.7) 1
5023100	$CuCO_3$	1.000	231	1.000	140		10.34	1	D(0) 1
5023101	Malachite	2.000	231	1.000	140	-2.000 330	4.48	2	LM 1,62
5023102	Azurite	3.000	231	2.000	140	-2.000 330	13.98	2	LM 1
5028000	Siderite	1.000	280	1.000	140		9.64	2	LM 1
5036000	Hg_2CO_3	1.000	360	1.000	140		14.62	1	D(0) 1

5046000	Nesquehonite	1.000	460	1.000	140			3.51	1	D(0) 1
5047000	Rhodochrosite	1.000	470	1.000	140			8.52	4	LM 1
5054000	$NiCO_3$	1.000	540	1.000	140			5.50	2	LM 1
5060000	Cerrusite	1.000	600	1.000	140			11.30	4	LM 1
5060001	$Pb_3(OH)_2(CO_3)$	3.000	600	2.000	140	-2.000	330	15.74	1	D(0.3) 1
5080000	Strontianite	1.000	800	1.000	140			7.93	1	D(0) 1
5095000	Smithsonite	1.000	950	1.000	140			8.73	1	D(0) 1
6002000	Ag_2SO_4	2.000	20	1.000	732			3.72	1	D(0) 1
6007000	Barite	1.000	70	1.000	732			8.51	1	$SrSO_4$(0) 1
6015000	Gypsum	1.000	150	1.000	732			2.97	5	LM 1
6023100	Brochantite	1.000	231	0.250	732	-1.500	330	-4.46	1	D(0) 1
6036000	Hg_2SO_4	1.000	360	1.000	732			4.62	2	LM 1
6060000	Anglesite	1.000	600	1.000	732			6.29	2	LM 1
6080000	Celestite	1.000	800	1.000	732			5.05	6	LM 1
7002000	Ag_3PO_4	3.000	20	1.000	580			15.29	1	D(0) 1
7003000	Berlinite	1.000	30	1.000	580			17.81	1	D(0) 63
7015000	Brushite	1.000	150	1.000	580	1.000	330	16.51	1	D(0) 1
7015002	$Ca_3(PO_4)_2$	3.000	150	2.000	580			23.68	1	D(0) 1
7028000	Vivianite	3.000	280	2.000	580			30.76	1	D(0) 1
7028100	Strengite	1.000	281	1.000	580			23.61	1	D(0) 1
7036000	Hg_2HPO_4	1.000	360	1.000	580	1.000	330	22.13	1	D(0) 1
7036100	$HgHPO_4$	1.000	361	1.000	580	1.000	330	24.36	1	D(3) 1
7036101	$Hg_3(PO_4)_2$	3.000	361	2.000	580			47.50	1	D(3) 1
7036102	$(HgOH)_3PO_4$	3.000	361	1.000	580	-3.000	330	20.74	1	D(3) 1
7046000	Bobierrite	3.000	460	2.000	580			18.38	1	D(0) 1
7046001	Newberyite	1.000	460	1.000	580	1.000	330	15.80	2	LM 1
7060006	$PbHPO_4$	1.000	600	1.000	580	1.000	330	21.25	1	D(0) 1
7089300	UO_2HPO_4	1.000	893	1.000	580	1.000	330	22.26	1	D(0) 1

7089301	$(UO_2)_3(PO_4)_2$	3.000	893	2.000	580			43.76	1	D(0)	1
7095000	α-Hopeite	3.000	950	2.000	580			30.06	1	D(0)	1
7402000	Ag_2CrO_4	2.000	20	1.000	210			10.48	1	D(1)	1
7407000	$BaCrO_4$	1.000	70	1.000	210			8.44	4	LM	1
7423100	$CuCrO_4$	1.000	231	1.000	210			4.23	1	$BaCrO_4$(0)	1
7436000	Hg_2CrO_4	1.000	360	1.000	210			6.49	1	$BaCrO_4$(0)	1
7460000	$PbCrO_4$	1.000	600	1.000	210			12.47	1	$BaCrO_4$(0)	1
8003000	Kaolinite	2.000	770	2.000	30	-2.000	330	35.25	1	D(0)	64
8003001	$KAl_3Si_3O_{10}$..	3.000	770	3.000	30	1.000	410	47.07	1	D(0)	64
		-4.000	330								
8033000	am-SiO_2	1.000	770	2.000	330			24.84	1	D(0)	64
8046000	Illite	3.500	770	-1.000	330	2.300	30	65.34	1	D(0)	64
		0.250	460	0.600	410						
8046001	Chlorite	3.000	770	2.000	30	5.000	460	-9.48	1	D(0)	64
		-10.000	330								
8050000	Mg-Montmorillonite	3.666	770	2.333	30	0.166	460	73.31	1	D(0)	64
Redox Reactions											
2102110	CrO_4^{2-}/Cr^{3+}	1.000	210	8.000	330	3.000	1	74.37	1	D(0)	61
		-1.000	211								
2302310	Cu^+/Cu^{2+}	1.000	231	1.000	1	-1.000	230	2.03	1	D(0)	61
2812800	Fe^{3+}/Fe^{2+}	1.000	281	-1.000	280	1.000	1	12.44	1	D(0)	61
3603610	Hg_2^{2+}/Hg^{2+}	2.000	361	2.000	1	-1.000	360	30.28	1	D(0)	61
3803810	IO_3^-/I^-	1.000	381	6.000	330	6.000	1	108.97	1	D(0)	61
		-1.000	380								
Gaseous Reactions											
3301403	CO_2 (g)	1.000	140	2.000	330			17.07	6	LM	1,65

References

1: The critical compilations of Martell and Smith (Mar74a, Smi75, Mar76, Smi76, Smi82, Smi89);
2: Bae76; 3: Lin79; 4: Lan79; 5: Mil82; 6: Rea76, 7: Har37; 8: Rog88; 9: Pyt74; 10: Joh79a;
11: Atl76; 12: VdB84a; 13: Bil76; 14: Hef90a; 15: Cos82; 16: Zho76; 17: Bon80; 18: Byr85;
19: Syl79; 20: Sun79b; 21: Pau80; 22: Kri68; 23: Dav79; 24: Elr89; 25: Sek72; 26: Dyr73;
27: Rob78; 28: Bus80; 29: Mas66; 30: Dan91; 31: Due72; 32: Pau55; 33: McG73; 34: Cha84; 35: Con54;
36: Hog82; 37: Sip80; 38: Bil82; 39: Fer87b; 40: Hef90b; 41: Syl80 (including reworking of Olin);
42: Har53; 43: Sta90; 44: Mor90; 45: Mar90; 46: Mot89; 47: Mae90; 48: Dan85b; 49: Koz90;
50: Moh79; 51: Kot85; 52: Dah88; 53: Laj83; 54: Cas84; 55: Nou83; 56: Hyn87; 57: Eri90; 58: Bis87;
59: Bis89; 60: Bus84; 61: Mil78; 62: Sym85b; 63: Mor83b; 64: Hel69; 65: Ber78; 66: Bru92;
67: Pal93

ADSORPTION CONSTANTS FOR REACTIONS ON HYDROUS FERRIC OXIDE

These are taken from the compilation of Dzombak and Morel [Dzo90].

=FeOH represents a site on the surface of HFO;

s: refers to a high affinity (strong) site;

w: refers to a low affinity (weak) site;

Constants are corrected to an ionic strength of 0.7 mol dm^{-3} at 25°C;

*: indicates that the constants compiled by Dzombak and Morel [Dzo90] were obtained from a linear free energy relationship.

The waters in the species defintion were left out of the MINTEQA2 database.

SURFACE ACIDITY

$=FeOH + H^+$	$\leftrightarrow$	$=FeOH_2^+$	log K = 7.14
$=FeOH$	$\leftrightarrow$	$=FeO^- + H^+$	log K = -8.78

Note the stability constants for the protonation/deprotonation of HFO are the same for strong and weak sites.

ALKALINE EARTH CATIONS

$=Fe^sOH + M^{2+}$	$\leftrightarrow$	$=Fe^sOHM^{2+}$	log K_1
$=Fe^wOH + M^{2+}$	$\leftrightarrow$	$=Fe^wOHM^{2+} + H^+$	log K_2

Ion	log K_1	log K_2
Mg^{2+}§	4.42	-5.03*
Ca^{2+}	4.39	-6.28
Sr^{2+}	4.43	-7.01
Ba^{2+}	4.88	-7.63

§ This constant is an estimate based on the trend observed for the adsoprtion of alkaline earth cations to goethite and other iron oxides.

Strontium undergoes a further reaction:

$$=Fe^{W}OH + Sr^{2+} + H_2O \leftrightarrow =Fe^{W}OSrOH + 2H^{+} \qquad \log K = -17.88$$

CONSTANTS FOR DIVALENT TRACE METALS

$$=Fe^{S}OH + M^{2+} \leftrightarrow =Fe^{S}OM^{+} + H^{+} \qquad \log K_1$$

$$=Fe^{W}OH + M^{2+} \leftrightarrow =Fe^{W}OM^{+} + H^{+} \qquad \log K_2$$

Ion	$\log K_1$	$\log K_2$
Co^{2+}	-0.89	-3.44
Ni^{2+}	-0.06	-2.93*
Zn^{2+}	0.56	-2.42
Cu^{2+}	2.46	0.17*
Pb^{2+}	4.22	0.13*
Sn^{2+}	7.57*	5.47*
Cd^{2+}	0.04	-3.33
Hg^{2+}	7.33	6.02
Mn^{2+}	-0.83*	-3.93*
UO^{2+}	4.77*	2.37*

Silver(I) undergoes the following reactions

$$=Fe^{S}OH + Ag^{+} \leftrightarrow =Fe^{S}OAg + H^{+} \qquad \log K = -1.72$$

$$=Fe^{W}OH + Ag^{+} \leftrightarrow =Fe^{W}OAg + H^{+} \qquad \log K = -5.3^{*}$$

Chromium(III) undergoes the following reaction

$$=Fe^{S}OH + Cr^{3+} + H_2O \leftrightarrow =Fe^{S}OCrOH^{+} + 2H^{+} \qquad \log K = 1.05$$

ANION ADSORPTION CONSTANTS

Reactions are the same on both high and low affinity sites

$=FeOH + PO_4^{3-} + 3H^+ \leftrightarrow =FeH_2PO_4 + H_2O$ log K = 29.53

$=FeOH + PO_4^{3-} + 2H^+ \leftrightarrow =FeHPO_4^- + H_2O$ log K = 23.78

$=FeOH + PO_4^{3-} + H^+ \leftrightarrow =FePO_4^{2-} + H_2O$ log K = 16.26

$=FeOH + B(OH)_4^- + H^+ \leftrightarrow =FeH_2BO_3 + 2H_2O$ log K = 9.47

$=FeOH + F^- + H^+ \leftrightarrow =FeF + H_2O$ log K = 8.7*

$=FeOH + F^- \leftrightarrow =FeOHF$ log K = 1.45*

$=FeOH + SO_4^{2-} + H^+ \leftrightarrow =FeSO_4^- + H_2O$ log K = 7.05*

$=FeOH + SO_4^{2-} \leftrightarrow =FeOHSO_4^{2-}$ log K = 0.21*

$=FeOH + SiO_2(OH)_2^{2-} + H^+ \leftrightarrow =FeH_2SiO_4^- + H_2O$ log K = 15.17*

$=FeOH + SiO_2(OH)_2^{2-} \leftrightarrow =FeOHH_2SiO_4^{2-}$ log K = 7.72*

$=FeOH + SiO_2(OH)_2^{2-} + 2H^+ \leftrightarrow =FeH_3SiO_4 + H_2O$ log K = 27.52*

$=FeOH + CrO_4^{2-} + H^+ \leftrightarrow =FeCrO_4^- + H_2O$ log K = 10.09

$=FeOH + CrO_4^{2-} \leftrightarrow =FeOHCrO_4^{2-}$ log K = 3.32

$=FeOH + TIPP^{2-} + H^+ \leftrightarrow =FeTIPP^- + H_2O$ log K = 13.37

$=FeOH + TIPP^{2-} \leftrightarrow =FeOHTIPP^{2-}$ log K = 6.52

APPENDIX 1.2: Stability constants used in the model at various ionic strengths

Code	Species	Ionic Strength (mol dm^{-3})							
		0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7
Aqueous Inorganic Species									
200900	$AgB(OH)_4$	1.20	0.95	0.88	0.83	0.80	0.77	0.74	0.72
201300	AgBr	4.70	4.47	4.42	4.39	4.38	4.37	4.37	4.37
201301	$AgBr_2^-$	7.50	7.20	7.12	7.08	7.05	7.03	7.01	7.00
201302	$AgBr_3^{2-}$	8.07	8.00	7.97	7.96	7.95	7.95	7.96	7.97
201303	$AgBr_4^{3-}$	8.50	8.69	8.69	8.67	8.67	8.66	8.66	8.66
201304	$AgIBr_2^{2-}$	10.46	10.39	10.35	10.33	10.32	10.32	10.32	10.32
201305	AgI_2Br^{2-}	12.37	12.30	12.25	12.23	12.21	12.21	12.20	12.20
201306	$AgI_2Br_2^{3-}$	12.08	12.26	12.26	12.24	12.23	12.22	12.21	12.21
201307	$AgCl_2Br_2^{3-}$	7.24	7.45	7.45	7.45	7.45	7.45	7.46	7.47
201308	$AgClBr_3^{3-}$	8.08	8.28	8.28	8.27	8.27	8.27	8.27	8.28
201309	$AgCl_3Br^{3-}$	6.05	6.26	6.27	6.27	6.28	6.28	6.30	6.31
201310	$AgIBr_3^{3-}$	10.50	10.69	10.69	10.67	10.66	10.65	10.65	10.65
201311	AgI_3Br^{3-}	13.30	13.48	13.48	13.46	13.45	13.44	13.43	13.42
201800	AgCl	3.31	3.08	3.03	3.00	2.99	2.98	2.98	2.98
201801	$AgCl_2^-$	5.25	5.14	5.05	5.07	5.11	5.07	5.12	5.11
201802	$AgCl_3^{2-}$	5.20	5.14	5.12	5.11	5.11	5.12	5.13	5.13
201803	$AgCl_4^{3-}$	4.43	4.65	4.66	4.67	4.68	4.69	4.71	4.73
201804	$AgClBr^-$	6.68	6.44	6.39	6.36	6.35	6.35	6.35	6.36
201805	$AgClBr_2^{2-}$	7.59	7.52	7.50	7.49	7.48	7.48	7.49	7.50
201806	$AgCl_2Br^{2-}$	6.64	6.57	6.55	6.54	6.53	6.54	6.54	6.55
201807	$AgClI^2$	8.42	8.22	8.17	8.15	8.15	8.15	8.16	8.16

201808	$AgClI_2^{2-}$	11.42	11.34	11.30	11.28	11.27	11.26	11.26	11.25
201809	$AgCl_2I^{2-}$	8.55	8.48	8.45	8.43	8.43	8.43	8.43	8.43
202700	AgF	0.40	0.12	0.01	-0.06	-0.12	-0.17	-0.21	-0.24
203300	AgOH	-12.00	-12.02	-12.04	-12.06	-12.08	-12.10	-12.12	-12.14
203301	$Ag(OH)_2^-$	-24.01	-23.80	-23.77	-23.77	-23.78	-23.79	-23.81	-23.84
203800	AgI	8.43	8.19	8.12	8.09	8.06	8.04	8.02	8.01
203801	AgI_2^-	10.99	10.75	10.69	10.66	10.64	10.63	10.62	10.61
203802	AgI_32^-	13.81	13.73	13.68	13.65	13.63	13.62	13.61	13.60
203803	AgI_4^{3-}	14.10	14.28	14.27	14.26	14.24	14.23	14.22	14.20
203806	$AgIBr^-$	9.55	9.28	9.21	9.17	9.15	9.13	9.12	9.11
203807	$AgCl_2I_2^{3-}$	10.04	10.24	10.24	10.24	10.24	10.24	10.24	10.24
203808	$AgClI_3^{3-}$	12.28	12.48	12.47	12.46	12.45	12.45	12.44	12.43
203809	$AgCl_3I^{3-}$	7.45	7.66	7.66	7.67	7.67	7.68	7.69	7.70
203810	$AgIO_3$	0.63	0.40	0.33	0.30	0.27	0.25	0.23	0.22
203811	$Ag(IO_3)_2^-$	1.90	1.68	1.64	1.61	1.60	1.60	1.60	1.60
204920	$AgNO_3$	-0.10	-0.33	-0.39	-0.41	-0.43	-0.44	-0.45	-0.45
207320	$AgSO_4^-$	1.30	0.84	0.71	0.64	0.58	0.54	0.50	0.47
207321	$Ag(SO4)_2^{3-}$	0.76	0.54	0.43	0.36	0.36	0.28	0.25	0.23
207322	$Ag(SO4)_3^{5-}$	0.42	0.75	0.65	0.58	0.52	0.48	0.44	0.42
301400	$Al2(OH)_2CO_3^{2+}$	3.74	2.38	2.13	1.96	1.85	1.75	1.68	1.62
301401	$Al3(OH)_3CO_3^{4+}$	1.16	0.02	-0.22	-0.39	-0.49	-0.58	-0.64	-0.69
302700	AlF^{2+}	7.00	6.43	6.25	6.16	6.12	6.11	6.10	6.10
302701	AlF_2^+	12.60	11.63	11.45	11.32	11.21	11.12	11.04	10.97
302702	AlF_3	16.70	15.50	15.30	15.17	15.07	15.00	14.94	14.89
302703	AlF_4^-	19.10	18.30	18.06	18.00	17.99	18.00	18.02	18.06
302704	AlF_5^{2-}	20.59	19.70	19.54	19.46	19.42	19.40	19.39	19.39
302705	AlF_6^{3-}	20.61	20.00	19.88	19.83	19.81	19.80	19.81	19.82
303300	$AlOH^{2+}$	-4.99	-5.31	-5.39	-5.47	-5.54	-5.53	-5.52	-5.52

303301	$Al(OH)_2^+$	-10.10	-10.62	-10.76	10.88	-10.98	-10.99	-11.00	-11.02
303302	$Al(OH)_3$	-16.30	-16.87	-17.04	-17.18	-17.29	-17.32	-17.35	-17.37
303303	$Al(OH)_4^-$	-23.00	-23.46	-23.56	-23.62	-23.65	-23.66	-23.67	-23.68
303304	$Al_2(OH)_2^{4+}$	-7.70	-7.78	-7.82	-7.85	-7.88	-7.90	-7.92	-7.94
303305	$Al_3(OH)_4^{5+}$	-13.94	-13.69	-13.62	-13.58	-13.54	-13.52	-13.49	-13.47
304920	$AlNO_3^{2+}$	0.12	-0.35	-0.42	-0.45	-0.48	-0.49	-0.50	-0.50
305800	$AlHPO_4^+$	19.75	18.04	17.66	17.45	17.29	17.17	17.08	17.03
305801	$AlH_2PO_4^{2+}$	22.65	21.02	20.68	20.47	20.32	20.20	20.11	20.05
307320	$AlSO_4^+$	3.90	3.45	2.46	2.90	2.75	2.63	2.53	2.45
700900	$BaB(OH)_4^+$	1.49	1.02	0.88	0.78	0.69	0.61	0.55	0.48
701400	$BaCO_3$	2.22	1.37	1.17	1.05	0.96	0.90	0.85	0.81
701401	$BaHCO_3^+$	11.85	11.04	10.85	10.71	10.61	10.53	10.47	10.42
702320	$BaSO_4$	2.20	1.33	1.12	1.00	0.91	0.84	0.79	0.75
702321	$Ba(SO4)_2^{2-}$	3.07	2.15	1.92	1.78	1.68	1.61	1.55	1.51
702700	BaF^+	0.49	-0.07	-0.14	-0.17	-0.18	-0.19	-0.19	-0.19
703300	$BaOH^+$	-13.36	-13.57	-13.63	-13.68	-13.70	-13.73	-13.77	-13.78
703810	$BaIO_3^+$	1.10	0.69	0.60	0.55	0.51	0.49	0.47	0.46
704920	$BaNO_3^+$	0.90	0.47	0.37	0.31	0.27	0.24	0.22	0.20
704921	$Ba(NO_3)_2$	1.04	0.41	0.26	0.18	0.12	0.08	0.05	0.03
902700	$B(OH)_3F^-$	8.86	8.59	8.56	8.54	8.52	8.51	8.51	8.52
902701	$B(OH)_2F_2^-$	16.62	16.18	16.13	16.09	16.06	16.07	16.07	16.09
902702	$B(OH)F_3^-$	22.99	22.36	22.27	22.23	22.21	22.22	22.23	22.25
902703	BF_4^-	28.95	28.15	28.03	27.98	27.96	27.97	27.98	28.02
1500900	$CaB(OH)_4^+$	1.80	1.40	1.29	1.23	1.18	1.13	1.09	1.06
1501400	$CaHCO_3^+$	11.58	10.75	10.51	10.32	10.18	10.05	9.94	9.83
1501401	$CaCO_3$	3.15	2.38	2.25	2.20	2.18	2.18	2.19	2.21
1501402	$CaMgCO_3^{2+}$	4.18	3.40	3.25	3.16	3.11	3.07	3.04	3.02
1502700	CaF^+	1.10	0.72	0.65	0.62	0.61	0.60	0.60	0.60

1503300	$CaOH^+$	-12.70	-12.89	-12.94	-12.98	-13.00	-13.03	-13.05	-13.08
1503810	$CaIO_3^+$	0.89	0.51	0.43	0.39	0.36	0.34	0.33	0.32
1504920	$CaNO_3^+$	0.70	0.29	0.20	0.14	0.10	0.06	0.03	0.01
1504921	$Ca(NO_3)_2$	0.60	-0.03	-0.15	-0.25	-0.31	-0.35	-0.37	-0.38
1505800	$CaPO_4^-$	6.46	5.20	4.92	4.76	4.65	4.58	4.53	4.50
1505801	$CaHPO_4$	15.01	13.54	13.18	12.97	12.81	12.61	12.61	12.56
1505802	$CaH_2PO_4^+$	20.55	19.07	18.68	18.43	18.25	18.09	17.98	17.88
1507320	$CaSO_4$	2.30	1.48	1.29	1.19	1.13	1.08	1.05	1.03
1507700	$CaSiO_2(OH)_2$	4.36	3.58	3.41	3.32	3.25	3.21	3.17	3.14
1507701	$CaSiO(OH)_3^+$	14.08	13.31	13.13	13.08	13.02	12.98	12.96	12.94
1507702	$Ca(SiO(OH)_3)_2$	30.02	28.65	28.39	28.24	28.13	28.06	28.02	27.99
1600900	$CdB(OH)_4^+$	1.99	1.61	1.53	1.49	1.46	1.44	1.43	1.42
1600901	$Cd(B(OH)_4)_2$	3.61	3.01	2.88	2.81	2.76	2.73	2.71	2.70
1601300	$CdBr^+$	2.17	1.79	1.67	1.62	1.58	1.55	1.54	1.54
1601301	$CdBr_2$	3.00	2.40	2.25	2.17	2.12	2.10	2.09	2.08
1601302	$CdBr_3^-$	3.10	2.48	2.37	2.33	2.30	2.30	2.31	2.32
1601303	$CdBr_4^{2-}$	2.90	2.47	2.41	2.40	2.41	2.44	2.48	2.53
1601304	CdI_2Br^-	4.98	4.36	4.25	4.21	4.18	4.18	4.19	4.20
1601305	$CdI_2Br_2^{2-}$	5.23	4.79	4.73	4.72	4.72	4.75	4.77	4.79
1601306	$CdIBr_3^{2-}$	4.28	3.84	3.78	3.77	3.78	3.81	3.84	3.87
1601307	$CdCl_2Br_2^{2-}$	3.08	2.63	2.54	2.51	2.49	2.50	2.52	2.54
1601308	$CdClBr_3^{2-}$	3.20	2.76	2.69	2.67	2.66	2.68	2.71	2.75
1601309	$CdCl_3Br^{2-}$	2.61	2.14	2.04	2.00	1.97	1.97	1.97	1.98
1601400	$CdCO_3$	4.33	3.50	3.39	3.30	3.23	3.17	3.13	3.09
1601800	$CdCl^+$	1.98	1.52	1.44	1.39	1.37	1.35	1.34	1.34
1601801	$CdCl_2$	2.60	1.97	1.83	1.76	1.72	1.70	1.69	1.68
1601802	$CdCl_3^-$	2.40	1.76	1.63	1.56	1.52	1.49	1.48	1.48
1601803	$CdCl_4^{2-}$	1.70	1.23	1.11	1.06	1.02	1.01	1.00	1.00

1601804	$CdClBr$	3.10	2.49	2.34	2.27	2.22	2.20	2.19	2.18
1601805	$CdClBr_2^-$	3.34	2.72	2.60	2.55	2.52	2.51	2.51	2.52
1601806	$CdCl_2Br^-$	3.11	2.48	2.35	2.29	2.26	2.24	2.23	2.24
1601807	$CdClI$	3.56	3.02	2.88	2.81	2.77	2.75	2.74	2.73
1601808	$CdClI_2^-$	4.75	4.06	4.01	3.95	3.92	3.91	3.91	3.92
1601809	$CdCl_2I^-$	3.81	3.15	3.06	2.99	2.96	2.94	2.93	2.94
1602700	CdF^+	1.20	0.80	0.71	0.64	0.60	0.57	0.55	0.54
1602701	CdF_2	1.48	0.85	0.72	0.64	0.60	0.57	0.55	0.54
1603300	$CdOH^+$	-10.08	-10.31	-10.37	-10.39	-10.41	-10.42	-10.42	-10.42
1603301	$Cd(OH)_2$	-20.35	-20.59	-20.65	-20.68	-20.71	-20.73	-20.74	-20.75
1603302	$Cd(OH)_3^-$	-32.06	-32.12	-31.14	-32.15	-32.18	-31.19	-32.30	-32.21
1603303	$Cd(OH)_4^{2-}$	-47.35	-46.91	-46.82	-46.79	-46.77	-46.77	-46.78	-46.79
1603304	Cd_2OH^{3+}	-9.39	-9.16	-9.10	-9.06	-9.04	-9.02	-9.01	-9.00
1603305	$Cd_4(OH)_4^{4+}$	-32.85	-32.36	-32.23	-32.15	-32.08	-32.03	-31.99	-31.96
1603800	CdI^+	2.40	2.00	1.92	1.89	1.87	1.86	1.86	1.86
1603801	CdI_2	4.10	3.47	3.33	3.26	3.22	3.20	3.19	3.18
1603802	CdI_3^-	5.21	4.59	4.48	4.43	4.40	4.40	4.41	4.42
1603803	CdI_4^{2-}	6.00	5.55	5.50	5.48	5.48	5.50	5.50	5.50
1603804	$CdIBr$	3.85	3.24	3.09	3.02	2.97	2.95	2.94	2.93
1603805	$CdIBr_2^-$	4.28	3.66	3.55	3.51	3.48	3.48	3.49	3.50
1603806	CdI_3Br^{2-}	5.83	5.38	5.33	5.31	5.31	5.34	5.35	5.36
1603807	$CdCl_2I_2^{2-}$	4.63	4.17	4.08	4.05	4.03	4.03	4.03	4.03
1603808	$CdClI_3^{2-}$	5.53	5.07	5.00	4.98	4.97	4.98	4.98	4.98
1603809	$CdCl_3I^{2-}$	3.38	2.91	2.81	2.77	2.74	2.73	2.73	2.73
1603810	$CdIO_3^+$	1.20	0.79	0.69	0.64	0.60	0.58	0.56	0.54
1603811	$Cd(IO_3)_2$	2.52	1.89	1.75	1.67	1.62	1.59	1.56	1.55
1604920	$CdNO_3^+$	0.50	0.09	0.00	-0.04	-0.07	-0.08	-0.09	-0.10
1604921	$Cd(NO_3)_2$	0.20	-0.44	-0.58	-0.66	-0.72	-0.75	-0.78	-0.80

1605800	$CdHPO_4$	16.73	15.23	14.85	14.62	14.45	14.32	14.23	14.17
1605801	$CdH_2PO_4^+$	20.93	19.46	19.08	18.85	18.69	18.56	18.46	18.39
1607320	$CdSO_4$	2.46	1.60	1.38	1.25	1.15	1.08	1.03	1.00
1607321	$Cd(SO_4)_2^{2-}$	3.65	2.70	2.42	2.25	2.10	2.00	1.91	1.83
1901300	$CoBr^+$	0.46	0.07	-0.01	-0.06	-0.09	-0.11	-0.12	-0.13
1901400	$CoCO_3$	4.51	3.68	3.49	3.38	3.31	3.25	3.21	3.17
1901401	$CoHCO_3^+$	12.29	11.50	11.33	11.19	11.11	11.03	10.98	10.93
1901800	$CoCl^+$	0.60	0.20	0.10	0.05	0.02	0.00	-0.02	-0.03
1902700	CoF^+	1.26	0.86	0.76	0.71	0.67	0.65	0.63	0.62
1903300	$CoOH^+$	-9.65	-9.80	-9.82	-9.83	-9.84	-9.84	-9.85	-9.85
1903301	$Co(OH)_2$	-18.18	-18.40	-18.44	-18.48	-18.51	-18.54	-18.56	-18.58
1903302	$Co(OH)_3^-$	-31.50	-31.51	-31.52	-31.54	-31.56	-31.58	-31.60	-31.62
1903303	$Co(OH)_4^{2-}$	-46.30	-45.05	-45.98	-45.94	-45.90	-45.88	-45.85	-45.83
1903304	$Co_{2O}H^{3+}$	-11.20	-10.95	-10.88	-10.84	-10.80	-10.78	-10.75	-10.73
1903305	$Co_4(OH)_4^{3+}$	-30.53	-30.04	-29.90	-29.81	-29.74	-29.68	-29.64	-29.60
1904920	$CoNO_3^+$	0.20	-0.20	-0.29	-0.34	-0.37	-0.40	-0.42	-0.43
1904921	$Co(NO_3)_2$	0.66	0.03	-0.12	-0.20	-0.26	-0.30	-0.33	-0.36
1905800	$CoHPO_4$	15.37	13.90	13.53	13.32	13.15	13.03	12.94	12.89
1907320	$CoSO_4$	2.34	1.48	1.27	1.13	1.03	0.95	0.89	0.83
2111800	$CrCl^{2+}$	0.11	-0.35	-0.42	-0.46	-0.48	-0.49	-0.50	-0.50
2112700	CrF^{2+}	5.20	4.69	4.57	4.49	4.42	4.36	4.30	4.25
2112701	CrF_2^+	9.18	8.21	8.03	7.90	7.79	7.70	7.62	7.55
2112702	CrF_3	11.90	10.70	10.50	10.37	10.27	10.20	10.14	10.09
2113300	$CrOH^{2+}$	-4.00	-4.27	-4.30	-4.31	-4.32	-4.33	-4.33	-4.34
2113301	$Cr(OH)_2^+$	-9.62	-10.10	-10.19	-10.23	-10.27	-10.30	-10.32	-10.35
2113302	$Cr(OH)_3$	-18.00	-18.72	-18.91	-19.03	-19.11	-19.17	-19.22	-19.26
2113303	$Cr(OH)_4^-$	-27.40	-27.88	-28.01	-28.09	-28.15	-28.20	-28.23	-28.26
2113304	$Cr_2(OH)_2^{4+}$	-5.06	-5.05	-5.03	-5.02	-5.00	-4.99	-4.98	-4.96

2113305	$Cr_3(OH)_4^{2+}$	-8.15	-7.94	-7.89	-7.88	-7.87	-7.88	-7.88	-7.89
2113810	$Cr(IO_3)_2^{+}$	3.23	2.40	2.26	2.18	2.14	2.11	2.09	2.08
2115800	$CrH_2PO_4^{2+}$	22.53	21.10	20.76	20.55	20.41	20.28	20.19	20.13
2301300	$CuBr_2^{-}$	5.90	5.68	5.63	5.60	5.59	5.58	5.58	5.59
2301301	$CuBr_3^{2-}$	6.46	6.41	6.39	6.38	6.39	6.39	6.40	6.41
2301307	$CuIBr^{-}$	7.46	7.24	7.19	7.16	7.14	7.14	7.13	7.14
2301308	$CuIBr_2^{2-}$	7.93	7.88	7.86	7.85	7.86	7.86	7.87	7.88
2301309	CuI_2Br^{2-}	8.92	8.87	8.85	8.84	8.85	8.85	8.86	8.87
2301800	$CuCl$	2.84	2.62	2.56	2.53	2.51	2.50	2.49	2.48
2301801	$CuCl_2^{-}$	5.29	5.08	5.04	5.02	5.02	5.02	5.02	5.03
2301802	$CuCl_3^{2-}$	4.16	4.12	4.12	4.13	4.15	4.17	4.19	4.22
2301803	$Cu_2Cl_4^{2-}$	11.66	11.39	11.32	11.30	11.29	11.29	11.30	11.31
2301804	$CuCl_4^{3-}$	2.33	2.55	2.56	2.57	2.58	2.59	2.61	2.63
2301804	$CuClBr^{-}$	5.90	5.68	5.64	5.61	5.61	5.60	5.60	5.61
2301805	$CuClBr_2^{2-}$	6.32	6.12	6.11	6.11	6.12	6.13	6.14	6.16
2301806	$CuCl_2Br^{2-}$	5.40	5.36	5.35	5.36	5.37	5.39	5.40	5.43
2301807	$CuClI^{-}$	7.15	6.94	6.89	6.87	6.86	6.86	6.85	6.86
2301808	$CuClI_2^{2-}$	8.16	8.11	8.10	8.09	8.11	8.11	8.13	8.14
2301809	$CuCl_2I^{2-}$	6.40	6.35	6.35	6.35	6.37	6.38	6.40	6.42
2303800	CuI^{2-}	8.41	8.19	8.14	8.11	8.09	8.09	8.08	8.08
2303801	CuI_3^{2-}	9.44	9.39	9.37	9.36	9.37	9.37	9.38	9.39
2303802	CuI_4^{3-}	7.62	7.85	7.87	7.88	7.90	7.92	7.94	7.96
2303807	$CuClI_3^{3-}$	6.90	7.13	7.14	7.15	7.17	7.19	7.21	7.23
2303808	$CuCl_2I_2^{3-}$	5.75	5.98	5.99	6.00	6.02	6.03	6.05	6.07
2303809	$CuCl_3I^{3-}$	4.25	4.48	4.49	4.50	4.51	4.52	4.54	4.56
2310900	$CuB(OH)_4^{+}$	4.02	3.64	3.56	3.52	3.49	3.47	3.46	3.43
2310901	$Cu(B(OH)_4)_2$	7.04	6.44	6.31	6.24	6.19	6.16	6.14	6.13
2311300	$CuBr^{+}$	-0.03	-0.40	-0.47	-0.50	-0.51	-0.52	-0.52	-0.51

2311400	$CuCO_3$	6.80	6.00	5.85	5.79	5.76	5.74	5.73	5.73
2311401	$Cu(CO_3)_2^{2-}$	10.80	9.70	9.54	9.44	9.39	9.35	9.32	9.30
2311402	$CuHCO_3^+$	12.13	11.33	10.58	10.95	10.83	10.72	10.64	10.57
2311403	$CuOHCO_3^-$	-2.41	-3.09	-3.20	-3.28	-3.32	-3.36	-3.38	-3.40
2311800	$CuCl^+$	0.35	-0.04	-0.12	-0.16	-0.18	-0.19	-0.20	-0.20
2311801	$CuCl^2$	0.48	-0.15	-0.29	-0.36	-0.42	-0.45	-0.48	-0.50
2312700	CuF^+	1.46	1.06	0.96	0.91	0.87	0.85	0.83	0.82
2313300	$CuOH^+$	-7.50	-7.71	-7.75	-7.78	-7.80	-7.82	-7.83	-7.84
2313301	$Cu(OH)_2$	-16.22	-16.48	-16.54	-16.59	-16.63	-16.66	-16.68	-16.70
2313302	$Cu(OH)_3^-$	-28.00	-28.00	-28.01	-28.01	-28.02	-28.02	-28.02	-28.03
2313303	$Cu(OH)_4^{2-}$	-39.60	-39.12	-39.00	-39.92	-39.93	-38.87	-38.80	-38.78
2313304	$Cu_2(OH)_2^{2+}$	-10.75	-10.99	-11.05	-11.09	-11.11	-11.13	-11.15	-11.17
2313810	$CuIO3^+$	0.68	0.30	0.22	0.18	0.15	0.13	0.12	0.11
2314920	$CuNO3^+$	0.50	0.11	0.03	-0.02	-0.05	-0.07	-0.08	-0.09
2314921	$Cu(NO_3)^2$	0.43	-0.20	-0.34	-0.42	-0.47	-0.51	-0.54	-0.56
2315800	$CuHPO_4$	16.39	14.92	14.55	14.34	14.17	14.05	13.96	13.91
2315811	$CuH_2PO_4^+$	21.25	19.78	19.42	19.20	19.05	18.92	18.83	18.76
2317320	$CuSO_4$	2.34	1.49	1.29	1.16	1.07	1.00	0.95	0.90
2801400	$FeCO_3$	4.86	4.03	4.86	3.71	3.64	3.58	3.54	3.50
2801401	$FeHCO_3^+$	11.43	10.65	10.47	10.34	10.25	10.17	10.12	10.07
2801800	$FeCl^+$	0.14	-0.25	-0.33	-0.38	0.41	-0.43	-0.44	-0.45
2802700	FeF^+	1.46	1.06	0.96	0.91	0.87	0.85	0.83	0.82
2803300	$FeOH^+$	-9.50	-9.71	-9.74	-9.76	-9.77	-9.77	-9.78	-9.79
2803301	$Fe(OH)_2$	-20.60	-20.82	-20.86	-20.90	-20.93	-20.96	-20.98	-21.00
2803302	$Fe(OH)_3^-$	-31.00	-31.01	-31.02	-31.04	-31.06	-31.08	-31.10	-32.12
2803303	$Fe(OH)_4^{2-}$	-46.00	-45.55	-45.44	-45.38	-45.34	-45.32	-45.32	-45.31
2805800	$FeH_2PO_4^+$	22.25	20.80	20.44	20.22	20.06	19.93	19.84	19.77
2805801	$FeHPO_4$	15.95	14.44	14.11	13.89	13.73	13.61	13.52	13.46

2807320	$FeSO_4$	2.20	1.34	1.12	0.99	0.89	0.82	0.77	0.74
2810900	$FeB(OH)_4^{2+}$	7.44	6.99	6.92	6.89	6.87	6.86	6.85	6.85
2810901	$Fe(B(OH)_4)_2^{+}$	14.17	13.32	13.18	13.11	13.06	13.03	13.01	13.00
2811300	$FeBr^{2+}$	0.60	0.12	0.03	-0.02	-0.06	-0.09	-0.12	-0.14
2811301	$FeBr_2^{+}$	0.85	-0.01	-0.16	-0.24	-0.37	-0.32	-0.35	-0.36
2811400	$FeOHCO_3$	-3.83	-4.93	-5.16	-5.29	-5.39	-5.46	-5.52	-5.56
2811401	$Fe(CO_3)_2^{-}$	7.40	5.91	5.60	5.43	5.31	5.23	5.16	5.11
2811800	$FeCl^{2+}$	1.24	0.78	0.71	0.67	0.65	0.64	0.63	0.63
2811801	$FeCl_2^{+}$	2.13	1.26	1.09	0.99	0.93	0.88	0.85	0.82
2811802	$FeCl_3$	0.93	-0.16	-0.37	-0.48	-0.56	-0.61	-0.64	-0.67
2811803	$FeClBr^{+}$	1.79	0.93	0.77	0.67	0.62	0.58	0.55	0.53
2812100	$FeCrO_4^{+}$	7.52	6.47	6.26	6.13	6.03	5.97	5.92	5.89
2812700	FeF^{2+}	6.00	5.45	5.34	5.26	5.21	5.18	5.17	5.17
2812701	FeF_2^{+}	10.61	9.64	9.46	9.33	9.22	9.13	9.05	8.98
2812702	FeF_3	13.60	12.40	12.20	12.07	11.97	11.90	11.84	11.79
2813300	$FeOH^{2+}$	-2.19	-2.60	-2.64	-2.68	-2.70	-2.72	-2.73	-2.74
2813301	$Fe(OH)_2^{+}$	-5.06	-5.54	-5.63	-5.68	-5.72	-5.75	-5.78	-5.81
2813302	$Fe(OH)_4^{-}$	-21.60	-21.88	-21.90	-21.91	-21.18	-21.91	-21.90	-21.90
2813303	$Fe_2(OH)_2^{4+}$	-3.00	-2.88	-2.80	-2.74	-2.70	-2.68	-2.68	-2.67
2813304	$Fe_3(OH)_4^{5+}$	-6.30	-6.05	-5.98	-5.94	-5.91	-5.88	-5.85	-5.83
2813305	$Fe(OH)_3$	-13.50	-14.00	-14.08	-14.12	-14.14	-14.16	-14.18	-14.20
2814920	$FeNO_3^{2+}$	1.00	0.45	0.29	0.17	0.06	-0.04	-0.14	-0.23
2815800	$FeHPO_4^{+}$	22.21	20.50	20.12	19.89	19.73	19.61	19.52	19.47
2815802	$FeH_2PO_4^{2+}$	23.60	22.07	21.73	21.52	21.37	21.25	21.16	21.10
2817320	$FeSO_4^{+}$	4.04	2.90	2.63	2.45	2.33	2.24	2.18	2.13
2817321	$Fe(SO_4)_2^{-}$	5.38	3.83	3.49	3.28	3.13	3.01	2.91	2.83
2817322	$FeHSO_4^{2+}$	2.57	1.75	1.64	1.58	1.54	1.52	1.49	1.48
2817700	$FeSiO(OH)_3^{2+}$	22.44	21.62	21.48	21.41	21.36	21.33	21.32	21.30

3300020	OH^-	-14.00	-13.79	-13.76	-13.75	-13.74	-13.74	-13.75	-13.76
3300900	$B(OH)_3$	9.24	8.97	8.93	8.90	8.87	8.86	8.85	8.85
3300901	$B_2O(OH)_5^-$	9.12	8.84	8.80	8.77	8.73	8.71	8.70	8.69
3300902	$B_3O_3(OH)_4^-$	20.69	20.14	20.05	19.99	19.92	19.88	19.86	19.85
3300903	$B_4O_5(OH)_4^{2-}$	20.66	20.32	20.31	20.30	20.30	20.31	20.31	20.32
3301400	HCO_3^-	10.33	9.93	9.83	9.74	9.68	9.62	9.58	9.54
3301401	H_2CO_3	16.68	16.07	15.92	15.81	15.72	15.65	15.59	15.54
3302100	$HCrO_4^-$	6.50	6.09	5.98	5.91	5.85	5.81	5.79	5.77
3302101	H_2CrO_4	6.30	5.65	5.48	5.38	5.29	5.23	5.20	5.17
3302102	$Cr_2O_7^{2-}$	14.53	13.90	13.72	13.61	13.51	13.46	13.45	13.43
3302700	HF	3.17	2.97	2.94	2.93	2.93	2.93	2.93	2.94
3302701	HF_2^-	3.65	3.54	3.51	3.50	3.50	3.50	3.51	3.52
3302702	SiF_6^{2-}	53.19	52.05	51.85	51.75	51.70	51.69	51.73	51.78
3302703	$Si(OH)_2F_2$	34.38	33.42	33.23	32.13	32.04	32.01	32.02	32.02
3303810	HIO_3	0.77	0.59	0.55	0.54	0.53	0.52	0.52	0.52
3305800	HPO_4^{2-}	12.35	11.72	11.55	11.45	11.37	11.31	11.27	11.25
3305801	$H_2PO_4^-$	19.55	18.48	18.20	18.02	17.89	17.78	17.70	17.64
3305802	H_3PO_4	21.70	20.42	20.10	19.88	19.73	19.63	19.52	19.43
3307320	HSO_4^-	1.99	1.55	1.45	1.38	1.33	1.29	1.25	1.22
3307700	$SiO(OH)_3^-$	13.10	12.72	12.65	12.61	12.58	12.56	12.55	12.54
3307701	$Si(OH)_4$	22.96	22.36	22.23	22.14	22.06	22.02	22.01	22.00
3603300	Hg_2OH^+	-4.51	-4.77	-4.86	-4.92	-4.96	-5.00	-5.03	-5.06
3603301	$(Hg_2)_2OH^{3+}$	-2.08	-2.08	-2.16	-2.21	-2.25	-2.28	-2.31	-2.34
3603302	$(Hg_2)_5OH_4^{6+}$	-7.14	-6.56	-6.80	-6.97	-7.07	-7.17	-7.29	-7.38
3604920	$Hg_2NO_3^+$	0.79	0.34	0.23	0.16	0.11	0.08	0.05	0.03
3607320	Hg_2SO_4	2.68	1.82	1.60	1.47	1.37	1.30	1.25	1.22
3607321	$Hg_2(SO_4)_2$	4.19	4.24	3.96	3.79	3.64	3.54	3.45	3.37
3611300	$HgBr^+$	9.56	9.15	9.07	9.03	9.01	9.00	9.00	9.00

