THE RELATIONSHIP BETWEEN ATMOSPHERIC DEPOSITION AND WATER QUALITY IN A SMALL UPLAND CATCHMENT

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Report to the

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EXECUTIVE SUMMARY

This project commenced in January 1992, and forms part of a larger programme of the Water Research Commission which aims to look at the salinisation of the Vaal Dam. The Vaal Dam is the most important source of water for the Gauteng Province.

The project was basically concerned with the relationship between atmospheric deposition and water quality in a small upland catchment. The four main components of the study are : Atmospheric studies, Water chemistry, Soil chemistry and Hydrology of the catchment.

The main purpose was to use a small undisturbed catchment to investigate the fate of atmospheric deposition (which includes both wet and dry deposition), and in so doing develop an understanding of the influence of atmospheric deposition on the water quality of the Vaal Dam.

The main objectives of this project were :

(i) to investigate the atmospheric inputs into, as well as the chemical export from, a small undisturbed upland catchment :

(ii) to use the information so gained to estimate the chemical load due to atmospheric deposition from other similar catchments in the Vaal Dam drainage basin;

(iii) to contribute to the estimation of the proportion of the salinisation of the Vaal Dam that may be due to atmospheric deposition; and

(iv) to investigate the relationship between wet deposition and total atmospheric deposition within a selected catchment.

Atmospheric deposition occurs in two forms: wet and dry deposition. Wet deposition includes the atmospheric pollutants dissolved in the rainfall, whereas dry deposition is the fallout of particles and the adsorption of gaseous sulphur dioxide (or more simply, all deposition that is not 'wet').

The most important anthropogenic pollutants in atmospheric deposition are sulphur dioxide, particulates, and nitrous oxides.

The emphasis in this study has been placed on the sulphate component of atmospheric deposition. Nitrogen compounds are largely taken up in biological processes, whereas sulphate tends to be more inert.

The study was undertaken at a catchment at the Suikerbosrand Nature Reserve, approximately 80 km south-east of Johannesburg. The study site was a small upland catchment (32.5 ha) which had a quartz/sandstone geology, and a loamy sand soil with an average depth of 15 cm.

Approximately 54% of the catchment was exposed rock with the remaining 46% being predominantly grassland interspersed with areas of bare soil.

The study was undertaken over two 'wet' periods and one 'dry' period between October 1992 and March 1994. These were Period A (October 1992 - March 1993), Period B (April 1993 - September 1993) and Period C (October 1993 - March 1994).

The amounts of rainfall recorded during the study period were 491.5 mm (Period A), 62.0 mm (Period B) and 843.5 mm (Period C). Comparing Periods A and C, which covered the same months of the year, Period C was 40% 'wetter' than Period A, indicating the variability of rainfall on an annual basis which is characteristic of the region.

Various techniques were employed to measure and estimate the wet and dry deposition.

The wet deposition was sampled using an automatic wet sampler, which is a standard method widely used throughout South Africa (Kiepersol Acid Rain network) and internationally.

The dry deposition was measured using bulk samplers, rock runoff plots, ambient sulphur dioxide measurements, surface runoff and stem collar runoff. Most of the techniques employed for dry deposition estimates were of total deposition whereby the amount of wet deposition was extracted to give the net dry deposition. The exception to this was the estimation of dry deposition using sulphur dioxide measurements, in which deposition velocities for sulphur dioxide of 0.3 and 1.3 cm.sec^{-1} for winter (Period B) and summer (Periods A and C) were used to calculate the potential deposition rates.

The collection of rock runoff was a unique method of estimating dry deposition and worked successfully with at least 94% of the potential runoff collected.

In the calculation of the dry deposition into the catchment, three of the techniques were employed. These were : the rock runoff estimates for 54% of the catchment which was exposed rock; and a combination of ambient SO_2 (gaseous deposition) and net bulk deposition (particulate deposition) for the remaining 46% of the catchment which was covered in primarily grassland.

A V-notch weir was constructed at the site to collect and measure the runoff.

The main findings of the study were that the total atmospheric deposition rates of sulphate to the site were 31.2 kg.ha^{-1}.yr^{-1} (Period A) and 8.6 kg.ha^{-1}.yr^{-1} (Period B) and 45.0 kg.ha^{-1}.yr^{-1} (Period C). This is within the range expected for the region.

The proportion of dry deposition to total atmospheric deposition was 62% (Period A), 91% (Period B) and 39% (Period C). These proportions of dry deposition to total deposition were related to the amount of rainfall - the higher the rainfall, the lower the percentage of dry deposition and vice versa.

The stream at Suikerbosrand was a seasonal stream only flowing after storm events of at least 20 mm. The flows were characterised by being of short duration and high intensity (average time of flow was 130 hours). In many of the flows the commencement of flow was often less than one hour after the rainfall causing the event.

The total outputs of sulphate from the catchment were 2.8 kg.ha^{-1} (Period A) and 7.6 kg.ha^{-1} (Period C). No flow was recorded in Period B. These represented approximately 9% (Period A) and 17% (Period C) of the total inputs of sulphate into the catchment. Comparing two overlapping annual cycles (Periods A and B, and Periods B and C), 93% of the total estimated sulphate inputs into the catchment were not exported from the catchment in the first annual cycle and 86% were not exported in the second. The loads were either retained in the catchment (most likely) or recirculated into the atmosphere as dust.

The total dissolved salt loads from the catchment were 10.7 $kg.ha^{-1}.yr^{-1}$ (Period A) and 413.9 $kg.ha^{-1}.yr^{-1}$ (Period C) as calculated from the electrical conductivity.

The most important variables of atmospheric origin in the surface waters of the catchment were sulphate and nitrate. Sulphate salts were responsible for 54% (Period A) and 44% (Period C) of the catchments' total salt load. Nitrate on the other hand contributed 14% (Period A) and 9% (Period B) of the total catchment salt load. The sulphate load was considerably higher than the 10% reported for the Vaal Dam catchment. The effect of these high proportions of sulphate and nitrate and the total flow of Suikerbosrand were, however, insignificant in the total load and flow of the Vaal Dam. Sulphate and nitrate play a much more important role in the load of the Suikerbosrand catchment and other similar upland catchments than for the Vaal Dam catchment.

Suikerbosrand is probably the most sensitive undisturbed upland catchment in the region. The Suikerbosrand catchment is an unusual catchment and cannot be considered to be representative of many upland catchments in the region. It should be considered to be an extreme case in terms of sulphate and nitrate loads.

When comparing the water quality data of the Suikerbosrand catchment with other calibrated catchments in the northern hemisphere, there were many similarities and also significant differences.

Variable	**Catchment**				
	Suikerbosrand (South Africa)	**Birkeness (Norway)**	**L. Gardsjon (Sweden)**	**Hubbard Brook (USA)**	**Sudbury (Canada)**
pH	4.2 - 6.3	4.5	4.2	4.9	4.7
Na $mg.l^{-1}$	0.6	2.8	6.5	0.9	2.1
K $mg.l^{-1}$	1.1	0.3	0.6	0.2	0.5
Ca $mg.l^{-1}$	1.6	1.3	1.5	1.7	5.7
Mg $mg.l^{-1}$	0.7	0.5	1.4	0.4	1.3
Cl $mg.l^{-1}$	1.6	4.4	11.0	0.5	5.7
S $mg.l^{-1}$	3.0	2.4	1.5	2.1	5.7
NO_3-N $mg.l^{-1}$	0.6	0.1	0.1	0.4	-

The Suikerbosrand had higher levels of potassium and lower levels of sodium than any of the other catchments. The levels of sulphate and nitrate were, however, generally higher in comparison to the average values for the four other catchments. One important difference between Suikerbosrand and the other catchments is the low runoff at Suikerbosrand (8.7%) as compared to greater than 50% for the other catchments. This would have implications for the concentration of salts at Suikerbosrand but would not influence the relative proportions of the main chemical variables in the catchment salt load.

The levels of aluminium were also examined during Period C, and were found to be inversely related to pH. The levels were found to be at their highest at times of low pH, which also coincided with peaks in flow.

A preliminary investigation of the wind patterns at the catchment revealed the levels of sulphur dioxide to be greatest when the wind direction was from nearby source areas (the Johannesburg/Vosloorus/Kelvin Power station area, and the Witbank/Eastern Transvaal Power Station area).

This study was unique in many ways. It was the first calibrated study in South Africa designed specifically with the aim of assessing the effects of atmospheric deposition on water quality in southern Africa. Internationally it is unique in that it is the first study to examine a catchment with a relatively low runoff, high evaporation, a seasonal stream and periodic drying out of the catchment with long periods of no rainfall.

The recommendations of this study are :

1. The influence of the catchment soils should be examined in more detail.
2. The nitrogen balance of the catchment and the process involved should be investigated.
3. Other upland catchments along a pollution gradient should be compared to the Suikerbosrand catchment to be able to assess the potential impacts of atmospheric deposition in the region.

4. The feasibility of using or modifying existing hydro-geochemistry models, such as the Birkeness or MAGIC models, which have been developed in Europe, should be investigated.

5. The hydrology of the catchment should be examined in detail using an appropriate small catchment model, to determine the retention times of water in the catchment.

6. A dry deposition model should be calibrated using the Suikerbosrand data and a comparison drawn between recently derived estimates of dry deposition calculated for the highveld using an inferential model.

7. The sulphate content of the rock in the catchment as well as the weathering rate should be examined.

8. The potential for re-circulation of sulphate into the atmosphere should be investigated.

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ABBREVIATIONS AND ACRONYMS

Cumecs	cubic metres per second ($m^3.s^{-1}$)
DWAF	Department of Water Affairs and Forestry
IWQS	Institute for Water Quality Studies
ISCW	Institute for Soil, Climate and Water (formerly SIRI)
m^3	cubic metres
$m^3.s^{-1}$	cubic metres per second
$mg.l^{-1}$	milligrammes per litre
$mS.m^{-1}$	milliSiemens per metre
SIRI	Soil and Irrigation Research Institute
$\mu eq.l^{-1}$	microequivalents per litre
UV	Ultra-Violet

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The Steering Committee responsible for this project, consisted of the following persons :

Mr H M du Plessis	Water Research Commission (Chairman)
Mr D Huyser	Water Research Commission (Secretary)
Dr P J Ashton	CSIR (Division of Water of Technology)
Prof. M V Fey	University of Cape Town
Mr B J Gore	ESKOM
Dr G C Green	Water Research Commission
Dr C E Herold	Stewart Scott Incorporated
Mr C R Turner	ESKOM
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1. INTRODUCTION AND OBJECTIVES

This project commenced in January 1992, and forms part of a larger programme of the Water Research Commission which aims to look at the salinisation of the Vaal Dam. The Vaal Dam is the most important source of water for the Gauteng Province.

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The main objectives of this project are as follows:

(i) To investigate the atmospheric inputs into, as well as the chemical export from, a small undisturbed upland catchment.

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Atmospheric deposition occurs in two forms: wet and dry deposition. Wet deposition is the atmospheric pollutants dissolved in the rainfall, whereas dry deposition is the fallout of particles and the adsorption of gaseous sulphur dioxide.

The most important anthropogenic pollutants in atmospheric deposition are sulphur dioxide, particulates, nitrous oxide and carbon monoxide (Els, 1987).

The emphasis in this study has been placed on the sulphate component of atmospheric deposition as nitrogen compounds are largely taken up in biological processes, whereas sulphate tends to be more inert.

The desired characteristics of the study site were as follows :

(i) it should not be subjected to significant anthropogenic inputs other than atmospheric

(ii) it should be a small catchment (<100 ha), which would facilitate the examination of a whole catchment under the set financial and practical constraints

(iii) it should have a geology which was sensitive to atmospheric inputs which implies a shallow soil underlain by a relatively inert geology. The retention capacity of the system would therefore be relatively low.

(iv) it should have a permanent water course whereby a continuous flow record could be obtained and from which 20 rainfall related flow events could be measured.

(v) it should be representative of the upland regions of the Vaal Dam catchment.

(vi) should be within easy access to the researcher's home base.

Originally, a small catchment near to Dullstroom was the preferred study site. However on inspection, together with M Fey (University of Cape Town), this catchment was found to be unsuitable due to the depth and probable high sulphate retention capacity of the soils. Further potential catchments were then examined.

A suitable site was found at the Suikerbosrand Nature Reserve which met most of the above requirements. The catchment, however, had only a temporary stream. This had significant consequences in the design and implementation of the sampling programme as there would not be a continuous flow record and flow events were likely to be of short duration and high intensity.

After selection of the site, the project developed to include more emphasis on the importance of dry deposition in developing a catchment budget as it was thought that dry deposition would be a significant component of the total atmospheric deposition.

Studies of the international and local literature indicated that the concept of studying a small upland catchment has been undertaken in many instances, most notably at Birkeness in Norway and Hubbard Brook in the U S A. There have been no studies of this nature undertaken in the southern hemisphere.

An important difference between studies in the northern hemisphere and the highveld region of the Gauteng, Eastern Transvaal and Free State Province is the low runoff (5 - 15%), high evaporation (8 mm/day) in the summer months and long dry periods with little or no rainfall in the winter (DWAF, 1986). This has consequences for the importance of dry deposition in that the drier the climate, the more significant is the proportion of dry deposition. The estimation of dry deposition is an area which is poorly developed.

The estimates that are available for the Transvaal highveld have as yet not been verified in the field. The whole question of the measurement of dry deposition itself has many problems such as the nature of the receiving surface (wetness, smoothness, stickiness and chemical reactivity) and the use of man-made as opposed to natural surfaces.

There are two basic concepts that should be understood to appreciate the complexities of this study, namely the water and sulphur cycles. In the water cycle, rainfall is the primary input into a catchment. The water is then either retained in the catchment, lost by evaporation/evapotranspiration, or leaves by runoff.

In the sulphur cycle there are two types of input into the catchment (wet and dry deposition). Sulphur is either retained in the catchment (as storage) or exported in the runoff. It has been suggested that recirculation of sulphate in the air takes place (Held, 1994).

The report is organised into six main sections. These include a Literature Review, a description of the Study Area, the Methodology used to meet the objectives, the Results and Catchment budget as well as a General Discussion.

2. LITERATURE REVIEW

Water for the Gauteng Province is mainly supplied by the Vaal Dam. Signs of salinization of this important water source have, however, been noticed over the past thirty years. It has been suggested that this increase in salinity could be associated with sulphate deposition in the catchment due to the combustion of fossil fuels in the Eastern Transvaal Highveld (Taviv *et al.*, 1989).

Several issues were identified from the literature as being relevant to atmospheric pollution and its effect on water quality, providing background information for the rest of the study. Each of these issues will be addressed in a separate section of the literature review. The first section is a brief overview of current knowledge on emissions and air quality in the Eastern Transvaal Highveld. The second section deals with atmospheric inputs of pollutants to a catchment, and the third section with the catchment response to these pollutants. In the fourth section the effect of atmospheric inputs on stream chemistry is discussed. In each section a general discussion on findings elsewhere is followed by an assessment of the situation in the Vaal Dam catchment specifically.

2.1 Emissions and Air Quality in the Eastern Transvaal Highveld

Sources of atmospheric pollutants in the Eastern Transvaal Highveld include power stations, petrochemical plants, smaller industries (e.g. brick works, ferro/alloy works, steelworks, foundries, fertilizer plants, sawmills, pulp and paper mills and chemical works), domestic combustion, motor vehicles, discard coal dumps as well as veld burning.

Considering the spatial distribution of the various atmospheric pollution sources and their emissions, the larger emissions originate within a relatively small area of the former Eastern Transvaal Highveld (Tyson *et al.*, 1988). Data for the Eastern Transvaal Highveld showed that SO_2 emission densities are between five and just under ten times greater than the rest of the former Transvaal - at between 30 and 40 tons of $SO_2.km^{-2}.yr^{-1}$ (Tyson *et al.*, 1988).

Nevertheless, data for the period 1979 - 1986 revealed that hourly, daily and annual mean SO_2 concentrations generally complied with local ambient air quality limits set by the Department of National Health and Population Development. Limits for hourly and daily means were occasionally exceeded, but never for annual means. Incidents of high doses of SO_2 were isolated and associated with certain wind directions (Tyson *et al.*, 1988).

Rainfall acidity recorded in the Eastern Transvaal Highveld and adjacent regions was found to be similar to that in north-eastern North America and Europe (Tyson *et al.*, 1988). Rainfall pH in these areas is lower than in areas free from anthropogenic pollution. In a study in the Blesbok- and Leeuspruit catchments, which are secondary catchments of the Vaal Dam catchment, Bosman (1990) found that precipitation pH ranged from pH 3 to 5.5 for 60% of the sample collection during a dry year. During wetter seasons precipitation pH was in the same range for 80% of time. It has been suggested that pH 5.6, which is the equilibrium pH for atmospheric carbon dioxide and water is the critical point for acidic deposition. Values beneath this suggest an anthropogenic influence.

2.2. Atmospheric Inputs

In order to assess the impact of pollutants on the environment, it is vital that the processes controlling the pathways and fate of atmospheric pollutants in the environment are understood. Important processes in this regard are the transportation and chemical transformation of atmospheric pollutants, as well as deposition on the earth's surface (Tyson *et al.*, 1988). Atmospheric deposition occurs as both wet and dry deposition.

2.2.1 *Wet deposition*

A major portion of the fine particulates in the atmosphere, especially sulphate and nitrate aerosols, are removed from the atmosphere by rainfall and transferred to the earth's surface by a process called wet deposition.

The amount of wet deposition can be determined by using wet-only samplers whereby the concentration of various ionic species are multiplied by the corresponding rainfall figures to give the wet deposition load. This component of atmospheric deposition measurement is the most reliable with established methods and techniques with consistently repeatable results (Snyman *et al.*, 1991). Wet deposition is, however, only part of the total atmospheric deposition.

