OPTIMIZING WATER QUALITY MONITORING : A CASE STUDY ON THE SOUTH AFRICAN HIGHVELD

O.W.Paul

B.Sc. (Hons.) (Geology), Bristol.

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

Department of Geological Sciences,
University of Cape Town,
Republic of South Africa.

December, 1995.

PREFACE

The theoretical work described in this study was conducted in the Department of Geological Sciences, University of Cape Town, Republic of South Africa from August 1995 to December 1995. The thesis was under the supervision of Dr. Martin Fey and Assoc. Prof. James Willis.

The studies in this thesis represent original work by the author and have not been submitted for the purpose of a degree to any other University. Where research of other workers was used acknowledgement occurs in the text.

Signed

19. XII. 95

Oliver Paul.

ACKNOWLEDGEMENTS

The author would like to extend his sincere gratitude to those listed below. Not only for their input to this thesis but for all the help provided over the Masters Course.

Dr. Martin Fey, for his inexhaustible theories, enthusiasm, humour and stimulating discussions on far reaching subjects.

Assoc. Prof. James Willis, for his expert guiding influence and his commitment to scientific excellence.

SASOL Ltd., for their financial support, patronage and willingness to abet me throughout the study period.

Martin Ginster, of SASTECH R&D, as my liaison officer, for his inspiration and guidance, and for the valuable time he allocated to me and my contemporaries on the Masters course.

Kobus du Toit, of SASTECH R&D, for his efficient response to my questions concerning the monitoring operation.

All the personnel at SASOL Ltd. who helped me, must receive thanks, especially Jaques Venter, Johan de Graaf and Flip du Bruyn.

Prof. Theo Stewart, for his patient explanation of statistical procedures and their application. Prior to the discussions with him I had never relished studying statistical theories.

Dr. Lindsay McNeill, for her kind help and enlightenment on some statistical rationales. Her warnings of potential pitfalls maintained the quality of my work.

Dr. Frank Hodgson, for his generous explanations of repeated queries I sent via the electronic highway.

Reinier de Vos, of the Computing Centre for Water Research (CCWR), for the valuable suggestions and pointers he gave, particularly the contacts he referred me to and for provision of WQStat II software.

Dr. Jenny Day for the valuable insight into bioassays she gave me.

Finally, I must thank all the friends I have made in South Africa for maintaining the humour and making this such an enjoyable year.

This thesis is dedicated to Calvin and Hobbs in respect of their theoretical work in exploring the environment, science and life in general.

ABSTRACT

Water quality monitoring is an essential part of environmental management, supplying information for decision making processes. Monitoring operations can, however, be inefficient and produce either inadequate or excessive information. There are three criteria determining the size of a monitoring network: the spatial scope (area monitored and density of sampling); the temporal dimension (sampling frequency and duration of the project) and the level of detail (number of analytes measured, interpretation techniques, *etc.*). Several workers have developed ways to optimize these criteria and increase the cost-effectiveness of data acquisition.

There is a parity of literature on research into industrial monitoring networks. This study focused on an industrial operation in Mpumalanga on the South African Highveld which has established a ground and surface water monitoring network to measure the environmental impact of its activities over an area of 140 km^2. Physiographic, legislative and management (including financial) factors were considered in relation to the design of the monitoring network.

An appraisal of the water quality data demonstrated that the different waste operations have varying impacts. Most of the waste sites were not seen to cause damage. An analysis of the percentage ion balance errors from the existing database shows that 27% of the analyses were characterized by an ion imbalance of > 10 %. Periods of both high precision but low accuracy and low precision, low accuracy were identified. The quality of analysis has not improved significantly over the last four years. Ca and Mg concentrations coincide with the large ion imbalance errors and techniques for determining these analytes should be investigated.

A multiple criteria system was developed to compare unrelated environmental factors and produce a composite and quantitative score for each of the waste operations. The weightings of the waste sites represent their environmental significance and were used in the allocation of sampling resources. Statistical procedures, based on pre-specified criteria, determined the number of samples required: a budget of R 40,000 per year would allow 136 samples to be collected; 115 samples would need to be collected to ensure a standard deviation of 55 $mS.m^{-1}$ on the mean EC value and if the acceptable margin of error on the EC was 100 (at a 95% confidence level) then 132 samples should

be collected. The sample requirements were objectively allocated to the waste operations based on the different weighting criteria.

The temporal variation in monitoring data was studied but no seasonal patterns in water quality were identified. It is, therefore, not possible to decrease the sampling frequency during any season of the year. Some trends are found in the data sets which aid in the environmental appraisal of the area.

A technique of hypothetically thinning the data (from weekly to fortnightly, and so on) was used to assess the decrease in information resolution resulting from less frequent sampling. For some sites the same conclusions would be drawn with less sampling, while for other monitoring sites the water quality characteristics inferred are significantly different from reality, suggesting that sampling should be done more often.

A study of the detail of the monitoring operation indicated that EC (or TDS) is the best pollution indicator. Automated telemetric analyzing equipment would allow a more realistic image of water quality to be obtained. The dominant ions can be inferred from mean relative proportions. The minor ions tend to have more aberrant behaviour and therefore require greater attention in the monitoring operation. Further work could produce chemical signatures of pollution allowing for events to be attributed to specific waste sites.

TABLE OF CONTENTS

LIST OF APPENDICES

LIST OF FIGURES

LIST OF TABLES

LIST OF ABBREVIATIONS, IMPORTANT UNITS AND TERMS

Abbreviations:

CCWR	The Computing Centre for Water Research, University of Natal, Pietermaritzburg, RSA.
CSIR	The Council for Scientific and Industrial Research, RSA.
DWAF	The Department of Water Affairs and Forestry, RSA.
EMU	Environmental Management Unit.
ISO 9000	International standard for quality management, 9000 series.
MCDA	Multiple criteria decision analysis.
REGM	Sampling sites 'receiving environmental ground water monitoring'.
RESM	Sampling site 'receiving environmental surface water monitoring'.
PPSM	'Potential pollution source monitoring' of waste operations. Analysis of the waste, effluent and associated raw leachate.
U.S.EPA	The United States Environmental Protection Agency.
VISA	Visual interactive sensitivity analysis.

Some common chemical abbreviations are used in this thesis, namely: COD (chemical oxygen demand), BOC (biological oxygen demand) SAR (sodium adsorption ratio) and TDS (total dissolved solids).

Important units:

mg.dm^{-3}	Milligrams per decimeter cubed, mg/l is also used in some figures where computer packages do not allow the use of superscripts.
mS.m^{-1}	Millisiemens per metre at 25°C, this is used as the electrical conductivity unit, mS/m is also used in some figures where computer packages do not allow the use of superscripts.

Terms:

Analyte	is synonymous with a chemical parameter, variable or component.
HydroCom	is the trade name of a hydrochemical computer database package.
Spruit	is a colloquial name for a stream.

INTRODUCTION

In 1852, Chief Seattle wrote an often quoted letter in response to US Government requests for title to his peoples land. It said:

> *"How can you buy or sell the sky? The land? .... If we do not own the freshness of the air and the sparkle of the water, how can you buy it? .... The rivers are our brothers. They quench our thirst .... So you must give the rivers the kindness that you would give any brother."*

Extracts from history are often used as passionate reminders of our duty to preserve the quality of water. Strong emotional conflicts are increasingly common between industrialists and 'environmentalists'. In South Africa, like much of the world, the waters have been bought and sold under a system of private management. Problems relating to the use water and maintenance of its quality have become increasingly vexing. New technology has continually been developed to progress towards a sustainable usage of this resource. The fundamental procedure of water quality management is monitoring of the hydrochemistry and associated biology. Water quality monitoring is a rational, scientific and objective process of supplying information to aid the decision making operation.

Scientific literature referring to monitoring operations lacks examples from industry. Publications tend to centre on specific pollution events which have generated some exciting research work, such as the data worth assessments conducted by James and Gorelick (1994) and Istok *et al.* (1993). Most monitoring, however, applies to the more mundane, industrial type of environmental evaluation. Protocols and procedures to be followed in the design of such monitoring networks have been outlined by many workers, for example Keith (1988), Loaiciga *et al.* (1992) and Weaver (1992). It can be assumed that the acquisition of information by industrial monitoring operations will be inefficient to some degree. Strategies for monitoring are often dynamically designed to allow for improvement, since it is usually only with the benefit of hindsight that inefficiency can be identified.

Most industrial companies recognize the value of monitoring but require some economic accountability from the operation. A monitoring network that is financially responsible will ensure information is obtained in an optimal way. However, monitoring designs too often lead to data-rich but information-poor operations. Monitoring is required to produce a representative image of the overall environment and therefore cannot involve whimsical data gathering - *i.e.* it is a logical and methodical process. Considering the financial constraints and the information which is expected, monitoring must follow the rationale of collecting the maximum amount of information for the minimum expenditure of energy (time, effort, money, *etc.*). The optimization of a monitoring network is therefore vital in improving environmental management.

Much of the energy put into the monitoring operation could, in theory, be saved and / or produce a better return. The performance of a monitoring operation has three facets which can theoretically be optimized:

(i) Sampling sites (the spatial scope) could be reduced and/or sited more judiciously.

(ii) The frequency of sampling (the temporal dimension) could be reduced and/or the time of sampling selected more judiciously.

(iii) Analytical and data interpretation (level of detail) considerations could be thought through more carefully in terms of appropriate methods and the type of information required.

The approach of this study has been to address ways of effecting improvements in these three aspects of monitoring. Previous workers have used one of three possible approaches in optimizing the acquisition of water quality information by monitoring: monetary value (Istok *et al.*, 1993); statistical uncertainty (Freeze *et al.*, 1992) and benefit to environmental management (James and Gorelick, 1994).

An appraisal of the geochemistry in the industrial area is an inherent part of reviewing the design of the monitoring network. The crux of the present study, however, is to draw together a number of concepts which address the process of information gathering, the objective being to recommend ways in which the monitoring network can be improved by reducing error and inaccuracies in the environmental data and decreasing the cost of the resultant information. The study was also considered an ideal opportunity to attempt some hitherto apparently untried approaches to the assessment of environmental monitoring data, namely the so called multiple criteria decision analysis (MCDA) and the simulation of sampling frequency variation through temporal thinning of data.

1. PRINCIPLES AND STRATEGIES FOR MONITORING WATER QUALITY - A REVIEW

1.1 INTRODUCTION

Much of the time, effort and money devoted to environmental assessment has been wasted on studies that lack specific objectives and / or use inappropriate appraisal designs (Bernstein and Zalinski, 1983). Such investigations run the risk of either having little chance of detecting anything but catastrophic changes, or of sampling far in excess of what is necessary. Neither excessive or inadequate strategies are cost effective.

The aim of this literature review is to develop an appreciation of the factors which contribute to the efficiency of water quality monitoring in addition to the manner these factors can be accommodated in the development of specific monitoring strategies.

1.2 PRINCIPLES OF MONITORING

1.2.1 Concepts

Monitoring consists of the repetitive and continued observation, measurement and evaluation of environmental data to follow changes over time (Porteous, 1992). It is multi-disciplinary (Vrba and Pekny, 1991) and may involve a wide variety of media (Sittig, 1974), for example: air, water, effluent, soil and sediment (Howarth and Thornton, 1983).

The actual procedures adopted can vary. For example, Loaiciga *et al.* (1992) define a water quality monitoring network so as to include the selection of sampling points and temporal sampling frequency to determine the physical, chemical and biological characteristics of water but not to include the evaluation of the data. Most workers consider monitoring to have a temporal dimension, as opposed to risk or impact assessment which is a one-off environmental appraisal. The latter is sometimes included in the concept of monitoring (DWAF, 1994; Lawrence and Williams, 1991).

Monitoring is generally considered to involve three operations: sampling, analysis and interpretation, each requiring different skills. Figure 1.1 depicts the typical flow of information, pertaining to water quality conditions in time and space, and how this ultimately influences management decisions. The concept allows for a dynamic element to be incorporated in the strategy, whereby continual improvements to procedures can be effected. Considering the diversity of environments monitored, the varying scope of monitoring programmes and the techniques required, monitoring can be a highly complex procedure.

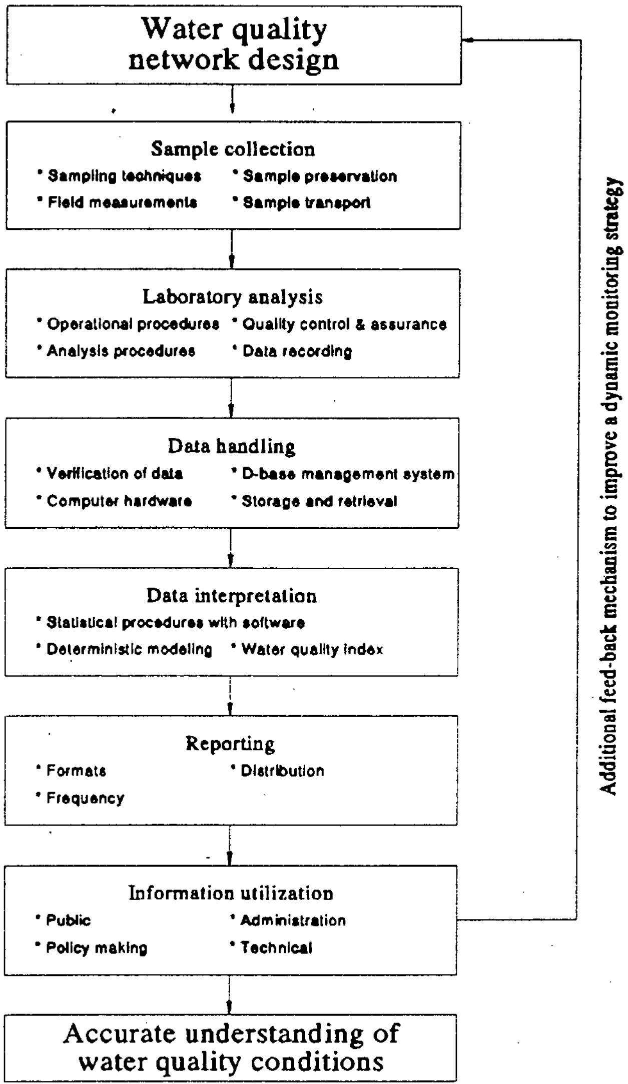


Figure 1.1. The flow of information in a water quality monitoring system. Adapted from Ward (1986) to include a feed back mechanism from the reporting stage to the water quality network design.

The overall objective of monitoring is firstly to detect environmental changes irrespective of whether these are desirable or undesirable, natural or anthropogenic (Sittig, 1974), and then to evaluate these changes in the context of the desired use of the medium being monitored (McBride, 1986). Examples of environmental evaluations include assessing: the ambient conditions, environmental criteria requiring remediation, the progress of mitigating measures and compliance with statutory requirements.

1.2.2 Criteria determining the size of monitoring programmes

The size of monitoring operations may be gauged in terms of three criteria: space, time and detail (number of analytes, precision *etc.*). The criteria vary in size and determine the size of the monitoring operation, as illustrated in Equation 1.1.

$$\textit{Total size of monitoring operation} = S + T + D$$

Equation 1.1.

Where: S = Spatial scope, (*i.e.* area/volume of sampling and density of sample sites).
T = Temporal dimension, (*i.e.* the length of time the region is monitored and frequency of sampling).
D = Detail, (*i.e.* number of analytes measurements, depth of interpretation procedures, size of the quality control operation *etc.*).

The spatial scope, S, not only varies in total area (and depth) but also in the density of the sampling points, and can apply on the local level (*e.g.* monitoring an industrial plant, Schweiter and Black, 1985), regionally (*e.g.* monitoring the catchment basin of a river, Droppo and Jaskot, 1995) or nationally (Parsons and Tredoux, 1995).

With regard to the temporal dimension, T, the longer the history of monitoring, the larger the data base, the more expensive is the operation but the greater the value of the information. The temporal aspect also includes the frequency of sampling - whether the samples are taken weekly, monthly or quarterly, for example. The higher the frequency the greater are the costs.

The third criterion is the number of analytes or parameter determinations, D. The design of a monitoring strategy needs to optimize the number of samples and test for the right indicators of pollution that furnish a sufficient but not excessive amount of data to characterize a pollution problem (Schweiter and Black, 1985). In addition, the strategy must provide the degree of confidence in the quality of the information necessary to support the intended use.

1.2.3 Applications

The potential applications of a monitoring activity are numerous. This thesis is concerned with the use of monitoring in the assessment of fluvial and ground water. McBride (1986) raised the point that a monitoring network's overall aim is distinct from its objectives. The aim might be to monitor water quality, while the objectives could be to assess the quality of water from an industrial plant and to determine the suitability of the same water for recreation or drinking. The monitoring strategy must resolve the conflict between objectives by developing the most effective method to assess the water quality. The result of the monitoring programme should provide the water quality management process with a clear classification of the problems (Figure 1.1).

1.2.3.1 Surface water

Fuggle and Rabie (1992) note that the demands for water range from the support of life, to the sustenance of material needs. The most valuable source of water for all human needs are our streams, rivers and lakes.

The importance of evaluating these waters is reflected by a significant increase in the establishment of monitoring networks of varying scales (Parsons and Tredoux, 1995). McBride (1986) identified faults in the evolution of water quality monitoring in New Zealand and presented concepts on the rationale behind monitoring. The 'why' is the goal of the monitoring programme and can easily be quantified. More elusive are the 'what', 'when' and 'where' to measure. These concepts should evolve dynamically and flexibly.

1.2.3.2 Ground water

The monitoring of ground water essentially has the same rationale as surface water monitoring. The acquisition of the data is, however, considerably more complicated. Loaiciga *et al.* (1992) prepared a 'review of ground water monitoring network design'. Many of their ideas coincide with those of McBride (1986). In particular, Loaiciga *et al.* (1992) highlighted the need for a consideration of:

- The spatial and temporal coverage of sampling sites.
- The competing objectives of a monitoring program.
- The complex nature of geologic, hydrologic and other environmental factors.
- The uncertainty about parameters needed in the design process.
- The range of applicability of the various methods for network design.

There are many parallels seen in the literature between surface water and ground water monitoring networks, but these really only exist on a conceptual level. The physical procedures of acquiring samples, preserving the specimens and the analytical techniques vary considerably. Surface and ground water, however, interact in the environment. A monitoring strategy must, therefore, study both media in conjunction with each other. Freeze *et al.* (1992) are not alone in acknowledging that every network design is unique and hence investigation strategies must mature in their own context.

1.3 PROCEDURES FOR MONITORING WATER QUALITY

It is important to bear in mind the objective of a monitoring programme. A tendency to concentrate on the acquisition of samples has led to data-rich, information-poor operations (McBride, 1986). If the programme is not structured to meet expectations, the information which can be inferred is inadequate and inappropriate for management decisions. Expectations or objectives are formulated through consultation between the network designers, water quality managers, the analysts and those who fund the monitoring programme.

The first stage in the construction of a monitoring network is to establish the overall goal of the monitoring programme. The network is designed with consideration for the specific objectives of the monitoring programme. Barcelona (1988) suggests the formulation of a sampling and an analytical protocol, enabling progression to the final stage of interpreting the results (Figure 1.2). He also identifies the need for a feed-back mechanism from the evaluation of the data to correct the protocols. This confirms the need for a return loop to adapt a monitoring network, as illustrated in Figure 1.1. Figure 1.2 has been modified slightly (indicated by italics) to show that the interpretation stage also has different methods, techniques and procedures (for example graphics or different statistics). The interpretation would also require a clearly defined protocol.

1.3.1 Sampling

There is a multitude of recommended procedures for acquisition of environmental data. Most governments produce advisory documents (for example, DWAF, 1993a-d; 1994a-c), which need to be followed if the monitoring programme is to have legal standing. A particularly comprehensive example is Weaver's (1992) manual on ground water sampling. It outlines the careful planning required, in addition to pilot runs, selection of determinants, quality assurance and other factors.

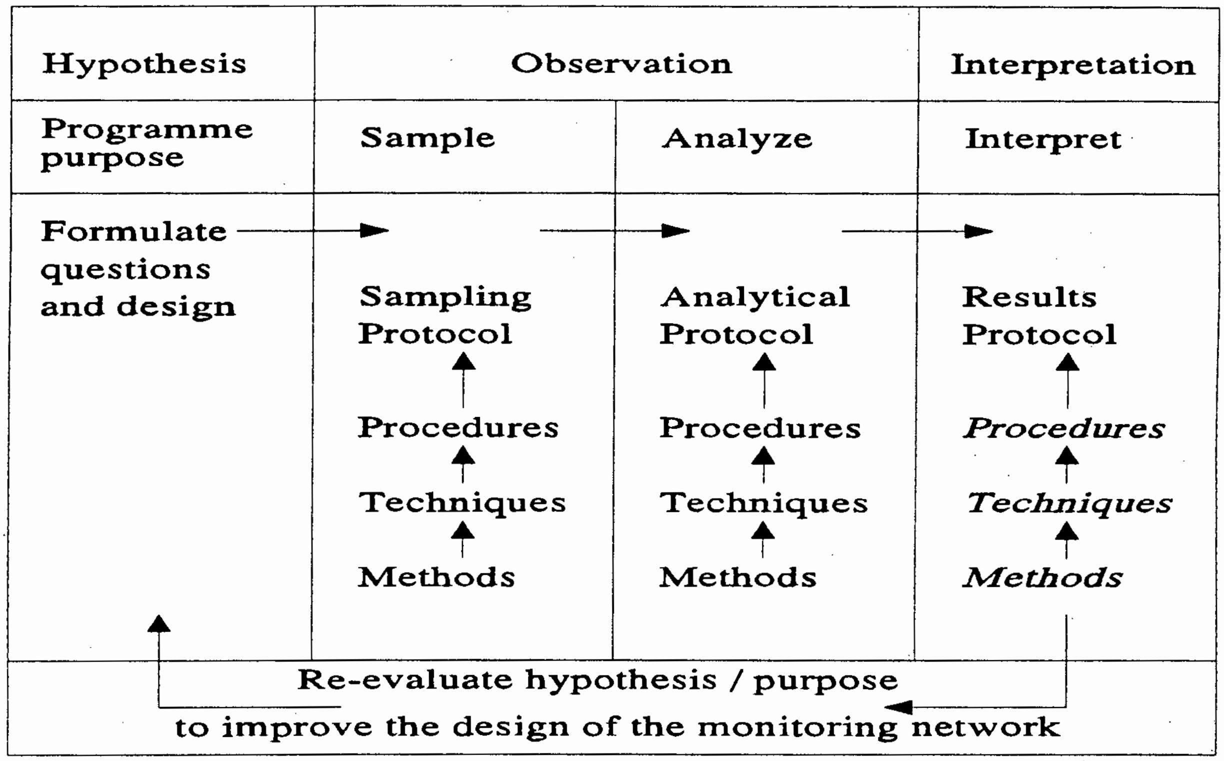


Figure 1.2. Relationship of program purpose (overall objective) and protocols to the monitoring method, modified from Barcelona (1988).

Monitoring is a scientific procedure and requires attention to the smallest detail. It is imperative to minimize misrepresentation and sample contamination, analytical errors and erroneous evaluations, so that management decisions are valid, even in law. Ultimately, choice of the different sampling techniques is dependent on the unique context of the monitoring programme. Somlyody *et al.* (1986) state that 'common uniform sampling strategies may not correctly or cost effectively describe the water quality information needed, as determined in the monitoring objectives.'

1.3.1.1 Frequency of sampling

Of all the design parameters, the frequency is the most flexible. The frequency of measurements can be analyzed by computer algorithms (such as WQStat II, chapter 3) and treated objectively using statistical optimization (James and Gorelick, 1994; Ben-Jemaa *et al.*, 1994). The other parameters of network design tend to be more subjective and site-specific. It is possibly because the frequency of sampling represents a large influence on the cost and can be rationalized, that the literature pays a significant amount of attention to this subject.

Droppo and Jaskot (1995) consider the impact a river's transport system has on the pollutant load distribution and highlight the fact that elevated concentrations may be seasonal. This suggests the use of different frequencies when sampling temporally. A non-aquatic example is the photochemical smog project in Cape Town, when sampling is only done a day before, a day after and on the actual brown haze day (Willis, 1995). Many monitoring programmes have a two-tier frequency network: a low frequency while measuring ambient conditions and a higher frequency targeted at one location when a pollution event is detected. There are other variations in sampling frequency strategies, for example double sampling (Gilbert, 1987).

Spacing samples evenly over time is logistically convenient but random sampling has benefits for statistical analysis (Sittig, 1974). Graphical representation of information is much clearer with periodic sampling, *i.e.* with regular time intervals (Steele, 1986). This paradox leads to further discussion in chapter 3. The absolute intervals are specific to the monitoring programme and range from seconds, providing near continuous monitoring (Andrew *et al.*, 1994), to a few years.

Bernstein and Zalinski (1983), unlike some other workers, stress the importance of replicating sampling through time, particularly in environments prone to variability. They provide a statistical model and a rationale for incorporating the variability between sampling location and over time into an error term of the analysis. This is based on the idea that an impact on the environment can be detected by changes in abundance of biological species or groups of species.

1.3.1.2 Location of site

The location of the sampling site is crucial. If the sample collected is not representative of the water body the whole monitoring operation becomes redundant. In aquatic environments, pollution may be derived from two types of sources: point sources, where the pollutant load may be readily quantified; and diffuse sources, where the programme needs to cope with low concentrations imprecise contaminant origins and on varying spatial scales.

McBride (1986) notes that the objective of monitoring will also influence the location. A broad scale monitoring programme will have dispersed sampling sites (Parsons and Tredoux, 1995), whereas an area in which there is potential for environmental dispute will have a concentration of monitoring at key locations, *e.g.* the habitability of homes near the Love Canal, New York, USA, which was contaminated with chlorinated organics (Schweiter and Black, 1985). The spatial variability of a pollutant can be quite large over a short distance. Two examples illustrate this:

- Droppo and Jaskot (1995) sampled the Nith River of southern Ontario, Canada. They established that contaminants have transport modes and relationships were found between dissolved and particulate concentrations and discharge and between load distribution and sediment particle size, over a cross section of the river. Such relations can have a significant bearing on sampling site selection.
- Parker and Foster (1986) showed the tendency of nitrate and sulphate diffuse pollution towards stratification in ground water. Ground may show inhomogeneous pollution related to the heterogeneous nature of the aquifer (Figure 1.3). The pollution is stratified in the aquifer profile and the quality of pumped supplies does not reflect the severity of pollution in the aquifer.

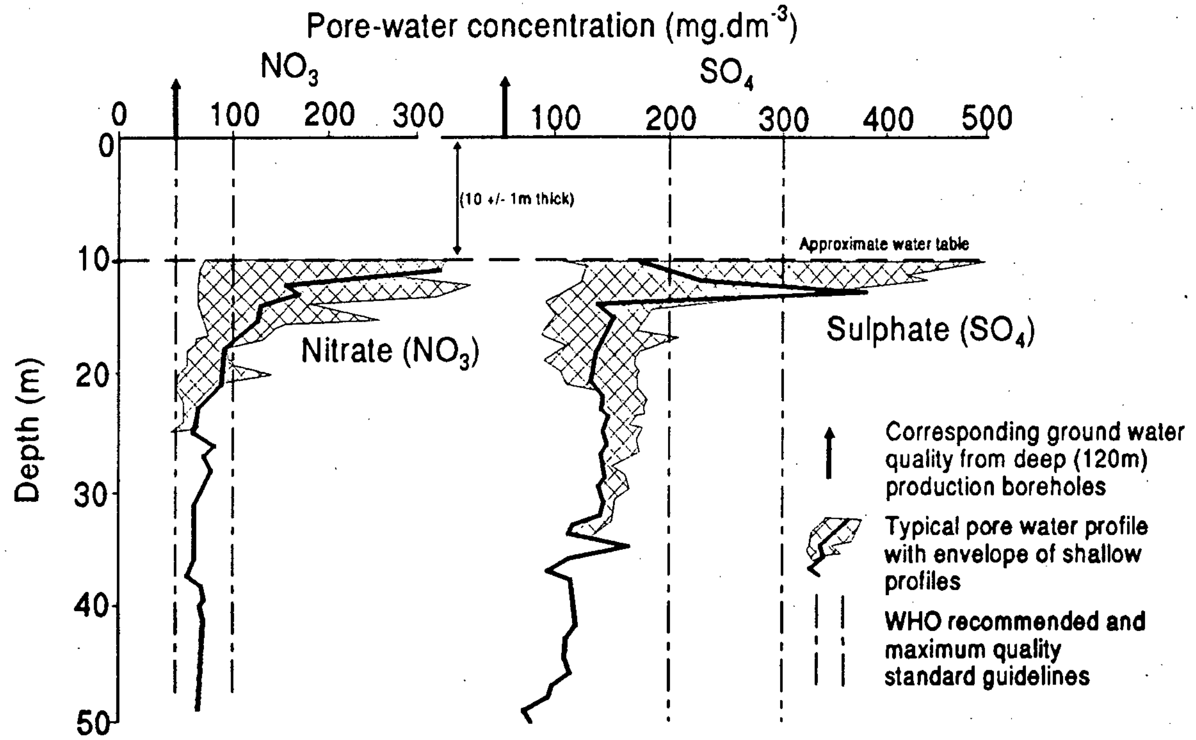


Figure 1.3. Saturated zone pore water from an aquifer in Yorkshire, UK, with diffuse pollution from agriculture and aerial deposition, (Parker and Foster, 1986).

The above examples highlight the importance of an initial risk assessment to identify the possible spatial variations in contaminant concentration. With regard to ground water monitoring, the location of sites must be chosen after considering the hydrogeological conditions and the areas of pollution vulnerability. Systems (such as that of LeGrand and Brown, 1990; Appendix IV) can be used to aid the design of the monitoring strategy. For fluvial water quality assessment, the characteristics of the water course and the potential for pollution must be accounted for in the monitoring network design.

Geostatistical methods have been used to optimize the location of sampling sites by many workers. Palmer and MacKenzie (1985) developed a classical analysis of variance (ANOVA) model, in which an interactive optimization procedure is applied in selecting monitoring designs which maximize the geostatistical power of a network for a specified budget. Similar methods employed by Gilbert (1987) are explored in chapter 2. The latter author explains how to statistically allocate samples to strata of a monitoring operation using pre-determined criteria. Such models enable a more effective selection of sampling location.

1.3.1.3 Acquisition of data

Ideally, water samples should be collected without changing their physical, chemical or biological characteristics. There is no universal procedure for sampling all waters. The methods must specifically match the monitoring programme. Cole *et al.* (1991) found that traditional sampling procedures revolved around the analytical laboratory. Physical specimens are often collected on site, packaged and preserved, and transported to the laboratory under a chain of custody restriction - a process which is laborious. In addition, it is costly, time consuming and many opportunities to incur errors and to lose data are present. Information loss will include systematic and random errors.

Methods to reduce the inconsistencies in sampling are important to the efficiency of a monitoring programme. Keith *et al.* (1983) provide a comprehensive guide to the favoured procedures employed for sample collection through to data interpretation. The appraisal of every potential problem and its solution prior to network design is crucial (Parker and Foster, 1986).

1.3.2 Analysis

There are numerous manuals providing guidance on sample preservation, handling and analysis (for example, Barcelona, 1988). Often the procedures are geared to adhere to prescribed (governmental) guidelines. For example, the minimum requirements for waste site monitoring in South Africa require that 'water samples must be analyzed by a recognized analytical laboratory that uses approved analytical procedures' (DWAF, 1994c). Statutory requirements and the programme's objectives should be accommodated in the construction of the analytical protocol (Barcelona, 1988).

1.3.2.1 Selection of analytes

The last few decades have seen significant advances in analytical techniques and equipment, in accuracy and precision, and in the analysis of an increasing diversity of media. Much of the impetus for these developments has come from environmental monitoring. In the construction of a programme there are now a large variety of techniques to choose from and analytes which could potentially be investigated. In practise, while the information obtained from analyses must fulfil the network's objectives, financial constraints must be considered.

Howarth and Thornton (1983), in an encyclopedic review of geochemical mapping, submit that it is difficult to generalize on the advantages and disadvantages of different sampling media and different analytes. A central concept can, however, be identified. The choice of variables can be adjusted to optimize a programme. The reduction in the number of analytes must not, however, jeopardize the information accuracy beyond an acceptable limit. One method to accomplish this is by establishing covariant parameters, which can be identified in the initial impact assessment. This removes the need for complete analysis of all variables.

A useful example of this principles provided by Istok *et al.* (1993). They found a positive correlation between the measured concentrations of nitrate and metabolites of the herbicide Dacthal in an unconfined aquifer and suggest that future monitoring should include a large number of the less expensive nitrate analyses to support the interpretation of fewer, more expensive, Dacthal analyses. A simple economic analysis demonstrated that more cost effective monitoring could thus be obtained (section 1.4.2).

Similarly, Ben-Jemaa *et al.* (1995) adopted a technique which incorporated spatial variations in addition to determinant correlations. The aim was to improve the prediction and estimation of variable abundances. Their method was applied to Clear Lake, California, USA, to design a network for determining mercury concentrations. The programme design took advantage of the cross correlation between mercury abundance and sediment grain size. Particle size distribution, therefore, was a valuable indicator of pollution.

1.3.2.2 Analytical techniques

Errors in analytical data can arise in the sampling procedure, sample handling and in laboratory analysis itself. To improve the efficiency of monitoring, each of these stages should be considered individually and as a whole. Important factors such as sample preservation and preparation, holding times and quality control, all require attention in the context of the analytical method. Problems such as the oxidation of organic substances and the precipitation of metals may be encountered. This has increasingly led to the integration of sampling and analysis so that the storage of samples is obviated. Three examples show the benefits of this approach:

1. Kuharic *et al.* (1993) describe the use of field portable X-ray fluorescence to determine the spatial distribution of lead concentrations in residential soils, in Leadville, Colorado, USA. Properly calibrated and with quality control, their method produces quantitative data of known quality, albeit, often of lower quality than provided by intensive laboratory analysis. Cole *et al.* (1991) list the advantages of this monitoring strategy as:

- A much greater number of readings can be taken in a given time period;
- The cost of analysis is often much less;
- The data acquisition time is effectively instantaneous, allowing a more flexible monitoring programme; and
- The expense and inconvenience associated with logistical procedures and sample handling are eliminated.

2. A battery powered, micro-controller based FI monitor has been shown to provide a versatile and reliable system for the determination of chemical parameters in natural waters (Andrew *et al.*, 1994). The deployment of pilot

monitoring stations with automatic data acquisition systems in Czechoslovakia has optimized 'monitoring methods, design of monitoring networks, sampling techniques and selection of variables' (Vrba and Pekny, 1991).

3. Barber and Davis (1986) developed a technique to monitor an organic pollution plume without the need to directly sample the ground water. The mapping of the distribution of contaminants, by determining trace concentrations of methane in soil gas at shallow depths, was investigated at a liquid disposal site near Perth, Australia. The persistence of methane in ground water suggested that dissolved CH_4 could be used as an indicator of ground water contamination.

In recent years formalization of regulatory control in the United Kingdom has led to considerable interest in the field of biological monitoring (Lawrence and Williams, 1991). The features in favour of bioassays are that they indicate biological responses to physicochemical changes in water condition, avoiding issues of synergism, additiveness or antagonism. In addition, they can be easy to conduct and cheaper than chemical analysis (Day, 1995; pers.com.). There are, however, several problems with bioassays: they are often not reproducible and difficult to interpret; different test systems with different indicator species yield different numerical results; and they do not identify the toxic component. Some monitoring networks stress the value of bioassays as indicators of ambient conditions, and chemical analyses are used when a pollution event is identified (Lawrence and Williams, 1991).

1.3.2.3 Quality control

Keith *et al.* (1983) wrote a paper to aid in the evaluation of the many options available in designing and conducting analytical measurements and in the intelligent choice of those that will meet the requirements. Such situations would range from semi-quantitative screening analyses to those involving strict quality assurance programmes intended to document the accuracy of data for regulatory enforcement or legal purposes (Fuggle and Rabie, 1992).

Good planning is an essential principle of environmental analysis, avoiding biased, meaningless or unreliable results. Keith *et al.* (1983) considered the decisions which must be followed:

- The level of confidence required regarding the analyte's identity. This is generally directly proportional to the analytical cost (Mar *et al.* 1986).
- The determinants required to be measured, both qualitatively and quantitatively. This decision defines the volume of material sampled, the degree and type of pre-treatment and the method of analysis. Generally, the lower the measurement levels, the higher is the cost.
- The degree of precision and accuracy required. The decision influences the method, the number of replicates and the design of the quality assurance programme. The more rigorous the assurance is, the higher the cost.
- The validity of the method. An appraisal of the chosen method is needed, with either intra- or inter-laboratory validation.
- The quality assurance of the laboratory and the procedures employed to conduct the monitoring programme.

Keith *et al.* (1983) and Sargent and Mackay (1995) elaborate on the methodology of quality assurance and quality control, verification and validation, precision and accuracy and measurements. Such publications are often furnished with a complete set of guidelines that would help improve the overall quality of environmental analytical measurements.

1.3.3 Data interpretation

The final stage of a monitoring programme is to present the information in a form which can be understood and used in water quality management (Figure 1.1). This requires the interpretation of data through statistical, graphical and written means. To utilize the information acquired by the monitoring network the data needs to be effectively communicated from collector to decision maker. This is generally done in the form of reports. The format, frequency and distribution of reports should be related to the programme's objectives. The presentation of information must be concise, accurate and appropriate (Keith *et al.*, 1983). A useful protocol to follow in the interpretation of data was stated by Aristotle in the 4th century BC (cited in Lawrence and Williams, 1991): *'It is the mark of an instructed mind to rest easy with that level of precision which the decision maker requires, and not to try an exactness which is unnecessary for the problem'.*

Prior to producing a report, the information needs to be processed and prepared. In fact, the expense and time of monitoring is negated if data is incorrectly stored, insufficiently analyzed, or if it does not include up-to-date material. The process of data interpretation has been greatly simplified by the advent of computers. Databases, statistics and graphics packages are all used in this procedure. Graphical and tabular visualisation of information increases the impact and can be adapted to effectively target the relevant party (Demayo and Whitlow, 1986).

Water quality indices are used to compare the variables spatially and temporally. An index combines the various indicator parameters to derive a composite value, often using weighting factors, for example the sodium adsorption ratio (SAR). The advantage of an index is that it provides a quantified reference of water quality, understandable by all those concerned. Fuggle and Rabie (1992) give the example of the index used by the CSIR in South Africa (Table 1.1). The disadvantage of an index, however, is the subjectivity related to criterion selection and weighting.

Table 1.1. Components of the South Africa water quality index as at mid-1990. After Fuggle and Rabie, 1992.

Variable		Weight
Total dissolved solids		0.27
E. coli		0.21
Dissolved oxygen		0.16
Chlorophyll - alpha		0.13
pH		0.12
Turbidity		0.11
	TOTAL	1.00

An alternative from of interpretation is modelling, which covers a range of calculation schemes from simple formulae to complex computer programmes. Recently, many workers have utilized this form of evaluation (Loaiciga *et al.*, 1992), particularly with feedback mechanisms to review and improve the original monitoring strategy (Ben-Jemaa *et al.*, 1995; Bernstein and Zalinski, 1983; Freeze *et al.*, 1992; James and Gorelick, 1994; Palmer and MacKenzie, 1985). Statistical methods are regularly used in the evolution of a monitoring network design, as they can identify areas which require modification. Algorithms that are designed to detect change use different statistics from those required by networks to identify simple statistics, *e.g.* means (Mar *et al.*, 1986).

Statistical interpretation of water quality information is an important aspect of water resource management. In the design of monitoring programmes, reliance on subjective professional judgements unaccompanied by objective information has become less acceptable to enforcement agencies and the scientific community (Schweiter and Black, 1985). The use of statistics is now considered necessary in determining the location of sampling sites, the frequency of sampling and the representativeness of individual specimens. Statistical analysis is also used for quality assurance, both in the field and in the laboratory. In addition, the estimation of spatial and temporal averages and trends represents a significant element of the interpretation of data (Gilbert, 1987; Somlyody *et al.*, 1986).

The quality of evaluated data will depend on the integrity of the measurements. An active quality assurance effort can, however, usually guarantee that the results reflect the true state of nature and not some property of sampling or analysis. Management dilemmas do occur where the hydrochemistry cannot be measured precisely, *e.g.* when the levels are below the detection limits and contain analytical errors (Porter, 1986). Water quality managers have not remedied the limit of detection paradox but have developed methods to account for the errors.

Gibbons (1991) advises the U.S.EPA, if they are really interested in controlling errors, that they must replicate sampling and analysis, and they must limit the amount of comparisons per sampling event. (Mar *et al.*, 1986, describe statistical errors in detail). These conclusions were based on Gibbon's comparison of statistical prediction and tolerance limits in the context of ground water monitoring applications. Gibbons (1991) believes that his statistical decision rule, for monitoring network design, incorporates the strengths of both *a priori* prediction and *a posteriori* tolerance limits. James and Gorelick (1994) also used *a priori* statistics. They were incorporated into a monitoring plan used to discover a contaminant plume, cost effectively (Figure 1.4). Freeze *et al.* (1992) also developed a decision framework. Figure 1.5 shows the processes of acquiring information on water quality and assessing the value of the information to determine the continuation of the monitoring exercise. The decision making scheme uses the initial interpretation of the physical environment, followed by the repeated acquisition of more information until it is considered that the monitoring process has gained enough data.

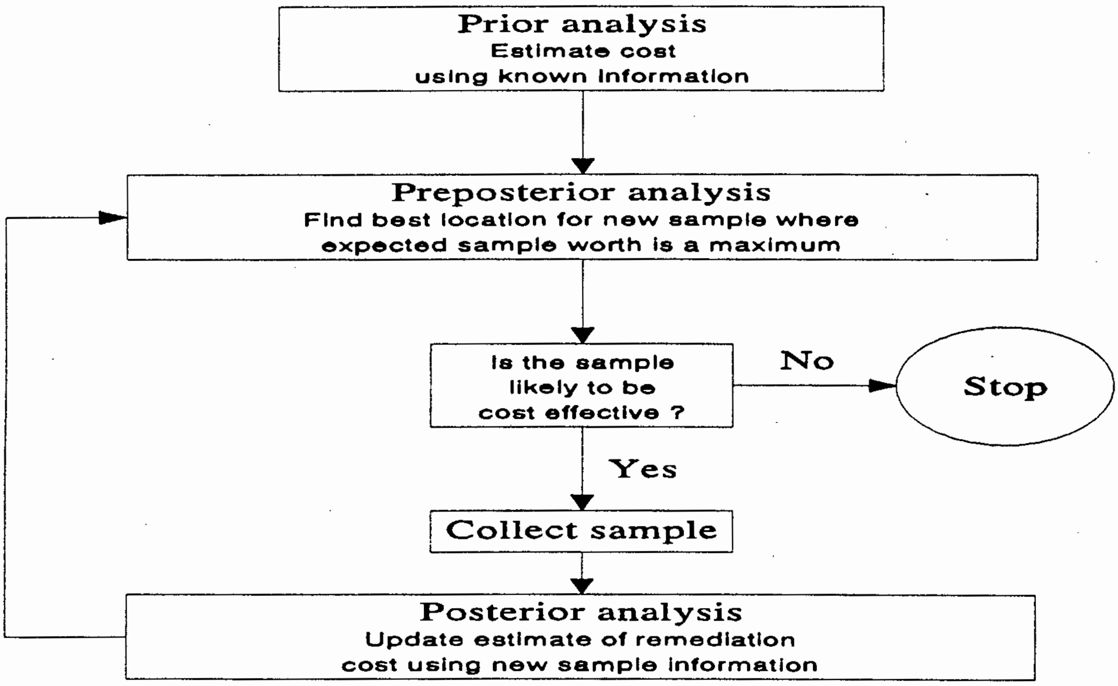


Figure 1.4. An outline of steps in using statistical analysis to search for a contamination plume, (after James and Gorelick, 1994).

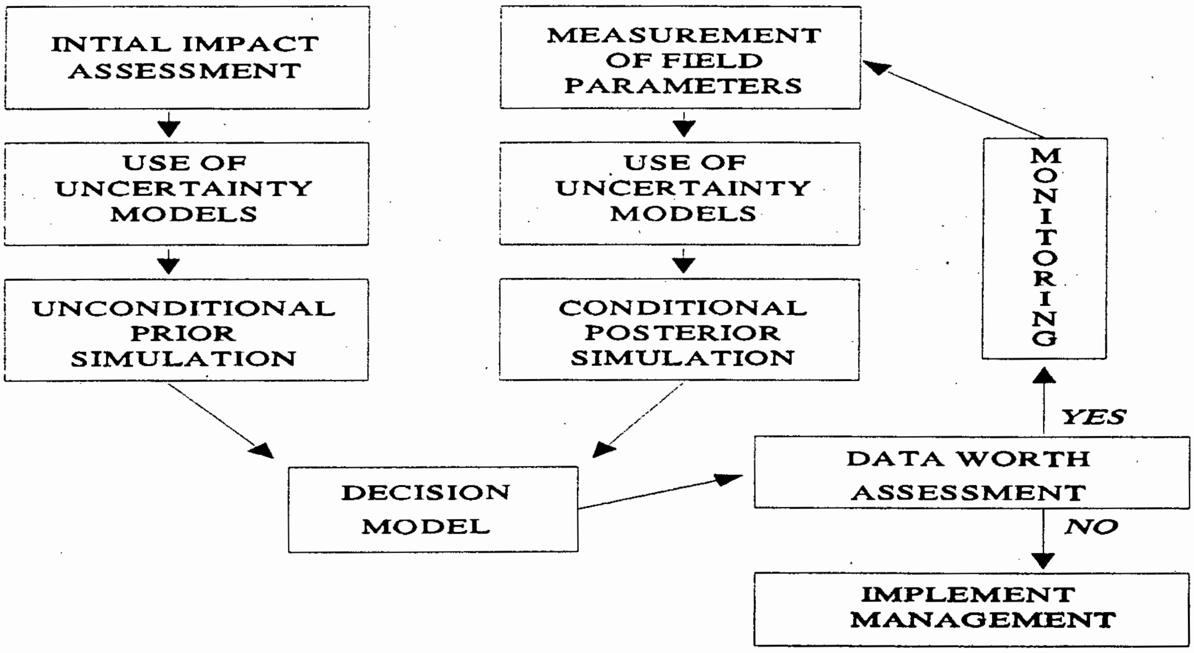


Figure 1.5. A summary of the decision framework, adapted from Freeze *et al.* (1992), who specifically apply this framework to evaluating and modelling pollution in ground water. The concept of assessing the 'worth of data' can be extrapolated to all monitoring strategies.

The development of statistical analyses has increased the objectivity of monitoring strategies, possibly easing the process of network design. The growth in the number of statistical procedures has, however, increased the complexity of monitoring strategies. Networks now need to be designed by integrated teams of environmental scientists and statisticians.

1.4 EFFICIENCY OF MONITORING

1.4.1 Costs and benefits of monitoring

The process of environmental monitoring has many inherent costs, of varying magnitudes. The areas of expenditure occur throughout the monitoring operation from the logistics of a field sampling crew, to the procurement and handling of samples, to the cost of the analytical technique, to the requirements of personnel for evaluation of data. The traditional sampling pathway has many operations within monitoring, all of which cost time and money. The importance of reducing parameter uncertainty by monitoring an environmentally sensitive site, however, cannot be overstated (James and Gorelick, 1994). Conversely, an overly conservative monitoring design may needlessly waste money or lead to an increase in environmental damage. As important as data collection is, the costs can be immense, typically accounting for one of the largest components of the clean up cost of a site (Figure 1.6).

The initial capital costs of developing a monitoring programme to meet the defined objectives can be very high. Steele (1986) suggests the use of statistics, *a priori*, to lower the capital investment required (this is supported by Freeze *et al.*, 1992; Gibbons, 1991; James and Gorelick, 1994 and others). Once the monitoring network is established, costs will decline sharply as the optimal sampling strategy evolves towards a minimal number of analytes providing as much information as possible (Droppo and Jaskot, 1995). One of the principal objectives of a quality assurance programme is to review the procedures and reduce costs.

Freeze *et al.* (1992) provide examples of the economic trade-offs which are possible between the resources assigned to a programme for the initial site investigation, the design of the monitoring network and the actual construction of the facility in question.

Mar *et al.* (1986) state that there are two types of 'cost data' that may be useful in determining the trade-off between costs and increasing information. It is useful to know the cost of acquiring the sample and the cost of analyzing the sample. In addition, it is probably also useful to know the cost of processing the data produced by analyzing the sample.

1.4.2 Attitudes towards efficiency

The optimization of monitoring networks can be improved by considering the network design as a dynamic process. A network is optimized given the current level of knowledge on the monitored parameters (Müller, 1991). The construction of a dynamic monitoring programme, as suggested by Mar *et al.* (1986), contains the following steps:

- Identification of environmental changes of interest.
- Formulation of hypotheses, definition of variables and identification of techniques by which these changes may be studied and quantified.
- The design of a cost effective monitoring programme.
- The integration of the hypothesis by multi-objective ranking of the information acquired from the quality assurance policy. This requires the use of multiple criteria decision analysis, of which further details are provided in chapter 2.

The literature review of James and Gorelick (1994) showed that contributions to the use of statistics in optimizing monitoring networks achieve two goals:

1. The statistical framework evaluates the monetary value of spatially and temporally correlated measurements (*e.g.* Istok *et al.*, 1993; Mar *et al.*, 1986).
2. The optimum number of measurements is estimated so as to provide a means of addressing questions of broad data worth (*e.g.* Palmer and MacKenzie, 1985; Bernstein and Zalinski, 1983).

James and Gorelick (1992) emphasize that it is important to make data collection as cost-effective as possible, the ultimate objective being to minimize the overall cost of the project. Their aim was to find the cheapest combination of monitoring and remediation (Figure 1.6). The sensitivity of a monitored environmental parameter to a change in the number of samples is used to identify an optimum. The idea is to first select each sample based on its value in reducing potential or actual remediation costs, and then to cease monitoring a variable when its cost of acquisition becomes greater than the benefit (Figure 1.4).

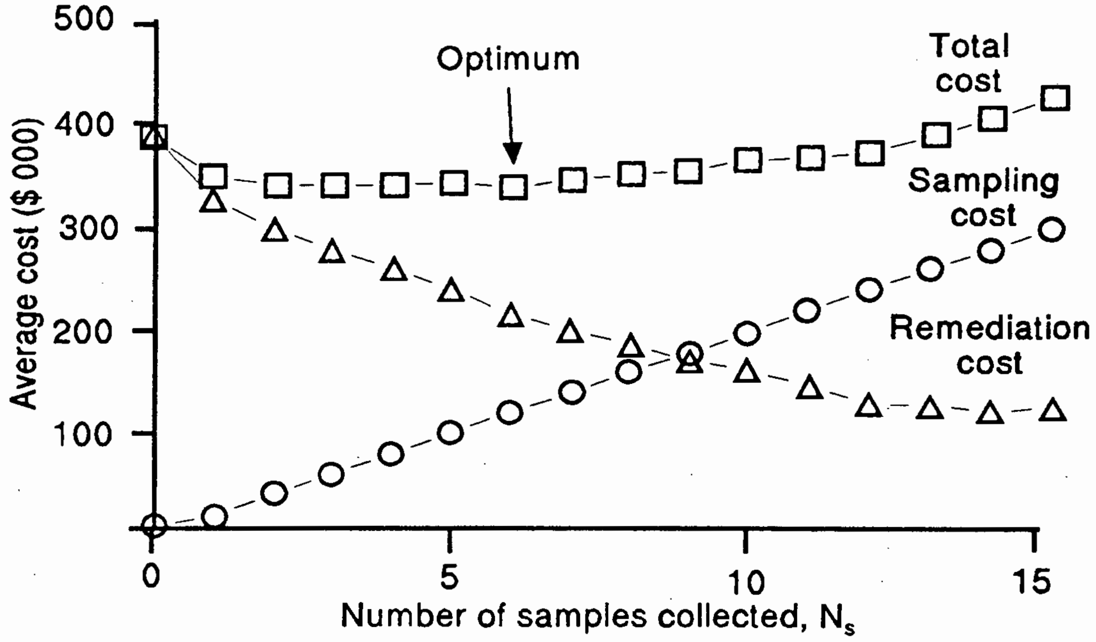


Figure 1.6. **Average total cost, average remediation cost and sampling cost as a function of the number of samples collected in 20 pseudo-operations of ground water monitoring and remediation, (after James and Gorelick, 1994).**

Water quality management decision options can be compared quantitatively by using functions such as that described by Freeze *et al.* (1992). This function (Equation 1.2) is simplified by assuming that if a pollution event occurs it will happen relatively quickly, so removing time considerations. The aggregate benefit, B, is offset by the costs, C, and the risks which are calculated as the probability product of a pollution event occurring plus a failure to detect the event by the monitoring facility, P_f, and the cost associated with the failure and the remediation, C_f.

$$\textit{Net benefit} = B - C - P_f \,.\, C_f$$

Equation 1.2.

In effect the function represents the net benefit as the gross benefit less the fixed cost, less the accidental cost. Subjectivity may occur in the use of Equation 1.2 due to the intangible nature of the parameters, for example pricing environmental criteria. The benefits and hypothetical costs associated with un-monitored pollution are identified for each of the decision options and compared. Freeze *et al.* (1992) illustrate the use of search theory and how Bayesian updating can be applied to provide a 'stopping rule' for the collection of additional data (Figure 1.5). They stress that their aim is not to design monitoring networks that minimize statistical uncertainty, rather, programmes should minimize economic regret with respect to management decisions.

Several workers approach optimization of monitoring strategies by estimating statistical uncertainty. For example, Istok *et al.* (1993) used multivariate statistics to assess the relative benefit of additional sampling. They expressed the function as simply R / C_r. Where R is the reduction in maximum estimation variance obtained by measuring one variable (the concentration of Dacthal) or the other variable (the concentration of nitrate), and C_r is the Dacthal:nitrate analysis cost ratio. In their study into using nitrate as an indicator of herbicide contamination, they conclude that at cost ratios equal to or greater than 5:1 *i.e.* Dacthal analysis is five times more expensive than nitrate analysis, the additional five nitrate samples per monitoring event, required to reduce the estimation of variance for Dacthal, are justified (Figure 1.7). Istok *et al.* (1993) use this covariance to locate the pollution plume by kriging procedures. Other authors also demonstrate optimization by establishing correlations (for example Ben-Jemaa *et al.*, 1994, Ben-Jemaa *et al.*, 1995).

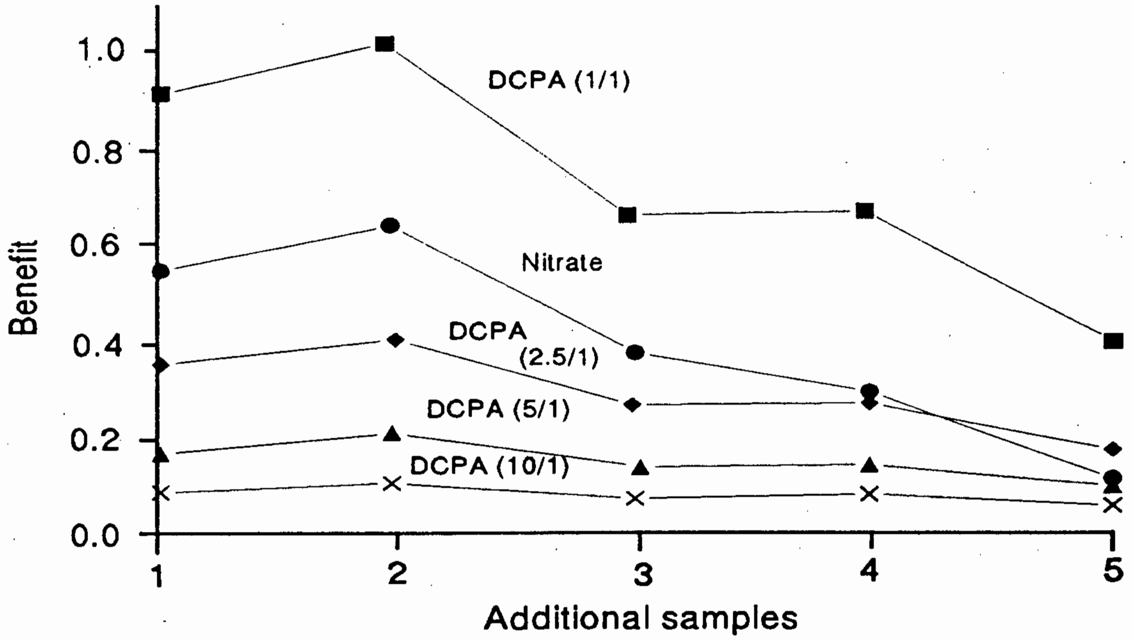


Figure 1.7. **Benefit of additional Dacthal and nitrate samples for several Dacthal : nitrate measurement cost ratios. Istok *et al.* (1993).**

1.5 GENERAL DISCUSSION AND CONCLUSIONS

Monitoring is crucial to environmental management but must develop an economic accountability to retain its integrity. Monitoring operations are unique strategies to sample, analyze and interpret, and are outlined after an initial impact assessment. Water quality monitoring principally applies to fluvial and ground water and requires consideration of the spatial scope, temporal dimensions, the level of detail of the operation, the overall aim and objectives, physiographic and anthropogenic factors, statistical uncertainties, resources and applicability of methods. The monitoring network design is completed by an appropriate team who must outline protocols and ensure expectations will be met. Many monitoring procedures are outlined in guidebooks and statutory documents.

The location of the sampling site is crucial and will vary depending on the physical factors in the monitoring region, the pollution vulnerability, the nature of pollution, the type of source, *etc*. In addition, the objective of monitoring will influence the location, whether it is to investigate spatial trends or resolve conflicts. Geostatistical methods are used to optimize the location of sample sites.

The sampling frequency of the operation can be adjusted which has a strong influence on the total cost. Monitoring is required to study seasonality and trends over time which can be accomplished by two tier or double sampling strategies.

The level of detail can be altered by choosing different analytes, analytical methods and interpretation procedures. The selection of these criteria is helped by establishing analyte covariances. The representativeness of the sample and the resulting data must be maintained which is done with a quality assurance programme. Recent work has led to the development of alternative strategies such as flow injection monitoring and bioassays. Presenting information in a form useable by water quality management is highly important. This involves the selection of graphical, statistical and written techniques. Statutory requirements can include reporting styles.

Capital costs of a monitoring operation can be high but optimization techniques will reduce running costs. There are different attitudes to 'data worth', for example monetary value, statistical uncertainty and benefit to remediation. All these approaches rely on adopting a dynamic monitoring network.

2. A DESCRIPTION OF THE STUDY AREA AND AN ANALYSIS OF FACTORS INFLUENCING THE PHYSICAL DESIGN OF THE MONITORING OPERATION

2.1 INTRODUCTION

The industrial area under study is situated in the upper reaches of the Vaal dam catchment in Mpumalanga (formerly the Eastern Transvaal) on the South African Highveld (Figure 2.1). A monitoring network has been installed to assess the impact of the industrial operation. The environmental evaluation being carried out is derived from a methodology prescribed by the United States Environmental Protection Agency (U.S.EPA) with additions to include surface and effluent monitoring (Müller, 1991). The overall objective of monitoring is to supply water quality information for environmental management.

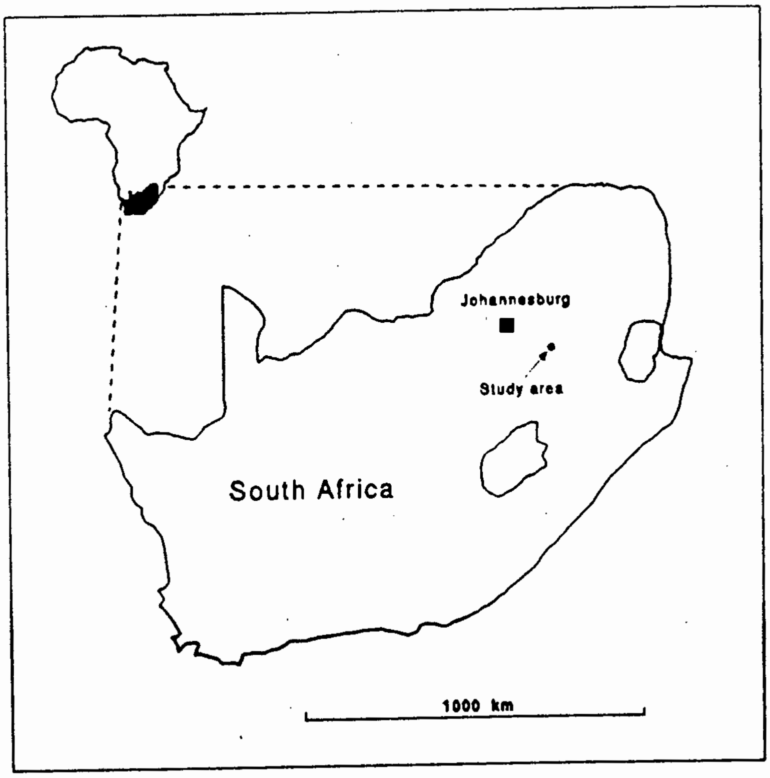


Figure 2.1. **Map of South Africa locating the study area.**

The design of the monitoring network is flexible and dynamic in two aspects (Müller, 1991). Firstly, the monitoring operation is divided into sequential programmes, facilitating upgrading and updating. Secondly, site specific details can be added to the database. The monitoring exercise is part of a commitment 'to act responsibly and with due regard to the effects of the company's operations and products on the environment', as stated in the company's environmental policy. The monitoring system is computerized to provide continuous accessible information on the environment around the plant.

2.2 NATURAL FEATURES OF THE STUDY AREA

The purpose of this section is to examine the physiographic situation around the industrial area. The lay-out of the industrial plant, the waste operations, the neighbouring town and both the surface and ground water monitoring sites in relation to natural features is shown in Figures 2.2 and 2.3.

2.2.1 Climate

The climate may be described as sub-humid with summer rainfall. Continuous monthly rainfall data was obtained from the Bethal dam weather station, covering the period 1964 to 1988 (CCWR, 1995; Appendix I). Bethal dam (26°27'S, 29°28'E) lies about 25 km from the study area and is 1636 m above sea level.

The mean monthly maximum temperature is 25.4°C in January and 16.4°C in June, while the mean monthly minimum ranges from 13.8°C in January to 8.0°C in June. The mean monthly evaporation ranges from 164.5 mm in December to 60.8 mm in June. The water budget shows a net loss of water by evapotranspiration. The wettest season is from November through December to January with mean monthly rainfall at 129.6, 109.5 and 148.3 mm, respectively. The least rain falls in June and July with an average of 5.7 and 5.5 mm per month, respectively. The mean annual precipitation is recorded at 703.4 mm (CCWR, 1995). All relevant climatic data are given in Appendix I.

2.2.2 Surface hydrology

In order to understand the dynamics of surface water pollution within a selected monitoring area it is necessary to have a fundamental appreciation of the hydrological environment. The area has a dendritic drainage pattern with small streams or spruits (Figure 2.3a). The industrial plant is near a major watershed and therefore the catchments of the streams are small. The fluvial water response time is quick with a short lag time after precipitation and a rapid decline in the subsequent spate (Ginster, 1995; pers.com.).

2.2.3 Topography

In order to delineate surface drainage routes and to predict pollution spill traces, runoff and fluvial water flow directions need to be determined. The hydrological assessment of this included flow vectors, *i.e.* the directions and the absolute velocities, as an overlay map (Muller, 1991).

The area being monitored has an undulating landscape. The ridges around the plant reach an elevation of about 1640 m, while the perimeter exit point of the main stream (the lowest point) is ~ 1570 m (Geological Survey, 1971). This has implications for the ground water conditions as the water table is a subdued reflection of topography.

2.2.4 Geology

The geological succession in the industrial area forms part of the Ecca series of the Karoo sequence, with formations of Dwyka, Pietermaritzburg and Vryheid present (Stratten, 1986). These formations consist of interbedded shale, sandstone, arkose, clays, conglomerates, marl and sandy limestone. Coal exploitation occurs in the area with extraction of two seams of the five-seam Vryheid formation. The sedimentary rocks of the Karoo sequence have been intruded by a series of post-Karoo coarse-grained dolerite sills and dykes. Dolerite caps are the salient features of the topography (Geological Survey, 1971). The post-Karoo and Karoo deposits are either sub-horizontal or gently dipping to the south west.

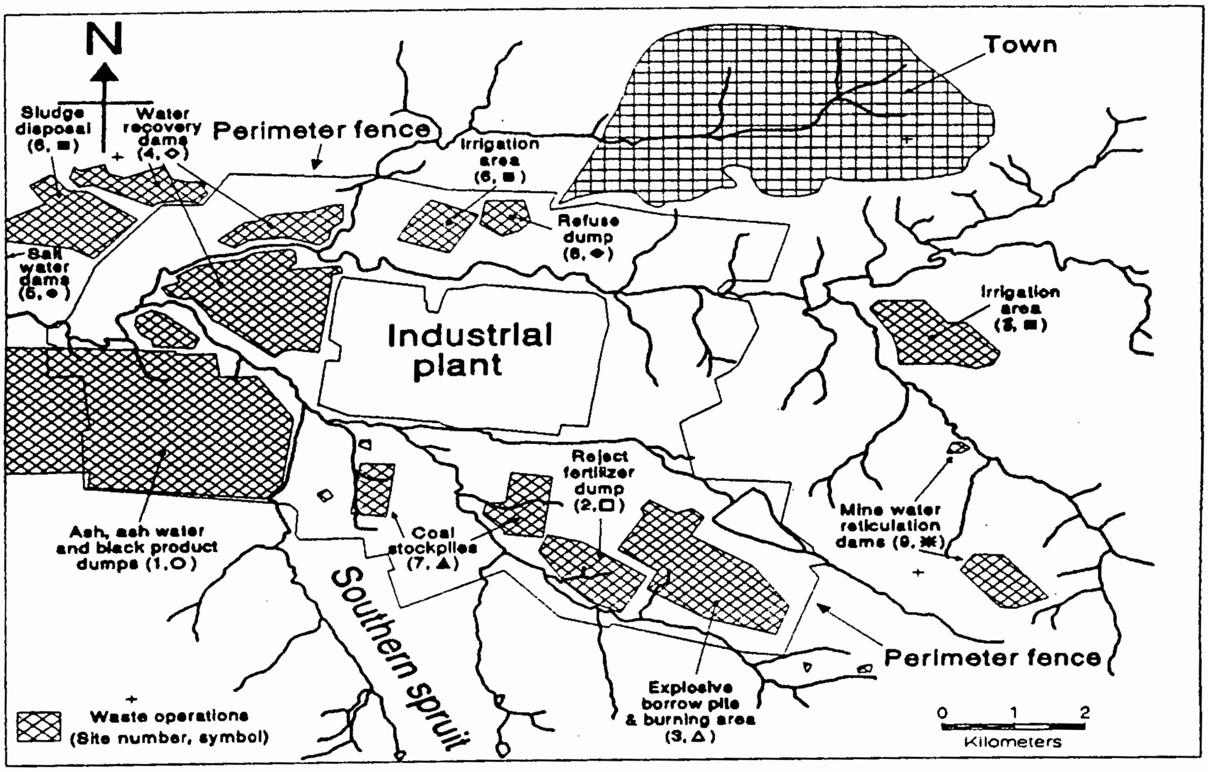


Figure 2.2a. Overlay map of the monitoring area outlining the nine waste operations. This Figure is repeated in Appendix IX and can be folded out for continued reference.

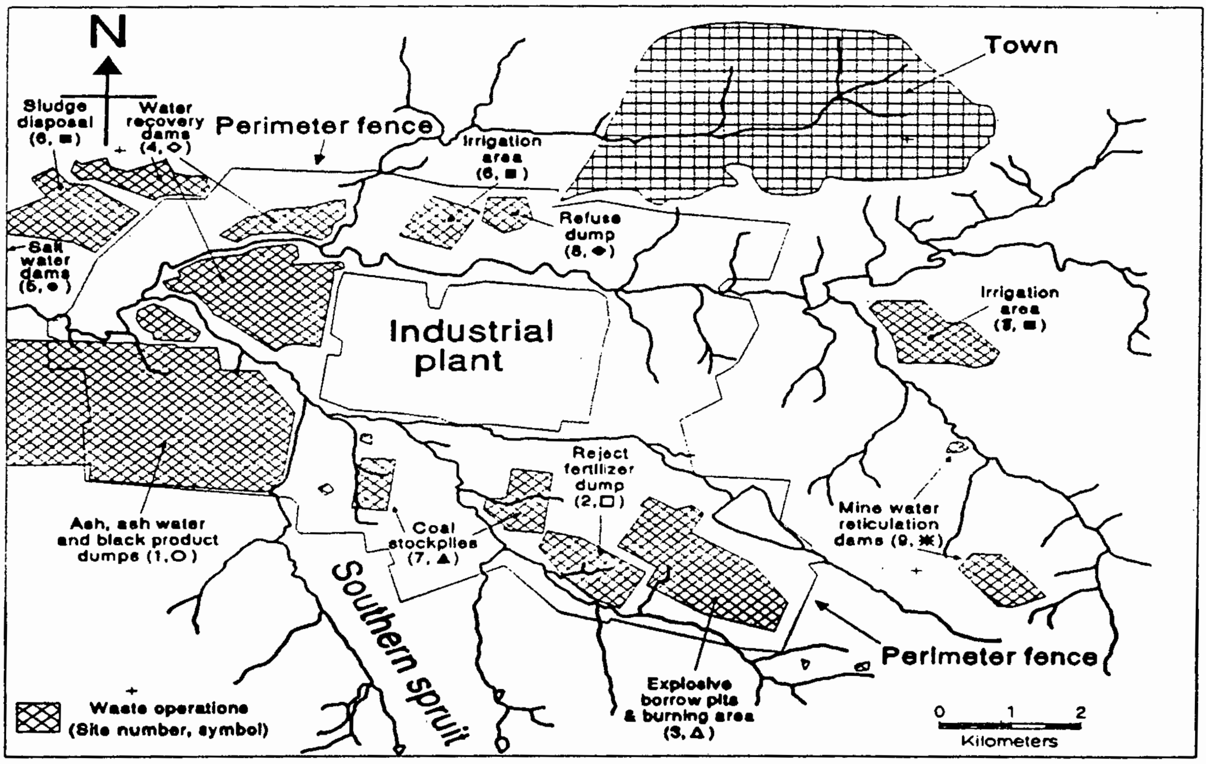


Figure 2.2b. The map is repeated as an overlay of the monitoring area outlining the nine waste operations.

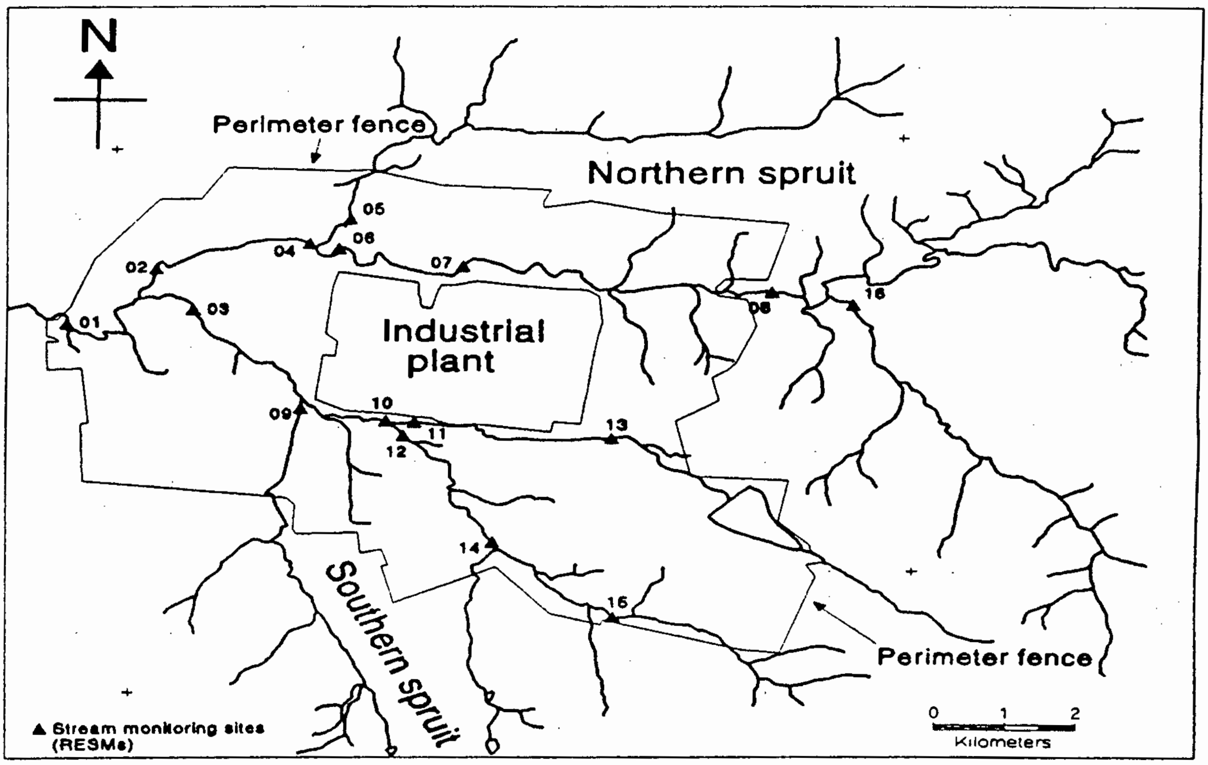


Figure 2.3a. Map of the monitoring area showing the hydrological pattern and the surface water monitoring locations (RESMs). Fold out copy is in Appendix IX.

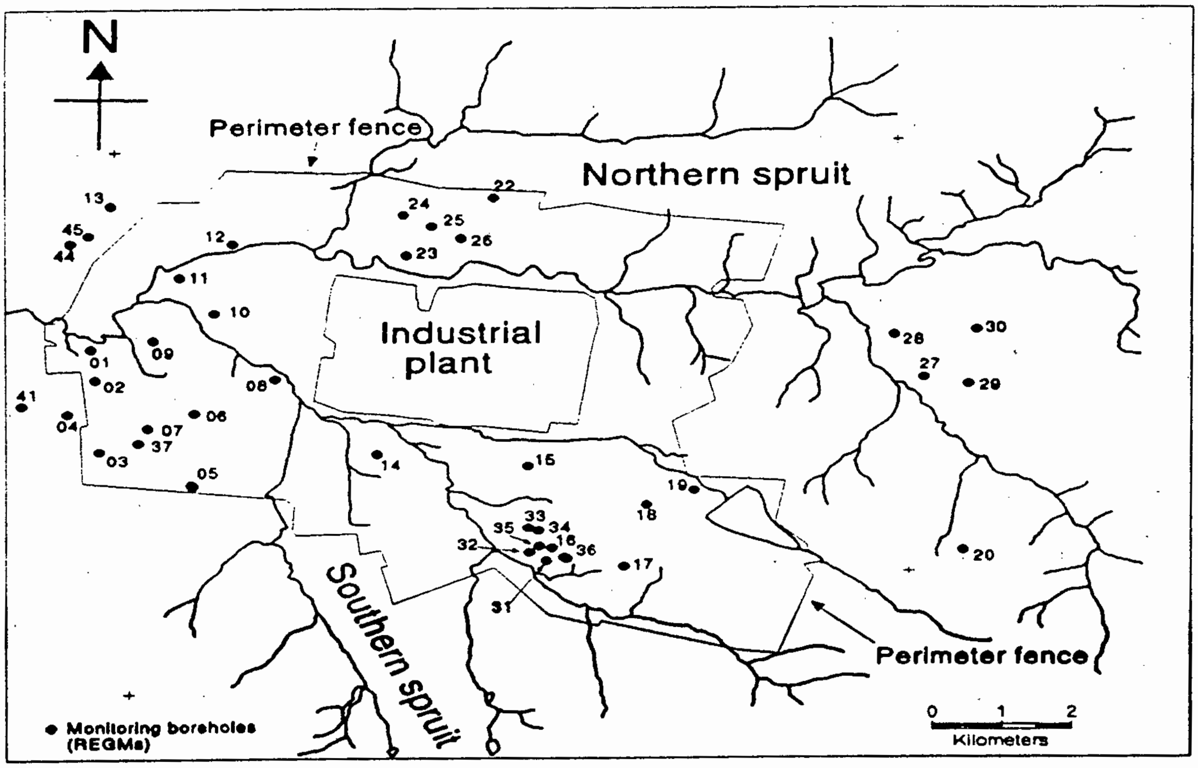


Figure 2.3b. Map of the monitoring area showing the sites of the waste operations the borehole monitoring locations (REGMs). Fold out copy is in Appendix IX.