3611301	$HgBr_2$	17.92	17.30	17.18	17.13	17.11	17.10	17.10	17.12
3611302	$HgBr_3^-$	20.15	19.55	19.44	19.40	19.39	19.40	19.42	19.45
3611303	$HgBr_4^{2-}$	21.57	21.12	21.04	21.00	20.99	21.00	21.02	21.04
3611304	HgOHBr	6.28	5.83	5.73	5.68	5.65	5.63	5.62	5.61
3611305	HgI_2Br^-	26.24	25.61	25.47	25.40	25.37	25.34	25.34	25.33
3611306	$HgCl_2Br^-$	17.19	16.59	16.48	16.43	16.41	16.41	16.41	16.41
3611307	$HgCl_2Br_2^{2-}$	19.41	18.99	18.93	18.89	18.87	18.88	18.89	18.91
3611308	$HgClBr_3^{2-}$	20.70	20.27	20.20	20.16	20.14	20.15	20.17	20.19
3611309	$HgCl_3Br^{2-}$	17.77	17.34	17.31	17.27	17.25	17.25	17.26	17.28
3611310	$HgI_2Br_2^{2-}$	26.82	26.36	26.26	26.21	26.18	26.18	26.18	26.19
3611311	$HgIBr_3^{2-}$	24.41	23.95	23.86	23.82	23.80	23.80	23.81	23.83
3611312	HgI_3Br^{2-}	28.88	28.41	28.30	28.25	28.21	28.20	28.20	28.20
3611400	$HgCO_3$	12.29	11.44	11.25	11.13	11.05	11.00	10.96	10.92
3611401	$HgHCO_3^+$	16.33	15.53	15.33	15.20	15.10	15.02	14.96	14.91
3611402	$Hg(CO_3)_2^{2-}$	15.87	14.99	14.78	14.65	14.56	14.50	14.45	14.41
3611403	$HgOHCO_3^-$	5.41	4.75	4.60	4.50	4.44	4.40	4.37	4.33
3611800	$HgCl^+$	7.30	6.89	6.81	6.77	6.75	6.74	6.73	6.72
3611801	$HgCl_2$	14.00	13.40	13.30	13.25	13.23	13.22	13.21	13.21
3611802	$HgCl_3^-$	15.00	14.40	14.28	14.23	14.21	14.20	14.19	14.18
3611803	$HgCl_4^{2-}$	15.70	15.30	15.26	15.22	15.20	15.20	15.21	15.22
3611804	HgOHCl	4.32	3.89	3.79	3.74	3.72	3.70	3.69	3.68
3611805	HgClBr	16.26	15.65	15.54	15.49	15.47	15.46	15.46	15.47
3611806	$HgClBr_2^-$	18.91	18.31	18.20	18.15	18.14	18.14	18.15	18.17
3611807	HgClI	19.71	19.08	18.96	18.89	18.85	18.82	18.80	18.79
3611808	$HgClI_2^-$	24.52	23.89	23.75	23.68	23.64	23.61	23.58	23.58
3611809	$HgCl_2I^-$	20.00	19.38	19.25	19.19	19.16	19.14	19.12	19.11
3612700	HgF^+	1.60	1.19	1.11	1.07	1.04	1.03	1.02	1.02
3613300	$HgOH^+$	-3.40	-3.59	-3.63	-3.66	-3.67	-3.67	-3.68	-3.68

3613301	$Hg(OH)_2$	-6.17	-6.34	-6.34	-6.35	-6.35	-6.35	-6.35	-6.35
3613302	$Hg(OH)_3^-$	-21.10	-21.10	-21.10	-21.11	-21.11	-21.11	-21.12	-21.12
3613303	$Hg_2OH_3^+$	-3.33	-3.08	-3.01	-2.97	-2.94	-2.91	-2.88	-2.86
3613304	$Hg_3(OH)_3^{3+}$	-6.47	-6.42	-6.43	-6.43	-6.44	-6.44	-6.45	-6.45
3613800	HgI^+	13.51	13.09	12.99	12.94	12.90	12.87	12.85	12.83
3613801	HgI_2	24.81	24.16	24.01	23.92	23.86	23.82	23.79	23.77
3613802	HgI_3^-	28.57	27.92	27.77	27.69	27.64	27.60	27.58	27.56
3613803	HgI_4^{2-}	30.51	30.04	29.92	29.86	29.82	29.80	29.79	29.78
3613804	$HgOHI$	9.63	9.17	9.04	8.97	8.92	8.87	8.83	8.80
3613805	$HgIBr$	21.67	21.03	20.90	20.83	20.79	20.76	20.75	20.75
3613806	$HgIBr_2^-$	23.43	22.82	22.69	22.64	22.62	22.61	22.62	22.63
3613807	$HgCl_2I_2^{2-}$	23.88	23.49	23.37	23.32	23.29	23.28	23.28	23.28
3613808	$HgClI_3^{2-}$	27.41	26.96	26.86	26.80	26.77	26.75	26.75	26.74
3613809	$HgCl_3I^{2-}$	20.00	19.59	19.53	19.48	19.46	19.45	19.46	19.46
3614920	$HgNO_3^+$	0.70	0.30	0.22	0.18	0.15	0.13	0.12	0.11
3614921	$Hg(NO_3)_2$	0.93	0.30	0.16	0.08	0.03	-0.01	-0.04	-0.06
3615800	$HgPO_4^-$	12.27	10.95	10.62	10.42	10.27	10.16	10.07	10.00
3615801	$HgHPO_4$	22.85	21.35	20.97	20.74	20.57	20.44	20.35	20.29
3617320	$HgSO_4$	2.72	1.86	1.64	1.51	1.41	1.34	1.29	1.26
3617321	$Hg(SO_4)_2^{2-}$	4.05	3.10	2.82	2.65	2.50	2.40	2.31	2.23
4101400	KCO_3^-	1.27	0.85	0.76	0.71	0.68	0.65	0.64	0.63
4101401	$KHCO_3$	10.08	9.47	9.33	9.21	9.14	9.07	9.03	8.99
4102100	$KCRO_4$	0.80	0.36	0.25	0.19	0.11	0.08	0.06	0.04
4102700	KF	-0.91	-1.11	-1.19	-1.25	-1.29	-1.32	-1.33	-1.34
4103300	KOH	-14.46	-14.48	-14.50	-14.52	-14.54	-14.56	-14.58	-14.60
4103810	KIO_3	-0.27	-0.49	-0.55	-0.58	-0.60	-0.61	-0.62	-0.63
4104920	KNO_3	-0.19	-0.37	-0.43	-0.45	-0.46	-0.46	-0.46	-0.45
4105800	KPO_4^{2-}	1.73	1.00	0.80	0.68	0.59	0.52	0.47	0.42

4105801	$KHPO_4^-$	13.00	11.93	11.65	11.49	11.36	11.27	11.20	11.16
4107320	KSO_4^-	0.85	0.42	0.34	0.30	0.29	0.29	0.29	0.30
4400900	$LiB(OH)_4$	0.55	0.29	0.21	0.14	0.09	0.04	-0.01	-0.05
4402700	LiF	0.23	0.03	-0.05	0.11	0.00	-0.18	-0.17	-0.15
4403300	LiOH	-13.64	-13.65	-13.66	-13.68	-13.69	-13.70	-13.71	-13.72
4407320	$LiSO_4^-$	0.77	0.34	0.24	0.18	0.14	0.11	0.09	0.07
4600900	$MgB(OH)_4^+$	1.63	1.28	1.22	1.19	1.16	1.15	1.14	1.13
4601400	$MgCO_3$	2.92	2.19	2.07	2.03	2.01	2.02	2.03	2.05
4601401	$MgHCO_3^+$	11.41	10.59	10.37	10.19	10.06	9.95	9.84	9.75
4601402	$Mg_2CO_3^{2+}$	3.68	2.94	2.80	2.72	2.67	2.63	2.61	2.59
4602700	MgF^+	1.82	1.46	1.40	1.36	1.34	1.33	1.32	1.32
4603300	$MgOH^+$	-11.79	-11.99	-12.05	-12.10	-12.13	-12.16	-12.23	-12.23
4603301	$Mg_4(OH)_4^{4+}$	-39.71	-39.26	-39.17	-39.12	-39.10	-39.09	-39.09	-39.09
4603810	$MgIO_3^+$	0.72	0.38	0.32	0.30	0.28	0.27	0.27	0.26
4605800	$MgH_2PO_4^+$	20.68	19.20	18.71	18.56	18.38	18.22	18.11	18.01
4605801	$MgHPO_4$	15.16	13.73	13.39	13.19	13.04	12.91	12.84	12.79
4605802	$MgPO_4^-$	5.86	4.60	4.32	4.16	4.05	3.98	3.93	3.90
4607320	$MgSO_4$	2.23	1.46	1.29	1.19	1.11	1.07	1.04	1.01
4607700	$MgSiO_2(OH)_2$	5.32	4.58	4.43	4.35	4.30	4.26	4.23	4.21
4607701	$MgSiO(OH)_3^+$	14.20	13.48	13.35	13.28	13.24	13.21	13.19	13.18
4607702	$Mg(SiO(OH)_3)_2$	30.82	29.50	29.26	29.12	29.03	28.96	28.93	28.90
4701300	$MnBr^+$	0.25	-0.17	-0.27	-0.31	-0.34	-0.37	-0.39	-0.40
4701400	$MnHCO_3^+$	11.60	10.80	10.62	10.47	10.38	10.29	10.22	10.17
4701401	$MnCO_3$	4.32	3.61	3.49	3.30	3.12	3.06	3.02	2.98
4701800	$MnCl^+$	0.35	-0.04	-0.12	-0.12	-0.18	-0.19	-0.20	-0.20
4702700	MnF^+	1.46	1.06	0.96	0.91	0.87	0.85	0.83	0.82
4703300	$MnOH^+$	-10.59	-10.79	-10.81	-10.83	-10.85	-10.85	-10.86	-10.86
4703301	$Mn(OH)_4^{2-}$	-48.30	-47.85	-47.74	-47.68	-47.64	-47.62	-47.62	-47.61
4703302	$Mn(OH)_2$	-22.20	-22.42	-22.46	-22.50	-22.5	-322.56	-22.58	-22.60

4703303	$Mn(OH)_3^-$	-34.80	-34.81	-34.82	-34.84	-34.86	-34.88	-34.90	-34.92
4703304	Mn_2OH^{3+}	-10.56	-10.32	-10.24	-10.20	-10.16	-10.14	-10.11	-10.09
4703305	$Mn_2(OH)_3^+$	-23.90	-24.40	-24.53	-24.63	-24.69	-24.75	-24.79	-24.83
4704920	$MnNO_3^+$	0.20	-0.20	-0.28	-0.32	-0.35	-0.37	-0.39	-0.40
4704921	$Mn(NO_3)_2$	0.60	-0.04	-0.20	-0.30	-0.37	-0.43	-0.47	-0.50
4705800	$MnHPO_4$	15.29	13.82	13.45	13.24	13.07	12.95	12.86	12.81
4707320	$MnSO_4$	2.26	1.40	1.18	1.00	0.84	0.77	0.73	0.70
5000900	$NaB(OH)_4$	0.24	-0.02	-0.10	-0.17	-0.22	-0.27	-0.32	-0.36
5001400	$NaCO_3^-$	1.27	0.85	0.76	0.71	0.68	0.65	0.64	0.63
5001401	$NaHCO_3$	10.08	9.47	9.33	9.21	9.14	9.07	9.03	8.99
5002100	$NaCrO_4$	0.70	0.26	0.15	0.09	0.01	-0.02	-0.04	-0.06
5002700	NaF	-0.26	-0.46	-0.54	-0.60	-0.64	-0.67	-0.68	-0.69
5003300	NaOH	-14.18	-14.20	-14.22	-14.24	-14.26	-14.28	-14.30	-14.32
5003810	$NaIO_3$	-0.40	-0.61	-0.66	-0.69	-0.70	-0.71	-0.72	-0.72
5004920	$NaNO_3$	-0.55	-0.77	-0.83	-0.86	-0.88	-0.89	-0.90	-0.91
5005800	$NaHPO_4^-$	13.20	12.13	11.85	11.69	11.56	11.47	11.40	11.36
5005801	$NaPO_4^{2-}$	1.83	1.10	0.90	0.78	0.69	0.62	0.57	0.52
5005802	NaH_2PO_4	21.48	19.99	19.62	19.38	19.21	19.09	18.98	18.89
5007320	$NaSO_4^-$	1.03	0.60	0.50	0.43	0.40	0.37	0.35	0.33
5401300	$NiBr^+$	0.60	0.18	0.08	0.04	-0.01	-0.02	-0.04	-0.05
5401400	$NiCO_3$	4.91	4.08	3.89	3.78	3.71	3.65	3.61	3.57
5401401	$NiHCO_3^+$	12.29	11.50	11.33	11.19	11.11	11.03	10.98	10.93
5401800	$NiCl^+$	0.55	0.16	0.14	0.04	0.02	0.01	0.00	0.00
5402700	NiF^+	1.16	0.96	0.66	0.61	0.57	0.55	0.53	0.52
5403300	$NiOH^+$	-9.86	-10.06	-10.10	-10.13	-10.15	-10.17	-10.18	-10.19
5403301	$Ni(OH)_2$	-19.00	-19.2	-219.26	-19.30	-19.3	-319.36	-19.38	-19.40
5403302	$Ni(OH)_3^-$	-30.00	-30.01	-30.02	-30.04	-30.06	-30.08	-30.10	-30.12
5403303	Ni_2OH^{3+}	-10.70	-10.45	-10.38	-10.34	-10.30	-10.28	-10.25	-10.23

5403304	$Ni_4(OH)_4^{4+}$	-27.74	-27.28	-27.16	-27.09	-27.05	-27.02	-27.00	-26.99
5404920	$NiNO_3^+$	0.50	0.10	-0.00	-0.05	-0.10	-0.13	-0.15	-0.17
5404921	$Ni(NO_3)_2$	0.00	-0.63	-0.76	-0.84	-0.89	-0.94	-0.96	-0.97
5405800	$NiH_2PO_4^+$	20.43	18.98	18.62	18.40	18.25	18.12	18.03	17.96
5405801	$NiHPO_4$	15.29	13.82	13.45	13.24	13.07	12.95	12.86	12.81
5407320	$NiSO_4$	2.34	1.47	1.27	1.13	1.03	0.95	0.89	0.83
5407321	$Ni(SO_4)_2^{2-}$	3.47	2.52	1.24	2.07	1.92	1.82	1.76	1.65
6000900	$PbB(OH)_4^+$	2.77	2.39	2.31	2.27	2.24	2.22	2.21	2.20
6000901	$Pb(B(OH)_4)_2$	5.32	4.72	4.59	4.52	4.47	4.44	4.42	4.41
6001300	$PbBr^+$	1.75	1.33	1.23	1.19	1.16	1.13	1.11	1.10
6001301	$PbBr_2$	2.55	1.90	1.75	1.68	1.64	1.62	1.61	1.60
6001302	$PbBr_3^-$	3.00	2.37	2.23	2.16	2.13	2.10	2.09	2.08
6001303	$PbBr_4^{2-}$	2.30	1.83	1.73	1.68	1.67	1.67	1.68	1.70
6001304	$PbI_2Br_2^{2-}$	4.18	3.70	3.60	3.55	3.53	3.53	3.53	3.55
6001305	$PbIBr_3^{2-}$	3.45	2.98	2.88	2.83	2.81	2.81	2.82	2.84
6001306	PbI_3Br^{2-}	4.55	4.07	3.97	3.92	3.90	3.89	3.89	3.91
6001307	$PbCl_2Br_2^{2-}$	2.48	2.00	1.89	1.84	1.81	1.80	1.81	1.82
6001308	$PbClBr_3^{2-}$	2.60	2.13	2.02	1.97	1.95	1.95	1.96	1.97
6001309	$PbCl_3Br^{2-}$	2.00	1.52	1.41	1.35	1.32	1.30	1.31	1.31
6001400	$Pb(CO_3)_2^{2-}$	10.50	9.60	9.38	9.21	9.12	9.05	9.00	8.96
6001401	$PbCO_3$	7.00	6.10	5.89	5.75	5.65	5.63	5.62	5.61
6001402	$PbOHCO_3^-$	-3.30	-3.58	-3.73	-3.83	-3.89	-3.93	-3.96	-3.98
6001800	$PbCl^+$	1.51	1.09	0.99	0.94	0.90	0.92	0.88	0.88
6001801	$PbCl_2$	2.16	1.48	1.34	1.27	1.22	1.21	1.19	1.18
6001802	$PbCl_3^-$	2.00	1.36	1.22	1.15	1.12	1.10	1.09	1.09
6001803	$PbCl_4^{2-}$	1.10	0.61	0.50	0.44	0.40	0.38	0.38	0.38
6001804	$PbClBr$	2.66	1.99	1.85	1.78	1.73	1.71	1.70	1.69
6001805	$PbClBr_2^-$	3.14	2.51	2.37	2.30	2.27	2.24	2.23	2.23

6001806	$PbCl_2Br^-$	2.81	2.17	2.03	1.96	1.93	1.91	1.90	1.90
6001807	$PbClI$	2.34	1.79	1.67	1.61	1.56	1.54	1.53	1.52
6001808	$PbClI_2^-$	3.74	3.10	2.97	2.91	2.88	2.88	2.88	2.89
6001809	$PbCl_2I^-$	3.11	2.47	2.33	2.27	2.24	2.23	2.22	2.23
6002700	PbF^+	2.10	1.70	1.60	1.55	1.51	1.49	1.47	1.46
6002701	PbF_2	3.64	2.99	2.83	2.74	2.68	2.64	2.60	2.58
6003300	$PbOH^+$	-7.65	-7.86	-7.90	-7.93	-7.95	-7.97	-7.98	-7.99
6003301	$Pb(OH)_2$	-17.10	-17.36	-17.43	-17.46	-17.49	-17.50	-17.52	-17.52
6003302	$Pb(OH)_3^-$	-28.10	-28.12	-28.15	-28.18	-28.20	-28.22	-28.24	-28.26
6003303	Pb_2OH^{3+}	-6.36	-6.16	-6.14	-6.13	-6.14	-6.15	-6.16	-6.17
6003304	$Pb_3(OH)_4^{2+}$	-23.40	-23.91	-24.03	-24.08	-24.08	-24.10	-24.10	-24.09
6003305	$Pb_4(OH)_4^{4+}$	-20.84	-20.40	-20.33	-20.19	-20.12	-20.07	-20.03	-20.02
6003306	$Pb_6(OH)_8^{4+}$	-43.43	-43.38	-43.33	-43.28	-43.23	-43.18	-43.13	-43.12
6003800	PbI^+	1.92	1.50	1.40	1.34	1.30	1.28	1.26	1.25
6003801	PbI_2	3.20	2.56	2.42	2.34	2.30	2.27	2.26	2.24
6003802	PbI_3^-	3.90	3.26	3.13	3.08	3.05	3.05	3.06	3.07
6003803	PbI_4^{2-}	4.50	4.02	3.92	3.86	3.84	3.83	3.83	3.84
6003804	$PbIBr$	3.18	2.53	2.39	2.31	2.27	2.25	2.24	2.22
6003805	$PbIBr_2^-$	3.78	3.14	3.01	2.94	2.91	2.89	2.89	2.89
6003806	PbI_2Br^-	4.08	3.44	3.31	3.25	3.22	3.21	3.21	3.22
6003807	$PbCl_2I_2^{2-}$	3.58	3.09	2.99	2.93	2.90	2.88	2.88	2.89
6003808	$PbClI_3^{2-}$	4.25	3.77	3.67	3.61	3.58	3.57	3.57	3.58
6003809	$PbCl_3I^{2-}$	2.55	2.06	1.96	1.90	1.86	1.84	1.84	1.85
6004920	$PbNO_3^+$	1.17	0.72	0.61	0.54	0.49	0.45	0.47	0.39
6004921	$Pb(NO_3)_2$	1.40	0.75	0.59	0.50	0.44	0.41	0.39	0.38
6005800	$PbH_2PO_4^+$	21.05	19.55	19.17	18.94	18.77	18.63	18.53	18.45
6005801	$PbHPO_4$	15.45	13.94	13.55	13.31	13.14	13.01	12.93	12.85
6007320	$PbSO_4$	2.70	1.90	1.80	1.65	1.52	1.44	1.37	1.30

6007321	$Pb(SO_4)_2^{2-}$	4.74	3.79	2.51	3.34	3.19	3.09	3.00	2.92
7801300	$SnBr^+$	1.16	0.78	0.72	0.70	0.37	0.68	0.69	0.70
7801301	$SnBr_2$	1.70	1.10	0.97	0.90	0.87	0.85	0.85	0.85
7801302	$SnBr_3^-$	1.61	1.00	0.45	0.81	0.77	0.75	0.73	0.73
7801303	$SnBr_4^{2-}$	-0.30	-0.72	-0.80	-0.82	-0.83	-0.81	-0.79	-0.77
7801304	$SnIBr$	2.07	1.46	1.33	1.25	1.21	1.18	1.17	1.16
7801305	$SnIBr_2^-$	2.37	1.76	1.63	1.57	1.52	1.50	1.48	1.48
7801306	SnI_2Br^-	2.66	2.04	1.91	1.85	1.80	1.77	1.75	1.75
7801307	$SnI_2Br_2^{2-}$	1.66	1.23	1.14	1.10	1.08	1.08	1.09	1.10
7801308	$SnIBr_3^{2-}$	0.89	0.47	0.38	0.35	0.34	0.35	0.36	0.38
7801309	SnI_3Br^{2-}	2.08	1.64	1.54	1.50	1.47	1.46	1.47	1.47
7801800	$SnCl^+$	1.64	1.23	1.15	1.10	1.07	1.05	1.04	1.04
7801801	$SnCl_2$	2.35	1.72	1.58	1.50	1.44	1.42	1.43	1.44
7801802	$SnCl_3^-$	2.00	1.39	1.27	1.20	1.17	1.15	1.14	1.15
7801804	$SnClBr$	2.33	1.70	1.58	1.50	1.46	1.44	1.44	1.45
7801805	$SnClBr_2^-$	2.22	1.61	1.48	1.42	1.38	1.36	1.34	1.35
7801806	$SnCl_2Br^-$	2.35	1.74	1.61	1.55	1.51	1.49	1.48	1.49
7801807	$SnClI$	2.40	1.77	1.63	1.55	1.50	1.47	1.46	1.46
7801808	$SnClI_2^-$	2.79	2.17	2.05	1.98	1.93	1.91	1.89	1.89
7801809	$SnCl_2I^-$	2.63	2.02	1.90	1.83	1.79	1.77	1.75	1.76
7802700	SnF^+	4.74	4.34	4.24	4.19	4.15	4.13	4.11	4.10
7802701	SnF_2	7.64	7.03	6.89	6.82	6.77	6.74	6.72	6.70
7802702	SnF_3^-	10.38	9.77	9.64	9.58	9.54	9.52	9.50	9.49
7803300	$SnOH^+$	-3.40	-3.64	-3.70	-3.74	-3.77	-3.79	-3.81	-3.82
7803301	$Sn(OH)_3^-$	-16.61	-16.62	-16.63	-16.64	-16.65	-16.67	-16.68	-16.69
7803302	$Sn_3(OH)_4^{2+}$	-6.88	-7.33	-7.42	-7.47	-7.49	-7.50	-7.50	-7.50
7803303	$Sn_2(OH)_2^{2+}$	-4.77	-4.99	-5.03	-5.04	-5.05	-5.04	-5.04	-5.03
7803304	$Sn(OH)_2$	-7.06	-7.31	-7.38	-7.42	-7.46	-7.48	-7.51	-7.53

7803800	SnI^+	1.19	0.79	0.71	0.66	0.63	0.61	0.59	0.58
7803801	SnI_2	1.84	1.22	1.08	1.00	0.95	0.91	0.89	0.87
7803802	SnI_3^-	2.47	1.85	1.72	1.65	1.60	1.57	1.55	1.54
7803803	SnI_4^{2-}	2.07	1.62	1.52	1.47	1.44	1.42	1.42	1.42
7804920	$SnNO_3^+$	1.10	0.67	0.58	0.55	0.52	0.50	0.48	0.47
8000900	$SrB(OH)_4^+$	1.55	1.08	0.94	0.84	0.75	0.61	0.61	0.54
8001400	$SrCO_3$	2.81	1.96	1.76	1.64	41.5	1.49	1.44	1.40
8001401	$SrHCO_3^+$	11.54	10.73	10.54	10.40	10.30	10.22	10.16	10.11
8002700	SrF^+	0.65	0.27	0.20	0.17	0.16	0.15	0.15	0.15
8003300	$SrOH^+$	-13.18	-13.39	-13.45	-13.49	-13.52	-13.54	-13.57	-13.59
8003810	$SrIO_3^+$	1.00	0.59	0.50	0.45	0.41	0.39	0.37	0.36
8004920	$SrNO_3^+$	0.80	0.37	0.28	0.22	0.18	0.15	0.12	0.10
8004921	$Sr(NO_3)_2$	0.80	0.15	0.00	-0.09	-0.15	-0.19	-0.22	-0.24
8007320	$SrSO_4$	2.20	1.40	1.25	1.18	1.15	1.14	1.15	1.16
8931300	UO_{2Br+}	-0.20	-0.62	-0.72	-0.76	-0.79	-0.82	-0.84	-0.85
8931400	UO_2CO_3	9.50	8.69	8.51	8.41	8.35	8.30	8.27	8.24
8931401	$UO_2(CO_3)_2^{2-}$	16.60	15.73	15.59	15.50	15.45	15.43	15.41	15.40
8931402	$UO_2(CO_3)_3^{4-}$	22.12	21.75	21.61	21.55	21.51	21.50	21.50	21.51
8931405	$(UO_2)_2(OH)_3CO_3^-$	-0.10	-1.05	-1.14	-1.25	-1.32	-1.37	-1.41	-1.44
8931406	$(UO_2)_3(CO_3)_6^{6-}$	55.82	54.53	54.10	53.88	53.76	53.70	53.68	53.69
8931800	UO_2Cl^+	0.21	-0.17	-0.23	-0.26	-0.28	-0.28	-0.28	-0.28
8932700	UO_2F^+	5.20	4.80	4.70	4.65	4.61	4.59	4.57	4.56
8932701	UO_2F_2	8.93	8.32	8.18	8.11	8.06	8.03	8.01	7.99
8932702	$UO_2F_3^-$	11.43	10.82	10.69	10.63	10.59	10.57	10.55	10.54
8932703	$UO_2F_4^{2-}$	12.55	12.12	12.03	11.98	11.96	11.95	11.95	11.96
8933300	UO_2OH^+	-5.93	-6.10	-6.09	-6.10	-6.10	-6.11	-6.10	-6.10
8933301	$(UO_2)_2(OH)_2^{2+}$	-5.62	-5.84	-5.88	-5.90	-5.91	-5.92	-5.92	-5.92
8933302	$(UO_2)_3(OH)_5^+$	-15.63	-16.20	-16.25	-16.30	-16.30	-16.31	-16.32	-16.33

8933810	$UO_2(IO_3)_2$	3.45	2.85	2.73	2.66	2.62	2.59	2.57	2.56
8933811	$UO_2(IO_3)_3^-$	4.37	3.78	3.67	3.61	3.58	3.56	3.55	3.55
8934920	$UO_2NO_3^+$	0.00	-0.40	-0.48	-0.52	-0.55	-0.57	-0.58	-0.59
8935800	$UO_2H_2PO_4^+$	23.20	21.75	21.39	21.17	21.01	20.88	20.79	20.72
8935801	$UO_2(H_2PO_4)_2$	44.70	41.94	41.25	40.80	40.48	40.22	40.03	39.88
8935802	$UO_2H_7(PO_4)_3$	67.40	63.37	62.40	61.74	61.31	61.04	60.73	60.49
8935803	$UO_2H_3PO_4^{2+}$	23.00	21.73	21.42	21.21	21.07	20.98	20.88	20.80
8937320	UO_2SO_4	2.95	2.14	1.98	1.89	1.84	1.81	1.80	1.79
8937321	$UO_2(SO_4)_2^{2-}$	4.00	3.12	2.90	2.78	2.70	2.64	2.59	2.56
8937700	$UO_2SiO(OH)_3^+$	21.06	20.30	20.15	20.07	20.01	19.97	19.95	19.93
9500900	$ZnB(OH)_4^+$	1.47	1.09	1.01	0.97	0.94	0.92	0.91	0.90
9500901	$Zn(B(OH)_4)_2$	4.23	3.63	3.50	3.43	3.38	3.35	3.33	3.32
9501300	$ZnBr^+$	-0.23	-0.60	-0.67	-0.70	-0.71	-0.72	-0.72	-0.71
9501400	$ZnHCO_3^+$	11.97	11.15	10.07	10.78	9.86	10.55	10.47	10.69
9501401	$ZnCO_3$	4.75	3.90	3.70	3.57	3.48	3.41	3.35	3.30
9501800	$ZnCl^+$	0.05	-0.24	-0.32	-0.36	-0.38	-0.39	-0.40	-0.40
9501801	$ZnCl_2$	0.60	0.00	-0.15	-0.20	-0.24	-0.26	-0.28	-0.30
9501802	$ZnCl_3^-$	0.50	-0.10	-0.25	-0.30	-0.35	-0.37	-0.39	-0.40
9501803	$ZnCl_4^{2-}$	0.20	-0.27	-0.38	-0.45	-0.50	-0.53	-0.55	-0.55
9502700	ZnF^+	1.20	0.80	0.70	0.65	0.61	0.59	0.57	0.56
9503300	$ZnOH^+$	-9.00	-9.14	-9.16	-9.17	-9.18	-9.18	-9.17	-9.17
9503301	$Zn(OH)_2$	-18.90	-19.08	-19.18	-19.23	-19.26	-19.29	-19.33	-19.37
9503302	$Zn(OH)_3^-$	-28.40	-28.39	-28.39	-28.39	-28.40	-28.41	-28.42	-28.43
9503303	$Zn(OH)_2^{2-}$	-38.02	-37.61	-37.58	-37.58	-37.58	-37.58	-37.61	-37.65
9503304	$Zn_2(OH)_3^+$	-9.00	-8.96	-8.94	-8.94	-8.94	-8.95	-8.95	-8.95
9503800	ZnI^+	-0.94	-1.34	-1.42	-1.47	-1.50	-1.52	-1.54	-1.55
9504920	$ZnNO_3^+$	0.40	0.01	-0.07	-0.12	-0.15	-0.17	-0.18	-0.19
9504921	$Zn(NO_3)_2$	0.65	0.00	-0.18	-0.27	-0.35	-0.41	-0.46	-0.50

9505800	$ZnHPO_4$	15.59	14.12	13.75	13.54	13.37	13.25	13.16	13.11
9505801	$ZnH_2PO_4^+$	21.15	19.68	19.32	19.10	18.95	18.82	18.73	18.66
9507320	$ZnSO_4$	2.34	1.50	1.30	1.15	1.05	1.00	0.95	0.90
9507321	$Zn(SO_4)_2^{2-}$	3.60	2.65	2.35	2.18	2.03	1.90	1.79	1.70
Fulvic Acid Ligand Interactions									
209050	AgALA	3.64	3.42	3.36	3.33	3.31	3.30	3.29	3.28
209051	$Ag(ALA)_2^-$	7.20	7.00	6.95	6.93	6.92	6.92	6.92	6.92
209060	$AgHBEAL^+$	10.57	9.39	9.37	9.35	9.36	9.36	9.38	9.39
209061	AgOHBEAL_	-6.11	-6.15	-6.16	-6.18	-6.18	-6.19	-6.19	-6.19
209062	AgBEAL	3.66	3.44	3.40	3.37	3.36	3.35	3.35	3.35
209063	$Ag(BEAL)_2^-$	7.38	7.17	7.13	7.11	7.10	7.10	7.10	7.11
209170	AgBENZ	0.91	0.67	0.60	0.57	0.55	0.54	0.53	0.53
209171	$Ag(BENZ)_2^-$	0.77	0.57	0.53	0.52	0.51	0.51	0.51	0.51
209450	$AgETA^+$	3.20	3.18	3.16	3.15	3.14	3.13	3.12	3.11
209451	$Ag(ETA)_2^+$	6.76	6.73	6.72	6.70	6.69	6.68	6.67	6.66
209600	AgHMP	0.59	0.37	0.32	0.28	0.26	0.25	0.24	0.23
209601	$Ag(HMP)_2^-$	0.35	0.14	0.10	0.07	0.06	0.06	0.06	0.06
209670	AgMET	13.42	13.20	13.15	13.11	13.09	13.08	13.07	13.06
209671	$Ag(MET)_2^-$	18.11	17.90	17.86	17.83	17.82	17.82	17.82	17.82
209672	$Ag_2MET=+$	19.43	19.20	19.15	19.11	19.09	19.08	19.07	19.07
209700	AgPHEN	0.37	0.18	0.16	0.16	0.18	0.20	0.22	0.25
209710	AgPROP	0.73	0.50	0.45	0.41	0.39	0.37	0.36	0.35
209711	$Ag(PROP)_2^-$	0.64	0.41	0.35	0.31	0.28	0.26	0.24	0.23
209750	$AgPN^+$	5.35	5.34	5.34	5.34	5.34	5.34	5.35	5.35
209751	$AgHPN^{2+}$	11.94	12.18	12.24	12.29	12.34	12.38	12.42	12.46
209752	$AgH_2(PN)_3^{2+}$	23.93	24.57	24.73	24.85	24.94	25.06	25.16	25.23
209753	AgOHPN	-3.96	-4.01	-4.03	-4.04	-4.06	-4.07	-4.08	-4.09

209754	Ag_2PN^{2+}	6.94	7.11	7.14	7.16	7.18	7.19	7.21	7.23
209755	$Ag_2(PN)_2^{2+}$	12.50	12.67	12.71	12.74	12.77	12.79	12.82	12.85
209800	$AgTMA^{2-}$	8.41	7.85	7.74	7.67	7.63	7.60	7.58	7.56
309100	$AlACAC^{2+}$	8.68	8.13	8.07	8.04	8.02	8.02	8.01	8.01
309101	$Al(ACAC)_2^{+}$	16.64	15.80	15.66	15.59	15.55	15.52	15.50	15.49
309120	$AlHASP^{2+}$	12.73	11.94	11.80	11.73	11.71	11.69	11.69	11.68
309121	$Al(OH)ASP$	9.26	8.25	8.05	7.95	7.90	7.85	7.83	7.80
309170	$AlOHBENZ^{+}$	-0.78	-1.40	-1.52	-1.59	-1.62	-1.65	-1.68	-1.70
309200	$AlCAT^{+}$	18.03	16.60	16.33	16.17	16.05	15.98	15.91	15.87
309201	$Al(CAT)_2^{-}$	32.29	30.10	29.69	29.46	29.28	29.20	29.11	29.07
309204	$AlH(CAT)_2$	38.45	36.15	35.68	35.45	35.28	35.20	35.12	35.11
309650	$AlMAL^{+}$	4.87	3.84	3.66	3.55	3.49	3.44	3.40	3.37
309651	$AlOHMAL$	2.26	1.20	0.99	0.87	0.79	0.73	0.68	0.64
309710	$AlPROP^{2+}$	2.26	1.81	1.75	1.72	1.70	1.69	1.69	1.69
309730	$AlPHTH^{+}$	4.61	3.58	3.40	3.30	3.23	3.18	3.14	3.12
309731	$Al(PHTH)_2^{-}$	8.31	6.89	6.63	6.48	6.39	6.32	6.27	6.23
309950	$AlSAL^{+}$	14.33	13.33	13.11	13.01	12.93	12.88	12.83	12.80
309951	$Al(SAL)_2^{-}$	25.49	24.14	23.81	23.66	23.56	23.48	23.41	23.37
309952	$AlOH(SAL)_2^{2-}$	15.69	14.70	14.44	14.32	14.25	14.18	14.12	14.08
309980	$AlSUCC^{+}$	4.70	3.64	3.44	3.33	3.25	3.20	3.16	3.13
309980	$AlOHSUCC$	1.05	-0.05	-0.26	-0.39	-0.49	-0.55	-0.60	-0.65
309981	$AlHSUCC^{2+}$	7.62	6.78	6.64	6.57	6.53	6.51	6.51	6.50
708650	$BaMAL$	2.20	1.42	1.27	1.20	1.16	1.14	1.14	1.14
708651	$BaHMAL^{+}$	6.18	5.35	5.20	5.10	5.01	4.97	4.93	4.91
709050	$BaALA^{+}$	0.77	0.36	0.26	0.21	0.18	0.15	0.14	0.12
709100	$BaACAC^{+}$	2.09	1.70	1.61	1.56	1.52	1.50	1.48	1.47
709120	$BaASP$	1.95	1.14	0.96	0.86	0.79	0.73	0.69	0.66
709160	$BaAET^{+}$	1.78	1.37	1.28	1.23	1.19	1.17	1.15	1.14

709300	BaDEM	2.41	1.60	1.42	1.32	1.24	1.19	1.15	1.12
709400	$BaDHMB^+$	1.31	0.89	0.80	0.75	0.71	0.69	0.67	0.66
709550	$BaHBT^+$	0.94	0.52	0.43	0.38	0.38	0.37	0.32	0.30
709600	$BaHMP^+$	1.03	0.62	0.53	0.47	0.44	0.41	0.40	0.38
709601	$Ba(HMP)_2$	1.47	0.85	0.72	0.65	0.60	0.57	0.54	0.53
709710	$BaPROP^+$	0.85	0.43	0.34	0.29	0.26	0.23	0.21	0.20
709730	BaPHTH	2.33	1.52	1.34	1.24	1.16	1.11	1.07	1.04
709950	$BaHSAL^+$	13.95	13.20	13.01	12.93	12.86	12.82	12.78	12.76
709980	BaSUCC	2.02	1.18	0.99	0.88	0.80	0.74	0.69	0.65
909200	$B(OH)_2CAT^-$	27.46	26.47	26.32	26.24	26.18	26.17	26.16	26.18
909201	$B(CAT)_2^-$	51.38	49.37	49.07	48.94	48.84	48.85	48.87	48.90
909950	$B(OH)_2SAL_-$	24.25	23.66	23.54	23.48	23.44	23.42	23.40	23.41
909951	$B(SAL)_2^-$	43.26	42.17	41.94	41.84	41.78	41.75	41.72	41.74
1509050	$CaALA^+$	1.24	0.85	0.78	0.73	0.71	0.69	0.68	0.67
1509060	$CaBEAL^+$	2.18	1.79	1.71	1.67	1.64	1.62	1.61	1.60
1509100	$CaACAC^+$	2.71	2.32	2.24	2.20	2.17	2.15	2.14	2.13
1509120	CaASP	2.38	1.60	1.44	1.34	1.28	1.23	1.19	1.17
1509160	$CaAET^+$	2.60	2.21	2.13	2.09	2.06	2.04	2.03	2.02
1509170	$CaBENZ^+$	0.73	0.34	0.27	0.22	0.20	0.18	0.17	0.16
1509300	CaDEM	2.55	1.77	1.60	1.51	1.44	1.40	1.36	1.33
1509400	$CaDHMB^+$	1.64	1.26	1.18	1.14	1.11	1.09	1.08	1.07
1509550	$CaHBT^+$	1.06	0.67	0.60	0.55	0.53	0.51	0.51	0.50
1509600	$CaHMP^+$	1.51	1.12	1.04	1.00	0.97	0.95	0.94	0.93
1509601	$Ca(HMP)_2$	2.29	1.70	1.58	1.52	1.48	1.46	1.44	1.43
1509650	CaMAL	2.66	1.96	1.81	1.74	1.70	1.67	1.66	1.66
1509651	$CaHMAL^+$	6.52	5.71	5.63	5.56	5.53	5.51	5.50	5.50
1509710	$CaPROP^+$	0.96	0.57	0.50	0.45	0.43	0.41	0.40	0.39
1509730	CaPHTH	2.42	1.64	1.47	1.38	1.31	1.27	1.23	1.20

1509731	$CaHPHTH^{+}$	6.43	5.55	5.40	5.30	5.25	5.20	5.16	5.14
1509900	$CaSER^{+}$	1.43	1.05	0.97	0.93	0.91	0.89	0.88	0.87
1509950	CaSAL	5.03	4.25	4.12	4.03	3.96	3.92	3.88	3.85
1509951	$CaHSAL^{+}$	14.84	13.38	13.21	13.13	13.81	13.03	13.74	13.72
1509980	CaSUCC	2.00	1.20	1.01	0.91	0.83	0.78	0.74	0.71
1509981	$CaHSUCC^{+}$	6.57	5.78	5.63	5.55	5.49	5.46	5.45	5.44
1609050	$CdALA^{+}$	4.47	4.06	3.97	3.91	3.88	3.85	3.84	3.82
1609051	$Cd(ALA)_2$	8.06	7.44	7.31	7.24	7.19	7.16	7.13	7.12
1609100	$CdACAC^{+}$	3.83	3.50	3.42	3.39	3.39	3.40	3.41	3.43
1609101	$Cd(ACAC)_2$	6.70	6.15	6.06	6.03	6.02	6.04	6.06	6.09
1609120	CdASP	5.22	4.35	4.23	4.13	4.06	4.00	3.96	3.93
1609121	$Cd(ASP)_2^{2-}$	8.35	7.55	7.38	7.29	7.23	7.18	7.15	7.13
1609160	$CdAET^{+}$	11.38	10.97	10.88	10.83	10.79	10.77	10.75	10.74
1609161	$Cd(AET)_2$	17.72	17.10	16.97	16.89	16.85	16.82	16.79	16.78
1609170	$CdBENZ^{+}$	1.82	1.40	1.30	1.23	1.18	1.14	1.11	1.08
1609171	$Cd(BENZ)_2$	2.56	1.96	1.84	1.77	1.73	1.70	1.68	1.66
1609200	CdCAT	8.89	8.08	8.14	7.80	7.96	7.67	7.87	7.84
1609250	CdCYS	13.97	13.18	13.03	12.95	12.91	12.88	12.86	12.86
1609251	$Cd(CYS)_2^{2-}$	20.72	19.92	19.75	19.65	19.59	19.55	19.52	19.50
1609300	CdDEM	3.35	2.54	2.36	2.26	2.19	2.13	2.09	2.06
1609400	$CdDHMB^{+}$	2.03	1.62	1.53	1.48	1.44	1.42	1.40	1.39
1609401	$Cd(DHMB)^2$	3.72	3.10	2.97	2.89	2.85	2.82	2.79	2.78
1609450	$CdETA^{2+}$	2.56	2.54	2.54	2.54	2.54	2.54	2.55	2.55
1609451	$Cd(ETA)_2^{2+}$	4.53	4.52	4.53	4.54	4.55	4.56	4.58	4.59
1609550	$CdHBT^{+}$	1.87	1.45	1.36	1.31	1.28	1.25	1.23	1.22
1609551	$Cd(HBT)_2$	3.00	2.39	2.25	2.18	2.13	2.10	2.08	2.06
1609600	$CdHMP^{+}$	1.91	1.50	1.41	1.35	1.32	1.29	1.28	1.26
1609601	$Cd(HMP)_2$	3.12	2.50	2.37	2.30	2.25	2.22	2.19	2.18

1609650	CdMAL	3.07	2.36	2.18	2.08	2.00	1.95	1.91	1.88
1609651	$CdHMAL^{+}$	6.85	6.05	5.87	5.76	5.68	5.63	5.60	5.57
1609670	$CdMET^{+}$	6.51	6.10	6.01	5.96	5.92	5.90	5.88	5.87
1609671	$Cd(MET)_2$	13.03	12.41	12.28	12.20	12.16	12.13	12.10	12.09
1609710	$CdPROP^{+}$	1.75	1.33	1.29	1.25	1.22	1.21	1.20	1.18
1609711	$Cd(PROP)_2$	2.83	2.21	2.08	2.01	1.96	1.92	1.90	1.88
1609730	CdPHTH	3.32	2.50	2.31	2.20	2.11	2.05	2.00	1.96
1609731	$Cd(PHTH)_2^{2-}$	4.14	3.34	3.17	3.07	3.01	2.97	2.94	2.92
1609732	$CdHPHTH^{+}$	6.56	5.68	5.49	5.38	5.32	5.26	5.23	5.19
1609733	$CdH(PHTH)_2^{-}$	8.26	7.10	6.86	6.73	6.64	6.59	6.55	6.53
1609750	$CdPN^{2+}$	5.20	5.25	5.29	5.33	5.37	5.41	5.45	5.49
1609751	$Cd(PN)_2^{2+}$	9.50	9.59	9.68	9.76	9.84	9.92	10.01	10.11
1609800	$CdTMA^{-}$	11.44	10.29	10.05	9.92	9.82	9.75	9.70	9.66
1609801	$Cd(TMA)_4^{2-}$	14.35	13.67	13.51	13.42	13.37	13.33	13.30	13.28
1609900	$CdSER^{+}$	4.18	3.85	3.79	3.76	3.75	3.74	3.74	3.75
1609901	$Cd(SER)_2$	7.92	7.30	7.17	7.10	7.05	7.02	7.00	6.98
1609980	CdSUCC	2.72	1.92	1.77	1.69	1.65	1.63	1.63	1.63
1609981	$Cd(SUCC)_2^{2-}$	4.05	3.25	3.08	2.98	2.92	2.88	2.85	2.83
1609982	$CdHSUCC^{+}$	7.30	6.49	6.33	6.23	6.17	6.13	6.11	6.10
1909050	$CoALA^{+}$	4.71	4.32	4.24	4.20	4.17	4.15	4.14	4.13
1909051	$Co(ALA)_2$	8.40	7.80	7.68	7.62	7.58	7.55	7.54	7.53
1909060	$CoBEAL^{+}$	4.21	3.74	3.58	3.45	3.34	3.24	3.15	3.06
1909061	$Co(BEAL)_2$	6.85	6.26	6.14	6.08	6.04	6.01	5.99	5.98
1909100	$CoACAC^{+}$	5.43	5.43	4.96	4.96	4.89	4.87	4.86	4.85
1909101	$Co(ACAC)_2$	9.60	9.01	8.89	8.83	8.79	8.76	8.75	8.74
1909120	CoASP	6.73	5.95	5.79	5.69	5.63	5.58	5.54	5.52
1909121	$Co(ASP)_2^{2-}$	11.00	10.23	10.08	9.99	9.94	9.90	9.87	9.86
1909150	$CoACPH^{+}$	4.59	4.20	4.12	4.08	4.05	4.03	4.02	4.01