Tyson *et al.*(1988) undertook a comparison of wet deposition of ionic species in the Eastern Transvaal Highveld with north-eastern North America and Europe. It was found that the H^+ deposition values were similar, but that the SO_4^{2-}, NO_3^- and NH_4^+ values were at the lower end of mean ranges reported elsewhere. However, in parts of the Eastern Transvaal Highveld, e.g. at Topfontein near Secunda and the forestry plantations at Sabie, high SO_4 concentrations were found. At these sites the critical limit of 20 kg SO_4 ha^{-1} yr^{-1} wet deposition, suggested in Canada to protect sensitive aquatic ecosystems, was exceeded. At other sites in the Eastern Transvaal Highveld this limit was approached.

It was also found that the levels of wet deposition in the north-eastern Orange Free State and north-western Natal are similar to that in the Eastern Transvaal Highveld. These results suggest that export of atmospheric pollution from the Eastern Transvaal Highveld is taking place, taking into account the general wind directions and the point sources of pollution.

High-level emissions in the Eastern Transvaal Highveld result in an elevated layer of polluted air. Unfortunately, it is not known whether the link between emissions from high-level sources and wet deposition is linear or non-linear, i.e. whether reductions in high-level source emissions would result in proportionate or disproportionate reductions in wet deposition (Tyson *et al.*, 1988).

2.2.2 *Dry deposition*

Dry deposition is the removal from the atmosphere of gaseous pollutants, such as SO_2 or particulate pollutants, by processes other than dissolution in rain (Wells, 1989). It is termed 'dry' in the sense that it does not form part of 'wet' deposition. This occurs through the gases being adsorbed onto, or being absorbed by, particles in the air, or terrestrial surfaces. The airborne particles are removed from the atmosphere by the impact of gravitational settling, depending on their size (Tyson *et al.*, 1988). It also includes the direct capture of SO_2 gas by plant stomata.

The rate of dry deposition can vary according to a number of factors including the nature of the receiving surface (smoothness, wetness, stickiness, chemical reactivity, and turbulence), temperature and time of day (diurnal variation).

Dry deposition can be determined using bulk collection methods in conjunction with wet deposition sampling. However, the use of unnatural inert surfaces always results in an under-estimation of dry deposition as adsorption to the surface of the collecting surface is restricted.

Unfortunately, no accurate methodology for the routine measurement of dry deposition exists. An approach often used is to determine the product of the near-surface concentration of a given pollutant (such as SO_2), and the deposition velocity appropriate to the area of interest. The deposition velocity (V_d) is an experimentally derived parameter. It is highly variable and depends upon the physical and chemical characteristics of the particular substance; the nature of the surface with which it is interacting and meteorological factors. Typical values range from 0.3 to 2.3 $cm.s^{-1}$ for SO_2. V_d values have, however, been experimentally determined for several natural surfaces. These include values for grassland of 1.3 $cm.s^{-1}$ in summer and 0.3 $cm.s^{-1}$ in winter (Shepherd, 1974). Tyson *et al.* (1988) assumed an average value of 0.8 $cm.s^{-1}$ for the Eastern Transvaal Highveld.

The determination of the actual level of dry deposition is important in catchment studies as it is often responsible for significant amounts of additional SO_4 loading onto the catchment (Whitehead *et al.*, 1988). Evidence from observations and calculations indicates that dry deposition may equal wet deposition over western Europe and north America (Tyson *et al.*, 1988). In the Eastern Transvaal Highveld, which has long dry spells and rainstorms of short duration, dry deposition probably plays an even more prominent role than in the wetter northern hemisphere countries. It is likely to be an important feature during the dry winter, when little or no rain falls.

2.2.3 *Total Deposition*

Total atmospheric deposition is determined using bulk collection methods. A container is left out in the open for a fixed period before the sample is collected and returned to the laboratory for analysis. This method has the advantages of being simple, resulting in fewer samples for analysis, and includes the important dry deposition component. However, as the containers are exposed to the air at all times, evaporation of the sample inevitably occurs, resulting in a concentration of the sample.

There are two major problems associated with this method. Firstly, due to problems mentioned earlier, the dry deposition component will always be underestimated due to the nature of the inert receiving surface which allows for little or no adsorption of gases such as SO_2. Secondly, chemical changes take place whilst the sample is standing in the collection container.

Snyman *et al.* (1991) therefore do not recommend bulk sampling, as the uncertainties associated with bulk collectors are particularly high for the Highveld with its long, dry, dusty winters and the isolated nature of major summer rain events. When compared to wet-only collectors, errors in the range of 2 - 192% have been reported for bulk collectors.

Tyson *et al.* (1988) found that bulk SO_4 deposition loads in the eastern parts of the Vaal Dam catchment and the mountain catchments near the Eastern Transvaal Highveld are similar to localities in north-eastern North America. Whether this poses a threat to water quality in the catchment depends on the catchment response and the fate of the SO_4 deposited on these catchments.

2.3 Catchment Response

The impact of atmospheric pollution on water quality is determined by catchment response characteristics such as soil processes, land use and catchment hydrology.

2.3.1 *Soil Processes*

The effect of atmospheric pollution on water chemistry may be direct through precipitation onto streams and lakes, but the effect is more often secondary, since water often reaches a stream after draining through soil profiles. The impact of atmospheric pollution on water quality and aquatic ecosystems is consequently determined in the first instance by soil processes.

If anions such as SO_4^{2-}, NO_3^- and Cl^- from atmospheric deposition are accompanied by H^+, as is the case for acidic deposition, excess H^+ will initially displace the base cations (Na^+, K^+, Ca^{2+} and Mg^{2+}) from the soil exchange sites. As the anions adsorbed onto the soil increase in concentration, there will be an equivalent increase in cation concentration to maintain a charge balance. As the base saturation declines, aluminium and H^+ ions become progressively more important in maintaining the ionic charge balance in solution. The result is that the water eventually delivered to the stream becomes more acidic with a higher Al content (Whitehead *et al.*, 1988).

SO_4 dynamics within the soil are a major determinant of stream chemistry. One of the major difficulties is to accurately determine the quantity and quality of inputs, since both are highly variable from year to year and difficult to measure (Jenkins *et al.*, 1988). The adsorption and exchange of SO_4 depends on soil type and soil characteristics. Organic soil types (e.g. peat) shows the most variable response as a result of its low maximum adsorption capacity, therefore the response to changing acidic input usually is rapid. Mineral soils, on the other hand, respond more smoothly due to their ability to adsorb and store sulphate on the soil (Jenkins *et al.*, 1988).

This ability of catchment soils to adsorb and store atmospheric pollutants often results in a build up of the pollutant in the catchment, which could be stored in dissolved form in the groundwater, adsorbed to the soil particles, cycled within the vegetation or deposited on the plant canopy. Pollutant adsorption to the soil also provides a buffering mechanism, resulting in a relatively small variation in streamwater concentration when compared to the often wide range in rainfall concentration. In cases where rainfall concentration does correlate to runoff concentration, a rapid transfer to the stream is inferred, i.e. little storage in the catchment (Neal *et al.*, 1988).

In the Vaal River catchment the low SO_4 concentration in surface soils indicate that leachable sulphate does not accumulate in surface layers, and the sulphate ion appears to be fairly mobile (Bosman, 1990).

Fey and Guy (1994) made a study of the sulphate retention capacities of soils in the Vaal Dam catchment. The technique used estimated the sorption capacity of the most sorptive soil, thereafter ranking all of the other soil types. It is not known whether the sulphate concentrations found in the soil solutions which were greater by a factor of almost 2 times when compared to soils of southern Natal, are due to anthropogenic sources or not.

2.3.2 *Land use*

The impact of atmospheric pollution on water quality and aquatic ecosystems in a specific catchment is also determined by land use. The effect of afforestation on acidification trends can be highly significant. Firstly, hydrological flowpaths usually change following a decrease in runoff. Secondly, enhanced evapotranspiration concentrates solutes. Thirdly, once canopy closure is complete, a major additional influx of sulphate and other pollutants into the catchment is achieved via dry deposition. In this regard, Whitehead *et al.* (1988) found that dry deposition factors were the dominant processes controlling water quality in an upland forest catchment in Wales.

2.3.3 *Catchment Hydrology*

Catchment hydrology has been identified as a major control of stream water quality in upland areas (Muscutt *et al.*, 1990). Since rainfall may induce changes in the predominant water pathways, resulting in a change in supply of ions to surface waters, knowledge of the processes of flow generation is important to gain an insight into causes of episodic changes in water quality.

There is considerable uncertainty about flow generation mechanisms. Although there is no consensus on the processes of subsurface flow generation in upland catchments, it is generally accepted that surface runoff from relatively small areas of the catchment contributes to rapid increases in flow and consequently to changes in water chemistry (Muscutt *et al.*, 1990).

In the Vaal Dam catchment increased runoff causes atmospherically deposited SO_4 to be washed out of the soil and released into surface waters. During dry periods atmospherically deposited SO_4 is retained on the soil (Bosman, 1990). A four year study in two secondary catchments of the Vaal Dam catchment indicated that only 36% of the atmospherically deposited SO_4 was exported during dry years, but that 92% was exported during wet years (Bosman, 1990). As we have more 'dry' years than 'wet' years this would suggest a considerable accumulation of sulphate soils.

2.4 Surface Water Quality

Depending on the catchment response, surface water quality is sooner or later affected by atmospheric deposition.

Surface water quality may respond to increased runoff from the catchment by either a decrease or an increase in solute concentrations.

A decrease in solute concentrations after a rainstorm could give an indication of no or very little atmospheric pollution in the particular catchment. In other words unpolluted rain would dilute the concentration of dissolved substances in the stream. Also, if a storm event follows a wet period, pollutants would already have been washed from the atmosphere. In cases where the catchment has a limited storage capacity, more runoff after a wet period would also result in a dilution of stream concentration.

An increase in solute concentrations in the stream could be the result of washout from the atmosphere after a relatively dry period, causing rainfall concentrations and consequently stream concentrations to rise. Also, if a storm event follows a wet period, pollutants would have been washed from the atmosphere and the rainfall concentration would be low. If this is the case, but the stream concentration increases in spite of low rainfall concentrations, the catchment probably has a high storage capacity. In this way accumulated dry deposition pollutants can contribute substantial amounts of pollutants to runoff and result in an increase in stream solute concentration (Muscutt *et al.*, 1990).

Surface water quality may also show an increase in certain ionic species concurrent with a decrease in other species after increased runoff. Adsorbed (organic and inorganic) aluminium concentrations have been observed to be very low during dry weather, but increased sharply during high flows (Goenaga and Williams, 1988). At the same time the inorganic aluminium concentration in solution was reduced. This phenomenon is due to the fact that suspended solids act as a sink for substantial amounts of inorganic aluminium.

As mentioned in the previous section, the most serious effects of atmospheric deposition on catchment surface water quality are those of decreased pH and alkalinity. Acidification may be accompanied by the mobilization of metals from the soil, of which aluminium especially is toxic to fish and other biota.

The process of acidification in a freshwater system proceeds in several stages. Initially the acidity of water draining through the soil is neutralized or buffered in the soil, with the consequent leaching of cations such as calcium and magnesium. As acidification proceeds, bicarbonate concentrations are reduced and replaced by sulphate. The sensitivity of a water body to effects of acid precipitation may therefore be predicted from alkalinity levels. The internationally accepted definition of alkalinity for the assessment of surface water sensitivity due to acidic inputs is the Acid Neutralising Capacity (ANC) which is defined as the sum of the base cations less the sum of acidic anions (sulphate and nitrate).

Lakes undergoing acidification have been found to move relatively slowly down to a pH of 6, after which the pH in the lake corresponds more directly to the pH of the precipitation as the buffering capacity is exhausted (Dickson, 1975).

The whole stream acidification problem involves two time scales. In the first instant acidity is observed as short-term pulses in the stream. These occur on a hourly timescale in small upland catchments and reflect hydrological changes in the catchment, such as flushing after storm events or snowmelt. Such acid pulses may be severe, causing damage to fisheries (Whitehead *et al.*, 1988; Jenkins *et al.*, 1988).

In the second instance acidification is observed as a longer term process. Short lived events are superimposed upon the longer term acidification processes. The buffering ability of the soils and rocks in a catchment can delay stream water acidification for many decades. The magnitude of observed short-term pulses are dependent on how far the long-term process of acidification has progressed within a specific catchment. It is therefore important in any atmospheric pollution study to evaluate the current status of catchment acidity and historical trends and processes that have occurred.

In the Vaal Dam catchment the precipitation falling over the catchment is within the definition of acid rain with pH ranging between 4.8 and 7. In spite of this, the rivers remain alkaline and well buffered. Only in the upland areas are poorly buffered streams seen. It is suspected that the soil is buffering acid input at this stage, and that there still remains much buffer capacity in the soils of the catchment (Bosman, 1990). Sub-surface catchment storage during dry years and hydrological variations are masking the short term response of the Vaal Dam catchment to atmospheric pollution to a large extent. It is therefore believed that the observed trend in water quality deterioration in the catchment is still in the lower part of an ascending curve (Taviv *et al.*, 1989).

3. DESCRIPTION OF THE STUDY AREA

The Suikerbosrand Small Catchment falls within the Suikerbosrand Nature Reserve, and is approximately 80 km south-east of Johannesburg and 30 km north of the Vaal Dam. The temporary stream in the catchment flows into the Suikerbosrand river via the Blesbok spruit and finally into the Vaal River at Vereeniging.

The catchment was surveyed using aerial photographs and a contour map was produced (*Figure 1*). The catchment is 32.5 ha in extent, has a north-south axis of 500 m and an east-west axis of 700m, with the highest point of the catchment being 98 m above the weir.

3.1 Catchment Land Cover

A survey of the percentage cover of vegetation, rock and bare soil was undertaken (*Figure 2*). Approximately 54% of the catchment was found to be exposed rock, 35% to be covered by vegetation (primarily grass species with a few *Protea sp.* trees) and 11% bare soil with no vegetation cover.

3.2 Geology and Soils

The geology of the catchment is quartzite, which is an inert slow-weathering rock. Visual inspection of rock samples revealed the presence of pyrites. In the opinion of a professional geologist (B. Eglington, CSIR) this was unlikely to be higher than 0.5% of the total mass of rock. In a preliminary analysis, no sulphate was detected. The potential weathering rate of the rock was not determined.

The soils are characterised as loamy sand with three main soil types (*Figure 3*), Mispah (80%), Oakleaf (18%) and Clovelly (2%).

