An investigation into vanadium contamination of soil and its effects on plants

Heather A. Dodds

B.Sc. (Agriculture)

Submitted in partial fulfilment of the
requirements for the degree of
Master of Science in Environmental Geochemistry

in the
Department of Geology
University of Cape Town

December 1994

Contents

Acknowledgements

I would like to express my gratitude to the following people and institutions :

ESKOM Human Resources Group and the Foundation for Research Development, for financial support;

SASOL, South Africa, for their contribution towards project running expenses;

Mr Martin Ginster of SASOL, for bringing the study topic to attention and for assistance in the collection of soils;

Dr Martin Fey, for valuable guidance, discussion and advice, and assistance with the plant growth experiments;

Associate Professor James Willis, for advice and assistance with HPIC and XRF analysis;

Professor Joe Cruywagen of the Department of Chemistry, University of Stellenbosch, for discussion of the general chemistry and analysis of vanadium;

Mrs Marian McKay of the Department of Chemistry, University of Cape Town, for assistance with ICP analysis;

Lesley Petrik and Katerina Johannsen of the Department of Chemical Engineering, University of Cape Town, for use of centrifugation facilities, and for surface area analysis, respectively;

Barbara Baard of the Elsenburg Agricultural Development Institute, for dry biomass digestion;

Mr Desmond Barnes of the Botany Department, University of Cape Town, for provision of phytotron facilities;

Mr Patrick Sieas for assistance with HPIC analysis and general laboratory work;

Mr Peter Meyer, for assistance with soil preparation;

Mr Andrew Menzies for assistance with the CoPlot and Quattro-Pro computer programmes;

Professor Andy Duncan, Rob Hounsome, Rory Tomlinson and Terry Harck, for valuable discussion.

Finally, I would like to thank my family for their continued encouragement, support and faith in my ability.

Abstract

This study constitutes a preliminary assessment of the behaviour of effluent-associated vanadium, and its possible effects on the biotic components of land treatment sites, used for the disposal of liquid industrial wastes from a chemical plant in the eastern Transvaal. A review of the literature showed that although the emission of vanadium into the environment is on the increase, very little information is available regarding its behaviour and impact as an environmental pollutant. This study is therefore important not only in the context of the land treatment operation in question, but clearly in a more universal context as well.

The study involved a three-phase approach to the problem. Firstly, vanadium sorption was considered in four soils encountered on the sites in question. Secondly, an investigation was conducted into the potential toxicity of vanadium to relevant plant species. Finally, the potential inhibition of soil biological activity at increasing levels of vanadium was examined, although the results of this experiment were inconclusive.

The sorption of vanadium, applied as ammonium vanadate, was found to be fairly complex. More than one sorption mechanism appeared to operate at high vanadate concentrations, possibly in response to altered vanadate speciation. The Freundlich adsorption isotherm was found to fit vanadate sorption very well under the experimental conditions employed in this study. Clay type and soil surface area may be important determinants of the extent of vanadate sorption in different soils, since 1:1 layer silicates appeared to bind much more vanadate per given amount of clay and surface area than 2:1 layer silicates. This situation is similar to that of phosphate sorption. Vanadate binding on soils with very large surface areas and clay contents may be as extensive, however, even though 1:1 clay minerals are absent. The trace element concentration of a soil, as well as its organic material content may be important in determining the extent to which vanadium is removed from the solution phase.

Vanadate sorption was found to increase on acidification of the adsorption systems, and decrease under alkaline conditions. These changes were attributed to altered vanadate speciation, and to changes in the surface-associated charge of soil colloids. The extent of vanadate sorption appeared to be intermediate between that of fluoride and borate, which are other potentially limiting anions with respect to land treatment of the effluents under consideration. This may imply that borate would be more of a threat to groundwater than other components of the land treatment systems concerned, but the effective loading rates and relative toxicities of these elements must be taken into account before such a conclusion can be confirmed.

In the plant growth trials, the growth of *Lolium perenne* (ryegrass) and *Zea mays* (maize) was considered at increasing levels of applied ammonium vanadate in Rensburg and Swartland soil. Inhibition of ryegrass emergence was observed, but whether this was a result of vanadate toxicity is unclear, since any such effects would have been obscured by the influence of soil moisture content, which had not been adequately controlled.

Maize germination and emergence, under properly controlled conditions, was unhindered at increasing NH_4VO_3 concentrations in the soil, but at the higher treatment levels, the seedlings did not develop past the emergent coleoptile phase. After 22 days of growth, a dramatic reduction in relative yield at higher NH_4VO_3 concentrations in both Rensburg and Swartland soil was apparent. Increasing soil salinity, acidity and potentially, soil ammonia at higher application of NH_4VO_3 were found to make no contribution to this trend. Maize grown in Swartland soil was more tolerant to applied vanadate than maize grown in Rensburg soil, and this was explained in terms of greater vanadate sorption, and lower solution-phase vanadate concentrations in the Swartland soil than in the Rensburg soil.

Two important issues need to be resolved in future work. Firstly, the potential inhibition of seed germination at higher vanadium levels should be clarified. Secondly, whether the high vanadium concentrations observed in plant material were a result of efficient uptake of the element by plants, or were a result of sample contamination remains uncertain and needs to be resolved.

Chapter 1

Introduction

Land farming or land treatment of effluents is a common, accepted strategy for the disposal and treatment of liquid and sludge wastes. It relies on the physical, chemical and biological components of the soil matrix to attenuate and/or immobilise waste constituents. The success of this process relies on careful planning and management of land treatment sites, so that the capacity of the soil to accept the waste is not overcome. This entails monitoring and predicting when priority pollutants in the effluent reach critical levels in the soil environment. Although standards have been set for a number of environmentally important chemicals, there are a number which have received scant attention. Vanadium is one of these. Since this element is often enriched in effluents generated by coal, oil and associated industries, its fate and effect in land treatment systems, which are commonly employed in these trades, requires assessment.

Land treatment has been described as 'an engineered delivery of wastes to a designated site with prescribed objectives' (Page *et al.*, 1986), those objectives generally being the attenuation and immobilisation of organic and inorganic waste components. Bender (1980) conducted a comprehensive survey of land treatment systems in operation in the United States of America. He found that a wide variety of processes are utilised, but the three main systems in use were slow rate infiltration, rapid rate infiltration and overland flow.

In the slow rate system, vegetation is important in the management of both water and waste constituents, which may be utilised as plant nutrients (Bender, 1980). Wastewater is applied to the soil either by strip flooding or sprinkler irrigation and is treated as it slowly moves through the soil matrix (Bender, 1980). Surface runoff may or may not be contained, and evaporation and transpiration are important in the removal of up to 50% of the water volume during treatment, the remainder being discharged to groundwater, or recycled for crop irrigation or other re-use purposes (Thomas, 1986).

Rapid rate infiltration systems are similar to slow rate systems but are designed to prevent surface run-off (Thomas, 1986), and their main aim is to remove insoluble wastewater constituents by filtration (Bender, 1980). Evaporative losses are minimal because loading rates are high and most of the treated effluent percolates to groundwater (Thomas, 1986). As such, this treatment strategy is inapproriate for wastewaters containing significant amounts of soluble material, and slow rate infiltration is preferred (Thomas, 1986).

In overland-flow systems, wastewater is applied to a sloped surface and allowed to flow across the soil to collection ditches, where it is collected for recycling purposes or discharged (Bender, 1980). Treatment is by means of physical, biological and chemical processes in the top part of the soil, and percolation is minimised either by utilising impermeable soil types or engineered subsurface barriers (Bender, 1980).

Land treatment of sludges may involve simply pumping the effluent onto the land surface where it either remains, or is ploughed into the soil. A more favoured method is to pump sludge into trenches which are backfilled, in this way dealing with problems of odour.

The effectiveness of soils as waste treatment systems is highly variable and will depend on the physical, chemical and biological properties of each soil type involved, and as such, the development of a land treatment system must take into account site- and waste-specific parameters (Page *et al.*, 1986). The most limiting constituent of the effluent will determine the rate of effluent application, and a threshold relating to this constituent will exist above which land application of waste is no longer acceptable (Page *et al.*, 1986).

In sewage sludges, it is often the trace metal content which is limiting and which defines both the capacity of the soil to deal with the waste, as well as the life-span of a land treatment site (Page *et al.*, 1986). It is conceivable that this constraint will apply to *any* land treatment operation. Setting the maximum tolerable limits of trace elements in a site utilised for the treatment of effluents is difficult, however, and relies on toxicity data which is often inappropriate or unavailable. Most studies of trace elements in the environment have centred around such species as zinc, cadmium, arsenic, lead, molybdenum and a few other metals. A number of elements, though, have been largely ignored and it has only been recognised recently that efforts to determine their fate and effect in the environment are required. Vanadium is one such element. This study was therefore initiated to gain some insight into the possible effects of vanadium in a particular land treatment scheme in the Eastern Transvaal.

Chapter 2

The distribution, toxicity and chemistry of vanadium - a review

Before embarking on a study of the potential environmental impacts of any element, consideration of its natural distribution in the environment, its potential targets and toxicity, as well as its chemistry and speciation is required. This chapter presents a review of relevant literature covering these aspects, with specific reference to vanadium.

2.1 Distribution

Vanadium is classified in group VB of the periodic table, and has an atomic number of 23 and an atomic weight of 50.92 (Baroch, 1983). It is widely distributed throughout the Earth, and has been identified in the spectra of many stars, and our Sun (Baroch, 1983). It occurs in over 65 minerals, the most important of which are listed in Table 2.1. Generally, vanadium is associated with uranium-bearing minerals in Colorado, with phosphatic shales and phosphate rocks in the western regions of America, and is a constituent of titaniferous magnetites which are widely distributed with large deposits in the former USSR, South Africa, Finland, China, America and Australia (Baroch, 1983). The element is used as an alloy in various steel products and as a catalyst in a number of industrial processes. Vanadium tends to associate with, and accumulate in organic-rich deposits like coal, and is often enriched in waste streams after the combustion or processing of these materials (*eg*. Dreesen *et al*., 1977) (Table 2.2).

Release of vanadium to the environment is receiving some attention. Nriagu and Pacyna (1988) consider the increased circulation of trace metals through the biosphere as a result of man's activities to be an important environmental issue, and conducted an investigation into the release of these elements into the environment on a global scale.

Table 2.1: Important vanadium minerals and the environments in which they are associated (adapted from Burkart-Baumann, 1972).

MINERAL	COMPOSITION	ASSOCIATION
Patronite	VS_4	Bituminous sedimentary deposits
Sulvanite	$CuVS_4$	Hydrothermal systems
Colusite	$Cu(As,Fe,Sn,V,Te)V_4$	Hydrothermal systems
Coulsonite	$(Fe,V)_3O_4$	Magnetite differentiations
Vanadinocker	V_2O_5	Oxidation zones
Montroseite	$(V,Fe)OOH$	Oxidation zones
Vanadinite	$Pb_5Cl(VO_4)_2$	Oxidation zones
Descloizite	$Pb(Zn,Cu)(VO_4)(OH)$	Oxidation zones
Mottramite	$Pb(Cu,Zn)(VO_4)(OH)$	Oxidation zones
Carnotite	$K_2(UO_2)_2(VO_4)_2.3H_2O$	In pores of sandstones
Tyuyamunite	$Ca(UO_2)_2(VO_4)_2.nH_2O$	In pores and fractures in limestones
Roscoelite	$KV_2(AlSi_2O_{10})(OH,F)_2$	In sandstone pores and in gold and telluride veins

Table 2.2: Concentration ranges ($mg.kg^{-1}$ solid) for vanadium in fossil fuel waste, coal and soil (adapted from Eary *et al.*, 1990).

MATERIAL	CONC ($mg.kg^{-1}$ solid)
Fly ash	12 - 1180
Bottom ash	12 - 540
Flue-gas desulph. sludge	<50 - 260
Oil ash	10 - 460000
Coal	0 - 1280
Soil *	20 - 500

* The concentration of vanadium in soil has been found to correlate with the concentration of the element in the parent material from which the soil was derived (Burkart-Baumann, 1972).

Of the thirteen elements they considered, vanadium is ranked third in terms of total emissions to the atmosphere, with only lead and zinc emissions being greater. Input of vanadium into aquatic systems is ranked ninth, and into soil systems is ranked sixth. The main source of vanadium pollution seems to be oil, coal and related industries, as well as iron and steel industries. The inventory of Nriagu and Pacyna (1988) for vanadium is summarised in Table 2.3.

Table 2.3: World-wide vanadium emissions from various sources (adapted from Nriagu and Pacyna, 1988).

RECEIVING COMPARTMENT	POLLUTION SOURCE	EMISSIONS (tonnes per year)
ATMOSPHERE	Coal combustion: electric utilities	310 - 4650
	industry & domestic	990 - 9900
	Oil combustion: electric utilities	6960 - 52200
	industry & domestic	21480 - 71600
	Cu-Ni Production	43 - 85
	Steel & Iron manufacturing	71 - 1420
	Sewage sludge incineration	300 - 2000
	TOTAL *	30150 - 141860
HYDROSPHERE	Domestic wastewater	4500
	Steam electric utilities	600
	Mining, smelting and refining	1200
	Manufacturing processes	1100
	Atmospheric fallout	9100
	Dumping of sewage sludges	4300
	TOTAL	20800
LITHOSPHERE	Agricultural & food wastes	300 - 22000
	Wood wastes & urban refuse	1700 - 15100
	Organic wastes & sludges	2330 - 13260
	Solid wastes & metal	30 - 220
	manufacturing	110 - 1830
	Fertiliser & peat usage	11000 - 67000
	Coal fly ash & bottom ash	3200 - 21000
	Atmospheric fallout	18570 - 140410
	TOTAL	37240 - 280820

* Ranked third largest emission, with lead and zinc ranked first and second, respectively.

2.2 Toxicity

Although there seems to be a fairly widespread release of the element into the environment, no bio-accumulation of vanadium has been documented in the human food chain (Bradford *et al.*, 1990). Very little information is available concerning the role of vanadium in animal systems, and toxicity data is even more scarce. Generally, the element is found in very low quantities in mammalian tissue. The requirement for vanadium in human diets may be in the order of 0.116 mg per 24 hours (Jorgensen, 1979) and it may be involved in the mobilisation of iron to the liver and calcium to bones (Maccioli & Risby, 1978). More recently, attention has been focused on the role of vanadium in sugar metabolism, and it is undergoing testing as a therapeutic replacement for insulin in the treatment of diabetes (Sekar & Govindasamy, 1991).

Tissues of the respiratory system seem to be most sensitive to the toxic effects of vanadium. Threshold limits of vanadium in the air have been set at 0.5 $mg.m^{-3}$ for dust and 0.05 $mg.m^{-3}$ for fumes, and vanadium concentrations above these limits result in respiratory tract tissue damage (Rosenbaum, 1983). Oral toxicity is limited by the fact that up to 99% of an ingested dose may be excreted (Jorgensen, 1979). If sufficient vanadium is ingested, though, in the order of 4 to 5 mg per day, gastrointestinal tissues, blood and liver tissues, as well as essential coenzymes and cofactors will be damaged (Maccioli & Risby, 1978; Hansen *et al.*, 1986). In addition, the toxic effects of vanadate may be cumulative. This was concluded by Al-Bayati *et al.* (1989), when they observed acute toxic signs and death in rats after the injection of 0.9 $mg.kg^{-1}.day^{-1}$ for 16 days.

With growing evidence that vanadium release to the environment is on the increase and that it may be as toxic as inorganic arsenic, fluorine, nickel and perhaps lead and cadmium (Tables 2.4 and 2.5), it is not surprising that vanadium has been placed on priority chemical pollutant lists in the United Kingdom (Abbasi, 1981) and in America (Petrie, 1994).

Table 2.4: Data relating to plant and animal tolerances of various trace metals (adapted from Sommers & Barbarick, 1986).

ELEMENT	LEVEL IN PLANT FOLIAGE ($mg.kg^{-1}$ dry weight)		MAXIMUM LEVELS CHRONICALLY TOLERATED			
	NORMAL	TOXIC	CATTLE	SHEEP	SWINE	FOWL
V	0.1-1	10	50	50	10*	10
Cd	0.1-1	5-700	0.5	0.5	0.5	0.5
As	0.01-1	3-10	50	50	50	50
Co	0.01-0.3	25-100	10	10	10	10
F	1-5	-	40	60	150	200
Mo	0.1-3	100	10	10	20	100
Pb	2-5	-	30	30	30	30
Se	0.1-2	100	2*	2*	2	20
Ni	0.1-5	50-100	50	50*	100*	300*

* estimated values as a result of insufficient data.

Table 2.5: Toxic dosages for various trace metals in the human diet (Alloway & Ayres, 1993).

ELEMENT	TOXIC DOSE ($mg.day^{-1}$)
Vanadium	18
Chromium	200
Mercury	0.4
Lead	1
Arsenic	5 - 50
Cadmium	3 - 330
Zinc	150 - 600

2.3 Chemistry and speciation

Vanadium is extremely sensitive to redox and pH fluctuations and can exist in one of five oxidation states, from +II to +VI. The most important oxidation states of vanadium in natural systems appear to be the +III, +IV and +V species, and the complexity of their speciation is evident in Table 2.6.

Table 2.6: Vanadium aqueous and solid species likely to be found in natural systems (adapted from Wanty & Goldhaber, 1992).

VANADIUM (III)	VANADIUM (IV)		VANADIUM (V)
V^{3+}	VO^{2+}	VOF_3^-	$H_4VO_4^+$
VOH^{2+}	$VO(OH)^+$	VOF_4^{2-}	$H_3VO_4^0$
$V(OH)_2^+$	$(VO(OH)_2)^{2+}$	$VOCl^+$	$H_2VO_4^-$
$V(OH)_3^0$	$VO(OH)_2^0$	$VOSO_4^0$	HVO_4^{2-}
$V_2(OH)_2^{4+}$	VOF^+	$VOCO_3^0$	VO_4^{3-}
V_2O_3	VOF_2^0	$VO(OH)CO_3^-$	
VSO_4^+			

2.3.1 *Vanadium(III) species*

Vanadium(III) solubility in water is controlled by the formation of hydroxide or oxyhydroxide solid phases which hydrolyse to yield species in the form $V_i(OH)_j^{3i-j}$ (Wanty & Goldhaber, 1992). The most important solid phases of vanadium(III) from a geological point of view are $V(OH)_3$ and VO(OH) (montroseite), with $V(OH)_3$ existing as an amorphous solid, and perhaps in a far less soluble form than previously thought (Wanty & Goldhaber, 1992). Little work has been done on vanadium(III) complexation, apart from some investigations into vanadium(III)sulphate which is extremely weak, but modelling experiments predict the occurrence of strong vanadium(III)chloride complexes (Wanty & Goldhaber, 1992). Vanadium(III) species may occur across the pH scale, but are limited to conditions where the redox potential is below 0.4V (Figure 2.1). Above pH~5 and below an Eh of 0.2 V, one would expect vanadium to be in the insoluble $V(OH)_3^0$ form (Figure 2.1). Vanadium(III) species are much less soluble than oxidised forms of V(IV) and V(V) (Wanty & Goldhaber, 1992).

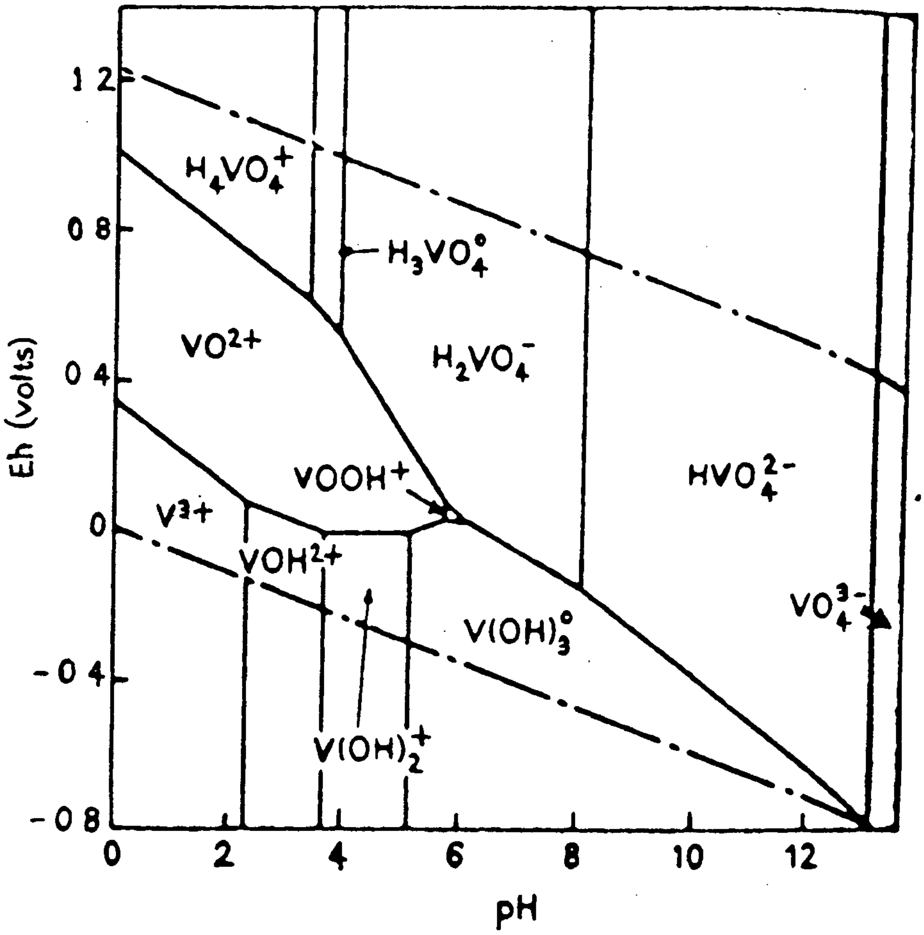


Figure 2.1: Eh-pH diagram for vanadium at 25°C, with a total dissolved metal activity of 10^{-5} mM and total dissolved C and S at 1 mM. Long dashed lines indicate the stability field for water. (Eary *et al.*, 1990).

2.3.2 *Vanadium(IV) species*

The VO^{2+} ion is a fairly robust species because it has a π-bonding arrangement between the vanadium and oxygen atoms (Wanty & Goldhaber, 1992). Vanadyl hydroxide, $VO(OH)_2$, is extremely insoluble, with a solubility product of $10^{-21.9}$ at zero ionic strength (Wanty & Goldhaber, 1992) and may therefore be important in determining vanadyl solubility in aqueous systems. The most important species in vanadyl ion hydrolysis appear to be $VO(OH)^+$ and $[VO(OH)]_2^{2+}$ at low ionic strength, but at higher vanadium concentrations, more complex species like $HV_4O_9^-$, $V_4O_9^{2-}$ and $VO(OH)_3^-$ become important (Wanty & Goldhaber, 1992).