1909151	$Co(ACPH)_2$	7.63	7.04	6.92	6.86	6.82	6.79	6.78	6.77
1909160	$CoAET^+$	8.27	7.88	7.80	7.76	7.73	7.71	7.70	7.69
1909161	$Co(AET)_2$	15.58	14.99	14.87	14.81	14.77	14.75	14.73	14.72
1909170	$CoBENZ^+$	1.08	0.69	0.62	0.57	0.55	0.53	0.52	0.51
1909200	CoCAT	10.03	8.88	8.67	8.56	8.48	8.44	8.41	8.40
1909201	$Co(CAT)_2^{2-}$	16.90	15.38	15.12	14.99	14.88	14.85	14.82	14.83
1909250	CoCYS	8.78	8.00	7.84	7.74	7.68	7.63	7.59	7.57
1909251	$Co(CYS)_2^{2-}$	14.97	14.20	14.05	13.96	13.91	13.87	13.84	13.83
1909270	$CoDAP^+$	6.65	6.28	6.22	6.20	6.20	6.20	6.21	6.22
1909271	$Co(DAP)_2$	11.93	11.36	11.26	11.22	11.20	11.20	11.22	11.21
1909272	$CoHDAP^{2+}$	12.35	12.30	12.30	12.32	12.35	12.37	12.40	12.43
1909273	$CoH(DAP)_2^+$	18.50	17.96	17.88	17.86	17.85	17.87	17.90	17.90
1909300	CoDEM	3.03	2.25	2.09	1.99	1.93	1.88	1.84	1.82
1909400	$CoDHMB^+$	1.98	1.59	1.51	1.47	1.44	1.42	1.41	1.40
1909401	$Co(DHMB)_2$	3.41	2.82	2.70	2.64	2.60	2.57	2.56	2.55
1909450	$CoETA^{2+}$	2.19	2.20	2.21	2.22	2.22	2.23	2.24	2.25
1909451	$Co(ETA)_2^{2+}$	3.48	3.53	3.59	3.66	3.73	3.79	3.84	3.89
1909550	$CoHBT^+$	1.39	1.00	0.93	0.88	0.86	0.84	0.83	0.82
1909551	$Co(HBT)_2$	1.91	1.33	1.21	1.14	1.11	1.08	1.06	1.05
1909600	$CoHMP^+$	2.04	1.65	1.57	1.53	1.50	1.48	1.47	1.46
1909601	$Co(HMP)_2$	3.30	2.81	2.59	2.53	2.49	2.47	2.45	2.44
1909650	CoMAL	3.58	2.86	2.73	2.64	2.57	2.53	2.49	2.46
1909651	$CoHMAL^+$	7.12	6.35	6.18	6.09	6.01	5.98	5.95	5.92
1909710	$CoPROP^+$	1.29	0.89	0.81	0.77	0.75	0.74	0.73	0.73
1909711	$Co(PROP)_2$	1.39	0.81	0.64	0.62	0.59	0.56	0.54	0.53
1909730	CoPHTH	2.83	2.03	1.83	1.71	1.61	1.53	1.46	1.40
1909731	$CoHPHTH^+$	7.24	6.37	6.21	6.12	6.06	6.01	5.98	5.95
1909750	$CoPN^{2+}$	5.45	5.50	5.60	5.65	5.65	5.70	5.76	5.81

1909751	$Co(PN)_2^{2+}$	10.03	10.10	10.17	10.23	10.30	10.37	10.43	10.50
1909800	$CoTMA^-$	7.83	6.71	6.49	6.36	6.27	6.21	6.16	6.12
1909801	$Co(TMA)_2^{-4}$	11.80	11.15	11.01	10.93	10.88	10.84	10.82	10.81
1909901	$CoSER^+$	4.74	4.36	4.29	4.26	4.25	4.24	4.24	4.24
1909902	$Co(SER)_2$	8.36	7.80	7.71	7.67	7.67	7.67	7.68	7.70
1909950	CoSAL	7.61	6.83	6.70	6.61	6.54	6.50	6.46	6.43
1909951	$Co(SAL)_2^{2-}$	12.29	11.49	11.34	11.25	11.20	11.16	11.13	11.12
1909980	CoSUCC	2.32	1.52	1.33	1.23	1.15	1.10	1.06	1.03
1909981	$CoHSUCC^+$	7.01	6.23	6.08	6.00	5.94	5.91	5.90	5.89
2119170	$CrPROP^{2+}$	5.24	4.79	4.73	4.70	4.68	4.68	4.67	4.67
2119171	$Cr(PROP)_2^+$	8.09	7.25	7.11	7.04	7.00	6.97	6.95	6.94
2119750	$Cr(PN)_2^{2+}$	12.64	12.75	12.81	12.85	12.89	12.92	12.96	12.99
2319050	$CuALA^+$	8.53	8.14	8.09	8.05	8.04	8.36	8.03	8.04
2319051	$Cu(ALA)_2$	15.50	14.92	14.85	14.81	14.80	14.80	14.81	14.83
2319052	$CuHALA^{2+}$	10.69	10.46	10.49	10.51	10.53	10.56	10.59	10.61
2319060	$CuBEAL^+$	7.43	7.04	6.96	6.92	6.89	6.87	6.86	6.85
2319061	$Cu(BEAL)_2$	13.13	12.54	12.42	12.36	12.32	12.29	12.28	12.27
2319100	$CuACAC^+$	8.30	7.96	7.93	7.91	7.92	7.94	7.97	8.00
2319101	$Cu(ACAC)_2$	15.15	14.60	14.52	14.49	14.47	14.48	14.49	14.51
2319120	CuASP	9.66	8.88	8.78	8.72	8.69	8.67	8.66	8.66
2319121	$CuHASP^+$	13.33	12.58	12.50	12.46	12.44	12.44	12.44	12.45
2319122	$Cu(ASP)_2^{2-}$	16.62	15.87	15.73	15.66	15.60	15.55	15.57	15.60
2319123	$CuH(ASP)_2^-$	20.98	19.87	19.66	19.56	19.48	19.41	19.42	19.45
2319124	$Cu_2(ASP)^{2+}$	11.16	10.39	10.30	10.25	10.23	10.22	10.22	10.23
2319125	$Cu_2(ASP)_2$	21.00	19.47	19.17	19.00	18.88	18.78	18.76	18.77
2319150	$CuACPH^+$	6.78	6.49	6.41	6.37	6.34	6.32	6.31	6.30
2319151	$Cu(ACPH)_2$	12.33	11.74	11.62	11.56	11.52	11.49	11.48	11.47
2319170	$CuBENZ^+$	2.14	1.76	1.69	1.65	1.62	1.60	1.59	1.59

2319200	CuCAT	14.69	13.92	13.78	13.70	13.66	13.63	13.61	13.60
2319201	$Cu(CAT)_2^{2-}$	25.72	24.98	24.86	24.82	24.80	24.80	24.80	24.82
2319270	$CuDAP^+$	10.95	10.56	10.48	10.44	10.41	10.39	10.38	10.37
2319271	$Cu(DAP)_2$	20.41	19.82	19.70	19.64	19.60	19.57	19.56	19.55
2319272	$CuHDAP^{2+}$	15.74	15.57	15.55	15.55	15.55	15.55	15.56	15.57
2319273	$CuH(DAP)_2^+$	25.89	25.33	25.23	25.19	25.16	25.15	25.15	25.15
2319274	$CuH_2(DAP)_2^{2+}$	30.42	30.08	30.04	30.04	30.04	30.05	30.07	30.09
2319300	CuDEM	5.74	4.96	4.80	4.70	4.64	4.59	4.55	4.53
2319301	$Cu(DEM)_2^{2-}$	8.49	7.72	7.57	7.48	7.43	7.39	7.36	7.35
2319400	$CuDHMB^+$	3.01	2.62	2.54	2.50	2.47	2.45	2.44	2.43
2319401	$Cu(DHMB)_2$	4.88	4.29	4.17	4.11	4.07	4.04	4.03	4.02
2319450	$CuETA^{2+}$	4.48	4.50	4.53	4.55	4.57	4.60	4.63	4.65
2319451	$Cu(ETA)_2^{2+}$	8.53	8.55	8.57	8.58	8.60	8.61	8.63	8.64
2319550	$CuHBT^+$	2.44	2.05	1.98	1.93	1.91	1.89	1.88	1.87
2319551	$Cu(HBT)_2$	3.69	3.11	2.99	2.92	2.89	2.86	2.84	2.83
2319600	$CuHMP^+$	3.19	2.82	2.76	2.73	2.71	2.71	2.71	2.71
2319601	$Cu(HMP)_2$	5.21	4.62	4.50	4.44	4.40	4.37	4.36	4.35
2319650	CuMAL	4.14	3.42	3.30	3.25	3.23	3.23	3.24	3.25
2319651	$Cu(MAL)_2^{2-}$	9.57	8.80	8.64	8.56	8.50	8.47	6.39	8.42
2319652	$CuHMAL^+$	7.47	6.71	6.56	6.47	6.43	6.41	6.43	4.39
2319653	$Cu_2OH(MAL)_2^-$	6.43	5.06	4.80	4.68	4.61	4.58	4.57	4.57
2319654	$Cu_2(OH)_2MAL_2^{2-}$	1.85	0.82	0.60	0.49	0.41	0.37	0.34	0.32
2319710	$CuPROP^+$	2.22	1.91	1.83	1.78	1.74	1.72	1.71	1.70
2319711	$Cu(PROP)_2$	3.50	2.91	2.79	2.73	2.69	2.66	2.64	2.63
2319730	CuPHTH	4.04	3.22	3.05	2.94	2.87	2.81	2.76	2.73
2319731	$Cu(PHTH)_2^{2-}$	6.23	5.46	5.31	5.22	5.17	5.13	5.10	5.09
2319732	$CuHPHTH^+$	7.08	6.22	6.08	6.00	5.96	5.93	5.92	5.90
2319750	$CuPN^{2+}$	10.49	10.55	10.62	10.67	10.71	10.76	10.81	10.87

2319751	$Cu(PN)_2^{2+}$	19.50	19.62	19.74	19.86	19.98	20.10	20.24	20.34
2319900	CuHSER2+	12.75	12.60	12.58	12.57	12.58	12.58	12.59	12.60
2319901	$CuSER^+$	8.25	7.89	7.84	7.84	7.85	7.87	7.89	7.92
2319902	$Cu(SER)^2$	15.04	14.50	14.44	14.44	14.45	14.48	14.52	14.57
2319903	$CuOH(SER)_2^-$	5.10	4.69	4.61	4.57	4.53	4.51	4.50	4.49
2319951	CuSAL	11.38	10.60	10.35	10.20	10.12	10.05	10.19	9.93
2319952	$CuHSAL^+$	14.86	14.13	13.95	13.87	13.81	13.78	13.74	13.72
2319952	$Cu(SAL)_2$	19.30	18.50	18.26	18.09	17.98	17.89	18.14	17.74
2319980	CuSUCC	3.30	2.60	2.42	2.32	2.25	2.19	2.15	2.12
2319981	$CuHSUCC^+$	7.88	7.09	6.94	6.86	6.80	6.77	6.76	6.75
2809050	$FeALA^+$	4.09	3.70	3.62	3.58	3.55	3.53	3.52	3.51
2809051	$Fe(ALA)_2$	6.50	5.91	5.81	5.75	5.71	5.68	5.67	5.66
2809100	$FeACAC^+$	5.11	4.72	4.65	4.60	4.58	4.55	4.51	4.50
2809101	$Fe(ACAC)^2$	8.77	8.17	8.05	7.99	7.95	7.92	7.91	7.90
2809120	FeASP	5.61	4.83	4.67	4.57	4.51	4.46	4.43	4.40
2809200	FeCAT	9.42	8.30	8.11	8.02	7.97	7.96	7.95	7.96
2809201	$Fe(CAT)_2^{2-}$	15.39	13.81	13.68	13.58	13.51	13.52	13.52	13.56
2809250	FeCYS	7.08	6.30	6.14	6.04	5.98	5.93	5.87	5.87
2809300	FeDEM	2.88	2.10	1.94	1.84	1.78	1.73	1.69	1.65
2809450	$FeETA^{2+}$	1.50	1.51	1.52	1.53	1.54	1.55	1.56	1.57
2809600	$FeHMP^+$	1.92	1.53	1.45	1.45	1.38	1.36	1.35	1.34
2809650	FeMAL	3.38	2.60	2.48	2.39	2.31	2.27	2.27	2.20
2809710	$FePROP^+$	1.40	1.00	0.91	0.86	0.82	0.79	0.76	0.74
2809750	$Fe(PN)^{2+}$	4.20	4.21	4.22	4.23	4.24	4.25	4.26	4.27
2809751	$Fe(PN)_2^{2+}$	7.38	7.40	7.42	7.44	7.46	7.48	7.50	7.52
2809900	$FeSER^+$	4.10	3.72	3.65	3.61	3.59	3.58	3.57	3.57
2809901	$Fe(SER)_2$	7.05	6.50	6.41	6.38	6.37	6.38	6.40	6.42
2809950	FeSAL	7.44	6.66	6.53	6.44	6.37	6.33	6.29	6.26

2809951	$Fe(SAL)_2^{2-}$	12.06	11.29	11.14	11.05	11.00	10.96	10.93	10.92
2809980	FeSUCC	2.33	1.55	1.42	1.33	1.26	1.22	1.18	1.15
2819050	$FeALA^{2+}$	10.81	10.36	10.30	10.27	10.25	10.24	10.24	10.24
2819100	$FeACAC^{2+}$	9.88	9.33	9.27	9.24	9.22	9.22	9.21	9.21
2819101	$Fe(ACAC)_2^{+}$	18.94	18.10	17.96	17.89	17.85	17.82	17.80	17.79
2819120	$FeASP^{+}$	12.83	11.80	11.62	11.51	11.45	11.40	11.36	11.33
2819150	$FeACPH^{2+}$	10.95	10.50	10.44	10.41	10.39	10.38	10.38	10.38
2819200	$FeCAT^{+}$	21.67	20.40	20.29	20.30	20.34	20.42	20.52	20.63
2819201	$Fe(CAT)_2^{-}$	37.49	35.37	35.23	35.18	35.17	35.24	35.32	35.44
2819300	$FeDEM^{+}$	9.29	8.26	8.08	7.98	7.91	7.86	7.82	7.80
2819600	$FeHMP^{2+}$	3.47	3.02	2.96	2.96	2.91	2.90	2.90	2.90
2819650	$FeMAL^{+}$	8.19	7.13	6.93	6.82	6.74	6.69	6.65	6.62
2819651	$Fe_2(OH)_2MAL_2$	14.97	14.97	12.45	12.22	12.06	11.95	11.86	11.78
2819700	$FePHEN^{2+}$	8.20	7.78	7.76	7.77	7.78	7.81	7.84	7.87
2819710	$FePROP^{2+}$	3.84	3.39	3.33	3.30	3.28	3.28	3.27	3.27
2819711	$Fe(PROP)_2^{+}$	7.15	6.31	6.17	6.10	6.06	6.03	6.01	6.00
2819800	$FeHTMA^{+}$	20.40	18.79	18.45	18.25	18.10	17.97	17.85	17.75
2819900	$FeSER^{2+}$	9.75	9.32	9.26	9.23	9.21	9.20	9.20	9.20
2819950	$FeSAL^{+}$	17.44	16.30	16.22	16.16	16.12	16.10	16.08	16.07
2819951	$FeHSAL^{2+}$	18.58	17.80	17.64	17.58	17.53	17.50	17.48	17.47
2819952	$Fe(SAL)_2$	29.56	28.14	23.81	27.73	27.64	27.57	27.52	27.49
2819980	$FeSUCC^{+}$	8.38	7.32	7.12	7.01	6.93	6.88	6.84	6.81
3309050	HALA	9.87	9.71	9.68	9.66	9.65	9.65	9.66	9.67
3309051	H_2ALA^{+}	12.22	12.02	11.99	11.97	11.96	11.96	11.96	11.98
3309060	HBEAL	10.29	10.10	10.09	10.08	10.08	10.09	10.10	10.11
3309061	H_2BEAL^{+}	13.84	13.63	13.62	13.63	13.64	13.66	13.69	13.72
3309100	HACAC	8.98	8.80	8.77	8.75	8.75	8.75	8.76	8.76
3309120	$HASP^{-}$	10.00	9.65	9.58	9.54	9.53	9.52	9.52	9.52

3309121	H_2ASP	13.90	13.35	13.24	13.19	13.17	13.16	13.16	13.16
3309122	H_3ASP^+	15.89	15.25	15.14	15.09	15.07	15.06	15.06	15.06
3309150	HACPH	10.02	9.87	9.87	9.88	9.91	9.93	9.96	9.99
3309160	HAET	10.90	10.73	10.71	10.70	10.70	10.70	10.70	10.71
3309161	H_2AET^+	19.13	18.98	18.98	18.99	19.00	19.02	19.03	19.05
3309170	HBENZ	4.20	4.01	3.97	3.96	3.96	3.96	3.97	3.97
3309200	$HCAT^-$	13.68	13.30	13.22	13.18	13.14	13.12	13.10	13.09
3309201	H_2CAT	23.51	22.60	22.45	22.38	22.33	22.32	22.31	22.32
3309250	$HCYS^-$	10.74	10.36	10.29	10.24	10.21	10.19	10.17	10.15
3309251	H_2CYS	19.10	18.52	18.44	18.38	18.34	18.32	18.30	18.38
3309252	H_3CYS^+	20.91	20.37	20.32	20.28	20.26	20.26	20.26	20.26
3309270	HDAP	9.58	9.40	9.37	9.36	9.35	9.35	9.35	9.35
3309271	H_2DAP^+	16.28	16.08	16.02	15.98	15.93	15.90	15.86	15.83
3309272	H_3DAP^{2+}	17.36	17.38	17.38	17.38	17.36	17.35	17.33	17.32
3309300	$HDEM^-$	7.42	6.96	6.86	6.80	6.75	6.71	6.67	6.64
3309301	H_2DEM	9.57	8.96	8.76	8.65	8.60	8.61	8.62	8.64
3309400	HDHMB	3.69	3.51	3.48	3.47	3.47	3.47	3.47	3.48
3309450	$HETA^+$	9.50	9.52	9.55	9.58	9.60	9.62	9.64	9.66
3309550	H(HBT)	4.50	4.32	4.30	4.29	4.30	4.31	4.32	4.32
3309600	H(HMP)	4.03	3.79	3.78	3.76	3.75	3.75	3.75	3.75
3309650	$HMAL^-$	5.10	4.68	4.62	4.57	4.52	4.50	4.48	4.47
3309651	H_2MAL	8.56	7.92	7.82	7.75	7.68	7.65	7.63	7.61
3309670	HMET	9.72	9.40	9.37	9.35	9.34	9.34	9.34	9.34
3309700	HPHEN	9.98	9.82	9.74	9.70	9.68	9.66	9.64	9.62
3309710	HPROP	4.87	4.69	4.66	4.64	4.63	4.63	4.64	4.65
3309730	$HPHTH^-$	5.41	4.92	4.84	4.79	4.76	4.73	4.71	4.69
3309731	H_2PHTH	8.36	7.68	7.54	7.49	7.44	7.40	7.37	7.34
3309750	HPN^+	9.72	9.78	9.81	9.84	9.87	9.90	9.93	9.95

3309751	H_2PN^{2+}	16.33	16.63	16.73	16.82	16.89	16.96	17.03	17.08
3309800	$HTMA^{2-}$	10.95	10.39	10.26	10.17	10.10	10.04	9.98	9.93
3309801	H_2TMA^{-}	15.89	14.97	14.77	14.65	14.56	14.48	14.41	14.36
3309802	H_3TMA	19.18	18.06	17.81	17.66	17.55	17.45	17.36	17.28
3309850	$HTLA^{-}$	10.45	10.08	10.01	9.97	9.95	9.93	9.92	9.91
3309851	H_2TLA	14.13	13.56	13.45	13.38	13.34	13.31	13.28	13.26
3309900	HSER	9.21	9.05	9.02	9.00	9.00	8.99	8.99	8.99
3309901	H_2SER^{+}	11.40	11.18	11.16	11.15	11.15	11.16	11.16	11.17
3309950	$HSAL^{-}$	13.74	13.40	13.30	13.26	13.23	13.21	13.19	13.18
3309951	H_2SAL	16.71	16.20	16.08	16.03	16.00	15.98	15.96	15.96
3309980	$HSUCC^{-}$	5.64	5.24	5.17	5.13	5.10	5.09	5.09	5.09
3309981	H_2SUCC	9.85	9.24	9.15	9.09	9.03	9.01	9.02	9.03
3619050	$HgALA^{+}$	10.96	10.51	10.40	10.34	10.29	10.26	10.23	10.21
3619051	$Hg(ALA)_2$	19.96	19.37	19.25	19.18	19.15	19.12	19.10	19.09
3619100	$Hg(ACAC)_2$	22.43	21.83	21.71	21.67	21.63	21.59	21.59	21.58
3619250	HgCYS	15.21	14.40	14.22	14.12	14.05	13.99	13.95	13.92
3619270	$HgDAP^{+}$	8.78	8.37	8.28	8.23	8.19	8.17	8.15	8.14
3619271	$Hg(DAP)_2$	16.52	15.90	15.77	15.69	15.65	15.62	15.59	15.58
3619272	$HgHDAP^{2+}$	14.37	14.18	14.15	14.14	14.13	14.13	14.13	14.14
3619273	$HgH(DAP)_2^{+}$	22.53	21.94	21.83	21.77	21.74	21.73	21.71	21.73
3619450	$HgETA^{2+}$	8.56	8.54	8.52	8.52	8.51	8.51	8.51	8.51
3619451	$Hg(ETA)_2^{2+}$	17.33	17.31	17.31	17.31	17.32	17.32	17.33	17.33
3619550	$HgHBT^{+}$	4.88	4.46	4.37	4.32	4.29	4.26	4.24	4.23
3619551	$Hg(HBT)_2$	9.14	8.52	8.39	8.32	8.27	8.24	8.22	8.20
3619700	$HgPHEN^{+}$	8.91	8.50	8.41	8.35	8.32	8.29	8.28	8.26
3619701	$HgPHEN_2$	16.71	16.09	15.96	15.89	15.84	15.81	15.78	15.77
3619710	$HgPROP^{+}$	4.40	3.78	3.74	3.74	3.75	3.78	3.81	3.85
3619711	$Hg(PROP)_2$	9.58	8.96	8.83	8.76	8.71	8.68	8.66	8.64

3619750	$Hg(PN)_2^{2+}$	23.42	23.51	23.60	23.68	23.76	23.84	23.93	24.01
3619751	$HgPN^{2+}$	14.32	14.30	14.30	14.30	14.30	14.31	14.31	14.32
3619800	$HgTMA^-$	11.09	9.94	9.70	9.57	9.47	9.40	9.35	9.31
3619801	$Hg(TMA)_2^{4-}$	18.75	18.07	17.91	17.82	17.77	17.73	17.70	17.68
4109300	$KDEM^-$	0.94	0.54	0.45	0.40	0.37	0.34	0.33	0.31
4109650	$KMAL^-$	0.40	0.00	-0.09	-0.14	-0.17	-0.20	-0.21	-0.23
4109710	KPROP	-0.19	-0.41	-0.46	-0.49	-0.51	-0.52	-0.53	-0.53
4109730	$KPHTH^-$	0.70	0.30	0.21	0.16	0.13	0.10	0.09	0.07
4109950	KHSAL	13.50	12.96	12.81	12.75	12.71	12.68	12.65	12.64
4109980	$KSUCC^-$	0.50	0.07	-0.03	-0.09	-0.13	-0.16	-0.18	-0.20
4409300	$LiDEM^-$	0.93	0.55	0.48	0.44	0.41	0.39	0.38	0.37
4409600	LiHMP	-0.11	-0.40	-0.43	-0.45	-0.46	-0.47	-0.47	-0.38
4409710	LiPROP	0.09	-0.11	-0.14	-0.15	-0.19	-0.18	-0.18	-0.18
4409730	$LiPHTH^-$	0.90	0.52	0.45	0.41	0.38	0.36	0.35	0.34
4409980	$LiSUCC^-$	0.80	0.39	0.30	0.26	0.22	0.20	0.18	0.17
4609050	$MgALA^+$	1.96	1.62	1.56	1.52	1.51	1.50	1.50	1.50
4609100	$MgACAC^+$	3.65	3.35	3.25	3.22	3.21	3.20	3.19	3.19
4609101	$Mg(ACAC)_2$	6.30	5.80	5.68	5.61	5.58	5.56	5.55	5.55
4609120	MgASP	2.96	2.43	2.34	2.29	2.27	2.26	2.25	2.25
4609160	$MgAET^+$	2.64	2.30	2.24	2.21	2.20	2.19	2.18	2.18
4609170	$MgBENZ^+$	0.54	0.20	0.14	0.11	0.10	0.09	0.08	0.08
4609300	MgDEM	2.63	1.89	1.75	1.67	1.61	1.57	1.55	1.52
4609400	MgDHMB	1.26	0.92	0.86	0.83	0.81	0.80	0.80	0.80
4609550	$MgHBT^+$	1.00	0.66	0.60	0.57	0.56	0.56	0.55	0.54
4609600	$MgHMP^+$	1.27	0.93	0.87	0.84	0.83	0.82	0.81	0.81
4609601	$Mg(HMP)_2$	2.22	1.67	1.58	1.53	1.50	1.48	1.47	1.47
4609650	MgMAL	2.44	1.71	1.56	1.51	1.47	1.45	1.43	1.42
4609651	$MgHMAL^+$	6.34	5.58	5.46	5.38	5.32	5.29	5.26	5.25

4609710	$MgPROP^{+}$	0.94	0.60	0.54	0.51	0.50	0.49	0.48	0.48
4609750	$MgPN^{2+}$	0.09	0.15	0.18	0.20	0.22	0.24	0.26	0.27
4609900	$MgSER^{+}$	1.37	1.02	0.97	0.94	0.92	0.91	0.91	0.90
4609950	MgSAL	5.50	4.97	4.89	4.84	4.82	4.81	4.80	4.80
4609980	MgSUCC	2.05	1.28	1.11	1.01	0.94	0.89	0.85	0.81
4609981	$MgHSUCC^{+}$	6.56	5.82	5.69	5.62	5.58	5.56	5.55	5.55
4709050	$MnALA^{+}$	2.96	2.56	2.49	2.44	2.42	2.40	2.39	2.38
4709051	$Mn(ALA)_2$	4.72	4.13	4.01	3.95	3.91	3.88	3.87	3.86
4709100	$MnACAC^{+}$	4.21	3.90	3.82	3.80	3.80	3.81	3.82	3.84
4709101	$Mn(ACAC)_2$	7.30	6.81	6.70	6.67	6.66	6.67	6.69	6.71
4709120	MnASP	4.48	3.70	3.54	3.44	3.38	3.33	3.29	3.27
4709200	MnCAT	9.03	7.90	7.68	7.61	7.54	7.52	7.50	7.51
4709201	$Mn(CAT)_2^{2-}$	14.91	13.40	13.12	13.01	12.91	12.89	12.86	12.87
4709250	MnCYS	5.48	4.70	4.54	4.44	4.38	4.33	4.29	4.27
4709300	MNDEM	2.73	1.95	1.79	1.69	1.63	1.58	1.54	1.50
4709450	$MnETA^{2+}$	0.80	0.81	0.82	0.83	0.84	0.85	0.86	0.87
4709600	$MnHMP^{+}$	1.49	1.10	1.02	0.98	0.95	0.93	0.92	0.91
4709601	$Mn(HMP)_2$	2.35	1.76	1.64	1.58	1.54	1.52	1.50	1.49
4709650	MnMAL	3.14	2.35	2.19	2.09	2.03	1.98	1.95	1.92
4709710	$MnPROP^{+}$	1.40	0.90	0.82	0.76	0.75	0.74	0.73	0.72
4709730	MnPHTH	2.74	1.96	1.79	1.70	1.63	1.59	1.55	1.52
4709750	$MnPN^{2+}$	2.74	2.74	2.74	2.75	2.75	2.75	2.76	2.76
4709751	$Mn(PN)_2^{2+}$	4.79	4.80	4.81	4.82	4.82	4.83	4.84	4.85
4709900	$MnSER^{+}$	2.93	2.56	2.50	2.47	2.46	2.46	2.47	2.47
4709901	$Mn(SER)_2$	4.63	4.07	3.98	3.94	3.93	3.93	3.95	3.96
4709950	MnSAL	6.79	6.01	5.88	5.79	5.72	5.68	5.64	5.61
4709951	$Mn(SAL)_2^{2-}$	10.66	9.89	9.74	9.65	9.60	9.56	9.53	9.52
4709980	MnSUCC	2.26	1.46	1.27	1.17	1.09	1.04	1.00	0.97

4709981	$MnHSUCC^{+}$	6.84	6.05	5.91	5.82	5.77	5.74	5.73	5.72
5009300	$NaDEM^{-}$	0.89	0.50	0.42	0.37	0.34	0.32	0.31	0.30
5009650	$NaMAL^{-}$	0.70	0.31	0.23	0.18	0.15	0.13	0.12	0.11
5009710	NaPROP	-0.05	-0.26	-0.30	-0.33	-0.34	-0.35	-0.36	-0.36
5009730	$NaPHTH^{-}$	0.80	0.41	0.33	0.28	0.25	0.23	0.22	0.21
5009950	NaHSAL	13.50	12.96	12.81	12.75	12.71	12.68	12.65	12.64
5009980	$NaSUCC^{-}$	0.40	-0.02	-0.11	-0.17	-0.21	-0.23	-0.25	-0.27
5409050	$NiALA^{+}$	5.80	5.40	5.34	5.32	5.31	5.31	5.32	5.33
5409051	$Ni(ALA)_2$	10.50	9.90	9.81	9.77	9.76	9.76	9.77	9.78
5409060	$NiBEAL^{+}$	4.99	4.54	4.48	4.46	4.46	4.46	4.45	4.45
5409061	$Ni(BEAL)_2$	8.42	7.87	7.86	7.86	7.85	7.84	7.82	7.80
5409100	$NiACAC^{+}$	6.04	5.65	5.58	5.53	5.51	5.49	5.48	5.47
5409101	$Ni(ACAC)_2$	10.69	10.09	9.97	9.91	9.87	9.84	9.83	9.82
5409120	$NiHASP^{+}$	11.92	11.20	11.09	11.04	11.02	11.02	11.02	11.04
5409121	NiASP	7.90	7.15	7.02	6.95	6.92	6.90	6.89	6.90
5409122	$Ni(ASP)_2^{2-}$	13.13	12.40	12.29	12.26	12.25	12.26	12.28	12.31
5409150	$NiACPH^{+}$	4.75	4.36	4.28	4.24	4.21	4.19	4.18	4.17
5409151	$Ni(ACPH)_2$	7.79	7.20	7.08	7.02	6.98	6.95	6.94	6.93
5409160	$NiAET^{+}$	10.64	10.25	10.17	10.13	10.10	10.08	10.07	10.06
5409161	$Ni(AET)_2$	20.68	20.09	19.97	19.91	19.87	19.85	19.83	19.82
5409171	$NiBENZ^{+}$	1.28	0.90	0.83	0.79	0.76	0.74	0.73	0.73
5409200	NiCAT	9.67	8.92	8.79	8.74	8.71	8.70	8.70	8.71
5409201	$Ni(CAT)_2^{2-}$	15.17	14.40	14.25	14.16	14.11	14.07	14.04	14.03
5409250	NiCYS	10.57	9.82	9.68	9.62	9.59	9.57	9.56	9.57
5409251	$Ni(CYS)_2^{2-}$	20.84	20.07	19.92	19.83	19.78	19.74	19.71	19.70
5409252	$NiHCYS^{+}$	15.44	14.72	14.60	14.56	14.54	14.54	14.54	14.56
5409270	$NiDAP^{+}$	8.54	8.15	8.07	8.03	8.00	7.98	7.97	7.96
5409271	$Ni(DAP)_2$	15.80	15.21	15.09	15.03	14.99	14.96	14.95	14.94

5409272	$NiHDAP^{2+}$	13.61	13.44	13.42	13.42	13.42	13.42	13.45	13.46
5409273	$NiH(DAP)_2^{+}$	21.79	21.13	21.03	20.99	20.96	20.95	20.95	20.95
5409274	$NiH_2(DAP)_2^{2+}$	26.75	26.41	26.37	26.37	26.37	26.38	26.40	26.42
5409300	NiDEM	3.15	2.37	2.21	2.11	2.05	2.00	1.96	1.94
5409400	$NiDHMB^{+}$	2.20	1.81	1.73	1.69	1.66	1.64	1.63	1.62
5409401	$Ni(DHMB)_2$	3.63	3.04	2.92	2.86	2.82	2.79	2.78	2.77
5409450	$NiETA^{2+}$	3.00	3.02	3.04	3.06	3.07	3.09	3.11	3.12
5409451	$Ni(ETA)_2^{2+}$	5.32	5.37	5.42	5.46	5.51	5.56	5.61	5.66
5409550	$NiHBT^{+}$	1.56	1.17	1.10	1.05	1.03	1.01	1.00	0.99
5409551	$Ni(HBT)_2$	2.14	1.56	1.44	1.37	1.34	1.31	1.29	1.28
5409600	$NiHMP^{+}$	2.26	1.87	1.79	1.75	1.72	1.70	1.69	1.68
5409601	$Ni(HMP)_2$	3.67	3.08	2.96	2.90	2.86	2.84	2.82	2.81
5409650	NiMAL	4.05	3.17	3.04	2.95	2.88	2.84	2.80	2.77
5409651	$NiHMAL^{+}$	7.31	6.54	6.37	6.27	6.20	6.17	6.14	6.11
5409671	$Ni_2(MET)_2^{2+}$	11.5	10.94	10.81	10.78	10.75	10.73	10.73	10.7
5409710	$NiPROP^{+}$	1.33	0.93	0.86	0.82	0.80	0.79	0.78	0.78
5409711	$Ni(PROP)_2$	1.59	1.01	0.89	0.82	0.79	0.76	0.74	0.73
5409730	$NiHPHTH^{+}$	6.66	5.79	5.63	5.54	5.48	5.43	5.40	5.37
5409731	NiPHTH	2.95	2.17	1.98	1.86	1.77	1.70	1.64	1.59
5409750	$NiPN^{2+}$	7.29	7.34	7.38	7.42	7.46	7.50	7.54	7.58
5409751	$Ni(PN)_2^{2+}$	13.42	13.51	13.60	13.68	13.76	13.84	13.93	14.03
5409800	$NiTMA^{-}$	8.79	7.67	7.45	7.32	7.23	7.17	7.12	7.08
5409801	$Ni(TMA)_4^{2-}$	14.53	13.88	13.74	13.66	13.61	13.57	13.55	13.53
5409802	NiHTMA	13.47	12.17	11.92	11.79	11.68	11.62	11.57	11.53
5409850	NiTLA	7.20	6.42	6.26	6.16	6.10	6.05	6.01	5.99
5409851	$Ni(TLA)_2^{2-}$	14.24	13.47	13.32	13.23	13.18	13.14	13.11	13.10
5409900	$NiSER^{+}$	5.78	5.40	5.33	5.30	5.29	5.28	5.28	5.28
5409901	$Ni(SER)_2$	10.46	9.90	9.81	9.73	9.76	9.76	9.77	9.79

5409950	NiSAL	7.84	7.06	6.93	6.84	6.77	6.73	6.69	6.66
5409951	$Ni(SAL)_2^{2-}$	12.59	11.79	11.64	11.55	11.50	11.46	11.43	11.42
5409980	NiSUCC	2.34	1.60	1.39	1.29	1.22	1.16	1.12	1.09
5409981	$NiHSUCC^+$	6.94	6.15	6.01	5.92	5.87	5.84	5.83	5.82
6009050	$PbALA^+$	5.86	5.43	5.33	5.27	5.24	5.21	5.19	5.17
6009051	$Pb(ALA)_2$	8.98	8.35	8.21	8.13	8.08	8.04	8.02	8.00
6009052	$PbHALA^{2+}$	11.54	11.33	11.29	11.27	11.27	11.26	11.26	11.27
6009100	$PbACAC^+$	5.00	4.57	4.47	4.41	4.37	4.34	4.32	4.31
6009101	$Pb(ACAC)_2$	7.91	7.28	7.14	7.06	7.01	6.97	6.95	6.93
6009120	PbASP	8.09	7.28	7.10	6.99	6.92	6.87	6.83	6.80
6009121	$Pb(ASP)_2^{2-}$	10.52	9.72	9.55	9.45	9.39	9.35	9.32	9.30
6009160	$PbAET^+$	11.59	11.16	11.06	11.00	10.96	10.93	10.91	10.89
6009170	$PbBENZ^+$	2.41	2.00	1.92	1.88	1.86	1.85	1.85	1.85
6009171	$Pb(BENZ)_2$	3.86	3.24	3.10	3.03	2.98	2.95	2.93	2.91
6009250	PbCYS	13.30	12.51	12.36	12.28	12.24	12.21	12.19	12.19
6009251	$PbHCYS^+$	18.00	17.20	17.04	16.94	16.91	16.86	16.79	16.76
6009252	$Pb(CYS)_2^{2-}$	19.72	18.92	18.75	18.65	18.59	18.55	18.52	18.50
6009253	$PbH(CYS)_2^-$	28.40	27.21	26.98	26.83	26.78	26.71	26.63	26.59
6009254	$PbOH(CYS)_2^{3-}$	7.78	7.50	7.42	7.36	7.33	7.31	7.32	7.28
6009300	PbDEM	3.13	2.30	2.11	2.00	1.93	1.87	1.83	1.79
6009400	$PbDHMB^+$	3.26	2.83	2.73	2.68	2.64	2.61	2.59	2.57
6009401	$Pb(DHMB)_2$	4.73	4.10	3.96	3.88	3.82	3.79	3.76	3.75
6009450	$PbETA^{2+}$	4.13	4.10	4.09	4.08	4.08	4.08	4.08	4.08
6009550	$PbHBT^+$	2.86	2.43	2.33	2.28	2.24	2.21	2.19	2.17
6009551	$Pb(HBT)_2$	4.17	3.54	3.40	3.32	3.26	3.23	3.20	3.19
6009600	$PbHMP^+$	2.67	2.25	2.16	2.11	2.08	2.06	2.04	2.03
6009601	$Pb(HMP)_2$	4.27	3.63	3.49	3.40	3.34	3.30	3.27	3.25
6009650	$PbHMAL^+$	8.27	7.45	7.26	7.16	7.07	7.02	6.98	6.95

6009651	PbH_2MAL_2	14.91	13.44	13.14	19.34	12.85	19.07	19.00	12.67
6009652	PbMAl	3.28	2.45	2.26	2.15	2.08	2.02	1.98	1.94
6009670	$PbMET^+$	7.13	6.70	6.60	6.54	6.50	6.47	6.45	6.44
6009671	Pb_2MET^{3+}	8.74	8.70	8.74	8.79	8.86	8.94	9.02	9.11
6009710	$PbPROP^+$	2.88	2.45	2.35	2.30	2.26	2.23	2.21	2.19
6009711	$Pb(PROP)_2$	4.19	3.56	3.42	3.34	3.28	3.25	3.22	3.21
6009730	PbPHTH	4.19	3.36	3.18	3.06	2.99	2.93	2.89	2.85
6009731	$Pb(PHTH)_2^{2-}$	5.18	4.41	4.25	4.17	4.11	4.08	4.05	4.03
6009732	$PbHPHTH^+$	7.16	6.28	6.12	6.03	5.97	5.92	5.89	5.86
6009733	$PbH(PHTH)_2^-$	9.57	8.34	8.11	8.00	7.91	7.87	7.83	7.81
6009750	$Pb(PN)_2^{2+}$	8.44	8.53	8.62	8.70	8.78	8.86	8.95	9.03
6009751	$PbPN^{2+}$	5.06	5.04	5.04	5.04	5.04	5.04	5.05	5.05
6009900	$PbSER^+$	5.08	4.75	4.69	4.66	4.65	4.64	4.64	4.65
6009901	$Pb(SER)_2$	8.33	7.71	7.58	7.51	7.46	7.43	7.41	7.39
6009980	PbSUCC	3.60	2.80	2.66	2.59	2.57	2.56	2.57	2.59
6009981	$PbHSUCC^+$	8.14	7.32	7.16	7.09	7.01	6.98	6.96	6.95
6009982	$Pb(SUCC)_2^{2-}$	5.27	4.42	4.23	4.13	4.07	4.03	4.01	3.99
6009984	$PbH_2(SUCC)_2$	14.92	13.50	13.23	13.09	12.99	12.94	12.93	12.93
6009985	$PbH(SUCC)_2^-$	10.57	9.36	9.11	8.99	8.91	8.86	8.84	8.82
7809710	$SnPROP^+$	3.97	3.58	3.51	3.46	3.44	3.42	3.41	3.40
7809711	$Sn(PROP)_2$	6.70	6.11	5.99	5.93	5.89	5.86	5.85	5.84
8009050	$SrALA^+$	0.74	0.33	0.23	0.18	0.15	0.12	0.11	0.09
8009100	$SrACAC^+$	2.16	1.75	1.66	1.61	1.57	1.55	1.53	1.52
8009120	SrASP	2.29	1.48	1.30	1.20	1.13	1.07	1.03	1.00
8009160	$SrAET^+$	1.96	1.55	1.46	1.41	1.37	1.35	1.33	1.32
8009300	SrDEM	2.41	1.60	1.42	1.32	1.24	1.19	1.15	1.12
8009400	$SrDHMB^+$	1.40	0.98	0.89	0.84	0.80	0.78	0.76	0.75
8009550	$SrHBT^+$	0.98	0.56	0.47	0.42	0.39	0.39	0.36	0.34

8009600	$SrHMP^{+}$	1.22	0.81	0.72	0.66	0.63	0.60	0.59	0.57
8009601	$Sr(HMP)_2$	1.69	1.07	0.94	0.87	0.82	0.79	0.76	0.75
8009650	SrMAL	2.29	1.52	1.38	1.31	1.28	1.27	1.26	1.27
8009651	$SrHMAL^{+}$	6.31	5.48	5.33	5.23	5.14	5.10	5.06	5.04
8009710	$SrProp^{+}$	0.94	0.52	0.43	0.38	0.35	0.32	0.30	0.29
8009980	SrSUCC	2.05	1.24	1.06	0.96	0.88	0.83	0.79	0.76
8009981	$SrHSUCC^{+}$	6.63	5.82	5.66	5.56	5.50	5.46	5.44	5.43
8937930	UO_2PHTH	5.65	4.87	4.70	4.61	4.54	4.50	4.46	4.43
8939050	UO_2ALA^{+}	7.72	7.33	7.25	7.21	7.18	7.16	7.15	7.14
8939051	$UO_2(ALA)_2$	15.56	14.97	14.85	14.79	14.75	14.72	14.71	14.70
8939060	UO_2HBEAL^{2+}	12.12	11.94	11.94	11.94	11.95	11.97	11.99	12.01
8939061	$UO_2H_2(BEAL)_2^{2+}$	23.82	23.46	23.46	23.46	23.48	23.52	23.56	23.60
8939100	UO_2ACAC^{+}	7.60	7.20	7.13	7.08	7.06	7.04	7.03	7.02
8939101	$UO_2(ACAC)_2$	14.05	13.45	13.33	13.27	13.23	13.20	13.19	13.18
8939102	$UO_2H(ACAC)_2^{+}$	18.42	17.80	17.75	17.71	17.68	17.67	17.67	17.67
8939120	$UO_{2A}SP$	4.74	3.95	3.79	3.69	3.63	3.58	3.55	3.52
8939121	$UO_{2H}ASP^{+}$	13.09	12.35	12.19	12.10	12.05	12.01	11.99	11.97
8939122	$UO_2H_2(ASP)_2$	25.01	23.72	23.46	23.32	23.26	23.22	23.20	23.19
8939200	UO_2CAT	16.55	15.77	15.60	15.51	15.44	15.40	15.36	15.33
8939201	UO_2HCAT^{+}	20.37	19.60	19.44	19.36	19.29	19.25	19.22	19.20
8939202	$UO_2H(CAT)_2^{-}$	35.23	34.08	33.84	33.72	33.62	33.57	33.52	33.49
8939250	UO_2HCYS^{+}	16.97	16.20	16.05	15.96	15.90	15.86	15.83	15.80
8939251	$UO_2H^2(CYS)_2$	33.92	33.57	33.2.	32.15	32.05	31.98	31.93	31.88
8939300	UO_2DEM	8.01	7.23	7.07	6.97	6.91	6.86	6.82	6.80
8939301	$UO_2(DEM)_2^{2-}$	12.14	11.37	11.22	11.13	11.08	11.04	11.01	11.01
8939550	UO_2HBT^{+}	2.97	2.58	2.50	2.46	2.43	2.41	2.40	2.39
8939551	$UO_2(HBT)_2$	5.22	4.63	4.51	4.45	4.41	4.39	4.37	4.36
8939600	UO_2HMP^{+}	3.76	3.37	3.30	3.25	3.23	3.21	3.20	3.19