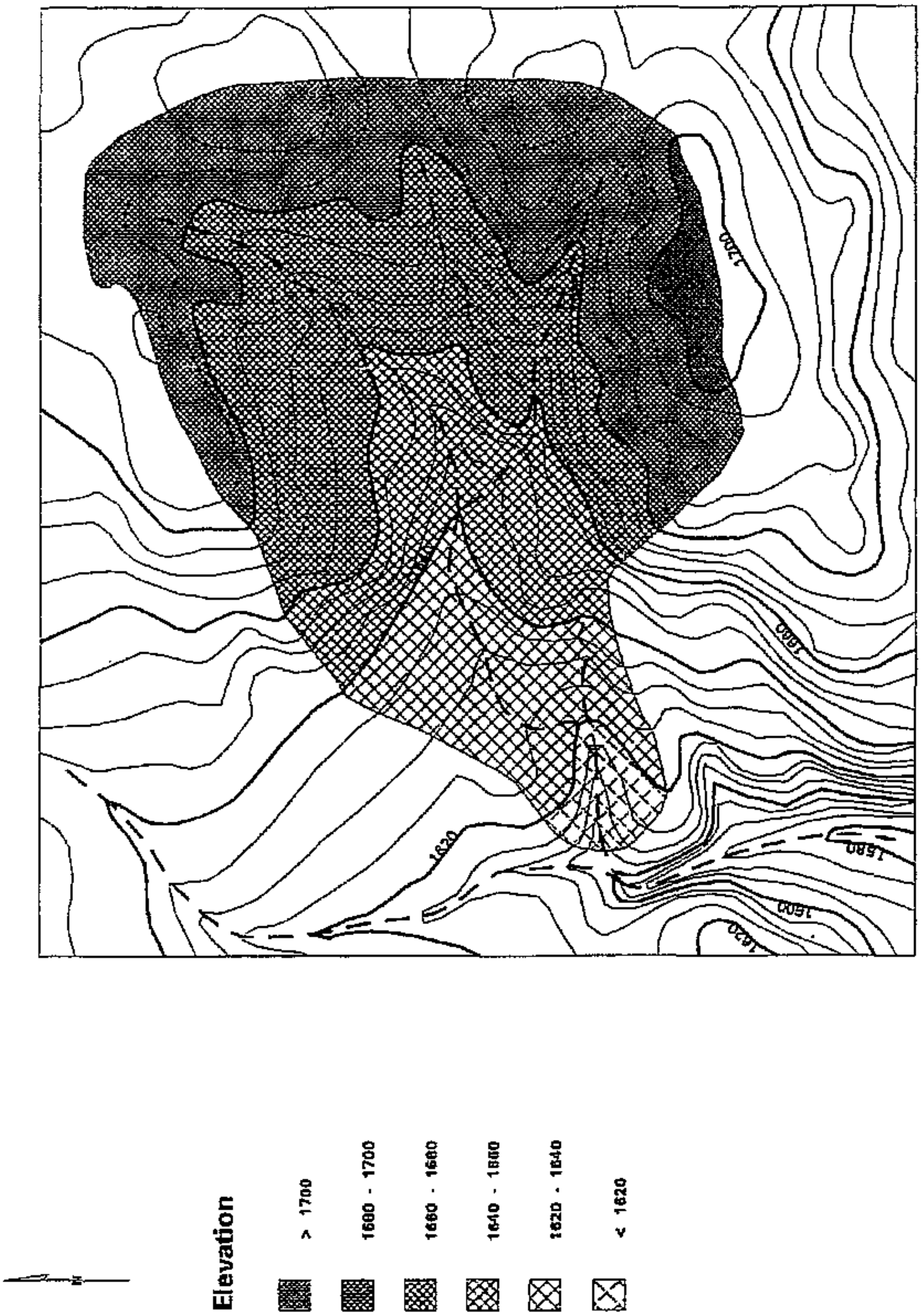


Figure 1. Map showing contour lines

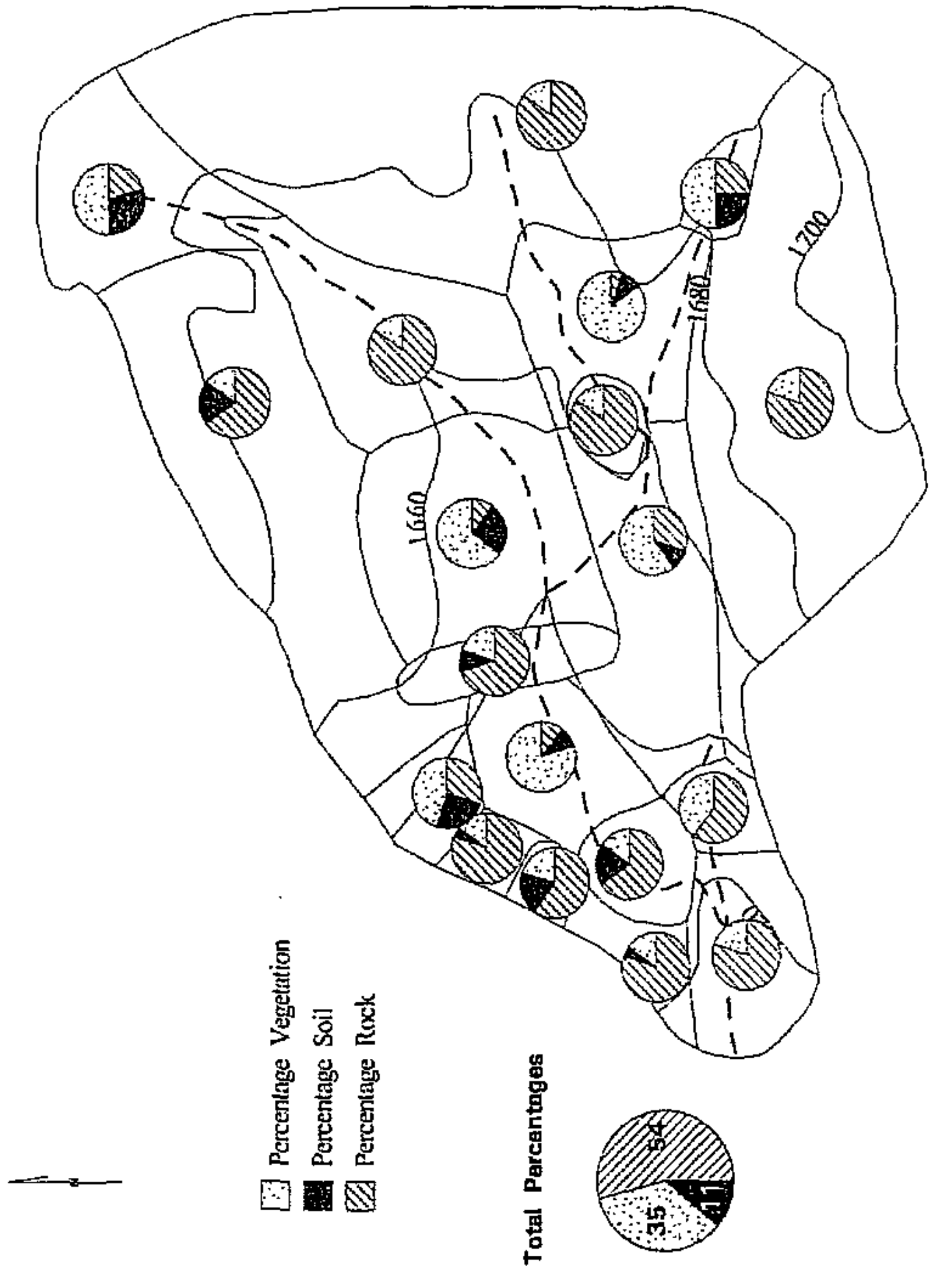


Figure 2: Map showing percentage vegetation, rock, soil

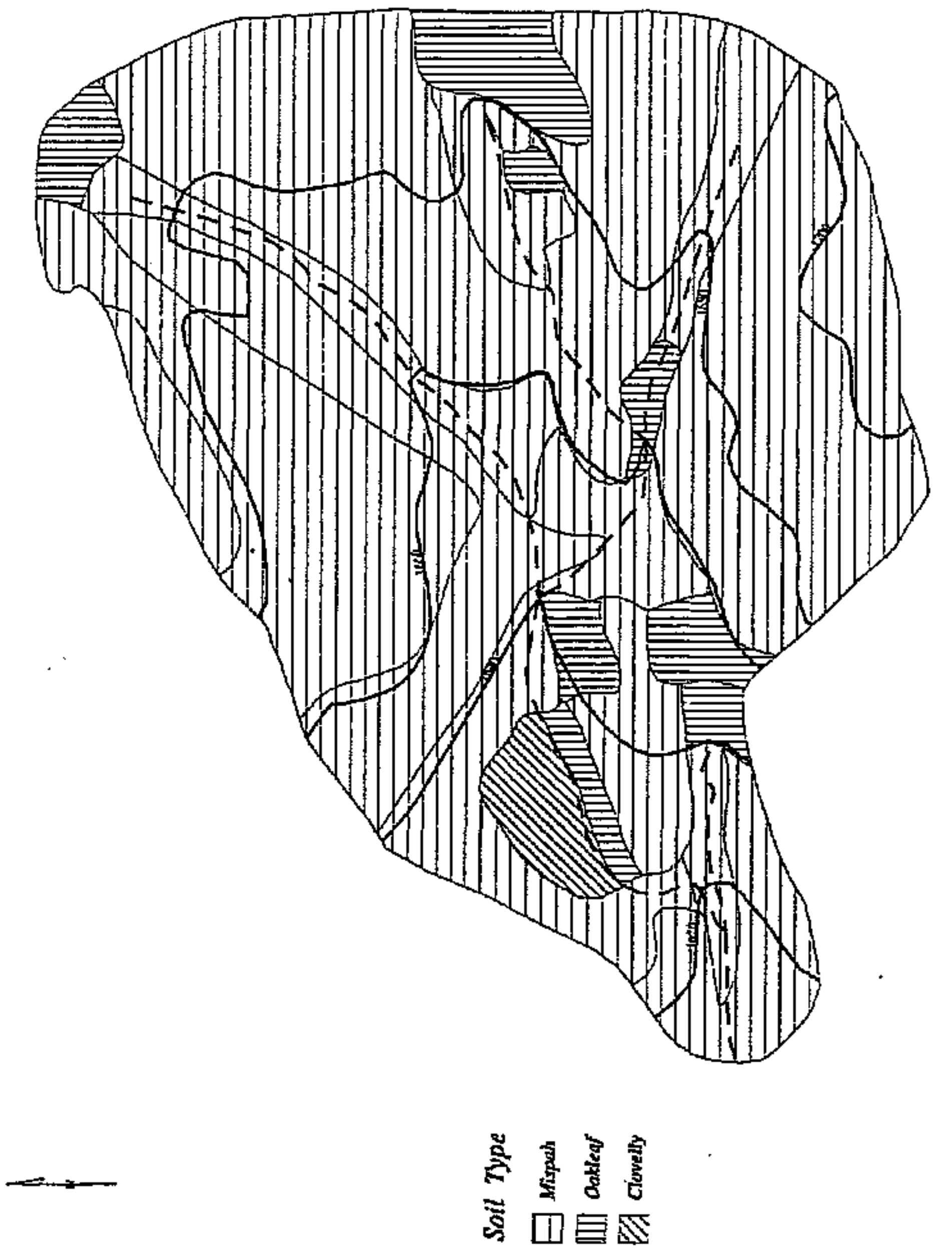


Figure 3: Map of soil type

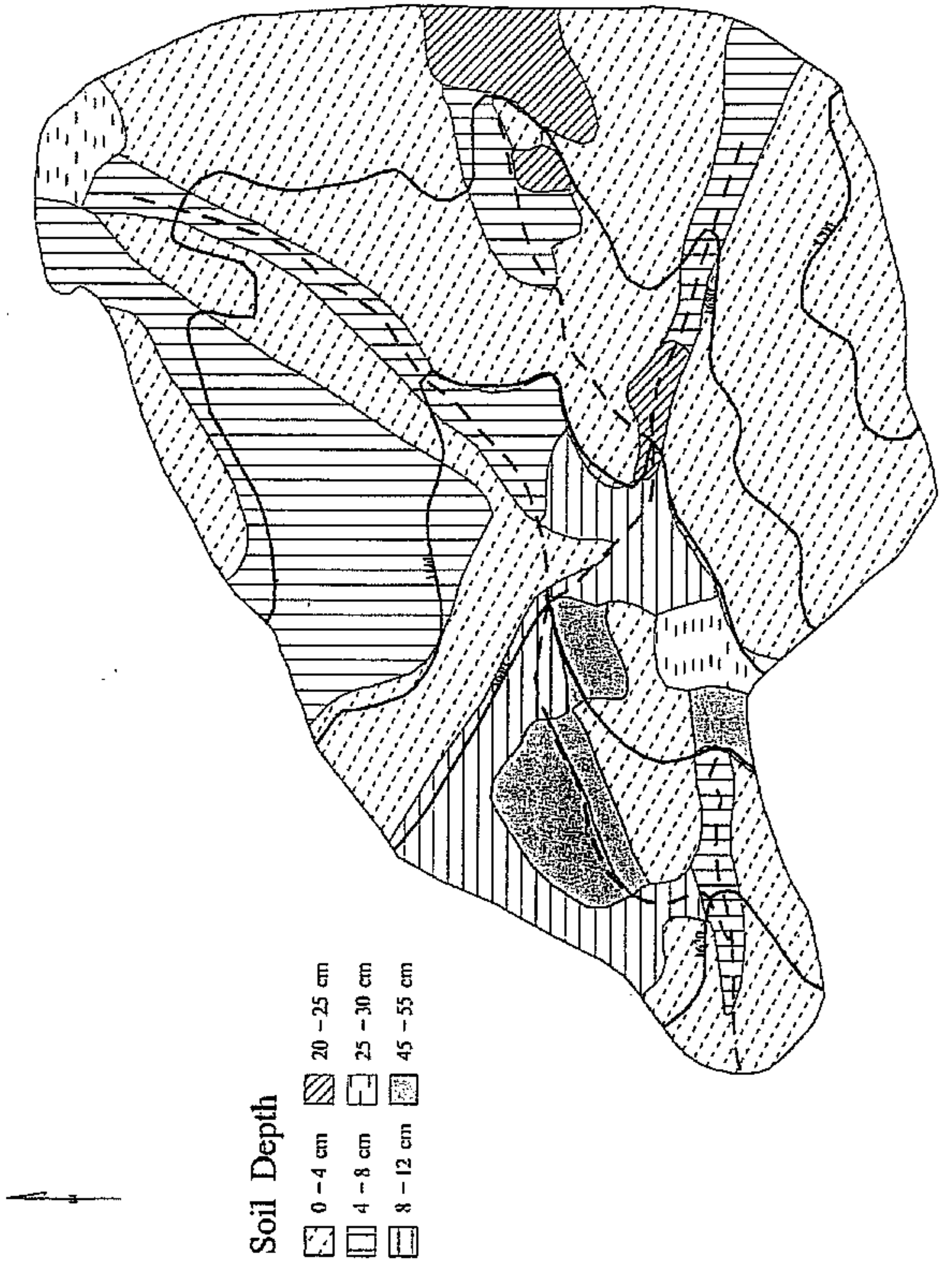


Figure 4: Map of soil depth

(i) Most of the catchment has a very shallow soil covering comprising a loamy sand orthic A-horizon associated with a substantial percentage of exposed rock (the Mispah 1100 form/family)

(ii) The Oakleaf soils generally have a thin A-Horizon overlaying a red, non-luvic neocutanic B-horizon. A neocutanic B-horizon is one which occurs in unconsolidated material, usually transported, which has undergone a small degree of pedogenesis.

(iii) The deepest soils were classified as orthic A-horizon over a yellow-brown apedal B-horizon (Clovelly form/family combination). The B-horizon in this case has a very weak structure and a loamy sand texture.

The average depth of the soils in the catchment was 15 cm (*Figure 4*).

3.3 Location of Field Equipment

Various pieces of equipment were installed for the duration of the study at either the catchment site (*Figure 5*) or at a nearby Ranger's house, which was situated approximately 2 km south-east of the catchment. Equipment located in the catchment included automatic tipping bucket rain gauges (2), a permanent V-notch weir, automatic samplers (2), rock (5) and surface runoff plots (2).

Equipment sited at the Rangers house required daily servicing, which was possible as the house was permanently occupied during the study period. This equipment included an automatic aerochemetrics wet-sampler, a bulk sampler (as used by the Institute for Water Quality Studies (IWQS)) and a mist sampler.

Most of the field measurements were taken at the catchment. These included the measurement of flow, water chemistry, rainfall, and rock and surface runoff.

Three standard South African rain gauges (to calibrate the automatic rain gauges) and an aerochemetrics sampler (to provide a comparison between the wet deposition and the catchment and the Rangers house) were also used in the catchment during Period C.

These pieces of equipment were only serviced on an irregular basis when the site was visited.

The measuring apparatus at the Ranger's site was serviced at approximately 06h00 each day. The apparatus at the catchment was serviced at various times of the day.

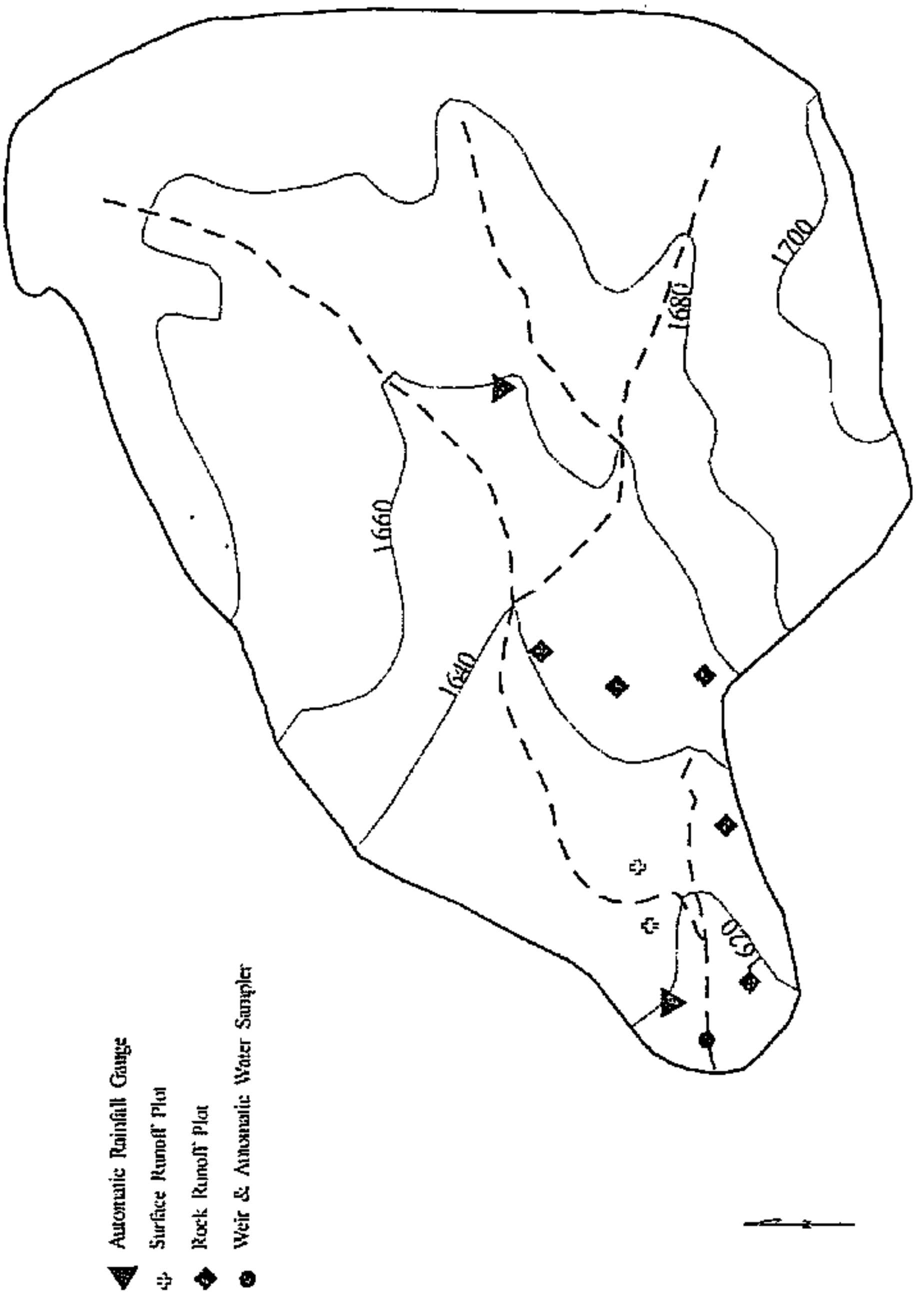


Figure 5: Location of the equipment

4. MATERIALS AND METHODS

This section describes the techniques applied and developed for this study. These include rainfall measurement and various techniques to measure wet and dry deposition. Measurements of the flow from the catchment (hydrology), predominant wind speed and direction (meteorology) and soils analysis are also described.

4.1 Rainfall Measurements

The amount of rainfall into the catchment was measured in mm using two automatic tipping bucket rain gauges. Standard South African rain gauges were used to check the calibration of these gauges.

Two automatic rain gauges were used to ensure a complete rainfall record (each as a backup to the other).

The automatic tipping bucket rain gauges recorded the amount of rainfall in 0.5 mm amounts every 10 minutes using a data logger. The amount of rainfall was also recorded at the nearby Rangers' house, where the wet and bulk samplers were situated. The rainfall was recorded using a standard South African rain gauge for each 24 hour period beginning at 06h00 each day.