Although the Karoo sequence has some sandstone beds with high porosity, the transmissivities are generally low. Most of the water resources are from secondary fissures (Hodgson, 1995; pers.com.). It is believed that some pre-Karoo faults have been re-activated to cause displacements, otherwise, there is little structural disturbance of the Karoo beds. The Karoo sediments are underlain by quartzite and shales with contorted and ferruginous beds of the Witwatersrand system. In addition, there is a basement of metamorphosed lava and gneiss (Stratten, 1986).

2.2.5 Soils

The lithology throughout the area, with exception of the higher eastern region, is capped by clay of varying thickness between 1 m and 13 m (Müller, 1991). Other quaternary deposits of unconsolidated overburden are also encountered. The recorded depth of saprolitic material is from 7 m to 30 m, with an average of 17 m below the surface. This large variation in depth of weathering is important when considering pollution migration into the ground. Hodgson (1995, pers.com.) estimated the effective porosity of the weathered zone at 15 % and the hydraulic conductivity at 0.01 $m.d^{-1}$.

The soils of the area are described as one or more vertic, melanic or red structured diagnostic horizons (SIRI, 1976). This reflects the parent materials with dolerite being the major influence in vertic horizons leading to the development of smectitic soils. The melanic and red structured soils have a greater abundance of kaolinite relative to smectite. The origin of these soil types is generally the Karoo Ecca series leading to a more loamy texture but still with ped formation through clay and climatic influences (Fey, 1995; pers.com.). Clearly, the pedosphere is not a direct reflection of the lithology as colluvial mixing will have occurred.

2.2.6 Hydrogeology

An investigation into the hydrochemistry of an aquifer for monitoring is different from an appraisal of ground water as a resource. A hydrogeological assessment is not an ultimate goal of a monitoring strategy but a component used to facilitate the design and implementation of a ground water quality monitoring network.

Geological and hydrogeological detail was obtained during the drilling of 45 boreholes (Figure 2.3b), in addition to regional information from maps, surveys and reports. Experience and the drilling programme have demonstrated that the primary hydraulic conductivity of the Karoo sediments is poor (Müller, 1991). It can be assumed that the pre-Karoo formations are aquicludes. Weathering and fracturing of the lithology will, however, have increased the storage capacity of the formations. The porosity of the sediments is ~ 10 %. However, this has no bearing on the flow rate of pollution (Hodgson, 1995; pers.com.).

The clay overburden will undoubtedly retard the vertical flow of water. Clays will also play an important role in the limiting migration of pollutants. As the confining dolerite intrusions are only semi-continuous over the Karoo series, the hydraulic condition of the sediments could be described as semi-confined secondary aquifers.

The direction of pollution flow will probably be towards the streams but will depend on the relative hydraulic pressures of parts of the aquifer. These pressures are not known but, in the simplest case, greater pressures would occur in the deeper part of the aquifer compared to the weathered zone (Hodgson, 1995; pers.com.). The majority of pollution migration will probably occur in the top, weathered part of the aquifer, particularly in fissures or preferred flow paths. Dilution from rainfall will take place at an estimated 3 % (21 mm.yr^{-1}) of the annual precipitation.

2.3 CURRENT ACTIVITIES WHICH AFFECT WATER QUALITY

2.3.1 Major industrial pollution sources

Effluents and solid waste products from various processes in the industrial plant are disposed of in the nine types of waste site (Figure 2.2). Samples taken from these sites are encoded PPSM (potential pollution source monitoring) and have been analyzed. The network design established surface and ground water monitoring localities at as many potential pollution sources as was possible, given available time and funds for the initial risk assessment by Müller (1991). The potential pollution sources are summarized in Table 2.1.

Additional information was gained during a visit to the monitoring area. In the cases where waste operations consisted of solid wastes, laboratory analyses of leachate were tested in order to obtain a chemical fingerprint. Some compositions, however, had to be inferred due to low availability of samples.

Table 2.1. Identification and classification of potential pollution sources (the waste operations) around the industrial plant. Table 2.1 is divided into four sections (2.1a to 2.1d), each pertaining to a different class of potential pollutant.

Table 2.1a. Liquid waste effluents.

CATEGORY	DESCRIPTION	PPSM site	Area Code
The liquid wastes include all liquid forms which are disposed of by containment and evaporation, recycling and recovery or sludge disposal and irrigation.			
Fertilizer plant process water dams.	Effluents originate from the plant as backwash water, scrubber water and spillages. They are highly saline with suspendoids. Overspill is a potential pollution mechanism although not common. Ground water contamination is severe but will hopefully be reduced by mitigating measures. Large ranges of some water quality variables are due to modification by natural processes active in the unsaturated zone. Seepage of solutes into the ground water is a reality and efforts to contain the leachate have been made.	11, 12, 13 & 14.	2 □
Water recovery diversion dams.	These contain effluent solutions enriched in inorganic and organic constituents. Pollution mechanisms are comparable to those of the fertilizer dams.	15, 16, 17, 18, 19, 20, 21, 22, 23 & 24.	4 ◇
Salt water dams.	There are two saline water dams. Although unlikely to spill into the surface water, their contents may percolate into the ground water. Leakages are suspected of causing a noticeable impact on the ground water. Obviously these dams have a high salinity.	25 & 26.	5 ●

Clear effluent dams / evaporation ponds.	These contain seepage originating from the course and fine ash dams, together with ash transport water. Such fluid in these effluent dams may become leachate.	27, 28 & 29.	1 ○
Mine water dams.	These dams store water pumped from underground mines. The dams are linked through an extensive reticulation system. Seepage is evident at some dams and probably occurs at others. The averages are listed but some of these samples may be diluted by surface water runoff.	30, 31, 32, 33, 34, 35, 36, 37, 38 & 39.	9 ★
Irrigation schemes.	Some water has a beneficial quality for irrigation of grass and hence is a viable method for disposal. Surface runoff at both sites is minimized through effective irrigation scheduling, but seepage into the ground water system remains a potential pollution mechanism.		6 ■
Vehicle washing area.	Waste washing water flows into an earth dam which has obnoxious odours emanating from it. Seepage occurs from this earthen dam.	03.	3 △
Sewage maturation pond.	The sewage works are currently out of commission and thus not actively creating effluent. The water in this area is of a poor quality, although new effluent is not being generated.	40.	6 □

Table 2.1 was compiled from selected information from Ginster (1995 and pers.com.) and Müller (1991), and notes taken during a site visit.

Table 2.1b. Liquid / slurry waste.

<table>
<tr><th>CATEGORY</th><th>DESCRIPTION</th><th>PPSM site</th><th>Area Code</th></tr>
<tr><td colspan="4">This category of waste is mixed and transported as a slurry to be disposed of in containment dams. It is considered that these wastes have a high pollution potential. The pollution mechanisms will include both surface runoff caused by spillages, ruptured pipes or overflows from dams and seepage of leachate into, through and from the ground water system.</td></tr>
<tr><td>Fine ash dams.</td><td>Spillages may occur including pipe rupturing, in addition to leakage from the dams. Impacts on the ground water quality are probably the largest in the area, however, contamination is generally localised. New fine ash handling areas are of a superior design.</td><td></td><td>1
O</td></tr>
<tr><td>Fine coal storage dams.</td><td>Surplus fine coal is piped to dams and stored under ash water. Seepage from the dams is a reality, which will migrate into the ground water system. The chemical composition of the water may be modified by the fine coal itself.</td><td>10.</td><td>1
O</td></tr>
</table>

Table 2.1c. Waste black products.

<table>
<tr><th>CATEGORY</th><th>DESCRIPTION</th><th>PPSM site</th><th>Area Code</th></tr>
<tr><td colspan="4">The black by-products are placed in a separate category as they are a variety of solids and highly viscous material. Seepage is dependent on the solubility of the individual components. The dams are located in the centre of the coarse ash dump, fine ash dams and fine coal storage dams. This will have some bearing on the nature of pollutants produced. There is an extreme diversity of products made in the industrial plant.</td></tr>
<tr><td>Pitch dams.</td><td>Filled with residue products of the tar distillation unit, the bulk of this black product is residual material and is relatively immobile. Heavy transport is used to carry the tar and spillages can easily be contained. The main mechanism for water pollution is from the few mobile fractions.</td><td></td><td>1
O</td></tr>
<tr><td>Tar dams.</td><td>The main four constituents disposed of are tar sludge, interphase sulphur, synthol gunk and catalyst overflow. Similarly, the main mechanism for water pollution is leachate migration.</td><td></td><td>1
O</td></tr>
<tr><td>Oil dams.</td><td>Waste oils, oily water mixtures and sludge from various sources are present. There is possibly leakage from the dam.</td><td></td><td>1
O</td></tr>
</table>

Table 2.1d. Dry solid waste / stockpiles.

CATEGORY	DESCRIPTION	PPSM site	Area Code
This type of material is the final disposal stage of a dry deposit. The type of pollution these solids could potentially cause is through precipitation generated leachate containing dissolved and suspended material. Such leachate might migrate into the ground water or disperse in the surface water.			
Fertilizer reject dump.	Reservoirs of waste where surface runoff and seepage are likely to occur. Due to the high solubility of the granulated fertilizer, mobilization of the chemical components into aquatic environments is a real possibility.		2 □
Explosives burning area.	Salts and ash left are after burning. Ash residue is washed into the borrow pits and diluted by precipitation and standing water. The hydrochemistry of the pit is summarized.	02.	3 △
Explosives borrow pits.	The pits are entirely or partially filled with a variety of solid wastes, including reject coal, builders rubbish, steel and ash. The majority of the pits have standing water which could produce pollutant migration. Averages of water monitored in the variety of borrows in the area are listed.	04, 05, 06, 07, 08 & 09.	3 △
Domestic type refuse.	Leachate seepage is potentially a major contributor towards water pollution. Due to the extreme diversity of waste material being dumped it is impossible to obtain a single representative chemical image, or even a realistic range. For this reason this site is not presently included in source monitoring.		8 ◆
Coal stockpile.	Coal is stored before it is fed by conveyor belts into the plant. The fine coal dust will pollute surface runoff and may eventuate in the fluvial system. In addition, pyrite decomposition will lead to acidified drainage. Due to the inherent transient nature of pollution formation, it is not easy to simulate the leaching process in a coal stockpile. No hydrochemistry has been obtained.		7 ▲
Coarse ash dumps.	Ash is deposited dry but precipitation on the dump will generate leachate. With parallels to the coal stockpiles, pollutants are generated as they percolate through the dump. The soluble chemical constituents will be derived from the leachable solid components of the coarse ash dump.		1 ○

2.3.2 Other pollution sources

Pollution in this part of the Vaal dam catchment is often almost entirely attributed to the industrial operations present. Other human activities, however, also have an effect.

The region is well known for its primary industry. There are coal and gold mines in the vicinity of the industrial plant. In addition, local farming may have an impact on water quality. Residential areas near to the area monitored include the town to the north (Figure 2.2), work hostels within the perimeter and an informal settlement. The individual and composite effects of all these potential pollution sources is unknown. Other criteria also need to be noted, such as the effect of atmospheric pollution, some of which may be derived from remote sources. The potential impact these source have on the environment are illustrated in Figure 1.3.

2.4 CRITERIA FOR ESTABLISHING THE MONITORING NETWORK

The onus of environmental management is predominantly on the industrial company. A policy of self regulation implies that most environmental actions implemented will entail more than the minimum statutory requirements. The selection of the monitoring criteria were largely based on company policy with regard to environmental management objectives, subject to administrative, physiographic, legal and resource considerations (Müller, 1991).

2.4.1 Management

The company's responsibilities for water quality management resides with the Environmental Management Unit (EMU). The legal liabilities, however, are carried by the relevant production divisions of the corporation (Müller, 1991). The many potential pollution waste streams increase the complexity of the operation. In addition, some pollution sources may be diffuse in nature and the impact on water quality may be detected in most of the localities monitored.

2.4.2 Physiographic

In order to be able to isolate the contribution of the plant to potential water quality degradation from all the sources, a large area (~ 140 km^2) was designated for monitoring.

The physiographic conditions are described in section 2.2. During the design of the monitoring network, natural features were considered in relation to potential pollution sources. This is evident by comparing Figures 2.2 and 2.3.

2.4.3 Legislative

Any industry that could potentially degrade water quality should implement meaningful and effective water quality management (DWAF, 1993c). Management requires qualitative and quantitative information on water resource application and utilization both within the industrial plant and downstream. The usage of water external to the plant will strongly influence waste load allocation by the Department of Water Affairs and Forestry (DWAF) as far as future effluent discharges are concerned. Based on inquiries carried out by Müller (1991) the following types of surface water utilization were identified in the area of study: domestic, agricultural (both stock watering and irrigation), and industrial use.

DWAF are responsible for maintaining the quality of South African waters. Much of this is done with permits. Statutory obligations must be complied with in the design of the monitoring network. Hence, legislation has a strong influence on the evolution of a monitoring strategy and in the construction of waste facilities. Most of the requirements are laid out in government documents (DWAF 1994a; b; c). The statutory requirements are still in an interim stage of development and therefore the strategy must be dynamic to adjust to changes in legislation.

The original permit compliance of the monitoring operation with DWAF standards is not currently valid. Due to an interim change in DWAF requirements, the monitoring operation is not bound to detailed regulatory specifications (du Toit, 1995; pers.com.). The onus of monitoring rests with the EMU and their rationale is to follow, where feasible, the previous DWAF guidelines. For this reason it is important to 'spell out' the water quality compliance requirements of 1994.

- The overall compliance surface water monitoring locality is RESM01 (Appendix V), the fluvial water perimeter exit point (Figure 2.3a).
- Continuous in-stream monitoring of EC at RESM01 is required. Grab samples should be collected at fortnightly intervals.

- The compulsory analytes are: pH, EC, TDS, Suspended solids, SO_4, Cl, F, B, COD, free and saline ammonia as N, Nitrate, P, Phenols, Total hardness, Na, Mg, Ca, Hg, Fe, Mn and Al. The last three should be analyzed as total acid and dissolved fractions. Interestingly, no HCO_3^- or alkalinity analysis is required.
- Specific to the industrial area under study and the monitoring operation some guideline levels are listed in Table 2.2. These levels are based on the water quality in the area between 1991 and 1993. Analytes not listed in Table 2.2 means the interim water quality variable objective has not been set, however data will be required by DWAF to set values for the long term. Some guidelines based on environmental impacts of the chemical components are listed in Table 2.3. The guidelines based on toxicity and utilization of the water are considered to be a preferable goal for water quality management.

Table 2.2 Compliance values estimated by DWAF from monitoring data from October 1991 to August 1993.

Analytes	Units for reporting	50 Percentile X_{50}	95 Percentile X_{95}	Permissible maximum X_{max}
TDS	$mg.dm^{-3}$	460	540	610
SO_4	$mg.dm^{-3}$	85	102	120
Na	$mg.dm^{-3}$	64	80	92
Cl	$mg.dm^{-3}$	55	69	80
F	$mg.dm^{-3}$	0.87	1.28	1.64
EC	$mS.m^{-1}$	70	80	92
SAR		2.2	2.7	3.1

X is the analyte mean for that percentile of the data distribution.

The procedures outlined by DWAF used to calculate the analyte requirements (Table 2.2; X_{50}, X_{95} and X_{max}) are applicable to normally distributed data sets. Contrary to the expectations of DWAF the data set for RESM01 has a skewed distribution (as will be shown in chapter 3, Figure 3.2 and Table 3.1b) and therefore the validity of these methods of reporting may be to question. There are further requirements from DWAF:

- With regard to irrigation water, grab samples should be taken once a week and analyzed for a broad spectrum of variables. Soil and plant conditions in these areas must also be monitored according to clear specifications.

Table 2.3. South African water quality guidelines (DWAF, 1993a to 1993d).

Analyte	General Standard	Domestic use	Industrial use (Petrochem.Ind)	Agricultural use (Livestock)
Alkalinity	~	~	0 - 100	~
Al	~	0 - 0.15	~	0 - 5
NH_4	10	~	~	~
B	1.0	~	~	0 - 5
Ca	~	~	~	0 - 1000
Cd	0.5	~	~	0 - 0.1
COD	75	~	0 - 10	~
Cl	~	250 #	0 - 20	0 - 1500
Cr ^{VII}	0.05	0.05 #	~	0 - 1
Co	~	~	~	0 - 1
Cu	1.0	1.0 #	~	0 - 0.5
CN	0.5	~	~	~
DOC	~	0 - 5	~	~
EC	~	0 - 70	10 - 70	0 - 154
F	1.0	0 - 1.0	~	0 - 2
Fe	~	0 - 0.1	0.0 - 0.5	0 - 10
Pb	0.1	0.05 #	~	0 - 0.1
Mg	~	~	~	0 - 500
Mn	0.4	0 - 0.05	0.0 - 0.2	0 - 10
Hg	0.02	0 - 0.005	~	0 - 0.002
Mo	~	0 - 6	~	0.0 - 0.01
Ni	~	~	~	0 - 1
NO_3	~	44 #	~	0 - 100
pH	5.5 - 9.5	6.0 - 9.0	7.5 - 8.5	~
Phenols	0.1	~	~	~
Salinity	~	~	~	0 - 1000
Na	90 + intake value	200 #	~	0 - 2000
SO_4	~	400 #	0 - 100	0 - 1000
TOC	~	~	~	~
V	~	~	~	0 - 0.1
Zn	5.0	5.0 #	~	0 - 20

General standards are from the DWAF requirements to the EMU but are unspecific and not qualified. Additional guidelines were obtained from WHO (1984, Tables 2 and 4) denoted by #. A tilder (~) indicates no guideline could be found. Units are mg.l^{-1}, except for EC (units: mS.m^{-1}) and pH.

- Ground water samples must be taken every 3 months and analyzed for most of the same variables as surface water.
- Raw surface water data must be submitted to DWAF every month accompanied by date, time and location of samples. Quality and quantity of effluent discharges also need to be included.
- A 'compliance assessment' report on the water quality at RESM01 should be conducted quarterly and submitted to DWAF. It should consider the in-stream monitoring of EC and the grab samples. Samples studied should be

from at least the pervious six months up to the last year. Concentration values need to be calculated for the mean (X_{mean}), the median (X_{50}), the 95 percentile (X_{95}) and the maximum (X_{max}).

- Every 6 months a report containing analysis of trends in river water quality is required by DWAF. Ground water quality data and trends are also requested on a biennial basis, in addition to information on the irrigation practice.

2.4.4 Resource allocation

The features of greatest importance were considered to be the water resident in the catchment and the sensitivity of the water. In addition, the company's policy with regard to environmental impact management and self regulation were taken into consideration, as well as the availability of funds for constructing the network (Müller, 1991). A step-wise implementation method was adapted for commissioning the current water quality monitoring and management system in order to facilitate a meaningful compromise between policies, physical features and funds. It is here that the flexible modular design of the strategy, together with the dynamic environmental management policy, will ensure optimization of the implemented system. During the initial construction of the network a U.S.EPA guideline (LeGrand and Brown, 1990) was used to allocate resources (time, money, effort, *etc.*) to the nine waste disposal operations. This allocation is reviewed in section 2.7.

2.5 A DESCRIPTION OF THE MONITORING PROCEDURES

2.5.1 Sampling strategy

At an early stage of this study, a site visit was conducted to make a first-hand assessment of the monitoring operation. The plant has an extensive monitoring programme that has been implemented as part of the environmental management schedule to limit the amount of pollution generated in the area and consists of:

- 47 boreholes, sampled quarterly. However, some are now collapsed or are covered. These borehole sites are called REGMs ('receiving environmental ground water monitoring', Figure 2.3b). Examples of data sets are listed in Appendix V, Table V.3.

- 22 surface water monitoring locations, called RESMs ('receiving environmental surface water monitoring', Figure 2.3a). Only about 15 of these are accessible and can be monitored weekly Two examples are listed in Tables V.1 and V.2.
- There are also 2 telemetric monitoring sites (RESM01 and RESM03; Figure 2.3a), which semi-continuously record EC and flow rate and transmit the results to a central computer. The EMU plans to increase the number of automated monitoring sites and the number of analytes tested.

During the site visit the technician in charge of sampling was consulted. The sample collection methods are relatively standard. Samples are collected at pre-specified times, simultaneously with field measurements of pH, EC and temperature. The accounting department keeps a detailed record of all the costs involved in the sampling procedure, for which information is supplied in Appendix II.

2.5.2 Analytical protocol

All the chemical analyses are done in-house by the company laboratories. The routine determinations are done by one laboratory with on-line automated equipment. The main analytical technique for cations is flame atomic absorption spectroscopy while most anion concentrations are measured by titrimetric methods. Primarily these analytes are: Na, K, NH_4^+, Mg, Ca, Fe_{Total}, Si, Cl^-, F^-, NO_3^-, PO_4^-, SO_4^{2-}, HCO_3^-, CO_3^{2-} and chemical oxygen demand (COD). Several of these analytical determinations are done over and above those required by DWAF (section 2.4.3). Additional *ad hoc* analysis (when considered appropriate) is done on the samples by a specialized laboratory. These determinations include: B, Cd, Cr, CN^-, *E.coli*, Pb, Mn, Se, V and Zn. The costs of these procedures are in Appendix III. Both the routine and the specialised laboratories mainly deal with samples from the production processes within the plant. It is difficult to gauge a laboratory's efficiency without an quality assurance programme, however, both laboratories are working towards achieving ISO 9000 status.

2.5.3 Data interpretation

The sample results are entered into a database called HydroCom. This calculates the percentage ion-balance error, %E. Supposedly the laboratory checks the results of every sample and re-runs any tests that might be erroneous. %E values in the database are, however, regularly greater than 10% and are sometimes over 50%.

With the data available in HydroCom, various temporal graphs can be constructed. HydroCom also has other useful features for interpreting and reporting data. Reports are, however, not produced on a frequent basis and hence the author suspects that the data are not studied often or closely enough. In addition, on average chemical values enable one to plot the monitoring sites on a series of Piper diagrams. Composite diagrams are recommended for data interpretation (Müller, 1991; section 2.6.2.2).

2.6 RESULTS OF THE FIRST FOUR YEARS OF MONITORING

2.6.1 An assessment of the data

The monitoring operation described in section 2.5 includes a database which allows some statistical and graphical manipulations to be made. For this study, however, only the original data was acquired and then assessed independently of the database

Due to logistical difficulties of travelling between the University and the study area, a single trip was carefully planned to collect information. In order to avoid incompleteness in data or information, very large volumes of data were collected. Subsequent inquiries were dealt with through a liaison officer at the company. The material consisted of field notes on the physical environment, the monitoring operation; and about 4 megabytes of water quality data and several papers and reports relevant to the monitoring operation. Examples of a few data sets are listed in Appendix V.

The initial geochemical evaluation of the data primarily involved the description of analyte concentrations over time and space. This was done using spreadsheets (Quattro Pro, version 4.0 and 6.0 for the more complex graphs) to produce time series plots for the different sample locations. Later in this dissertation, statistics are applied and a more complete geochemical appraisal is made.

2.6.2 Interpretation of the data

2.6.2.1 Surface water monitoring

It is much harder to draw inferences on the quality of the surface water (Table 2.4) compared to the ground water conditions (Table 2.5). Guideline values are given in Table 2.3 for comparison. The residence time of fluvial water in this industrial area is relatively short as the district is in the upper reaches of the catchment with a relatively small drainage area (SIRI, 1976). Some conclusions can be made by the comparison of time series plots over the course of the stream.

Basic statistics for each of the surface water monitoring sites (RESMs) are listed in Table 2.4. Reference to Figure 2.3a (also in Appendix IX). of the monitoring localities may be necessary. The fluvial monitoring location where the spruit leaves the industrial zone (RESM01), *i.e.* the perimeter fence, is the most important site. RESM01 is the station which records the pollution released from the plant downstream. Figures 2.4a and 2.4b show that the pollution has roughly remained constant for the last three years. There was a major pollution period in 1991. Figures 2.4a and 2.4b show that Ca^{2+} and Na^{+} are the dominant cations and HCO_3^- and SO_4^{2-} are the dominant anions.

Table 2.4. A summary of the water quality at the surface water monitoring locations (RESMs) over the last four years.

Site No.	Site description	Area code & symbol	EC (mS.m^{-1}) Mean	EC (mS.m^{-1}) Std. Dev.
RESM 01	West side perimeter fence.	1 ○ 2 □	58	25
RESM 02	Northern spruit end, below water dams.	2 □ 5 ●	54	9
RESM 04	Above water dams, after confluence.	6 ■ 8 ♦	54	17
RESM 05	Upstream of confluence, below town.	Town	56	17
RESM 06	Above confluence, below irrigation.	6 ■ 8 ♦	45	16
RESM 07	Above irrigation & refuse disposal.	6 ■ 8 ♦	52	17
RESM 08	Above of the whole plant bar irrigation.	6 ■	53	36
RESM 16	Above RESM08 confluence.	6 ■	32	29
	Average:		*51*	*19*
RESM 03	Southern spruit end, after ash/BP dam.	1 ○	78	86
RESM 09	Below confluence 2nd, after coal stocks.	7 ▲	324	147
RESM 10	Below confluence 1st, after coal stocks.	7 ▲	67	33
RESM 11	Above coal stockpiles.	2 □ 3 △	56	17
RESM 12	Below coal stockpiles and fertilizer areas.	2 □ 9 ★	128	85
RESM 13	Above stockpiles and fert./explo. dumps.	9 ★	55	20
RESM 14	Above stockpiles, below fert./explo. area.	2 □ 3 △	201	108
RESM 15	Above fertilizer and explosive dumps.		51	38
	Average:		*120*	*67*

Figures 2.5a and 2.5b show the northern spruit rarely has a high pollutant load (>70 mS.m^{-1}) at RESM02. There appears to be episodic dilution events when the water quality improves. Figures 2.6a and 2.6b indicate the southern stream is much more polluted. Figures 2.7a and 2.7b of RESM08, in addition to other graphs of the northern stream, suggest that the pollution source is probably from the water recovery division dams. Analyses show that they are rich in calcium and sodium, carbonate and sulphate. The contaminant load is high over the length of the spruit in the area of the waste operations (Figures 2.8a and 2.8b, in addition to Figure 2.1). The effluent in the southern stream is diluted at the confluence of the spruits, decreasing the contaminant load at RESM01, the exit point.

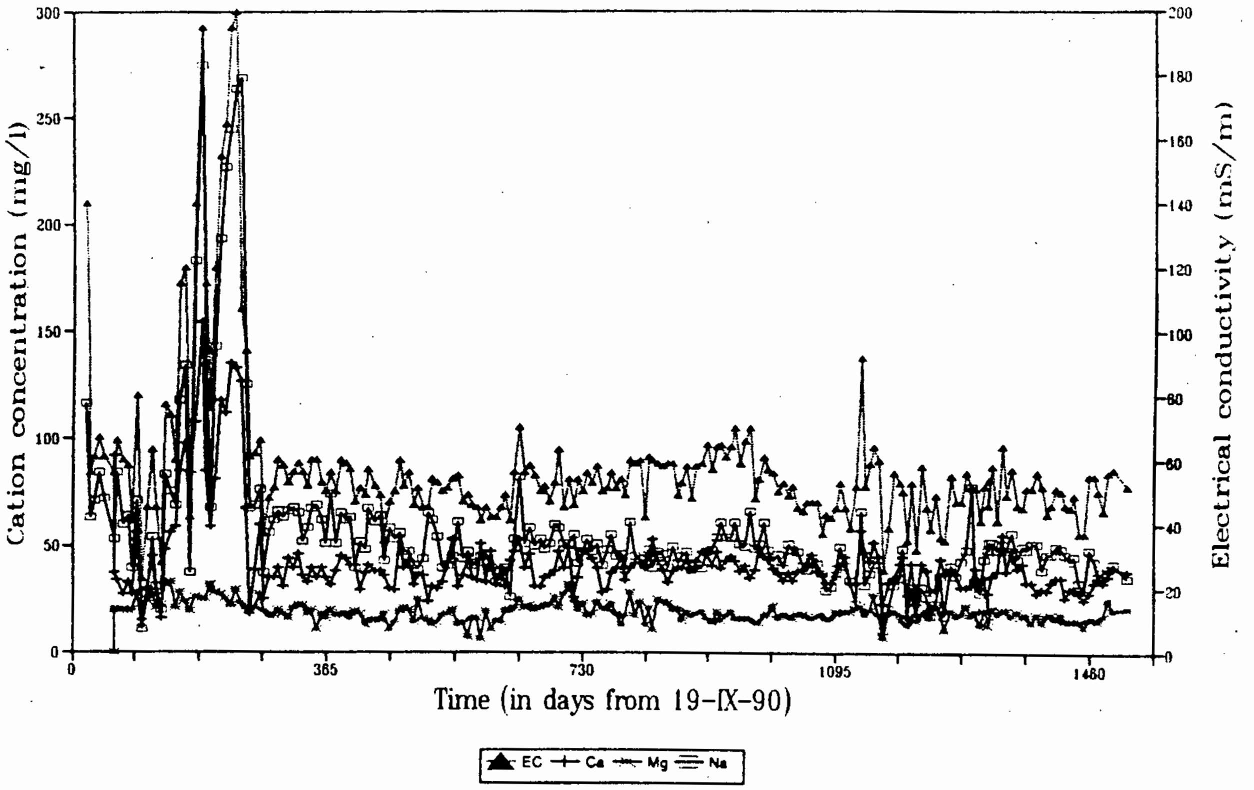


Figure 2.4a. Time series plot of electrical conductivity and the major cations at surface water monitoring site number RESM01, the stream exit point. (Appendix V).

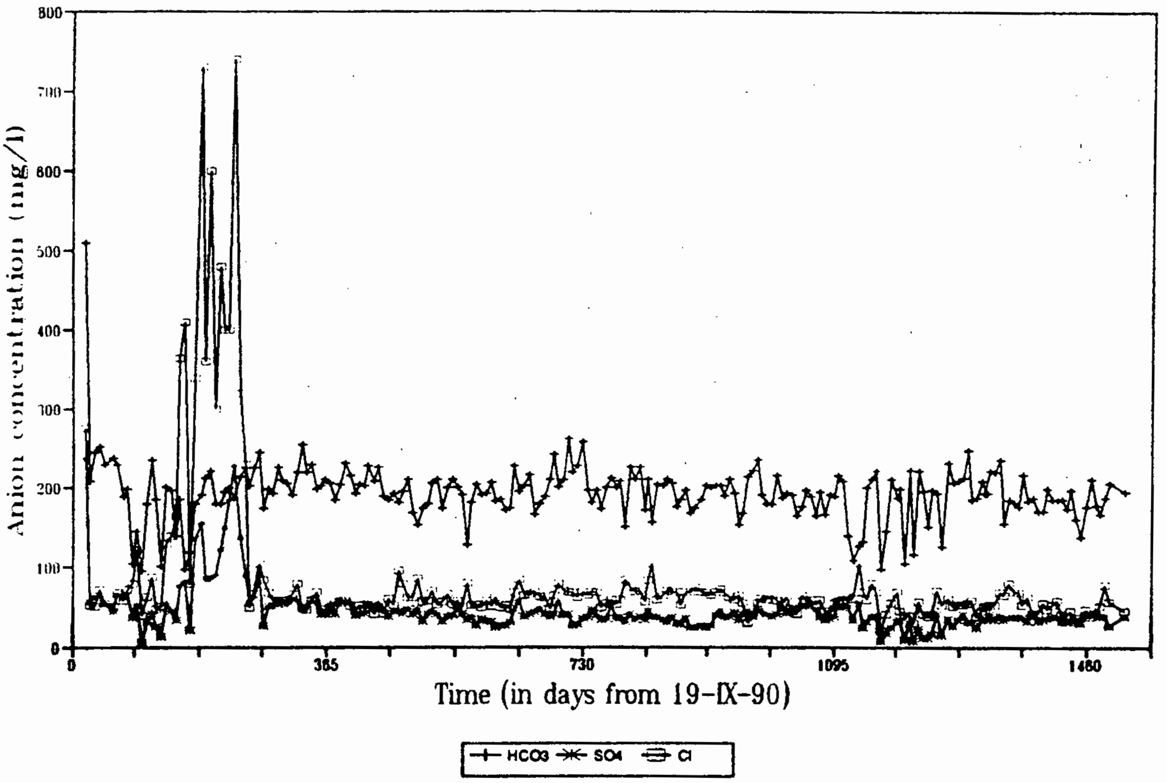


Figure 2.4b. Time series plot of the major anions at surface water monitoring site number RESM01, the stream exit point from the industrial area. (Appendix V).

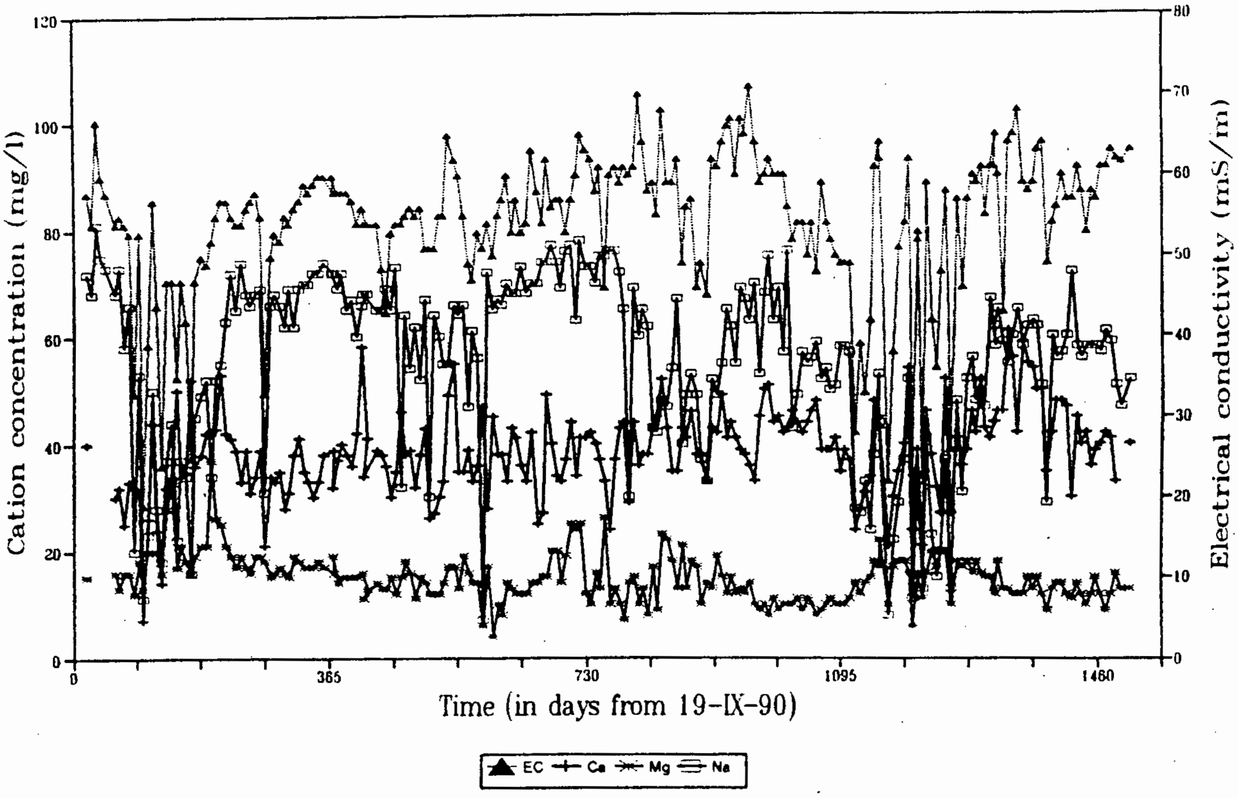


Figure 2.5a. Time series plot of EC and the major cations at surface water monitoring site number RESM02, on the northern spruit below the water recovery dams.

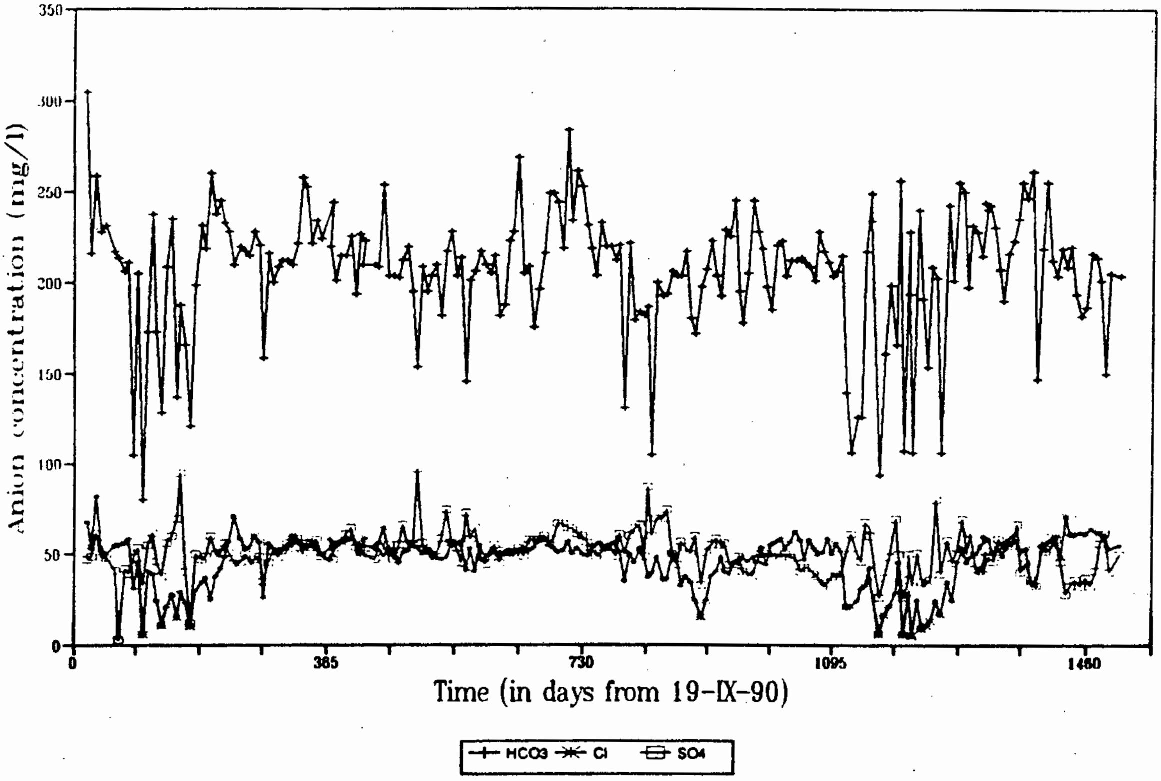


Figure 2.5b. Time series plot of the major anions at surface water monitoring site number RESM02, the end of the northern spruit below the water recovery division dams.

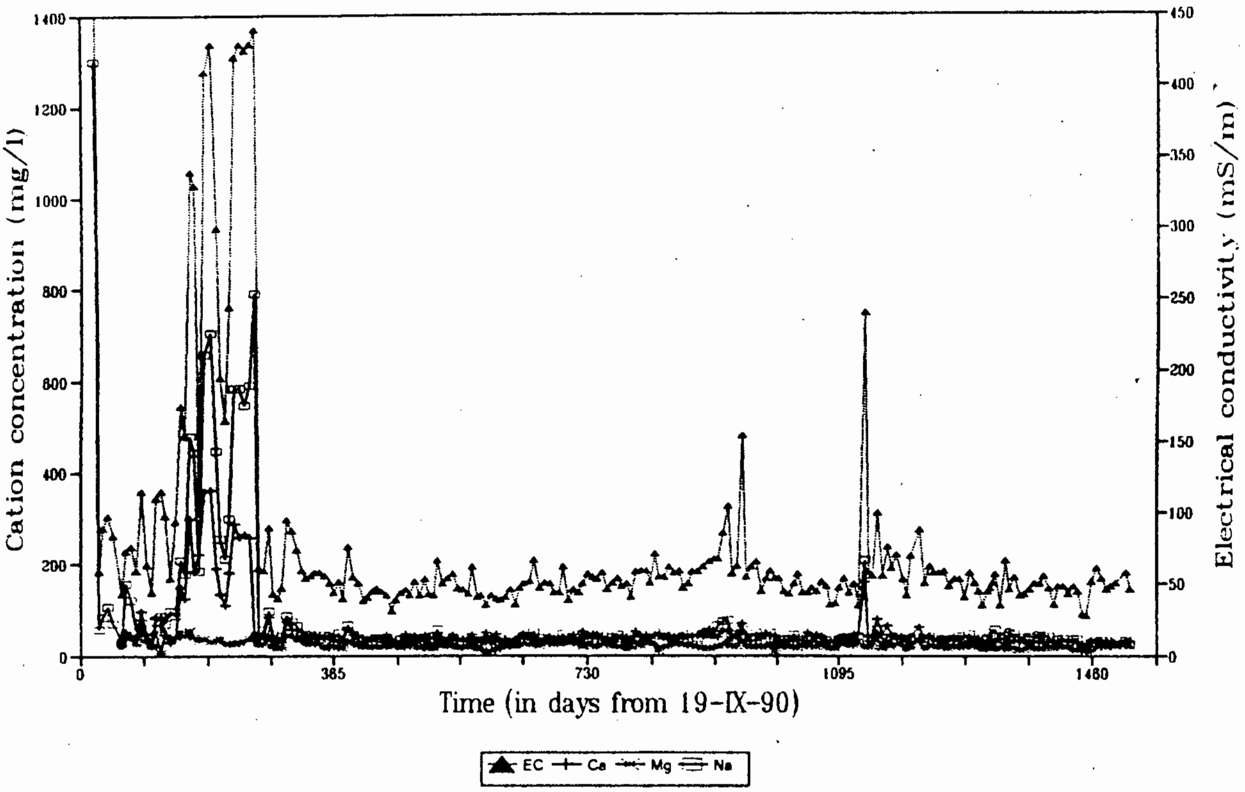


Figure 2.6a. Time series plot of EC and the major cations at surface water site RESM03, on the southern spruit below the ash, black product and fertilizer dams.

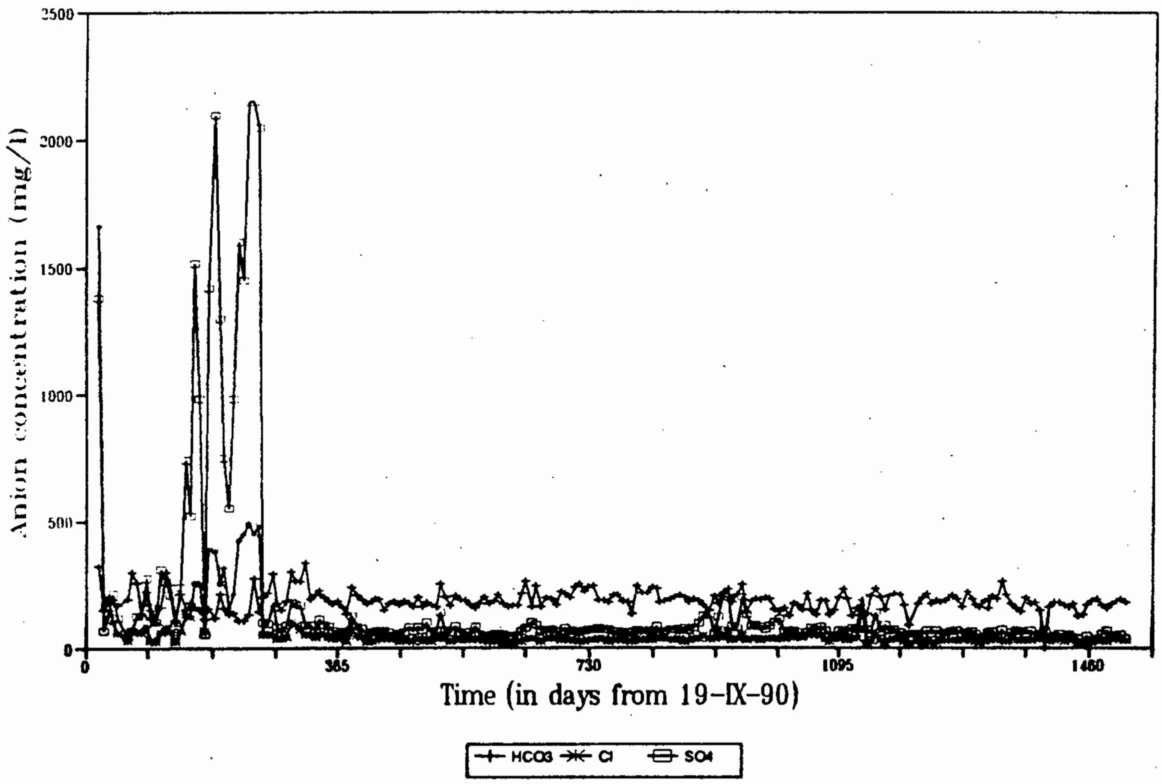


Figure 2.6b. Time series plot of the major anions at surface water site RESM03, on the southern spruit below the ash, black product, fertilizer and explosives dams.

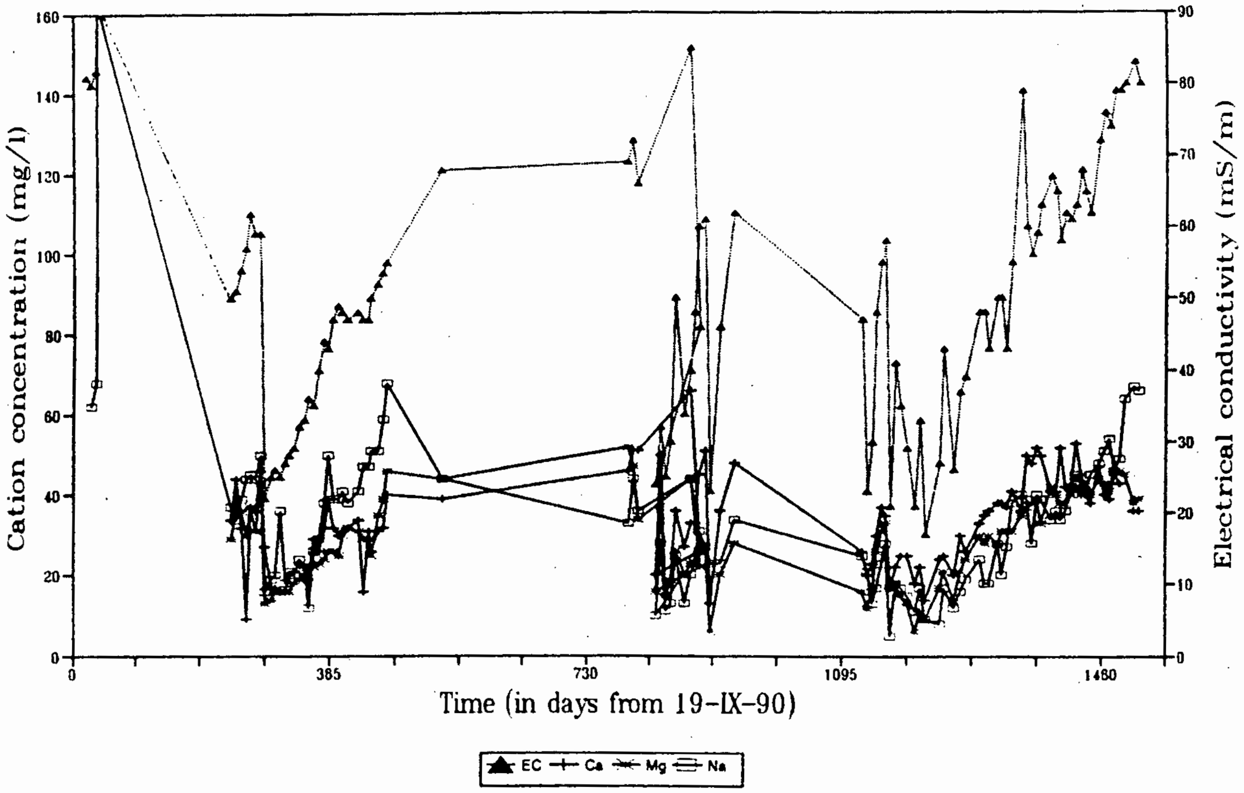


Figure 2.7a. Time series plot of EC and the major cations at surface water site RESM08, the northern stream above the industrial area bar some effluent irrigation.

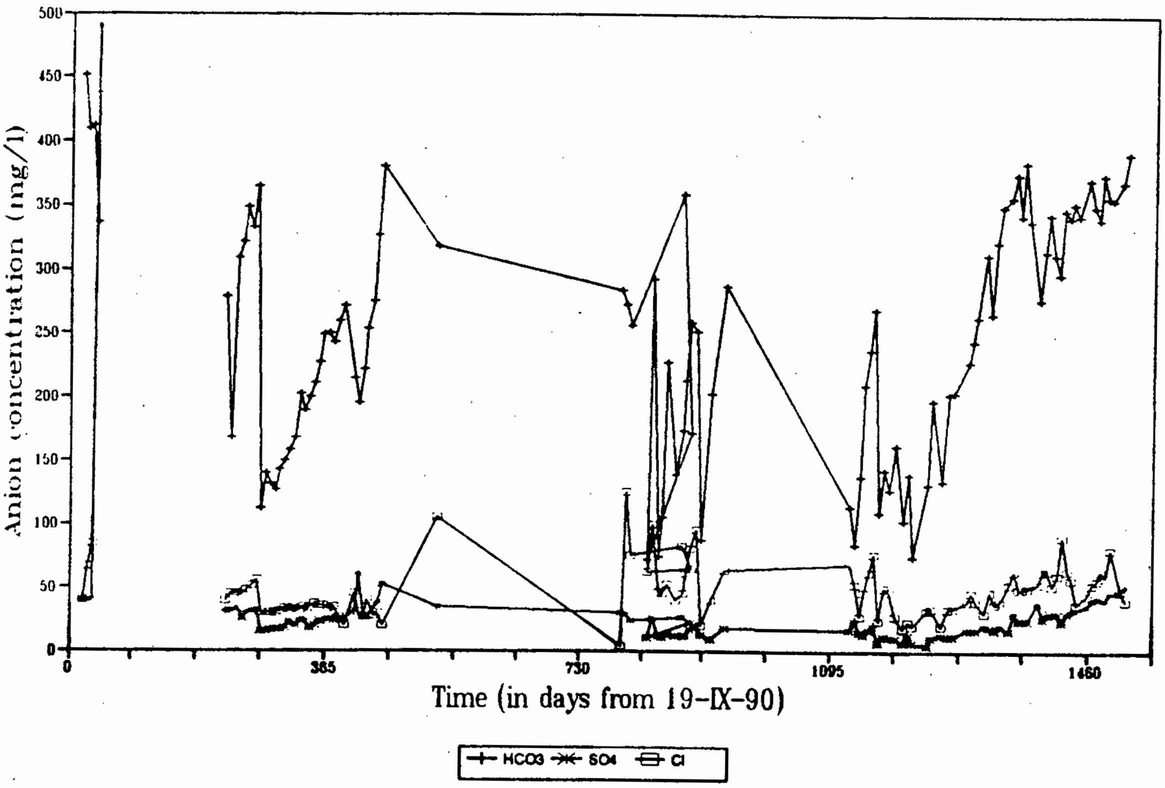


Figure 2.7b. Time series plot of the major anions at surface water site RESM08, the top end of the northern stream above the industrial area bar some effluent irrigation.

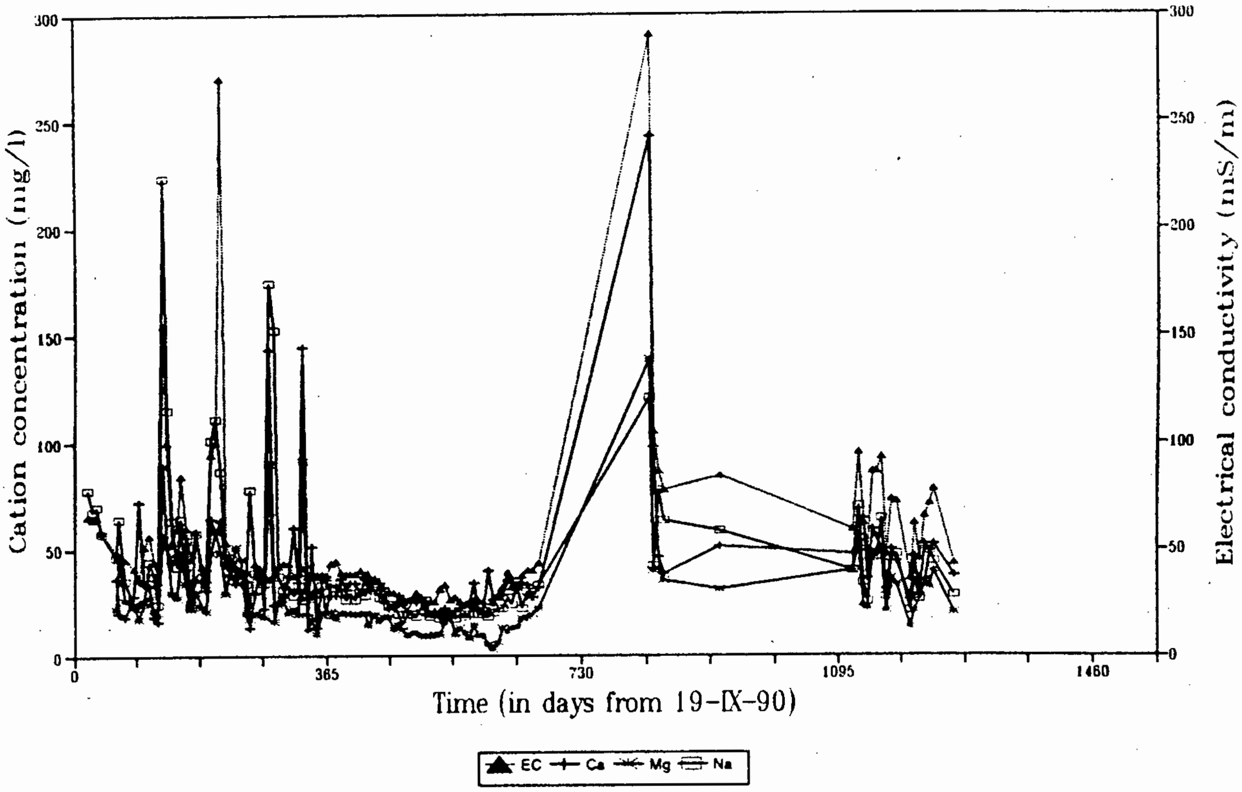


Figure 2.8a. Time series plot of EC and the major cations at surface water site RESM15, above the industrial area including the fertilizer and explosives dumps.

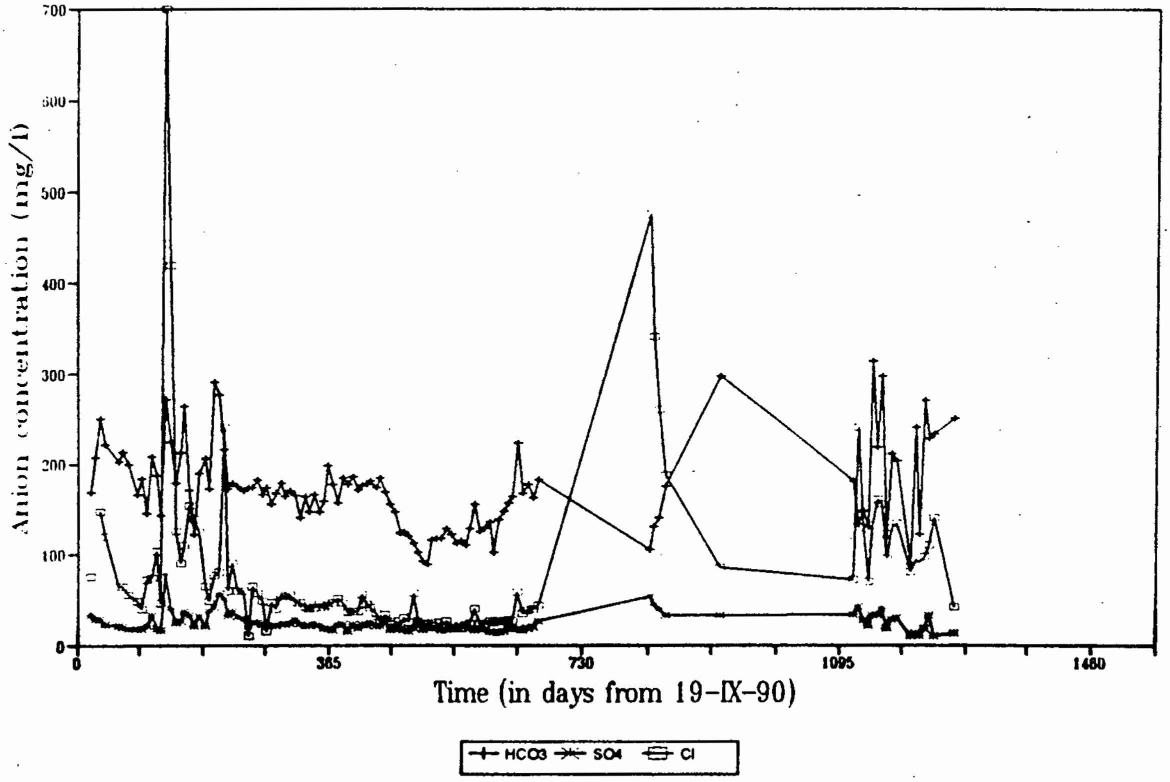


Figure 2.8b. Time series plot of the major anions at surface water monitoring site RESM15, above the industrial area including the fertilizer and explosives dumps.

2.6.2.2 Ground water monitoring

The ground water geochemical interpretation of the area must consider each waste operation individually before assessing the overall impact. Piper diagrams are often used, to compare relative ion abundances. Figure 2.9 shows the ionic composition of all the boreholes averaged over the last four years of data. The plots indicate the chemical signature of the ground water quality but not absolute concentrations. The magnitude of contamination is evident from EC values which are plotted against time in Figures 2.10 to 2.27 for the individual boreholes.

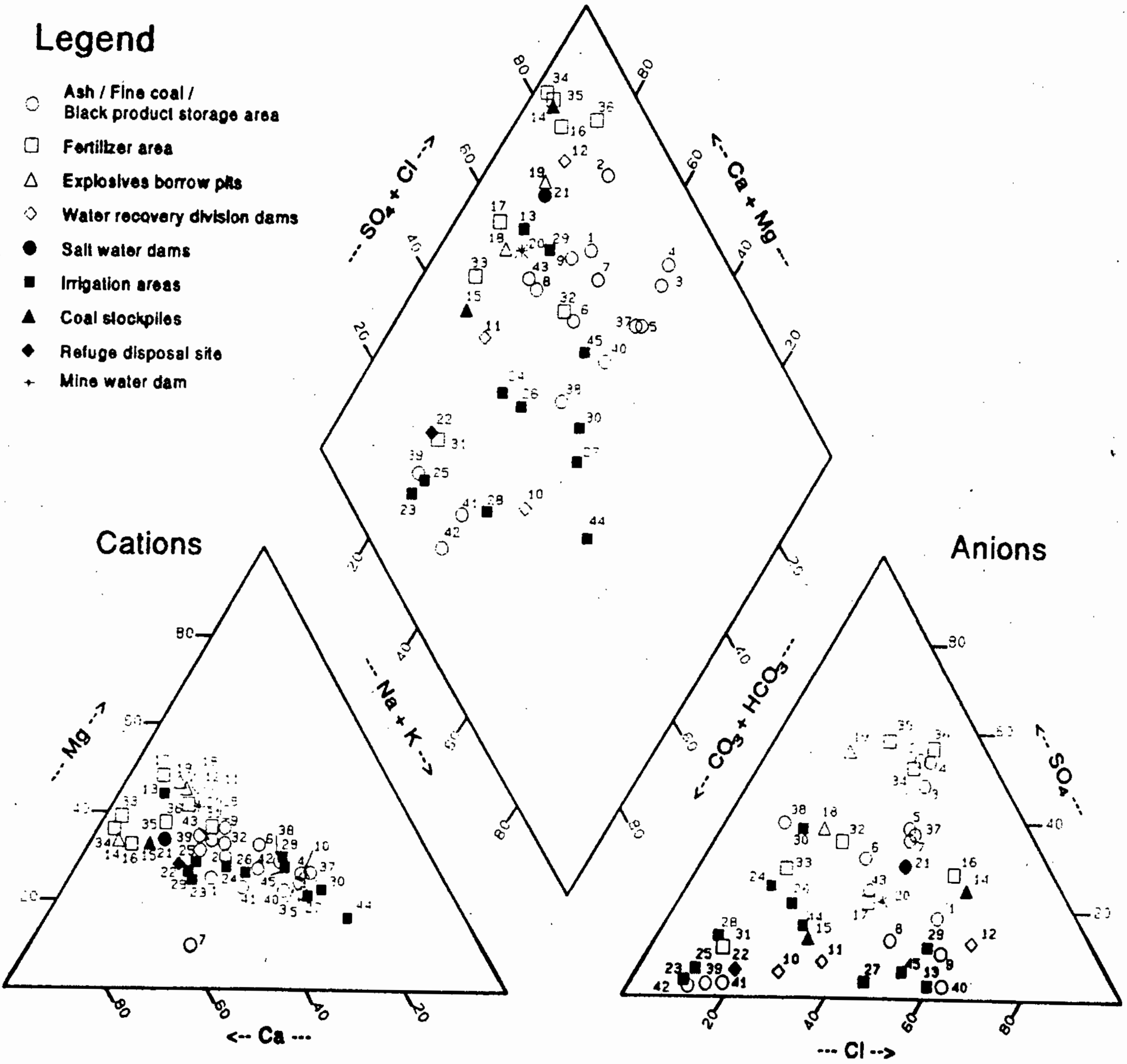


Figure 2.9. Piper diagram of the mean borehole (REGM) composition, categorized by the waste operations.

Figures 2.10 to 2.27 are time / concentration plots using mg.dm^{-3} values which is the convention for reporting water quality data (DWAF, 1994c). The relative proportions of the ions are not directly comparable in these figures as the values are not in moles. Figure 2.9, however, has been constructed using molar data.

Figure 2.9 is useful as an overall comparison of water composition from the different boreholes, if only to indicate that there is no clear separation based on the type of waste operation being monitored The impact of waste operations on ground water would appear to be quite large, although varying widely between boreholes (Figures 2.10 to 2.27). The ground water quality below the ash / black product dams is illustrated in Figure 2.10 and 2.11. The dominant ion species are Ca and SO_4 and one pollution event with Na levels. The two major episodes of REGM03 contamination in the first half of 1992 (Figure 2.10) were not appropriately analyzed and the composition is not recorded in Figure 2.11.

Ground water around the fertilizer reject dump is severely polluted (Figure 2.12; Appendix V), particularly in REGM16. Figure 2.13 shows that only two samples have been analyzed from borehole REGM17 over the last four years. Similarly only one determination has been done for REGM16 which has heavier pollution (Figure 2.12). The plots for the fertilizer area in the Piper diagram (Figure 2.9) therefore represent mean relative chemical abundances calculated from only a few samples. Boreholes 16, 34, 35 and 36 (top corner of upper section) are high in Ca / Mg and SO_4 / Cl. The other parts of the aquifer which are further away from the centre of the dump (Figure 2.3) tend to have relatively more carbonate and Na / K.

The carbonate influence seen in the outer boreholes of the fertilizer dump (REGMs 17, 31, 32 and 33; Figure 2.9) probably emanates from the explosives borrow pits. Although the EC of pollution from the pits is not particularly high (Figure 2.14), the pollution mixes with that of the fertilizer dump. Figure 2.18 illustrates that HCO_3 is the dominant ion which is probably a product of burning. The fertilizer and explosive waste operation are environmentally linked, confusing the interpretation. This is not helped by the fact that the EC fluctuations seen in Figure 2.14 were not further investigated and are therefore not apparent in the ion analyses in Figure 2.15. Some feature caused a dramatic drop in the EC (Figure 2.14) which might be enlightening in the design of remediation procedures.

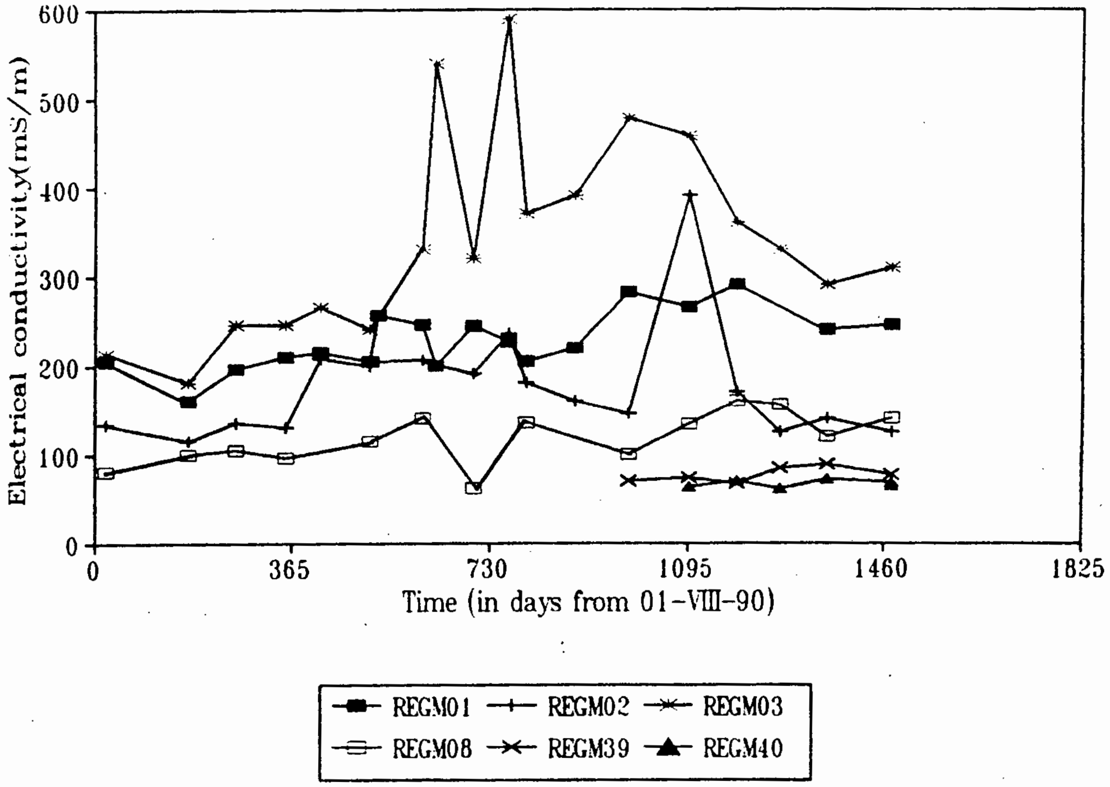


Figure 2.10. Time series plots of electrical conductivity in some of the boreholes around the ash, ash water and black product dams. Area code 1 O.

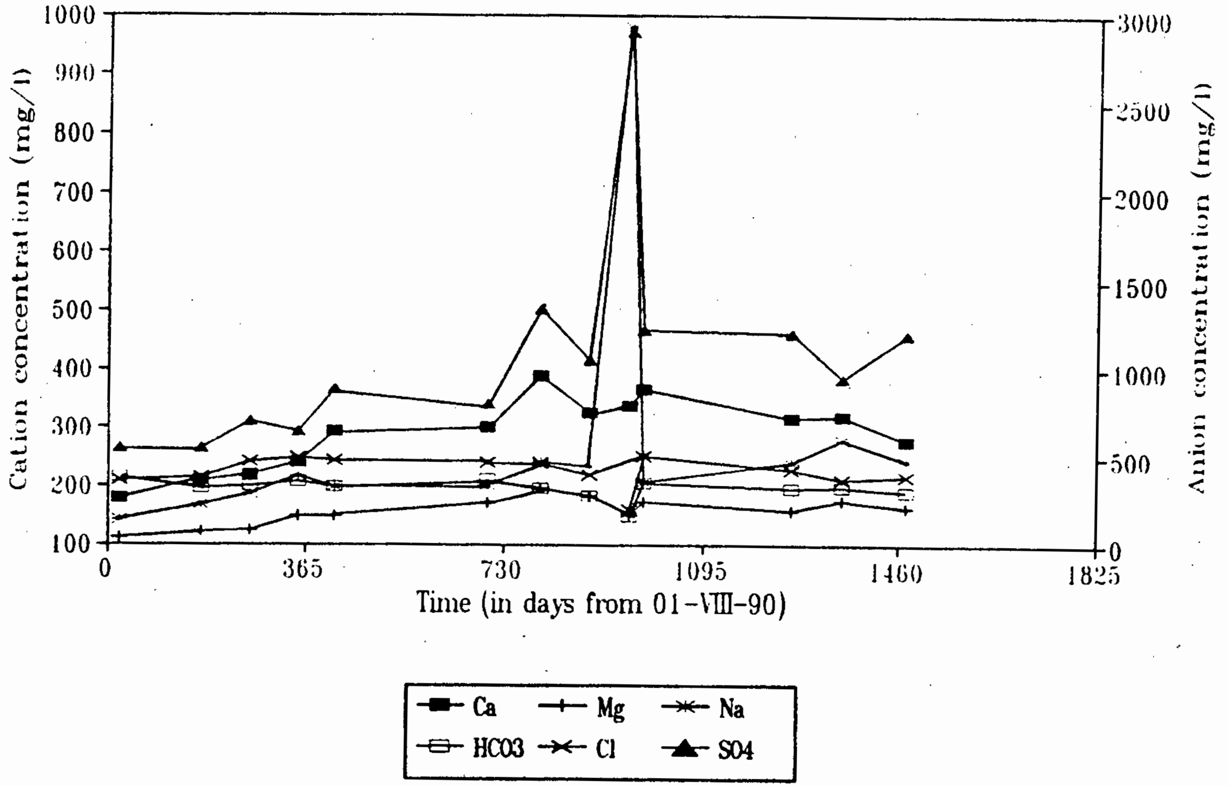


Figure 2.11. Time series plots of ion concentration in borehole REGM03 near the ash, ash water and black product dams. Area code 1 O.

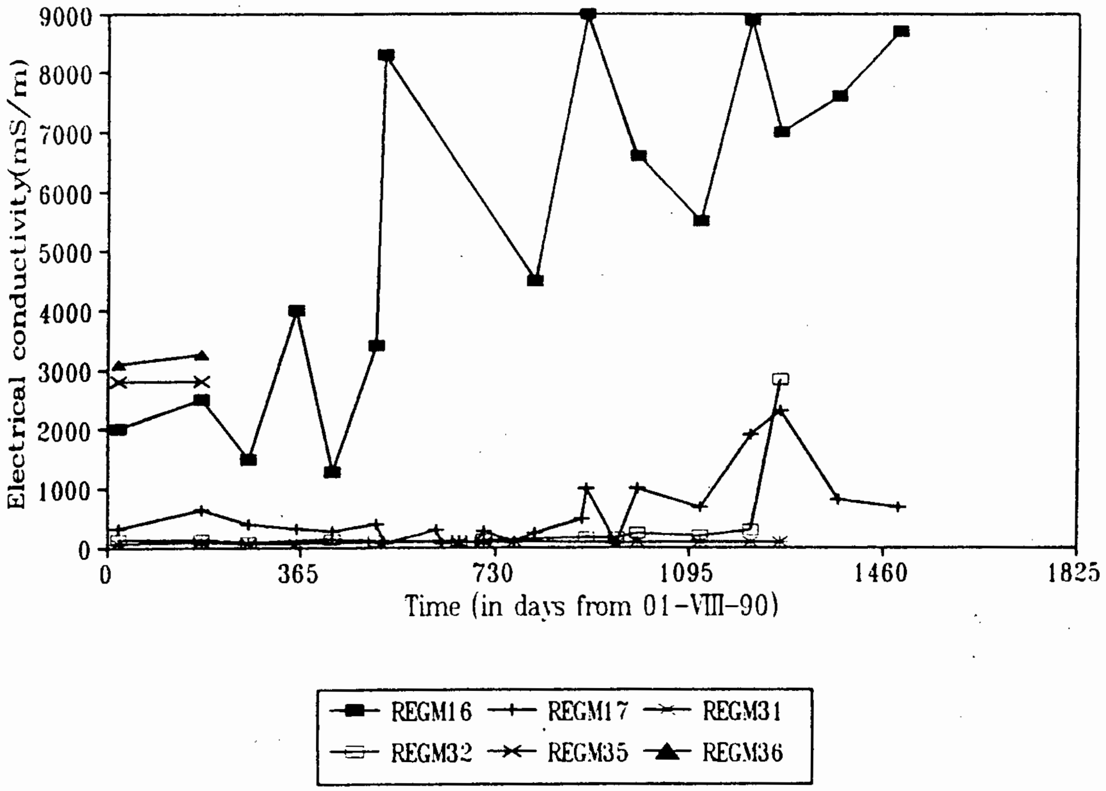


Figure 2.12. Time series plots of electrical conductivity in the boreholes around the reject fertilizer dumps. Area code 2 ☐.

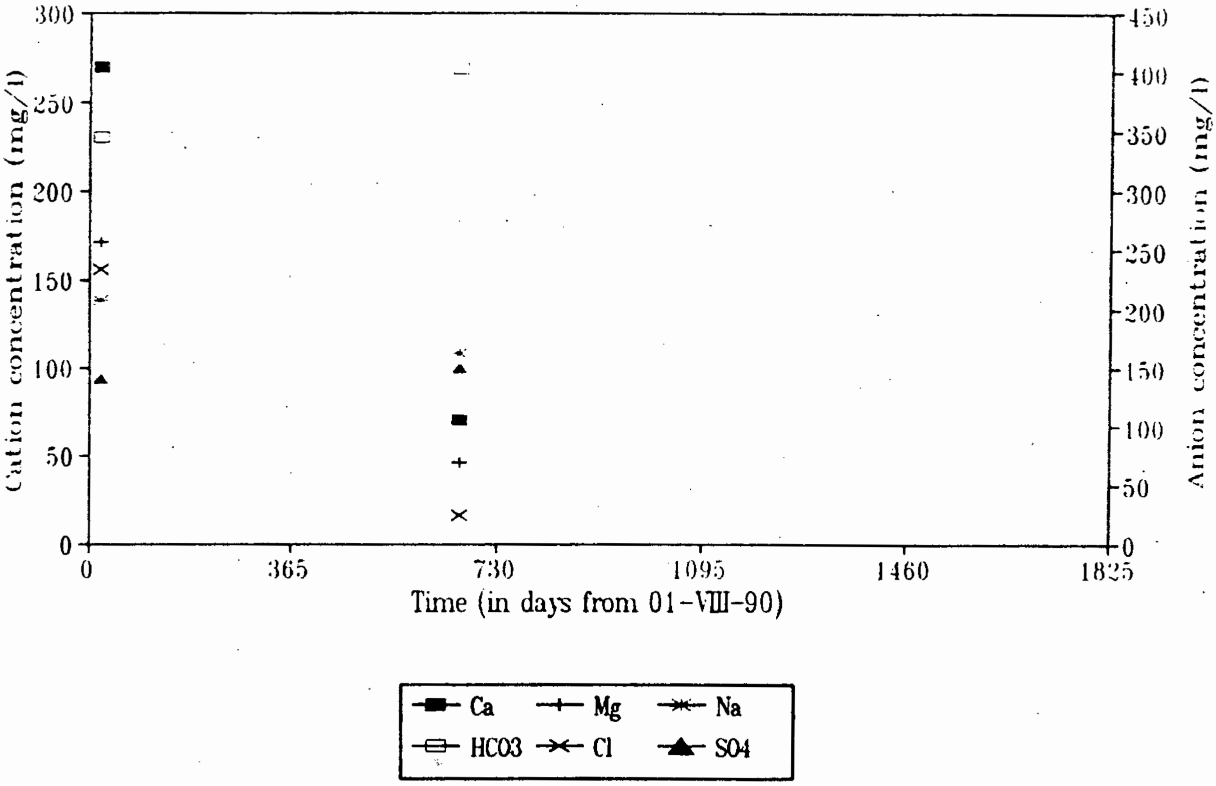


Figure 2.13. Time series plots of ion concentration in borehole REGM17 near the reject fertilizer dump. Area code 2 ☐.