8939601	$UO_2(HMP)_2$	6.00	5.42	5.30	5.23	5.20	5.17	5.15	5.14
8939650	UO_2OHMAL^-	3.27	2.57	2.41	2.32	2.23	2.17	2.13	2.08
8939651	$(UO_2)_2(OH)_2MAL_2$	9.08	7.93	7.71	7.61	7.50	7.46	7.44	7.42
8939700	UO_2PHEN^+	6.20	5.81	5.74	5.69	5.67	5.65	5.64	5.63
8939710	UO_2PROP^+	2.90	2.51	2.44	2.39	2.37	2.35	2.34	2.33
8939711	UO_2PROP_2	5.42	4.64	4.52	4.45	4.42	4.39	4.37	4.36
8939900	UO_2HSER^{2+}	10.03	9.88	9.86	9.85	9.86	9.86	9.87	9.88
8939901	UO_2SER^+	9.05	8.66	8.58	8.54	8.51	8.49	8.48	8.47
8939902	$UO_2(SER)_2$	15.25	14.66	14.54	14.48	14.44	14.41	14.40	14.39
8939950	UO_2HSAL^+	16.32	15.60	15.42	15.34	15.28	15.24	15.21	15.19
8939951	UO_2SAL	12.88	12.10	11.97	11.88	11.81	11.77	11.73	11.70
8939952	$UO_2(SAL)_2^{2-}$	21.60	20.83	20.68	20.59	20.54	20.50	20.47	20.46
8939980	UO_2SUCC	5.14	4.32	4.13	4.02	3.93	3.87	3.82	3.78
8939981	UO_2HSUCC^+	8.14	7.39	7.28	7.23	7.21	7.22	7.24	7.27
8939982	$UO_2H(SUCC)_2$	12.98	11.77	11.52	11.38	11.27	11.21	11.17	11.14
9509051	$ZnALA^+$	4.95	4.58	4.57	4.56	4.56	4.56	4.55	4.55
9509052	$Zn(ALA)_2$	9.20	8.63	8.54	8.51	8.50	8.50	8.13	8.53
9509060	$ZnBEAL^+$	4.45	4.07	3.99	3.95	3.92	3.90	3.89	3.88
9509061	$Zn(BEAL)_2$	8.04	7.45	7.33	7.26	7.23	7.20	7.18	7.17
9509100	$ZnACAC^+$	5.05	4.68	4.61	4.58	4.57	4.57	4.57	4.57
9509101	$Zn(ACAC)_2$	8.65	8.10	8.02	8.01	8.01	8.02	8.05	8.08
9509120	$ZnASP$	6.75	5.97	5.81	5.71	5.65	5.60	5.56	5.54
9509121	$Zn(ASP)_2^{2-}$	11.10	10.33	10.18	10.09	10.04	10.00	9.97	9.96
9509122	$ZnHASP^+$	11.67	10.92	10.78	10.70	10.65	10.62	10.59	10.58
9509160	$ZnAET^+$	10.25	9.92	9.90	9.91	9.94	9.98	10.02	10.07
9509161	$Zn(AET)_2$	19.33	18.79	18.71	18.69	18.70	18.72	18.74	18.78
9509170	$ZnBENZ^+$	1.28	0.90	0.83	0.79	0.76	0.74	0.73	0.73
9509200	$ZnCAT$	10.67	9.90	9.75	9.67	9.62	9.59	9.57	9.55

9509201	$Zn(CAT)_2^{2-}$	18.12	17.40	17.30	17.27	17.27	17.29	17.32	17.36
9509250	ZnCYS	9.95	9.17	9.01	8.91	8.85	8.80	8.76	8.74
9509251	$Zn(CYS)_2^{2-}$	18.84	18.12	18.02	17.98	17.98	18.00	18.02	18.06
9509252	$ZnHCYS^+$	15.63	14.86	14.71	14.62	14.56	14.52	14.49	14.46
9509253	$ZnH(CYS)_2^-$	25.55	24.46	24.28	24.20	24.17	24.17	24.17	24.19
9509254	$ZnH_2(CYS)_2$	31.21	29.96	29.76	29.68	29.66	29.67	29.69	29.72
9509270	$ZnDAP^+$	6.80	6.31	6.23	6.19	6.16	6.14	6.13	6.12
9509271	$Zn(DAP)_2$	12.27	11.66	11.54	11.48	11.44	11.41	11.40	11.39
9509272	$ZnHDAP^{2+}$	12.76	12.59	12.57	12.57	12.57	12.57	12.58	12.59
9509273	$ZnH(DAP)_2^+$	18.99	18.43	18.23	18.29	18.26	18.25	18.25	18.25
9509274	$ZnH2(DAP)_2^{2+}$	24.96	24.62	24.58	24.58	24.58	24.59	24.61	24.63
9509300	ZnDEM	3.22	2.44	2.28	2.18	2.12	2.07	2.03	2.01
9509450	$ZnETA^{2+}$	2.39	2.41	2.43	2.45	2.48	2.50	2.51	2.53
9509452	$Zn(ETA)_2^{2+}$	4.65	4.67	4.70	4.73	4.75	4.78	4.81	4.83
9509550	$ZnHBT^+$	1.55	1.16	1.09	1.04	1.02	1.00	0.99	0.98
9509551	$Zn(HBT)_2$	2.50	1.92	1.80	1.73	1.70	1.67	1.65	1.64
9509600	$ZnHMP^+$	2.29	1.90	1.82	1.78	1.75	1.73	1.72	1.71
9509601	$Zn(HMP)_2$	3.86	3.27	3.15	3.09	3.05	3.03	3.01	3.00
9509650	ZnMAL	3.66	2.93	2.80	2.71	2.64	2.60	2.56	2.53
9509651	$ZnHMAL^+$	7.14	6.37	6.20	6.10	6.03	6.00	5.97	5.94
9509710	$ZnPROP^+$	1.30	0.90	0.84	0.81	0.80	0.80	0.81	0.81
9509711	$Zn(PROP)_2$	2.21	1.61	1.48	1.41	1.36	1.32	1.29	1.27
9509730	ZnPHTH	2.91	2.13	1.96	1.87	1.80	1.76	1.72	1.69
9509731	$Zn(PHTH)_2^{2-}$	4.20	3.43	3.28	3.19	3.14	3.10	3.07	3.06
9509750	$ZnPN^{2+}$	5.64	5.72	5.75	5.79	5.83	5.87	5.91	5.96
9509751	$Zn(PN)_2^{2+}$	10.62	10.73	10.85	10.96	11.08	11.20	11.32	11.43
9509800	$ZnTMA^-$	9.37	8.24	8.01	7.88	7.78	7.71	7.66	7.62
9509801	$Zn(TMA)_2^{4-}$	15.21	14.56	14.42	14.34	14.29	14.25	14.23	14.21

9509802	$ZnOHTMA^{2-}$	0.62	0.12	-0.26	-0.34	-0.39	-0.43	-0.45	-0.46
9509803	ZnHTMA	12.05	10.54	10.28	10.14	10.03	9.96	9.91	9.87
9509850	ZnTLA	8.00	7.22	7.06	6.96	6.90	6.85	6.81	6.79
9509851	$Zn(TLA)_2^{2-}$	15.44	14.67	14.52	14.43	14.38	14.34	14.31	14.30
9509901	$ZnSER^{+}$	4.97	4.60	4.54	4.51	4.50	4.49	4.49	4.50
9509902	$Zn(SER)_2$	9.06	8.50	8.41	8.38	8.37	8.37	8.38	8.40
9509950	ZnSAL	7.74	6.96	6.83	6.74	6.67	6.63	6.59	6.56
9509980	ZnSUCC	2.52	1.74	1.59	1.52	1.48	1.46	1.45	1.45
9509981	$Zn(SUCC)_2^{-}$	3.34	2.51	2.33	2.23	2.16	2.11	2.07	2.05
9509982	$ZnHSUCC^{+}$	6.98	6.20	6.05	5.97	5.91	5.88	5.87	5.86
9509050	ZNOHALA	-3.75	-3.73	-3.70	-3.68	-3.65	-3.64	-3.64	-3.64
	Protonation constants for organics adsorbent								
9993300	$HTIPP^{-}$	4.40	4.06	3.96	3.92	3.89	3.87	3.85	3.84
9993301	$H_{2=T}IPP$	5.10	4.59	4.47	4.42	4.39	4.37	4.37	4.37
	Solid Precipitation Reactions								
2002000	Ag_2O	-12.58	-12.62	-12.70	-12.76	-12.82	-12.86	-12.92	-12.97
2003000	Gibbsite	-8.50	-9.19	-9.36	-9.45	-9.51	-9.54	-9.57	-9.58
2007000	$Ba(OH)_2$	-24.40	-24.60	-24.71	-24.76	-24.77	-24.79	-24.83	-24.86
2015001	$Ca(OH)_2$	-22.80	-22.97	-23.06	-23.10	-23.12	-23.14	-23.17	-23.20
2016000	$Cd(OH)_2$	-13.65	-13.89	-13.95	-13.99	-14.01	-14.03	-14.04	-14.06
2019000	$Co(OH)_2$	-13.20	-13.42	-13.45	-13.48	-13.51	-13.54	-13.57	-13.60
2021100	$Cr(OH)_3$	-12.00	-12.72	-12.90	-13.03	-13.11	-13.18	-13.22	-13.26
2023000	Cu_2O	1.60	1.52	1.46	1.41	1.35	1.36	1.32	1.32
2023100	$CU(OH)_2$	-8.70	-8.84	-8.92	-8.96	-8.98	-8.99	-9.02	-9.04
2028000	$Fe(OH)_2$	-12.85	-13.07	-13.13	-13.17	-13.20	-13.22	-13.25	-13.26
2028100	$am\text{-}Fe(OH)_3$	-3.20	-3.58	-3.75	-3.79	-3.74	-3.82	-3.82	-3.80

2028101	$Fe(OH)_2NO_3$	-1.04	-1.75	-1.89	-1.97	-2.03	-2.07	-2.11	-2.13
2036100	HgO	-2.56	-2.73	-2.73	-2.74	-2.74	-2.74	-2.74	-2.74
2046000	Brucite	-16.84	-17.09	-17.16	-17.20	-17.24	-17.26	-17.28	-17.31
2047000	$Mn(OH)_2$	-15.20	-15.42	-15.45	-15.48	-15.51	-15.54	-15.57	-15.60
2047001	MnO_2	-41.37	-41.26	-41.27	-41.31	-41.34	-41.38	-41.42	-41.47
2054000	$Ni(OH)_2$	-13.00	-13.22	-13.25	-13.28	-13.11	-13.34	-13.37	-13.40
2060000	Litharge	-12.72	-12.92	-13.00	-13.05	-13.09	-13.13	-13.17	-13.21
2078000	SnO	-1.76	-2.00	-2.05	-2.09	-2.12	-2.13	-2.15	-2.16
2089300	$UO_2(OH)_2$	-5.60	-5.83	-5.88	-5.90	-5.92	-5.93	-5.93	-5.93
2095000	$ZN(OH)_2$	-12.45	-12.65	-12.68	-12.70	-12.71	-12.72	-12.73	-12.74
4002000	AgBr	12.30	12.10	12.02	11.98	11.96	11.95	11.94	11.93
4023000	CuBr	8.30	8.09	8.05	8.03	8.02	8.02	8.03	8.04
4023100	$Cu(OH)_{1.5}Br_{0.5}$	-3.43	-3.71	-3.80	-3.85	-3.87	-3.90	-3.93	-3.95
4036000	Hg_2Br_2	22.25	21.57	21.40	21.29	21.22	21.17	21.13	21.10
4036100	$HgBr_2$	19.84	19.20	19.06	18.98	18.93	18.90	18.88	18.87
4060000	$PbBr_2$	5.68	5.03	4.88	4.79	4.74	4.70	4.68	4.66
4102000	Chloroargyrite	9.75	9.56	9.55	9.58	9.60	9.62	9.64	9.66
4123000	CuCl	6.73	6.52	6.48	6.46	6.46	6.46	6.47	6.47
4123100	$Cu(OH)_{1.5}Cl_{0.5}$	-3.70	-3.90	-3.92	-3.91	-3.85	-3.80	-3.76	-3.71
4136000	Hg_2Cl_2	17.91	17.24	17.08	16.98	16.92	16.88	16.85	16.83
4160000	$PbCl_2$	4.78	4.16	4.04	3.99	3.97	3.96	3.97	3.99
4195000	$Zn(OH)_{1.5}Cl_{0.5}$	-7.60	-7.88	-7.97	-8.02	-8.04	-8.07	-8.10	-8.12
4203000	$AlOHF_2$	8.60	7.68	7.47	7.33	7.24	7.21	7.21	7.20
4207000	BaF_2	5.82	5.19	5.05	4.98	4.93	4.91	4.89	4.98
4215000	Fluorite	10.50	9.90	9.77	9.71	9.67	9.65	9.64	9.63
4244000	LiF	2.77	2.57	2.54	2.52	2.52	2.52	2.53	2.53
4246000	MgF_2	8.13	7.57	7.47	7.42	7.39	7.38	7.37	7.37
4260000	PbF_2	7.44	6.77	6.60	6.50	6.43	6.38	6.34	6.30

4278000	SrF_2	8.58	7.95	7.81	7.74	7.69	7.67	7.65	7.64
4302000	AgI	16.08	15.85	15.81	15.78	15.77	15.76	15.76	15.77
4336000	Hg_2I_2	28.33	27.69	27.56	27.51	27.48	27.47	27.47	27.49
4336100	HgI_2	28.89	28.25	28.11	28.03	27.98	27.95	27.93	27.92
4360000	PBI_2	8.10	7.47	7.34	7.28	7.25	7.23	7.23	7.24
4378000	SnI_2	5.39	4.78	4.65	4.58	4.54	4.51	4.50	4.49
4402000	$AgIO_3$	7.51	7.28	7.22	7.18	7.15	7.13	7.12	7.10
4407000	$Ba(IO_3)_2$	8.81	8.16	8.00	7.89	7.82	7.76	7.71	7.68
4415000	$Ca(IO_3)_2$	6.06	5.40	5.27	5.17	5.12	5.07	5.03	5.00
4416000	$Cd(IO_3)_2$	7.64	7.06	6.98	6.95	6.95	6.97	7.00	7.03
4419000	$Co(IO_3)_2$	5.63	5.03	4.90	4.84	4.80	4.77	4.75	4.73
4421100	$Cr(IO_3)_3$	6.69	5.65	5.47	5.38	5.33	5.30	5.28	5.28
4423100	$Cu(IO_3)_2$	6.93	6.34	6.22	6.16	6.13	6.11	6.10	6.09
4423101	$CuOHIO_3$	-3.44	-3.71	-3.80	-3.85	-3.87	-3.89	-3.92	-3.94
4436000	$Hg_2(IO_3)_2$	17.89	17.24	17.10	17.01	16.96	16.93	16.91	16.89
4441000	KIO_3	1.64	1.43	1.38	1.36	1.35	1.35	1.35	1.35
4454000	$Ni(IO_3)_2$	5.01	4.42	4.30	4.23	4.19	4.17	4.16	4.15
4460000	$Pb(IO_3)_2$	12.41	11.82	11.70	11.63	11.59	11.57	11.56	11.55
4480000	$Sr(IO_3)_2$	6.35	5.71	5.58	5.49	5.43	5.40	5.36	5.34
4489300	$UO_2(IO_3)_2$	7.71	7.12	7.01	6.95	6.92	6.90	6.89	6.89
4495000	$Zn(IO_3)_2$	5.23	4.63	4.53	4.45	4.42	4.40	4.39	4.38
5002000	Ag_2CO_3	11.09	10.43	10.27	10.18	10.12	10.08	10.05	10.03
5007000	$BaCO_3$	8.69	7.85	7.66	7.55	7.47	7.42	7.38	7.35
5015000	ARAGONITE	8.30	7.55	7.24	6.82	6.83	6.46	6.30	6.15
5016000	$CdCO_3$	13.74	12.90	12.71	12.60	12.52	12.47	12.43	12.40
5019000	$CoCO_3$	10.78	9.28	9.22	9.23	9.28	9.35	9.43	9.52
5023100	$CuCO_3$	11.50	10.70	10.54	10.45	10.40	10.37	10.35	10.34
5023101	Malachite	5.55	4.64	4.47	4.42	4.42	4.43	4.45	4.48

5023102	Azurite	16.90	15.11	14.67	14.42	14.27	14.16	14.04	13.98
5028000	Siderite	10.68	9.90	9.75	9.69	9.65	9.64	9.64	9.64
5036000	Hg_2CO_3	16.05	15.18	14.97	14.84	14.76	14.70	14.65	14.62
5046000	Nesquehonite	4.67	3.90	3.74	3.66	3.60	3.56	3.53	3.51
5047000	Rhodochrosite	10.60	9.66	9.36	9.14	8.95	8.79	8.64	8.52
5054000	$NiCO_3$	6.87	6.04	5.85	5.73	5.65	5.59	5.54	5.50
5060000	Cerrusite	13.13	12.20	11.95	11.80	11.65	11.50	11.40	11.30
5060001	$Pb_3(OH)_2(CO_3)_2$	19.02	17.09	16.59	16.30	16.11	15.97	15.84	15.74
5080000	Strontianite	9.27	8.43	8.24	8.13	8.05	8.00	7.96	7.93
5095000	Smithsonite	10.00	9.18	9.01	8.91	8.84	8.79	8.76	8.73
6002000	Ag_2SO_4	4.83	4.15	3.98	3.89	3.82	3.78	3.75	3.72
6007000	Barite	9.96	9.06	8.84	8.72	8.63	8.57	8.53	8.51
6015000	Gypsum	4.23	3.41	3.23	3.13	3.06	3.02	2.99	2.97
6023100	Brochantite	-3.84	-4.17	-4.28	-4.34	-4.37	-4.40	-4.44	-4.46
6036000	Hg_2SO_4	6.13	5.24	5.01	4.88	4.79	4.72	4.66	4.62
6060000	Anglesite	7.79	6.91	6.69	6.56	6.47	6.40	6.34	6.29
6080000	Celestite	6.50	5.60	5.38	5.26	5.17	5.11	5.07	5.05
7002000	Ag_3PO_4	17.59	16.22	15.88	15.67	15.53	15.43	15.35	15.29
7003000	Berlinite	20.60	18.85	18.47	18.24	18.09	17.97	17.88	17.81
7015000	Brushite	18.93	17.47	17.11	16.90	16.75	16.64	16.58	16.51
7015002	$Ca_3(PO_4)_2$	28.92	25.73	24.98	24.54	24.23	24.00	23.83	23.68
7028000	Vivianite	36.00	32.81	32.06	31.62	31.31	31.08	30.91	30.76
7028100	Strengite	26.40	24.65	24.27	24.04	23.89	23.77	23.68	23.61
7036000	Hg_2HPO_4	24.75	23.23	22.83	22.60	22.42	22.29	22.20	22.13
7036100	$HgHPO_4$	26.85	25.36	24.99	24.77	24.61	24.49	24.41	24.36
7036101	$Hg_3(PO_4)_2$	53.02	49.78	48.95	48.46	48.10	47.83	47.63	47.50
7036102	$(HgOH)_3PO_4$	24.11	22.11	21.61	21.31	21.09	20.93	20.82	20.74
7046000	Bobierrite	23.28	20.23	19.54	19.14	18.86	18.66	18.50	18.38

7046001	Newberyite	18.15	16.73	16.38	16.18	16.04	15.93	15.85	15.80
7060006	$PBHPO_4$	23.88	22.28	21.90	21.61	21.51	21.39	21.30	21.25
7089300	$UO_{2H}PO4$	24.68	23.22	22.86	22.65	22.50	22.39	22.33	22.26
7089301	$(UO_2)_3(PO_4)$	49.00	45.81	45.06	44.62	44.31	44.08	43.91	43.76
7095000	α-Hopeite	35.30	32.11	31.36	30.92	30.61	30.38	30.21	30.06
7402000	Ag_2CrO_4	11.59	10.91	10.74	10.65	10.58	10.54	10.51	10.48
7407000	$BaCrO_4$	9.67	8.96	8.75	8.65	8.57	8.51	8.47	8.44
7423100	$CuCrO_4$	5.44	4.73	4.52	4.42	4.34	4.28	4.24	4.23
7436000	Hg_2CrO_4	8.70	7.81	6.78	6.66	6.60	6.54	6.50	6.49
7460000	$PbCrO_4$	13.70	13.00	12.78	12.68	12.60	12.54	12.50	12.47
8003000	Kaolinite	38.29	36.19	35.81	35.60	35.47	35.37	35.30	35.25
8003001	$KAl_3Si_3O_{10}$..	51.83	48.64	48.53	47.69	47.46	47.29	47.17	47.07
8033000	Am-SiO_2	25.70	25.11	25.00	24.92	24.86	24.83	24.84	24.84
8046000	Illite	70.02	66.87	66.27	65.94	65.71	65.55	65.43	65.34
8046001	Chlorite	-4.32	-7.88	-8.53	-8.89	-9.12	-9.28	-9.39	-9.48
8050000	Mg-Montmoril..	78.09	74.86	74.25	73.91	73.69	73.53	73.40	73.31
	Redox Reactions								
2102110	CrO_4^{2-}/Cr^{3+}	74.90	74.30	74.21	74.20	74.22	74.26	74.31	74.37
2302310	Cu^{+}/Cu^{2+}	2.60	2.21	2.14	2.09	2.07	2.05	2.04	2.03
2812800	Fe^{3+}/Fe^{2+}	13.03	12.57	12.51	12.48	12.46	12.45	12.44	12.44
3603610	Hg_2^{2+}/Hg^{2+}	31.10	30.51	30.40	30.34	30.31	30.29	30.28	30.28
3803810	$IO_3^{-}/I\_$	110.05	109.00	108.86	108.82	108.83	108.86	108.91	108.97
	Gaseous Reactions								
3301403	CO_2 (g)	18.15	17.59	17.44	17.33	17.25	17.18	17.12	17.07

APPENDIX TWO

THE RANDOM PROGRAM

Appendix 2.1: Discussion of the procedures underlying RANDOM

The TURBO PASCAL listing of the RANDOM program can be found in Appendix 2.2. The purpose of the program is to generate "random" molecules of fulvic acid according to certain rules and then identify possible metal binding sites in these molecules. The RANDOM program thus consists of a number of sections: the input of control parameters including characteristics of the fulvic acid; the generation of structures and the allocation of functional groups to the structures; the identification and counting of binding sites and the output of results.

Because the program is designed to be run on a computer with a graphics screen the program uses the unit GrDriver which comes from the book *Mastering Turbo Pascal* by Tom Swan [Swa89]. This unit recognizes the graphics card (hercules, cga, ega or vga) in use and loads the necessary driver. Compatibility problems have been experienced with some hercules cards. The unit is listed after the random program. All other units are those supplied with TURBO PASCAL v 5.5 and higher.

Section one - Input of data

This can either be done interactively using RANDOM or by creating an input file using an editor. By using RANDOM, two options are offered. An input file may be created from scratch or one might be created by using another as a seed file. Figure A.2.1 is a sample input file for RANDOM while Figure A.2.2 is an explanation of the various numbers in Figure A.2.1. It should be noted that RANDOM formats the input file which it creates, so some comments are necessary for the user who wishes to create the file from scratch.

1) The ratio oo:mm:pp or the ratio of ortho:meta:para rings must contain no spaces and must contain the two colons shown in Figure A:2.1.

Figure A.2.1: A sample input file for RANDOM

```
2:2:1
BRIEF
26
30 33 20 31 26 21 09 32 22 24 25 27 34 10 13 11 12 15 14 03
05 04 06 08 07 16
100000
1
51.25 0.05 9.0 0.2 0
5 3 0.7 0 0 2 3 0.05
```

Figure A.2.2: Explanation of the input file

```
Line 1    RO:RM:RP              { Ratio of ortho to meta to
                                para rings, note the colons }
Line 2    OUTPUT OPTION         { BRIEF, INTERMEDIATE OR FULL}
Line 3    NO of GROUPS TO BE COUNTED
Line 4    1st LINE OF COUNTING ORDER     { Note spaces }
Line 5    2nd LINE of COUNTING ORDER
Line 6    NUMBER OF STRUCTURES TO BE GENERATED
Line 7    NUMBER OF FULVIC ACIDS         { Repeat next pair
                                         of lines this many
                                         times }
Line 8    5 NUMBERS SEPARATED BY A SPACE
                    PERCENTAGE CARBON
                    FRACTION OF -COOHs ON AROMATIC RINGS
                    PERCENTAGE AROMATIC CARBON
                    FRACTION OF ALIPHATIC C IN METHYL GROUPS
                    FRACTION OF QUINONES IN ORTHO
                              ARRANGEMENTS
Line 9    8 NUMBERS SEPARATED BY A SPACE
                    CONCENTRATION OF KETONES IN MEQ/G
                    CONCENTRATION OF CARBOXYLS
                    CONCENTRATION OF PHENOLS
                    CONCENTRATION OF METHOXYLS
                    CONCENTRATION OF QUINONES
                    CONCENTRATION OF ALIPHATIC HYDROXYLS
                    CONCENTRATION OF ALIPHATIC AMINES
                    CONCENTRATION OF ALIPHATIC THIOLS
```

2) The output options available are BRIEF, INTERMEDIATE or FULL.

3 The third line contains the number of binding sites listed in lines 4 and 5. Line 4 contains the first 20 sites and line 5 the rest. If their are less than 21 sites line 5 is blank. Note the SINGLE space between site numbers while site numbers (X < 10) are entered as 0X.

4 Obviously the number of structures and number of fulvic acids must be integers greater than 0.

5 The functional group data given in lines 8 and 9 must be positive real numbers. Note again the SINGLE space between entries.

Section two - Generation of the structures

Use is made of the PC's own random number generator. These are in the interval [0,1) and are stored in the array XX which has 800 entries. RANDOM assumes a molecular mass of 2000 g mol^{-1}.

The first procedure RANDOM performs is to test for incompatabilities in the input data. The number of aromatic rings must be less than 15 (this is equivalent to an input percentage aromatic carbon of 100% assuming 54% C elemental composition). The number of aliphatic carbons must be less than 100. This means that at most 60% of the total composition is made up of aliphatic carbons. Samples with aliphatic carbons in excess of 100 and rings in excess of 15 per mole do not fall within the normal range of fulvic acid measurements. Lastly the number of carbons atoms in rings, carboxylates and ketones must not exceed the number of carbon atoms predicted by the elemental composition.

The program will then generate the number of structures in the input file. For each structure, the functional group concentration is calculated using the procedure discussed

earlier but which will be explained again here. The program also calculates the number of carbon atoms from the elemental composition and the number of rings. The program also calculates the number of quinone pairs. Because the program can use only integral concentration values the non-integral input data must be converted. The example will be discussed for the number of phenol groups. Suppose the input concentration is 0.63 meq g^{-1} (= FD). The number per fulvic acid molecule is therefore 1.26 phenols (= FC) since the molar mass is assumed to be 2000 g mol^{-1}. The truncated value is put into IFMIN (i.e. 1) and IFMAX = IFMIN + 1 (i.e. 2). RANDOM then uses the array XX[JJ] and selects the next number in the array. If this number, in the example, is less than (FC-IFMIN) (i.e. 0.26) the concentration used will be IFMIN phenol groups per structure else it will be IFMAX groups per structure. The net effect is that over all the structures generated the average phenol concentration will be FC (1.26 groups per molecule) (See later for an exception).

The program then decides how many of the IR rings are ortho, meta or para. This is again done randomly using the input data (RO:RM:RP) such that the probability of a ring being ortho is RO/(RO+RM+RP). Over all the structures the types of ring junctions will be in the ratio RO:RM:RP.

The first functional groups to be assigned are the IQ quinone groups which are assigned in pairs. Using the fraction of quinones that are ortho pairs, the program randomly decides whether each pair is in an ortho or a para arrangement. These pairs are then randomly allocated to one of the aromatic rings. Following this the IA phenolic hydroxyls, IE methoxyls and IB1 aromatic carboxyl groups are randomly assigned to the remaining "available" aromatic carbons. If the aromatic carbon that RANDOM chooses to allocate a functional group to, already has an allocated group RANDOM searches again for an "available" carbon.

However, RANDOM obviously cannot search forever so there are cut off values for the number of times that RANDOM will search for an "available" aromatic carbon. If this cutoff number is exceeded, the structure is aborted and recorded as an aromatic incompatibility. The cutoff points are indicated by IF JJ = xxx THEN yyInComp = 0 statements where xxx is the cutoff and yy = Ar, Br, Al indicating aromatic, branching or aliphatic incompatibilities. Obviously in fulvic acids with high functional group concentrations these cutoffs are more likely to be exceeded. In that case the cutoffs should be increased and the program recompiled. The number of elements in the random number array XX[JJ] should also be increased. Note that the cutoffs used in the present version of RANDOM are greater than in the original program.

Functional groups for aromatic rings are assigned to the array IAR[2,60] which comprises two rows. At present the second row will be ignored as it is used for site counting. Functional groups are allocated to the first row of IAR and this procedure will now be explained. The interpretation of the array IAR has changed from the original program and has been somewhat simplified.

The example given is the same as that given by Murray [Mur81] but as will be observed IAR is different. Assume there are 6 aromatic rings (i.e. there are 24 (6 x 4) "available carbons" in IAR. Assume now that of those rings two are ortho, 2 are meta and 2 are para. Previously RANDOM used an interlocking system of carbon allocation to IAR but this has been simplified. All 4 carbons of an individual ring follow each other in a set of four. Thus in the example, the first set of 4 refers to the first ortho ring, the second set to the second ortho ring, the third set of 4 to the first meta ring and so on. If there are no ortho rings the first set of four will be a meta ring unless there are no meta rings as well, in which case the set defines a para ring. IAR is printed out in the FULL output option of RANDOM. Above the IAR row is the number of ortho, meta and para rings so that it is easy to discover which set belongs to which type as all ortho rings are listed before meta

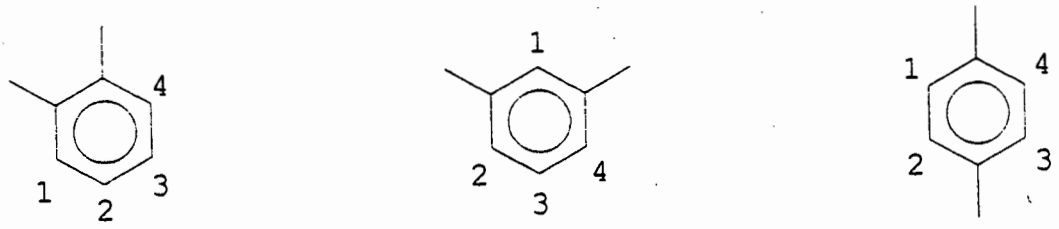
rings before para rings. Figure A.2.3 is an example of IAR that was used by Murray [Mur81]. As can be seen IAR is different even though the structures are the same.

Various integers are used in the arrays (IAR and IAL (for aliphatic carbons)) to indicate functional groups. These can be found in Table A.2.1

After the assignment of the aromatic functional groups, the carbon skeleton is generated. The skeleton is represented in the array IAL[4,100]. The first row contains the carbon atom type, the second and third rows functional groups bound to that atom and the last row is used for site identification.

Firstly the ketones are allocated to the carbon skeleton (row 1 of IAL). Care is taken that two ketones are not allocated to adjacent carbons so that α-diketone arrangements are avoided. After this the IR rings are allocated to the skeleton. At this stage, nothing is known about which of these are ortho, meta or para. RANDOM then randomly decides which of the allocated rings are ortho, meta or para. The first ortho ring in the IAL list thus represents the first ortho ring set in IAR, the second ortho ring represents the second set etc.

After the rings are allocated the methyl groups are allocated to the skeleton. This is based on the fraction of aliphatic carbons that are input as methyl groups. The carbon before every methyl is allocated as a =CH- group which is bonded to the methyl group as well as two other carbons in the skeleton. After these groups have been allocated the remaining carbons in IAL are allocated as $-CH_2-$ groups. It is possible that there may not be sufficient carbons in IAL for all the methyl groups to be allocated. In this case a branching incompatibility occurs.



ORTHO RINGS : 2 META RINGS : 2 PARA RINGS :2

0	7	1	7	7	7	7	0	1	1	1	7
0	0	0	0	0	0	0	0	0	0	0	0

15	715	0	1	7	0	0	7	7	3
0	0	0	0	0	0	0	0	0	0

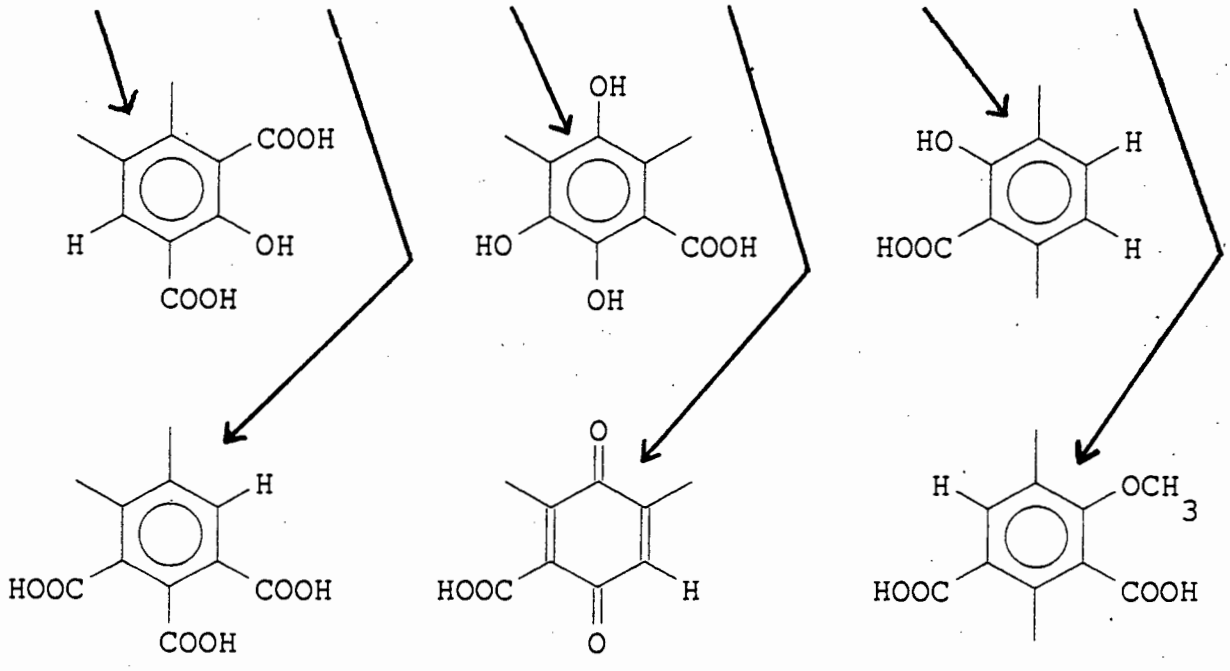


Figure A.2.3: (Top) The numbering of atoms on ortho, meta and para rings. These numbers refer to the position in the appropriate rings set of four. (Bottom) Array IAR with the relevant groups positioned, showing the structures represented by the codes

Table A.2.1: The code integers used in RANDOM to indicate carbon types and functional groups.

	Functionality	Integer
Aromatic groups (1st row array IAR)	Phenolic -OH	1
	Methoxyl -OCH_3	3
	Aromatic -COOH	7
	Quinone C=O	15
Carbon skeleton (1st row array IAL)	-CH_3	1
	-CH_2-	2
	=CH-	3
	Ortho aromatic ring	5
	Meta aromatic ring	6
	Para aromatic ring	7
	Ketone C=O	8
Aliphatic groups (2nd, 3rd rows of array IAL)	Amine -NH_2	1
	Alcoholic -OH	3
	Aliphatic -COOH	4
	Thiol -SH	9

Lastly all the aliphatic carboxyl, hydroxyl, amine and thiol groups are allocated to the =CH-, $-CH_2-$ and $-CH_3$ carbons. These funcional groups are assigned to the second and third rows of IAL. Firstly the second row is checked for the presence of a functional group. If it is occupied the group is then allocated to the third row unless it too is occupied. In this case a new carbon atom is sought. One restriction to the allocation of carboxyl groups is that β-keto-acid type arrangements are avoided. Note that a maximum of two functional groups are allocated to methyl carbons while only one group can be allocated to =CH- carbons.

One change to the original program is that the code in lines 980 to 990 has been left out. In the old RANDOM, this code was used to speed the program up. If the carbon type chosen in row 1 of IAL was not aliphatic (i.e. it was a ketone or a ring), the program searched an adjacent carbon until an aliphatic carbon was found. This, however, is not a purely RANDOM selection of carbons as functional groups are more likely to end up next to ketones or rings in this arrangement. Binding sites involving two carbons are disadvantaged and consequently have lower concentrations. This code is removed in the new RANDOM, which searches for an aliphatic carbon by picking a new carbon in IAL, randomly. Incompatibilities are thus more likely so the cutoffs were set higher than in the original program.

Section three - Binding site counting

The binding sites are counted in the order listed in the input file. After each individual structure is generated, the sites are identified and counted. Once a site is identified it is flagged so that a carbon atom cannot be counted in more than one binding site. The site number is allocated to row 2 of IAR (for aromatic sites) and to row 4 (for aliphatic sites) to indicate flagging.

Because the allocation of groups to IAR has changed from the method used in the original RANDOM program, the counting of aromatic sites is slightly more complicated. RANDOM checks ortho, meta and para rings separately in the procedure AROCOUNT. To identify sites, the values in adjacent columns of IAR are added. If the sum is equal to an identifying number for the relevant site, the site is identified. In ortho rings the columns added together are (1&2,2&3,3&4), meta rings (2&3,3&4) and para rings (1&2,3&4). Note that column 1 in a meta ring represents an available carbon which cannot have a functional group on an adjacent carbon. In a para ring it can be seen that there are two pairs (Figure A.2.3). The sums for the relevant site can be found in Table A.2.2

Table A.2.2: Expected values for the sum of adjacent columns in IAR representing aromatic sites

Site No	Functional group			
	Phen OH	COOH	C=O	Sum
1			15+15	30
2	1		15	16
3	1+1			2
4		7+7		14
5	1	7		8

The 2-acetylphenol site is counted in a separate procedure while the residual aromatic sites (phenol and benzoic acid) are counted in the procedure MONARO in which phenol or carboxylate groups are found in row 1 of IAR while row 2 must be empty.

The program searches for the acetylacetone site in the procedure ACAC. Care is taken that there is a proton on the carbon between the two ketones. If there is no proton (a zero in the 2nd or 3rd row of IAL indicates a proton) acetylacetone is not identified. Note that the ketones in an acetylacetone arrangement may be represented in IAL by 828 or 8418. In the first case the middle carbon is $-CH_2-$, in the second it is =CH-. 878 is not an acetylacetone arrangement since there is a ring between the ketones.

The propanoate site is counted in the procedure PROP which looks for -COOH groups on untagged carbons. The remaining sites are counted in the procedures BIDENSAME, BIDENDIFF, TRIDEN. The first procedure looks for bidendate sites on the same carbon (e.g. ALA), the second bidendate sites on adjacent carbons (e.g. SUCC) and the last tridendate sites. These procedures are different to the original RANDOM. In BIDENSAME and TRIDEN RANDOM adds together the 2nd and 3rd rows of IAL. If this sum is the same as an identifying number for the site, RANDOM identifies a site for bidendate sites on the same carbon. For tridentate sites RANDOM looks at the adjacent carbon to check if the third functional group is there. With BIDENDIFF, RANDOM checks adjacent carbons for the pair of functional groups that makes up the site.

It should be noted that the codes in Table A.2.1 are chosen such that the sums of rows 2 and 3 of IAL are unique. This actually is not so because if the second row contains a carboxylate group (IAL = 4) and the third row is empty (IAL = 0) the sum is 4. If the second row contains a $-NH_2$ groups (IAL = 1) and the third a -OH (IAL = 3) the sum is also 4. However, none of the RANDOM binding sites contains an amine and a hydroxyl group on the same carbon so this problem is avoided. All other combinations are unique. If a site with an amine and a hydroxyl on the same carbon were to be added in the future, a special counting procedure would have to be written for that site or the codes in Table A.2.1 would have to be changed.

Random calculates the mean site concentration by dividing the total number of sites counted by the molar mass and the number of structures generated. Standard deviations of single determinations are calculated using the formula

$$(S.D.)^2 = [\Sigma (x^2) - (\Sigma x)^2/N] / [N-1]$$

where x is the site concentration

N is the number of structures generated.

RANDOM then quotes the standard deviation of the mean by dividing S.D. by the square root of N. This formula simplifies the calculation of standard deviations used in the original program where deviations from the mean in individual structures were calculated. The original procedure necessitates keeping site concentrations in an array for each structure generated. Over 100000 structures, this uses up too much memory so the above formula is obviously preferable.

RANDOM also calculates an average percentage carbon, hydrogen, oxygen, nitrogen and sulphur as well as a number average molecular weight for the structures generated. These are quoted with a standard deviation for a single determination.

Section four - Output

The output of RANDOM includes the input data from the input file. Depending on the output option RANDOM then provides variable output. If the output option is FULL, RANDOM prints out the number of ortho, meta and para rings followed by the array IAR for each structure. Random also prints the array IAL and the number of each site identified in each structure. Lastly RANDOM lists each site with its concentration and the standard deviation thereof. The INTERMEDIATE output does not include the listing

of IAR and IAL for each structure but includes site concentrations for each structure. The BRIEF output lists only the site concentrations and standard deviations.

Random also includes elemental composition for the structures calculated as well as a number-average molecular mass. Because the elemental composition is calculated from the input data, discrepancies with experimental observations may occur. This may result from ether oxygen being ignored. The molecular mass should be close to 2000 g mol^{-1} which is assumed by the program. Variation from this number means that oxygen, nitrogen and sulphur in the input functional groups do not account for all the O, N and S in the fulvic acid if the molecular mass is < 2000 g mol^{-1}. If it is greater than 2000 g mol^{-1}, input functional group concentrations are too large.

RANDOM also gives a distribution pattern for carbon and hydrogen in fulvic acid (i.e the percentage of aliphatic, aromatic hydroxyl hydrogens etc.). These distributions can then be compared with experimental data.

Lastly RANDOM provides the average site concentrations used in the structures generated by the program. If these values are the same as the input data, RANDOM has functioned properly. Where discrepancies occur, the results of RANDOM should be viewed with care. As an example consider the case in which there are 4.2 phenol groups per molecule and just one ring per molecule (no other aromatic functional groups). There are thus only 4 "available" aromatic carbons, thus when RANDOM tries to allocate 5 phenol groups, an incompatibility occurs. Only when 4 phenol groups are allocated do successful structures occur. Thus over all the successful structures generated the average phenol concentration is 4.0 and not 4.2 phenols per molecule. Thus any difference between the output average functional group concentrations and the input to RANDOM would indicate incompatibilities in the input data. In these cases, the output of RANDOM should not be used but the input data should be reviewed.