The vanadyl ion may interact with several ligands but only a few complexes are strong enough to be important under natural conditions, and these include F^-, Cl^- and SO_4^{2-} (Wanty & Goldhaber, 1992). Thermodynamic considerations suggest that vanadyl-carbonate complexes are likely to exist, with possible species being $VOCO_3^0$, $VO(CO_3)_2^{2-}$ and $VO(OH)CO_3^-$. Alberico and Micera (1994) showed that VO^{2+} complexation with phosphate species occurs readily, giving a wide variety of vanadium-phosphorus complexes. Such complexation is extremely pH-dependent. In neutral to basic systems (pH 4.5 to 8.5) precipitation occurs, resulting in the depletion of solution-phase vanadium. Outside of these limits soluble vanadium-phosphate complexes occurs, for example $[VO(H_2PO_4)(HPO_4)]^-$.

Vanadium(IV) species appear to occur below pH 6 under oxidising conditions (Figure 2.1). However, complexation of vanadium in other oxidation states may involve a redox reaction, whereby vanadium is converted to the +IV state and held by the complexing ligand as VO^{2+} (Figure 2.2), implying that the distribution of vanadium(IV) in natural systems may be wider than is suggested by Figure 2.1.

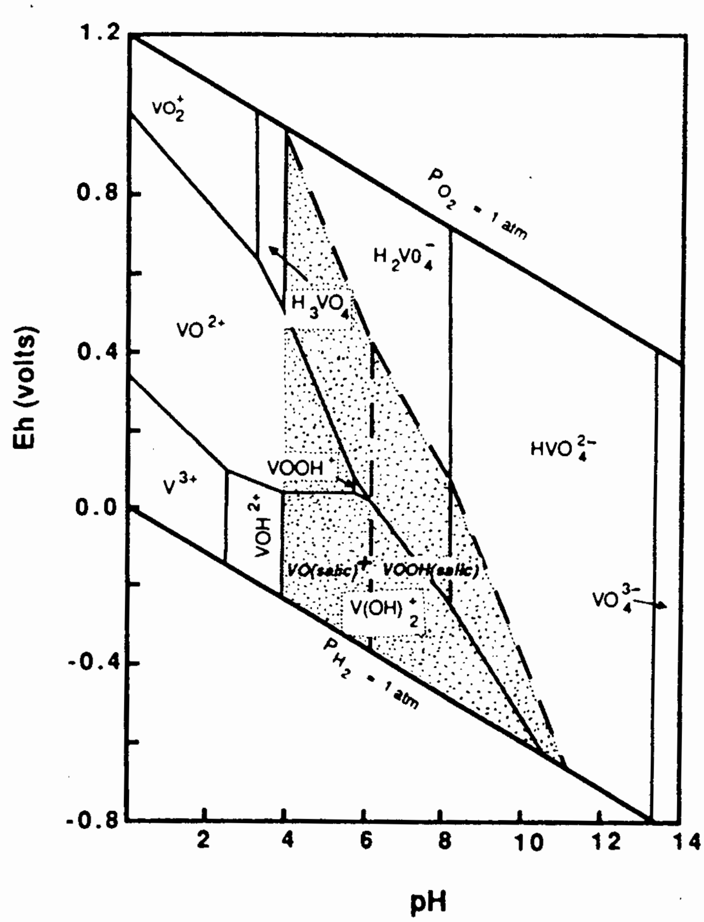


Figure 2.2: Eh-pH diagram of vanadium-water (solid lines) and vanadium-water-salicylate (dashed lines, dotted area) at 0.01 mM and vanadium at 0.01 mM (Breit & Wanty, 1991).

2.3.3 *Vanadium(V) species*

In most natural systems, the predominant vanadium(V) species are of the $H_nVO_4^{n-3}$ vanadate hydrolysis series (Wanty & Goldhaber, 1992). Anionic vanadium(V) species tend to exist above pH ~5 under oxidising and reducing conditions (Figure 2.1), but at higher redox potential may occur in cationic forms like VO_2^+ and $H_4VO_4^{2+}$ below this pH limit (Figures 2.1 & 2.2). An important aspect of vanadium(V) chemistry is its tendency to form polymerised species at higher vanadium concentrations, especially between pH 2 and 8 (Figure 2.3). Complexation of vanadium(V) with organic ligands may be important under certain conditions, and the solubilities of oxidised V(IV) and V(V) species may be significantly enhanced by complexation with short-chain organic acids (Wanty & Goldhaber, 1992).

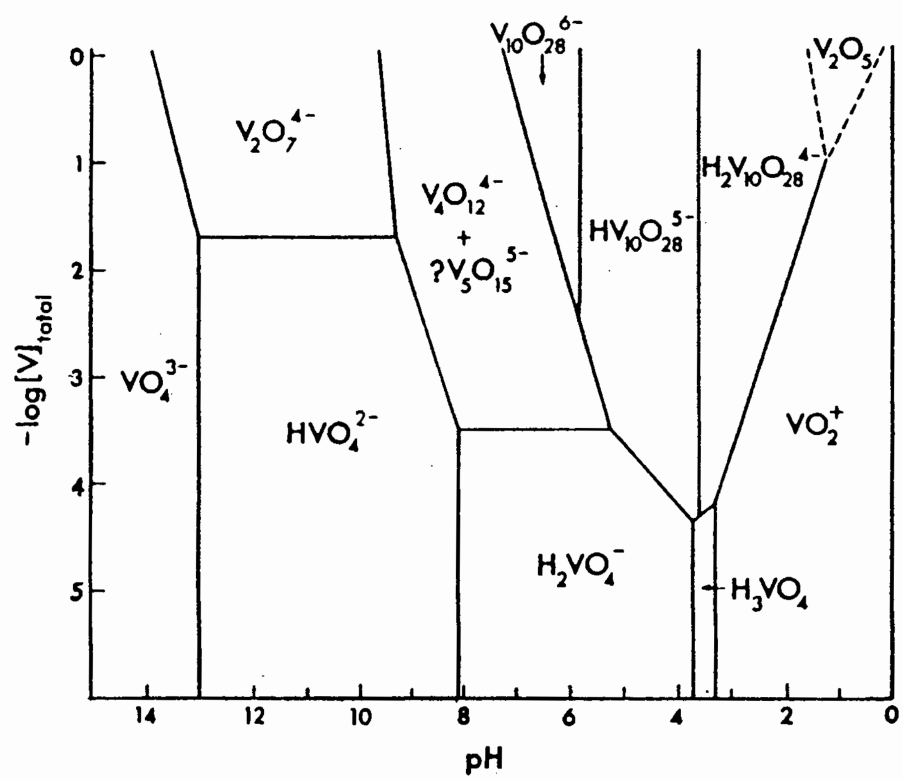


Figure 2.3: Distribution diagram for polymerised vanadium species. This diagram is based on equilibrium data obtained from experimentation with vanadium compounds in NaCl or $NaClO_4$ matrices, with ionic strength between 0.5 and 3.0M (Pope, 1983).

Speciation of vanadium in aqueous systems appears to be quite complex, with controlling factors being pH, redox potential, vanadium concentration, and the presence of inorganic or organic ligands. The situation is even more intricate if one considers that the solubility of those vanadium species which control solution-phase vanadium may be modified to a large extent by the nature and concentration of complexing ligands (Wanty & Goldhaber, 1992). The degree of such modification will also depend on the effects of prevailing pH, redox potential and concentration on ligand speciation.

2.3.4 *Redox conditions*

Fluctuating redox potentials will occur in soils with a high content of swelling clay, and in soils periodically amended with organic-rich effluents. Since the redox state of a system will affect the types of solubility-controlling solids which might form, as well as the sorption-desorption characteristics of trace elements (Eary *et al.*, 1990), particularly for vanadium, it is important to consider in more detail the behaviour of this element under different redox conditions.

Eary *et al.* (1990) decided that the redox states of minor elements in waste solids and leachates, including vanadium, are not well known, and took some steps to improve current knowledge. It seems, though, that a degree of uncertainty still remains, illustrated for example by their claim that V(IV) can be reduced to V(III) by organics, which directly contradicts Wanty and Goldhaber's (1992) conclusion in this regard.

Aqueous vanadium species under reducing conditions include various hydroxylated vanadium(III) species, the solution-phase concentrations of which are dependent to a large degree on pH (Eary *et al.*, 1990). This is because the degree of protonation and deprotonation of associated hydroxyl groups will influence their charge and therefore their solubility and sorption behaviour.

Generally, though, it seems that vanadium is more insoluble under reducing conditions, because it is here that cationic vanadium forms tend to dominate, and these are able to form insoluble hydroxide or oxide solids like $V(OH)_3$ (Eary *et al.*, 1990) and V_2O_4

(Middelburg *et al.*, 1988). It has been noted by Amrhein *et al.* (1993), for example, that a gradual decrease occurs in soluble vanadium concentration in evaporation pond soils under reducing conditions, and this was attributed to the slow precipitation of vanadyl hydroxide, $VO(OH)_2$.

Another factor which may control vanadium solubility under reducing conditions is H_2S. Under reducing conditions there is great potential for H_2S production as a result of anaerobic microbial metabolism. Vanadium(IV) can be reduced to vanadium(III) by H_2S, to yield $V(OH)_2^+$ with subsequent precipitation of insoluble vanadium(III) species (Wanty & Goldhaber, 1992). Bloomfield and Kelso (1973) found that vanadate was immobilised during anaerobic incubation of sulphate-reducing bacteria, and was remobilised on subsequent aeration. They attributed these changes in mobility to the precipitation and/or co-precipitation of vanadium with sulphides, and their dissolution upon oxidation.

Under oxidising conditions, the dominant vanadium species are anionic +V species (Eary *et al.*, 1990). Figure 2.4 gives an indication of the variability of vanadate speciation under oxidising conditions, all parameters besides pH being constant. The vanadates are soluble over a wide pH range, but are prone to local precipitation with cations like Pb, Zn and Cu, to form common vanadium minerals like vanadinite, descloizite and mottramite (Burkart-Baumann, 1972).

It is important to note the observation of Eary *et al.* (1990) that in most natural situations, redox reactions may be in a state of disequilibrium because of slow reaction rates, or because of microbially-mediated catalysis, and as such, interpretation of Eh-pH diagrams like Figures 2.1 and 2.2 should be considered very carefully, because they relate to equilibrium conditions in very controlled systems. Another point to consider is that redox potential may control the solubility of an element not by directly influencing its speciation, but by controlling the solubility of the substrate to which that element is sorbed (Amrhein *et al.*, 1993). This is especially true for vanadium because it has been shown to have an affinity for iron oxides in the soil environment (Section 3.4.2 and 3.4.3), the solubility of which is sensitive to redox potential.

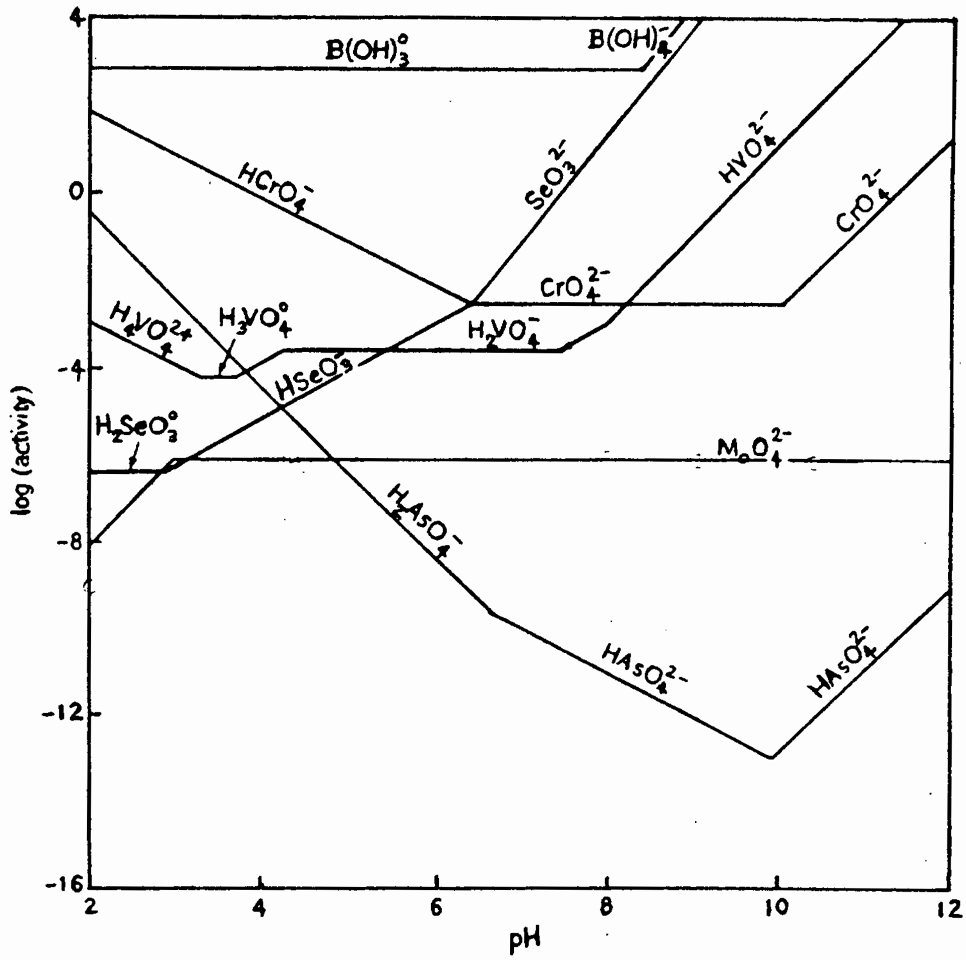


Figure 2.4: Aqueous speciation of elements that form oxyacids at 25°C, with $CO_{2(g)}$ at $10^{-3.5}$ atm and SO_4^{2-} at 1 mM (Eary *et al.*, 1990).

2.3.5 *Ammonium metavanadate*

The vanadium compound considered in this study was ammonium metavanadate, since time and cost constraints precluded the use of other vanadium compounds. Because +V vanadate species appear to be the most mobile forms of vanadium in natural environments, any conclusions drawn from this work would most likely be relevant to a worst case scenario. Since vanadate derived from ammonium metavanadate would be expected to behave similarly to that derived from sodium ammonium vanadate, the results presented in this study will have a bearing on situations where the source of vanadium in effluents is sodium ammonium vanadate, a commonly employed desulphurisation catalyst.

Ammonium metavanadate (NH_4VO_3) is an anhydrous metavanadate in which the V atoms are tetrahedrally co-ordinated to four oxygen atoms, two of which are terminal, and the other two are bridging, so that there is no discrete "metavanadate ion" unit in the solid state (Clark, 1973). Aqueous-phase speciation of the vanadate has been represented in Figures 2.3 and 2.4.

2.4 Conclusions

The chemistry of vanadium is complex, characterised by various oxidation states and a large number of possible chemical forms. On the basis of this review, forms of vanadium present in the soil solution at common soil pH (4-8) and under oxidising conditions would be $H_2VO_4^-$, with the precipitation of more insoluble vanadium(III) hydroxides under more reducing conditions. In more acidic soils, a fair proportion of total soluble vanadium would be expected to occur in the VO^{2+} form, which would behave as other cations of the soil solution, and become associated with cation binding sites on mineral or organic colloids. At higher total solution-phase vanadium concentrations, complex polymerised species may dominate, especially under oxidising conditions where the stability of vanadium(V) species is favoured.

The importance of vanadium as an environmental contaminant appears to be on the increase, but little definitive, quantitative information regarding its role in biological systems, and its toxicity, is readily available. This is partly because the work has not yet been done, and partly because a number of reports which seem to be highly relevant in this regard, are inaccessible, being housed in private libraries.

The general objective of this study then, was to conduct a preliminary assessment of the behaviour of applied vanadium in a particular land treatment scheme in the Eastern Transvaal, and its possible effects on the biotic components of the sites in question. In light of the previous discussion of global vanadium emissions and toxicity, it is clear that this project is also relevant in a more universal context, and as such, may serve to broaden the foundation of scientific knowledge relating to the environmental geochemistry of this trace element.

Chapter 3

Sorption of vanadate on selected soils

3.1 Introduction

There are two fundamental mechanisms by which anions adsorb to soil surfaces, namely specific and non-specific adsorption, and the extent to which either of these occurs for a particular anion species will determine its strength of association with a soil surface, as well as its mobility in the soil environment and potential threat to groundwater.

Species involved in non-specific adsorption include $HClO_4^-$, NO_3^-, Cl^- and Br^-, and these are retained in the double diffuse layer associated with charged surfaces (Mott, 1988). As such, those factors which influence the double diffuse layer at a soil surface will also influence the adsorption of these anions. The most important factor in this regard is the solution electrolyte concentration, since at greater dilution of the soil solution, a greater degree of anion exclusion from the surface will occur (Mott, 1988). Non-specifically binding anions tend to be relatively mobile in soil environments, and may pose a significant threat to groundwater.

Almost all other anions "form firmly bound surface species by making partly covalent bonds at hydroxyl sites, not by addition, but by complete replacement of the charged group at the surface" (Mott, 1988). This is the fundamental concept underlying specific sorption, and is a mechanism termed ligand exchange.

The most important surface functional group in soils is the OH group, which will have different chemical properties and reactivities according to stereochemistry (Sposito, 1989). As far as anion adsorption is concerned, the most important of these OH groups are the so-called Lewis acid sites (Figure 3.1), present on metal oxide surfaces, 1:1 clays and 2:1 clay mineral edges (Sposito, 1989). In theory, the high reactivity of Lewis acid sites is a consequence of the surface metal atom being associated with an unstable water molecule. This water molecule exchanges readily for solution-phase organic or inorganic anions, which then form stable bonds with the surface metal atom (Sposito, 1989).

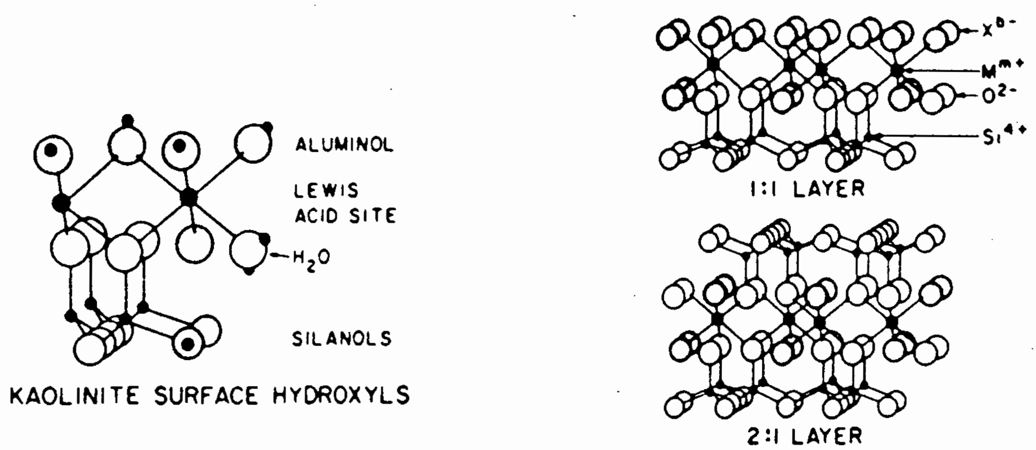


Figure 3.1: Schematic illustration of Lewis acid sites on both 1:1 and 2:1 layer silicates (adapted from Sposito, 1989).

Within more common soil pH ranges, however, the ligands that predominate in these sites are not unstable water molecules, but are more stable, covalently bound hydroxyl groups which require protonation before ligand exchange can proceed, and it is for this reason that the anions participating in this type of sorption are generally oxyanions of weak acids, like phosphoric acid and silicic acid, since they have at least one protonated form (Mott, 1988). Surface hydroxyl groups often carry a partial negative charge and this promotes the removal of a proton from an oxyanion, which is consequently in the immediate vicinity of an unstable water ligand, and participates in ligand exchange (Mott, 1988).

Anions which form more than one ligand bond become bound very tightly to surfaces, do not desorb easily, and include such species as fulvic and humic acids, orthophosphate and selenite (Mott, 1988). Species like borate, fluoride and silicate form only one ligand bond, and so become fairly strongly-associated surface complexes, but are more easily desorbed than the species mentioned above (Mott, 1988). Species also exist which form ligand bonds to some extent, but also form outer-sphere complexes, and as such are the most easily desorbed of all. Such species include carbonate and sulphate (Mott, 1988).

Anions which bind by specific adsorption tend to become immobilised in the soil environment, and once bound are unlikely to desorb and wash through into groundwater. An important consideration, though, is the rate of the complexation reaction, since if this is fairly slow, then wash-through may occur before adsorption/immobilisation has any effect.

Three important mathematical functions have been derived to relate the solution-phase concentration of an ion to its sorbed-phase concentration after a suitable equilibration period. These are the Langmuir, (Von Bemmelen-)Freundlich, and the less applied Tempkin, adsorption isotherms (Mott, 1988). All of these describe so-called L-curve isotherms, which are characterised by a slope which is initially steep, and then becomes shallower, approaching horizontal (Sposito, 1989). Because of the generality of these mathematical expressions, they cannot be used to decide on the specific mechanisms involved in ion adsorption (Mott, 1988), but they can still yield useful information on the comparative extent of ion adsorption in systems which are similar, and allow very general inferences to be made on possible mechanisms of ion adsorption.

In this study, only two papers were encountered which dealt specifically with vanadium(V) sorption to soil colloids. Mikkonen and Tummavuori (1993) considered the retention of vanadium(V) on kaolinite over a pH range of 2 to 7.5, and found that it was sorbed to a certain extent, with maximum retention occurring in the region of pH 4 (Figure 3.2). Szalay and Szilagyi (1967) reported the reduction of VO_3^- to VO^{2+} by insoluble humic acids under laboratory conditions similar to those of natural environments, and found that reduced vanadium concentrated on the humic acids with a geochemical enrichment factor of roughly 50 000:1. A number of authors have proposed mechanisms for such reduction, for example complexation and reduction by catechols (Templeton & Chasteen, 1980), and reduction by organic thiol groups (Legrum, 1986).

