THE CAPACITY OF SOILS IN THE VAAL DAM CATCHMENT TO RETAIN SULPHATE FROM ATMOSPHERIC POLLUTION

A Report to the Water Research Commission

by

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EXECUTIVE SUMMARY

This report presents the results of a one-year study to assess the way in which the soils of the Vaal Dam catchment react with atmospheric additions of sulphate and other solutes (so-called acid deposition) and, in so doing, modify the salt load in runoff from the catchment.

The objectives of the study were: to collect, and investigate the sulphate retention capacity of representative soils in the Vaal Dam catchment; to compare them with soils elsewhere to find out whether sulphate enrichment from atmospheric additions may have taken place; and to explore the possibility of describing the salt flux through the soil mantle of the catchment by means of computer models. All of these objectives have been met, although the modelling work was curtailed when it was discovered that the scope for chemical (as opposed to purely physical) prediction of solute movement is limited unless new subroutines are written into the models.

The study began with the computer-processing of information on land types of the area, obtained from existing maps and memoirs. This allowed the areal extent of each soil series occurring within the catchment to be calculated. Soil series were then grouped into a small number of *ad hoc* classes based on profile morphology, texture and other properties. A manageable number of representative soils (19 profiles) was then sampled in the field and characterized physically and chemically in the laboratory.

The soils were subsequently investigated in detail with respect to their sulphate retention characteristics by contacting them with sulphate-containing solutions (dilute sulphuric acid or neutral salts) in different ways: as saturated pastes, as dilute suspensions, or by leaching through columns. Chemical composition data from rainfall monitoring stations in the catchment were used as a basis for deciding on appropriate concentrations of the equilibrating solutions.

It was found that the saturated paste data were of little value in estimating sulphate sorption because the narrow soil:solution ratio would have required unrealistically large sulphate concentrations for the estimation of sorption capacity. Sulphate retention capacity was therefore determined initially using data from dilute suspensions (equilibration of 4 g soil with 200 ml of a solution containing about 6 mg L^{-1} sulphate). This wide soil: solution ratio is equivalent to 50 years of rainfall (1000 mm per annum) reacting all at once with a 1 m thick soil mantle.

The sulphate retention capacity of most of the soils could not be determined accurately by this method because of low sorptivity and the simultaneous desorption of significant concentrations of sulphate already present in the soil. Furthermore, many of the soils treated in this way were prone to strong clay dispersion and the supernatants proved impossible to clarify sufficiently for analysis of sulphate by ion liquid chromatography.

However, after having accurately estimated sulphate sorption capacity of the most sorptive soil by the suspension equilibration method described above, it was possible to rank all of the soils on a relative scale by measuring their retention behaviour with the much more sensitive leaching column method, which also proved to be free of the clay dispersion problem. This measurement consisted of counting the number of pore volumes of leachate required before the breakthrough of sulphate occurred (as measured by an upturn in EC which had been correlated with sulphate concentration) from an influent sulphuric acid solution containing 12 mg L^{-1} sulphate. The sulphate retention characteristics of all the soils was thus estimated, and then related to land type data (broad classes of soils and their depths) so that a relative index of sulphate retention could be calculated for each of the subcatchments. This index will be valuable in monitoring the historical and future trends in Vaal Dam water quality by comparing it with the runoff composition in each of the monitored subcatchments.

The soils of the catchment show some signs of having possibly been influenced already by the enhanced atmospheric additions of sulphate which characterise the ETH, in that they contain twice as much sulphate, relative to TDS in the saturation extract, as a comparable set of soils from southern Natal. A more systematic and extensive sampling will be needed, however, to ascertain whether this trend is not confounded by a maritime influence.

The overall capacity of the catchment soils to retain sulphate, and thus limit the translation of atmospheric additions into an increment of salts in the drainage, is small. Most of the soils studied had a negligible capacity to retain sulphate. As much as two-thirds of the catchment consists of soils having less than 40% of the maximum retention capacity for any one catchment (nominally about 11 g m^{-2} in Wilge 1), while only about one-sixth of the catchment's area is taken up by subcatchments with a significant capacity to retain sulphate. These subcatchments are the wettest, however, and will consequently make a disproportionate contribution to water quality in the dam.

Soil acidity, and especially the acid saturation of the exchangeable cation suite, appears to relate strongly to sulphate sorption capacity. This commonly measured property may prove to be an effective means of extrapolating the results of this study to other areas in South Africa, although the relationship needs to be tested against a larger number of soils because the relationship could be confounded by the fact that sulphate may accumulate in less weathered soils as soluble salts, simply on account of a lower degree of leaching.

The prognosis made by Herold and co-workers regarding drainage water salinisation resulting from atmospheric additions of sulphate to soils of the catchment, warrants discussion in the light of these results. On the one hand, it seems clear that sulphate retention by the soil mantle is insufficient to invalidate the assumption of mass equivalence between sulphate input from the atmosphere and TDS output in the drainage water. On the other hand, after considering the data pertaining to water-soluble salts, it is difficult to anticipate a degree of atmospherically induced salinisation, even in the longer term, which would be detectable above the natural background concentration of salts being released by normal leaching processes. This suggests that factors such as climatic variation, which will alter - both seasonally and over longer periods - the degree of dilution of the natural salt flux in the catchment, may have a greater impact on water quality changes than will air pollution. The question which remains to be answered, however, is whether the soluble salt (and sulphate) concentrations in the Vaal Dam catchment soils are indeed of natural origin, or whether their almost twofold greater magnitude, on average, than that of the southern Natal soils is a legacy of increased anthropogenic impact over the past few decades. A new research programme initiated by ESKOM is examining the geographic distribution of soluble salts and sulphate in South African soils. Hopefully this will shed more light on the matter.

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Mr F P Marais	Water Research Commission (Secretary)
Dr G C Green	Water Research Commission
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LIST OF ABBREVIATIONS

AAS : Atomic absorption spectrophotometry

AMBIC: Ammonium bicarbonate

CCWR : Computing Centre for Water Research

EC : Electrical conductivity

ETH : Eastern Transvaal Highveld

GIS : Geographical information system

HRI : Hydrological Research Institute

ILC : Ion liquid chromatography

ISCW : Institute for Soil, Climate and Water (formerly SIRI)

PWV : Pretoria-Witwatersrand-Vereeniging region

PZC : Point of zero charge

SAR : Sodium adsorption ratio

SIRI : Soil & Irrigation Research Institute (now ISCW)

TDS : Total dissolved solids

WRC : Water Research Commission

CHAPTER ONE

INTRODUCTION

1.1 Rationale

Atmospheric deposition of sulphate emanating from the combustion of fossil fuels has been implicated as a significant contributing factor in the increased TDS load in water from the Vaal Dam catchment (Taviv & Herold, 1989; Herold & Gorgens, 1991). It is vitally important to assess the potential for such deterioration of Vaal Dam water quality, since it will result in greater water treatment costs from an industrial point of view. A monthly time step hydro-salinity model was used by Herold and Gorgens to predict the continued increase in salinity, given the load of sulphate already stored in the catchment from pre-1988 deposition, and the prevailing hydrological conditions (*ca.* 2 x 10^6t salt - i.e. 1.4 x 10^6t of SO_4). In this simulation, soil solution storage capacities consistent with soil water depths of 500 and 1000mm were catered for. The deeper storage was suggested as a means of crudely mimicking the effect of sulphate sorption by soil. It was clear, however, that uncertainty regarding such reaction of deposited SO_4 with the soil mantle had resulted in a significant range of possible catchment response times and absolute surface water TDS loads, and it was therefore recommended that these interactions be assessed. This project, initiated and funded by the Water Research Commission of South Africa, aims to provide a basis for such an assessment by identifying the dominant soil types in the Vaal Dam catchment and establishing the extent of their chemical interaction with solutes - chiefly sulphate - which are added from the atmosphere.

1.2 Project objectives

The objectives of the study were to:
(i) Obtain representative samples of the major soil types in the Vaal Dam catchment.

(ii) Conduct a laboratory investigation into their capacity for sulphate attenuation.

(iii) Make use, where appropriate, of computer models to calculate the salt flux through the catchment soil mantle, adjusting the estimates as far as possible to include the effects of plant uptake and microbial attenuation.

(iv) Compare unadulterated soil profiles in the catchment (and especially in the proximity of the Pretoria-Witwatersrand-Vereeniging (PWV) and eastern Transvaal highveld (ETH) regions) with similar soils elsewhere (e.g. southern Natal) to assess whether significant accumulations of sulphate have already occurred due to atmospheric pollution.

CHAPTER TWO

LITERATURE SURVEY

2.1 Introduction

The chemical composition of atmospheric precipitation is complex. The diverse chemical reactions which follow the infiltration of rain water into soil further add to the complexity of assessing surface water salinisation potential arising from atmospheric deposition. There may, however, be some opportunity for reducing this complexity in experiments designed to simulate the effects of polluted rain - without sacrificing applicability. The review of published literature on acid rain and related subjects which follows is guided by this objective as well as by the need to assess current knowledge of processes and their likely consequences in the Vaal Dam catchment.

2.2 Atmospheric deposition

2.2.1 Chemical composition

Pollutants washed from the atmosphere by rain, dew, hail, snow, etc. are termed **wet deposition**. The sum of the wet deposition and the particulate matter which gravitates towards the earth's surface is termed **bulk deposition**. Composition data for bulk deposition indicate that the major anions are CO_3^{2-}, SO_4^{2-}, NO_3^- and Cl^-, and that the cations NH_4^+, Ca^{2+}, Na^+, H^+, Mg^{2+}, and K^+ are all well represented (Tyson *et al.*,1988; see also Table 4 in Chapter 4). The extent to which dust from the catchment contributes to the electrolyte load in bulk deposition is uncertain, but the deposition may nevertheless be assumed to consist of acids (H_2CO_3, H_2SO_4, HNO_3, and HCl) which are at least partially neutralised (Peterson, 1986). Important components of **gaseous deposition** include the oxides of sulphur (SO_x, and particularly SO_2), oxides of nitrogen (NO_x), and ammonia (NH_3). These components are adsorbed on soil or plant surfaces (and even absorbed within foliage) and it can be anticipated that in an unharvested, well drained system they will ultimately be oxidised and released to the soil solution as SO_4^{2-} or NO_3^- (Reuss & Johnson, 1986), further boosting the atmospherically derived quantities of these ions. The sum of gaseous and bulk deposition is termed the **total deposition.** Gaseous deposition is the most difficult to quantify and the recently presented range of estimates of sulphate deposition in the Vaal Dam catchment, from 3.12 to 6.62 g $m^{-2}yr^{-1}$, attests to the uncertainty of estimation (Herold & Gorgens, 1991). No regional estimates of total N deposition appear to be available, although the data presented in Chapter 4 give some indication of the N flux and the implications are discussed in the next section.

2.2.2 Chemical simulation

Simulating the reaction of acid rain with soil demands a leaching procedure, which can be performed in two ways: either by passage of the solution through a column of soil and analysis of the effluent (usually in pore volume increments), or by equilibration of a fixed proportion of soil to solution (usually by preparing a dilute suspension, shaking overnight, and then separating a supernatant for analysis). The latter method, if conducted over a range of sulphate concentrations, permits adsorption isotherms to be constructed for each soil.

Reuss and Johnson (1986) have the following to say about estimating the SO_4^{2-} sorption capacity of soils:

> "There seems to be no reasonable alternative to the experimental determination of adsorption isotherms, at least for the most common soil series. This could be supplemented by a concerted effort to relate SO_4^{2-} adsorption properties, including reversibility, to characteristics that are routinely available from standard soil surveys."

On the other hand, many investigations of SO_4^{2-} attenuation have made use of soil columns and the plotting of characteristic breakthrough curves which are usually of great diagnostic value (David et *al.*, 1991; Huete & McColl, 1984; Gaston *et al.* 1987 , Bloom, Mansell, Rhue & Volk, 1987; Fuller & Warrick, 1985). Ideally, both approaches should be followed since they provide complementary information about soil behaviour.

While the SO_4^{2-} anion constitutes a greater fraction of the total atmospheric anion load and is therefore the most important to include in simulated deposition, there are still significant quantities of the NO_3^- anion (Tyson *et al.*, 1988) and it is therefore appropriate to assess whether loading of this anion must also be modelled. The NO_3^- anion is unlikely to leach into surface waters in N limited systems (Reuss & Johnson, 1986) and is therefore unlikely to contribute to the salinisation of these waters. In their consideration of the Vaal Dam catchment, Herold and Gorgens (1991) have followed this rationale, proposing that essentially complete biological attenuation of atmospherically deposited NO_3^- is occurring, based on the observation that the NO_3^- concentration in surface waters is negligible.

Chloride is also fairly well represented in the anion suite of atmospheric deposition (Tyson et *al.*, 1988). The possibility of sorption site competition and an ionic strength effect on solution pH and cation exchange reactions suggests that at least some consideration should be given to estimating its contribution to reactions which affect the salinity of drainage from the soil.

Apart from H^+, the main cations added to soil by acid deposition are NH_4^+, Ca^{2+}, Mg^{2+}, K^+, and Na^+ (Tyson *et al.*, 1988; Patel et *al.*, 1989; see also Chapter 4). The salts of basic cations are usually considered to have originated to a large extent from the reaction of atmospheric acids with the exchangeable cations in suspended dust. For this reason it may be unnecessary for simulation experiments to include salt solutions since in any mass balance type of calculation it could be assumed that the dust particles contributing to the salt load emanated from the soil surface in the catchment. Some comparison of neutral salt solutions with acids may nevertheless be instructive.

Unlike the base cations, NH_4^+ will acidify the soil through nitrification (Reuss & Johnson, 1986). Since it can be expected that the NH_4-derived N will be biologically attenuated, simulation experiments which omit a vegetation component could well be simplified by substituting H^+ for NH_4^+ in the leaching solution.

Intermittent concentration of the soil solution by evaporation is another factor which needs to be accounted for since sorption of SO_4^{2-} is affected both by its own concentration and by the background ionic strength. Laboratory simulation should therefore also be conducted with solutions more concentrated than those typical of rainwater composition.

The pH of simulated leaching solutions can best be taken as the default value arising from a charge balance calculation. The acidification potential from gaseous deposition of SO_2 would therefore be included ($SO_2 + H_2O = H_2SO_3$, $H_2SO_3 + 1/2\ O_2 = H_2SO_4$). The consideration of pH *per se* is not likely to be critical, however, in view of the buffering effect of soil surfaces as well as biological mediation of pH in field soils. A comparison of acid and neutral salt solutions having the same sulphate concentration should nevertheless be conducted to assess the effect of pH on leachate composition.

2.2.3 Soil and biological attenuation

It can be anticipated that the capacity of the Vaal Dam catchment to buffer salinity generated by atmospheric pollution will be closely related to its capacity to attenuate sulphate, either in the biomass or within the soil mantle. Any sulphate not thus immobilised can participate as an accompanying anion in the leaching of metal cations displaced by protons from soil surfaces according to the following exchange reaction:

$$\text{Soil-}[\textbf{Metal}]_2 + \textbf{H}_2\text{SO}_{4(aq)} = \text{Soil-}(\textbf{H})_2 + [\textbf{Metal}]_2\text{SO}_{4(aq)} \qquad (1)$$

The following discussion explores the nature of the various sulphate sinks which are responsible for diminishing the salinisation process represented by reaction (1).

a) Soil attenuation

The adsorption of sulphate in highly weathered soils differs significantly from that in less weathered soils because of the comparatively small amount of permanent negative charge associated with kaolinitic clay in the former soils, and due to the presence of amphoteric hydrous metal oxides (Mott, 1981). Adsorption of sulphate by the typical 2:1 layer silicate clays (mica, smectite, etc.) found in less weathered soils is negligible. According to Mott (1981), the adsorption of sulphate on kaolinite is specific but reversible and it is this reversibility which contributes to the so-called "first flush effect" observed after heavy rains where the initial runoff is relatively saline. The metal hydrous oxides, most commonly occurring as the minerals gibbsite, goethite and hematite, sorb SO_4^{2-} strongly when they acquire a net positive surface charge under acidic conditions. Such amphoteric behaviour is well known and is explained in a number of texts, including those of Parfitt (1978) and Mott (1988). In effect, if the solution pH is below the PZC (point of zero charge) of the soil (Metson, 1979; Skeffington & Brown, 1986), protonation of hydroxyl groups is favoured and sulphate adsorption occurs by displacement of more labile water ligands as follows:

$$\text{Soil-(OH)}_2 + H_2SO_{4(aq)} = \text{Soil-}(OH_2^+)_2 + SO_4^{2-} \qquad (2a)$$

$$\text{Soil-}(OH_2^+)_2 + SO_{4\,(aq)}^{2-} = \text{Soil-}SO_4 + 2H_2O_{(aq)} \qquad (2b)$$

Sulphate is thus adsorbed on hydrous oxide surfaces more strongly than on the surface of kaolinite, forming an inner-sphere complex (Parfitt, 1978; Sposito, 1986). Such sorption is irreversible to some degree at sufficiently low pH (Mott, 1981). Reactions 2a and 2b clearly indicate that acidity and sulphate attenuation are complementary, which means that more retention can be expected from sulphuric acid than from a solution of a neutral salt having the same sulphate concentration.

Other factors which modify the sorption behaviour of sulphate are crystallinity of the Al and Fe compounds, often assessed by the ratio of oxalate- to dithionite-extractable Fe and Al (Johnson *et al.*, 1986), and the presence of humic substances. The latter have a low PZC and can therefore be expected to repel SO_4^{2-} even at relatively low soil pH values (David *et al.*, 1991). It is also known (David *et al.*, 1991) that sulphate sorption by sesquioxidic soils is relatively sensitive to the SO_4^{2-} concentration in solution, with higher SO_4^{2-} concentrations giving rise to higher adsorption capacities at a given pH. This has potentially important implications for computing the effects of future increases in atmospheric pollution. Specifically, the attenuation capacity of the soil will increase as the sulphate load increases.

An alternative mechanism by which sulphate immobilisation can be explained is the precipitation of an aluminium sulphate mineral such as alunite, jurbanite or basaluminite which, in high sulphate, low pH environments, assumes a greater stability than that of existing aluminium solids such as gibbsite and kaolinite (Adams & Rawajfih, 1977; Fey *et al.*, 1990). The effects of factors such as concentration and pH on sulphate solubility will be the same as those applying to adsorption.

Calcium carbonate has the capacity to exchange CO_3^{2-} for SO_4^{2-} at its surface, an exchange that may lead to the incorporation of the sulphate anion into the crystal lattice (Mott, 1981; Metson, 1979). Calcareous soils are relatively common in the Vaal Dam catchment and may constitute a possible sink for sulphate. The reaction is relatively weak compared with that of the sesquioxides, however, and is therefore unlikely to contribute significantly to sulphate attenuation. Concerning salinisation, the release of carbonate as sulphate is adsorbed, implies that the overall TDS flux will not be reduced.

Huete & McColl (1984) found that a good estimate of the SO_4^{2-} adsorption capacity of a soil, which takes into account both the amphoteric and the permanent charge characteristics of the soil components, is the value of the PZC of the soil relative to the soil pH. According to Metson (1979) it has been shown that the difference between the suspension pH in 1M KCl and in water could also be used to indicate the net charge on soil colloids. In particular, if this difference is small or negative (for the subtraction of pH(KCl) from that in water), a strongly sesquioxidic colloidal fraction with relatively large anion exchange capacity is indicated. Conversely, a large, positive difference signifies predominantly negative charge and a small capacity to retain sulphate. As these two pH measurements constitute part of the routine preliminary assessment of soils, they could be employed as a crude but useful guide to SO_4^{2-} sorption capacity.

Barium sulphate is characterised by an exceedingly low solubility, and it is possibile that soils endowed with a sufficient concentration of exchangeable Ba will attenuate sulphate (and the attendant salinity). There has been one locally reported case of possible Ba control of sulphate solubility [1], while Tabatabai (1982) has also drawn attention to the possible role of Ba in reducing the extractability of sulphate - in some soils - with a calcium phosphate solution.

Most reports have shown that subsoils generally contain more [1]native, sorbed sulphate and also show greater sulphate retention

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[1] C.C. du Preez, University of the Orange Free State: personal communication.

capacities than their overlying topsoils. The commonly higher clay content and often lower pH of subsoils, as well as the paucity of organic matter, could all contribute to this partitioning (Metson, 1979). The consideration of soil depth at sampling is therefore important.

b) Biological attenuation

The extent to which atmospheric additions of NO_3^- and SO_4^{2-} are absorbed by plants will depend on whether or not soil N and/or S concentrations are naturally deficient. An example illustrating the potential magnitude of SO_4^{2-} removal in crops was given by Suarez & Jones (1982), who reported that large atmospheric doses (15 kg ha^{-1}) of sulphur in the south-eastern U.S.A. were not sufficient to replace all of the sulphur removed by harvests. Thompson (1984) has noted that S deficiencies anticipated in crops growing on soils derived from sandstone, granite and dolomite are uncommon in South Africa, whereas in Zimbabwe fertilizers contain a mandatory 6.5% S to correct what would otherwise presumably be a widespread problem of S deficiency. This constitutes circumstantial evidence for a regional atmospheric contribution to the S requirement of crops. Herold & Gorgens (1991), however, have concluded from a computation of the agricultural S balance in the Vaal Dam catchment that less S is removed by crops, on average, than is applied incidentally in the form of fertilizers containing compounds such as gypsum and ammonium sulphate. This suggests that all atmospherically derived S effectively remains within the catchment. Some of the added S may be incorporated in the unharvested biomass. The transfer of S both to and from the organic pool may lag by a number of decades depending on climatic conditions and the intensity of microbial activity. Organic S may thus represent a long-term repository for added sulphate; this fraction usually represents the main sulphur pool in soils (Reuss & Johnson, 1986). However, the rate of biological sulphur accumulation may be limited by the relatively small annual biomass requirement. In systems subjected to heavy atmospheric deposition (e.g. 80 kg kg ha^{-1} per annum is the high estimate for the Vaal Dam catchment - Herold & Gorgens, 1991), and where hydrological processes are conducive to solute transport, biological assimilation will probably be of far less importance than soil chemical properties in restricting the efflux of sulphate.

Microbial incorporation of S and N into the organic pool and subsequent remineralisation can be affected by acid rain, although there are contrasting reports as to the nature of the response (Killham *et al.*, 1983; Bitton & Boylan, 1985; Lee, 1985; Skeffington & Brown, 1986). Short-term microbial influences should, however, be small enough to be discounted in brief laboratory experiments - at least as far as sulphur is concerned.

2.3 Atmospheric deposition impacts in Europe and North America

Taviv & Herold (1989) pointed out that the impact of acid rain in industrialised countries has so far been assessed primarily in terms of acidification rather than salinisation of surface waters. Once basic cations have been depleted, soil pH drops sufficiently for the dissociation of Al to occur (Reuss & Johnson, 1986) and the acidic percolate, loaded with soluble aluminium, sulphate, chloride and nitrate and with a reduced organic acid and bicarbonate content (Johnson *et al.*, 1984; Wright, 1984) gives rise to the acidification of surface waters (Krug & Frink, 1984) which is reputed to have had disastrous environmental consequences (see, for example, a number of articles cited by Skoroszewski & Chutter, 1988). The extent to which water acidification occurs naturally as opposed to being induced by acid rain has been debated by Krug & Frink (1984), Johnson & co-workers (1984), Seip & Dillon (1984) and Wright (1984). The conclusions of a major American project, documented in a 6000 page report, were that the effects of acid rain on aquatic biota are clearly less severe than was initially believed and that the only really threatened ecosystems were those with very low buffering capacities (Roberts, 1991a). The high base status of much of the Vaal Dam catchment soil mantle implies strong buffering against acidity and one could thus deduce that surface water acidification is unlikely to result from current acid deposition inputs.

2.4 Conclusions

There has apparently been no investigation focussing specifically on surface water salinity as a problem caused by atmospheric pollution. The present study is thus possibly unique in an international context, which lends weight to the potential impact its findings may have on the development of pollution control policies. Although there are no empirical precedents to go by, there is a sound body of knowledge on the chemistry of sulphate and acids in soil and there is therefore good reason to believe that the assumptions inherent in making hydrological prognoses about salt build-up should be fairly easy to test by column leaching and suspension equilibration techniques. These methods would be applied to representative surface and sub-surface soil samples from the Vaal Dam catchment, using solutions to simulate the effect of sulphate (as an acid or neutral salt) in rainfall or in more concentrated soil solutions. The next chapter describes the experimental approach which was devised after reviewing the literature on acid rain and its effects on soil.

CHAPTER THREE

SAMPLING, DATA COLLECTION AND EXPERIMENTAL METHODS

3.1 Introduction

In this chapter the soil sampling localities and techniques, data gathering and experimental approaches are described. A total of 19 soil profiles from the Vaal Dam catchment were identified and sampled. Data from atmospheric deposition sampling stations were procured in order to calculate the chemical composition of precipitation, which could then be simulated in laboratory leaching experiments. Two other sets of soil samples were procured: about 30 benchmark profiles from the land type survey in areas within the Vaal Dam catchment were selected, and samples of these soils were obtained from the ISCW; and a further set of 40 profiles were identified and sampled in southern Natal for comparison with the Vaal Dam catchment, specifically to investigate the degree of sulphate accumulation which may have occurred as a result of protracted atmospheric additions. The experiments themselves comprised a variety of chemical extractions for purposes of sample characterisation, followed by a series of equilibration experiments involving (i) saturated pastes, (ii) dilute soil suspensions, and (iii) column leaching with solutions of a composition designed to simulate the chemical impact of atmospheric inputs under a variety of conditions.

3.2 Soil inventory and sampling

3.2.1 Inventory of Vaal Dam catchment soils

To ascertain the range of soil series in the Vaal Dam catchment and their extent, land type maps and memoirs produced by the ISCW were consulted. A land type is defined as a region of uniform terrain type, soil pattern and climate. Its locality is given on a land type **map**. In the land type **inventories**, the portion of the land type and geomorphic position occupied by each soil series are described, as well as soil series, depth and clay content. To arrive at the area of each soil series as a percentage of the Vaal Dam catchment as a whole, the Arcinfo GIS package was used, first to digitise (trace by mouse) the land type boundaries from land type maps and then to calculate both the area and percentage area occupied by each land type in the catchment. This information was then interfaced with a Fortran programme similar to that described by Schulze, Angus & Guy (1991) to calculate the percentage of each soil series in the catchment by weighting its percentage in a land type as given in the land type memoirs with the percent of the catchment occupied by the land type. Additional information that the programme was designed to access were soil depth and clay content in the 15-25 and 25-35% ranges, neither of which are conveyed automatically by the soil series classification booklet. Figure 1 shows the final digitised land type map of the catchment. Appendices to this report in the form of computer discs containing the digitised map data have been lodged with the WRC to save report production costs. It should be noted that the land type information is based on the earlier, binomial system for South African soil classification (MacVicar *et al.*, 1977).

A summary of the main categories into which the soil series were grouped, together with their total area in the catchment, is given in Table 1. The areal extent of each soil category was used as the basis for ensuring that the soil samples collected were as representative of the catchment as possible. While the entire operation described above was fairly laborious, it produced very worthwhile information in a form which, because of ease of computer retrieval, is likely to be of some value for other land-use planning purposes in the region.