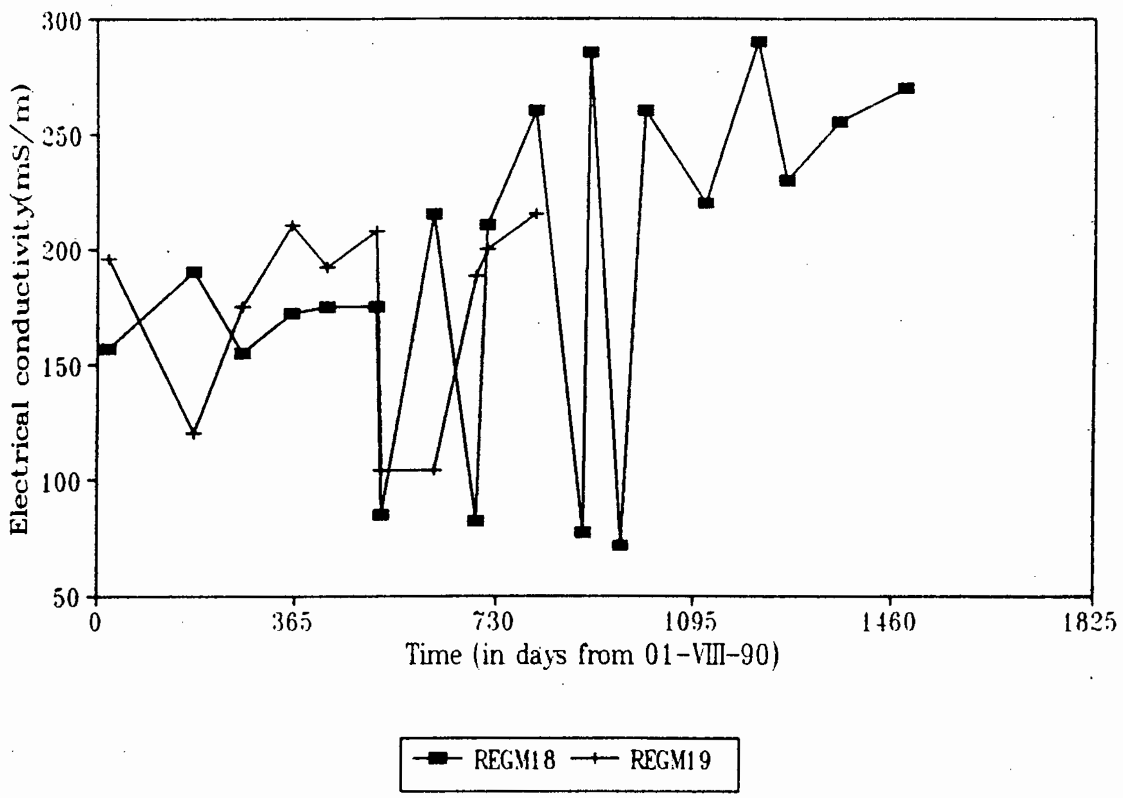


Figure 2.14. Time series plots of electrical conductivity in the two boreholes around the explosives burning area and borrow pits. Area code 3 △.

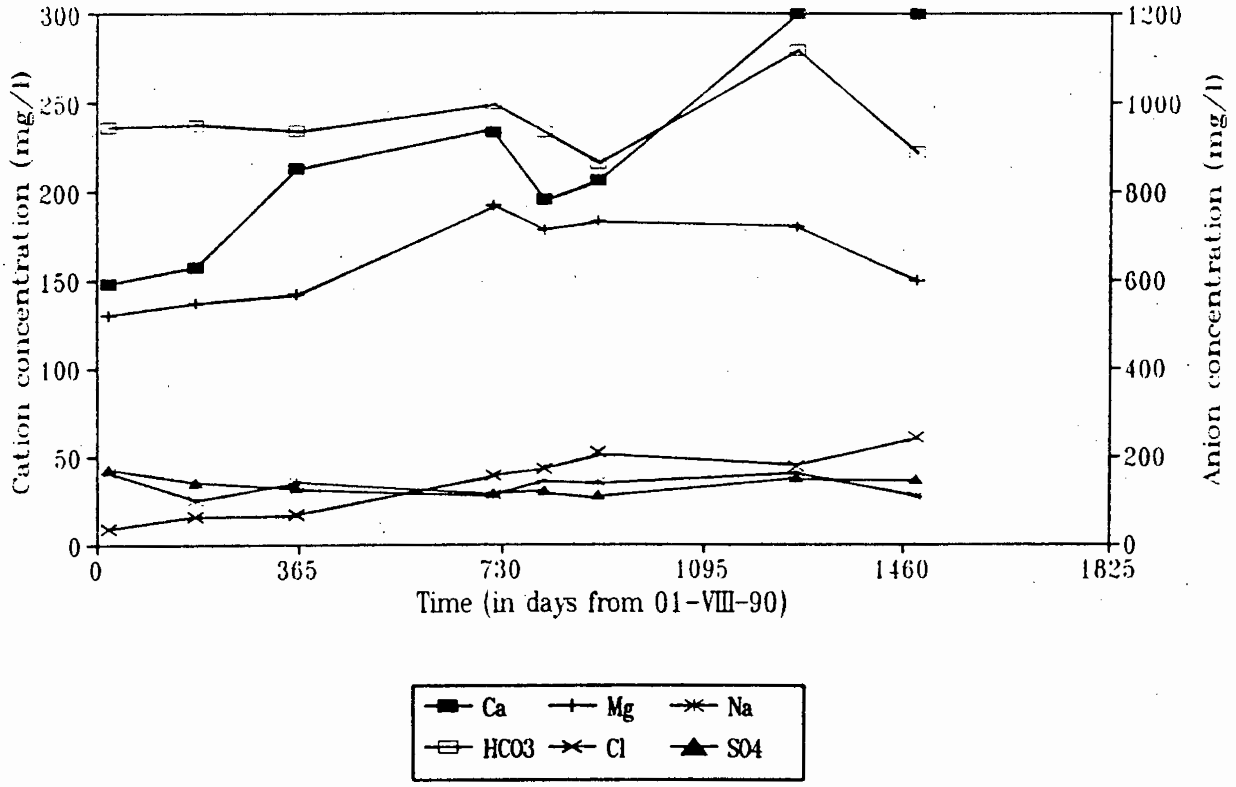


Figure 2.15. Time series plots of ion concentration in borehole REGM18 near the explosives burning area and borrow pits . Area code 3 △.

Although there are only three boreholes around the water recovery division dams (REGMs 10, 11 and 12) they show there is a large variation in the chemical make-up of the ground water (Figure 2.9). The impact on the aquifer water quality (in terms of EC) is not the largest of the waste operations but the dams occur over a large area and so the pollution is probably diluted. The dominant species are Na and HCO_3 in REGM10 (Figure 2.17; Appendix V) while borehole REGM11 has an increased influence from a source rich in Ca, Mg and Cl (Figure 2.9) and REGM12 has an even greater concentration of Ca and Cl.

Chemical analysis of the effluent in the water recovery division area suggests that contaminated ground water would also be high in phosphate and nitrate levels. There are, however, mechanisms (phosphate sorption by clay minerals; biological denitrification) which might preferentially reduce the concentrations of these constituents before the pollution plume reaches the ground water. Clearly, the water recovery division of the industrial operation although dealing with different waste streams is not the largest pollution culprit.

The contamination around the salt water dam has been gradually increasing in the aquifer at least since August 1990, with only a slight temporary improvement in water quality during mid-1994 (Figure 2.18). Only one borehole monitors this waste site and indicates an alarming level of contamination. Ca and Mg are the main cations and Cl as the anion. The DWAF water quality guidelines (Table 2.3) do not specify Ca and Mg concentrations. These metals are usually treated as benign but the Cl levels are clearly excessive.

Borehole data associated with various irrigation areas, including the sludge disposal site, are illustrated in Figure 2.20. Figure 2.9 shows that the chemical signature of water from boreholes in these areas is varied. The EC for all of the sites is around that of the DWAF recommended level of $154\,mS.m^{-1}$. A comparison of the values in Table 2.3 and the time series plot of Figure 2.21 shows that Na and Cl levels are lower than domestic use guideline. Ground water from these areas could not, however, be used directly for industrial purposes because of corrosivity associated with high HCO_3 levels.

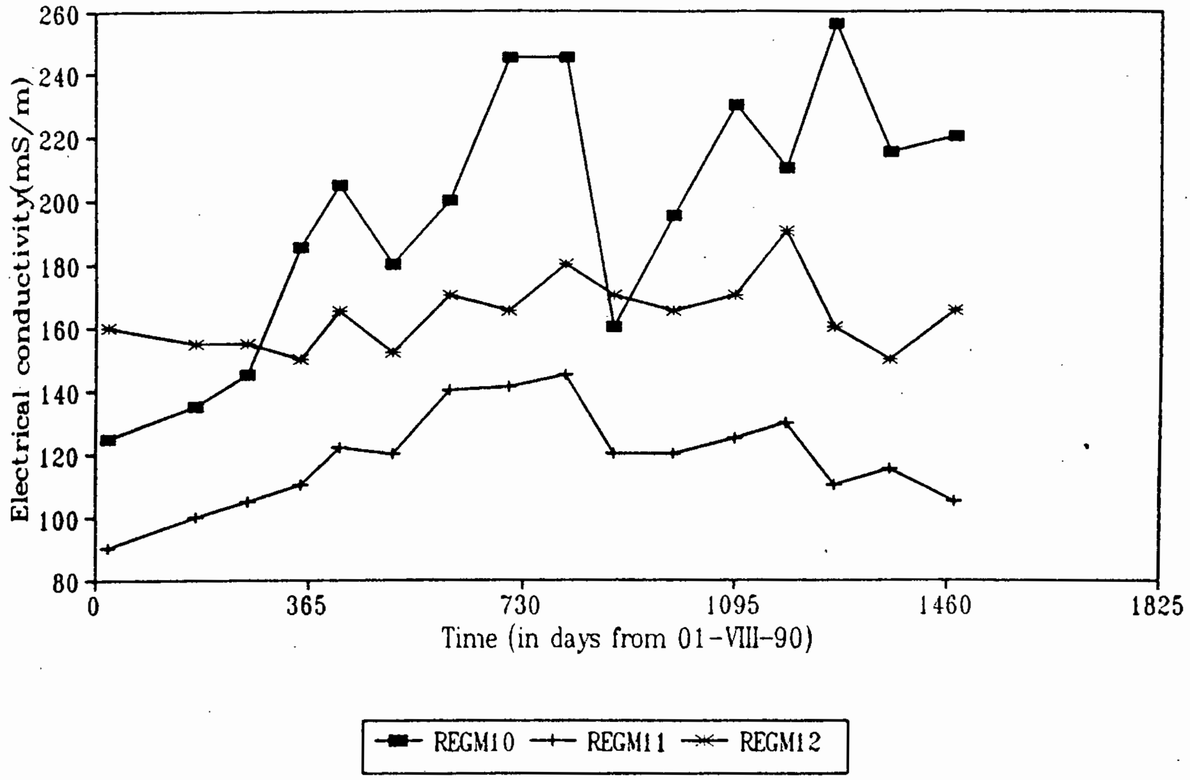


Figure 2.16. Time series plots of electrical conductivity in the three boreholes around the water recovery division dams. Area code 4 ◇.

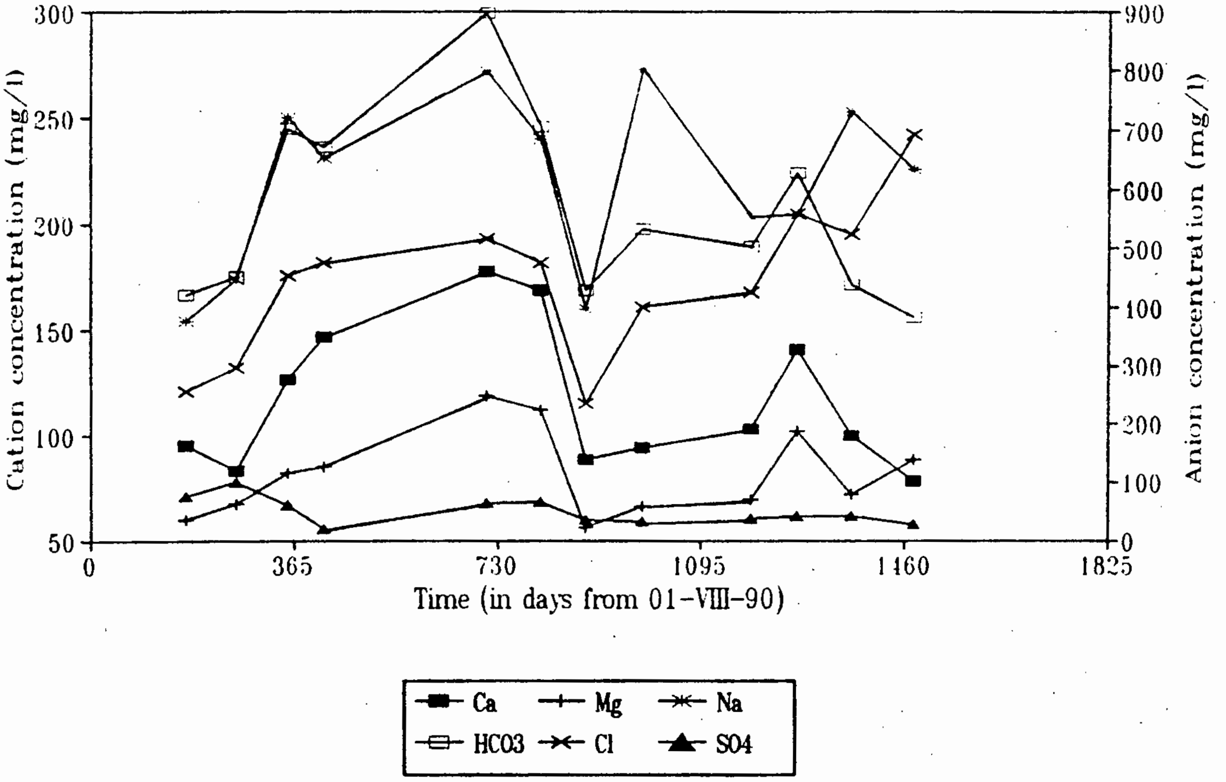


Figure 2.17. Time series plots of ion concentration in borehole REGM10 near the water recovery division dams. Area code 4 ◇. (Appendix V).

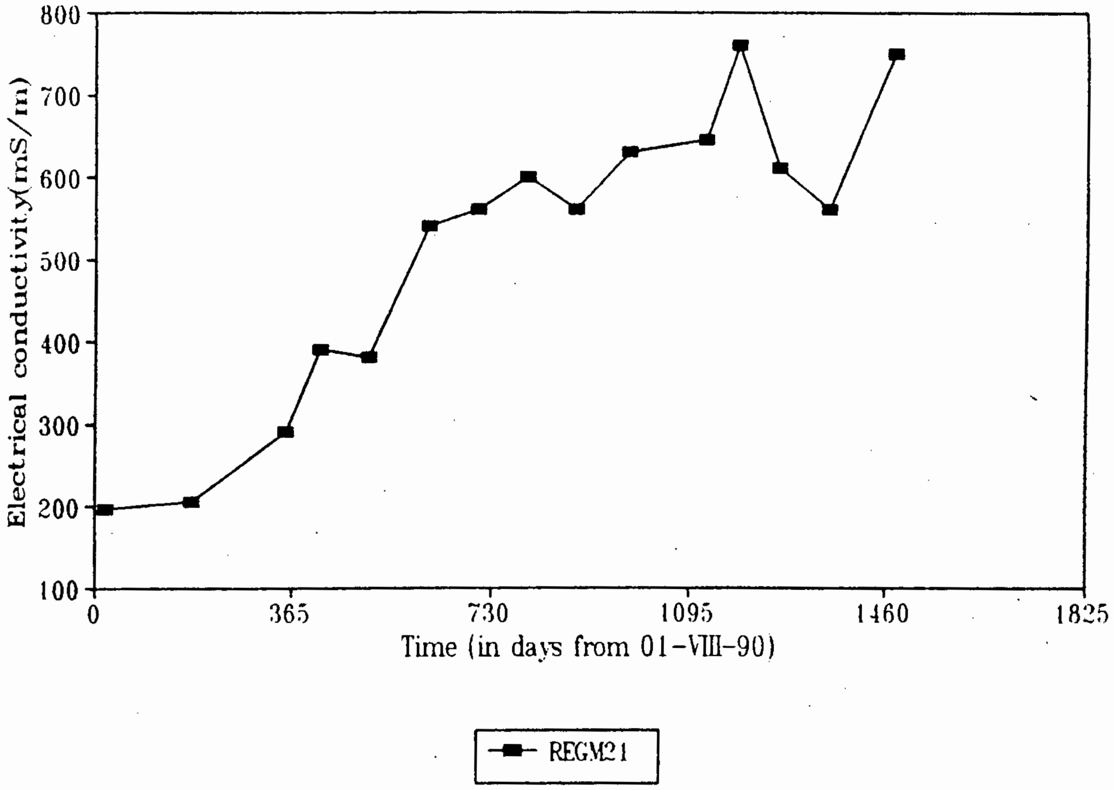


Figure 2.18. Time series plots of electrical conductivity in the borehole at the salt water dam. Area code 5 ●.

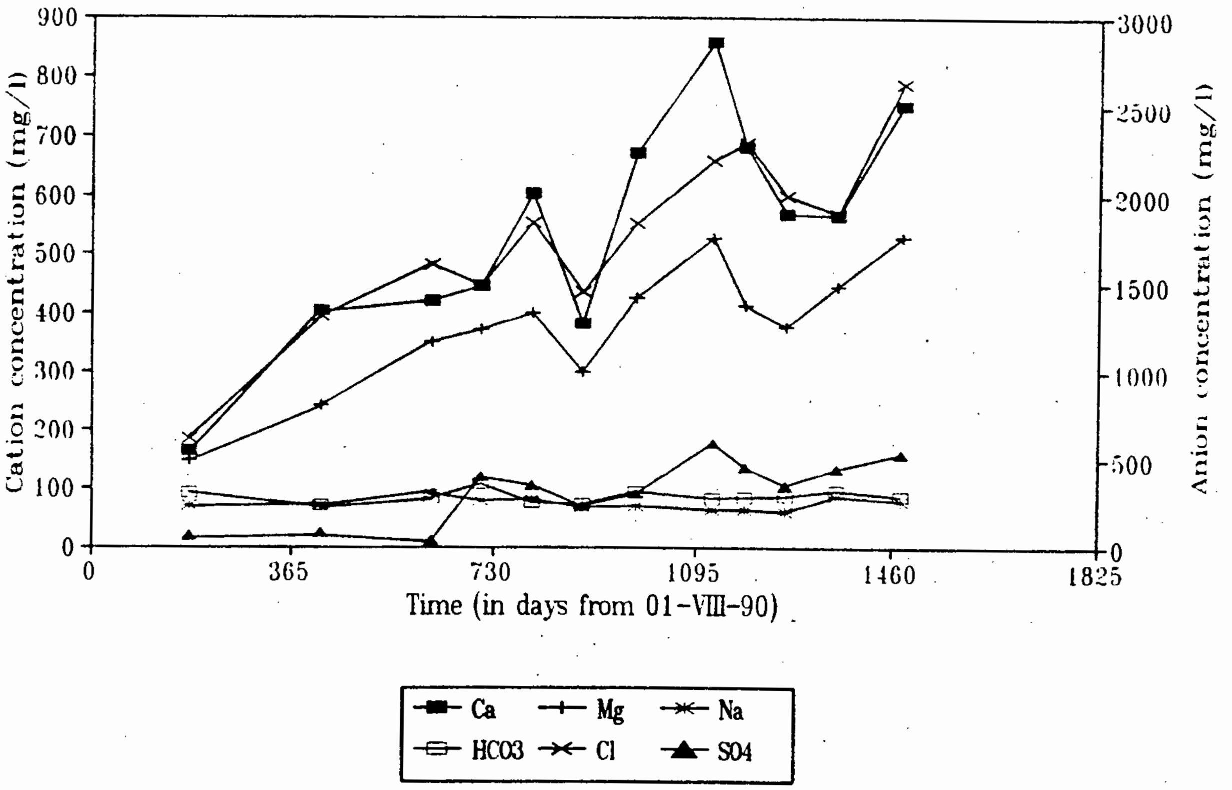


Figure 2.19. Time series plots of ion concentration in borehole REGM21 near the salt water dam. Area code 5 ●.

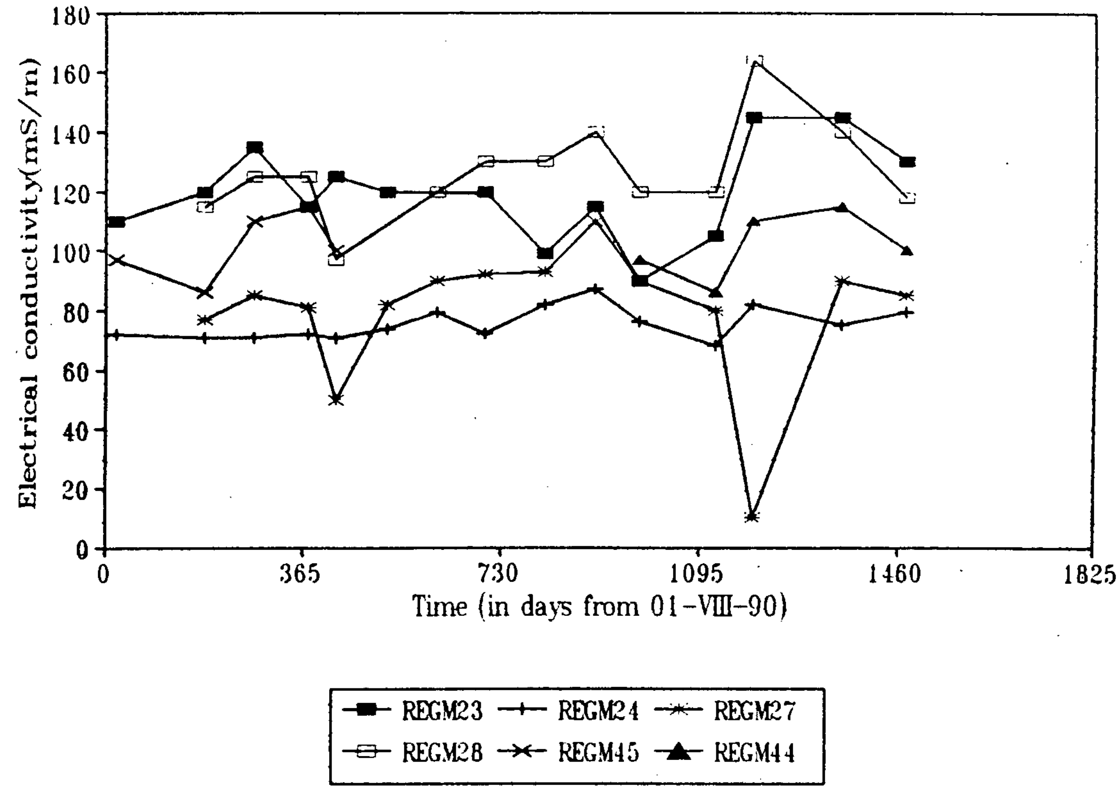


Figure 2.20. Time series plots of electrical conductivity in the two boreholes around each of the sludge disposal area and the two irrigation areas. Area code 6 ■.

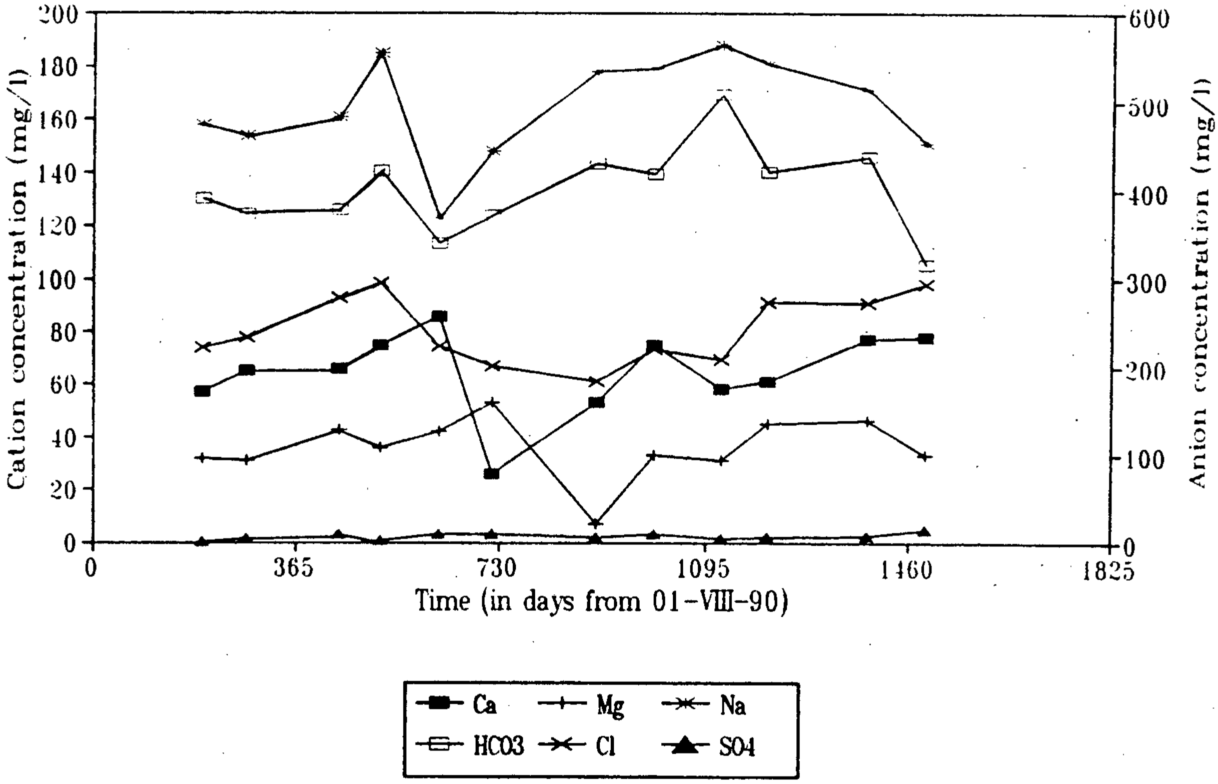


Figure 2.21. Time series plots of ion concentration in borehole REGM28 near an irrigation area. Area code 6 ■.

Contamination below the coal stockpile fluctuates in EC although not alarmingly (Figure 2.22). HCO_3, Ca and Cl are the most abundant components of the ground water in this area (Figure 2.23). Surprisingly, SO_4 is a relatively minor contaminant, which was not expected as the degradation of pyrite in the coal should increase sulphate levels. It is suggested, therefore, that there is pollution migrating into this area, probably from the reject fertilizer dumps and the explosive borrow pits which are upstream. This is supported by the location of REGM14 on the Piper diagram very close to points representing some of the boreholes around the fertilizer / explosive dump. The coal stockpile leachate does not appear to pollute to a significantly greater degree than the other waste operations.

The refuse dump in the northern part of the industrial area (Figure 2.2) is not perceived to be a major environmental hazard. The EC values, which are considered to be good pollution indicators, are the lowest on average in the whole area (Figure 2.24 and Table 2.5). Figure 2.25 records to the major ions in the ground water of this area. The relative ion abundance is erratic which is probably a manifestation of the heterogeneous nature of the waste.

There are a number of mine water dams within the reticulation system in the area monitored (Figure 2.2). Only one of these is monitored (Figure 2.3b) at borehole site REGM20. Over the last four years the ground water quality in this well has declined, although there have been temporary improvements (Figure 2.26). It would be interesting to determine what has caused these dilution events - whether they are simply the result of recharge by rainfall or the result of amelioration by water quality management procedures. There is no indication that the chemical signature from mine water contamination is similar to that of the coal stockpile leachate, which is useful as an indication that the borehole near the coal pile is being influenced from elsewhere. The compositions on the Piper diagram (Figure 2.9) are dissimilar for REGM14 and REGM20. The high SO_4 levels (Figure 2.27) are probably the product of pyrite weathering and render the mine water quite potent (400 $mg.dm^{-3}$ is the domestic use guideline - Table 2.3).

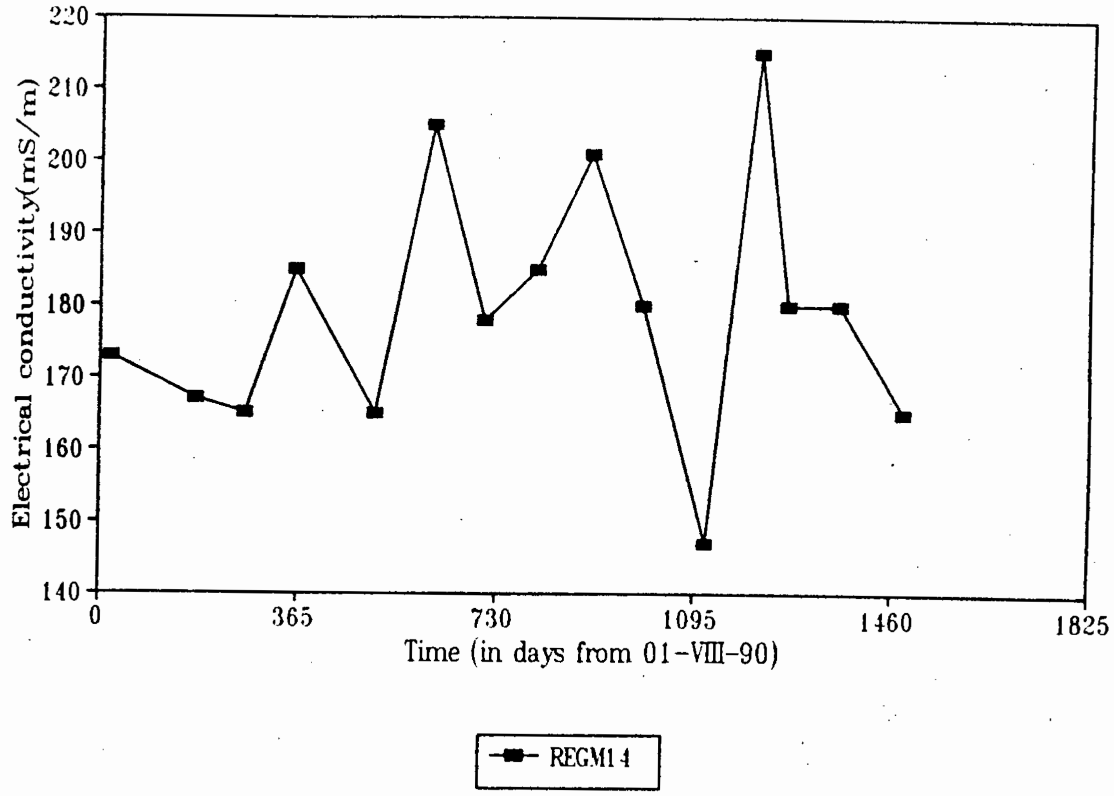


Figure 2.22. Time series plot of electrical conductivity in the borehole at the coal stockpile. Area code 7 ▲.

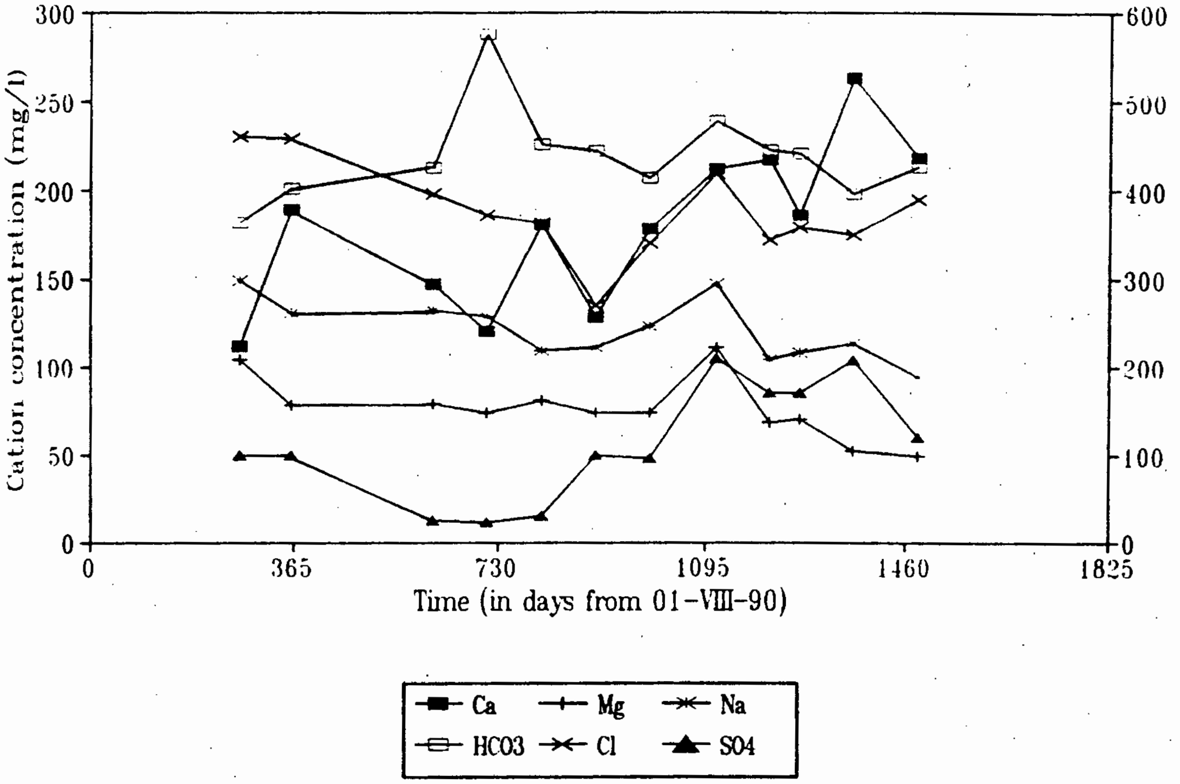


Figure 2.23. Time series plots of ion concentration in borehole REGM14 near the coal stockpile. Area code 7 ▲.

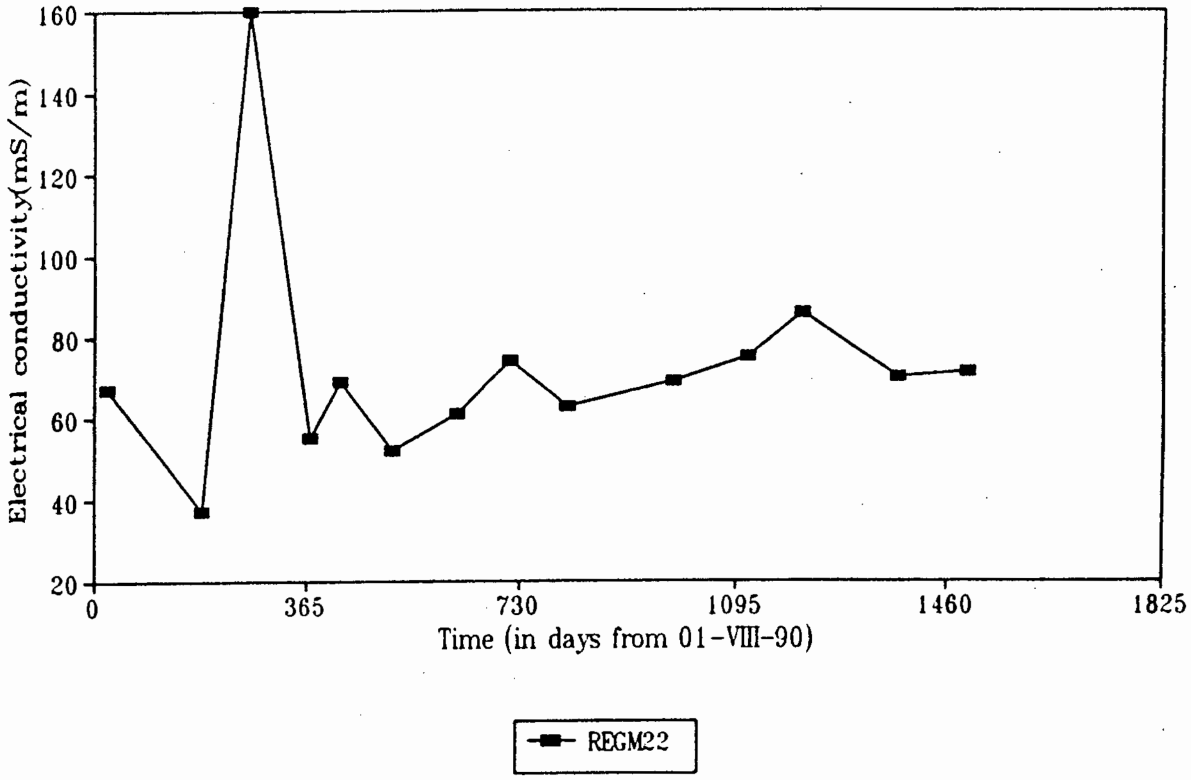


Figure 2.24. Time series plot of electrical conductivity in the boreholes at the domestic type refuse dump. Area code 8 ♦.

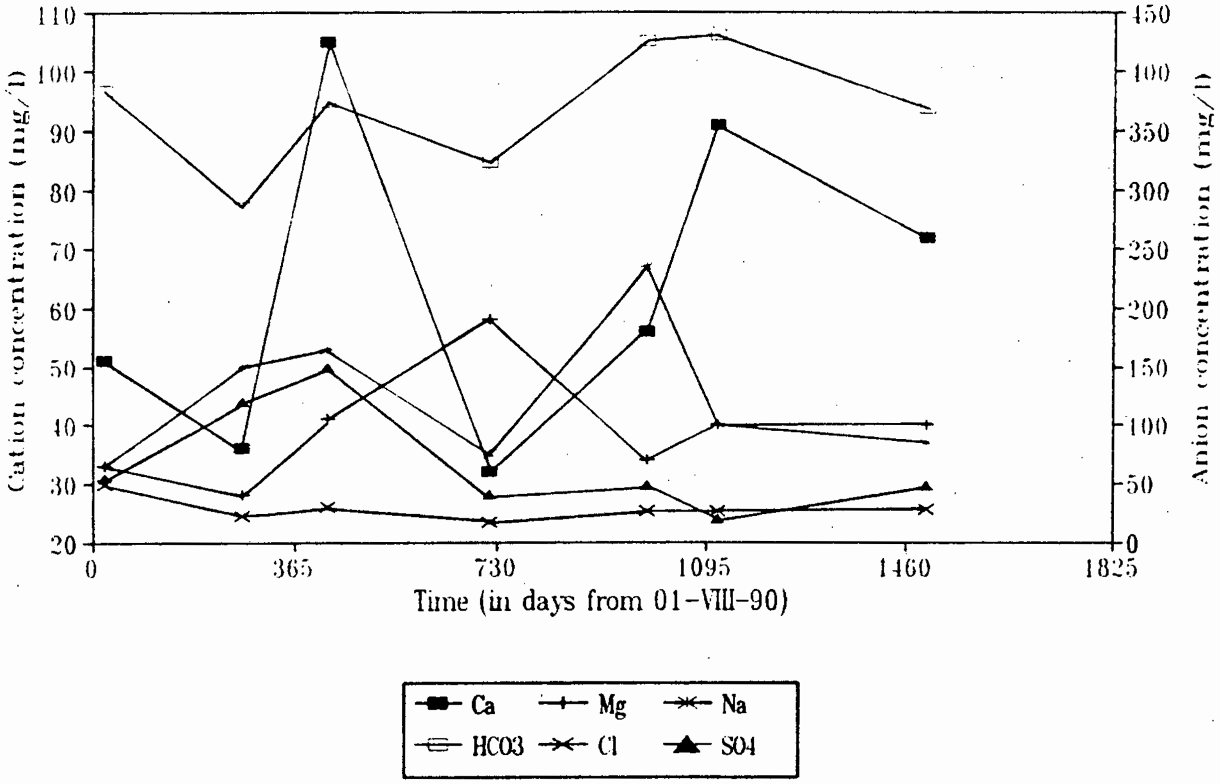


Figure 2.25. Time series plots of ion concentration in borehole REGM22 near the domestic refuse dump. Area code 8 ♦.

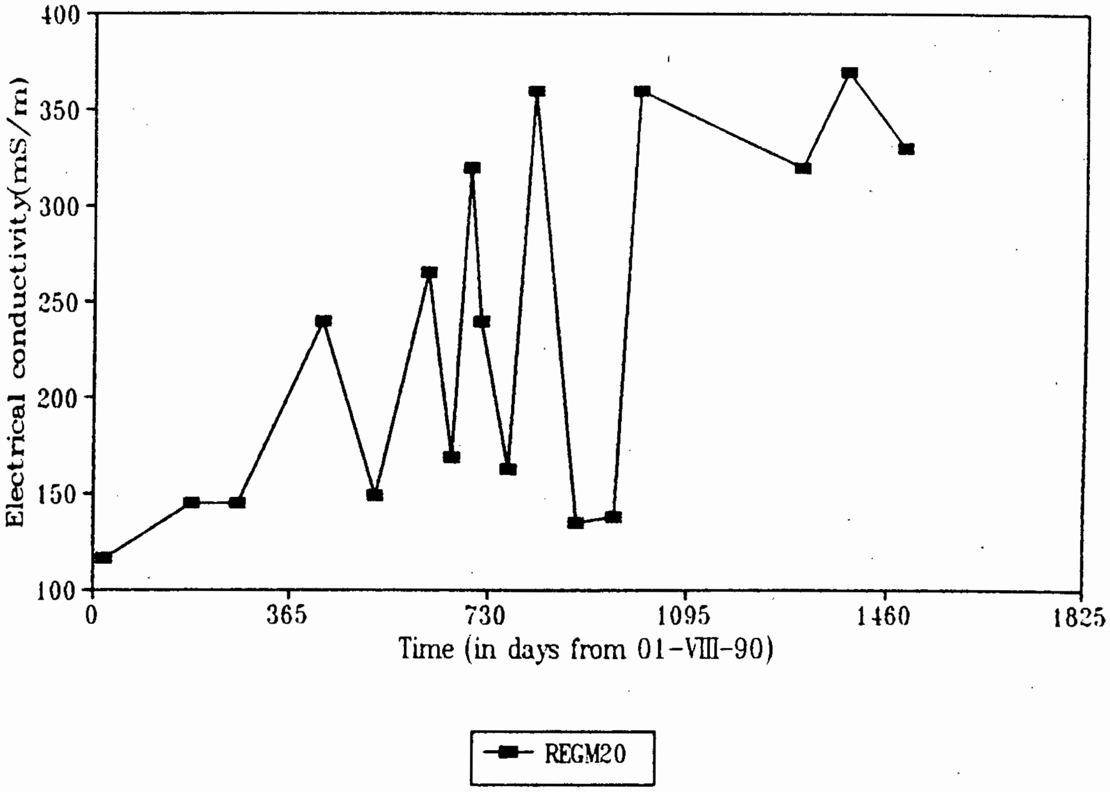


Figure 2.26. Time series plot of electrical conductivity in the borehole at the mine water reticulation dam. Area code 9 ★.

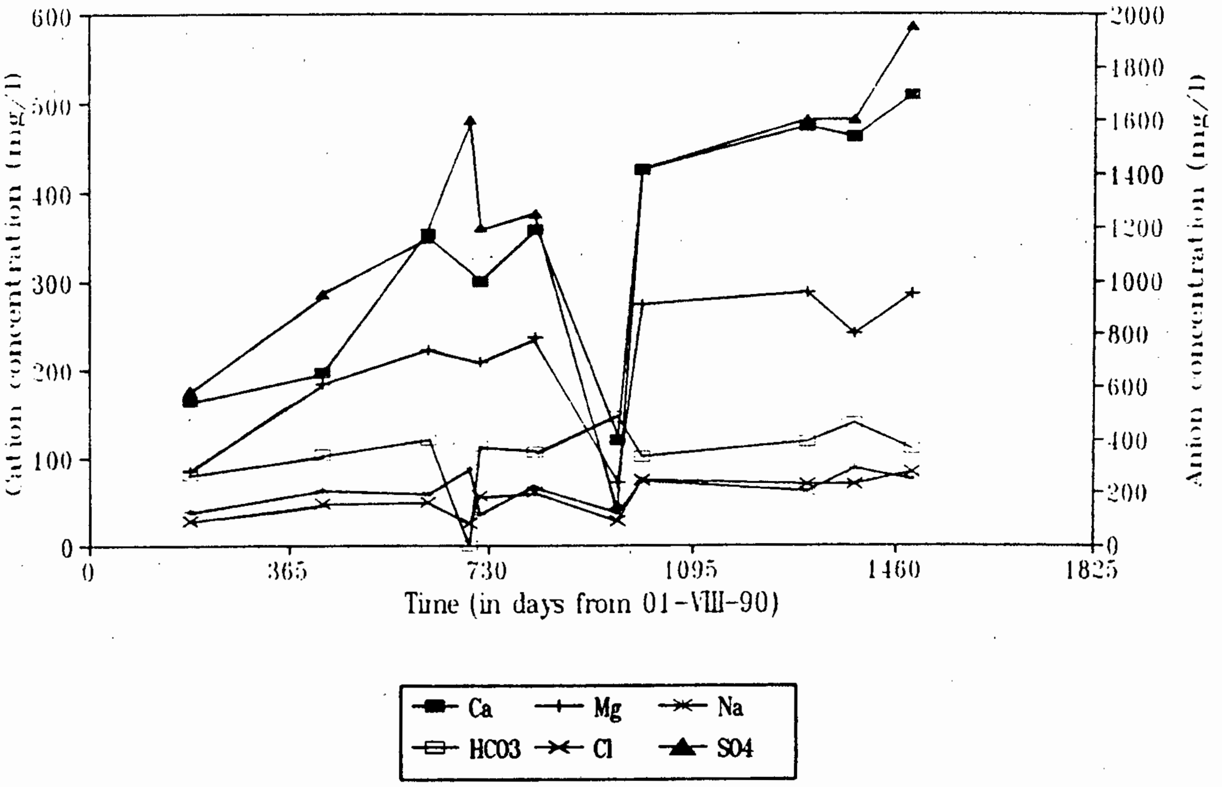


Figure 2.27. Time series plots of ion concentration in borehole REGM20 near the mine water reticulation dam. Area code 9 ★.

Table 2.5. A summary of the water quality at the ground water monitoring boreholes (REGMs) over the last four years.

Site No.	Site description	Area code & symbol		EC ($mS.m^{-1}$) Mean	EC ($mS.m^{-1}$) Std. Dev.
REGM 01	Ash water evaporation dam	1	○	228	34
REGM 02	Fine ash dam	1	○	171	65
REGM 03	Fine coal storage dam	1	○	292	62
REGM 08	Coarse ash dump	1	○	117	28
REGM 37	Black product dams	1	○	350	15
REGM 39	Fine ash dam No. 4	1	○	76	9
REGM 40	Fine ash dam No. 4	1	○	95	34
REGM 41	Fine ash dam No. 4	1	○	147	13
REGM 42	Ash water return dam No. 4	1	○	52	6
REGM 43	Ash water return dam No. 4	1	○	65	4
	Average:			*159*	*34*
REGM 16	Liquid fertilizer dams	2	□	5385	2832
REGM 17	Fertilizer reject dump	2	□	538	574
REGM 31	Liquid fertilizer dams	2	□	79	9
REGM 32	Liquid fertilizer dams	2	□	358	744
	Average:			*1590*	*1491*
REGM 18	Explosives borrow pits	3	△	192	71
REGM 19	Explosives borrow pits	3	△	174	43
	Average:			*183*	*59*
REGM 10	Water dam unit 52	4	◇	196	44
REGM 11	Water recovery division dams	4	◇	119	15
REGM 12	Water recovery division dams	4	◇	164	11
	Average:			*159*	*28*
REGM 21	Salt water dam	5	●	512	179
REGM 23	Irrigation area B	6	■	120	16
REGM 24	Irrigation area B	6	■	74	5
REGM 25	Irrigation area B	6	■	90	50
REGM 26	Irrigation area B	6	■	85	7
REGM 27	Irrigation area A	6	■	80	23
REGM 28	Irrigation area A	6	■	118	34
REGM 29	Irrigation area A	6	■	97	48
REGM 30	Irrigation area A	6	■	263	194
REGM 44	Dam 10 irrigation	6	■	271	413
REGM 45	Dam 10 irrigation	6	■	136	13
	Average:			*134*	*147*
REGM 14	Coal stockpile	7	▲	179	18
REGM 22	Domestic-type refuse dump	8	◆	72	28
REGM 20	Mine water reticulation dam	9	★	232	89

2.6.3 Data quality

The collection of samples, their preservation and transport all contribute to error. Sampling errors can, however, be kept to a minimum provided that a prescribed protocol is carefully followed. During initial design of the monitoring strategy the sampling procedures were specified and it is assumed that these have subsequently been followed correctly. It would be difficult to assess the efficiency of the sampling stage without a highly detailed investigation.

With regard to analytical accuracy, a widely accepted indicator is percentage ion balance error (%E), which approaches zero if the analysis of major ions is both complete and accurate. If variations of %E are common, then queries arise such as 'why were the samples not re-tested' or 'why has the instrumental precision not been tested'.

The efficiency of interpreting the resulting data is also a subjective judgement. Just as in the assessment of the sampling technique, a number of assumptions concerning the interpretation procedures used have to be made. Assumptions include: procedures recommended by DWAF to acquire information are the most effective method; the appropriate tools used to draw conclusions and implement decisions have the smallest margin of error to providing the wrong inference. The validity of assumptions relating to interpretation procedures has not been contended as it would require the assessment of the HydroCom database and its associated tools.

The ion balance error, %E, was calculated for the data sets as follows:

$$\%E = \left(\frac{Cations - Anions}{Cations + Anions} \right) * 100$$

Equation 2.1

The frequency histogram in Figure 2.28 shows the number of samples from the full set of over 3000 which fall into each 5 % class interval. In research laboratory only a 5% ion balance error is usually deemed acceptable (Willis, 1995; pers.com.). It is probably difficult to achieve such excellence in an industrial laboratory. Time and money constraints limit the amount of attention which can be paid to each analytical determination. In such cases 10 %E might be considered acceptable. It was calculated that 72.7 % of the analyses have fallen within the %E range of - 10 to + 10. The majority of large %E aberrations from 0 being positive (the skew of Figure 2.28).

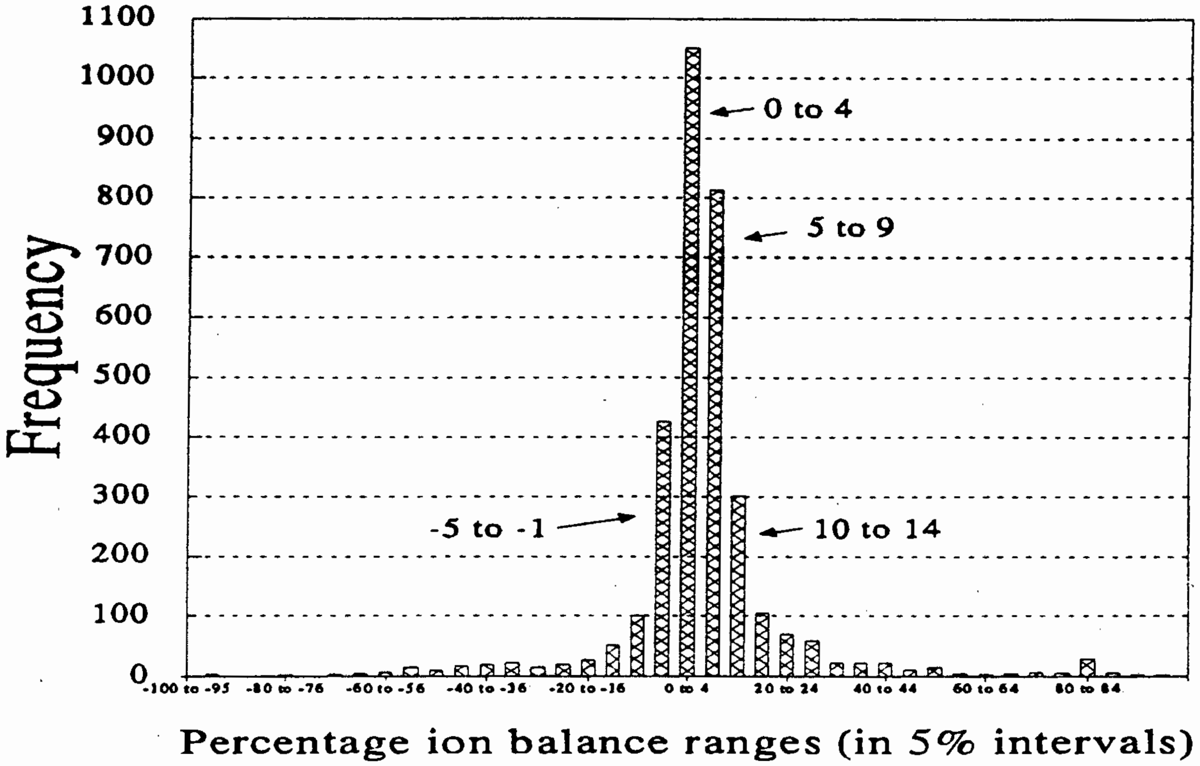


Figure 2.28. Frequency distribution histogram of the percentage ion balance error, % E, of data produced in the laboratory from 1990 to 1994. Number of samples = 3288.

The large number (27.3 %) of analyses characterized by an ion balance error of more than 10 % raises two questions:

- Has the error changed with time?
- Which analytical methods are responsible?

Figure 2.29 demonstrates that some periods, for example around July / August 1991, may be identified during which there were analytical problems which were subsequently corrected. Similarly during late-1990 a continued period of high % E (around 84 %) indicates high precision but very low accuracy in analyses. There is some indication that the 1993/4 period is less beset by erratic analysis than the earlier 1990/1 period. Even during this later period, however, the positive skewness in % E is still clearly evident.

Figure 2.30 is a time series plot of the % E irrespective of sign, *i.e.* the absolute value of % E. From a visual inspection of the plot it would appear that there is no significant improvement in analytical procedures. The slope is estimated to be (calculated from % E + 100 values to avoid the introduction of any bias) $7.08*10^{-4}$, with an R^2 value of 0.019 which indicates that the change in % E is not significant.

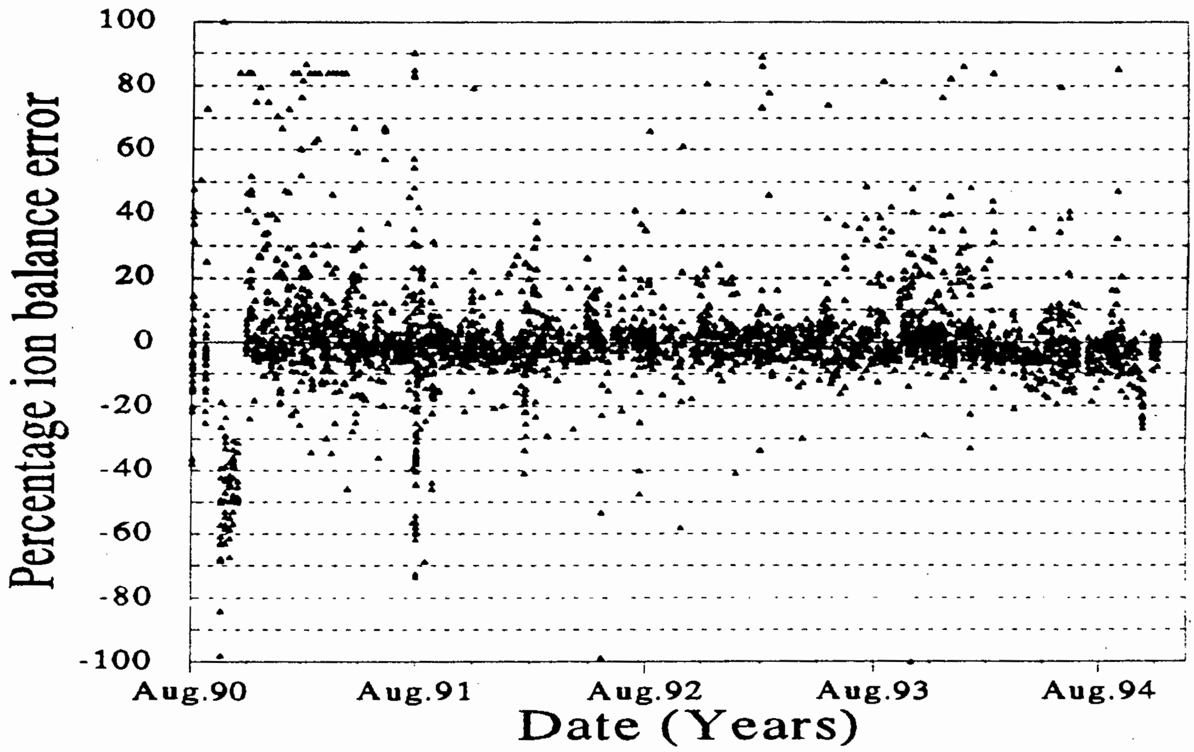


Figure 2.29. Percentage ion balance errors of results from the laboratory over the duration of the monitoring period.

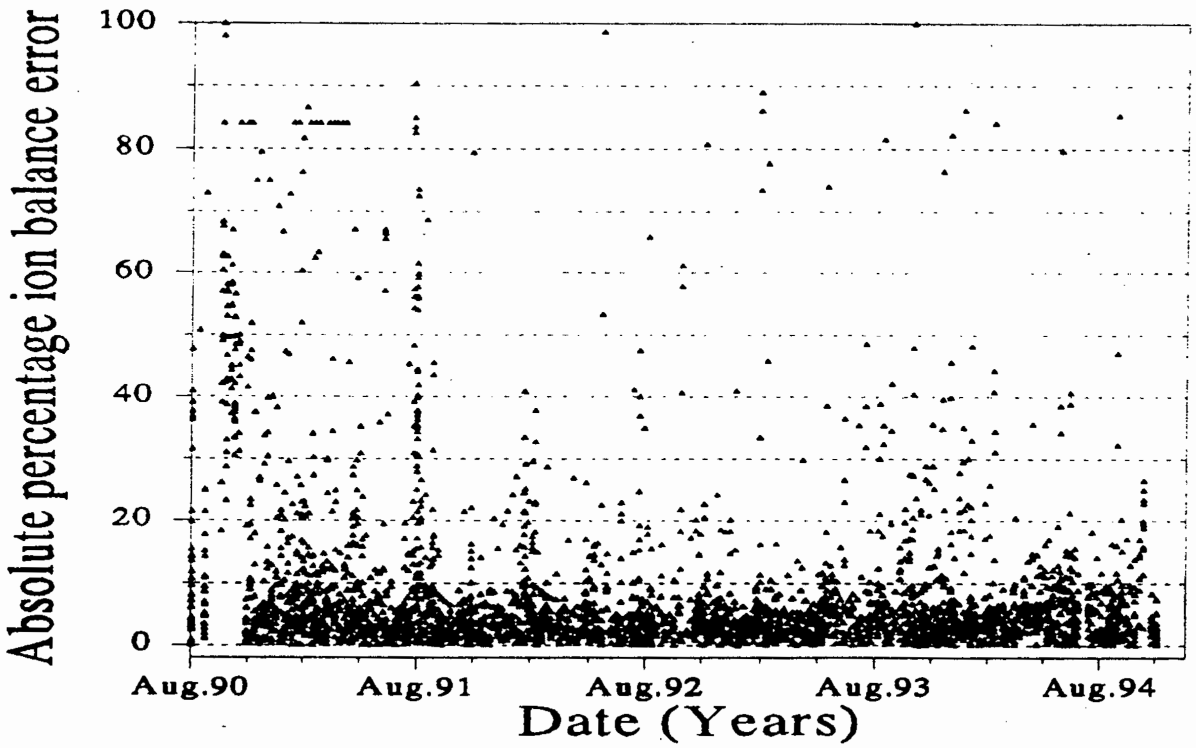


Figure 2.30. Absolute ion balance errors of results from the laboratory over the duration of the monitoring period.

Figures 2.31 and 2.32 show the concentration of individual analytes plotted against %E. The positively skewed distribution of %E shown in Figure 2.18, suggests that, in general, the analytical techniques tend to either over-estimate cation abundance or under-estimate anion concentration.

A comparison of Figure 2.31 (cations) and 2.32 (anions) suggests that cation over-estimation is a more frequent cause of charge imbalance than anion under-estimation, with Ca and, to a much lesser extent, Mg being the culprit analytes. It would, therefore, be useful to reexamine the analytical protocols for these ions in particular, in attempting to improve the quality of the data.

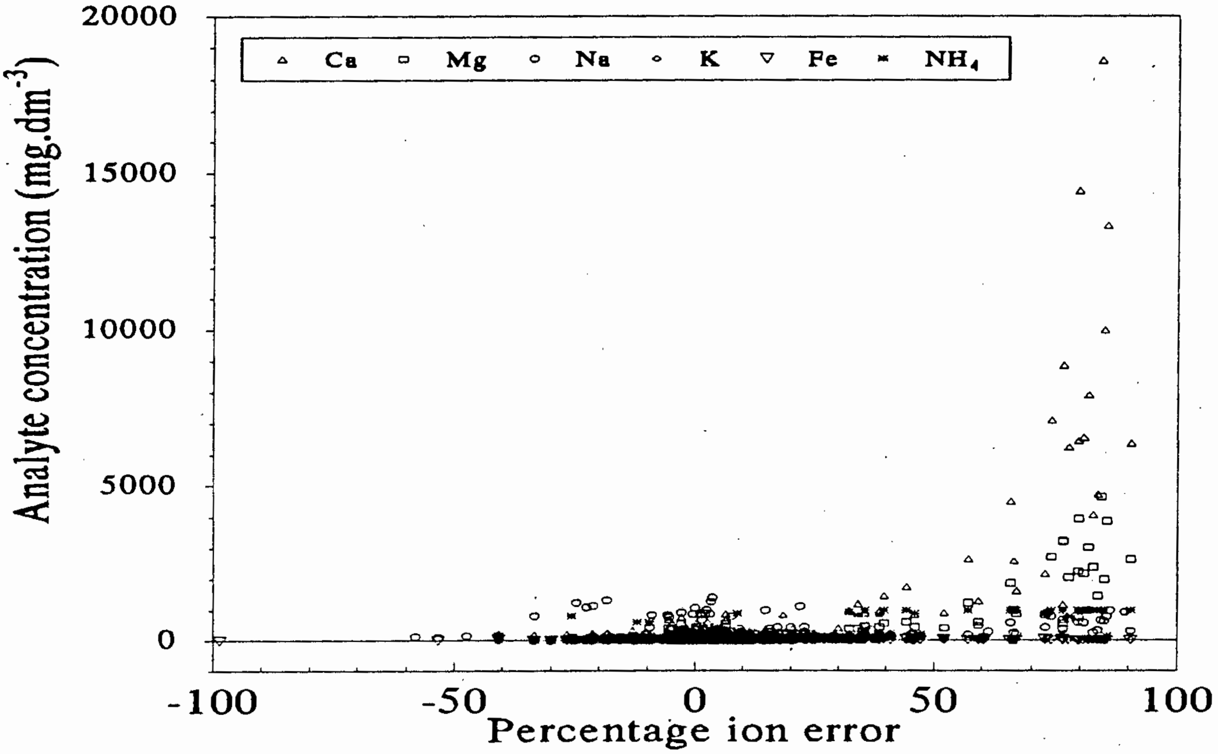


Figure 2.31. Concentrations of the dominant cations in ground water compared to the percentage ion balance error.

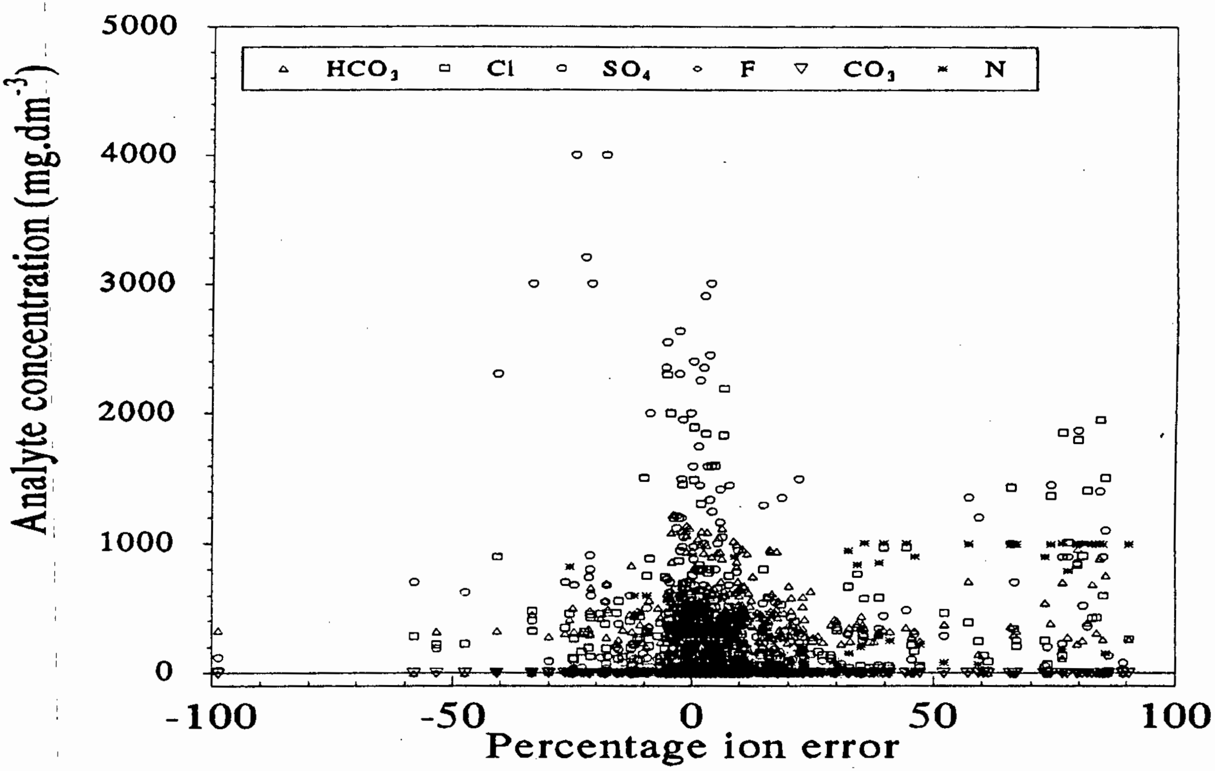


Figure 2.32. Concentrations of the dominant anions in ground water compared to the percentage ion balance error.

2.7 EVALUATION OF THE PHYSICAL DESIGN OF THE NETWORK

A useful and flexible design for a monitoring strategy is proposed by Gilbert (1987, pp. 45-57) and is termed stratified sampling. The method of stratification requires a decision, *a priori*, to divide the area or 'target population' into sub-populations. Each sub-population (stratum) is then sampled to assess environmental quality for the area which it represents. As part of Müller's (1991) report, an assessment of the relative importance of the sections monitored in the industrial area was carried out in order to best allocate monitoring resources. Although the resource allocation recommended by Müller (1991) appears to be objectively based, a number of palpably subjective decisions are involved in the scheme (LeGrand and Brown, 1990; Appendix IV) which was employed. The overall scheme is standardized and cannot be altered. The relative environmental importance of different waste operations can, however, be assessed statistically with a view to the effective allocation of resources.

2.7.1 Statistical concepts of sampling

As already mentioned, the target monitoring area can be divided into non-overlapping sub-populations. In this approach it is assumed that variability of a particular environmental parameter intra-stratum is less than inter-strata. In the model of Gilbert (1987) the total population, N, of the monitored area is divided into L strata, with sub-populations labelled N_1, N_2, ..., N_L. N therefore denotes the total potential population that could be sampled. Weightings, W, are calculated for each particular stratum (section 2.7.3.3), *e.g.* the hth stratum. The strata and criteria needed to produce weightings are listed by Müller (1991).

The nine different waste disposal sites (Figure 2.2, also in Appendix IX) constitute the strata. Gilbert (1987) states that strata can be considered as consisting of specimen units, n_h. For example, in the industrial area where ground water is monitored, the total water volume is effectively a multiple of unit (*e.g.* one cubic decimeter) water samples. The total number of sample units over all L strata is defined as:

$$n = \sum_{h=1}^{L} n_h$$

Equation 2.2

Where: n = sample population.
L = number of strata (the nine waste operations).
n_h = number of sample units within each stratum.

One objective of monitoring is to calculate the overall water quality in an industrial area using a weighted average. This is based on the assumption that stratification has been effective in delimiting relatively homogeneous strata and the weighting reflects the differing impacts the waste operations have on the individual sub-populations. The concept can also be used to review a monitoring network design. Information obtained in an initial impact assessment is used as a feed-back mechanism to modify the monitoring strategy by correcting the environmental rating of the nine areas monitored. It is difficult to apply these concepts to surface water monitoring as fluvial water has a short residence time in the area of concern. In the case of ground water quality, the target population (N) is therefore equivalent to, or synonymous with, all the ground water associated with the area over time. In order to monitor the target population every unit (say dm^3) water in the area would be collected and analyzed during every sampling event. Clearly, only a sample population, n, is taken from the target or total population, N.

2.7.2 Stratification of the monitoring area

Ideally, spatial statistical examination of the area monitored should be influenced by the relative environmental importance of the different waste operations. Not only is the likelihood of contamination important but also the severity of the pollution and the capacity of the locale to absorb it.

The 'prioritization' performed by Müller (1991) on the potential pollution sources was based on an integrated evaluation of all the information generated in the initial risk assessment. Although Müller describes the prioritization as inadequate and incomplete due to lack of information, he does provide criteria and data to rate the waste operations and to clearly stratify the zones. He stresses that the prioritization scheme is dynamic and will tend towards an optimum as more information becomes available. Updating the rank of potential pollution sources has, however, not yet been carried out and will be attempted in the ensuring sections.

2.7.2.1 Environmental significance of the monitored zones

The initial integrated evaluation (Müller, 1991) was completed by the utilization of an alpha-numeric rating system applicable to waste disposal sites or potential pollution sources. The system was developed for the U.S.EPA by LeGrand and Brown (1990; Appendix IV). The prioritization can be described as a semi-objective classification which is less prone to bias than the method proposed by the DWAF (1994a). The DWAF recommend the formation of a multi-disciplinary committee (including academics and representatives from the community) to classify waste disposal sites.

The U.S.EPA system uses a rating system which focuses on weighting physical features in the vicinity of the contamination source. This produces clear and concise definitions but there is some subjectiveness attached to the scheme (Appendix IV). Numerical values are assigned to four key geological and hydrological characteristics which are combined with letters referring to the type and condition of the waste.

The numerical and alphabetic values are together describe the relative contamination potential and acceptability and permit the location of the waste site in a matrix diagram of aquifer sensitivities and contamination spread. From this a situation rating can be calculated, which is a numerical value pertaining to a general description of the site and the waste (Table 2.6 and Appendix IV). The relative importance of the sites can then be considered and the waste zones ranked. The scheme used to calculate the situation ratings does not include all the environmentally important criteria. Müller (1991) did not determine the situation ratings in the same categorization of monitoring areas as is used in this study as the network has evolved since the initial impact assessment, therefore some have had to be inferred (explanatory notes of Table 2.6).

Table 2.6. The stratification of potential pollution zones (Müller, 1991).

Name of zone monitored	Area code & symbol	Situation rating (Müller, 1991)
Liquid fertilizer dams	2 □	+ 8
Explosives area (1)	3 △	+ 8
Water recovery dams (2)	4 ◇	+ 5
Black product dams & ash dumps (3)	1 ○	− 1
Salt water dams	5 ●	− 3
Irrigation areas	6 ■	− 6
Mine water dams	9 ★	− 6
Coal stockpiles (4)	7 ▲	− 6
Domestic type refuse (5)	8 ♦	− 6

Explanatory notes:

(1) The explosives dump is very close to the fertilizer disposal site and so the physical features are considered to be similar. The nature of the pollution is also very similar.

(2) There are several water recovery dams with slightly different effluents. The characteristics of the most severe waste, the worst case scenario, have been used.

(3) The black product dams and the ash dumps are situated in the same area and are therefore classified together.

(4) No evaluation of the coal stockpiles was done, but such solid material was classified as not posing as great a threat as the liquid disposal sites. The chemical behaviour of coal pile leachate is likely to be similar to that of the mine water.

(5) No evaluation of the domestic refuse dump was done. Although rubbish dumps can be highly hazardous pollution sources the monitoring operation is concerned with the impact from the industry and the landfill is relatively inert and unimportant. It is also fairly well separated from the other disposal sites.

2.7.3 The use of multiple criteria analysis

A key question when considering the allocation of resources is the relative environmental importance of the waste operations. In order to address this problem a number of criteria need to be considered. The report compiled by LeGrand and Brown (1990) uses a series of criteria to provide a rating of a site. The U.S.EPA method, however, does not produce a definitive scale of the environmental importance of the nine waste operations. A variety of criteria should be considered when estimating the relative impact of a site. Some of these criteria are used by LeGrand and Brown (1990) but there are also others. In order to consider the many factors simultaneously and the weightings attached to each criterion, the present study made use of a 'multiple criteria decision analysis' (MCDA) programme. [1]

The resulting aggregated criteria produced a weighted score for each site. The statistics explained in Gilbert (chapter 5, 1987) show how weightings can be used in the allocation of sampling sites. The expense incurred in drilling a borehole, however, is far greater than the cost of sampling. The sampling technician will be under pressure to 'produce results' from commissioned wells if they are in operation. The weighted scores can, nevertheless, be used to identify a number of aspects relating to the monitoring strategy:

- Whether the allocation of sampling locations to the waste operations was done correctly in the past, using professional judgement;
- What the importance of a waste operation is in affecting the environment and therefore how often the boreholes around the site should be sampled;
- How much attention should be given to the samples taken from each waste site *i.e.* what analyses the samples should be subjected to;
- When reporting composite information on the water quality of the area monitored, how average values should be calculated. Clearly, the waste operations with worst pollution will have the greatest effect on overall environmental quality.

---

[1] In use of MCDA for the thesis the advice of Professor Theo Stewart, Head of the Department of Statistical Sciences at the University of Cape Town is gratefully acknowledged.