4.2 Wet Deposition

4.2.1 *Rainfall Chemistry*

The quality of the wet deposition was measured using an aerochemetric automatic sampler which was installed at the Ranger's house. The sampler was emptied on a daily basis each morning at 06h00 and the samples stored in polypropylene bottles. After use the sample buckets were washed using distilled water. During the first period of collection (October 1992 - June 1993), the samples were immediately frozen on site and thawed in the laboratory. During the second period (July 1993 - March 1994) the samples were stored unfrozen at 4 °C in a fridge on site. In the laboratory, the parameters measured included pH, electrical conductivity (EC), Na^+, K^+, Ca^{2+}, Mg^{2+}, F^+, SO_4^{2-}, Cl^-, NH_4^+ and NO_3^- as well as formate and acetate during the second period of collection. All of the analysis was undertaken by the Institute of Soil, Climate & Water (ISCW) using ion exchange chromatography and atomic absorption spectrometry.

The sulphate deposition rates were calculated by multiplying the measured sulphate concentration(ppm or mg.l^{-1}) for each rainfall event measured by the amount of rainfall in mm and multiplying by 1×10^{-2} to convert to kg sulphate.ha^{-1}. The monthly weighted deposition loads were calculated by adding the deposition rates for each event measured, dividing this value by the total number of mm measured and then multiplying by the total rainfall. This standard procedure allows for the calculation of monthly loads when not all of the rainfall events have been analyzed. Reasons for not sampling all rainfall events include small events where the sample is not large enough for analysis, equipment failure, contamination of sample or operator error.

4.3 Dry Deposition

Estimates of dry deposition were made either directly through measurement of ambient sulphur dioxide or indirectly through the use of combined deposition techniques (rock runoff and bulk samples).

4.3.1 *Sulphur Dioxide Measurements*

Two techniques for measuring sulphur dioxide were used during this study: the peroxide method (Kemeny and Halliday, 1974) between October 1992 and March 1994: as well as an automatic sulphur dioxide sampler as was used by the Department of National Health and Population Development (February 1994 to March 1994).

As a consequence of the visit of Dr Muniz (Norwegian Institute for Nature Research) and a meeting held with Martin Lloyd of the Department of Health and Population Development in December 1993, an offer of the loan of a UV Fluorescence sulphur dioxide sampler was received. In February 1994 this extra sulphur dioxide sampling equipment was installed on site to provide a comparison with the peroxide method which was used throughout the study period.

(i) Peroxide method

The basic principle behind this method is that measured volumes of air are drawn through a gas washing bottle containing a dilute solution of hydrogen peroxide (Kemeny and Halliday, 1974). The SO_2 is absorbed and oxidised to sulphuric acid.

The sampling solutions were changed three times a week, after either two or three day periods.

Initially, the test and control samples were titrated to give an estimation of SO_2. However, on five occasions in October 1992, the pH of the test sample was higher than that of the control and so no reading could be obtained. This was probably due to interference by ammonia in the atmosphere. It was therefore decided to determine the SO_4 concentration in the samples directly using ion exchange chromatography. It was not possible to measure SO_4 directly as well as using the titration method, as H_2SO_4 is used in the titration.

The peroxide method is a relatively inexpensive method, although time consuming.

(ii) Automatic SO_2 sampler

A UV Fluorescence sampler was used at the end of the study period which measured the SO_2 concentrations in the air over 10 minute intervals, allowing the detection of at least hourly peaks in concentration.

4.3.2 *Rock Runoff*

Five rock runoff plots were installed in the catchment. These were randomly located throughout the lower part of the catchment. A consideration in siting the plots was their accessibility for frequent sampling. Each plot consisted of a delineated area of rock from which runoff was directed into a sealed polypropylene bucket. The boundaries of these plots were demarcated using concrete strips approximately 5 cm high. The concrete edge was painted with an inert paint, to prevent contamination of the rainwater by the concrete.

The area of the five plots were as follows : -

Plot A - 0.54 m^2
Plot B - 0.60 m^2
Plot C - 0.57 m^2
Plot D - 0.59 m^2
Plot E - 0.74 m^2

The runoff from rainwater falling onto these plots was collected in sealed polypropylene buckets which had a capacity of 26.5 litres . Polypropylene tubing (20 mm diameter) was used to connect the plots with the collecting buckets. There was a small hole on top of each bucket where the pipe was connected. This small hole prevented any pressure build up in the container.

The plots were designed to cope with 50 mm rainfall in events (this was only exceeded on one occasion - 6 October 1993).

The drainage rate of the plots was approximately 2 litres in 20 seconds. A rainfall intensity of 10 mm per minute would cause overflow and spillage (this rate was never experienced during the study period).

During the dry winter months (May to September 1993), three of these plots (A, C and E) were irrigated using distilled water and the washoff collected. The purpose of this was to collect all of the dry deposition that had accumulated during this period. Two of the plots were not irrigated to serve as a control to determine whether irrigation caused a change in the amount of dry deposition deposited.

The samples were analyzed for sulphate using ion exchange chromatography by ISCW.

The volume of the runoff (l) was multiplied by the sulphate concentration ($mg.l^{-1}$) and then by a factor for each plot (1/area of plot in m^2). This value was then multiplied by $1x10^{-2}$ to convert to $kg.ha^{-1}$ to give the sulphate deposition load per hectare.

4.3.3 *Surface Runoff Plots*

The purpose of the surface runoff plots was to measure the volume and sulphate concentration of surface runoff.

Two surface runoff plots were constructed at the catchment each with an enclosed area of 30 m^2. They were demarcated with strips of asbestos and were positioned in such a way that any runoff was collected using four 50l plastic drums per plot. The asbestos strips were embedded in the soil to a depth of between 3 and 5 cm and any gaps sealed with concrete to prevent any leakage of surface runoff. The asbestos strips were then painted with an inert marine paint to remove any possibility of contamination.

The percentage runoff (surface runoff {mm}/rainfall{mm}x100) for each of the flow events was measured. The ratio of the sulphate concentration in the runoff to the sulphate concentration in the rainfall was also calculated.

The data for only one of the runoff plots was used in the study as, in October 1994, runoff was seen flowing across one of the plots during a period of heavy rainfall. The plot from which data was obtained was located approximately 2 m down-slope of a natural rock ridge. This plot had an average soil depth of 9 cm with loosely compacted soil allowing for rapid infiltration.

4.3.4 *Bulk Sampler*

A bulk sampler was obtained from the Institute for Water Quality Studies (IWQS) and set up at the Rangers House. The main purpose of using the bulk sampler was to provide a comparison of a bulk sampler with an artificial inert collecting surface with 'natural' collecting surfaces. It would also provide a comparison for the IWQS for their own sites. For this reason, the same procedure was used as employed by the IWQS (formerly the Hydrological Research Institute). The only difference was that 500 ml distilled water was used to rinse the collector instead of 300 ml .

This apparatus consists of an open plastic funnel of 0.30 cm diameter. The rainfall was collected in a 1 litre plastic bottle, supported by a 1.8 m metal cylinder. This apparatus is always open and thus will collect even small rainfall events. All of the deposition (wet and dry) was collected after each rainfall event on a daily basis (at 6.00 am). At the end of each month, the collecting funnel was rinsed with 500 ml distilled water, whether it had rained or not.

The samples were analyzed for sulphate, initially by the IWQS and later (January 1993 onwards) by the ISCW.

The total sulphate deposition was calculated for each rainfall event by multiplying the sulphate concentration in the sample collected by the rainfall (mm) for each event. The sulphate deposition values were totalled monthly. The net dry deposition was the total bulk deposition minus the wet sulphate deposition as measured by the wet-only automatic sampler. The sulphate deposition collected in the monthly rinses was calculated by multiplying the concentration of sulphate ($mg.l^{-1}$) by 7.07 (to convert to $mg.m^{-2}$) and then 10^{-2} (to convert to $kg.ha^{-1}$).

4.3.5 *Stem Collars*

Polypropylene collars of 9 cm diameter were placed around the base of upright clumps of grass. The area between the collars and the grass stems was filled as follows: 1 cm of diatomaceous earth covered with 3 cm of ion exchange resin, with a 1 cm layer of polypropylene beads. The diatomaceous earth is an inert substance and was used as an interface between the resin and soil. This was to prevent possible contamination of the resin. A schematic representation of the experimental set-up is shown in *Figure 6.*

Clumps of grass were selected which almost completely filled the collars leaving little exposed polypropylene beads. DOWEX resin was used as the ion exchange resin to collect sulphate. This was prepared by washing twice with 1M NaOH (100 ml for 3 g of resin) followed by two washes with distilled water. After each wash the suspension was poured off through a 20 micron filter using vacuum filtration.

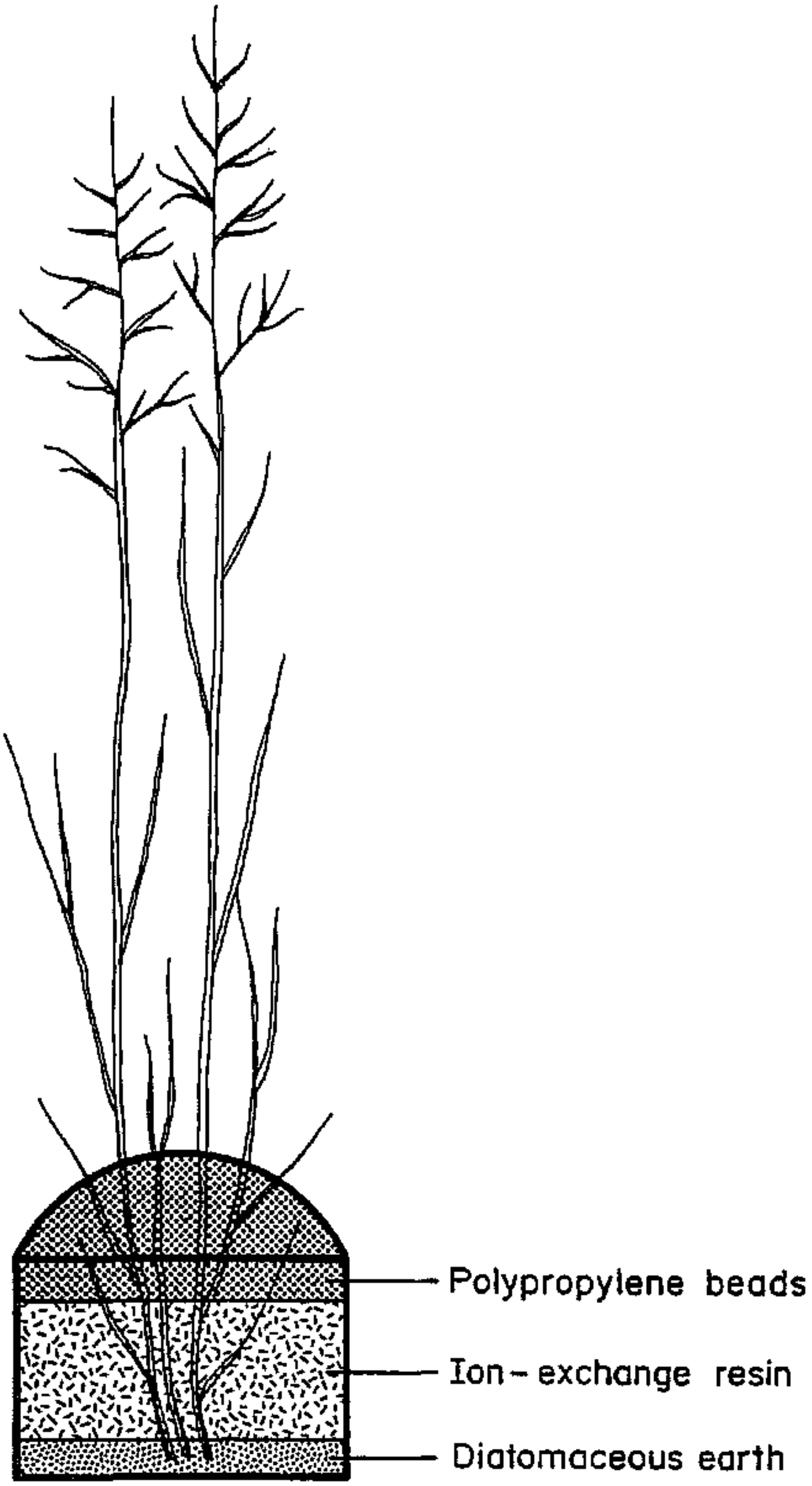


Figure 6: Schematic representation of the stem collars.

The collars were placed in the field for varying periods after which the grass clumps were cut at ground level and the collars were removed. The resin was separated by the North-Western Co-operative and the sulphate extracted using 0.1 M HCl (40 ml to 3 g resin). The mass of resin was recorded together with the sulphate content per gram of resin. The sulphate concentrations for unexposed washed resin were also determined as a control.

The amount of dry deposition was then calculated as the total amount of sulphate extracted per collar (area of 64 cm^2) less the input from the rainfall over the specific measurement period (all in $kg.ha^{-1}$).

4.3.6 *Dew*

The purpose of dew sampling was primarily to test for the occurence of dew formation and secondly to assess the significance of this in terms of the total wet deposition load.

Between August and October 1993 a mist sampler was used at the Ranger's house. This apparatus consists of nylon threads suspended from a 20 cm diameter polypropylene disc. The whole collecting apparatus is suspended beneath a 1.2 m polypropylene lid. The dew collects on these nylon threads and is directed into a polypropylene collecting bottle.

The polypropylene disc was placed in the apparatus overnight, examined the following morning and any sample collected. The volume of each sample was recorded and the amount of sulphate analyzed.

The sulphate deposition rate was calculated by multiplying the SO_4 concentration by the volume collected and the area of the disc (314 cm^2) and then converting to $kg.ha^{-1}$.

4.4 Meteorology

During the study period, wind speed and direction were obtained from an anemometer located on top of the Heidelberg microwave tower (H Langenberg, Division of Earth, Marine and Atmospheric Sciences, CSIR). Initially, this work was due for completion in June 1993, but was extended until March 1994 as part of this project.

An anemometer was placed on top of a 10 m mast which was itself on top of the Heidelberg Microwave tower. The total height above ground level was 90 m.

Wind speed and direction were recorded between November 1992 and March 1994. The wind charts were processed at EMATEK, CSIR.

4.5 Hydrology

An 80° V-Notch weir was constructed at the catchment by the Department of Water Affairs & Forestry (DWAF) which complied with their specifications. The weir was designed to ensure the accuracy at both low and high flows. The height of the water above the base of the V-notch was measured using a level recorder. After calibration the water level readings were used to calculate the flow in $m^3.sec^{-1}$.

The maximum flow measurable at the weir was 1.07 $m^3.sec^{-1}$.

The retaining pond behind the weir was surveyed to determine the volume of water retained as well as to calculate the leakage rate of the weir.

Two ISCO Automatic Samplers were sited at the weir. The first sampler was set to sample at regular intervals of between 1 and 6 hours whether there was any flow or not. The second sampler was attached to a ultrasonic water level sensor which triggered the sampler to begin collection when the level of water in the weir reached the base of the V-notch and at varying time intervals of between 5 and 15 minutes. The samplers were set to collect sample sizes of 100 ml . The samples were collected in polypropylene bottles and stored at 4 °C before being analyzed.

The samples were analyzed for the following chemical variables using ion exchange chromatography and atomic adsorption spectrophotometry : Na^+, K^+, Ca^{2+}, Mg^{2+}, SO_4^{2-}, Cl^-, NH_3-N, NO_3-N, NO_2-N, PO_4^{2-}, Al^+, (October 1993 - March 1993) and Total Alkalinity (TAL). A full metal screening analysis was also undertaken by the IWQS using ICP analysis on two samples.

4.6 Soils

As part of the soils survey undertaken by R Guy of the University of Natal, soil samples were collected for analysis. Similar soils were mixed together into composites for laboratory analysis.

Altogether five composites were selected as typical of soils in the catchment, namely two soils of the Mispah form, two of the Oakleaf form and one of the Clovelly form. Particle size and sulphate retention breakthrough analyses were undertaken at the University of Natal.

Sulphate retention breakthrough analyses were carried out using column leaching tests with sulphate solution using the same method as that employed by Fey and Guy (1993).

In summary, the experiment involved a leaching and loading procedure using prepared soil columns. The columns were first leached using distilled water to remove all excess salts. The endpoint of this part of the experiment is when the leachates' electrical conductivity (EC) value showed no change between successive pore volumes. Thereafter a dilute solution of H_2SO_4 was drained through the columns and the EC measured as before. The breakthrough point is that point where the attenuating capacity of the soil for sulphate is reached and corresponds to a sharp increase in EC.

5. RESULTS

The study was undertaken between October 1992 and March 1994. The study period comprised two 'wet' summer periods and one 'dry' winter period.

These periods are referred to as follows : -

Period A (October 1992 - March 1993) - 'wet'
Period B (April 1993 - September 1993) - 'dry'
Period C (October 1993 - March 1994) - 'wet'

5.1 Rainfall at Suikerbosrand

The daily rainfall data collected is shown in Table A1 of the appendix. Monthly summaries are shown in **Table 1** below and graphically represented in *Figure 7*.

The data from the automatic rainfall gauge located close to the weir were used for the calculations as this rainfall gauge had the most complete record. No significant differences were found between the two automatic rain gauges located at the catchment using the T test at $p = 0.05$.

Table 1: Monthly Rainfall at Suikerbosrand (October 1992 - March 1994)

Period A		**Period B**		**Period C**	
Month	**Rainfall (mm)**	**Month**	**Rainfall (mm)**	**Month**	**Rainfall (mm)**
Oct 92	17.0	Apr 93	39.0	Oct 93	280.5
Nov 92	140.5	May 93	5.0	Nov 93	110.5
Dec 92	66.5	Jun 93	0.0	Dec 93	119.5
Jan 93	69.0	Jul 93	0.0	Jan 94	113.0
Feb 93	91.0	Aug 93	1.0	Feb 94	125.5
Mar 93	107.5	Sep 93	16.0	Mar 94	94.5
Totals	**491.5**		**62.0**		**843.5**

Most of the rainfall occurred during the two ‘wet’ periods - Periods A and C (491.5 mm) and C (843.5 mm). Period B had the lowest rainfall (62.0 mm) with no rainfall recorded in June and July 1993.