Appendix 2.2: The TURBO PASCAL listing of RANDOM

..... at the beginning of a line indicates the line is actually part of the previous line but the the page-width is too small, so it has been typed on the next line here. To compile the PASCAL version they must be combined in one line

```
PROGRAM FARANDOM;
  { The program is called FARANDOM (Fulvic Acid Random)
    because RANDOM is reserved by TURBO PASCAL }

  { PROGRAM PURPOSE : This program generates random
                      molecules of fulvic acid
    As input it requires experimental elemental and
    functional group compositions. From this estimates of
    the number of metal binding sites occurring on an
    average molecule are estimated.

    SOURCE          : The original FORTRAN program RANDOM

    DEVELOPED AT    : Department of Chemistry
                      University of Cape Town
                      South Africa

    DEVELOPED BY    : Kevin Murray (for the original FORTRAN
                                    version)
                      Christopher Woolard (this version)

    DATE            : 1981 (original)
                      1994 (new)

    DIFFERENCES     : This new version includes nitrogen and
    WITH THE          sulphur binding sites. The site
    ORIGINAL PROGRAM  counting procedure has also been
                      altered slightly while the data input
                      and output procedures have been
                      totally revamped }

USES Graph, Crt, GrDrivers;

TYPE
  { These TYPE statements allow arrays TO be passed TO
    PROCEDURES }
  ArIAL             = ARRAY [ 1 .. 4, 1 .. 100] of INTEGER;
  ARIAR             = ARRAY [ 1 .. 4, 1 .. 60] of INTEGER;
  ArS               = ARRAY [ 1 .. 40] of INTEGER;

VAR
  Opt               : STRING;    { RANDOM operation chosen }
  UserQuits         : BOOLEAN;   { Used TO test for program
                                   exit }


FUNCTION PosX (Frxn : REAL) : INTEGER;
  { This function converts X positions on the screen for any
    type }
```

```
BEGIN
  PosX := ROUND (Frxn * (GETMAXX+1));
END;


FUNCTION PosY (Frxn : REAL) : INTEGER;
  { This function converts Y positions on the screen for any
    type }

BEGIN
  PosY := ROUND (Frxn * (GETMAXY+1));
END;


PROCEDURE FetchInp (VAR GrIn : STRING);
  { This procedure reads input from a graphics screen one
    character at a time }
VAR
  Lett              : CHAR;      { Input from the KeyBoard }
  LastLett          : STRING;    { Last letter of GrIn which
                                   is erased by backspace }
  AscLett           : INTEGER;   { ASCII code for Lett }
  LenGrIn           : INTEGER;   { LENGTH of GrIn }
  NewLen            : INTEGER;   { LenGrIn - 1 }

BEGIN
 Lett := ' ';
 AscLett := 1000;
 GrIn := '';
 WHILE Lett <> Chr (13) DO
 BEGIN
  CASE AscLett OF
  32 .. 126 : BEGIN
               MOVEREL (PosX (-0.01252), 0);
               SETCOLOR (0);
               OUTTEXT ('_');
               SETCOLOR (15);
               MOVEREL (PosX (-0.01252), 0);
               GrIn := GrIn + Lett;
               OUTTEXT (Lett);
              END;
  { Backspace may be used for corrections }
   8        : BEGIN
               MOVEREL (PosX (-0.01252), 0);
               SETCOLOR (0);
               OUTTEXT ('_');
               SETCOLOR (15);
               MOVEREL (PosX (-0.01252), 0);
               LenGrIn := LENGTH (GrIn);
               IF LenGrIn > 0 THEN
                BEGIN
                 NewLen := LenGrIn - 1;
                 LastLett := COPY (GrIn, LenGrIn, 1);
                 GrIn := COPY (GrIn, 1, NewLen);
                 MOVEREL (PosX (-0.01252) , 0);
                 SETCOLOR (0);
                 OUTTEXT (LastLett);
```

```
                MOVEREL (PosX (-0.01252), 0);
                SETCOLOR (15);
               END;
              END;
  { Disable Esc key }
  27          : BEGIN
                MOVEREL (PosX (-0.01252), 0);
                SETCOLOR (0);
                OUTTEXT ('_');
                SETCOLOR (15);
                MOVEREL (PosX (-0.01252), 0);
               END;
  { Disable keys with ASCII code 0 e.g. cursors }
   0          : BEGIN
                MOVEREL (PosX (-0.01252), 0);
                SETCOLOR (0);
                OUTTEXT ('_');
                SETCOLOR (15);
                MOVEREL (PosX (-0.01252), 0);
               END;
  { To prevent a leading blank }
1000          : BEGIN
                MOVEREL (PosX (-0.01252), 0);
                SETCOLOR (0);
                OUTTEXT ('_');
                SETCOLOR (15);
                MOVEREL (PosX (-0.01252), 0);
               END;
  END;
  OUTTEXT ('_');
  Lett := READKEY;
  AscLett := ORD (Lett);
  IF (GrIn = '') AND (Lett = ' ') THEN AscLett := 1000;
 END;
 MOVEREL (PosX (-0.01252), 0);
 SETCOLOR (0);
 OUTTEXT ('_');
 SETCOLOR (15);
 MOVEREL (PosX (-0.01252), 0);
END;


PROCEDURE ClearOld (X, Y : REAL; OldTEXT : STRING);
          {This procedure overWRITEs old text on the screen}

BEGIN
 SETCOLOR (0);
 OUTTEXTXY (PosX (X-0.01252), PosY (Y), OldTEXT);
 SETCOLOR (15);
END;


PROCEDURE CheckStr (X,Y : REAL; RealINT : INTEGER; VAR Inpt
: STRING);
  { This procedure checks that data is input as numbers
    where equired }
VAR
```

```
  NumInpt           : REAL;     { Inpt converted TO a real
                                  number }
  NoInpt            : LONGINT;  { inpt converted TO an
                                  integer }
  ErrINT            : INTEGER;  { Error variable TO check if
                                  an integer has been input
                                  where required }
  ErrInpt           : INTEGER;  { An error checking variable}
  ErrString         : INTEGER;  { An error checking variable}
  I                 : INTEGER;  { Counter }

BEGIN
 ErrInpt := 1;
 WHILE ErrInpt <> 0 DO
 BEGIN
  ErrString := 1;
  MOVETO (PosX (X), PosY (Y));
  FetchInp (Inpt);
  ErrINT := 0;
  VAL (Inpt, NumInpt, ErrInpt);
  IF ErrInpt <> 0 THEN
  BEGIN
   OUTTEXTXY (PosX (0.156), PosY (0.917), 'YOU HAVE ENTERED
..... A STRING AND NOT A NUMBER, PLEASE RETYPE');
   FOR I := 1 TO 5 DO
   BEGIN
    SETBKCOLOR (Blue);
    DELAY (500);
    SETBKCOLOR (Black) ;
    DELAY (500);
   END;
   SETCOLOR (0);
   OUTTEXTXY (PosX (X), PosY (Y), Inpt);
   OUTTEXTXY (PosX (0.156), PosY (0.917), 'YOU HAVE ENTERED
..... A STRING AND NOT A NUMBER, PLEASE RETYPE');
   SETCOLOR (15);
   ErrString := 0;
  END;
  IF REALINT = 0 THEN VAL (Inpt, NoInpt, ErrInt);
  IF ErrINT = 0 THEN ErrString := 0;
  IF (ErrINT <> 0) AND (ErrString <> 0) THEN
  BEGIN
   ErrInpt := 1;
   OUTTEXTXY (PosX (0.078), PosY (0.917), 'YOU HAVE ENTERED
..... A REAL NUMBER AND NOT AN INTEGER, PLEASE RETYPE');
   FOR I := 1 TO 5 DO
   BEGIN
    SETBKCOLOR (Blue);
    DELAY (500);
    SETBKCOLOR (Black) ;
    DELAY (500);
   END;
   SETCOLOR (0);
   OUTTEXTXY (PosX (X), PosY (Y), Inpt);
   OUTTEXTXY (PosX (0.078), PosY (0.917), 'YOU HAVE ENTERED
..... A REAL NUMBER AND NOT AN INTEGER, PLEASE RETYPE');
   SETCOLOR (15);
```

```
  END;
  ClearOld (X, Y, Inpt);
 END;
 I := 1;
 WHILE Inpt[1] = ' ' DO Inpt := COPY(Inpt,2,LENGTH(Inpt)-1);
END;


PROCEDURE Intro;
  { This procedure draws the graphics screen used as an
    introduction }
VAR
  grDriver, grMode : INTEGER;   {graphics control variables}
  RK               : CHAR;      { Key entered }

BEGIN
 grDriver := Detect;
 INITGRAPH (grDriver, grMode, '');
 RECTANGLE(PosX (0.03),PosY (0.03),PosX (0.97),PosY (0.97));
 {WRITE Random on the screen}
   {R}
   MOVEREL (PosX (0.188), PosY (0.354));
   LINEREL (          0 , PosY(-0.208));
   LINEREL (PosX (0.070), 0);
   LINEREL (PosX (0.008), PosY (0.010));
   LINEREL (          0 , PosY (0.083));
   LINEREL (PosX(-0.008), PosY (0.010));
   LINEREL (PosX (-0.07), 0);
   MOVEREL (PosX (0.047), 0);
   LINEREL (PosX (0.031), PosY (0.104));
   {A}
   MOVEREL (PosX (0.031), 0);
   LINEREL (          0 , PosY(-0.198));
   LINEREL (PosX (0.008), PosY (-0.01));
   LINEREL (PosX (0.063), 0);
   LINEREL (PosX (0.008), PosY (0.010));
   LINEREL (          0 , PosY (0.198));
   MOVEREL (PosX(-0.078), PosY(-0.104));
   LINEREL (PosX (0.078), 0);
   {N}
   MOVEREL (PosX (0.031), PosY (0.104));
   LINEREL (          0 , PosY(-0.208));
   LINEREL (PosX (0.078), PosY (0.208));
   LINEREL (          0 , PosY(-0.208));
   {D}
   MOVEREL (PosX (0.031), 0);
   LINEREL (PosX (0.070), 0);
   LINEREL (PosX (0.008), PosY (0.010));
   LINEREL (          0,  PosY (0.188));
   LINEREL (PosX(-0.008), PosY (0.010));
   LINEREL (PosX (-0.07), 0);
   LINEREL (          0 , PosY(-0.208));
   {O}
   MOVEREL (PosX (0.117), 0);
   LINEREL (PosX (0.063), 0);
   LINEREL (PosX (0.008), PosY (0.010));
   LINEREL (           0, PosY (0.188));
```

```
   LINEREL (PosX(-0.008), PosY (0.010));
   LINEREL (PosX(-0.063), 0);
   LINEREL (PosX(-0.008), PosY (-0.01));
   LINEREL (          0, PosY(-0.188));
   LINEREL (PosX (0.008), PosY (-0.01));
   {M}
   MOVEREL (PosX (0.102), PosY (0.208));
   LINEREL (          0, PosY(-0.208));
   LINEREL (PosX (0.039), PosY (0.104));
   LINEREL (PosX (0.039), PosY(-0.104));
   LINEREL (          0, PosY (0.208));
 OUTTEXTXY (PosX (0.328), PosY (0.490), 'Designed in the
..... DEPARTMENT OF CHEMISTRY');
 OUTTEXTXY (PosX (0.531), PosY (0.542), 'UNIVERSITY OF CAPE
..... TOWN');
 OUTTEXTXY (PosX (0.531), PosY (0.594), 'SOUTH AFRICA');
 OUTTEXTXY (PosX (0.492), PosY (0.729), 'by KEVIN MURRAY');
 OUTTEXTXY (PosX (0.531), PosY (0.781), 'and');
 OUTTEXTXY (PosX (0.531), PosY (0.833), 'CHRISTOPHER
..... WOOLARD');
 OUTTEXTXY (PosX (0.078), PosY (0.917), 'HIT ANY KEY TO
..... CONTINUE');
 RK := READKEY;
 SETCOLOR (15);
END;


PROCEDURE Mainmenu;     { This brings up the menu of RANDOM
                          operations }

BEGIN
 CLEARVIEWPORT;
 OUTTEXTXY (PosX (0.461), PosY (0.156), 'RANDOM');
 OUTTEXTXY (PosX (0.445), PosY (0.208), 'MAIN MENU');
 OUTTEXTXY (PosX (0.203), PosY (0.313), '1.  CREATE an input
..... file for RANDOM');
 OUTTEXTXY (PosX (0.203), PosY (0.417), '2.  EDIT an
..... existing input file');
 OUTTEXTXY (PosX (0.203), PosY (0.521), '3.  RUN RANDOM to
..... obtain fulvic acid structures');
 OUTTEXTXY (PosX (0.203), PosY (0.573), '    and binding
..... site concentrations');
 OUTTEXTXY (PosX (0.203), PosY (0.677), 'Q.  QUIT');
RECTANGLE(PosX(0.125),PosY(0.104),PosX(0.875),PosY (0.750));
 MOVETO (PosX (0.125), PosY (0.260));
 LINEREL (PosX (0.750), 0);
 OUTTEXTXY (PosX (0.258),  PosY (0.833), 'ENTER YOUR CHOICE
..... OF OPERATION');
END;


PROCEDURE Error;
  { Performed if an incorrect key is hit at a menu }
VAR
  I                 : INTEGER;    { Counter }

BEGIN
```

```
 OUTTEXTXY (PosX (0.35), PosY (0.938), 'INCORRECT CHOICE
..... MADE');
 FOR I := 1 TO 5 DO
 BEGIN
  SETBKCOLOR (Blue);
  DELAY (500);
  SETBKCOLOR (Black);
  DELAY (500);
 END;
END;


PROCEDURE ErrArRat (VAR ArErr : INTEGER; Rat : STRING);
  { Checks for an error in the entry of ArRat }
VAR
  Ch             : INTEGER;       { Counter }
  I              : INTEGER;       { Counter }
  Colon          : INTEGER;       { Counter for number of
                                    colons }

BEGIN
 Ch := 0;
 Colon := 0;
 WHILE Ch < LENGTH (Rat) DO
 BEGIN
  Ch := Ch + 1;
  CASE Rat[Ch] OF
   '0' .. '9' :;
   '.'        :;
   ':'        : Colon := Colon + 1;
   ' '        : BEGIN
                 ArErr := 1;
                 Ch := LENGTH (Rat);
                 OUTTEXTXY (PosX (0.219), PosY (0.833),
.....'YOUR ENTRY CONTAINS SPACES, PLEASE RETYPE');
                 FOR I := 1 TO 5 DO
                 BEGIN
                  SETBKCOLOR (Blue);
                  DELAY (500);
                  SETBKCOLOR (Black);
                  DELAY (500);
                 END;
                 Colon := 2;
                END;
   ELSE BEGIN
         ArErr := 1;
         Ch := LENGTH (Rat);
         OUTTEXTXY (PosX (0.078), PosY (0.833), 'YOUR ENTRY
..... CONTAINS ILLEGAL CHARACTERS (LETTERS, ETC), PLEASE
..... RETYPE');
         FOR I := 1 TO 5 DO
         BEGIN
          SETBKCOLOR (Blue);
          DELAY (500);
          SETBKCOLOR (Black);
          DELAY (500);
         END;
```

```
          Colon :=2;
         END;
  END;
 END;
 IF Colon <> 2 THEN
 BEGIN
  ArErr := 1;
  OUTTEXTXY (PosX (0.156), PosY (0.833), 'YOUR ENTRY DOES
..... NOT CONTAIN TWO COLONS, PLEASE RETYPE');
  FOR I := 1 TO 5 DO
  BEGIN
   SETBKCOLOR (Blue);
   DELAY (500);
   SETBKCOLOR (Black);
   DELAY (500);
  END;
 END;
END;


PROCEDURE AroRatio (VAR AR : STRING);
  { Procedure in which ratio of o:m:p aromatic linkages is
    entered }
VAR
  Err            : BOOLEAN;      { Error testing variable }
  XErr           : INTEGER;      { Error testing variable }

BEGIN
 Err := False;
 REPEAT
  XErr := 0;
  CLEARVIEWPORT;
  OUTTEXTXY (PosX (0.078), PosY (0.208), 'ENTER THE RATIO OF
..... ORTHO:META:PARA LINKAGES ON AROMATIC RINGS');
  OUTTEXTXY (PosX (0.180), PosY (0.417), 'ENTER IT IN THE
..... FORM oo:mm:pp (INCLUDE THE COLONS)');
  OUTTEXTXY (PosX (0.172), PosY (0.625), '(2:2:1 IS
..... RECOMMENDED AS THE TOTALLY RANDOM CHOICE)');
  OUTTEXTXY (PosX (0.185), PosY (0.521), 'MAKE SURE YOU DO
..... NOT INCLUDE SPACES IN YOUR INPUT');
  MOVETO (PosX (0.46), PosY (0.313));
  FetchInp (AR);
  ErrArRat (XErr , AR);
  IF XErr = 0 THEN Err := True;
 UNTIL Err;
END;


PROCEDURE PrintOption (VAR PO : STRING);
 { Procedure to enter the desired print option for the
   output }
VAR
  Kwit             : BOOLEAN;    { Monitors whether entry is
                                   correct }
  Opt              : STRING;     { Option chosen }

BEGIN
```

```
 Kwit := False;
 REPEAT
  CLEARVIEWPORT;
  OUTTEXTXY (PosX (0.078), PosY (0.208), 'ENTER THE DESIRED
..... PRINT OPTION FOR THE OUTPUT');
  OUTTEXTXY (PosX (0.078), PosY (0.260), 'THESE ARE :');
  OUTTEXTXY (PosX (0.117), PosY (0.313), '1.  BRIEF
..... (ONLY MEAN SITE CONCENTRATIONS ARE SUPPLIED)');
  OUTTEXTXY (PosX (0.117), PosY (0.365), '2.  INTERMEDIATE
..... (AS IN 1, THE OCCURRENCE OF SITES ON INDIVIDUAL');
  OUTTEXTXY (PosX (0.117), PosY (0.417), '
..... STRUCTURES IS ALSO SHOWN)');
  OUTTEXTXY (PosX (0.117), PosY (0.469), '3.  FULL
..... (AS IN 2, THE POSITION OF INDIVIDUAL GROUPS ON');
  OUTTEXTXY (PosX (0.117), PosY (0.521), '
..... OF THE GENERATED STRUCTURES IS ALSO SHOWN)');
  OUTTEXTXY (PosX (0.078), PosY (0.625), 'PRINT OPTION :');
  MOVETO (PosX (0.27), PosY (0.625));
  FetchInp (Opt);
  IF Opt ='1' THEN PO := 'BRIEF';
  IF Opt = '2' THEN PO := 'INTERMEDIATE';
  IF Opt = '3' THEN PO := 'FULL';
  IF (Opt<>'1') AND (Opt<>'2') AND (OPT<>'3') THEN Error;
  IF Opt = '1' THEN Kwit := True;
  IF Opt = '2' THEN Kwit := True;
  IF Opt = '3' THEN Kwit := True;
 UNTIL Kwit;
END;


PROCEDURE CountOrder (VAR CO1, CO2 : STRING; VAR NoSites :
INTEGER);
  { This procedure determines the site counting order TO be
    used by the program }
VAR
  Site, SSite      : STRING;     { The next site to be added
                                   to the counting
                                   order }
  ValSite          : INTEGER;    { Site converted to an
                                   integer }
  ErrSite          : INTEGER;    { Error code in case Site is
                                   typed in wrongly}
  ErrSites         : INTEGER;    { Test that NoSites < 31 }
  RK               : CHAR;       { Key read from Keyboard }
  XPosn            : REAL;       { Used to detemine where to
                                   print }

BEGIN
 ErrSites := 1;
 WHILE ErrSites <> 0 DO
 BEGIN
  NoSites := 0;
  CLEARVIEWPORT;
  Site := '';
  CO1 := '';
  CO2 := '';
  LINE (0, PosY (0.042), PosX (1), PosY (0.042));
```

```
  LINE (0, PosY (0.125), PosX (1), PosY (0.125));
  OUTTEXTXY (PosX (0.383), PosY (0.078), 'METAL BINDING
..... SITES');
  OUTTEXTXY (PosX (0.078), PosY (0.137), ' 1. 1,2-
..... benzoquinone');
  OUTTEXTXY (PosX (0.078), PosY (0.168), ' 2. 3-hydroxy-1,4-
..... benzoquinone');
  OUTTEXTXY (PosX (0.078), PosY (0.199), ' 3. catechol');
  OUTTEXTXY (PosX (0.078), PosY (0.230), ' 4. phthalic
..... acid');
  OUTTEXTXY (PosX (0.078), PosY (0.262), ' 5. salicylic
..... acid');
  OUTTEXTXY (PosX (0.078), PosY (0.293), ' 6. 2-
..... acetylphenol');
  OUTTEXTXY (PosX (0.078), PosY (0.324), ' 7. benzoic .....
acid');
  OUTTEXTXY (PosX (0.078), PosY (0.355), ' 8. phenol');
  OUTTEXTXY (PosX (0.078), PosY (0.387), ' 9.
..... acetylacetone');
  OUTTEXTXY (PosX (0.078), PosY (0.418), '10. malic acid');
  OUTTEXTXY (PosX (0.078), PosY (0.449), '11. 2,3-dihydroxy-
..... 2-methylbutanoic');
  OUTTEXTXY (PosX (0.078), PosY (0.480), '    acid');
  OUTTEXTXY (PosX (0.078), PosY (0.512), '12. succinic
..... acid');
  OUTTEXTXY (PosX (0.078), PosY (0.543), '13. diethylmalonic
..... acid');
  OUTTEXTXY (PosX (0.078), PosY (0.574), '14. 3-
..... hydroxybutanoic acid');
  OUTTEXTXY (PosX (0.078), PosY (0.607), '15. 2-hydroxy-2-
..... methylpropanoic');
  OUTTEXTXY (PosX (0.078), PosY (0.638), '    acid');
  OUTTEXTXY (PosX (0.578), PosY (0.137), '16. propanoic
..... acid');
  OUTTEXTXY (PosX (0.578), PosY (0.168), '17. citric acid');
  OUTTEXTXY (PosX (0.578), PosY (0.199), '20. 2,3-
..... diaminopropanoic acid');
  OUTTEXTXY (PosX (0.578), PosY (0.230), '21. aspartic
..... acid');
  OUTTEXTXY (PosX (0.578), PosY (0.262), '22. serine');
  OUTTEXTXY (PosX (0.578), PosY (0.293), '23. isoserine');
  OUTTEXTXY (PosX (0.578), PosY (0.324), '24. alanine');
  OUTTEXTXY (PosX (0.578), PosY (0.355), '25. '#225'-
..... alanine');
  OUTTEXTXY (PosX (0.578), PosY (0.387), '26. 1,2-
..... propylenediamine');
  OUTTEXTXY (PosX (0.578), PosY (0.418), '27.
..... ethanolamine');
  OUTTEXTXY (PosX (0.578), PosY (0.449), '30. cysteine');
  OUTTEXTXY (PosX (0.578), PosY (0.480), '31. thiomalic
..... acid');
  OUTTEXTXY (PosX (0.578), PosY (0.512), '32. thiolactic
..... acid');
  OUTTEXTXY (PosX (0.578), PosY (0.543), '33. 2-
..... aminoethanethiol');
  OUTTEXTXY (PosX (0.578), PosY (0.574), '34. 2-
..... mercaptoethanol');
```

```
  LINE (0, PosY (0.67), PosX (1), PosY (0.67));
  OUTTEXTXY (PosX (0.078), PosY (0.719), 'SITE COUNTING
..... ORDER');
  XPosn := 0.117;
  OUTTEXTXY (PosX (0.3125), PosY (0.844), 'ENTER THE NUMBER
..... FOR THE NEXT SITE:');
  OUTTEXTXY (PosX (0.3125), PosY (0.875), '(ENTER 0 (ZERO)
..... WHEN COMPLETE)');
  WHILE Site <> '0' DO
  BEGIN
   If NoSites = 20 THEN XPosn := 0.117;
   CheckStr (0.771, 0.844, 0, Site);
   NoSites := NoSites + 1;
   VAL (Site, ValSite, ErrSite);
   IF NoSites < 21 THEN
   BEGIN
    CASE ValSite OF
     0       :;
     1 .. 9 : BEGIN
               STR (ValSite, SSite);
               CO1 := CO1 + '0' + SSite;
               XPosn := XPosn + 0.01252;
               OUTTEXTXY (PosX (XPosn),PosY (0.750),SSite);
               XPosn := XPosn + 0.02504;
               CO1 := CO1 + ' ';
              END;
     ELSE     BEGIN
               CO1 := CO1 + Site;
               OUTTEXTXY (PosX (XPosn), PosY (0.750), Site);
               XPosn := XPosn + 0.03756;
               CO1 := CO1 + ' ';
              END;
    END;
   END;
   IF NoSites > 20 THEN
   BEGIN
    CASE ValSite OF
     0       :;
     1 .. 9 : BEGIN
               STR(ValSite, SSite);
               CO2 := CO2 + '0' + SSite;
               XPosn := XPosn + 0.01252;
               OUTTEXTXY (PosX (XPosn),PosY (0.781),SSite);
               XPosn := XPosn + 0.02504;
               CO2 := CO2 + ' '
              END;
     ELSE     BEGIN
               CO2 := CO2 + Site;
               OUTTEXTXY (PosX (XPosn),PosY (0.781),Site);
               XPosn := Xposn + 0.03756;
               CO2 := CO2 + ' ';
              END;
    END;
   END;
  END;
  NoSites := NoSites - 1;
  ErrSites := 0;
```

```
  IF NoSites > 30 THEN
  BEGIN
   ErrSites := 1;
   CLEARVIEWPORT;
   OUTTEXTXY (PosX (0.234), PosY (0.313), 'YOUR NUMBER OF
..... SITES EXCEEDS THE MAXIMUM');
   OUTTEXTXY (PosX (0.234), PosY (0.417), 'ALLOWABLE (30),
..... PLEASE REENTER');
   OUTTEXTXY (PosX (0.3125), PosY (0.625), 'HIT ANY KEY TO
..... CONTINUE');
   RK := READKEY;
  END;
 END
END;


PROCEDURE NoStruct (VAR NS : STRING);
  { This procedure gets the number of structures to be
    generated per fulvic acid }

BEGIN
 CLEARVIEWPORT;
 OUTTEXTXY (PosX (0.157), PosY (0.208), 'ENTER THE NUMBER OF
..... STRUCTURES TO BE GENERATED');
 OUTTEXTXY (PosX (0.157), PosY(0.3125), 'PER FULVIC ACID
..... MODELLED:');
 OUTTEXTXY (PosX (0.157), PosY (0.521), '(A VALUE OF AT
..... LEAST 1000 IS RECOMMENDED FOR A');
 OUTTEXTXY (PosX (0.157), PosY (0.625), ' TRUELY RANDOM
..... DISTRIBUTION)');
 CheckStr (0.485, 0.3125, 0, NS);
END;


PROCEDURE NoFA (VAR NF : STRING);
  { This procedure gets the number of different fulvic acid
    models to be performed }

BEGIN
 CLEARVIEWPORT;
 OUTTEXTXY (PosX (0.157), PosY (0.208), 'ENTER THE NUMBER OF
..... DIFFERENT FULVIC ACID MODELS');
 OUTTEXTXY (PosX (0.157), PosY(0.3125), 'THAT NEED TO BE
..... PERFORMED:');
 CheckStr (0.5, 0.3125, 0, NF);
END;


PROCEDURE Firstpage (VAR ArRat, PrintOp , CountOrd1,
.....CountOrd2,NoStr, NoFul : STRING ; VAR NoGrp : INTEGER);
  { This procedure obtains the data which is common to all
    the fulvic acid models }
VAR
  Opt                : STRING;     { Option chosen }

BEGIN
 Opt := '1';
```

```
 WHILE Opt <> '0' DO
 BEGIN
  CLEARVIEWPORT;
  LINE (0, PosY (0.052), PosX (1.000), PosY (0.052));
  OUTTEXTXY (PosX (0.3125), PosY (0.104), 'INPUT DATA FOR
..... RANDOM, PAGE ONE');
  LINE (0, PosY (0.156), PosX (1.000), PosY (0.156));
  OUTTEXTXY (PosX (0.078), PosY (0.208), '1.  RATIO OF ORTHO
.....:META:PARA LINKAGES');
  OUTTEXTXY (PosX (0.8125),PosY (0.208), ArRat);
  OUTTEXTXY (PosX (0.078), PosY (0.260), '2.  PRINT OPTION
..... FOR OUTPUT');
  OUTTEXTXY (PosX (0.8125),PosY (0.260), PrintOp);
  OUTTEXTXY (PosX (0.078), PosY (0.313), '3.  SITE COUNTING
..... ORDER');
  OUTTEXTXY (PosX (0.125), PosY (0.365), CountOrd1);
  OUTTEXTXY (PosX (0.125), PosY (0.417), CountOrd2);
  OUTTEXTXY (PosX (0.078), PosY (0.469), '4.  No. OF
..... STRUCTURES GENERATED PER FULVIC ACID MODELLED');
  OUTTEXTXY (PosX (0.8125),PosY (0.469), NoStr);
  OUTTEXTXY (PosX (0.078), PosY (0.521), '5.  No. OF FULVIC
..... ACIDS TO BE MODELLED');
  OUTTEXTXY (PosX (0.8125),PosY (0.521), NoFul);
  LINE (0, PosY (0.625), PosX (1), PosY (0.625));
  OUTTEXTXY (PosX (0.078), PosY (0.729), 'ENTER THE NUMBER
..... FOR WHICH YOU WOULD LIKE TO SUPPLY DATA :');
  OUTTEXTXY (PosX (0.078), PosY (0.781), '(ENTER 0 (ZERO)
..... WHEN YOU ARE COMPLETE)');
  MOVETO (PosX (0.820), PosY (0.729));
  FetchInp (Opt);
  IF OPT = '1' THEN AroRatio (ArRat);
  IF OPT = '2' THEN PrintOption (PrintOp);
  IF OPT = '3' THEN CountOrder (CountOrd1,CountOrd2, NoGrp);
  IF OPT = '4' THEN NoStruct (NoStr);
  IF OPT = '5' THEN NoFA (NoFul);
  IF (Opt<>'0') AND (Opt<>'1') AND (Opt<>'2') AND (Opt<>'3')
..... AND (Opt<>'4') AND (Opt<>'5') THEN Error;
 END;
END;


PROCEDURE FetchData (X1, Y1, X2, Y2 :REAL;VAR Dat : STRING);
  { This procedure gets the data for secondpage }
VAR
  OldDat            : STRING;     { Old data that needs TO be
                                    erased }

BEGIN
 OldDat := Dat;
 CheckStr (X1, Y1, 1, Dat);
 ClearOld (X2+0.01252, Y2, OldDat);
 OUTTEXTXY (PosX(X2), PosY(Y2), Dat);
END;


PROCEDURE SecondPage (ModNo : INTEGER; VAR PC, FAC, PA, FAM,
.....OQ, CO, COOH, POH, OCH, QCO, OH, NH, SH : STRING);
```

```
  { This procedure obtains the data for each of the fulvic
    acid models :
    functional group characteristics etc }
VAR
  ModNum              : STRING;     { STRING of ModNo }
  XPosn               : INTEGER;    { XPosn on screen }
  YPosn               : INTEGER;    { YPosn on screen }
  Opt                 : STRING;     { Option chosen }
  Err                 : INTEGER;    { Error checking variable }

BEGIN
 CLEARVIEWPORT;
 Opt := ' ';
 STR (ModNo, ModNum);
 LINE (0, PosY (0.042), PosX (1.000), PosY (0.042));
 LINE (0, PosY (0.125), PosX (1.000), PosY (0.125));
 OUTTEXTXY (PosX (0.3125), PosY (0.083), 'INPUT DATA FOR
..... FULVIC ACID NO');
 OUTTEXTXY (PosX (0.703), PosY (0.083), ModNum);
 OUTTEXTXY (PosX (0.015), PosY (0.167), '1 PERCENTAGE
..... CARBON');
 OUTTEXTXY (PosX (0.015), PosY (0.208), '2 FRACTION OF COOH
..... GROUPS');
 OUTTEXTXY (PosX (0.015), PosY (0.250), '       ON AROMATIC
..... RINGS');
 OUTTEXTXY (PosX (0.015), PosY (0.292), '3 PERCENTAGE
..... AROMATICITY');
 OUTTEXTXY (PosX (0.015), PosY (0.333), '4 FRACTION OF
..... ALIPHATIC CARBONS');
 OUTTEXTXY (PosX (0.015), PosY (0.375), '                IN
..... METHYL GROUPS');
 OUTTEXTXY (PosX (0.015), PosY (0.417), '5 FRACTION OF
..... QUINONE PAIRS');
 OUTTEXTXY (PosX (0.015), PosY (0.458), '       ORTHO TO
..... EACH OTHER');
 OUTTEXTXY (PosX (0.531), PosY (0.167), ' 6 CARBONYL
..... GROUPS');
 OUTTEXTXY (PosX (0.531), PosY (0.208), ' 7 CARBOXYLATE
..... GROUPS');
 OUTTEXTXY (PosX (0.531), PosY (0.250), ' 8 PHENOL GROUPS');
 OUTTEXTXY (PosX (0.531), PosY (0.292), ' 9 O-CH  GROUPS');
 OUTTEXTXY (PosX (0.531), PosY (0.302), '       3');
 OUTTEXTXY (PosX (0.531), PosY (0.333), '10 QUINONE .....
GROUPS');

 OUTTEXTXY (PosX (0.531), PosY (0.375), '11 ALIPHATI
.....C OHs');
 OUTTEXTXY (PosX (0.531), PosY (0.417), '12 ALIPHATI
.....C NHs');
 OUTTEXTXY (PosX (0.531), PosY (0.427), '                2');
 OUTTEXTXY (PosX (0.531), PosY (0.458), '13 ALIPHATI
.....C SHs');
 FOR YPosn := 1 TO 8 DO OUTTEXTXY (PosX (0.922), PosY
.....(0.125+ YPosn*0.04166), 'meq/g');
 LINE (0, PosY (0.500), PosX (1.000), PosY (0.500));
 OUTTEXTXY (PosX (0.430), PosY (0.167), PC);
 OUTTEXTXY (PosX (0.430), PosY (0.208), FAC);
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```
 OUTTEXTXY (PosX (0.430), PosY (0.292), PA);
 OUTTEXTXY (PosX (0.430), PosY (0.333), FAM);
 OUTTEXTXY (PosX (0.430), PosY (0.417), OQ);
 OUTTEXTXY (PosX (0.8125),PosY (0.167), CO);
 OUTTEXTXY (PosX (0.8125),PosY (0.208), COOH);
 OUTTEXTXY (PosX (0.8125),PosY (0.250), POH);
 OUTTEXTXY (PosX (0.8125),PosY (0.292), OCH);
 OUTTEXTXY (PosX (0.8125),PosY (0.333), QCO);
 OUTTEXTXY (PosX (0.8125),PosY (0.375), OH);
 OUTTEXTXY (PosX (0.8125),PosY (0.417), NH);
 OUTTEXTXY (PosX (0.8125),PosY (0.458), SH);
 WHILE Opt <> '0' DO
  BEGIN
  OUTTEXTXY (PosX (0.078), PosY (0.583), 'ENTER THE NUMBER
..... FOR WHICH YOU WOULD LIKE TO SUPPLY DATA :');
  OUTTEXTXY (PosX (0.078), PosY (0.635), '(ENTER 0 (ZERO)
..... WHEN YOU ARE COMPLETE)');
  MOVETO (PosX (0.825), PosY (0.583));
  FetchInp (Opt);
  Err := 1;
  IF Opt = '1' THEN
  BEGIN
   Err :=0;
   OUTTEXTXY (PosX (0.078), PosY (0.729), 'ENTER THE
..... PERCENTAGE CARBON IN THIS FULVIC ACID');
   FetchData (0.695, 0.729, 0.430, 0.167, PC);
  END;
  IF Opt = '2' THEN
  BEGIN
   Err :=0;
   OUTTEXTXY (PosX (0.078), PosY (0.729), 'ENTER THE
..... FRACTION OF CARBOXYLATE GROUPS THAT ARE');
   OUTTEXTXY (PosX (0.078), PosY (0.771), 'ON AROMATIC
..... RINGS');
   FetchData (0.380, 0.771, 0.430, 0.208, FAC);
  END;
  IF Opt = '3' THEN
  BEGIN
   Err :=0;
   OUTTEXTXY (PosX (0.078), PosY (0.729), 'ENTER THE
..... PERCENTAGE AROMATICITY');
   FetchData (0.547, 0.729, 0.430, 0.292, PA);
  END;
  IF Opt = '4' THEN
  BEGIN
   Err :=0;
   OUTTEXTXY (PosX (0.078), PosY (0.729), 'ENTER THE
..... FRACTION OF ALIPHATIC CARBONS THAT OCCUR');
   OUTTEXTXY (PosX (0.078), PosY (0.771), 'IN METHYL
..... GROUPS');
   FetchData (0.3125,0.771, 0.430, 0.333, FAM);
  END;
  IF Opt = '5' THEN
  BEGIN
   Err :=0;
   OUTTEXTXY (PosX (0.078), PosY (0.729), 'ENTER THE
..... FRACTION OF QUINONE PAIRS THAT ARE ORTHO');
```

```
   OUTTEXTXY (PosX (0.078), PosY (0.771), 'TO EACH OTHER');
   FetchData (0.281, 0.771, 0.430, 0.417, OQ);
  END;
  IF Opt = '6' THEN
  BEGIN
   Err :=0;
   OUTTEXTXY (PosX (0.078), PosY (0.729), 'ENTER THE NUMBER
..... OF CARBONYL GROUPS');
   OUTTEXTXY (PosX (0.726), PosY (0.729), 'meq/g');
   FetchData (0.633, 0.729, 0.8125, 0.167, CO);
  END;
  IF Opt = '7' THEN
  BEGIN
   Err :=0;
   OUTTEXTXY (PosX (0.078), PosY (0.729), 'ENTER THE NUMBER
..... OF CARBOXYLATE GROUPS');
   OUTTEXTXY (PosX (0.719), PosY (0.729), 'meq/g');
   FetchData (0.625, 0.729, 0.8125, 0.208, COOH);
  END;
  IF Opt = '8' THEN
  BEGIN
   Err :=0;
   OUTTEXTXY (PosX (0.078), PosY (0.729), 'ENTER THE NUMBER
..... OF PHENOLIC GROUPS');
   OUTTEXTXY (PosX (0.719), PosY (0.729), 'meq/g');
   FetchData (0.625, 0.729, 0.8125,0.250, POH);
  END;
  IF Opt = '9' THEN
  BEGIN
   Err :=0;
   OUTTEXTXY (PosX (0.078), PosY (0.729), 'ENTER THE NUMBER
..... OF AROMATIC METHOXYLS');
   OUTTEXTXY (PosX (0.719), PosY (0.729), 'meq/g');
   FetchData (0.625, 0.729, 0.8125,0.292, OCH);
  END;
  IF Opt = '10' THEN
  BEGIN
   Err :=0;
   OUTTEXTXY (PosX (0.078), PosY (0.729), 'ENTER THE NUMBER
..... OF QUINONE GROUPS');
   OUTTEXTXY (PosX (0.719), PosY (0.729), 'meq/g');
   FetchData (0.625, 0.729, 0.8125,0.333, QCO);
  END;
  IF Opt = '11' THEN
  BEGIN
   Err :=0;
   OUTTEXTXY (PosX (0.078), PosY (0.729), 'ENTER THE NUMBER
..... OF ALIPHATIC HYDROXYLS');
   OUTTEXTXY (PosX (0.719), PosY (0.729), 'meq/g');
   FetchData (0.625, 0.729, 0.8125, 0.375, OH);
  END;
  IF Opt = '12' THEN
  BEGIN
   Err :=0;
   OUTTEXTXY (PosX (0.078), PosY (0.729), 'ENTER THE NUMBER
..... OF ALIPHATIC AMINES');
   OUTTEXTXY (PosX (0.719), PosY (0.729), 'meq/g');
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    FetchData (0.625, 0.729, 0.8125, 0.417, NH);
   END;
   IF Opt = '13' THEN
   BEGIN
    Err :=0;
    OUTTEXTXY (PosX (0.078), PosY (0.729), 'ENTER THE NUMBER
..... OF ALIPHATIC THIOLS');
    OUTTEXTXY (PosX (0.719), PosY (0.729), 'meq/g');
    FetchData (0.625, 0.729, 0.8125, 0.458, SH);
   END;
   IF Opt = '0' THEN Err :=0;
   IF Err = 1 THEN
   BEGIN
    Error;
    ClearOld(PosX(0.35),PosY(0.938),'INCORRECT CHOICE MADE');
    SetFillStyle (EmptyFill, 0);
    Bar (0, PosY(0.85), PosX (1),  PosY (1));
   END;
   SetFillStyle (EmptyFill, 0);
   Bar (PosX(0.063), PosY (0.6875), PosX (1),  PosY (0.833));
   ClearOld (0.825, 0.583, Opt);
 END;
 IF PC = '' THEN PC := '0';
 IF FAC = '' THEN FAC := '0';
 IF PA = '' THEN PA := '0';
 IF FAM = '' THEN FAM := '0';
 IF OQ = '' THEN OQ := '0';
 IF CO = '' THEN CO := '0';
 IF COOH = '' THEN COOH := '0';
 IF POH = '' THEN POH  := '0';
 IF OCH = '' THEN OCH := '0';
 IF QCO = '' THEN QCO := '0';
 IF OH = '' THEN OH := '0';
 IF NH = '' THEN NH := '0';
 IF SH = '' THEN SH := '0';
END;


PROCEDURE Creat;
  { This procedure creates an input file }
VAR
  FileCr            : STRING;    { File name TO be created }
  FileName          : TEXT;
  Ratio             : STRING;    { Ratio of ortho : meta :
                                   para linkages }
  PrOpt             : STRING;    { Print Option chosen for
                                   the output }
  CouOrd1           : STRING;    { Count Order chosen (1st 20
                                   sites) }
  CouOrd2           : STRING;    { Count Order chosen
                                   (remaining sites) }
  NumSites          : INTEGER;   { The number of sites TO be
                                   counted }
  NumStruct         : STRING;    { Number of structures
                                   generated per fulvic
                                   acid modelled }
  NumFA             : STRING;    { Number of different fulvic
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```
                                        acids modelled }
  NumberFA          : INTEGER;    { NumFA as an integer }
  ErrFA             : INTEGER;    { Error variable for
                                    conversion }
  Count             : INTEGER;    { Counter }
  PerC              : STRING;     { Percentage carbon in
                                    Fulvic Acid }
  FrxnArC           : STRING;     { Fractrion COOH on aromatic
                                    rings }
  PerAro            : STRING;     { Percentage aromaticity }
  FrxnAlM           : STRING;     { Fraction aliphatic carbons
                                    as methyls }
  FrxnOQ            : STRING;     { Fraction ortho quinones }
  Keto              : STRING;     { Number of carbonyl groups}
  Carbox            : STRING;     { Number of carboxylate
                                    groups }
  Phen              : STRING;     { Number of phenolic groups}
  Meth              : STRING;     { Number of Methoxy groups }
  Quinon            : STRING;     { Number of quionone groups}
  Hyd               : STRING;     { Number of hydroxyl groups}
  Ami               : STRING;     { Number of amine groups }
  Thio              : STRING;     { Number of thiol groups }
  RK                : CHAR;       { Key read from keyboard }

BEGIN
 CLEARVIEWPORT;
 Ratio := '';
 PrOpt := '';
 CouOrd1 := '';
 CouOrd2 := '';
 NumStruct := '';
 NumFA := '';
 OUTTEXTXY (PosX (0.406),PosY (0.208), 'FILE CREATION');
 RECTANGLE(PosX(0.328),PosY(0.156),PosX(0.656),PosY(0.260));
 OUTTEXTXY (PosX (0.266),PosY (0.365), ' Enter the name of
..... the file you');
 OUTTEXTXY (PosX (0.266),PosY (0.469), ' would like to
..... create from scratch :');
 MOVETO (PosX (0.735),PosY (0.469));
 FetchInp (FileCr);
 ASSIGN (FileName, FileCr);
 REWRITE (FileName);
 FirstPage (Ratio, PrOpt, CouOrd1, CouOrd2, NumStruct,
.....NumFA, NumSites);
 WRITELN (FileName, Ratio);
 WRITELN (FileName, PrOpt);
 WRITELN (FileName, NumSites);
 WRITELN (FileName, CouOrd1);
 WRITELN (FileName, CouOrd2);
 WRITELN (FileName, NumStruct);
 WRITELN (FileName, NumFA);
 VAL (NumFA, NumberFA, ErrFA);
 FOR Count := 1 TO NumberFA DO
 BEGIN
  PerC := '';
  FrxnArC := '';
  PerAro := '';
```

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  FrxnAlM := '';
  FrxnOQ := '';
  Keto := '';
  Carbox := '';
  Phen := '';
  Meth := '';
  Quinon := '';
  Hyd := '';
  Ami := '';
  Thio := '';
  SecondPage (Count, PerC, FrxnArC, PerAro, FrxnAlM, FrxnOQ,
.....Keto, Carbox, Phen, Meth, Quinon, Hyd, Ami, Thio);
  WRITELN (FileName, PerC, ' ', FrxnArc, ' ', PerAro, ' ',
.....FrxnAlM, ' ', FrxnOQ);
  WRITELN (FileName, Keto, ' ', Carbox, ' ', Phen, ' ',
.....Meth, ' ', Quinon, ' ', Hyd, ' ', Ami, ' ', Thio);
 END;
 CLOSE (FileName);
END;


PROCEDURE Edit;
  { This procedure edits an input file }
VAR
  FileCr            : STRING;    { File name TO be edited }
  FileSd            : STRING;    { File name TO be used as
                                   seed }
  FileSeed          : TEXT;      { Seed file }
  FileNew           : TEXT;      { New file TO store changed
                                   data }
  Ratio             : STRING;    { Ratio of ortho : meta :
                                   para linkages }
  PrOpt             : STRING;    { Print Option chosen for
                                   the output }
  CouOrd1           : STRING;    { Count Order chosen (1st 20
                                   sites) }
  CouOrd2           : STRING;    { Count Order chosen
                                   (remaining sites) }
  NumSites          : INTEGER;   { The number of sites TO be
                                   counted }
  NumStruct         : STRING;    { Number of structures
                                   generated per fulvic
                                   acid modelled }
  NumFA             : STRING;    { Number of different fulvic
                                   acids modelled }
  NumberFA          : INTEGER;   { NumFA as an integer }
  ErrFA             : INTEGER;   { Error variable for
                                   conversion }
  Count             : INTEGER;   { Counter }
  PerC              : STRING;    { Percentage carbon in
                                   Fulvic Acid }
  FrxnArC           : STRING;    { Fraction COOH on aromatic
                                   rings }
  PerAro            : STRING;    { Percentage aromaticity }
  FrxnAlM           : STRING;    { Fraction aliphatic carbons
                                   as methyls }
  FrxnOQ            : STRING;    { Fraction ortho quinones }
```

```
  Keto              : STRING;     { Number of carbonyl groups}
  Carbox            : STRING;     { Number of carboxylate
                                    groups }
  Phen              : STRING;     { Number of phenolic groups}
  Meth              : STRING;     { Number of Methoxy groups }
  Quinon            : STRING;     { Number of quionone groups
  Hyd               : STRING;     { Number of hydroxyl groups}
  Ami               : STRING;     { Number of amine groups }
  Thio              : STRING;     { Number of thiol groups }
  FirstLine         : STRING;     { First line of data read }
  Secondline        : STRING;     { Second line of data read }
  I,J               : INTEGER;    { Counters }
  Blanks            : ARRAY[ 1 .. 7] OF INTEGER; { Position
                                    of blanks in text read }

BEGIN
 CLEARVIEWPORT;
 OUTTEXTXY (PosX (0.406), PosY (0.208), 'FILE EDITING');
 RECTANGLE(PosX(0.328),PosY(0.156),PosX(0.656),PosY(0.260));
 OUTTEXTXY (PosX (0.266), PosY (0.365), ' Enter the name of
..... the file you');
 OUTTEXTXY (PosX (0.266), PosY (0.469), ' would like to
..... create :');
 MOVETO (PosX (0.573), PosY (0.469));
 FetchInp (FileCr);
 OUTTEXTXY (PosX (0.266), PosY (0.625), ' Enter the name of
..... the file you');
 OUTTEXTXY (PosX (0.266), PosY (0.729), ' would like use as
..... seed file :');
 MOVETO (PosX (0.665), PosY (0.729));
 FetchInp (FileSd);
 ASSIGN (FileSeed, FileSd);
 RESET (FileSeed);
 ASSIGN (FileNew, FileCr);
 REWRITE (FileNew);
 READLN (FileSeed, Ratio);
 READLN (FileSeed, PrOpt);
 READLN (FileSeed, NumSites);
 READLN (FileSeed, CouOrd1);
 READLN (FileSeed, CouOrd2);
 READLN (FileSeed, NumStruct);
 READLN (FileSeed, NumFA);
 FirstPage (Ratio, PrOpt, CouOrd1, CouOrd2, NumStruct,
.....NumFA, NumSites);
 WRITELN (FileNew, Ratio);
 WRITELN (FileNew, PrOpt);
 WRITELN (FileNew, NumSites);
 WRITELN (FileNew, CouOrd1);
 WRITELN (FileNew, CouOrd2);
 WRITELN (FileNew, NumStruct);
 WRITELN (FileNew, NumFA);
 VAL (NumFA, NumberFA, ErrFA);
 FOR Count := 1 TO NumberFA DO
 BEGIN
  IF NOT EOF(FileSeed) THEN
  BEGIN
   READLN (FileSeed, FirstLine);
```