2.7.3.1 Weighting the different waste sites

There are nine waste sites in the monitoring area (Figure 2.3). Each has its own environmental significance pertaining to the likelihood of pollution and the impact of any subsequent contamination. If weightings can be attached to the sites then it should be possible to efficiently allocate resources which includes time, effort, expertise and ultimately money. The problem is to identify the criteria which should be used to produce a weighting for each site and how these criteria should be integrated to produce an overall score for each waste operation.

The method which was followed in addressing this problem is outlined by Goodwin and Wright (1991); and was implemented using the Visual Interactive Sensitivity Analysis (VISA, 1994) computer programme. The procedures required for the effective use of MCDA (Stewart, 1995; pers.com.) are as follows:

1. Define criteria with explanations.
2. Rank all sites (on an ordinal scale) in terms of each criterion. This makes it easier to complete the next stage, which is the most subjective part.
3. Assign units of an interval scale to each site (Table 2.8). An interval scale is where one unit represents an equal degree of change in environmental importance. For example, an increase in distance (to the nearest river) from 1 to 10 m has the same environmental significance (in terms of not polluting a water course) as an increase from 1000 to 2000 m (Table 2.7).
4. Use the VISA computer algorithm to adjust the weightings applied to each criterion and to calculate the aggregated scores for each type of waste disposal site. This allows an assessment of the sensitivity of the different operations to the adjustment of weightings applied to the criteria.
5. A judgement can then be made on is the best allocation of weightings which does not make the aggregated score aberrant.

Table 2.7. Interval scales for environmental criteria devised for use in MCDA from the U.S.EPA document (LeGrand and Brown, 1990). Abbreviations are described below.

CRITERIA SCORES	Distance from site to water supply (m)	Depth to water table below (m)	Water table gradient to supply	Thickness of uncon. material (m)	Clay (%)	Risk	Accept. of pollution	Mobility of pollution
100	2000 +	150 +	Away	50 +	100	Beneficial		Solid
90	1000-2000	60-149		45-50			Prob.accept.	
80	300-999	30-59	Flat	35-40	50	Rel. Low		Sludge
70	299-150	20-29		30-35			Margin. unaccept	
60	75-149	12-19	< 2% n.f.d	25-29	15-30	Mod. Low		
50	50-74	8-11		20-24			Accept. uncertain	
40	35-49	5-7	< 2% f.d	15-19	< 15	Mod. High		
30	20-34	3-4		10-14			Margin. accept.	
20	10-19	1.5-2.9	> 2% n.f.d	5-9	F. sand	High		
10	5-9	0.5-1.4		0.5-5			Prob. unaccept	
0	0-4	0-0.4	< 2% f.d	0-0.4	C. sand	Extre. High		Liquid effluent

Abbreviations:
n.f.d. indicates the water table gradient is not in the flow direction.
f.d indicates the gradient is in the flow direction.
F. and C. represent fine and course when referring to sand.
Rel. (Relative), Mod. (Moderate), Extre. (Extremely), Prob. (Probably), accept. (acceptable), Margin. (Marginal) and unaccept. (unacceptable).

Table 2.8. Scores assigned to the environmental criteria for each waste operation under the schedule listed in Table 2.7 and using the information in Müller (1991).

CRITERIA SITES		Distance from site to water supply (m)	Depth of water table below (m)	Water table gradient	Thick. of uncon. material (m)	Clay (%)	Risk	Accept. of pollution	Mobility of pollution
Ash / B.P	1○	90	10	40	20	100	20	50	80
Fert.	2□	70	20	0	10	60	0	50	0
Explo.	3▵	70	20	0	10	60	0	50	0
Water Rec.	4◇	70	20	40	20	100	40	30	0
Salt water	5●	70	10	40	20	80	40	50	0
Irri.	6■	80	40	40	10	80	60	70	20
Coal S.P.	7▴	70	50	0	10	60	60	70	100
Refuse pit	8♦	80	40	40	10	80	60	70	100
Mine water	9★	70	50	0	10	60	60	70	0

2.7.3.2 Explanations of the criteria

Explanations of the criteria listed in Tables 2.7 and 2.8, and the assumptions associated with then are as follows:

(i) *Distance from the waste operation to the nearest water supply.* This is derived from Müller (1991), who measured actual distances to the nearest well, borehole or stream. The interval scale is extracted from LeGrand and Brown (1990).

(ii) *Depth of water table below the site.* Müller (1991) estimated the 'water table height at more than 5% of the year', which is assumed to be the average depth of the water table in the annual 95% percentile, and produced interval values from the U.S.EPA interval scale.

(iii) *Water table gradient from the waste disposal area.* This is the hydraulic gradient which includes the hydraulic conductivity and the flow direction. The values are from Step 3 of Müller's report following U.S.EPA specifications.

(iv) *Thickness of unconsolidated material.* This criterion is essentially a representation of pollution retardation. Müller (1991) used thickness and particle size distribution to classify the solum under the disposal site. The U.S.EPA scale of metres was adapted to an interval scale by assuming an equal benefit for every successive 5 m of homogeneous regolith.

(v) *Percentage clay.* The attenuation by clay colloids makes this an important criterion. An interval scale was constructed based on U.S.EPA criteria.

(vi) *Risk, the degree of seriousness.* This is an interval scale from beneficial to extremely serious. It takes into account the sensitivity of the aquifer to contamination and the nature of the hazard.

(vii) *The acceptability of pollution.* This is a somewhat arbitrary classification adapted from Müller's report. It represents a combination of the potency of the waste and the likely impact it would have on the environment. It has been adapted from the situation rating and the par value in Step 9 of the U.S.EPA document.

(viii) *The mobility or inertia of the waste.* This is a manifestation of the phenomenon that wastes of low viscosity and low head will move slowly causing less contamination and *vice versa.* It is a subjective weighting.

The following three criteria were not considered to be applicable to this monitoring network and are not, therefore, included in Tables 2.7 and 2.8.

(ix) *Distance from disposal site to nearest settlement.* The region surrounding the industrial area is mainly rural apart from the town to the north. Ground water flows away from the town at all waste disposal sites. At settlements further downstream the individual impact of the sites causing pollution will effectively be the same when only considering distance from source. Hence distance to habitation is not a relevant criterion in the evaluation of this monitoring network.

(x) *Dilution factor of the contamination into the underlying aquifer.* This was a difficult criterion to select. The area has very different wastes, so the amount of leachate (from an effluent dam or a solid stockpile) is very hard to gauge and the amount of dilution is difficult to estimate. There will be varying lag times for plume migration, and varying mixing. Plumes often displace ground water rather than mix with it. Due to the many complications it was considered expedient and assumed that the scores for each site are equal.

(xi) *Rainfall dilution.* This is the same over the whole area and works out to be about 3% of the total annual precipitation (Hodgson, 1995; pers.com.). This criterion would only need to be considered if there was a gradient in precipitation over the area monitored.

2.7.3.3 Discussion and conclusions from the use of MCDA

It can be argued that the MCDA method of providing a conclusive answer from a data series is subjective and biased by personal judgement. The method allows for decisions to be based on a number of smaller separate decisions made initially for each criterion. Some of the scores applied to sites for criteria can be objectively calculated, such as a distance or a percentage (Table 2.7). There may be some subjectivity due to the classification of an interval scale for a criterion. The interval scales used in this discussion have, however, been drawn from a credible document (LeGrand and Brown, 1990). The author is therefore satisfied that the scores for the waste operations using each criterion are probably the best representations available. It is accepted, nevertheless, that the weightings of the criteria are strongly influenced by personal judgement. MCDA is increasingly being used to address decisions which are not based on a quantitative scale. It is an efficient method, useful for complex tasks, in which criteria can be added to account for remedial actions and mitigating measures implemented by the EMU to change the impact of the various waste operations.

The criteria for decision analysis can be divided into three main types: those pertaining to the characteristics of the water around the site (i, ii & iii); those concerned with the physical nature of the regolith underneath the waste operations (iv & v); and the last three which relate to minor decisions with regard to the type of waste, the area it might damage and the acceptability of pollution (vi, vii & viii). Before weights were assigned to the criteria, careful consideration was given to the relative importance of the decisions themselves. The method of ranking the criteria and then assessing the importance of criteria individually was completed in the manner described by Goodwin and Wight (1991). This also involved consideration of the environmental protocol practised by the EMU. The concern of the EMU is not so much with the environmental quality within the confines of the perimeter fence but with what pollution is emitted (via air or water) from the industrial area. The author, therefore, considers that the primary concerns of the EMU with regards to the monitoring strategy are:

- the aquifer sensitivity to pollution;
- the hazard potential of the waste;
- the degree of acceptability if a pollution event occurs and
- the mobility or inertia of the contaminant depending on the physical nature of the waste and the confines in which the waste is stored.

The waste related criteria were, therefore, given the largest weightings. The attenuation of pollution is considered to be the second most important criterion, and estimates of the weightings were made accordingly (Figure 2.33a). After the first aggregate source had been calculated (left-hand section of Figure 2.33a) the weightings were revised in order to assess the sensitivity of the aggregate scores to the change in criterion weight (Figure 2.33b). A third arrangement of weightings between the criteria is demonstrated in Figure 2.33c.

What is clear from Figures 2.33a, b & c is that the rank *order* changes very little with different weightings on the criteria. The *spacing* of aggregated scores between waste locations, however, does vary. Considering the concerns of the EMU and the clear separation produced by the higher weighting of waste related criteria (Figure 2.33a) the first set of weightings was chosen as representing values of the relative environmental importance of the nine waste operations.

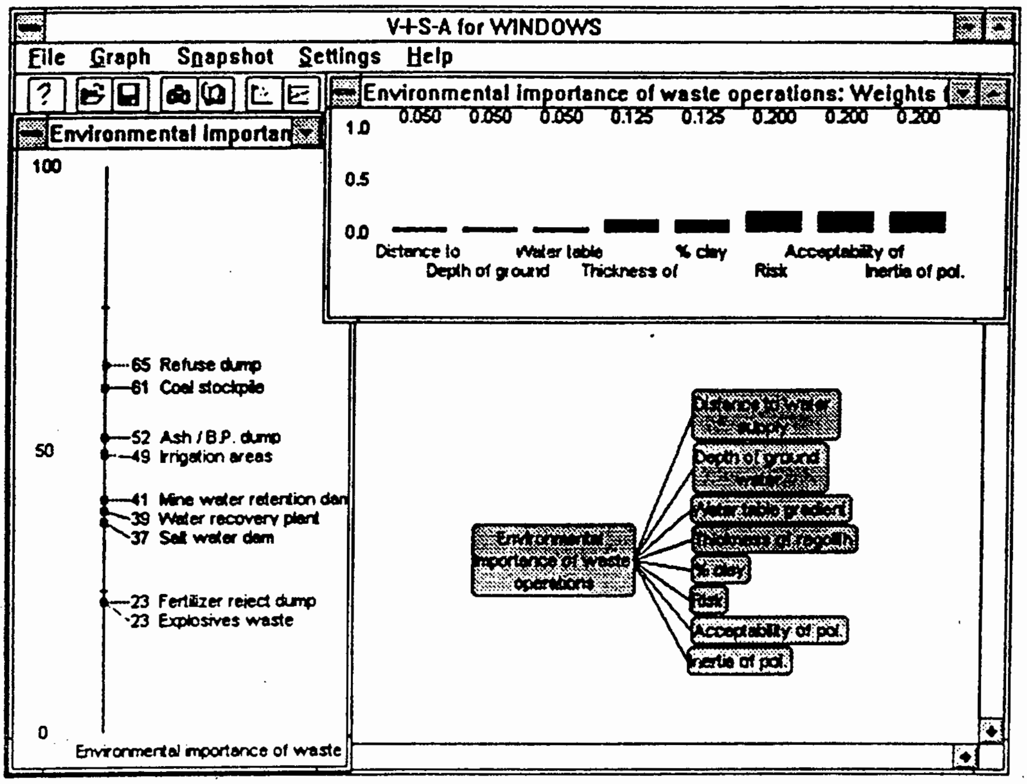


Figure 2.33a. Aggregate scores of environmental importance criteria for the nine waste operations with preferential weightings given to factors pertaining to the nature of the waste. (criteria vi to ix)

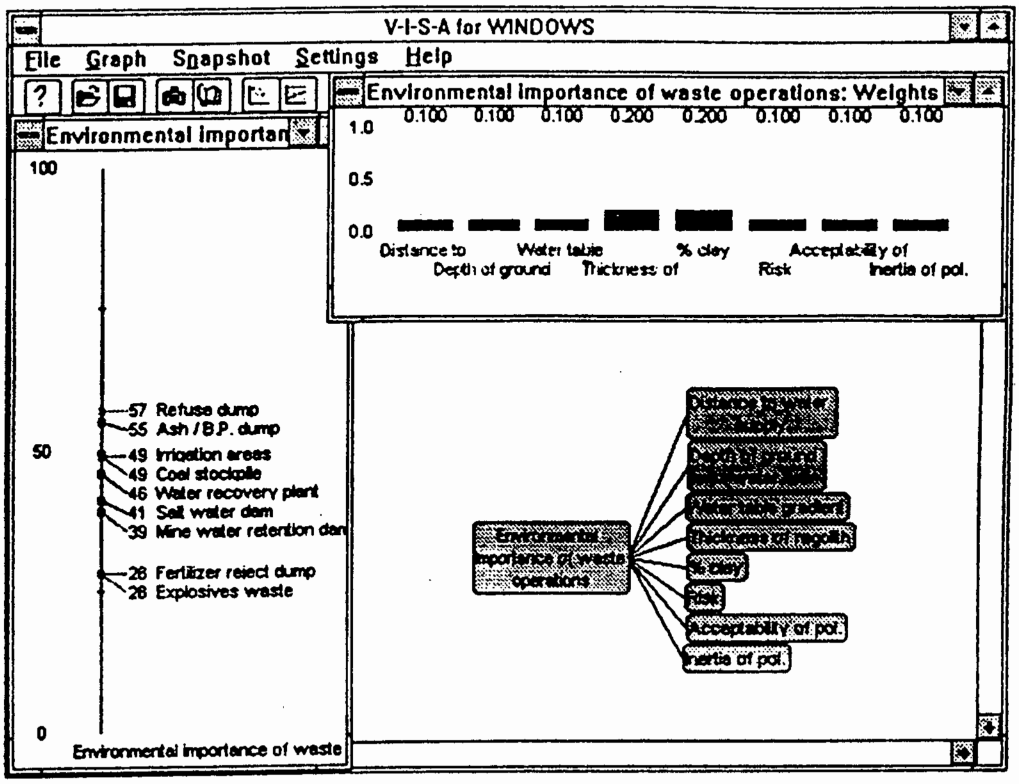


Figure 2.33b. Aggregate scores of environmental importance criteria for the waste operations, more weighting given to factors regarding to the soil. (Criteria iv and v).

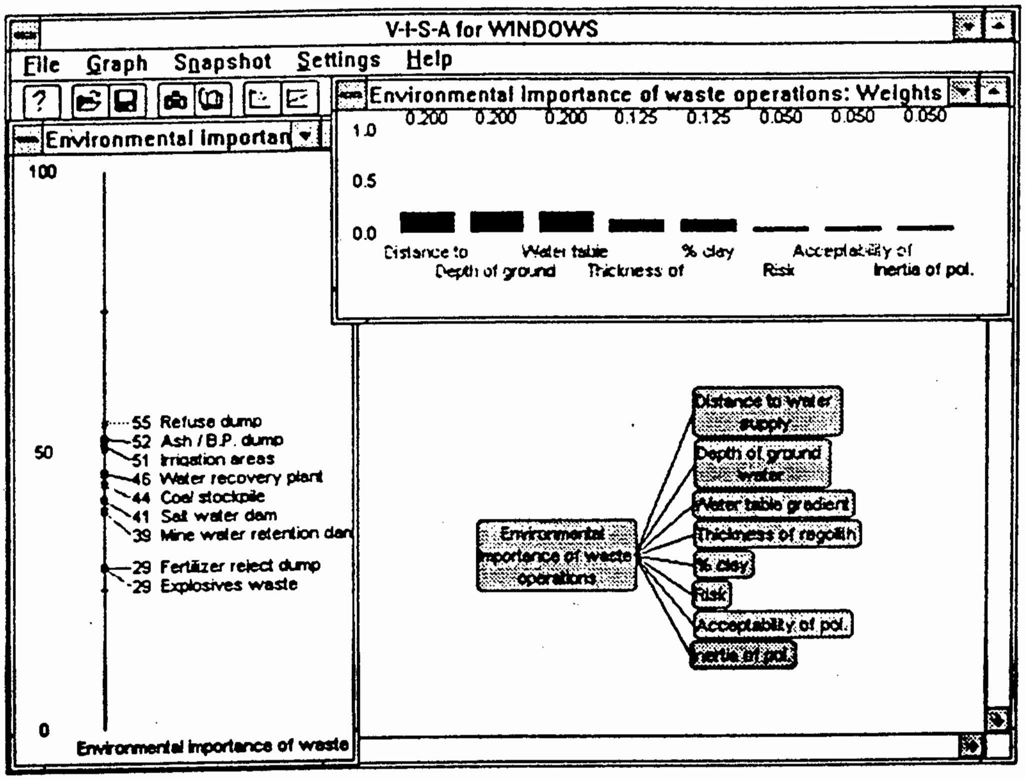


Figure 2.33c. Aggregate scores of environmental importance criteria for the nine waste operations with preferential weightings given to factors pertaining to the nature of the surface and ground water surrounding the sites. (Criteria i to iii).

The aggregate scores enabled relative environmental weightings to be calculated as fractions of the total score, shown in Table 2.9. Scores for the sites were obtained by MCDA and are the highest for the best waste operations, *i.e.* the areas with the smallest environmental impact. With respect to the allocation of resources, the most attention needs to be given to the operation with the largest impact. Weightings were accordingly calculated for use in statistical allocation procedures. These weights could be used in many other environmental management decision tools, such as estimating the water quality of the entire area using a weighted average.

Table 2.9. Weightings calculated from MCDA for the nine waste operations.

Name of zone monitored	Area code & symbol	Aggregated score (MCDA)	100 - Ag. score	Weighting
Liquid fertilizer dams	2 □	23	77	0.151
Explosives area	3 △	23	77	0.151
Salt water dams	5 ●	37	63	0.124
Water recovery dams	4 ◇	39	61	0.120
Mine water dams	9 ★	41	59	0.116
Irrigation areas	6 ■	49	51	0.100
Black product & ash dumps	1 ○	52	48	0.094
Coal stockpiles	7 ▲	61	39	0.077
Domestic type refuse	8 ◆	65	35	0.069

The relative order of the nine waste operations is slightly different from the one estimated by Müller (1991; Table 2.6). The MCDA environmental rating (Table 2.9) should be more reliable since more criteria have been considered and more attention has been given to individual decisions.

2.7.4 Use of statistical analysis to allocate sampling resources

The weightings determined by MCDA may be used to provide a quantitative stratification of the waste zones monitored in the area around the industrial plant. Quantifying the environmental significance of each zone allows for a statistical assessment to be made of the monitoring strategy. The purpose of this section is to provide a summary of the statistical approach described by Gilbert (1987) and to apply this approach to the task of devising a sampling strategy for the monitoring area.

2.7.4.1 Descriptive statistics for the whole area

For a given environmental variable (with its associated weighting) in a certain stratum its importance over the whole industrial area can be assessed. This assessment includes the determination of mean values in addition to the development of inventories of chemical abundance at specific localities. Means can be calculated for each stratum to give an estimate of the whole target population.

Stratification of the monitored area has achieved a definition of monitoring zones in terms of various criteria (section 2.7.3.3). From these zones or strata samples are collected on a regular basis. According to Gilbert (1987), if the sample populations in each stratum are n_1, n_2, to n_L, an unbiased estimator, $\bar{x}_{st}$, of the true mean, μ, of the total population (*i.e.* over the whole monitoring area is) can be obtained by the relation:

$$\bar{x}_{st} = \sum_{h=1}^{L} W_h \bar{x}_h$$

Equation 2.3

in which W_h is the weighting factor associated with the *h*th stratum (Table 2.9) and $\bar{x}_h$ is an estimate of the *h*th stratum mean (Tables 2.3 and 2.4). $\bar{x}_{st}$ is a weighted mean, the weights (W_h) representing the relative importance of the strata or monitored operations.

In the context of the present case study, the sampling can be assumed to be random even though samples are taken at regular intervals (McNeill, 1995; pers.com.), since water quality characteristics will be determined by random interaction of the physical environment with sporadic disposal activities of the industrial plant (section 3.2.3). Because only a portion of the population over the entire area has been measured in each stratum, the weighted mean $\bar{x}_{st}$ has a variance associated with the random sampling procedure which can be calculated as:

$$s^2 = \sum_{h=1}^{L} \frac{W_h^2 s_h^2}{n_h}$$

Equation 2.4

in which, n_h and s_h are the sample population and variance, respectively, in the *h*th stratum. This represents an estimate of the standard error associated with sampling.

2.7.4.2 Allocation of samples by pre-specified criteria

Before allocating the number of samples to be taken from each waste operation (stratum), the total number of samples required from the monitoring area must be ascertained. In statistical terms, this is the total number of sample units, n (one sample unit is designated to be one 1 dm^3 water sample) required to achieve satisfactory results either at a pre-specified cost, variance or margin of error. The use of these criteria will be explained more fully in the ensuing sections.

(i) Fixed cost

If the budget, C, for sampling is fixed *a priori*, it will limit the number of samples. The unit cost, c_h, of samples in the hth stratum is, in this case, assumed to be constant. The standard deviation, s_h, for the hth stratum can be estimated from prior studies, following which the sample number can be obtained as:

$$n = \frac{C \cdot \sum_{h=1}^{L} \left(\frac{W_h s_h}{\sqrt{c_h}} \right)}{\sum_{h=1}^{L} (W_h s_h \sqrt{c_h})}$$

Equation 2.5

(ii) Variance

In designating the monitoring strategy, an alternative basis to the use of cost might be specify an acceptable standard deviation of the results. If the variance associated with the weighted mean, $\bar{x}_{st}$, is assigned a pre-specified value, V, then n can be computed, on the assumption that sample allocation is proportional to the weighting, as:

$$n = \frac{\sum_{h=1}^{L} W_h s_h^2}{V + \frac{1}{N} \left(\sum_{h=1}^{L} W_h s_h^2 \right)}$$

Equation 2.6

in which N is the target or total population (*i.e.* the volume of potentially polluted water in the aquifer).

(iii) Margin of error

Rather than specifying the variance, it may be preferable to specify a tolerable margin of error, d, and an acceptable probability, α, of being exceeded. The objective is then to choose a sample population, n, such that *probability* $[\ |\bar{x}-\mu| \geq d\ ] \leq \alpha$. Where $\bar{x}$ is the mean of the n data collected and d is defined as $|\bar{x}_{st} - \mu|$. Both d and α are therefore pre-specified. As was the case with pre-specified variance, it is assumed that samples are allocated to monitoring zones in proportion to weighting factors and that $\bar{x}_{st}$ is normally distributed. The sample population is then given by:

$$n = \frac{Z^2_{1-\alpha/2} \sum_{h=1}^{L} \left(\frac{W_h\ s_h^2}{d^2} \right)}{1 + Z^2_{1-\alpha/2} \sum_{h=1}^{L} \left(\frac{W_h\ s_h^2}{d^2\ N} \right)}$$

Equation 2.7

in which $Z_{1-\alpha/2}$ is the standard normal deviate which cuts off $(100\,\alpha\,/\,2)\,\%$ of the upper tail of a standard distribution (obtained from Appendix A of Gilbert, 1987). For example, if $d = 10\,\text{mg.dm}^{-3}$ and $\alpha = 0.05$, a value for n must found so that there is only a $100\,\alpha = 5\%$ chance that the absolute difference (positive or negative) between the estimate $\bar{x}$ (obtained from the n data to be collected) and the true mean μ is greater than or equal to $10\,\text{mg.dm}^{-3}$.

2.7.4.3 Calculation of descriptive statistics

A common requirement by regulatory bodies is a complete hydrochemical description of water quality in an industrial area. Sometimes a simple average is reported but in the case of the present monitoring network it is obviously preferable to use a weighted average based on the relative impact of the different waste operations. The weighted mean and variance for the TDS load (as EC) associated with the monitoring of each waste operation are shown in Table 2.10 alongside weighting coefficients used to calculate the weighted average for the area as a whole.

Table 2.10. Mean electrical conductivity ($mS.m^{-1}$) and variance in ground water of the entire industrial area. (Table 2.4 has a breakdown of the EC in each area).

Name of zone monitored	Area code	EC ($mS.m^{-1}$) Mean	Variance	Weighting
Liquid fertilizer dams	2 □	1590	1491	0.151
Explosives area	3 △	183	59	0.151
Salt water dams	5 ●	512	179	0.124
Water recovery dams	4 ◇	159	28	0.120
Mine water dams	9 ★	232	89	0.116
Irrigation areas	6 ■	134	147	0.100
Black product dams & ash dumps	1 ○	159	35	0.094
Coal stockpiles	7 ▲	179	18	0.077
Domestic type refuse	8 ♦	72	28	0.069
	Simple average:	*358*	*230*	
	Weighted average:	*424*	*291*	

2.7.4.4 Allocation of samples to strata

Gilbert (1987) describes the procedures for choosing the number of samples per stratum, n_h, that will optimize the monitoring network. The methods first calculate the total number of samples to be collected per year in terms of specified criteria. This number can then be allocated to the operations in one of two ways:

(i) Simple allocation, solely using the environmental weight assigned to the strata.

(ii) The so called Neyman allocation, which combines the weighting with the variance of an *a priori* data set. This attaches greater importance to the variability of the analyte, *i.e.* how often pollution events are detected.

It is assumed that the cost of sampling is the same in every stratum or disposal zone monitored. If this were not the case, Gilbert (1987) describes a sample allocation formula that accounts for different sampling costs in different areas. In reality the cost of collecting samples will probably vary for simple reasons (such as varying distances for the sampling technician to travel) in addition to more subtle costs (for example, time taken to collect the sample once the technician is at the site). To consider varying costs, in addition to fixed costs, a detailed financial audit of the monitoring strategy would have to be completed. This would probably require a full assessment over at least a year and so has not been attempted in the present study. The total cost is obtained by:

$$C = c_o + \sum_{h=1}^{L} c_h n_h$$

Equation 2.8

where c_h is the cost per population unit (*i.e.* the cost of taking one sample) in the *h*th stratum and c_o is the fixed overhead cost. The accounting department of the industrial plant considers the costs of the monitoring exercise as whole 'service' units. Service units are composite values (or fractions thereof) representing the complete process, including all overhead costs (*e.g.* vehicle maintenance, building expenses, salaries; Appendix II).

Without considering the cost implications of a monitoring strategy, the allocation of samples to different monitoring zones is based purely on the relative environmental importance of the zone, *i.e.* simple allocation. Since the cost per sample is assumed to be equal for each monitoring zone only weightings need to be considered. Alternatively, the following equation, the Neyman allocation, can be used to allocate samples:

$$n_h = \frac{n\, W_h\, \sigma_h}{\sum_{h=1}^{L} W_h\, \sigma_h}$$

Equation 2.9

in practise, σ_h the variance of the *h*th stratum, is replaced with an estimate, s_h, obtained from previous studies.

The results of calculations using the equations described above (Equations 2.3 to 2.9) are shown in Tables 2.11, 2.12 and 2.13 for the three pre-specified criteria. The number of samples required for an efficient monitoring strategy is listed for different specifications of the sampling budget, variability of data and tolerable margin of error, respectively. (It should be noted that Tables 2.11 to 2.13 are specimen output files from the spreadsheet computer package, Quattro Pro. The inability of the software to display superscripts *etc.* means some symbols do not appear correctly. For example, Wh instead of W_h and Sh rather than S_h. Equations 2.5 to 2.7 show the correct symbols.

Table 2.11. Sample allocation in the monitoring network determined by pre-specified cost. Equation 2.5.

Site name	Site number	Wh	Sh	Ch	(Wh*Sh)/sq.C	Wh*Sh*sq.Ch
Ash/B.P.	1	0.0941	34.6	293.43	0.19	55.77
Fert.	2	0.1510	1492.3	293.43	13.15	3859.98
Explo.	3	0.1510	58.6	293.43	0.52	151.57
Water rec.	4	0.1196	27.8	293.43	0.19	56.95
Salt dams	5	0.1235	179.9	293.43	1.30	380.58
Irrig.	6	0.1000	146.9	293.43	0.86	251.64
Coal S.P.	7	0.0765	17.6	293.43	0.08	23.06
Refuse dump	8	0.0686	27.9	293.43	0.11	32.79
Mine water	9	0.1157	88.6	293.43	0.60	175.60
Sum		1			17.00	4987.95

n = C * sum(Wh*Sh/sqrt.Ch) / sum (Wh*Sh*sqrt.Ch)
Calculation at different budgets

Budgets (C)	50000	40000	30000	(Rands/year)
n =	170	136	102	

Simple allocation of ground water samples to monitor the waste operation sites:

Site name	Site number	Wh	Budget 50000	Budget 40000	Budget 30000
Ash/B.P.	1	0.0941	16	13	10
Fert.	2	0.1510	26	21	15
Explo.	3	0.1510	26	21	15
Water rec.	4	0.1196	20	16	12
Salt dams	5	0.1235	21	17	13
Irrig.	6	0.1000	17	14	10
Coal S.P.	7	0.0765	13	10	8
Refuse dump	8	0.0686	12	9	7
Mine water	9	0.1157	20	16	12
Sum			170	136	102

Neyman allocation of samples to monitor the waste operation sites:

Site name	Site number	Wh	Sh	Wh*Sh	Budget 50000	Budget 40000	Budget 30000
Ash/B.P.	1	0.0941	34.6	3.26	2	2	1
Fert.	2	0.1510	1492.3	225.34	132	105	79
Explo.	3	0.1510	58.6	8.85	5	4	3
Water rec.	4	0.1196	27.8	3.32	2	2	1
Salt dams	5	0.1235	179.9	22.22	13	10	8
Irrig.	6	0.1000	146.9	14.69	9	7	5
Coal S.P.	7	0.0765	17.6	1.35	1	1	0
Refuse dump	8	0.0686	27.9	1.91	1	1	1
Mine water	9	0.1157	88.6	10.25102	6	5	4
Sum				291.18565	170	136	102

Table 2.12. Sample allocation in the monitoring network determined by pre-specified variance. Equation 2.6. [2]

Site name	Site number	Wh	Sh^2	Wh*Sh^2
Ash/B.P.	1	0.0941	1198.1	112.74
Fert.	2	0.1510	2225830.0	336100.33
Explo.	3	0.1510	3436.5	518.91
Water rec.	4	0.1196	770.1	92.10
Salt dams	5	0.1235	32177.0	3973.86
Irrig.	6	0.1000	21574.0	2157.40
Coal S.P.	7	0.0765	308.7	23.62
Refuse dump	8	0.0686	778.9	53.43
Mine water	9	0.1157	7848.2	908.04
Sum				343940.43

n = sum(Wh*Sh^2) / V+(1/N)(sum Wh*Sh^2)
Calculation at different variances.
N = 3.55 E+12 litres

Variances (V)	5000	3000	1000
n =	69	115	344

Simple allocation of ground water samples to monitor the waste operation sites:

Site name	Site number	Wh	Variance 5000	Variance 3000	Variance 1000
Ash/B.P.	1	0.0941	6	11	32
Fert.	2	0.1510	10	17	52
Explo.	3	0.1510	10	17	52
Water rec.	4	0.1196	8	14	41
Salt dams	5	0.1235	8	14	42
Irrig.	6	0.1000	7	11	34
Coal S.P.	7	0.0765	5	9	26
Refuse dump	8	0.0686	5	8	24
Mine water	9	0.1157	8	13	40
Sum			69	115	344

Neyman allocation of ground water samples to monitor the waste operation sites:

Site name	Site number	Wh	Sh	Wh*Sh	Variance 5000	Variance 3000	Variance 1000
Ash/B.P.	1	0.0941	34.61	3.26	1	1	4
Fert.	2	0.1510	1491.92	225.28	53	89	266
Explo.	3	0.1510	58.62	8.85	2	3	10
Water rec.	4	0.1196	27.75	3.32	1	1	4
Salt dams	5	0.1235	179.38	22.15	5	9	26
Irrig.	6	0.1000	146.88	14.69	3	6	17
Coal S.P.	7	0.0765	17.57	1.34	0	1	2
Refuse dump	8	0.0686	27.91	1.91	0	1	2
Mine water	9	0.1157	88.59	10.25	2	4	12
Sum				**291.06**	**69**	**115**	**344**

---

[2] The amount of ground water, *N*, is estimated to be $3.55*10^{12}$ dm^3 after consultation with Hodgson (1995, pers.com.). Industrial area = 140.8 km. Average aquifer thickness = 168 m (Geological Survey, 1971). Effective porosity = 15% (Hodgson, 1995; pers.com.).

Table 2.13. Sample allocation in the monitoring network determined by pre-specified margin of error. Equation 2.7.

		Weighting	Variance	(A)	(A)	(B)	(B)	(C)	(C)
Site name	Site number	Wh	Sh^2	Wh*Sh^2/d^2	Wh*Sh^2/d^2*N	Wh*Sh^2/d^2	Wh*Sh^2/d^2*N	Wh*Sh^2/d^2	Wh*Sh^2/d^2*N
Ash/B.P.	1	0.0941	1198	0.01	3.1758E-13	0.01	3.5287E-13	0.02	3.9698E-13
Fert.	2	0.1510	2225830	33.61	9.4676E-10	41.49	1.052E-09	52.52	1.1835E-09
Explo.	3	0.1510	3437	0.05	1.4617E-12	0.06	1.6241E-12	0.08	1.8272E-12
Water rec.	4	0.1196	770	0.01	2.5945E-13	0.01	2.8828E-13	0.01	3.2431E-13
Salt dams	5	0.1235	32177	0.40	1.1194E-11	0.49	1.2438E-11	0.62	1.3992E-11
Irrig.	6	0.1000	21574	0.22	6.0772E-12	0.27	6.7524E-12	0.34	7.5965E-12
Coal S.P.	7	0.0765	309	0.00	6.6523E-14	0.00	7.3914E-14	0.00	8.3153E-14
Refuse dump	8	0.0686	779	0.01	1.5051E-13	0.01	1.6724E-13	0.01	1.8814E-13
Mine water	9	0.1157	7848	0.09	2.5578E-12	0.11	2.8421E-12	0.14	3.1973E-12
Sum				34.39	9.6885E-10	42.46	1.0765E-09	53.74	1.2111E-09

n = (Z^2 * sum(Wh*Sh^2/d^2)) / (1 + Z^2 * sum(Wh*Sh^2/d^2*N))

Calculation at prespecified margins of error and alpha values

Z {1-(alpha/2)} obtained from Table A1 (Gilbert, 1987, p254)

Alpha		0.20	0.10	0.05	0.01
Z {1-(alpha/2)}		1.2816	1.6449	1.9600	2.5758
n = when	d (A)	56	93	132	228
n = when	d (B)	70	115	163	282
n = when	d (C)	88	145	206	357

Margin of error = Probability
[|mean.samp. - mean.pop.| > X mS/m]

Margin of error, d (A) = 100
Margin of error, d (B) = 90
Margin of error, d (C) = 80
N (litre) = 3.55E+12

Simple allocation of ground water samples to monitor the waste operation sites:
With an alpha value of 0.10.

Site name	Site number	Wh	d (A)	d (B)	d (C)
Ash/B.P.	1	0.0941	9	11	14
Fert.	2	0.1510	14	17	22
Explo.	3	0.1510	14	17	22
Water rec.	4	0.1196	11	14	17
Salt dams	5	0.1235	11	14	18
Irrig.	6	0.1000	9	11	15
Coal S.P.	7	0.0765	7	9	11
Refuse dump	8	0.0686	6	8	10
Mine water	9	0.1157	11	13	17
Sum			93	115	145

Neyman allocation of ground water samples to monitor the waste operation sites:
With an alpha value of 0.10.

					d (A)	d (B)	d (C)
Site name	Site number	Wh	Sh	Wh*Sh	100	90	80
Ash/B.P.	1	0.0941	34.61	3.26	1	1	2
Fert.	2	0.1510	1491.92	225.28	72	89	113
Explo.	3	0.1510	58.62	8.85	3	3	4
Water rec.	4	0.1196	27.75	3.32	1	1	2
Salt dams	5	0.1235	179.38	22.15	7	9	11
Irrig.	6	0.1000	146.88	14.69	5	6	7
Coal S.P.	7	0.0765	17.57	1.34	0	1	1
Refuse dump	8	0.0686	27.91	1.91	1	1	1
Mine water	9	0.1157	88.59	10.25	3	4	5
Sum				291.08	93	115	145

2.8 Discussions and conclusions

Piper diagrams a valuable method for illustrating, in one diagram, water quality at several sites (Figure 2.9), however, relative proportions are only apparent and time series plots, or another type of graph, have to be used to demonstrate the magnitude of the variables (Figures 2.4 to 2.8 and 2.10 to 2.28). The surface and ground water quality over the last four years has varied in space and time. Trends (spatial and temporal) are difficult to determine. Most of the concentration fluctuations are episodic events. Specific pollution phenomena can be identified and should be studied in detail by the EMU and the source traced. For example, the pollution high recorded at RESM01 in the first half of 1991 (Figure 2.4) was from a waste operation in the south of the area (Figure 2.6) and not from the northern stream (Figure 2.5) nor from outside the industrial area (Figure 2.8). The contamination source was high in Na and Cl (Figure 2.4) which suggests that the waste operation at fault was the water recovery division or possibly the fine coal storage dams.

The dominant anion in surface water is HCO_3 of which only minor amounts will originate from natural sources (section 2.2). SO_4 and Cl are also present but smaller quantities. There are some exceptional pollution events, *e.g.* the Cl high in Figure 2.8b. Cations species in the surface water are mainly Na with subordinate amounts of Ca and Mg. Conversely, the ground water quality is dominated by Ca and then Mg with less Na (Figure 2.9). The exceptions are boreholes REGM28 in an irrigation area (Figure 2.21) and the water recovery division REGM10 monitoring site (Figure 2.17). This feature is caused by the preferential attenuation of Na (and K) ions by the solum. The anions in the ground water vary greatly in relative abundance which causes the spread of data points in Figure 2.9. The ash / B.P. dams, fertilizer dump and explosives borrow pits tend to more SO_4 and Cl, while the irrigation areas and water recovery dams are dominated by HCO_3. The other waste operations are divergent.

The weighted statistics in Table 2.10 probably represent a more realistic image of the ground water quality in monitored area as a whole. The sample allocation to the waste operations can be compared to the present distribution of sample localities (Table

2.4). Sampling resource allocation will be discussed further in chapter 5. The Neyman allocation is not considered to be a favoured method since it attaches too much importance to the variability of the data set. Variance, *i.e.* pollution occurrence, has already been accounted for in the MCDA. In addition, analyte concentrations are expected to vary with pollution events and the data sets of the monitored waste operations will have varying distributions. Water quality may also improve, although present studies show a relatively sustained level of poor water quality. The Neyman allocation is biased by the characteristics of water quality in the past and assumes that the trends are unlikely to change. The implementation of mitigating measures to improve water quality or some other change in the waste operations will alter the variance of readings taken at a borehole. This could give rise to a spurious allocation of resources by the Neyman method.

Figure 2.34 shows the present allocation of samples to the monitoring zones compared with those calculated by the environmental significance (weighting) of the waste operation in terms of particular pre-specified criteria. Figure 2.34 is an example of the suggested distribution of samples over the operations in a year, calculated using precise criteria. The total number of samples changes with the values assigned to the pre-specified criteria (Tables 2.11 to 2.13). The criteria should be identified in the monitoring objectives. The relative allocation of samples will only vary if the environmental criteria scores are changed. If need be, the calculation of new weightings (Table 2.10) is an easy process. Figure 2.34, specifies the proportional allocation of samples to waste operations, even though the total number may change.

The optimized sample allocation must be considered in relation to the existing monitoring network. It does not make financial sense to discount the present boreholes and start a whole new programme. Any drilling of new boreholes, however, should be concentrated in the most important areas, *i.e.* the fertilizer and explosives dumps.

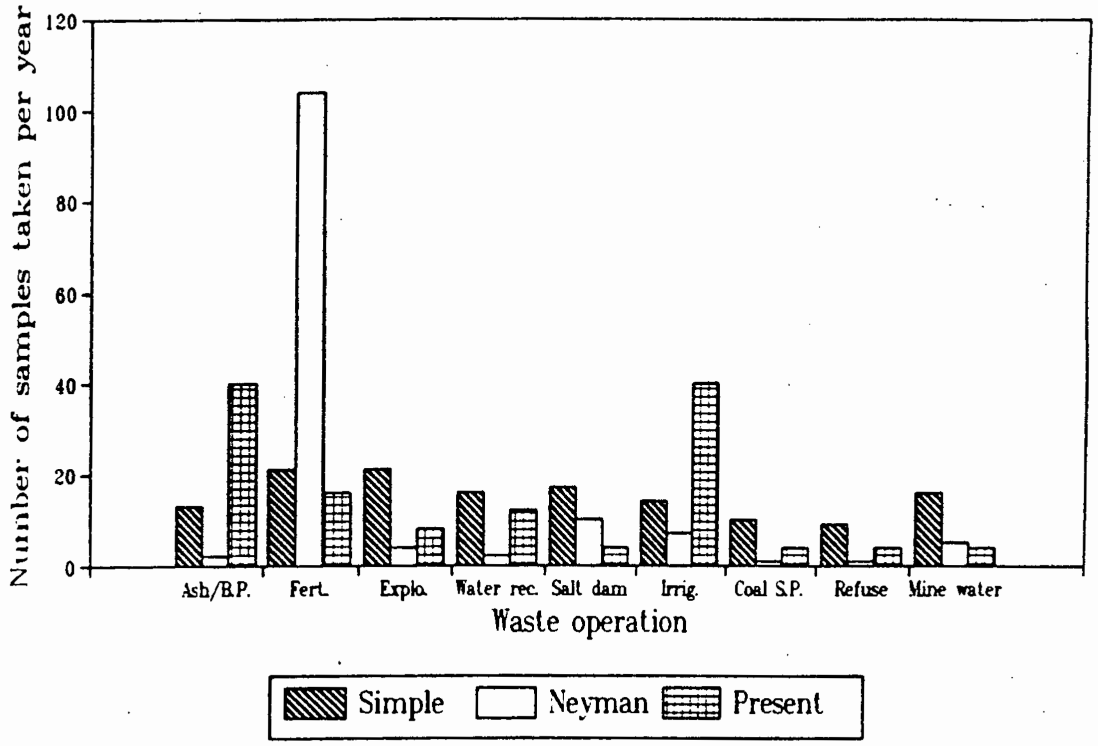


Figure 2.34. **A comparison of sample allocations to the nine waste operations monitored.**

The present allocation of samples per year is compared with a simple allocation (just using environmental significance weightings) and the Neyman allocation (Equation 2.9) in Figure 2.34. The total number of samples per year for the two suggested allocations were determined using weightings and a pre-specified budget of R 40 000 yr^{-1} (Table 2.11).

Figure 2.34 has implications for the amount of attention needed for each sample collected. The samples which will be the most environmentally revealing are those from the most strongly weighted sites. The optimum frequency of collecting samples and the detail of subsequent analysis performed are dealt with in the next two chapters.

3. A STATISTICAL APPRAISAL OF THE FREQUENCY OF SAMPLING

3.1 INTRODUCTION

In this chapter, two approaches are described which assess the temporal variability of the environment being monitored. Firstly, a selection of sample locations were studied using a computer algorithm which applies statistical tests to a time series of data. Secondly, data worth was assessed on the basis of the change in information resolution after thinning of the data.

3.2 ANALYSIS OF TEMPORAL PATTERNS USING STATISTICAL ALGORITHMS

The water quality statistics programme, WQStat II (1989), was developed by Colorado State University and is available on a shareware basis. Many of the statistical procedures are similar to those described by Gilbert (1987, chapter 17). Gilbert gives the listings for a series of statistical algorithms in a programme called Trend (Gilbert, 1987, Appendix B). Trend was initially applied to the present data set but because of difficulties with code modification and the lack of 'user friendliness', it was decided to use WQStat II.

3.2.1 Tests for significance of temporal patterns

As part of the statistical procedures WQStat II generally associates results with confidence levels. In the testing of statistical hypotheses nothing is ever known with absolute certainty. A confidence level is the probability that the test will correctly accept the null hypothesis when it is true in reality. Similarly, the confidence level represents the probability that the test in question will conclude that a trend is not significant when it is indeed not significant. The programme computes values of each test statistic, for a series of confidence levels, with which it then compares the test statistic derived from the data.

For the purpose of this dissertation a 90 % confidence level was considered acceptable, leaving a 10 % chance of the algorithm rejecting a null hypothesis when in fact it is true. The 90 % confidence level was chosen after studying the results from the data sets and determining which levels yielded significant values. The 90 % level was deemed to have a high enough power to detect significance within an acceptable error. The 95% confidence level was found to be too rigorous, in that virtually no patterns were revealed in the data. Conversely, 80% was deemed to low, in that most of the tests performed produced significant results.

The null hypothesis, H_0, of the tests is generally to suggest that no temporal feature is evident. From the significance values, one can conclude either that the statistical procedure rejects the null hypothesis (*i.e.* the data shows a statistically visible trend or pattern) or confirms it. A 'significant' conclusion leads to the rejection of the hypothesis and hence it is possible to identify significant regularities in the data.

In order to perform the more advanced statistical calculations available in WQStat II, some basic knowledge of data distribution is required. Output from the programme includes descriptive information and an evaluation of the data distribution. Other procedures of WQStat II make it possible to study the data with respect to changes over time and to identify extreme or outlier values. Temporal analysis involves the detection either of continuous trends or of a fluctuating pattern (*e.g.* seasonality). Fluctuations may follow a pattern of regular periods (*e.g.* seasonal cycles) but may also include episodic changes such as intermittent, irregular pollution events.

Usually 'unadjusted' data for a particular site are used for initial exploratory analysis before other tests are executed. If a temporal pattern is identified, it may be favourable to remove the trend and / or seasonality prior to conducting subsequent tests. The trend is removed by subtracting the data set mean or Sen estimate trend component (see below) from each data point. The resulting data series then has a mean of zero with the episodic fluctuations as salient features. Seasonality is removed by subtracting the seasonal means from each data point. In other words the mean of all observations in a given month or quarter is subtracted from each reading in that given period. This will result in each period having a mean of zero. After running tests with unadjusted data series (*i.e.* without the temporal patterns accounted for) it was not considered necessary to perform subsequent tests as the regularities did not warrant further investigation. The results of applying WQStat II tests to electrical conductivity data from 6 ground water (REGM) sites and from 11 surface water (RESM) sites are presented in Tables 3.1a, b and c. Prior to examining the results in the Tables the explanatory notes following Table 3.1c should be consulted.

Table 3.1. Results from the statistical tests performed in WQStat II (1989). Footnotes included.

Table 3.1a. Temporal statistical analysis of electrical conductivity data (units = mS.m^{-1}) from ground water monitoring locations (REGMs) around the industrial plant.

SITE NUMBER:	REGM01EC	REGM11EC	REGM14EC	REGM17EC	REGM21EC	REGM23EC
AREA CODE & SYMBOL:	1 ○	4 ◇	7 ▲	2 □	5 ●	6 ■
MEAN:	236.32	118.63	179.40	652.27	511.73	116.58
MEDIAN:	235.00	120.00	178.00	380.00	560.00	115.00
STANDARD DEVIATION:	29.63	15.36	17.56	625.90	179.384	14.93
SKEWNESS (1):						
Statistic:	0.311	0.091	0.371	1.628	-0.518	0.110
α value (@ 90% C.L.) test:	| 0.828 |	| 0.845 |	| 0.862 |	> 0.845	| 0.862 |	| 0.888 |
Conclusion on Sig:	Not sig.	Not sig.	Not sig.	Sig.	Not sig.	Not sig.
KURTOSIS (2):						
Statistic:	1.83	2.34	2.82	4.69	2.18	2.77
α value (@ 90% C.L.) test:	1.7<x<4.1	1.7<x<4.1	1.7<x<4.1	> 4.14	1.7<x<4.1	1.6<x<4.0
Conclusion on Significance:	Not q. sig.	Not sig.	Not sig.	Just sig.	Not sig.	Not sig.
K-W SEASONALITY (3):						
Statistic:	0.130	1.260	4.63	0.120	0.36	3.99
α value (@ 90% C.L.) test:	< 6.25	< 6.25	< 6.25	< 6.25	< 6.25	< 6.25
Conclusion on Significance:	Not sig.	Not sig.	Not q. sig.	Not sig.	Not sig.	Not sig.
SLOPE EST. (4) (units/year):	11.00	3.75	0.00	216.08	149.67	0.00
KENDALL TAU TREND (5):						
Statistic:	2.357	1.087	0.350	2.211	3.927	-0.624
α value (@ 90% C.L.) test:	> 1.645	| 1.645 |	| 1.645 |	> 1.645	> 1.645	| 1.645 |
Conclusion on Significance:	Sig.	Not sig.	Not sig.	Sig.	Sig.	Not sig.
KENDALL SEN TREND (6):						
Statistic:	2.479	0.978	0.000	1.379	3.381	0.000
α value (@ 90% C.L.) test:	> 1.625	| 1.645 |	| 1.645 |	| 1.645 |	> 1.645	| 1.645 |
Conclusion on Significance:	Sig.	Not sig.	Not sig.	Not q. sig.	Sig.	Not sig.
ANAL. OF COVARIANCE (7):						
Statistic:	2.570	1.226	0.746	2.580	7.390	-0.712
α value (@ 90% C.L.) test:	> 1.782	| 1.796 |	| 1.812 |	| 1.796 |	> 1.812	| 1.895 |
Conclusion on Significance:	Sig.	Not sig.	Not sig.	Sig.	Sig.	Not sig.
EST. MEDIAN DIFF (8):	28.75	12.50	10.00	582.17	305.00	-20.00
WILCOXON TEST (9):						
Statistic:	-1.680	-1.524	-1.153	-1.521	-2.201	0.677
α value (@ 90% C.L.) test:	< -1.625	| 1.645 |	| 1.645 |	| 1.645 |	< -1.645	| 1.645 |
Conclusion on significance:	Just sig.	Not q. sig.	Not sig.	Not q. sig.	Sig.	Not sig.
MANN-WHITNEY SUM (10):						
Statistic:	-2.027	-1.686	0.975	-1.969	-3.112	1.212
α value (@ 90% C.L.) test:	> -1.645	< -1.645	| 1.645 |	< -1.645	< -1.645	| 1.645 |
Conclusion on Significance:	Sig.	Sig.	Not sig.	Sig.	Sig.	Not sig.

Table 3.1b. Temporal statistical analysis of electrical conductivity data (units = $mS.m^{-1}$) from surface water monitoring locations (RESMs) on the northern side of the plant.

SITE NUMBER:	RESM01EC	RESM02EC	RESM04EC	RESM05EC	RESM06EC	RESM07EC
CLOSEST WASTE SITE (No.+Sym.):	1 ○	4 ◇	4 ◇ and 6 ■	6 ■	6 ■	6 ■ and 8 ♦
MEAN:	58.45	55.02	57.60	58.10	49.81	55.94
MEDIAN:	53.26	57.27	53.90	52.30	45.18	52.5
STANDARD DEVIATION:	20.50	5.26	14.87	16.25	15.35	14.79
SKEWNESS (1):						
Statistic:	3.317	-0.738	0.762	0.485	1.068	0.283
α value (@ 90% C.L.) test:	> 0.811	| 0.811 |	| 0.811 |	| 0.845 |	> 0.845	| 0.811 |
Conclusion on Sig:	Sig.	Not sig.	Not sig.	Not sig.	Sig.	Not sig.
KURTOSIS (2):						
Statistic:	13.150	2.39	2.57	2.38	2.95	1.55
α value (@ 90% C.L.) test:	> 4.15	1.8<x<4.2	1.8<x<4.2	1.7<x<4.1	1.7<x<4.1	< 1.78
Conclusion on Significance:	Sig.	Not sig.	Not sig.	Not sig.	Not sig.	Sig.
K-W SEASONALITY (3):						
Statistic:	0.32	0.76	4.20	2.26	1.23	6.85
α value (@ 90% C.L.) test:	< 6.25	< 6.25	< 6.25	< 7.81	< 6.25	> 6.25
Conclusion on Significance:	Not sig.	Not sig.	Not sig.	Not sig.	Not sig.	Just sig.
SLOPE EST. (4) (units/year):	-2.48	1.26	-0.07	-1.54	-0.18	1.20
KENDALL TAU TREND (5):						
Statistic:	-2.576	1.630	0.076	-0.405	0.045	0.644
α value (@ 90% C.L.) test:	< -1.645	| 1.645 |	| 1.645 |	| 1.645 |	| 1.645 |	| 1.645 |
Conclusion on Significance:	Sig.	Not sig.	Not sig.	Not sig.	Not sig.	Not sig.
KENDALL SEN TREND (6):						
Statistic:	-2.669	1.545	-0.140	-0.326	0.000	0.000
α value (@ 90% C.L.) test:	< -1.645	| 1.645 |	| 1.645 |	| 1.645 |	| 1.645 |	| 1.645 |
Conclusion on Significance:	Sig.	Not sig.	Not sig.	Not sig.	Not sig.	Not sig.
ANAL. OF COVARIANCE (7):						
Statistic:	-3.008	1.202	0.138	-0.545	0.138	0.670
α value (@ 90% C.L.) test:	< -1.771	| 1.771 |	| 1.771 |	| 1.796 |	| 1.796 |	| 1.771 |
Conclusion on Significance:	Sig.	Not sig.	Not sig.	Not sig	Not sig.	Not sig.
EST. OF MEDIAN DIFF (8):	-3.115	2.934	-10.875	-13.231	-0.947	3.07
WILCOXON TEST (9):						
Statistic:	2.383	-0.560	1.680	2.20	0.734	0.840
α value (@ 90% C.L.) test:	> 1.645	| 1.645 |	> 1.645 |	> 1.645	| 1.645 |	| 1.645 |
Conclusion on significance:	Sig.	Not sig.	Just sig.	Sig.	Not sig.	Not sig.
MANN-WHITNEY SUM (10):						
Statistic:	1.510	-1.422	1.365	2.236	0.703	0.525
α value (@ 90% C.L.) test:	< 1.645	| 1.645 |	| 1.645 |	> 1.645	| 1.645 |	| -1.645 |
Conclusion on Significance:	Not sig.	Not sig.	Not q. sig.	Sig.	Not sig.	Not sig.

Table 3.1c. Temporal statistical analysis of electrical conductivity data (units = $mS.m^{-1}$) from surface water monitoring locations (RESMs) on the southern side of the plant. RESM01 is repeated for comparison.

SITE NUMBER: CLOSEST WASTE SITE (No.+Sym.):	RESM01EC 1 ○	RESM03EC 1 ○ and 4 ◊	RESM09EC 1 ○ and 7 ▴	RESM10EC 2 □ and 7 ▴	RESM13EC 9 ★	RESM14EC 2 □ and 3 ▵
MEAN:	58.45	81.29	271.46	68.14	56.45	209.04
MEDIAN:	53.26	51.91	231.37	68.54	52.86	172.00
STANDARD DEVIATION:	20.50	68.87	131.91	16.84	10.72	73.60
SKEWNESS (1):						
Statistic:	3.317	2.600	0.010	-0.001	0.181	0.277
α value (@ 90% C.L.) test:	> 0.811	> 0.811	| 0.879 |	| 0.811 |	| 0.828 |	| 0.888 |
Conclusion on Sig:	Sig.	Sig.	Not sig.	Not sig.	Not sig.	Not sig.
KURTOSIS (2):						
Statistic:	13.150	8.89	1.51	2.05	1.70	1.80
α value (@ 90% C.L.) test:	> 4.15	> 4.15	< 1.66	1.8<x<4.2	< 1.76	1.6<x<4.0
Conclusion on Significance:	Sig.	Sig.	Sig.	Not sig.	Just sig.	Not sig.
K-W SEASONALITY (3):						
Statistic:	0.32	0.31	4.01	3.56	4.54	4.71
α value (@ 90% C.L.) test:	< 6.25	< 6.25	< 6.25	< 6.25	< 6.25	< 6.25
Conclusion on Significance:	Not sig.	Not sig.	Not sig.	Not sig.	Not q. sig.	Not q. sig.
SLOPE EST. (4) (units/year):	-2.48	-9.19	-35.36	6.23	5.23	16.33
KENDALL TAU TREND (5):						
Statistic:	-2.576	-1.667	-1.281	1.970	1.524	-0.069
α value (@ 90% C.L.) test:	< -1.645	< 1.645	| 1.645 |	> 1.645	| 1.645 |	| 1.645 |
Conclusion on Significance:	Sig.	Just sig.	Not sig.	Sig.	Not q. sig.	Not sig.
KENDALL SEN TREND (6):						
Statistic:	-2.669	-1.545	-1.919	2.107	1.184	0.436
α value (@ 90% C.L.) test:	< -1.645	< 1.645	| 1.645 |	> 1.645	| 1.645 |	| 1.645 |
Conclusion on Significance:	Sig.	Not sig.	Just sig.	Sig.	Not sig.	Not sig.
ANAL. OF COVARIANCE (7):						
Statistic:	-3.008	-1.743	-1.622	2.348	1.690	0.670
α value (@ 90% C.L.) test:	< -1.771	| 1.771 |	| 1.860 |	> 1.771	| 1.782 |	| 1.895 |
Conclusion on Significance:	Sig.	Not sig.	Not q. sig.	Sig.	Not q. sig.	Not sig.
EST. OF MEDIAN DIFF (8):	-3.115	-12.818	-42.077	18.993	6.873	39.79
WILCOXON TEST (9):						
Statistic:	2.383	1.120	1.572	-1.960	-1.352	-0.405
α value (@ 90% C.L.) test:	> 1.645	| 1.645 |	| 1.645 |	< 1.645	| 1.645 |	| 1.645 |
Conclusion on significance:	Sig.	Not sig	Not q. sig.	Sig.	Not q. sig.	Not sig.
MANN-WHITNEY SUM (10):						
Statistic:	1.510	0.533	0.571	-2.521	-1.390	-0.244
α value (@ 90% C.L.) test:	< 1.645	| 1.645 |	| 1.645 |	< -1.645	| 1.645 |	| 1.645 |
Conclusion on Significance:	Not sig.	Not sig.	Not sig.	Sig.	Not q. sig.	Not sig.

Explanatory notes:

The statistical procedures were executed with no prior adjustment for trends or seasonality. The temporal distribution was considered on a quarterly basis which represents the seasons. The seasons were determined from a mean rainfall graph (Appendix I) as follows: November 1st to January 31st = summer; February 1st to April 30th = autumn; May 1st to July 31st = winter; August 1st to October 31st = spring.

Sig denotes significance, showing the test has rejected the null hypothesis at the confidence level, while *Not sig* symbolizes an acceptance of the statistical hypothesis. Other annotations are used (for example, *Just* *sig*) to explain the significance of the test statistic. The calculated test statistic is compared with an acceptable value at a 90% confidence level (alpha, $\alpha = 0.10$). The α significance value is shown as a comparative figure as greater than (>) or less than (<) or as a range (*e.g.* $-1.00 < X < 2.00$) or as the modulus of a value (*e.g.* $|2.00|$, *i.e.* $-2.00 < X < 2.00$) depending on the conclusion, with respect to significance, drawn from each test. C.L. symbolizes confidence limit.

The important tests are the Kendall Tau as a trend indicator, the Sen slope estimate of the magnitude of a trend, the Kruskal-Wallace test for seasonality, the Hodges-Lehman estimate of median difference between the first half of the monitoring period and the second and the significance of this difference in the Wilcoxon test (WQStat II, 1989).

H_0 is listed for each test. A 'significant' value leads to a rejection of the H_0 hypothesis.

(1) Skewness: H_0 = the data distribution is normal.

(2) Kurtosis: H_0 = the data distribution is mesokurtic.

(3) Kruskal-Wallis test for seasonality: H_0 = means of the seasons are the same.

(4) Seasonal Kendall Sen slope estimate in units ($mS.m^{-1}$) per year.

(5) Kendall Tau test for trend (preferred when data set < 5 years long): H_0 = the values at the beginning of the data set are the same as those at the end.

(6) Kendall Sen test for trend (preferred when data set > 5 years long): H_0 = the values at the beginning of the data set are the same as those at the end.

(7) Analysis of covariance (a multiple linear regression on the ranks of the data estimating a slope and testing its significance, Kendall tests are generally preferred): H_0 = the trend slope is zero.

(8) Seasonal Hodges-Lehman estimate of median difference in two time periods.

(9) Wilcoxon signed rank test (where data periods can be paired) for the significance of median difference: H_0 = the medians are the same.

(10) Mann-Whitney (Wilcoxon Rank sum) test with unpaired data periods for significance of median difference: H_0 = the medians are the same.

3.2.2 Analysis of temporal patterns

3.2.2.1 Normality of data

Many statistical procedures rely on a normal distribution of data. Most of the tests used in WQStat II are, however, non-parametric and therefore do not depend on a Gaussian distribution of data values. To test for normality, two procedures were used:

- A frequency histogram should be a bell shaped curve if the data are normally distributed. Outliers are identified as violations of normality.
- Tests producing skew and kurtosis values were included in the exploratory statistics. If either of the values is significantly different from those pertaining to a normal distribution, the assumption of normality is probably unjustified within the confidence level specified.

The skewness and kurtosis values listed in Tables 3.1a to 3.1c show that the data for about one third of the monitoring locations are not normally distributed. The use of non-parametric statistics is therefore important for all datasets to ensure that the results are comparable.

The use of WQStat II helped in understanding the frequency distribution of data sets which is discussed in more detail in section 4.1.2. Figures 3.1 to 3.4, however, are included in this section to demonstrate the variation involved. The monitoring operation is inherently unlikely to produce data displaying a Gaussian distribution. Skewed distributions should be expected for one of two reasons. Either the data will be influenced by sporadic pollution events (Figure 3.2), or the data will be influenced by occasional dilution (Figure 3.3). Normality in data sets can be found (Figure 3.1), in addition to a spread distribution of low kurtosis which could be inferred as bimodal (Figure 3.4). The variety of distributions in the data sets lead to a lack of confidence by author in assuming normality. Non-parametric statistics were there chosen where possible.

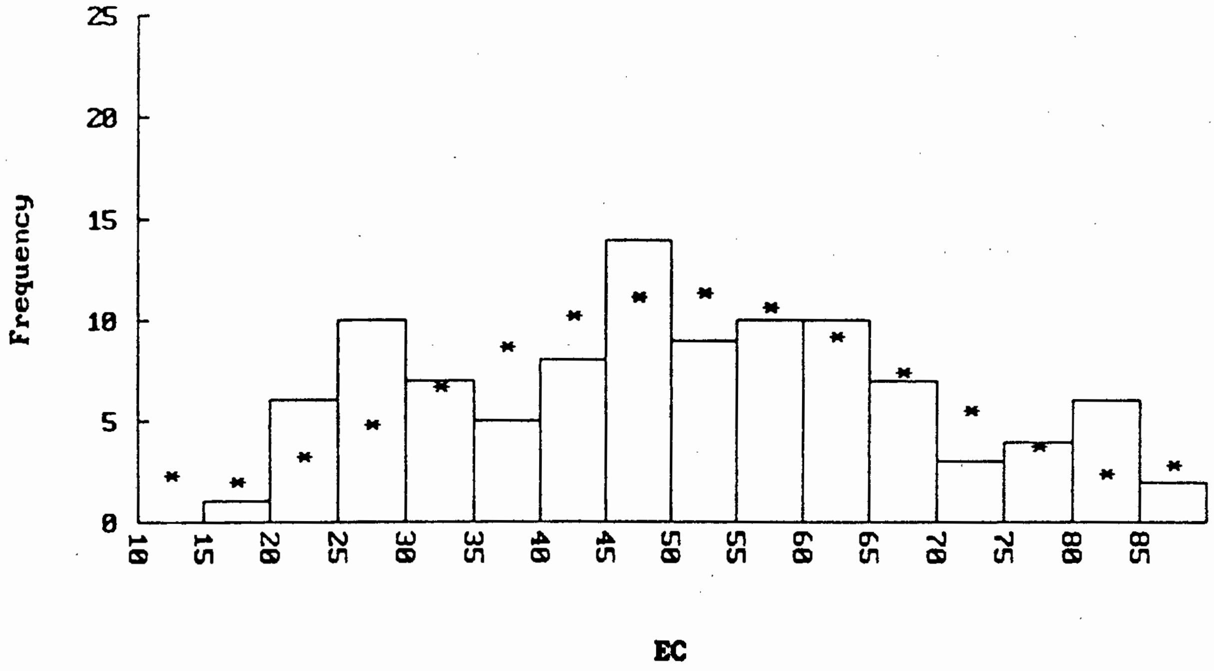


Figure 3.1. **A frequency distribution histogram of electrical conductivity (mS.m^{-1}) at surface water site RESM08 over the duration of the monitoring operation. * = calculated normal distribution from the data set.**

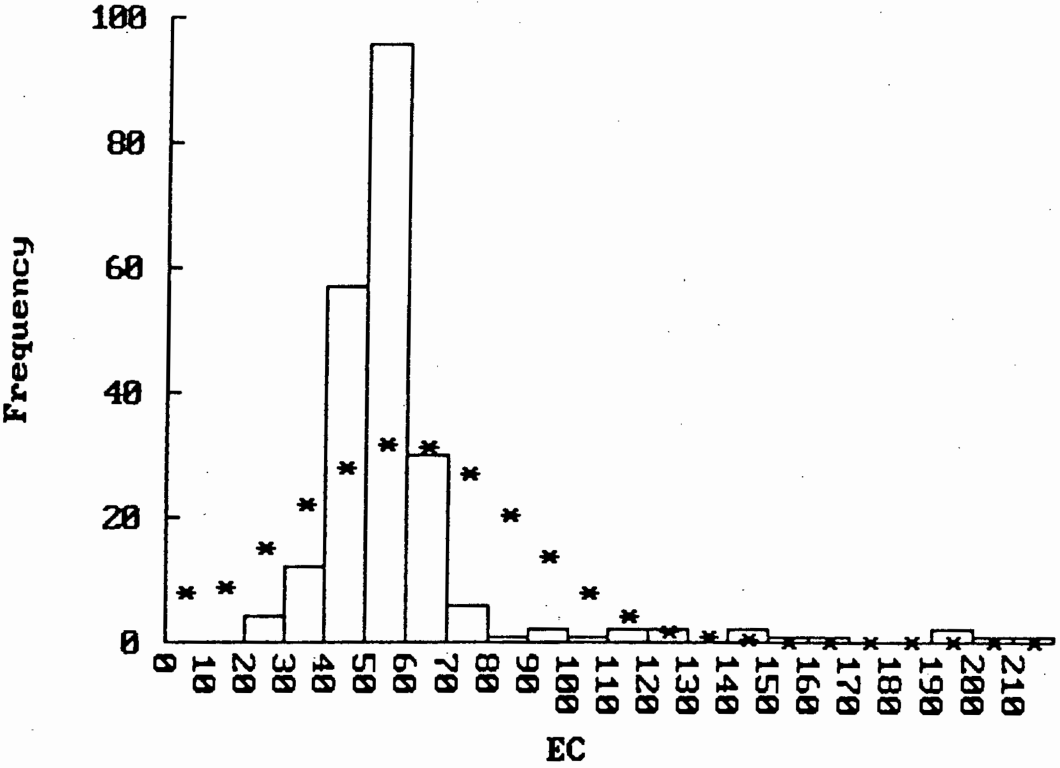


Figure 3.2. A frequency distribution histogram of electrical conductivity (mS.m^{-1}) at surface water site RESM01 over the duration of the monitoring operation. * = calculated normal distribution from the data set.

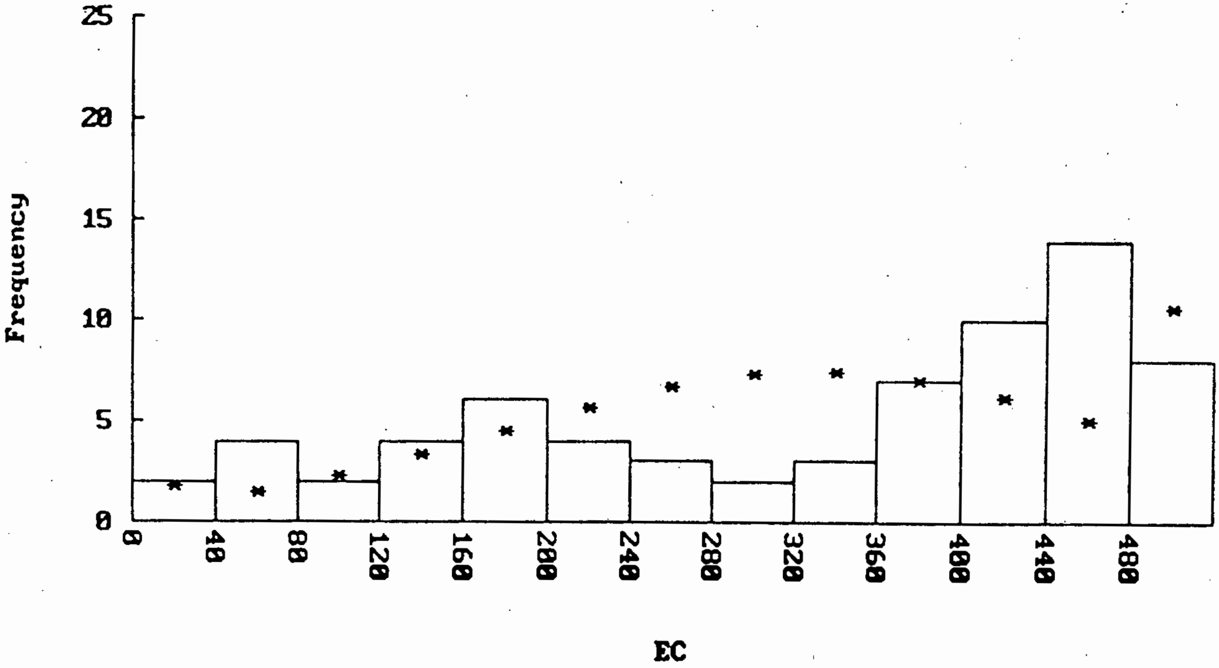


Figure 3.3. A frequency distribution histogram of electrical conductivity (mS.m^{-1}) at surface water site RESM02 over the duration of the monitoring operation. * = calculated normal distribution from the data set.

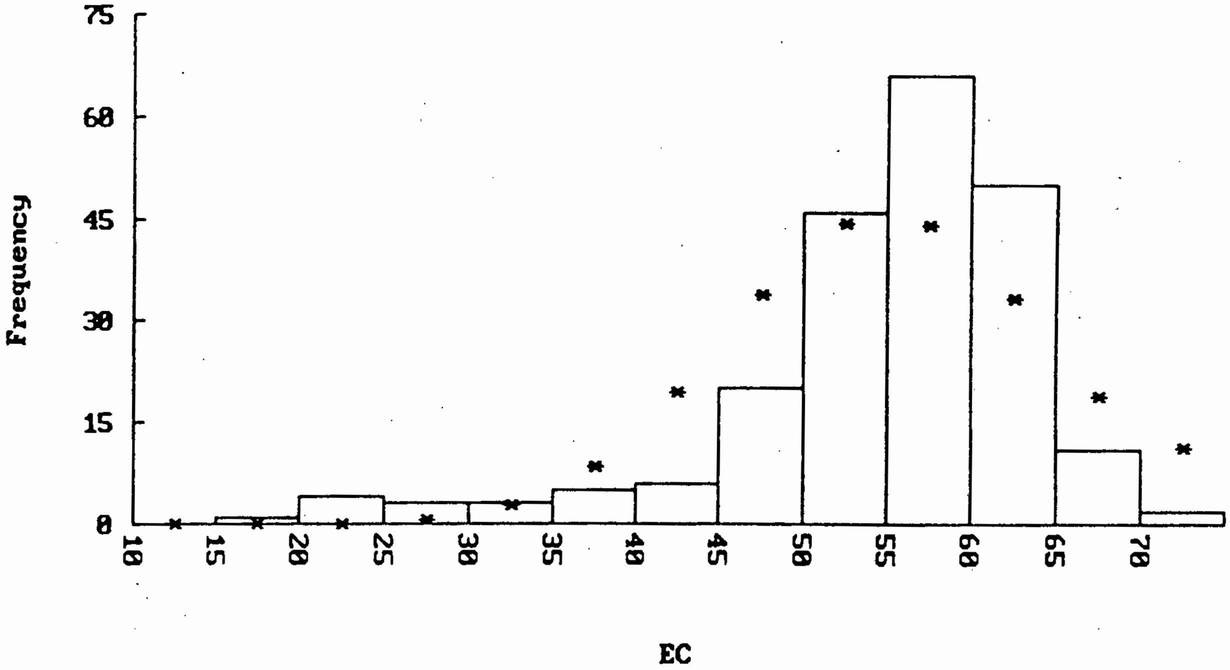


Figure 3.4. A frequency distribution histogram of electrical conductivity (mS.m^{-1}) at surface water site RESM09 over the duration of the monitoring operation. * = calculated normal distribution from the data set.

3.2.2.2 The analysis of trends in the data

For the purpose of this study, a trend is considered to be evident if the values of a data set generally increase or decrease with time. Three graphical procedures were used to look at trends in the summary statistics section of WQStat II:

(i) A time series plot may reveal obvious trends which can be identified visually (Figure 3.5). Such time verses concentration plots may also identify cyclic fluctuations although no suitable examples were found in this study.

(ii) Annual box and whisker plots show the medians, interquartile ranges and maximum and minimum values for each year within a data series (Figure 3.6). Trends are sometimes more obvious in B+W plots than XY graphs.

(iii) A trend may be observed by the use of a correlogram. The data need to be adjusted for seasonal means, however, which is not always possible. A successfully constructed correlogram will indicate a trend through a large positive value at lag one with a gradual decay of values at lags (or time periods; section 3.2.2.3) thereafter (Figure 3.7).

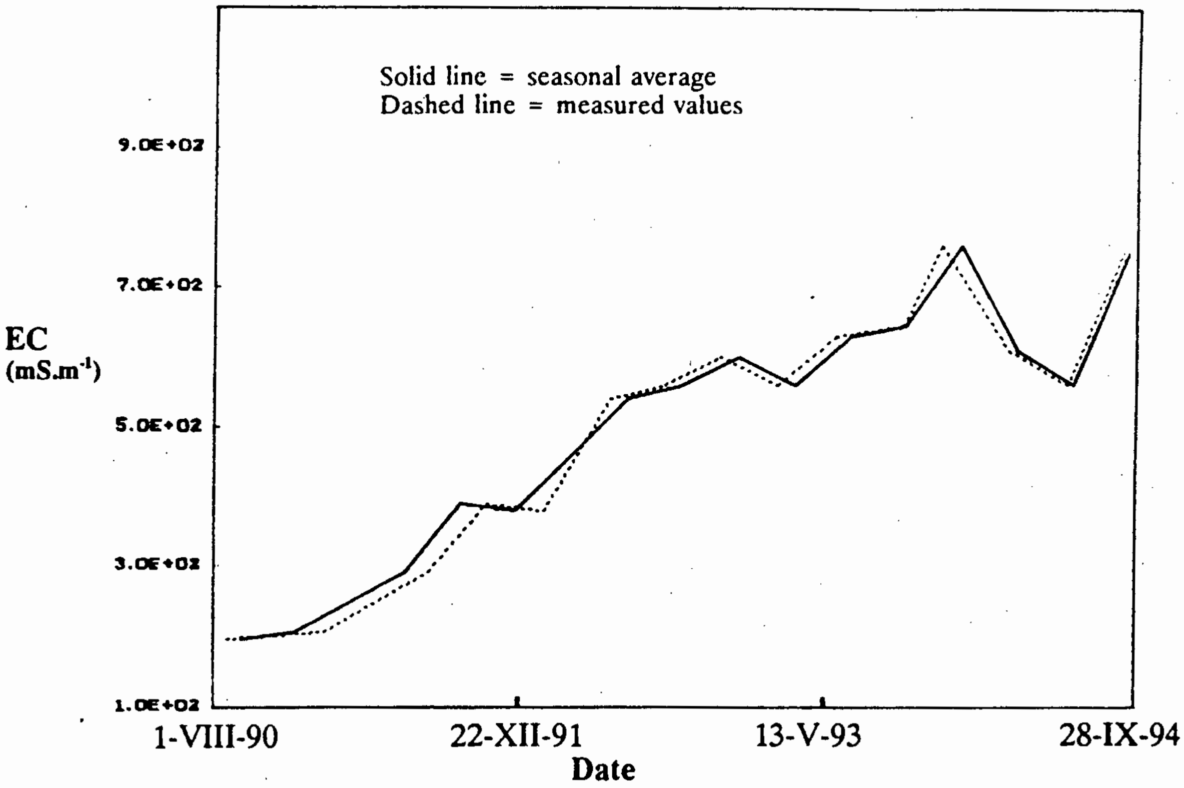


Figure 3.5. An example of a time series plot (from ground water site REGM21) produced by WQStat II which enables the qualitative identification of a trend and possible inference of cyclic fluctuations.