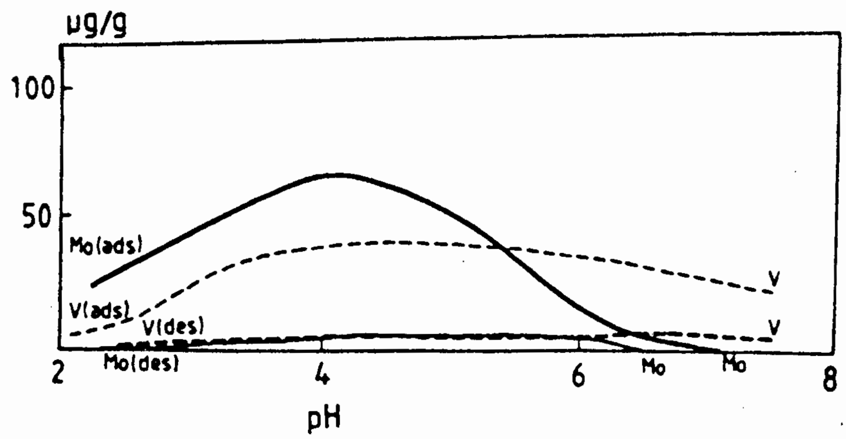


Figure 3.2: Adsorption of vanadium(V) on kaolin from 10^{-5} M solutions. Results from a separate experiment with Mo are also shown. The solutions initially contained 50.94 µg of V, and 95.94 µg Mo in 0.02M KCl. Adsorption results are indicated by 'ads', and desorption results are indicated by 'des'. (Mikkonen & Tummavuori, 1993).

Crans and Shin (1994) investigated the complexation of vanadate with ligands containing oxygen and nitrogen chelating functional groups, and found that very stable complexes were formed, generally containing only one ligand and one vanadate moiety, even at high total vanadium concentration. In addition, the stability of these complexes was found to vary with ligand type and reaction conditions, especially pH, which was also observed by Ehde *et al.* (1986, 1989).

It seems that a great deal of effort has been directed at elucidating the specific mechanism of vanadium-organic interactions, with particular emphasis on the VO^{2+} species (*eg.* Branca *et al.*, 1990), which binds very strongly to humic materials (McBride, 1978). This association involves the insertion of organic, anionic functional groups into the inner hydration sphere of the VO^{2+} molecule in its axial plane, where weakly-bound water molecules can easily be displaced. Such close electrostatic association is not possible with clay surfaces, because the negative charge associated with clays is buried within the clay structure (McBride, 1978). When VO^{2+} is associated with the permanent charge sites of fully-hydrated clays, therefore, its mobility may be very close to that of solution phase VO^{2+}.

The binding of vanadium(IV) to organic material occurs fairly rapidly. The reaction of VO^{2+} with oxalate, for example, was found to have an equilibrium constant in the order of 10^{12} (Wanty & Goldhaber, 1992), and at solution pH values of 3, 3.5 and 4, Shimmack and Bunzl (1985) observed half times for VO^{2+} sorption to soil organic matter of 0.4, 0.9 and 1.0 minutes, respectively, and equilibrium was attained after an hour. No such quantitative data was encountered for vanadate sorption.

Because of the apparent scarcity of information specific to vanadate sorption and immobilisation in the soil environment, it was considered highly relevant to consider vanadate sorption in four soils present on the sites in question, and interpret these results in terms of the land treatment scheme concerned. Since pH appears to influence vanadium sorption to a fairly large extent, vanadate sorption under three different conditions of acidity was also investigated.

3.2 Materials and methods

3.2.1 *Soils studied*

The soils considered in this study are of the Rensburg and Swartland soil forms, which are common in the Eastern Highveld area. The Rensburg soil can be described as a heavy, black clay soil, with the clay fraction containing a minor proportion of mica, but dominated by a smectitic component. The sample used was obtained from a pile of supposedly clean Rensburg soil which was being stored for use in a remediation operation. The Swartland soil is an acidic brown loam, with a predominantly kaolinitic clay fraction, and the sample used in this study was obtained from the edge of a land treatment site. Both of these soil types were extensively characterised by Ginster (1993) and Bester (1993).

The third soil examined was not classified, and has arbitrarily been termed the Sasolburg soil in this study for purposes of identification. It can be described as a sandy clay soil, having a clay fraction dominated by a smectitic component, but with a large proportion of micaceous minerals, and a small contribution from a kaolinitic fraction. Two samples of the Sasolburg soil were obtained, one from a supposedly clean, undisturbed area, as well as one from an area which has been routinely used as a sludge disposal site. Effectively, then, four soils were tested in this study.

Preparation of the Rensburg and Swartland soils involved air drying and crushing to pass a 4 mm pore diameter sieve for the plant growth experiments, and a 2 mm pore diameter sieve for the sorption work. The two Sasolburg soils were simply passed through the 2 mm sieve. Details of the soil characterisation tests conducted in this study, along with clay mineralogical determinations, are presented in Appendix A, and the results are summarised in Table 3.1.

3.2.2 *Sorption experiments*

The basic protocol for the sorption experiments involved placing 2.5 g aliquots of prepared soil into 50 ml plastic centifuge tubes and adding 25 ml of ammonium vanadate solution. These tubes were then sealed with a parafilm-covered cork bung and were placed on a horizontal shaker. After a set shaking period, the tubes were centrifuged at 6000 rpm for 5 minutes, and the electrical conductivity (EC) and pH of the supernatants were determined. The supernatant of each tube was decanted and passed through a 0.22 μm pore diameter Millipore membrane filter, diluted 20x using deionised water, and submitted for vanadium determination. The amount of vanadium sorbing to the soil was determined by subtraction.

Vanadium analysis was conducted on a Jobin Yvon 70C inductively-coupled plasma spectrometer (ICP) using a standard method for vanadium and reading the peak occurring at 309.311 nm. Calibration employed standards prepared up to a concentration of 500 $mg.l^{-1}$ NH_4VO_3 in 0.1M NaCl, and vanadium concentrations as low as 1 $mg.l^{-1}$ were determined with reasonable accuracy.

Table 3.1: Data relevant to the four soils examined in this study, summarised from Appendix A.

DETERMINATION	SOIL TYPE			
	RENSBURG	SWARTLAND	SASOLBURG (clean)	SASOLBURG (contaminated)
Elemental analysis				
Al_2O_3 (%)	7.76	8.53	10.22	7.50
Fe_2O_3 (%)	4.31	6.61	4.91	4.34
MnO (%)	0.08	0.17	0.07	0.05
V ($mg.kg^{-1}$)	109	200	121	248
Mn ($mg.kg^{-1}$)	769	1630	645	505
Pb ($mg.kg^{-1}$)	13	15	16	43
Zn ($mg.kg^{-1}$)	45	60	59	355
Cu ($mg.kg^{-1}$)	27	37	26	54
Particle size distribution (%)				
Sand	43.9	53.2	55.4	nd
Coarse silt	0	6.3	9.4	
Fine silt	32.8	17.5	16.7	
Clay	23.3	23.0	18.5	
Clay mineralogy				
Major	Smectite	1:1 interstratified clays	Smectite Mica	nd
Minor	Mica	Mica	Kaolinite	
Soil organic material (%)	0.17	2.17	0.91	7.33
Soil moisture holding capacity (ml)	0.637	0.447	nd	nd
Soil pH				
H_2O	6.29	9.28	6.95	6.60
1M KCl	5.85	7.71	6.15	6.19
0.01M $CaCl_2$	5.45	7.59	5.64	6.36
BET surface area ($m^2.g^{-1}$)	49.14	38.43	24.87	nd

Note:

1. Elemental analysis was conducted using X-Ray fluorescence spectroscopy;
2. Particle size analysis was determined using a standard Lowy pipetted method (SSSSA, 1990);
3. Clay mineralogy of separated clay was investigated using X-Ray diffractometry.
4. Soil organic material content was determined using the standard Walkley-Black method (SSSSA, 1990);
5. Soil moisture holding capacity was determined by measuring the amount of water held by air-dried soil at its sticky point, where the soil surface just begins to glisten;
6. Soil pH determinations involved a soil to solution ratio of 1:10, and an equilibration period of 10 minutes on horizontal shaker;
7. BET surface area was determined by nitrogen adsorption.

nd : not determined

The 14 ammonium vanadate solutions used to draw up initial adsorption isotherms covered a range from 0 to 1000 $mg.l^{-1}$ NH_4VO_3 and were made up in 0.1M NaCl solution (Appendix B), and the tubes were shaken for 24 hours. Subsequent work was limited to between 0 and 500 $mg.l^{-1}$ NH_4VO_3 in 0.1M NaCl solution (Appendix B), and equilibration time was reduced to 12 hours. A matrix of 0.1M NaCl was utilised to minimise the influence on vanadate sorption of the diffuse double layer (Sposito, 1989). In addition, this matrix encourages flocculation and sedimentation of clay during centrifugation, so that colloid-free supernatants can be collected.

Because the chemistry of vanadium is extremely pH-dependent, sorption experiments were conducted under acidified conditions, where nitric acid was incorporated into the ammonium vanadate solutions to bring them up to 0.01M HNO_3. A similar procedure was carried out in a further set of experiments to consider vanadate sorption under basic conditions, and the ammonium vanadate solutions were adjusted to 0.01M Na_2CO_3. Sorption work conducted in a 0.1M NaCl matrix was termed the control set, while that carried out in the 0.1M NaCl/0.01M HNO_3 matrix was termed the acidified set. The alkaline set involved the 0.1M NaCl/0.01M Na_2CO_3 matrix. It should be noted that because of the preliminary nature of this study, these adsorption experiments were unreplicated.

3.3 Results and discussion

3.3.1 *Initial vanadate sorption isotherms*

Although this experiment was conducted to help decide what levels of vanadium should be utilised in the plant growth trials, and to refine the approach under consideration in the sorption work, it provided valuable information in its own right.

Firstly, the two soils under consideration appear to sorb vanadate to differing degrees (Figure 3.3). For the same equilibrium solution concentration, the Rensburg soil appeared to sorb a greater amount of vanadium than did the Sasolburg soil, although this observation only really applies above solution-phase vanadium concentrations of about

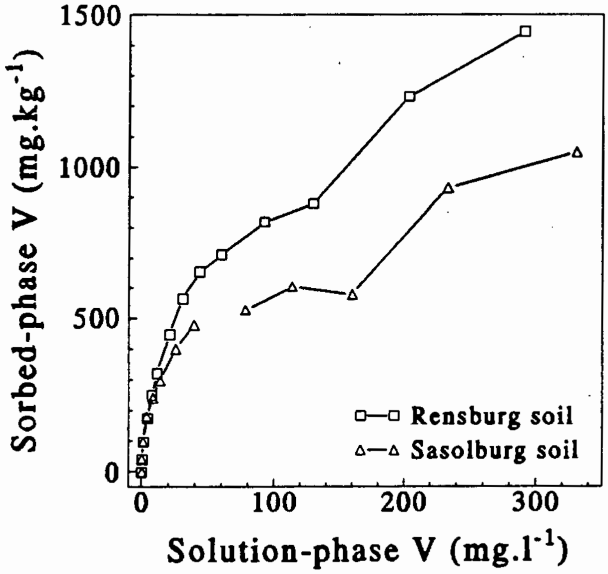


Figure 3.3: Initial sorption isotherms of vanadium, applied as NH_4VO_3 in a 0.1M NaCl matrix, on Rensburg and Sasolburg soil at a soil to solution ratio of 1:10.

10 mg.l^{-1}. It may be that since these soil types have similar, largely smectitic clay fractions, the difference in their ability to sorb vanadate could be a result of the much lower clay content and surface area of the Sasolburg soil.

It is because of the apparent two-phase sorption evident in Figure 3.3, and for the sake of clarity, that the vanadium concentrations considered in the subsequent sorption work were limited to the range 0 to 500 mg.l^{-1} NH_4VO_3 (i.e. 0 to 218 mg V per litre).

3.3.2 *Final vanadate sorption isotherms*

Calculations showed that the Freundlich adsorption isotherm best described vanadate sorption in the control, acidified and alkaline sorption sets, with R coefficients for the test criteria ranging between 0.941 and 0.999 (Table 3.2). It is relevant to note that

Table 3.2: Langmuir and Freundlich adsorption constants, and the linear regression R co-efficients for the appropriate plots in each case (see Appendix C for equations).

PARAMETER	SOIL TYPE			
	Rensburg	Swartland	Sasolburg (clean)	Sasolburg (contaminated)
CONTROL SET				
Freundlich				
a	114.3	114.8	113.5	125.8
b	0.473	0.418	0.375	0.387
R	0.995	0.997	0.999	0.993
Langmuir				
K	0.058	0.089	0.078	0.082
b	1058.0	982.3	696.0	789.2
R	0.943	0.915	0.916	0.951
ACIDIFIED SET				
Freundlich				
a	121.4	374.7	240.2	323.7
b	0.448	0.207	0.287	0.232
R	0.996	0.988	0.992	0.980
Langmuir				
K	0.035	0.374	0.112	0.226
b	1197.9	925.6	940.3	918.5
R	0.875	0.927	0.945	0.976
ALKALINE SET				
Freundlich				
a	46.4	71.7	13.8	25.6
b	0.607	0.545	0.741	0.665
R	0.989	0.941	0.992	0.941
Langmuir				
K	0.012	0.016	0.005	0.007
b	1364.0	1448.9	1283.9	1444.9
R	0.974	0.830	0.938	0.643

because the Langmuir equation is not applicable with as much accuracy in these cases, and because a second sorption mechanism appears to be operative at higher vanadium applications (Figure 3.3), to report a maximum sorption limit for vanadate in these systems would be unreasonable. It may even be conceivable that at still higher vanadate concentrations, more extensive complexation and precipitation reactions will occur.

Figure 3.4 shows vanadate sorption by the four soils in the control set. The most conspicuous feature of this graph is that the curves representing vanadate sorption by the Rensburg and Swartland soils are almost coincidental. This can perhaps be explained in

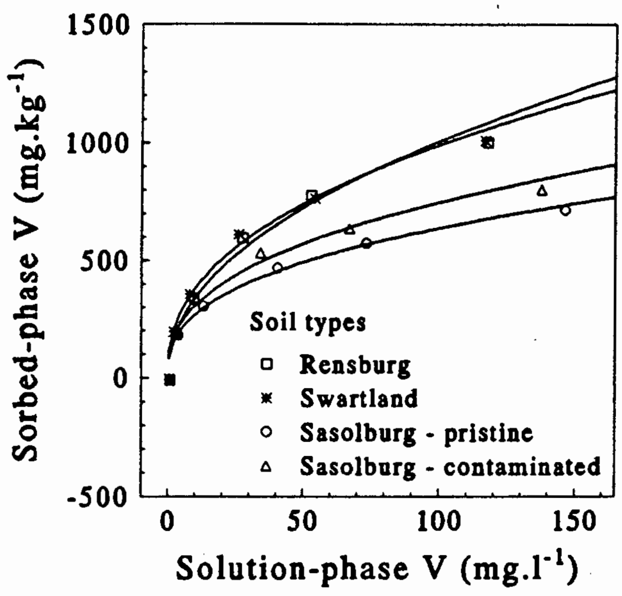


Figure 3.4: Freundlich adsorption isotherms calculated for vanadium sorption on four soils. Vanadium was applied as NH_4VO_3 in a 0.1M NaCl matrix, at a soil to solution ratio of 1:10.

terms of the clay fractions of the soils involved, since a number of studies have illustrated an association of vanadium with clay minerals (Norrish, 1975; Korte *et al.*, 1976; Greca, 1986; Xiao-Quan & Bin, 1993). Particle size distribution analysis of these soil samples (Table 3.1) showed the clay contents of the Rensburg and Swartland soils to be virtually identical at 23.3 and 23.0%, respectively. This fact in itself may explain the coincidental curves, but when one considers surface area analysis, there appears to be some discrepancy. The Rensburg soil has a far greater surface area (49.1 $m^2.g^{-1}$) than the Swartland soil (38.4 $m^2.g^{-1}$) and on this basis, one would expect sorption in the latter soil to be less than it is.

Breit and Wanty (1991) reported that in the pH range of most natural waters, vanadate sorbs strongly to kaolinite. Furthermore, Mikkonen and Tummavuori (1993) found vanadate to sorb on kaolinite in the pH range 2 to 7.5, and that desorption in the presence of 0.02M KCl was extremely limited. Such sorption behaviour is very similar to that of phosphate, so it may be reasonable to assume that vanadate and phosphate behave in a similar manner on clay particles. Bainbridge *et al.* (1994) reported phosphate adsorption on 1:1 clay minerals like kaolinite to be much more extensive than on 2:1 clay minerals like smectite. Thus, by assumption, greater sorption of vanadate per unit area may be expected to occur in the kaolinitic Swartland soil, so that the extent of vanadate sorption in this soil appears to be virtually the same as that in the Rensburg soil, despite the difference in surface area between these two soils.

It is relevant to note here that Ginster (1993) observed clay contents of 49.2% and 29.4% in the Rensburg and Swartland soils, respectively, and these are somewhat different from the values obtained in this study, especially for the Rensburg soil. The two different clay contents observed in Swartland soil are sufficiently similar to be attributable to variance between samples. However, the discrepancy between the two reported clay contents for the Rensburg soil is too large to be explained in this way. Since the accuracy of the particle size distribution analysis conducted for the Rensburg soil is questionable, it might be more reasonable to consider the value presented by Ginster (1993). If this is the case, then in light of the arguments presented above for vanadate sorption, sorption in the Swartland soil must be even more extensive than before, if it is to be equivalent to that in the Rensburg soil with its higher clay content and surface area. This may lend further evidence for a specific binding mechanism for vanadate on the 1:1 layer silicate.

Vanadium has also been reported to associate with various oxide minerals in soil environments (*eg.* Buchter *et al.*, 1989). More specifically, Breit and Wanty (1991) reported that V(IV) and V(V) species sorb strongly to ferric and aluminium oxides, and Xiao-Quan and Bin (1993) suggested that sorption to manganese oxides may also occur. Since the Swartland soil has a greater amount of Fe and Mn than the other soils (Table 3.1) it is conceivable that these soil constituents contribute to the relatively more extensive vanadate sorption apparent in this soil.

If surface area, clay content and clay type are important factors controlling vanadate sorption, then the Sasolburg soil would be expected to show the least amount of vanadium sorption, since it has the lowest surface area of the four soils (24.9 $m^2.g^{-1}$), possibly because it has the lowest content of clay (18.5%), the mineralogical character of which is predominantly smectitic with only a small kaolinitic component (Table 3.1). Figure 3.4 shows that the extent of vanadate sorption in both of the Sasolburg soils is indeed less than that in the Rensburg and Swartland soils.

It is interesting that the contaminated Sasolburg soil displays greater apparent vanadate sorption than does its uncontaminated counterpart (Figure 3.4). This could possibly be explained in terms of trace element enrichment of the contaminated soil by consecutive sludge applications (Appendix A). Burkart-Baumann (1972) reported that the precipitation of vanadate with cations like lead, zinc and copper would occur readily, forming common vanadium minerals like vanadinite, descloizite and mottramite (Table 2.1). The contaminated Sasolburg soil has twice or more the concentration of lead, zinc and copper in particular, than does the undisturbed Sasolburg soil (Table 3.1). Thus, the precipitation mentioned by Burkart-Baumann (1972) would be expected to occur more extensively in the contaminated soil, removing a greater amount of vanadium from solution and causing an apparent increase in the amount of vanadate sorbed. Such precipitation may be enhanced further on the basis of mass balance, since the contaminated soil also contains twice the concentration of vanadium than the clean Sasolburg soil (Table 3.1).

An additional explanation could be the reduction of vanadate to VO^{2+} and its immobilisation on the soil organic material of the contaminated Sasolburg soil, in a similar situation as that observed by Szalay and Szilagyi (1967). This may indeed be a feasible explanation because the soil organic material content of the contaminated Sasolburg soil is 8 times higher than the clean soil.

3.3.3 *Vanadate sorption in acidified systems*

In the case of anions which protonate (like vanadate), changes in pH, which reflect changing hydrogen ion activity, will influence sorption by modifying the speciation and charge of the anion, as well as by modifying the surface-associated charge of soil cooloids. Both of these factors need to be considered in explaining altered sorption of particular anions under different pH conditions.

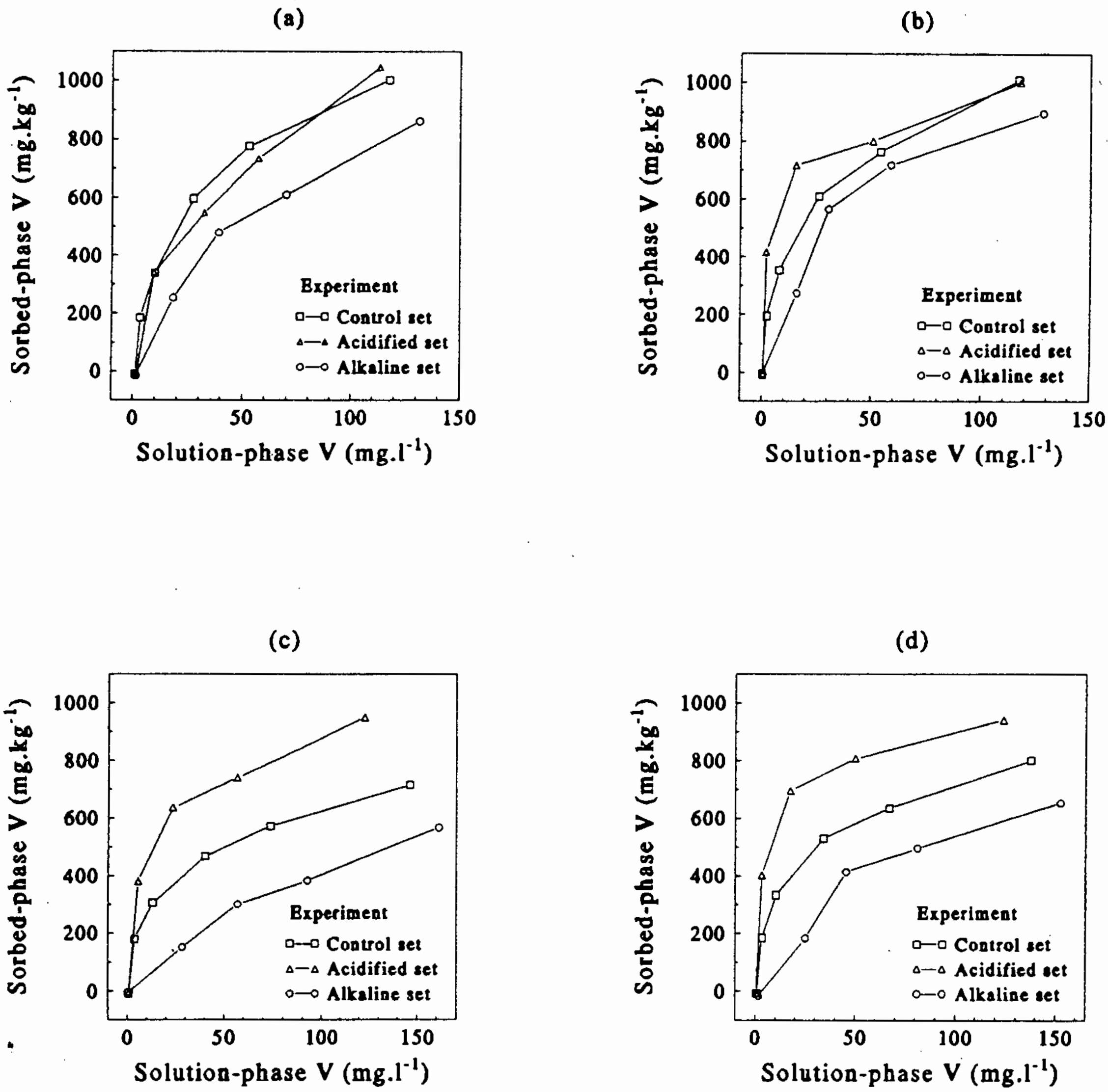


Figure 3.5: Sorption of vanadium in (a) Rensburg, (b) Swartland, (c) clean Sasolburg and (d) contaminated Sasolburg soils under different conditions of acidity. Vanadium was applied as NH_4VO_3 either in a 0.1M NaCl matrix (control set), in a 0.1M NaCl/0.01M HNO_3 matrix (acidified set), or in a 0.1M NaCl/0.01M Na_2CO_3 matrix (alkaline set).