Forty per cent more rain was recorded in Period C than in Period A, even though both periods covered the same months of the year (October - March), thereby illustrating the annual variability of rainfall in the region.

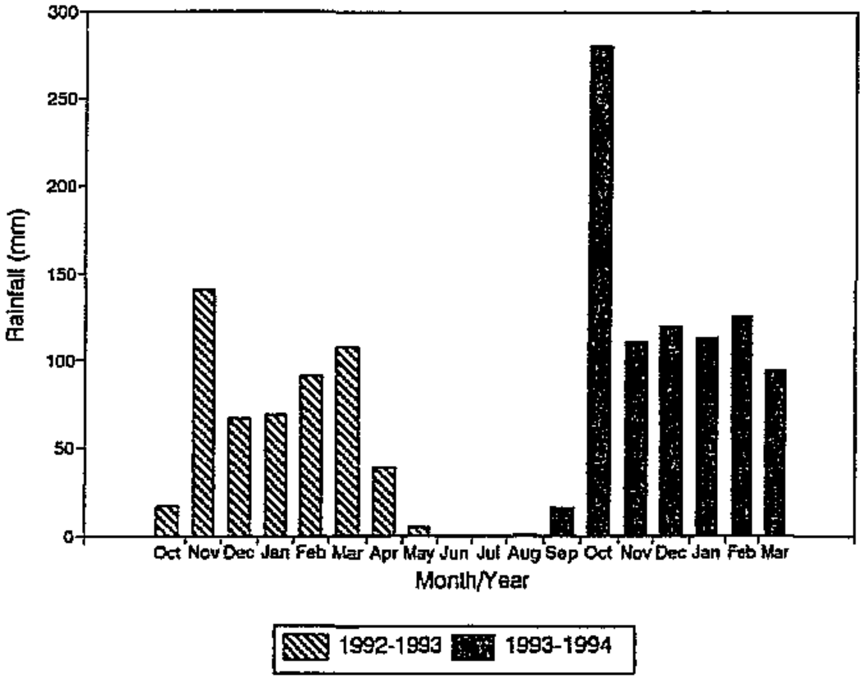


Figure 7 : Monthly rainfall at Suikerbosrand

The highest monthly total (280.5 mm) was recorded in October 1993, when rainfall was recorded on 18 days during the month. This was 236 mm more than occurred in October 1992.

The highest rainfall months (>100 mm) were November 1992 and March 1993 (Period A) and October 1993 to February 1994 (Period C).

A rainfall record was also kept at the Ranger's house which is approximately 2 km from the catchment (no measurements were made between 4 and 28 March 1993). The rainfall recorded at the Ranger's house amounted to 534 mm (Period A), 34 mm (Period B) and 882.0 mm (Period C - adjusted to include missing data). These rainfall data were used in the calculation of the bulk deposition and are shown in Table A7 of the appendix.

The rainfall at the Ranger's house was approximately 10% higher than measured at the main catchment in Period A, 40% less in Period B, and 3% more in Period C. Over the whole study period there was very little difference between the two sites (<5%). Smaller events (0.5 mm) are more accurately measured using an automatic rainfall sampler as the rainfall is measured as it occurs, whereas losses may occur with daily readings where evaporation of the sample may occur. The higher levels recorded at the Ranger's house were partly due to higher readings in two heavy rainfall events (on 9 November 1992 and 8 February 1993).

5.2 Wet Deposition

The wet deposition analysis for all variables measured is shown in Tables A2 and A3 of the appendix. A summary of the main chemical variables is shown below (**Table 2**). Approximately 95% of the rainfall events were collected for analysis.

The total sulphate loads were 11.78, 0.81 and 27.54 kg.ha^{-1} for periods A, B and C respectively. On an annualized basis these were 12.59 and 28.35 kg.ha^{-1} for Periods A and B, and B and C respectively.

The concentrations of sulphate in individual rainfall events were often found to be highest in small rainfall events (<5 mm). The highest concentrations of sulphate in the rainfall (>10 mg.l) were mostly found in rainfall events of less than or equal to 5 mm. The highest monthly sulphate deposition rates (>3 kg.ha^{-1}) occurred during the months of highest rainfall (November 1992, October and November 1993, and January and February 1994).

The rainfall samples for analysis were collected at the Ranger's house. To determine whether there was any difference in rainwater chemistry between the Suikerbosrand catchment and the Ranger's house, a second automatic rainfall sampler was installed at the catchment in Period C. Five samples were collected over the same period and were found to be not significantly different using the t test at $p = 0.05$. It was not possible to install a wet deposition sampler permanently at the main catchment as daily servicing would have been required. Data are shown in Table A4 of the appendix.

Table 2: Mean monthly volume weighted loads of the main chemical variables analysed in the rainfall

Month	Rainfall (mm)	Mean Monthly Volume Weighted Loads (Kg.ha^{-1})							
		NO_3^-	Cl^-	SO_4^{2-}	Na^+	K^+	Ca^{2+}	Mg^{2+}	NH_4^+
Period A									
Oct 92	17	0.83	0.12	0.84	0.21	0.07	0.35	0.07	0.14
Nov 92	140.5	2.17	0.40	3.33	0.77	0.13	2.29	0.51	0.01
Dec 92	66.5	1.80	0.24	2.50	0.03	0.11	1.04	0.17	0.01
Jan 93	69	1.15	0.17	1.77	0.51	2.97	0.64	0.06	0.00
Feb 93	91	1.10	0.21	1.97	0.29	0.16	0.62	0.03	0.01
Mar 93	107.5	0.66	0.16	1.37	0.49	0.10	0.37	0.11	0.00
Totals	491.5	7.71	1.3	11.78	2.30	3.54	5.31	0.95	0.17
Period B									
Apr 93	39	0.23	0.04	0.47	0.00	0.04	0.12	0.04	0.00
May 93	5	0.11	0.04	0.28	0.02	0.06	0.03	0.01	0.00
June 93	0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
July 93	0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Aug 93	1	0.10	0.02	0.03	0.01	0.03	0.04	0.01	0.00
Sep 93	4.5	0.23	0.10	0.03	0.11	0.18	0.04	0.00	0.00
Totals	49.5	0.67	0.20	0.81	0.14	0.31	0.21	0.06	0.00
Period 3									
Oct 93	264.5	4.92	1.01	8.26	0.06	0.30	0.19	0.07	0.34
Nov 93	110.5	1.45	1.95	5.62	0.09	0.06	0.29	0.03	0.41
Dec 93	119.5	2.85	0.29	2.76	0.16	0.40	0.33	0.10	0.75
Jan 94	113	2.64	0.39	4.52	0.15	0.62	0.64	0.18	0.09
Feb 94	125.5	1.88	0.23	4.01	0.04	0.94	0.77	0.18	0.67
Mar 94	94.5	1.39	0.18	2.37	0.10	0.54	0.46	0.12	0.67
Totals	827.5	15.13	4.05	27.54	0.60	2.86	2.68	0.68	2.93
Grand Totals	1368.5	23.51	5.55	40.13	3.04	6.71	8.22	1.69	3.10

5.3 Dry Deposition

The dry deposition at Suikerbosrand was estimated either directly (sulphur dioxide) or indirectly through the estimation of total deposition (rock runoff, bulk deposition, surface runoff, stem flow or mist sampling) whereby the dry deposition is derived by the subtraction of measured wet deposition.

5.3.1 *Sulphur Dioxide*

The data are shown in Table A5 of the appendix and summarised below in **Table 3**. They have been graphically represented in *Figure 8*.

The highest mean SO_2 values were found in the winter months of 1993. The mean SO_2 levels were significantly lower in the 'wetter' summer of 1993 - 1994 than the summer of 1992 - 1993.

The lowest mean SO_2 levels were recorded in January and October 1993 and February 1994.

The automatic sulphur dioxide sampler gave a mean SO_2 concentration of $4.4 \mu g.m^{-3}$ for February and March 1994 as compared to $4.2 \mu g.m^{-3}$ using the peroxide method. The automatic sampler thus gave an SO_2 measurement of approximately 5% higher than the peroxide method at relatively low concentrations. The level of accuracy at higher concentrations of SO_2 is not known.

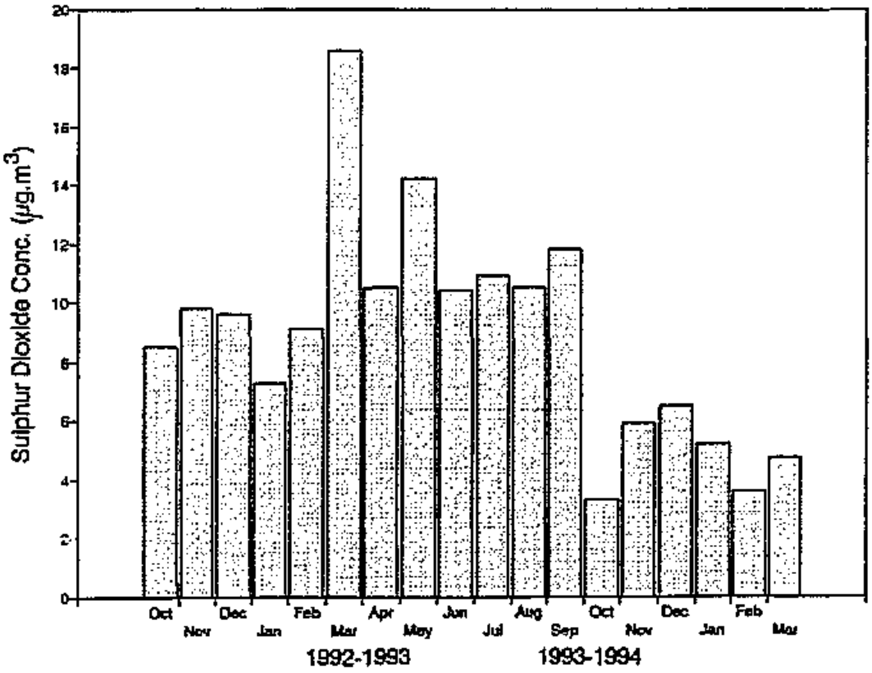


Figure 8: Mean monthly SO_2 concentrations at Suikerbosrand

Table 3 : Mean monthly SO_2 concentrations in $\mu g.m^{-3}$

Period A (Oct 92 - Mar 93)		Period B (Apr 93 - Sept 93)		Period C (Oct 93 - Mar 94)	
Month/Year	SO_2 Conc. ($\mu g.m^{-3}$)	Month/Year	SO_2 Conc. ($\mu g.m^{-3}$)	Month/Year	SO_2 Conc. ($\mu g.m^{-3}$)
Oct 92	8.5	Apr 93	10.5	Oct 93	3.3
Nov 92	9.8	May 93	14.2	Nov 93	5.9
Dec 92	9.6	Jun 93	10.4	Dec 93	6.5
Jan 93	7.3	Jul 93	10.9	Jan 94	5.2
Feb 93	9.1	Aug 93	10.5	Feb 94	3.6
Mar 93	18.6	Sep 93	11.8	Mar 94	4.7

The mean annual SO_2 concentrations were 10.9 $\mu g.m^{-3}$ (Periods A and B) and 7.0 $\mu g.m^{-3}$ (Periods B and C).

Using a deposition velocity of 0.3 cm.sec^{-1} for the winter months (Period B) and 1.3 cm.sec^{-1} for the summer months (Periods A and C), which are calculated values for grassland (Shepherd, 1974) the deposition rates were calculated as follows (Wells, 1989):

$$SO_2 \text{ deposition} = V_d \times c \times 3.154 \text{ kg.ha}^{-1}.\text{year}^{-1} \times 1.5 \times \text{m}.365^{-1}$$

where V_d is the deposition velocity (0.3 cm.sec^{-1} in winter or 1.3 cm.sec^{-1} in summer)
c is the SO_2 concentration in µg.m^{-3}
m is the number of days in the month
and 1.5 is the ratio of the molecular weight of SO_4 to SO_2
(96/64 = 1.5)

The calculated values are shown in **Table 4.**

Table 4 : Deposition rates using a deposition velocity of 0.3 cm.sec^{-1} (Period B) and 1.3 cm.sec^{-1} (Periods A and C).

Period A (Oct 92 - Mar 93)		Period B (Apr 93 - Sep 93)		Period C (Oct 93 - Mar 94)	
Month/ Year	**Deposition Rate (kg.ha^{-1})**	**Month/ Year**	**Deposition Rate (kg.ha^{-1})**	**Month/ Year**	**Deposition Rate (kg.ha^{-1})**
Oct 92	4.4	Apr 93	1.2	Oct 93	1.7
Nov 92	5.0	May 93	1.7	Nov 93	3.0
Dec 92	5.0	Jun 93	1.2	Dec 93	3.4
Jan 93	3.8	Jul 93	1.3	Jan 93	2.7
Feb 93	4.3	Aug 93	1.3	Feb 94	1.7
Mar 93	9.7	Sep 93	1.4	Mar 94	2.5
Totals	**32.2**		**8.1**		**15.0**

When the levels of sulphur dioxide are compared to the rainfall, as shown in *Figure 9*, it can be seen that the concentration of sulphur dioxide is inversely proportional to the amount of rainfall i.e. the higher the rainfall the lower the sulphur dioxide concentration. This is due to the scavenging of sulphur dioxide by rainfall.

The linear regression of the points has been plotted to show clearly the relationship ($r^2 = 0.59$).

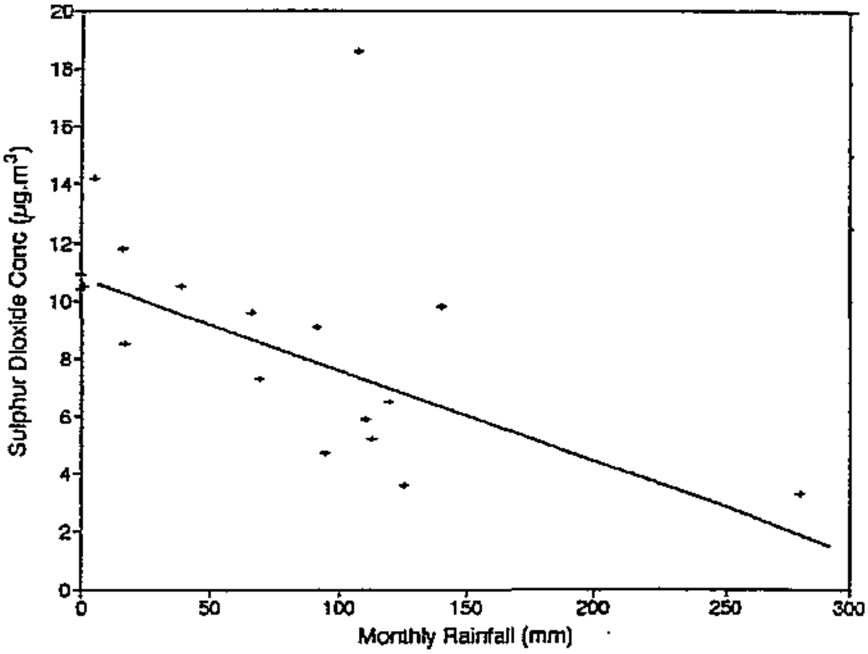


Figure 9: Sulphur dioxide vs rainfall at Suikerbosrand

5.3.2 *Rock runoff plots*

The data are shown in Table A6 of the appendix. Monthly summaries are shown in **Table 5** and graphically represented in *Figure 10* below.

Table 5: Total runoff/wet deposition/net dry deposition of sulphate for the rock runoff plots

Month	Sulphate Load (kg.ha^{-1})		
	Total Runoff	Wet Deposition	Net Dry Dep
Period A (Nov 92 - Mar 93)			
Nov	3.42	3.10	0.32
Dec	4.82	2.50	2.32
Jan	3.03	1.77	1.26
Feb	1.43	1.97	-0.54
Mar	3.99	1.37	2.62
Totals	**16.69**	**10.71**	**5.98**
Period B (Apr 93 - Sep 94)			
Apr	2.73	0.47	2.26
May	0.90	0.28	0.62
Jun	0.35	0.00	0.35
Jul	0.36	0.00	0.36
Aug	0.36	0.03	0.33
Sep	1.88	0.03	1.85
Totals	**6.58**	**0.81**	**5.77**
Period C (Oct 93 - Mar 94)			
Oct	8.74	6.60	2.14
Nov	5.52	5.62	-0.10
Dec	6.26	2.76	3.50
Jan	8.53	4.52	4.01
Feb	10.08	4.01	6.07
Mar	3.80	2.37	1.43
Totals	**42.93**	**25.88**	**17.05**

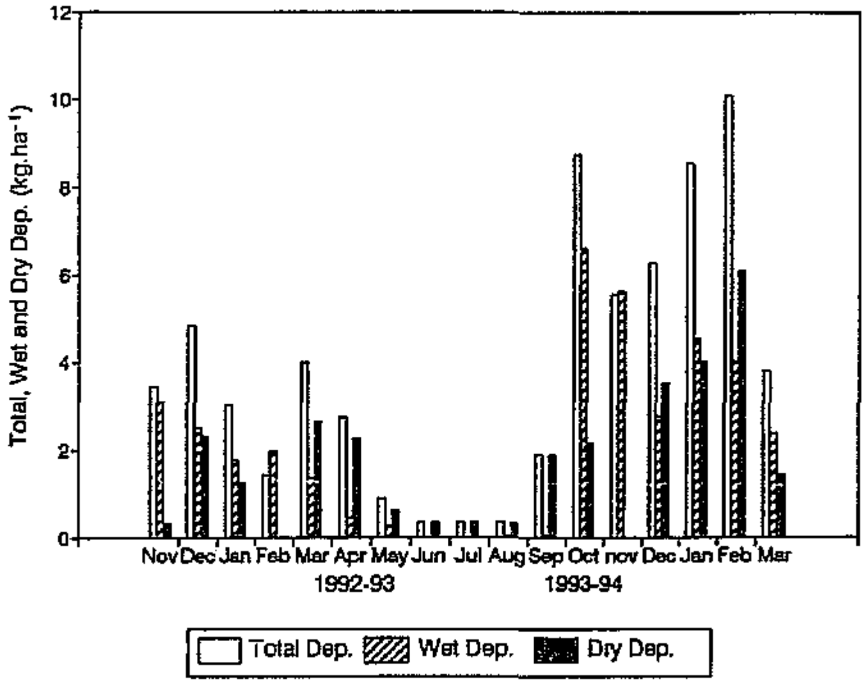


Figure 10: Total, wet and dry deposition measured using the rock run-off plots.