3.2.2 Sample collection in the Vaal Dam catchment

Samples were collected during the last week of December, 1991. The sample site locations are shown in Figure 2a. The geographic co-ordinates of each sample site, its position in the landscape

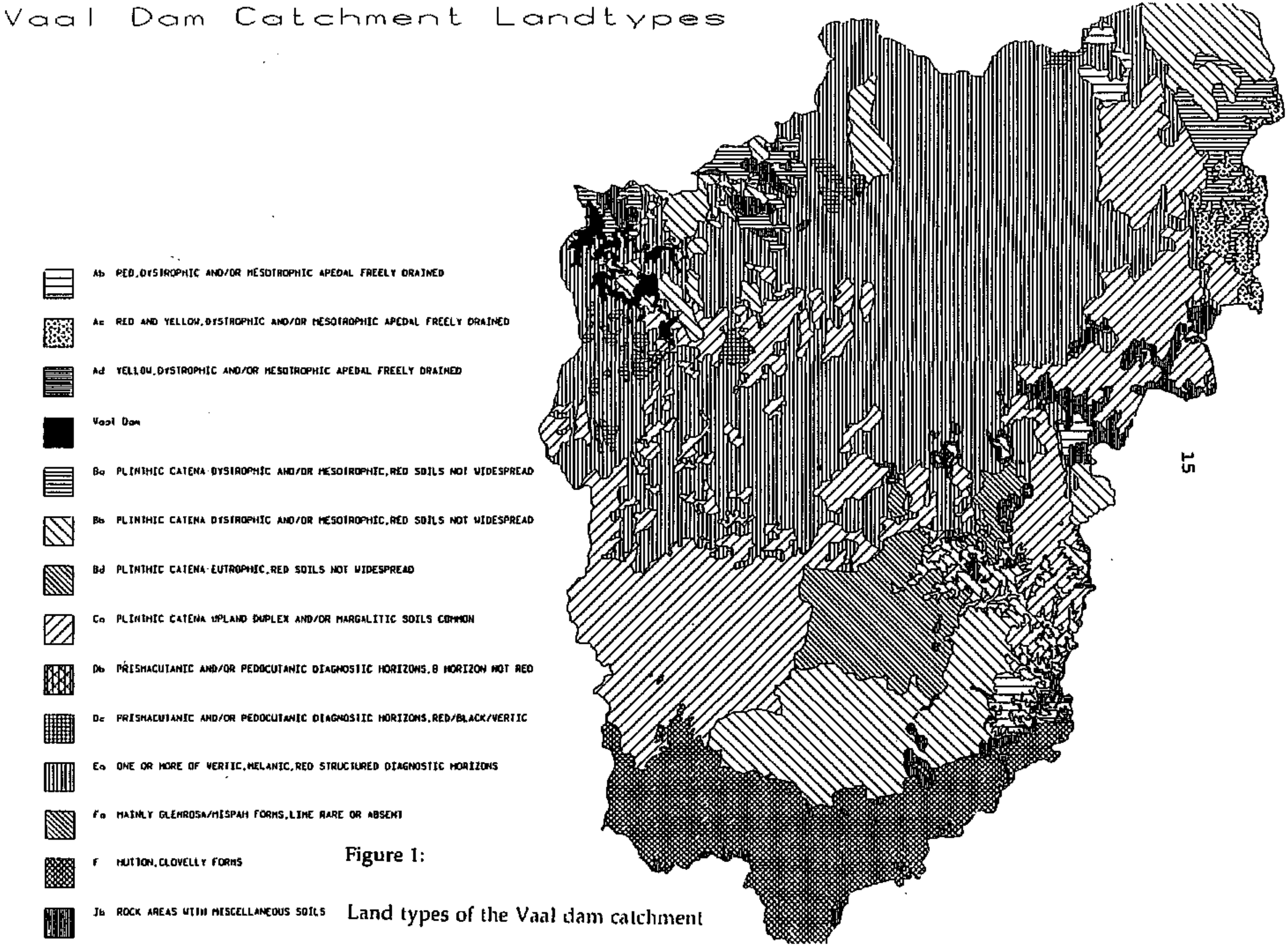

Figure 1:

Land types of the Vaal dam catchment

Table 1. Distribution of major soil classes in the catchment

Soil category		areal extent (%)
1 Grey soils		
1.1 - sands		9.3
1.2 - clays		9.8
1.3 - loams		15.2
	Total	34.3
2. Black clay soils		
2.1 - calcareous		10.7
2.2 - non-calcareous		14.0
	Total	24.7
3. Red and Yellow soils		
3.1 - plinthic:		
3.11 sands		1.9
3.12 clays		1.9
3.13 loams		7.8
3.2 - humic:		
3.21 sands		1.1
3.22 clays		2.2
3.23 loams		4.5
3.3 - neither humic nor plinthic		2.3
	Total	19.4
Balance of area (rocky, swamps, eroded etc)		21.6
	Total	100

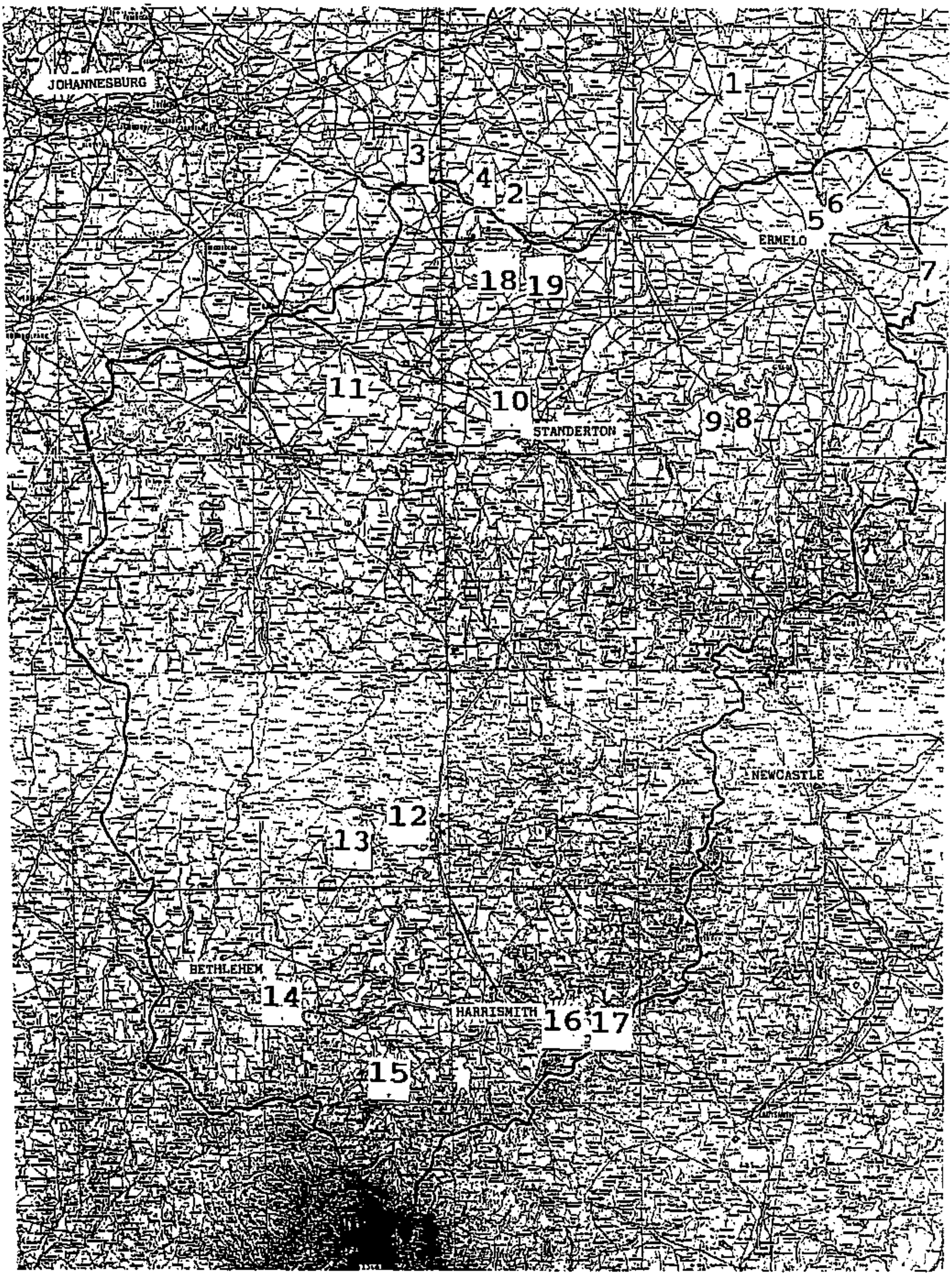

Figure 2a. Soil sampling sites in the Vaal Dam catchment

(terrain morphological unit), the depths of the A and B horizons, and a brief site description were recorded. In general, samples were collected to ensure a good spread across the categories in Table 1, by identifying those areas in which preselected soil types were known to occur with a high incidence. Planned routes were then followed and road cuttings inspected at intervals until suitable sampling sites were found. Samples of approximately 10kg were taken from topsoil and (in most cases) subsoil horizons of excavated profiles. The classification of the sampled soils is presented alongside characterisation data in Chapter 4.

3.2.3 Land type soil samples

Land type memoirs pertaining to the Vaal Dam catchment were searched for benchmark profiles of soils which were similar to those which had been sampled in the field, and small samples of surface and subsurface horizons of these profiles were procured from the ISCW in Pretoria which houses a sample bank of all soils collected during the land type surveys. The objective was to obtain an enlarged collection of soils from the catchment and, especially, to take advantage of the detailed chemical and mineralogical characterisation documented in the memoirs. Further information on these soils appears in Chapter 4.

3.2.4 Soil sampling in southern Natal

The humid and sub-humid interior of southern Natal and East Griqualand between Bulwer and Matatiele is characterised by climatic conditions and a range of soil types which is similar to much of the Vaal Dam catchment and the ETH. To test the hypothesis that the historical atmospheric deposition load has already affected soil chemical properties (and especially the sulphate levels) in the Vaal Dam catchment, a matching suite of soils was needed, for the purpose of comparison, from an area in which the impact of atmospheric deposition could be expected to be considerably lower.

A private soil surveyor, W Z Heathman, was commissioned to collect samples from soil profiles selected for their similarity to those from the Vaal Dam catchment and a total of about 30 profiles (60 samples) were classified, described and sampled (Figure 2b). Further information appears in Chapter 4.

3.3 Atmospheric deposition data

A hard copy of bulk deposition data from six monitoring stations, the locations of which are shown in Figure 3, was acquired from the Hydrological Research Institute (HRI) and a total of over 700 chemical analyses of this deposition were processed on a spreadsheet (Quattro Pro) to give a precipitation-weighted mean composition for the bulk deposition at each recording station. The purpose of this exercise, which has apparently not been carried out on this data set before, was to establish realistic values for the composition of simulated acid deposition to be used in equilibration experiments with the soil collection in order to assess their capacity to buffer deposition salinity. A disc containing the processed information in spreadsheet form has been lodged with the WRC.

3.4 Soil characterisation

3.4.1 Diagnostic properties

The soils were air-dried, crushed to pass a 2mm screen and the water content determined by oven-drying. Samples were analysed for standard characterisation properties including particle size distribution (pipette method after sedimentation and screening for sand grades), organic carbon (wet oxidation), pH (1:2.5 soil to solution ratios of water and 1M KCl), exchangeable basic cations, acidity, available phosphorus (KCl or AMBIC extraction and volumetric titration, AAS or colorimetry), EC, soluble basic cations and SAR (in a saturated paste extract made with distilled water). These analyses were performed in the laboratories of the Department of Agricultural Development (Natal Region) at Cedara.

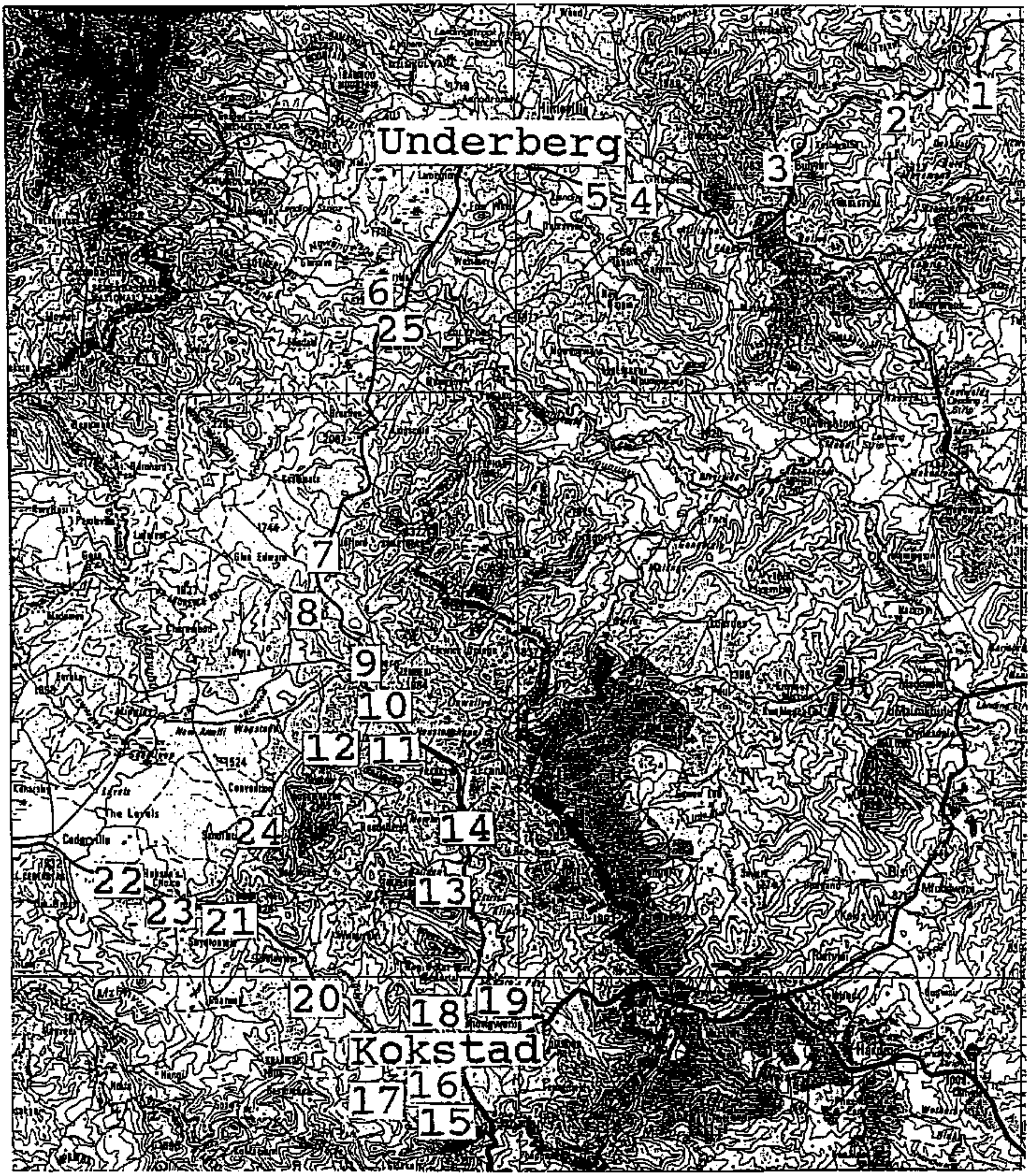

Figure 2b. Soil sampling sites in southern Natal

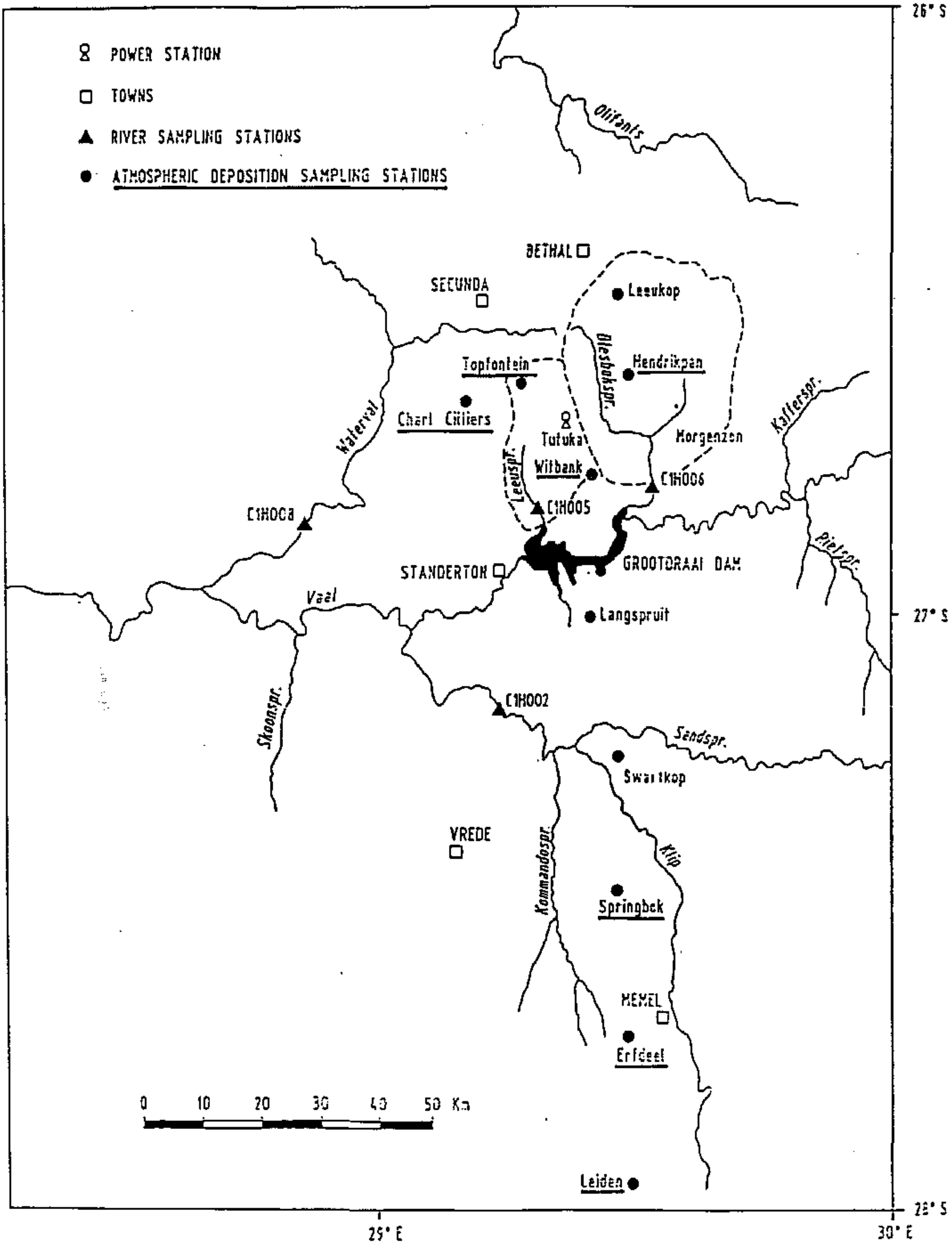

Figure 3. Atmospheric deposition sampling stations for which average bulk deposition data were calculated

Oxalate-extractable iron and aluminium (Mehra and Jackson method described in Page, 1982) and hot, 5M HCl-soluble iron (Fey & Dixon, 1983) were determined on the Vaal Dam catchment soils.

Exchangeable barium was extracted using a pH 7 ammonium acetate solution (Page, 1982). A 5g subsample of soil was equilibrated with 50ml of 1N NH_4OAc for 30 min. The solution was centrifuged, filtered, 2ml of suppressant (50 g L^{-1} KCl) was added, and the extract made up to 50ml. Barium was determined by AAS.

3.4.2 pH response to salt treatment

As mentioned in Chapter 2, an indirect, relative measure of the sulphate sorption capacity of a soil may be provided by the difference in pH measured in water and a concentrated salt solution. In particular, if pH(water) - pH(salt) is small or negative, a strongly sesquioxidic colloidal fraction with relatively large anion exchange capacity is indicated. Conversely, a large, positive difference signifies predominantly negative charge and a small capacity to retain sulphate. Furthermore, if the salt used is a sulphate rather than, say, a chloride, a higher pH in a suspension of the former salt relative to the latter would indicate some degree of specific sorption of sulphate over and above that attributable to indifferent anion exchange.

A 1:2.5 soil to solution ratio was therefore used to equilibrate samples in distilled water, 1M KCl and 0.5M K_2SO_4 solution. The solutions were stirred rapidly initially, and then again after 50 minutes. The pH of the supernatant was taken 10 minutes later, after an electrode contact time of 20 seconds.

3.4.3 Adsorbed sulphate

Adsorbed sulphate was determined in all the soils by extraction with a calcium phosphate solution and analysis by reduction-distillation using the methylene blue procedure (Tabatabai, 1982). Samples of 5g of soil were extracted with 50ml of 500 mg L^{-1} $Ca(HPO_4).H_2O$ by shaking at constant temperature (22°C) for 30 minutes. Where necessary, a 20ml aliquot of the extract was evaporated down in an oven and made up to 2ml for the reductive distillation, to bring the sulphate levels to within detection limits.

3.5 Equilibration experiments

3.5.1 Saturated pastes

Saturated pastes were prepared using distilled water and three increasingly concentrated, simulated acid deposition treatment solutions, details of which appear in Chapter 4. The soil pastes were allowed to stand at constant temperature overnight (21°C) before extraction.

The extracts were frozen immediately after collection and were thawed prior to measurement of pH and HCO_3^- concentration. The pH was measured using a Radiometer PHM Standard pH meter. The HCO_3^- concentration was determined using a Radiometer Autotitrator assembly (PHM meter, TTT 80 Titrator, and ABU Autoburette), according to the Radiometer Applications Manual Method No. 918-354. Sample volumes were 5ml, the maximum burette volume was 0.25ml, and 0.01M HCl was used as titrant. The Titrator settings were: Proportional Band 0.5; Delay Sec. 10; Autoburette speed 40 (or 20 if very low titrant volumes were obtained).

The paste extracts were also analysed for EC, cations by AAS and anions by ILC, details of which are provided below.

3.5.2 Soil suspensions

A 4g sample of the A horizon of each soil from the Vaal Dam catchment was equilibrated overnight with 200ml of either distilled water or sulphate solutions (as sulphuric acid or sodium sulphate) containing between 6 and 24 mg L^{-1} sulphate. The solutions were centrifuged, and 100ml of the supernatant was equilibrated overnight with 2g of the corresponding B horizon (if sampled), while the remainder was collected after filtration for analysis. The supernatant of the B horizon equilibration was also collected for analyses which included measurement of EC, pH, anion composition, and in some cases cation composition.

Similar equilibrations of the East Griqualand soils, with distilled water only, were performed. The equilibrations of the Vaal soils were repeated using 10g soil and 100ml of the treatment solution containing 6 mg L^{-1} sulphate as sulphuric acid.

All equilibrations took place at a constant temperature of ca. 22°C.

3.5.3 Column leaching

Standard perspex leaching columns (5.4cm diameter) were carefully packed with soil according to the method recommended by Fuller & Warrick (1985). Five rounds of glass wool sheeting were placed at the bottom of the columns. Above these were 7cm of the A horizon for soils consisting only of A horizons; if a B horizon had also been sampled, a 7cm depth of B horizon soil was packed first, followed by 7cm of A horizon. The mass of soil was recorded. Two rounds of glass wool were placed on top of the packed soil columns to protect their surfaces from disturbance. The soil columns were sealed with rubber stoppers and wet up from the base prior to leaching to remove air and enhance column stability. The columns were stripped with distilled water until the leachate gave a constant EC reading prior to the application of the treatment solutions. Treatments were applied continuously until breakthrough occurred, as determined by increasing EC values which then levelled off. After breakthrough, distilled water was reapplied in order to study desorption behaviour. The leachate was collected in pore volume aliquots and flow rates were monitored periodically, having been controlled by delivery of the leaching solution through a manifold connected to a constant head Mariotte bottle (Fig.4), and enhanced if necessary by lowering the column height so that the leaching rate was similar for each soil. All the column work was done at a constant temperature of ca. 22°C. (The hydraulic conductivities of the soil samples 2A and 9AB were prohibitively low and they were therefore mixed with 50% m/m sand (soil 14), before packing).

All pore volumes of leachate were analysed for EC and selected fractions were taken for determination of pH, anion and cation composition.

3.5.4 Analytical procedures

For all samples from the various equilibration experiments, EC was measured with a Radiometer CDM83 conductivity meter and pH using a Radiometer ION85 Ionalyser. Cation concentrations (Ca, Mg, Na and K) were determined by standard working conditions for flame spectroscopy with a Varian 275 Atomic Absorption Spectrophotometer (AAS). Anion concentrations were determined using a Waters Ion Liquid Chromatograph (ILC) configuration, *viz.* 714 WISP injection system, 590 Programmable HPLC Pump, Model 430 Conductivity Detector, 745 Data Module, and an IC Pak A Column.

The solutions subjected to ILC analysis were cleaned up by removal of water-soluble organics and divalent cations, the former by passage of the sample through a Millipore C18 Sep-Pak cartridge, and the latter by injecting the sample through a NaEDTA-purged Millipore Accell Sep-Pak filter. Suspended colloid was removed by filtration (0.45μm Millipore filter). ILC is a method particularly well suited to sulphate analysis in aqueous solutions, supplanting the classical turbidimetric method with its greater reliability and sensitivity.

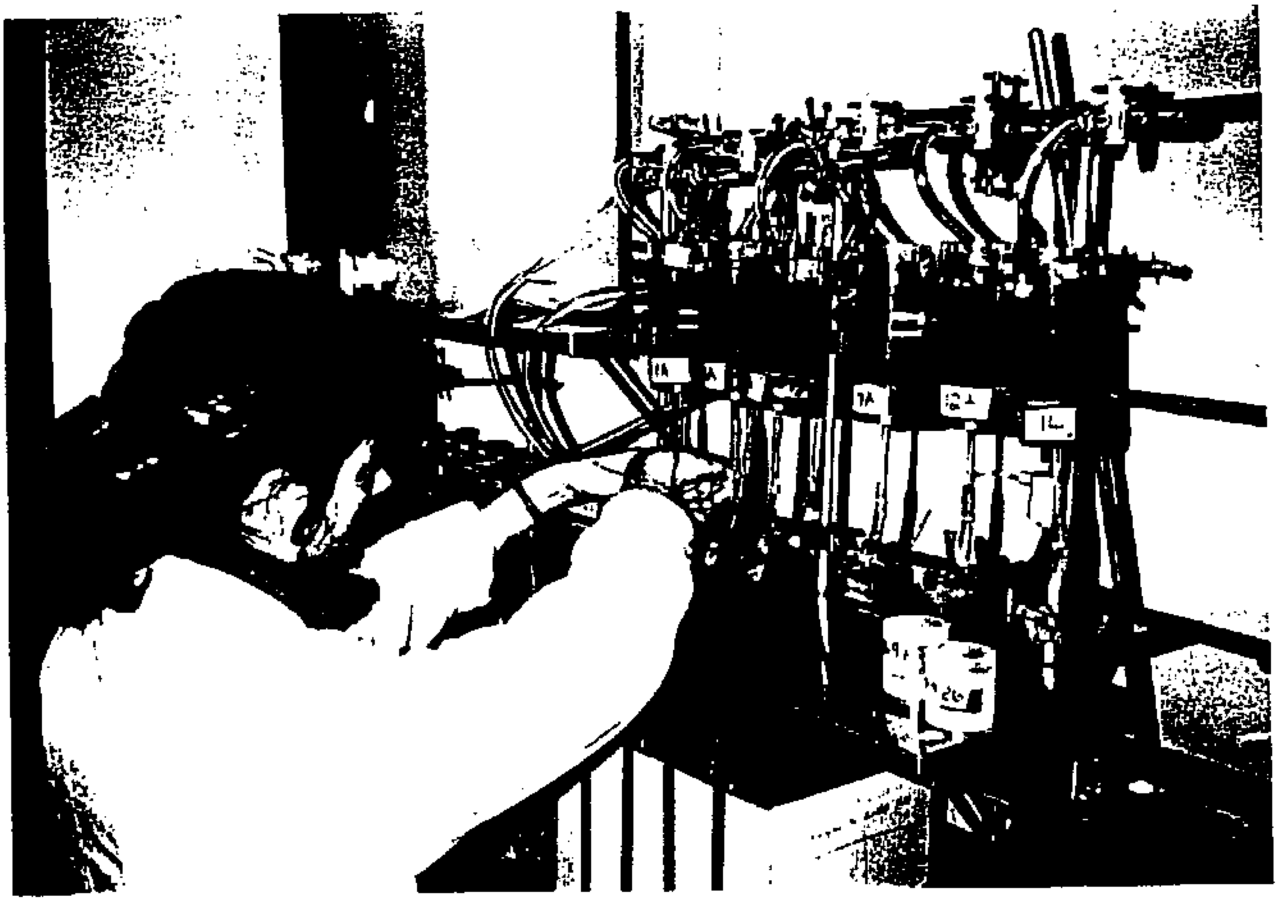

Figure 4. Soil columns connected to manifold leading from constant head reservoir of leaching solution

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Introduction

In presenting the results of this study, consideration will first be given to the properties of the soil collection likely to have an influence on their capacity to attenuate sulphate and thus to buffer the salt load. The results of equilibration experiments designed to evaluate this capacity will then be reported and discussed.

4.2 Nature and properties of catchment soils

The 19 profiles sampled in the Vaal Dam catchment are classified in Table 2 which, together with Table 3, lists pertinent physical and chemical properties of the sample collection. Wide ranges in texture (between 8 and 76% clay), organic carbon content (0.02 to 8%C), acidity (pH 4.7 to 7.5 in water) and saturation extract salinity (EC 7 to 118 mS m^{-1}) are evident. The main objective of obtaining a comprehensive soil characterisation was to investigate whether sulphate sorbing capacity could be related to one or more soil properties in a manner which would permit extrapolation of the results to soil types not included in the study. Other properties, such as the concentrations of barium and amorphous and crystalline Fe and Al compounds, were also assessed and the data are included in subsequent sections.

4.3 Composition of bulk precipitation in the catchment

The precipitation weighted mean chemical composition of bulk deposition collected at seven stations (Fig.3) within the catchment was calculated, and the results are shown in Table 4. It is interesting that the two stations with the lowest sulphate and total electrolyte load (Leiden and Erfdeel) are located furthest from the PWV industrial area (south of Memel in Fig.3).