Figure 3.5 shows that the acidification of the test systems in this study generally caused an increase in vanadate sorption, relative to the control set, although this only occurred at the highest vanadium application in the Rensburg soil (Figure 3.5a), and the significance of the apparent sorption increase in the Swartland and Rensburg soils can be questioned. Sorption in the two Sasolburg soils, however, was markedly enhanced under acidified conditions.

Because the equilibrium supernatant pH of the Rensburg suspension hardly changed on acidification (Table 3.3), one would not expect vanadate speciation in the acidified set to differ from that in the control set. In addition, a minor change only in pH reflects little change in proton activity, so an increase in the extent of ligand exchange reactions would not be expected. Any free H^+ ions would become associated with and attenuated on cation exchange sites on the smectite clay surface. Thus the observed minor, if any, difference in vanadate sorption between the Rensburg control and acidified systems is as expected.

Table 3.3: Average pH values of equilibrium supernatants measured during an investigation of vanadate sorption under conditions of different pH, obtained from Appendix B.

SET	SOIL TYPE			
	Rensburg	Swartland	Sasolburg (clean)	Sasolburg (contaminated)
CONTROL	8.00	6.57	6.48	6.59
ACIDIFIED	7.80	3.97	3.11	4.24
ALKALINE	9.53	8.91	9.53	9.32

In comparison to the Rensburg soil, vanadate sorption in the two Sasolburg soils (Figure 3.5a & d) was markedly enhanced by acidification. This may be attributed to intensified ligand exchange in response to increased H^+ activity at low pH, or to altered vanadate speciation in response to changes in pH.

At the vanadium concentrations involved ($-\log[V]_{total}$ between 2 and 3) and the equilibrium pH values observed in the acidified Sasolburg set (pH 3 to 4.5, Table 3.3), vanadate is expected to be in the forms $HV_{10}O_{28}^{5-}$ and $H_2V_{10}O_{28}^{4-}$ (Figure 2.3). If any precipitation of these species occurred, which is likely, especially at the higher vanadium concentrations, it would remove a substantial amount of vanadium from the solution phase since 10 vanadium atoms are incorporated into one ion, and this would result in an apparent increase in vanadate sorption. In addition, the stability domains of these species are very close to that of VO_2^+ (Figure 2.3), and the reaction

$$[H_2V_{10}O_{28}]^{4-} + 16H^+ = 10[VO_2]^+ + 8H_2O$$

has a log K value of 6.75 (Pope, 1983), meaning that the forward reaction is favoured. Decreases in solution-phase VO_2^+ as a result of sorption, and increases in H^+ activity would promote the forward reaction even more. It is therefore fair to assume that a certain proportion of the vanadate may be in cationic form under these low pH conditions, and this would sorb to negatively-charged soil surfaces much more readily than anionic vanadate. Such modification of vanadate speciation may account for the apparent increase in vanadate sorption on acidification of the Sasolburg systems.

On the basis of the argument just presented, it is surprising that no real change in vanadate sorption in the Swartland system occurred on acidification (Figure 3.5b). The equilibrium solution pH was low (~3.9, Table 3.3), so H^+ activity was high and ligand exchange should have been promoted. Vanadate speciation would have been similar to that in the Sasolburg soil, so the reasoning applied in the Sasolburg set should apply equally here. Furthermore, the Swartland soil has a higher iron and manganese content than the other soils (Table 3.1), and the hydroxide mineral of these elements would carry a greater proportion of positively-charged sites at lower pH, so both non-specific anion adsorption and ligand exchange should have been promoted.

Russell (1961), however, observed manganese solubility to increase under conditions of acidification, and McKenzie (1989) observed an enrichment of vanadium in manganese nodules compared to whole soil, indicating co-precipitation of natural soil vanadium with manganous oxides. If a reasonable proportion of these oxides dissolved on acidification, not only would a proportion of sorption sites become unavailable, but natural soil vanadium would become part of solution-phase vanadium, and would be indistinguishable from applied vanadate under ICP analysis. The sum effect of these events, especially the dissolution of soil vanadium already present, would be to cause vanadate adsorption to appear less than it is. This may explain why there is little difference in apparent vanadate sorption between the control and acidified Swartland soil sets.

Since vanadium co-precipitates with iron and aluminium oxides as well (Sposito, 1989), an argument for these soil minerals, similar to that presented above for manganese, may apply to all the soils under consideration here. However, the Swartland soil is distinguished from the others by a considerably higher Mn content, which possibly accounts for a great deal of vanadate sorption in the control set. Thus, dissolution of hydroxide minerals would have a much more profound effect on vanadate sorption in the Swartland soil than in the others.

3.3.4 *Vanadate sorption in alkaline systems*

Less vanadate adsorption was observed in all soils under alkaline conditions than in the control sets (Figure 3.5). This can be explained in terms of greater surface-associated negative charge on soil colloids, as a result of surface-bound hydroxyl groups becoming deprotonated in response to lower solution-phase hydrogen ion activity. This would limit the extent to which anions could approach and complex with negatively charged surfaces. In addition, reduced solution-phase hydrogen ion activities would suppress the forward reaction presented in Section 3.3.3, so that ligand exchange would not be favoured.

Furthermore, interference of matrix anions with vanadate sorption may well have occurred in this experiment. Initially, matrices for the acidified and alkaline sets were chosen for their non-specific adsorption character, so that interference of matrix anions with vanadate sorption would be minimised. Almost all authors are in agreement that nitrate associates non-specifically with soil surfaces. The situation is not so clear, however, in the case of carbonate.

Greenland and Hayes (1981) reported that the dominant anions of the soil solution included nitrate and bicarbonate, and that both of these were weakly adsorbed by clay particles, implying a fairly large degree of non-specific binding. Sposito (1989), however, reported that CO_3^{2-} sorbs non-specifically, either in the double diffuse layer or as an outer-sphere surface complex, *to some extent*, implying that a degree of specific binding may indeed occur. Furthermore, Mott (1988) observed that anions involved in ligand exchange are oxyanions derived from weak acids having at least one protonated form.

Carbonate/bicarbonate fits this category, especially at the pH values of around 9 observed in these sets, since the protonated, bicarbonate species would dominate. Reduced vanadate sorption in the alkaline sets could therefore be partly attributed to competition between specifically binding bicarbonate and HVO_3^{2-} anions present in these systems under the given conditions.

3.3.5 *Borate, fluoride and vanadate sorption*

It is highly relevant to compare vanadate sorption in these soils to that of other potentially limiting constituents in the effluents under consideration. Ginster (1993), in a study centered on the same land treatment scheme, considered boron and fluoride to be the most important potentially toxic elements in this regard, and prepared adsorption isotherms for these elements using Rensburg and Swartland saturated paste extracts from a plant growth experiment of approximately 120 days duration.

Combining his results with those obtained in this study (Figure 3.6), it appears that vanadate sorbs to the two soils to an extent intermediate between that of borate and fluoride. It is conceivable that had the vanadate sorption experiments been incubated for

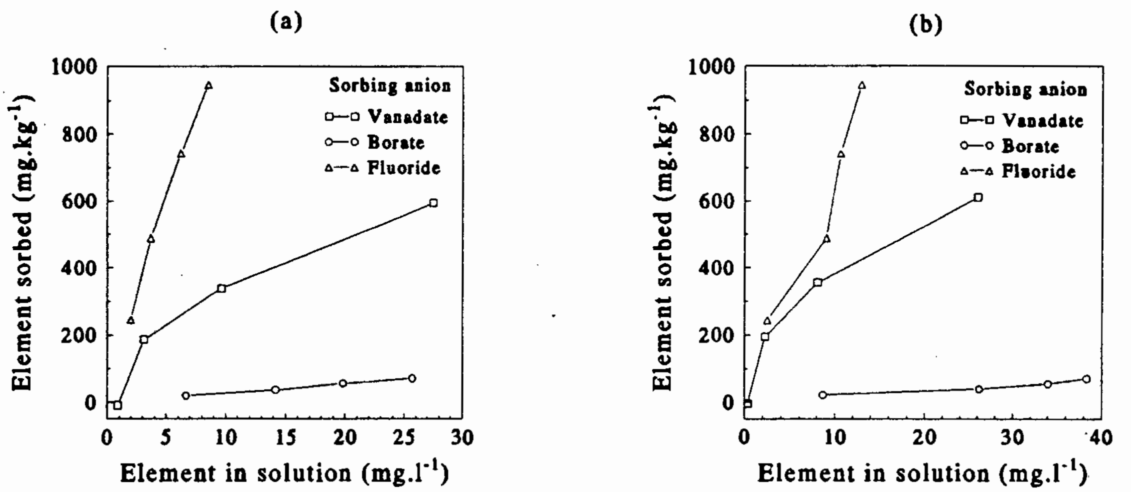


Figure 3.6: Borate, fluoride and vanadate sorption on (a) Rensburg and (b) Swartland soil. Borate and fluoride data from Ginster (1993) and vanadate data from the control sets of this study.

a few days instead of 12 hours, vanadate sorption may have occurred to a greater degree. Nevertheless, of the three anions, borate sorption appears to be the least intensive, whereas fluoride is sorbed more strongly than vanadate.

Before interpreting the relative strength of borate, fluoride and vanadate sorption in terms of which element is likely to be the most mobile and therefore the most environmentally hazardous, a number of other factors must be taken into account. Firstly, the relative toxicities of these elements towards plant growth and in aquatic systems need to be compared, since these will be the primary targets of vanadate, borate or fluoride contamination of soil and migrating groundwater. Secondly, the effective loading rates of these elements in the land treatment environment requires assessment in order to determine whether vanadate, borate or fluoride sorption capacity will be saturated first. The potential for competition between these anions for binding sites would also be an important factor to consider.

3.4 Conclusions

The sorption of vanadate appears to be fairly complex with more than one sorption mechanism coming into operation at high vanadate concentrations, possibly in response to altered vanadate speciation. The Freundlich adsorption isotherm fits vanadate sorption very well under the experimental conditions employed in this study. Clay type and soil surface area may be important determinants of the extent of vanadate sorption in different soils, with 1:1 layer silicates appearing to bind much more vanadate per given amount of clay and surface area than 2:1 layer silicates. This situation is similar to that of phosphate sorption. Vanadate binding on soils with very large surface areas and clay contents may be as extensive, however, even though 1:1 clay minerals are absent. The trace element concentration of a soil, as well as its organic material content may be important in determining the extent to which vanadium is removed from the solution phase.

Vanadate sorption generally increases on acidification of the adsorption system, and the extent of this increase is probably attributable more to changes in vanadate speciation than to changes in the proportions of anion and cation binding sites in the soil, although these will definitely make a contribution. Vanadate sorption may be hindered under more alkaline conditions, because of increased repulsion between the anions and the negatively-charged surface of soil colloids. In addition, reduced hydrogen ion activity and participation in ligand exchange mechansims will limit anion binding. Competition between vanadate and other ions of the soil solution, for example bicarbonate, may limit vanadate adsorption.

The extent of vanadate sorption appears to be intermediate between that of fluoride and borate, which are other potentially limiting anions with respect to land treatment of the effluents under consideration. This may imply that borate would be more of a threat to groundwater than other components of the land treatment systems concerned, but the effective loading rates and relative toxicities of these elements must be taken into account before such a conclusion can be confirmed.

The conclusions reached here are of a preliminary nature. Future work involving more replications is required to ensure that the results on which they are based are statistically sound.

Chapter 4

Response of plants to vanadium amendment of soil

4.1 Introduction

If a land treatment scheme is to be operated successfully, the inhibition of plant growth or destruction of already established vegetation by effluent constituents must be avoided. This can only be accomplished by taking into account plant toxicity data for potentially limiting components of the waste, and their effective loading rates on the sites under consideration.

There appears to be little understanding of the behaviour and effect of vanadium in plant systems, and there is some doubt as to whether this element is essential or not (Kabata-Pendias & Pendias, 1984). Its toxic effects have been attributed to its similarity to phosphate (Wever & Kustin, 1990), a ubiquitous biological co-factor. Morrell *et al.* (1985), however, detected vanadium in the +IV state in plant tissue, irrespective of the form or manner in which it was applied, and vanadium in this oxidation state is very different to biologically active phosphate, both in charge and structure. The mechanism of vanadium toxicity apparently requires clarification.

Plants seem to take up soluble vanadium from the soil solution and cationic forms occurring under acidic conditions are more easily absorbed than the anionic species which predominate under neutral and alkaline conditions (Kabata-Pendias and Pendias, 1984). This may support the observation of Morrell *et al.* (1985), since preferred +IV cationic species would be more easily, and therefore more rapidly absorbed. The ability of both cationic and anionic species to be chelated, however, may influence vanadium uptake by plants (Kabata-Pendias and Pendias, 1984), possibly explaining the observation of Yaroshevskii *et al.* (1982) that the vanadium content of wheat and barley grain was not dependent on the vanadium content of the Chernozem soil in which the plants were grown.

In their review, Kabata-Pendias and Pendias (1984) reported that vanadium is taken up easily by plants roots, where it is usually immobilised. To illustrate this, they cited a study involving vanadium uptake by bush bean plants from a culture solution, where final absorbed concentrations were 13, 8 and 880 $mg.kg^{-1}$ (dry mass) in leaves, stem and roots, respectively. Alloway and Ayres (1993) reported normal leaf vanadium concentrations between 0.001 and 1.5 $mg.kg^{-1}$, and concentrations considered to be toxic between 5 and 10 $mg.kg^{-1}$.

Critical levels of vanadium in the root environment depend to a large extent on the rooting medium. Vanadium concentrations to be considered phytotoxically excessive have been reported to range between 50 and 500 $mg.kg^{-1}$ (Kabata-Pendias and Pendias, 1984; Torrey, 1978). Whether these figures represent total soil vanadium or applied vanadium is unclear, although one would assume the latter. In hydroponic systems, plants may exhibit chlorosis and dwarfing at vanadium concentrations of 0.5 $mg.l^{-1}$ in the liquid substrate and growth may be significantly inhibited at concentrations of 2.5 to 5.0 $mg.l^{-1}$ (Kabata-Pendias and Pendias, 1984). Vanadium concentrations having similar chlorotic and growth-inhibiting effects in the soil solution have been reported at 140 $mg.l^{-1}$ (Kabata-Pendias and Pendias, 1984).

A further complication to bear in mind is that soil in the immediate vicinity of the roots is often substantially different from the general soil environment (Cataldo *et al.*, 1987). This is because roots exude organic and inorganic compounds which modify the chemistry and resident microbial population of the rhizosphere. Both of these factors will influence the speciation and solubility of trace elements in the rhizosphere, thereby influencing their availability to plants (Cataldo *et al.*, 1987). The degree to which trace element behaviour will be modified in the rhizosphere will depend on the nature of the root exudates, and is therefore likely to be a plant species-specific parameter.

A number of studies have pointed to plant uptake of vanadium from pollution sources (*eg*. Biernacka, 1989; Ward, 1990; Jorgensen, 1979). Swiss chard, for example, grown in potted soils amended with power plant bottom ash and fly ash absorbed significantly higher concentrations of vanadium and other elements, compared to control pots (Bache *et al.*, 1991). Rates of ash amendment higher than 2% for the bottom ash and 1% for the fly ash were phytotoxic, but whether vanadium or some other component of the ash was the critical factor in determining this toxicity level requires clarification.

From the brief review just presented, it appears that a number of factors will influence vanadium uptake and toxicity in plants. These include plant species, vanadium speciation and possible chelation, as well as the particular soil environment in which the plants are established. The aim of this part of the study, therefore, was to consider the tolerance to vanadium displayed by *Lolium perenne* (ryegrass) and *Zea mays* (maize) in the Rensburg and Swartland soils, so that the possible impact of increased vanadium on vegetation in the particular land treatment scheme of interest, might be evaluated.

The approach taken was to consider ryegrass germination in the presence of increased amounts of applied ammonium vanadate, and subsequently, to assess the growth of maize in the same soil. A parallel trial was conducted to evaluate the effects of salinity, ammonia and potential pH trends which are simultaneously introduced into the soil along with added ammonium vanadate. A further clarification step involved preparing saturated pastes of the soil used in the pot trials, and analysing the extract for anion concentrations, pH, electrical conductivity and vanadate concentration. Finally, the concentration of vanadium in the harvested maize was determined to assess vanadium uptake in these systems.

4.2 Materials and methods

4.2.1 *Soil preparation*

Rensburg and Swartland soil was air-dried, crushed to pass a 4mm sieve, and then separated into 1.2 and 1.0 kg aliquots, respectively. A different quantity of each soil was used to obtain similar soil volumes in the pots, Rensburg soil being denser than Swartland soil. Each soil aliquot was spread into a layer a few millimetres thick and treated with nitrogen and phosphate fertilisers, as well as a basal fertiliser incorporating magnesium and potassium (Appendix D). The characteristically acidic Swartland soil (Ginster, 1993) was not limed, since the pH of this particular sample (1M KCl, Appendix A) was considered suitable for plant growth.

After fertilisation, each soil aliquot was thoroughly mixed and transferred to the phytotron for vanadium treatment. Nine levels of vanadium were considered in this trial, namely 0, 44, 87, 174, 261, 348, 435, 609 and 784 mg V per kg of dry soil, the different soil mass per aliquot of Rensburg and Swartland soil was taken into account in both fertilisation and vanadium application, so that the treatments in each soil were parallel. It should be noted that because of the highly preliminary nature of this work, only two replications were employed, and results presented in Section 4.3 are based on means of the two replications.

Vanadium was added to the soils using a stock solution of 7 g NH_4VO_3 per litre of distilled water. Because the stock solution was close to saturation at room temperature (Broul *et al.*, 1981), its concentration could not be increased much further without risk of NH_4VO_3 precipitation, which would cause vanadium application to be inaccurate. For the higher vanadium treatments, then, it was necessary to apply a fairly large volume of stock solution to the soil (Appendix D), the larger volumes being added as a succession of smaller applications, with evaporation steps inbetween.

Evaporation of excess water necessitated a second crushing of the Rensburg soil, but not of the Swartland soil because of its friable nature. The loose, treated soil was then passed through a 4 mm sieve and transferred into pots which had been lined with plastic, and tared. The amount of soil added could thus be accurately determined by subtraction, for the establishment of a watering regime by mass balance. The field capacity of each soil was estimated by halving its moisture holding capacity (Table 3.1). According to M.V. Fey (personal communication), Dr P. Grant, formerly of the Division of Research and Specialist Services in Zimbabwe, advised the use of this procedure for watering plants in sealed pots as a reliable method of ensuring sufficient water availability and aeration for plant growth.

Rensburg soil was brought to field capacity over a number of days, by the successive addition of small volumes of water, to prevent the surface layer from sealing. During this time, Swartland soil was prepared and treated. Because of the much sandier nature of the Swartland soil, it could be brought to field capacity within a day.

4.2.2 *Plant care and maintenance*

All plant growth experiments were conducted under controlled conditions of temperature, light intensity and humidity in a phytotron chamber (Appendix D). Ryegrass (*Lolium perenne*) seeds were planted in the Swartland soil by dropping them into ~1 cm deep holes formed by a glass rod, and tamping the soil down. Somewhat shallower holes were made in the Rensburg soil because of hard crust formation on the soil surface. A total of 20 seeds were planted per pot.

Delayed seedling emergence in the Rensburg soil, as well as its very hard surface crust, was cause for some concern. In discussion with I.R. Tomlinson of the Department of Geological Sciences, UCT, who had grown ryegrass in a previous study, a more frequent watering regime was suggested to keep the soil sufficiently moist and soft for germination. This would cause the water content of the pots to increase above field capacity, but it was assumed that the effect of this on the germinating seeds would be negligible, since they were so close to the soil surface, and the development of anaerobic, reducing conditions at such a shallow depth was assumed to be unlikely. Once sufficient seedling emergence had occurred, the idea was to reduce the watering volume, and the pots would slowly return to field capacity. Water contents and saturation status could be tracked in a daily log.

The ryegrass trial was run with watering twice daily for a total of 15 days, during which period the number of seedlings emerging per pot was noted. The trial was terminated on the 15th day because plant growth was extremely slow and insufficient biomass for analysis would have been obtained in the time available.

The ryegrass seedlings were uprooted and the pots were re-planted with maize (*Zea mays*) seeds which had been soaked in distilled water for 12 hours. A total of 8 seeds per pot were planted to a depth of about 2 to 3 cm, and these were allowed to grow for 10 days, during which seedling emergence was noted. The plants were then thinned to 4 seedlings per pot and maize growth continued for a further 12 days, with daily watering up to field capacity.

Because of the problems caused by crust formation in the Rensburg soil during the ryegrass trial, maize emergence was assisted by carefully removing, crushing and replacing soil which had formed into a surface crust, on a daily basis. Watering was also conducted using a fine spray nozzle instead of by pouring from a beaker, to encourage water to soak into the surface crust and soften it, instead of flowing into cracks and bypassing the crust.

4.2.3 *Maize yield and vanadium uptake*

At the end of the 22 day growth period, maize plants were harvested by cutting their stems ~1 cm above the soil surface. Harvested shoots were placed in paper bags which had been punched for ventilation and appropriately marked, and the plant material was dried by leaving the bags in a flow-through oven at 82°C for 2 days.