```
   READLN (FileSeed, SecondLine);
  END;
  I := 1;
  J := 0;
  WHILE I < LENGTH (FirstLine) DO
  BEGIN
   IF FirstLine[I] = ' ' THEN
   BEGIN
    J := J + 1;
    Blanks[J] := I;
   END;
   I := I + 1;
   IF J = 4 THEN I := LENGTH (FirstLine);
  END;
  PerC := COPY (FirstLine, 1, Blanks[1]-1);
 FrxnArC:=COPY(FirstLine,Blanks[1]+1,Blanks[2]-Blanks[1]-1);
  PerAro:=COPY(FirstLine,Blanks[2]+1,Blanks[3]-Blanks[2]-1);
 FrxnAlM:=COPY(FirstLine,Blanks[3]+1,Blanks[4]-Blanks[3]-1);
 FrxnOQ:=COPY(FirstLine,Blanks[4]+1,LENGTH(FirstLine)-
.....Blanks[4]);
  I := 1;
  J := 0;
  WHILE I < LENGTH (SecondLine) DO
  BEGIN
   IF SecondLine[I] = ' ' THEN
   BEGIN
    J := J + 1;
    Blanks[J] := I;
   END;
   I := I + 1;
   IF J = 7 THEN I := LENGTH (SecondLine);
  END;
  Keto := COPY (SecondLine, 1, Blanks[1]-1);
 Carbox:=COPY(SecondLine,Blanks[1]+1,Blanks[2]-Blanks[1]-1);
  Phen :=COPY(SecondLine,Blanks[2]+1,Blanks[3]-Blanks[2]-1);
  Meth :=COPY(SecondLine,Blanks[3]+1,Blanks[4]-Blanks[3]-1);
 Quinon:=COPY(SecondLine,Blanks[4]+1,Blanks[5]-Blanks[4]-1);
  Hyd := COPY(SecondLine,Blanks[5]+1,Blanks[6]-Blanks[5]-1);
  Ami := COPY(SecondLine,Blanks[6]+1,Blanks[7]-Blanks[6]-1);
  Thio:=COPY(SecondLine,Blanks[7]+1,LENGTH(SecondLine)-
.....Blanks[7]);
  SecondPage (Count, PerC, FrxnArC, PerAro, FrxnAlM, FrxnOQ,
.....Keto, Carbox, Phen, Meth, Quinon, Hyd, Ami, Thio);
  WRITELN (FileNew, PerC, ' ', FrxnArc, ' ', PerAro, ' ',
.....FrxnAlM, ' ', FrxnOQ);
  WRITELN (FileNew, Keto, ' ', Carbox, ' ', Phen, ' ', Meth,
.....' ', Quinon, ' ', Hyd, ' ', Ami, ' ', Thio);
 END;
 CLOSE (FileNew);
 CLOSE (FileSeed);
END;

PROCEDURE MonoAro (II : INTEGER; NoAroC : REAL; VAR S: ArS;
VAR IAR : ArIAR);
  { This procdure counts the monodentate aromatic sites
    (BENZ and PHEN) }
VAR
```

```
  I                 : INTEGER;    { Carbon Position Counters }
  CC                : INTEGER;    { Code identifying phenol or
                                    carboxylate }

BEGIN
 IF II = 7 THEN CC := 7 ELSE CC := 1;
 FOR I := 1 TO TRUNC (NoAroC) DO
 BEGIN
  IF (IAR[1,I]=CC) AND (IAR[2,I]=0) THEN
  BEGIN
   S[II] := S[II]+1;
   IAR[2,I] := II;
  END;
 END;
END;


PROCEDURE AroCount (II, SUM, IRO, IRM, IRP : INTEGER; VAR S
.....: ArS; VAR IAR : ArIAR);
  { This procedure counts the occurrence of the didentate
    aromatic binding sites }
VAR
  I,J               : INTEGER;    { Carbon Position Counters }
  I1                : INTEGER;    { Carbon position }
  I2                : INTEGER;    { Adjacent carbon TO I1 }
  Add               : INTEGER;    { Sum of IAL[1,I] of I1 and
                                    I2; used to see if there
                                    is a match with the site
                                    in question }

BEGIN

{ Count the sites on ortho rings }

 IF IRO <> 0 THEN
 BEGIN
  FOR I := 1 TO IRO DO
  BEGIN
   FOR J := 1 TO 3 DO
   BEGIN
    I1 := (I-1)*4+J;
    I2 := I1 + 1;
    IF (IAR[2,I1]=0) AND (IAR[2,I2]=0) THEN
    BEGIN
     Add := IAR[1,I1] + IAR[1,I2];
     IF Add = Sum THEN
     BEGIN
      S[II] := S[II]+1;
      IAR[2,I1] := II;
      IAR[2,I2] := II;
      IF (Sum = 16) AND (J=1) THEN IAR[2,I1+3] := 2;
      IF (Sum = 16) AND (J=3) THEN IAR[2,I1-2] := 2;
     END;
    END;
   END;
  END;
 END;
```

```
{ Count the sites on meta rings }

 IF IRM <> 0 THEN
 BEGIN
  FOR I := 1 TO IRM DO
  BEGIN
   FOR J := 2 TO 3 DO
   BEGIN
    I1 := (I-1+IRO)*4+J;
    I2 := I1 + 1;
    IF (IAR[2,I1]=0) AND (IAR[2,I2]=0) THEN
    BEGIN
     Add := IAR[1,I1] + IAR[1,I2];
     IF Add = Sum THEN
     BEGIN
      S[II] := S[II]+1;
      IAR[2,I1] := II;
      IAR[2,I2] := II;
      IF Sum = 16 THEN IAR[2,(I-1+IRO)*4+1] := 2;
     END;
    END;
   END;
  END;
 END;

{ Count the sites on para rings }

 IF IRP <> 0 THEN
 BEGIN
  FOR I := 1 TO IRP DO
  BEGIN
   FOR J := 0 TO 1 DO
   BEGIN
    I1 := (I-1+IRO+IRM)*4+2*J+1;
    I2 := I1 + 1;
    IF (IAR[2,I1]=0) AND (IAR[2,I2]=0) THEN
    BEGIN
     Add := IAR[1,I1] + IAR[1,I2];
     IF Add = Sum THEN
     BEGIN
      S[II] := S[II]+1;
      IAR[2,I1] := II;
      IAR[2,I2] := II;
      IF (Sum=16) AND (J=0) AND (IAR[1,I1]=15) THEN
..... IAR[2,I1+2]:=2;
      IF (Sum=16) AND (J=0) AND (IAR[1,I2]=15) THEN
..... IAR[2,I2+2]:=2;
      IF (Sum=16) AND (J=1) AND (IAR[1,I1]=15) THEN
..... IAR[2,I1-2]:=2;
      IF (Sum=16) AND (J=1) AND (IAR[1,I2]=15) THEN
..... IAR[2,I2-2]:=2;
     END;
    END;
   END;
  END;
 END;
```

```
END;


PROCEDURE BidenSame (II, Sum, MMM : INTEGER; VAR S : ArS;
.....VAR IAL : ArIAL);
  { This procedure  counts bidentate sites with functional
    groups on the same carbon }
VAR
  I                 : INTEGER;    { Carbon Position counter }
  Add               : INTEGER;    { Sum of IAL[2,I] and
                                    IAl[3,I] used to see if
                                    there is a match with the
                                    site in question }

BEGIN
 FOR I := 1 TO MMM DO
 BEGIN
  Add := IAL[2,I]+IAL[3,I];
  IF (Add=Sum) AND (IAL[4,I]=0) THEN
  BEGIN
   IAL[4,I] := II;
   S[II] := S[II] + 1;
  END;
 END;
END;


PROCEDURE BidenDiff (II, MM, NN, MMM : INTEGER; VAR S : ArS;
.....VAR IAL : ArIAL);
  { This procedure  counts bidentate sites with functional
    groups on different carbons }
VAR
  I                 : INTEGER;    { Carbon Position counter }
  IPrev             : INTEGER;    { Previous carbon in
                                    sequence }
  INext             : INTEGER;    { Next carbon in sequence }
  Chk               : INTEGER;    { Check variable to test if
                                    a site has already been
                                    found }

BEGIN
 FOR I := 1 TO MMM DO
 BEGIN
  IF IAL[4,I] = 0 THEN
  BEGIN
   Chk := 1;
   IF (IAL[2,I]=MM) OR (IAL[3,I]=MM) THEN
   BEGIN
    IPrev := I-1;
    IF IPrev = 0 THEN IPrev := MMM;
    IF IAL[1,IPrev] = 1 THEN IPrev := IPrev - 1;
    IF IPrev = 0 THEN IPrev := MMM;
    IF IAL[4,IPrev] = 0 THEN
    BEGIN
     IF (IAL[2,IPrev]=NN) OR (IAL[3,IPrev]=NN) THEN
     BEGIN
```

```
      Chk := 0;
      S[II] := S[II]+1;
      IAL[4,I] := II;
      IAL[4,IPrev] := II;
     END;
    END;
    IF (Chk <> 0) AND (IAL[1,I] <> 1) THEN
    BEGIN
     INext := I + 1;
     IF I = MMM THEN INext := 1;
     IF IAL[4,INext] = 0 THEN
     BEGIN
      IF (IAL[2,INext]=NN) OR (IAL[3,INext]=NN) THEN
      BEGIN
       Chk := 0;
       S[II] := S[II]+1;
       IAL[4,I] := II;
       IAL[4,INext] := II;
      END;
     END;
     IF (IAL[1,I]=4) AND (Chk<>0) THEN
     BEGIN
      INext := I+2;
      IF I = MMM-1 THEN INext := 1;
      IF I = MMM Then Inext := 2;
      IF IAL[4,INext] = 0 THEN
      BEGIN
       IF (IAL[2,INext]=NN) OR (IAL[3,INext]=NN) THEN
       BEGIN
        S[II] := S[II]+1;
        IAL[4,I] := II;
        IAL[4,INext] := II;
       END;
      END;
     END;
    END;
   END;
  END;
 END;
END;


PROCEDURE Citric (MMM:INTEGER; VAR S:ArS; VAR IAL : ArIAL);
  { This procedure counts citric acid sites }
VAR
  I                : INTEGER;   { Carbon Position counter }
  IPrev            : INTEGER;   { Previous carbon in
                                  sequence }
  INext            : INTEGER;   { Next carbon in sequence }
  Add              : INTEGER;   { Sum of IAL[2,I] and
                                  IAL[3,I] to see if a
                                  match with the site in
                                  question is found }
BEGIN
 FOR I := 1 TO MMM DO
 BEGIN
  IF (IAL[4,I] = 0) AND (IAL[1,I]=2) THEN
```

```
  BEGIN
   Add := IAL[2,I] + IAL[3,I];
   If Add = 7 THEN
   BEGIN
    IPrev := I - 1;
    INext := I + 1;
    IF I = MMM THEN INext := 1;
    IF IPrev = 0 THEN IPrev := MMM;
    IF IAL[1,IPrev] = 1 THEN IPrev := IPrev - 1;
    IF IPrev = 0 THEN IPrev := MMM;
    IF (IAL[4,IPrev]=0) AND (IAL[4,INext]=0) THEN
    BEGIN
     IF (IAL[2,IPrev]=4) AND (IAL[2,INext]=4) THEN
     BEGIN
      IAL[4,I] := 17;
      IAL[4,IPrev] := 17;
      IAL[4,INext] := 17;
      S[17] := S[17]+1;
     END;
    END;
   END;
  END;
 END;
END;


PROCEDURE Triden (II, Sum, NN, MMM : INTEGER; VAR S : ArS;
.....VAR IAL : ArIAL);
  { This procedure counts tridentate sites }
VAR
  I                 : INTEGER;   { Carbon Position counter }
  IPrev             : INTEGER;   { Previous carbon in
                                   sequence }
  INext             : INTEGER;   { Next carbon in sequence }
  Chk               : INTEGER;   { Check variable to test if
                                   a site has already been
                                   found }
  Add               : INTEGER;   { Sum of IAL[2,I] and
                                   IAL[3,I] to see if a
                                   match with the site in
                                   question is found }

BEGIN
 FOR I := 1 TO MMM DO
 BEGIN
  IF IAL[4,I] = 0 THEN
  BEGIN
   Chk := 1;
   Add := IAL[2,I] + IAL[3,I];
   IF Add = Sum THEN
   BEGIN
    IPrev := I-1;
    IF IPrev = 0 THEN IPrev := MMM;
    IF IAL[1,IPrev] = 1 THEN IPrev := IPrev - 1;
    IF IPrev = 0 THEN IPrev := MMM;
    IF IAL[4,IPrev] = 0 THEN
    BEGIN
```

```
      IF (IAL[2,IPrev]=NN) OR (IAL[3,IPrev]=NN) THEN
      BEGIN
       Chk := 0;
       S[II] := S[II]+1;
       IAL[4,I] := II;
       IAL[4,IPrev] := II;
      END;
     END;
     IF (Chk <> 0) AND (IAL[1,I] = 2) THEN
     BEGIN
      INext := I + 1;
      IF I = MMM THEN INext := 1;
      IF IAL[4,INext] = 0 THEN
      BEGIN
       IF (IAL[2,INext]=NN) OR (IAL[3,INext]=NN) THEN
       BEGIN
        S[II] := S[II]+1;
        IAL[4,I] := II;
        IAL[4,INext] := II;
       END;
      END;
     END;
    END;
   END;
  END;
END;


PROCEDURE PROP (MMM:INTEGER; VAR S : ArS; VAR IAL : ArIAL);
  { This procedure looks for site 16 propionic acid }
VAR
  I                : INTEGER;   { Carbon Position Counter }

BEGIN
 FOR I := 1 TO MMM DO
 BEGIN
  IF IAL[4,I] = 0 THEN
  BEGIN
   IF (IAL[2,I] = 4) OR (IAL[3,I] = 4) THEN
   BEGIN
    S[16] := S[16] + 1;
    IAL[4,I] := 16;
   END;
  END;
 END;
END;


PROCEDURE ACAC (MMM:INTEGER; VAR S : ArS; VAR IAL : ArIAL);
  { This procedure looks for site 9 acetylacetone }
VAR
  I, I1, I2, I3    : INTEGER;   { Carbon Position Counters }

BEGIN
 FOR I := 1 TO MMM DO
 BEGIN
  IF IAL[1,I] = 8 THEN
```

```
  BEGIN
   IF IAL[4,I] = 0 THEN
   BEGIN
    I1 := I+1;
    I2 := I+2;
    I3 := I+3;
    IF I = MMM-2 THEN I3 := 1;
    IF I = MMM-1 THEN
    BEGIN
     I2 := 1;
     I3 := 2;
    END;
    IF I = MMM THEN
    BEGIN
     I1 := 1;
     I2 := 2;
     I3 := 3;
    END;
    IF IAL[1,I1] = 2 THEN
    BEGIN
     IF (IAL[1,I2]=8) AND (IAL[4,I2]=0) AND (IAL[4,I1]=0)
..... AND (IAL[3,I1]=0) THEN
     BEGIN
      IAL [4,I] := 9;
      IAL [4,I1] := 9;
      IAL [4,I2] := 9;
      S[9] := S[9] + 1;
     END;
    END;
    IF IAL[1,I1] = 4 THEN
    BEGIN
     IF (IAL[1,I3]=8) AND (IAL[4,I3]=0) AND (IAL[4,I2]=0)
..... AND (IAL[4,I1]=0) AND (IAL[2,I1]=0) THEN
     BEGIN
      IAL [4,I] := 9;
      IAL [4,I1] := 9;
      IAL [4,I2] := 9;
      IAL [4,I3] := 9;
      S[9] := S[9] + 1;
     END;
    END;
   END;
  END;
 END;
END;


PROCEDURE ACPH (IRO, IRM, MMM : INTEGER; VAR S : ArS; VAR
..... IAR : ArIAR; VAR IAL : ArIAL);
  { This procedure looks for site 6 (acetylphenol) }
VAR
  I, I1              : INTEGER;   { Carbon Position Counters }
  J                  : INTEGER;   { Ring counter }
  Chk                : INTEGER;   { Check Variable }
  RingType           : INTEGER;   { Indicates type of ring }
  NIR                : INTEGER;   { Used to indicate ring
                                    position }
```

```
  NN                : INTEGER;    { Position marker }

BEGIN
 FOR I := 1 TO MMM DO
 BEGIN
  IF (IAL[1,I]=8) AND (IAL[4,I]=0) THEN
  BEGIN
   Chk := 1;
   I1 := I+1;
   IF I = MMM THEN I1 := 1;
   IF (IAL[1,I1]>4) AND (IAL[1,I1]<8) THEN
   BEGIN
    RingType := IAL[1,I1];
    NIR := 0;
    FOR J := 1 TO I1 DO
    BEGIN
     IF IAL[1,J] = RingType THEN NIR := NIR + 1;
    END;
    IF RingType = 5 THEN
    BEGIN
     NN := 4*NIR-3;
     IF (IAR[1,NN] = 1) AND (IAR[2,NN]=0) THEN
     BEGIN
      Chk := 0;
      S[6] := S[6]+1;
      IAL[4,I] := 6;
      IAR[2,NN] := 6;
     END;
    END;
    IF RingType = 6 THEN
    BEGIN
     NN := 4*(NIR+IRO)-3;
     IF (IAR[1,NN] = 1) AND (IAR[2,NN]=0) THEN
     BEGIN
      Chk := 0;
      S[6] := S[6]+1;
      IAL[4,I] := 6;
      IAR[2,NN] := 6;
     END;
    IF (IAR[1,NN+1]=1) AND (IAR[2,NN+1]=0) AND (Chk<>0) THEN
     BEGIN
      Chk := 0;
      S[6] := S[6]+1;
      IAL[4,I] := 6;
      IAR[2,NN+1] := 6;
     END;
    END;
    IF RingType = 7 THEN
    BEGIN
     NN := 4*(NIR+IRO+IRM)-3;
     IF (IAR[1,NN] = 1) AND (IAR[2,NN]=0) THEN
     BEGIN
      Chk := 0;
      S[6] := S[6]+1;
      IAL[4,I] := 6;
      IAR[2,NN] := 6;
     END;
```

```
 IF (IAR[1,NN+3]=1) AND (IAR[2,NN+3]=0) AND (Chk<>0) THEN
  BEGIN
   Chk := 0;
   S[6] := S[6]+1;
   IAL[4,I] := 6;
   IAR[2,NN+3] := 6;
  END;
 END;
END;
I1 := I-1;
IF I = 1 THEN I1 := MMM;
IF (IAL[1,I1]>4) AND (IAL[1,I1]<8) AND (Chk<>0) THEN
BEGIN
 RingType := IAL[1,I1];
 NIR := 0;
 FOR J := 1 TO I1 DO
 BEGIN
  IF IAL[1,J] = RingType THEN NIR := NIR + 1;
  END;
 IF RingType = 5 THEN
 BEGIN
  NN := 4*NIR;
  IF (IAR[1,NN] = 1) AND (IAR[2,NN]=0) THEN
  BEGIN
   Chk := 0;
   S[6] := S[6]+1;
   IAL[4,I] := 6;
   IAR[2,NN] := 6;
  END;
 END;
 IF RingType = 6 THEN
 BEGIN
  NN := 4*(NIR+IRO)-3;
  IF (IAR[1,NN] = 1) AND (IAR[2,NN]=0) THEN
  BEGIN
   Chk := 0;
   S[6] := S[6]+1;
   IAL[4,I] := 6;
   IAR[2,NN] := 6;
  END;
 IF (IAR[1,NN+3]=1) AND (IAR[2,NN+3]=0) AND (Chk<>0) THEN
  BEGIN
   Chk := 0;
   S[6] := S[6]+1;
   IAL[4,I] := 6;
   IAR[2,NN+3] := 6;
  END;
 END;
 IF RingType = 7 THEN
 BEGIN
  NN := 4*(NIR+IRO+IRM)-2;
  IF (IAR[1,NN] = 1) AND (IAR[2,NN]=0) THEN
  BEGIN
   Chk := 0;
   S[6] := S[6]+1;
   IAL[4,I] := 6;
   IAR[2,NN] := 6;
```

```
      END;
     IF (IAR[1,NN+1]=1) AND (IAR[2,NN+1]=0) AND (Chk<>0) THEN
      BEGIN
       Chk := 0;
       S[6] := S[6]+1;
       IAL[4,I] := 6;
       IAR[2,NN+1] := 6;
      END;
     END;
    END;
   END;
 END;
END;


PROCEDURE TooManyInc (VAR FileNam : TEXT);
  { Output error writing procedure }
BEGIN
 WRITELN (FileNam);
 WRITELN (FileNam, 'THE MAXIMUM NUMBER OF INCONSISTENT
 ..... STRUCTURES');
 WRITELN (FileNam, 'HAS BEEN EXCEEDED, PLEASE CHECK YOUR
INPUT DATA');
END;


PROCEDURE TooManyQui (VAR FileNam : TEXT);
  { Output error writing procedure }
BEGIN
 WRITELN (FileNam);
 WRITELN (FileNam, 'RANDOM ACCEPTS A MAXIMUM OF ONE QUINONE
..... PAIR');
 WRITELN (FileNam, 'PER AROMATIC RING. YOUR INPUT DATA IS
..... INCOMPATIBLE');
 WRITELN (FileNam, 'WITH THIS REQUIREMENT. YOUR QUINONE
..... CONCENTRATION');
 WRITELN (FileNam, 'IS TOO HIGH.');
END;


Procedure PoorArom (VAR FileNam : TEXT);
  { Output error writing procedure }
BEGIN
 WRITELN (FileNam);
 WRITELN (FileNam, 'THE AROMATICITY AND PERCENTAGE CARBON
..... REQUIRED');
 WRITELN (FileNam, 'BY YOUR INPUT DATA EXCEEDS THE PROGRAM
..... LIMITS');
 WRITELN (FileNam, 'I.E 7.5 meq/g OF AROMATIC RINGS');
END;


PROCEDURE ToomanyGrp (VAR FileNam : TEXT);
  { Output error writing procedure }
BEGIN
 WRITELN (FileNam, 'THE CARBONS IN RINGS, COOH, OCH3 AND
..... KETONE GROUPS');
```

```
 WRITELN (FileNam, 'EXCEED THE NUMBER OF CARBONS
..... AVAILABLE.');
 WRITELN (FileNam, 'THIS RUN HAS BEEN TERMINATED.');
END;


PROCEDURE ToomanyAli (VAR FileNam : TEXT);
  { Output error writing procedure }
BEGIN
 WRITELN (FileNam);
 WRITELN (FileNam, 'THE NUMBER OF ALIPHATIC SITES REQUIRED
..... EXCEEDS');
 WRITELN (FileNam, 'THE PROGRAM LIMITS. CHECK THAT YOUR
..... PERCENTAGE');
 WRITELN (FileNam, 'CARBON IS NOT UNCHARACTERISTICALLY
..... HIGH');
 WRITELN (FileNam, 'FOR FULVIC ACID. (IT SHOULD BE LESS');
 WRITELN (FileNam, 'THAN 60%.');
END;


PROCEDURE Calc;                    {This procedure runs RANDOM}
VAR
  FileOut          : STRING;     { File TO send output TO }
  FileName         : TEXT;
  FileIn           : STRING;     { File from which input is
                                   read }
  FileRead         : TEXT;
  Ratio            : STRING;     { Ratio of ortho : meta :
                                   para linkages }
  I,J,NS           : INTEGER;    { Counter }
  Colons           : ARRAY[ 1 .. 2 ] of INTEGER; { Posn of
                                   colons in Ratio }
  RO               : REAL;       { Ortho part of Ratio }
  RM               : REAL;       { Mtea part of Ratio }
  RP               : REAL;       { Para part of Ratio }
  Err              : INTEGER;    { Error variable }
  PrOpt            : STRING;     { Print Option chosen for
                                   the output }
  CouOrd1          : STRING;     { Count Order chosen (1st 20
                                   sites) }
  CouOrd2          : STRING;     { Count Order chosen
                                   (remaining sites) }
  NumSites         : INTEGER;    { The number of sites TO be
                                   counted }
  NumStruct        : LONGINT;    { Number of structures
                                   generated per fulvic
                                   acid modelled }
  NumFA            : INTEGER;    { Number of different fulvic
                                   acids modelled }
  Order            : ARRAY[ 1 .. 30 ] of INTEGER; { Site
                                   counting order }
  FirstLine        : STRING;     { First line of data read }
  Secondline       : STRING;     { Second line of data read }
  LastSpace        : INTEGER;    { Posn of last space }
  BC               : ARRAY[ 1 .. 5 ] of REAL; { Bulk
                                   characteristics of the
```

```
                                  Fulvic acid
                                  1: Percentage carbon
                                  2: Fraction aromatic COOH
                                  3: Percentage aromaticity
                                  4: Fraction aliphatic
                                     methyls
                                  5: Fraction ortho quinones}
FD              : ARRAY[ 1 .. 8 ] of REAL; { Functional
                                    groups characteristics
                                  expressed as meq/g
                                  1: Carbonyl groups
                                  2: Carboxylate groups
                                  3: Phenolic groups
                                  4: Methoxy groups
                                  5: Quinones
                                  6: Aliphatic hydroxyls
                                  7: Aliphatic amines
                                  8: Aliphatic thiols }
FC              : ARRAY[ 1 .. 10 ] of REAL; { Functional
                                    groups characteristics
                                    expressed as meq/molecule
                                  As in FD but
                                  9: No of carbon atoms
                                  10: No of aromatic rings}
IFMIN           : ARRAY[ 1 .. 10 ] of REAL; { This and
                                  IFMAX are used so }
IFMAX           : ARRAY[ 1 .. 10 ] of REAL; { integer
                                values for the functional
                                group concentrations are
                                used by the program }
MaxAro          : INTEGER;    { Maximum no of aromatic
                                  rings }
FGTest          : REAL;       { Test if functional groups
                                  concns does not
                                  exceed max allowable }
R2              : REAL;       { The no of rings per FA in
                                  meq/g }
INAR            : LONGINT;    { No of aromatic
                                  incompatibilities }
INAL            : LONGINT;    { No of aliphatic
                                  incompatibilities }
NARH            : LONGINT;    { No of aromatic hydrogens
                                  allocated }
NST             : LONGINT;    { No of successful
                                  structures completed }
NOSTR           : LONGINT;    { Total No of incompatible
                                  structures }
MXNOST          : LONGINT;    { Max number of incompatible
                                  structures }
MAX             : LONGINT;   { Max no of total structures}
JJJ             : LONGINT;    { Counter of total
                                  structures }
S               : ArS;        { No of each site counted
                                  per structure }
SSUM            : ARRAY [ 1 .. 40 ] of LONGINT; { Sum of
                                  S }
SSQ             : ARRAY [ 1 .. 40 ] of LONGINT; { Sum of
```

```
                                    S*S }
StdDev          : ARRAY [ 1 .. 40 ] of REAL; { Standard
                                    Deviation of S }
JJ              : INTEGER;    { Counter }
XX              : ARRAY [ 1 .. 800 ] of REAL; { Set of
                                    random numbers }
FM              : ARRAY [ 1 .. 10 ] of REAL; { IFMAX[I] -
                                    FC[I] }
IM              : ARRAY [ 1 .. 10 ] of REAL; { REAL
                                    parameters for
                                    functional group concns
                                    used by RANDOM }
IA              : REAL;       { INTEGER value for phenols}
IB              : REAL;       { INTEGER value for COOHs }
IC              : REAL;       { INTEGER value for
                                    carbonyls }
ID              : REAL;       { INTEGER value for
                                    hydroxyls }
IE              : REAL;       { INTEGER value for
                                    methoxyls }
IQ              : REAL;      { INTEGER value for quinones}
INH             : REAL;       { INTEGER value for amines }
IS              : REAL;       { INTEGER value for thiols }
N               : REAL;       { INTEGER value for number
                                    of carbons }
IR              : REAL;       { INTEGER value for rings }
ICA             : REAL;       { Number of aliphatic
                                    carbons }
B1              : REAL;       { Number of aromatic COOHs
                                    per molecule }
IB1MIN          : REAL;       { Truncated B1 }
IB1MAX          : REAL;       { IB1MIN + 1 }
FB1             : REAL;       { IB1MAX - FB1 }
IB1             : REAL;       { INTEGER value for aromatic
                                    COOHs }
IB2             : REAL;       { INTEGER value for
                                    aliphatic COOHs }
IAR             : ArIAR;      { ARRAY containing info
                                    about groups on aromatic
                                    carbons }
IRP             : INTEGER;    { Number of para rings
                                    allocated }
IRM             : INTEGER;    { Number of meta rings
                                    allocated }
IRO             : INTEGER;    { Number of ortho rings
                                    allocated }
TR              : REAL;       { Sum of RO, RM, RP }
K               : REAL;       { Random no * TR + 1
                                    truncated }
IAROM           : REAL;       { Max no of aromatic binding
                                    positions }
IIP             : INTEGER;    { Counter of para rings
                                    allocated }
IIM             : INTEGER;    { Counter of meta rings
                                    allocated }
IIO             : INTEGER;    { Counter of ortho rings
                                    allocated }
```

```
Chk              : INTEGER;   { Test variable }
IQA              : INTEGER;   { Position TO allocate a
                                quinone }
ArInComp         : INTEGER;   { Test variable for aromatic
                                incompatibilities }
M                : INTEGER;   { Counter }
MN               : REAL;      { No of relevant functional
                                group }
II               : INTEGER;   { Position or site marker }
IAL              : ArIAL;    { ARRAY of aliphatic carbons}
MaxAli           : INTEGER;   { Max no of aliphatic
                                carbons }
Ali              : REAL;      { No of aliphatic carbons }
MMM              : INTEGER;   { No of aliphatic carbons
                                allocated }
IJ               : INTEGER;   { Position marker }
JI               : INTEGER;   { Position marker }
IRR              : REAL;      { ring assigment variable }
R                : ARRAY [ 1 .. 15 ] of INTEGER; { ARRAY
                                used TO arrange rings

                                randomly }
R1               : ARRAY [ 1 .. 15 ] of INTEGER; { ARRAY
                                used TO arrange rings

                                randomly }
NN               : INTEGER;   { Site condition }
XCA              : REAL;      { No of methyl carbons as
                                real no }
NXCA             : REAL;      { No of methyl carbons as
                                integer }
DIF              : REAL;      { XCA-NXCA }
BrInComp         : INTEGER;   { Test variable for
                                branching
                                incompatibilities }
AlInComp         : INTEGER;   { Test variable for
                                aliphatic
                                incompatibilities }
INST             : INTEGER;   { No of branching
                                incompatibilities }
MM               : REAL;      { Site Condition }
NG               : INTEGER;   { Group No }
QuinTest         : BOOLEAN;   { test variable that quinone
                                concn is within limits }
SumIA            : LONGINT;   { These are the Sum over all
                                structures of the }
SumIB1           : LONGINT;   { Relevant variable }
SumIB2           : LONGINT;
SumIC            : LONGINT;
SumID            : LONGINT;
SumIE            : LONGINT;
SumIQ            : LONGINT;
SumIR            : LONGINT;
SumINH           : LONGINT;
SumIS            : LONGINT;
Di               : INTEGER;   { Used for full output }
TNN              : REAL;      { Total number of nitrogen
```

```
                                    atoms }
TNH                 : REAL;          { Total number of hydrogen
                                       atoms }
TNO                 : REAL;          { Total number of oxygen
                                       atoms }
TNS                 : REAL;          { Total number of sulphur
                                       atoms }
TWTC                : REAL;          { Total weight of carbon }
TWTN                : REAL;          { Total weight of nitrogen }
TWTO                : REAL;          { Total weight of oxygen }
TWTH                : REAL;          { Total weight of hydrogen }
TWTS                : REAL;          { Total weight of sulphur }
ElCom               : ARRAY [ 1 .. 6 ] OF REAL; { ARRAY of
                                       element compositions
                                       per structure
                                       1: carbon
                                       2: oxygen
                                       3: hydrogen
                                       4: nitrogen
                                       5: sulphur
                                       6: molar weight }
ECSUM               : ARRAY [ 1 .. 6 ] OF REAL; { Cumulative
                                       sum of ElCom }
ECSQ                : ARRAY [ 1 .. 6 ] OF REAL; { Sum of
                                       ElCom*ElCom }
SDEC                : ARRAY [ 1 .. 6 ] OF REAL; { Std Dev of
                                       ElCom }
RNC                 : REAL;          { Mean no of carbon atoms
                                       per structure }
RNH                 : REAL;          { Mean no of hydrogen atoms
                                       per structure }
HC                  : REAL;          { H/C Ratio }
AROMC               : REAL;          { Mean no of aromatic
                                       carbons }
COOHC               : REAL;          { Mean no of carboxyl
                                       carbons }
COC                 : REAL;          { Mean no of carbonyl
                                       carbons }
OCH3C               : REAL;          { Mean no of methoxyl
                                       carbons }
ALPHC               : REAL;          { Mean no of aliphatic
                                       carbons }
QUINC               : REAL;         { Mean no of quinone carbons}
AROMH               : REAL;          { Mean no of aromatic
                                       hydrogens }
COOHH               : REAL;          { Mean no of carboxyl
                                       hydrogens }
OHH                 : REAL;          { Mean no of hydroxyl
                                       hydrogens }
ANHH                : REAL;         { Mean no of amine hydrogens}
SHH                 : REAL;         { Mean no of thiol hydrogens}
OCH3H               : REAL;          { Mean no of methoxyl
                                       hydrogens }
ALPHH               : REAL;          { Mean no of aliphatic
                                       hydrogens }
PHENH               : REAL;          { Mean no of phenolic
                                       hydrogens }
```

```
  NPOH              : INTEGER;    { No of phenols allocated }
  NOH               : INTEGER;    { No of hydroxyls allocated}
  NNH               : INTEGER;    { No of amines allocated }
  NSH               : INTEGER;    { No of thiols allocated }
  NALCOOH           : INTEGER;    { No of aliphatic carboxyls
                                    allocated }
  NARCOOH           : INTEGER;    { No of aromatic carboxyls
                                    allocated }
  NQO               : INTEGER;    { No of quinones allocated }
  NCO               : INTEGER;    { No of ketones allocated }
  NRING             : INTEGER;    { No of rings allocated }
  NOCH3             : INTEGER;    { No of methoxyls allocated}
  NXC               : INTEGER;    { No of aliphatic methyls
                                    allocated }
  SumMF             : REAL;       { Average fraction of Cs in
                                    methyls }
  SumICA            : LONGINT;    { Total no of aliphatic Cs }
  SumIRO            : LONGINT;    { Total no of ortho rings }
  SumIRM            : LONGINT;    { Total no of meta rings }
  SumIRP            : LONGINT;    { Total no of para rings }
  SumRing           : LONGINT;    { Total no of rings }
  Code              : Array [1 .. 40] of String [4]; { Ligand
                                    Codes }

BEGIN

{ INPUT OF DATA }
 CODE[ 1] := '12BQ';
 CODE[ 2] := '3HBQ';
 CODE[ 3] := 'CAT ';
 CODE[ 4] := 'PHTH';
 CODE[ 5] := 'SAL ';
 CODE[ 6] := 'ACPH';
 CODE[ 7] := 'BENZ';
 CODE[ 8] := 'PHEN';
 CODE[ 9] := 'ACAC';
 CODE[10] := 'MAL ';
 CODE[11] := 'DHMB';
 CODE[12] := 'SUCC';
 CODE[13] := 'DEM ';
 CODE[14] := '3HBT';
 CODE[15] := '2HMP';
 CODE[16] := 'PROP';
 CODE[17] := 'CIT ';
 CODE[20] := 'DAP ';
 CODE[21] := 'ASP ';
 CODE[22] := 'SER ';
 CODE[23] := 'ISER';
 CODE[24] := 'ALA ';
 CODE[25] := 'BEAL';
 CODE[26] := 'PN  ';
 CODE[27] := 'ETA ';
 CODE[30] := 'CYS ';
 CODE[31] := 'TMA ';
 CODE[32] := 'TLA ';
 CODE[33] := 'AET ';
 CODE[34] := 'MET ';
```

```
 CLEARVIEWPORT;
 RANDOMIZE;
 MaxAro := 15;
 MaxAli := 100;
 OUTTEXTXY (PosX(0.375),PosY(0.208),'RANDOM CALCULATIONS');
 RECTANGLE(PosX(0.328) PosY(0.156),PosX(0.656),PosY(0.260));
 OUTTEXTXY (PosX (0.157), PosY (0.365), ' Enter the name of
..... the file from which the');
 OUTTEXTXY (PosX (0.157), PosY (0.469), ' fulvic acid
..... characteristics should be read:');
 MOVETO (PosX (0.725), PosY (0.469));
 FetchInp (FileIn);
 ASSIGN (FileRead, FileIn);
 RESET (FileRead);
 READLN (FileRead, Ratio);
 J := 1;
 FOR I := 1 TO LENGTH(Ratio) DO
 BEGIN
  IF Ratio[I] = ':' THEN
  BEGIN
   Colons[J] := I;
   J := J + 1;
  END;
 END;
 VAL (COPY (Ratio, 1, Colons[1]-1), RO, Err);
 VAL (COPY(Ratio,Colons[1]+1,Colons[2]-1-Colons[1]),RM,Err);
VAL(COPY(Ratio,Colons[2]+1,LENGTH(Ratio)-Colons[2]),RP,Err);
 READLN (FileRead, PrOpt);
 READLN (FileRead, NumSites);
 READLN (FileRead, CouOrd1);
 READLN (FileRead, CouOrd2);
 IF NumSites < 21 THEN
 BEGIN
  FOR I := 1 TO NumSites DO VAL (COPY (CouOrd1, (I-1)*3+1,
.....2), Order[I], Err);
 END;
 IF NumSITES > 20 THEN
 BEGIN
  FOR I := 1 TO 20 DO VAL (COPY (CouOrd1, (I-1)*3+1, 2),
.....Order[I], Err);
  FOR I := 21 TO NumSites DO VAL (COPY (CouOrd2, (I-21)*3+1,
.....2), Order[I], Err);
 END;
 READLN (FileRead, NumStruct);
 READLN (FileRead, NumFA);
 OUTTEXTXY (PosX (0.157),PosY (0.625), ' Enter the name of
..... the file to which');
 OUTTEXTXY (PosX (0.157), PosY (0.729), ' you would like to
..... send output: ');
 MOVETO (PosX (0.562), PosY (0.729));
 FetchInp (FileOut);
 ASSIGN (FileName, FileOut);
 REWRITE (FileName);
 CLEARVIEWPORT;
 OUTTEXTXY (PosX (0.475), PosY (0.521), 'PROCESSING');
 FOR NS := 1 TO NumFA DO
 BEGIN
```

```
  READLN (FileRead, FirstLine);
  LastSpace := 0;
  J := 1;
  FOR I := 1 TO LENGTH(FirstLine) DO
  BEGIN
   IF FirstLine[I] = ' ' THEN
   BEGIN
    VAL (COPY (FirstLine, LastSpace+1, I-LastSpace-1),
.....BC[J], Err);
    LastSpace := I;
    J := J + 1;
   END;
  END;
  VAL(COPY (FirstLine, LastSpace+1, LENGTH (FirstLine)-
.....LastSpace), BC[5], Err);
  READLN (FileRead, SecondLine);
  LastSpace := 0;
  J := 1;
  FOR I := 1 TO LENGTH (SecondLine) DO
  BEGIN
   IF SecondLine[I] = ' ' THEN
   BEGIN
    VAL (COPY (SecondLine, LastSpace+1, I-LastSpace-1),
.....FD[J], Err);
    LastSpace := I;
    J := J + 1;
   END;
  END;
  VAL (COPY (SecondLine, LastSpace+1, LENGTH (SecondLine)-
.....LastSpace), FD[8], Err);
  FOR I := 1 TO 8 DO FC[I] := FD[I]*2;
  FC[5] := FC[5]/2;
  FC[9] := 2000*BC[1]/1201.1;
  FC[10] := FC[9]*BC[3]/600;
  WRITELN (FileName);
  WRITELN (FileName, '                          MODEL ', NS);
  FOR I := 1 TO 10 DO
  BEGIN
   IFMIN[I] := INT (FC[I]);
   IFMAX[I] := IFMIN[I]+1;
  END;
  FGTest := 6*IFMAX[10]+IFMAX[2]+IFMAX[1]+IFMAX[4];
  Ali := IFMIN[9]-5*IFMAX[10]-IFMAX[2]-IFMAX[4];
  IF (FC[10]<MaxAro) AND (FGTest<IFMIN[9]) and (Ali<MaxAli)
.....THEN
  BEGIN
   WRITELN (FileName);
   WRITELN (FileName, 'INPUT DATA');
   WRITELN;
   WRITELN (FileName, 'PERCENTAGE CAR
.....BON                    = ', BC[1]:9:3, ' %');
   WRITELN (FileName);
   WRITELN (FileName, 'FRACTION OF ALIPHATIC
..... CARBONS AS CH3 = ', BC[4]:9:3);
   WRITELN (FileName);
   WRITELN (FileName, 'FRACTION OF ORTHO QUIN
.....ONES           = ', BC[5]:9:3);
```

```
   WRITELN (FileName);
   WRITELN (FileName, 'FRACTION AROMATIC CO
.....OH                = ', BC[2]:9:3);
   WRITELN (FileName);
   WRITELN (FileName, 'PERCENTAGE AROMATIC CAR
.....BON           = ', BC[3]:9:3, ' %');
   R2 := FC[10]/2;
   WRITELN (FileName);
   WRITELN (FileName, 'GROUPS:  KET   COOH   PHEN OH  OC
.....H3    QUIN    ALC OH   NH2     SH     RINGS');
   WRITE (FileName, '    ');
   FOR J := 1 TO 8 DO WRITE (FileName, FD[J]:8:3);
   WRITELN (FileName, R2:8:3);
   WRITELN (FileName);
   WRITELN (FileName, 'COUNTING ORDER: ', CouOrd1);
   WRITELN (FileName, '                ', CouOrd2);

{ GENERATION OF STRUCTURES }
   SumIA := 0;
   SumIB1 := 0;
   SumIB2 := 0;
   SumIC := 0;
   SumID := 0;
   SumIE := 0;
   SumIQ := 0;
   SumIR := 0;
   SumINH := 0;
   SumIS := 0;
   SumMF := 0;
   SumICA := 0;
   SumIRO := 0;
   SumIRM := 0;
   SumIRP := 0;
   INAR :=0;
   INAL :=0;
   INST :=0;
   NARH :=0;
   NST :=0;
   NOSTR :=0;
   MXNOST := 2*NumStruct;
   MAX := 3*NumStruct;
   JJJ := 0;
   FOR I := 1 TO 40 DO SSUM[I] :=0;
   FOR I := 1 TO 40 DO SSQ[I] :=0;
   FOR I := 1 TO 6 DO ECSUM[I] := 0;
   FOR I := 1 TO 6 DO ECSQ[I] := 0;
   QuinTest := True;
   IF (FC[5] > FC[10]) THEN QuinTest := False;
   WHILE (JJJ < MAX) and (QuinTest) DO
   BEGIN
    IRO := 0;
    IRM := 0;
    IRP := 0;
    NPOH := 0;
    NOH := 0;
    NNH := 0;
    NSH := 0;
```

```
    NALCOOH := 0;
    NARCOOH := 0;
    NQO := 0;
    NCO := 0;
    NRING := 0;
    NOCH3 :=0;
    NXC := 0;
    FOR I := 1 TO 40 DO S[I] := 0;
    ArInComp := 1;
    BrInComp := 1;
    AlInComp := 1;
    JJ := 0;
    FOR I := 1 TO 800 DO XX[I] := Random;

{ Choose the parameters IR, IA, IB, IC, ID, IN, IS }
    FOR I := 1 TO 10 DO
    BEGIN
     FM[I] := IFMAX[I] - FC[I];
     JJ := JJ + 1;
     IM[I] := IFMIN[I];
     IF XX[JJ] >= FM[I] THEN IM[I] := IFMAX[I];
    END;
    IA := IM[3];
    IB := IM[2];
    IC := IM[1];
    ID := IM[6];
    IE := IM[4];
    IQ := IM[5];
    INH := IM[7];
    IS := IM[8];
    N  := IM[9];
    IR := IM[10];
    ICA := N-6*IR-IB-IC-IE;
    B1 := BC[2]*IB;
    IB1MIN := INT (B1);
    IB1MAX := IB1MIN + 1;
    FB1 := IB1MAX-B1;
    JJ := JJ + 1;
    IB1 := IB1MIN;
    IF XX[JJ] >= FB1 THEN IB1 := IB1MAX;
    IB2 := IB - IB1;

{ DETERMINE NUMBER OF EACH TYPE OF RING }
    FOR J := 1 TO 2 DO
    BEGIN
     FOR I := 1 TO 40 DO IAR[J,I] := 0;
    END;
    IF BC[3] <> 0 THEN
    BEGIN
     TR := RO + RM + RP;
     FOR I := 1 TO TRUNC (IR) DO
     BEGIN
      JJ := JJ + 1;
      K := (XX[JJ]*TR);
      IF K < RO THEN IRO := IRO + 1;
      IF (K < (RO+RM)) AND (K >= RO) THEN IRM := IRM + 1;
      IF K >= (RO+RM) THEN IRP := IRP + 1;
```

```
      END;
      IAROM := 4*IR;

{ Assign  Quinone groups }
      IIP := 0;
      IIM := 0;
      IIO := 0;

{ Choose whether quinone groups are ortho or para }
      IF IQ <> 0 THEN
      BEGIN
       IF IQ > IR THEN ArInComp := 0;
       J := 0;
       WHILE (ArInComp <> 0) AND (J < IQ) DO
       BEGIN
        Chk := 1;
        JJ := JJ + 1;