Table 2. Soil identification and key properties - catchment soils

Sample	Soil	Soil	Soil	COLOUR	TEXTURE						
no.	form	series	category	Moist	Clay	Silt	CoSa	MeSa	FiSa	Org. C	S value
(a)			(b)		%					%	meq/100g clay
1A	Cv	26	3.2.3	5YR 3/2	16.54	14.60	12.72	15.98	39.62	1.15	12.34
1B				7.5YR 6/8	19.61	13.26	11.95	16.92	37.97	0.35	6.69
2A	Ar	30	2.2	7.5YR 2/0	34.31	21.34	10.27	7.42	26.86	1.85	59.94
3A	Gs	18	1.3	10YR 3/7	22.72	10.94	14.03	23.15	28.24	0.81	23.77
4A	Va	31	1.2	10YR 2/2	23.40	12.69	13.68	11.92	38.06	0.92	19.49
4B				10YR 3/1	40.55	10.13	13.8	11.15	25.61	0.45	31.82
5A	Hu	26	3.2.3	5YR 4/6	18.05	12.22	10.65	13.92	45.4	0.75	13.92
5B				2.5YR 4/6	28.03	13.88	8.49	10.74	39.41	0.21	2.57
6A	Av	26	3.1.3	10YR 3/2	14.36	10.50	10.37	16.63	47.31	0.72	4.86
6B				10YR 6/6	19.82	9.22	9.07	15.26	46.86	0.25	6.89
7A	No	11	3.2.2	7.5YR 2/0	35.93	32.87	7.15	4.09	17.78	7.94	7.72
8A	Sd	22	3.2.3	2.5YR 2.5/4	58.09	26.65	1.93	1.57	10.33	2.56	26.96
8B				2.5YR 3/3	75.81	12.38	0.99	0.93	7.97	0.88	23.96
9A	Rg	10	2.2.2	7.5YR 3/0	33.89	17.66	3.03	7.39	36.84	1.22	46.08
9B				7.5YR 2.5/0	42.25	28.75	0.95	2.61	37.53	0.64	53.88
10A	Va	40	1.2	10YR 3/2	40.39	37.55	2.57	2.79	17.05	1.66	19.86
10B				10YR 3/2	52.89	26.45	2.19	2.14	15.49	0.86	24.75
11A	We	22	1.3	2.5YR 3/6	25.50	8.13	9.6	15.6	39.47	0.68	26.88
11B				5YR 4/6	31.63	11.39	10.1	13.6	32.79	0.39	22.32
12A	Cv	26	3.2.3	10YR 4/3	15.95	14.29	2.67	4.64	61.91	0.81	21.71
12B				7.5YR 5/6	25.76	16.34	1.35	3.38	53.77	0.02	10.54
13A	Av	36	3.1.3	7.5YR 3/4	9.31	13.15	1.42	7.03	69.66	0.29	21.82
13B				7.5YR 4/4	15.11	15.38	3.88	4.91	60.29	0.24	16.27
14	Fw	10	1.1	10YR 4/4	8.21	9.57	4.01	13.23	64.46	0.12	39.74
15A	Pn	36	3.3	10YR 5/4	22.42	21.04	2.79	2.62	50.95	1.09	16.58
15B				2.5YR 5/4	24.84	25.11	6.29	3.66	41.13	0.27	21.51
15C				10YR 4/2	36.74	28.55	4.06	3.21	27.55	0.12	23.50
16B	Hu	18	3.2.2	2.5YR 4/8	50.78	22.02	0.45	0.91	26.74	0.22	1.66
17A				10YR 3/3	43.77	18.63	1.98	3.41	29.7	2.46	4.67
18A	Rg	20	2.1	7.5YR 3/2	36.35	30.71	6.56	6.52	21.58	1.21	23.40
18B				2.5Y 3/2	48.17	29.55	4.89	4.35	14.09	0.90	31.44
19A	Sw	31	2.2	10YR 2/1	50.55	28.21	3.16	2.89	15.68	1.07	32.39

(a) symbols A,B and C refer to A, upper B and lower B horizons, of the profile, respectively

(b) as defined in Table 1

Table 3: Additional properties - Vaal Dam catchment soils

Sample	pH	pH	-------	-SATURATION EXTRACTS--------					AMBIC		--KCl EXTRACT.--			Sample
no.	(H2O)	(KCl)	E.C.	Na	Ca	Mg	K	SAR	P	K	Ca	Mg	(Al + H)	Density
			mS/m	--------	--me/l	-----------			——	-----mg/L---		-------	cmol /L	g/ml
1A	5.22	4.41	33.3	0.17	0.67	0.49	0.86	0.2	3	177	266	75	0.30	1.18
1B	5.01	4.39	23.6	0.18	0.52	0.53	0.55	0.3	0	130	139	75	0.45	1.26
2A	6.47	5.11	58.9	3.49	0.82	1.92	0.06	3.0	1	72	1410	1797	0.13	1.08
3A	5.41	4.33	19.1	0.20	0.64	0.54	0.21	0.3	0	145	717	303	0.37	1.20
4A	5.09	4.15	27.1	0.59	0.99	0.80	0.07	0.6	1	74	624	254	0.76	1.19
4B	7.25	5.47	44.2	3.23	0.44	0.43	0.05	4.9	0	194	1479	787	0.08	1.12
5A	5.89	4.81	18.5	0.09	0.70	0.32	0.33	0.1	3	111	423	83	0.07	1.23
5B	4.88	4.21	7.0	0.17	0.16	0.14	0.03	0.4	0	21	81	48	1.11	1.19
6A	4.75	4.05	12.9	0.07	0.31	0.31	0.15	0.1	2	48	86	40	1.08	1.27
6B	4.88	4.11	13.7	0.19	0.29	0.52	0.04	0.3	1	32	115	126	0.67	1.25
7A	5.64	4.70	10.1	0.29	0.13	0.15	0.06	0.8	1	32	246	79	0.62	0.71
8A	5.75	4.87	30.4	0.22	1.17	1.29	0.10	0.2	1	131	1732	762	0.17	0.98
8B	6.42	5.24	20.1	0.45	0.56	0.63	0.02	0.6	0	55	1829	1087	0.07	1.01
9A	6.29	5.31	72.5	0.33	3.75	2.19	0.08	0.2	0	86	2155	667	0.00	1.06
9B	7.31	5.96	41.3	0.33	2.03	1.39	0.04	0.3	0	68	2783	1287	0.08	1.09
10A	5.87	4.92	53.2	0.22	1.91	1.43	0.94	0.2	2	524	938	306	0.05	1.07
10B	6.16	4.93	29.6	1.12	0.91	0.63	0.08	1.3	0	185	1795	657	0.10	1.14
11A	6.30	5.25	53.8	0.42	1.57	1.41	0.79	0.3	0	283	917	358	0.07	1.21
11B	6.87	5.40	64.0	4.30	0.40	0.48	0.06	6.5	0	96	800	507	0.04	1.20
12A	5.92	4.75	35.2	0.16	0.74	0.54	1.37	0.2	2	343	408	115	0.09	1.12
12B	5.26	4.29	35.1	1.04	0.50	0.62	0.18	1.4	0	86	332	162	0.96	1.19
13A	6.10	5.04	28.3	0.12	0.50	0.43	0.64	0.2	13	128	338	82	0.13	1.33
13B	5.90	4.83	9.6	0.09	0.45	0.14	0.12	0.2	3	90	483	69	0.09	1.31
14	7.06	5.86	17.8	0.17	0.97	0.30	0.30	0.2	3	102	693	97	0.07	1.39
15A	5.90	4.89	32.0	0.13	1.58	1.09	0.84	0.1	1	226	487	129	0.10	1.10
15B	6.55	5.29	13.7	0.42	0.44	0.25	0.03	0.7	0	66	784	266	0.02	1.18
15C	7.12	5.61	16.2	0.58	0.45	0.28	0.03	1.0	0	101	1290	459	0.04	1.22
16B	5.16	3.89	****	0.07	0.03	0.02	0.03	0.4	1	86	48	57	8.49	1.11
17A	4.92	4.00	13.4	0.12	0.29	0.17	0.30	0.3	4	71	246	71	3.25	0.98
18A	5.12	4.11	33.2	0.27	1.49	1.12	0.18	0.2	13	194	1148	456	0.92	1.18
18B	5.11	5.74	33.4	1.15	0.99	0.97	0.05	1.2	2	115	1974	743	0.08	1.08
19A	7.45	5.25	118.0	7.23	1.95	2.54	0.73	4.8	0	36	2541	724	0.06	1.15

Table 4. Composition of bulk precipitation in the catchment

Station code	Station name	Na	Mg	Ca	F	Cl	NO3/2-	SO4	PO4	T. alk.	Si	K	NH4-N	pH
		PRECIPITATION WEIGHTED MEANS												
		mg/l												
C1E118	C.Cilliers	0.57	0.29	1.15	0.10	1.14	0.52	3.64	0.05	4.12	0.16	0.20	0.70	4.78
C8E14B	Leiden	0.69	0.23	0.82	0.03	0.73	0.34	1.28	0.07	4.89	0.25	0.38	0.25	5.24
C1E13B	Springbok	0.77	0.30	1.07	0.05	1.16	0.68	2.84	0.17	5.49	0.43	0.63	1.21	5.04
C1E16B	Erfdeel	0.62	0.23	0.85	0.04	0.68	0.44	1.07	0.11	1.65	0.20	0.35	0.29	4.61
C1E128	Witbank	0.70	0.42	1.26	0.09	1.17	0.56	3.70	0.03	5.70	0.24	0.32	0.56	4.95
C1E09B	Hendrikspan	0.61	0.33	1.67	0.12	0.97	0.57	3.80	0.12	7.19	0.22	0.56	0.83	5.18
C1E10B	Topfontein	1.06	0.30	1.22	0.11	0.94	0.44	3.93	0.08	6.43	0.24	0.34	0.71	4.75
MEAN		0.72	0.30	1.15	0.08	0.97	0.51	2.89	0.09	5.07	0.25	0.40	0.65	4.94

The charge difference between cations and anions in these analyses was closely matched by the calculated H^+ ion concentration, indicating that these results are analytically sound and have formed a useful basis for establishing a realistic composition of solutions used in some of the equilibration experiments. To the authors' knowledge a synthesis of these bulk deposition data has not been previously conducted. The low sulphate concentrations at Leiden and Erfdeel would appear to be matched by correspondingly low concentrations of chloride, nitrate, fluoride, calcium, magnesium and ammonium. The other constituents do not show the same relationship. A closer examination of individual events may be warranted.

4.4 Adsorbed sulphate in catchment and other soils

Tables 5, 6 and 7 respectively document the results of the phosphate-extractable (adsorbed) sulphate-S determination for the catchment soils, the southern Natal collection and the land type profile samples, along with a selection of other data which will be referred to later. A conspicuous feature of these results is the greater average concentration of sulphate in the soils from the Vaal Dam catchment area, although the range of S concentrations is also quite wide in the southern Natal soils. No significant correlation could be found between adsorbed sulphate and any of the other properties recorded in Tables 5 to 7. This is not surprising in view of the fact that in less weathered soils sulphate may accumulate as soluble salts because the degree of leaching is subdued, whereas in highly weathered soils accumulation may occur through adsorption associated with low pH and the presence of Al and Fe colloids. Phosphate will obviously extract both types of accumulated sulphate.

4.5 Extractable barium in catchment and other soils

Exchangeable Ba determinations were performed on all the soils and the results are shown in Tables 5, 6 and 7. The insolubility of barium sulphate is such that an inverse relationship might be

Table 5. Adsorbed S and Ba, oxalate-extractable Fe and Al and HCl-soluble Fe in the catchment soils

Soil	Sample No	Sulfate-S (mg/kg	Barium (mg/kg)	Fe oxalate	Al oxalate (%)	Fe HCl
Cv26	1A	16	27	0.22	0.16	1.00
	1B	67	14	0.18	0.20	0.89
Ar30	2A	15	55	0.80	0.17	1.23
Gs18	3A	0	39	0.25	0.19	0.95
Va31	4A	20	25	0.48	0.19	0.90
	4B	57	29	0.25	0.19	1.18
Hu26	5A	5	27	0.15	0.16	0.87
	5B	20	29	0.22	0.19	1.08
Av26	6A	10	26	0.28	0.18	0.40
	6B	33	30	0.10	0.14	0.50
No11	7A	13	32	0.83	2.63	1.27
Sd22	8A	24	54	0.99	0.31	1.69
	8B	24	94	0.78	0.40	2.26
Rg10	9A	19	44	0.43	0.10	1.18
	9B	13	50	0.88	0.12	1.18
Va40	10A	16	50	0.42	0.16	0.88
	10B	19	87	0.46	0.19	1.03
We22	11A	20	39	0.28	0.20	1.19
	11B	18	41	0.44	0.19	1.43
Cv26	12A	0	56	0.14	0.13	0.62
	12B	22	54	0.20	0.25	0.91
Av36	13A	0	38	0.09	0.07	0.29
	13B	6	46	0.18	0.09	0.62
Fw10	14	1	48	0.12	0.03	0.26
Pn36	15A	0	52	0.22	0.11	0.50
	15B	5	64	0.11	0.09	0.57
	15C	1	92	0.10	0.09	0.64
Hu18	16B	0	70	0.75	0.37	0.98
	16A	24	47	0.32	0.32	0.92
Sw31	18A	10	55	0.51	0.18	0.84
	18B	18	65	0.43	0.19	1.09
Rg20	19A	63	51	0.38	0.15	1.19

Table 6. pH of southern Natal soil suspensions and extractable sulphate and barium data

Soil Form	Lab No	pH of 1:2.5 suspension			Extractable (mg/kg):	
		Water	1M KCl	.5M K2SO4	S	Ba2+
Cv 27	1A	5.31	4.09	4.62	4.6	37.1
	1B	5.19	4.15	4.71	4.6	38.2
Cv 26	12A	5.42	4.35	4.76	10.6	13.5
	12B	5.00	4.23	4.69	10.0	23.7
Ar 10	23A	6.66	5.18	5.82	2.0	17.2
Gs 18	2A	5.79	4.24	4.68	3.0	75.7
Gs 18	3A	5.05	4.09	4.57	0.0	19.6
Va 31	6A	5.35	3.97	4.51	3.6	31.9
	6B	5.53	4.06	4.59	2.0	33.0
Hu 27	9A	5.97	4.91	5.30	3.6	20.2
	9B	5.99	4.67	5.07	13.8	20.3
Hu 27	20A	5.89	4.78	5.15	2.0	52.1
	20B	5.82	4.21	4.74	2.4	63.2
Hu 26	22A	6.28	5.15	5.50	4.6	14.9
	22B	6.17	5.23	5.60	3.6	23.9
Av 26	19A	5.75	4.37	4.85	11.6	9.0
	19B	5.25	4.44	4.96	2.0	25.4
Sd 12	13A	5.75	4.64	5.09	8.0	31.2
	13B	6.06	4.78	5.38	4.6	49.3
Sd 12	17A	6.34	5.25	5.72	4.6	75.3
	17B	6.41	5.10	5.75	19.6	123.6
Rg 10	15A	7.39	5.82	6.42	2.0	7.1
	15B	6.81	5.84	6.46	2.4	34.4
Va 41	8A	6.01	4.90	5.37	3.0	12.9
	8B	5.75	4.81	5.48	20.0	26.6
We 13	11A	6.09	4.82	5.27	8.2	61.5
	11B	6.73	5.15	5.62	5.8	62.0
We 13	14A	6.03	4.97	5.37	7.2	37.4
	14B	6.01	5.07	5.37	4.6	28.2
Pn 24	24A	6.21	5.31	5.53	2.4	2.5
	24B	6.23	5.19	5.49	2.4	1.4
Hu 18	25A	5.42	4.32	4.85	55.0	18.7
	25B	5.45	4.35	4.96	40.4	29.0
Sw 31	4A	5.88	4.77	5.24	8.8	40.6
	4B	5.80	4.75	5.20	4.0	45.4
Ia 11	5A	5.36	4.24	4.76	3.6	30.9
	5B	5.46	4.33	4.95	4.0	26.7
Ss 26	7A	6.22	5.10	5.50	2.4	40.2
	7B	6.72	5.17	5.81	2.4	87.0
Ss 26	16A	6.63	5.73	6.17	3.6	7.7
	16B	7.90	6.24	6.80	11.0	23.3
Bv 26	10A	5.98	4.96	5.34	4.6	15.8
	10B	5.46	4.99	5.47	3.6	15.5
Gf 22	18A	5.99	5.01	5.34	8.4	25.1
	18B	5.78	4.54	5.03	6.8	25.6
Es 14	21A	5.93	4.67	5.01	10.0	13.5
	21B	6.80	5.27	5.83	51.0	36.7

Table 7. Extractable sulphate, barium and other properties of soils from the land type survey sample bank (ISCW) for the Vaal dam catchment region

Soil	Sample (ISCW)	Sulfate-S (mg/kg)	Ba (mg/kg)	Clay	Fe(CBD)	Al(CBD) (%)	Org. C	CEC (me/kg)	pH H2O	pH CaCl2
Ar20	P640	9		57	1.96	0.17	-	494	7	6.5
	P640sub	12	58	53	2.32	0.15	-	438	7.8	7.1
	P641	152	10	45	3.5	0.25	1.3	413	8.1	7.1
	P641sub	210	16	63	3.5	0.28	0.8	465	8.2	7.9
Gs17	P1102	8	16	17	0.9	0.15	0.6	50	5.7	4.9
	P1102sub	31	22	46	3.3	0.5	0.5	96	5.5	4.5
	P1062	13	6	23	1.4	0.15	1.4	76	5.6	4.7
	P1062sub	13	4	23	1.2	0.16	0.7	71	5.4	4.8
	P1101	7	25	25	1.2	0.19	1.5	81	5.3	5.5
	P1101sub	7	13	38	3.1	0.36	0.4	71	4.5	4.9
Va31	P1113	6	22	17	0.8	0.1	0.9	82	6	5.4
	P1113sub	20		37	1.6	0.25	0.6	120	6.2	5.4
Hu26	P124	19	34	29	2.8	0.2	0.6	60	5.9	5.1
	P124sub	53	25	34	2.8	0.2	0.4	44	5.5	4.7
	P132	12	25	27	1.8	0.1	1.1	68	6.1	5.4
	P132sub	13	21	30	2	0.1	0.7	66	6	5.4
Av26	P1045	14	12	22	1.9	0.49	2.3	70	5.3	4.3
	P1045sub	7	4	27	2.2	0.55	0.7	45	5.4	4.2
	P1046	25	14	25	2.1	0.6	1.5	64	5.4	4.5
	P1046sub	4	10	31	2.2	0.64	0.6	48	5.2	4.3
Va41	P130	6		24	0.5	0.3	0.7	11	6.4	5.6
	P130sub	9	105	50	2.9	0.3	0.5	11	7.4	6.7
We12	P117	2		15	0.8	-	0.6	57	6.5	5.1
	P117sub	4	18	35	1	-	0.4	166	7.2	6
	P112	5		12	0.8	-	0.7	40	8.2	6.9
	P112sub	11	22	25	0.85	-	0.4	103	6.4	5.9
	P948sub	7	45				0.9	72	6.7	6.2
Av36	P1096	10	49	15	-	-	0.4	85	7.4	6.4
Fw10	P46	2		7	0	-	0.2	15	6.2	5
	P46sub	2	6	6	0.1	-	0.1	11	5.7	4.7
Pn36	P220	2	8	13	0.4	0	0.6	57	6.4	5.4
	P220sub	6	6	27	1	0.1	0.4	82	5.8	4.5
Hu18	P1151sub	14	1	63	7.5	1.61	2	154	5.6	4.5
	P1060sub	12	6	67	9.8	1.51	1	80	5.6	4.9
	P1095sub	15	28	56	6.4	1.21	2.4	160	5.3	4.5
	P1151	25	12	58	6.3	1.3	3.7	182	5.4	4.4
	P1060	18	4	63	8.2	1.24	1.6	111	5.4	4.6
	P1095	11	41	51	6.9	1.17	3.3	187	5.4	4.7
Sw31	P1078	10	60	27	-	-	1	193	7.4	6.6
	P1078sub	15	104	42	-	-	0.5	227	7.4	6.3
Rg20	P1104	8	44	37	2.5	0.21	1.8	233	6.1	5.4
	P1104sub	2	15	65	4.5	0.38	0.3	153	7.9	6.7

expected between the quantities of barium and sulphate which can be extracted from soil. There is some indication (to be discussed later in relation to Figure 10) that this is so. The range in barium concentrations is quite wide (from 1 to 124 mg kg^{-1}) but falls below 1 mmol kg^{-1} and Ba is therefore not a significant contributor to the overall suite of exchangeable cations. It is probable that at the higher end of the concentration range, barium may constitute a significant sink for atmospheric sulphate additions to soils.

4.6 Salt effect on suspension pH as an index of sulphate sorption

The pH of soil suspensions in water, potassium chloride and potassium sulphate solutions is compared in Table 6 for the southern Natal soils and in Table 8 for the catchment soils. As explained in Chapter 3, the purpose of these determinations was to find out whether a simple index of sulphate sorption capacity could be derived from the difference in pH (water) and pH (salt solution), since this difference is widely known to be related to the proportion of positive to negative surface charge. It subsequently transpired that there was no significant correlation between the salt-induced pH differential and sulphate sorption (Section 4.9). There is, however, a strong correlation between the chloride effect and that of sulphate (Figure 5), although the difference, pH(salt) - pH(water), is smaller in the case of sulphate, as would be expected in view of the greater specificity of sulphate for sites of adsorption by ligand exchange with hydroxyl groups.

4.7 Equilibration experiments

Three types of equilibration of sulphate solutions with catchment soils were undertaken. In the first of these, saturated pastes were prepared in water and mixed salt solutions. A second set of equilibrations was performed in dilute suspensions of soil with water, sulphuric acid and sodium sulphate, while the third involved leaching columns of soil in order to investigate the

Table 8. pH in suspensions of catchment soils in 1M KCl, 0.5M K_2SO_4 and distilled water

Sample	pH(KCl)	pH(K2SO4)	pH(H2O)
1A	4.32	4.87	5.21
1B	4.35	4.95	4.90
2A	5.10	5.51	6.32
3A	4.26	4.79	5.37
4A	4.09	4.62	5.00
4B	5.42	6.09	6.52
5A	4.75	5.21	5.86
5B	4.19	4.75	4.85
6A	4.02	4.55	4.60
6B	4.12	4.68	4.80
7A	4.68	5.14	5.58
8A	4.90	5.35	6.15
8B	5.19	5.84	6.25
9A	5.35	5.97	6.34
9B	5.94	6.54	6.92
10A	4.89	5.32	5.92
10B	4.86	5.45	6.11
11A	5.11	5.71	6.07
11B	5.26	6.06	6.65
12A	4.55	5.08	5.82
12B	4.17	4.85	5.24
13A	4.94	5.52	6.11
13B	4.65	5.32	5.79
14	5.96	6.49	6.77
15A	4.70	5.23	5.88
15B	5.16	5.93	6.28
15C	5.52	6.34	6.78
16B	3.80	4.41	4.97
17A	3.88	4.49	4.87
18A	3.99	4.63	5.06
18B	5.05	5.74	6.47
19A	6.01	6.57	7.42

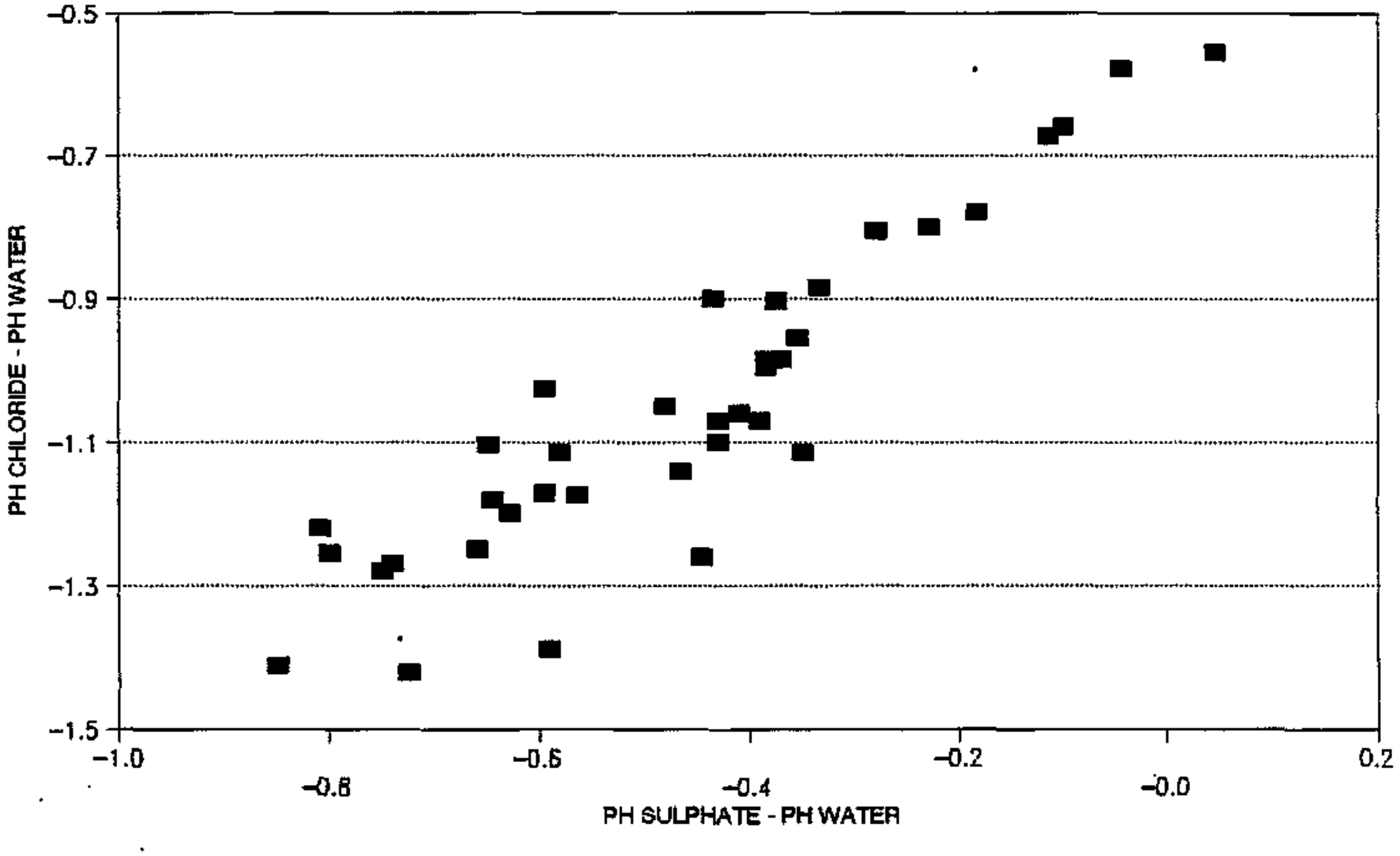

Figure 5. Relationship between the suspension pH response to the presence of KCl (chloride-water) and that due to the presence of K_2SO_4 (sulphate-water) for the catchment soils

sulphate breakthrough characteristics of each soil.

4.7.1 Saturated pastes

Four treatments were employed in preparing saturated pastes, and the solution compositions are shown in Table 9. Treatment B was made up with a composition approximating that of the mean bulk deposition shown in the last row of Table 4. Treatments C and D were prepared to simulate the effect of solution B becoming progressively more concentrated through evaporation, although D probably represents an exaggerated degree of concentration and was mainly included for reference purposes. The composition of the saturated paste extracts from these treatments is shown in Tables 10 a-f.

The results in Table 10 do not alone permit a quantitative estimate of sulphate retention or salinity buffering. The results for treatment A, however, provide a useful characterisation of the existing soil solution composition at equilibrium, while the treatments B, C and D show that there is considerable variation in the response to treatment with salt solutions of different concentrations, some soils showing a very clear sulphate- and salinity-buffering effect (especially 7A and 16B in Tables 10a,c) while others are sufficiently endowed with natural salts to mask the effect of even the most concentrated of the treatments.