The dry mass of the bag contents wass then determined, and the plant material from the first 4 Rensburg and first 5 Swartland pots was digested in preparation for ICP analysis of plant tissue-associated vanadium. Biomass from separate replications was combined to obtain sufficient material for analysis. Biomass digestion involved milling and ashing the dry plant material, resuspending a measured mass of it in 5 ml of a 1:1 HCl solution, and diluting with 35 ml of distilled water. These solutions were then filtered through Whatman (No. 1) filters, and then through 0.22 μm pore diameter Millipore filters in preparation for vanadium analysis, which was conducted as outlined in Section 3.4, but using a set of standards with the same matrix as the samples (Appendix E).

4.2.4 *Comparison between vanadate and sulphate application*

Only Rensburg soil was considered in this trial, since insufficient Swartland soil was available to fill the required number of pots. Aliquots of Rensburg soil (1.5 kg) were measured into buckets and fertilised with phosphate, nitrate and basal solution up to the concentrations presented in Appendix D. For all except the control pots, a measured quantity of solid NH_4VO_3 or $(NH_4)_2SO_4$ (Table 4.1) was thoroughly mixed into the soil in each bucket. A portion of the soil (1 kg) was then transferred to plastic-lined, tared pots, and the remaining 500 g was transported in plastic bags to the laboratory for analysis. The soil was then slowly brought to field capacity, and 8 maize seeds, which had been soaked for 24 hours, were planted to a depth of 2 to 3 cm in each pot.

The seeds were allowed to germinate and grow for a total of 14 days, with daily watering by fine spray up to field capacity on a mass balance basis. Seedling emergence was assisted by carefully removing, crushing and replacing the surface crust, as before. The plants were not thinned since germination was excellent, with all eight seedlings emerged in each pot. The plants were harvested on their 14th day of growth for dry matter determination as outlined in Section 4.2.3.

Table 4.1: Quantities of solid NH_4VO_3 and $(NH_4)_2SO_4$ added to 1.5 kg Rensburg soil in a trial comparing the growth of *Zea mays* in soil amended with these salts.

MAIN TRIAL TREATMENT	VANADIUM $mg.kg^{-1}$	NH_4VO_3 mg in 1.5 kg	$(NH_4)_2SO_4$ mg in 1.5 kg	NITROGEN $mg.kg^{-1}$
1	0	0	0	0
3	200	689	83	55
5	600	2068	247	165
7	1000	3446	412	275
9	1800	6203	742	495

4.2.5 *Soil solution composition*

After harvesting, potted soil from the main growth trial was spread and dried in the phytotron, and the two replicates of each treatment were thoroughly mixed before saturated pastes were prepared. Saturated pastes were also prepared from the 500 g of treated soil which had been set aside in the vanadate/sulphate trial.

Initially, saturated pastes were prepared by hand according to standard criteria (SSSSA, 1990), but problems were experienced with the Rensburg soil because of its strongly swelling nature, so that extract collection by filtration was unsuccessful. Centrifugation was therefore utilised to separate saturated paste extracts (SPE) from the soil paste.

This modified method involved accurately measuring dried soil, in the order of 300 g, into plastic jars, and then adding a calculated volume of distilled water so that the theoretical saturation point of the soil (Appendix A) was reached. The soil was thoroughly mixed and allowed to equilibrate for two days in the sealed jars. The paste was then stirred and transferred to tubes for centrifugation, after which the supernatant SPE was collected. Saturated pastes from the main growth trial were extracted by spinning at 3850 rpm for 15 minutes, while those from the vanadate/sulphate trial were spun at 6000 rpm for 10 minutes. Collected SPE was also centrifuged at 6000 rpm for 10 minutes as a cleaning step. Swartland saturated pastes were prepared and extracted in the same way as the Rensburg soil pastes.

The electrical conductivity (EC_e) and pH of the SPE were determined using a Crison micro pH 2001 meter and a Crison micro CM2201 conductivity meter, respectively. The first four Rensburg soil SPEs and the first five Swartland soil SPEs from the main growth trial were then filtered through 0.22 μm Millipore membrane filters. An aliquot of each Rensburg SPE was diluted 20 times using deionised water, and analysed for anions by high-performance ion chromatography (HPIC) (Appendix F). Sub-samples of each Swartland SPE were diluted 150 times for the same purpose. Vanadium analysis of SPE was conducted by ICP using the method outlined in Section 3.4.

4.3 Results and discussion

4.3.1 *Seedling emergence in vanadium-amended soil*

Germination of the ryegrass seeds was poor, with less than 50% of the seedlings emerging at all treatment levels (Figure 4.1). The overall downward trend in seedling emergence evident in Figure 4.1 was initially attributed to increased levels of ammonium vanadate, with the fluctuations between points being explained in terms of natural variation in seed germination potential. However, the between-point fluctuation was found to have a negative correlation with the water content of the Rensburg soil, and a positive correlation with the water content of the sandier, Swartland soil. The assumption that was made regarding the negligible effect of an altered watering strategy on seed

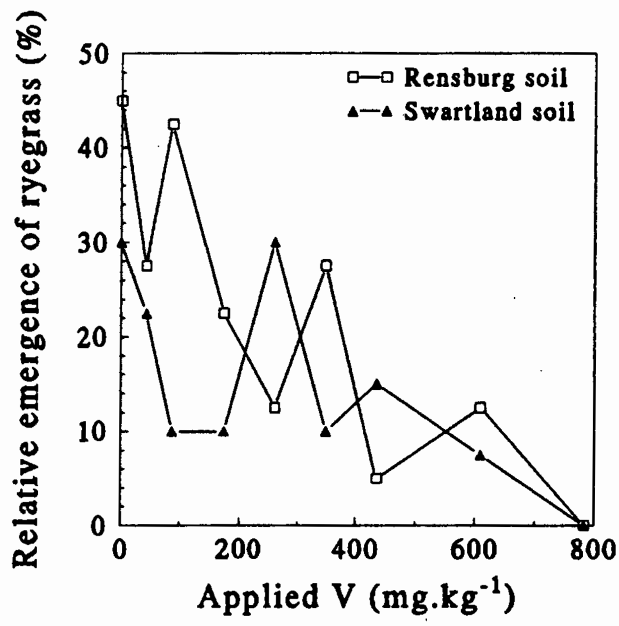


Figure 4.1: Ryegrass emergence 12 days after seeds were planted in Rensburg and Swartland soil treated with ammonium vanadate, expressed as a percentage of the total number of seeds planted.

germination (Section 4.2.2) was therefore not sound, and this probably explains the wide variation in seedling emergence between the two replications. For this reason, it is not possible to make any conclusion as to the potential effects of applied ammonium vanadate on ryegrass germination, based on the results of this trial.

By the time the maize seeds were planted, the Swartland soil and most of the Rensburg soil was being maintained at field capacity with daily watering. The few Rensburg soil pots that were above field capacity were only very slightly so, and there was no correlation between soil moisture content and the success of seedling emergence (Figure 4.2). It is interesting to note, though, that the fluctuations in germination success apparent in the maize trial appear to occur mainly at the higher ammonium vanadate applications, while germination is consistently high at the lower vanadate treatments (Figure 4.2, and also observed in the Swartland soil). This trend is also evident in the greater variation in emergence between the two replicates at higher vanadate applications, especially in the Rensburg soil (Table D.5), highlighting the necessity for increased replication. A potential negative influence of high vanadate concentrations on seed germination and emergence may thus be indicated, but cannot be concluded with much confidence based on these results.

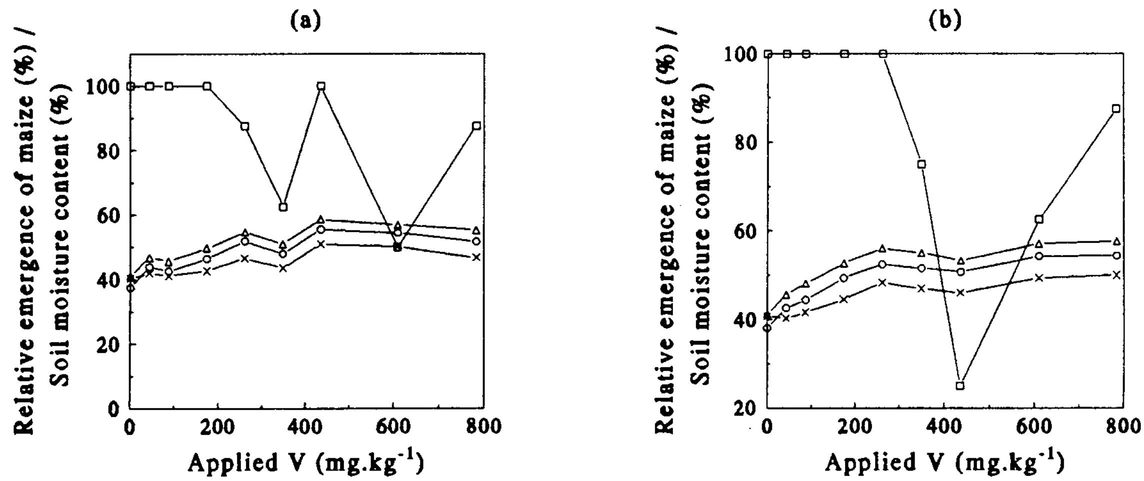


Figure 4.2: Maize emergence 5 days after seeds were planted in Rensburg soil treated with NH_4VO_3 at various levels. (a) First replication; (b) second replication. Legend: relative emergence of maize (squares); soil moisture on day 1 (triangles), day 3 (circles) and day 6 (crosses).

4.3.2 *Maize growth in vanadium-amended soil*

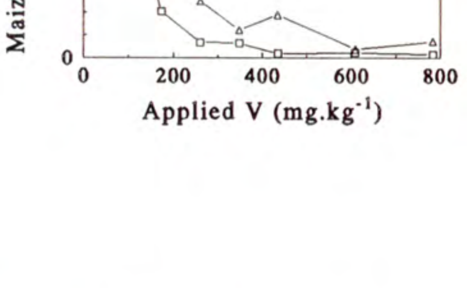
The growth of maize in Rensburg and Swartland soil which had been amended with ammonium vanadate is represented in Figure 4.3. A clear trend of deteriorating plant performance with increasing ammonium vanadate application is evident in Figure 4.3a and this is reflected in Figures 4.3b and c. Maize growth in the control pots was healthy, but at the higher NH_4VO_3 levels, particularly 1.4 and 1.8 g NH_4VO_3 per kg of soil, the plants did not develop past the emergent coleoptile phase. This downward trend in plant yield could be interpreted in terms of vanadium phytotoxicity, but other factors exist which could have been equally responsible.

In applying increasing quantities of NH_4VO_3 to soil, a trend of increasing soil vanadium is established, as well as a trend of increasing salinity, which may be potentially growth inhibiting. In addition, a trend of increasing soil ammonia, a potential plant toxin (Voss, 1993), may be established if soil conditions favour the reaction

$$NH_4^+ + OH^- = NH_3\uparrow + H_2O\,.$$

(a)

(b)



(c)

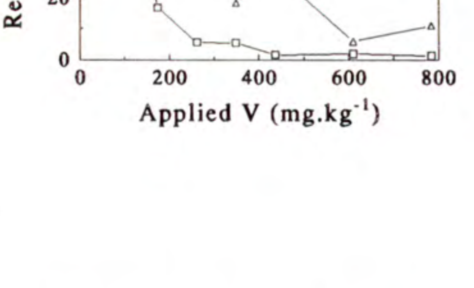


Figure 4.3: Maize yield after 22 days of growth in Rensburg and Swartland soil amended with NH_4VO_3.

This may be particularly relevant in the more alkaline Rensburg soil. Furthermore, if the applied ammonium ion is converted to nitrate by nitrifying microorganisms, a release of hydrogen ion into the soil environment will occur, since the first phase of nitrification involves the reaction (Schlegel, 1990)

$$NH_4^+ + 1\frac{1}{2}O_2 = NO_2^- + 2H^+ + H_2O$$

and a trend of increasing soil acidity may also be established across the NH_4VO_3 treatments. Deteriorating plant performance evident in Figure 4.3 could therefore be in response to increased soil vanadate, increased soil salinity or acidity, or to increased soil ammonia, either alone or in combination. To clarify the situation, a trial was conducted comparing maize growth in NH_4VO_3-amended Rensburg soil to that in $(NH_4)_2SO_4$-amended Rensburg soil.

4.3.3 *Comparison between vanadate and sulphate application*

Figure 4.4 represents plant growth in Rensburg soil amended with either NH_4VO_3 or $(NH_4)_2SO_4$. From visual observation (Figure 4.4a) it is clear that no growth inhibition occurred in the sulphate-amended soil, and at higher levels of $(NH_4)_2SO_4$, growth even appeared to be promoted above that in the control. This is clearly evident in Figure 4.4b. The NH_4VO_3 treatment, however, gave the same result observed in the main growth trial, with seedlings at the higher NH_4VO_3 levels not developing past the emergent coleoptile phase.

Because the ammonium content of parallel vanadate and sulphate treatments in this trial was equivalent, ammonia phytotoxicity as a cause of reduced maize yield can be discounted on the basis of the results presented in Figure 4.4. Furthermore, since soil ammonium was equivalent in parallel vanadate and sulphate treatments, so too would be the extent of any soil acidity development, and this factor can also be discounted. In fact, SPE pH was found to be most acidic in the highest $(NH_4)_2SO_4$ treatment (Table 4.2), and maize growth in this soil was as good as that in the control (Figure 4.4b).

Because the vanadate- or sulphate-treated soil used for SPE preparation had not been incubated under the same conditions or for the same length of time as the potted soil, its properties (Table 4.2) may not have been representative of soil conditions in the potted soil. For this reason, the SPE of the potted Rensburg and Swartland soil used in the main growth trial was analysed for pH and EC_e after the 22 day growth period (Table 4.3).

Table 4.2: Electrical conductivity (EC; $mS.cm^{-1}$) and pH of saturated Rensburg soil paste extracts prepared from soil amended with different amounts of ammonium sulphate and ammonium vanadate.

mg $N.kg^{-1}$ soil	$(NH_4)_2SO_4$		NH_4VO_3		Corresponding main growth trial treatment
	EC	pH	EC	pH	
0	2.41	7.16	2.41	7.18	1
55	2.68	7.29	-	-	3
165	3.56	7.13	2.14	7.77	5
275	4.17	7.11	2.42	7.43	7
495	5.22	6.56	2.60	7.87	9

Table 4.3: Electrical conductivity (EC_e) and pH of saturated paste extracts prepared from Rensburg and Swartland soil which had been amended with NH_4VO_3 and planted to maize for 22 days.

TREAT-MENT	APPLIED V $mg.kg^{-1}$	RENSBURG SOIL			SWARTLAND SOIL		
		EC_e $mS.cm^{-1}$	pH	BIOMASS YIELD %	EC_e $mS.cm^{-1}$	pH	BIOMASS YIELD %
1	0	1.54	7.58	100	10.82	7.38	87
2	44	1.53	7.67	83	11.32	7.42	64
3	87	1.64	7.65	68	10.08	7.63	82
4	174	2.18	7.31	17	11.47	5.96	100
5	261	3.50	6.99	5.6	14.02	6.27	37
6	348	4.00	6.91	5.4	-	-	18
7	435	3.48	6.94	1.6	14.88	6.36	28
8	609	2.42	6.83	1.9	12.77	6.19	5.9
9	784	-	-	1.3	13.34	6.41	11

(a)

(b)

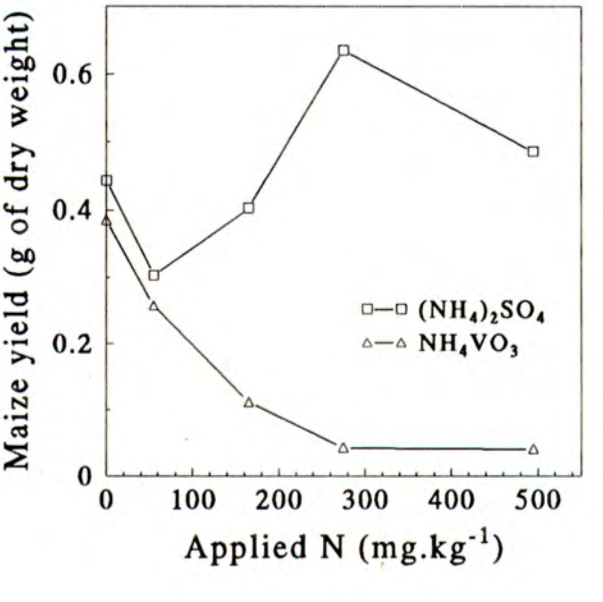


Figure 4.4: Maize yield after 14 days of growth in Rensburg soil amended with NH_4VO_3 or $(NH_4)_2SO_4$.

All of the Rensburg EC_e values were below those observed in the highest $(NH_4)_2SO_4$ treatment, and although a trend of decreasing pH was indeed observed, the lowest value measured was still above the lowest SPE pH in the sulphate trial. Thus pH and salinity can be discounted as factors contributing to reduced maize yields in NH_4VO_3-amended Rensburg soil.

The situation is not so clear, however, in the case of the Swartland soil. A trend of decreasing pH to below 6.56 (the minimum pH measured in the sulphate-amended soil) is apparent at the higher treatment levels (Table 4.3). Because of this, it is difficult to draw any conclusions from the sulphate trial regarding the influence of pH on maize yield in the Swartland soil. However, the highest maize yield obtained from the Swartland soil (100% relative yield) grew from soil with a very low SPE pH of 5.96. On the basis of this observation, a contribution of soil acidity to declining biomass yield in the Swartland soil is doubtful.

A trend of increasing EC_e was also observed in Swartland SPE (Table 4.3), and this may indeed have affected maize growth, because these EC_e values are extremely high. For the *Zea mays* strains they considered, Ayers and Westcot (1985) predict a 100% relative decrease in grain yield at an EC_e of 10 $mS.cm^{-1}$, clearly illustrating a negative effect of salinity on plant reproductive growth. However, the extent to which this would have contributed to the growth trend observed in Figure 4.3 is questionable, because the effects of salinity are not the same for vegetative and reproductive growth. In addition, the EC_e of treatment 5 was 14 $mS.cm^{-1}$ and the biomass yield was 37%, whereas the EC_e of treatment 8 was *lower* at 12.8 $mS.cm^{-1}$, but biomass yield plummeted to 6%, instead of improving in response to a slight reduction in salinity. The pH difference between these two treatments was only 0.08 pH units. From these values, the effect of changing salinity appears to have little, if any affect on maize yield in the Swartland soil.

4.3.4 *Anions of the soil solution*

One other factor exists which may contribute to poor maize performance, and that is the disruption of anion chemistry in the soil by high applications of vanadate. To investigate this possibility, anion concentrations in the first four Rensburg and the first five

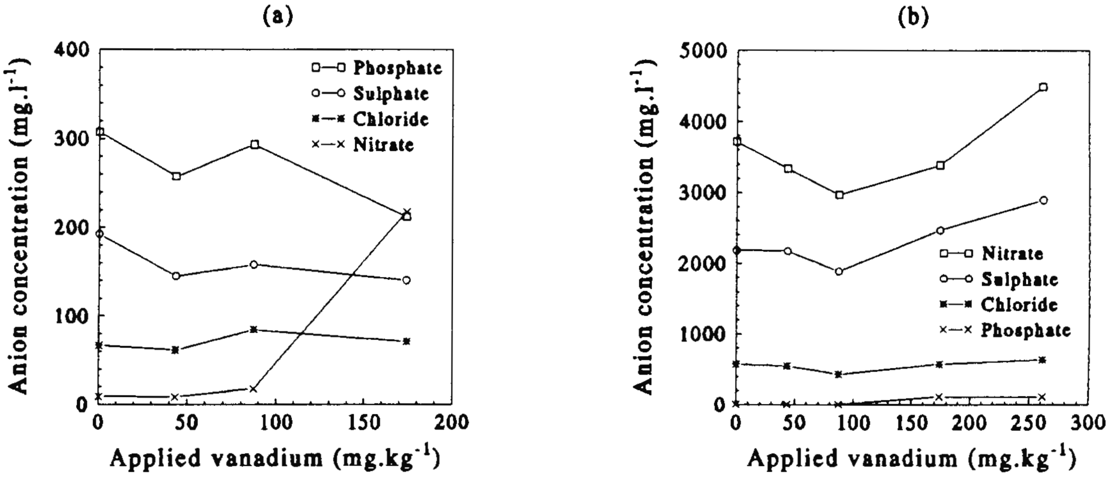


Figure 4.5: Anion concentrations in (a) Rensburg and (b) Swartland saturated paste extract, determined by high performance ion chromatography.

Swartland SPEs were determined by HPIC (Appendix F). This limited set of SPEs was analysed because treatments 1 to 4 in the Rensburg soil were associated with a biomass reduction from 100% to below 50% relative yield, and this was considered the critical range of treatments. Swartland SPEs of treatment 1 to 5 were selected for the same reason. It was considered unnecessary to analyse the remaining SPEs, which were outside the critical range.

The Swartland SPE displayed very high anion concentrations, particularly for nitrate and sulphate, and to a lesser extent, chloride (Figure 4.5b). These, and the very high EC_e values observed in this soil suggest that it must have been contaminated at some stage. The sample had been collected from the edge of a land treatment site, and may have received nitrate- and sulphate-rich effluent, either directly or by uncontrolled, wind-driven migration of spray-irrigated effluent. In any event, the concentration of these anions across the range of applied NH_4VO_3 is sufficiently constant to preclude their contribution to the very definite downward trend in maize yield. The initial slight suppression of chloride, sulphate and nitrate concentration at the lower vanadate levels is probably a consequence of plant uptake of these anions.

Anion concentrations in Rensburg SPE (Figure 4.5a) were much lower than in Swartland SPEs, and also did not alter sufficiently to suggest a contribution to the decline in plant performance at higher NH_4VO_3 applications. Nitrate was found to rise dramatically at the fourth treatment level, but this increase is not to levels which are phytotoxic (Bennett, 1993). Phosphate concentrations were extremely high in this soil, and perhaps reflect a previous contamination or fertilisation event.

From the results of the vanadate/sulphate trial and consideration of pH, EC_e and anion concentrations in saturated paste extracts, it seems reasonable to conclude that ammonia phytotoxicity, increased soil acidity and salinity, and changed anion concentrations in the soil environment were not responsible for the dramatic reduction in maize growth at higher NH_4VO_3 applications, evident in Figures 4.3 and 4.4. It can therefore be concluded with a fair degree of confidence that the observed trend was indeed in response to vanadate phytotoxicity, alone.