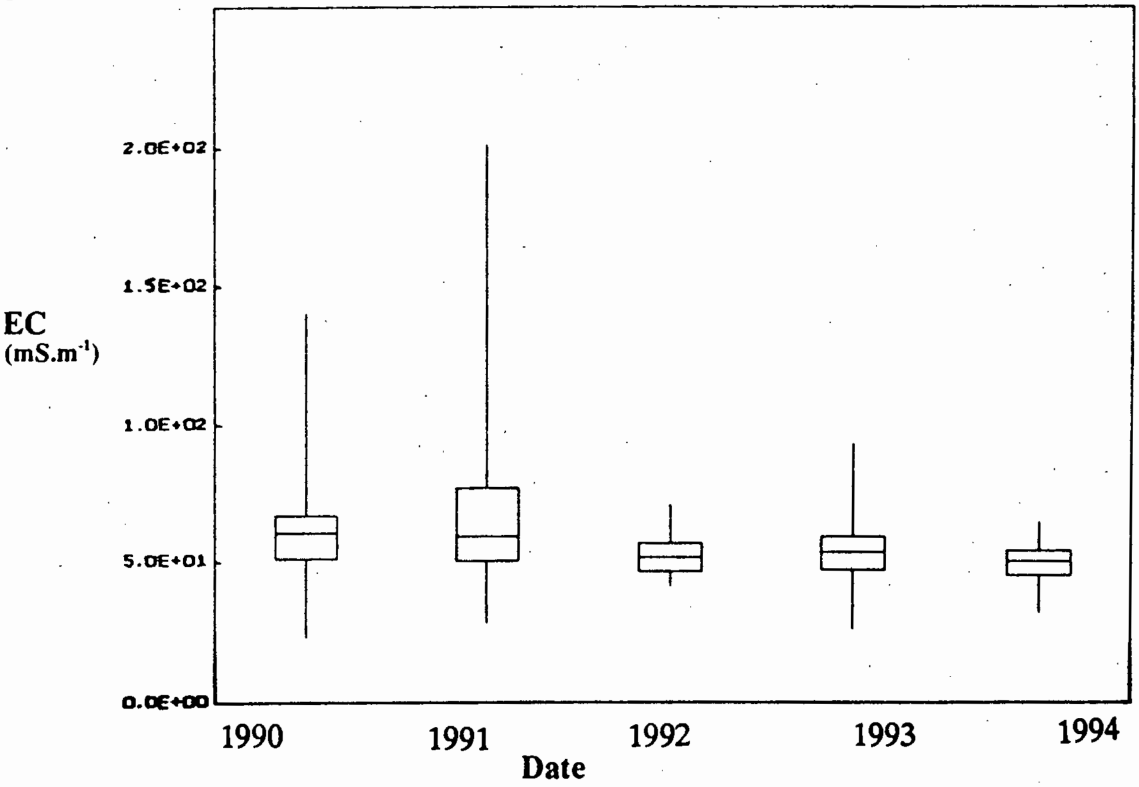


Figure 3.6. An example of an annual box and whisker (B+W) plot using the RESM01 electrical conductivity data set. A clear trend would be evident if the medians and ranges did not overlap.

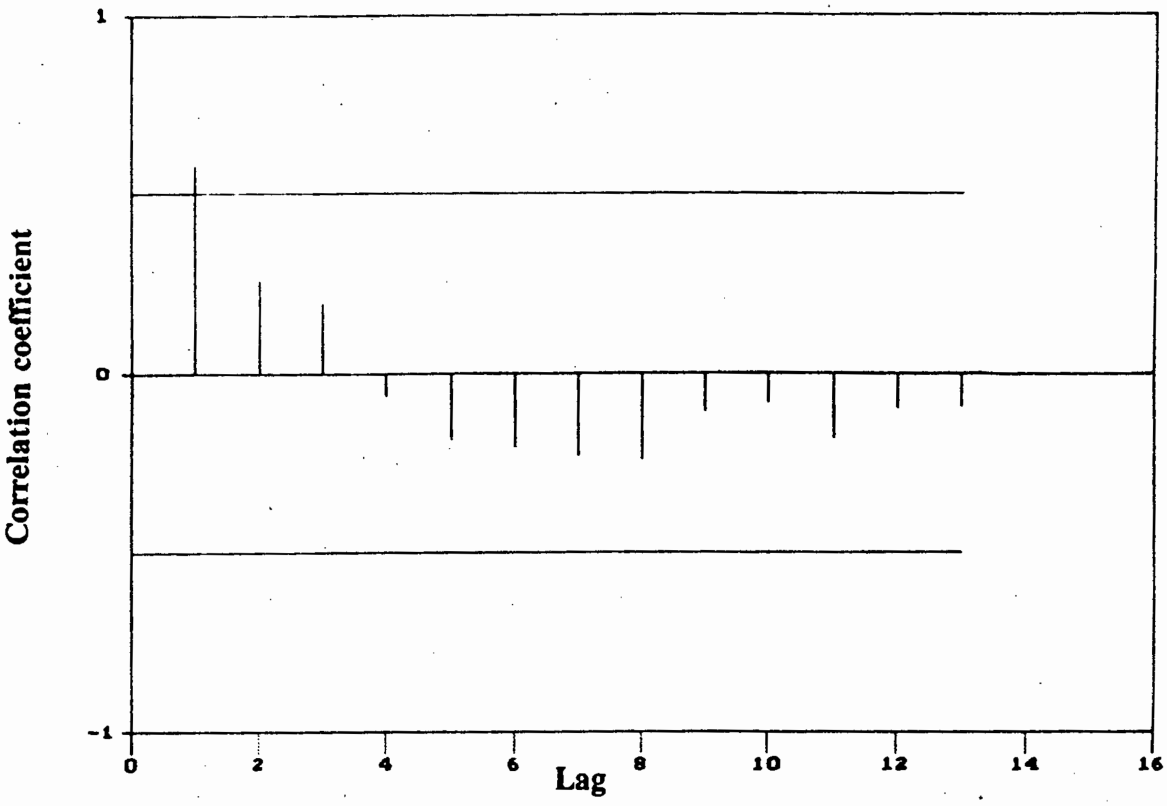


Figure 3.7. **An example of a correlogram constructed by WQStat II. Temporal regularities are difficult to identify using a correlogram if seasonality cannot be determined from the data set and accounted for in the construction of the graph.**

In addition to graphical analysis of the data series, three types of statistical tests can be performed. The manual for WQStat II suggests that usually the Kendall procedures are preferred over analysis of covariance but the explanation is unclear (WQStat II, 1989). The tests are:

(i) Both the Kendall Tau and the seasonal Kendall Sen procedures test whether data values at the beginning of the data are significantly larger or smaller than values later in the set. The Kendall Tau test is recommended if the duration of the data series is not longer than five years (Gilbert, 1987), implying that the analyst is unlikely to be confident about the expression of seasonality.

(ii) The seasonal Kendall procedure is beneficial for a data set with more than five years of information, coupled with fluctuations of values between seasons.

(iii) The analysis of covariance is a multiple linear regression on the ranks of the data with terms to account for trend and seasonality.

The estimated Sen Slope is then tested for significance. The slope estimate can also be used as an overall indicator of the trend, not only showing the trend direction (positive or negative) but also the magnitude of change (Figure 3.8).

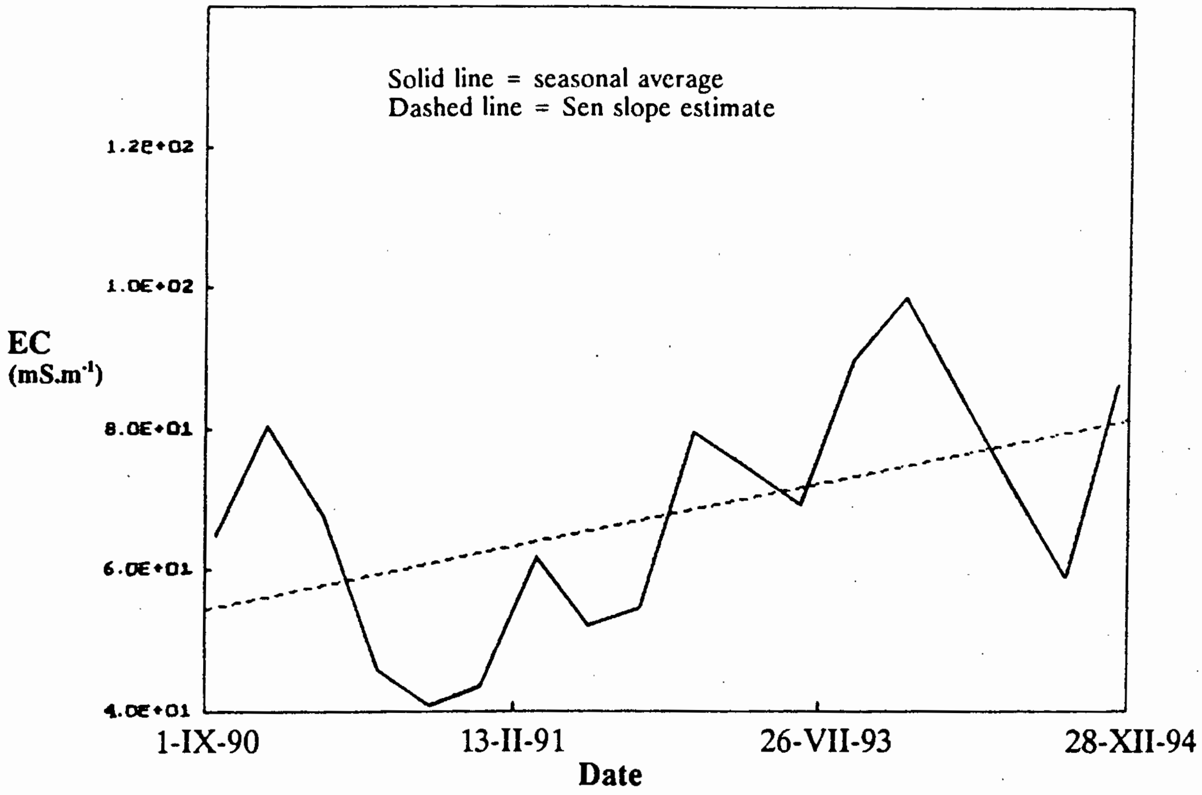


Figure 3.8. An example of a Sen slope estimate with the use of the RESM10 electrical conductivity data set.

WQStat II has the great benefit of producing an explanatory graph after running each statistical test. When considering the Sen slope, a simple graph will support the conclusion of the test. For example, Figure 3.8 shows the estimated Sen slope, indicative of the overall trend, for the surface water monitoring site RESM10. In this case, the Kendall Tau test result is 1.97, indicating a significant trend, and the slope estimate is +18.99 $mS.m^{-1}.yr^{-1}$ (Table 3.1c). Of all the monitoring localities, the largest slope estimates are for ground water data from REGMs 17 and 21, with Sen slopes of 216 and 149 $mS.m^{-1}.yr^{-1}$, respectively. These values reflect a considerable increase in pollution over the last four years.

3.2.2.3 Analysis of seasonality

Seasonality represents a predictable annual cycle in the data due to the regular time periods between events, and is inferred when the mean or variance of one period is significantly different from the mean or variance of other periods. WQStat II enables seasonality to be analyzed in a variety of ways:

(i) Seasonality is considered to be present if an annual cycle exists in the time series graph (Figure 3.9). If, however, this observation cannot be supported by a statistical test, it could be argued that the observation of periodicity is subjective.

(ii) A seasonal box and whisker plot has a centre line for the mean of each season, the ends of the boxes are the interquartile ranges (the middle 50% of the data) and the ends of the whiskers are the maximum and minimum values (Figure 3.10). Seasonality, with regard to the mean of data sets from different time periods, might be significant if the boxes do not overlap. Seasonality in the variance, however, might be significant if boxes are much different lengths. Figure 3.10 is the best example of seasonality found in the study. It appears that seasonality cannot be conclusively inferred for any of the monitoring locations. An inspection of Figure 3.10, however, might lead to the conclusion that there is biennial seasonality. The six-monthly periods are a wet spring and summer, with low mean and high variance in electrical conductivity due to dilution, and a dry autumn and winter, with sustained pollution events.

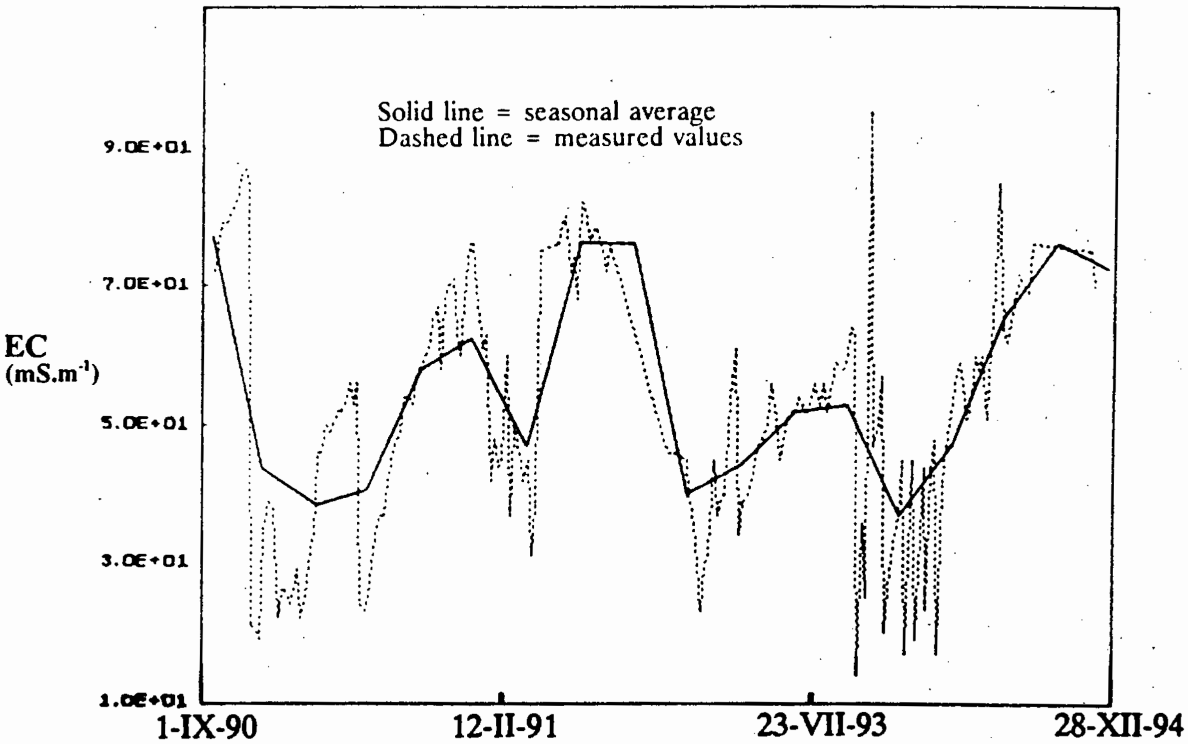


Figure 3.9. **A time series plot of electrical conductivity data from surface location RESM07 demonstrating seasonality. Although seasonal (regular) fluctuations could be concluded from this graph, objective statistical support should be applied. The Kruskal-Wallace test (Table 3.1b) confirms the seasonality as just significant.**

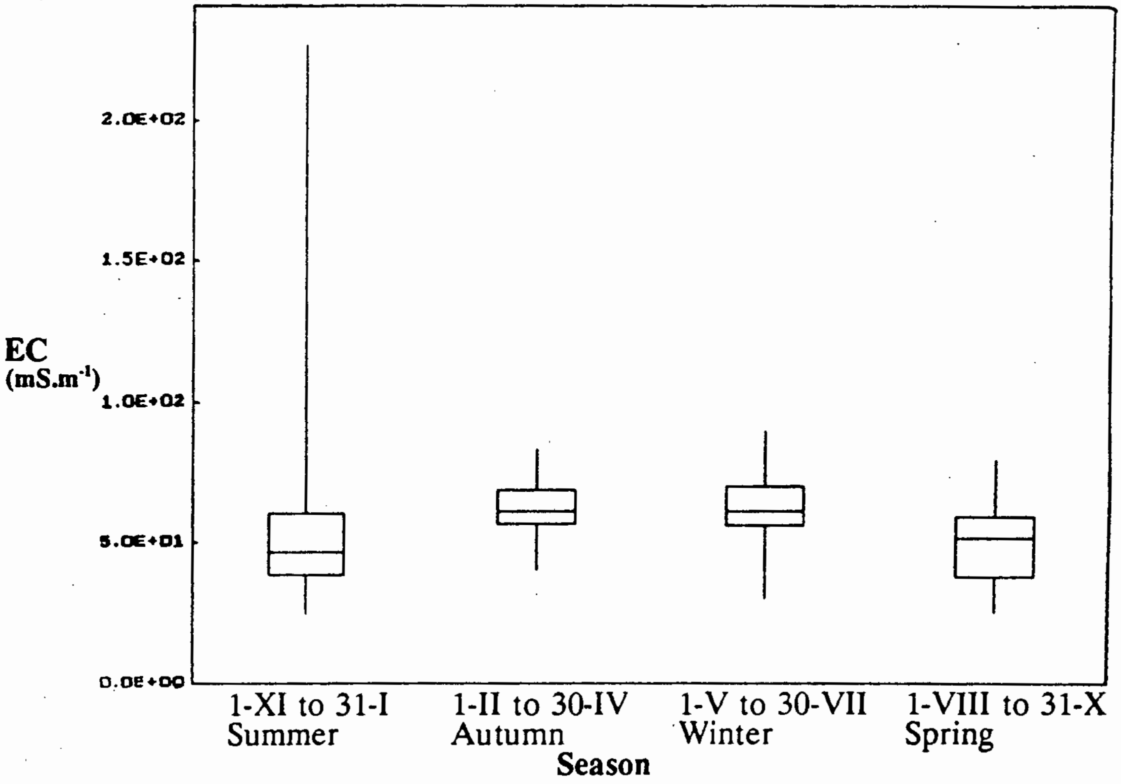


Figure 3.10. A seasonal box and whisker plot. If the boxes did not overlap there would be a significant difference in the means of each season. If the boxes where different lengths the seasonal variances could be considered as different.

(iii) A correlogram shows the correlation of a variable with itself in different time periods. The ordinate of the graph at lag N (Figure 3.7) is the correlation coefficient corresponding to data points N times apart. Seasonality is present if a significant negative correlation exists at half year intervals. For example, 2, 6, 10, ... lags for quarterly data, or 6 and 18 lags for monthly data. A significant positive correlation exists at yearly intervals if there is a similar trend in the correlation coefficients. *e.g.* 4, 8, 12, ... for quarterly data, or 12 and 24 for monthly data. For a more complete explanation the reader is referred to the WQStat II manual.

No suitable correlogram example could be found in the data sets of the monitoring operation under study. It is possible, however, to understand the theory by looking at Figure 3.7. **This graphical evaluation procedure might be applicable to other monitoring networks and is highly recommended when seasonality is present.**

(iv) A Kruskal-Wallace test checks for significant differences in medians across seasons. The test will indicate a significant difference if one or more of the medians varies from the others (Tables 3.1a to 3.1c.)

A section in the WQStat II manual suggests that if any of the four above tests indicate seasonality, or if there is some physical reason to believe that the water quality series under study should vary seasonally, it is 'safest to assume that seasonality is present'. This, however, could be dangerous when the pollution events occur randomly but monitoring is only done in certain seasons. No clear seasonality was found in the data sets studied, although there is some evidence for biennial periodicity.

3.2.2.4 Within-data series correlation analysis

As a follow-on from an assessment of trend within a data set, a comparison of two time intervals within the series can be made. An example is the need to compare the first half of a monitoring period with the second half to see if an overall change in a water quality variable is significant. One option in WQStat II provides for comparison of data sets over time. The two data sub-sets are both extracted from the same data series and a seasonal Hodges-Lehman estimate of the median difference between the sub-sets is calculated. This procedure produces a graph which shows the median differences (Figure 3.11). If the data sets can be paired (*i.e.* January to January, February to February, *etc.* for monthly data or a spring to spring, summer to summer, *etc.* pairing for quarterly data) then the WQStat II manual suggests the use of the Wilcoxon signed rank test. The calculated test statistics for within correlation analysis are also listed in Tables 3.1a to 3.1c.

The Wilcoxon test accounts for seasonality without prior adjustment of the data and provides a test statistic on the significance between the data set medians. If the data sets cannot be paired (January to January, *etc.*) and one is confident that the data shows no seasonality, then WQStat II suggests the use of the Mann-Whitney test. This statistic will also identify the significance of the median difference. The favoured test for the monitoring operation under study is the Wilcoxon.

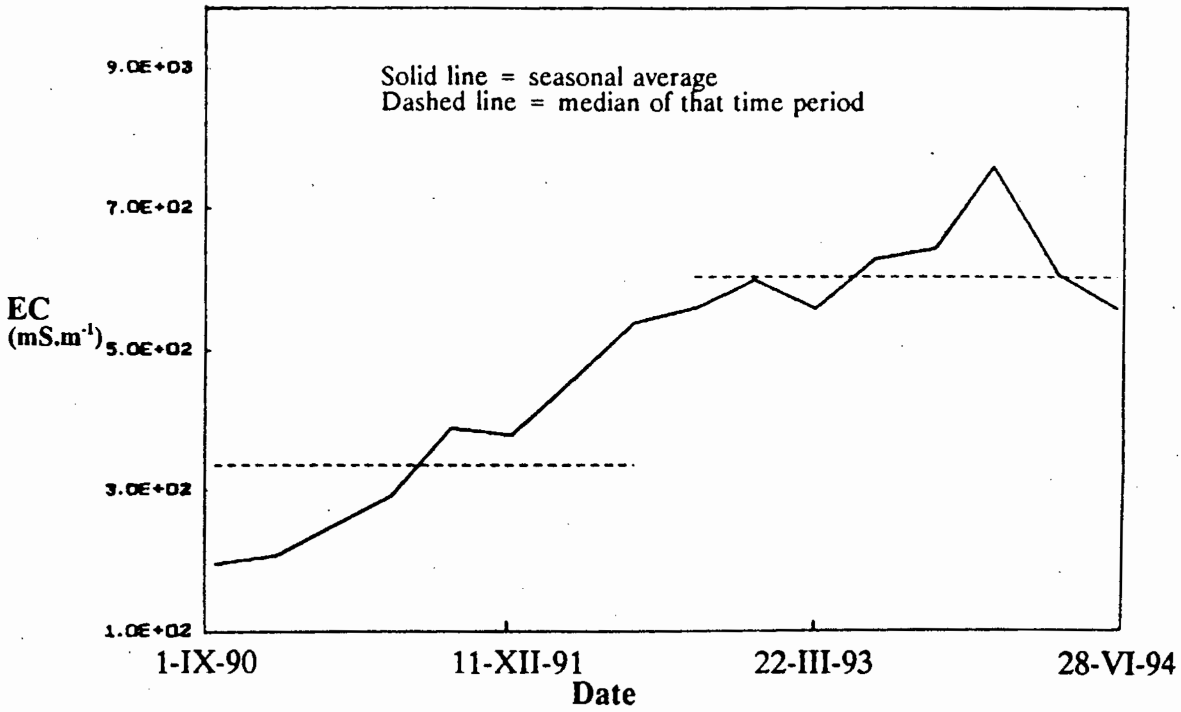


Figure 3.11. **An example of the median difference of the first and second halves of the monitoring period. This demonstrates the Hodges-Lehman estimate (Table 3.1a) of a 305 mS.m^{-1} deterioration in water quality (increase in EC) in borehole REGM21.**

3.2.2.5 Excursion limit determinations

Before the author fully understood the abilities of WQStat II, the significance of monitoring site values exceeding guideline thresholds was to be studied in a different way. If the mean of a component is obtained from a number of sites, a ratio can be calculated and compared with a recommended value or with one pertaining to the ambient conditions. This would demonstrate the relative magnitude of the analytes exceeding the guideline. This method, however, would take account neither the variance of the data (*i.e.* how often the value is greater than the recommended level) nor when the values are exceeded (*i.e.* the seasonality).

WQStat II has an automatic facility for comparing a data set with a defined standard. This standard might be a statutory concentration, an excursion limit or an action level. The 'proportion of excursion' procedure computes the fraction of observations above a certain limit, along with confidence intervals around this proportion. The proportion of excursion is computed for each season and for the total period.

This procedure is parametric and depends on a normal distribution. Normality is not an acceptable assumption for this monitoring operation (section 3.2.2.1) and therefore there may be errors associated with the results given in this section. For a data set chosen at random, the probability shown at either the 95% or 99% confidence level that the proportion of excursion will in reality fall within the stated limits.

WQStat II is also able to estimate the tolerance interval, *i.e.* the data value with a certain proportion (*e.g.* 75%) of a data set below it. The calculations associated with tolerance intervals have complications, however, when no baseline water quality values are known. Without an 'unaffected' monitoring location (up-gradient) with samples collected at nearly the same times (so that logical pairing exists between the baseline and the affected sample site) the seasonality and other external effects cannot be adjusted for. This highlights the importance of background sampling, which has not been done as part of the monitoring operation.

DWAF (1993a and 1993d) have specified relevant water quality guidelines which are applicable to the monitoring area under study. It is, therefore, not necessary to use the tolerance level calculations that can also be performed by WQStat II. The proportion of excursion determines the fraction of observations, over a time period, which occurs above the pre-defined limit. Confidence intervals are assigned to this proportion. Three guidelines were chosen from the DWAF documents. Since EC is probably the best single indicator of water quality, the recommended levels relate to the total ionic concentration.

- 70 $mS.m^{-1}$ is the DWAF (1993a, p.32) guideline for domestic used water. It is the limit of salt concentration with no health or aesthetic effects, although the water may taste slightly salty. The level takes into account the higher water consumption expected in hot climates, such as South Africa (Appendix VII, Table VII.1). The value of 70 $mS.m^{-1}$ is also the permit guideline for the 95 percentile prescribed by DWAF.
- 154 $mS.m^{-1}$ is the guideline value below which suitability for livestock watering is indicated (DWAF, 1993d, p.88; Table VII.2).
- 270 $mS.m^{-1}$ is the maximum salinity level which could be expected to cause a 90% relative yield in moderately salt-sensitive crops. A low frequency irrigation application is required, with a leaching fraction of up to 0.15, and wetting of sensitive crops prevented (DWAF, 1993d, p.35; Table VII.3)

A selection of data sets that are representative of the overall monitoring operation were analyzed for statistical temporal patterns. Tables 3.1a to 3.1c contain the results of most of the tests. An overall assessment was ensured by studying one borehole (REGM) from six of the more important waste operations (Table 3.1a) and six surface (RESMs) sampling localities each from the northern (Table 3.1b) and southern spruits (Table 3.1c)). Appendix VII (Tables VII.1 to VII.3) show, for different threshold values, the proportion of excursion of the monitoring sites for seasons and for the year as a whole. The more important results of this analysis are displayed in Figures 3.12 to 3.15.

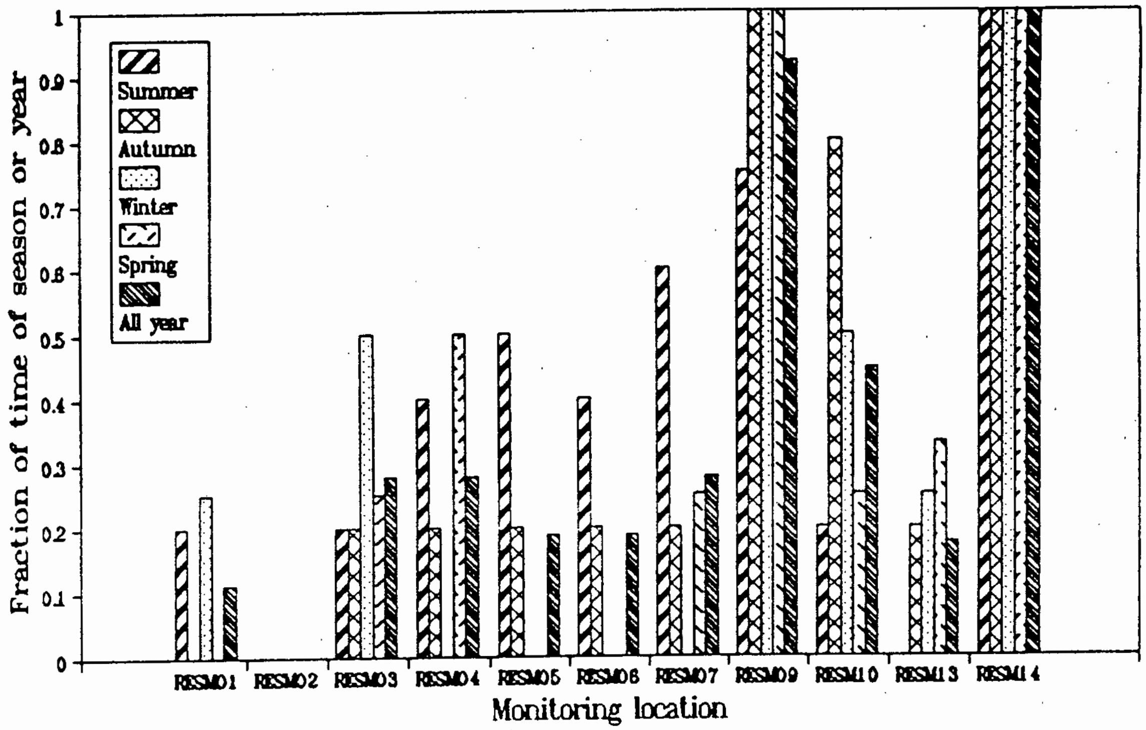


Figure 3.12. A selection of electrical conductivity data sets from surface water (RESMs) for which the proportion of excursion over 70 $mS.m^{-1}$ has been estimated for different seasons and for the total monitoring period.

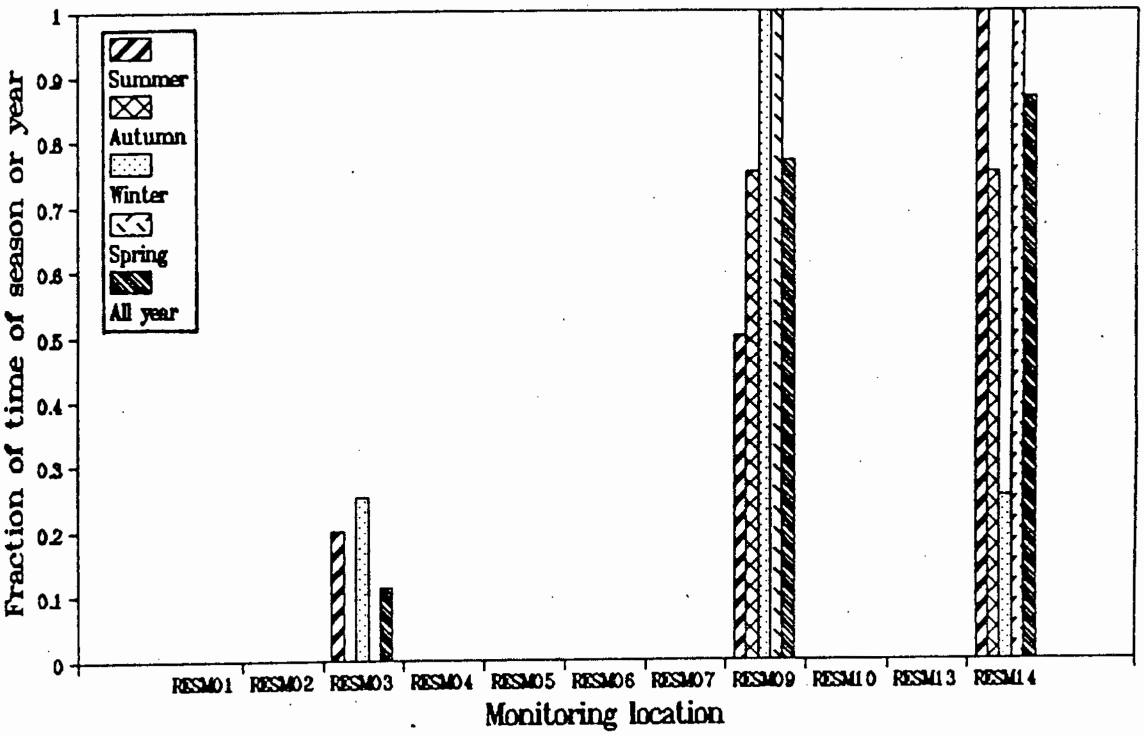


Figure 3.13. A selection of electrical conductivity data sets from surface water (RESMs) for which the proportion of excursion over 154 mS.m^{-1} has been estimated for different seasons and for the total monitoring period.

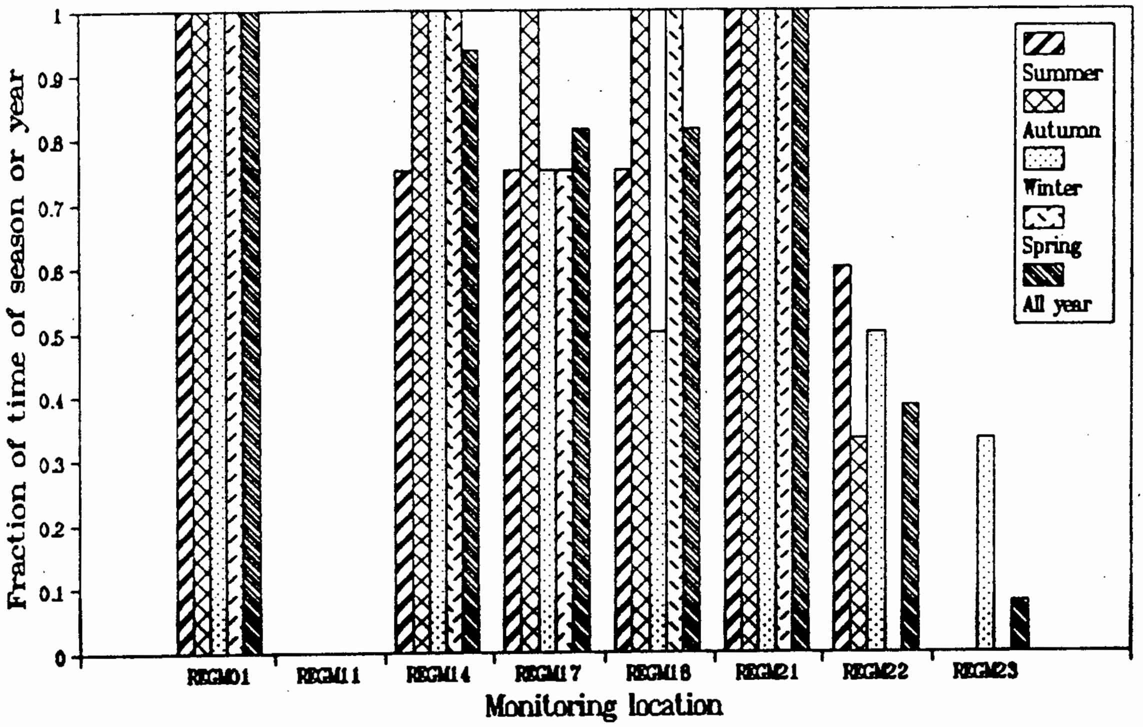


Figure 3.14. A selection of electrical conductivity data sets from boreholes (REGMs) surrounding different waste operations for which the proportion of excursion over 154 mS.m^{-1} has been estimated for different time periods.

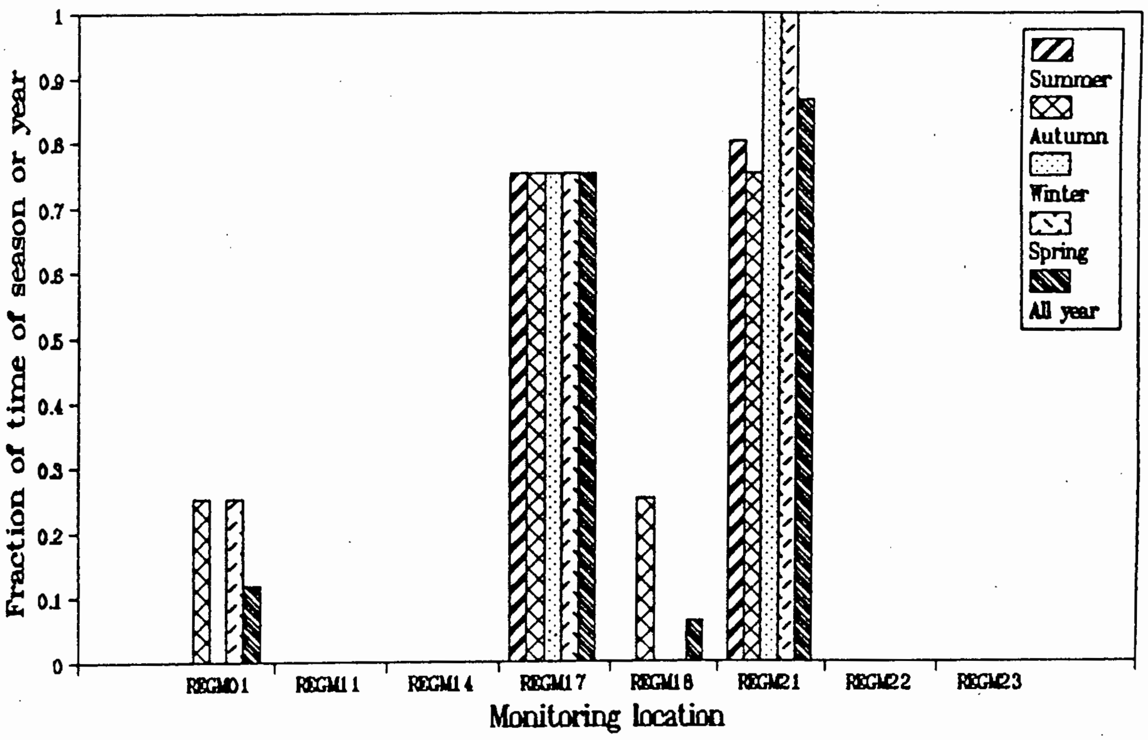


Figure 3.15. **A selection of electrical conductivity data sets from boreholes (REGMs) surrounding different waste operations for which the proportion of excursion over 270 mS.m^{-1} has been estimated for the different time periods.**

3.2.3 Discussion

Figures 3.12 to 3.15 show that at many of the monitoring localities, one or more of the recommended EC guidelines is exceeded. The data sets do not display true periodic seasonality. There is no temporal pattern exhibited by the ground water monitoring sites with regard to guideline exceedance. Surface water sites, however, did show some indication of climatic fluctuation. The seasons were delineated by studying meterological information obtained from the CCWR database (Appendix I, Figure I.2). No pattern emerged which could be identified as statistically significant, it was therefore concluded that episodic anthropogenic factors are the dominant cause of EC perturbations.

The most frequently polluted surface water sites are RESM09 and RESM14 (Figure 3.12), both of which are heavy influenced by the reject fertilizer dump. These two sites exceed the guideline for livestock drinking water (154 mS.m^{-1}) about 65 to 80% of the time (Figure 3.13). Other surface sites monitored, however, do not display such evidence of a major impact. The ground water in the area is much more heavily contaminated (Figures 3.14 and 3.15). The exceedance of 270 $mS.m^{-1}$ (crop irrigation quality guideline) is greatest in REGM17 and REGM21 (Figure 3.15) which monitor the fertilizer dump and salt water dam, respectively. For over 70% of the period, the EC in this part of the aquifer has been higher than the recommended threshold for irrigation water. Of the borehole data studied, most of them exceed the guideline for livestock watering over 75% of the time (Figure 3.14), Three exceptions are REGM11, REGM22 and REGM23.

Table 3.1a indicates that the ground water quality in the area is worse than the surface water. Averages are often high, and highly variable. By far the most polluted areas are the fertilizer and explosives dumps and the salt water dam, represented by REGMs 17 and 21 respectively. The frequency of pollution at the ground water site REGM17 is so high that it produces a positive skew of the data distribution.

The slow response time of ground water to a change in climatic conditions prohibits manifestation of seasonal fluctuations. The water quality of an aquifer is stabilised by attenuation and buffering capacity. The one exception might be REGM14 which monitors the coal stockpile. Pollution at this site is leachate-generated. Contamination will, therefore, be directly related to precipitation, which possibly leads to the identification of seasonality. Although not significant at 90% confidence, REGM14 shows the strongest seasonality of all the ground water data sets (Table 3.1a).

The seasonality may not be detected in the data sets because of large fluctuations in the transitional seasons, *i.e.* in spring and autumn. The distribution of the data over time is clearly punctuated by periodic highs and lows. The data sets often show episodic fluctuations of high frequency, possibly superimposed on a seasonal variation in concentration. Obviously, this is harder to statistically identify.

The estimate of median difference (Table 3.1a) shows all of the ground water sites to have deteriorated in water quality except REGM23. Boreholes 01, 11 and 10 have, however, only slightly worsened. This observation of trend is supported by the median slope estimate but not always statistically conclusive in terms of the Wilcoxon test. The worst borehole studied by WQStat II procedures is clearly REGM17 which, although not statistically proven, has suffered an EC increase of about 580 $mS.m^{-1}$ in the last two years. Some mitigating measures need to be implemented. The clear exception, REGM23, monitors an irrigation area and is an excellent example of how waste can be handled and disposed of without affecting the environment. The Kendall Tau test statistic of REGM23 shows a negative trend but it is not statistically significant. It cannot, therefore, be assumed that water quality has improved in the vicinity of REGM23. Environmental management of the irrigation area has nevertheless probably helped to maintain ground water quality.

The appraisal of surface water monitoring sites (Tables 3.1b and 3.1c) reveals a different pattern to that found for ground water quality. The means are much lower, at around 50 $mS.m^{-1}$, with smaller variance within the data sets. This smaller deviation may be due to more frequent sampling accounting for the decreased variability of the analyte. The two exceptions, of those statistically studied, to generally good surface water quality are RESM09 and RESM14 (Table 3.1c). The high standard deviation shows that RESMs 09 and 14 occasionally have very high electrical conductivity. These sample sites are situated near the fertilizer dump (RESM14) and below the coal stockpile, the ash dams and the reject fertilizer area (RESM09).

Surface water quality is far more likely to display seasonality due to the greater influence of rainfall on runoff and surface flow rate compared to ground water flow. Only monitoring site RESM01 (Table 3.1c) shows significant seasonality, however, this suggests that climate is not the dominant factor in quality fluctuations, which implicates anthropogenic factors (section 2.1). This conclusion supports that of the guideline excursion analysis.

There is considerable variation in the temporal trends in water quality at the monitoring sites. Some show increases and others decreases, suggesting that site-specific factors are involved. The magnitudes do not, however, represent an environmental hazard. The area is clearly not subjected to catastrophic pollution, but the problem is growing. The most important feature, perhaps, is the overall improvement in water quality at RESM01 with the EC dropping an average of -2.48 $mS.m^{-1}.yr^{-1}$. An improvement is also a feature of RESM03 and RESM09, although not yet significant.

3.3 EFFECTS OF THINNING TEMPORAL DATA ON INTERPRETATION

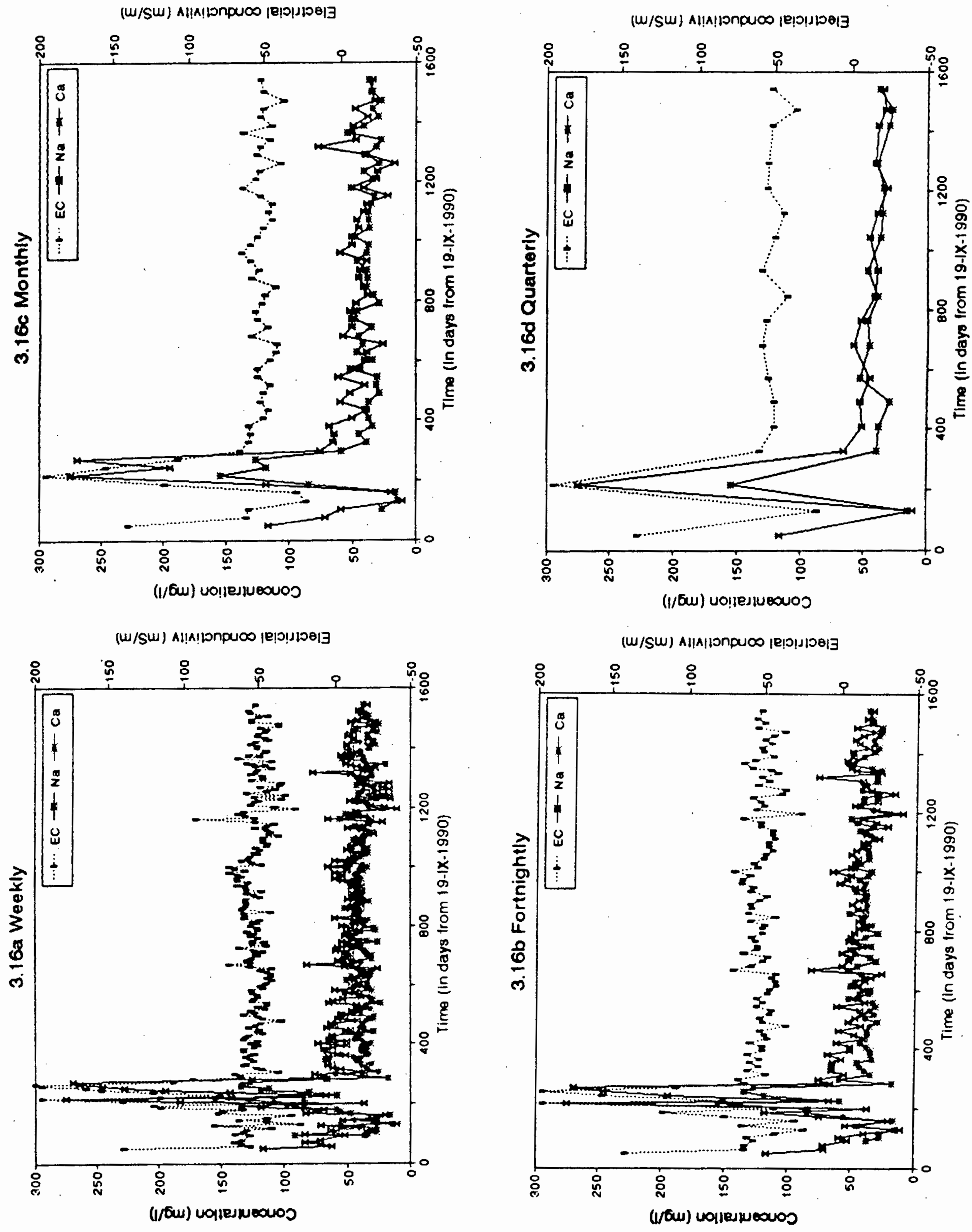
It was hypothesized that the effect of reducing the sampling frequency can be tested by systematically eliminating the values of a sampling site over time. With the current availability of monitoring data, the frequency of sampling can be reduced from weekly to fortnightly, monthly or quarterly and time series plots of data can be reconstructed to demonstrate the reduction in resolution associated with the data thinning. The questions of concern are:

- What is the information loss associated with the reduction of sampling frequency?
- Can the same inferences on water quality be drawn from a data series for monthly-sampled water, for example, as from one which contains results of weekly samples?
- If so, then to what degree and with what confidence can the periodicity of sampling be reduced while still maintaining an acceptable information reliability?

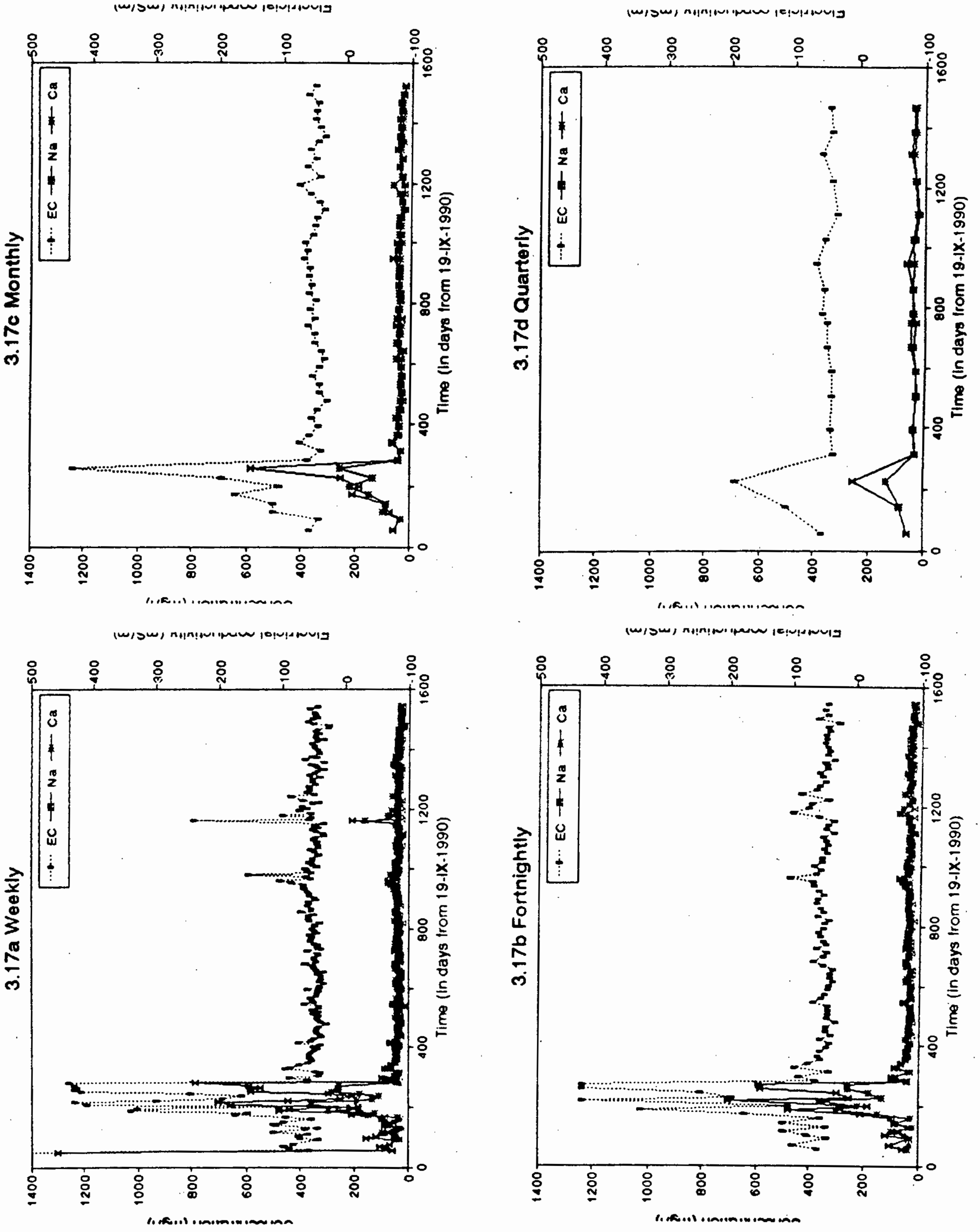
The present cost of collecting one surface water sample is estimated at R 273 (Appendix II). To completely analyze one water sample costs approximately R 763 (Appendix III). If 15 surface water monitoring sites are sampled weekly the annual cost would be about R 213 000. This budget requirement would decrease to R 107 000 for fortnightly samples, R 49 000 for monthly and R 16 000 for quarterly sampling and analysis.

Systematic manual thinning of a selection of data sets (observations of water quality parameters over time) was performed. The only area of concern arose around the thinning of a data series which had missing values. To avoid this problem only near-complete weekly data sets where chosen. Despite this, the presence of missing values is exaggerated by the thinning procedure, as illustrated in Figure 3.18. The decision only to select a few sites with good data sets is justified since the objective of this section is simply to demonstrate the effect of sampling frequency and is not site-specific.

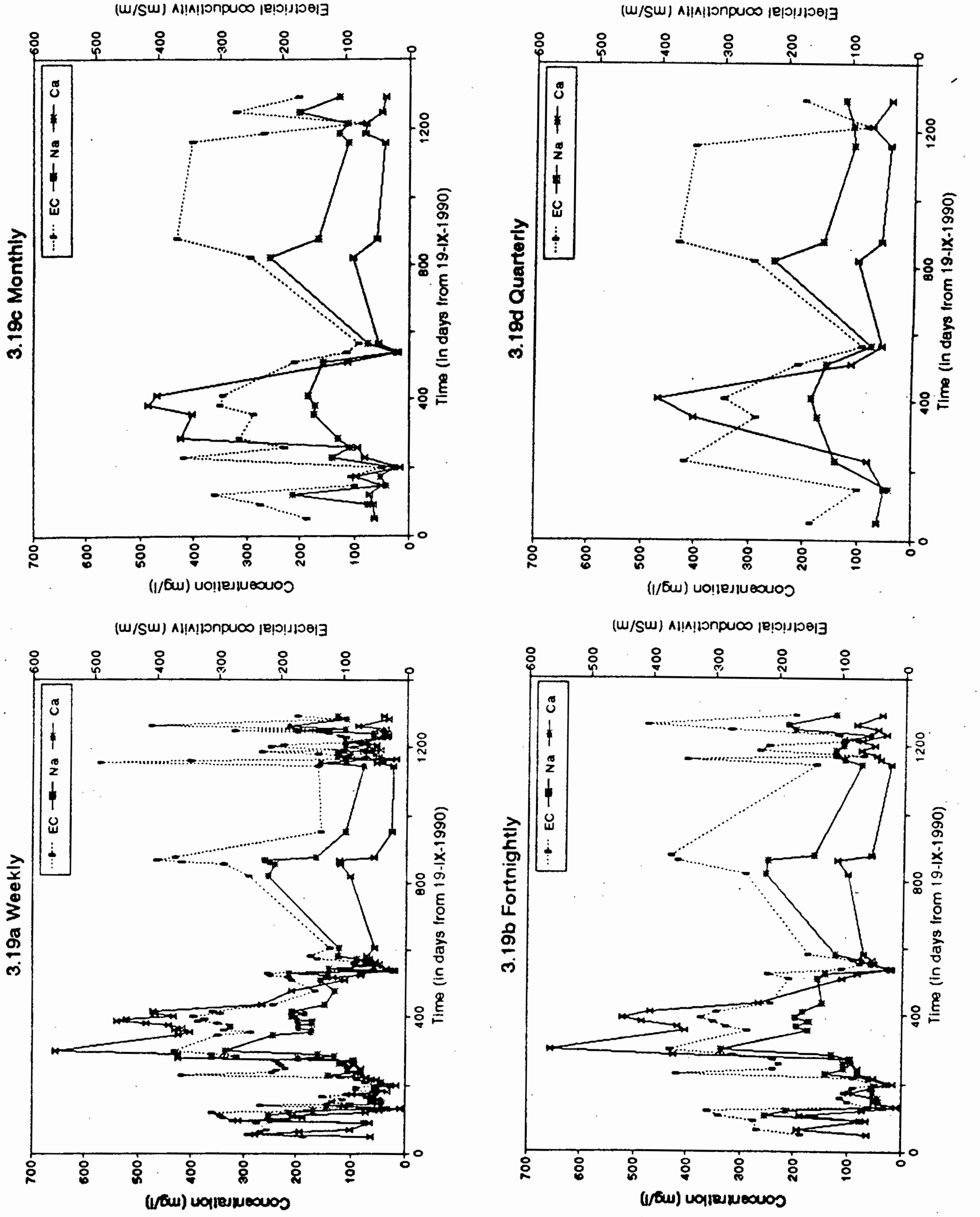
Figures 3.16 to 3.19 show examples of data thinning. The data entered for weekly sampling (Figures a) were systematically reduced to fortnightly sampling (Figures b), to monthly (Figures c) and then quarterly (Figures d). The concentrations of the dominant cations and EC have been used to demonstrate the effect of thinning, which required the sampling dates to be scrutinized to ensure that the correct periodicity (weeks, fortnights *etc.*) was maintained between sample dates.



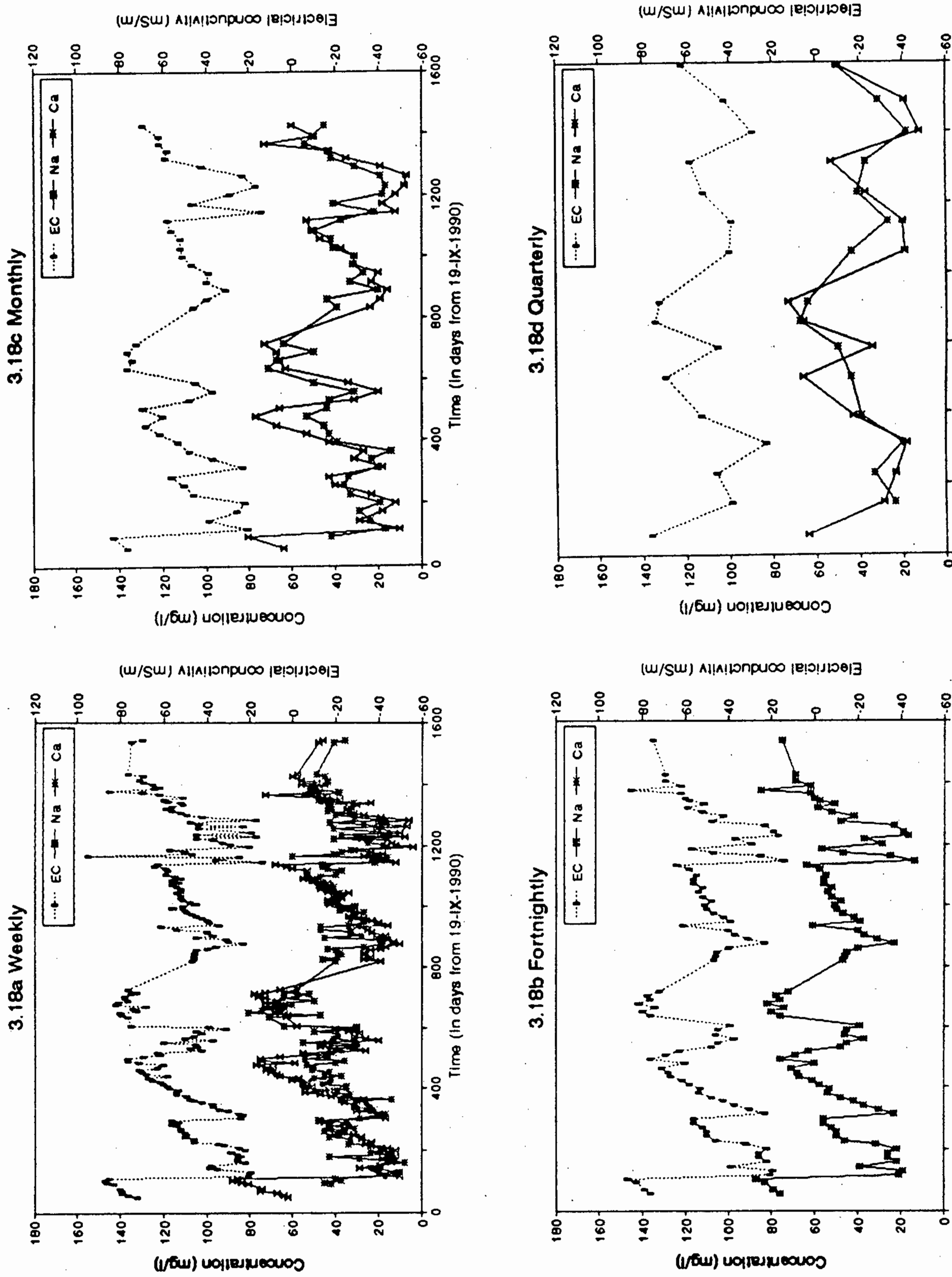
Figures 3.16a to 3.16d. **Electrical conductivity ($mS.m^{-1}$) and the dominant cations ($mg.dm^{-3}$) from the data set of surface water monitoring site RESM01 sampled weekly (3.16a) and hypothetical sampled fortnightly (3.16b), monthly (3.16c) and quarterly (3.16d) by retrospectively removing data for selected sampling dates.**



Figures 3.17a to 3.17d. Electrical conductivity (mS.m^{-1}) and the dominant cations (mg.dm^{-3}) from the data set of surface water monitoring site RESM03 sampled weekly (3.17a) and hypothetical sampled fortnightly (3.17b), monthly (3.17c) and quarterly (3.17d) by retrospectively removing data for selected sampling dates.



Figures 3.19a to 3.19d. **Electrical conductivity (mS.m^{-1}) and the dominant cations (mg.dm^{-3}) from the data set of surface water monitoring site RESM14 sampled weekly (3.18a) and hypothetical sampled fortnightly (3.18b), monthly (3.18c) and quarterly (3.18d) by retrospectively removing data for selected sampling dates.**



Figures 3.18a to 3.18d. Electrical conductivity (mS.m^{-1}) and the dominant cations (mg.dm^{-3}) from the data set of surface water monitoring site RESM07 sampled weekly (3.18a) and hypothetical sampled fortnightly (3.18b), monthly (3.18c) and quarterly (3.18d) by retrospectively removing data for selected sampling dates.

Figures 3.16 to 3.19 show the change in resolution with varying sampling frequency. Two methods were used to describe the change in the quality of the data. Correlation coefficients were calculated for the different period data sets (Figure 3.20 and Table VIII.1). A non-parametric alternative was used to calculate R^2 values, for reasons of non-normality of the data distribution (section 3.2.2.1). In addition, the change in the mean and standard deviation were estimated for the different sampling periods. The simple statistics and correlation values are listed in Appendix VIII (Table VIII.1) and illustrated in Figures 3.21a and 3.21b.

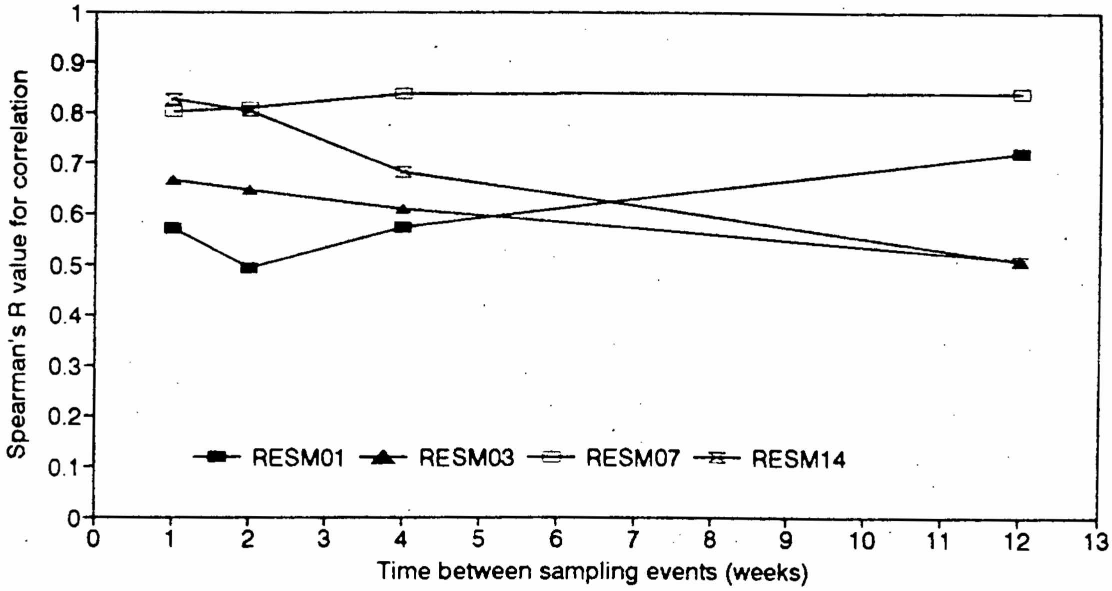


Figure 3.20. **Coefficient of correlation between EC and Ca concentration in data sets from different surface water monitoring locations, with weekly sampling or hypothetical fortnightly, monthly or quarterly sampling.**

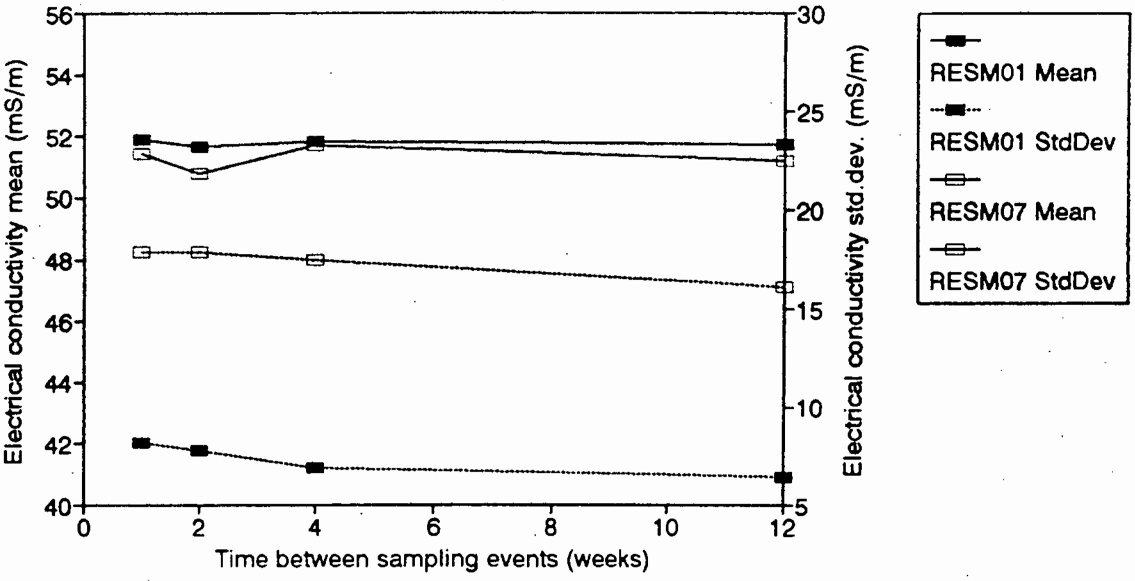


Figure 3.21a. Changes in the mean and standard deviation of electrical conductivity data sets for surface water monitoring sites RESM01 and RESM07, with the recognition of different sampling frequencies. This graph suggests the sampling interval has no effect on the information obtained.

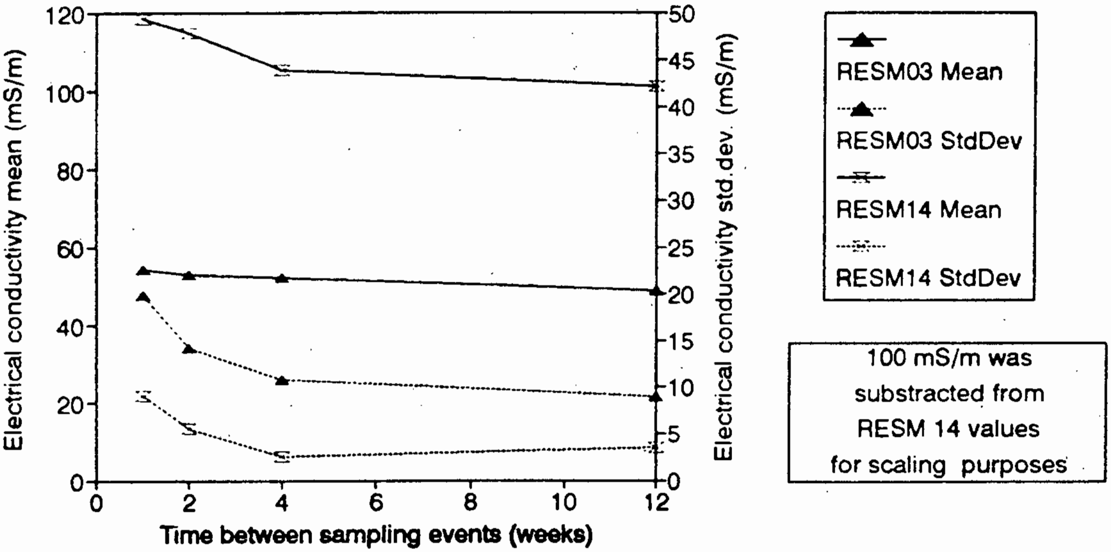


Figure 3.21b. Changes in the mean and standard deviation of electrical conductivity data sets for surface water monitoring sites RESM03 and RESM14, with the recognition of different sampling frequencies. This graph suggests that increasing sampling interval will profoundly decrease the accuracy of information.

Figure 3.21a, with data sets of surface monitoring sites RESM01 and RESM07, shows that the summary statistics do not significantly change with an increase in time interval between sampling events. The information gained from the weekly data set is not much different from that of the fortnightly or even the monthly data set. This would infer that the sampling frequency can be decreased without an adverse effect on the information. This is supported by correlation information in Figure 3.20, showing that an increase in sampling interval (decreasing frequency) may actual lead to some obscure events not being monitored and so the correlation coefficient between two analytes improves, fortuitously.

Figure 3.21b on the other hand, shows that the summary statistics may change drastically if the sampling frequency is reduced even by one step to fortnightly. The change in information resolution is also expressed by the decrease in the R^2 value (EC correlated with Ca) for the two locations (Figure 3.20). The monitoring operation at low frequency is not intense enough to detect the true correlation between analytes (EC and Ca are used as examples). If the lines in Figure 3.21b were extrapolated toward smaller sampling intervals, it might be suggest that the mean and standard deviation would increase along a near exponential curve. A similar extrapolation could be done on the RESM03 and RESM14 plots in Figure 3.20, and one could expect a stronger correlation between EC and Ca. The higher mean values, with an increase in sampling frequency, infer that pollution events would be determined more accurately, *i.e.* more high values would be recorded with greater distribution. A monitoring strategy with high frequency is, therefore, more realistic, as might be expected.

3.4 CONCLUSIONS

The first half of this chapter is devoted to explaining the features available in the WQStat II computer programme and their application to this case study. Arising from this, a closer insight was obtained into the regularities present in the data sets of the monitoring network.

There is a large variety in trends and in amplitude of fluctuations of environmental parameters at the different monitoring locations, both for surface and ground water

(Table 3.1). The main cause of pulses in analyte concentrations is probably anthropogenic, since seasonality was discounted in the data. Higher rainfall in the spring and summer does, however, introduce a degree dilution of the chemical constituents in the surface water.

The temporal statistical analysis completed on the series of sampling localities, both surface and ground water, shows that pollution patterns are relatively unpredictable. Appraisal in terms of water quality criteria indicated that caution is required before utilizing water in this industrialized area, since the water quality is quite often worse than recommended guidelines for various uses.

Overall, the water quality of the area has shown an improvement at the exit point from the industrial area since monitoring began. The RESM01 (exit point) data set shows high variability, inferring that there are still some major pollution events occurring at that locality. In addition, many zones within the area have increased the pollution loading or at least do not show signs of improving, most notably the reject fertilizer dump, the salt water dam and parts of the ash dump. Mitigating measures must be developed to stop or slow this increase in environmental degradation before it gets beyond remediation.

The four surface monitoring sites used as examples were chosen randomly. One case suggested that sample frequency can be decreased, while another showed that weekly sampling, as is presently done, falls short of monitoring reality, *i.e.* the information acquired is not complete. It could be proposed that each monitoring locality should be studied by systematic thinning of the data set in order to comprehensively revise the sampling frequency. This would require a detailed evaluation and has one major drawback. The conclusions would be based entirely on the previous 'track record' or signature of the monitoring site. In order to be valid, the sampling frequency determined by the method of systematic retrospective data reduction would have to assume a similar overall pattern to the data that will occur in the future.

Extrapolation of trends was used to demonstrate that there may be some benefit in increasing the sampling frequency. A decrease in sampling interval would more accurately identify the true mean and standard deviation of water quality and greater frequency should be attempted at a few monitoring points in order to more rigorously assess the advantage of doing so.

4. CRITERIA FOR ASSESSING WATER QUALITY

4.1 INTRODUCTION

Chapters 2 and 3 have dealt with the sampling stage of the monitoring operation, studying the spatial and temporal aspects of sampling, respectively. This chapter addresses the last two aspects of monitoring, namely analysis and interpretation. Strategies for optimizing analytical procedures will be examined. Following this, covariance between analytes will be sought in order to determine suitable pollution indicators. Finally, strategies for assessing and reporting environmental information, which are specific to this case study, are described.

4.2 RATIONALIZING THE ANALYTICAL PROCEDURE

4.2.1 Analytical strategies

Gilbert (1987, chapter 9) discusses the statistical benefits arising from what he terms 'double sampling'. Double sampling is the philosophy of running two sampling and analytical programmes in parallel to form a single monitoring strategy. Financial benefits can also accrue from developing different strategies. Frequently, two or more analytical techniques may be available for measuring the concentration of a pollutant. Raab *et al.* (1989) discuss an example, in which a mobile laboratory is used in the field to produce less time consuming and cheaper results, although with lower accuracy and more fallible techniques. The shortened turn-around time from sampling to decisive action has a significant advantage when compared to a time-consuming, fixed laboratory strategy. A second example of double sampling is the precise analyses done by a fixed laboratory on a small number of specimens supplemented with more measurements from the laboratory by a quicker method. This is particularly beneficial when determining averages over a large area. Double sampling is an approach which will be cost effective if the linear correlation between measurements obtained by both techniques on the same samples is sufficiently high, and if the fallible method is substantially cheaper than the more accurate method (Gilbert, 1987).

A broad assessment of the overall cost associated with a monitoring programme will show that the greatest expense lies in the analytical stage (Appendices II and III). Sampling is a relatively simple process, although a strictly prescribed protocol must be followed. Data interpretation may require considerable capital investment for equipment, such as computer packages, but is cheap to run relative to an analytical laboratory. The overall expenses incurred are a combination of the high laboratory start-up costs, the maintenance of equipment, the large consumption of materials and the use of qualified personnel (Willis, 1995; pers.com.).

Based on the premise that analysis is the most expensive stage, it is suggested that selective analyses can be performed. Monitoring involving the use of a fixed laboratory is generally not a design for 'early warning' because of the long residence times of specimens before analysis. Monitoring strategies frequently use portable or field measuring devices, which are often automated, as notification of a pollution event. Electrical conductivity measurement is a common indicator. An analytical laboratory is employed to help study trends and chemical behaviour, in addition to other phenomena, so decisions can be made pertaining to pollution source mitigation and the remediation of contamination.