In periods A, B and C, the estimated net dry deposition of sulphate (total rock runoff minus measured wet deposition) was 5.98, 5.77 and 17.05 kg.ha^{-1} respectively

In periods A and C (wet periods) the proportion of dry deposition to the total deposition was 36 and 40% respectively. In period B (dry period) the proportion of dry deposition was 88% of the total deposition.

The volumes collected for each runoff plot were compared using two-way analysis of variance to determine whether there was any significant difference between the different plots. No significant difference was found (p less than 0.05).

Three of the rock plots (A,C and E) were washed on two occasions in the winter of 1993 (2.8.93 and 25.9.93) as shown in **Table 6**. The plots were washed with 1 litre of distilled water on 2 August 1993 and 2 litres on 25 August 1993.

The purpose of the experiment was twofold - 1. to determine the effect of washing on the deposition of sulphate; 2. to determine the accumulation of sulphate on the rock surfaces.

Table 6 : Rock runoff wash

Plot	10.09.93 SO_4^{2-} Conc. (mg.l^{-1})	Volume (l) Wash with 1 litre	Total Runoff (kg.ha^{-1})	15.09.93 SO_4^{2-} Conc. (mg.l^{-1})	Volume (l) Wash with 2 litres	Total Runoff (kg.ha^{-1})
A	58.8	0.71	0.77	58.6	1.79	1.94
C	16.1	0.75	0.21	30.5	1.86	0.99
E	58.6	0.68	0.54	52.8	1.65	1.18
Mean	44.5	0.71	0.51	47.3	1.77	1.37

The mean deposition rate was calculated by multiplying the sulphate concentration by the volume collected and by the appropriate factor for each plot to convert to one m^2 (1.85, 1.75 and 1.35 for Rock Plots A, C and E respectively).

The mean deposition rate on 10 August 1993 was 0.51 kg.ha^{-1}, as compared to 1.37 kg.ha^{-1} on 15 September 1993. The deposition rates were much higher for the second wash than for the first. This was probably due to the more thorough washing that took place (two litres were used on 15 September 1993 as opposed to one litre on 10 August 1993).

The loss in volume after water is poured over the plots was between 29% for one litre and 12% for two litres and can be ascribed to the 'wettability' of the rocks.

The total sulphate runoff for the washed plots was approximately 1.8 kg.ha^{-1} higher than for the unwashed plots (**Table 7**).

The rock surfaces are not smooth and dry deposition particles and gases accumulate or are absorbed onto the rock surfaces and in crevices. Washing removed accumulated sulphate and hence created a greater capacity for subsequent accumulation of sulphate on the cleaned surfaces.

Table 7 : Comparison of washed and unwashed rock plots

Plot	Sulphate Deposition ($kg.ha^{-1}$)			Totals
	Date of Wash			
	02.08.93	15.09.93	25.09.93	
A	0.77	1.94	1.28	3.99
B	unwashed		1.16	1.16
C	0.21	0.99	1.24	2.44
D	unwashed		1.96	1.96
E	0.54	1.18	1.91	3.63

The total runoff collected for all plots was 2456 l (491.2 l/plot). During the period when rock runoff was collected, the total rainfall was 1256.5 mm (or 1256 litres.m^{-2}). This excludes the one event when the plots overflowed (6 October 1993). The average area of the plots was 0.60 m^2.

Thus, the maximum runoff that could be collected is :

1256.5 l x 0.60 = 753.9 l

Taking into account that 13.5% of the plots were not used for various reasons including interference by baboons. The maximum runoff that could be expected is :

753.9 x 0.865 = 652.0 l

A further loss due to 'wettability' of approximately 20%

652.01 x 0.8 = 521.6 l

Thus, the percentage of runoff collected over the study period was:

491.2 / 521.6 = 94%

5.3.3 *Surface Runoff Plots*

The surface runoff plot data, in which the volume of runoff, the respective rainfall events as well as the sulphate analyses are shown in **Table 8** below. Only those events that sampled the whole event were analyzed. Events where the sampling bottles overflowed or the collecting tubes became blocked were not analyzed.

Table 8 : Soil surface runoff events - based on individual rainfall events

Date of Event	Runoff Event						Ratio SO_4 conc. in runoff : SO_4 conc. in rainfall
	SO_4 conc. of runoff ($mg.l^{-1}$)	Volume collected (l)	Days since last event	Amount of rainfall causing runoff event (mm)	% Runoff	Sulphate conc. of rainfall causing event ($mg.l^{-1}$)	
Period B							
01.10.93	15.4	46.0	172	35.5	4.3	3.9	3.95
Period C							
07.10.93	5.88	35	1	26.5	4.4	3.1	1.90
08.10.93	3.54	81	1	14.0	19.3	2.9	1.22
14.10.93	8.82	10.5	2	11.5	3.0	5.4	1.63
28.10.93	11.5	2	2	7.5	5.1	3.6	1.78
16.12.93	4.69	5.6	12	7.5	2.5	3.3	1.42
21.12.93	3.75	55	5	18.5	9.9	2.3	1.63
30.12.93	3.60	45	8	23.5	6.4	1.6	2.29
06.02.94	4.07	52	3	32.5	5.3	1.1	3.70

Only one of the plots was used, as surface runoff was seen to flow across the second plot in periods of high rainfall.

The runoff rates varied between 2.5 and 19.3%. The runoff rate is affected by several factors including the intensity of the rainfall, the infiltration capacity of the soil as well as its moisture content.

The average soil depth in the plot was 9 cm. The loamy sand soil was loosely compacted allowing for rapid infiltration.

The ratio of sulphate in the runoff to the rainfall for period B was 3.95 and between 1.22 and 3.7 for period C. This represents the increase in sulphate concentration as the rainfall flows across and through the surface of the soil.

The volume weighted concentration ratio of the surface runoff to the rainfall for Period C was 1.49.

5.3.4 *Bulk Deposition*

The data from the bulk sampler, which was located at the Rangers house, are shown in Table A7 of the appendix. The data are summarised in **Table 9** and graphically represented in *Figure 11* below. The samples collected in August and September were discarded due to contamination (phosphate levels of >50 mg.l^{-1}).

Over the whole sampling period, the total bulk deposition of sulphate measured was 44.0 kg.ha^{-1}, of which approximately 19.5 % was dry or particulate deposition. The total estimated dry deposition rates for periods A, B and C were 3.03, 2.39 and 3.13 kg.ha^{-1} respectively.

The annualised totals were 5.42 and 5.52 kg.ha^{-1} for periods A and B, and B and C respectively.

In period A (wet), the proportion of dry to the total deposition was 19.5 %, in Period B (dry) it was 94.4 %, and in Period C (wet) it was 12.7%.

The bulk sampler primarily measures the deposition of particulate sulphate with little or no adsorption of gaseous sulphur dioxide. The collecting surface is made of polypropylene which is an inert surface to adsorption of SO_2 gas.

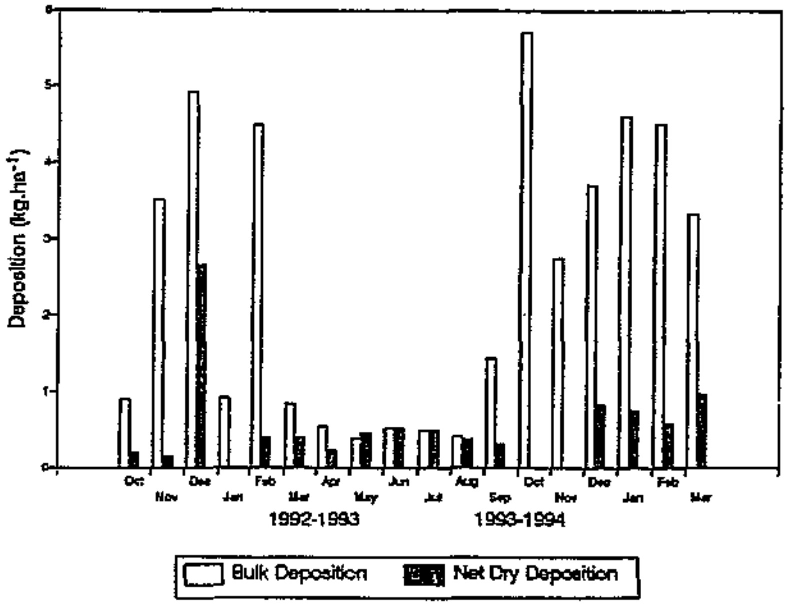


Figure 11 : Total bulk and net dry sulphate deposition

Table 9 : Total bulk, wet and dry deposition at Ranger's House

Year/Month	Total bulk sulphate deposition (kg.ha^{-1})	Wet deposition (kg.ha^{-1})	Net dry deposition (kg.ha^{-1})
Period A			
Oct	0.90	0.71	0.19
Nov	3.52	3.37	0.15
Dec	4.91	2.25	2.66
Jan	0.92	1.70	0.00
Feb	4.48	4.07	0.40
Mar	0.85	0.45	0.40
Totals	**15.58**	12.55	**3.03**
Period B			
Apr	0.55	0.32	0.23
May	0.38	0.21	0.46
Jun	0.52	0.00	0.52
Jul	0.49	0.03	0.38
Aug*	0.41	0.03	0.38
Sept*	1.44	1.13	0.31
Totals	**3.79**	**1.69**	**2.39**
Period C			
Oct	5.71	6.92	0.00
Nov	2.75	5.53	0.00
Dec	3.71	2.88	0.83
Jan	4.60	3.84	0.76
Feb	4.51	3.93	0.57
Mar	3.33	2.36	0.97
Totals	**24.69**	25.46	**3.13**

* some samples were excluded because of contamination.

5.3.5 *Stem Collars*

The stem flow data, in terms of the measured sulphate deposition, are shown below in **Table 10.**

Table 10 : Total stem flow (May 1993 - September 1993)

Period	Replicates	Total stem flow (kg.ha^{-1})	Wet deposition (kg.ha^{-1})	Net dry deposition (kg.ha^{-1})	Days	Dry dep/day (kg.ha^{-1})
B (18.05.93 -25.09.93)	11	7.10	0.03	7.04	130	0.05
C (11.03.94 -12.04.94)	5	17.32	1.78	15.54	22	0.71

The estimated net dry deposition over the two periods was 7.04 and 15.54 kg.ha^{-1}.

The higher rate obtained in Period C was probably due to stomatal activity of the plants when the grass clumps were actively growing, whereas in Period B the grass clumps were dry and dormant.

It is not realistic to extrapolate the data to the whole catchment as the clumps of grass selected for sampling were isolated from each other and standing alone, allowing for more effective scavenging of the SO_2. A group of closely spaced stands may give a much lower deposition rate.

5.3.6 *Dew Sampling*

Dew sampling was undertaken over a period of three months (August, September and October 1993). Dew formation occurred on six occasions during this period. These are shown below in **Table 11.**

The occurrence of dew at Suikerbosrand was at best occasional. The occurrences corresponded to those days on which rainfall occurred and hence the presence of sufficient moisture for dew formation.

The total deposition of sulphate associated with dew over the three month sampling period was 1.14 kg.ha^{-1}. This was 12.0% of the total sulphate deposited in the rainfall over the same period (9.36 kg.ha^{-1}).

The period during which dew formation occurred (late winter/early summer) was a period when dew formation is most likely. Other times of the year, it is unlikely that the above levels as a percentage of wet deposition would be exceeded.

Table 11: Dew samples collected and calculated deposition rates

Date	SO_4 Conc mg.l^{-1}	Volume (ml)	mm equiv.	Deposition (kg.ha^{-1})
06.09.93	53.81	6.5	0.20	0.11
25.09.93	55.02	22	0.67	0.37
01.10.93	55.62	12.5	0.38	0.21
07.10.93	55.62	6	0.18	0.10
08.10.93	8.16	87	2.64	0.22
15.10.93	55.62	7.9	0.24	0.13
Total				**1.14**

Note : Area of sampler = 0.033 m^2 and 1 mm mist = 33 ml sample

5.4 Summary of Catchment Inputs

The measured and estimated catchment inputs are summarised below in **Table 12.**

Table 12 : Summary of catchment inputs

Period	Wet Deposition of Sulphate (kg.ha^{-1})	Dry Deposition of sulphate (kg.ha^{-1})				
		SO_2 (0.3 and 1.3 m.sec^{-1})	Rock Runoff	Surface Runoff	Bulk Deposition	Stem Collar
A	11.78	32.2	7.6*	-	3.03	-
B	0.81	8.1	5.77	2.4	2.39	7.04
C	27.54	15.00	17.05	14.0	3.13	15.54

* adjusted to include October 1992

The rock runoff, SO_2 and bulk samples were made continuously over the three periods. The other two methods (surface runoff and leaf stem) were undertaken in only parts of Periods B and C.

The potential rates of SO_2 deposition are inversely proportional to the amount of rainfall and hence wet deposition as SO_2 is scoured from the atmosphere by the rainfall.

The rock runoff plots on the other hand are directly proportional to the amount of wet deposition in the two 'wet' periods (B and C). In Period B, when there was little deposition, the amount of dry deposition measured was probably comprised mostly of particulates.

The bulk deposition estimates were primarily of particulate dry deposition and consistently gave the lowest estimates.

The surface runoff and stem collar estimates should only be regarded as indications of total dry deposition. It is considered likely that the surface runoff estimates were underestimates as it would be expected that the potential for dry deposition was higher for the grassland than for the rock runoff plots.

The dry deposition rates for the grassland part of the catchment (46% of catchment area) are assumed to be equal to the combined totals of the SO_2 estimated deposition rates together with the particulate deposition rates measured by the bulk sampler.

5.5 Catchment Outputs

5.5.1 *Hydrology*

During the two study periods, 14 separate flow events occurred. The hydrograph of Flow 1A together with the associated rainfall record is shown in *Figure 12* below. The hydrographs for Flows A2 to C14 are shown in the appendix (Figs A1 to A13). The flow data has been summarised below in **Tables 13 and** 14.

Table 13 : Flow events - Period A (November 1992 - March 1993)

Flow	Period	Duration (hours)	Maximum discharge ($m^3.sec^{-1}$)	Volume (m^3)	Rainfall (mm)	% Runoff
A-1	08.11.92 - 10.11.92	30	0.478	2 044.2	56.5	11
A-2	13.11.92 - 15.11.92	51	0.026	226.5	32	2
A-3	12.12.92 - 12.12.92	35	0.001	44.2	21	1
A-4	21.12.92 -23.12.92	45	0.038	107.8	23	1
A-5	03.01.93 - 31.02.93	26	1.070	4 720.5	29.5	51
A-6	08.02.93 - 11.02.93	69	0.009	361.9	31.5	4
A-7	01.03.93 - 09.03.93	186	1.12	5 484.5	87	21
Total discharge = 12 989.6 m^3						

Table 14 : Flow events - Period C (October 93 - Mar 94)

Flow	Period	Duration (hours)	Maximum discharge ($m^3.sec^{-1}$)	Volume (m^3)	Rainfall	% Runoff
C-8	06.10.93 - 23.10.93	413	0.080	7 159.3	187.5	12
C-9	25.10.93 -02.11.93	186	0.019	2 168.4	32	21
C-10	28.11.93 - 02.12.93	95	0.343	1 648.1	39	13
C-11	02.12.93 - 09.12.93	160	0.028	384.0	37	3
C-12	23.01.94 - 28.01.94	121	0.001	271.2	58.5	1
C-13	02.02.94 - 19.02.94	404	0.037	12 083.2	107.5	35
C-14	28.03.94 - 30.03.94	29	0.175	620.5	42	5
Total discharge = 24 334.7 m^3						

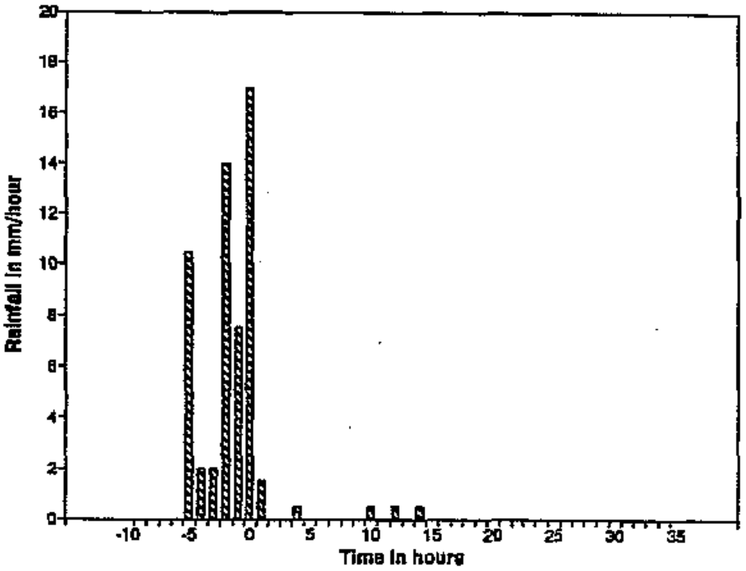


Figure 12a: Rainfall - Flow A1 - 56.5 mm

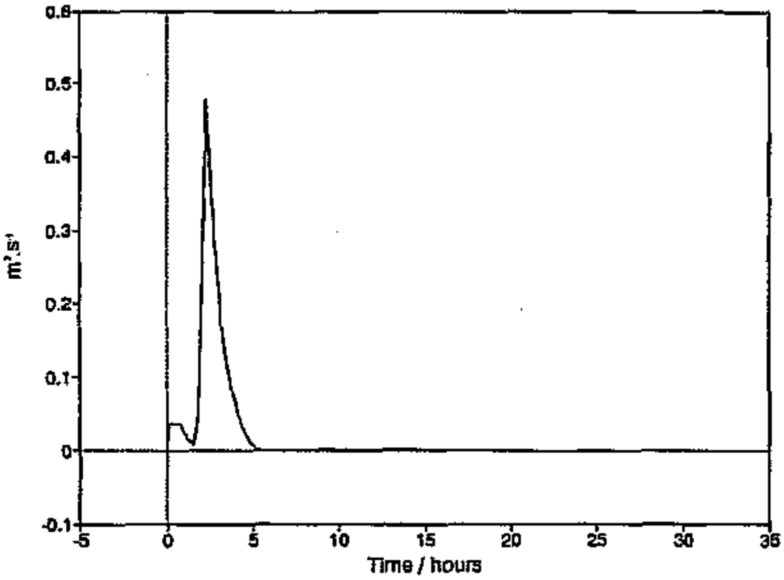


Figure 12b: Flow A1 (8 - 10 Nov 92)

All of the flows were measured during the two periods. In the first period (Period A), the flows were predominantly of short duration occurring after a single rainfall event. The exceptions were Flows A3 and A7, which flowed in response to a period of general rainfall. Flows A7 also responded to a rainfall event after commencement of flow.