4.3.5 *Vanadium phytotoxicity*

4.3.5.1 *Maize yields*

At most of the NH_4VO_3 treatment levels in the main growth trial (Figure 4.3c), relative yield in the Swartland soil was greater than that in the Rensburg soil. This correlates with the vanadium concentrations observed in Rensburg and Swartland SPE (Table 4.4). The steady, fairly rapid increase in Rensburg SPE vanadium, to concentrations higher than in Swartland SPE, implies that more vanadate would be present in the Rensburg than in the Swartland soil solution. Such a result is to be expected, based on the more efficient sorption of vanadate to Swartland soil, observed in Chapter 3, which could be exaggerated with greater incubation time. Since plants generally take up vanadium from the solution phase (Kabata-Pendias and Pendias, 1984), the greater tolerance of maize to applied vanadate in the Swartland soil, compared to that in the Rensburg soil, is therefore to be expected.

It is interesting that the control Swartland soil (treatment 1) which did not receive any NH_4VO_3 amendment had quite a high SPE vanadium concentration compared to the Rensburg control soil (Table 4.4). This might attest to the development of reducing conditions in the Swartland saturated paste during equilibration, with consequent dissolution of a proportion of its large amount of manganese minerals, and release of natural soil vanadium (Section 3.5.3). If this indeed occurred, then the concentration of vanadium in the Swartland soil solution might be lower than is suggested by the SPE data, and even less vanadate would be available for plant uptake in this soil, hence the better performance of maize in the Swartland soil compared to that in the Rensburg soil.

Mammalian toxicity trials often involve a parameter called the LD_{50}, which is the lethal dose of a chemical which causes a 50% reduction in the population of a test species. The apparent difference in vanadate tolerance displayed by maize in this trial can be quantified by utilising this concept. Using Figure 4.3c, an LD_{50} for maize yield can be estimated at 120 $mg.kg^{-1}$ V and 245 $mg.kg^{-1}$ V, for the Rensburg and Swartland soils, respectively, although greater refinement of these preliminary values is certainly required.

Table 4.4: Vanadium concentration in saturated paste extracts prepared from Rensburg and Swartland soil which had been amended with NH_4VO_3.

TREATMENT	Concentration (mg $V.l^{-1}$)	
	RENSBURG SOIL	SWARTLAND SOIL
1	1.1	16.4
2	13.5	17.2
3	37.6	14.7
4	72.0	13.8
5	-	30.5

An important issue is raised by these LD_{50} values with regard to the setting of maximum tolerable limits for elements in land treatment systems. The United States of America's Environmental Protection Agency (EPA) has set a maximum tolerable limit of 500 $mg.kg^{-1}$ for total vanadium in land treatment sites (Brown *et al.*, 1985). If the natural vanadium content of the Rensburg soil is added to the LD_{50} estimated in this study (Table 4.5) it appears that a 50% reduction in plant growth could occur at *half* the maximum tolerable limit, and if land application of effluent is allowed to continue until the official limit is reached, it is possible that no vegetation will survive at all. This will have a bearing on the future fertility of the site, as well as on its potential for further effluent treatment.

Furthermore, the *total* soil vanadium concentration in soils with naturally high vanadium contents, may be much higher than that stipulated by the maximum tolerable limit after an LD_{50} vanadium dose has been applied. In these cases, the closure of a land treatment site in compliance with official regulations, would be premature and would have important economic consequences for the industrial concern involved. The problems associated with setting maximum tolerable limits for particular soil contaminants, as illustrated here, raise serious implications for the management of land treatment operations using general guideline values, which do not take into account site- and effluent-specific parameters.

Table 4.5: Natural vanadium concentrations of the Rensburg and Swartland soil samples used in this study, and the approximate LD_{50} value as applied to maize growing in these soils.

VANADIUM CONCENTRATIONS	RENSBURG SOIL	SWARTLAND SOIL
NATURAL LD_{50}	109 120	200 245
TOTAL	229	445
EPA maximum tolerable limit	500	

4.3.5.2 *Maize uptake of vanadium*

No significant change in the vanadium concentration of dry plant material was apparent at higher soil NH_4VO_3, even though relative maize yield dropped to below 50% (Figure 4.6). This seems to be consistent with the literature, where vanadium is reported to be

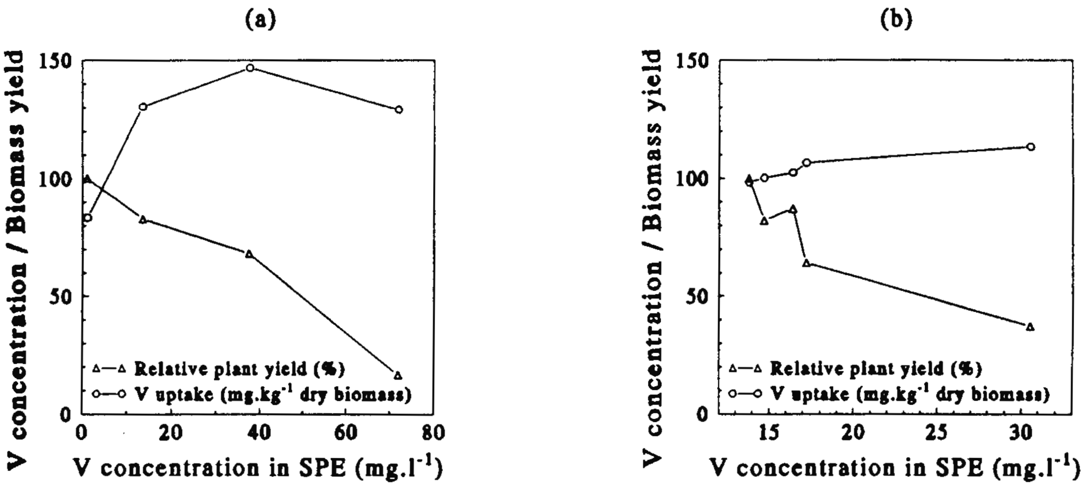


Figure 4.6: Relative yield and uptake of vanadium in maize grown in (a) Rensburg and (b) Swartland soil which had been amended with NH_4VO_3.

immobilised in plant roots, so an excess of the element in the soil environment would not necessarily be reflected in its concentration in aerial plant organs. However, normal leaf vanadium concentrations are in the $\mu g.kg^{-1}$ range, with toxic levels between 5 and 10 $mg.kg^{-1}$ (Alloway & Ayres, 1993). The vanadium concentrations observed here, in the order of 100 to 150 $mg.kg^{-1}$ (Figure 4.6) seem to be excessively high in comparison, especially since they also pertain to soil which was not treated with vanadium.

In their review, Kabata-Pendias and Pendias (1984) point out that soil contaminated with metals may produce crops which appear to be normal, but which are in fact unsafe to be used as a food source. They also report that certain bryophytes and fungi may contain as much as 180 $mg.kg^{-1}$ V on a dry weight basis when grown in mineralised areas. They also state that other accumulator plant species are known, but since they did not identify these, and the reference they cited was unavailable at time of writing, whether *Zea mays* strains are vanadium accumulator plants or not, could not be established.

It is interesting to note, though, that biomass-associated vanadium concentrations are somewhat higher in maize established in Rensburg soil than in maize grown in Swartland soil. This may reflect a greater uptake of vanadium from Rensburg soil solution which appears to have greater vanadium concentrations at higher NH_4VO_3 application than the Swartland soil solution, based on SPE vanadium concentrations (Table 4.4).

Very high and very similar vanadium concentrations, however, also raise the suspicion of possible contamination of sample material with vanadium at some stage during sample preparation. A possible source of such contamination could have been the milling apparatus, if it had been composed of vanadium-strengthened steel, a common tool material. This is because dry plant material is milled into an extremely fine powder, so contact between the mill and the sample is extensive and the transfer of any vanadium-enriched steel dust would have been unhindered.

If contamination of sample material can be eliminated, then the results presented in Figure 4.6 suggest that the maize grown in this study may indeed be a vanadium-accumulating strain. However, milling was conducted by the Elsenburg Agricultural Development Institute using undocumented mills, and the possibility of sample contamination could not be confidently ruled out. The results of this experiment are therefore inconclusive.

4.4 Conclusions

Inhibition of ryegrass emergence was observed in NH_4VO_3-amended Rensburg and Swartland soil, but whether this was a result of vanadate toxicity is unclear, since any such effects would have been obscured by the influence of soil moisture content, which had not been adequately controlled.

Maize germination and emergence, under properly controlled conditions, was unhindered at increasing NH_4VO_3 concentrations in the soil, but at the higher treatment levels, the seedlings did not develop past the emergent coleoptile phase. After 22 days of growth, a dramatic reduction in relative yield at higher NH_4VO_3 concentrations in both Rensburg and Swartland soil was apparent. Increasing soil salinity, acidity and potentially, soil ammonia at higher application of NH_4VO_3 were found to make no contribution to this trend, which could therefore be attributed to vanadate phytotoxicity with a fair degree of confidence.

Maize grown in Swartland soil was more tolerant to applied vanadate than maize grown in Rensburg soil. This can be explained in terms of greater vanadate sorption, and lower solution-phase vanadate concentrations in the Swartland soil than in the Rensburg soil. Vanadate was effectively more available, and therefore more toxic, to plants established in the Rensburg soil.

LD_{50} values of 120 $mg.kg^{-1}$ and 245 $mg.kg^{-1}$ were estimated for ammonium vanadate, with reference to maize grown in Rensburg and Swartland soil, respectively.Vanadium uptake by these plants appeared to be very efficient, with very high vanadium concentrations in the aerial plant organs. Whether these high values point to the maize used in this work as being an accumulator strain, or whether they point to vanadium contamination of sample material, remains uncertain.

The aim of this preliminary study was to obtain some idea of the potential impact of vanadium in a particular land treatment system, and to gain a greater understanding of its behaviour as an environmental pollutant in a more general context. That the goal of this study was realised to a reasonable degree is evident in the observations of vanadate sorption and phytotoxicity discussed in the preceding chapters. A number of issues exist, however, which still require clarification. Firstly, it would be instructive to complete the investigation of potential vanadate inhibition of soil biological activity (Appendix G), which could not be completed in this study in the time available. The potential inhibition of seed germination by vanadate application needs to be investigated more thoroughly, since this may have a bearing on the fertility of the soil to which vanadium-containing effluent is applied. Finally, the uptake of vanadium by crops established on the sites should be measured accurately, especially if these are to be used periodically as a livestock feed.

Literature cited

Abbasi, S.A. 1981. Pollution due to vanadium and a new spot test for detection of traces of vanadium in water, plants, soils and rocks. Int. J. Environ. Studies **18**: 51-52.

Al-Bayati, M.A., S.N. Giri, O.G. Raabe, L.S. Rosenblatt and M. Shifrine. 1989. Time and dose response study of the effects of vanadate on rats: morphological and biochemical changes in organs. J. Environ. Path., Toxicol. Oncol. **9**: 435-455.

Alberico, E. and G. Micera. 1994. Phosphate complexation of oxovanadium(IV). Evidence of bidentate chelation of orthophosphate. Inorg. Chim. Acta **215**: 225-227.

Alloway, B.J. and D.C. Ayres. 1993. Chemical principles of environmental pollution. Blackie Academic and Proessional, London.

Amrhein, C., P.A. Mosher and A.D. Brown. 1993. The effects of redox on Mo, U, B, V and As solubility in evaporation pond soils. Soil Sci. **155**: 249-255.

Anderson, J.P.E. 1982. Soil Respiration. In: A.L. Page (ed.). Methods of soil analysis (Part 2): Chemical and microbiological properties (2nd ed.). American Society of Agronomy and the Soil Science Society of America, Madison. pp 831-902.

Ayers, R.S. and D.W. Westcot. 1985. Water quality for agriculture. Food and Agriculture Organisation of the United Nations, Rome.

Bache, C.A., M. Rutzke and D.J. Lisk. 1991. Absorption of vanadium, nickel, aluminium and molybdenum by Swiss chard grown on soil amended with fly ash or bottom ash. J. Food Saf. **12**:79-84. Chemical Abstracts **116**: 172589d.

Bainbridge, S.H., Miles, R. Praan and M.A. Johnston. 1994. Phosphorous sorption in Natal soils. Awaiting publication.

Baroch, E.F. 1983. Vanadium and vanadium alloys. *In*: Kirk-Othmer. Encyclopedia of Chemical Technology (3rd ed.). Vol. 23. John Wiley & Sons, New York. pp 673-687.

Bender, J.H. 1980. Operation and maintenance considerations of land treatment systems. Municipal Environmental Research Laboratory, USEPA, Cincinnati, Ohio. pp 1-12.

Bennett, W.F. 1993. Plant nutrient utilization and diagnostic plant symptoms. *In*: W.F. Bennett (ed.). Nutrient deficiencies and toxicities in crop plants. APS Press, Minnesota. pp 1-10.

Bester, H.C. 1993. Mobility and phytotoxicity of boron in two highveld soils. M.Sc thesis, department of agronomy, University of Natal, Pietermaritzburg.

Biernacka, E. 1989. Effect of refinery-petrochemical works on the content of trace elements in grassy vegetation. Zesz. Probl. Postepow Nauk Roln. **325**: 251-257. Chemical Abstracts **112**: 83199b.

Bloomfield, C. and W.I. Kelso. 1973. The moblisation and fixation of molybdenum, vanadium, and uranium by decomposing plant matter. J. Soil Sci. **24**: 368-379.

Bradford, G.R., D. Bakhtar and D. Westcot. 1990. Uranium, vanadium and molybdenum in saline waters of California. J. Environ. Qual. **19**: 105-108.

Branca, M., G. Micera, A. Dessi and D. Sanna. 1990. Complexation of oxovanadium(IV) by humic and tannic acids. J. Inorg. Biochem. 39: 109-115.

Breit, G.N. and R.B. Wanty. 1991. Vanadium accumulation in carbonaceous rocks: a review of geochemical controls during deposition and diagenesis. Chem. Geol. 91: 83-97.

Broul, M., J. Nyvlt and O. Söhnel. 1981. Solubility in inorganic two-component systems. Elsevier Scientific Publishing Company, Amsterdam. p 99.

Brown, K.W., L.E. Deuel, Jr. and J.C. Thomas. 1985. Distribution of inorganic constituents in soil following land treatment of refinery wastes. Water Air Soil Poll. 25: 285-300.

Buchter, B., B. Davidoff, M.C. Amacher, C. Hinz, I.K. Iskandar and H.M. Selim. 1989. Correlation of Freundlich K_d and *n* retention parameters with soils and elements. Soil Sci. 148: 370-379.

Bühmann, C. 1986. Investigation of 2:1 layer silicate clays in selected Southern African soils. PhD thesis, department of soil science and agronomy, University of Natal, Pietermaritzburg.

Burkart-Baumann, I. 1972. Vanadium: Element and Geochemistry. *In*: R.W. Fairbridge (ed.). The Encyclopedia of Geochemistry and Environmental Sciences. Van Nostrand Reinhold Company, New York. pp 1234-1236.

Cataldo, D.A., R.E. Wildung and T.R. Garland. 1987. Speciation of trace inorganic contaminants in plants and bioavailability to animals: An overview. J. Environ. Qual. 16: 289-295.

Clark, R.J.H. 1973. Vanadium. *In*: J.C. Bailar, H.J. Emeléus, R. Nyholm and A.F. Trotman-Dickenson (eds.). Comprehensive inorganic chemistry. Pergamon Press, Oxford.

Crans, D.C. and P.K. Shin. 1994. Characterization of vanadium(V) complexes in aqueous solutions: ethanolamine- and glycine-derived complexes. J. Am. Chem. Soc. 116: 1305-1315.

Dreesen, D.R., E.S. Gladney, J.W. Owens, B.L.Perkins, C.L.Wienke and L.E. Wangen. 1977. Comparison of levels of trace elements extracted from fly ash and levels found in effluent waters from a coal-fired power plant. Environ. Sci. Technol. 11: 1017-1019.

Eady, R., R.Robson and J. Postgate. 1987. Vanadium puts nitrogen in a fix. New Scientist, 18 June 1987 issue, pp 59-62.

Eary, L.E., D.Rai, S.V. Mattigod and C.C. Ainsworth. 1990. Geochemical factors controlling the mobilisation of inorganic constituents from fossil fuel combustion residues: II. Review of the minor elements. J. Environ. Qual. 19: 202-214.

Ehde, P.M., I. Andersson and L. Pettersson. 1986. Multicomponent polyanions. 40. A Potentiometric and ^{51}V NMR study of equilibria in the H^+-$H_2VO_4^-$-$C_2O_4^{2-}$ system in 0.6 M Na(Cl) medium. Acta Chem. Scand. A 40: 489-499.

Ehde, P.M., I. Andersson and L. Pettersson. 1989. Multicomponent polyanions. 43. A study of aqueous equilibria in the vanadocitrate system. Acta Chem. Scand. 43: 4136-143.

Fu, M.H. and M.A. Tabatabai. 1989. Nitrate reductase activity in soil: Effects of trace elements. Soil Biol. Biochem. 21: 943-946.

Ginster, M. 1993. Soil chemical and plant growth studies with liquid industrial wastes. M.Sc thesis, department of agronomy, University of Natal, Pietermaritzburg.

Greca, M.C. 1986. Geochemical studies of sediments of the Barreiras group, Itaborai region - Rio de Janeiro. Ceramica (Sao Paulo) **32**: 245-254. Chemical Abstracts **106**: 53522k

Greenland, D.J. and M.H.B. Hayes. 1981. Soil processes. *In*: D.J. Greenland and M.H.B. Hayes (eds.). The chemistry of soil processes. John Wiley & Sons, London. pp 1-35.

Hansen, T.V., J. Aaseth and V. Skaug. 1986. Hemolytic activity of vanadyl sulphate and sodium vanadate. Acta Pharmacol. Toxicol., Suppl. **59**: 562-565. Chemical Abstracts **106**: 45357v.

Jorgensen, S.E. 1979. Handbook of environmental data and ecological parameters. Pergammon Press, Oxford. pp C509, D1, D85, D361, D391, D436, D483, D507 and G39.

Kabata-Pendias, A. and H. Pendias. 1984. Trace elements in soils and plants. CRC Press, Boca Raton.

Korte, N.E., J. Skopp, W.H. Fuller, E.E. Niebla and B.A. Alsii. 1976. Trace element movement in soils: Influence of soil physical and chemical properties. Soil Sci. **122**: 350-359.

Legrum, W. 1986. The mode of reduction of vanadate(+V) to oxovanadium(+IV) by glutathione and cysteine. Toxicology **42**: 281-289. Chemical Abstracts **106**: 133317n.

Ma, W. 1987. Microbial transformation and toxicity change of vanadium(V). Nanjing Daxue Xuebao, Ziran Kexue **23**: 195-191. Chemical Abstracts **107**: 34545z.

Maccioli, F.J. and T.H. Risby. 1978. Determination of toxic metals and metalloids in ambient air. The Pennsylvania State University Press, Pennsylvania, pp 11-12.

McBride, M.B. 1978. Transition metal bonding in humic acid: An ESR study. Soil Sci. **126**: 200-209.

McKenzie, R.M. 1989. Manganese oxides and hydroxides. *In*: J.B. Dixon and S.B. Weed (eds.). Minerals in soil environments (2nd ed.). Soil Sci. Soc. America, Madison. pp 439-465.

Middelburg, J.J., C.H. Van Der Weijden and J.R.W. Woittiez. 1988. Chemical processes affecting the mobility of major, minor and trace elements during weathering of granitic rocks. Chem. Geol. **68**: 253-273.

Mikkonen, A. and J. Tummavuori. 1993. Retention of vanadium(V), molybdenum (VI) and tungsten(VI) by kaolin. Acta Agric. Scand., Sect. B, Soil & Plant Sci **43**: 11-15.

Morrell, B.G., N.W. Lepp, D.A. Phipps and C.A. Hampson. 1985. Reduction of vanadium by higher plant roots. Heavy Met. Environ., Int. Conf., 5th (2): 277-279. Chemical Abstracts **106**:155452e.

Mott, C.J.B. 1988. Surface chemistry of soil particles. *In*: A. Wild (ed.). Russell's soil conditions and plant growth (11th ed.). Longman Scientific and Technical, New York. pp 239-281.

Norrish, K. 1975. The geochemistry and mineralogy of trace elements. *In*: D.J.D. Nicholas and A.R. Egan (eds.). Trace elements in soil-plant-animal systems. Academic Press, New York. pp 60-61.

Nriagu, J.O. and J.M. Pacyna. 1988. Quantitative assessment of worldwide contamination of air, water and soils by trace metals. Nature **333**: 134-139.

Page, L.A., C. Lue-Hing and A.C. Chang. 1986. Utilisation, Treatment and Disposal of Waste on Land. *In*: E.C.A. Runge. Utilisation, Treatment and Disposal of Waste on Land. Proceedings of a Conference held in Chicago, 1985. Soil Sci. Soc. Am., Madison, Wisconsin. pp 1-12.

Petrie, J. 1994. Verbal communication.

Pope, M.T. 1983. Heteropoly and isopoly oxometalates. Springer-Verlag, Berlin. pp 34-35.

Rosenbaum, J.B. 1983. Vanadium compounds. *In*: Kirk-Othmer. Encyclopedia of Chemical Technology (3rd ed.). Vol. 23. John Wiley & Sons, New York. pp 688-704.

Russell, E.W. 1961. Soil conditions and plant growth (9th ed.). Longmans, London. pp 523-525.

Schlegel, H.G. 1990. General microbiology (6th) ed.). Cambridge University Press, Cambridge. pp 352-355.

Sekar, N. and S. Govindasamy. 1991. Insulin mimetic role role of vanadate on plasma membrane insulin-receptors. Biochem. Int. 23: 461-466.

Shimmack, W. and K. Bunzl. 1985. The sorption of vanadium by soil organic matter. Heavy Met. Environ., Int. Conf., 5th (2): 522-524. Chemical Abstracts **106**: 155456j.

Soil Science Society of South Africa (SSSSA). 1990. Handbook of standard soil testing methods for advisory purposes. Soil Science Society of South Africa, Pretoria.

Sommers, L.E. and K. Barbarick. 1986. Constraints to land application of sewage sludge. *In*: E.C.A. Runge. Utilisation, Treatment and Disposal of Waste on Land. Proceedings of a Conference held in Chicago, 1985. Soil Sci. Soc. Am., Madison, Wisconsin. pp 193-216.

Sposito, G. 1989. The chemistry of soils. Oxford University Press, Oxford.

Szalay, A. and M. Szilagyi. 1967. The association of vanadium with humic acids. Geochim. Cosmochim. Acta 31: 1-6.

Templeton, G.D. and N.D. Chasteen. 1980. Vanadium-fulvic acid chemistry: Conformational and binding studies by electron spin probe techniques. Geochim. Cosmochim. Acta **44**: 741-752.

Thomas, R.E. 1986. Land treatment of wastewaters: Some perspectives. *In*: E.C.A. Runge. Utilisation, Treatment and Disposal of Waste on Land. Proceedings of a Conference held in Chicago, 1985. Soil Sci. Soc. Am., Madison, Wisconsin. pp 13.