If the laboratory's rationale is not for pollution detection but for pollution appraisal, it is not essential that chemical determinations are done immediately after sampling, providing appropriate sample preservation is completed (Willis, 1995; pers.com.). Sample preservation involves rendering specimens biologically, physically and chemically stable, by the use of cold storage for example. One scenario might be the collection of samples weekly, but only with monthly analyses. If an interesting phenomenon is identified which warrants investigation, the stored samples can be returned to for further analysis. The preservation of samples is also valuable in the event of legal disputes.

In this study, no comparisons of alternative methods have been done. Application of the philosophies of double sampling or of sample storage to this monitoring operation would require further investigation. This should include comparison of different fixed laboratory procedures for any specific analyte with potential field based techniques and studies of the chemical changes incurred by sample storage. The EMU of the industrial plant has plans to increase the amount of telemetric automated analytical equipment, which is cheaper but potentially more fallible. Further work is required to determine the loss of accuracy incurred by changing the strategy compared to the financial implications.

Analytical costs are often around US$150 per sample (Cole *et al.*, 1991), but the quality of results can only be as good as that of the samples collected. There are, however, many factors within the analytical procedure which may decrease the quality of results. The control of these factors, limiting those which are detrimental, is the objective of a quality assurance (QA) programme (Sargent and Mackay, 1995). There are various QA and QC (quality control) protocols which laboratories must adhere to.

This thesis is not concerned with methods used to achieve analytical excellence. Any environmental management department should have analytical acumen and the laboratory conducting the determinations must be tested with repeats and blind standards to ensure quality. An effective symbiosis is easily established between an EMU and the laboratory by constant good communication. The EMU needs results with an acceptable degree of guarantee. For this reason, monitoring networks often choose to use contract laboratories which are tightly held to QA. The author would refer any interested parties to documentation pertaining to QA and QC programmes, particularly ISO 9000 guidelines and associated literature, for example Sargent and Mackay (1995). The EMU should always be inquisitive about results. This will involve enquiring about techniques used, the associated errors and the limits of detection. Simple reference to a catalogue of potential analytical techniques is inadequate.

The list of analytes to be measured, and with what accuracy, will depend on management information requirements. The objective of this thesis was to optimize a monitoring network, therefore it is assumed that the EMU would desire the maximum amount of high quality information at the cheapest cost. Costs can be greatly reduced by analyzing only for the chemical components which are really necessary. The critical analytes are those which are the best indicators of pollution, *i.e.* those which identify the contaminants and those describing the magnitude of the event. The next section is concerned with ways to select the most important analytes.

4.2.2 Correlations between analytes

The information obtained in the monitoring strategy consists mainly of data sets of analyte concentrations over time, permitting statistical analysis. Some implications of non-normally distributed data are discussed in chapter 3. The lack of normality complicates correlation analysis and non-parametric statistics must be used. In addition, it is important to know the implications of reducing the number of analytical determinations permitted by covariance.

The majority of the data sets have distributions with most of the values in a cluster. Some individual events are, however, separated from the data mass (Figure 4.1a). These outlying data points often number 5 or 10 in a total of 500 + observations. In order to study relationships between analyte concentrations, correlation analyses can be performed. The correlation will be strongly influenced by the outlying points, lowering the confidence associated with the resultant statistic. The influence these points have does not discount the correlation, but produces a spurious result. A small error in the outliers would greatly alter the correlation and hence the regression line (Figure 4.1b).

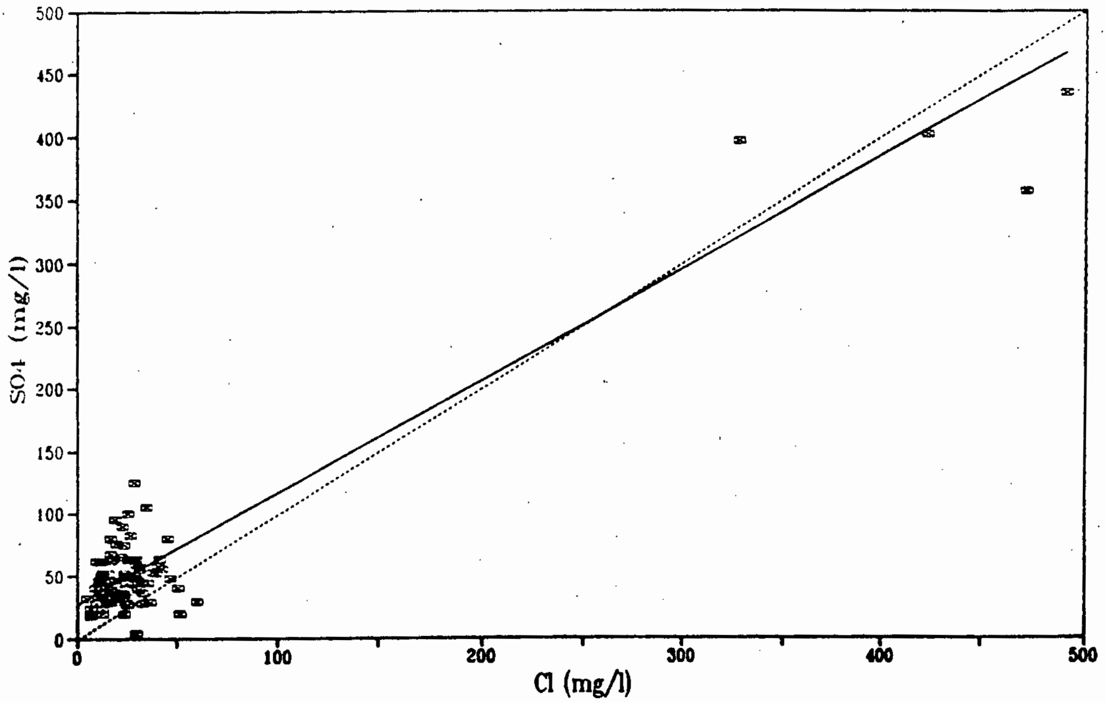


Figure 4.1a. An example graph (from surface water monitoring site RESM08) of two analytes (sulphate and chloride) showing how data sets have a clustered majority of observations with some outlying events.

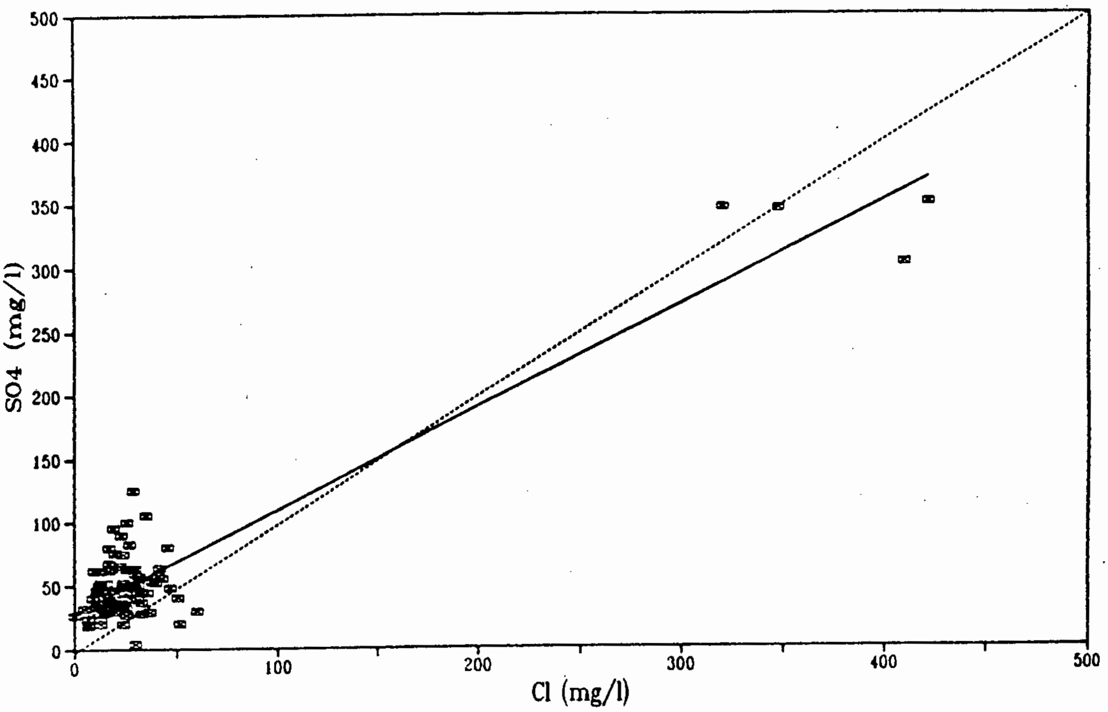


Figure 4.1b. Artificially altering the data set of RESM08 demonstrates how the correlation and regression line are greatly influenced. The real correlation is shown in Figure 4.1a

Aside from pollution events, another reason for spurious correlations among variables is the presence of detection limit values. For example, many analyses for NH_4 fall below 0.4 mg.dm^{-3}, which would clearly affect the correlation calculation (Figure 4.2). Although the predicted P values associated with the correlation will be close to zero for abnormally distributed data (0.0094 in Figure 4.2, for example), the test effectively considers only a few observations and regards the mass cluster as a single observation (Stewart, 1995; pers.com.). Caution is, therefore, required in using correlation statistics.

No statistical test is mechanical and capable of generate certainty. Rather, statistics are used as flags to suggest important features meriting further study. Statistics are a simplification of the true picture. Correlation coefficients fail to reflect certain parts of a data set, for example by masking outliers. Masking occurs when a correlation does not adequately weight towards one clear outlier, and can easily be detected by using XY or box and whisker plots. This is demonstrated in Figures 4.3a and 4.3b, where a calculated correlation would not allocate sufficient importance to monitored observations plotting far off the regression line. Several of the data records have such outliers.

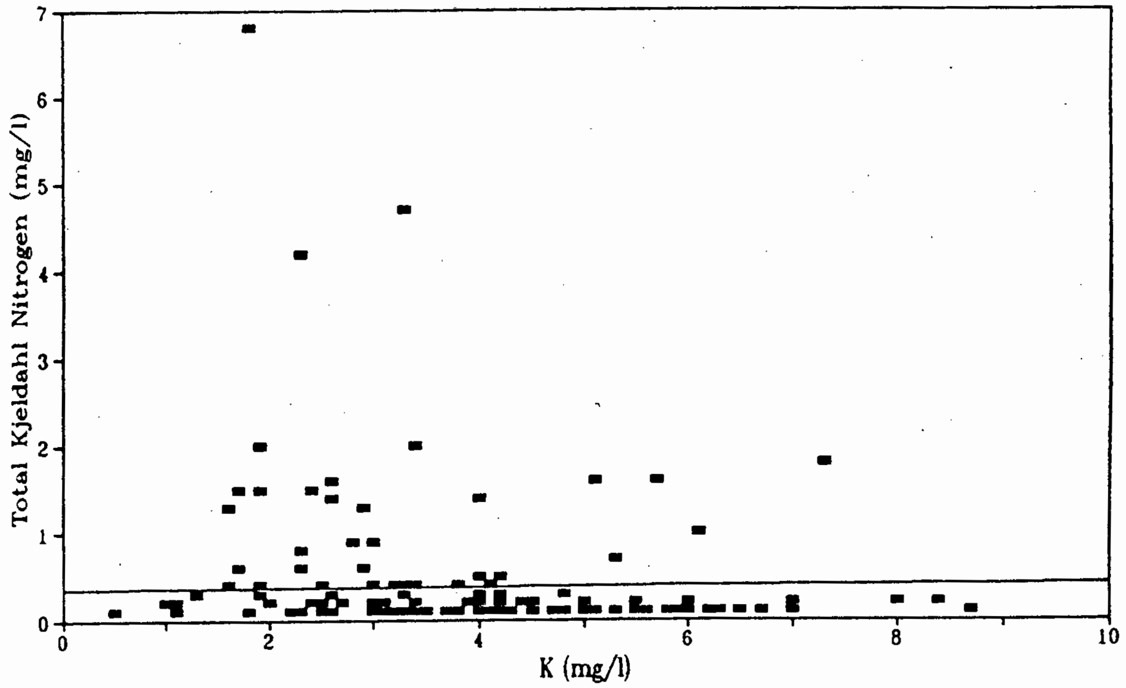


Figure 4.2. A graph of Total Kjeldahl nitrogen (TKN) and potassium at surface water site RESM13 to demonstrate how the distributions and hence subsequent statistical calculations are strongly influenced by clusters of observations produced by limits of detection values entered in sets of data.

The outliers in Figure 4.3a and 4.3b are clearly of interest to the monitoring operation. The identification of their occurrence would warrant further investigation. These graphs highlight a potential pitfall in establishing covariances. A strong correlation may be found between two analytes, discounting the need to always analyze for both. Observation of the complete data set, however, shows some outliers, as in Figures 4.3a and 4.3b. These are pollution events of a different signature and reflect a different problem. The reduction in analytical determinations by established covariances would not notify the EMU of the outlier occurrence, *i.e.* a change in pollution signature.

The data sets obtained from the monitoring operation inherently do not conform to a Gaussian distribution. Frequency distribution plots are often skewed or even bimodal (Figures 3.1 to 3.4). There are three approaches to the analysis of such data:

(i) **The data could be separated into ambient and pollution distributions and investigated as individual sub-sets. This is easiest when the data is of bimodal** distribution.

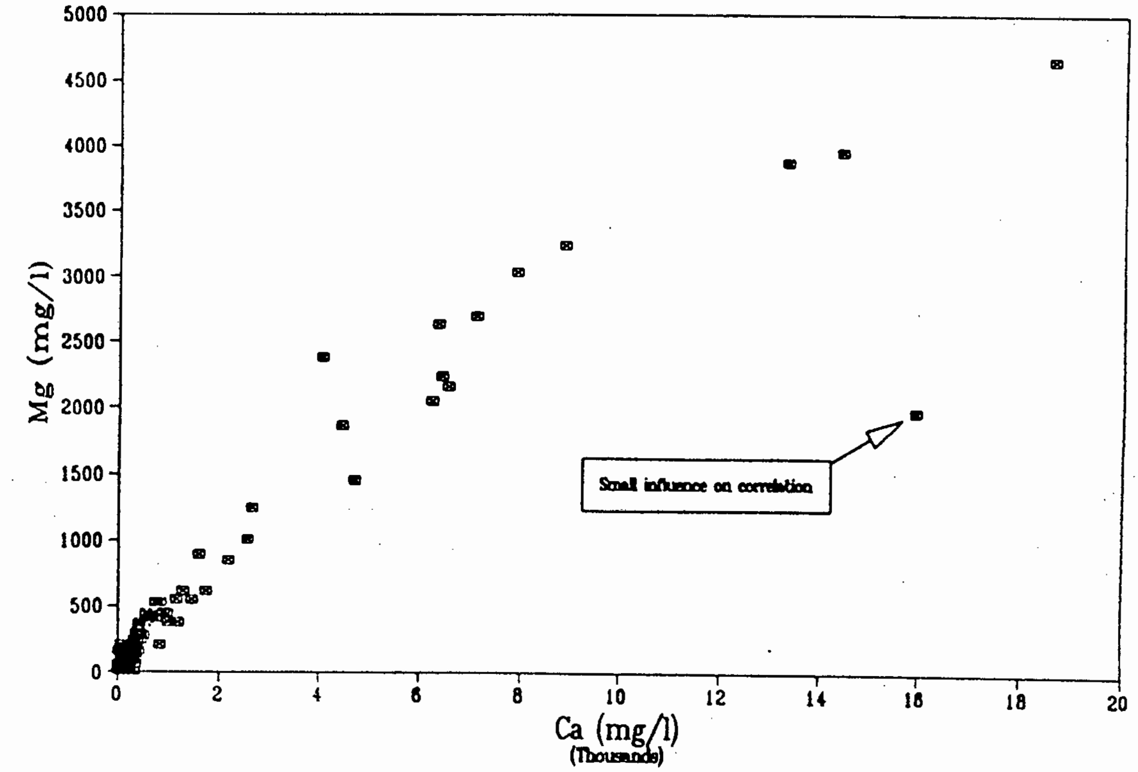


Figure 4.3a. A graph of ground water data (REGMs) to demonstrate the effect a large cluster of observations has in 'masking' a few clear outliers and hence affecting correlation calculations.

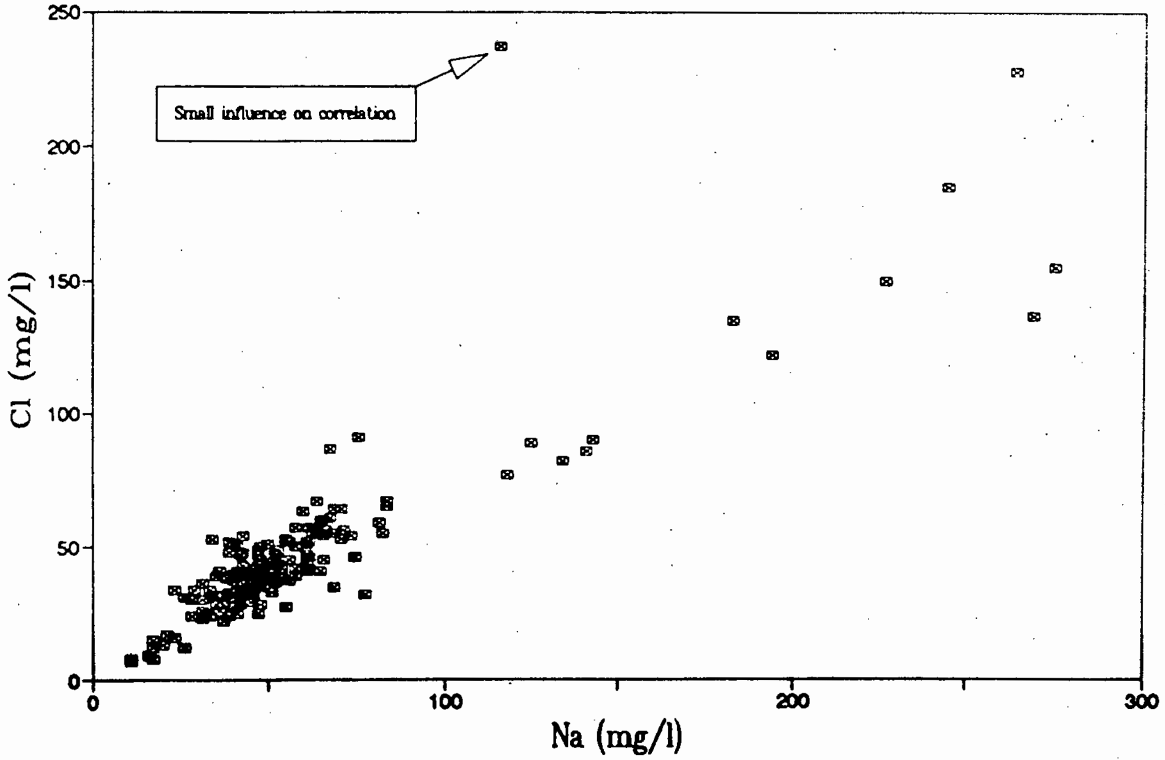


Figure 4.3b. A graph of surface water monitoring site RESM01 to demonstrate the effect a large cluster of observations has in 'masking' a few clear outliers and hence affecting correlation calculations.

(ii) The data could be modified and then analyzed by parametric statistics. For example the observations can be altered by conversion to log values.

(iii) Non parametric statistics could be used as they do not rely on the assumption that the data is normally distributed.

The latter procedure was chosen since it does not involve much manipulation of the data nor any marked subjective judgement. Although there is less subjectivity, there is some loss in power. It is not possible to state the precise reduction in power incurred using non-parametric statistics, since the vigour of the statistic is very specific to the data set under study (Stewart, 1995; pers.com.). Importantly, however, by using the non-parametric alternative one is able to 'buy safety'. It would not be possible to guarantee the validity of P values calculated by parametric statistics on the sets of data from this monitoring network. Two non-parametric correlation calculations can be used for non-normally distributed data:

- The Kendall Tau test works by tying pairs of values between observations for variables. This test, however, has problems with repeated analyte values during the pairing stage of the algorithm, including values entered as detection limits. The problem leads to noise in the system. The test is also computationally clumsy and less commonly used.
- The Spearman test works with ranked data. After the data observations are assigned to an ordinal scale, the originals are discarded. A loss in information is, therefore, incurred. Resulting correlation coefficients and P values can, however, be calculated on the constructed normally distributed data set.

In this section, the P value assigned to a correlation was calculated by a statistics package (CoStat, 1995). The P values are tabulated in Tables 4.1a to 4.1d for a selection of monitoring sites which give an overview of the whole monitoring network. If the P value is < 0.05 it indicates the variables are probably correlated. As stated above, however, some of the values may be spurious due to mass clustering of data observations and / or masking. Outliers may not be visible in univariant plots, such as frequency histograms, hence XY plots were used in Quattro Pro to identify spurious correlations. The low P values, not highlighted by shading, are considered spurious (Table 4.1a to 4.1d). If $P < 0.05$ then the calculated R statistic (not listed) is significantly different from 0 and the two analyte variables are probably correlated (at a 95% confidence level). The shaded areas (Table 4.1) indicate a probable correlation which is confirmed after visual inspection of an XY plot.

Table 4.1. Correlation matrix of P values for analytes calculated using Spearman's non-parametric correlation tests on analytes which had a sufficient number of measurements recorded. Footnotes included.

Table 4.1a. Analytes measured from the surface water monitoring site RESM01.

	pH	TDS	Ca	Mg	Na	K	Si	HCO_3	Cl	SO_4	F	Fe	CO_3	TKN	COD	NH_4	PO_4
EC	.4299	.0000	.0000	.0000	.0000	.0000	.8141	.0000	.0000	.0000	.5011	.0070	.0001	.0075	.0000	.0000	.0005
pH	-	.4444	.0219	.5351	.1310	.1254	.0042	.4281	.8646	.6112	.0505	.4277	.0000	.2700	.0084	.4690	.0001
TDS	-	-	.0000	.0000	.0000	.0000	.6455	.0000	.0000	.0000	.7604	.0776	.0005	.0045	.0000	.0000	.0000
Ca	-	-	-	.0000	.0000	.0000	.0002	.0004	.0000	.0000	.0004	.0014	.0167	.0021	.2816	.0000	.0169
Mg	-	-	-	-	.0001	.0006	.0190	.0011	.0000	.0000	.0050	.0584	.0002	.0029	.0016	.0000	.2723
Na	-	-	-	-	-	.0000	.2014	.0000	.0000	.0000	.0167	.7087	.0000	.4816	.0000	.0000	.0000
K	-	-	-	-	-	-	.6202	.0000	.0000	.0000	.1105	.4192	.0000	.2483	.0003	.0000	.0004
Si	-	-	-	-	-	-	-	.1060	.9883	.0512	.0295	.0739	.1695	.1280	.9304	.0004	.0435
HCO_3	-	-	-	-	-	-	-	-	.0000	.5345	.6144	.1289	.0006	.0168	.3249	.0009	.0098
Cl	-	-	-	-	-	-	-	-	-	.0000	.0476	.1035	.0029	.3058	.0000	.0000	.0000
SO_4	-	-	-	-	-	-	-	-	-	-	.0007	.2282	.0014	.0017	.0029	.0000	.0179
F	-	-	-	-	-	-	-	-	-	-	-	.0586	.0001	.0763	.3816	.0726	.0808
Fe	-	-	-	-	-	-	-	-	-	-	-	-	.8057	.7862	.3333	.0082	.6931
CO_3	-	-	-	-	-	-	-	-	-	-	-	-	-	.0000	.0009	.0000	.4868
TKN	-	-	-	-	-	-	-	-	-	-	-	-	-	-	.1634	.0000	.8387
COD	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	.0000	.0001
NH_4	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	.0000

Table 4.1b. Analytes measured from the surface water monitoring site RESM08.

	pH	TDS	Ca	Mg	Na	K	Si	HCO_3	Cl	SO_4	F	Fe	CO	TKN	COD	NH_4	PO_4
EC	.0000	.0000	.0000	.0000	.0000	.1608	.0000	.0000	.0000	.0000	.0654	N/A	.0000	.9358	.5291	.0376	.0002
pH	-	.0000	.0038	.0000	.0000	.0020	.0000	.0000	.0000	.9687	.0424	N/A	.0000	.1158	.4355	.0000	.1063
TDS	-	-	.0000	.0000	.0000	.2025	.0000	.0000	.0000	.0000	.2095	N/A	.0000	.7667	.4112	.0413	.0001
Ca	-	-	-	.0000	.0000	.6945	.0000	.0002	.0004	.0000	.0703	N/A	.0001	.3793	.2597	.9278	.0017
Mg	-	-	-	-	.0000	.2426	.0000	.0000	.0000	.0000	.3402	N/A	.0000	.4816	.0000	.0000	.0000
Na	-	-	-	-	-	.0055	.0000	.0000	.0000	.0004	.4953	N/A	.0000	.0443	.4489	.0000	.0109
K	-	-	-	-	-	-	.4978	.0683	.0083	.0294	.8618	N/A	.1934	.4371	.3484	.4942	.5453
Si	-	-	-	-	-	-	-	.0000	.0000	.0001	.1307	N/A	.0017	.0349	.0370	.3520	.0007
HCO_3	-	-	-	-	-	-	-	-	.0000	.0000	.6384	N/A	.0000	.1570	.0010	.1996	.0000
Cl	-	-	-	-	-	-	-	-	-	.0008	.3070	N/A	.0000	.0032	.4556	.0000	.0271
SO_4	-	-	-	-	-	-	-	-	-	-	.0576	N/A	.0134	.8490	.6641	.8216	.0232
F	-	-	-	-	-	-	-	-	-	-	-	N/A	.0749	.3919	.1104	.2790	.8491
Fe	-	-	-	-	-	-	-	-	-	-	-	-	N/A	N/A	N/A	N/A	N/A
CO_3	-	-	-	-	-	-	-	-	-	-	-	-	-	.0044	.0044	.0000	.1845
TKN	-	-	-	-	-	-	-	-	-	-	-	-	-	-	.0848	.0000	.0000
COD	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	.0811	.0012
NH_4	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	.0063

Table 4.1c. Analytes measured from the surface water monitoring site RESM13.

	pH	TDS	Ca	Mg	Na	K	Si	HCO_3	Cl	SO_4	F	Fe	CO_3	TKN	COD	NH_4	PO_4
EC	.6455	.0000	.0000	.0000	.0000	.4852	.2122	.0000	.0000	.0014	.0023	N/A	.0013	.3611	.5688	N/A	.0223
pH	-	.4195	.6965	.0202	.0067	.9369	.0000	.1401	.0003	.0003	.0000	N/A	.0065	.7567	.7281	N/A	.1859
TDS	-	-	.0000	.0000	.0000	.5999	.5643	.0000	.0000	.0007	.0025	N/A	.0065	.7567	.7281	N/A	.0699
Ca	-	-	-	.0000	.0000	.3605	.9623	.0000	.0000	.0001	.0123	N/A	.0054	.7995	.2271	N/A	.1001
Mg	-	-	-	-	.0000	.3686	.7662	.0000	.0000	.0520	.7196	N/A	.0000	.5273	.9475	N/A	.1311
Na	-	-	-	-	-	.1856	.8865	.0000	.0000	.7459	.4718	N/A	.0000	.6687	.4461	N/A	.2848
K	-	-	-	-	-	-	.0013	.9371	.0004	.8690	.1754	N/A	.0267	.0094	.9161	N/A	.0708
Si	-	-	-	-	-	-	-	.8002	.1090	.0557	.0017	N/A	.0488	.0016	.4808	N/A	.0005
HCO_3	-	-	-	-	-	-	-	-	.0000	.1958	.0882	N/A	.0000	.6008	.6860	N/A	.0470
Cl	-	-	-	-	-	-	-	-	-	.6577	.1295	N/A	.0000	.8816	.0891	N/A	.0863
SO_4	-	-	-	-	-	-	-	-	-	-	.0153	N/A	.5466	.7361	.0193	N/A	.1578
F	-	-	-	-	-	-	-	-	-	-	-	N/A	.4114	.8283	.1902	N/A	.4389
Fe	-	-	-	-	-	-	-	-	-	-	-	-	N/A	N/A	N/A	N/A	N/A
CO_3	-	-	-	-	-	-	-	-	-	-	-	-	-	.0000	.0009	N/A	.0085
TKN	-	-	-	-	-	-	-	-	-	-	-	-	-	-	.0052	N/A	.0000
COD	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	N/A	.0001
NH_4	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	N/A

Table 4.1d. Analytes measured at all the ground water monitoring sites (REGMs).

	pH	TDS	Ca	Mg	Na	K	Si	HCO_3	Cl	SO_4	F	Fe	CO_3	TKN	COD	NH_4	PO_4
EC	.0000	.0000	.0000	.0000	.0000	.0001	.0000	.0001	.0000	.0000	.7530	.0000	.0000	.2279	.0000	.0000	.0009
pH	-	.0000	.0219	.0000	.8450	.0509	.0002	.0333	.0000	.0000	.0000	.0000	.0000	.4222	.0000	.1683	.9916
TDS	-	-	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.8549	.0000	.0000	.0170	.0000	.0000	.0001
Ca	-	-	-	.0000	.0000	.0019	.0000	.0000	.0000	.0000	.0275	.0002	.0000	.0000	.0000	.0000	.0000
Mg	-	-	-	-	.0000	.0023	.0000	.0504	.0000	.0000	.0824	.0000	.0000	.0003	.0000	.0000	.0001
Na	-	-	-	-	-	.0001	.9758	.0083	.0000	.0000	.0006	.0001	.0000	.0000	.0000	.0000	.0059
K	-	-	-	-	-	-	.2102	.0099	.0239	.0000	.4478	.9490	.0000	.0000	.0030	.0000	.0000
Si	-	-	-	-	-	-	-	.0966	.0001	.0000	.0086	.0907	.0000	.0000	.0000	.0000	.0000
HCO_3	-	-	-	-	-	-	-	-	.0000	.0000	.0542	.0691	.0000	.0850	.0045	.0319	.0237
Cl	-	-	-	-	-	-	-	-	-	.0000	.7759	.0000	.0029	.3058	.0000	.0000	.0000
SO_4	-	-	-	-	-	-	-	-	-	-	.0007	.0000	.0000	.3624	.0000	.0000	.0000
F	-	-	-	-	-	-	-	-	-	-	-	.0112	.0000	.0019	.3451	.0259	.0193
Fe	-	-	-	-	-	-	-	-	-	-	-	-	.0000	.0598	.0000	.0000	.0000
CO_3	-	-	-	-	-	-	-	-	-	-	-	-	-	.0000	.0000	.0000	.0000
TKN	-	-	-	-	-	-	-	-	-	-	-	-	-	-	.3213	.0000	.0000
COD	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	.0000	.0000
NH_4	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	.0000

TKN = Total Kjeldahl nitrogen.

N/A indicates the correlation test is not applicable as there were too few values.

Returning to the first of the three methods to study correlations among data with a non-Gaussian distribution, it might be possible to manipulate the data sets. The inspection of an XY plot, the use of correspondence analysis or even a frequency distribution diagram (for example Figure 3.4) will identify groups of data observations. Two clear examples are shown in Figures 4.4a and 4.4b. The figures indicate ambient conditions and different types of pollution. Such a data set could be separated and correlation analysis on each sub-set completed to establish the analyte relations for that particular chemical signature. This would lead to a detailed chemical signature of the background water chemistry and that of pollution. The complexity of the data sets from this monitoring network, however, inhibited the use of this procedure in the time available for the study. One would require several analytes to categorize the pollution and separate clusters. In addition, the many environmental factors and the diffuse nature of the pollution events leads to a blurring of analyte groupings.

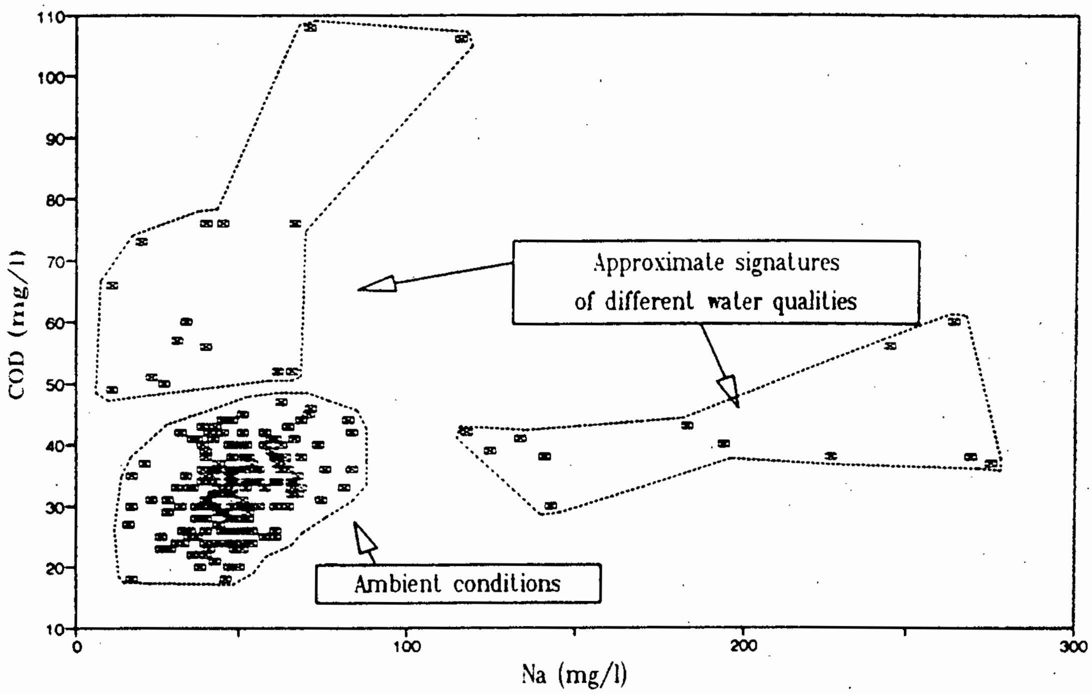


Figure 4.4a. A plot of a selection of chemical oxygen demand (COD) and Na data to demonstrate pollution signatures and ambient conditions observed in the data set of surface water monitoring locality RESM01. (Data from August 1990 to November 1994).

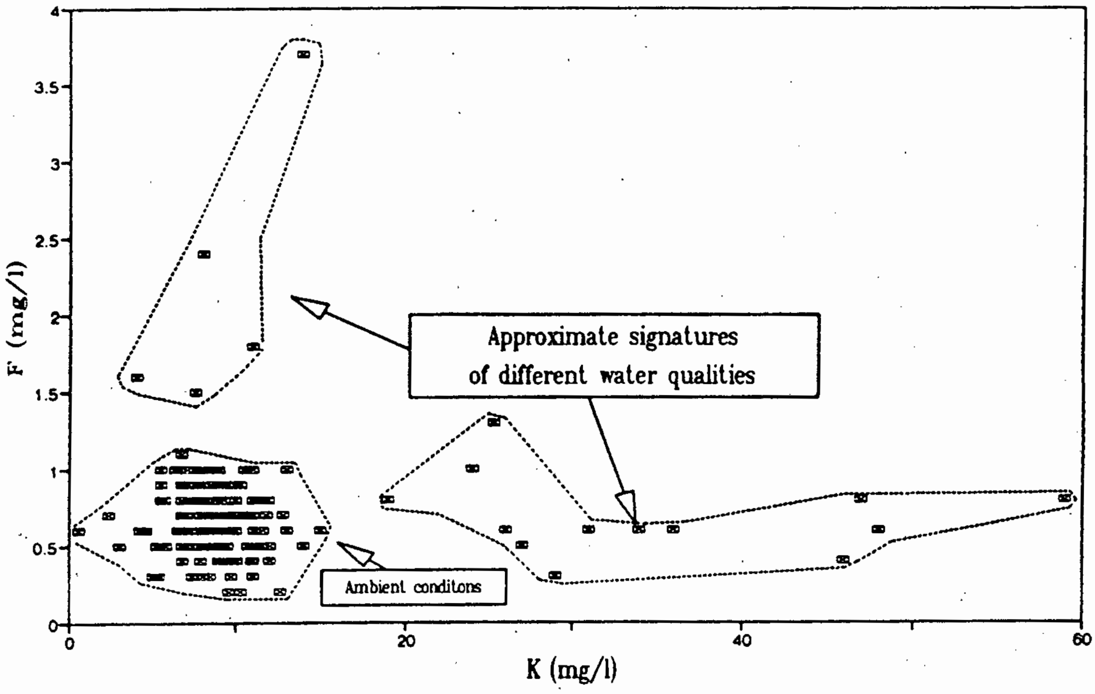


Figure 4.4b. A plot from selection of F and K data to demonstrate pollution signatures and ambient conditions observed in the data set of surface water monitoring locality RESM01. (Data from August 1990 to November 1994).

Tables 4.1a to 4.1c demonstrate that many of the correlations observed between analytes are similar in the different surface water monitoring sites as well as in the boreholes (Table 4.1d). Some of the analytes do not have enough observations for a successful correlation calculation, for example Fe in Tables 4.1b and 4.1c and other variables not included in the listings. It may be that some of these analytes, particularly the heavy metals, are the best indicators of pollution. The components of lower abundance, irrespective of their relative environmental impact, are not determined regularly. Without the benefit of a large data set of analytes, for example including a range of trace metals such as Zn, Pb, Hg, *etc.*, it is not possible to do a retrospective investigation to establish the environmental importance of the analyte. Conversely, without studying the component's environmental significance, one does not know if it is worth setting up a large database for the analyte or not. It is a 'catch 22' situation.

From the data sets which are available, some useful conclusions can be drawn. Most of the correlation matrices show a strong covariance between EC (or TDS) and the dominant ion concentrations, which serves to confirm that EC is a very good indicator, as would be expected in view of the fact that most of the pollution is of an ionic nature. The concentrations of most of the ions correlate with each other. If the standard proportions of ions in a pollution signature were estimated with hindsight, it would not always be necessary to determine ionic concentrations - EC would suffice. The ion proportions of pollution events would require checking much less frequently than EC tests.

Figures 4.5a and 4.5b demonstrate the dominant cation and anion proportions at all the surface water monitoring sites (RESMs). The overall height of the bar is an approximation of the total dissolved solids (TDS). The two graphs were constructed separately for monitoring sites with a low EC (Figure 4.5a) and those with a high EC (Figure 4.5b). Not only was this for scaling purposes but it also shows that no matter what the EC value is the ion proportions do not vary significantly. The only exception is the abundance of SO_4 and Ca, the dominant contaminants, in the highly polluted areas.

The idea that a strong correlation between the major ions permits the determination of only one ion is not necessarily justified. Analytical procedures are often multi-element in character and produce determinations for one ion almost as easily as for all the major ions, *e.g.* ion chromatography or simultaneous ICP spectrometry. It is only favourable to reduce the number of analyses, based on correlations, if cheaper methods can be used, although they may be more fallible. Automated telemetric measurements are an example (Andrew *et al.*, 1994).

The correlation matrices (Tables 4.1a to 4.1d) indicate the variables which do not show a regular relationship with others. With regard to monitoring, statistically significant correlations are perhaps not as important as non-correlations. Covariance between parameters means there is a certain amount of predictability in the monitoring operation. Analytes which do not show covariance are unpredictable and therefore should be the focus of monitoring. The important analytes which in the past have had erratic concentrations are F, COD, PO_4 and occasionally NH_4. These components often have relatively low abundances compared to the other ions. Analytical errors, therefore, may increase the variability in their concentration which may have counteracted any environmentally inherent correlation. The low abundance ions (F, NH_4, PO_4 in addition to B, heavy metals, *etc.*) often have the most significant impact when concentrations are elevated. These analytes should receive closer attention than the others.

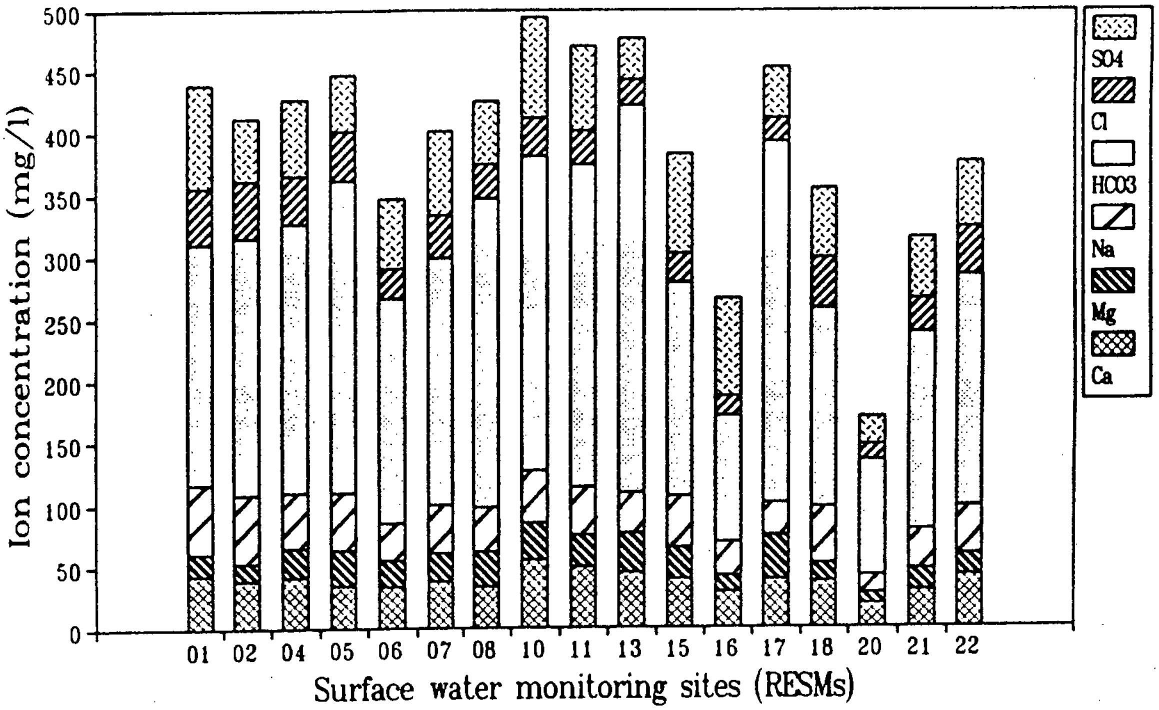


Figure 4.5a. Mean ion concentrations at the surface water monitoring sites (RESMs) which have a low (< 500 mS.m^{-1}) electrical conductivity.

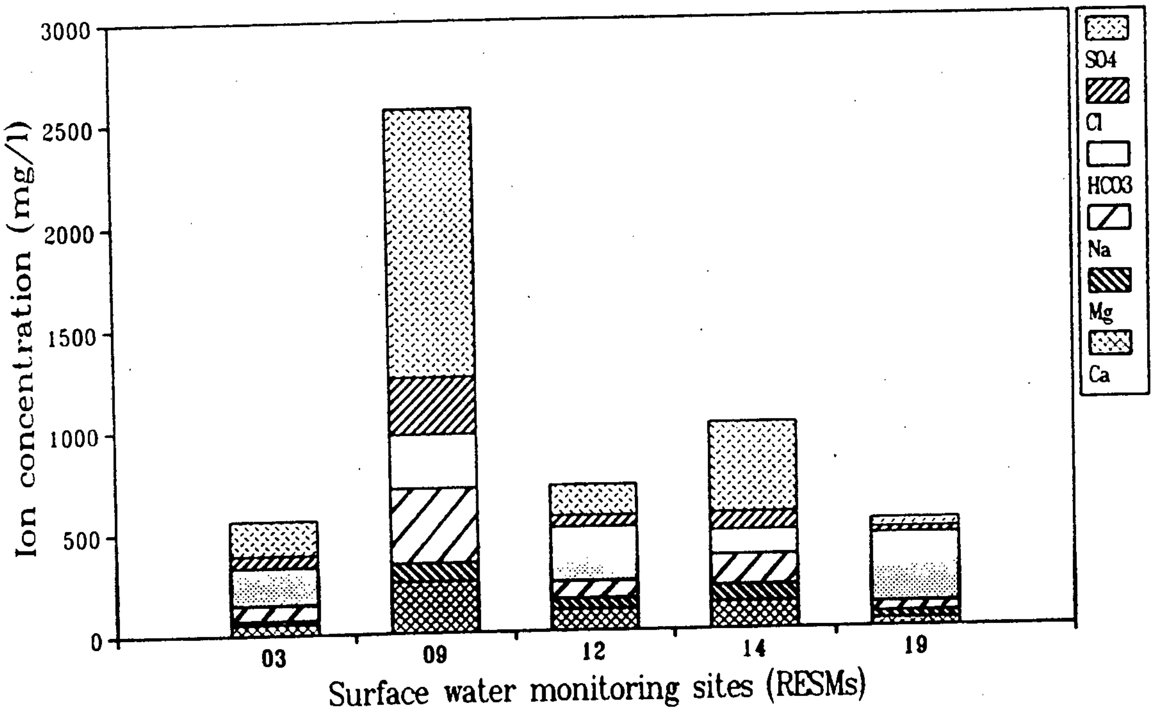


Figure 4.5b. Mean ion concentrations at the surface water monitoring sites (RESMs) which have a high (> 500 mS.m^{-1}) electrical conductivity.

4.3 APPROACHES TO INTERPRETING DATA

After completing the sampling and analysis stages of a monitoring exercise, the information must still be converted into a useful format (Ward, 1986). Uninterpreted raw data are almost as useless as no data at all. It is imperative to implement sound interpretation procedures. Interpretation does not simply consist of data management or maintenance of a database - it must involve a number of techniques, graphical, statistical and / or written, to appraise the data within resource limitations. Requirements external to the monitoring network must also be considered. These will primarily involve statutory regulations but may also include other reasons for interpreting data *e.g.* for research purposes.

Raw data need to be presented in a usable or palatable form for management purposes. The first step is to simplify and summarize the information. There are many ways in which this can be done (Ward, 1986). The HydroCom database, in which the information from the present monitoring network is stored, has packages to facilitate graphical summaries. These include time series plots, Piper and Durov diagrams, *etc.* In addition, the database permits calculation of simple descriptive statistics. These methods are important for reporting purposes. Other computer packages are available for more complex statistics. These are important for comprehensive reviews of the monitoring network and the area monitored. WQStat II (1989) was found to be particularly valuable in this respect.

The style of reports will be specific to management and / or regulatory body requirements. DWAF (1994a, p.24) state that the system of reporting will be specified in waste disposal permit conditions. Data processing and interpretation *must* be carried out after each sampling and analysis exercise. DWAF also suggest that reports should be submitted at least as regularly as every six months. The objectives of water quality management by the EMU have not been considered for this thesis. The author would like to have been able to clearly identify an overall goal and the individual objectives required to achieve that goal, but this will require a decision from high level management.

4.4 CONCLUSIONS

Analytical strategies can be greatly improved by reviewing them after a few years of operation. The operation can be optimized by obtaining the required information more cheaply. This could be done by using the more fallible telemetric monitoring stations which have a relatively low operating cost. Laboratory analytical measurements do not always need to be as rigorous as they have been. It is more important to have high quality assurance. The collection, preservation and safe storage of samples will ensure that important, conspicuous and legally salient parameters can be evaluated in future.

Rationalizing analytical procedures benefits from establishing covariances. Despite the pitfalls of correlation calculation (*e.g.* non-normal distributions, masking and detection limit values), highlighted in this chapter, covariances between chemical components were authenticated. EC (or TDS) is the best indicator of pollution. Non-correlations provide equally if not more important information. The analyte correlations which have high P values are less predictable and therefore should be the focus of monitoring. This must also be considered in relation to the potency of the chemical constituent. It is not as important to study the dominant ions as it is the less abundant ones. The analytes of lower concentration often have more episodic occurrence and can be more environmentally significant.

The work reported in this chapter has not clearly defined the chemical signatures of pollution events in the area monitored. It is a strong recommendation that further work should be carried out to identify traces of contamination. Correspondence analysis would be a very useful tool for this purpose. Ideally, clear chemical signatures evident at monitoring sites could be used to locate a pollution source and lead to rapid and effective mitigating measures.

5. DISCUSSION AND RECOMMENDATIONS

Based on the results of this study and literature reviewed in chapter 1, a summary of the considerations required for the design of a monitoring operation has been prepared (Figure 5.1). The rationales of several workers, including Barcelona (1988), Bernstein and Zalinski (1983), Freeze *et al.* (1992), McBride (1986), Ward (1986) are incorporated in this summary. The EMU of the company will need to consider carefully the extent to which monitoring has accomplished each operation or goal depicted in Figure 5.1.

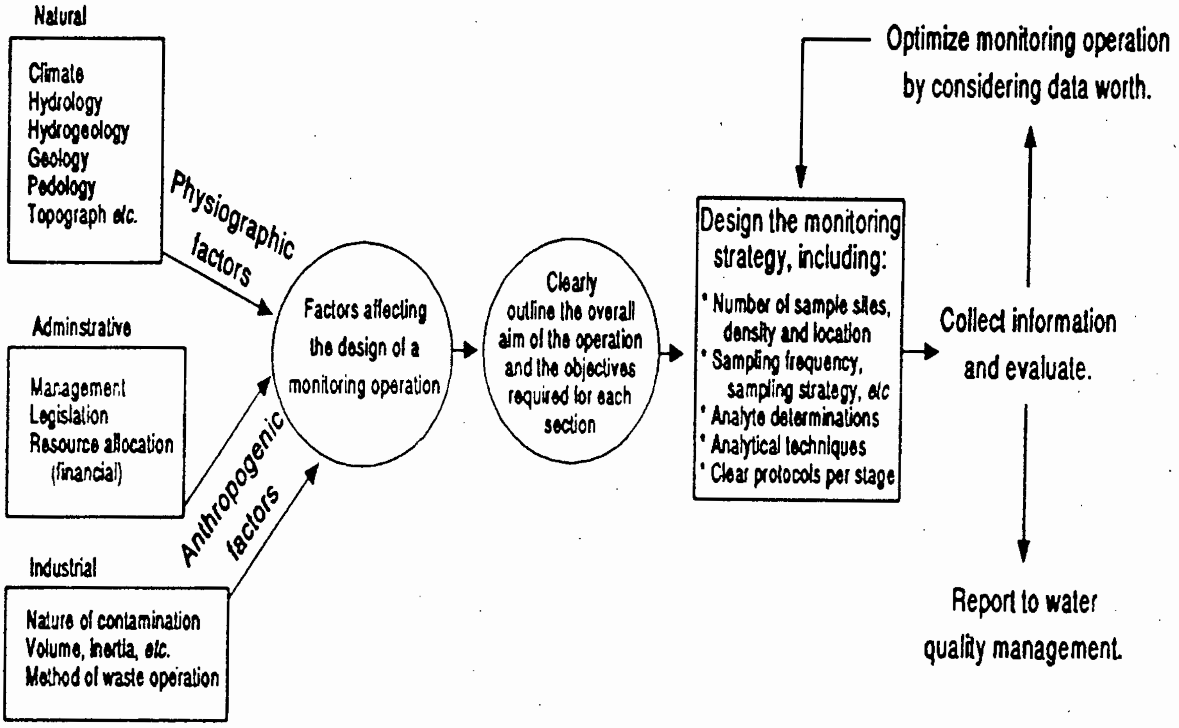


Figure 5.1 A summary of the factors that need to be considered in the design of a monitoring operation.

The physiographic factors are generally fixed and can only be altered by extensive engineering practices. Anthropogenic factors can, however, be varied to alter the network design. The industrial activities of waste generation and disposal can be rationalised by engineers. The administrative variables can also be altered by a change in management or regulatory policy, which includes the allocation of funds. A monitoring strategy essentially weights all these factors in defining the monitoring operation. The objective of the present study was to consider ways to increase efficiency of data acquisition by evaluating the optimization process - the feedback loop of Figure 5.1.

Errors incurred during the monitoring were investigated. It was assumed that mistakes and inaccuracies are minimal in the sampling and interpretation stages of the network as prescribed protocols are followed. The analytical stage, however, has regularly suffered errors manifested as ion imbalances in the database. As much as 27 % of the sample determinations exceed an acceptable error of 10 % ion imbalance. Trends in the ion balance error identify periods of low precision and of low accuracy. Overall, there has been no significant improvement in the analytical techniques.

Correlations of high ion balance errors with anion abundances do not exist. Cations, however, show that large errors coincide with large Ca and Mg concentrations suggesting the analytical procedures for these elements are responsible for the errors in the data. Cation determinations are done by flame spectroscopy, which could have a number of problems associated with: ionization inferences; or the use of releasing agents. Alternatively, dilution and other techniques for obviating instrument sensitivity to high concentrations (*e.g.* burner rotation) may the source of the problem.

A system of weighting the nine waste operations of the monitored area was devised. The weights, obtained by the use of MCDA, allow for more realistic mean values for the whole area to be estimated and for a more objective allocation of resources. The initial risk assessment used the U.S.EPA scheme described by LeGrand and Brown (1990; Appendix IV) to produce an alpha-numeric site rating of the waste operations. The codes of this rating are effectively a synoptic description of the area. Müller (1991) used the rating to allocate sampling resources to the waste operations by professional judgement. The MCDA system applied in the present study used the criteria from the U.S.EPA scheme to calculate weights for each site. The weights enabled objective ground water sample allocation by three different statistical procedures described by Gilbert (1987). The illustrative examples of Gilbert (1987) used stratum population sizes (volumes of water in different zones) to weight the areas sampled. The multiple criteria weight is a more complete indication of the environmental significance of the waste operation. The three allocation procedures used have different limiting factors: cost, variance and margin of error. Some examples of varying these limiting factors are illustrated in Table 5.1.

Table 5.1 Number of samples to be collected per year (n) as defined by three statistical procedures each with 3 examples of acceptable limits (the variance and error values are derived from electrical conductivity data in mS.m^{-1}.

COST (Rands)	50 000	40 000	30 000
n =	170	136	102

VARIANCE STANDARD DEVIATION (mS.m^{-1})	5000 ~ 71	3000 ~ 55	1000 ~ 32
n =	69	115	344

MARGIN OF ERROR (Alpha = 0.10)	100	90	80
n =	93	115	145

Two types of calculation for allocating samples to boreholes at the waste sites were used. The simple allocation solely uses the environmental weight, whereas the Neyman method includes the variance of the data from the operation. If the sample total was estimated at 132 samples / year, as it presently is, then the allocation would be as illustrated in Table 5.2. The present status of the sampling is characterized by a cost of R 38 000 per year, a global standard deviation in EC data of 51 mS.m^{-1} and a margin of error of 84 mS.m^{-1}.

Table 5.2 Sample allocation for the year to the nine waste operations. Samples are collected quarterly.

Site	No.	Sym.	Simple Allocat'n	Neyman Allocat'n	Present Allocat'n
Ash and black product dams	1	○	12	1	40
Reject fertilizer dump	2	□	20	102	16
Waste explosives pits	3	△	20	4	8
Water recovery division	4	◇	16	2	12
Salt water dams	5	●	16	10	4
Irrigation areas	6	■	13	7	40
Coal stockpile	7	▲	10	1	4
Refuse disposal	8	◆	9	1	4
Mine water	9	★	15	5	4
Sum			132	132	132

The Neyman allocation is considered to place to much emphasis on the variability of the data. Data distribution is a manifestation of the variability of the water quality *i.e.* pollution event occurrence. This likelihood of pollution occurring has been accounted for in the calculation of the weights by MCDA.

The sample allocation in Table 5.2 indicates the relative importance of each site and where more attention is required. The reject fertilizer and explosives dumps are particularly important areas. In addition, the weights allow for a meaningful estimate of the overall electrical conductivity in the aquifer. At 424 mS.m^{-1} this is alarmingly high.

Normal distribution cannot be assumed for the data sets, This was expected due to the nature of the monitoring operation, and was generally found to be true after exploratory statistical analysis. This finding was important for the temporal analysis done in the study and will be important as well for reports prepared by the EMU To the extent that these reports make use of statistics, the tests should be non-parametric.

The temporal variability of the data was addressed to determine an optimal sampling frequency. Two approaches were used: a computer algorithm which enabled graphics and statistics to be done and a hypothetical system of thinning data sets. The temporal statistical analysis of data sets and the use of simple graphs revealed several features about the monitoring area. Positive and negative trends have occurred at both surface and ground water monitoring localities. The majority of the boreholes show a slight decline in water quality. The worst sites of those studied are REGM17 and REGM21 located near the reject fertilizer dump and the salt water dam, respectively (Figure 5.2). The majority of the surface water sites show an increase in water quality. The improved quality at RESM01 is mainly due to cleaner water from the northern stream over the last four years. The pollution load in the southern stream has decreased at RESM03 but the overall improvement is hampered by large steady increases in EC over the last four years at RESM10, RESM13 and particularly RESM14, next to the fertilizer dump (Figure 5.3). The water quality of the southern spruit has been ameliorated due to dilution at RESM09 by the tributary from the south.

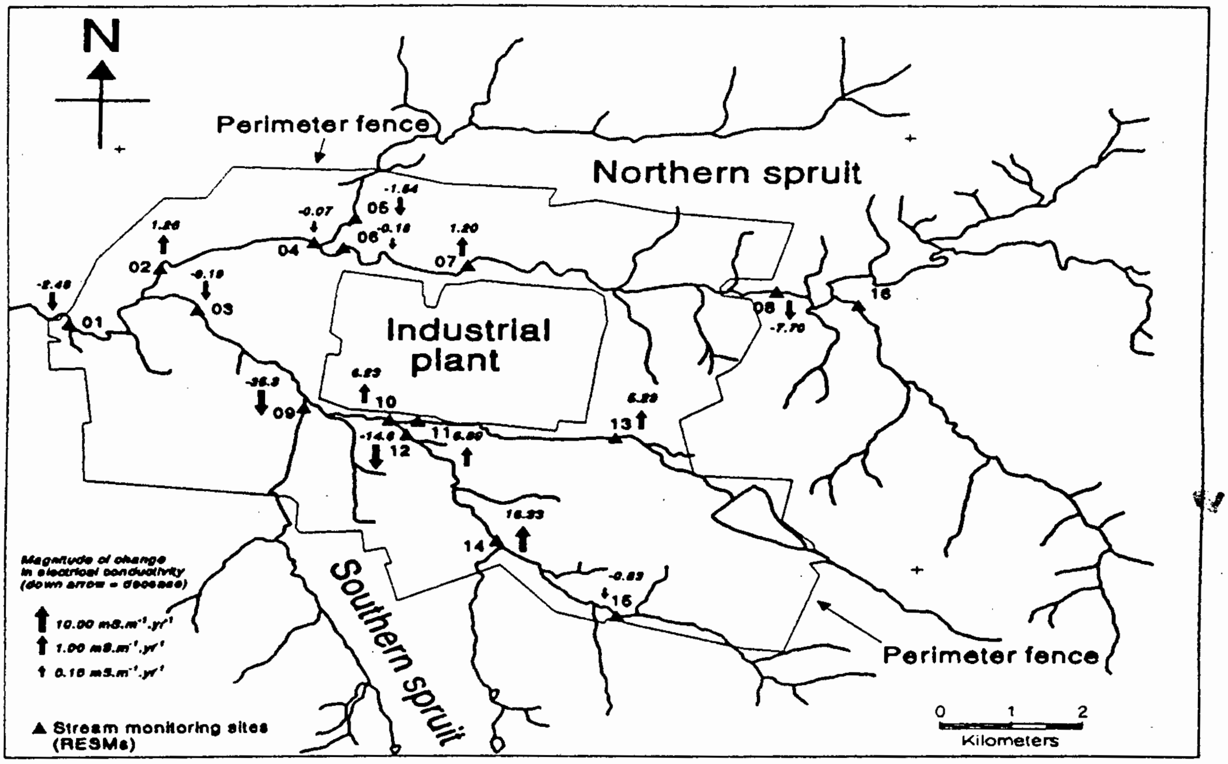


Figure 5.2. Slope estimates of electrical conductivity trend (mS.m^{-1}.yr^{-1}) at some of the ground water monitoring boreholes illustrated by proportional arrows. *Italic* value are not necessarily statistical significant but is a good indicator of aquifer water quality.

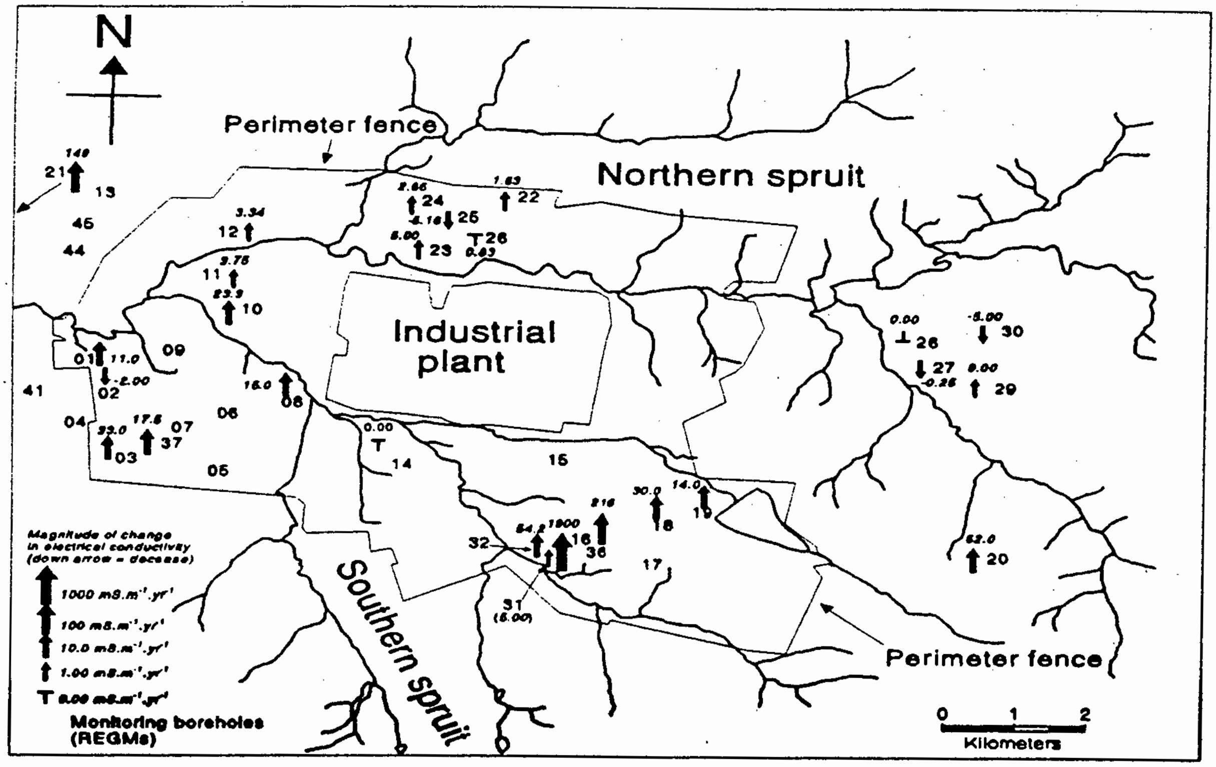


Figure 5.3. Slope estimate of electrical conductivity trend (mS.m – l^{-1}.yr^{-1}) at some of the surface water monitoring locations illustrated by proportional arrows. *Italic* values are not necessarily statistical significant but is a good indicator of stream water quality change (Tables 3.1b and 3.1c).

The temporal statistics programme also allowed the illustration of some valuable information regarding the water quality related to recommended thresholds. Borehole water from near the salt water dam (REGM21) and the fertilizer / explosives reject dump (REGM17) would not be fit for irrigation (greater than 270 mS.m^{-1}). The stream water occasionally exceeds the 70 mS.m^{-1} permit requirement, the same level as for domestic usage. The only stream locations that violate this level over 90% of the time are RESM09 and RESM14. The results of analysis for excursion from guidelines did not indicate any clear seasonality. Concentration highs, however, are less common in the summer. The statistical tests for seasonality did not discover any significant periodic fluctuations either.

Returning to the concept of optimizing the sampling frequency, periods of the year in which pollution is more likely occur cannot be identified. A two-frequency sampling strategy (longer time intervals between sampling events in the wetter months) could not, therefore, be adopted with any confidence. Climate is not the dominant factor in causing contamination events, which leads to the conclusion that the generally high analyte concentrations are anthropogenic.

Reducing the overall sampling frequency was also considered. Four data sets were thinned from weekly to fortnightly sampling, to monthly and then to quarterly. Two of the four data series chosen (RESM01 and 07) lead to the conclusion that the thinning procedure did not significantly affect the information resolution, *i.e.* the mean and the standard deviation were not greatly altered. The correlation values actual improved as thinning had removed some of the unusual water quality composition events where analytes deviated from the normal relative abundance. The two other data sets, however, showed a significant loss in information resolution with an annual sampling budget decrease. It is suggested that the present weekly sampling interval fails to effectively represent the situation it monitors. An increase in frequency of samples would produce a higher mean and greater variance, inferring a better detection of the extremes in water quality.

The sampling frequency can, of course, be increased without incurring steeper cost increases. Automated sampling could be increased, coupled with a decrease in classic sample collection, as Vrba and Pekny (1991) have been suggested. The implementation of more automated monitoring sites supported by low frequency laboratory tests is a common method of double sampling (Andrew *et al.*, 1994). Before justifying this strategy, two requirements need to be met: the automated station must produce results which correlate closely with laboratory data and the automated system needs to be substantially cheaper.

Theoretically and experimentally (Istok *et al.*, 1993) it is possible to reduce the cost of monitoring by establishing analyte covariances and cutting back on some analytical determinations. The calculation of correlation coefficients has a number of pitfalls which include clustering and masking of data and detection limit values. Nevertheless, the analytes which had enough values for a correlation calculation were tested against one other. The major cations and anions generally have *inter-* and *intra-* positive correlation. In addition, the major ions show a good covariance with EC. It is therefore safe to assume that EC is probably the best indicator of contamination in this network.

An interesting feature of the correlation procedure are those analytes which show no covariance. This infers their concentration levels are aberrant and would, therefore, require more attention. The chemical components of interest are K^+, Si, F^-, Fe_{Total}, NO_3^-, COD NH_4^+ and EC. The mean chemical signature, with regard to the major ions, shows that an EC value can be used to produce a good estimate of *relative* ion abundances.

It is recommended that more work is done on the potential exploitation of covariances. Some analytes of low abundance, like the heavy metals, are often the most environmentally significant. The proportion of such analytes should be related to the major ion concentrations. Unfortunately, the present data sets do not have enough records of the minor ion concentrations. A detailed study of one or two carefully chosen monitoring localities could be used as an example to explore minor ion abundances without incurring the high costs of a complete appraisal. Several pieces of research, specifically Kralik (1994), Droppo and Jaskot (1995) and Ben-Jemaa *et al.* (1995), have focused on correlations between physical and chemical phenomena, for example particle size distribution and analyte abundance.

Further work is also encouraged in chemical signature identification, including cluster analysis and multi-dimension graphs, which could be used to classify pollution sources expressed at monitoring locations. A simple example was illustrated for the surface water location where the stream leaves the industrial area (RESM01) using COD, F, Na and K as delineators. Different signatures have been expressed at RESM01. The common water quality or ambient condition has relatively low analyte levels. Two other situations, however, have also been found to exist. One has a relatively high COD and F abundance while Na and K concentration is low and the other is the opposite, with low COD and F but relatively high Na and K concentrations. It might be suggested that the high COD and F correlations originate from the water recovery division dams, while high K is representative of the reject fertilizer dam. There may well be other sources simultaneously expressed in these signatures and further work could produce some valuable results.

REFERENCES

Andrew, K.N., Blundell, N.J., Price, D. and Worsfold, P.J. 1994. Flow injection techniques for water monitoring. *Analytical chemistry.* **66**, (18), 916-922.

Barber, C. and Davis, G.B. 1986. The subsurface distribution of methane as an indicator of ground water polluted by waste. Proceedings of the Budapest Symposium 1986 *Monitoring to detect changes in water quality.* IAHS Publ. No. 157, 3-12.

Barcelona, M.J. 1988. Overview of the sampling process. In: Keith, L.H. (ed) *Principles of environmental sampling* American Chemical Society. Salem, M.A. USA.

Ben-Jemaa, F., Marino, M.A. and Loaiciga, H.A. 1994. Multivariate geostatistical design of ground water monitoring networks. *Journal of Water Resources Planning and Management-ASCE.* **120**, (4), 505-522.

Ben-Jemaa, F., Marino, M.A. and Loaiciga, H.A. 1995. Sampling design for contaminant distribution in lake-sediments. *Journal of Water Resources Planning and Management-ASCE.* **121**, (1), 71-79.

Bernstein, B.B. and Zalinski, J. 1983. An optimum sampling design and power tests for environmental biologists. *Journal of Environmental Management.* **16**, 35-43.

CCWR, Computing Centre for Water Research. 1995. Selected information from the South African Weather Bureau on the CCWR 'Daily temperature and evaporation database.'

Cochran, W.G. 1977. *Sampling techniques.* Third edition. J.Wiley & Sons, New York, USA.

Cole (III), W.H., Enwall, R.E., Raab, G.A., Kuharic, C.A., Engelmann, W.H. and Eccles, L.A. 1991. Rapid assessment of superfund sites for hazardous materials with x-ray fluorescence spectrometry. In: *Second international symposium: Field screening methods for hazardous waste site investigations.* U.S. Environmental Protection Agency and U.S Army Toxic and Hazardous Materials Agency.

CoStat, 1995. *Costat, Statistical software and manual.* CoHort Software, Minneapolis, USA.

Demayo, A. and Whitlow, S. 1986. Graphical presentation of water quality data. In: Proceedings of the Budapest Symposium 1986 *Monitoring to detect changes in water quality.* IAHS Publ. No. 157, 13-27.

Droppo, I.G. and Jaskot, C. 1995. Impact of river transport characteristics on contaminant sampling error and design. *Environmental Science and Technology.* **29**, 161-170.

DWAF, Department of Water Affairs and Forestry, RSA. 1994a. *Waste management series. Document 1: Minium requirements for waste disposal.*

DWAF, Department of Water Affairs and Forestry, RSA. 1994b. *Waste management series. Document 2: Minimum requirements for the handling and disposal of hazardous waste.*

DWAF, Department of Water Affairs and Forestry, RSA. 1994c. *Waste management series. Document 3: Minimum requirements for monitoring at waste management facilities.*

DWAF, Department of Water Affairs and Forestry, RSA 1993 a to d. *South African water quality guidelines. Volumes 1 to 4: Domestic use, Recreational use, Industrial use and Agricultural use.*

Flatman, G.T., Englund, E. and Yfantis, A. 1988. Geostatistical approaches to the design of sampling regimes. In: Keith, L.H. (ed) 1988 *Principles of environmental sampling.* American Chemical Society, Salem, MA., USA.

Freeze, R.A., James, B., Massmann, J., Sperling, T. and Smith, L. 1992. Hydrogeological decision analysis: 4. the concept of data worth and its use in the development of site investigation strategies. Ground Water, **30**, (4), 574-588.

Friedman, D. 1990. Testing methodology in environmental monitoring. *Environmental Science and Technology,* **24**, (6), 796-798.

Fuggle, R.F. and Rabie, M.A. 1992. *Environmental management in South Africa.* Juta & Co., Ltd. Wetton, RSA.

Geological Survey. 1971. *Geological map, 2629C-Standerton.* Geological survey, Department of Mines, RSA.

Gibbons, R.D. 1991. Statistical tolerance limits for ground-water monitoring. *Ground Water,* **29**, (4), 563-570.

Gilbert, R.O. 1987. *Statistical methods for environmental pollution monitoring.* Van Nostrand Reinhold, New York, USA.

Ginster, M. 1995. *An assessment of the ground water quality deterioration at and around the Sasol Secunda industrial complex using monitoring data from the Secunda water quality monitoring and management system.* Internal report produced for SASTECH (PTY) Limited.

Goodwin, P. and Wright, G. 1991. *Decision analysis for management judgement - Chapter 2: Decisions involving multiple objectives.* J. Wiley, London, U.K.

Howarth, R.A. and Thornton, I. 1983. In: *Applied environmental geochemistry.* 1983 Thornton, I. (ed)

Istok, J.D., Smyth, J.D. and Flint, A.L. 1993. Multivariate geostatistical analysis of ground water contamination - A case history. *Ground Water,* **31**, (1), 63-74.

James, B.R. and Gorelick, S.M. 1994. When enough is enough - The worth of monitoring data in aquifer remediation design. *Water Resources Research,* **30**, (12), 3499-3513.

Keith, L.H., Libby, R.A., Crummett, W., Taylor, J.K., Deegan, J. and Wentler, G. 1983. Principles of environmental analysis. *Analytical Chemistry,* **55**, 2210-2218. American Chemical Society on Environmental Quality

Keith, L.H. (ed) 1988. *Principles of environmental sampling.* American Chemical Society, Salem, MA., USA.

Kralik, M. 1994. Quick and simple sample collection and evaluation of polluted sediments and soils. In: *The third international symposium on environmental geochemistry.* Krakow, Poland.

Kuharic, C.A., Cole (III), W.H., Singh, A.K., Gonzales, D. and Brown, K.W. 1993. *An x-ray fluorescence survey of lead contaminated residential soils in Leadville, Colorado: A case study.* U.S. Environmental Protection Agency, EPA/600/R-93/073.

Lawrence, J. and Williams, B. 1991. Monitoring water quality. *Chemistry and Industry,* 18 March 1991, 209-213.

LeGrand, H. and Brown, C. 1990. *Numerical site rating system for evaluating waste disposal sites.* U.S.EPA contact number 68-01-4405. Cited in: Müller, J. 1991. *Secunda water quality monitoring and management system - project report.* Internal report produced for SASOL Limited.

Loaiciga, H.A., Charbeneau, R.J., Everett, L.G., Fogg, G.E., Hobbs, B.F and Rouhani, S. 1992. Review of ground-water quality monitoring network design. *Journal of Hydraulic Engineering,* **118**, (1), 11-37.

Mar, B.W., Horner, R.R., Richey, J.S., Palmer, R.N. and Lettenmaier, D.P. 1986. Data acquisition. *Environmental Science and Technology,* **20**, (6), 545-551.

McBride, G.B. 1986. Requirements of a water quality information system for New Zealand. In: Proceedings of the Budapest Symposium 1986. *Monitoring to detect changes in water quality.* IAHS Publ. No. 157, 29-35.

Müller, J. 1991. *Secunda water quality monitoring and management system - project report.* Internal report produced for SASOL Limited.

Palmer, R.N. and MacKenzie, M.C. 1985. Optimization of water quality monitoring networks. *Journal of Water Resources Planning and Management-ASCE,* **111**, (4), 478-493.

Parker, J.M. and Foster, S.S.D. 1986. Ground water monitoring for early warning of diffuse pollution. In: Proceedings of the Budapest Symposium 1986. *Monitoring to detect changes in water quality.* IAHS Publ. No. 157, 37-46.

Parsons, R. and Tredoux, G. 1995. Monitoring ground water quality in South Africa: Development of a national strategy. *Water SA,* **21**, (2), 113-116.

Porteous, A. 1992. *Dictionary of environmental science and technology.* J.Wiley & Sons, Chichester, UK.

Porter, P.S. 1986. A description of measurement error near limits of detection. In: Proceedings of the Budapest Symposium 1986. *Monitoring to detect changes in water quality.* IAHS Publ. No. 157, 305-316.

Quattro Pro. 1987. *Spreadsheet computer package and associated manuals.* Borland, California, USA.

Sargent, M. and Mackay, G. 1995. (eds) *Guidelines for achieving quality in trace analysis.* The Royal Society of Chemistry, UK.

Schweiter, G.E. and Black, S.C. 1985. Monitoring statistics. *Environmental Science and Technology,* **19**, (11), 1026-1030.