The interpretation of the results of saturated paste equilibration are also limited by the fact that the cumulative effects of long-term atmospheric additions to soil cannot easily be simulated. Sulphate sorption is concentration dependent and it is therefore not realistic to work at elevated concentrations as a means of compressing the time scale. The ionic strength of all but one or two of the soil solutions is so high relative to that of even the most concentrated acid rain solution, however, that adding enough of this solution to achieve saturation of the soil with water does little to alter the ambient ionic strength

Table 9. Composition of solutions used for preparing saturated paste extracts, simulating rainwater composition (B), or evaporative concentrates thereof (C, D)

Compound	Treatment* B	C	D
	(µmol/L)		
H2SO4	17	236	708
HCl	27	315	945
NaHCO3	19	220	661
NaNO2	12	141	422
MgSO4.7H2O	3	0	0
Mg(NO3)2.6H2O	9	105	315
KNO2	6	69	208
KF	4	48	145
CaCO3	18	203	609
CaSO4.2H2O	10	111	334
Ca(H2PO4).2H2O	1	17	50
NH4HCO3	46	535	1605
Mg(OH)2	0	37	111

* Treatment A: deionized water

Table 10a. Composition of saturated paste extracts prepared by mixing water or salt solutions(*) with Vaal Dam catchment soils

Soil No	Bicarbonate alkalinity (meq/L)				Electrical conductivity (mS/m)			
	A	B	C	D	A	B	C	D
1A	0.45	0.57	-	0.41	28.7	47.4	54.9	76.4
1B	0.15	0.07	-	0.02	26.2	22.0	36.4	54.2
2A	3.78	4.39	3.75	0.72	67.3	79.7	77.2	88.7
3A	0.30	0.31	0.16	0.24	16.2	19.8	27.6	54.9
4A	0.22	0.35	0.14	0.00	31.2	28.8	43.5	61.9
4B	0.46	0.45	0.60	0.42	40.0	42.5	58.3	82.3
5A	0.67	0.88	0.81	0.49	30.4	25.0	39.7	62.2
5B	0.10	0.07	0.17	0.12	10.5	8.6	19.2	29.5
6A	0.12	0.32	0.15	0.17	19.9	18.6	32.8	49.6
6B	0.09	0.09	0.22	0.13	15.8	13.5	26.3	40.9
7A	0.15	0.42	0.00	0.21	16.3	17.6	22.4	35.2
8A	0.86	1.22	0.85	0.68	36.2	31.0	46.1	62.4
8B	0.25	0.22	-	0.33	19.4	17.4	40.7	57.7
9A	1.85	1.87	-	2.68	63.1	58.3	120.0	85.4
9B	1.48	1.37	1.86	1.51	39.0	30.1	49.6	87.6
10A	1.56	2.12	2.04	0.71	51.6	55.6	57.1	78.9
10B	0.39	0.70	0.34	0.51	36.5	24.3	35.0	58.8
11A	0.66	0.72	0.83	0.80	74.3	44.3	67.6	88.3
11B	0.24	0.30	0.47	0.42	67.9	51.1	69.3	95.8
12A	0.30	1.13	0.18	0.34	41.0	58.8	45.0	78.4
12B	0.07	0.08	0.11	0.30	30.1	31.9	40.8	56.7
13A	1.82	2.19	1.57	0.80	35.3	36.2	45.3	76.4
13B	0.39	0.39	0.34	0.44	15.2	12.5	29.6	47.3
14	1.34	1.18	-	1.61	29.6	27.2	45.5	74.2
15A	1.12	1.66	0.24	0.48	39.7	34.6	43.9	69.6
15B	0.23	0.31	0.34	0.46	15.4	13.1	25.6	49.4
15C	0.27	0.20	0.41	0.30	14.3	14.5	28.8	52.2
16B	0.04	0.06	0.09	0.12	3.0	4.2		17.9
17A	0.15	0.31	0.42	0.08	16.1	17.6	26.4	41.2
18A	0.64	0.59	0.50	0.29	38.7	42.8	43.7	67.4
18B	0.94	1.34	0.98	0.65	35.4	41.7	50.7	72.2
19A	2.72	3.28	2.71	1.85	119.5	118.3	127.8	150.0
Treatment Solution	0.03	0.06	0.51	0.48	-	2.6	22.2	60.0

Treatment A:Deionised water; B, C and D as in Table 9.

Table 10b. Composition of saturated paste extracts prepared by mixing water or salt solutions(*) with Vaal Dam catchment soils

Soil No	pH				Water content (%)			
	A	B	C	D	A	B	C	D
1A	5.30	5.67	-	6.29	31	30	31	32
1B	6.23	5.88	-	4.60	26	31	27	27
2A	7.47	7.53	7.56	6.37	66	63	65	73
3A	6.11	6.51	5.94	5.60	38	35	33	72
4A	5.57	6.73	5.39	4.47	29	32	31	36
4B	7.04	7.12	7.48	7.02	75	68	67	76
5A	6.68	7.02	7.02	6.80	23	29	26	26
5B	6.15	6.17	6.89	6.38	31	38	30	-
6A	4.99	7.26	6.40	5.64	15	24	24	27
6B	5.81	6.45	6.89	6.20	33	30	28	32
7A	6.40	6.90	4.21	5.95	86	81	91	89
8A	6.38	6.96	6.66	6.01	82	84	66	74
8B	6.93	7.05	-	5.46	94	111	-	93
9A	7.88	7.98	-	7.82	56	63	-	63
9B	7.99	8.21	8.30	7.88	72	76	76	74
10A	7.19	7.27	7.93	6.00	51	59	56	55
10B	6.70	7.39	6.67	6.94	63	72	66	70
11A	7.28	7.35	7.65	7.09	33	39	32	36
11B	6.75	7.24	7.52	7.07	49	52	44	52
12A	6.06	5.57	4.86	5.36	30	30	28	33
12B	5.57	6.25	6.62	6.75	40	33	35	37
13A	7.63	7.68	7.79	6.77	18	24	22	24
13B	7.21	7.34	7.11	7.11	25	25	24	24
14	7.04	7.93	-	7.53	21	24	-	-
15A	6.84	5.77	4.86	5.75	59	40	36	34
15B	6.68	7.12	7.07	7.21	41	42	40	35
15C	6.97	6.90	7.38	6.86	62	63	58	55
16B	5.80	6.39	6.64	6.63	77	52	52	61
17A	5.85	7.09	7.25	4.77	55	58	56	27
18A	6.92	6.45	7.17	5.16	48	44	41	36
18B	7.20	7.56	7.29	6.69	71	64	66	66
19A	7.81	8.17	7.68	7.42	92	94	96	94
Treatment Solution	5.48	6.30	7.66	7.50	-	-	-	-

Table 10c. Composition of saturated paste extracts prepared by mixing water or salt solutions(*) with Vaal Dam catchment soils

Soil No	Sulphate (mg/L)				Chloride (mg/L)			
	A	B	C	D	A	B	C	D
1A	75.0	76.8	86.4	116.0	30.6	28.4	35.6	65.2
1B	57.6	53.2	61.6	81.6	15.4	11.3	27.2	54.4
2A	61.6	81.2	106.0	195.2	22.4	56.7	22.8	81.2
3A	29.8	34.2	60.0	86.0	8.4	28.4	45.2	47.2
4A	100.8	86.6	98.2	119.2	12.8	10.6	13.2	43.6
4B	70.0	139.2	180.8	221.6	119.6	32.0	16.0	32.0
5A	42.6	30.6	55.6	107.2	29.1	13.4	21.4	41.6
5B	17.2	13.0	12.6	16.6	6.9	5.6	12.9	23.6
6A	32.9	32.1	40.4	72.8	11.8	9.8	20.4	39.2
6B	36.9	27.5	33.6	45.2	11.5	7.6	11.6	41.0
7A	9.9	4.8	4.5	8.0	25.1	15.0	23.7	40.4
8A	50.6	25.2	57.4	99.6	22.6	9.0	20.2	68.8
8B	31.1	27.4	56.0	94.0	15.4	11.1	27.4	46.8
9A	112.4	100.4	193.2	114.8	57.6	49.6	84.8	65.6
9B	-	64.2	111.2	137.2	-	8.6	120.8	24.8
10A	64.4	74.4	120.0	176.4	56.0	29.6	52.0	67.6
10B	59.6	46.8	65.6	96.0	17.0	7.8	16.2	56.0
11A	104.8	65.4	86.8	113.2	101.6	48.8	82.4	72.8
11B	100.8	67.2	78.8	116.4	55.2	27.2	48.8	58.8
12A	39.4	37.2	59.6	128.8	36.4	36.0	45.2	71.2
12B	17.2	11.8	17.0	29.6	52.8	51.4	78.6	78.0
13A	28.0	31.8	32.8	148.4	55.2	11.6	66.0	57.2
13B	18.6	16.5	23.6	52.4	16.2	6.8	27.2	42.6
14	18.1	25.2	66.0	135.2	11.2	9.6	21.8	12.4
15A	27.2	14.8	49.8	99.2	4.4	11.6	57.6	36.4
15B	22.7	21.9	29.6	62.4	15.3	7.5	18.8	44.4
15C	13.7	12.2	26.6	64.8	14.8	12.7	36.6	9.2
16B	0.7	0.9	0.6	0.7	2.9	6.0	5.3	3.9
17A	18.0	19.2	31.8	34.0	13.8	15.5	46.4	31.5
18A	76.0	85.2	104.2	128.0	16.2	17.6	45.6	49.6
18B	66.6	62.6	88.8	129.2	4.4	13.6	26.4	42.4
19A	268.4	302.4	239.6	249.6	55.2	48.0	64.0	48.0

Table 10d. Composition of saturated paste extracts prepared by mixing water or salt solutions(*) with Vaal Dam catchment soils

Soil No	Nitrate (mg/L)				Nitrite (mg/L)			
	A	B	C	D	A	B	C	D
1A	0.2	3.6	20.8	14.8	1.4	0.8	1.6	13.6
1B	8.2	3.9	26.4	57.2	0.4	0.3	4.0	0.4
2A	7.2	7.7	11.2	10.4	0.0	0.6	1.2	48.8
3A	3.4	1.7	36.0	49.2	-	0.4	2.8	8.4
4A	7.2	4.0	39.4	71.6	0.1	0.1	3.4	0.1
4B	4.6	5.2	23.6	49.2	-	0.3	15.6	31.2
5A	8.7	2.6	20.4	45.6	0.1	0.2	10.0	19.2
5B	8.4	6.7	31.1	35.8	-	0.4	4.8	16.4
6A	10.2	5.9	45.2	65.6	0.1	0.4	0.4	0.8
6B	5.5	3.1	29.2	43.4	0.2	0.6	4.4	17.4
7A	4.8	1.4	25.9	52.6	0.1	0.1	-	3.2
8A	4.4	1.4	15.6	38.8	1.6	-	7.8	11.2
8B	7.1	4.1	7.4	48.0	0.3	0.7	8.6	3.2
9A	7.2	3.6	23.2	6.4	0.8	-	104.8	42.8
9B	-	2.6	16.0	5.6	-	0.2	54.4	58.4
10A	5.6	4.0	5.2	19.2	-	0.2	0.8	20.4
10B	11.8	4.4	13.6	40.4	0.1	0.1	13.0	26.8
11A	24.0	4.8	16.0	57.2	20.4	0.2	48.4	32.8
11B	115.6	93.2	131.6	111.6	3.6	6.0	12.0	27.2
12A	6.6	-	0.4	2.8	-	-	7.2	6.8
12B	5.4	2.4	20.6	35.6	-	-	4.6	20.4
13A	1.6	0.6	0.8	1.2	0.8	-	46.0	24.4
13B	6.0	4.0	22.8	43.4	0.2	0.1	9.2	20.8
14	9.5	2.6	11.8	16.4	0.1	0.4	11.0	16.4
15A	6.4	0.2	-	3.2	0.2	1.0	-	19.6
15B	5.2	2.8	15.4	42.4	0.1	0.1	7.8	25.2
15C	12.2	11.4	22.0	42.4	0.1	1.1	14.0	9.2
16B	3.7	6.2	13.2	25.9	0.0	0.3	2.6	4.5
17A	2.4	2.2	8.6	26.2	-	-	0.4	0.1
18A	5.6	2.4	7.8	42.8	0.4	0.2	-	2.8
18B	21.2	3.6	13.2	40.8	5.6	0.2	1.2	29.6
19A	5.2	-	5.6	3.2	-	0.4	0.8	26.0

Table 10e. Composition of saturated paste extracts prepared by mixing water or salt solutions(*) with Vaal Dam catchment soils

Soil No	Calcium (mg/L)				Magnesium (mg/L)			
	A	B	C	D	A	B	C	D
1A	1.9	1.9	2.8	6.8	0.8	0.7	-	3.0
1B	1.3	1.0	-	4.6	0.6	0.5	-	2.9
2A	2.3	2.8	2.6	5.3	3.0	4.0	3.7	7.2
3A	1.5	1.6	2.3	7.4	0.5	0.6	1.2	3.8
4A	2.2	2.0	3.0	8.5	0.9	0.9	1.5	4.1
4B	0.4	1.2	1.9	4.9	0.0	0.4	0.9	3.0
5A	2.5	2.4	3.0	10.7	0.7	0.6	0.9	3.5
5B	1.1	0.9	1.2	1.8	0.2	0.2	0.8	1.1
6A	1.5	1.5	1.9	5.2	0.5	0.5	0.8	3.0
6B	1.4	1.2	1.7	2.8	0.6	0.5	1.0	3.3
7A	1.4	1.5	1.5	2.1	0.3	0.5	0.5	1.7
8A	3.4	2.8	3.7	10.3	1.8	1.6	2.4	5.7
8B	2.0	1.8	-	9.1	0.7	0.7	-	5.8
9A	7.2	6.5	-	23.3	2.9	2.6	-	7.6
9B	4.1	3.1	4.9	19.4	1.8	1.4	2.3	5.5
10A	4.1	4.6	4.7	14.3	2.1	2.3	2.3	5.9
10B	2.6	1.8	2.3	8.0	0.9	0.7	1.0	3.1
11A	5.1	3.0	4.3	12.0	2.5	1.5	2.5	5.2
11B	2.4	1.5	2.0	4.4	0.9	0.4	0.8	2.5
12A	2.6	3.0	2.4	9.2	0.8	1.3	1.0	3.7
12B	1.5	1.4	2.1	5.6	0.7	0.6	1.0	2.6
13A	3.4	3.3	3.9	13.3	1.1	1.0	1.1	3.6
13B	1.9	1.8	3.2	9.0	0.3	0.2	0.6	1.6
14	3.6	3.6	-	16.3	0.5	0.5	-	2.7
15A	3.4	4.1	1.7	8.6	1.4	1.8	0.6	3.3
15B	1.3	1.2	2.8	7.0	0.3	0.3	0.7	2.9
15C	1.2	1.3	2.0	6.3	0.3	0.3	0.6	2.5
16B	0.8	0.9	1.1	1.3	0.1	0.1	0.1	0.5
17A	1.4	1.6	1.9	2.9	0.2	0.3	0.4	1.1
18A	3.6	3.6	3.7	11.4	1.6	1.5	1.5	5.1
18B	2.8	3.1	3.6	9.5	1.4	1.6	1.9	5.3
19A	3.9	3.8	3.5	7.9	3.5	3.3	2.8	6.1
Treatment Solution	-	0.2	1.2	4.6	-	0	0.3	1.9

Table 10f. Composition of saturated paste extracts prepared by mixing water or salt solutions(*) with Vaal Dam catchment soils

Soil No	Potassium (mg/L)				Sodium (mg/L)			
	A	B	C	D	A	B	C	D
1A	7.9	7.9	-	7.8	1.7	1.5	-	-
1B	4.1	3.7	-	5.2	1.9	1.5		4.9
2A	0.5	0.6	0.6	0.9	19.6	23.0	19.4	20.7
3A	1.3	1.4	2.1	2.9	1.2	1.3	2.1	2.6
4A	0.7	0.6	1.0	0.9	3.7	3.5	4.4	4.1
4B	0.2	0.4	0.8	0.7	10.9	14.3	18.2	23.0
5A	3.9	3.7	4.0	4.7	1.8	1.3	2.1	3.6
5B	0.3	0.1	0.8	0.5	1.6	1.5	2.5	4.5
6A	1.6	1.6	2.8	2.7	1.8	2.0	2.6	4.5
6B	0.3	0.3	0.7	0.7	1.7	1.5	2.0	4.3
7A	0.5	0.8	0.7	1.0	2.0	2.3	2.1	4.1
8A	1.0	1.1	1.3	1.3	2.0	1.8	2.2	3.4
8B	0.1	0.1	-	1.2	2.2	2.1	-	2.8
9A	0.7	0.7	-	0.9	2.1	2.2	-	2.7
9B	0.0	0.0	0.5	0.0	2.2	1.8	2.5	1.9
10A	6.8	7.6	6.8	7.5	1.8	1.8	2.3	3.2
10B	0.5	0.8	0.5	0.8	6.0	4.9	5.8	6.3
11A	5.3	5.2	6.2	6.2	5.4	2.6	2.9	27.0
11B	0.3	0.2	0.3	0.5	19.5	17.4	23.5	24.0
12A	8.8	13.0	9.9	13.8	1.0	1.6	1.7	3.7
12B	1.3	1.0	1.1	1.8	4.9	4.7	5.5	7.1
13A	5.8	5.4	5.9	7.4	1.6	1.0	2.1	4.6
13B	1.0	0.8	2.0	2.2	1.2	0.8	1.9	3.5
14	3.3	3.2	-	5.0	1.6	1.1	-	4.0
15A	6.2	7.0	4.9	6.1	1.1	1.1	2.1	3.6
15B	0.1	0.0	0.2	0.5	2.3	2.0	3.1	5.3
15C	0.0	0.0	0.3	0.4	2.6	2.7	4.0	6.0
16B	0.0	0.1	0.3	2.7	0.4	0.5	1.0	0.6
17A	2.0	3.1	3.5	3.4	0.7	1.1	1.5	4.6
18A	1.5	1.4	1.1	2.9	1.9	1.8	1.7	25.0
18B	0.5	0.4	0.4	8.2	6.1	6.4	7.2	0.4
19A	0.5	0.3	-	20.5	-	-	-	-
Treatment Solution	-	0	0.8	2.1	-	0.4	2.2	6.4

or composition of the saturation extract. This of course begs the question whether there is any substance to the claim, discussed in the Introduction, that atmospheric inputs of acid will displace native salts in the soil and give rise to enhanced salinity levels in water draining from the catchment. Discussion of this subject will be deferred to the concluding section of this report.

4.7.2 Soil suspensions

The next step in seeking a means of simulating **protracted** periods of **low level** inputs was to equilibrate a small quantity of soil with a large volume of dilute sulphate solution. The concentrations of sulphate chosen were 0, 6, 12 and 24 mg L^{-1} as sulphuric acid and 24 mg L^{-1} as sodium sulphate, which was included to test the pH effect on sulphate sorption. It was anticipated that the 6 mg L^{-1} concentration would have the most relevance because it is the closest to the prevailing bulk deposition level of about 3 mg L^{-1} (up to nearly 4 at the Topfontein station - Table 4). On the other hand, the 12 and 24 mg L^{-1} concentrations, besides accommodating the possibility of intermittent enhancement of sulphate concentrations during drier phases, offer the opportunity of calculating adsorption maxima from isotherms which would not be available if only a single concentration of sulphate were used.

In designing the equilibration experiment, 4g soil with 200ml solution was reckoned to be equivalent to taking 50 years of acid rain (at 1000mm per annum) and reacting it with a 1 metre depth of soil. On the other hand 10g soil with 100ml solution, used as an alternative ratio for the 6 mg L^{-1} treatment, can be viewed as representing a 10 year period instead of 50. It must be emphasised that the above line of thinking is not strictly accurate, even besides the fact that 10 or 50 years' worth of rain does not fall in one night and reach equilibrium with the top metre of soil by the next afternoon! However, it does represent equilibration at both a realistic sulphate concentration (intensity) and a meaningful total quantity, and the results should therefore be far more applicable than those derived from narrower soil to solution ratios. To add a further touch of realism to the reaction, B horizon samples were equilibrated not with the original solution in each case, but with some of the supernatant following equilibration of this solution with the corresponding A horizon.

The results are presented in Tables 11a-g. The equilibrium conductivity values (EC - Table 11a) are not easily interpreted in isolation because, as can be seen from the large difference in values for the original sulphuric acid and sodium su solutions at the 24 mg L^{-1} sulphate concentration (19.7 compared with 5.61 mS m^{-1}, respectively) the EC is much higher if the dominant cation in solution is hydrogen as opposed to sodium, meaning that for a particular concentration of sulphate the decrease in EC following equilibration with soil will be as much due to the exchange of hydrogen ions for basic cations on soil colloid surfaces as it will to the adsorption of sulphate. Consequently, it is the sulphate concentrations which are the most instructive, and an interpretation of the results in Table 11c will now be attempted. The column headed "Water" in Table 11c gives the equilibrium concentrations of sulphate which the soils themselves subtend when equilibrated with distilled water at the same soil to solution ratio of 1:50. Initially the sulphate concentration value in this column was used as a correction value by subtracting it from the sulphate concentration which resulted from equilibration with any particular sulphate solution. Subsequently, however, it was found that this approach is fallible because the water supernatants have a higher pH than those resulting from equilibration with sulphate solutions (Table 11b), and sulphate retention is sensitive to pH. Thus the soils equilibrated with water release more sulphate into solution than they would if the pH was as low as that resulting from reaction with the sulphate solution. Consequently, subtracting the "water" value as described above would in most cases over-correct for the naturally soluble sulphate in the soil and result in an

Table11 a Electrical conductivity of soil suspensions equilibrated with sulphuric acid or sodium sulphate solutions (4g soil + 200ml solution)

Soil	Lab	Initial sulphate concentration (mg/L)					
Form	No	0	24	24	12	6	6
		Water	Acid	Salt	Acid	Acid	Acid*
		--- EC (mS/m) ---					
Clovelly	1A	2.26	9.93	8.31	4.90	3.06	4.99
	1B	3.22	8.34	7.67	5.88	3.86	7.02
Arcadia	2A	2.92	8.40	8.93	4.90	3.39	7.31
Glenrosa	3A	1.75	9.10	8.01	4.52	3.62	3.73
Valsrivier	4A	2.26	9.37	7.48	4.81	2.76	3.80
	4B	3.33	8.62	7.26	5.45	3.74	6.78
Hutton	5A	1.99	10.62	7.39	4.56	2.48	2.97
	5B	2.42	7.98	6.86	3.82	2.48	4.05
Avalon	6A	2.02	11.79	7.36	6.42	2.78	2.81
	6B	2.19	9.14	6.86	4.94	3.23	4.32
Nomanci	7A	2.29	6.41	7.43	3.87	2.56	3.26
Shortlands	8A	2.59	8.17	7.82	4.69	3.00	4.46
	8B	3.41	8.37	7.92	5.45	3.66	7.46
Rensburg	9A	3.20	9.02	8.44	5.26	3.80	7.16
	9B	4.82	9.70	9.30	7.05	5.54	11.50
Valsrivier	10A	2.93	7.53	8.38	5.30	3.48	4.82
	10B	3.24	8.48	8.03	5.69	3.98	6.50
Westleigh	11A	2.52	7.45	8.04	4.13	2.22	4.98
	11B	3.28	8.49	8.06	4.66	2.57	6.73
Clovelly	12A	2.27	8.16	7.74	4.68	2.76	4.51
	12B	2.55	8.82	7.59	5.27	3.41	6.16
Avalon	13A	2.48	8.32	7.07	4.78	2.55	3.74
	13B	2.07	8.27	6.90	5.18	2.83	3.67
Fernwood	14	1.94	8.83	7.10	4.21	2.49	3.31
Pinedene	15A	1.94	8.93	7.48	4.73	2.64	3.57
	15B	2.23	7.99	7.46	4.79	3.12	3.96
Hutton	16A	2.36	8.69	7.68	4.07	1.17	4.02
	16B	1.71	7.45	6.09	3.35	1.44	2.45
Swartland	18A	2.22	9.21	8.03	4.91	2.84	4.74
	18B	3.45	7.99	8.11	5.99	3.98	8.19
Rensburg	19A	5.22	8.32	9.68	6.78	5.51	15.30
Solution only		0.22	19.70	5.61	11.83	5.20	5.32

* 10g soil + 100ml solution

Table11b Supernatant pH of soil suspensions equilibrated with sulphuric acid or sodium sulphate solutions (4g soil + 200ml solution)

Soil Form	Lab No	Initial sulphate concentration (mg/L)					
		0	24	24	12	6	6
		Water	Acid	Salt	Acid	Acid	Acid*
		Final pH					
Clovelly	1A	5.95	4.19	5.84	5.12	5.79	5.70
	1B	5.63	4.78	5.43	5.70	5.61	5.26
Arcadia	2A	6.41	5.62	6.43	6.24	6.48	6.55
Glenrosa	3A	6.02	4.50	5.78	5.25	6.23	5.52
Valsrivier	4A	5.79	4.40	5.33	5.43	5.40	5.33
	4B	6.47	5.65	5.24	6.18	6.32	6.46
Hutton	5A	5.59	3.90	5.59	4.46	5.10	5.17
	5B	5.46	4.48	5.22	5.28	5.41	5.10
Avalon	6A	5.73	3.69	5.09	4.14	5.01	5.02
	6B	5.49	4.06	5.15	5.61	5.46	5.19
Nomanci	7A	6.23	5.45	6.16	5.57	5.98	5.92
Shortlands	8A	6.39	5.41	6.29	5.90	6.37	6.33
	8B	6.46	6.06	6.38	6.16	6.33	6.34
Rensburg	9A	6.30	5.13	6.49	6.55	6.46	6.59
	9B	6.77	6.39	6.69	6.63	6.78	6.98
Valsrivier	10A	6.04	5.31	6.12	6.00	6.24	6.44
	10B	6.29	5.76	6.21	6.16	6.23	6.22
Westleigh	11A	6.34	4.67	6.17	5.47	6.01	6.41
	11B	6.53	5.58	6.45	6.30	6.29	6.74
Clovelly	12A	6.05	4.33	5.65	5.44	6.17	6.20
	12B	5.84	4.64	5.48	5.60	5.76	5.43
Avalon	13A	6.34	4.23	5.57	5.41	6.10	6.13
	13B	6.22	4.81	5.55	5.61	5.93	6.12
Fernwood	14	6.37	4.10	5.89	4.74	5.73	6.42
Pinedene	15A	6.28	4.29	6.00	5.60	5.97	6.33
	15B	6.29	5.19	6.26	6.14	6.28	6.32
Hutton	16A	5.72	4.30	5.50	4.90	5.23	5.30
	16B	5.76	4.45		5.28	5.50	5.38
Swartland	18A	5.13	4.48	5.06	5.19	5.37	5.38
	18B	6.25	6.09	6.09	6.07	6.11	6.35
Rensburg	19A	6.57	6.39	6.70	6.53	6.44	6.99
Solution only			3.37	5.63	3.59	3.98	3.95

* 10g soil + 100ml solution

Table 11c Supernatant sulphate in soil suspensions equilibrated with sulphuric acid or sodium sulphate solutions (4g soil + 200ml solution)

Soil Form	Lab No	Initial sulphate concentration (mg/L)					
		0 Water	24 Acid	24 Salt	12 Acid	6 Acid	6 Acid*
		Final sulphate concentration (mg/L)					
Clovelly	1A	1.2	24.3	23.2	14.3	7.1	9.9
	1B	4.5	24.0	25.5	16.0	9.5	20.7
Arcadia	2A	1.5	24.6	22.9	14.4	7.3	11.1
Glenrosa	3A	0.7	23.3	22.8	13.8	7.1	8.5
Valsrivier	4A	1.2	23.7	25.2	14.8	7.4	10.5
	4B	3.5	24.2	25.6	15.6	10.0	22.8
Hutton	5A	2.2	19.9	23.1	10.8	6.0	7.5
	5B	3.6	22.7	24.7	10.6	4.6	9.6
Avalon	6A	0.7	21.8	20.9	13.0	6.2	8.2
	6B	2.3	23.2	25.0	13.8	7.4	12.9
Nomanci	7A	0.7	19.3	23.4	10.9	5.6	4.7
Shortlands	8A	1.6	24.9	25.2	11.6	7.7	12.5
	8B	4.0	25.7	26.6	17.3	9.7	20.4
Rensburg	9A	6.5	25.8	26.5	13.2	7.3	12.1
	9B	2.1	27.0	25.5	15.8	8.3	14.7
Valsrivier	10A	1.8	25.8	26.1	15.0	7.9	15.4
	10B	3.0	26.4	26.7	15.3	9.1	22.3
Westleigh	11A	3.8	24.7	25.3	12.8	6.0	8.8
	11B	2.6	25.4	24.7	13.9	6.7	12.2
Clovelly	12A	3.3	24.7	25.0	13.3	6.1	7.5
	12B	2.3	24.5	25.4	14.6	7.9	13.5
Avalon	13A	0.0	24.3	24.2	14.1	5.9	6.1
	13B	0.4	24.1	23.6	14.6	6.3	7.6
Fernwood	14	3.0	24.9	22.9	12.6	6.1	6.7
Pinedene	15A	0.0	22.4	24.2	13.4	6.1	6.5
	15B	0.8	24.0	23.7	13.7	6.7	9.5
Hutton	16A	3.8	23.4	25.1	12.5	6.4	8.9
	16B	1.0	16.7	20.7	8.3	4.1	1.4
Swartland	18A	5.3	25.3	25.4	13.9		12.8
	18B	3.0	27.3	24.4	15.0	8.8	22.2
Rensburg	19A	5.5	29.6	28.8	18.7	9.0	30.3
Solution only		0.0	24.0	22.8	12.2	5.6	

* 10g soil + 100ml solution

Table 11d Supernatant nitrate in soil suspensions equilibrated with sulphuric acid or sodium sulphate solutions (4g soil + 200ml solution)