During the second period of flow (Period C), where the rainfall was considerably higher, the flows were of much longer duration, mostly responding to periods of rainfall, with the exception of flows C10, C11 and C14 which all flowed in response to an individual rainfall event.

The total volumes for Period A and Period C were 12989.6 m^3 and 24 334.7 m^3 respectively, representing a runoff percentage of 8.4% (Period A) and 8.9% (Period C).

The stream at Suikerbosrand is a temporary stream, and was found to respond quickly to rainfall events that caused flow (often <1 hour).

The retaining pond behind the weir was surveyed and the rate of leakage estimated.

The drop in level at zero flow was measured during the two periods of flow and the leakage rate was estimated to be 0.0008 $m^3.sec^{-1}$ during the first period and 0.0005 $m^3.sec^{-1}$ during the second period. These values were included in the calculation of the final flows. It was assumed that the leakage rate above zero flow was constant. Evaporation from the weir pond was taken into consideration when calculating these leakage rates.

The percentage losses for each flow are shown in **Table 15** below.

The overall effect of the leak on the combined flows of Period A was 1.83%, and 2.58% on the combined flows of Period B.

Although the effect of the leakage on the total flows was relatively small it was significant for the very low flows (Flows A3, A4 and B10) where the loss due to the leakage was in excess of 10%.

Table 15 : Weir leakage as a percentage of flow

Flow	% Leakage	Flow	% Leakage
A-1	0.05	C-8	1.1
A-2	7.5	C-9	1.7
A-3	25.3	C-10	13.2
A-4	12	C-11	8.8
A-5	0.1	C-12	9.4
A-6	5.5	C-13	0.7
A-7	0.8	C-14	0.9

5.5.2 *Surface Water Chemistry*

The chemical characteristics of the catchment discharge are discussed.

The volume-weighted concentrations of the main water quality variables were calculated by multiplying the concentrations in $mg.l^{-1}$ by the corresponding flow volume and dividing by the total flow. These data for each flow are shown below in **Table 16** ($mg.l^{-1}$) and **Table 17** ($\mu eq.l^{-1}$). A metals screening analysis is shown in the appendix (Table A8).

The water chemistry of Suikerbosrand stream was in many ways characteristic of a pristine upland stream in the region, with a low alkalinity (often less than 5 $mg.l^{-1}$), mostly undetectable levels of PO_4, and low concentrations of heavy metals.

The concentrations of the chemical variables were generally lower in Period C than Period A (which also corresponded to the higher rates of flow recorded in Period C resulting in higher dilution).

The levels of sulphate (mostly > 8 $mg.l^{-1}$) did, however, not show a reduction in Period C. The pH levels were acid and mostly less than pH 6.0 (4.2 - 6.3). The low ANC values of less than 130 $\mu eq.l^{-1}$ (**Table 17**) indicate that the stream has a high sensitivity to acid inputs.

Table 16 : Mean volume weighted concentration (mg.l^{-1})

Flow	Volume (m^3)	Variable								
		Na^+	K^+	Ca^{2+}	Mg^{2+}	SO_4^{2-}	NO_3^-	Cl^-	TAL	pH Range
Period A										
A1	2 044.2	-	-	-	-	-	-	-	-	-
A2	226.5	1.2	2.4	4.0	1.9	9.4	17.0	3.4	5.0	4.2 - 5.5
A3	44.2	1.4	1.5	3.5	1.6	13.9	15.0	4.6	4.7	4.7 - 5.4
A4	107.8	1.4	1.6	2.8	1.2	7.7	7.7	3.5	5.3	5.0 - 5.7
A5	4 720.5	0.2	4.5	1.4	0.5	5.1	2.5	1.7	8.0	4.3 - 5.7
A6	361.9	3.5	0.9	3.7	1.7	11.7	7.6	2.7	7.0	4.2 - 5.5
A7	5 484.5	1.0	0.9	2.7	1.3	10.9	4.1	2.3	5.6	4.7 - 6.0
Period C										
C8	7 159.3	1.2	1.3	3.0	1.3	10.2	5.8	3.2	2.6	4.6 - 5.6
C9	2 168.4	1.4	0.5	2.5	1.1	10.4	1.5	3.0	3.4	4.7 - 5.4
C10	1 648.1	0.6	1.2	2.6	0.9	11.5	3.0	1.2	2.9	4.8 - 5.8
C11	384.0	1.0	0.4	2.3	1.0	9.1	1.1	1.8	2.9	4.7 - 5.9
C12	271.2	1.0	0.8	2.7	1.2	11.7	0.4	1.9	4.0	5.2 - 5.9
C13	12 083.2	1.1	0.4	2.3	0.9	10.0	0.1	2.1	3.0	4.7 - 6.3
C14	620.5	0.3	2.2	1.5	0.5	6.0	1.7	1.0	4.0	5.2 - 5.4

The highest mean volume-weighted levels of nitrate occurred in flows A2 and A3 (>15 mg.l^{-1}) - Flow A1 was not sampled. These flows were, however, the first flows of the summer season after the catchment has largely dried out. Subsequent flows in the same period had much lower levels. The highest levels of nitrate in Period C were also seen in the first flow after the dry winter months.

The most important variables (Na, K, Ca, Mg, SO_4, NO_3, Cl, EC, pH and ANC have been plotted for Flow A-6 and are shown below in *Figure 13a-d.*

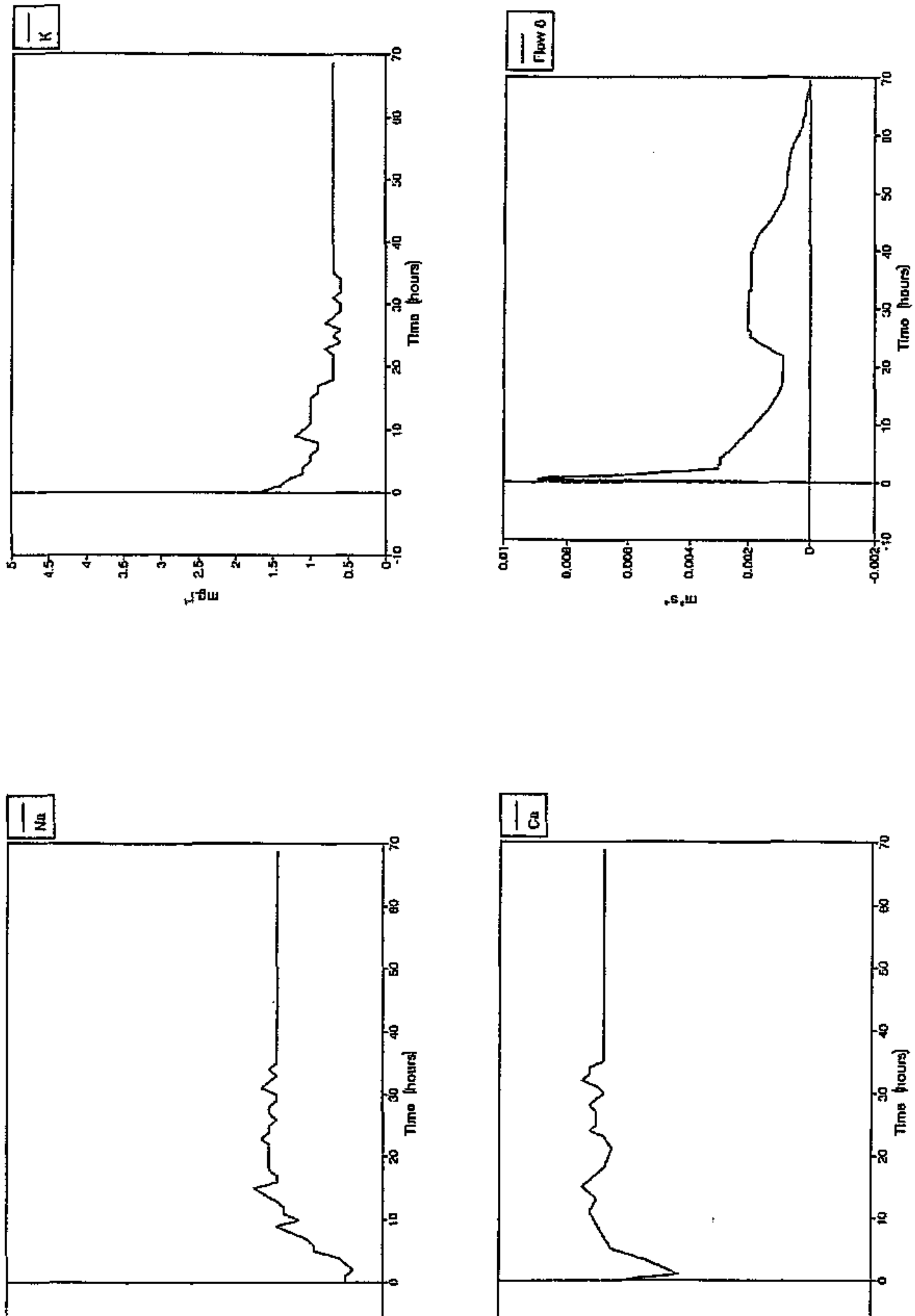


Figure 13a: Flow A6 (Na, K, Ca and Flow)

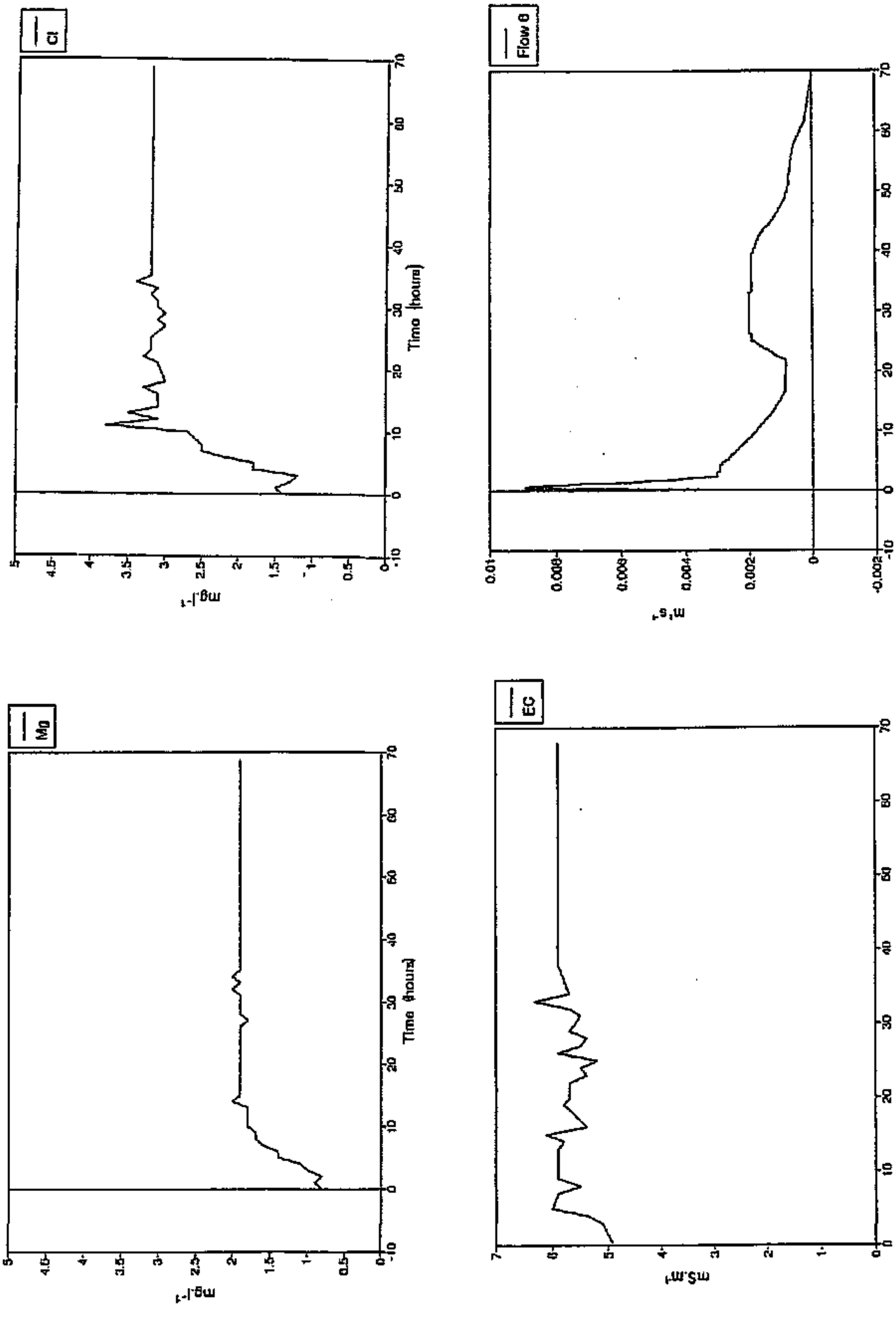


Figure 13b: Flow A6 (Mg, Cl, EC and Flow)

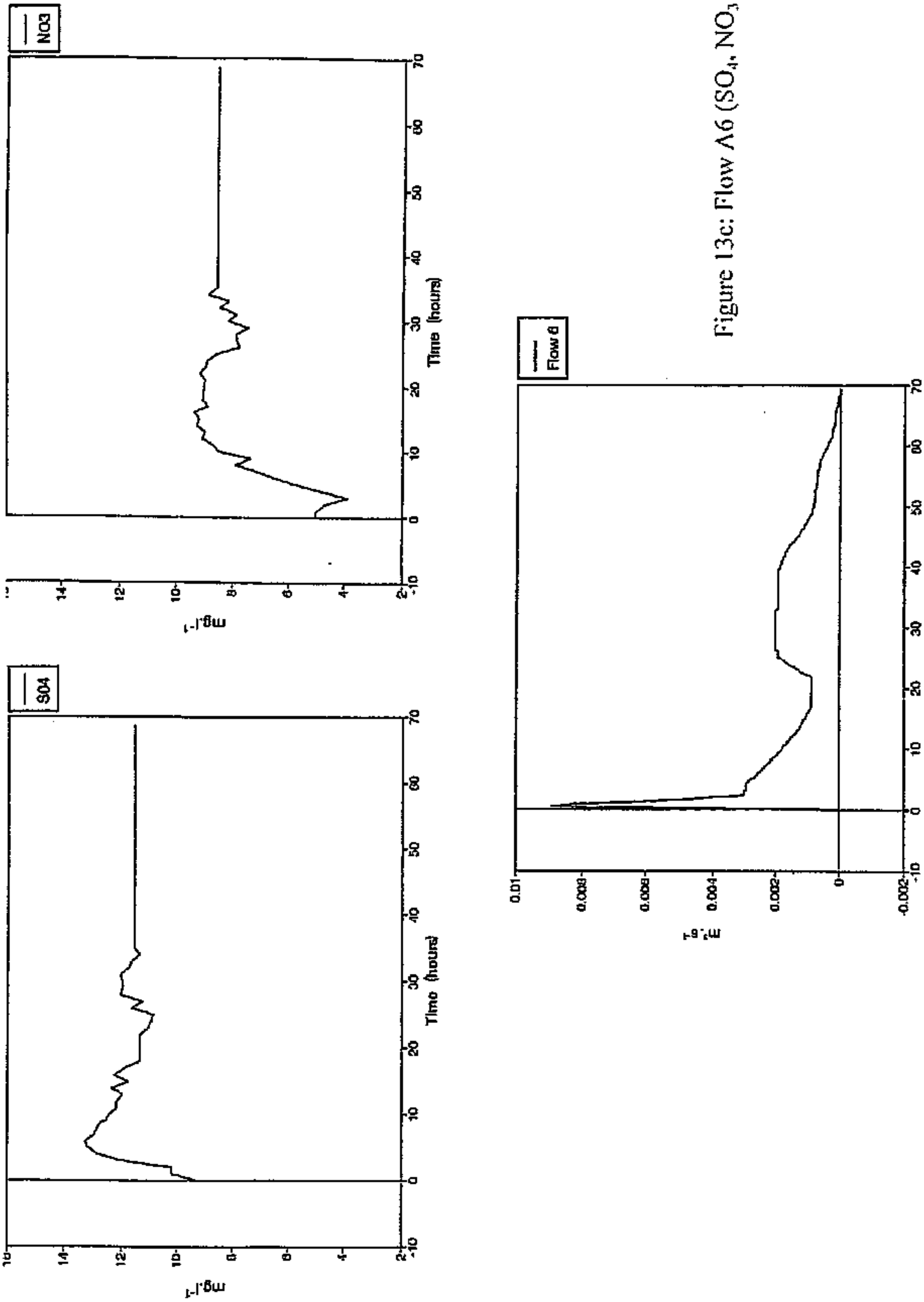
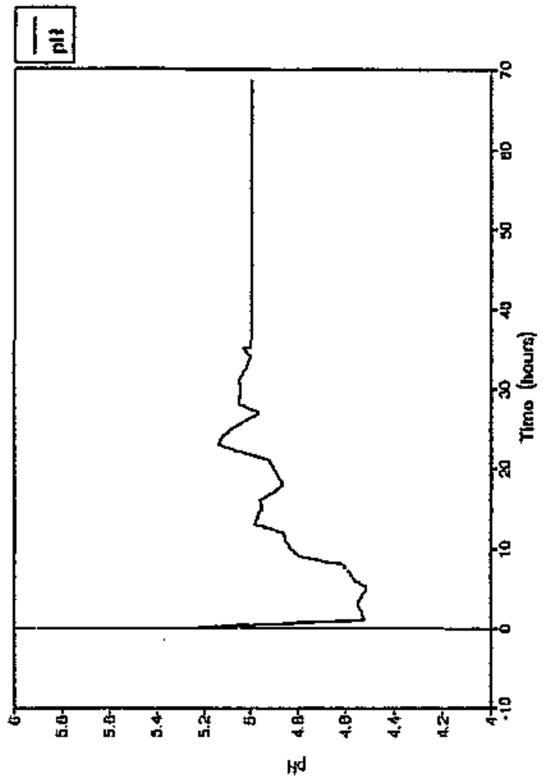
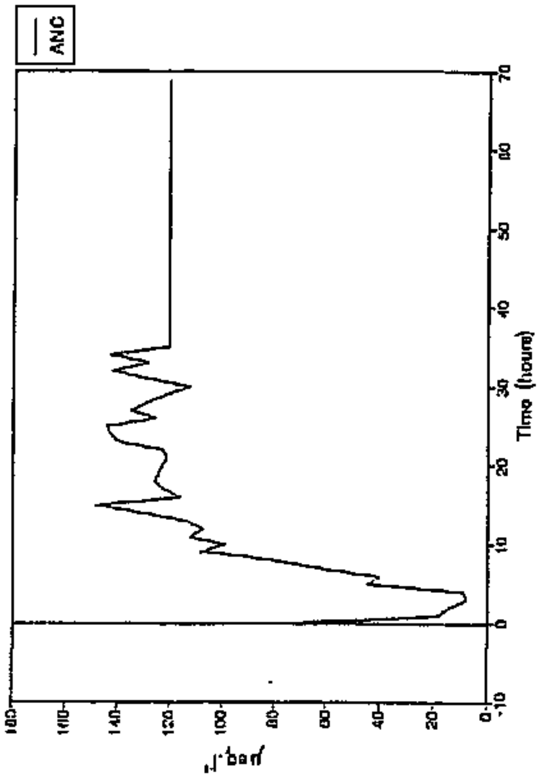