Torrey, S. 1978. Trace contaminants from coal. Noyes Data Corporation, New Jersey. pp 185-194.

Voss, R.D. 1993. Corn. *In*: W.F. Bennett (ed.). Nutrient deficiencies and toxicities in crop plants. APS Press, Minnesota. pp 11-14.

Wanty, R.B. and M.B. Goldhaber. 1992. Thermodynamics and kinetics of reactions involving vanadium in natural systems: accumulation of vanadium in sedimentary rocks. Geochim. Cosmochim. Acta **56**: 1471-1483.

Ward, N.I. 1990. Multielement contamination of British motorway environments. Sci. Total Environ. **93**:393-401. Chemical Abstracts **113**: 11393h.

Wever, R. and K. Kustin. 1990. Vanadium: A biologically relevant element. Adv. Inorg. Chem. **35**: 81-115.

Xiao-Quan, S. and C. Bin. 1993. Evaluation of sequential extraction for speciation of trace metals in model soil containing natural minerals and humic acid. Anal. Chem. **65**: 802-807.

Yaroshevskii, B.N., E.A. Derkachev and E.V. Mashkina. 1982. Critical permissible levels of manganese and vanadium in soils of south-eastern Ukraine. Khim. Sel'sk. Khoz. 3: 25-26. Chemical Abstracts **96**: 161494m.

APPENDIX A

Soil characterisation procedures

A.1 Soil organic material content

A.1.1 *Materials and methods*

Prepared soil was ground to pass a 0.5 mm sieve using an agate mortar and pestle, and 1 g of Rensburg, 0.5 g of Swartland, 1 g of clean Sasolburg and 0.2 g of contaminated Sasolburg soil was placed into separate 500 ml Erlenmeyer flasks. Two replications were carried out for each soil. $K_2Cr_2O_7$ (10ml of 0.167M) was added to each flask, and the contents wre swirled. Concentrated H_2SO_4 (20ml) was rapidly added and the flasks were swirled again for a minute, and then allowed to cool for 30 minutes, after which 150ml deionised water and 10ml concentrated orthophosphoric acid was added to each flask. Ba-diphenylamine sulphonate indicator (0.4g per 100 ml water) was added to each flask, the contents of which were then titrated with Fe(II)ammonium sulphate solution. This procedure is termed the Walkley-Black soil organic material determination and is a standard method (SSSSA, 1990).

A.1.2 *Calculations*

$$\text{Concentration of } Fe(NH_4)_2(SO_4)_2 = \frac{10 \text{ ml } K_2Cr_2O_7 \times 0.167 \times 6}{20.59 \text{ ml } Fe(NH_4)_2(SO_4)_2}$$

$$= 0.487M$$

$$\% \text{ Organic Carbon} = \frac{(A-B) \times C \times 0.3 \times D}{E} \quad \text{where:}$$

A = ml $Fe(NH_4)_2(SO_4)_2$ blank

B = ml $Fe(NH_4)_2(SO_4)_2$ sample

C = concentration of $Fe(NH_4)_2(SO_4)_2$ = 0.487

D = factor accounting for the inherent incompleteness of the reaction, set at 1.3

E = amount of soil used (g)

A.1.3 *Results*

Using the equation given above and the relevant titration volumes, the organic carbon content of the soils was calculated and presented in Table A.1.

Table A.1: Organic carbon content of the four soils examined in this study, determined using the Walkley-Black standard method (SSSSA, 1990).

SOIL TYPE	SOIL ORGANIC CARBON (%)
Rensburg	0.17
Swartland	2.17
Sasolburg - clean	0.91
Sasolburg - contaminated	7.33

A.2 Clay mineral separation and characterisation

A.2.1 *Materials and methods*

Aliquots of the Rensburg, Swartland and clean Sasolburg soils (100g each) was placed in separate 250ml plastic centrifuge bottles. The bottles were then filled to the neck with distilled water and the pH adjusted to around 9 after a brief shaking. After shaking overnight on a horizontal shaker, the slurries were then transfered into large buckets filled with pH 10 Na_2CO_3 solution, were vigorously stirred and left overnight. Approximately half of the supernatant was siphoned into a smaller bucket, where the dispersed clay was flocculated by salt addition, and left to stand overnight. The clear supernatant was discarded and the clay suspension concentrated by centrifugation. To remove excess salt from the final clay suspension, it was dialysed with tap water for 48 hours.

The concentration of the final clay suspension was determined, and a 5ml aliquot was prepared to a clay concentration of 10 $mg.l^{-1}$ by dilution. This was then dropped onto a rough-surfaced glass slide and allowed to air dry, before being stored in a desiccator. Clay characterisation was conducted using a Phillips X-Ray Diffractometer and Cu K_{α},

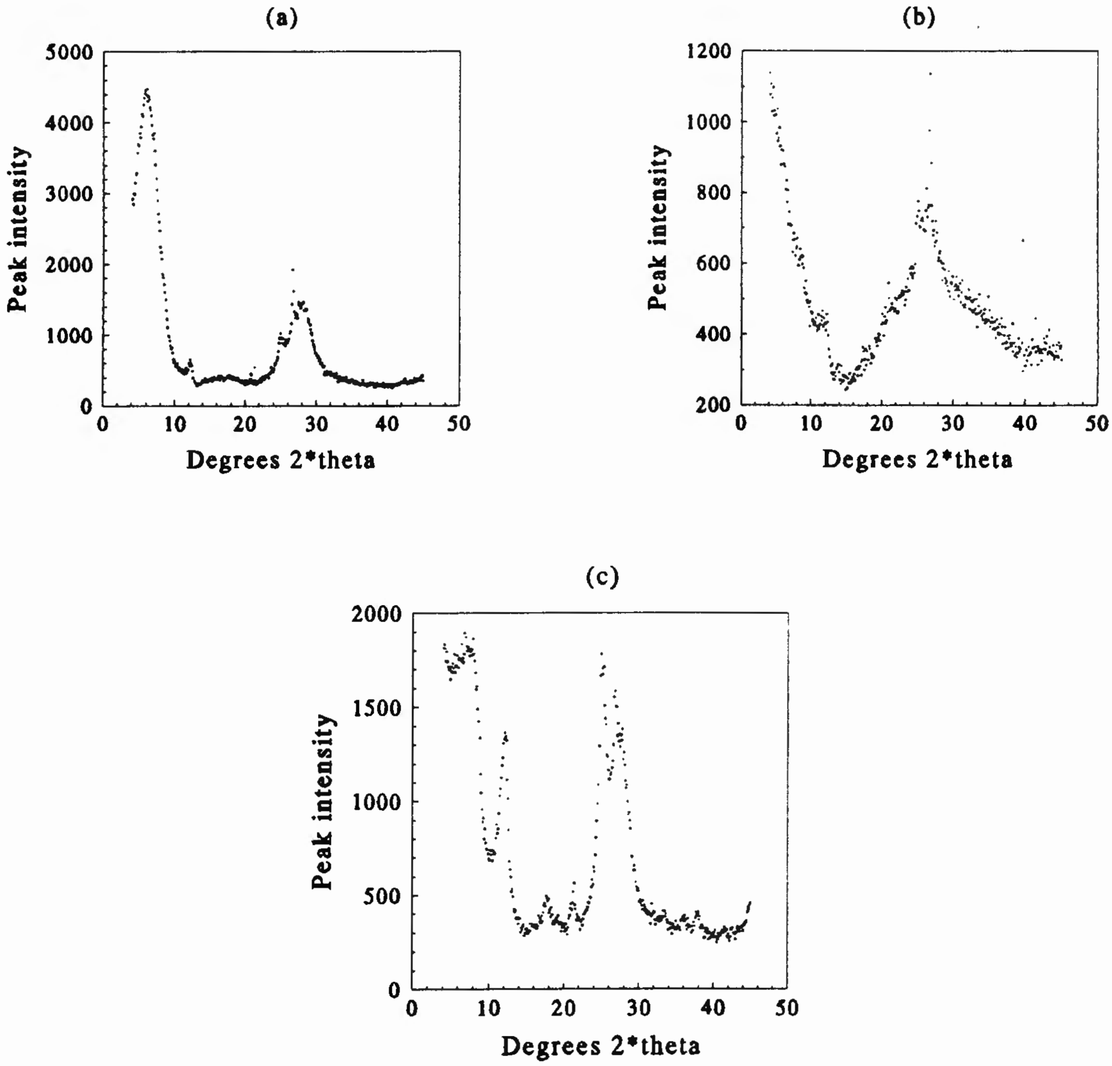


Figure A.1: X-Ray Diffractometry scans using a copper tube, of the clay fractions from (a) Rensburg, (b) Swartland and (c) Sasolburg soil, separated by pH-controlled dispersion and flocculation.

operating at 25 mA and 40 kV, and reading at 0.05°2ϴ step increments between 4.00° and 45.00°. Count time was 1 second and the time constant was set at 1.

A.2.2 *Results*

The Rensburg clay fraction appears to be dominated by 2:1 layer silicate minerals of the smectite group, since the only strong features of the XRD scan (Figure A.1a) is the first order peak at 6°2ϴ and the second order peak at 28°2ϴ corresponding to these minerals. A small peak at 12.2°2ϴ implies the presence of a micaceous component in the clay fraction, and that occurring at 27°2ϴ represents one of the higher order quartz peaks.

No distinct peaks are evident on the Swartland clay fraction XRD scan (Figure A.1b), except for a minor peak at 12°2ϴ representing a micaceous contribution. A very broad shouldered peak is evident, with its maximum centred around the 27°2ϴ. Such broad shoulders are indicative of interstratified clay mineralogy, with increased ramdomisation of layering resulting in reduced peak intensities and sometimes peak extinction (Bühmann, 1986). Ginster (1993) identified kaolinite as the dominant clay mineral in this soil form, with smectite as an accessory mineral. From this observation, and the fact that the major peak in Figure A.1b is centred around the region where the second order smectite peak should emerge, it may be reasonable to suggest that the dominant clay fraction in the Swartland soil is of a randomly interstratified kaolinite-smectite character.

High peak intensities around 8°2ϴ evident on Figure A.1c point to a large smectitic component in the Sasolburg clay fraction. Smaller peaks at 18°2ϴ and 38°2ϴ represent a minor contribution by kaolinite, and a higher order quartz peak is evident at 27°2ϴ. A relatively large second order smectite peak is present at 28°2ϴ.

A.3 Particle size distribution analysis

A.3.1 *Materials and methods*

A standard method using a Lowy pipette was used, as outlined by the SSSSA (1990). Aliquots (10g) of air-dried and crushed soil were passed through a 2 mm pore diameter sieve and then treated with sodium acetate to remove carbonate cementing agents, H_2O_2 to remove organic binding materials, and finally citrate-bicarbonate buffer to remove iron oxides. The treated samples were dried overnight at 105°C and their mass was noted. The samples were then shaken overnight in Calgon dispersing solution and tipped into a 63 μm pore diameter sieve held over a collecting tray. Fine material was washed through the sieve using distilled water, and the sieve was placed briefly in the oven to dry. The slurry in the collecting tray was tipped into a plastic cylinder for sedimentation and withdrawal using the Lowy pipette as prescribed by SSSSA (1990). The dry sand fraction remaining on the sieve was weighed separately, and the coarse silt fraction was calculated by different after the other particle percentages were known.

A.3.2 *Results*

Calculations were conducted as presented in SSSSA (1990), and the results of these are presented in Table A.1.

Table A.2: Particle size distributions in the Rensburg, Swartland and clean Sasolburg soils (%) determined by a standard method involving a Lowy pipette.

FRACTION	RENSBURG	SWARTLAND	SASOLBURG
SAND	43.9	53.2	55.4
COARSE SILT	0	6.3	9.4
FINE SILT	32.8	17.5	16.7
CLAY	23.3	23.0	18.5
"FINES"	56.1	40.5	35.2
IRON OXIDES	6.6	11.5	11.3

The Rensburg soil appears to have no coarse silt fraction since the sum of the other, experimentally determined fractions was greater than 100% because problems relating to the extreme swelling properties of the smectitic clay of this soil were experienced. For this reason, the percentages of the fine silt and clay fractions were determined by relative apportionment of the 56.1% part of the clay which was not accounted for by the accurately-measured sand fraction. Thus a value for "fines" is given, which is a sum of the fine silt and clay percentages and is probably a more accurate basis on which to compare the three soils. The iron oxide percentages given are calculated from soil sample mass before and after the citrate-bicarbonate buffer treatment.

A.4 Determination of soil moisture holding and field capacity

A.4.1 *Materials and method*

Rensburg and Swartland soil was finely crushed using a mortar and pestle, and then transfered to tared beakers. The mass of the dry soil was noted, and then water was added drop-wise over a period of roughly 30 minutes until the surface of the soil was observed to glisten. The amount of water which had been added in this way, termed the sticky point moisture content (SPMC) was noted. A soil water content of half the SPMC is known to give a good estimation of soil water content at field capacity (see pg 45).

The SPMC of the Rensburg soil was found to be 0.637 $ml.g^{-1}$ of soil, and its field capacity was 0.319 $ml.g^{-1}$ of soil. The corresponding values for the Swartland soil were 0.447 $ml.g^{-1}$ and 0.223 $ml.g^{-1}$ of soil, respectively. The water holding capacity of the Sasolburg soils was not determined.

A.5 Measurement of soil pH

A.5.1 *Materials and methods*

Aliquots (2.5 g) of the Rensburg soil were placed in 3 centrifuge tubes and suspended in 25 ml of either distilled water, 0.01M $CaCl_2$ or 1M KCl. The tubes were stoppered, sealed and shaken on a horizontal shaker for 10 minutes. The tubes were then centrifuges at 6000 rpm for 5 minutes, and the pH of the supernatant was determined using a Crison micro pH 2001 meter. This procedure was repeated for the three remaining soils.

A.5.2 *Results*

Table A.3: Supernatant pH of 1:10 soil to solution slurries of Rensburg, Swartland, clean and contaminated Sasolburg soil.

SLURRY SOLUTION	SOIL TYPE			
	RENSBURG	SWARTLAND	CLEAN SASOLBURG	CONTAMINATED SASOLBURG
H_2O	6.29	9.28	6.95	6.60
1M KCl	5.85	7.71	6.15	6.19
0.01M $CaCl_2$	5.45	7.59	5.64	6.36

A.6 Soil elemental analysis

A.6.1 *Materials and methods*

Dry soil samples were crushed to a face powder consistency using a ball and ring sieb mill. Powder briquettes were then prepared by compressing an aliquot of the milled soil surrounded by boric acid powder, under an applied pressure of 10 tonnes. Fusion discs were also prepared according to the Norrish Fusion method. Briefly, soil powder (~2g) was oven-dried overnight, and then roasted at 1000°C over a second night. Oven-dried lithium-boron flux (1.500 ± 0.002 g) and sodium nitrate (0.020 ± 0.002 g) was then weighed out and mixed with the roasted sample (0.2800 ± 0.002 g). The sample mixture was then melted in gold-platinum crucibles at a temperature above 980°C, poured into a mould and cooled, firstly over a hot plate, and then in a desiccator.

Major element composition was then determined using the fusion discs and a Siemens SRS 303 AS X-Ray Fluorescence (XRF) spectrophotometer fitted with a rhodium tube. The minor elements Mo, Nb, Zr, Y, Sr, U, Rb, Th and Pb were also analysed for on this instrument, using the powder briquettes. A Phillips 1400 XRF spectrophotometer, fitted with a tungsten tube was used to determine Co, Cr, V and Mn concentrations in the powder briquettes, and Zn, Cu and Ni were determined on the same instrument, but fitted with a gold tube.

A.6.2 *Results*

Primary XRF data was routinely processed, and the final elemental composition of the soils is given in Table A.3.

Table A.4: Elemental composition of the four soils under consideration in this study, as determined by X-ray fluorescence spectrophotometry.

	SWARTLAND	RENSBURG	CLEAN SASOLBURG	CONTAMINATED SASOLBURG
%				
SiO_2	68.33	77.94	73.49	73.85
TiO_2	1.09	0.87	0.49	0.41
Al_2O_3	8.53	7.76	10.22	7.50
Fe_2O_3	6.61	4.31	4.91	4.34
MnO	0.17	0.08	0.07	0.05
MgO	0.77	0.95	0.58	0.43
CaO	1.26	0.78	0.51	0.97
Na_2O	0.52	0.52	0.24	0.22
K_2O	1.20	0.96	0.94	0.44
P_2O_5	0.13	0.02	0.07	0.08
H_20	5.22	1.52	3.14	2.07
LOI	6.26	4.34	5.13	9.49
TOTAL	100.09	100.05	99.79	99.86
$mg.kg^{-1}$				
V	200	109	121	248
Mo	1.5	<0.5	2.5	42
Nb	11	9.7	11	7.6
Zr	319	398	231	206
Y	21	26	27	17
Sr	82	75	48	75
U	1.5	1.3	1.5	<1.2
Rb	61	52	54	25
Th	7.9	7.0	11	7.6
Pb	15	13	16	43
Zn	60	45	59	355
Cu	37	27	26	54
Ni	49	41	53	118
Co	40	22	22	25
Mn	1630	769	645	505
Cr	204	197	139	190

A.7 Soil surface area analysis

Surface area analysis of the Rensburg, Swartland and clean Sasolburg soil was conducted at the Department of Chemical Engineering (UCT) using a Micrometrics ASAP 2000 instrument and nitrogen as the analytical gas under standard operating conditions. Results are presented in Table A.4.

Table A.5: BET and single point surface areas ($m^2.g^{-1}$) of three soils used in this study, determined using nitrogen sorption.

SOIL TYPE	BET SURFACE AREA ($m^2.g^{-1}$)	SINGLE POINT SURFACE AREA ($m^2.g^{-1}$)
Rensburg	49.14	48.17
Swartland	38.43	37.39
Clean Sasolburg	24.87	23.78

APPENDIX B

Raw data from vanadate sorption trials

B.1 Calculations for initial vanadate sorption isotherms

RENSBURG SOIL

mg/l salt added	total mg applied V	solution V mg/l	sorbed V mg/kg
0	0	0.187	-2
10	0.109	0.4	40
25	0.272	1.232	97
50	0.544	4.266	175
75	0.816	7.705	249
100	1.088	11.448	321
150	1.632	20.677	446
200	2.176	30.645	564
250	2.721	43.355	655
300	3.265	59.635	710
400	4.353	92.283	818
500	5.441	129.718	879
750	8.162	203.283	1232
1000	10.882	290.777	1445

SASOLBURG SOIL

mg/l salt added	total mg applied V	solution V mg/l	sorbed V mg/kg
0	0	0.17	-2
10	0.109	0.165	42
25	0.272	0.988	99
50	0.544	3.683	181
75	0.816	8.532	241
100	1.088	13.886	296
150	1.632	25.291	400
200	2.176	39.307	478
300	3.265	77.918	527
400	4.353	113.612	605
500	5.441	159.753	579
750	8.162	233.318	932
1000	10.882	330.389	1049

CONTROL SET		Ammonium vanadate in 0.1M NaCl				
		RENSBURG SOIL			final	
applied V salt	applied V element				solution	sorbed
mg/l	mg/l	Sample No.	pH	EC	V mg/l	V mg/kg
0	0	1	8.01	11.03	0.91	-9.14
100	43.53	5	8.02	11.15	9.66	338.66
200	87.06	7	8.03	11.11	27.51	595.48
300	130.59	9	8.00	10.93	52.93	776.57
500	217.65	11	7.97	11.09	117.53	1001.18
		SWARTLAND SOIL			final	
applied V salt	applied V element				solution	sorbed
mg/l	mg/l	Sample No.	pH	EC	V mg/l	V mg/kg
0	0	13	6.52	11.09	0.35	-3.48
100	43.53	17	6.55	11.18	8.05	354.77
200	87.06	19	6.75	11.32	26.03	610.28
300	130.59	21	6.36	11.27	54.24	763.51
500	217.65	23	6.66	11.42	116.66	1009.89
		CLEAN SASOLBURG SOIL			final	
applied V salt	applied V element				solution	sorbed
mg/l	mg/l	Sample No.	pH	EC	V mg/l	V mg/kg
0	0	25	6.43	11.52	0.78	-7.84
100	43.53	29	6.49	11.50	13.06	304.71
200	87.06	31	6.48	11.44	40.31	467.51
300	130.59	33	6.51	11.58	73.30	572.85
500	217.65	35	6.49	11.50	146.26	713.88
		CONTAMINATED SASOLBURG SOIL			final	
applied V salt	applied V element				solution	sorbed
mg/l	mg/l	Sample No.	pH	EC	V mg/l	V mg/kg
0	0	37	6.51	12.05	0.65	-6.53
100	43.53	41	6.61	12.01	10.27	332.57
200	87.06	43	6.59	12.05	34.13	529.32
300	130.59	45	6.62	12.09	67.12	634.66
500	217.65	47	6.60	12.31	137.55	800.94

B.2 Continued....