Soil Form	Lab No	Initial sulphate concentration (mg/L)					
		0	24	24	12	6	6
		Water	Acid	Salt	Acid	Acid	Acid*
		Final nitrate concentration (mg/L)					
Clovelly	1A	3.4	3.7	3.1	1.0	0.9	1.4
	1B	3.6	2.4	2.9	2.3	1.4	1.5
Arcadia	2A	3.5	3.1	3.6	0.7	0.8	1.0
Glenrosa	3A	2.8	3.2	3.1	0.7	0.8	0.7
Valsrivier	4A	4.6	3.6	3.8	0.8	1.2	1.1
	4B	3.4	2.5	3.1	1.3	1.5	2.0
Hutton	5A	3.0	0.2	3.8	0.6	0.9	1.0
	5B	2.8	4.9	2.4	0.7	0.5	1.3
Avalon	6A	4.1	0.8	3.2	0.9	0.7	1.1
	6B	3.0	7.1	2.6	1.2	1.7	1.4
Nomanci	7A	3.9	3.7	4.4	0.8	1.4	1.8
Shortlands	8A	3.8	6.7	3.8	0.7	0.8	1.0
	8B	3.2	6.2	3.2	1.2	0.6	1.2
Rensburg	9A	6.3	8.8	5.2	2.0	2.1	7.0
	9B	5.2	8.1	4.9	3.4	3.4	9.1
Valsrivier	10A	4.1	2.6	4.0	0.8	1.1	2.7
	10B	3.5	5.7	3.0	1.3	1.2	2.9
Westleigh	11A	4.6	2.0	4.8	0.9	0.8	2.4
	11B	4.1	7.2	4.5	1.6	1.4	9.1
Clovelly	12A	0.0	2.0	4.2	0.5	0.7	1.2
	12B	3.7	6.3	4.2	1.2	1.2	1.3
Avalon	13A	4.4	1.8	3.6	0.7	0.8	0.9
	13B	3.4	6.4	3.3	1.3	1.3	1.5
Fernwood	14	4.0	1.2	3.4	0.6	0.7	0.8
Pinedene	15A	3.2	3.4	3.6	0.8	0.7	1.1
	15B	3.0	5.8	3.6	1.3	1.4	1.3
Hutton	16A	4.6	5.0	4.0	0.6	0.6	1.6
	16B	2.6	7.9	2.7	0.8	1.0	2.0
Swartland	18A	3.1	7.4	5.0	1.0		1.3
	18B	3.7	2.0	3.7	1.7	0.9	1.3
Rensburg	19A	3.0	1.1	3.9	0.8	0.7	1.0

* 10g soil + 100ml solution

Table 11e Supernatant chloride in soil suspensions equilibrated with sulphuric acid or sodium sulphate solutions (4g soil + 200ml solution)

Soil Form	Lab No	Initial sulphate concentration (mg/L)					
		0 Water	24 Acid	24 Salt	12 Acid	6 Acid	6 Acid*
		Final chloride concentration (mg/L)					
Clovelly	1A	0.3	0.4	0.5	0.4	0.7	1.2
	1B	0.4	0.8	1.0	3.4	1.0	1.3
Arcadia	2A	0.5	0.4	0.3	1.0	1.1	3.3
Glenrosa	3A	0.3	0.4	0.7	0.4	1.6	2.6
Valsrivier	4A	0.6	0.2	0.3	0.8	0.4	0.6
	4B	0.6	0.3	0.4	0.4	0.7	0.8
Hutton	5A	0.4	0.3	0.8	0.2	0.4	0.5
	5B	0.2	0.9	1.5	0.3	0.2	0.6
Avalon	6A	0.6	0.5	1.2	0.3	0.6	0.7
	6B	0.2	0.8	0.3	1.0	0.5	0.6
Nomanci	7A	0.5	0.9	0.5	0.5	0.7	1.2
Shortlands	8A	0.5	0.7	0.6	0.7	0.4	0.8
	8B	0.5	0.7	0.8	0.9	0.5	1.9
Rensburg	9A	0.8	1.0	0.8	0.5	1.4	2.1
	9B	0.6	0.8	4.1	1.1	1.3	2.6
Valsrivier	10A	0.5	0.6	0.6	0.8	0.9	1.6
	10B	0.8	0.6	0.6	0.8	1.3	2.5
Westleigh	11A	0.8	0.5	0.6	0.7	0.7	2.3
	11B	0.9	0.7	0.8	1.0	1.0	3.1
Clovelly	12A	0.5	0.4	0.5	0.4	0.4	0.9
	12B	0.8	0.8	1.0	0.9	1.1	4.4
Avalon	13A	0.1	0.8	0.4	0.3	0.4	0.8
	13B	0.7	0.4	0.4	0.7	0.7	0.6
Fernwood	14	0.2	1.2	0.4	0.3	0.4	1.0
Pinedene	15A	0.4	0.3	0.5	0.5	0.6	0.6
	15B	0.7	0.5	0.5	0.5	1.1	0.9
Hutton	16A	0.3	1.3	0.5	0.5	0.3	0.8
	16B	0.6	0.5	0.5	0.4	0.5	1.3
Swartland	18A	5.1	1.2	1.2	0.6		0.8
	18B	0.8	0.5	0.4	1.0	1.0	1.4
Rensburg	19A	5.1	0.6	0.8	0.9	0.8	2.9

* 10g soil + 100ml solution

Table 11f Supernatant Ca & Mg in soil suspensions equilibrated with sulphuric acid (4g soil + 200ml solution)

Soil Form	Lab No	Initial sulphate concentration (mg/L)					
		0	6	6	0	6	6
		Water	Acid	Acid*	Water	Acid	Acid*
			Ca (mg/L)			Mg (mg/L)	
Clovelly	1A	0.2	0.9	2.2	0.0	0.2	0.9
	1B	0.3	0.9	2.2	0.1	0.4	1.3
Arcadia	2A	0.7	1.2	8.0	0.8	1.1	7.3
Glenrosa	3A	0.3	1.2	5.8	0.0	1.9	1.3
Valsrivier	4A	0.3	1.6	4.2	0.0	0.7	1.1
	4B	1.9	3.6	8.9	0.4	0.8	22.4
Hutton	5A	0.2	0.9	1.1	0.1	0.4	0.7
	5B	0.4	1.0	1.6	0.2	0.6	1.0
Avalon	6A	0.2	0.8	1.3	0.0	0.2	0.4
	6B	0.3	0.6	1.6	0.2	0.1	1.6
Nomanci	7A	0.3	0.9	1.3	0.1	0.6	0.9
Shortlands	8A	0.6	1.9	5.3	0.1	1.0	1.8
	8B	0.9	3.1	3.4	0.7	0.8	1.7
Rensburg	9A	2.1	3.7	17.8	0.8	1.1	7.6
	9B	3.0	4.7	11.1	1.2	1.6	5.4
Valsrivier	10A	0.8	1.8	5.0	0.3	0.8	2.2
	10B	1.3	4.6	9.0	0.3	1.1	16.9
Westleigh	11A	0.4	1.3	6.2	0.0	0.3	4.7
	11B	0.8	1.8	5.8	0.0	0.6	12.4
Clovelly	12A	0.1	0.7	1.8	0.0	0.1	0.0
	12B	0.2	1.0	1.8	0.0	0.4	1.0
Avalon	13A	0.3	1.4	2.2	0.0	0.2	0.0
	13B	0.4	1.2	5.9	0.0	0.2	1.1
Fernwood	14	0.3	1.8	5.3	0.0	0.3	0.7
Pinedene	15A	0.3	1.0	2.9	0.0	0.2	0.2
	15B	0.6	1.8	4.1	0.0	0.6	3.0
Hutton	16A	0.2	1.0	1.8	0.0	0.1	0.2
	16B	0.1	0.6	0.9	0.0	0.1	0.0
Swartland	18A	0.4	1.8	6.9	0.2	0.4	1.6
	18B	1.6	2.2	10.1	0.8	1.3	21.6
Rensburg	19A	2.2	2.9	14.2	1.7	1.4	6.9
Solution only							

* 10g soil + 100ml solution

Table 11g Supernatant Na & K in soil suspensions equilibrated with sulphuric acid (4g soil + 200ml solution)

Soil Form	Lab No	Initial sulphate concentration (mg/L)					
		0	6	6	0	6	6
		Water	Acid	Acid*	Water	Acid	Acid*
		Na (mg/L)			K (mg/L)		
Clovelly	1A	0.4	0.6	0.2	1.4	2.3	12.6
	1B	0.1	0.4	0.2	2.4	4.0	8.7
Arcadia	2A	3.6	4.2	12.2	0.6	1.0	13.0
Glenrosa	3A	0.2	4.6	0.4	1.0	1.1	29.3
Valsrivier	4A	0.7	0.6	2.7	0.4	1.6	15.0
	4B	4.1	3.6	21.2	15.3	20.0	147.2
Hutton	5A	3.6	0.3	0.2	0.0	0.0	0.0
	5B	0.0	0.1	0.7	0.0	0.1	0.0
Avalon	6A	0.2	0.7	0.0	0.2	0.8	7.3
	6B	0.3	0.1	0.6	0.4	1.4	0.7
Nomanci	7A	0.7	0.4	1.1	0.0	0.1	0.0
Shortlands	8A	0.4	0.1	0.9	0.7	2.2	7.0
	8B	1.6	1.1	3.7	0.3	6.2	0.6
Rensburg	9A	0.3	0.3	0.9	0.4	1.1	11.0
	9B	0.7	0.8	1.8	1.0	2.8	4.4
Valsrivier	10A	0.4	0.2	0.8	4.9	8.7	73.8
	10B	1.4	1.4	6.2	4.4	15.8	164.7
Westleigh	11A	0.2	0.4	0.9	2.3	5.8	35.0
	11B	4.4	3.1	19.4	2.8	7.8	100.7
Clovelly	12A	0.0	0.2	0.2	2.2	4.0	24.0
	12B	0.3	0.7	2.8	1.9	5.1	4.1
Avalon	13A	0.6	0.2	0.2	1.2	2.6	13.7
	13B	0.6	0.2	0.1	2.0	4.4	28.3
Fernwood	14	0.4	0.1	0.0	1.7	2.4	17.2
Pinedene	15A	0.6	0.1	0.0	2.8	3.3	25.3
	15B	0.6	0.7	1.8	2.1	7.4	39.4
Hutton	16A	0.2	0.2	0.2	1.4	11.0	19.3
	16B	0.4	0.3	0.6	0.7	1.7	1.3
Swartland	18A	0.1	0.6	0.4	1.0	2.7	26.0
	18B	2.1	2.2	8.6	1.3	9.0	71.6
Rensburg	19A	8.1	8.7	31.6	3.8	2.2	17.8
Solution only							

* 10g soil + 100ml solution

overestimation of sulphate retention capacity. The problem is intractable in the sense that any attempt to adjust the pH of the "water" system (e.g. with HCl or some other acid) would entail the addition of an anion with the potential to exchange for sulphate, and introduce as much uncertainty into the interpretation of the result as is currently associated with pH differences. On the other hand, ignoring the natural, water-soluble sulphate content would inevitably result in the sulphate retention capacity being underestimated. Ultimately a clearer picture would emerge if each soil were subjected to an elaborate experiment in which the pH, accompanying cation and background ionic strength effects were all compared simultaneously with a number of sulphate concentrations. Such work would be laborious enough if performed on only one or two soils. To perform it on all 19 soils was therefore deemed impractical.

Instead, the following approach was adopted. The most strongly sulphate-sorbing profile in the collection, and which also is likely to be influenced minimally by desorption of native sulphate, is the Hutton soil (no.16). The equilibrium concentrations of sulphate after contacting the A horizon supernatant with the B horizon are 4.1 and 1.4 mg L^{-1} at soil solution ratios of 1:50 and 1:10, respectively (from the final two columns in Table 11c). Subtracting these values from the initial sulphate concentration of 5.6 (by chemical analysis, as opposed to the nominal value of 6) gives calculated values of 75 and 32 mg kg^{-1}, respectively for adsorbed sulphate. (It is useful to recall here that the two cases represent, respectively, 50 and 10 years of 1000mm per annum rainfall containing 5.6 mg L^{-1} of sulphate reacting with a 1m depth of soil). For a bulk density of 1000 kg m^{-3}, these figures translate into a sulphate retention capacity of 75 and 32 g m^{-2}, respectively -i.e. 1.5 and 3.2 g m^{-2} per annum. If naturally soluble sulphate is taken into account (which, as expained above, would result in sulphate sorption being underestimated) the lower figure of 1.5 would be revised downward to 0.5 g m^{-2}.

These calculations serve to bracket a realistic range of values which might be anticipated for this soil over a period of one to five decades, and it is on this basis that a working value for sulphate retention of 1 g m^{-2} per annum per metre soil depth was adopted for later incorporation into catchment-scale calculations (and which would be valid for, say, 30 to 50 years hence).

What remains to be done is to establish comparable values for sulphate retention in the other soils. As already explained, the equilibration data in Table 11c are unsatisfactory for this purpose because of the magnified error associated with water-soluble sulphate interference in establishing marginal differences between initial and final sulphate concentrations. What is needed is a reliable basis for ranking, quantitatively, each soil **relative to profile 16** so that the calculations which could be made confidently for this soil, in view of its strong sulphate retention, could be applied to all the others.

Before describing such an approach in the next section, it should be mentioned that while soil 16 has the greatest sulphate sorbing capacity of those soils sampled, there are undoubtedly soils which, although not widespread, would adsorb sulphate even more strongly. For example, a red subsoil from the Natal midlands (Balmoral series) was subjected, for reference purposes, to the same 6 mg L^{-1} sulphate treatment at a soil solution ratio of 1:10 and no sulphate could be detected in the equilibrium supernatant, indicating complete adsorption. This would work out at 5.6 g m^{-2} per annum, per metre soil depth (for a rainfall of 1000mm and a sulphate concentration of 5.6 mg L^{-1}), compared with the working value of 1, and the range of 0.5 to 3.2, referred to above.

A suspension equilibration of the southern Natal soils was also performed at the same soil:solution ratio (1:50) with distilled water only, so that the water-soluble sulphate levels could be compared with those of the catchment soils shown in Figure 11c. The results are shown in Table 12, and will be discussed in a later section.

Table 12. Composition of southern Natal soil suspension supernatants (4g soil + 200ml distilled water)

Soil Form	Lab No	EC (mS/m)	pH	Concentration (mg/L)		
				SO_4^{2-}	Cl^-	NO_3^-
Cv 27	1A	0.75	6.19	0.3	0.5	0.6
	1B	0.94	6.12	1.1	0.7	-
Cv 26	12A	1.25	6.00	0.7	1.1	0.8
	12B	2.23	5.77	1.3	2.7	1.0
Ar 10	23A	0.92	6.30	0.2	0.5	0.5
Gs 18	2A	0.69	6.33	0.0	0.1	0.5
Gs 18	3A	0.79	6.27	0.0	0.5	0.6
Va 31	6A	0.72	5.88	0.0	0.4	0.7
	6B	0.90	6.07	0.4	0.6	1.1
Hu 27	9A	0.68	6.39	0.0	0.1	0.5
	9B	0.99	6.38	0.4	1.3	1.2
Hu 27	20A	0.75	6.00	0.0	0.4	0.5
	20B	0.85	5.87	0.4	0.6	1.1
Hu 26	22A	1.20	6.17	0.0	0.4	0.5
	22B	1.73	6.17	0.3	0.3	1.2
Av 26	19A	1.09	5.95	0.7	0.5	0.6
	19B	1.66	5.84	0.7	1.7	0.9
Sd 12	13A	0.75	6.65	0.2	0.2	0.5
	13B	1.15	6.58	0.5	0.4	1.0
Sd 12	17A	1.37	6.68	0.3	0.4	0.5
	17B	1.84	6.74	1.2	0.4	1.5
Rg 10	15A	1.27	6.65	0.0	0.1	0.5
	15B	2.69	6.89	0.4	1.1	1.2
Va 41	8A	0.66	6.32	0.0	0.1	0.6
	8B	1.35	6.25	1.1	1.0	1.2
We 13	11A	1.04	6.55	0.3	0.4	1.0
	11B	1.94	6.70	0.7	0.6	1.4
We 13	14A	1.32	6.54	0.4	0.3	0.8
	14B	1.83	6.52	0.7	0.4	1.8
Pn 24	24A	0.64	6.06	0.0	0.3	0.6
	24B	0.91	6.12	0.0	0.3	1.2
Hu 18	25A	1.05	5.56	1.9	0.5	0.6
	25B	1.22	5.49	1.7	0.7	1.0
Sw 31	4A	0.81	6.57	0.6	0.7	0.6
	4B	1.37	6.45	0.8	1.1	1.0
Ia 11	5A	0.68	6.33	0.0	0.5	0.5
	5B	0.78	6.27	0.0	0.4	1.1
Ss 26	7A	1.13	6.43	0.0	0.4	1.4
	7B	1.70	6.64	0.4	0.8	0.8
Ss 26	16A	1.38	6.60	0.4	0.5	1.4
	16B	0.80	7.13	1.2	1.3	1.6
Bv 26	10A	0.57	6.42	0.0	0.3	0.6
Gf 22	18A	1.02	6.01	0.3	0.2	0.5
	18B	1.13	5.81	1.0	0.3	1.1
Es 14	21A	0.96	6.07	0.4	0.8	1.0
	21B	1.74	6.37	1.0	1.4	1.4

4.7.3 Leaching columns

The column leaching procedure has been described in detail in Chapter 3. In many respects this is the most realistic basis for comparing the sulphate sorption characteristics among the different soils, provided that a similar rate of loading is applied in each case. Breakthrough curves are presented for four of the soils at a 24 mg L^{-1} sulphate input concentration as sulphuric acid in Figures 6a and 6b, and as sodium sulphate in Figures 7a and 7b. Breakthrough curves for 16 of the soils at 12 mg L^{-1} sulphate (as sulphuric acid) are given in Figures 8a, b, c and d. All these curves show the initially low EC associated with the distilled water pre-leach, a sustained low concentration for a variable number of pore volumes until the EC begins to rise - gradually or sharply depending on whether the sulphate retention capacity is strong or weak - and then to level off at a value which depends upon the intensity of the residual sulphate sorption. The influent sulphate solution was replaced with water at this stage and the EC dropped again to a new steady state. A comparison of all the curves reveals that, as would be expected, steeper breakthrough slopes and high, flat plateaux correspond to short approaches (i.e. a small number of pore volumes before EC responds to the applied sulphate), indicating a small capacity to retain sulphate; conversely, more gradual increases in EC, lower, more inclined plateaux and longer approaches (many pore volumes) to breakthrough indicate strong retention. For the 12 mg L^{-1} H_2SO_4 treatments (Figures 8a-d), the number of pore volumes from initiation of leaching to the beginning of breakthrough varied from 1 (the minimum possible, indicating negligible retention) to 21 (soil 16), and **this value was used as the quantitative criterion for ranking the soils according to their sulphate retention capacity**. A summary of the soil rankings is given in Table 13.

The breakthrough curves in Figures 6a and 6b indicate that, in general, there is a tendency for acid input solutions to result in more sulphate sorption than neutral salt (Na) solutions of the

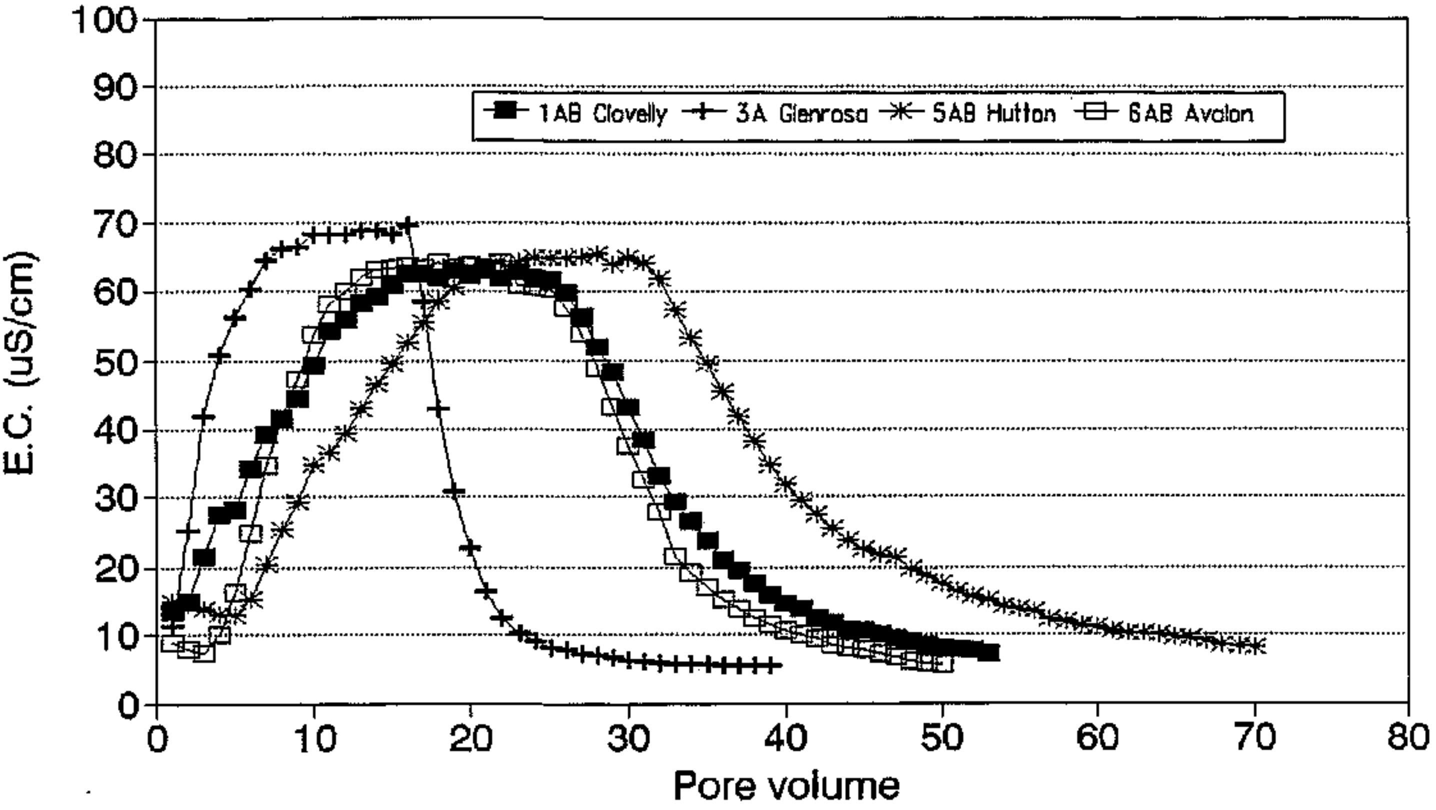

Figure 6a. Breakthrough curves for catchment soils (1, 3, 5 and 6) with H_2SO_4 (24mg/L sulphate) followed by distilled water

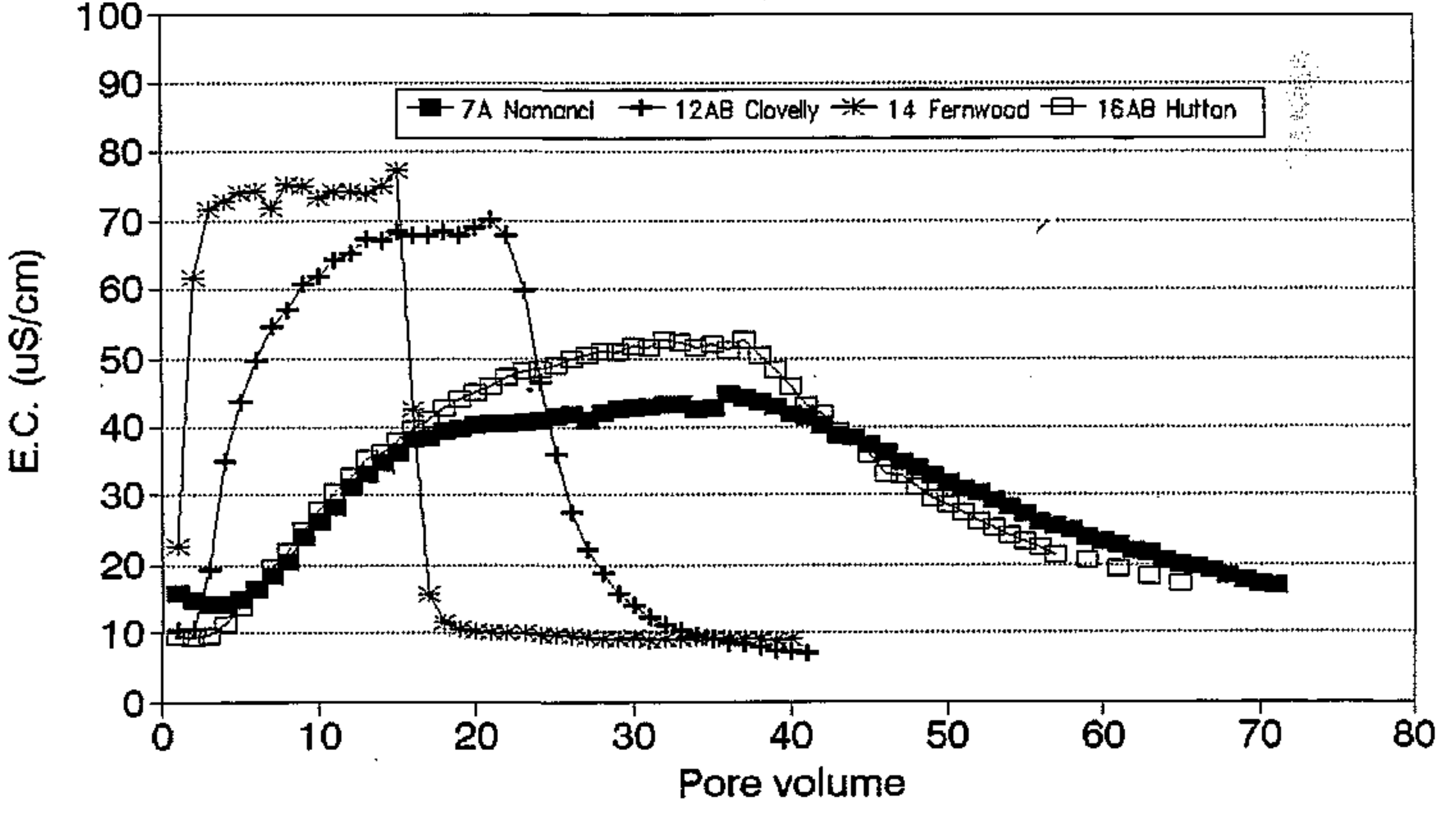

Figure 6b. Breakthrough curves for catchment soils (7, 12, 14 and 16) with H_2SO_4 (24mg/L sulphate) followed by distilled water

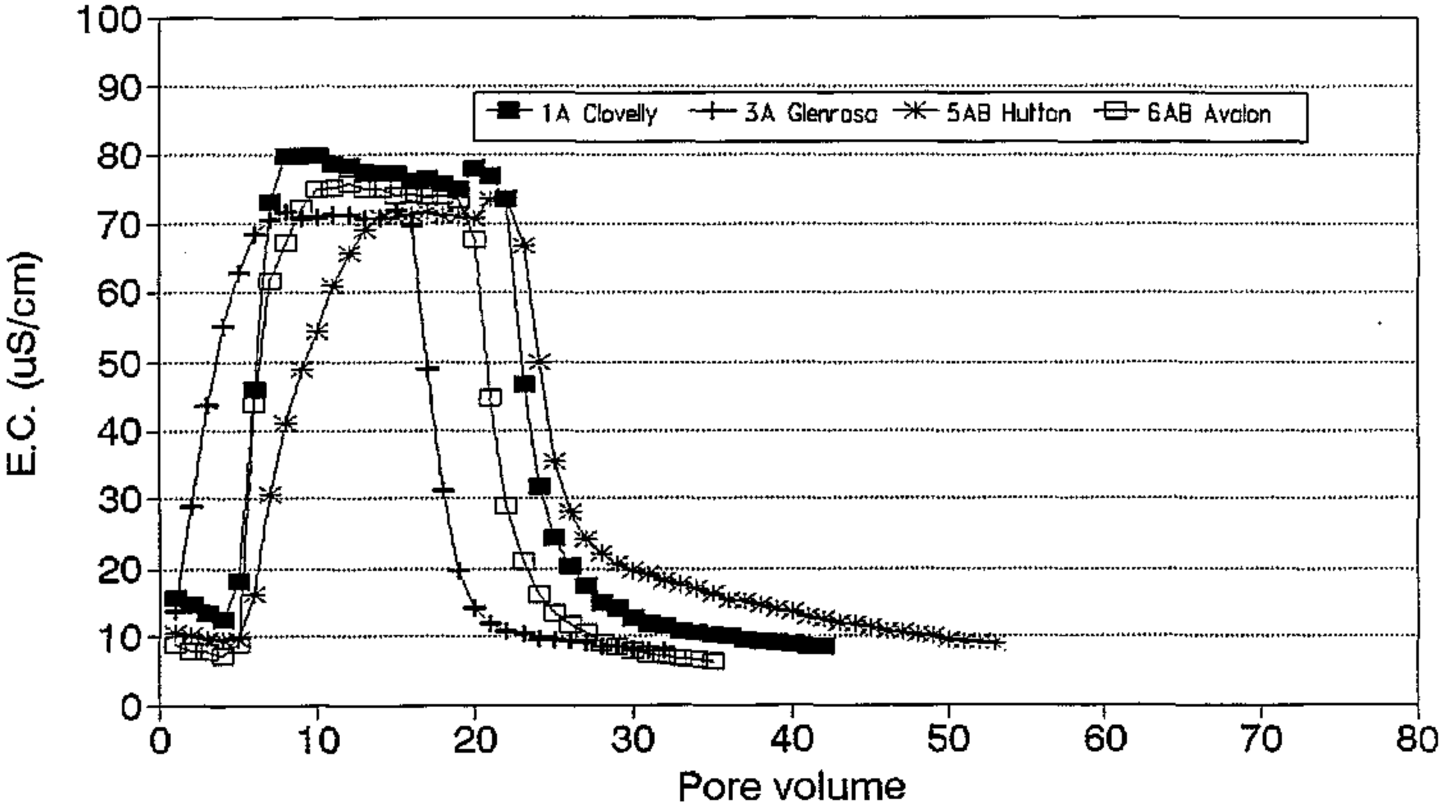

Figure 7a: Breakthrough curves for the same soils as in Fig. 6a, but with Na_2SO_4 in place of H_2SO_4 (24 mg L^{-1} sulphate)