Selinus, O. 1994. Large scale monitoring in environmental geochemistry. In: *The third international symposium on environmental geochemistry.* Krakow, Poland.

Sittig, M. 1974. *Pollution detection and monitoring handbook.* Noyes Data Corporation, Park Ridge, New Jersey, USA.

SIRI. 1976. *Land type map, 2628-East Rand.* Department of Agricultural Technical Services, Soil and Irrigation Research Institute, (now the Institute for soil, climate and water, ISCW), RSA.

Somlyody, L., Pinter, J., Koncsos, L., Hanagsek, I. and Juhasz, I. 1986. Estimating averages and detecting trends in water quality data. In: Proceedings of the Budapest Symposium 1986. *Monitoring to detect changes in water quality.* IAHS Publ. No. 157, 61-69.

Steele, T.D. 1986. Convertising water quality information goals into design criteria. In: Proceedings of the Budapest Symposium 1986. *Monitoring to detect changes in water quality.* IAHS Publ. No. 157, 71-78.

Stratten, T. 1986. Environmental stratigraphic setting of the Karoo Basin and its mineral deposits. In: Anhaeusser, C.R. and Maske, S. (eds). *Mineral deposits of Southern Africa.* pp 1863-1873. Geological Society of Southern Africa, Johannesburg, RSA.

VISA. 1994. *Visual interactive sensitivity analysis (VISA) for multi-criteria decision support.* Belton, V. and Visual Thinking International Limited, Glasgow, UK.

Vrba, J. and Pekny, V. 1991. Ground water quality monitoring - Effective method of hydrogeological system pollution prevention. *Environmental Geology and Water Science,* 17, (1), 9-16

Ward, R.C. 1986. Framework for designed water quality information systems. In: Proceedings of the Budapest Symposium 1986. *Monitoring to detect changes in water quality.* IAHS Publ. No. 157, 89-100.

Weaver, J.M.C. 1992. *Ground water sampling.* WRC Project No. 339. Ground water programme, Division of Water Technology, CSIR, RSA.

WHO. 1984. *Guidelines for drinking-water quality. Vol. 1. Recommendations.* World Health Organization, Geneva, Switzerland.

WQStat II. 1989. *Water quality statistics programme and manual.* Prepared by: Phillips R.D. Loftis J.C. and Hotto H.P. Colorado State University, USA.

APPENDICES

APPENDIX I - CCWR climatic data

Table I.1 Mean monthly climatic data from the Bethal dam weather station.

	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Maximum temperature	25.4	25.1	24.5	21.6	19.4	16.4	17.1	19.8	22.8	23.6	23.9	25
Minimum temperature	13.8	13.1	11.8	8.6	4.4	0.8	0.9	3.7	7.3	9.8	11.7	13
Mean Evaporation	15.68	130.4	127.8	92.7	80.7	66.8	78.3	110.6	137.5	137.8	147.4	164.5
Mean precipitation	148.3	80.2	62.8	47.1	14.8	5.7	5.5	12.7	24.6	82.9	129.6	109.5
Median precipitation	134.6	64.1	50.8	40.3	10.1	1.6	1.4	8.7	15	87.9	114.1	98.8

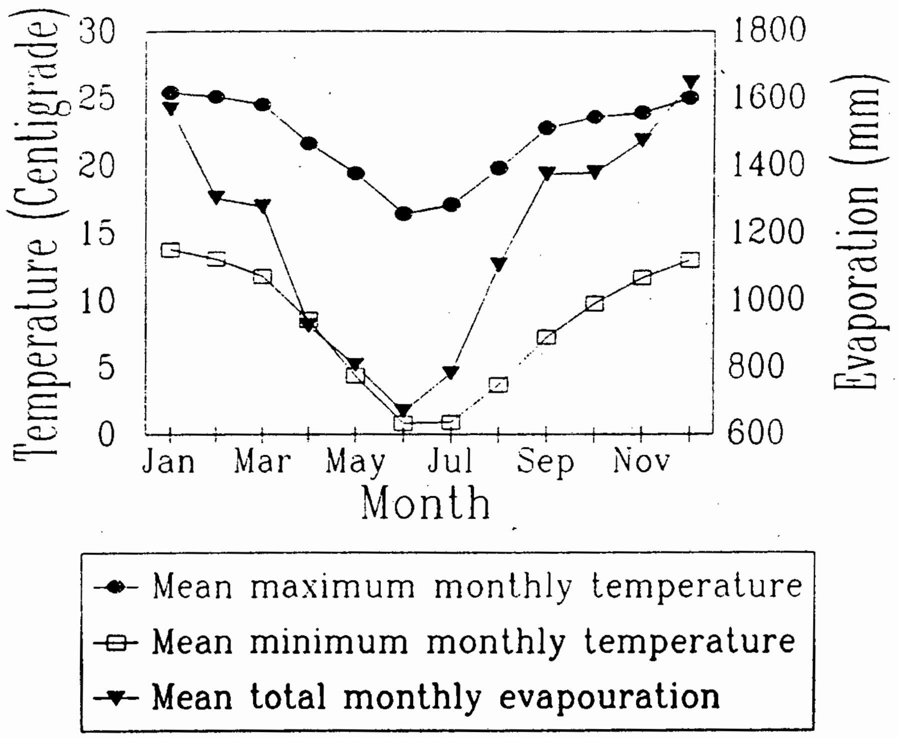


Figure I.1 The mean maximum and minium monthly temperature and evaporation between 1964 and 1987 at the Bethal dam weather station about 20 km from the study area.

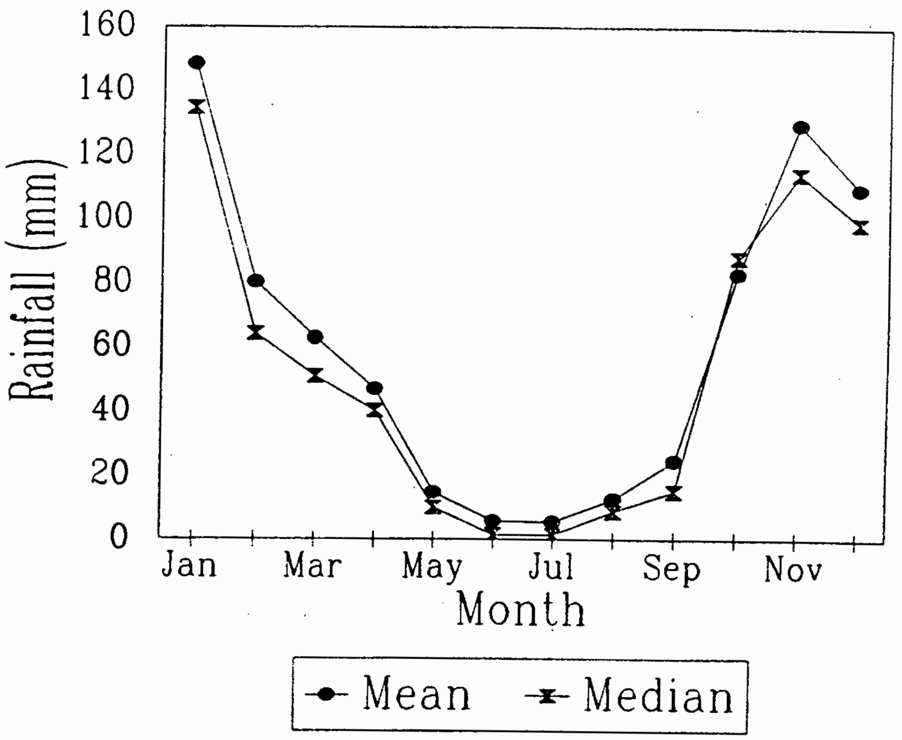


Figure I.2 The mean and median monthly rainfall between 1964 and 1987 at the Bethal dam weather station about 20 km from the study area.

APPENDIX II - Costs of sampling

COSTS OF SAMPLING

Cost of technician to sample per hour (Rands):	
(including EC and pH measurements)	80

APPROXIMATE ESCALATED BUDGET OF EQUIPMENT REQUIRED FOR MONITORING

	Costs of equip. (Rands/month)	Costs of equip. (R/month)	Costs of sampling (R/month)
Lab services	19297.00	19297.00	(included in lab.costs)
Synref services	19297.00	19297.00	9648.50
Intercommpany services	19297.00	19297.00	9648.50
Solvents & material	28.00	28.00	14.00
Cleaning material	28.00	28.00	14.00
Direct lab material	124.00	124.00	62.00
Lab material	124.00	124.00	62.00
Operating material	152.00	152.00	76.00
Vehicle fuel	**445.00**	**445.00**	**222.50**
Vehicle maintenance cost	**420.00**	**420.00**	**210.00**
Vehicle running costs	**865.00**	**865.00**	**432.50**
Cost I.R.O. fixed assets	**865.00**	**865.00**	**432.50**
Total per month (R/ma.)	**60942.00**	**60942.00**	**20822.50**
Cost per year (R/an.)	**731304.00**	**731304.00**	**249870.00**

APPROXIMATE MAGNITUDE OF SAMPLING

	No. of sample sites	# sites/event	Sampl. frequency	Sampl.events/year	Sample /year	
RESM	22	15	weekly	52	780	
REGM	47	38	quarterly	4	152	
PPSM	15	0	(biannually)	0	0	Discontinue
Misc.			randomly		60	Ad hoc
Total					992	

APPROXIMATE UNIT SAMPLE TIME

	# sites/event	Time /event (hrs/event)	Unit sample time (mins/smp.)	
RESM	15	4	16.0	
REGM	38	15	23.7	
PPSM	0	4		
Misc. (ad hoc)			16.0	(Estimate)

APPROXIMATE TIME TAKEN TO COLLECT SAMPLES AND COST OF THE SAMPLING TECHNICIAN

	# samples/year	Unit sample time (mins/sample)	Tot.time (hours/year)	Unit cost of tech. (R/hour)	Cost of tech.time (R/year)
RESM	780	16.0	208	80.00	16640.00
REGM	152	23.7	60	80.00	4800.00
PPSM	0	0.0	0	80.00	0.00
Misc. (ad hoc)	60	16.0	16	80.00	1280.00
Total	992		284		22720.00

APPROXIMATE COST PER SAMPLE

	Samples/year	Cost of tech.time (R/year)	Unit cost of equip. (R/sample)	Cost of equip. (R/year)	Total cost (R)	Cost / sample
RESM	780	16640.00	251.89	196470.36	213110.36	273.22
REGM	152	4800.00	251.89	38286.53	43086.53	283.46
PPSM	0	0.00	251.89	0.00	0.00	
Misc. (ad hoc)	60	1280.00	251.89	15113.10	16393.10	273.22
Total	992	22720.00		249870.00	272590.00	

APPENDIX III - Costs of analysis

Value of a service unit (R)	179.60
Size of a service unit (min)	100

ANALYTICAL DETERMINATION	Service unit size	No.samples analyzed	Service unit cost	Cost of analyses
Ammonia as nitrogen (TKN)	0.20	1	35.92	35.92
Arsenic (As)	0.30	1	53.88	53.88
Bicarbonate (HCO3)	0.05	1	8.98	8.98
Boron (B)	0.10	1	17.96	17.96
Cadmium (Cd)	0.10	1	17.96	17.96
Calcium (Ca)	0.05	1	8.98	8.98
Carbonate (CO3)	0.05	1	8.98	8.98
Chemical oxygen demand (COD)	0.10	1	17.96	17.96
Chloride (Cl)	0.10	1	17.96	17.96
Chromium (Cr)	0.10	1	17.96	17.96
Copper (Cu)	0.05	1	8.98	8.98
Cyanide (CN)	0.10	1	17.96	17.96
E.coli	1.00	1	179.60	179.60
Electrical conductivity (EC)	*	1	0.00	0.00
Fluoride (F)	0.05	1	8.98	8.98
Hydrogen sulphide (H2S)	0.05	1	8.98	8.98
Iron (total) (Fe tot.)	0.10	1	17.96	17.96
Lead (Pb)	0.10	1	17.96	17.96
Magnesium (Mg)	0.05	1	8.98	8.98
Manganese (Mn)	0.10	1	17.96	17.96
Mercury (Hg)	0.30	1	53.88	53.88
Methyl-orange alkalinity (M-O Alk)	0.10	1	17.96	17.96
Nitrite as nitrogen (NO3)	0.05	1	8.98	8.98
Non acidic chemicals (NAC)	0.05	1	8.98	8.98
pH	*	1	0.00	0.00
Phenolphtlen alkalinity (P Alk)	0.10	1	17.96	17.96
Phenols	0.05	1	8.98	8.98
Phosphate (PO4)	0.05	1	8.98	8.98
Potassium (K)	0.05	1	8.98	8.98
Selenium (Se)	0.30	1	53.88	53.88
Silicon (Si)	0.05	1	8.98	8.98
Sodium (Na)	0.05	1	8.98	8.98
Sulphate (SO4)	0.05	1	8.98	8.98
Temperature	*	1	0.00	0.00
Total dissolved solids (TDS)	0.05	1	8.98	8.98
Vanadium (V)	0.20	1	35.92	35.92
Zinc (Zn)	0.05	1	8.98	8.98
			Total cost	763.30

(* Included in the sampling costs)

APPENDIX IV – Description of the alpha-numerical site rating system

For the construction of the original monitoring strategy a numerical rating system was used to evaluate the potential pollution sources, the waste operations. For the purpose of this thesis it is important to have an understanding of the methodology behind the rating procedure, both for reference and for comparison with the multiple criteria decision analysis performed in Section 2.4. Many of the criteria used in the U.S.EPA procedure (LeGrand and Brown, 1990) where chosen, scrutinized and deployed in the resource decision making procedure of this thesis. The numerical rating system was described by Müller (1991). Its objective is to evaluate and rank potential of ground water contamination from waste disposal sites. This has the purpose of comparing different sites and is valuable in the selection of a disposal site. It can, however, be utilized in the allocation of monitoring resources, or prioritization as Müller (1991) refers to it.

The system focuses on weighting four key geological and hydrological characteristics in the vicinity of the contamination source. The rating, however, does not provide a definitive value for the waste site but is more of a descriptive set of alpha-numerical figures. It could be argued that a single figure or score for a site is a constricted classification and the waste site, which will be unique, is being stereotyped. A score, however, provides an all-inclusive assessment of the site which can be used in objective and statistical procedures. These options of using the U.S.EPA scheme the DWAF recommended procedure and MCDA are discussed in the thesis (Section 2.4.3.3). This Appendix is a worked example of the U.S.EPA system. It outlines the stages in the evaluation process using the reject fertilizer dump site as a case study.

Four digits and four additional letter codes concisely describe characteristics of a site for standardized interpretation and the values indicate the relative contamination potential. Geohydrological features are identified on a scale of various aquifer sensitivities to pollution spread, in addition to the particular waste's toxicity, concentration, volume and constituents. The parameters are then integrated into a matrix in which the hazard potential is graphically displayed. The location of the point on the graph reveals the degree of seriousness a waste operation would have if it was situated on that particular site. The probability of contamination can be determined by correlating the site's numerical description with a synthetic numerical standard constructed by LeGrand and Brown (1990). Acceptance or rejection rating limits are suggested which are based firstly on the unaltered natural setting and then on the rating including modifications to the site by specific engineering practices. The entire procedure is divided into four stages

IV.1. Stage 1 - Site description

A standard geohydrological and pedological description.

Step 1. Determine the distance on the ground from the source of contamination to the nearest well, borehole, spring, surface stream or property boundary. Then read the point values from Table IV.1. The value for the reject fertilizer dumps is shaded.

Table IV.1. Scale to determine the distance on ground between contamination source and water supply (LeGrand and Brown 1990).

Point Value	0	1	2	3	4	5	6	7	8	9
Distance in meters	2000 +	1000-2000	300-999	150-299	75-149	50-74	35-49	20-34	15-19	0-14

Step 2. Estimate the depth to the water table below the base of the contamination source for more than 5% of the year. This estimate is assumed to be the average water table depth within the 95 percentile of the distribution of depths as Müller does not specify the criteria. The point value for the depth is read from Table IV.2 as indicated by the example of the reject fertilizer dams.

Table IV.2. Scale to estimate the depth to the water table below the base of the site at more than 5% of the year (LeGrand and Brown 1990).

Point Value	0	1	2	3	4	5	6	7	8	9
Distance in meters	60+	30-60	20-19	12-19	8-11	5-7	3-4	1.5-2.5	0.5-1	0

Step 3. Estimate the water table gradient and flow direction from the contamination source and read the point value from Table IV.3. The point value for the reject fertilizer dumps is 5.

Table IV.3. Scale to estimate the water table gradient from the waste site (LeGrand and Brown 1990).

Point Value	0	1	2	3	4	5
Water table gradient and flow direction.	Gradient away from all water supplies that are closer than 1000m.	Gradient almost flat.	Gradient less than 2 percent toward water supply but not the anticipated direction of flow.	Gradient less than 2 percent toward water supply and is the anticipated direction of flow.	Gradient greater than 2 percent toward water supply but not the anticipated direction of flow.	Gradient greater than 2 percent toward water supply and is the anticipated direction of flow.

Step 4. Estimate the permeability-sorption characteristics of the site using Table IV.4. The attenuation properties of the reject fertilizer dump are indicated by the shading on 5D.

Table IV.4. The permeability-sorption characterization of the soil underlying the site (LeGrand and Brown 1990).

Thickness of unconsolidated material over bed rock in meters.	Clay(1)		Clay with no more than 50% sand		Sand with 15-30% clay		Sand with less than 15% clay		Clean fine sand		Clean gravel or coarse sand	
More than 30	OA(2)		2A		4A		6A		8A		9A	
	I(3)	II(4)	I	II	I	II	I	II	I	II	I	II
25 - 29	OB	1C	1D	2F	3E	4G	5F	6E	7F	8E	9G	9M
20 - 24	OC	2C	1E	3D	4D	5E	5G	6F	7G	8F	OH	9N
15 - 19	OD	3B	1F	4C	4E	6C	5H	7D	7H	8G	9I	9O
10 - 14	OE	4B	2D	5B	4F	6D	5I	7E	7I	9D	9J	9P
3 - 9	1B	6B	2E	7B	5C	7C	5J	8D	7J	9F	9K	9Q
Less than 3	2B	8B	2C	9B	5D	9B	5K	9C	7K	9F	9L	9R
Bedrock at land surface: I = 5Z, II = 9Z.												

(1) U.S. Department of Agriculture particle size classification.
(2) Top row (suffix A) is for site areas where no consolidated rock occurs closer than 30m below land surface.
(3) Category I: unconsolidated material overlies shale or other poorly permeable consolidated rock.
(4) Category II: unconsolidated material overlies permeable consolidated rock (fractured or cavernous limestone).

Step 5. Determine the degree of confidence in accuracy of values in the first 4 steps of the procedure. This is done by choosing an appropriate category from A and C.

A • Confidence in estimates of values for the parameters is high and estimated values are considered fairly accurate.

B • Confidence is fair.

C • Confidence in estimates of values for the parameters is low and estimated values are not considered to be accurate.

The parameter of the reject fertilizer dump's environ, which were originally estimated by Müller (1991) are considered to be fair (B).

Step 6. Combine letters and numbers (from Steps 1 to 5) to form a code which is used to complete the description of the site. To this a letter representing the nearest physical feature the contamination source could pollute is recorded, for example a borehole or well (W), stream or perennial stream (S) or property boundary (B). Finally, further letter(s) are use to describe appropriate phenomena:

C • Special conditions that require that a comment or explanation be added to the evaluation.

D • A cone of depression near to the waste site may cause pollution to migrate towards a pumped borehole.

E • The distance recorded is that from a water supply to the estimated closest edge of an existing plume, rather than to the original source of contamination.

F • The contamination source is located on a ground water discharge area, such as a flood plain, and would likely cause a minimal source of contamination.

K • The site is located in karst topography or is underlain by cavernous limestone.

M • Mounding of the water table occurs beneath the site, which is common beneath sites where there is liquid input or reduced infiltration capacity.

P • Percolation may not be as adequate as the permeability-sorption digit suggests. A value of 3 or less being a warning of poor percolation.

Q • The recharge or transmission part of an aquifer is exposed the to pollution source, which may also be expressed by a high permeability-sorption value.

T • The water table is in fractured cavernous rock.

Y • One or more confined aquifers underlie the water table aquifer.

Z • Acid rock drainage is a problem.

The reject fertilizer dump is assigned an M from this Step.

Step 7. Completion of the site numerical description is done by adding all point values determined in Steps 1 to 4. The total point value determined relates to the physical characteristics of the area. Note that no weighting system is used when the values of Steps 1 to 4 are added. The composite value is followed, in sequence, by the four individual values for the key geological criteria. The special site identifier suffixes, from Steps 5 and 6 are placed at the end of the code. After the site rating, the code for the value of the hazard potential matrix (see Stage 2) is added.

The reject fertilizer dump, for example has the rating description of:

20 : 3 7 5 5D B S M + F

Where:

20 = Total points for the physical features around the site.
3 = Step 1 - distance to water supply is between 150 to 299 m.
7 = Step 2 - depth to the water table is a around 1.5 to 2.5 m deep.
5 = Step 3 - the water table gradient is greater than 2% and flow is expected to be towards the stream.
5D = Step 4 - a permeability-sorption value of a soil less than 3 m deep and sand with 15 to 30% clay.
B = Step 5 - the confidence attached to the values is fair.
S M = Step 6 - the other identifiers are that the direction of the plume is moving towards a stream and water table mounding will occur.
\+ F = Stage 2 - The hazard potential is moderately high as the site is moderate in area or quantity and of moderate consequence (not to be confused with Table IV.5).

Table IV.5 shows general value categories based on the geohydrological conditions only, *i.e.* without regard for the type or severity of the contaminant. Water table and gradient values could be listed but on aggregate they should not be large enough to allow the site to exceed the total points listed. For example, if a site had a total of 17 points and the distance value was less than 2 and the permeability-sorption code was 4 or below then the site could be graded as 'good'. The values pertaining to the water should not be large enough to having a bearing on this classification. The reject fertilizer dump has a total of 20 points which is very poor.

Table IV.5. Generalized site grade based on critical geohydrological parameters (LeGrand and Brown, 1990).

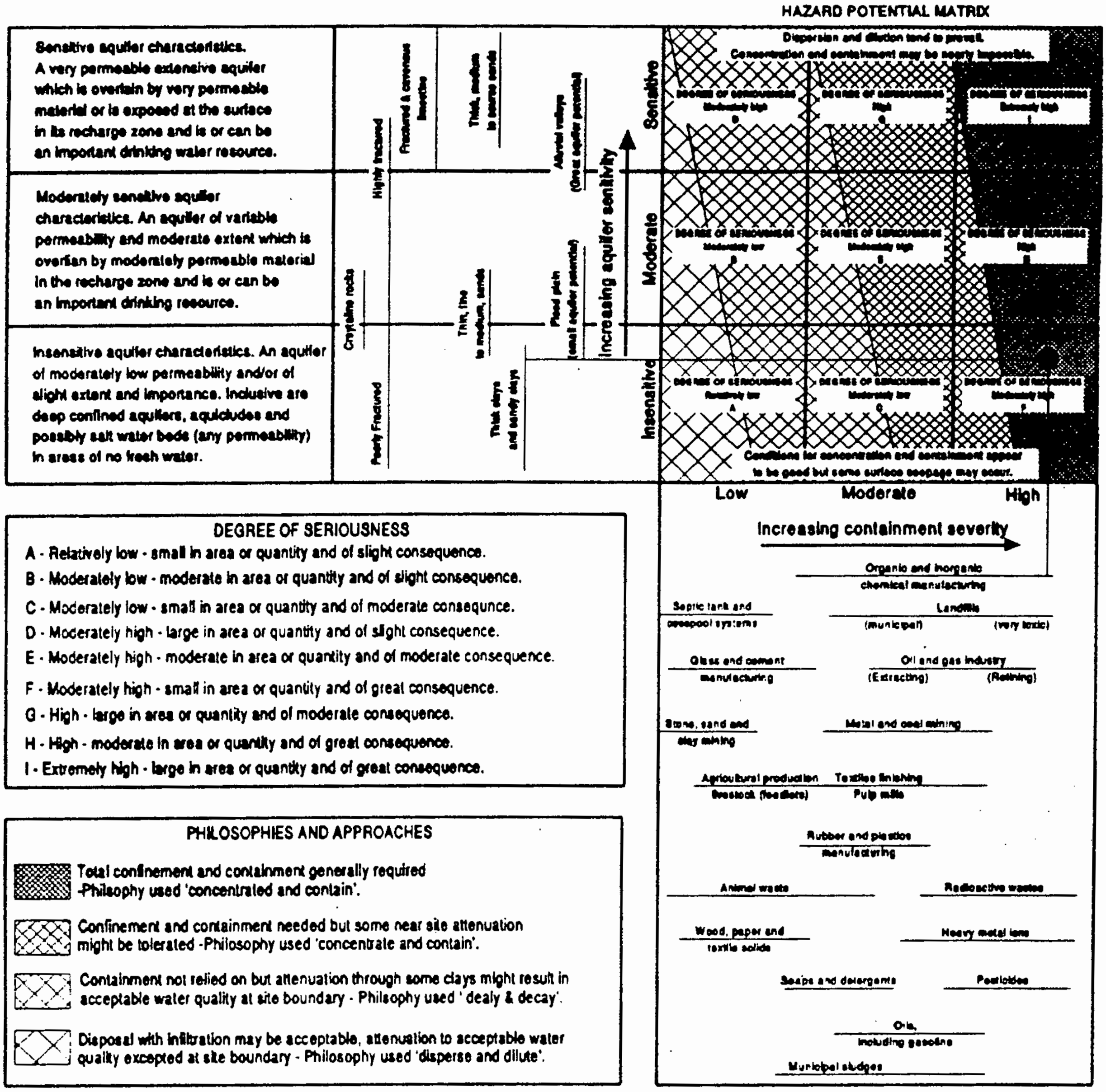
Grade	Descriptn	Total points	Distance (max)	Water table	Gradient	Perm-sorption (max)
A	Excellent	< 10	0	-	-	2
B	Very good	11 - 14	1	-	-	3
C	Good	15 - 17	2	-	-	4
D	Fair	18 -20	3	-	-	5
E or F	Poor or very poor	> 20	-	-	-	-

IV.2 Stage 2 - Evaluate the degree of seriousness

Step 8. The degree of seriousness of contamination is one of the two aspects of the total hazard potential, the probability of a pollution event occurring being the other, as defined by LeGrand and Brown (1991). Figure IV.1 is somewhat independent of the site rating description of Stage 1 but essential to the overall evaluation of the potential ground water impact. Figure IV.1 shows a perception matrix which allows insight into several aspects of the ground water contamination problem. The analyses embodied in Figure IV.1 are made with a matrix including on one axis the sensitivity of the ground to pollution and on the other, the severity of the contaminant.

Aquifer sensitivity is a term used to indicate the likelihood of and the degree to which ground water resources may be polluted at a particular site. It also incorporates the aquifer's real extent and importance, or potential importance, as a ground water resource. For this rating system the aquifers are divided into sensitive, moderately sensitive and insensitive. Figure IV.1 shows the classification of sensitivities of near surface aquifers and rock materials to pollution. Ranges of sensitivities of various groups of regolith are also shown. Müller (1991) considered permeability, *i.e.* hydraulic conductivity, to be the chief factor in considering aquifer sensitivity.

Contaminant severity is a composite term which includes qualitative weighting of toxicity, concentration and volume, mobility in the water and persistence. The range of the contaminant severity scale can be gauged by considering effluent from a single septic tank, at the low end, to large volumes of radioactive waste, at the high end. Some sources and types of pollutants are shown in the bottom right of Figure IV.1. The interaction between contaminant severity and aquifer sensitivity is illustrated on the potential hazard matrix or grid (see the top right of Figure IV.1).



Sensitive aquifer characteristics. A very permeable extensive aquifer which is overlain by very permeable material or is exposed at the surface in its recharge zone and is or can be an important drinking water resource.

Moderately sensitive aquifer characteristics. An aquifer of variable permeability and moderate extent which is overlain by moderately permeable material in the recharge zone and is or can be an important drinking resource.

Insensitive aquifer characteristics. An aquifer of moderately low permeability and/or of slight extent and importance. Inclusive are deep confined aquifers, aquicludes and possibly salt water beds (any permeability) in areas of no fresh water.

DEGREE OF SERIOUSNESS

A - Relatively low - small in area or quantity and of slight consequence.
B - Moderately low - moderate in area or quantity and of slight consequence.
C - Moderately low - small in area or quantity and of moderate consequnce.
D - Moderately high - large in area or quantity and of slight consequence.
E - Moderately high - moderate in area or quantity and of moderate consequence.
F - Moderately high - small in area or quantity and of great consequence.
G - High - large in area or quantity and of moderate consequence.
H - High - moderate in area or quantity and of great consequence.
I - Extremely high - large in area or quantity and of great consequence.

PHILOSOPHIES AND APPROACHES

▩ Total confinement and containment generally required -Philosophy used 'concentrated and contain'.
▩ Confinement and containment needed but some near site attenuation might be tolerated -Philosophy used 'concentrate and contain'.
▨ Containment not relied on but attenuation through some clays might result in acceptable water quality at site boundary - Philosophy used ' dealy & decay'.
☒ Disposal with infiltration may be acceptable, attenuation to acceptable water quality excepted at site boundary - Philosophy used 'disperse and dilute'.

Figure IV.1. The hazard potential matrix indicating the degree of seriousness (LeGrand and Brown 1990).

The hazard potential matrix can be expressed in several ways. The overall degree of seriousness is divided into 9 categories which are described in the bottom left corner of Figure IV.1. The philosophies and approaches, shown as patterns on the matrix, indicate a range of actions which can be implemented to mitigate the waste problem. The distinctions between the four categories are gradational and appear somewhat arbitrary. The need for concentration and containment is obvious where hazardous materials are present in large volumes, of high persistence and high mobility. At the other extreme, materials of low toxicity that attenuate readily may be acceptable in a disperse and dilute situation.

The hazard potential matrix provides a useful framework for monitoring (Müller, 1991). A site's position in the matrix indicates the degree of seriousness of the hazard which in turn reflects the effort of monitoring. This indication, however, is only a qualitative guide to the amount of resources need to be applied to the particular site. Systematic, intensive monitoring is required for sites locating in blocks I, H and F and less rigorous monitoring is required for sites in less sensitive areas. The location of the reject fertilizer dump is plotted in Figure IV.1 illustrated by the circle. It location is determined by the containment severity and aquifer sensitivity (see the little arrows).

IV.3. Stage 3 - Evaluate the probability of contamination and degree of acceptance.

The same matrix that was constructed in Figure IV.1 is used in Figure IV.2. For a series of hypothetical systems, isometric lines have been drawn. These have a bearing on the degree of acceptance a site would have depending on where it would plot in the grid.

Step 9. The final situation rating of LeGrand and Brown (1990) scheme is calculated by comparison is the waste operation's rating with a set of artificial site ratings (see the code next to each isometric line in Figure IV.2). The comparison is done by locating the site relative to the isometric zones. This par rating, the hypothetical code, is subtracted from the site numerical description and results are combined to provide a situation rating. Only the total points and the permeability-sorption values, are subtracted. The two water parameters are not required for the calculation as they do not have a significant effect. The presence of the water table depth and gradient values are simple indicated by / in the isometric zone rating. A synthetic distance is also shown in the figure and can be used if one chooses to use the matrix for other purposes.

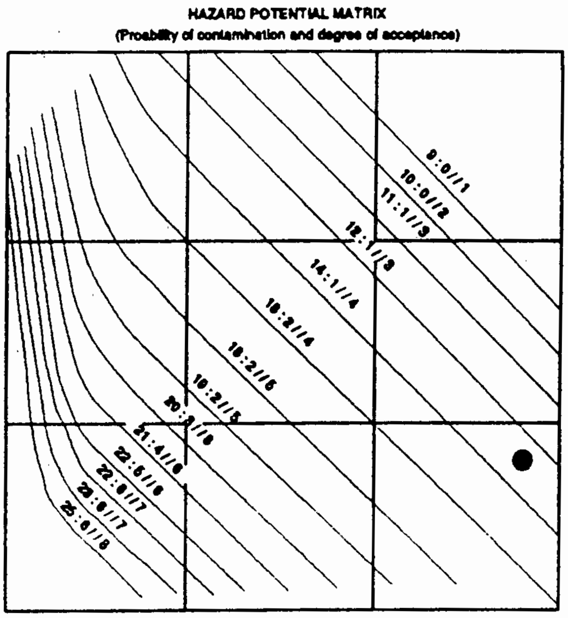


Figure IV.2. The hazard potential matrix used to estimate the probability of contamination and the degree of acceptance (LeGrand and Brown, 1990).

For the example of the reject fertilizer dump, the situation rating is calculated such:

Site rating: 13 : \ \ \ 3
Par rating: 13 : \ \ \ 4
Subtracted result: 0 : 0 0 0 -1
Combined value: -1

The degree of acceptability and the probability of pollution can be obtained from Table IV.6, which was estimated by LeGrand and Brown (1990). These criteria are used in the final assessment of a site's suitability for a waste operation.

Table IV.6. A table to show how the combined situation rating is used to provided the degree of acceptability and the probability of contamination a waste operation would have at a specific site (LeGrand and Brown, 1990).

Situation rating (combined value)	Probability of contamination	Degree of acceptability	Grade
-8 or less	Improbable	Probably acceptable	A
-4 to -7	?	Probably acceptable	B
+3 to -3	?	Acceptance uncertain	C
+4 to +7	Probable	Probably unacceptable	D
+8 or more	Very probable	Almost certainly unacceptable	F

The probability of contamination from situations having values between +3 and -7 is difficult to categorize satisfactorily. The range of values represented by grades B and C, therefore, are designated by only a question mark. Acceptance or rejection of a site for the intended waste operation is the responsibility of the particular regulatory agency. Permitting may depend on the requirements from the agency or on the feasibility of approved engineering modifications to a site. The example used, the reject fertilizer dump, therefore has a combined situation rating of C. This means that the acceptability of pollution from the site is uncertain but the rating is closer the unacceptable than acceptable. In addition, it is not possible to produce a satisfactory estimate on the probability of pollution occurring.

The MCDA technique, see Section 2.4, does not aim to produce such philosophical conclusions on the acceptability or probability of pollution occurs. MCDA provides a value, which is an overall relative classification. The resultant weighting from MCDA, however, does suggest that the reject fertilizer site will probably pollute and the environmental impact could be unacceptable.

IV.4. Stage 4 - Degree of acceptance for the modified site

Step 10. The final Step proposed by LeGrand and Brown (1990) allows for optional considerations and grading. The different options could be according to modifications as the result of anthropogenic inputs such as improvement resulting from engineering designs. The procedure is repeated but with the modified information producing a slight variation on the site description, plotted matrix location, par value and hence the situation rating.

Table V.1. Surface water monitoring site RESM01 data set.

Loc #	Samp.Date	Day	EC mS/m	pH	TDS	Ca mg/l	Mg mg/l	Na mg/l	K mg/l	Si mg/l	M.Alk meq.C	HCO3 meq.H	HCO3 mg/l	Cl mg/l	SO4 mg/l	F mg/l	B mg/l	Fe mg/l	Mn mg/l	Zn mg/l	Cu mg/l	P.Alk meq.C	CO3 meq.H	CO3 mg/l	N mg/l	COD	NH4 mg/l	Pheno mg/l	PO4 mg/l	Total Cation	Total Anion	Ion %E
ECRESM01	19900919	19	140	7.8	992			116			418	8.36	510	237	276	0.6						0	0	0	0.2	106	2		3.7	5.16	20.94	-60.48
ECRESM01	19900926	26	56	8.3	372			63			179	3.42	208.6	57	53	0.3						8	0.16	9.6		47	2			2.85	6.47	-38.79
ECRESM01	19901003	33	61	7.7	406			71			201	4.02	245.2	64	52	0.5						0	0	0	0.3	45	2		2.4	3.20	7.01	-37.35
ECRESM01	19901010	40	67	7.8	478			84			207	4.14	252.5	65	72	0.6						0	0	0	0.5	42	2		1.5	3.76	7.56	-33.50
ECRESM01	19901017	47	61	7.7	410			72			188	3.76	229.4	56	56	0.4						0	0	0	0.2	46	2		2.5	3.24	6.61	-34.16
ECRESM01	19901031	61	56	7.7	360	92	0	53	6.9		195	3.9	237.9	46	52	0.6						0	0	0						7.12	6.31	6.05
ECRESM01	19901101	61	56	7.7	360	37	20	53	6.9		195	3.9	237.9	46	52	0.6						0	0	0	1.4	38	2		2.4	6.14	6.41	-2.16
ECRESM01	19901106	66	66	7.9	431	34	20	64	11.5		188	3.76	229.4	67	68	0.5						0	0	0	0.6	36	2		3.6	7.40	7.22	1.26
ECRESM01	19901114	74	60	7.8	372	27	20	60	12.6		155	3.1	189.1	63	56	0.2						0	0	0	0.7	41	2		4.5	6.04	6.25	-1.72
ECRESM01	19901121	81	56	7.9	376	33	19	64	10.7		163	3.26	198.9	67	72	0.5						0	0	0	0.7	37	2		3.3	6.38	6.79	-3.12
ECRESM01	19901128	88	41	7.3	330	27	20	40	7.2		86	1.72	104.9	37	60	0.6						0	0	0	1.8	56	2		1.3	5.03	4.53	5.20
ECRESM01	19901205	95	60	7.8	630	56	26	71	10		119	2.38	145.2	53	122	0.7						0	0	0	10	106	2		1.4	8.55	6.66	12.47
ECRESM01	19901212	102	23	7.3	251	15	12	11	5.4		79	1.58	96.38	7	40	0.3						0	0	0	2	66	2		1.9	2.46	2.72	-4.91
ECRESM01	19901219	109	45	7.8	416	30	24	27	2.4		148	2.96	180.6	31	64	0.7						0	0	0	1.9	50	2		0.6	4.82	5.26	-4.37
ECRESM01	19901226	116	63	7.9	511	45	27	54	6.8		193	3.86	235.5	43	68	0.7						0	0	0	2.5	37	2		1.6	7.10	7.04	0.44
ECRESM01	19910102	122	45	7.8	376	27	21	31	5.2		153	3.06	186.7	26	48	0.3						0	0	0	0.4	33	2		1.7	4.67	4.87	-2.10
ECRESM01	19910109	129	28	7.2	227	16	22	20	6.5		84	1.68	102.5	13	52	0.6						0	0	0	3.6	73	9		1.8	4.14	3.28	11.71
ECRESM01	19910116	136	77	7.7	576	46	32	83	9.3		165	3.3	201.3	55	130	0.6						0	0	0	2.7	44	2		1.9	8.99	7.69	7.76
ECRESM01	19910123	143	74	7.8	500	56	33	75	13		162	3.24	197.6	46	140	0.6						0	0	0	3.9	31	2		2.6	9.22	7.63	9.42
ECRESM01	19910130	150	60	7.6	398	59	21	69	10		115	2.3	140.3	35	165	0.4						0	0	0	1.9	44	2		1	8.04	6.61	6.32
ECRESM01	19910206	156	115	7.6	876	65	28	118	24		153	3.06	186.7	77	365	1						0	0	0	1.6	42	2		0.6	12.40	12.93	-2.10
ECRESM01	19910213	163	120	7.8	489	96	24	134	31		80	1.6	97.6	82	410	0.6						0	0	0	2.7	41	2		0.9	13.60	12.55	4.00
ECRESM01	19910220	170	42	7.4	337	64	19	37	6.7		97	1.94	118.3	22	60	1.1						0	0	0	1.6	41	2		1.2	7.65	4.35	27.47
ECRESM01	19910227	177	140	7.6	1123	106	26	163	47		148	2.96	180.6	135	340	0.8						0	0	0	0.2	43	2		0.7	16.80	13.91	9.40
ECRESM01	19910306	186	195	7.8	1665	155	25	275	59		157	3.14	191.5	155	730	0.8						0	0	0	3.2	37	4		1.7	23.48	22.86	1.35
ECRESM01	19910313	193	115	7.4	855	65	25	141	25.3		175	3.5	213.5	86	360	1.3						0	0	0	3.2	38	2		1.6	13.19	13.60	-1.52
ECRESM01	19910319	199	76	7.8	566	59	32	66	17		181	3.62	220.8	87	600	0.2						0	0	0	2.3	32	2		1	9.06	18.64	-34.50
ECRESM01	19910326	206	120	7.8	893	61	26	143	27		148	2.96	180.6	90	300	0.5						0	0	0	10	30	2		14	13.37	12.37	3.86
ECRESM01	19910403	213	155	7.7	1061	118	27	194	29		148	2.96	180.6	122	480	0.3						0	0	0	4.6	40	2		3	17.40	16.56	2.42
ECRESM01	19910410	220	165	7.8	1328	112	25	227	34		160	3.2	195.2	150	400	0.6						0	0	0	4.2	36	2		3.5	18.50	15.97	7.35
ECRESM01	19910417	227	195	7.3	1269	135	22	245	36		164	3.28	200.1	165	400	0.6						0	0	0	3.9	56	3.9		2.9	20.34	17.01	8.91
ECRESM01	19910424	234	200	8	1470	133	29	264	46		154	3.08	187.9	226	740	0.6						0	0	0	17	60	2		4	21.64	25.36	-7.43
ECRESM01	19910502	242	107	7.9	786	127	23	269	46		176	3.52	214.7	137	320	0.4						0	0	0	3.5	36	2		5	21.22	14.28	19.54
ECRESM01	19910509	249	94	7.8	691	67	21	125	26		185	3.7	225.7	69	230	0.6						0	0	0	3.7	39	10		5.1	11.73	11.25	2.08
ECRESM01	19910515	255	61	8.1	396	16	19	67	6		167	3.34	203.7	56	50	0.5						0	0	0	2.7	76	1		5.7	5.64	6.21	-4.84
ECRESM01	19910522	262	62	7.9	424	39	21	69	12		185	3.7	225.7	64	75	0.4						0	0	0	4	33	1		7	7.04	7.37	-2.32
ECRESM01	19910529	269	66	8.4	446	60	27	76	19		209	4.02	245.2	91	105	0.6						8	0.16	9.6	1.5	36	2		5.3	9.12	9.33	-1.12
ECRESM01	19910605	275	37	8	246	25	19	37	5		143	2.86	174.5	28	85	0.3						0	0	0	0.2	28	2		1.1	4.66	5.47	-8.03
ECRESM01	19910613	283	46	8	366	35	17	56	9		163	3.26	198.9	52	70	0.4						0	0	0	1.6	34	1		3.6	5.87	6.36	-3.96
ECRESM01	19910619	289	51	7.8	395	35	17	62	10		158	3.16	192.6	52	60	0.4						0	0	0	2	34	2		3.2	6.21	6.03	1.47
ECRESM01	19910626	296	60	7.8	397	40	20	66	11		186	3.72	226.9	54	56	0.4						0	0	0	3.6	32	2		3.3	6.90	6.63	2.01
ECRESM01	19910703	303	56	8.1	411	31	18	83	12		172	3.44	209.8	55	60	0.4						0	0	0	2.8	36	2		4.4	6.19	6.44	-2.05
ECRESM01	19910710	310	53	7.7	361	44	16	66	11		169	3.38	206.2	54	60	0.3						0	0	0	3.4	34	2		5.2	6.78	6.39	2.95
ECRESM01	19910717	317	56	7.7	380	40	21	66	11		157	3.14	191.5	61	67	1.6						0	0	0	7	35	2		6.5	7.07	6.67	2.96
ECRESM01	19910724	324	59	7.7	366	46	22	65	9		180	3.6	219.6	59	79	0.6						0	0	0	2.4	36	2		5.6	7.27	7.16	0.76
ECRESM01	19910731	331	56	7.9	376	36	22	52	11		209	4.18	255	47	50	0.7						0	0	0	2.7	40	2		2.9	6.28	6.72	-3.52
ECRESM01	19910807	337	52	7.8	406	33	18	56	9.7		180	3.6	219.6	50	47	0.3						0	0	0	2.5	33	2		3	6.01	6.14	-1.06
ECRESM01	19910814	344	60	7.9	387	40	20	67	10		188	3.76	229.4	56	60	0.6						0	0	0	0.2	34	2		3	6.92	6.77	1.09
ECRESM01	19910821	351	60	8.2	323	35	11	69	12		163	3.26	198.9	55	70	0.5						0	0	0	1.2	38	2		2.5	6.07	6.39	-2.56
ECRESM01	19910828	358	53	8.1	371	40	18	62	14		167	3.34	203.7	42	48	0.5						0	0	0	1.1	37	2		2.6	6.64	5.65	8.06
ECRESM01	19910904	364	50	7.7	348	35	16	51	10		173	3.46	211.1	42	44	0.4						0	0	0	2.5	31	2		1.6	5.65	5.67	-0.21
ECRESM01	19910911	371	56	7.5	399	32	20	74	10		169	3.38	206.2	54	49	0.9						0	0	0	0.9	40	2		2.7	6.83	6.07	5.88
ECRESM01	19910918	378	50	7.7	367	38	17	51	10		152	3.04	185.4	42	57	0.9						0	0	0	1.2	45	2		2.5	5.88	5.56	2.83
ECRESM01	19910925	385	60	7.5	432	45	16	65	11		168	3.36	205	60	56	0.8						0	0	0	0.3	43	2		5.3	6.95	6.43	3.84
ECRESM01	19911002	392	59	7.8	440	44	16	62	11		189	3.78	230.6	57	56	1						0	0	0	0.8	62	1		3	6.71	6.75	-0.31
ECRESM01	19911009	399	57	7.9	387	41	16	63	13		177	3.54	215.9	57	51	1						0	0	0	0.3	40	1		5.5	6.49	6.44	0.39
ECRESM01	19911016	406	47	7.8	337	41	19	40	6.4		159	3.18	194	40	45	0.5						0	0	0	1	38	1		2.1	5.62	5.35	2.43
ECRESM01	19911023	413	51	7.8	361	29	16	52	9.6		168	3.36	205	43	53	0.6						0	0	0	0.2	40	1		5.4	5.49	5.86	-3.43

Table V.1. Continued.

ECRESM01	19911030	420	49	6.9	329	37	13	46	9.1		167	3.34	203.7	43	49	0.8	0	0	0	0.8	36	1	2	5.29	5.66	-3.53
ECRESM01	19911105	425	67	7.8	374	41	15	67	10		187	3.74	228.1	55	53	0.8	0	0	0	0.4	41	1	2.6	6.51	6.51	-0.06
ECRESM01	19911113	433	62	7.4	371	38	15	61	9.3		171	3.42	208.6	51	41	0.4	0	0	0	0.5	36	1	2.2	6.06	5.81	2.25
ECRESM01	19911120	440	49	7.4	345	38	15	64	10.1		186	3.72	226.9	55	50	0.4	0	0	0	0.4	36	1	1	6.23	6.37	-1.13
ECRESM01	19911127	447	35	8	289	36	16	43	6		156	3.12	190.3	48	43	0.3	0	0	0	0.6	36	1	0.9	5.41	5.42	-0.13
ECRESM01	19911204	454	47	7.7	292	30	11	56	7.3		152	3.04	185.4	39	61	0.8	0	0	0	0.4	25	1	1.2	5.17	5.50	-3.06
ECRESM01	19911211	461	50	7.7	340	29	14	53	9.5		158	3.16	192.8	45	53	0.5	0	0	0	0.4	30	1	1.1	5.20	5.60	-3.87
ECRESM01	19911218	468	60	7.8	401	54	19	56	9.3		149	2.98	181.8	45	97	0.7	0	0	0	1.5	36	1	1.1	6.99	6.36	4.67
ECRESM01	19911224	474	52	8	340	40	21	47	8.1		161	3.22	196.4	43	79	0.7	0	0	0	1.8	35	1	0.9	6.03	6.17	-1.15
ECRESM01	19920101	481	56	7.8	415	43	20	47	8.7		174	3.48	212.3	49	82	0.7	0	0	0	1.4	40	1	1.7	6.06	6.27	-1.64
ECRESM01	19920108	488	46	7.9	306	32	14	41	8.4		139	2.78	169.6	41	62	0.3	0	0	0	1.1	34	1	1.2	4.80	5.30	-4.91
ECRESM01	19920115	495	51	7.9	222	36	25	39	8.2		126	2.52	153 7	48	66	0.8	0	0	0	1.9	43	1	1.8	5.81	5.76	0.26
ECRESM01	19920122	502	45	8	257	38	16	44	7.4		143	2.86	174.5	33	57	0.3	0	0	0	1.2	27	1	0.8	5.27	5.04	2.27
ECRESM01	19920129	509	45	7.6	247	24	15	65	11.6		148	2.96	180.6	41	59	0.8	0	0	0	2.2	30	1	1.3	5.61	5.46	1.34
ECRESM01	19920205	516	54	8	331	31	13	62	12.8		169	3.38	206.2	46	71	0.7	0	0	0	0.6	36	1	2.7	5.70	6.29	-4.93
ECRESM01	19920212	522	53	8	350	30	14	54	12		173	3.46	211.1	42	54	0.5	0	0	0	0.9	34	1	2.8	5.36	5.90	-4.77
ECRESM01	19920219	529	50	7.2	265	33	17	40	8		143	2.86	174.5	33	57	0.6	0	0	0	0.3	76	1	1.2	5.05	5.05	-0.06
ECRESM01	19920226	536	51	7.9	335	42	16	41	8		164	3.28	200.1	39	67	0.5	0	0	0	1.6	30	1	9	5.62	6.11	-4.16
ECRESM01	19920304	544	54	8.1	268	53	20	45	8.6		173	3.46	211.1	40	54	0.5	0	0	0	1.2	24	1	3	6.53	5.85	5.46
ECRESM01	19920311	551	55	7.7	374	31	13	61	15		165	3.3	201.3	52	58	0.6	0	0	0	1.3	30	1	11	5.71	6.37	-5.50
ECRESM01	19920318	558	47	7.6	321	36	14	44	9.4		157	3.14	191.5	41	50	0.7	0	0	0	0.2	33	1	4.3	5.16	5.51	-3.32
ECRESM01	19920325	565	49	7.3	416	45	7	47	8		106	2.12	129 3	35	81	0.9	0	0	0	1	40	1	2.4	5.13	4.93	1.92
ECRESM01	19920401	571	46	7.3	337	35	16	41	7.4		149	2.98	181.8	39	53	0.8	0	0	0	1.5	42	1	4	5.09	5.38	-2.72
ECRESM01	19920408	578	45	7.3	371	34	16	42	7.4		168	3.36	205	28	54	0.8	0	0	0	1.6	35	1	2.2	5.06	5.41	-3.13
ECRESM01	19920415	585	41	6.4	302	51	6	45	9		157	3.14	191.5	36	50	0.5	0	0	0	0.9	26	1	8	5.28	5.43	-1.35
ECRESM01	19920422	592	45	7.9	318	33	19	46	8		159	3.18	194	33	58	0.5	0	0	0	1.2	28	1	2	5.47	5.43	0.41
ECRESM01	19920429	599	42	7.2	256	47	11	40	8		170	3.4	207.4	33	52	0.5	0	0	0	0.5	28	1	3	5.25	5.54	-2.70
ECRESM01	19920506	606	42	7.2	290	32	15	33	7		150	3	183	24	62	0.7	0	0	0	1.2	24	1	2	4.50	5.09	-6.11
ECRESM01	19920513	613	45	8	331	40	14	35	7		153	3.06	186 7	28	50	0.6	0	0	0	1.2	28	1	1.8	4.90	4.99	-0.87
ECRESM01	19920520	620	49	8.1	310	31	20	40	7	20	141	2.82	172	27	53	0.8	0	0	0	0.1	31	1	1.7	5.17	4.77	3.96
ECRESM01	19920527	627	41	7.5	266	43	19	26	7		143	2.86	174.5	31	49	0.5	0	0	0	0.9	23	1	1.1	5.07	4.83	2.47
ECRESM01	19920603	633	56	7.6	404	47	21	53	9.4		187	3.74	228.1	45	69	0.8	0	0	0	1.9	29	1	1.2	6.67	6.54	0.96
ECRESM01	19920609	639	70	8.2	490	53	25	62	9.3		161	3.22	196.4	59	65	0.6	0	0	0	1.6	33	1	1.2	6.56	6.76	11.77
ECRESM01	19920617	647	56	8	302	40	21	51	8.6		167	3.34	203.7	39	65	0.7	0	0	0	1.7	26	1	0.8	6.22	5.88	2 83
ECRESM01	19920624	654	56	7.6	434	46	22	58	8 9		178	3 56	217 2	42	67	0.7	0	0	0	0.9	40	1	1.7	6.91	6.24	5.06
ECRESM01	19920701	661	55	8.1	320	31	20	50	8.7		136	2.72	165 9	44	69	0.5	0	0	0	0.3	30	1	1.2	5.66	5.47	1.61
ECRESM01	19920708	668	50	7.4	379	31	21	53	9.2		148	2.96	180 6	49	64	0.7	0	0	0	2.2	28	1	0.9	5.87	5.77	0.83
ECRESM01	19920715	675	62	7.6	318	35	22	46	8.6		155	3.1	189.1	42	62	0.7	0	0	0	0.2	28	1	1.6	5.92	5.87	2.24
ECRESM01	19920722	682	47	6.5	300	36	22	51	8.1		174	3 48	212.3	39	49	0.6	5	0.1	6	0.1	24	1	0.7	6.09	5.85	1.95
ECRESM01	19920729	689	53	7.7	323	38	26	60	9.1		199	3.98	242 8	42	66	0.9	0	0	0	2.7	30	1	1.5	6.93	6.88	1.69
ECRESM01	19920805	695	63	7.2	326	47	21	58	10.5		165	3.3	201 3	57	79	1	0	0	0	2.2	42	1	1.1	6.92	6.87	1.61
ECRESM01	19920812	702	45	8	297	40	27	51	7.7		172	3.44	209.8	40	71	0.9	0	0	0	1.2	28	1	0.4	6.69	6.12	4.40
ECRESM01	19920819	709	54	8	389	49	32	51	8.7		215	4.3	262.3	42	69	0.8	0	0	0	1.6	34	1	0.8	7.57	7.01	3.85
ECRESM01	19920826	716	46	6.4	264	26	24	55	8.6		180	3.6	219.6	27	66	0.4	10	0.2	12	0.1	36	1	0.8	5.89	6.22	-2.68
ECRESM01	19920902	722	54	7.6	380	35	20	42	7.4		187	3.74	228 1	29	62	0.5	0	0	0	1	30	1	0.5	5.46	5.91	-3.89
ECRESM01	19920909	729	50	8.1	327	47	23	47	9		212	4.24	258.6	36	69	0.6	0	0	0	1.7	32	1	0.9	6.57	6.76	-1.56
ECRESM01	19920916	736	56	7.9	339	47	17	53	9.6		162	3.24	197 6	37	66	0.4	0	0	0	0.6	30	1	1.6	6.36	5.74	5.10
ECRESM01	19920923	743	53	7.7	380	44	16	47	10.6		149	2.98	181.8	47	70	0.7	0	0	0	1.3	34	1	1	6.05	5.85	1.69
ECRESM01	19920930	750	56	8	379	40	24	51	10.3		162	3.24	197.6	40	66	0.9	0	0	0	1.9	45	1	0.4	6.51	5.87	5.12
ECRESM01	19921007	757	50	6.7	369	26	21	41	7.3		142	2.84	173.2	34	50	0.6	11	0.22	13.2	0.7	30	1	2	5.15	5.39	-2.23
ECRESM01	19921014	764	61	8.1	342	29	20	46	8.4		164	3.28	200.1	36	56	1	0	0	0	1.5	35	1	0.8	5.45	5.56	-1.01
ECRESM01	19921021	771	56	8.2	340	37	23	55	10.1		175	3.5	213.5	53	60	0.7	0	0	0	0.6	34	1	1.5	6.44	6.34	0.64
ECRESM01	19921028	778	61	7.9	306	40	16	45	6.5		164	3.28	200.1	36	54	1	0	0	0	1	29	1	0.8	5.71	5.51	1.79
ECRESM01	19921104	784	54	7.6	354	45	13	46	8.6		171	3.42	208.6	37	60	1	0	0	0	1.2	36	1	0.7	5.59	5.81	-1.86
ECRESM01	19921111	791	49	8.2	317	34	17	39	6.9		124	2.48	151.3	31	65	0.9	0	0	0	1.3	40	1	0.5	5.02	5.21	-1.80
ECRESM01	19921118	798	60	7.2	360	40	26	61	9.5		186	3.72	226.9	41	75	0.9	0	0	0	1.6	41	1	0.8	7.25	6.54	5.19
ECRESM01	19921125	806	59	7.9	348	42	17	45	8.9		173	3.46	211.1	35	70	1	0	0	0	1.5	42	1	0.9	5.73	6.01	-2.33
ECRESM01	19921202	812	60	8	364	42	24	44	11		186	3.72	226 9	39	71	0.7	0	0	0	0.5	37	1	1.2	6.32	6.38	-0.46
ECRESM01	19921209	819	42	7.4	314	40	13	42	9		141	2.82	172	34	57	0.5	0	0	0	1	24	1	1	5.16	5.04	1.36
ECRESM01	19921216	826	61	7 5	398	45	21	46	7.9		174	3 48	212.3	45	64	0.8	0	0	0	2.9	36	1	0.6	6.32	6.61	-2.26

Table V.1. Continued.

ECRESM01	19921221	831	60	7	400	53	11	40	8		128	2.56	156.2	38	105	2.4	0	0	0	2.9	39	1	1.1	5.55	6.03	-4.11
ECRESM01	19921228	838	59	8.1	386	43	25	47	9		168	3.36	205	37	60	0.9	0	0	0	2.1	28	1	0.4	6.53	5.75	6.41
ECRESM01	19930106	846	56	9.2	355	39	24	48	8.5		166	3.32	202.5	34	66	0.7	0	0	0	3.9	29	1	1	6.19	5.76	3.43
ECRESM01	19930113	853	59	8.3	367	33	23	40	9.2		187	3.48	212.3	31	71	0.7	13	0.26	15.6	0.1	35	1	0.7	5.57	6.41	-7.03
ECRESM01	19930120	860	59	8.2	394	38	20	50	9.2		169	3.38	206.2	37	69	0.5	0	0	0	1.8	36	1	0.1	6.01	5.92	0.75
ECRESM01	19930127	867	49	7.9	318	40	21	42	8.8		145	2.9	176.9	30	70	1	0	0	0	0.5	24	1	0.6	5.77	5.28	4.45
ECRESM01	19930203	873	53	7.9	372	40	15	45	8.8		152	3.04	165.4	29	53	0.4	0	0	0	0.6	76	1	0.7	5.42	5.02	3.84
ECRESM01	19930210	880	56	8.3	378	43	19	47	0.8		171	3.24	197.6	38	69	0.8	9	0.18	10.8	0.6	32	1	1	5.62	6.12	-2.51
ECRESM01	19930217	887	48	7	304	39	17	39	8.7		138	2.76	166.4	24	69	0.9	0	0	0	1.4	36	1	0.9	5.27	4.97	2.90
ECRESM01	19930224	894	58	7.9	356	43	18	41	7.7		143	2.86	174.5	25	75	0.9	0	0	0	4	23	1	1.5	5.66	5.29	3.45
ECRESM01	19930303	903	59	7.9	385	47	19	40	10		152	3.04	165.4	27	70	0.8	0	0	0	2.2	22	1	0.7	5.96	5.35	5.42
ECRESM01	19930310	910	66	7.6	436	46	16	47	8.2		166	3.32	202.5	25	68	0.8	0	0	0	1.3	20	1	0.7	5.92	5.53	3.46
ECRESM01	19930317	917	67	7.6	382	41	14	46	8		164	3.28	200.1	28	66	0.8	0	0	0	1.2	26	1	0.1	5.56	5.50	0.44
ECRESM01	19930324	924	64	7.9	400	47	19	54	8.8		166	3.32	202.5	40	69	0.8	0	0	0	0.9	24	1	2.4	6.54	6.01	4.24
ECRESM01	19930331	931	66	7.7	405	40	15	61	10.9		166	3.32	202.5	46	72	0.4	0	0	0	1.3	25	1	4.9	6.22	6.31	-0.76
ECRESM01	19930407	937	61	8.4	390	43	17	54	8.9		162	3.12	190.3	37	68	0.4	6	0.12	7.2	0.5	26	1	0.6	6.16	5.67	2.52
ECRESM01	19930414	944	64	8.7	412	45	19	54	9.2		173	3.46	211.1	38	82	0.5	0	0	0	0.6	30	1	1.5	6.45	5.91	4.40
ECRESM01	19930421	951	70	8	455	43	16	61	8.9		158	3.16	192.8	44	60	0.4	0	0	0	3.3	34	1	0.6	6.40	5.75	5.35
ECRESM01	19930428	958	59	8.5	379	38	16	51	7.9		150	2.52	153.7	35	65	0.7	24	0.48	28.6	3.5	28	1	0.1	5.69	5.92	-1.96
ECRESM01	19930505	965	68	8.4	449	41	16	50	8.2		152	2.76	166.4	41	56	0.5	14	0.28	16.8	3.3	28	1	1.5	5.80	5.77	0.29
ECRESM01	19930512	972	70	7.5	379	35	16	66	8.8		176	3.52	214.7	45	30	0.8	0	0	0	2.4	33	1	1.3	6.21	5.52	5.66
ECRESM01	19930519	979	48	7.4	337	39	14	49	8.7		181	3.62	220.8	38	40	0.8	0	0	0	1.5	23	1	0.6	5.51	5.60	-0.82
ECRESM01	19930526	986	54	7.5	366	49	14	51	11		193	3.66	235.5	44	55	0.5	0	0	0	0.1	23	1	0.9	6.15	6.30	-1.20
ECRESM01	19930602	992	61	8.5	387	45	17	61	10.5		174	3.14	191.5	47	61	0.7	17	0.34	20.4	1.8	28	1	0.9	6.62	6.51	0.86
ECRESM01	19930609	999	57	8.3	381	44	16	46	7.9		152	2.96	180.6	42	60	0.4	4	0.08	4.8	2.7	34	1	0.7	6.02	5.64	3.28
ECRESM01	19930616	1006	56	7.5	385	40	22	43	11.8		147	2.94	179.3	39	66	0.8	0	0	0	2.4	32	1	0.2	6.03	5.49	4.66
ECRESM01	19930623	1013	50	7.7	326	37	16	48	8.8		177	3.54	215.9	42	59	0.8	0	0	0	1.5	33	1	0.7	5.44	6.03	-5.15
ECRESM01	19930630	1020	53	7.6	355	34	16	40	9.4		154	3.08	187.9	51	53	0.8	0	0	0	2.3	24	1	0.1	5.21	5.69	-4.40
ECRESM01	19930707	1027	49	7.1	314	37	17	51	8 9		159	3.16	194	43	64	0.8	0	0	0	2.5	28	1	0.1	5.75	5.80	-0.46
ECRESM01	19930714	1034	52	8.1	347	34	16	48	8.5		157	3.14	191.5	50	46	0.8	0	0	0	2.5	32	1	1	5.37	5.61	-2.16
ECRESM01	19930721	1041	45	7.6	306	38	18	47	8.7		135	2.7	164.7	49	42	0.8	0	0	0	1.6	28	1	1.2	5.70	5.06	5.93
ECRESM01	19930728	1048	44	7.4	293	39	18	41	8.3	14.4	145	2.9	176.9	51	65	0.7	0	0	0	2.4	30	1	1	5.46	5.80	-2.64
ECRESM01	19930804	1054	47	7.6	315	42	17	39	8.7	27	162	3.24	197.6	52	56	0.8	0	0	0	2.3	30	1	0.6	5.47	6.00	-4.64
ECRESM01	19930811	1061	47	7.6	303	46	16	43	9.5	38	155	3.1	189.1	54	60	0.7	0	0	0	2.2	30	1	0.2	5.76	5.95	-1.45
ECRESM01	19930818	1068	47	8	305	38	17	42	11.3	25	135	2.7	164.7	47	54	0.5	0	0	0	1.8	32	1	0.2	5.47	5.21	2.39
ECRESM01	19930825	1075	37	8.8	334	37	18	37	11.8	38	164	3.2	195.2	39	60	0.7	4	0.08	4.8	1.6	25	1	0.6	5.29	5.79	-4.50
ECRESM01	19930901	1081	43	8	284	33	16	29	8.6	12	136	2.72	165.9	34	45	0.8	0	0	0	1.6	23	1	1.2	4.45	4.71	-2.86
ECRESM01	19930908	1088	42	7.8	281	33	16	31	8.8	15	157	3.14	191.5	36	41	0.5	0	0	0	1.1	24	1	0.6	4.54	5.07	-5.52
ECRESM01	19930915	1095	45	7.6	275	36	19	40	7.9	16	155	3.1	189.1	39	55	0.8	0	0	0	1.5	31	1	0.6	5.36	5.44	-0.73
ECRESM01	19930922	1102	53	8.3	347	41	18	50	10	21	161	3.54	215.9	51	59	0.8	4	0.08	4.8	1.2	40	1	1	6.01	6.46	-3.58
ECRESM01	19930929	1109	45	7.6	326	45	19	41	8	22	171	3.42	208.6	50	60	0.8	0	0	0	1.5	30	1	0.6	5.65	6.16	-2.56
ECRESM01	19931006	1116	39	7.5	380	33	19	34	7.1	11.4	115	2.3	140.3	53	64	0.7	0	0	0	6.3	60	6	1.2	5.20	5.30	-0.95
ECRESM01	19931013	1123	52	7.4	348	33	21	23	7.9	16.4	89	1.78	108.6	34	61	1	0	0	0	11.5	61	10	2.4	5.13	4.32	8.56
ECRESM01	19931021	1131	92	7.6	592	57	22	66	13.9	16	104	2.08	126.9	55	106	3.7	0	0	0	29	52	16	1.7	6.86	6.55	15.07
ECRESM01	19931027	1137	52	7.3	341	47	16	32	8.1	16.6	109	2.18	133	24	70	1	0	0	0	9	42	1	1.6	5.46	4.57	9.06
ECRESM01	19931103	1143	59	7.9	386	43	20	37	8	16.4	164	3.28	200.1	32	60	0.9	0	0	0	3.4	30	1	0.6	5.66	5.56	0.91
ECRESM01	19931110	1150	64	7	411	52	27	42	8.4	11.2	173	3.46	211.1	39	60	1	0	0	0	6.4	36	1	0.7	6.86	6.40	3.46
ECRESM01	19931117	1157	60	8.5	391	45	18	44	7.1	15	161	3.62	220.8	39	70	1	0	0	0	2.9	32	1	1.1	5.88	6.31	-3.55
ECRESM01	19931124	1164	28	8.4	173	23	7	11	4.5	25	80	1.6	97.6	8	20	0.8	0	0	0	3.2	49	1	0.4	2.37	2.34	0.75
ECRESM01	19931201	1171	39	7.4	255	33	18	21	5.5	17	119	2.38	145.2	17	41	0.9	0	0	0	1.4	37	1	1	4.24	3.61	5.26
ECRESM01	19931208	1178	56	7.3	354	35	20	32	7.6	24	173	3.46	211.1	25	56	0.9	0	0	0	4.3	30	1	1.6	5.03	5.50	-4.40
ECRESM01	19931217	1187	53	7	326	42	18	35	8	15.4	154	3.08	187.9	32	70	1	0	0	0	1.6	33	6	1	5.64	5.55	0.76
ECRESM01	19931222	1192	50	7.9	335	45	15	49	8.7	14.8	163	3.26	198.9	35	46	0.8	0	0	0	2	24	1	5	5.84	5.44	3.56
ECRESM01	19931229	1199	36	7.8	229	27	13	18	5.2	11.5	86	1.72	104.9	9	40	0.5	0	0	0	9.6	27	4	2.2	3.47	3.06	6.25
ECRESM01	19940105	1205	83	7.8	292	42	17	31	5.5	17.2	163	3.66	223.3	30	40	0.8	0	0	0	2	33	1	0.85	5.04	5.44	-3.62
ECRESM01	19940112	1212	32	6.4	214	23	15	17	4 2	15	95	1.9	115.9	8	30	0.6	0	0	0	4.5	30	1	0.6	3.26	2.87	6.66
ECRESM01	19940119	1219	58	7.7	386	42	18	31	8.9	13.2	182	3.64	222	23	57	1	0	0	0	3.3	57	1	0.5	5.21	5.80	-3.59
ECRESM01	19940126	1226	46	7.7	294	39	20	26	3	16	161	3.22	196.4	12	42	0.5	0	0	0	2.9	25	1	0.7	4.85	4.53	3.49
ECRESM01	19940202	1232	36.5	7.5	262	29	17	17	4	17	124	2.48	151.3	12	39	1.6	0	0	0	2	35	1	1.2	3.74	3.76	-0.55
ECRESM01	19940209	1239	40	7.6	365	30	22	23	4 6	16.6	162	3.24	197.6	16	42	0.6	0	0	0	2	31	1	1	4.48	4.06	-1.96

Table V.1. Continued.

ECRESM01	19940216	1246	36	7.7	389	44	19	36	6.6	13	159	3.16	194	41	71	0.9						0	0	0	2.7	41	1		1.3	5.55	5.95	-3.41
ECRESM01	19940223	1253	35	7.6	229	37	11	17	5.5	14	103	2.06	125.7	15	53	1						0	0	0	2.3	16	1		1.9	3.69	3.74	-0.66
ECRESM01	19940302	1262	55	7.6	305	40	20	41	6.1	16	189	3.78	230.6	36	61	0.9						0	0	0	2.5	31	1		0.75	5.69	6.16	-4.12
ECRESM01	19940309	1269	47	7.7	314	37	17	36	5.7	16	169	3.38	206.2	26	51	0.6						0	0	0	0.1	22	1		1.2	5.01	5.26	-2.37
ECRESM01	19940316	1276	47	7.7	351	31	18	43	7.7	12.6	171	3.42	208.6	34	54	1						0	0	0	0.5	21	1		0.5	5.15	5.56	-3.99
ECRESM01	19940323	1283	56	8.3	375	31	22	48	10.3	13	191	3.5	213.5	42	54	0.2						16	0.32	19.2	2.4	28	1		0.4	5.76	6.51	-6.06
ECRESM01	19940330	1290	52	7.6	368	32	17	76	8.1	12.7	203	4.06	247.7	32	56	0.7						0	0	0	1.8	20	1		1.1	6.65	6.23	3.28
ECRESM01	19940406	1296	61	8.3	366	40	19	34	7.7	12.6	164	3.04	185.4	32	58	1						12	0.24	14.4	0.1	35	1		1.9	5.29	5.74	-4.10
ECRESM01	19940413	1303	41	7.5	262	31	13	26	5.8	9.7	154	3.06	187.9	24	38	0.5						0	0	0	0.2	29	1		0.2	4.04	4.56	-6.32
ECRESM01	19940420	1310	52	7.6	341	35	20	44	9.4	13.5	171	3.42	208.6	35	46	0.6						0	0	0	2.4	37	1		0.5	5.60	5.45	1.37
ECRESM01	19940427	1317	54	8.3	387	20	15	52	9.5	13.2	175	3.16	194	38	52	0.5						16	0.32	19.2	1.9	38	1		0.5	4.79	5.99	-11.11
ECRESM01	19940504	1314	46	8.1	308	26	13	48	8.7	13	159	3.18	194	35	51	0.6						0	0	0	1.8	24	1		0.4	4.83	5.30	-4.59
ECRESM01	19940511	1321	56	8.3	388	38	21	52	9.6	19.4	197	3.64	222	41	53	0.6						15	0.3	18	0.2	33	1		0.1	6.09	6.54	-3.56
ECRESM01	19940518	1328	41	8.5	270	38	18	48	6.4	16.9	195	3.6	219.6	35	53	0.9						15	0.3	18	2.8	30	1		0.9	5.74	6.41	-5.56
ECRESM01	19940525	1335	64	8.2	423	55	20	51	11.9	16.2	193	3.86	235.5	40	70	0.6						0	0	0	3.2	42	1		0.3	6.97	6.55	3.11
ECRESM01	19940601	1341	49	8.6	322	38	20	48	7.6	12	137	2.54	154.9	35	66	1.5		0.2	0.1			10	0.2	12	2.5	28	1		0.1	5.89	5.42	4.16
ECRESM01	19940608	1348	67	8.5	322	48	17	56	9	14.2	174	3.04	185.4	37	80	1		0.5	0.1			22	0.44	26.4	3.1	30	1		0.3	6.55	6.74	-1.46
ECRESM01	19940615	1355	46	8.5	310	40	19	44	7.6	14.7	159	2.98	181.8	37	70	0.8		0.3	0.1			10	0.2	12	1.8	29	1		0.6	5.74	5.97	-1.94
ECRESM01	19940622	1362	45	8.7	292	42	17	50	8.1	13.7	165	2 9	176.9	38	69	0.7		0.2				20	0.4	24	3.6	20	1		0.1	5.94	6.31	-2.96
ECRESM01	19940629	1369	51	8.8	342	33	18	48	9.6	11.7	200	3.56	217.2	37	53	0.4		0.2				22	0.44	26.4	2.5	33	1		0.6	5.53	6.67	-9.39
ECRESM01	19940706	1376	51	8.7	342	33	14	51	9.6	10.9	171	3	183	33	63	0.2		0.3				21	0.42	25.2	1.8	34	1		0.7	5.33	6.14	-7.05
ECRESM01	19940713	1383	56	8.5	360	26	18	51	11.1	6.6	206	3.06	187.9	43	41	0.6		0.2				52	1.04	62.4	1.9	40	1		0.3	5.45	7.30	-14.52
ECRESM01	19940720	1390	62	8.6	331	30	14	39	7.2	10.9	149	2.8	170.8	33	43	0.7		0.2				9	0.18	10.8	2.3	34	1		0.2	4.60	5.07	-4.86
ECRESM01	19940727	1397	43	9.2	345	29	17	46	9.7	11.3	159	2.8	170.8	35	56	0.7		0.1				19	0.38	22.8	2.9	16	1		0.7	5.16	5.62	-6.04
ECRESM01	19940803	1403	46	8.8	304	33	16	46	8.2	9.5	169	3.26	196.9	36	48	0.5		0.1				6	0.12	7.2	0.1	36	1		0.4	5.40	5.55	-1.42
ECRESM01	19940810	1410	51	8.5	323	35	16	50	9.8	11	162	3.04	185.4	39	53	0.6		0.1				10	0.2	12	1.9	36	1		1.1	5.55	5.74	-1.69
ECRESM01	19940817	1417	50	8.9	321	35	18	49	9	11	165	3.04	185.4	38	59	0.4		0.1	0.1			13	0.26	15.6	1.6	36	1		0.7	5.65	5.93	-2.37
ECRESM01	19940824	1424	46	8.4	301	26	15	46	9.3	10	157	3.06	186.7	32	42	0.4						4	0.08	4.8	2.6	32	1		0.4	4.83	5.07	-2.49
ECRESM01	19940831	1431	45	7.4	293	30	15	43	6.2	11.4	142	2.84	173.2	32	40	0.3		0.1				0	0	0	2	34	1		0.7	4.67	4.64	2.39
ECRESM01	19940907	1437	49	8.7	326	30	15	45	12.5	12.2	173	3.24	197.6	35	46	0.9		0.1				11	0.22	13.2	1.6	44	1		0.5	5.07	5.71	-5.97
ECRESM01	19940914	1444	37	8.2	247	28	15	33	6.9	10	132	2.64	161	34	33	0.4		0.1	0.1			0	0	0	1.1	26	1		0.3	4.31	4.33	-0.30
ECRESM01	19940921	1451	37	8.4	251	25	12	26	6.5	8.6	116	2.26	139.1	30	37	0.6		0.1				2	0.04	2.4	1.1	31	1		0.4	3.68	4.05	-4.77
ECRESM01	19940928	1456	56	8.5	341	26	16	48	7	10.2	168	2.9	176.9	40	47	0.4		0.1				23	0.46	27.6	2.1	44	1		0.5	5.04	6.00	-6.85
ECRESM01	19941005	1465	56	8.3	367	33	16	43	10.9	13	183	3.46	211.1	43	36	0.4						10	0.2	12	1.7	43	1		0.1	5.17	5.91	-6.74
ECRESM01	19941012	1472	50	7.9	320	35	15	36	8.3	11.4	146	2.92	178.1	41	43	0.6		0.6	0.1			0	0	0	1.3	33	1		0.3	4.85	5.03	-1.85
ECRESM01	19941019	1479	44	8	326	33	17	36	8.5	11.2	137	2.74	167.1	38	52	0.7		0.1				0	0	0	1.5	20	1		0.5	4.96	4.97	0.06
ECRESM01	19941026	1486	56	8.8	364	36	25	40	10.4	12.6	184	3.06	187.9	40	76	0.9						30	0.6	36	0.1	28	1		0.1	5.91	7.06	-8.99
ECRESM01	19941103	1493	57	7.6	368	40	20	42	9.7	13.3	169	3.38	206.2	26	57	0.6						0	0	0	1.5	41	1		0.6	5.77	5.44	2.95
ECRESM01	19941124	1514	52	7.6	349	38	21	35	9.2	11.2	160	3.2	195.2	39	46	0.9		2.4				0	0	0	0.6	25	1		0.6	5.57	5.33	2.14
ECRESM01	19941124	1514	52	7.6	349	38	21	35	9.2	11.2	160	3.2	195.2	39	46	0.9		2.4				0	0	0	0.6	25	1		0.6	5.57	5.33	2.14
Mean			57.82	7.616	393.6	42.39	16.69	56.26	10.31	15.12	161.7	3.168	194.5	45.85	64.26	0.662	ERR	0.405	0.1	ERR	ERR	2.317	0.046	2.76	2.14	35.47	1.497	ERR	1.727	6.36	6.452	-0.622
Std.Dev.			24.61	0.462	191.5	19.54	4.596	38 45	7.143	5.59	30.9	0.61	37.2	26.79	99.06	0.335	ERR	0.677	0	ERR	ERR	6.381	0.126	7.657	2.723	11.96	1.644	ERR	1.631	2.929	2.917	6.363
Number			216	216	216	213	213	216	213	70	216	216	216	216	216	216	0	21	6	0	0	216	216	216	216	217	217	0	216	216	216	216

Table V.2. Surface water monitoring site RESM10 data set.