        { Assign  Para Quinones }
        IF XX[JJ] >= BC[5] THEN
        BEGIN
         JJ := JJ + 1;

         { Assign  TO an ortho ring }
         IF XX[JJ]*IR < IRO THEN
         BEGIN
          IIO := IIO + 1;
          IF IRO >= IIO THEN
          BEGIN
           IQA := (IIO)*4-3;
           IAR[1,IQA] := 15;
           IAR[1,IQA+3] := 15;
           Chk := 0;
          END;
         END;

         { Assign  TO a meta ring }
         IF (XX[JJ]*IR < (IRO+IRM)) AND (XX[JJ]*IR >= IRO)
..... AND (Chk <> 0) THEN
         BEGIN
          IIM := IIM + 1;
          IF IRM >= IIM THEN
          BEGIN
           Chk := 0;
           IQA := 4*(IRO+IIM)-3;
           IAR[1,IQA] := 15;
           IAR[1,IQA+2] := 15;
          END;
         END;

         { Assign  TO a para ring }
         IF  (Chk <> 0) THEN
         BEGIN
          IIP := IIP + 1;
          IF IRP >= IIP THEN
          BEGIN
           IQA := 4*(IRO+IRM+IIP)-3;
```

```
          JJ := JJ+1;
          IF XX[JJ] < 0.5 THEN IQA := IQA+1;
          IAR[1,IQA+2] := 15;
          IAR[1,IQA] := 15;
          Chk := 0;
         END;
        END;
       END;

       {Assign  ortho quinones }
       IF Chk <> 0 THEN
       BEGIN
        JJ := JJ + 1;

        { Assign  TO an ortho ring }
        IF XX[JJ]*IR < IRO THEN
        BEGIN
         IIO := IIO + 1;
         IF IRO >= IIO THEN
         BEGIN
          IQA := (IIO)*4-2;
          JJ := JJ + 1;
          IF XX[JJ] < (1/3) THEN IQA := IQA-1;
          IF XX[JJ] >= 2/3 THEN IQA := IQA+1;
          IAR[1,IQA] := 15;
          IAR[1,IQA+1] := 15;
          Chk := 0;
         END;
        END;

        { Assign  TO a meta ring }
        IF (XX[JJ]*IR < (IRO+IRM)) AND (XX[JJ]*IR >= IRO)
..... AND (Chk< 0) THEN
        BEGIN
         IIM := IIM + 1;
         IF IRM >= IIM THEN
         BEGIN
          Chk := 0;
          IQA := 4*(IRO+IIM)-2;
          JJ := JJ+1;
          IF XX[JJ] < 0.5 THEN IQA := IQA+1;
          IAR[1,IQA+1] := 15;
          IAR[1,IQA] := 15;
         END;
        END;

        { Assign  TO a para ring }
        IF  (Chk <> 0) THEN
        BEGIN
         IIP := IIP + 1;
         IF IRP >= IIP THEN
         BEGIN
          IQA := 4*(IRO+IRM+IIP)-3;
          JJ := JJ + 1;
          IF XX[JJ] < 0.5 THEN IQA := IQA + 2;
          IAR[1,IQA+1] := 15;
          IAR[1,IQA] := 15;
```

```
          Chk := 0;
         END;
        END;
       END;
       J := J + 1;
       IF Chk = 0 THEN NQO := NQO + 1;
       IF Chk <> 0 THEN J := J - 1;
       IF JJ = 200 THEN ArInComp := 0;
      END;
     END;

{ Assign  the IA phenols, IE methoxyls and IB1 COOHs }

     FOR M := 1 TO 3 DO
     BEGIN
      IF M = 1 THEN MN := IA;
      IF M = 2 THEN MN := IE;
      IF M = 3 THEN MN := IB1;
      I := 0;
      WHILE (ArInComp <> 0) AND (I < MN) DO
      BEGIN
       JJ := JJ + 1;
       J := Trunc (XX[JJ]*IArom)+1;
       IF IAR[1,J] <> 0 THEN I := I-1;
       IF IAR[1,J] = 0 THEN
       BEGIN
        IF M = 1 THEN
        BEGIN
         IAR[1,J] := 1;
         NPOH := NPOH + 1;
        END;
        IF M = 2 THEN
        BEGIN
         IAR[1,J] := 3;
         NOCH3 := NOCH3 + 1;
        END;
        IF M = 3 THEN
        BEGIN
         IAR[1,J] := 7;
         NARCOOH := NARCOOH + 1;
        END;
       END;
       I := I + 1;
       IF JJ = 350 THEN ArInComp := 0;
      END;
     END;

    END;
    IF ArInComp = 0 THEN
    BEGIN
     INAR := INAR + 1;
     NOSTR := NOSTR + 1;
    END;

{ Assign  IC C=O Groups to Arbitrary positions }
    IF ArInComp <> 0 THEN
    BEGIN
```

```
      FOR I := 1 TO 4 DO
      BEGIN
       FOR II := 1 TO 100 DO IAL[I,II] := 0;
      END;
      MMM := TRUNC (N-5*IR-IB-IE);
      IF IC <> 0 THEN
      BEGIN
       I := 0;
       WHILE I < IC DO
       BEGIN
        JJ := JJ + 1;
        J := TRUNC (XX[JJ]*MMM)+1;
        IF IAL[1,J] <> 0 THEN I := I-1;
        IF IAL[1,J] = 0 THEN
        BEGIN
         IJ := J + 1;
         JI := J - 1;
         IF J = MMM THEN IJ := 1;
         IF J = 1 THEN JI := MMM;
         IF (IAL[1,JI]<>8) AND (IAL[1,IJ]<>8) THEN
         BEGIN
          IAL[1,J] := 8;
          NCO := NCO + 1;
         END;
         IF (IAL[1,JI]=8) OR (IAL[1,IJ]=8) THEN I := I - 1;
        END;
        I := I + 1;
       END;
      END;

{ Assign  the R Rings }
      IF IR <> 0 THEN
      BEGIN
       I := 0;
       WHILE I < IR DO
       BEGIN
        JJ := JJ + 1;
        J := TRUNC (XX[JJ]*MMM)+1;
        IF IAL[1,J] <> 0 THEN I := I-1;
        IF IAL[1,J] = 0 THEN
        BEGIN
         IAL[1,J] := 6;
         NRING := NRING + 1;
        END;
        I := I + 1;
       END;

{ Arbitrarily assign the rings as ortho, meta or para }
       NN := 0;
       FOR M := 1 TO 3 DO
       BEGIN
        IF M = 1 THEN IRR := IRO;
        IF M = 2 THEN IRR := IRM;
        IF M = 3 THEN IRR := IRP;
        IF IRR <> 0 THEN
        BEGIN
         FOR I := 1 TO TRUNC (IRR) DO
```

```
        BEGIN
         NN := NN + 1;
         IF M = 1 THEN R[NN] := 5;
         IF M = 2 THEN R[NN] := 6;
         IF M = 3 THEN R[NN] := 7;
        END;
       END;
      END;
      FOR I := 1 TO TRUNC (IR) DO R1[I] := 0;
      M := 0;
      WHILE M < IR DO
      BEGIN
       JJ := JJ + 1;
       J := TRUNC (XX[JJ]*IR)+1;
       IF R1[J] = 0 THEN
       BEGIN
        M := M + 1;
        R1[J] := R[M]
       END;
      END;
      NN := 0;
      FOR I := 1 TO MMM DO
      BEGIN
       IF IAL[1,I] = 6 THEN
       BEGIN
        NN := NN + 1;
        IAL[1,I] := R1[NN];
       END;
      END;
     END;

{ Assign  the CH3 groups and hence the -CH= groups }
     NXCA := INT(BC[4]*ICA);
     XCA := BC[4]*ICA;
     DIF := XCA-NXCA;
     JJ := JJ + 1;
     IF XX[JJ] < DIF THEN NXCA := NXCA + 1;
     IF NXCA <> 0 THEN
     BEGIN
      I := 0;
      While (BrInComp <> 0) AND (I < NXCA) DO
      BEGIN
       JJ := JJ + 1;
       Chk := 1;
       J := TRUNC (XX[JJ]*MMM)+1;
       IF IAL[1,J] = 0 THEN
       BEGIN
        IJ := J + 1;
        JI := J - 1;
        IF J = MMM THEN IJ := 1;
        IF J = 1 THEN JI := MMM;
        IF IAL[1,IJ] = 0 THEN
        BEGIN
         IAL[1,J] := 4;
         IAL[1,IJ] := 1;
         NXC := NXC + 1;
         Chk := 0;
```

```
          END;
          IF (IAL[1,JI] = 0) AND (Chk<>0) THEN
          BEGIN
           IAL[1,J] := 1;
           IAL[1,JI] := 4;
           NXC := NXC + 1;
           Chk := 0;
          END;
         END;
         IF JJ = 500 THEN BrInComp := 0;
         IF Chk <> 0 THEN I := I-1;
         I := I + 1;
        END;
       END;

{ Assign  the remaining carbons as -CH2- }
      FOR I := 1 TO MMM DO
      BEGIN
       IF IAL[1,I] = 0 THEN IAL[1,I] := 2;
      END;

{ Assign  the aliphatic COOHs }
      I := 0;
      II := 4;
      MM := IB2;
      IF IB2 <> 0 THEN
      BEGIN
       While (BrInComp <> 0) AND (AlInComp <>0) AND (I<MM) DO
       BEGIN
        JJ := JJ + 1;
        Chk := 1;
        J := TRUNC (XX[JJ]*MMM)+1;
        IF IAL[1,J] = 1 THEN
        BEGIN
         IF IAL[2,J] = 0 THEN
         BEGIN
          IAL[2,J] := II;
          Chk := 0;
         END;
         IF (Chk<>0) AND (IAL[3,J]=0) THEN
         BEGIN
          IAL[3,J] := II;
          Chk := 0;
         END;
        END;
        IF IAL[1,J] = 2 THEN
        BEGIN
         IJ := J+1;
         JI := J-1;
         IF J = MMM THEN IJ := 1;
         IF J = 1 THEN JI := MMM;
         IF (IAL[1,IJ]<>8) AND (IAL[1,JI]<>8) THEN
         BEGIN
          IF IAL[2,J] = 0 THEN
          BEGIN
           IAL[2,J] := II;
           Chk := 0;
```

```
          END;
          IF (Chk<>0) AND (IAL[3,J]=0) THEN
          BEGIN
           IAL[3,J] := II;
           Chk := 0;
          END;
         END;
        END;
        IF IAL[1,J] = 4 THEN
        BEGIN
         IJ := J+2;
         JI := J-1;
         IF J = MMM THEN IJ := 2;
         IF J = (MMM-1) THEN IJ := 1;
         IF J = 1 THEN JI := MMM;
         IF (IAL[1,IJ]<>8) AND (IAL[1,JI]<>8) THEN
         BEGIN
          IF IAL[2,J] = 0 THEN
          BEGIN
           IAL[2,J] := II;
           Chk := 0;
          END;
         END;
        END;
        I := I + 1;
        IF (Chk<>0) THEN I := I-1;
        IF JJ = 700 Then AlInComp := 0;
        IF Chk = 0 THEN NALCOOH := NALCOOH + 1;
       END;
      END;

{ Assign  the OHs, NH2s and SHs }
      FOR M := 1 TO 3 DO
      BEGIN;
       I := 0;
       IF M = 1 THEN
       BEGIN
        II := 3;
        MM := ID;
       END;
       IF M = 2 THEN
       BEGIN
        II := 1;
        MM := INH;
       END;
       IF M = 3 THEN
       BEGIN
        II := 9;
        MM := IS;
       END;
       IF MM <> 0 THEN
       BEGIN
        While (BrInComp<>0) AND (AlInComp<>0) AND (I<MM) DO
        BEGIN
         JJ := JJ + 1;
         J := TRUNC (XX[JJ]*MMM)+1;
         Chk := 1;
```

```
        IF (IAL[1,J] = 1) OR (IAL[1,J] = 2) THEN
        BEGIN
         IF IAL[2,J] = 0 THEN
         BEGIN
          IAL[2,J] := II;
          Chk := 0;
         END;
         IF (Chk<>0) AND (IAL[3,J]=0) THEN
         BEGIN
          IAL[3,J] := II;
          Chk := 0;
         END;
        END;
        IF IAL[1,J] = 4 THEN
        BEGIN
         IF IAL[2,J] = 0 THEN
         BEGIN
          IAL[2,J] := II;
          Chk := 0;
         END;
        END;
        I := I + 1;
        IF (Chk<>0) THEN I := I-1;
        IF Chk = 0 THEN
        BEGIN
         IF M = 1 THEN NOH := NOH + 1;
         IF M = 2 THEN NNH := NNH + 1;
         IF M = 3 THEN NSH := NSH + 1;
        END;
        IF JJ = 800 Then AlInComp := 0;
       END;
      END;
     END;
     IF BrInComp = 0 THEN
     BEGIN
      NOSTR := NOSTR + 1;
      INST := INST + 1;
     END;
     IF AlInComp = 0 THEN
     BEGIN
      NOSTR := NOSTR + 1;
      INAL := INAL + 1;
     END;
    END;
    JJJ := JJJ + 1;
    IF NOSTR = MXNOST THEN JJJ := MAX;
   IF (ArInComp<>0) AND (BrInComp<>0) AND (AlInComp<>0) THEN
    BEGIN
     NST := NST + 1;
     IF NST = NumStruct THEN JJJ := MAX;

{ Count the number of aromatic H's }
     IF IR <> 0 THEN
     BEGIN
      FOR I := 1 TO TRUNC (IAROM) DO
      BEGIN
       IF IAR[1,I] = 0 THEN NARH := NARH + 1;
```

```
      END;
     END;

{ Binding Site Counting }
     FOR NG := 1 TO NumSites DO
     BEGIN
       CASE Order[NG] OF
       1    : AroCount (1, 30, IRO, IRM, IRP, S, IAR);
       2    : AroCount (2, 16, IRO, IRM, IRP, S, IAR);
       3    : AroCount (3,  2, IRO, IRM, IRP, S, IAR);
       4    : AroCount (4, 14, IRO, IRM, IRP, S, IAR);
       5    : AroCount (5,  8, IRO, IRM, IRP, S, IAR);
6: IF (IC<>0) AND (IA<>0) THEN ACPH (IRO,IRM,MMM,S,IAR,IAL);
       7    : IF IB1 <> 0 THEN MonoAro (7, IAROM, S, IAR);
       8    : IF IA <> 0 THEN MonoAro (8, IAROM, S, IAR);
       9    : IF IC <> 0 THEN ACAC (MMM, S, IAL);
       10   : Triden (10, 7, 4, MMM, S, IAL);
       11   : Triden (11, 7, 3, MMM, S, IAL);
       12   : BidenDiff (12, 4, 4, MMM, S, IAL);
       13   : Bidensame (13, 8, MMM, S, IAL);
       14   : BidenDiff (14, 4, 3, MMM, S, IAL);
       15   : Bidensame (15, 7, MMM, S, IAL);
       16   : IF IB2 <> 0 THEN PROP (MMM, S, IAL);
       17   : Citric (MMM, S, IAL);
       20   : Triden (20, 5, 1, MMM, S, IAL);
       21   : Triden (21, 5, 4, MMM, S, IAL);
       22   : Triden (22, 5, 3, MMM, S, IAL);
       23   : Triden (23, 7, 1, MMM, S, IAL);
       24   : Bidensame (24, 5, MMM, S, IAL);
       25   : BidenDiff (25, 4, 1, MMM, S, IAL);
       26   : BidenDiff (26, 1, 1, MMM, S, IAL);
       27   : BidenDiff (27, 3, 1, MMM, S, IAL);
       30   : Triden (30, 5, 9, MMM, S, IAL);
       31   : Triden (31, 13, 4, MMM, S, IAL);
       32   : Bidensame (32, 13, MMM, S, IAL);
       33   : BidenDiff (33, 3, 9, MMM, S, IAL);
       34   : BidenDiff (34, 1, 9, MMM, S, IAL);
      END;
     END;
     FOR I := 1 TO 40 DO
     BEGIN
      SSUM[I] := SSUM[I] + S[I];
      SSQ[I] := SSQ[I] + S[I]*S[I];
     END;
     SumIA := SumIA + NPOH;
     SumIB1 := SumIB1 + NALCOOH;
     SumIB2 := SumIB2 + NARCOOH;
     SumIC := SumIC + NCO;
     SumID := SumID + NOH;
     SumIE := SumIE + NOCH3;
     SumIQ := SumIQ + NQO;
     SumIR := SumIR + NRING;
     SumINH := SumINH + NNH;
     SumIS := SumIS + NSH;
     SumMF := SumMF + NXC/ICA;
     SumICA := SumICA + TRUNC (ICA);
     SumIRO := SumIRO + TRUNC (IRO);
```

```
      SumIRM := SumIRM + TRUNC (IRM);
      SumIRP := SumIRP + TRUNC (IRP);

{ Determining elemental composition }
      TNO := IA + IC + ID + 2*IB + IE + 2*IQ;
      TNH := 2*(N - IB - IC - IQ - 4*IR) + INH;
      TNN := INH;
      TNS := IS;
      TWTO := 15.9994*TNO;
      TWTC := 12.01115*N;
      TWTN := 14.007*TNN;
      TWTS := 32.064*TNS;
      TWTH := 1.00797*TNH;
      ElCom[6] := TWTO + TWTC + TWTN + TWTS + TWTH;
      ElCom[1] := TWTC*100/ElCom[6];
      ElCom[2] := TWTO*100/ElCom[6];
      ElCom[3] := TWTH*100/ElCom[6];
      ElCom[4] := TWTN*100/ElCom[6];
      ElCom[5] := TWTS*100/ElCom[6];
      FOR I := 1 TO 6 DO
      BEGIN
       ECSUM[I] := ECSUM[I] + ElCom[I];
       ECSQ[I] := ECSQ[I] + ElCom[I]*ElCom[I];
      END;

{ Output for intermediate option }
      IF PrOpt = 'INTERMEDIATE' THEN
      BEGIN
       WRITELN (FileName);
       WRITELN (FileName, 'STRUCTURE NO : ', NST);
       WRITELN (FileName);
       IF NumSites < 21 THEN
       BEGIN
        WRITELN (FileName, 'SITE NO    : ', CouOrd1);
        WRITE (FileName, 'NO COUNTED :');
        FOR I := 1 TO NumSites DO
        BEGIN
         II := Order[I];
         WRITE (FileName, S[II]:3);
        END;
        WRITELN (FileName);
       END;
       IF NumSites > 20 THEN
       BEGIN
        WRITELN (FileName, 'SITE NO    : ', CouOrd1);
        WRITE (FileName, 'NO COUNTED :');
        FOR I := 1 TO 20 DO
        BEGIN
         II := Order[I];
         WRITE (FileName, S[II]:3);
        END;
        WRITELN (FileName);
        WRITELN (FileName, 'SITE NO    : ', CouOrd2);
        WRITE (FileName, 'NO COUNTED :');
        FOR I := 21 TO NumSites DO
        BEGIN
         II := Order[I];
```

```
        WRITE (FileName, S[II]:3);
       END;
       WRITELN (FileName);
      END;
     END;

{ Output for full print option }
     IF PrOpt = 'FULL' THEN
     BEGIN
      WRITELN (FileName);
      WRITELN (FileName, 'STRUCTURE NO : ', NST);
      WRITELN (FileName);
      WRITELN (FileName, 'ORTHO RINGS: ', IRO:3, ' META
..... RINGS: ', IRM:3, ' PARA RINGS: ', IRP:3);
      WRITELN (FileName);
      Di := TRUNC (IAROM/39);
      FOR I := 1 TO Di DO
      BEGIN
    FOR J:=1 TO 39 DO WRITE (FileName,IAR[1,39*(Di-1)+J]:2);
       WRITELN (FileName);
    FOR J:=1 TO 39 DO WRITE (FileName,IAR[2,39*(Di-1)+J]:2);
       WRITELN (FileName);
       WRITELN (FileName);
      END;
      FOR I:=1 TO TRUNC (IAROM-39*Di) DO WRITE
.....(FileName,IAR[1,39*(Di)+I]:2);
      WRITELN (FileName);
      FOR I := 1 TO TRUNC (IAROM-39*Di) DO WRITE (FileName,
.....IAR[2,39*(Di)+I]:2);
      WRITELN (FileName);
      WRITELN (FileName);
      Di := TRUNC (MMM/39);
      FOR I := 1 TO Di DO
      BEGIN
    FOR J:=1 TO 39 DO WRITE (FileName,IAL[1,39*(Di-1)+J]:2);
       WRITELN (FileName);
    FOR J:=1 TO 39 DO WRITE (FileName,IAL[2,39*(Di-1)+J]:2);
       WRITELN (FileName);
    FOR J:=1 TO 39 DO WRITE (FileName,IAL[3,39*(Di-1)+J]:2);
       WRITELN (FileName);
    FOR J:=1 TO 39 DO WRITE (FileName,IAL[4,39*(Di-1)+J]:2);
       WRITELN (FileName);
       WRITELN (FileName);
      END;
      FOR I:=1 TO (MMM-39*Di) DO WRITE (FileName,
.....IAL[1,39*(Di)+I]:2);
      WRITELN (FileName);
      FOR I := 1 TO (MMM-39*Di) DO WRITE (FileName,
.....IAL[2,39*(Di)+I]:2);
      WRITELN (FileName);
      FOR I := 1 TO (MMM-39*Di) DO WRITE (FileName,
.....IAL[3,39*(Di)+I]:2);
      WRITELN (FileName);
      FOR I := 1 TO (MMM-39*Di) DO WRITE (FileName,
.....IAL[4,39*(Di)+I]:2);
      WRITELN (FileName);
      WRITELN (FileName);
```

```
      IF NumSites < 21 THEN
      BEGIN
       WRITELN (FileName, 'SITE NO    : ', CouOrd1);
       WRITE (FileName, 'NO COUNTED :');
       FOR I := 1 TO NumSites DO
       BEGIN
        II := Order[I];
        WRITE (FileName, S[II]:3);
       END;
       WRITELN (FileName);
      END;
      IF NumSites > 20 THEN
      BEGIN
       WRITELN (FileName, 'SITE NO    : ', CouOrd1);
       WRITE (FileName, 'NO COUNTED :');
       FOR I := 1 TO 20 DO
       BEGIN
        II := Order[I];
        WRITE (FileName, S[II]:3);
       END;
       WRITELN (FileName);
       WRITELN (FileName, 'SITE NO    : ', CouOrd2);
       WRITE (FileName, 'NO COUNTED :');
       FOR I := 21 TO NumSites DO
       BEGIN
        II := Order[I];
        WRITE (FileName, S[II]:3);
       END;
       WRITELN (FileName);
      END;
     END;
    END;
   END;
  END;

{ Standard deviation calculation }
  IF NST > 1 THEN
  BEGIN
  { Note the Std Devs for ligand concentrations are SDs of
    the mean whereas for elemental composition they are the
    SDs of a single sample }
   FOR I := 1 TO 40 DO StdDev[I] := SQRT ((SSQ[I] -
.....SSUM[I]*SSUM[I]/NST)/((NST-1)*NST));
   FOR I := 1 TO 6 DO SDEC[I] := SQRT ((ECSQ[I] -
.....ECSUM[I]*ECSUM[I]/NST)/(NST-1));
  END;

{ Output }
  Chk := 1;
  IF NOT QuinTest THEN
  BEGIN
   TooManyQui (FileName);
   Chk := 0;
  END;
  IF Ali >= MaxAli THEN
  BEGIN
   ToomanyAli (FileName);
```

```
   Chk := 0;
  END;
  IF NOSTR >= MXNOST THEN
  BEGIN
   ToomanyInc (FileName);
  END;
  IF FC[10] >= MaxAro THEN
  BEGIN
   PoorArom (FileName);
   Chk := 0;
  END;
  IF FGTest >= IFMIN[9] THEN
  BEGIN
   ToomanyGrp (FileName);
   Chk := 0;
  END;
  IF (Chk <> 0) AND (NST > 1) THEN
  BEGIN
   WRITELN (FileName);
   WRITELN (FileName, 'BINDING SITE CONCENTRATIONS');
   WRITELN (FileName);
   WRITELN (FileName, 'SITE NO CODE    CONCENTRATION   STD
..... DEV.');
   WRITELN (FileName, '                    mmo
.....l/g      mmol/g ');
   FOR I := 1 TO NumSites DO
   BEGIN
    II := Order[I];
    WRITELN (FileName, '  ', II:2, '    ',Code[II],
.....'       ' , (SSUM[II]/(2*NST)):8:5, '     ',
...../(StdDev[II]2):8:5);
   END;
   WRITELN (FileName);
   WRITELN (FileName, 'ELEMENTAL COMPOSITION');
   WRITELN (FileName);
   WRITELN (FileName, '            %C      %O      %
.....H      %N      %S        MOL. WGT');
   WRITE (FileName, '          ');
   FOR I := 1 TO 5 DO WRITE (FileName, ECSUM[I]/NST:5:2,
.....' % ');
   WRITELN (FileName, '   ', ECSUM[6]/NST:9:2, ' g/mol');
   WRITE (FileName, 'STD DEV.  ');
   FOR I := 1 TO 5 DO WRITE (FileName, SDEC[I]:5:2, ' % ');
   WRITELN (FileName, '   ', SDEC[6]:9:2, ' g/mol');
   WRITELN (FileName);
   RNC := ECSUM[1]*ECSUM[6]/(1201.115*NST*NST);
   RNH := ECSUM[3]*ECSUM[6]/(100.797*NST*NST);
   HC := RNH/RNC;
   AROMC := SumIR*600/(RNC*NST);
   COOHC := (SumIB1+SumIB2)*100/(NST*RNC);
   COC := SumIC*100/(NST*RNC);
   OCH3C := SumIE*100/(NST*RNC);
   QUINC := SumIQ*200/(NST*RNC);
   ALPHC := 100-AROMC-COOHC-COC-OCH3C-QUINC;
   AROMH := NARH*100/(NST*RNH);
   COOHH := (SumIB1+SumIB2)*100/(NST*RNH);
   OHH := SumID*100/(NST*RNH);
```

```
   PHENH :=  SumIA*100/(NST*RNH);
   ANHH := SumINH*200/(NST*RNH);
   SHH := SumIS*100/(NST*RNH);
   OCH3H := SumIE*300/(NST*RNH);
   ALPHH := 100-AROMH-COOHH-OHH-SHH-ANHH-OCH3H-PHENH;
   WRITELN (FileName ,'PERCENTAGE DISTRIBUTION OF C AND H');
   WRITELN (FileName);
   WRITELN (FileName ,'GROUP       CARBON    HYDROGEN');
   WRITELN (FileName);
   WRITELN (FileName ,'ALIPHATIC   ',ALPHC:6:2,
.....'    ',ALPHH:6:2);
   WRITELN (FileName ,'AROMATIC    ',AROMC:6:2,
.....'    ',AROMH:6:2);
   WRITELN (FileName ,'QUINONE     ',QUINC:6:2);
   WRITELN (FileName ,'CARBONYL    ',COC:6:2);
   WRITELN (FileName ,'CARBOXYLATE ',COOHC:6:2,
.....'    ',COOHH:6:2);
   WRITELN (FileName ,'METHOXYL    ',OCH3C:6:2,
.....'    ',OCH3H:6:2);
   WRITELN (FileName ,'PHENOL                ',PHENH:6:2);
   WRITELN (FileName ,'HYDROXYL              ',OHH:6:2);
   WRITELN (FileName ,'AMINE                 ',ANHH:6:2);
   WRITELN (FileName ,'THIOL                 ',SHH:6:2);
   WRITELN (FileName);
   WRITELN (FileName ,'H/C RATIO: ',HC:4:2);
   WRITELN (FileName);
   WRITELN (FileName ,'INCOMPATIBILITY DATA');
   WRITELN (FileName ,'--------------------');
   WRITELN (FileName);
   WRITELN (FileName ,'NUMBER OF SUCCESSFUL STRUCTURE
.....S             : ', NST:6);
   WRITELN (FileName ,'NUMBER OF AROMATIC INCOMPATIBI
.....LITIES        : ', INAR:6);
   WRITELN (FileName ,'NUMBER OF STRUCTURES WHICH ARE TOO
..... BRANCHED : ', INST:6);
   WRITELN (FileName ,'NUMBER OF ALIPHATIC INCOMPATIBI
.....LITIES        : ', INAL:6) ;
   WRITELN (FileName);
   WRITELN (FileName, 'MEAN CONCENTRATIONS OVER THE
..... SUCCESSFUL STRUCTURES');
   WRITELN (FileName);
   WRITELN (FileName, 'GROUPS:  KET   COOH   PHEN OH  OC
.....H3    QUIN    ALC OH   NH2     SH     RINGS');
   WRITE (FileName, '    ');
   WRITE (FileName, SumIC/(2*NST):8:3);
   WRITE (FileName, (SumIB1+SumIB2)/(2*NST):8:3);
   WRITE (FileName, SumIA/(2*NST):8:3);
   WRITE (FileName, SumIE/(2*NST):8:3);
   WRITE (FileName, SumIQ/(NST):8:3);
   WRITE (FileName, SumID/(2*NST):8:3);
   WRITE (FileName, SumINH/(2*NST):8:3);
   WRITE (FileName, SumIS/(2*NST):8:3);
   WRITE (FileName, SumIR/(2*NST):8:3);
   WRITELN (FileName);
   WRITELN (FileName);
   WRITELN (FileName, 'FRACTION OF ALIPHATIC CARBONS IN
..... METHYL GROUPS ', SumMF/NST:5:3);
```

```
   WRITELN (FileName, 'NUMBER OF ALIPHATIC CARBONS PER
..... MOLECULE');
   WRITELN (FileName, 'THEORETICAL : ', (fc[9]-6*FC[10]-
.....FC[2]-FC[1]-FC[4]):8:3);
   WRITELN (FileName, 'MEASURED    : ', (SumICA/NST):8:3);
   WRITELN (FileName, 'FRACTION OF COOHS ON AROMATIC RIN
.....GS : ', SumIB2/(SumIB1+SumIB2):5:3);
   SumRing := SumIRO+SumIRP+SumIRM;
   IF SumRing = 0 THEN SumRing := 1;
   WRITE (FileName, 'RO:RM:RP', SumIRO*TR/(SumRing):6:3,
.....':',SumIRM*TR/(SumRing):6:3, ':');
   WRITELN (FileName, SumIRP*TR/(SumRing):6:3);
   WRITELN (FileName);
  END;
 END;
 CLOSE (FileName);
 CLOSE (FileRead);
END;

{ Main routine follows, Tests options chosen }
BEGIN
 Intro;
 UserQuits := False;
 REPEAT
  Mainmenu;
  MOVETO (PosX (0.665), PosY (0.833));
  FetchInp (Opt);
  IF Opt = '1' THEN Creat;
  IF Opt = '2' THEN Edit;
  IF Opt = '3' THEN Calc;
  IF (Opt = 'Q') OR (Opt = 'q') THEN UserQuits := True;
  IF (Opt<>'1') AND (Opt<>'2') AND (Opt<>'3') AND NOT
..... UserQuits THEN Error;
 UNTIL UserQuits;
 CLOSEGRAPH;
END.
```

The unit GrDrivers used by RANDOM to test the PC's graphics driver

```
UNIT GRDRIVERS;

INTERFACE

USES GRAPH;


IMPLEMENTATION

PROCEDURE CGADRIVERPROC; EXTERNAL;       {$L CGA.OBJ}
PROCEDURE EGAVGADRIVERPROC; EXTERNAL;    {$L EGAVGA.OBJ}
PROCEDURE HERCDRIVERPROC; EXTERNAL;      {$L HERC.OBJ}

PROCEDURE REPORTERROR( S : STRING );

BEGIN
     WRITELN;
     WRITELN(S,' : ',GRAPHERRORMSG(GRAPHRESULT));
     HALT(1);
END;