ACIDIFIED SET		Ammonium vanadate in 0.1M NaCl/0.01M Nitric acid				
		RENSBURG SOIL			final	
applied V salt	applied V element				solution	sorbed
mg/l	mg/l	Sample No.	pH	EC	V mg/l	V mg/kg
0	0	73	7.81	12.01	1.50	-14.97
100	43.53	75	7.89	12.22	9.40	341.27
200	87.06	76	7.78	12.02	32.47	545.86
300	130.59	77	7.80	11.96	57.20	733.91
500	217.65	78	7.73	12.10	113.18	1044.71
		SWARTLAND SOIL			final	
applied V salt	applied V element				solution	sorbed
mg/l	mg/l	Sample No.	pH	EC	V mg/l	V mg/kg
0	0	79	3.89	11.93	0.69	-6.88
100	43.53	81	3.89	12.28	1.92	416.14
200	87.06	82	3.83	11.95	15.50	715.63
300	130.59	83	3.96	11.89	50.49	800.94
500	217.65	84	4.27	11.88	117.53	1001.18
		CLEAN SASOLBURG SOIL			final	
applied V salt	applied V element				solution	sorbed
mg/l	mg/l	Sample No.	pH	EC	V mg/l	V mg/kg
0	0	85	2.96	11.72	0.82	-8.18
100	43.53	87	2.99	12.09	5.49	380.36
200	87.06	88	3.12	11.74	23.33	637.27
300	130.59	89	3.17	12.00	56.50	740.87
500	217.65	90	3.32	12.11	122.75	948.94
		CONTAMINATED SASOLBURG SOIL			final	
applied V salt	applied V element				solution	sorbed
mg/l	mg/l	Sample No.	pH	EC	V mg/l	V mg/kg
0	0	91	4.21	12.01	0.49	-4.88
100	43.53	93	4.16	12.36	3.26	402.74
200	87.06	94	4.17	12.13	17.50	695.60
300	130.59	95	4.30	12.10	49.88	807.04
500	217.65	96	4.34	12.32	123.62	940.24

ALKALINE SET		Ammonium vanadate in 0.1M NaCl/0.01M sodium carbonate				
		RENSBURG SOIL			final	
applied V salt	applied V element				solution	sorbed
mg/l	mg/l	Sample No.	pH	EC	V mg/l	V mg/kg
0	0	169	9.85	12.01	1.40	-14.02
100	43.53	170	9.77	12.05	18.20	253.34
200	87.06	171	9.44	11.87	39.18	478.83
300	130.59	172	9.38	11.93	69.65	609.41
500	217.65	173	9.21	12.22	131.46	861.89
		SWARTLAND SOIL			final	
applied V salt	applied V element				solution	sorbed
mg/l	mg/l	Sample No.	pH	EC	V mg/l	V mg/kg
0	0	174	9.50	12.95	0.59	-5.92
100	43.53	175	9.29	12.92	16.11	274.24
200	87.06	176	8.60	12.62	30.56	565.01
300	130.59	177	8.67	12.72	58.85	717.37
500	217.65	178	8.50	12.68	127.98	896.71
		CLEAN SASOLBURG SOIL			final	
applied V salt	applied V element				solution	sorbed
mg/l	mg/l	Sample No.	pH	EC	V mg/l	V mg/kg
0	0	179	9.96	12.09	0.37	-3.74
100	43.53	180	9.82	11.80	28.29	152.35
200	87.06	181	9.34	12.00	57.02	300.35
300	130.59	182	9.31	11.79	92.28	383.06
500	217.65	183	9.21	12.10	161.06	565.88
		CONTAMINATED SASOLBURG SOIL			final	
applied V salt	applied V element				solution	sorbed
mg/l	mg/l	Sample No.	pH	EC	V mg/l	V mg/kg
0	0	184	9.81	12.56	1.58	-15.84
100	43.53	185	9.65	12.58	25.16	183.69
200	87.06	186	9.03	12.12	45.62	414.40
300	130.59	187	9.09	12.23	81.05	495.37
500	217.65	188	9.03	12.49	152.35	652.94

APPENDIX C

Freundlich and Langmuir adsorption isotherms (Sposito, 1989)

The Freundlich function is: $x = ac^b$

The Langmuir function is: $x = (bKc)/(1+Kc)$

where x is the sorbed-phase concentration and c is the solution-phase concentration of a particular sorbing species after suitable equilibration. The parameter b is the value of x that is approached asymptotically as c increases, and K determines the initial slope of the isotherm.

For the Langmuir equation to apply, a plot of K_d against the sorbed-phase concentration of the sorbing species must be linear, where K_d is the sorbed-phase concentration divided by the appropriate solution-phase concentration of the species at equilibration.

For the Freundlich equation to apply, a plot of the logarithm of the sorbed-phase concentration against the logarithm of the solution-phase concentration at equilibrium, must be linear.

It is from these linear plots that R co-efficients are obtained to compare the relative fit of each adsorption isotherm.

APPENDIX D

Details of soil preparation, maize growth conditions and maize yield.

Table D.1: Controlled environmental conditions used in the phytotron, where all plant growth experiments were conducted.

PARAMETER	SETTINGS
DAY LENGTH	13 hours, from 06h00 to 19h00
PERCENTAGE RELATIVE HUMIDITY	set point: 50% actual values: 47-68%
TEMPERATURE	19H00-08H00: 20°C 08H00-09H00: steadily rising to 28°C 09H00-17H00: 28°C 17H00-19H00: steadily dropping to 20°C
LIGHT INTENSITY	between 350-450 $\mu mol.m^{-2}.s^{-1}$, varying with distance from lights.

Table D.2: Nutrients applied to Rensburg and Swartland soil in preparation for plant growth trials.

ELEMENT	STOCK SOLUTION	VOLUME OF STOCK APPLIED TO 1.2 kg RENSBURG SOIL	VOLUME OF STOCK APPLIED TO 1.0 kg SWARTLAND SOIL	FINAL SOIL CONCENTRATION $mg.kg^{-1}$
Mg	3.04 $g.l^{-1}$	5	4.2	12.5
K	9.80 $g.l^{-1}$	5	4.2	40.8
N *	0.25 $g.l^{-1}$	5	4.2	1.0 *
P *	62.5 $mg.l^{-1}$	20	16.6	1.0 *

* The concentration of N and P applied was very low due to a misinterpretation of the suggested fertilisation method that was followed.

Table D.3: Details relating to the NH_4VO_3 treatment of Rensburg and Swartland soil in preparation for plant growth trials.

TREATMENT	VANADIUM $mg.kg^{-1}$	NH_4VO_3 mg in 1.2 kg	ml of 7 $g.l^{-1}$ stock required	ml exceeding field capacity *
RENSBURG SOIL				
1	0	0	0	-
2	100	275	39.4	-
3	200	551	78.8	-
4	400	1103	157.5	-
5	600	1654	236.3	-
6	800	2205	315.1	45.1
7	1000	2757	393.8	123.8
8	1400	3859	551.3	281.3
9	1800	4962	708.9	438.9
SWARTLAND SOIL				
1	0	0	0	-
2	100	230	32.8	-
3	200	460	65.6	-
4	400	919	131.3	6.3
5	600	1378	196.9	71.9
6	800	1838	262.5	137.5
7	1000	2297	328.2	203.2
8	1400	3216	459.5	334.5
9	1800	4135	590.7	465.0

* takes into account the volume of fertiliser used.

Table D.4: Ryegrass (*Lolium perenne*) emergence in Rensburg and Swartland soil amended with NH_4VO_3, after 12 days of growth.

Treatment	REPLICATION 1			REPLICATION 2		
	Seedlings per pot	Soil moisture content (%)		Seedlings per pot	Soil moisture content (%)	
		Day 9	Day 13		Day 9	Day 13
RENSBURG SOIL						
1	9	58.0	46.5	9	60.3	47.4
2	6	69.2	52.7	5	65.7	51.4
3	10	64.3	51.3	7	66.8	54.0
4	1	68.8	55.5	8	73.2	58.2
5	1	71.2	59.6	4	70.7	61.0
6	9	65.4	56.2	2	69.2	59.6
7	2	78.9	63.8	0	80.4	58.1
8	0	78.1	63.8	5	76.4	62.6
9	0	72.4	61.7	0	74.9	63.6
SWARTLAND SOIL						
1	5	81.3	38.7	7	65.9	34.3
2	6	64.6	32.6	3	60.8	34.8
3	3	57.5	30.5	1	61.6	29.3
4	3	43.0	32.4	1	41.7	32.5
5	4	58.4	35.8	8	57.8	37.3
6	2	40.7	30.2	2	49.0	31.6
7	2	38.2	33.5	4	44.2	31.2
8	0	59.3	30.1	3	56.3	35.2
9	0	64.7	31.7	0	38.5	33.5

Note: 1. Soil moisture contents were calculated from the pot mass immediately before daily watering. Soil moisture therefore ranged between the percentage value given in the table above, and field capacity, which corresponds to a soil moisture content of 50%, except for the pots which were over-watered.

2. A total of 20 seeds were planted per pot.

Table D.5: Maize (*Zea mays*) emergence in Rensburg and Swartland soil amended with NH_4VO_3, after 7 days of growth.

Treatment	REPLICATION 1			REPLICATION 2		
	Seedlings per pot	Soil moisture content (%)		Seedlings per pot	Soil moisture content (%)	
		Day 1	Day 6		Day 1	Day 6
RENSBURG SOIL						
1	8	41.2	40.4	8	41.3	40.8
2	8	46.8	42.0	8	45.6	40.3
3	8	45.7	41.2	8	48.2	41.7
4	8	49.7	42.8	8	52.7	44.6
5	7	54.8	46.6	8	56.0	48.4
6	5	51.0	43.6	6	55.0	47.0
7	8	58.6	50.9	2	53.3	46.1
8	4	56.9	50.1	5	57.0	49.4
9	7	55.2	46.7	7	57.6	50.0
SWARTLAND SOIL						
1	8	43.5	43.7	7	44.1	36.3
2	8	46.8	34.3	8	40.2	36.6
3	8	37.7	35.3	8	36.2	35.9
4	8	40.6	35.3	7	35.9	35.4
5	8	47.1	37.2	8	51.6	38.3
6	8	36.1	33.9	8	37.9	36.6
7	7	36.5	34.3	8	40.2	32.6
8	8	33.9	33.9	7	38.7	37.6
9	8	34.2	36.0	6	32.3	33.8

Note: 1. Soil moisture contents were calculated from the pot mass immediately before daily watering. Soil moisture therefore ranged between the percentage value given in the table above, and field capacity, which corresponds to a soil moisture content of 50%, except for the pots which were over-watered.

2. A total of 8 seeds were planted per pot.

Table D.6: Maize yields in Rensburg and Swartland soil amended with NH_4VO_3, after 22 days of growth.

Treatment	Applied V mg.kg^{-1}	Dry weight yield g Replication 1	Dry weight yield g Replication 2	Dry weight yield g Average	Relative yield % of maximum average
RENSBURG SOIL					
1	0	1.310	1.139	1.224	100.0
2	44	0.956	1.071	1.014	82.8
3	87	0.833	0.833	0.833	68.1
4	174	0.211	0.198	0.204	16.7
5	261	0.062	0.074	0.068	5.6
6	348	0.076	0.055	0.066	5.4
7	435	0.027	0.013	0.020	1.6
8	609	0.026	0.021	0.024	1.9
9	783	0.009	0.024	0.017	1.3
SWARTLAND SOIL					
1	0	0.631	0.533	0.582	87.0
2	44	0.415	0.442	0.428	64.1
3	87	0.754	0.344	0.549	82.1
4	174	1.107	0.231	0.669	100.0
5	261	0.255	0.242	0.248	37.1
6	348	0.122	0.123	0.122	18.3
7	435	0.202	0.175	0.188	28.2
8	609	0.046	0.033	0.039	5.9
9	783	0.067	0.078	0.073	10.8

Table D.7: Maize yields in Rensburg soil amended with NH_4VO_3 or $(NH_4)_2SO_4$, after 14 days of growth.

AMENDMENT	APPLIED N mg.kg^{-1}	Dry weight yield g	Relative yield % of the maximum yield in g	Corresponding main growth trial treatment
$(NH_4)_2SO_4$	0	0.444	69.9	1
	55	0.303	47.7	3
	165	0.403	63.5	4
	275	0.635	100.0	7
	495	0.487	76.7	9
NH_4VO_3	0	0.385	100.0	1
	55	0.258	67.0	3
	165	0.112	29.1	5
	275	0.043	11.2	7
	495	0.041	10.6	9

APPENDIX E

Preparation of special NH_4VO_3 standard solutions in an acid matrix.

The acidic matrix of the sample solution needed to be matched by the standard solutions for ICP, since if the usual 0.1M NaCl matrix had been used, the flow rates of standard and sample solutions into the ICP plasma would have been different because of differing viscosities, resulting in inaccurate calibration.

Biomass digestion involved adding 35 ml of deionised water to 5 ml of a 1:1, concentrated HCl:water solution. Thus 2.5 ml conc HCl were present in a total volume of 40 ml, and the effective dilution of the acid was 1:16.

So to make 500 ml of a 100 $mg.l^{-1}$ V stock solution,

50 mg V = 0.11487 g NH_4VO_3 must be dissolved in
500/16 = 31.25 ml conc HCl and
500 - 500/16 = 468.75 ml deionised water.

It is important to note that NH_4VO_3 cannot be dissolved directly in strongly acidic solutions, since the solid salt is converted directly into poorly soluble species, and in this case, the dark red crystals of most probably pentavanadate ($M^I_3V_5O_{14}$) were observed (Clark, 1973). Ammonium vanadate had to be dissolved completely in some of the deionised water before the addition of the acid, and then finally made up to volume with the remaining deionised water.

Standard solutions of 0.5, 1, 2, 3 and 5 $mg.l^{-1}$ were prepared by dilution of the 100 $mg.l^{-1}$ stock, using a 1:16 conc HCl solution.

APPENDIX F

Determination of saturated paste extract anion concentration by high performance ion chromatography (HPIC)

Selected saturated paste extracts obtained from Rensburg and Swartland soil which had been amended with NH_4VO_3 and used to grow maize for 22 days, were diluted 20 and 150 times, respectively, to reduce their EC to below 100 $\mu S.cm^{-1}$. The diluted sub-samples were then analysed for anions using a Dionex DX300 series-suppressed ion chromatography system, coupled with A1450 chromatography software. An HPIC-AS4A separator column, fitted with an HPIC-AG4A guard column, was flushed with a sodium carbonate/bicarbonate eluant (1.80 mM Na_2CO_3; 1.70 mM $NaHCO_3$) at a flow rate of 2.0 $ml.min^{-1}$, and a MicroMembrane (AMMS) anion suppressor was used.

Table F.1: Anion concentrations ($mg.l^{-1}$) in selected saturated paste extracts of Rensburg and Swartland soil, amended with NH_4VO_3 and used to grow maize for 22 days. Elemental vanadium concentration, determined by ICP (Section 3.4) is included for completion.

Treatment	Applied V mg/kg^{-1}	Cl^-	NO_3^-	PO_4^-	SO_4^-	V
RENSBURG SOIL						
1	0	67	9.2	307	192	1.1
2	44	61	8.7	257	145	13.5
3	87	85	18	293	158	37.6
4	174	71	217	212	140	72.0
SWARTLAND SOIL						
1	0	573	3714	0	2182	16.4
2	44	545	3336	0	2170	17.2
3	87	432	2970	0	1888	14.7
4	174	571	3385	110	2466	13.8
5	261	636	4496	112	2894	30.5

APPENDIX G

Soil microorganisms and vanadium

The purpose of this appendix is to outline the work that was conducted in this study with regard to the potential effects of vanadium on the soil microbiota. The goal of the work was not achieved since problems experienced with the apparatus could not be resolved in the limited time available. What follows is an explanation of the aim of the experiment, and a description of the method employed. This information is included for the sake of completion.

G.1 Introduction

Kabata-Pendias and Pendias (1984) estimate that up to 7 tonnes of active microorganisms may be present per hectare of grassland soil. Taking this fact, as well as the very active metabolism of most soil microorganisms into account, it is clear that the influence of the microbiota in the soil environment will be important.

In land treatment systems, soil microorganisms are responsible for the biodegradation of organic wastes which may be applied to the site, and may also influence the cycling and mobility of inorganic waste constituents, either by accumulating them, or by excreting compounds that reduce or bind them. (Breit & Wanty, 1991). Inhibition of the soil population by toxic chemical species may therefore contribute to a reduction in the ability of the soil to attenuate and immobilise waste constituents. For this reason, it was considered highly relevant to investigate the effect of vanadium on soil respiration at different levels of applied NH_4VO_3 in the soils examined in this study.

G.2 Microorganisms and vanadium

Very little information is available concerning the role of vanadium in microorganisms, and its toxicity. It may be a cofactor in miscellaneous small molecules like antibiotics and porphyrins, and it may have a role in lipid metabolism (Kabata-Pendias and Pendias, 1984). Recently, some attention has been focused on the replacement of molybdenum by vanadium in the nitrogenase enzyme complex, responsible for atmospheric nitrogen fixation, in common soil organisms like *Azotobacter* species (Eady *et al.*, 1987).

Ma (1987) nurtured vanadium-enriched cultures of soil bacteria and observed their colours to "change interestingly", suggesting the microbially-mediated redox transformation of vanadium species. Such transformation in the soil environment would have an important effect on vanadium mobility, bearing in mind the greater mobility of vanadium(V) species, and the relative immobility of vanadium(IV) species in soil.

Only two papers concerning the inhibition of soil microbiological activity were encountered in this study. Fu and Tabatabai (1989) observed the inhibition of nitrate reductase by vanadium(IV) and other trace elements in soil. This enzyme system is responsible for the conversion of nitrate to gaseous nitrogen. Yaroshevskii *et al.* (1982) considered the effect of vanadium and manganese additions on soil biological activity, and found that the combined application of 500 $mg.kg^{-1}$ Mn and 50 $mg.kg^{-1}$ V had a toxic effect on *E. coli*, and that vanadium applied alone also caused changes in soil biological activity.

Although vanadium may be required for certain microbiological systems, concentrations of the element which are too high will inhibit their functioning, and it is evident from the above discussion that this could have important consequences in a land treatment system. The aim of this part of the study, therefore, was to consider the potential toxicity of vanadium in the soils under consideration, and compare this against the results obtained in the plant growth trials. In this way, a more holistic understanding of the potential impact of vanadium in the land treatment scheme in question, could be obtained.

G.3 Principle of soil respirometry

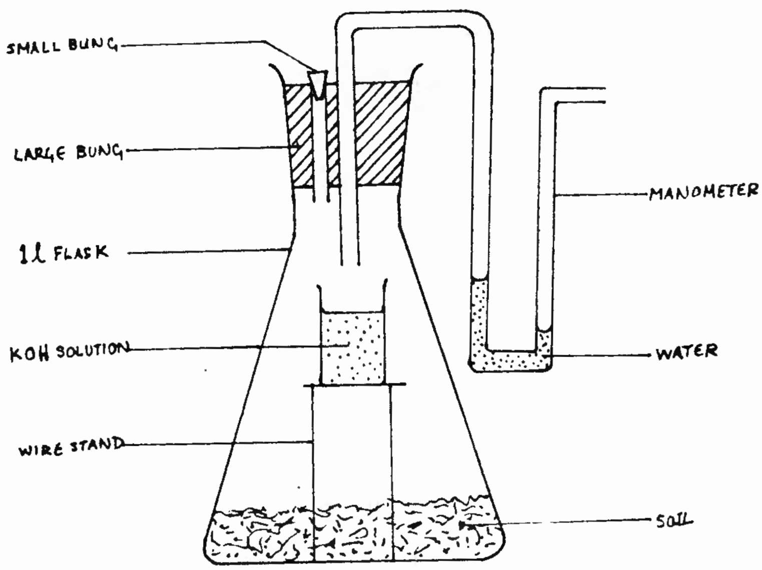
Microorganisms present in the soil actively respire, giving off CO_2 and using up O_2. If fresh soil, as well as a CO_2 sink like KOH solution, is contained in a sealed unit, the amount of O_2 utilised can be determined by measuring the change in internal pressure of the unit after a given period of time, using a manometer, for example. This change in pressure will effectively be the change in O_2 partial pressure. If increasing amounts of a toxic material are added to the soil, inhibition of the soil microbiota will be reflected in a reduction in the amount of O_2 consumed.

G.4 Materials and methods

Solid NH_4VO_3 was thoroughly mixed into aliquots of soil (250 g) so that seven vanadium treatments were obtained, namely 0, 100, 300, 500, 750, 1000 and 1500 $mg.kg^{-1}$ V. Distilled water was then added to the soil and thoroughly mixed in, to bring its water content close to field capacity, and the volume of the soil was determined by transferring it into a large measuring cylinder. The treated soil was then transferred into the soil respirometer unit illustrated in Figure G.1a. A 50ml beaker and a support stand were totally immersed in water to determine their volumes, dried and arranged in the units, and 10ml of 10g/100ml KOH solution was placed in the beaker. The large bung of the flask was replaced and water was introduced into the bend of the manometer. After the flasks had been allowed to equilibrate for 5 to 10 minutes, the flasks were sealed using the small bungs shown in Figure G.1a, and the water level in the manometer arm closest to the flask was marked.

The units were left to stand for a noted period of time, after which the change in the level of water in the manometer arm closest to each flask was noted. The temperature of the flask environment was noted both before and after the experiment.

(a)



(b)

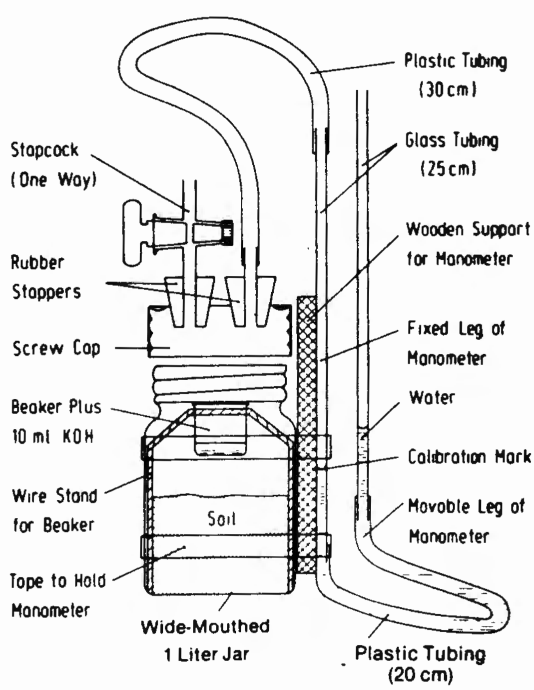


Figure G.1: Soil respirometer units (a) constructed and used in this study, which were modelled after (b) the units which are used commercially (Anderson, 1982).

The change in the manometer water level (mm) was converted to ml of O_2 consumed and plotted against time. This conversion involved multiplication by a flask constant, K, which had been determined as follows (Anderson, 1982):

$$K = \frac{V_g(273/T) + V_f\alpha}{P_o} \quad \text{units: } \mu l.ml^{-1}$$

where V_g is the volume of gas present in the flask up to the reference mark on the manometer, T is the temperature of the run in Kelvin, V_f is the total volume of fluid in the unit (water and KOH solution), α is the solubility of oxygen in water at the temperature of incubation (Table G.1), and P_o is a standard pressure set at 10.336 mm for distilled water.

G.5 Problems encountered with the respirometer units

Very erratic results were obtained from the respirometer units, and were attributed to the following problems:

1. The units were extremely sensitive to heat-related pressure changes, so much so that handling had to be kept to a minimum, and sufficient equilibration time had to be allowed before sealing.
2. The flasks had to be completely aerated between each run, and this involved removing everything from the flask, except the soil. This would have interfered with the flask constants determined at the beginning of the experiment, since soil was inevitably removed during this operation.
3. Saturation of the KOH solution after a number of runs may explain the lowered respiration rates observed in some of the runs.
4. The manometers used in this study may have been too small, and therefore too sensitive to small pressure changes.

Table G.1: Solubility of O_2 in water at various temperatures, with units of ml gas dissolved per ml of fluid, when gas is at 1 atm pressure (Anderson, 1982).

Temperature (°C)	O_2 solubility
0	0.04872
10	0.03793
15	0.03441
20	0.03091
25	0.02822
30	0.02612

If this work was to be continued in the future, a very specific method needs to be set out and followed carefully. It might also be useful to replace the delicate, sensitive manometers used in this study with more robust models, as depicted in Figure G.1b.