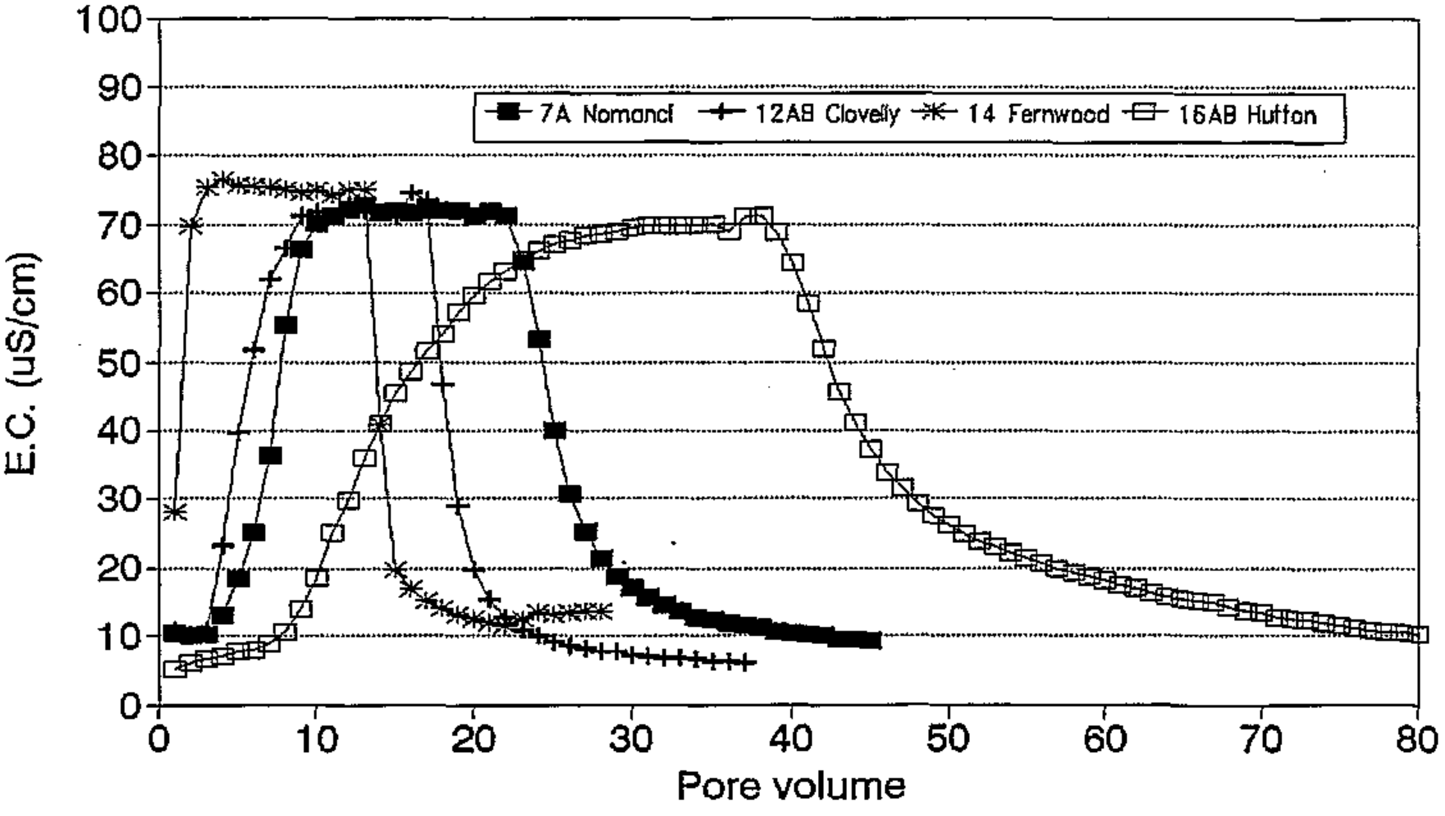

Figure 7b: Breakthrough curves for the same soils as in Fig. 6b, but with $Na_2 SO_4$ in place of H_2SO_4 (24 mg L^{-1} sulphate)

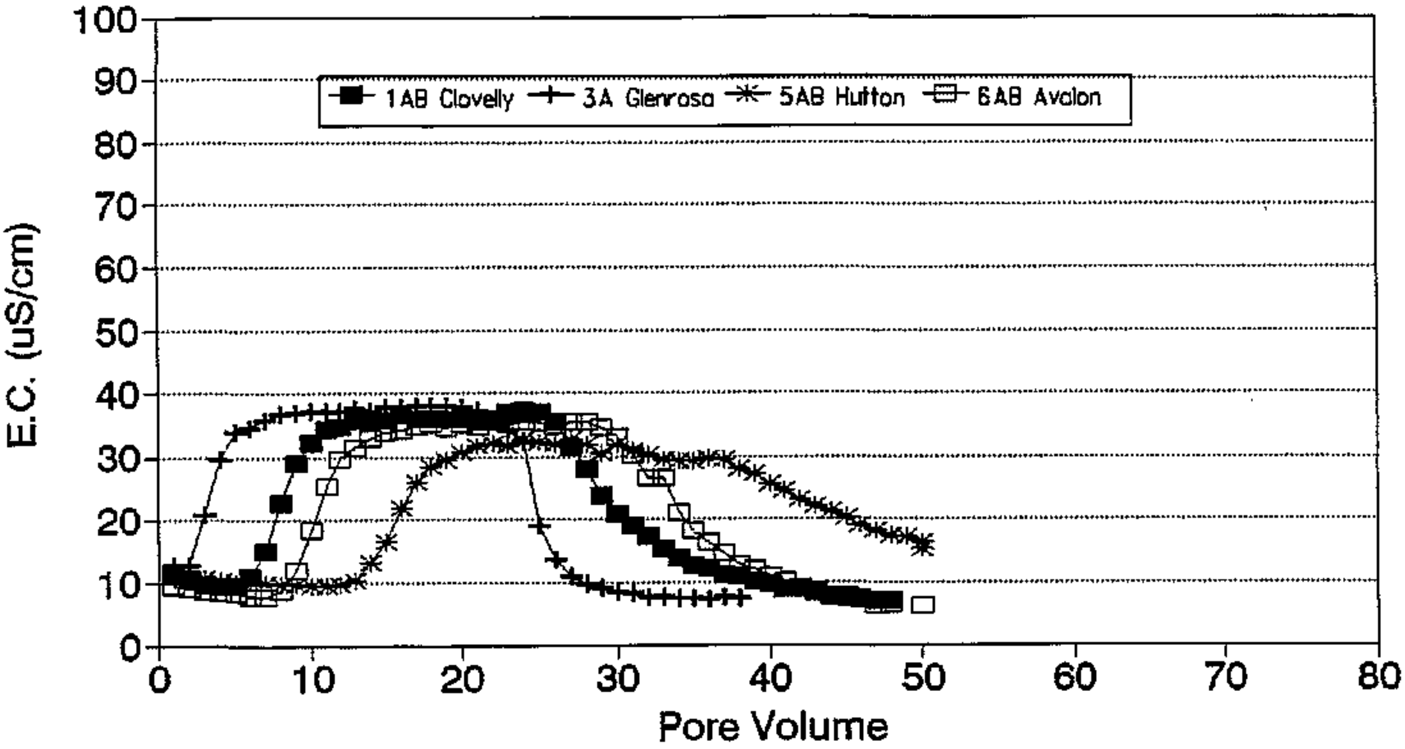

Figure 8a. Breakthrough curves for catchment soils (1, 3, 5, and 6) with H_2SO_4 (12mg/L sulphate) followed by distilled water

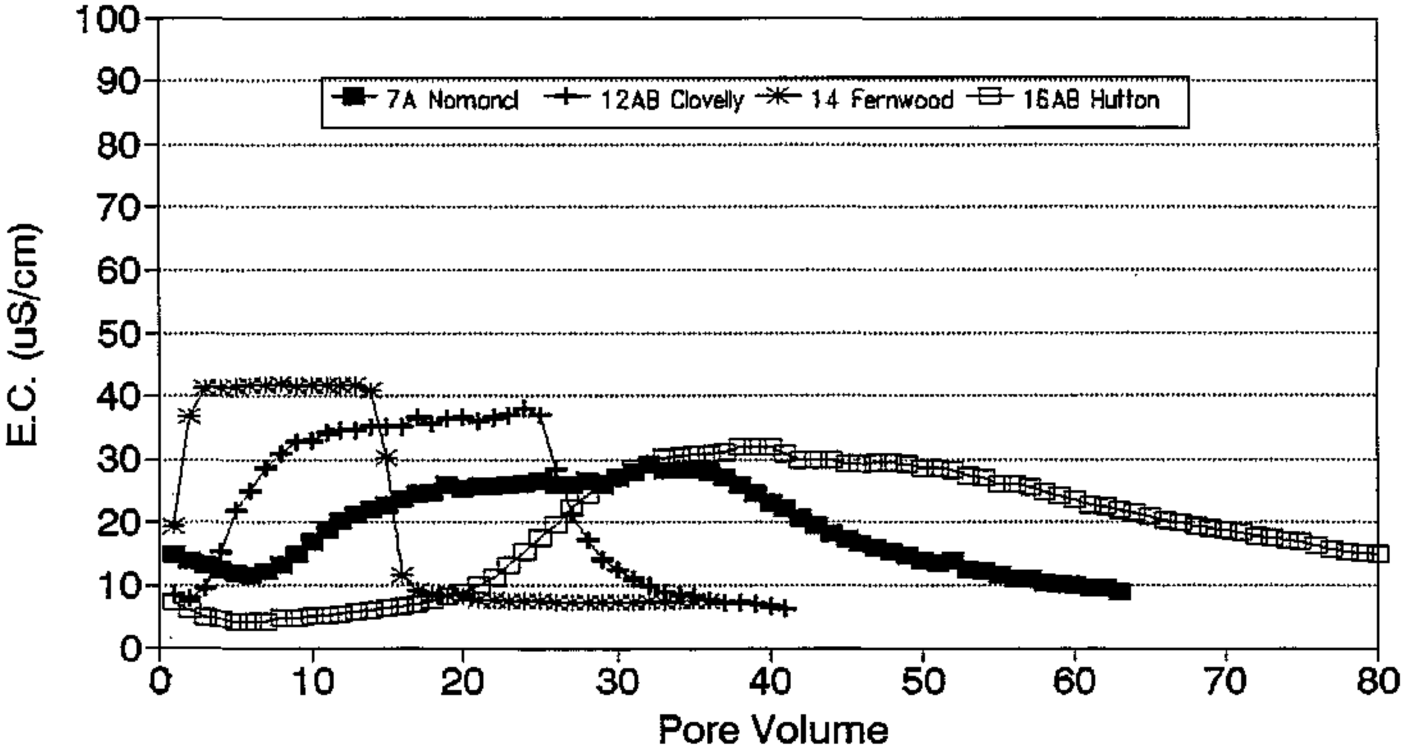

Figure 8b. Breakthrough curves for catchment soils (7, 12, 14 and 16) with H_2SO_4 (12mg/L sulphate) followed by distilled water

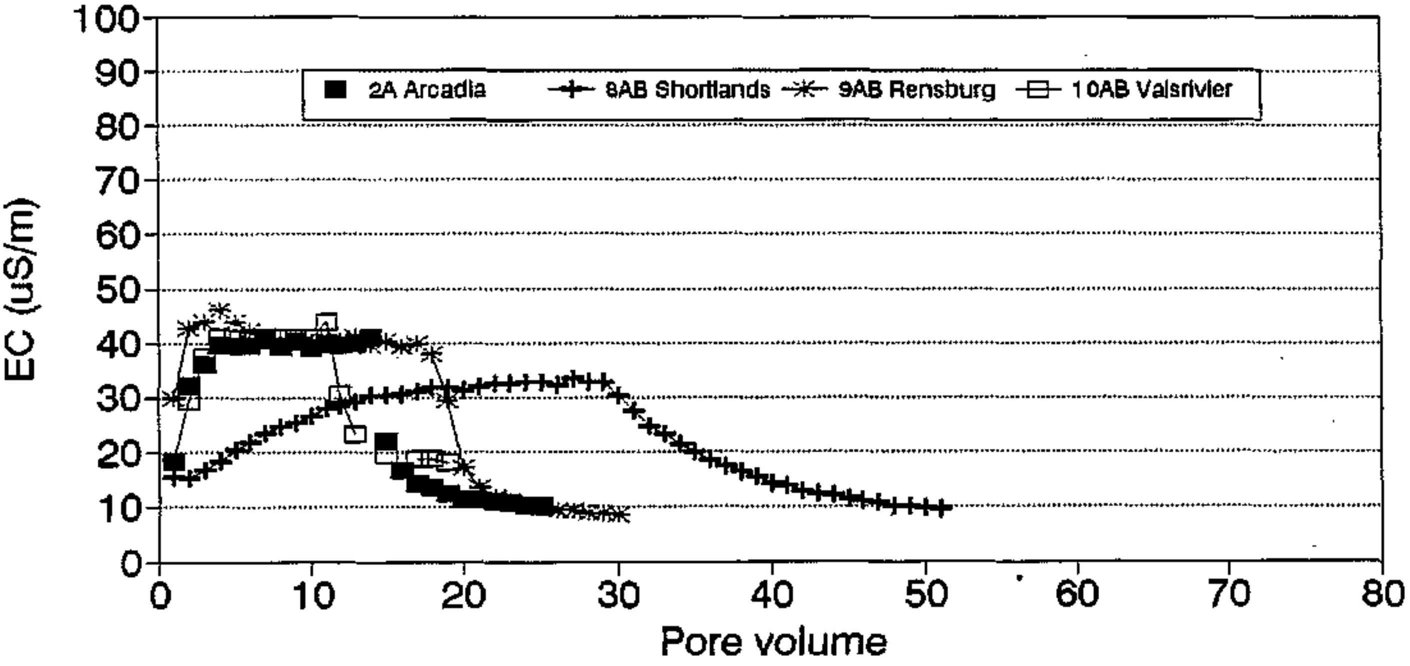

Figure 8c. Breakthrough curves for catchment soils (2, 8, 9 and 10) with H_2SO_4 (12 mg/L sulphate) followed by distilled water

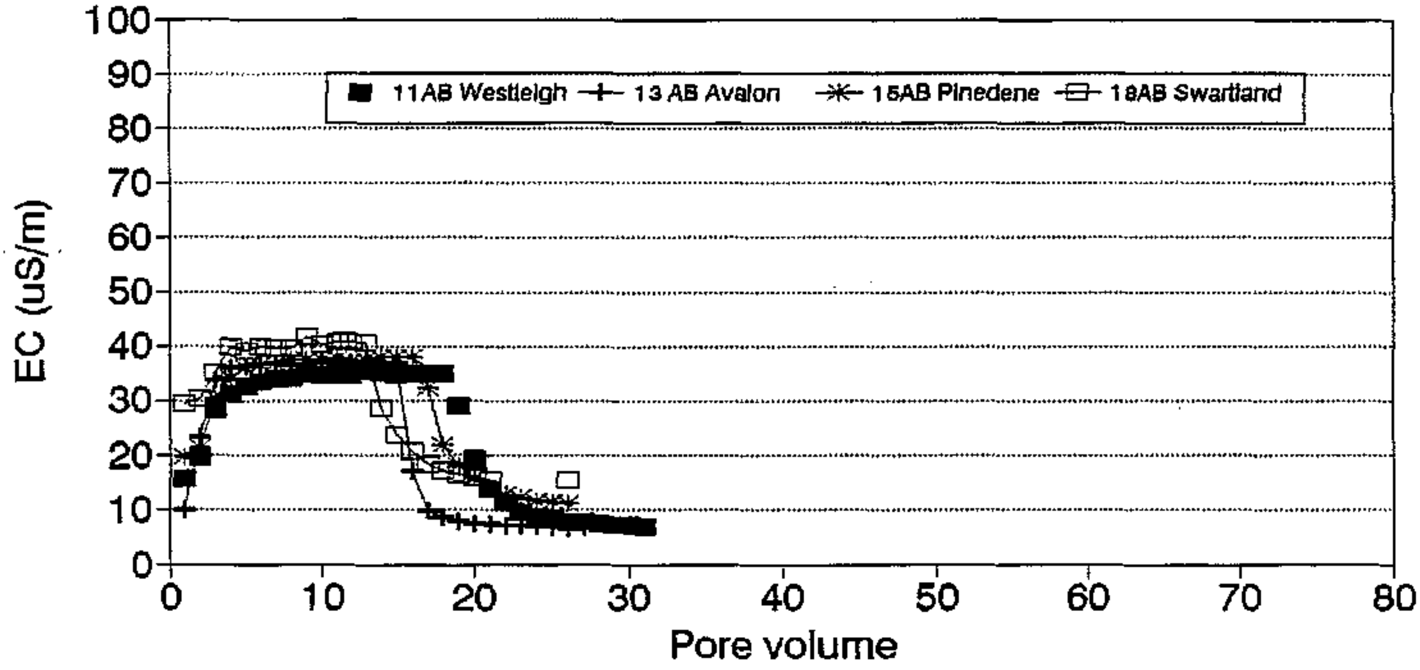

Figure 8d. Breakthrough curves for catchment soils (11, 13, 15 and 18) with H_2SO_4 (12mg/L sulphate) followed by distilled water

Table 13: Relative ranking of soils in terms of their sulphate breakthrough characteristics

No of pore volumes before breakthrough	Soil Profile Number
0	2, 4, 9, 10, 11, 13, 14, 15, 18, 19
2	3
3	8, 12
5	1
8	6, 7
13	5
21	16

same sulphate concentration. This is particularly the case for soil 7 which has an exceptionally high organic matter content.

In order to establish whether the measured EC of the leachate corresponded with sulphate concentration, a regression analysis was performed and the equations for the relationships shown in Figure 9a (24 mg L^{-1} sulphate as either sulphuric acid or sodium sulphate input) and 9b (12 mg L^{-1}) were effectively identical, with $r^2 = 0.95$. This implies that the breakthrough curves plotted using EC measurements could effectively be considered as representing the breakthrough of sulphate.

For the purpose of having a record of the composition (and especially of the cations accompanying sulphate) of the column leachates, selected pore volumes were analysed and the results are shown in Table 14. In the last two columns of Table 14 the charge balance between sulphate and total cations is compared, and it is of interest to note that the cation charge is matched closely by sulphate in the more acidic soil leachates, whereas there is a marked anion deficit in those leachates which have a higher pH, suggesting that in these samples there has been some exchange of sulphate for bicarbonate in the column and that where bicarbonate is available it tends to lead sulphate as the anion

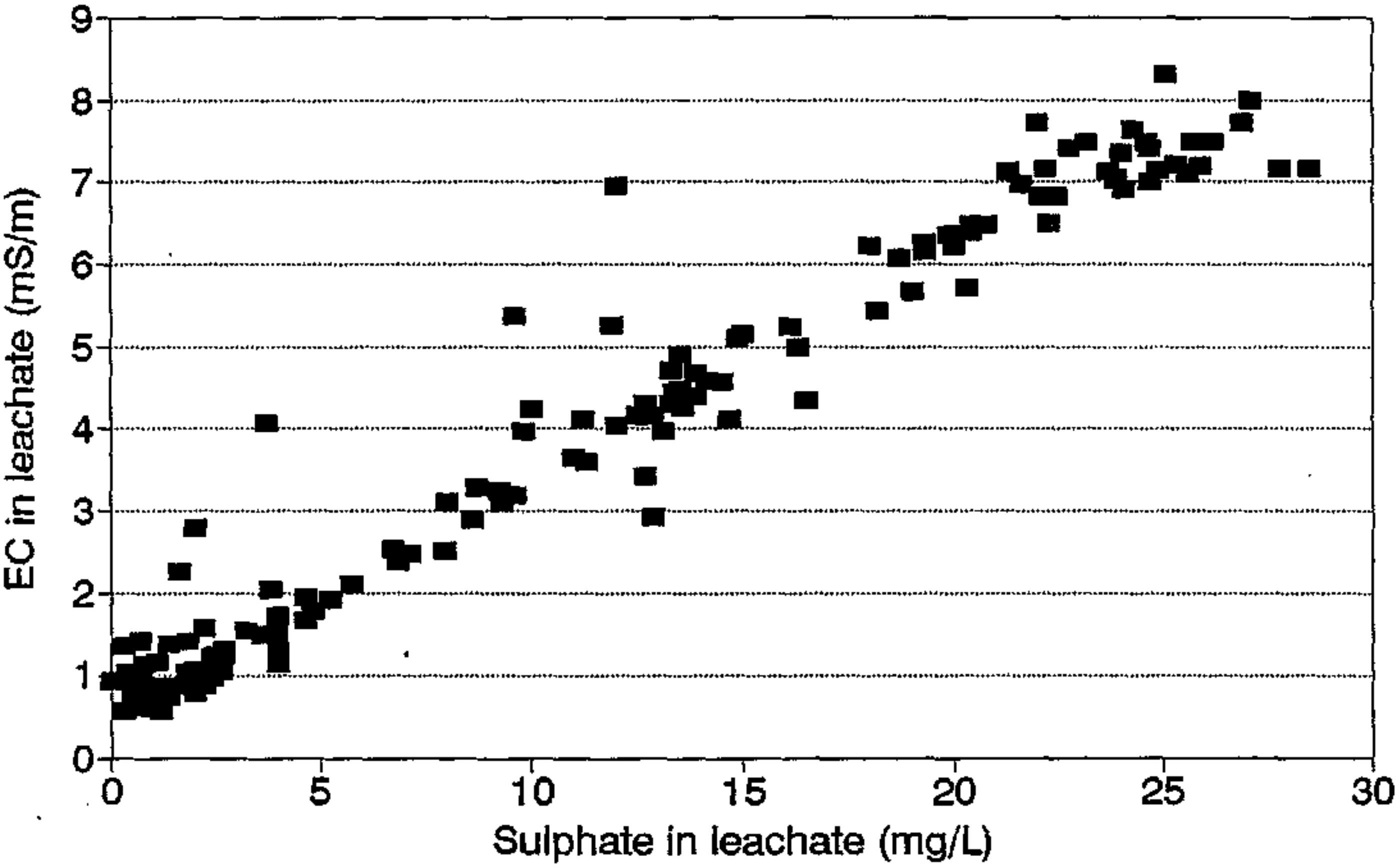

Figure 9a. Correlation of leachate conductivity with sulphate concentration of catchment soil breakthrough curves with H_2SO_4 and Na_2SO_4 (24mg/L sulphate input)

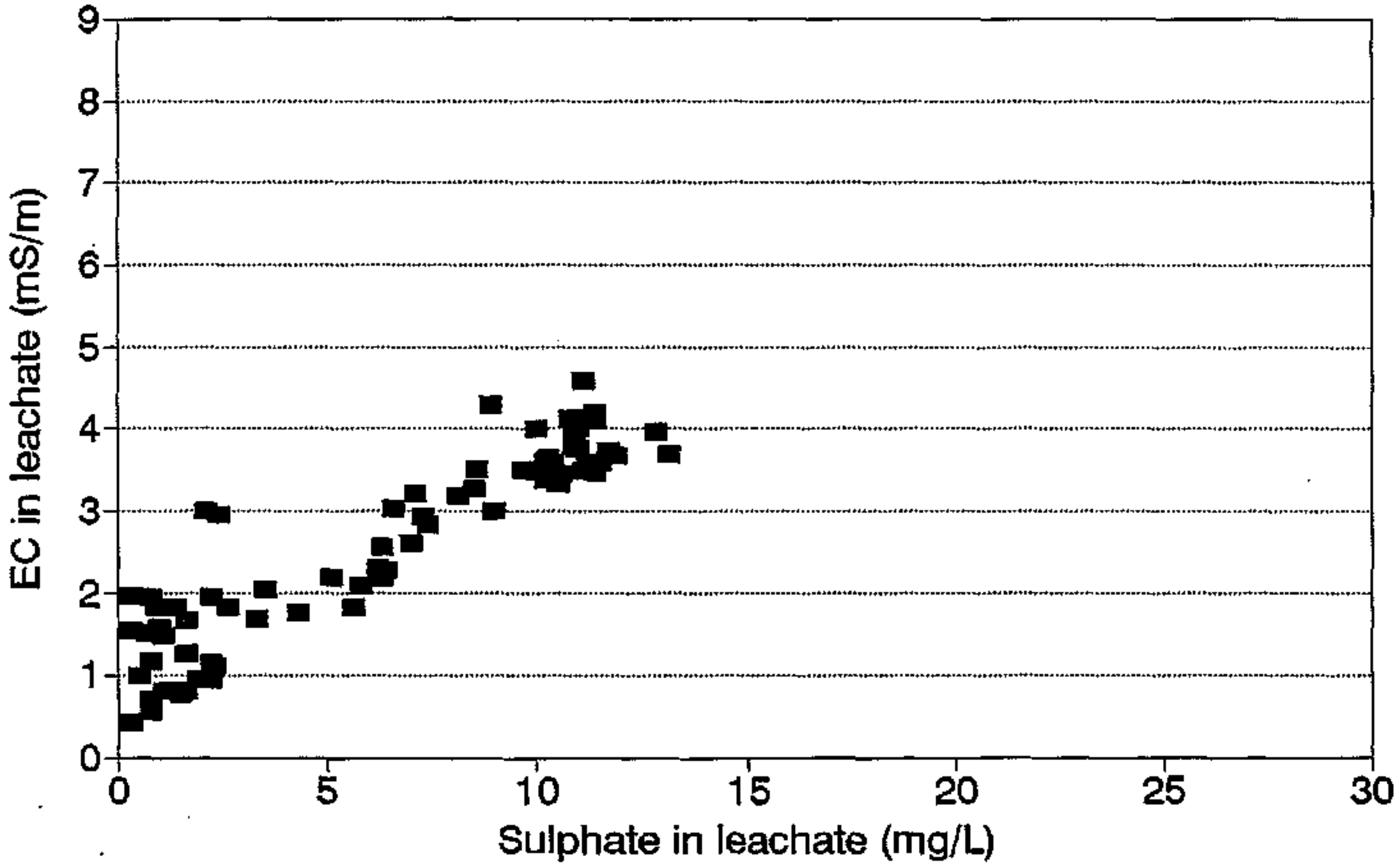

Figure 9b. Correlation of leachate conductivity with sulphate concentration of catchment soil breakthrough curves with H_2SO_4 (12mg/L sulphate input)

Table 14. Composition of selected pore volumes of leachate from soil columns leached with H_2SO_4 (12mg/L SO_4)

Soil	PV No	SO4 (mg/L)	pH	EC (mS/m)	Ca	Mg	Na	K	SO4	Cations
					(mg/L)				(mmolc/kg)	
1AB	4	2.2	6.23	0.96	0.3	0.1	0.0	0.9	0.05	0.05
	8	6.4	5.90	2.28	1.2	0.3	0.0	2.2	0.13	0.14
	14	10.4	5.69	3.59	0.9	0.4	0.0	4.0	0.22	0.18
2A	1	0.9	6.87	1.84	0.6	0.3	2.8	7.2	0.02	0.36
	2	7.1	6.79	3.23	0.8	0.4	4.0	0.9	0.15	0.27
	5	10.9	6.65	3.98	1.0	0.6	4.3	0.4	0.23	0.30
3A	2	1.6	6.61	1.28	0.6	0.2	0.0	1.0	0.03	0.07
	3	5.8	6.16	2.09	1.0	0.4	0.0	1.4	0.12	0.12
	13	11.0	5.90	3.76	2.2	0.8	0.1	2.4	0.23	0.24
5AB	12	2.1	5.58	0.96	0.4	0.2	0.0	0.1	0.04	0.04
	16	5.1	5.63	2.19	0.7	0.3	0.0	0.9	0.11	0.08
	24	8.5	5.32	3.27	0.9	0.3	0.0	3.2	0.18	0.15
6AB	7	1.5	5.72	0.79	0.6	0.3	0.0	0.0	0.03	0.06
	10	5.6	5.32	1.84	0.8	0.7	0.0	0.1	0.12	0.10
	18	9.7	5.36	3.51	1.2	1.1	0.0	0.6	0.20	0.17
7A	6	0.8	6.41	1.17	0.5	0.2	0.0	0.1	0.02	0.04
	10	3.3	6.33	1.69	0.6	0.4	0.1	0.2	0.07	0.07
	21	6.3	6.19	2.57	0.9	0.6	0.0	0.3	0.13	0.10
8AB	1	0.3	6.49	1.56	1.4	0.7	0.0	0.0	0.01	0.13
	2	0.7	6.81	1.52	1.3	0.7	0.0	14.4	0.01	0.48
	4	2.6	6.69	1.84	1.5	0.8	0.0	1.3	0.05	0.17
9AB	1	2.1	6.84	3.00	2.8	0.9	0.4	0.7	0.04	0.25
	2	8.9	6.63	4.29	3.4	1.2	0.2	1.4	0.19	0.31
	8	11.0	6.54	4.07	3.4	1.2	0.0	2.1	0.23	0.32
10AB	1	1.4	6.62	1.84	1.9	0.6	0.0	1.5	0.03	0.18
	2	7.3	6.59	2.94	2.3	0.8	0.0	2.4	0.15	0.24
	4	11.0	6.62	4.13	2.5	1.1	0.0	5.4	0.23	0.35
11AB	1	1.0	6.89	1.57	0.4	0.0	3.2	0.0	0.02	0.16
	3	7.4	6.85	2.83	0.9	0.0	4.4	0.0	0.15	0.24
	10	11.4	6.42	3.47	1.0	0.4	3.9	0.6	0.24	0.27
12AB	2	1.1	6.39	0.81	0.4	0.2	0.0	0.4	0.02	0.05
	5	6.3	6.03	2.19	1.1	0.6	0.0	0.9	0.13	0.13
	12	10.6	5.87	3.46	1.6	0.9	0.0	1.8	0.22	0.20
13AB	1	0.5	6.47	1.00	0.8	0.1	0.0	1.4	0.01	0.08
	2	6.2	6.33	2.31	1.4	0.2	0.0	2.3	0.13	0.14
	4	11.5	6.04	3.60	2.1	0.4	0.0	4.0	0.24	0.24
14	1	0.8	6.76	1.94	1.5	0.2	0.0	3.6	0.02	0.18
	3	11.3	6.48	4.12	2.5	0.4	0.0	3.3	0.24	0.24
	10	11.4	6.46	4.18	2.8	0.4	0.0	3.5	0.24	0.26
15AB	1	0.3	6.85	1.97	1.9	0.7	0.0	0.1	0.01	0.16
	3	6.6	6.66	3.04	2.5	0.9	0.0	0.1	0.14	0.20
	6	10.3	6.51	3.65	3.0	1.0	0.0	0.2	0.21	0.24
16AB	19	1.6	6.65	0.81	0.4	0.0	0.0	0.4	0.03	0.03
	25	4.3	5.18	1.76	0.5	0.2	0.0	1.4	0.09	0.08
	33	9.0	4.97	3.01	0.7	0.3	0.0	2.6	0.19	0.13
18AB	1	2.4	6.89	2.96	2.4	1.2	0.0	0.8	0.05	0.24
	3	8.6	6.70	3.51	2.7	1.3	0.0	1.2	0.18	0.27
	4	10.0	6.66	4.00	2.7	1.5	0.0	0.0	0.21	0.26

accompanying the initial discharge of basic cations from the column. After breakthrough is complete, however, sulphate dominates the anion suite.