BEGIN
IF REGISTERBGIDRIVER(@CGADRIVERPROC    )<0 THEN REPORTERROR('CGA');
IF REGISTERBGIDRIVER(@EGAVGADRIVERPROC )<0 THEN REPORTERROR('EGAVGA');
IF REGISTERBGIDRIVER(@HERCDRIVERPROC   )<0 THEN REPORTERROR('HERC');
END.
```

APPENDIX THREE

THE EXTRACTION OF FULVIC ACID FROM SEAWATER

A.3.1 INTRODUCTION

It was decided that the validation of the RANDOM approach could be successfully performed, using fulvic acid extracted from seawater. With this in mind, efforts were made to extract marine organic matter. Samples were extracted during two cruises. These were a cruise to the Agulhas Bank in March 1994 on the R.S. Algoa (samples extracted by C. Woolard and S. Bernard) and a cruise up the West Coast in May 1994 on the R.S. Africana (extraction by S. Bernard). The sampling locations are listed in Table A.3.1 together with conditions prevalent during sampling. The locations may also be seen in Figure A.3.1.

A.3.2 METHOD AND RESULTS OBTAINED

The method was similar to that used by Harvey et al. [Har83]. It was decided to follow this method closely and then to compare the extracted fulvic acids with those in the literature [Har83].

Samples were collected from surface seawater. The average depth from which water was pumped was 5 m. However, because of pitching and rolling of the cruise vessel, water was sampled in the range 10 m right up to the surface. The seawater was pumped directly into a 1650 litre stainless steel drum using a nitrogen-lift system. This involved lowering a stainless steel tube to sampling depth and then introducing compressed nitrogen. Seawater and gas then rose together to fill the tank. The system is described in detail by Tokar et al. [J.M. Tokar, G.R. Harvey and L.A. Chesal, "A gas lift system for large volume water sampling", *Deep Sea Res.*, 28A (1981) 1395-1399].

Table A.3.1: Sampling locations for fulvic acid extractions

Code	Ship	Date	Time	Latitude	Longitude	Temp(°C)	Max. Depth (m)
1	R.S. Algoa	3/3/94	Afternoon	34°52.21'S	22°16.58'E	18.1	102
2	R.S. Algoa	5/3/94	Afternoon	35°11.81'S	22°21.21'E	17.2	102
3	R.S. Algoa	8/3/94	Afternoon	35°44.75'S	20°40.79'E	20.8	85
4	R.S. Africana	17/5/94	Afternoon	St Helena Bay			
5	R.S. Africana	17/5/94	Night	60 km NW of St Helena Bay			

Note: Temperature and maximum depth data as well as exact locations were not recorded during the second cruise. All samples were extracted from surface seawater (depth < 10 m). The ship was not stationary for the last sampling location but was actually cruising in the region specified.

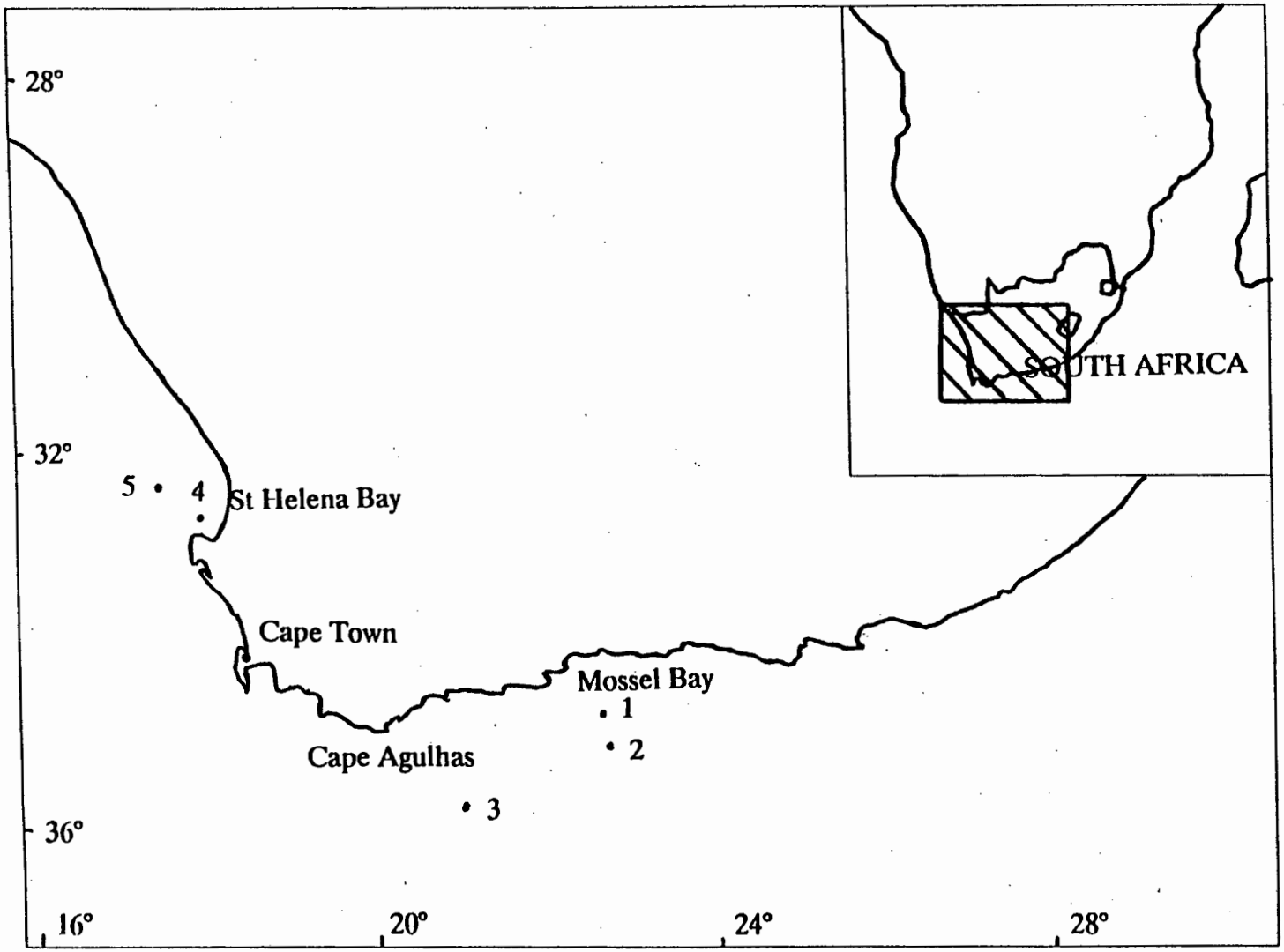

Figure A.3.1: Sampling locations off the South African coast for fulvic acid extractions

When about half of the seawater had been collected, concentrated (12M) HCl was added to the drum. Harvey et al. added 250 ml per 240 l of sample. In this study 110 ml was added per 100 litres of seawater collected. This was to acidify the seawater to pH = 2. The tank was then pressurized with nitrogen and the acidified seawater was discharged through columns containing Amberlite XAD-2 at a flow rate of 250 ml/min. The Amberlite XAD-2 had been cleaned before use by washing with acetone and methanol. Following this 5 l of 1.0 M NaOH was eluted through the packed columns. This was followed by 2 l of 1 M NH_3(aq) in methanol to remove any impurities in the resin. Finally the columns were acidified (to pH = 2) using concentrated HCl. The columns had glass wool plugs above and below to trap marine particles. The system is represented in Figure A.3.2

After the seawater was passed through the columns, the columns were deep frozen at a temperature of -20°C. Later they were thawed and each was rinsed with 2 l of 0.01 M HCl to remove salts. The humic material was collected by eluting each of the columns with 2.5 l of 1 M NH_3(aq) in methanol after an initial 4 hour soak in the eluent. To assure complete recovery the columns were then eluted with 2 l of methanol. The ammonia in methanol solution was made up by diluting 25% aqueous ammonia with methanol and not by bubbling ammonia gas through methanol.

The ammonia and methanol eluents were then combined and concentrated in a rotary evaporator below 40°C. They were not rotary-evaporated to dryness but rather till no more methanol was observed to be distilled. A murky solution of humic material in water was obtained. This crude material was then dissolved in a minimum of deionized water containing a few microlitres of NaOH to aid dissolution. (For sample C from the R.S. Algoa cruise and all from the Africana cruise no NaOH was added.) The solution was acidified to pH = 2 with 1.0 M HCl and then refrigerated for 72 hours (-5 °C) to allow the humic acid fraction to precipitate out. The humic acid fraction was separated

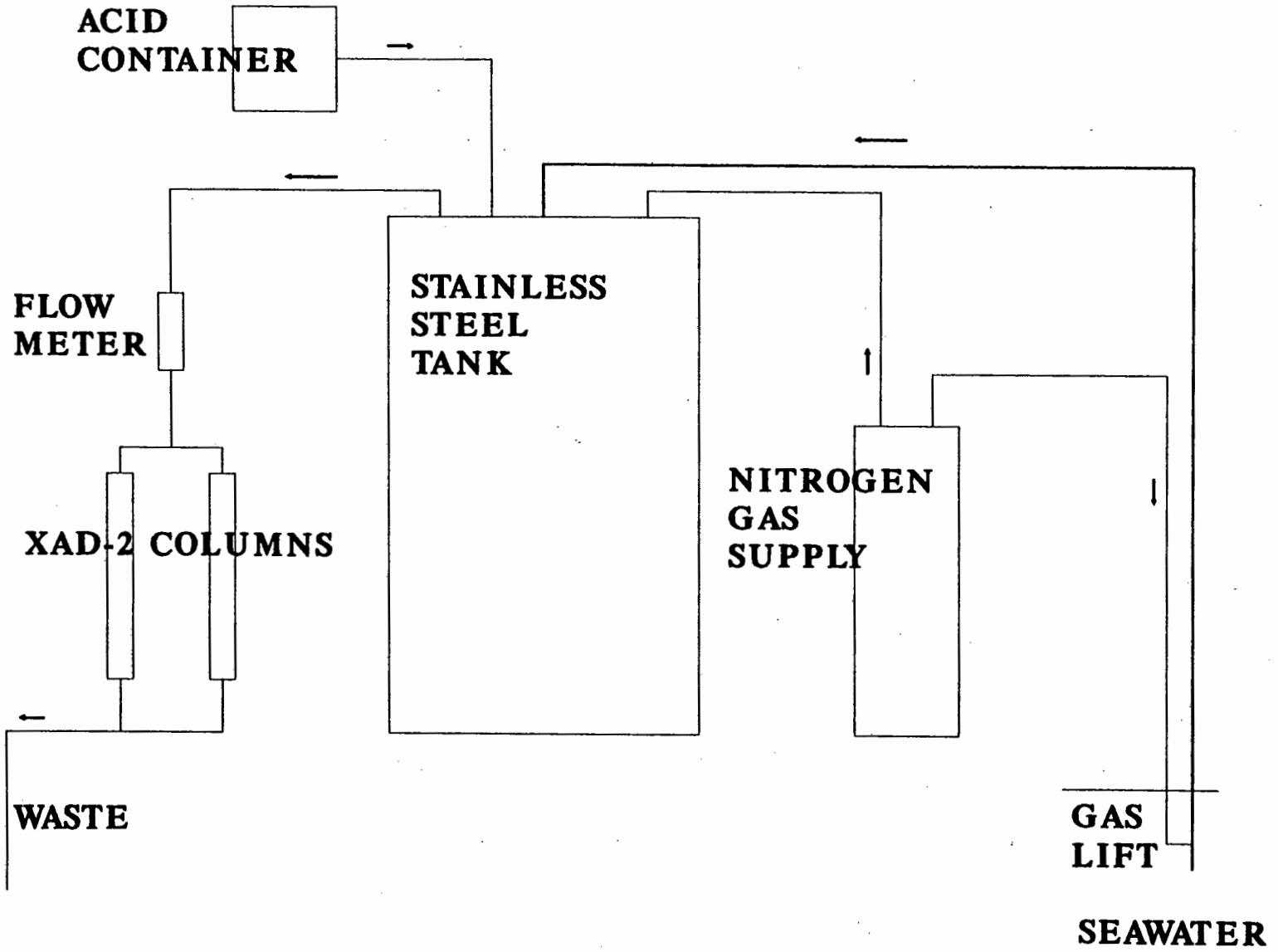

Figure A.3.2: Schematic representation of the system used for fulvic acid extraction from seawater.

from the soluble fulvic acids by centrifugation and decantation. Both fractions were freeze-dried and weighed.

At stations 1 and 2 only one column was used while at stations 3, 4 and 5 two columns were used. Table A.3.2 shows how much fulvic and humic acid was collected as well as the volume of seawater from which it was collected. Figures A.3.3 to A.3.6 are photographs of the extracted humic and fulvic acids. As can be seen the fulvic acids are lighter in colour than the humic material which was very dark.

The fulvic acid samples were submitted for CHN analysis. The results of this can be found in Table A.3.3. UV spectra of the fulvic acid samples in 0.001 M NaOH were also run. These were performed on a Philips PU 8000 UV-Vis spectrophotometer. The results of these runs can be found in Table A.3.4. The E_4/E_6 ratio is the ratio of the absorbance at 465 nm to that at 665 nm. The spectra for fulvic acid A can be found in Figure A.3.7.1 (190 - 360 nm) and A.3.7.2 (360 - 800 nm). It can be seen that the spectra are featureless except for a peak at 195 nm. All fulvic acid samples gave similar monotonic spectra in the range 210 - 800 nm with the absorbance increasing as wavelength decreased. The other samples also displayed single peaks in the 190 - 210 nm range.

Because the CHN results were unexpected, contamination of the samples was deemed likely. Fulvic acid sample D was dry-ashed. The ash content was discovered to be a very high 54.7 %. Sample D was then sent for ICP analysis. 17.5 mg was dissolved in 500 ml of 0.0001 M NaOH. This solution was filtered through 0.45 μm filter paper before ICP analysis.

Table A.3.2: Quantities of organic material extracted from seawater

Sample	Station Code	Approximate volume (l)	Mass of fulvics(g)	Mass of humics(g)
A	1	650	1.0975	0.0305
B	2	350	0.6401	0.0177
C	3	750	0.3204¶	0.0177
D	3	750	1.0587	0.0117
E	4	800	1.0119	0.0602
F	4	800	1.2015	0.0772
G	5	800	0.5961¶	0.0134
H	5	800	1.10182§	

¶: Sample was lost as a result of flasks cracking in the freeze-dryer.

§: This is a combined fulvic and humic acid sample

Table A.3.3: The results of CHN analysis on fulvic acid samples

Sample	%C	%N	%H
A	11.03	4.15	2.23
B	11.78	6.89	3.17
C	20.98	9.75	4.89
D	11.14	7.37	3.39
E	7.91	20.87	6.84
F	6.67	21.67	7.02
G	9.23	18.38	6.23
H	9.47	19.74	6.65

Figure A.3.3: Photograph of the fulvic acids extracted from the Algoa cruise. From the left: sample A, B, C and D.

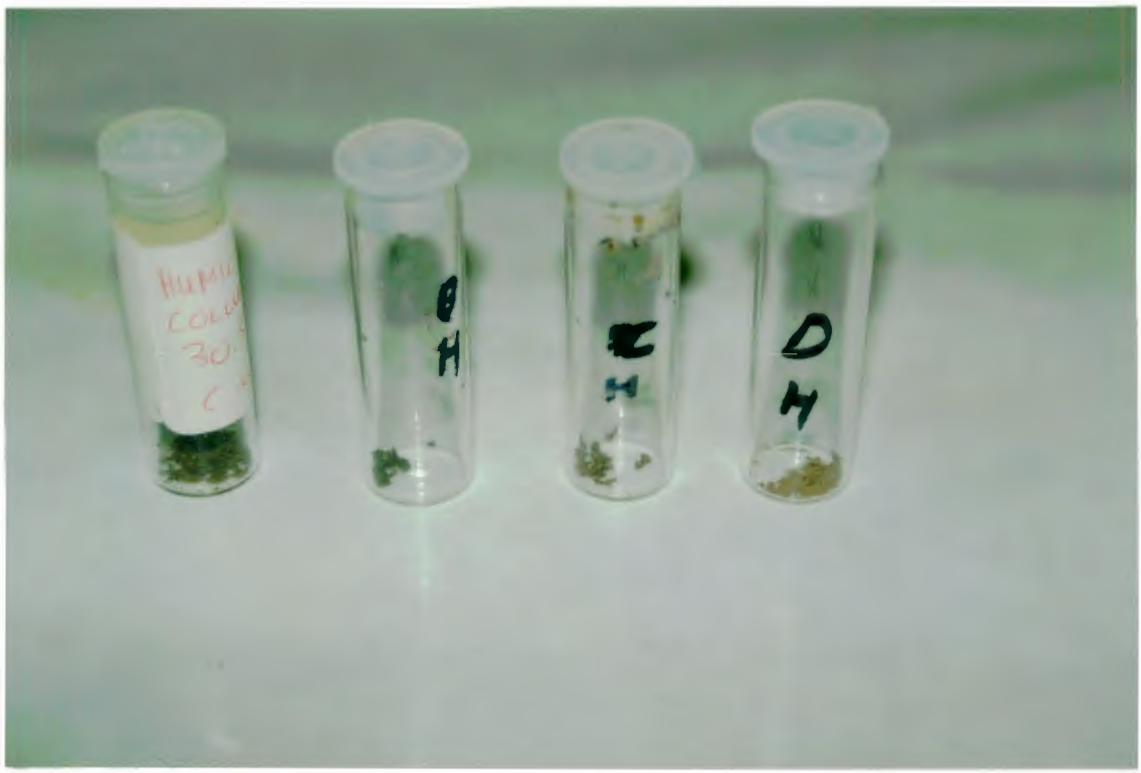

Figure A.3.4: Photograph of the humic acids extracted from the Algoa cruise. From the left: sample A, B, C and D.

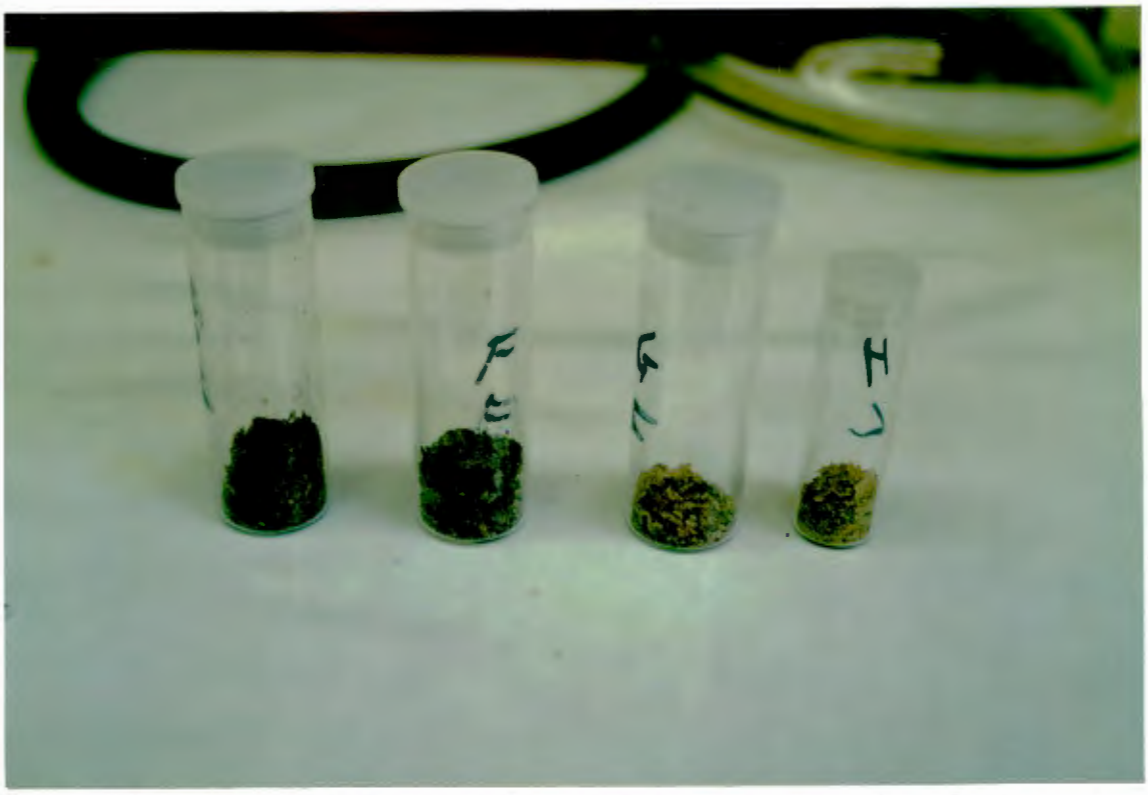

Figure A.3.5: Photograph of the fulvic acids extracted from the Afrikaner cruise. From the left: sample E, F, G and H. Sample H is an unfractionated sample (fulvic and humic acids combined).

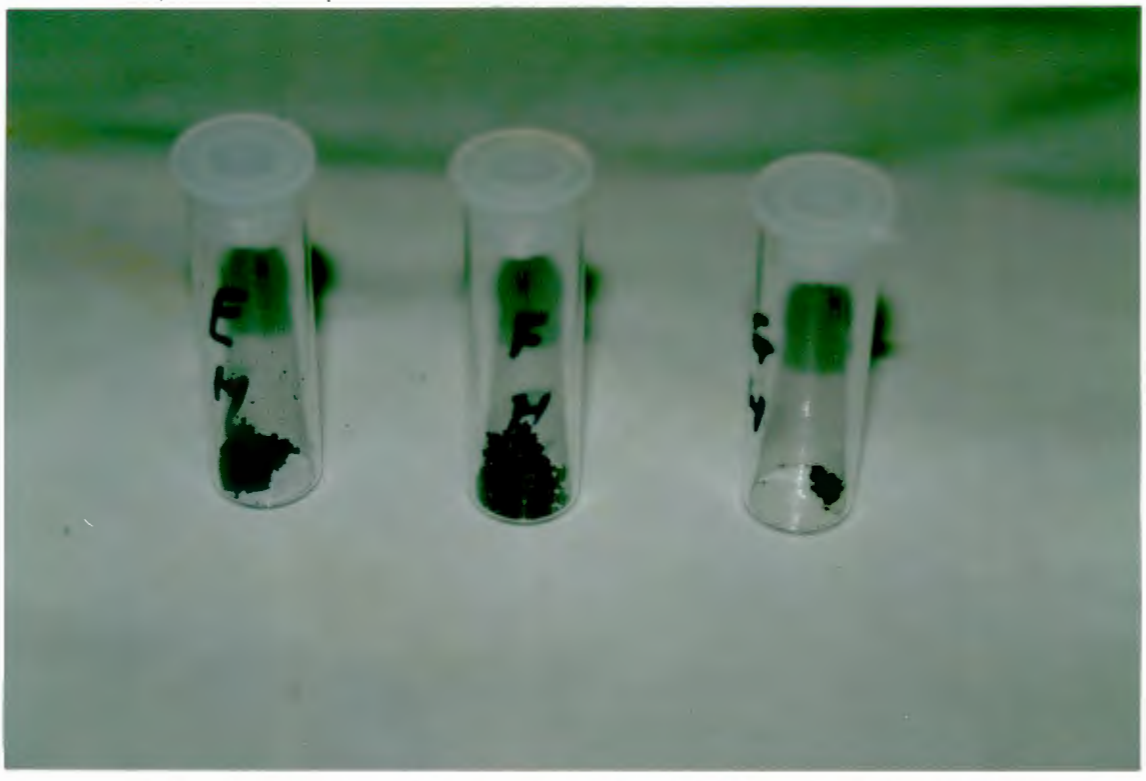

Figure A.3.6: Photograph of the humic acids extracted from the Afrikaner cruise. From the left: sample E, F and G.

Table A.3.4: UV absorbances of the various fulvic acid samples

The mass of sample indicated was dissolved in 5 ml of 0.0001 M NaOH

		Absorbance at wavelength				
Code	Mass (/mg)	360 nm	420 nm	465 nm	665 nm	E_4/E_6
A	32.1	0.740	0.287	0.153	0.031	4.94
B	21.5	0.345	0.148	0.096	0.038	2.53
C	20.7	0.794	0.295	0.157	0.035	4.49
D	21.8	0.366	0.113	0.061	0.013	4.69
E	22.4	0.437	0.160	0.083	0.019	4.37
F	27.4	0.703	0.237	0.127	0.023	5.52
G	22.7	0.373	0.126	0.062	0.13	4.77
H	27.4	0.693	0.268	0.136	0.035	3.89

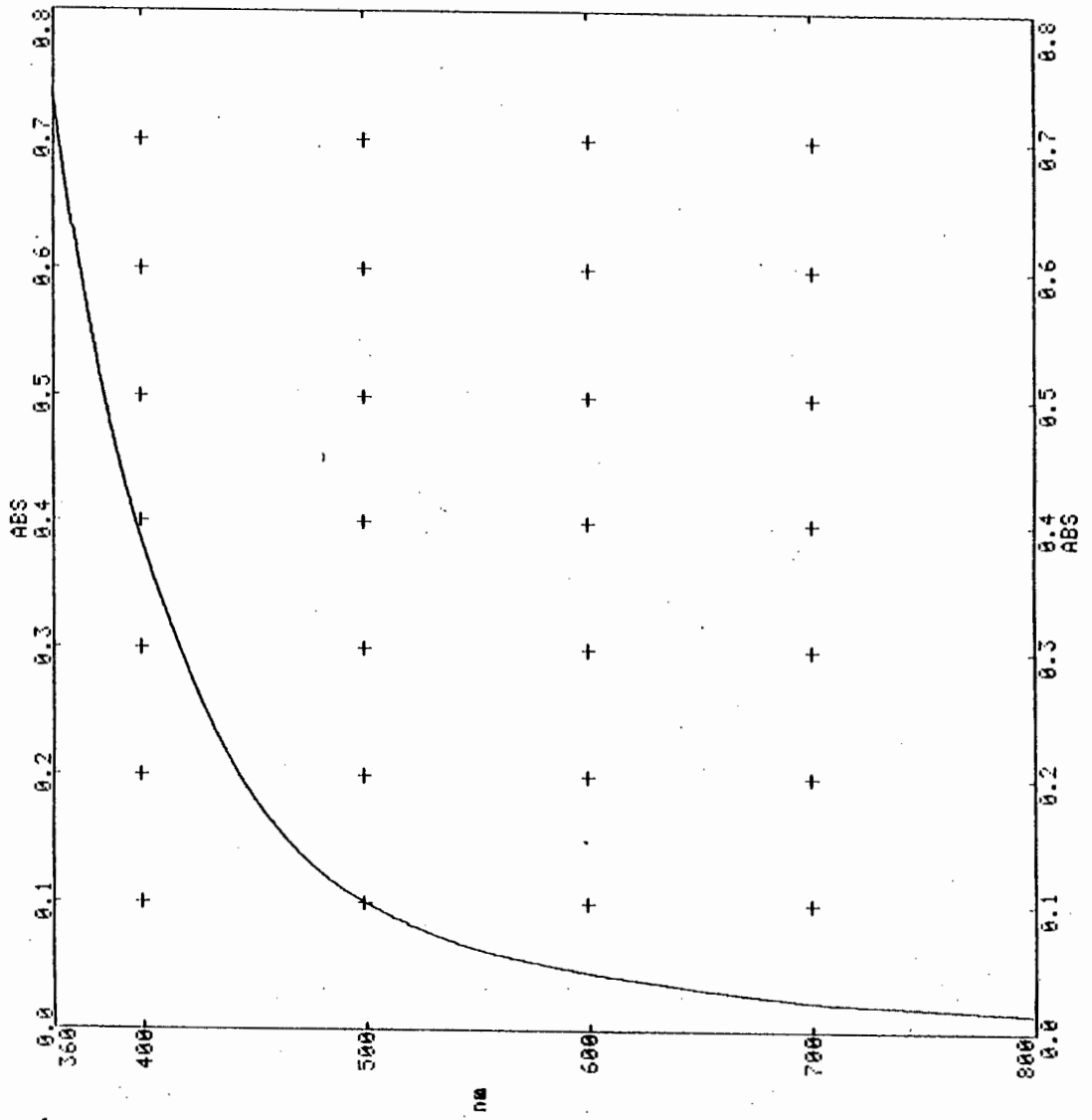

Figure A.3.7.1: UV-Vis absorbance spectrum (360-800 nm) of fulvic acid sample A. 32.1 mg dissolved in 5 ml of 0.001 NaOH. Reference: distilled water; Cell path: 1 cm glass cuvette.

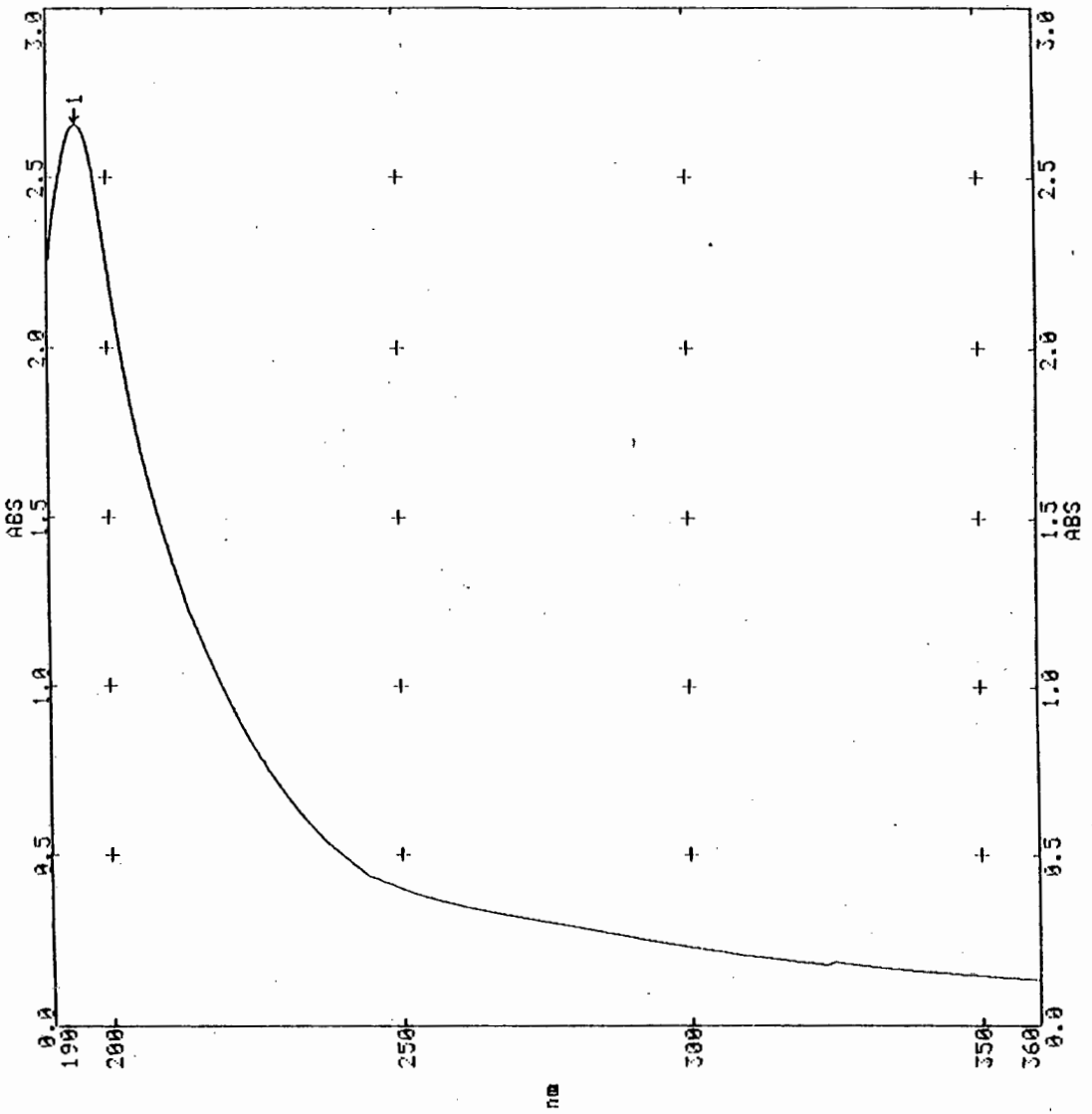

Figure A.3.7.2: UV absorbance spectrum (190-360 nm) of fulvic acid sample A. 32.1 mg dissolved in 5 ml of 0.001 NaOH (diluted a further 20 times). Reference: distilled water; Cell path: 1 cm glass cuvette.

The results obtained were:

Metal	Concentration (ppm)	% of original sample
Mg	0.169	0.48
Ca	1.69	4.83
Al	0.065	0.19
Cu	0.01	0.03
Si	2.41	6.89

If the silicon is expressed as SiO_2 it makes up 14.7% of the original sample. Lead, phosphorus and iron could not be detected. Trace quantities (ca. 0.01 ppm) of zinc and manganese were observed in an ICP profile.

Fulvic acid A was dissolved in 0.001 M NaOH. This was then passed through an ion exchange resin (Amberlite IR 120) to remove cations. The resultant solution was then freeze-dryed. The recovery from this process was 23.6%.

29 mg of fulvic acid C was dissolved in 50 ml of 0.001 M NaOH. This was then dialysed using Sigma dialysis tubing (cutoff 12000 g mol^{-1}) into distilled water (250 ml). The distilled water was sent for cation analysis using ion chromatography. The results were 16-17 ppm Na^+, 9.5-10 ppm NH_4^+, 1.4 ppm K^+, 1.5 ppm Mg^{2+}, 7.9 ppm Ca^{2+}. Subtracting the sodium contribution from the NaOH this gives percentages in the original sample of 10.3% Na^+, 8.4% NH_4^+, 1.2% K^+, 1.3% Mg^{2+} and 6.8% Ca^{2+}. The ammonium ion accounted for 67% of the total nitrogen from the CHN analysis.

A.3.3 DISCUSSION ON THE EXPERIMENTAL METHOD AND RESULTS OBTAINED

The samples extracted from seawater were intended for detailed characterization of marine fulvic acids. Unfortunately contamination of the samples by cations made this impossible. This contamination is the result of deficiencies in the extraction procedure used.

The extraction of fulvic acid from seawater proved more complicated than expected. It was hoped that when seawater was pumped aboard ship, the tank would be filled. However, at stations 1 and 2 the pumping rate was too slow. The volumes listed in Table A.3.2 were estimated from the flow rate into the tank as there was no apparatus for measuring volume fitted to the collection tank. At station 3, the ship's electric pump was used to rapidly fill the tank. About 100 l of seawater at this station was not passed through the columns.

The next step that proved troublesome was acidifying the seawater with HCl. The volume added was 110 ml of concentrated HCl per 100 l of seawater. Because the volume to be pumped into the tank was approximate, the volume of acid added was overestimated to obtain a lower pH. The pH of the acidified seawater in the tank was not tested as it was discovered that the tank did not have a valve that allowed a sample to be taken. Furthermore the seawater was pressurized with nitrogen which would have made sampling difficult.

The flow rate through both columns was a combined 250 ml min^{-1} (a maximum of 400 ml min^{-1} was obtained). This was much slower than that obtained by Harvey et al. [Har83] who obtained 500 ml min^{-1} through each column. This slow pumping speed limited seawater collection as the tank had to empty between runs.

Stuermer and Harvey (D.H. Stuermer and G.R. Harvey, "The isolation of humic substances and alcohol-soluble organic matter from seawater", *Deep-Sea Res.* 24 (1977) 303-309) state that the acidification of seawater is unlikely to precipitate the humic acid fraction in whole seawater because of the low concentration of marine humic acid. This acidification step serves two purposes. Firstly by protonating carboxylate groups, marine organic matter is made more hydrophobic and thus more likely to be adsorbed onto the XAD-2 resin. Secondly, the protonation of these groups should release bound cations. As the ICP and ion chromotography results indicate ions are still present in the samples extracted. It is possible that the seawater was not acidified to pH = 2 as the acid could have been used to dissolve the skeletons of organisms, present in the seawater. The sample areas (Agulhas bank and Benguella current along the Cape West coast) are known to have high primary productivity which might explain why Harvey et al. [Har83] did not have high cation contamination. Stuermer and Harvey (reference above) observed dark coloration in the glass wool plugs above and below the column but no discoloration of the columns. This was observed in this study. The glass wool was clogged with phytoplankton and had to be replaced regularly at sea. At station 4 (samples E and F) sampling was performed during a "red tide". In this case there was slight discoloration (olive-green) of the columns.

The high nitrogen content of the fulvic acid samples (from CHN measurements) indicated that nitrogen had in some way been incorporated into the samples. The most likely source was the ammonia in the methanol eluent. It was expected that this ammonia would be removed during the rotary evaporation and freeze-drying steps. However, the ion chromotography indicated that 67% of the nitrogen in sample C was present as ammonate. This ammonia had thus been complexed by the fulvic acid. Comparing the method of Harvey et al. [Har83] with the method used here, it was discovered that Harvey et al. dissolved ammonia in methanol by bubbling ammonia gas through methanol solution. In this study, aqueous ammonia was used. The water present

thus provided a source of protons for NH_4^+ ions to be formed and then complexed by fulvic acid. If ammonia gas was dissolved in methanol, ammonate ions should not have formed and the ammonia would then have been easily removed by rotary evaporation. However, it should be noted that in the original paper by Stuermer and Harvey (*Deep-Sea Res.* 24 (1977) 303-309) ammonia dissolved in distilled water was used, and no ammonia contamination was reported. Furthermore, it has been pointed out that even at the low temperature used for rotary evaporation (40°C), microorganisms are likely to oxidize ammonia to nitrate which may cause nitrate contamination [Professor James Willis, Geochemistry Department, UCT, personal communication]. The CHN analyses indicate higher N-content up the west coast. Because station 4 was sampled during a "red tide", microorganisms are likely to have been caught on the column. At station 5 the tank was not cleaned thoroughly after station 4, so the same problem of microbial contamination may also apply. Unfortunately nothing is known about biological activity during the sampling done by Harvey et al. [Har83], so these explanations for the differnces in results remain speculation.

The E_4/E_6 ratios are similar to those obtained by Kalinowski and Blondeau [Kal88] but lower than those obtained by Ertel and Hedges [Ert83]. Because a ratio is used, contamination by cations which do not absorb in the range scanned, should affect these results only slightly. Ertel and Hedges observed a shoulder in marine fulvic acid absorbance at 465 nm. This is not reported elsewhere as all other authors report monotonic spectra in line with that observed here. Thus Ertel and Hedges may have had falsely high absorbances at 465 nm and hence higher E_4/E_6 ratios.

When the samples were dissolved for UV-Vis spectrometry, not all dissolved in the 0.001 M NaOH. All had a white residue which refused to dissolve. It is suspected that this was siliceous material. The ICP results indicate high Si-content which accounts for 14.7% of the original sample D if it is taken as SiO_2. Because the sample was filtered before the

ICP analysis was performed, the silicate content may be much higher. The fact that the aluminium content is low would indicate that the silicate is opaline rather than aluminosilicate material. The high calcium content (10 (from ICP) and 5 (from ion chromotography) times magnesium despite magnesium's higher concentration in seawater (5 times greater)) would also seem to indicate that this contamination is likely to be the result of marine organisms and their breakdown products being caught on the XAD-2 columns. It is known that the skeletons of marine diatoms are made of $CaCO_3$ and SiO_2 [Bea89].

The recovery using an ion-exchange resin was 23.6% for sample A. If all the carbon present is organic and the %C in fulvic acid is 51.5% (mean of literature reported values) then the percentage fulvic acid in the sample is 21.4%. This would seem to indicate that the ion-exchange resin is efficient at purifying fulvic acid. Unfortunately the product obtained was not a fine powder like the original sample A. The photographs indicate that the fulvic acids are lighter in colour than humic acids. Only fulvic A and C and humic D were powders. All other extracts were plate-like material. However, the fulvic acid samples were easily crushed to a powder. The humic samples (sample D excluded) were sticky and did not dissolve easily in 0.001 M NaOH [Stewart Bernard, personal communication].

Contamination from the XAD-2 resin is unlikely as a clean column was eluted with NH_3 in methanol. The eluent was then rotary-evaporated. No solid material was obtained from this extraction.

Despite the contamination of the samples, the results indicate that in surface seawater fulvic acids are more common than humic acids. This is in line with the results obtained by Harvey et al. [Har83]. The XAD-2 columns also appeared to be efficient at extracting humic material. When the first ammonia eluent was added to the column, the column

was observed to warm to the touch. However, this warming occurred only at the top of the column but not lower down. This would seem to indicate that the columns used were large enough for the volume of seawater passed through them.

A.3.4: RECOMMENDATIONS

The technique of Harvey et al. [Har83] did not prove satisfactory for extracting fulvic acids from seawater and was prone to contamination. It is recommended that the pH of the acidified seawater be tested to make sure that pH= 2. This should lower cation complexation. Furthermore, the washing of the column with 0.01 M HCl to remove salts proved unsatisfactory. A greater volume at this step is recommended. A higher concentration would also be beneficial.

Harvey et al. [Har83] used ammonia in methanol as this reduced the need to desalt the final product. However, serious ammonia contamination was observed in this study. This could be overcome by dissolving ammonia gas in methanol so that ammonate ions are minimized. However, elution using NaOH solutions instead is recommended followed by dialysis to remove the salts. This may , however, result in the loss of low-molecular weight material. The use of ion-exchange resins (thoroughly cleaned to prevent resin bleed) could also be a viable option.

When the rotary-evaporated material is dissolved in NaOH, the resultant solution should be allowed to stand and then filtered to remove any precipitates. This should hopefully lower the ash content by removing silicate material.

The extraction of fulvic acid from seawater was thus not as simple as initially envisioned. Hopefully, insight into the process has been provided, especially considerations on the

impact of micro-organisms (both as oxidizers of ammonia and as sources of biological contamination).

APPENDIX FOUR

ADDITIONAL TURBO PASCAL PROGRAMS

PROGRAM ZHB

This program calculates experimental as well as calculated Z_H values. Calculations were done using RANDOM ligand concentrations and known protonation constants. The protonation constants were stored in the file KPROT.DBS which is listed after the ZHB program. The file RANDOM.DAT contained the number of RANDOM ligands used on the first line followed by pairs of lines which contained the ligand number code and the output concentration from RANDOM. The experimental data was input from the file ZHBAR.DAT which is listed after ZHB. The output (pH, Z_H^{exp} and Z_H^{calc}) was written to the program ZHBAR.OUT.

```
PROGRAM ZHB;

VAR
 FILINP          : TEXT;        { INPUT FILE ZHBAR.DAT }
 FILOUT          : TEXT;        { OUTPUT FILE ZHBAR.OUT }
 FILDBS          : TEXT;     {PROTONATION DATA FILE KPROT.DBS}
 FILRAN          : TEXT;        { RANDOM OUTPUT FILE }
 VINIT           : REAL;        { INITIAL VOLUME - EXPTL DATA}
 MLIG            : REAL;        { MASS OF FULVIC ACID - EXPTL}
 HLIG            : REAL;        { MOLES H PER G OF FA }
 CBAS            : REAL;        { CONCN OF BASE - EXPTL }
 NPH             : INTEGER;     { NO OF PH DATA POINTS }
 I               : INTEGER;     { COUNTER }
 II              : INTEGER;     { LIGAND CODE NO }
 J               : INTEGER;     { COUNTER }
 K               : INTEGER;     { COUNTER }
 M               : INTEGER;     { COUNTER }
 HC              : REAL;        { POWER OF H IN SPECIES }
 PH              : REAL;        { PH READ IN }
 MEQBAS          : REAL;        { MEQ OF BASE ADDED - EXPTL }
 VOL             : REAL;        { TOTAL SOLUTION VOLUME }
 VBAS            : REAL;        { VOLUME OF BASE ADDED }
 TL              : REAL;        { CONCN OF FA }
 TH              : REAL;        { CONCN OT TOAL H }
 NUMER           : REAL;        { NUMERATOR IN ZHBAR-EXPTL }
 ZHCALC          : REAL;        { ZHBAR - CALCULATED }
 ZHBAR           : REAL;        { ZHBAR - EXPERIMENTAL }
 NUM             : REAL;        { NUMERATOR IN ZHBAR-CALC }
 HCONC           : REAL;        { CONCN OF FREE H }
 DEN             : REAL;        { DENOMINATOR IN ZHBAR-CALC }
 NOGRP           : INTEGER;     { NO OF LIGANDS IN KPROT }
 KSTAB           : REAL;        { STABILITY CONSTANT (NOT
                                  LOGGED) }
 NOLIG           : INTEGER;     { NO OF LIGANDS IN RANDOM.DAT}
```

```
 LIGAND          : ARRAY [1..40] OF INTEGER;  { LIGAND NO }
 LIGCONC         : ARRAY [1..40] OF REAL;     { LIGAND CONCN}
 KH              : ARRAY [1..40] OF ARRAY [1..3] OF REAL;

BEGIN
 FOR I:= 1 TO 40 DO
 BEGIN
  FOR J:= 1 TO 3 DO KH[I,J] := 0;
  LIGAND [I] := 0;
  LIGCONC [I] := 0;
 END;
 ASSIGN ( FILDBS , 'KPROT.DBS');
 RESET (FILDBS);
 READLN ( FILDBS,NOGRP);
 FOR I := 1 TO NOGRP DO
 BEGIN
  READLN (FILDBS,II);
  FOR J := 1 TO 3 DO READLN (FILDBS,KH[II,J]);
 END;
 ASSIGN (FILRAN, 'RANDOM.DAT');
 RESET (FILRAN);
 READLN (FILRAN, NOLIG);
 FOR I:= 1 TO NOLIG DO
 BEGIN
  READLN (FILRAN,LIGAND[I]);
  READLN (FILRAN,LIGCONC[I]);
 END;
 CLOSE (FILRAN);
 CLOSE (FILDBS);
 ASSIGN (FILINP, 'ZHBAR.DAT');
 RESET (FILINP);
 ASSIGN (FILOUT, 'ZHBAR.OUT');
 REWRITE (FILOUT);
 READLN (FILINP, VINIT);
 READLN (FILINP, MLIG);
 READLN (FILINP, HLIG);
 READLN (FILINP, CBAS);
 READLN (FILINP, NPH);
 FOR I := 1 TO NPH DO
 BEGIN
  ZHCALC := 0;
  READLN (FILINP,PH);
  READLN (FILINP,MEQBAS);
  VBAS := MEQBAS * 0.001 * MLIG / CBAS;
    VOL := VINIT + VBAS;
  TL := MLIG / (1000*VOL);
  TH := HLIG * MLIG - CBAS * VBAS;
  TH := TH / VOL;
  HCONC := EXP (-PH*LN(10));
  NUMER := TH - HCONC + EXP ((PH-14)*LN(10));
  ZHBAR := NUMER / TL;
  FOR J := 1 TO NOLIG DO
  BEGIN
   NUM := 0;
   DEN := 1;
   FOR K := 1 TO 3 DO
   BEGIN
```

```
    IF KH[LIGAND[J],K] <> 0 THEN
    BEGIN
     HC :=1;
     FOR M := 1 TO K DO HC := HC * HCONC;
     KSTAB := EXP (KH[LIGAND[J],K]*LN(10));
     NUM := NUM + K*KSTAB*HC;
     DEN := DEN + KSTAB*HC;
    END;
   END;
   ZHCALC := ZHCALC + LIGCONC[J]*(NUM/DEN);
  END;
  WRITELN (FILOUT,PH:5:2, '   ', ZHBAR:5:3,
'.....'    ',ZHCALC:5:3);
 END;
 CLOSE (FILOUT);
 CLOSE (FILINP);
END.
```

FILE KPROT.DBS

```
26
3
13.68
23.51
0
4
5.41
8.36
0
5
13.74
16.71
0
6
10.02
0
0
7
4.2
0
0
8
9.98
0
0
9
8.98
0
0
10
5.1
8.56
0
```

```
11
3.69
0
0
12
5.64
9.85
0
13
7.42
9.57
0
14
4.5
0
0
15
4.03
0
0
16
4.87
0
0
20
9.58
16.28
17.36
21
10
13.9
15.89
22
9.21
11.4
0
24
9.87
12.22
0
25
10.29
13.84
0
26
9.72
16.33
0
27
9.5
0
0
30
10.74
19.1
20.91
31
```

```
10.95
15.89
19.18
32
10.45
14.13
0
33
10.9
19.13
0
34
9.72
0
0
```

FILE ZHBAR.DAT

```
0.002
0.00953
0.0100
0.0989
40
2.34
0
2.53
0.515
2.72
1
2.95
1.71
3.25
2.054
3.47
2.423
3.724
2.569
3.845
2.774
4
3.007
4.183
3.212
4.374
3.416
4.504
3.62
4.652
3.796
4.87
4.01
5.017
4.243
```

5.217
4.466
5.409
4.65
5.643
4.85
5.861
5.049
6.083
5.243
6.427
5.447
6.841
5.68
7.403
5.89
7.98
6.119
8.509
6.3
9.241
6.514
9.81
6.69
10.259
6.883
10.534
7.136
10.819
7.34
11.034
7.564
11.155
7.758
11.276
8
11.379
8.269
11.5
8.75
11.629
9.285
11.681
9.771
11.741
10.344
11.802
10.831
11.836
11.317

]PROGRAM DBSORDER

This program orders the MINTEQA2 input database files based on the MINTEQA2 species code. The input database files were read into MS-WORD 5.1 first and saved as TEXT files with LINE BREAKS. This was to prevent the program reading the input files as one long line.

```
PROGRAM DBSORDER;

TYPE
 LINEPAIR  =
  RECORD
        LINE1            : STRING;
        LINE2            : STRING
  END;

VAR
 PAIR                    : LINEPAIR;
 INP, OUT                : STRING;
 FILINP, FILOUT          : TEXT;
 CODE                    : STRING [7];
 CODEVAL                 : ARRAY [1..2] OF ARRAY [ 1.. 2000]
OF LONGINT;
 I,J,BOTTOM,TOP,MIDDLE   : INTEGER;
 TEMP                    : LONGINT;
 ERRCODE                 : INTEGER;
 K                       : INTEGER;
 N,M                     : INTEGER;
 L1,L2                   : STRING;
 C                       : LONGINT;
 TEMP2                   : LONGINT;
 FILTEMP                 : FILE OF LINEPAIR;

BEGIN
 WRITE ('WHAT IS THE INPUT FILE? ');
 READLN (INP);
 WRITE ('WHAT IS THE OUTPUT FILE? ');
 READLN (OUT);
 ASSIGN (FILINP, INP);
 ASSIGN (FILOUT, OUT);
 ASSIGN (FILTEMP, 'TEMP.DAT');
 RESET (FILINP);
 K := 0;
 C := 0;
 REWRITE (FILOUT);
 FOR M := 1 TO 3 DO
 BEGIN
  REWRITE (FILTEMP);
  IF C <> 0 THEN
```

```
BEGIN
 K := 1;
 SEEK (FILTEMP,K);
 WITH PAIR DO
 BEGIN
  LINE1 := L1;
  LINE2 := L2;
  WRITE (FILTEMP,PAIR);
  CODE := LINE1;
  VAL (CODE, C, ERRCODE);
  CODEVAL [1,K] := C;
  CODEVAL [2,K] := K;
 END;
END;
C := 100;
WHILE C <> 0 DO
BEGIN
 K := K + 1;
 SEEK (FILTEMP,K);
 WITH PAIR DO
 BEGIN
  READLN (FILINP,LINE1);
  READLN (FILINP,LINE2);
  WRITE (FILTEMP,PAIR);
  CODE := LINE1;
  VAL (CODE, C, ERRCODE);
  CODEVAL [1,K] := C;
  CODEVAL [2,K] := K;
 END;
END;
CLOSE (FILTEMP);
N := K - 1;
FOR I := 2 TO N DO
BEGIN
 TEMP := CODEVAL [1,I]; BOTTOM := 1; TOP := I - 1; TEMP2
.....:= CODEVAL[2,I];
 WHILE BOTTOM <= TOP DO
 BEGIN
  MIDDLE := (BOTTOM+TOP) DIV 2;
  IF TEMP < CODEVAL[1,MIDDLE]
     THEN TOP := MIDDLE - 1
     ELSE BOTTOM := MIDDLE + 1
 END;
 FOR J := I-1 DOWNTO BOTTOM DO
 BEGIN
  CODEVAL [1,J+1] := CODEVAL[1,J];
  CODEVAL [2,J+1] := CODEVAL[2,J];
 END;
 CODEVAL[1,BOTTOM] := TEMP;
 CODEVAL[2,BOTTOM] := TEMP2
END;
ASSIGN (FILTEMP,'TEMP.DAT');
RESET (FILTEMP);
FOR I := 1 TO N DO
BEGIN
 SEEK (FILTEMP,CODEVAL[2,I]);
 READ (FILTEMP,PAIR);
```

```
   WITH PAIR DO WRITELN (FILOUT,LINE1);
   WITH PAIR DO WRITELN (FILOUT,LINE2);
  END;
  SEEK (FILTEMP,N+1);
  READ (FILTEMP,PAIR);
  WITH PAIR DO
  BEGIN
   L1 := LINE1;
   L2 := LINE2;
  END;
  WHILE C=0 DO
  BEGIN
   WRITELN (FILOUT,L1);
   WRITELN (FILOUT,L2);
   IF NOT EOF (FILINP) THEN
   BEGIN
    READLN (FILINP,L1);
    CODE := L1;
    VAL (CODE, C, ERRCODE);
    READLN (FILINP,L2);
   END;
   IF EOF (FILINP) THEN C := 1;
  END;
 END;
 CLOSE (FILINP);
 CLOSE (FILOUT);
 CLOSE (FILTEMP);
END.
```

PROGRAM XTRACT

This program extracts data from the database to a file to be used as a basis for Appendix 1.1. Note that it uses an ordered input file called THERMO.SA7.

```
PROGRAM XTRACT;

VAR
 FILINP,FILOUT          : TEXT;
 CODE                   : STRING[7];
 NAME                   : STRING[22];
 L1,L2                  : STRING;
 I, LEN                 : INTEGER;
 COMP                   : STRING;
 LOGK                   : STRING;
 OUT                    : STRING;
 C                      : LONGINT;
 EC                     : INTEGER;

BEGIN
 ASSIGN (FILINP,'THERMO.SA7');
```

```
 ASSIGN (FILOUT,'THESIS.DB7');
 RESET (FILINP);
 REWRITE (FILOUT);
 C := 100;
 WHILE C <> 0 DO
 BEGIN
  READLN (FILINP,L1);
  READLN (FILINP,L2);
  NAME := L1;
  CODE := L1;
  VAL (CODE,C,EC);
  LEN := LENGTH(L2);
  COMP := COPY (L2,8,LEN-7);
  FOR I := 1 TO (50-LEN) DO COMP := COMP + ' ';
  LOGK := COPY (L1,33,6);
  OUT := NAME + COMP + LOGK;
  WRITELN (FILOUT,OUT);
 END;
 WHILE NOT EOF(FILINP) DO
 BEGIN
  READLN (FILINP,L1);
  READLN (FILINP,L2);
  NAME := L1;
  LEN := LENGTH(L2);
  COMP := COPY (L2,8,LEN-7);
  FOR I := 1 TO (64-LEN) DO COMP := COMP + ' ';
  LOGK := COPY (L1,33,6);
  OUT := NAME + COMP + LOGK;
  WRITELN (FILOUT,OUT);
 END;
 CLOSE (FILINP);
 CLOSE (FILOUT);
END.
```

POROGRAM COBINE

This programs combines input data into a file to be used as a basis for Appendix 1.2. It uses all the ordered databases which must be stored in the files THERMO.SAX where X = 0, 1, 2, 3, 4, 5, 6 or 7 (i.e. 10 times the ionic strength). It also looks for discrepancies in species names and MINTEQA2 species codes between files.

```
PROGRAM COMBINE;

USES CRT;

TYPE
 ENTRY =
  RECORD
```

```
    NAME                    : STRING[15];
    CODE                    : STRING[7];
    LOGK                    : ARRAY [0 .. 7] OF STRING[12];
   END;

VAR
 FILBASE                    : TEXT;
 CONS                       : ENTRY;
 I,J,K                      : INTEGER;
 KS                         : STRING[1];
 L1,L2                      : STRING;
 FILCOMB                    : FILE OF ENTRY;
 FILNAME                    : STRING;
 FILINP                     : TEXT;
 TEST                       : INTEGER;
 FILOUT                     : TEXT;
 C                          : STRING[7];
 N                          : STRING[15];
 MAXENT                     : INTEGER;
 LOOPOUT                    : INTEGER;
 ERR                        : INTEGER;
 CODEVAL                    : LONGINT;
 CVAL                       : LONGINT;

BEGIN
 ASSIGN (FILBASE,'THERMO.SA7');
 RESET (FILBASE);
 ASSIGN (FILCOMB,'COMB.DAT');
 REWRITE (FILCOMB);
 J := 0;
 WHILE NOT EOF (FILBASE) DO
 BEGIN
  J := J + 1;
  READLN (FILBASE,L1);
  READLN (FILBASE,L2);
  SEEK (FILCOMB,J);
  WITH CONS DO
  BEGIN
   CODE := L1;
   NAME := COPY (L1,9,13);
   FOR I := 0 TO 6 DO LOGK[I] := ' ????? ';
   LOGK[7] := COPY (L1,32,7);
  END;
  WRITE (FILCOMB,CONS);
 END;
 MAXENT := J;
 ASSIGN (FILOUT,'COMB.DBS');
 REWRITE (FILOUT);
 FOR K := 0 TO 6 DO
 BEGIN
  STR (K, KS);
  FILNAME := 'THERMO.SA'+KS;
  ASSIGN (FILINP,FILNAME);
  RESET (FILINP);
  WRITELN (FILOUT, FILNAME);
  J := 0;
  TEST := 0;
```

```
  LOOPOUT := 1;
  WHILE (NOT EOF (FILINP)) AND (LOOPOUT <> 0) DO
  BEGIN
   J := J + 1;
   IF TEST = 0 THEN
   BEGIN
    READLN (FILINP,L1);
    READLN (FILINP,L2);
   END;
   C := L1;
   VAL (C,CVAL,ERR);
   TEST := 0;
   N := COPY (L1,9,13);
   SEEK (FILCOMB,J);
   IF J <= MAXENT THEN READ (FILCOMB,CONS);
   IF J > MAXENT THEN LOOPOUT := 0;
   IF LOOPOUT <> 0 THEN
   BEGIN
    WITH CONS DO
    BEGIN
     VAL (CODE,CODEVAL,ERR);
     IF CVAL = CODEVAL THEN IF N = NAME THEN
     BEGIN
      LOGK[K] := COPY(L1,32,7);
      SEEK (FILCOMB,J);
      WRITE (FILCOMB,CONS);
     END;
     IF CVAL = CODEVAL THEN IF N <> NAME THEN WRITELN
..... (FILOUT,'  ',C,'  ',N, ' DIFF NAME');
     IF CVAL < CODEVAL THEN
     BEGIN
      J := J - 1;
      WRITELN (FILOUT,'  ',C,'  ',N,' UNKNOWN CODE');
     END;
     IF CVAL > CODEVAL THEN TEST := 1;
    END;
   END;
  END;
  CLOSE (FILINP);
 END;
 FOR J := 1 TO MAXENT DO
 BEGIN
  SEEK (FILCOMB,J);
  READ (FILCOMB,CONS);
  WITH CONS DO
  BEGIN
   WRITE (FILOUT,CODE,' ',NAME);
   FOR I := 0 TO 7 DO WRITE (FILOUT,LOGK[I]);
   WRITELN (FILOUT);
  END;
 END;
 CLOSE (FILBASE);
 CLOSE (FILCOMB);
 CLOSE (FILOUT);
END.
```