Loc #	Samp.Dat	EC mS/m	pH	TDS	Ca mg/l	Mg mg/l	Na mg/l	K mg/l	Si mg/l	M.Alk meq.C	HCO3 meq.H	HCO3 mg/l	Cl mg/l	SO4 mg/l	F mg/l	B mg/l	Fe mg/l	Mn mg/l	Zn mg/l	Cu mg/l	P.Alk meq.C	CO3 meq.H	CO3 mg/l	N mg/l	COD	NH4 mg/l	Pheno mg/l	PO4 mg/l	Total Cation	Total Anion	Ion %E
ECRESM10	19900919	34	8.5	222			22			133	2.14	130.5	21	90	0 7						26	0.52	31.2	0.2	24	2		0.2	1.07	5.69	-68.40
ECRESM10	19900926	67	8.6	266			38			172	3.18	194	31	100	0.4						13	0.28	16.8		31	2			1.76	6.66	-58.20
ECRESM10	19901003	45	8.4	306			30			176	2.98	181.8	44	1	1						27	0.54	32.4	2	28	2		0.6	1.42	6.42	-58.60
ECRESM10	19901010	71	8.2	490			61			170	3.4	207.4	46	66	1.1						0	0	0	1.5	66	2		1.1	2.76	6.29	-38.91
ECRESM10	19901017	118	8.3	1013			63			220	4.06	247.7	45	57	0.5						17	0.34	20.4	61	66	2		1.2	2.65	8.57	-50.05
ECRESM10	19901101	42	8	235	30	21	27	5.2		164	3.28	200.1	19	24	0.4						0	0	0	2.9	34	2		1.4	4.64	4.43	2.39
ECRESM10	19901108	190	7.7	1330	160	104	110	11.4		230	4.6	280.6	68	48	0.7						0	0	0	1.6	70	2		5.1	21.73	7.74	47.47
ECRESM10	19901114	58	8.1	397	33	33	40	5.2		162	3.24	197.6	31	68	0.4						0	0	0	6.4	35	2		0.7	6.35	6.05	2.38
ECRESM10	19901121	36	7.7	267	29	16	21	3.6		63	1.26	76.88	23	60	0.5						0	0	0	4.5	24	2		0.5	4.04	3.69	4.60
ECRESM10	19901128	43	7.8	276	24	35	22	5.3		117	2.34	142.7	22	76	0.6						0	0	0	6.1	30	2		1	5.28	4.70	5.76
ECRESM10	19901205	170	7.7	1600	164	96	64	7.7		115	2.3	140.3	52	118	0.6						0	0	0	120	44	2		1.4	19.17	8.23	39.91
ECRESM10	19901212	40	7.2	361	22	22	12	7.6		68	1.36	82.98	11	60	0 4						0	0	0	12.5	66	2		4	3.74	3.27	6.67
ECRESM10	19901219	118	7.8	1064	92	52	65	9.6		209	4.18	255	46	72	0.6						0	0	0	56	46	4		4	12.16	8.02	20.53
ECRESM10	19901226	90	7.8	626	48	27	59	7		219	4.38	267.2	38	130	0.5						0	0	0	25	38	2		0.9	7.37	8.62	-7.77
ECRESM10	19910102	74	8	606	26	52	46	2.7		230	4.6	280.6	32	116	0.6						0	0	0	2.2	31	2		1.1	7.86	8.03	-1.09
ECRESM10	19910109	68	7.4	528	27	51	41	12.5		86	1.72	104.9	29	116	0.6						0	0	0	14	62	6		16.2	7.96	5.72	16.48
ECRESM10	19910116	52	8	448	36	33	40	7		162	3.24	197.6	26	70	0.5						0	0	0	4.5	26	2		2	6.54	5.59	7.83
ECRESM10	19910123	65	7.5	467	50	37	60	10.7		143	2.86	174.5	37	114	0.6						0	0	0	17	34	2		13	8.53	6.99	9.92
ECRESM10	19910130	80	7.4	694	55	37	49	7		102	2.04	124.4	24	93	0.4						0	0	0	30.5	44	2		6	8.21	5.36	21.05
ECRESM10	19910206	70	7.8	587	61	37	49	6.8		206	4.12	251.3	30	40	0.7						0	0	0	40	36	2		7.6	8.50	6.73	11.67
ECRESM10	19910213	60	8.2	462	56	33	91	7.6		138	2.76	168.4	26	115	0.5						0	0	0	10	42	2		7	9.77	6.35	21.22
ECRESM10	19910220	45	7.5	364	33	22	33	4.5		123	2.46	150.1	16	160	0.5						0	0	0	6	45	2		7.4	5.12	6.63	-12.87
ECRESM10	19910227	61	8	448	46	32	45	5.8		190	3.8	231.8	29	90	0.5						0	0	0	1.8	31	2		9.3	7.24	6.84	2.90
ECRESM10	19910306	46	8.3	316	42	22	33	5.1		140	2.42	147.6	22	70	0.3						19	0.38	22.8	0.2	20	2		2.5	5.58	5.36	2.06
ECRESM10	19910313	53	7.9	361	57	26	44	5.3		209	4.18	255	27	55	0.6						0	0	0	1	20	2		0.2	7.14	6.14	7.56
ECRESM10	19910319	83	7.7	630	74	40	87	16		205	4.1	250.1	35	115	0 6						0	0	0	18.3	32	2		8.3	10.42	8.07	12.70
ECRESM10	19910326	125	7.8	887	75	56	71	16		164	3.28	200.1	51	135	0.7						0	0	0	79	29	34		60	13.79	11.37	9.62
ECRESM10	19910403	90	7.8	566	70	40	50	10		176	3.52	214.7	35	100	0.3						0	0	0	32	24	6		40	9.66	8.36	7.07
ECRESM10	19910410	57	8	368	53	26	40	5.4		191	3.82	233	39	165	0.5						0	0	0	3.4	26	2		3.4	6.94	8.96	-12.72
ECRESM10	19910417	56	8	389	53	23	44	4.8		187	3.74	228.1	37	120	0 5						0	0	0	1.3	25	1.3		1.3	6.65	7.37	-5.16
ECRESM10	19910424	66	8.4	450	57	29	46	5		212	4.16	253.8	47	70	0.5						4	0.08	4.8	1.9	30	2		6.3	7.56	7.36	1.34
ECRESM10	19910502	54	8	349	54	27	51	3.5		200	4	244	39	70	0.5						0	0	0	2	26	17		1	8.17	6.65	10.27
ECRESM10	19910509	56	8	395	51	27	45	53		228	4.56	278.2	35	50	0.6						0	0	0	1	32	2		1.4	8.19	6.68	10.16
ECRESM10	19910515	65	8	392	48	32	49	4.9		244	4.88	297.7	40	75	0.5						0	0	0	1.2	41	1		0.9	7.34	7.64	-2.02
ECRESM10	19910522	44	8	269	32	21	34	5		154	3.08	187.9	31	65	0.3						0	0	0	0.8	17	1		0.8	4.99	5.35	-3.56
ECRESM10	19910529	48	8.4	350	48	27	39	5		185	3.62	220.8	32	105	0.4						4	0.08	4.8	0.9	22	2		0.2	6.55	6.91	-2.66
ECRESM10	19910605	28	8.2	190	19	12	25	7		116	2.32	141.5	21	60	0.4						0	0	0	0.2	23	2		0.5	3.31	4.20	-11.82
ECRESM10	19910613	33	8	266	27	16	27	3		132	2.64	161	20	45	0.3						0	0	0	0.5	14	1		0.8	3.97	4.18	-2.61
ECRESM10	19910619	53	8	368	41	27	42	6		192	3.84	234.2	37	65	0.4						0	0	0	0.8	26	2		0.7	6.36	6.29	0.53
ECRESM10	19910626	44	8.5	305	29	23	32	5		158	3.06	186.7	28	50	0.4						6	0.1	6	1.1	20	2		0.6	4.97	5.15	-1.75
ECRESM10	19910703	50	8.2	361	41	30	36	4		203	4.06	247.7	35	57	0.5						0	0	0	0.7	19	2		0.6	6.29	6.29	0.03
ECRESM10	19910710	48	8.3	296	33	22	32	3.6		171	3.34	203.7	26	47	0.4						4	0.08	4.8	0.5	16	2		0.4	5.06	5.31	-2.43
ECRESM10	19910717	40	8.2	340	27	23	25	6		144	2.88	175.7	28	42	0.4						0	0	0	1	30	2		1	4.59	4.61	-0.22
ECRESM10	19910724	37	8	219	36	19	26	3		138	2.76	168.4	24	42	0.4						0	0	0	0.7	34	2		0.4	4.68	4.36	3.57
ECRESM10	19910731	42	8.2	246	57	22	43	5		174	3.48	212.3	26	35	0.4						0	0	0	0.2	26	2		0.2	6.76	4.97	15.27
ECRESM10	19910807	47	8.3	360	19	18	42	4		211	3.48	212.3	23	37	0 3						37	0.74	44.4	0.2	16	2		0.5	4.30	6.41	-19.67
ECRESM10	19910814	39	8.1	291	97	21	31	5		164	3.28	200.1	26	51	0.5						0	0	0	0.7	20	2		0.3	8.18	5.18	22.33
ECRESM10	19910821	32	8.4	166	23	14	22	4		102	1.96	119.6	24	47	0.4						4	0.08	4.8	0.2	26	2		0.2	3.47	3.81	-4.61
ECRESM10	19910828	32	8.3	222	27	16	26	6		94	1.68	102.5	21	45	0.4						10	0.2	12	0.3	19	2		0.4	4.06	3.65	5.34
ECRESM10	19910904	40	8.2	260	34	24	35	5		169	3.38	206.2	22	41	0.5						0	0	0	0.4	22	2		0.3	5.43	4.90	5.20
ECRESM10	19910911	51	8.1	305	36	29	41	7		176	3.52	214.7	34	49	0 6						0	0	0	2.9	28	2		3.7	6.28	5.69	4.71
ECRESM10	19910918	41	8.3	264	29	17	30	4		133	2.58	157.4	25	44	0.8						4	0.08	4.8	0.2	30	2		0.9	4.36	4.42	-0.68
ECRESM10	19910925	67	8.8	443	66	32	35	7		29	0.58	35.38	21	310	0.4						0	0	0	0.2	19	2		0.8	7.84	7.67	1.09
ECRESM10	19911002	34	8.1	222	29	16	23	3		133	2.66	162.3	20	29	0.3						0	0	0	0.2	34	2		0.5	4.12	3.86	3.19
ECRESM10	19911009	33	8.4	231	29	15	26	4		127	2.38	145.2	19	50	0.4						8	0.16	9.6	0.2	24	2		0.4	4.03	4.31	-3.45
ECRESM10	19911016	32	7.8	230	33	19	17	4.4		134	2.68	163.5	14	36	0.4						0	0	0	0.2	36	2		0.4	4.17	3.86	3.89
ECRESM10	19911023	43	8.6	315	36	17	46	4.3		184	3.38	206.2	26	57	0.5						15	0.3	18	0.2	28	2		1.1	5.52	6.02	-4.36
ECRESM10	19911030	36	8.3	253	33	20	24	3.9		161	3.1	189.1	16	36	0.4						6	0.12	7.2	0.2	26	2		0.2	4.56	4.63	-0.67

Table V.2. Continued.

ECRESM10	19911105	38	8.2	246	33	14	30	3		147	2.94	179.3	17	53	0.5	0	0	0	0.3	24	1	0.5	4.24	4.57	-3.79
ECRESM10	19911113	30	8.8	238	30	15	22	3		113	2.02	123.2	24	35	0 4	12	0.24	14.4	0.3	23	1	0.2	3.82	3.94	-1.51
ECRESM10	19911120	36	7.8	253	23	15	33	4.6		109	2.16	133	30	72	0.4	0	0	0	0.2	30	1	0.2	3.99	4.56	-6.61
ECRESM10	19911127	28	7.9	156	31	17	22	4.2		124	2.48	151.3	21	32	0.3	0	0	0	0.2	34	1	0.5	4.07	3.77	3.74
ECRESM10	19911204	39	8.2	106	27	23	33	3		96	1.92	117.1	18	120	0.5	0	0	0	0.2	22	1	0.2	4.61	4.98	-1.56
ECRESM10	19911211	34	8.1	236	21	13	32	2.4		124	2.48	151.3	18	40	0.4	0	0	0	0.2	24	1	0.4	3.63	3.86	-3.06
ECRESM10	19911218	41	8.1	274	41	22	28	4.1		145	2.9	176.9	18	55	0.4	0	0	0	0.2	22	1	4	5.23	4.70	5.35
ECRESM10	19911224	40	8.4	258	34	20	28	3.5		141	2.6	158.6	23	59	0.5	11	0.22	13.2	0.4	18	1	0.7	4.62	4.97	-3.66
ECRESM10	19920101	39	8.2	317	33	18	27	2.8		143	2.66	174.5	22	52	0.5	0	0	0	0.2	21	1	0.2	4.28	4.60	-3.76
ECRESM10	19920108	63	7.9	450	54	27	45	5.7		160	3.2	195.2	39	153	0.5	0	0	0	0.3	30	1	1	7.07	7.55	-3.23
ECRESM10	19920115	73	8	352	62	29	43	5.3		240	4.8	292.8	32	76	0.2	0	0	0	0.8	24	1	1.1	7.54	7.34	1.36
ECRESM10	19920122	49	7.9	213	43	17	40	5		174	3.48	212.3	27	76	0.5	0	0	0	0.5	26	1	2.3	5.47	5.93	-4.06
ECRESM10	19920129	56	8.1	345	48	20	43	6.6		182	3.64	222	43	108	1	0	0	0	2.5	34	1	0.2	6.14	7.20	-7.94
ECRESM10	19920205	64	8.3	43	45	26	69	7.2		248	4.54	276.9	47	100	1.2	19	0.38	22.8	0.2	36	1	3.7	7.63	6.89	-7.65
ECRESM10	19920212	60	7.7	420	55	27	44	6		208	4.16	253.6	32	110	0.6	0	0	0	0.2	30	1	0.1	7.09	7.40	-2.15
ECRESM10	19920219	74	8.8	516	60	29	44	6		85	1.7	103.7	29	100	7	0	0	0	33	60	1	1.5	7.50	5.55	14.96
ECRESM10	19920226	70	7.8	434	70	30	43	5		246	4.92	300.1	31	65	0.6	0	0	0	0.4	20	1	6	8.01	7.79	1.42
ECRESM10	19920304	67	8.2	399	73	27	70	5.4		332	6.64	405	45	88	0.7	0	0	0	0.8	25	1	1.4	9.10	9.63	-3.84
ECRESM10	19920311	70	7.8	334	67	26	67	7.3		286	5.72	348.9	47	39	0.7	0	0	0	0.2	44	1	5.1	8.60	8.06	4.43
ECRESM10	19920318	63	7.9	226	52	24	55	6.4		273	5.46	333.1	47	26	0.6	0	0	0	0.2	52	1	7.5	7.23	7.60	-2.46
ECRESM10	19920325	44	7.7	359	36	24	60	6.1		146	2.92	178.1	51	88	0.5	0	0	0	0.5	38	1	1.7	6.69	6.28	3.19
ECRESM10	19920401	66	7.6	473	52	21	51	6.2		265	5.3	323.3	39	46	0.6	0	0	0	0.6	36	1	6	6.81	7.63	-5.70
ECRESM10	19920408	42	7.8	312	39	31	42	7		229	4.58	279.4	22	44	0.7	0	0	0	0.7	38	1	1.2	8.56	8.20	2.80
ECRESM10	19920415	78	7.8	452	75	22	58	5		316	6.32	385.5	37	47	0.7	0	0	0	0.5	18	1	6	6.17	6.64	-2.77
ECRESM10	19920422	42	8	308	30	19	51	6		168	3.36	205	24	55	0.4	0	0	0	1	24	1	0.2	5.49	5.22	2.45
ECRESM10	19920429	41	7.8	276	45	11	31	6		170	3.4	207.4	24	58	0.5	0	0	0	0.2	24	1	0.3	4.71	5.32	-6.13
ECRESM10	19920506	48	7.8	301	42	18	36	6		189	3.78	230.6	26	60	0.7	0	0	0	0.8	24	1	0.1	5.35	5.81	-4.14
ECRESM10	19920513	53	8.2	367	46	21	35	8	0	181	3.62	220.8	24	57	0.7	0	0	0	1.4	23	1	0.6	5.75	5.56	1.71
ECRESM10	19920520	50	8.5	317	31	24	34	6.2		174	3.38	206.2	25	55	0.7	5	0.1	6	1.1	26	1	0.6	5.21	5.51	-2.75
ECRESM10	19920527	58	8	398	60	41	40	4.4		293	5.86	357.5	35	54	0.6	0	0	0	0.4	23	1	0.9	6.28	6.05	1.40
ECRESM10	19920603	66	8.1	476	67	37	59	5		356	7.12	434.3	44	88	0.6	0	0	0	0.6	21	1	3	9.14	9.91	-4.06
ECRESM10	19920609	49	8.3	359	45	26	42	6.4		247	4.76	291.6	30	88	0.6	8	0.16	9.6	0.5	29	1	0.6	8.60	7.43	-5.95
ECRESM10	19920617	49	8.2	296	40	22	38	6.5		191	3.82	233	25	55	0.6	0	0	0	0.4	40	1	0.9	5.68	5.74	-0.48
ECRESM10	19920624	50	8.3	255	44	24	37	6.6		182	3.6	219.6	24	55	0.7	2	0.04	2.4	0.3	35	1	0.2	6.00	5.55	3.94
ECRESM10	19920701	63	8.1	374	49	37	37	6		253	5.06	308.7	29	71	0.5	0	0	0	1.1	30	1	0.5	7.31	7.41	-0.73
ECRESM10	19920708	50	8.1	336	35	27	37	7.2		176	3.52	214.7	32	56	0.5	0	0	0	1	28	1	0.4	5.62	5.64	1.52
ECRESM10	19920715	47	8	312	36	27	37	6.7		165	3.3	201.3	34	50	0.5	0	0	0	0.1	22	0.1	0.1	5.90	5.33	5.11
ECRESM10	19920722	47	8.5	268	45	30	40	7		224	4.38	267.2	31	58	0.6	5	0.1	6	0.1	24	1	0.1	8.69	8.70	-0.07
ECRESM10	19920729	48	8.2	315	40	32	39	6.7		217	4.34	264.7	28	57	0.6	0	0	0	0.3	23	1	0.2	6.55	6.37	1.42
ECRESM10	19920805	59	8.1	384	50	21	41	7.7		207	4.14	252.5	40	72	0.5	0	0	0	1.7	35	1	0.6	6.28	6.65	-4.48
ECRESM10	19920812	43	8.4	263	43	25	34	6.2		162	3.34	203.7	29	61	0 4	15	0.3	18	0.4	26	1	0.6	5.90	6.06	-1.54
ECRESM10	19920819	46	8.1	268	47	32	28	4.1		237	4.74	289.1	26	57	0 3	0	0	0	0.5	16	1	0.3	6.36	6.69	-2.57
ECRESM10	19920826	60	8.4	440	48	37	29	3.7		232	4.36	266	24	59	0.4	14	0.28	16.8	0.5	28	1	0.4	6.65	6.67	-0.11
ECRESM10	19920902	52	8.3	352	45	26	33	6.2		203	3.76	230.6	24	60	0.5	14	0.28	16.8	0.4	24	1	0.1	6.20	6.30	-0.82
ECRESM10	19920909	52	8.3	221	47	23	28	4		205	4.1	250.1	20	60	0.5	0	0	0	0.3	34	1	0.5	5.61	5.96	-2.99
ECRESM10	19920916	69	8.1	455	62	31	49	4.6		220	4.4	268.4	25	58	0.4	0	0	0	0.1	20	1	0.5	7.95	6.35	11.16
ECRESM10	19920923	63	8.1	392	46	24	46	4.9		230	4.6	280.6	37	71	0.6	0	0	0	0.9	32	1	0.95	6.55	7.20	-4.69
ECRESM10	19920930	47	8.1	281	40	23	28	4.8		187	3.74	228.1	18	35	0.5	0	0	0	0.1	31	1	1.5	5.20	5.05	1.43
ECRESM10	19921007	46	9.1	257	32	31	30	3		235	4.04	246.4	20	28	1	33	0.66	39.6	0.1	22	1	0.2	5.58	6.52	-7.76
ECRESM10	19921014	62	8.4	432	56	30	46	4		289	5.2	317.2	29	58	0.7	29	0.58	34.8	0.1	18	1	0.4	7.42	6.43	-6.39
ECRESM10	19921104	62	8.1	409	60	23	42	4.4		212	4.24	258.6	28	75	1	0	0	0	0.5	20	1	0.7	6.68	6.87	1.54
ECRESM10	19921111	74	8.2	469	61	35	43	4.6		280	5.6	341.6	35	65	0.9	0	0	0	1.7	50	1	1.3	7.97	6.47	-3.03
ECRESM10	19921118	80	7.9	626	90	40	65	6.7		277	5.54	337.9	41	160	1	0	0	0	0.4	46	1	0.9	10.84	10.11	3.45
ECRESM10	19921125	39	7.9	220	37	12	18	4.1		132	2.64	161	13	20	0.7	0	0	0	0.2	52	1	0.6	3.76	3.49	3.96
ECRESM10	19921202	56	8	315	47	25	29	3.4		221	4.42	269.6	22	39	0.5	0	0	0	2.8	33	1	1.8	5.61	5.96	-1.45
ECRESM10	19921209	54.5	7.7	369	64	16	29	5		110	2.2	134.2	26	110	0 9	0	0	0	3.4	24	1	1	5.96	5.36	5.29
ECRESM10	19921216	63	7.8	560	68	27	47	4.9		219	4.38	267.2	32	140	0 9	0	0	0	7.9	26	1	0.9	7.84	6.40	-3.45
ECRESM10	19921221	66	7.5	546	61	24	46	5		227	4.54	276.9	46	140	0.9	0	0	0	4	30	1	4.45	8.29	9.06	-4.45
ECRESM10	19921228	88	8	660	80	48	56	4.7		303	6.06	369.7	34	190	0.6	0	0	0	7.3	22	1	1	10.39	11.15	-3.56
ECRESM10	19930106	106	7.7	1156	104	62	84	9		211	4.22	257.4	41	140	0.7	0	0	0	70	46	1	4.4	12.92	9.89	14.79

Table V.2. Continued.

ECRESM10	19930113	84	7.9	533	66	40	48	5		246	4.92	300.1	29	100	0.7		0	0	0	17	30	1	1	8.86	8.16	4.06
ECRESM10	19930120	84	8	574	59	37	61	4.1		260	5.2	317.2	41	110	0.6		0	0	0	3.8	27	1	0.1	8.80	8.74	0.35
ECRESM10	19930127	82	7.8	532	59	40	52	4.8		286	5.72	348.9	32	125	0.8		0	0	0	2.5	22	1	0.9	8.68	9.32	-3.60
ECRESM10	19930203	62	7.7	420	64	42	63	4.2		316	6.32	385.5	39	130	0.3		0	0	0	4.7	56	1	0.7	10.55	10.24	1.50
ECRESM10	19930213	88	7.9	572	76	40	63	4.1		313	6.26	381.9	41	125	1.1		0	0	0	0.1	24	1	0.8	9.98	10.10	-0.59
ECRESM10	19930217	91	7.8	556	87	46	60	5		304	6.08	370.9	35	145	1		0	0	0	3	30	1	0.9	10.92	10.21	3.34
ECRESM10	19930224	79	7.9	517	66	25	50	8.6		253	5.06	308.7	39	140	1		0	0	0	3	25	1	0.9	8.75	9.20	-2.54
ECRESM10	19930303	60	7.9	390	50	25	41	7		222	4.44	270.8	32	55	0.7		0	0	0	1.9	27	1	0.8	8.57	8.57	-0.02
ECRESM10	19930310	82	7.7	434	67	28	29	5.6		258	5.16	314.8	30	75	1		0	0	0	4.4	45	1	0.4	7.11	7.70	-4.02
ECRESM10	19930324	60	7.8	500	76	26	50	5.6		189	3.78	230.6	26	160	0.6		0	0	0	2.7	24	1	1.4	8.31	7.96	2.10
ECRESM10	19930519	78	7.9	506	65	32	65	1.1		357	7.14	435.5	41	82	0.9		0	0	0	0.1	19	1	0.1	8.79	10.05	-6.72
ECRESM10	19930728	61	7.9	409	53	29	42	6.1	15	252	5.04	307.4	52	50	0.7		0	0	0	1	28	1	0.4	7.07	7.61	-3.70
ECRESM10	19930804	52	8.2	346	52	24	35	5.3	37.5	198	3.96	241.6	29	63	0.7		0	0	0	0.5	26	1	4	6.28	6.28	0.16
ECRESM10	19930811	84	7.9	419	72	28	57	6.9	29	217	4.34	264.7	69	90	0.8		0	0	0	0.7	31	1	0.2	6.66	6.22	2.61
ECRESM10	19930818	61	8.1	395	64	32	45	6.2	31	225	4.5	274.5	51	72	0.6		0	0	0	0.1	24	1	0.1	8.00	7.47	3.39
ECRESM10	19930825	60	8.2	401	55	25	41	4.6	24	247	4.94	301.3	36	66	0.8		0	0	0	0.1	15	1	0.9	8.76	7.44	-4.76
ECRESM10	19930901	84	8.3	426	58	32	39	3.6	17	273	5.34	325.7	44	63	0.8		6	0.12	7.2	0.1	24	1	1.4	7.36	8.22	-5.41
ECRESM10	19930915	54	7.8	352	45	29	39	5.3	22	243	4.86	296.5	32	64	0.9		0	0	0	0.4	28	1	0.6	8.52	7.17	-4.73
ECRESM10	19930922	59	8.2	367	52	29	43	4.4	22	266	5.32	324.5	38	62	0.8		0	0	0	0.1	26	1	1	7.02	7.76	-4.99
ECRESM10	19930929	84	7.8	433	56	26	49	3.8	28	294	5.88	358.7	36	60	0.7		0	0	0	0.1	22	1	1.3	7.36	8.22	-5.36
ECRESM10	19931006	41	7.4	428	41	19	23	7.6	14.2	72	1.44	87.84	19	70	0.7		0	0	0	14	56	1	3.3	4.86	3.80	12.29
ECRESM10	19931013	185	7.3	1239	88	55	39	38	21.6	109	2.18	133	32	220	0.8		0	0	0	110	60	66	8.7	15.25	9.74	22.03
ECRESM10	19931020	299	7.5	1928	108	65	72	17.6	20.4	109	2.18	133	62	460	0.7		0	0	0	100	46	62	9.3	20.52	15.45	14.10
ECRESM10	19931027	77	7.1	502	59	29	24	0.5	20.4	91	1.82	111	15	68	0.7		0	0	0	30	54	4	5.2	6.61	4.34	20.69
ECRESM10	19931103	100	7.7	666	76	47	50	6.8	14.8	312	6.24	380.6	35	128	0.8		0	0	0	9.6	27	1	1.8	10.16	10.14	0.09
ECRESM10	19931110	100	7.5	703	62	48	46	6.9	15	229	4.58	279.4	30	134	0.7		0	0	0	33	32	1	4.3	10.27	8.92	7.05
ECRESM10	19931117	97	7.4	606	72	39	49	5.6	11.6	278	5.56	339.2	35	130	1		0	0	0	11.6	30	1	1.8	9.13	9.55	-2.23
ECRESM10	19931124	95	7	666	76	37	25	8.3	19.2	118	2.36	144	21	68	0.6		0	0	0	75	36	12	6.5	8.90	5.61	20.99
ECRESM10	19931201	115	7.6	715	93	52	59	10	19	275	5.5	335.5	39	150	1.1		0	0	0	39	32	4	4.9	11.96	10.56	6.21
ECRESM10	19931208	175	7.3	1124	91	57	59	26	24	182	3.64	222	42	175	2.2		0	0	0	100	36	30	6.6	14.13	10.47	14.85
ECRESM10	19931217	91	7.4	645	104	58	55	9	21.6	294	5.88	358.7	34	120	0.8		0	0	0	60	19	1	2	12.64	10.41	9.68
ECRESM10	19931222	71	7.5	476	74	27	42	2.6	21.2	315	6.3	384.3	21	75	1		0	0	0	1	31	1	0.6	7.86	6.54	-4.13
ECRESM10	19931229	79	7.2	508	45	16	30	9.3	17	69	1.38	84.18	17	70	0.9		0	0	0	46	31	16	9	6.10	4.39	16.33
ECRESM10	19940105	83	7.7	530	78	30	46	6.1	22.4	346	6.92	422.1	26	75	1.5		0	0	0	6.5	31	1	2.5	6.62	9.46	-4.70
ECRESM10	19940112	100	7.2	670	80	40	57	7.5	22	119	2.38	145.2	24	110	0.6		0	0	0	56	32	6	4	10.40	6.41	23.75
ECRESM10	19940119	91	7.6	609	81	39	50	5.3	16.4	302	6.04	368.4	21	90	0.7		0	0	0	1.5	51	1	2.5	9.62	8.64	5.32
ECRESM10	19940126	88	7.7	565	83	38	38	4.9	20	295	5.9	359.9	21	80	0.4		0	0	0	3	32	1	0.5	9.10	8.24	4.96
ECRESM10	19940202	156	7.4	676	82	40	43	6	17	191	3.82	233	28	112	1		0	0	0	30	32	15	5	10.29	7.63	14.81
ECRESM10	19940209	128	7.8	954	77	37	45	7	17.4	272	5.44	331.8	27	100	1		0	0	0	0.1	26	1	0.3	9.06	8.35	4.20
ECRESM10	19940216	99	8.1	701	64	42	59	3.6	17.2	358	7.16	436.8	31	128	0.9		0	0	0	12	30	1	1.2	10.36	10.96	-2.86
ECRESM10	19940223	40	7.8	265	42	13	14	4.5	14	91	1.82	111	15	70	1.2		0	0	0	2.7	27	1	1.6	3.94	3.86	1.04
ECRESM10	19940302	87	7.7	615	70	39	49	6.3	16	294	5.88	358.7	28	105	0.8		0	0	0	0.1	23	1	3.7	9.05	9.01	0.19
ECRESM10	19940309	87	7.9	562	69	42	57	5.1	20	324	6.48	395.3	31	110	1		0	0	0	7.8	23	1	1.6	9.56	9.87	-1.56
ECRESM10	19940316	80	7.8	542	88	42	60	4.6	16	364	7.28	444.1	37	106	1		0	0	0	1	18	1	0.7	9.63	10.86	-5.07
ECRESM10	19940323	63	8.1	422	55	30	43	3.2	16.8	257	5.14	313.5	29	70	0.6		0	0	0	0.6	15	1	0.5	7.22	7.48	-1.76
ECRESM10	19940330	63	7.6	323	58	32	39	6.3	15.1	213	4.26	259.9	24	124	0.6		0	0	0	1.4	24	1	0.5	7.44	7.60	-1.05
ECRESM10	19940406	76	7.9	501	64	30	46	3.5	15.6	299	5.98	364.8	35	80	0.9		0	0	0	0.1	24	1	0.8	7.81	8.71	-5.44
ECRESM10	19940413	84	7.6	551	77	34	53	4.6	15.7	286	5.72	348.9	46	100	0.7		0	0	0	0.2	30	1	0.3	9.12	9.15	-0.16
ECRESM10	19940420	71	7.7	464	52	32	48	4.9	15.5	283	5.66	345.3	35	80	0.8		0	0	0	0.1	36	1	0.2	7.50	8.36	-5.45
ECRESM10	19940427	78	7.9	513	62	32	53	4.6	15.5	327	6.54	398.9	39	83	0.6		0	0	0	0.1	27	1	0.3	8.21	9.42	-6.86
ECRESM10	19940504	83	7.9	556	69	33	72	5.5	23.9	354	7.08	431.9	50	80	0.5		0	0	0	0.2	26	1	0.3	9.49	10.19	-3.59
ECRESM10	19940511	75	8	503	66	33	51	4.6	19.6	332	6.64	405	45	74	1		0	0	0	0.1	26	1	0.8	8.50	9.52	-5.67
ECRESM10	19940518	78	8	500	77	47	69	5.6	16.8	394	7.88	480.7	56	127	0.9		0	0	0	0.1	23	1	0.1	10.91	12.15	-5.40
ECRESM10	19940525	79	7.9	409	76	40	54	5.9	12.6	350	7	427	42	109	1	0.1	0	0	0	0.1	20	1	0.1	9.74	10.51	-3.78
ECRESM10	19940622	81	8	396	81	33	40	3.5	9.2	279	5.58	340.4	36	75	1		0	0	0	0.4	23	1	0.1	7.64	8.22	-3.62
ECRESM10	19940629	66	8.2	449	63	33	51	4.4	8.6	290	5.8	353.8	37	67	0.6		0	0	0	0.1	21	1	0.6	8.25	8.30	-0.30
ECRESM10	19940706	70	8	47	83	33	42	4.5	9.3	302	6.04	368.4	38	79	0.7		0	0	0	0.1	25	1	0.1	6.65	6.60	0.33
ECRESM10	19940713	0.1	8	475	63	32	50	5.3	8.7	282	5.64	344	47	67	0.5		0	0	0	0.1	26	1	0.4	8.14	8.40	-1.56
ECRESM10	19940720	77	8.1	491	53	36	48	4.3	5.9	234	4.68	285.5	23	109	0.5		0	0	0	0.1	20	1	0.2	7.77	7.63	0.92
ECRESM10	19940727	56	8.1	374	46	33	43	5.4	13.4	257	5.14	313.5	35	71	0.4		0	0	0	0.1	9	1	0.3	7.17	7.64	-3.12

Table V.2. Continued.

ECRESM10	19940803	64	8.1	409	72	28	44	5.4	13.6	269	5.38	328.2	36	97	0.8						0	0	0	0.1	36	1		0.1	6.00	6.45	-2.71
ECRESM10	19940810	71	8.2	450	64	29	47	5 2	10.1	261	5 22	318.4	44	76	0 7						0	0	0	0.1	22	1		0.3	7.61	8.09	-1.74
ECRESM10	19940817	61	8.2	261	51	23	24	5.4	11	152	3.04	185.4	23	100	0.9						.0	0	0	0.2	27	1		0.4	5.67	5.63	-1.38
ECRESM10	19940824	45	8.1	266	41	22	27	4	3.9	194	3 88	236.7	21	42	0.8						0	0	0	0.1	22	1		0.1	5.19	5.39	-1.93
ECRESM10	19940831	53	7.9	344	42	22	31	4.1	2	206	4.16	253 8	23	42	0.7						0	0	0	0.1	21	1		0.2	5.41	5.73	-2.80
ECRESM10	19940907	49	8.1	333	41	26	27	4.2	5.6	224	4.48	273 3	22	33	1						0	0	0	0.1	22	1		0.1	5.52	5.84	-2.63
ECRESM10	19940914	56	8	378	40	26	40	4.5	5.2	227	4.54	278.9	28	45	0.9						0	0	0	0.1	21	1		0.2	6.05	6.32	-2.22
ECRESM10	19940921	35	8	219	27	17	17	8.7	12.2	105	2.1	128.1	21	43	0.5						0	0	0	1.8	31	1		0.5	3.71	3.66	0.73
ECRESM10	19940928	70	8.2	433	52	36	48	8.5	9.9	279	5.58	340.4	35	56	0.8						0	0	0	0.1	34	1		0.3	8.08	7.78	1.87
ECRESM10	19941005	56	8.3	351	40	30	31	4.8	10.6	237	4.7	286.7	22	40	0.8						2	0.04	2.4	0.1	40	1		0.1	5.99	6.27	-2.28
ECRESM10	19941012	72	8.3	460	56	31	48	4.2	10.5	273	5.34	325.7	35	43	0.5						6	0.12	7.2	0.1	21	1		0.1	7.51	7.51	0.01
ECRESM10	19941019	72	8.8	452	48	23	48	4.3	10.8	268	4.78	290.4	35	35	0.9						30	0.8	36	0.1	22	1		0.1	6.54	7.73	-8.31
ECRESM10	19941026	75	8.5	487	49	35	43	4.4	14.2	247	4.48	273.3	35	67	1						23	0.46	27.6	0.8	31	1		0.1	7.36	7.85	-3.18
ECRESM10	19941103	81.5	7.6	530		37	48	4.5	7.6	262	5.24	319.6	31	55	1.1						0	0	0	0.4	32	1		0.1	5.30	7.33	-16.02
ECRESM10	19941117	87	7.6	583	60	36	50	4.5	19.6	263	5.26	320.9	37	120	0.4						0	0	0		20	6			6.74	6.62	-0.44
ECRESM10	19941124	91	8.7	610	68	40	56	4.3	16.6	269	5.38	328.2	39	162	1.4						0	0	0		36	4		0.8	9.45	9.95	-2.57
Mean		66.6	7.953	447.4	55.2	30.47	42.88	6.169	15.95	210.2	4.159	253.7	31.63	62.26	0.695	ERR	0.1	ERR	ERR	ERR	2.253	0.045	2.703	6.173	29.73	2.806	ERR	2.373	7.28553	7.09322	-0.051
Std.Dev.		32.52	0.361	244.1	22.14	12.85	14.14	4.974	6.651	72.12	1.453	66.62	10.16	48.55	0.523	ERR	ERR	ERR	ERR	ERR	6.412	0.128	7.694	20.67	10.37	8.283	ERR	6.771	2.84029	2.02207	12.3507
Number		194	194	194	168	189	194	189	66	194	194	194	194	194	194	0	1	0	0	0	194	194	194	191	194	194	0	192	194	194	194

Table V.3. Data sets from ground water monitoring sites REGM01, REGM10, REGM16 and REGM 23.

Loc #	Samp.Date	pH	EC mS/m	TDS	Ca mg/l	Mg mg/l	Na mg/l	K mg/l	Si mg/l	M.Alk meq.Ca	HCO3 meq.H	HCO3 mg/l	Cl mg/l	SO4 mg/l	F mg/l	B mg/l	Fe mg/l	Mn mg/l	Zn mg/l	Cu mg/l	P.Alk meq.Ca	CO3 meq.H	CO3 mg/l	N mg/l	COD	NH4 mg/l	Phenol mg/l	PO4 mg/l	Total Cation	Total Anion	Ion %E
ECREGM01	19900822	7.8	205	1403	222	88	130	3.8	42	384	7.68	468.48	448	910	0.3	2.2	23	0.2			0	0	0	0.2	81	2	1	0.8	23.53	38.51	-21.30
ECREGM01	19910124	7.3	160	932	220	77	163	2.7	50	361	7.22	440.42	414	240	0.4	1.9	17	0.5		0.01	0	0	0	0.2	84	2	0.01	0.2	23.51	22.03	3.22
ECREGM01	19910423	7	195	1538	373	129	188	4.5	44	392	7.84	478.24	432	240	0.7	0.01	23.7			0.01	0	0	0	0.2	82	2	0.01	0.2	37.95	25.07	20.44
ECREGM01	19910723	7.1	210	1740	253	77	173	2	78	397	7.94	484.34	438	440	0.2	4.4	23		0.02	0.01	0	0	0	0.4	84	2	0.01	0.4	27.88	29.64	-3.08
ECREGM01	19911029	7.2	215	1794	279	79	174	2.1	8.4	387	7.74	472.14	447	325	0.3	2.59	38.8		0.04	0.02	0	0	0	0.3	100	2	0.01	0.4	30.13	27.15	5.21
ECREGM01	19920128	6.8	200	1184	160	19	68	1.4	38	371	7.42	452.62	477	400	2.4	0.04	20		0.17	0.02	0	0	0	0.8	80	1	0.01	0.01	14.58	29.34	-33.57
ECREGM01	19920505	7.5	245	1902	253	100	153	4.1	44	348	6.96	424.56	419	380	0.8	0.836	52.4		0.1	0.16	0	0	0	0.5	102	1	0.01	0.2	30.48	26.85	6.16
ECREGM01	19920811	7.3	244	2058	290	100	140	1.9		465	9.3	567.3	426	400	0.4	0.085	7		0.13	0.01	0	0	0	0.1	108	1	0.01	0.9	29.88	29.89	-0.02
ECREGM01	19921117	7.1	200	1239	208	69	140	1.8		259	5.18	315.98	383	260	0.8	1.307	50		0.03	0.01	0	0	0	0.1	69	1	0.01	0.8	24.83	21.40	7.40
ECREGM01	19930217	6.9	220	1488	230	79	135	1.1		333	6.66	406.26	328	372	0.4	2	20.6	0.01	0.27	0.2	0	0	0	0.1	114	1	0.01	0.1	26.82	23.68	6.40
ECREGM01	19930525	7.1	262	1808	383	80	148	1.2		376	7.52	458.72	438	425	0.5	0.907	14.1		0.1	0.01	0	0	0	0.1	90	1	0.01	0.1	30.80	28.75	3.56
ECREGM01	19930817	7	265	1637	308	101	153	2.1	88	389	7.78	474.58	452	530	0.5	0.283	31		0.07	0.03	0	0	0	0.1	116	1		0.1	32.01	31.39	0.98
ECREGM01	19931115	7.8	290	1904	286	89	183	1.2	48	384	7.68	468.48	530	420	0.4	0.537	20.6		0.11	0.08	0	0	0	0.6	98	1		0.1	29.86	31.42	-2.50
ECREGM01	19940308	7.2	240	1580	322	91	178	1.8	44	400	8	488	517	465	1.1	3.128	15.9		0.16		0	0	0	0.8	88	1		0.1	32.26	32.98	-1.07
ECREGM01	19940808	7.1	245	1842	300	87	184	2	23	342	6.84	417.24	519	488	0.5	1.111	16.8		0.11	0.01	0	0	0	0.1	79	14		0.1	31.82	31.25	0.90
ECREGM10	19900822	7.8	129	731	82	53	44	1.8	14	566	11.32	690.52	165	32	0.2	0.5	27	0.2			0	0	0	0.2	15	2	1	0.2	11.88	17.22	-17.94
ECREGM10	19910124	7.4	135	701	95	60	154	3.8	21	344	6.88	419.68	256	75	0.2	5.3	19	0.5		0.01	0	0	0	0.2	54	2	0.01	0.2	17.07	15.89	5.90
ECREGM10	19910423	7.2	145	1063	93	67	174	7.5	18	370	7.4	451.4	295	100	0.3	0.01	22			0.01	0	0	0	0.2	54	2	0.01	0.2	18.71	17.83	2.41
ECREGM10	19910723	7.2	195	1335	127	82	250	6	44	575	11.5	701.5	452	60	0.3	0.1	7.6		0.01	0.03	0	0	0	0.2	72	2	0.01	0.5	24.63	25.53	-1.79
ECREGM10	19911029	7.2	200	1388	147	85	231	5	11.4	550	11	671	475	20	0.3	0.87	35.5		0.01	0.01	0	0	0	0.2	80	2	0.01	0.2	26.52	24.84	3.28
ECREGM10	19920129	7.2	160	1370	101	39	122	5.6	10	403	8.06	491.66	463	125	0.2	0.04	22		0.09	0.04	0	0	0	2	108	1	0.01	0.2	16.59	23.77	-17.80
ECREGM10	19920505	7.7	200	1329	126	106	226	8.3	9	462	9.24	563.64	443	26	0.5	0.04	61.5		0.03	0.08	0	0	0	0.2	126	1	0.01	0.2	28.51	22.31	12.20
ECREGM10	19920818	7.3	245	1564	178	119	272	3.4		736	14.72	897.92	516	63	0.4	0.2	45		0.02	0.04	0	0	0	0.1	71	1	0.01	0.1	33.12	30.81	3.94
ECREGM10	19921124	6.8	245	1316	189	112	240	4.2		578	11.56	705.16	476	65	0.3	2.344	88		0.001	0.01	0	0	0	0.1	100	1	0.01	0.5	31.80	26.37	9.40
ECREGM10	19930217	7.5	180	1068	98	38	180	3.3		351	7.02	428.22	235	35	0.5	2.943	24.3	0.01	0.001	0.02	0	0	0	0.1	60	1	0.01	0.1	17.40	14.41	9.42
ECREGM10	19930601	7	195	1154	84	66	273	4.8		437	8.74	533.14	400	32	0.4	1.286	54.7	0.4	0.08	0.08	0	0	0	0.1	124	1		0.3	25.13	20.72	9.61
ECREGM10	19930817	7.1	230	1415	102	73	227	4.7	10.6	400	8	488	300	48	0.5	1.043	4.9		0.02	0.01	0	0	0	0.1	88	1		0.1	21.41	17.45	10.19
ECREGM10	19931115	7.4	210	1431	103	69	203	7.1	11	411	8.22	501.42	424	37	0.6	0.241	38.5		0.04	0.08	0	0	0	0.4	88	1		0.1	21.86	20.89	2.25
ECREGM10	19940307	7.3	256	1692	141	102	205	8.7	12.5	514	10.28	627.08	557	40	0.8	0.03	40.5		0.06	0.01	0	0	0	0.1	81	1	0.01	0.4	26.75	26.87	-0.22
ECREGM10	19940813	6.8	215	1388	100	72	253	4.9	9.1	359	7.18	437.98	523	41	0.9	0.04	7.4	0.2	0.15		0	0	0	0.1	89	1		0.1	22.51	22.82	-0.68
ECREGM10	19940805	7.2	220	1474	78	68	226	4.4	4.5	313	6.26	381.86	692	26	0.5	0.04	80.1	0.6	0.09		0	0	0	0.2	110	20		0.4	25.44	26.40	-1.86
ECREGM16	19900822	7.8	2000	15739	2181	653	440	13.6	48	444	8.88	541.68	246	50	0.2	4.2	31	0.9			0	0	0	800	38	2	1	1.3	200.30	31.43	72.88
ECREGM16	19910129	6.8	2500	13386	1158	569	373	9.8	90	93	1.86	113.46	130	225	0.2	2	22	0.7		0.1	0	0	0	182	140	2	0.01	1	121.57	13.19	80.43
ECREGM16	19910429	6.5	1500	10239	1267	626	480	5	80	118	2.36	143.96	244	1200	0.4	0.01	19.3			0.07	0	0	0	84	105	2	0.01	2.1	139.31	35.35	59.29
ECREGM16	19910730	6.8	4000	35178	15973	1884	631	12	50	207	4.14	252.54	601	900	0.3	61	9		0.2	0.08	0	0	0	999	29	2	0.01	1.8	888.48	38.02	89.28
ECREGM16	19911105	6.5	1275	20000	8431	2245	601	11	42	185	3.7	225.7	836	800	0.6	0.04	10.2		0.39	0.14	0	0	0	999	108	2	0.01	0.8	502.70	81.15	72.41
ECREGM16	19920128	6.8	3400	18785	218	77	420	8.5	40	163	3.26	198.86	748	500	0.2	1.3	20		0.05	0.04	0	0	0	800	88	1	0.01	2	38.83	44.58	-6.89
ECREGM16	19920818	6.8	6300	44853	4404	1871	584	11.8		290	5.8	353.8	1432	1000	0.3	13.7	11		0.18	0.08	0	0	0	999	108	1	0.01	0.5	404.94	83.28	65.88
ECREGM16	19921125	7.1	4500	28704	8004	2169	575	8.5		204	4.08	248.88	803	320	0.3	0.748	7		0.09	0.05	0	0	0	999.9	170	1	0.01	0.2	531.19	58.53	80.79
ECREGM16	19930302	6.8	9000	58047	6250	2058	718	11		224	4.48	273.28	1008	900	0.5	38.767	12.8	3.7	0.88	0.18	0	0	0	780	180	1	0.01	0.1	513.08	64.42	77.71
ECREGM16	19930609	7.2	8800	58310	7103	2700	783	12.2		313	6.26	381.86	1370	1450	0.2	4.107	6.8	2.1	0.45	0.25	0	0	0	999	120	1	0.01	0.7	611.47	91.24	74.03
ECREGM16	19930907	7	5500	28898	7685	3035	888	13.2	110	319	6.38	389.18	1412	380	0.4	88.888	4.8	2.7	0.06	0.02	0	0	0	999.9	200	1		1.7	687.82	68.91	81.50
ECREGM16	19931213	6.1	6800	58630	6876	3235	888	12.1	131.1	574	11.48	700.28	1854	900	0.4	10.33	8.6		0.55	0.17	0	0	0	999.9	420	8		1.3	740.27	88.70	78.47
ECREGM16	19940307	6.1	7000	48084	16585	4403	858	58	54	725	14.5	884.5	1952	1400	0.6	88.322	12.3		0.32	0.01	0	0	0	999.9	418	12		4.5	1342.22	115.01	84.22
ECREGM16	19940627	6.4	7800	50820	14418	3857	774	41.4	8	785	15.7	957.7	1798	1874	1	88.888	7.1		1.28	1	0	0	0	999.9	300	10		4.8	1080.84	121.79	79.74
ECREGM16	19940810	6.4	8700	57480	13333	3870	794	15.2	81	622	12.44	758.84	1505	1100	0.8	88.9	4.6	1.1	0.23	0.21	0	0	0	150	800	22		8.3	1020.15	80.45	85.38
ECREGM23	19900822	7.8	110	650	131	34	27	5.1	34	242	4.84	295.24	60	40	0.2	0.1	1	0.1		0.01	0	0	0	70	6	2	1	0.2	10.81	9.07	8.72
ECREGM23	19910205	7.2	120	1000	184	37	32	6.6	24	305	6.1	372.1	60	20	0.3	0.1	1.6	0.5		0.01	0	0	0	80	344	2	0.01	2	13.00	10.14	12.37
ECREGM23	19910508	6.7	135	1157	158	31	30	4.5	30	312	6.24	380.64	84	13	0.2	0.5	1.2			0.01	0	0	0	82	19	2	0.01	0.2	12.00	10.08	8.04
ECREGM23	19910912	7.8	115	919	214	35	29	4	120	228	4.56	278.16	109	8	0.2	0.2	2.2		0.001	0.001	0	0	0	84	20	0.2	0.01	0.2	15.06	9.35	23.39
ECREGM23	19911105	7.3	125	1084	144	40	37	3.6	26	321	6.42	391.62	89	12	0.4	1.823	2.5		0	0.001	0	0	0	40	16	2	0.01	0.2	12.43	10.13	10.17
ECREGM23	19920210	7.7	120	1013	248	58	30	5	25	342	6.84	417.24	82	10	0.6	0.04	4.6		0	0.01	0	0	0	80	10	1	0.01	0.3	18.84	10.29	29.39
ECREGM23	19920825	7.4	120	880	86	30	38	4.3		287	5.74	350.14	40	4	0.4	1.38	1.1		0.07	0.009	0	0	0	30	113	1	0.01	0.5	10.23	7.47	15.61
ECREGM23	19921201	7.5	99	581	77	26	39	2		331	6.62	403.82	45	12	0.4	0.04	34		0.03	0.01	0	0	0	20	35	1	0.01	0.1	9.81	8.48	8.22
ECREGM23	19930301	7.2	115	802	144	33	31	5.9		346	6.92	422.12	66	11	0.5	3.327	1.7		0.01	0.08	0	0	0	45	3	1		0.1	12.42	9.82	11.69
ECREGM23	19930801	7.5	90	583	134	29	44	4.3	30	250	5	305	61	7	0.4	0.314	0.4		0.03	0.01	0	0	0	50	8	1		0.1	11.17	7.70	18.44
ECREGM23	19931208	7.2	105	670	134	24	28	8.5	23	271	5.42	330.62	57	12	0.6	2.053	0.4		0.02	0.04	0	0	0	15	20	1		1.2	10.18	7.39	14.57
ECREGM23	19940411	7.1	145	623	148	35	27	5	27	319	6.38	389.18	65	16	1.9	6	0.2		0.08	0.01	0	0	0	35	25	1		1.8	11.89	9.83	9.48
ECREGM23	19940627	7.7	145	971	179	48	22	3.4	10.6	381	7.62	464.82	80	20	0.6	0.04	0.8		0.05		0	0	0	40	8	4		0.7	14.00	11.27	10.78
ECREGM23	19940808	7.4	130	871	184	37	29	4.4	20	235	4.7	286.7	84	22	0.6	0.777	0.9		0.06	0.01	0	0	0	91	80	1		0.1	13.71	9.08	20.27

APPENDIX VI - Electrical conductivity slope estimate

Table VI.1.Slope estimate of the electrical conductivity at the surface water monitoring locations (RESMs) over the last four years. < data denotes that there was less than the required amount of data for the statistical test.

Site No.	Site description	Area code & symbol	EC ($mS.m^{-1}$) Slope estimate	Significance (Alpha = 0.10)
RESM 01	West side perimeter fence.	1 ○ 2 □	-2.48	Sig.
RESM 02	Northern spruit end, after water dams.	2 □ 5 ●	1.26	Not sig.
RESM 04	Above water dams, after confluence.	6 ■ 8 ♦	-0.07	Not sig.
RESM 05	Upstream of confluence, below town.	Town	-1.54	Not sig.
RESM 06	Up from confluence, below irrigation.	6 ■ 8 ♦	-0.18	Not sig.
RESM 07	Upstream of irrigation & refuge.	6 ■ 8 ♦	1.20	Not sig.
RESM 08	Above of the whole plant bar irrigation.	6 ■	-7.70	Not sig.
RESM 16	Above RESM08 confluence.	6 ■	< data	-
	Average:		*-1.36*	
RESM 03	Southern stream end, post ash/BP.	1 ○	-9.19	Not sig.
RESM 09	Below confluence 2nd, after coal stocks.	7 ▲	-35.36	Sig.
RESM 10	Below confluence 1st, after coal stocks.	7 ▲	6.23	Sig.
RESM 11	Above coal stockpiles.	2 □ 9 ★	6.89	Sig.
RESM 12	Below coal stockpiles & fertilizer areas.	7 ▲ 2 □ 3 △	-14.81	Not sig.
RESM 13	Above stockpiles & fert./explo. dumps.	2 □ 3 △	5.23	Not sig.
RESM 14	Above stockpiles, below fert./explo.		16.33	Not sig.
RESM 15	Above fertilizer and explosive dumps.		-0.83	Not sig.
	Average:		*-3.19*	

Table VI.2. Slope estimate of electrical conductivity at the ground water monitoring boreholes (REGMs) over the last four years. < data denotes that there was less than the required amount of data for the statistical test.

Site No.	Site description	Area code & symbol		EC ($mS.m^{-1}$) Slope estimate	Significance
REGM 01	Ash water evaporation dam	1	○	11.00	Sig.
REGM 02	Fine ash dam	1	○	-2.00	Not sig.
REGM 03	Fine coal storage dam	1	○	33.00	Sig.
REGM 08	Coarse ash dump	1	○	15.00	Sig.
REGM 37	Black product dams	1	○	17.50	Sig.
REGM 39	Fine ash dam No. 4	1	○	< data	-
REGM 40	Fine ash dam No. 4	1	○	< data	-
REGM 41	Fine ash dam No. 4	1	○	< data	-
REGM 42	Ash water return dam No. 4	1	○	< data	-
REGM 43	Ash water return dam No. 4	1	○	< data	-
	Average:			*14.9*	
REGM 16	Liquid fertilizer dams	2	□	1900	Sig.
REGM 17	Fertilizer reject dump	2	□	216	Sig.
REGM 31	Liquid fertilizer dams	2	□	5.00	Sig.
REGM 32	Liquid fertilizer dams	2	□	54.16	Sig.
	Average:			*543*	
REGM 18	Explosives borrow pits	3	△	30.00	Sig.
REGM 19	Explosives burrow pits	3	△	14.00	Not sig.
	Average:			*22*	
REGM 10	Water dam unit 52	4	◇	23.33	Sig.
REGM 11	Water recovery division dams	4	◇	3.75	Not sig.
REGM 12	Water recovery division dams	4	◇	3.34	Sig.
	Average:			*10.14*	
REGM 21	Salt water dam	5	●	149	Sig.
REGM 23	Irrigation area B	6	■	5.00	Not sig.
REGM 24	Irrigation area B	6	■	2.66	Sig.
REGM 25	Irrigation area B	6	■	-5.16	Sig.
REGM 26	Irrigation area B	6	■	0.833	Not sig.
REGM 27	Irrigation area A	6	■	-0.25	Not sig.
REGM 28	Irrigation area A	6	■	0.00	Not sig.
REGM 29	Irrigation area A	6	■	9.00	Not sig.
REGM 30	Irrigation area A	6	■	-5.00	Not sig.
REGM 44	Dam 10 irrigation	6	■	< data	-
REGM 45	Dam 10 irrigation	6	■	< data	-
	Average:			*0.88*	
REGM 14	Coal stockpile	7	▲	0.00	Not sig.
REGM 22	Domestic type refuse dump	8	♦	1.83	Sig.
REGM 20	Mine water reticulation dam	9	★	52.00	Sig.

APPENDIX VII - Proportions of excursion in some of the data sets

The results of the statistical analysis by WQStat II for the proportions (of 1) of excursion (exceedance over time) by the values in a selection of data sets discussed in Section 3.1.1.5. The excursion values are displayed in Figures 3.12 to 3.15.

Table VII.1. EC guideline 70 $mS.m^{-1}$.

Site	Summer	Autumn	Winter	Spring	Total year
RESM					
01	0.200	0.000	0.250	0.000	0.111
02	0.000	0.000	0.000	0.000	0.000
03	0.200	0.200	0.500	0.250	0.278
04	0.400	0.200	0.000	0.500	0.278
05	0.500	0.200	0.000	0.000	0.188
06	0.400	0.200	0.000	0.000	0.188
07	0.600	0.200	0.000	0.250	0.278
09	0.750	1.000	1.000	1.000	0.923
10	0.200	0.800	0.500	0.250	0.444
13	0.000	0.200	0.250	0.333	0.178
14	1.000	1.000	1.000	1.000	1.000
REGM					
01	1.000	1.000	1.000	1.000	1.000
11	1.000	1.000	1.000	1.000	1.000
14	1.000	1.000	1.000	1.000	1.000
17	1.000	1.000	1.000	1.000	1.000
18	1.000	1.000	1.000	1.000	1.000
21	1.000	1.000	1.000	1.000	1.000
22	1.000	1.000	1.000	1.000	1.000
23	1.000	1.000	1.000	1.000	1.000

Table VII.2. EC guideline 154 $mS.m_{-1}$.

Site	Summer	Autumn	Winter	Spring	Total year
RESM					
01	0.000	0.000	0.000	0.000	0.000
02	0.000	0.000	0.000	0.000	0.000
03	0.200	0.000	0.250	0.000	0.111
04	0.000	0.000	0.000	0.000	0.000
05	0.000	0.000	0.000	0.000	0.000
06	0.000	0.000	0.000	0.000	0.000
07	0.000	0.000	0.000	0.000	0.000
09	0.500	0.750	1.000	1.000	0.769
10	0.000	0.000	0.000	0.000	0.000
13	0.000	0.000	0.000	0.000	0.000
14	1.000	0.750	0.250	1.000	0.867
REGM					
01	1.000	1.000	1.000	1.000	1.000
11	0.000	0.000	0.000	0.000	0.000
14	0.750	1.000	1.000	1.000	0.937
17	0.750	1.000	0.750	0.750	0.813
18	0.750	1.000	0.500	1.000	0.813
21	1.000	1.000	1.000	1.000	1.000
22	0.600	0.333	0.500	0.000	0.385
23	0.000	0.000	0.333	0.000	0.077

Table VII.3. EC guideline 270 $mS.m^{-1}$.

Site	Summer	Autumn	Winter	Spring	Total year
RESM					
01	0.000	0.000	0.000	0.000	0.000
02	0.000	0.000	0.000	0.000	0.000
03	0.000	0.000	0.000	0.000	0.000
04	0.000	0.000	0.000	0.000	0.000
05	0.000	0.000	0.000	0.000	0.000
06	0.000	0.000	0.000	0.000	0.000
07	0.000	0.000	0.000	0.000	0.000
09	0.000	0.000	0.000	0.000	0.000
10	0.000	0.000	0.000	0.000	0.000
13	0.000	0.000	0.000	0.000	0.000
14	0.333	0.250	0.000	1.000	0.250
REGM					
01	0.000	0.250	0.000	0.250	0.118
11	0.000	0.000	0.000	0.000	0.000
14	0.000	0.000	0.000	0.000	0.000
17	0.750	0.750	0.750	0.750	0.750
18	0.000	0.250	0.000	0.000	0.063
21	0.800	0.750	1.000	1.000	0.867
22	0.000	0.000	0.000	0.000	0.000
23	0.000	0.000	0.333	0.000	0.077

APPENDIX VIII - Statistics representing the data thinning procedure

Table VIII.1. Simple statistics and EC/Ca correlation values for different hypothetical sampling time intervals. These results are displayed in Figures 3.20 and 3.21a to 3.21b.

Site		Weeks	Mean	Standard deviation	Spearman correlation	Kendall Tau
RESM01	Weekly	1	51.90	8.17	0.5711	0.4674
	Fortnightly	2	51.67	7.76	0.4928	0.4048
	Monthly	4	51.85	6.91	0.5734	0.4664
	Quarterly	12	51.73	6.43	0.7218	0.6031
RESM03	Weekly	1	54.06	19.90	0.6669	0.5332
	Fortnightly	2	52.94	14.27	0.6457	0.5135
	Monthly	4	52.12	10.73	0.6106	0.4743
	Quarterly	12	48.71	8.96	0.5102	0.4530
RESM07	Weekly	1	51.44	17.90	0.8017	0.6472
	Fortnightly	2	50.81	17.88	0.8089	0.6559
	Monthly	4	51.69	17.48	0.8381	0.6919
	Quarterly	12	51.19	16.15	0.8393	0.7115
RESM14	Weekly	1	218.33	109.09	0.8261	0.6270
	Fortnightly	2	214.57	105.58	0.8041	0.6095
	Monthly	4	205.23	102.55	0.6834	0.4821
	Quarterly	12	201.23	103.55	0.5090	0.3818

APPENDIX IX - Maps of the area under study

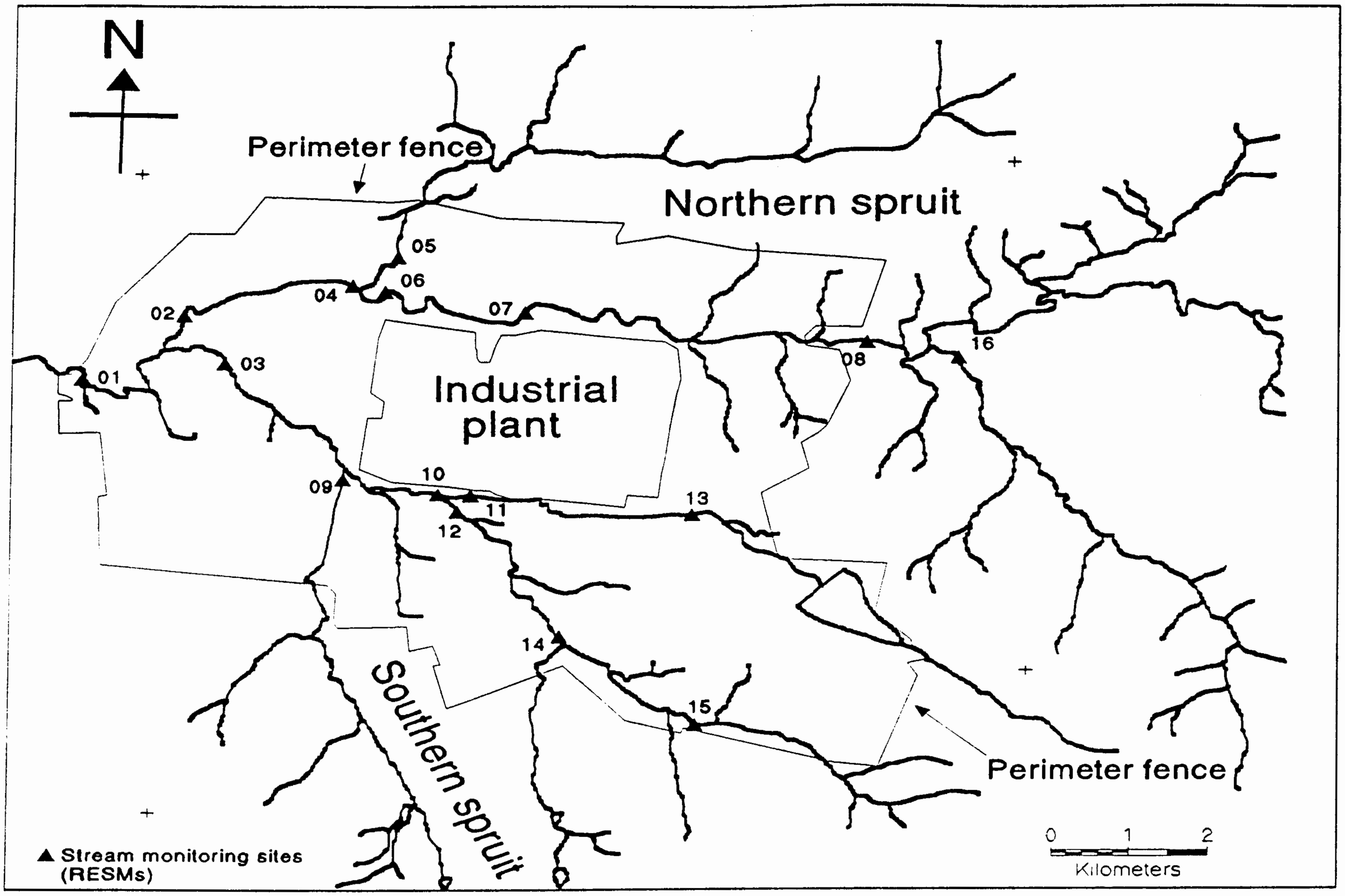


Figure IX.1. **Surface water monitoring sites, RESMs.**

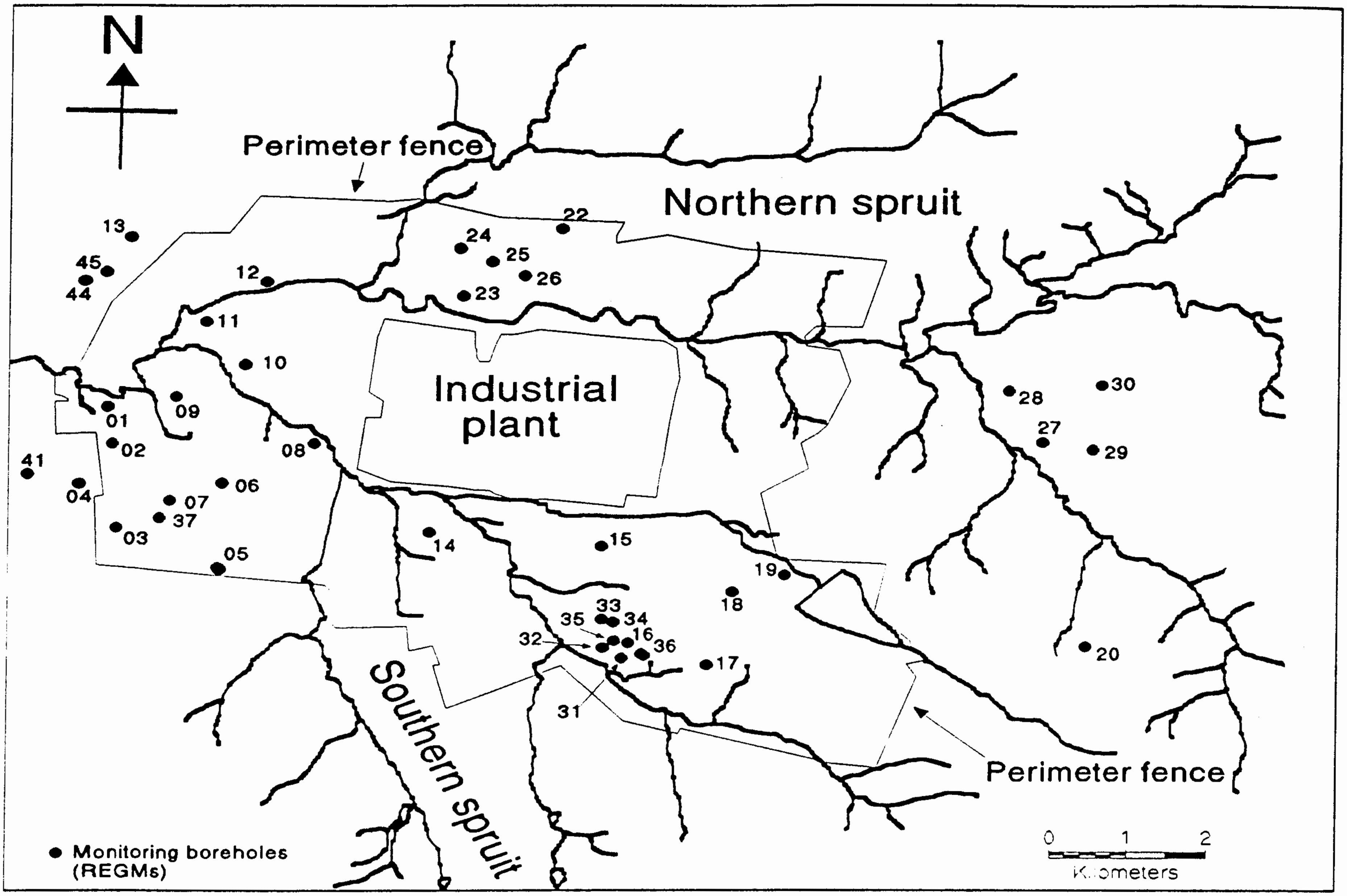


Figure IX.2. Ground water monitoring sites, REGMs.

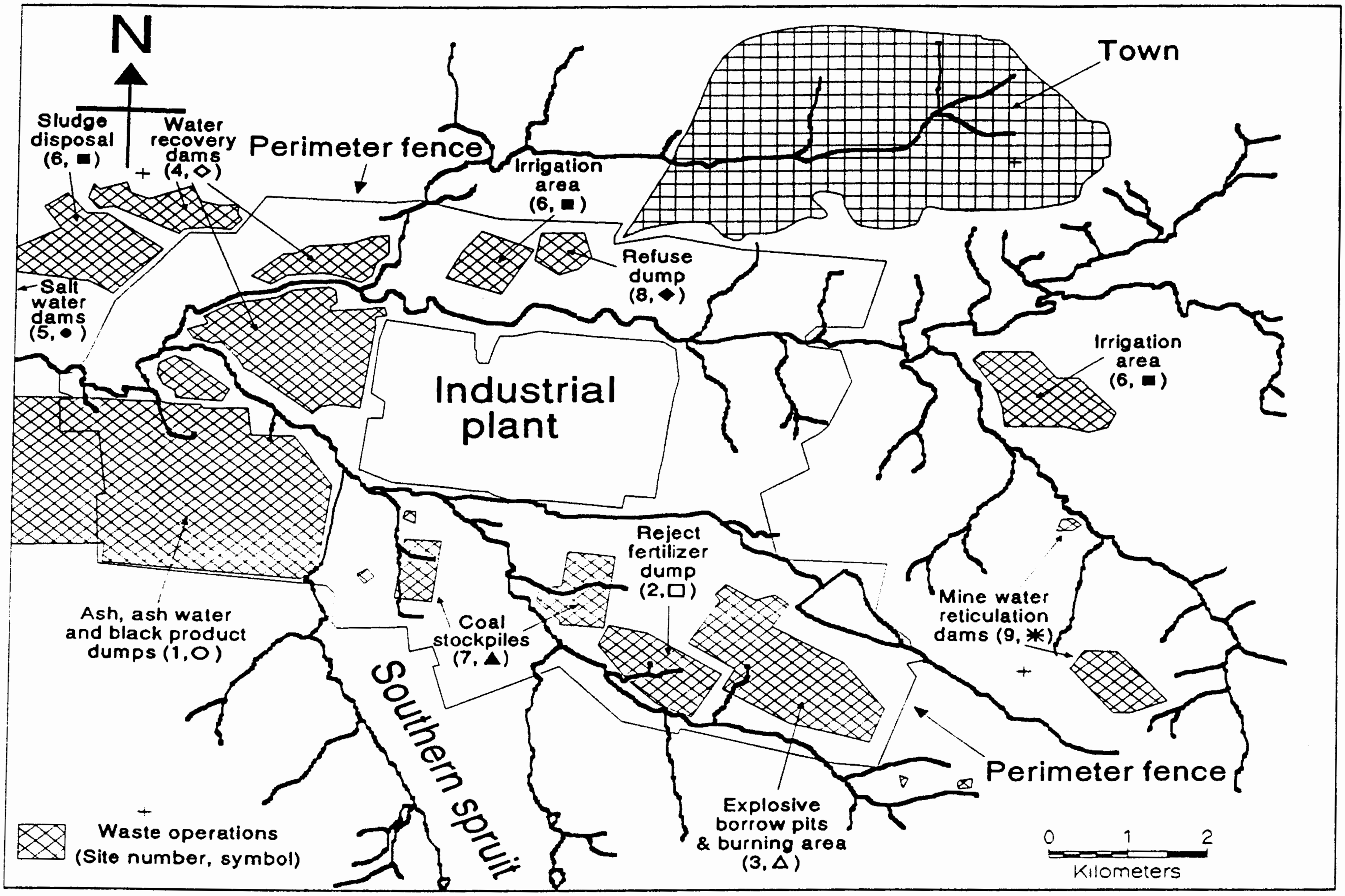


Figure IX.3. The waste operation in the area monitored.