4.8 Modelling sulphate movement in the soil profile

Mention should be made of the intention, stated in the original proposal for this project, to investigate the extent to which solute movement models such as LEACHM (J.L. Hutson and R.J. Wagenet, Dept. of Agronomy, Cornell University) might be applied to the question of sulphate movement in soil profiles.

The updated version of LEACHM housed in the CCWR at the University of Natal was examined for its capacity to deal with sulphate movement and it was found that, contrary to expectations, the model in its present form partitions sulphate between solid and solution phases by means of a distribution coefficient (K_d) which cannot be changed for different soils without having to rewrite a programme subroutine. It was decided that the main benefits of using LEACHM as a modelling tool for solute movement stem, to a large extent, from its elegant treatment of profile water movement. In this sense the exercise would have been more a hydrological than a soil chemical one and it was decided not to pursue this line any further in anticipation of future research on the hydrological modelling of solute movement in the catchment.

4.9 Sulphate attenuation in the Vaal Dam catchment

4.9.1 Historical

Adsorbed sulphate in the Vaal Dam catchment has already been discussed and compared to other soils from southern Natal. There was some suggestion that the sulphate concentrations were lower in southern Natal, although the evidence was not conclusive. Attempts to correlate adsorbed sulphate data with various soil properties met with little success. Figure 10 gives some indication

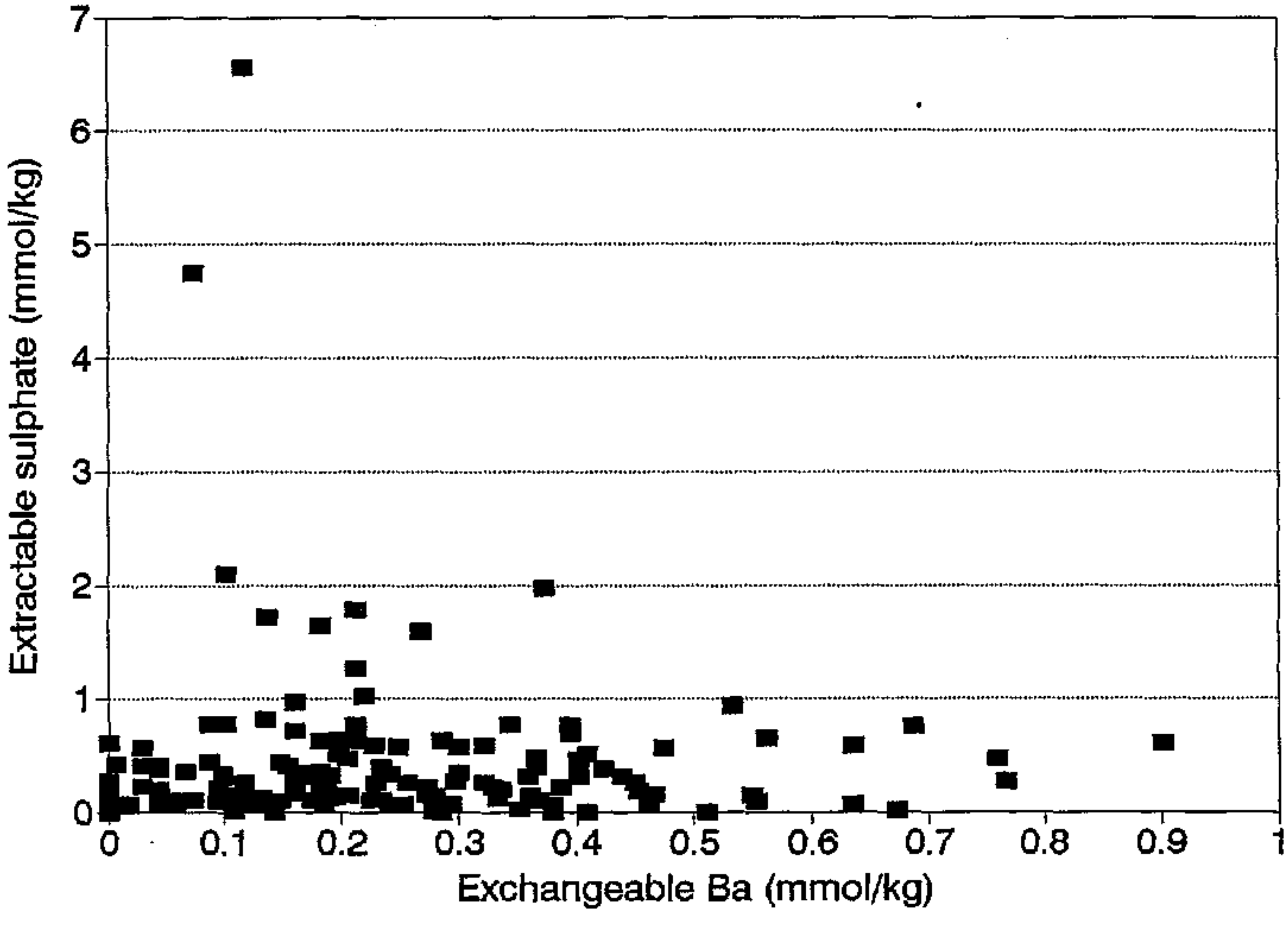

Figure 10. Relationship between phosphate-extractable sulphate and exchangeable barium for all soils

of the fact that high sulphate and high barium are mutually exclusive, as would be expected. However, the barium content did not correlate with the degree of sulphate adsorption indicated by the column leaching experiments. This implies that no serious emphasis need be placed on barium as a factor in determining sulphate attenuation.

A comparison of the composition of aqueous extracts of the catchment soils and those from southern Natal shows interesting differences between soils from the two regions. The data in Table 15 indicate that, on average, soil solutions in the Vaal Dam catchment are considerably more enriched with both soluble salts and sulphate than those from southern Natal. In making this comparison, however, it is assumed that the sample collections are made up of the same distribution of soil types, which may not be the case even though an attempt was made to select a range of soils in southern Natal which matched that collected in the Vaal Dam catchment in terms of soil series classification. A more realistic comparison of sulphate enrichment in the two soil sets is likely to be achieved by examining the sulphate concentration as a fraction of the total dissolved salts. The ratio in the last column of Table 15 provides such an index, from which it is evident that soluble sulphate enrichment in the Vaal Dam catchment soils is about double that in the southern Natal soils.

Table 15. Mean EC and sulphate concentrations in aqueous extracts of soils from the Vaal Dam catchment and southern Natal*

Soil collection	EC (mS m^{-1})	Sulphate (mg L^{-1})	Sulphate/EC ratio#
Vaal catchment	2.45	2.68	1.09
Southern Natal	1.16	0.48	0.41

* Calculated from data in Tables 11a&c and Table 12, respectively.

\# Numerical ratio of values in the middle and first columns

These results provide some preliminary evidence of a possible build-up of sulphates in the catchment soils, which warrants further investigation.

4.9.2 Future capacity to attenuate sulphate

In Section 4.7, a basis was described for ranking the soils according to their sulphate sorbing capacity relative to the measured capacity of the most strongly sorbing soil (no. 16). This now provides a method for calculating the sulphate retention capacity of portions of the catchment as a basis for future research and monitoring studies.

In Figure 11, the Land Type map of the catchment is reproduced (the monochrome version is presented on page 15 of this report) with boundaries of the sub-catchments superimposed on it. Each of these 15 sub-catchments is monitored by a weir at which water samples are regularly taken for analysis. The logical basis for calculating sulphate retention therefore seemed to be this division into sub-catchments. The procedure used to determine the soil series areal extent and depth for the Vaal Dam catchment as a whole was thus repeated to provide this information on the sub-catchment level. Each soil series in the data base was then assigned the same sulphate retention rating (in mg kg^{-1}), as that of the profile in the soil collection which it most resembled. Thereafter, it was a relatively simple task to calculate (taking into account depth estimates and a nominal bulk density of 1500 kg m^{-3}) the gross sulphate retention capacity of the soil mantle in each subcatchment. Because of the approximations involved it was decided to present the results as a classification of the subcatchments according to their relative sulphate retention capacity (as a percentage) and the final product is shown in Figure 12 (the actual figures being presented in Table 16 for reference purposes only). The summaries of the calculations for each subcatchment and other information from the soils data base have been lodged with the WRC on computer disc. The information in Figure 12 represents a satisfactory

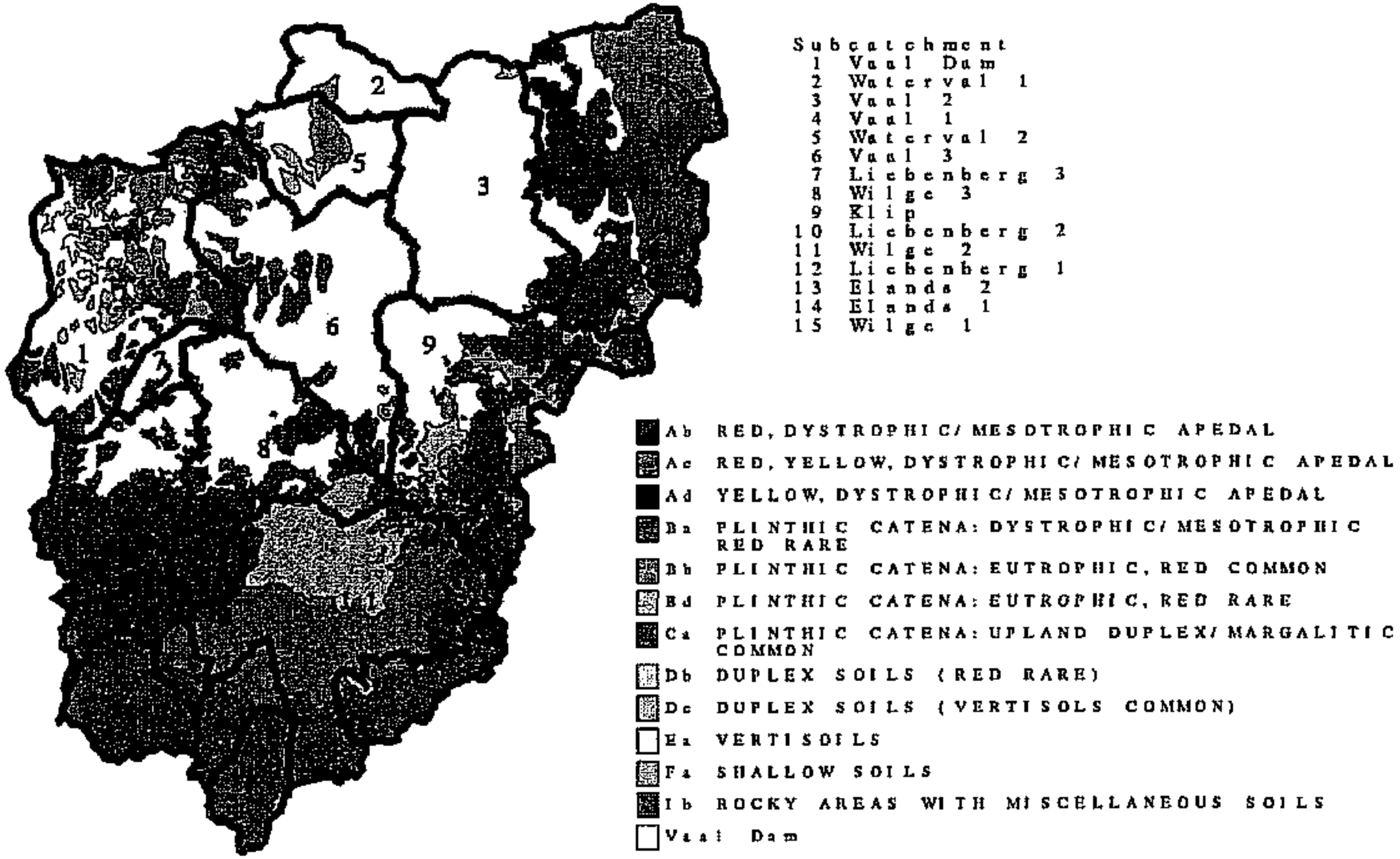

Figure 11 : Subcatchments of the Vaal dam catchment in relation to Land Types

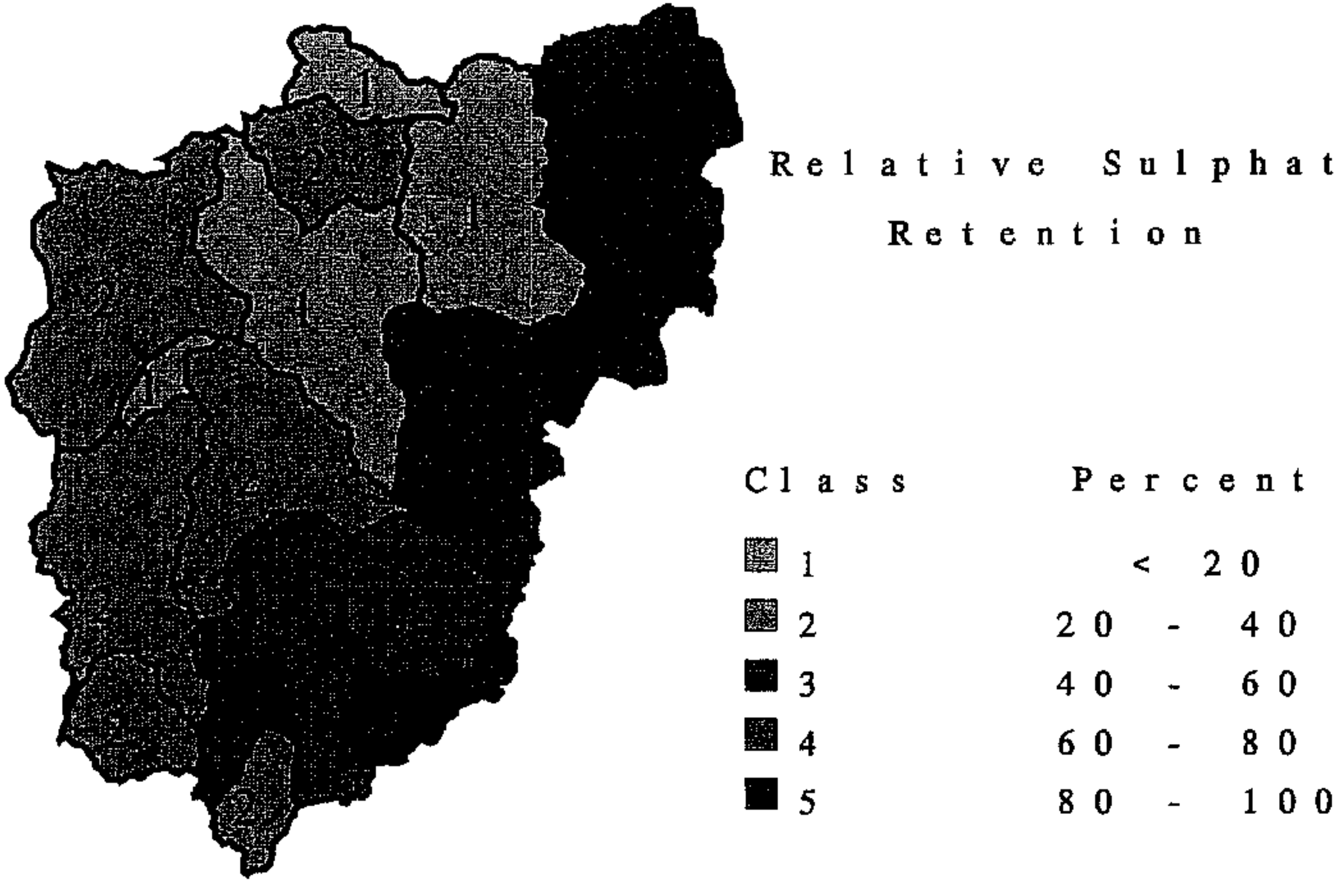

Figure 12 : Classification of the subcatchments of the Vaal dam catchment according to sulphate retention, calculated from soil type and depth

culmination to this project as it permits future monitoring of water quality data in a manner which should greatly increase the confidence with which trends can be interpreted as having resulted from diffuse- as opposed to point-source pollution. The actual sulphate retention values in Table 16, corresponding to the classes in Figure 12, are understandably not easy to present with confidence. The subcatchment with the highest retention value (Wilge 1, which is soil 15 in Figure 11), which is assigned a relative value of 100% for the purpose of classifying the subcatchments in Figure 12, retains about 11 g m^{-2} of sulphate (i.e. 100 kg ha^{-1}) in terms of the calculation scheme referred to above (i.e. for 50m of rainfall containing about 6 mg L^{-1} sulphate).

Table 16. Sulphate retention indices for subcatchments of the Vaal Dam catchment, nominally assigned units of g m^{-2} sulphate*

Subcatchment	Sulphate retention index
Vaal 1	9.1
Vaal 2	0.9
Vaal 3	1.7
Liebenberg 1	3.1
Liebenberg 2	3.3
Liebenberg 3	0.4
Waterval 1	1.2
Waterval 2	3.2
Elands 1	3.0
Elands 2	4.6
Wilge 1	11.0
Wilge 2	6.6
Klip	2.5
Vaal Dam	2.6

* These values will change if assumptions in the calculations about the period and intensity of atmospheric deposition are altered.

4.9.3 Predicting sulphate retention from soil properties

One final question which needs to be addressed is whether the soil characterisation data are in any way related to the sulphate retention behaviour of the soils. A comprehensive attempt was made to find correlations between individual soil properties and the capacity to retain sulphate, and the only properties which showed some indication of having predictive value were those related to soil acidity. The strongest relationship was that shown in Figure 13, in which the correlation between the sulphate retention index (derived from the column leaching study) and the degree of acid (largely aluminium) saturation of the exchangeable cation suite (calculated from data in Table 3) is highly significant. This suggests that the mechanism of retention has to do with the reaction of exchangeable Al with influent sulphate, although it may simply reflect a covariance both of Al solubility and sesquioxide surface reactivity with the acidic conditions which normally accentuate the retention of sulphate. What may be particularly useful about this relationship is the fact that Al or acid saturation is routinely determined on large numbers of soil samples both for the purpose of general characterisation and as a basis for fertilizer and lime recommendations. This suggests a basis for cost-saving in extrapolating the results of the study to new areas.

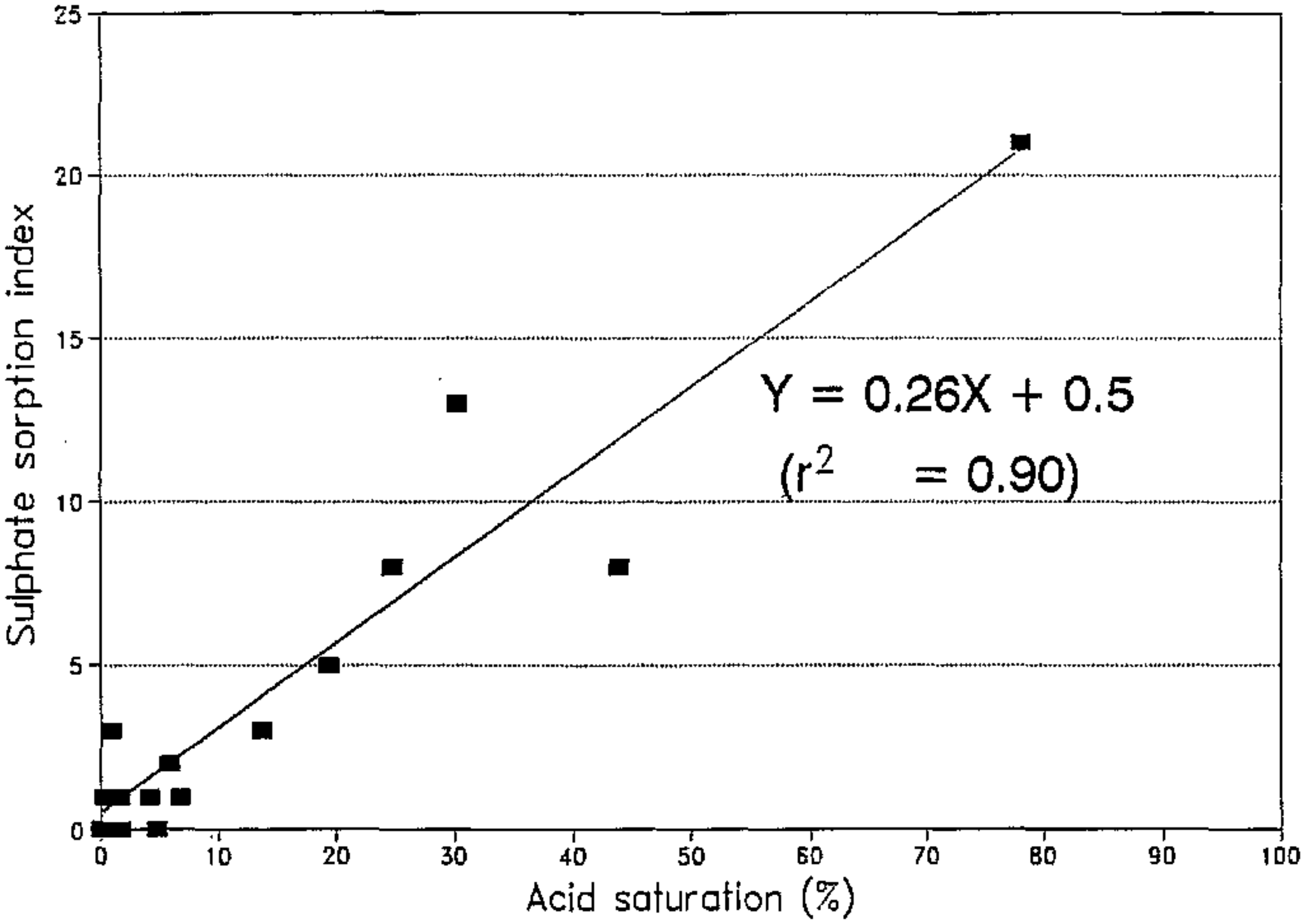

Figure 13. Relationship between sulphate sorption index of catchment profiles from column leaching data and acid saturation of the exchange complex

4.10 General discussion and conclusions

The objectives of this study were: to collect and to study the sulphate retention capacity of representative soils in the Vaal Dam catchment; compare them with soils elsewhere to find out whether sulphate enrichment had taken place; and to explore the possibilities of describing the salt flux through the soil mantle of the catchment by means of computer models. All these objectives have been met, although the modelling work was curtailed when it was discovered that the scope for chemical (as opposed to purely physical) prediction of solute movement is limited unless new subroutines are written into the models.

The project has provided a valuable synthesis of existing information on the soils of the catchment by identifying and characterising the dominant soil types, on both a catchment and subcatchment basis, which should prove useful for a variety of hydrological studies of erosion and water quality in the future. In particular, the map in Figure 11 represents the first published example of a digitised full-colour land-type map stored as a computer file available through the CCWR network. Enlarged land-type maps for subcatchments within the Vaal Dam catchment could be extracted from this file with little difficulty, along with the statistics on dominant soil series. Useful information has also been furnished on the precipitation-weighted mean chemical composition of rainwater at several locations within the catchment.

Nineteen soil profiles were selected to represent the dominant soils of the catchment. After being fully characterised both physically and chemically, these soils were then investigated in detail for their sulphate retention and salinity buffering characteristics by equilibration in pastes, suspensions and leaching columns with acidic and neutral sulphate solutions of different concentrations.

It was found that the saturated paste data were of little value in estimating sulphate sorption because the narrow soil solution ratio would have required unrealistically large sulphate concentrations for the estimation of sorption capacity. The sulphate retention capacity of the most strongly sorbing soil was therefore determined using data from the equilibration of 4g soil with 200ml of a solution containing about 6 mg L^{-1} sulphate. (The bulk deposition data showed that the average sulphate concentration in rainwater could be as high as 4 mg L^{-1}). This wide soil solution ratio is equivalent to 50 years of rainfall (1000mm per annum) reacting all at once with a 1m thick soil mantle, and the method was considered a realistic expedient in comparison to what would have been, for 19 soils, an exceedingly laborious alternative of developing sulphate sorption isotherms spanning a range of pH values for each soil.

The retention capacity of the other soils could not be determined with any certainty by this method because of their low sorptivity coupled with the desorption of significant concentrations of sulphate which was naturally present in the soil. This meant that the equilibrium sulphate concentration after adding the 6mg L^{-1} sulphate solution was not significantly different from that measured after equilibrating the soils in the same volume of distilled water. Furthermore, many of the soils treated in this way were prone to strong clay dispersion and the supernatants proved impossible to clarify sufficiently for analysis of sulphate.

Having estimated sulphate sorption capacity in the most sorptive soil by the equilibration method described in the preceding paragraph, it was possible to rank all of the soils on a relative scale by measuring their retention behaviour with the much more sensitive leaching column method (which also, incidentally, proved to be free of the clay dispersion problem which affected the equilibration experiments). This consisted of counting the number of pore volumes of leachate required before the breakthrough of sulphate occurred (as measured by an upturn in the EC values which correlated with sulphate concentration) from an influent sulphuric acid solution containing 12 mg L^{-1} sulphate. In this way the sulphate retention characteristics of all the soils was estimated and the information was then related to land type data (broad classes of soils and their depths) so that an index of sulphate retention could be calculated for each of the subcatchments. This index must necessarily be taken as a relative one, in view of the uncertainties concerning the accuracy of the original land type inventories (these are based on reconnaissance assessments), the approximations inherent in matching soil series to broad behavioural classes of soils, and the variation in sulphate retention as a function of the assumed period and intensity of atmospheric sulphate deposition. This is not really a disadvantage, however, because in monitoring the historical and future trends in Vaal Dam water quality the most useful approach will be one of comparing the drainage composition of the various subcatchments. To achieve this, only a relative estimate of sulphate retention in the soil mantle of each subcatchment is required.

The soils of the catchment show some signs of having possibly been influenced already by the enhanced atmospheric additions of sulphate which characterise the ETH, although a more systematic and extensive sampling will be needed to establish whether this trend is not confounded by a maritime influence.

The overall capacity of the catchment soils to retain sulphate, and thus limit the translation of atmospheric additions into an increment of salts in the drainage, is small. Most of the soils studied had a negligible capacity to retain sulphate. Figure 12 and the accompanying Table 16 show that as much as two-thirds of the catchment consists of soils having less than 40% of the maximum retention capacity for any one catchment (nominally about 11 g m^{-2} in Wilge 1), while only about one-sixth of the catchment's area is taken up by subcatchments with a significant capacity to retain sulphate. These subcatchments are the wettest, however, and will consequently make a disproportionate contribution to water quality in the dam.

Soil acidity, and especially the acid saturation of the exchangeable cation suite, appears to relate strongly to sulphate sorption capacity. This commonly measured property may prove to be an effective means of extrapolating the results of this study to other areas in South Africa, although the relationship needs to be tested against a larger number of soils.

To conclude this report we should return to the prognosis of Herold and co-workers regarding drainage water salinisation resulting from atmospheric additions of sulphate to soils of the catchment. On the one hand it seems clear that sulphate retention by the soil mantle is insufficient to invalidate the assumption of mass equivalence between sulphate input from the atmosphere and TDS output in the drainage water. On the other hand, after considering the data in Tables 10 and 11, especially those pertaining to water-soluble salts, it is difficult to anticipate a degree of atmospherically induced salinisation, even in the longer term, which would be detectable above the natural background concentration of salts being released by normal leaching processes. This suggests that there is little cause for concern and that factors such as climatic variation, which will alter both seasonally and over longer periods, the degree of dilution of the natural salt flux in the catchment, will have a considerably greater impact on water quality changes than will air pollution. The question which remains to be answered, however, is whether the soluble salt (and sulphate) concentrations in the Vaal Dam catchment soils are indeed of natural origin, or whether their almost twofold greater magnitude, on average, than those of the southern Natal soils (Table 15) is a legacy of increased anthropogenic impact over the past few decades. A new research programme initiated by ESKOM is examining the geographic distribution of soluble salts and sulphate in South African soils, so hopefully more light will be shed on the matter.

REFERENCES

Adams F. & Rawajfih Z. (1977). Basaluminite and alunite: A possible cause of sulfate retention by acid soils. *Soil Sci. Soc. Amer. J. 41*, 686-692.

Bitton G., & Boylan R.A. (1985). Effect of acid precipitation on soil microbial activity: I. Soil core studies. *J. Environ. Qual. 14, 66-71.*

David M.B., Fasth W.J. & Vance G.F. (1991). Forest soil response to acid and salt additions of sulfate: I. Sulfur constituents and net retention. *Soil Sci. 151*, 136-145.

Fey M.V. & Dixon J.B. (1983). Rapid estimation of irom oxides in soils and clays by spectrophotometric analysis. *Soil Sci. Am. J. 47, 1261-1263.*

Fey M.V., Manson A.D. & Schütte R. (1990). Acidification of the pedosphere. *S.Afr. J. Sci. 86*, 403-406.

Fuller W.H. & Warrick A.W. (1985). Soils in waste treatment and utilisation. Volume II: Pollutant containment, monitoring, and closure. CRC Press Inc. Boca Raton, Florida. pp. 99-119.

Gaston L.A., Mansell R.S., Rhue R.D., Bloom S.A. & Volk G.B.(1987). Cation leaching during application of sulphuric and nitric acids to an ultisol. In: Acid rain: scientific and and technical advances. (Perry R., Harrison R.M., Bell J.N. and Lester J.N., eds.) Selper Ltd., London.

Herold C.E. & Gorgens A. (1991). Vaal Dam salinity assessment with particular reference to atmospheric deposition. Dept. Water Affairs, Hydrological Res. Inst. Rep. No: NC120/13/DEQ0391.

Huete A.R. & McColl J.G. (1984). Soil cation leaching by "acid rain" with varying nitrate-to-sulfate ratios. *J. Environ. Qual. 13*, 366-371.

Johnson D.W., Cole D.W., van Miegroet H. & Horing F.W. (1986). Factors affecting anion movement and retention in four forest soils. *Soil Sci. Soc. Am. J. 50*, 776-783.

Johnson N.M., Likens, G.E., Feller M.C. & Driscoll C.T. (1984). Acid rain and soil chemistry. *Science 225*, 1424-1425.

Killham K., Firestone M.K., & McColl J.G. (1983). Acid rain and soil microbial activity: effects and their mechanisms. *J. Environ. Qual. 12*, 133-137.

Krug E.C. & Frink C.R. (1984). Acid rain and soil chemistry. *Science 225*, 1432-1434.

Lee J.L. (1985). Effect of simulated sulfuric acid rain on the chemistry of a sulfate adsorbing forest soil. *Water, Air & Soil Pollution 25*, 185-193.

MacVicar C.N., de Villiers J.M., Loxton R.F., Verster E., Lambrechts J.J.N., Merryweather E.R., Le Roux J., Van Rooyen T.H., & Harmse H.J. von M. (1977). Soil Classification: a binomial system for South Africa. Science Bull. 390, Dept. Agric. Development, Pretoria.

Metson A.J. (1979). Sulphur in New Zealand soils I. A review of sulphur in soils with particular reference to adsorbed sulphate-sulphur. *N.Z. J. Agric. Res. 22*, 95-114.

Mott C.J.B. (1981). Anion and ligand exchange. Ch. 5 In: The chemistry of soil processes. (D.J. Greenland & M.H.B. Hayes, eds.) John Wiley & Sons, New York.

Mott C.J.B. (1988) Surface chemistry of soil particles. Ch. 7 In: Russell's Soil Conditions and Plant Growth. 11th Ed. (A. Wild, ed.) Longman Scientific & Technical, London.

Page A.L. (ed.) (1982). Methods of Soil Analysis, Part 2 - Chemical and Microbiological Properties (2nd Ed.) Amer. Soc. Agronomy & Soil Sci. Soc. Amer., Madison, Wis.

Parfitt R.L. (1978). Anion adsorption by soils and soil materials. *Adv. Agron. 30*, 1-50

Patel S.G., Sarma V.A., & van Loon G.W. (1989). Acid rain, cation dissolution, and sulphate retention in three tropical soils, *J. Soil Sci. 40*, 85-93.

Petersen L. (1986). Effects of acid deposition on soil and sensitivity of the soil to acidification. *Experientia 42*, 340-344.

Reuss J.O. & Johnson D.W. (1986). Acid deposition and the acidification of soils and waters. *Ecological Studies 59*, 7-14.

Roberts L. (1991a). Learning from an acid rain programme. *Science 251*, 1302-1305.

Schulze R.E., Angus G.R. & Guy R.M. (1991). Making the most of soils information: a hydrological interpretation of SIRI land type information. Proc. 5th National Hydrological Symposium, SANCIAHS, Stellenbosch.

Seip H.M. & Dillon P.J. (1984). Acid rain and soil chemistry. *Science 225*, 1425-1426.

Skeffington R.A. & Brown K.A. (1986). The effect of five years acid treatment on leaching, soil chemistry and weathering of a humo-ferric podzol. *Water, Air & Soil Pollution 31*, 891-900.

Skoroszewski R.W. & Chutter F.M. (1988). Impact of atmospheric pollution on the quality of surface waters and their biota in the Eastern Transvaal Highveld. CSIR Division Water Technol. Rep., CSIR, Pretoria.

Sposito G. (1989) The chemistry of soils. Oxford Univ. Press.

Suarez E.W. & Jones U.S. (1982). Atmospheric sulphur as related to acid precipitation and soil fertility. *Soil Sci. Soc. Am. J. 46*, 976-980.

Tabatabai M.A. (1982). Sulphur. Ch. 28 In: Methods of Soil Analysis, Part 2 - Chemical and Microbiological Properties. 2nd Ed. (A.L. Page, ed.) Amer. Soc. Agronomy & Soil Sci. Soc. Amer., Madison, Wis. pp. 501-538.

Taviv I. & Herold C.E. (1989). Preliminary estimation of the impact of air pollution on the water quality in the Vaal Dam. SS&O Report to Dept. Water Affairs, Pretoria.

Thompson J.G. (1984). A note on the possible effects of acid rain on soils in South Africa. SIRI Information Bulletin, ARC, Pretoria, B 2/3, 3-5.

Tyson P.D., Kruger F.J. & Louw C.W. (1988). Atmospheric pollution and its implications in the Eastern Transvaal Highveld. South African National Scientific Programme. Report No. 150, CSIR, Pretoria.

Van der Merwe W. (1991). A review of water quality management in the Republic of South Africa. *Water Sewage & Effluent 11(2)*, 11-14.

Van Loon G.W., Hay G.W. & Goh R.H.T. (1987). Analysis of sulphur containing components of a soil treated with simulated acid rain. *Water, Air & Soil Pollution 34*, 233-240.

Wright R.F. (1984). Acid rain and soil chemistry. *Science 225*, 1426-1432.

APPENDIX I: Fortran programme for determining soil series percent, soil depth, and percent soils with clay content in the 15-25 and 25-35% ranges, in a region, given the areal composition of the landtypes in the region, and the land type inventory data.

```
      CHARACTER soil2*6, SOIL*4, SOIL1*4, CATCH*8
      DIMENSION XRETen(11), BULKDEN(11), RETEN(11), CODETOT(11),
&                   CODEDEP2(11), CODEP3 (11), CODEDEP4(11)


      OPRN(10,FILE='/u/guy/misc/vaalsoils')
      OPEN(20,FILE='/u/guy/misc/vaalsoil.output')
      OPEN(40,FILE='/u/guy/misc/bulk.output')
      OPEN(50,FILE='/u/guy/misc/catch.results')

      WRITE(*,*)'ENTER THE NAME OF THE CATCHMENT(A8)'
      READ(*,'(A8)')CATCH
      WRITE(*,*)'ENTER THE AREA OF THE CATCHMENT'
      READ(*,*)AREA
      READ(20,200)XPERC
      write(*,*)'xperc=',xperc
200   format(16x,f7.0)

      DO 1 IA=1,7
            READ(20,1100)SOIL2
1100        format(1x,a6)
            IF(SOIL2.EQ.'SOIL  ')THEN
             READ(20,100)SOIL,TOTAL,DEP2,DEP3,DEP4
100          format(1x,a4,f6.2,6x,3(f6.2))
             IF(SOIL.EQ.'ROCK')then
             adj=100/(xperc-total)
             write(*,*)'adj=',adj
             READ(20,100)SOIL,TOTAL,DEP2,DEP3,DEP4
             cNd if
            goto 888
        enDIF
1      CONTINUE
888    DO 2 IB=1,10000
        READ(10,1200,end=999)SOIL1,ICODE
1200    format(1x,a4,1x,i2)
        IF(SOIL1.EQ.SOIL)THEN
              CODETOT(ICODE)=CODETOT(ICODE)+TOTAL
              CODEDEP2(ICODE)=CODEDEP2(ICODE)+DEP2
              CODEDEP3(ICODE)=CODEDEP3(ICODE)+DEP3
              CODEDEP4(ICODE)=CODEDEP4(ICODE)+DEP4
              READ(20,100)SOIL,TOTAL,DEP2,DEP3,DEP4
            endif
       2 CONTINUE
999       continue
          DO 3 IC=1,11
              READ(40,400)RETEN(IC),BULKDEN(IC)
400           format(3x,f4.1,f4.2)
      XRETEN(IC)=XRETEN(IC)+(1000000*AREA*((CODEDEP2(IC)/100)
      &                   *ADJ*.25+(CODEDEP39IC)/100+ADJ*.75+
      &              (CODEDEP4(IC)/100)*ADJ*1.2)*RETEN(IC)*BULKDEN(IC))
          xtotret=xtotret+xreten(ic)
          codedep2(ic)=codedep2(ic)*adj
          codedep3(ic)=codedep3(ic)*adj
          codedep4(ic)=codedep4(ic)*adj
          codetot(ic)=codetot(ic)*adj
3      continue
      write(50,*)'SULPHATE RETENTION RESULTS FOR CATCHMENT',CATCH
      write(50,*)'SOILTYPE TOTAL% DEP2% DEP3% DEP4% SO4-RETENTION'
      DO 4 id=1,11
          write(50,500)id,codetot(id),codedep2(id),codedep3(id)
   &  ,codedep4(id),xreten(id)
4     continue
500    format(4x,i2,4x,f5.2,3(1x,f5.2),2x,f19.0)
      write(50,*)'TOTAL SULPHATE RETENTION CAPACITY =',XTOTRET
```

APPENDIX II: Example of soil series areal coverage (percent) in one of the Vaal Dam subcatchments in relation to soil depth class (Wordperfect file VAALSO4 on disc with WRC).

```
SOIL DEPTH CLASS COMBINATIONS
-----------------------------
DEP1=0.0  DEP2=<500  DEP3=500-1000  DEP4=>1000
SOIL  TOTAL DEP1  DEP2  DEP3  DEP4
ROCK 21.67 21.67   .00   .00   .00
Ar10   .09   .00   .00   .09   .00
Ar30   .58   .00   .00   .58   .00
Av13   .20   .00   .00   .20   .00
Av26  4.21   .00   .00  4.21   .00
Av27  1.57   .00   .00  1.57   .00
Av24  1.32   .00   .00  1.32   .00
Av23  1.52   .00   .00  1.52   .00
Bv26   .51   .00   .00   .51   .00
Bo41   .75   .00   .00   .75   .00
Bo30  1.08   .00   .33   .75   .00
Bo31  1.08   .00   .33   .75   .00
Bo10   .19   .00   .19   .00   .00
Bo11   .20   .00   .20   .00   .00
Bo40   .75   .00   .00   .75   .00
Cf10   .65   .00   .65   .00   .00
Cf12   .02   .00   .02   .00   .00
Cf11   .68   .00   .68   .00   .00
Cv16   .02   .00   .02   .00   .00
Cv23  1.52   .00   .00  1.52   .00
Cv26  1.90   .00   .00  1.90   .00
Cv24   .81   .00   .00   .81   .00
Cv13   .73   .00   .02   .71   .00
Du10   .38   .00   .00   .38   .00
Es13  1.80   .00  1.80   .00   .00
Es36   .12   .00   .12   .00   .00
Es14  1.52   .00  1.52   .00   .00
Es16  1.80   .00  1.80   .00   .00
Fw10   .36   .00   .00   .36   .00
Fw20   .36   .00   .00   .36   .00
Gs13  2.03   .00  2.03   .00   .00
Gs17  2.55   .00  2.55   .00   .00
Gs16  5.92   .00  5.92   .00   .00
Hu27   .01   .00   .00   .01   .00
Hu16   .36   .00   .00   .36   .00
Hu26   .68   .00   .00   .68   .00
Ik11   .11   .00   .00   .11   .00
Ik10   .20   .00   .00   .20   .00
Ik20   .25   .00   .00   .25   .00
Ka20   .09   .00   .00   .09   .00
My10  1.16   .00  1.07   .09   .00
My11  1.32   .00  1.32   .00   .00
Mw10  1.41   .00  1.32   .09   .00
Mw11  1.32   .00  1.32   .00   .00
Ms10  9.02   .00  9.02   .00   .00
Oa36  1.96   .00   .00  1.12   .85
Oa16  1.12   .00   .00  1.12   .00
```

APPENDIX III: Sulphate retention figures of major soil types in each sub-catchment (identified by weir name) in terms of depth class (mm) and in total (last column in nominal units of g m^{-3} sulphate over 50 years with an annual rainfall of 1000 mm.

Weir	Soil-Type	retention	0-500	500-1000	>1000	Total%	Total
Vaal1	Grey soils(sand)	2.	8.90	10.53	.00	19.42	.30
	Grey soils(clay)	2.	7.68	.52	.00	8.19	.07
	Grey soils(int.)	2.	6.60	4.00	1.00	11.61	.18
	Black clays	2.	9.67	7.54	1.23	18.47	.29
	Red/Yellow plinthic(sand)	2.	.00	4.57	.00	4.57	.10
	Red/Yellow plinthic(clay)	2.	.00	1.73	.68	2.41	.06
	Red/Yellow plinthic(int.)	19.	.00	8.16	1.30	9.47	2.19
	Red/Yellow humic(sand)	7.	.04	2.20	.00	2.23	.17
	Red/Yellow humic(clay)	36.	.42	4.89	3.93	9.25	4.58
	Red/Yellow humic(int.)	19.	.49	9.44	2.31	12.25	2.84
	Red/Yellow (other)	7.	.72	.77	.60	2.09	.15
Total			34.51	54.36	11.05	100.0	10.95
Vaal2	Grey soils(sand)	2.	5.54	1.33	.00	6.87	.07
	Grey soils(clay)	2.	19.39	.03	.00	19.42	.15
	Grey soils(int.)	2.	6.17	1.24	.16	7.58	.08
	Black clays	2.	27.60	29.42	1.33	58.35	.92
	Red/Yellow plinthic(sand)	2.	.00	.00	.00	.00	.00
	Red/Yellow plinthic(clay)	2.	.00	2.54	.00	2.54	.06
	Red/Yellow plinthic(int.)	19.	.00	2.63	.00	2.63	.56
	Red/Yellow humic(sand)	7.	.00	.00	.00	.00	.00
	Red/Yellow humic(clay)	36.	.19	.46	.00	.64	.21
	Red/Yellow humic(int.)	19.	.26	.71	.00	.96	.17
	Red/Yellow (other)	7.	1.00	.00	.00	1.00	.03
Total			60.15	38.36	1.48	100.0	2.24
Vaal3	Grey soils(sand)	2.	8.95	1.92	.43	11.31	.13
	Grey soils(clay)	2.	14.00	.01	.00	14.01	.11
	Grey soils(int.)	2.	8.60	1.93	.30	10.82	.12
	Black clays	2.	26.22	15.45	1.47	43.13	.60
	Red/Yellow plinthic(sand)	2.	.00	.64	.18	.82	.02
	Red/Yellow plinthic(clay)	2.	.00	1.83	.00	1.83	.04
	Red/Yellow plinthic(int.)	19.	.00	5.85	.00	5.85	1.25
	Red/Yellow humic(sand)	7.	.02	.19	.00	.21	.02
	Red/Yellow humic(clay)	36.	.09	.52	.06	.66	.27
	Red/Yellow humic(int.)	19.	.19	1.07	.17	1.42	.30
	Red/Yellow (other)	7.	.96	.13	.00	1.09	.04
Total			59.04	29.53	2.61	100.0	2.87
Liebl	Grey soils(sand)	2.	19.35	4.56	.00	23.92	.25
	Grey soils(clay)	2.	17.29	.00	.00	17.29	.13
	Grey soils(int.)	2.	12.73	4.64	6.44	23.82	.43
	Black clays	2.	2.19	2.45	1.15	5.79	.11
	Red/Yellow plinthic(sand)	2.	.00	8.25	.00	8.25	.19
	Red/Yellow plinthic(clay)	2.	.00	3.39	.00	3.39	.08
	Red/Yellow plinthic(int.)	19.	.00	13.32	.00	13.32	2.85
	Red/Yellow humic(sand)	7.	.00	1.63	.00	1.63	.13
	Red/Yellow humic(clay)	36.	.00	.04	.00	.04	.02
	Red/Yellow humic(int.)	19.	.00	2.21	.00	2.21	.47
	Red/Yellow (other)	7.	.00	.37	.00	.37	.03
Total			51.56	40.86	7.60	100.0	4.68

Weir	Soil-Type	retention	0-500	500-1000	>1000	Total%	Total
Lieb2	Grey soils(sand)	2.	18.31	6.79	.00	25.10	.29
	Grey soils(clay)	2.	4.30	.00	.00	4.30	.03
	Grey soils(int.)	2.	14.16	4.76	2.43	21.35	.30
	Black clays	2.	2.53	12.52	.21	15.26	.31
	Red/Yellow plinthic(sand)	2.	.00	2.30	.00	2.30	.05
	Red/Yellow plinthic(clay)	2.	.00	1.37	.00	1.37	.03
	Red/Yellow plinthic(int.)	19.	.00	14.64	.00	14.64	3.13
	Red/Yellow humic(sand)	7.	.00	.81	.00	.81	.06
	Red/Yellow humic(clay)	36.	.00	.00	.00	.00	.00
	Red/Yellow humic(int.)	19.	.00	1.91	.18	2.08	.47
	Red/Yellow (other)	7.	.00	.00	.00	.00	.00
Total			39.30	45.10	2.82	100.0	4.68
Lieb3	Grey soils(sand)	2.	14.87	1.90	.00	16.78	.15
	Grey soils(clay)	2.	10.89	.00	.00	10.89	.08
	Grey soils(int.)	2.	22.61	1.04	.21	23.85	.20
	Black clays	2.	17.14	28.50	.25	45.87	.78
	Red/Yellow plinthic(sand)	2.	.00	.52	.00	.52	.01
	Red/Yellow plinthic(clay)	2.	.00	.00	.00	.00	.00
	Red/Yellow plinthic(int.)	19.	.00	1.56	.00	1.56	.33
	Red/Yellow humic(sand)	7.	.00	.00	.00	.00	.00
	Red/Yellow humic(clay)	36.	.00	.11	.00	.11	.05
	Red/Yellow humic(int.)	19.	.00	.36	.06	.44	.10
	Red/Yellow (other)	7.	.00	.00	.00	.00	.00
Total			65.51	34.00	.52	100.0	1.71
Water1	Grey soils(sand)	2.	3.03	.15	.00	3.17	.03
	Grey soils(clay)	2.	19.75	.00	.00	19.75	.15
	Grey soils(int.)	2.	5.93	.06	.00	5.99	.05
	Black clays	2.	23.48	35.59	1.77	60.84	1.04
	Red/Yellow plinthic(sand)	2.	.00	.00	.00	.00	.00
	Red/Yellow plinthic(clay)	2.	.00	3.94	.00	3.94	.09
	Red/Yellow plinthic(int.)	19.	.00	3.55	.00	3.55	.76
	Red/Yellow humic(sand)	7.	.00	.00	.00	.00	.00
	Red/Yellow humic(clay)	36.	.00	.00	.31	.31	.20
	Red/Yellow humic(int.)	19.	.00	.00	1.06	1.06	.36
	Red/Yellow (other)	7.	1.41	.00	.00	1.41	.04
Total			53.60	43.29	3.14	100.0	2.71
Water2	Grey soils(sand)	2.	4.06	.48	.00	4.54	.04
	Grey soils(clay)	2.	20.08	.00	.00	20.08	.15
	Grey soils(int.)	2.	7.20	.20	.00	7.39	.06
	Black clays	2.	16.96	31.06	2.24	50.26	.91
	Red/Yellow plinthic(sand)	2.	.00	.00	.00	.00	.00
	Red/Yellow plinthic(clay)	2.	.00	4.13	.00	4.13	.09
	Red/Yellow plinthic(int.)	19.	.00	6.94	.00	6.94	1.48
	Red/Yellow humic(sand)	7.	.00	.00	.00	.00	.00
	Red/Yellow humic(clay)	36.	.09	.31	1.01	1.43	.79
	Red/Yellow humic(int.)	19.	.19	.25	3.39	3.85	1.23
	Red/Yellow (other)	7.	1.36	.02	.00	1.39	.04
Total			49.94	43.38	6.65	100.0	4.79

Weir	Soil-Type	retention	0-500	500-1000	>1000	Total%	Total
Eland1	Grey soils(sand)	2.	19.64	1.59	1.06	22.29	.22
	Grey soils(clay)	2.	10.56	.00	.00	10.56	.08
	Grey soils(int.)	2.	19.16	3.37	1.06	23.57	.26
	Black clays	2.	7.58	6.38	.00	13.96	.20
	Red/Yellow plinthic(sand)	2.	.00	7.07	.00	7.07	.16
	Red/Yellow plinthic(clay)	2.	.00	3.91	.00	3.91	.09
	Red/Yellow plinthic(int.)	19.	.00	10.86	.00	10.86	2.32
	Red/Yellow humic(sand)	7.	.02	3.78	.00	3.81	.30
	Red/Yellow humic(clay)	36.	.00	.01	.00	.01	.01
	Red/Yellow humic(int.)	19.	.02	3.66	.00	3.68	.78
	Red/Yellow (other)	7.	.00	.27	.00	.27	.02
Total			56.98	40.90	2.11	100.0	4.44
Eland2	Grey soils(sand)	2.	13.39	1.00	.45	14.85	.14
	Grey soils(clay)	2.	12.23	.10	.00	12.32	.09
	Grey soils(int.)	2.	20.15	3.42	.57	24.16	.25
	Black clays	2.	1.18	6.61	.02	7.81	.16
	Red/Yellow plinthic(sand)	2.	.00	3.29	.00	3.29	.07
	Red/Yellow plinthic(clay)	2.	.00	11.10	.00	11.10	.25
	Red/Yellow plinthic(int.)	19.	.00	18.65	.00	18.65	3.99
	Red/Yellow humic(sand)	7.	.00	3.64	.00	3.64	.29
	Red/Yellow humic(clay)	36.	.00	.00	.00	.00	.00
	Red/Yellow humic(int.)	19.	.00	4.06	.00	4.06	.87
	Red/Yellow (other)	7.	.00	.15	.00	.15	.01
Total			46.95	52.03	1.04	100.0	6.12
Wilge1	Grey soils(sand)	2.	13.28	.43	.05	13.76	.11
	Grey soils(clay)	2.	5.63	.02	.00	5.65	.04
	Grey soils(int.)	2.	16.84	1.89	4.87	23.59	.34
	Black clays	2.	2.03	2.60	.41	5.03	.09
	Red/Yellow plinthic(sand)	2.	.00	.59	.00	.59	.01
	Red/Yellow plinthic(clay)	2.	.00	1.66	3.31	4.97	.16
	Red/Yellow plinthic(int.)	19.	.00	19.92	3.31	23.23	5.39
	Red/Yellow humic(sand)	7.	.07	1.05	.00	1.12	.08
	Red/Yellow humic(clay)	36.	.00	10.00	.00	10.00	4.05
	Red/Yellow humic(int.)	19.	.07	11.90	.00	11.99	2.55
	Red/Yellow (other)	7.	.00	.06	.00	.06	.01
Total			37.92	50.12	11.94	100.0	12.83
Wilge2	Grey soils(sand)	2.	14.96	1.20	.11	16.26	.14
	Grey soils(clay)	2.	4.70	.00	.00	4.70	.04
	Grey soils(int.)	2.	17.76	2.42	2.25	22.44	.27
	Black clays	2.	1.33	2.37	2.76	6.47	.16
	Red/Yellow plinthic(sand)	2.	.00	5.46	.00	5.46	.12
	Red/Yellow plinthic(clay)	2.	.00	6.43	.00	6.43	.14
	Red/Yellow plinthic(int.)	19.	.00	22.23	.00	22.23	4.75
	Red/Yellow humic(sand)	7.	.01	4.23	.00	4.25	.33
	Red/Yellow humic(clay)	36.	.00	2.31	.00	2.31	.94
	Red/Yellow humic(int.)	19.	.01	6.33	.00	6.34	1.35
	Red/Yellow (other)	7.	.00	.00	.00	.00	.00
Total			38.77	52.98	5.12	100.0	8.25

Weir	Soil-Type	retention	0-500	500-1000	>1000	Total%	Total
Wilge3	Grey soils(sand)	2.	13.90	3.35	.00	17.25	.18
	Grey soils(clay)	2.	11.63	.02	.00	11.65	.09
	Grey soils(int.)	2.	16.05	3.54	.96	20.54	.23
	Black clays	2.	14.38	17.21	2.18	33.76	.57
	Red/Yellow plinthic(sand)	2.	.00	1.87	.00	1.87	.04
	Red/Yellow plinthic(clay)	2.	.00	1.48	.00	1.48	.03
	Red/Yellow plinthic(int.)	19.	.00	10.55	.00	10.55	2.25
	Red/Yellow humic(sand)	7.	.00	.89	.00	.89	.07
	Red/Yellow humic(clay)	36.	.00	.19	.00	.19	.08
	Red/Yellow humic(int.)	19.	.00	1.68	.14	1.83	.41
	Red/Yellow (other)	7.	.00	.00	.00	.00	.00
Total			55.95	40.78	3.28	100.0	3.96
Klip	Grey soils(sand)	2.	9.33	2.20	.00	11.52	.12
	Grey soils(clay)	2.	5.81	1.14	.00	6.94	.07
	Grey soils(int.)	2.	16.23	7.79	1.38	25.41	.35
	Black clays	2.	13.35	8.49	3.52	25.36	.42
	Red/Yellow plinthic(sand)	2.	.00	1.48	.00	1.48	.03
	Red/Yellow plinthic(clay)	2.	.00	2.02	.00	2.02	.05
	Red/Yellow plinthic(int.)	19.	.00	8.64	.00	8.64	1.85
	Red/Yellow humic(sand)	7.	.03	1.08	.00	1.10	.09
	Red/Yellow humic(clay)	36.	2.39	3.26	.00	5.62	1.64
	Red/Yellow humic(int.)	19.	1.84	5.34	.00	7.20	1.27
	Red/Yellow (other)	7.	.43	.00	.00	.44	.01
Total			49.42	41.43	4.90	100.0	5.89
Vaaldam	Grey soils(sand)	2.	9.98	2.74	1.19	13.93	.18
	Grey soils(clay)	2.	6.22	.00	.00	6.22	.05
	Grey soils(int.)	2.	14.85	2.32	.08	17.25	.17
	Black clays	2.	4.24	33.39	2.55	40.16	.87
	Red/Yellow plinthic(sand)	2.	.00	.38	.47	.85	.03
	Red/Yellow plinthic(clay)	2.	.00	.43	.00	.43	.01
	Red/Yellow plinthic(int.)	19.	.00	8.58	.11	8.70	1.87
	Red/Yellow humic(sand)	7.	.02	.04	.04	.12	.01
	Red/Yellow humic(clay)	36.	.11	.69	.07	.85	.34
	Red/Yellow humic(int.)	19.	.13	2.18	.42	2.77	.62
	Red/Yellow (other)	7.	.45	.13	.00	.59	.02
Total			36.01	50.90	4.92	100.0	4.16