Figure 13c: Flow A6 (SO_4, NO_3 and Flow)





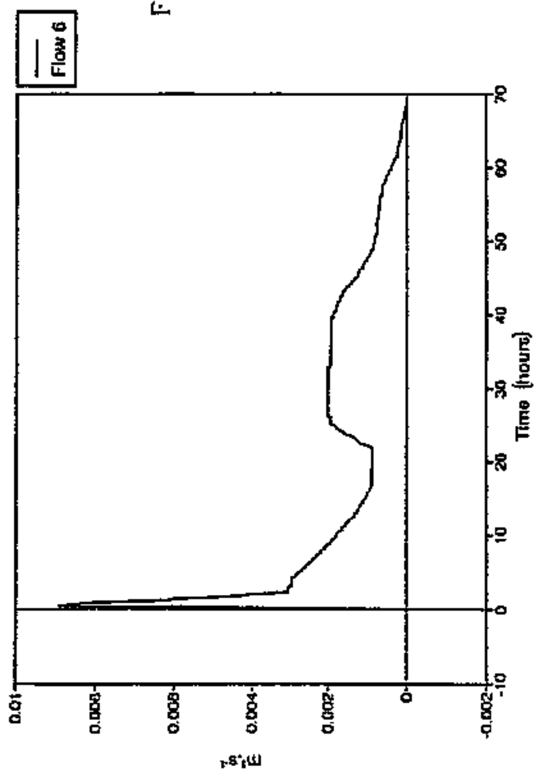


Figure 13d: Flow A6 (ANC, pH and Flow)

The measured variables were seen to vary according to the level of flow. Flow A6 was selected as it had a relatively uncomplicated flow hydrograph with one main peak, corresponding to a single rainfall event and a long tail-off in flow during which no further rainfall events were recorded.

Table 17 : **Mean volume weighted concentrations ($\mu eq.l^{-1}$)**

Flow	Volume (m^3)	Variable								
		Na^+	K^+	Ca^{2+}	Mg^{2+}	SO_4^{2-}	NO_3^-	Cl^-	TAL	ANC
Period A										
A1	2 044.2	-	-	-	-	-	-	-	-	-
A2	226.5	53.8	61.0	200.5	156.3	196.7	273.5	94.7	99.8	1.4
A3	44.2	60.0	39.4	176.1	128.5	289.4	242.0	129.8	94.0	0
A4	107.8	58.9	39.9	138.4	101.5	159.5	124.0	98.6	105.5	55.2
A5	4 720.5	9.4	115.6	70.5	43.9	107.0	40.9	49.2	159.6	91.5
A6	361.9	150.3	22.3	183.4	137.1	242.8	123.0	77.2	139.8	127.0
A7	5 484.5	43.4	23.8	134.9	107.0	227.5	66.8	64.7	112.2	14.8
Period C										
C8	7 159.3	51.7	33.0	151.0	109.5	213.0	92.9	90.9	52.1	39.3
C9	2 168.4	61.6	13.3	123.7	92.1	216.7	24.8	85.9	67.8	0
C10	1 648.1	25.4	30.7	131.3	74.6	239.6	48.2	35.3	59.0	0
C11	384.0	41.9	10.7	116.0	79.3	190.1	17.6	49.9	59.0	41.1
C12	271.2	43.9	20.9	135.4	94.7	244.4	6.1	52.5	80.5	44.6
C13	12 083.2	49.0	10.9	115.6	77.0	207.9	2.4	58.2	59.6	42.2
C14	620.5	14.3	55.7	73.5	40.2	124.0	27.8	28.2	79.6	31.9

Typically, the lowest concentrations were seen at the time of peak flow which was the time of maximum dilution, except for potassium (K) which was at its highest concentration at the start of flow. This could be due to the relatively low pH at the peak of flow. Low pH may enhance K release (Dixon and Weed, 1989), although the transformation is complex.

Comparing sulphate with nitrate, it can be seen that the dilution of nitrate at the time of peak flow was much greater than for sulphate. The levels of sulphate also peaked shortly after the peak in flow whereas the levels of nitrate, as with most other variables increased to their pot-flow concentrations at a slower rate. This could be explained by the fact that the surface runoff had a higher concentration of sulphate than nitrate.

In several flow events the concentration of variables were often higher at the immediate onset of flow. With a temporary stream, accumulated debris is often washed out at the start of flow, resulting in higher concentrations before the effect is negated by dilution when the peak of flow occurs.

The ANC was observed to be at its lowest shortly after the time of peak flow, which was a time when the concentration of the base cations were at or close to their lowest, but the levels of sulphate were already on an ascending trend. Similarly, pH was found to recover after the peak in flow at a slower rate than the other variables. The electrical conductivity (EC), which is a measure of the total dissolved salts, more closely follows the trend of sulphate which is the variable of primary interest.

The levels of sulphate in flows A1 - B14 (excluding Flow A6 which is shown in *Figure 13*) are shown in Figures A14 - A25 of the appendix.

The levels of sulphate in many of the flows were found to be highest at the start of flow - again, this is probably a characteristic of temporary streams as accumulated debris is washed out during the first flush.

Sulphate in many cases was found to be lowest at the time of peaks in flow (particularly when these peaks were in excess of 0.2 $m^3.sec^{-1}$). This can be attributed to the dilution effect of the runoff associated with rainfall.

The levels of sulphate in each flow were often found (as in Flow A7) to be lowest at the time of peak flow (particularly when these flows exceeded 0.02 $m^3.s^{-1}$). This can be attributed to the dilution effect of the runoff associated with rainfall.

Aluminium is another variable showing a response to flow as shown for Flow C11 in *Figures 14* below.

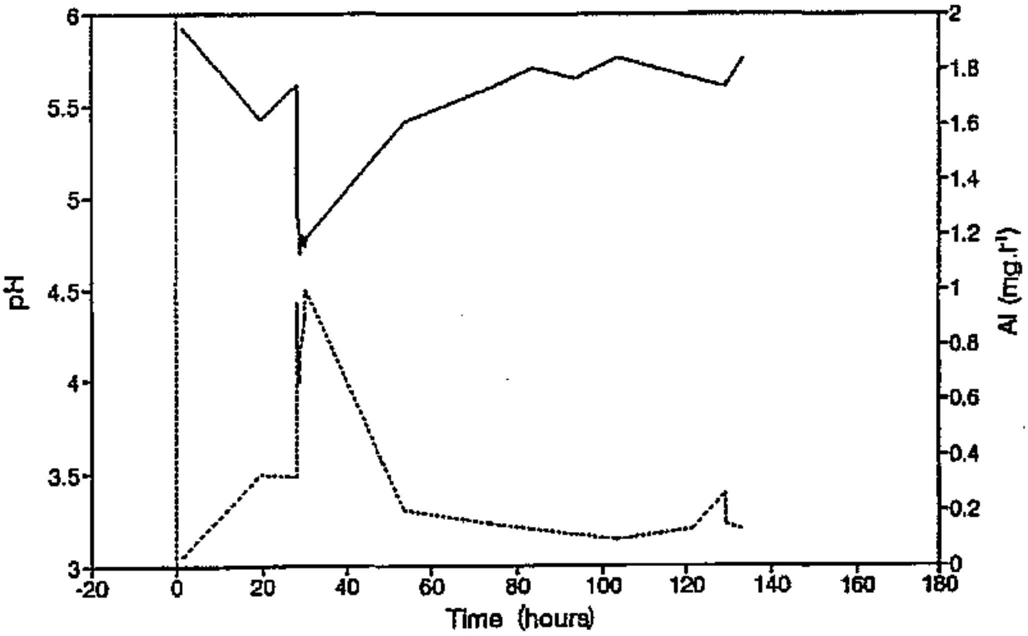


Figure 14(a): Aluminium and pH (Flow C-11)

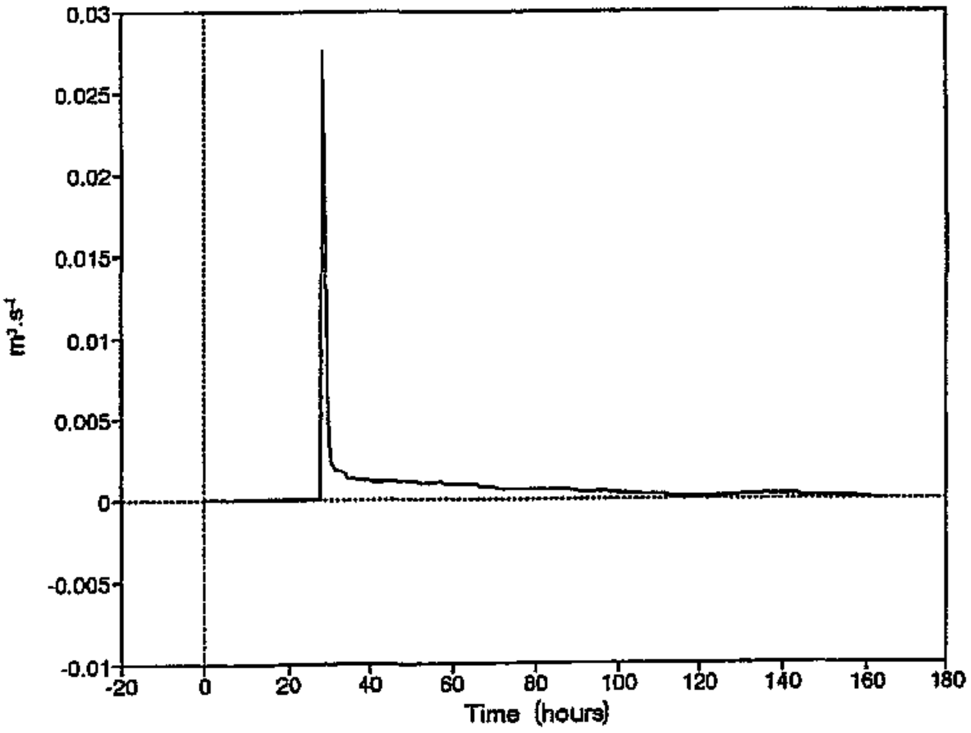


Figure 14(b): Flow C-11 (2 - 9 Dec 93)

The levels of aluminium measured show aluminium to be inversely related to pH (the lower the pH the higher the aluminium concentration). The lowest pH values were often seen at the times of peak flow. A maximum is seen at the time of lowest pH. This is characteristic of acidified waters and is one of the toxic effects of acidification of rivers and streams.

5.5.3 *Salt Load from Suikerbosrand*

The loads of the main salts (Na, K, Ca, Mg, SO_4, NO_3, Cl and TAL) were calculated for Flows A2 - C14 and are shown below in **Table 18**.

Table 18 : Salt load of Suikerbosrand (kg)

Flow	Total Flow (m³)	Total loads of salts (kg)							
		Na	K	Ca	Mg	SO_4	NO_3	Cl	TAL
Period A									
Flow A1	2 044.2								
Flow A2	226.5	0.3	0.5	0.9	0.4	2.1	3.8	0.8	1.1
Flow A3	44.2	0.1	0.1	0.2	0.1	0.6	0.5	0.2	0.2
Flow A4	107.8	0.1	0.2	0.3	0.1	0.83	0.8	0.4	0.6
Flow A5	4 720.5	1.0	21.3	6.7	2.5	24.1	12.0	8.2	37.7
Flow A6	361.9	1.3	0.3	1.3	0.6	4.2	2.8	1.0	2.5
Flow A7	5 484.5	5.5	5.1	14.8	7.1	59.8	22.7	12.6	30.8
Totals	12 989.6	8.3	27.5	24.2	10.8	91.6	42.6	23.2	72.9
Period C									
Flow C8	7 159.3	8.5	9.2	21.7	9.5	73.2	41.2	23.1	18.7
Flow C9	2 168.4	3.1	1.1	5.4	2.4	22.6	3.4	6.6	7.4
Flow C10	1 648.1	1.0	2.0	4.3	1.5	19.0	4.9	2.1	4.9
Flow C11	384.0	0.4	0.2	0.9	0.4	3.5	0.4	0.7	1.1
Flow C12	271.2	0.3	0.2	0.7	0.3	3.2	0.1	0.5	1.1
Flow C13	12 083.2	13.6	5.2	28.0	11.3	120.7	1.8	24.9	36.0
Flow C14	620.5	0.2	1.4	0.9	0.3	3.7	1.1	0.6	2.5
Totals	24 334.7	27.1	19.3	61.9	25.7	245.9	52.9	58.5	71.7

The total export of salts from the catchment in 347.5 kg (adjusted to include Flow A1) or 10.7 kg.ha^{-1} in Period A and 56.0 kg or 17.3 kg.ha^{-1} in Period C.

The difference between the two periods was smaller when compared to the large difference in total flow (12 990 m^3 in Period A and 24 335 m^3 in Period C).

The largest contributors in terms of kg salt load are sulphate and nitrate at contributes approximately 26% and 12% in Period A and 44% and 9% in Period C.

5.6 Meteorology

The wind speed and direction data collected for the period October to March 1994 are shown in the appendix (A43 - A48) and summarised in **Table 19**.

The wind directions were categorised as follows:

Sector 1 : WNW - NNE (including NW, NNW and N) - Johannesburg / Vosloorus
Sector 2 : NE - ESE (including, E and ESE) - Witbank / Main Power Stations in the Eastern Transvaal
Sector 3 : SE - W (including SSW, SSE, S, SSW, SW, WSW and W) - Orange Free State.

Table 19 : Predominant wind directions measured at Heidelberg Microwave Tower

Year/Month	Predominant Wind Direction
1992	
October	
November	Sector 1
December	Sectors 1 and 2
1993	
January	Sectors 2 and 3
February	Sectors 1 and 2
March	Sectors 2 and 3
April	Sectors 1 and 3
May	Sectors 1 and 3
June	
July	Sectors 1 and 3
August	Sector 1
September	Sectors 1 and 3
October	Sector 1
November	
December	Sector 1
1994	
January	Sectors 1, 2 and 3
February	
March	

The predominant wind direction is from Sector 1 (WNW - NNE).

5.6.1 *Comparison of SO_2 levels and associated wind direction*

The periods when the measured SO_2 concentrations were in excess of 50 µg.m^{-3}, and the associated wind direction sectors are shown below in Table 20.

Table 20 : Prevailing wind sector when SO_2 concentrations exceeded 50 µg.m^{-3}

Sector	No. Periods [SO_2] exceeds 50 µg.m^{-3}
1	8
2	6
3	6

There were 18 periods when the SO_2 concentrations exceeded 50 µg.m^{-3}. The predominant wind direction was either Sectors 1 or Sector 2. The predominant wind sectors were found to be 1 and 2 (i.e. from nearby source areas).

This analysis only took into account mean SO_2 concentrations over two and three day periods. No account was taken of wind speed. The general findings should thus be considered to be preliminary.

5.7 Soils

The soils analysis was undertaken by the University of Natal. A copy of the report is included in the appendix.

The soils were analyzed for total sulphur and the data are shown below in **Table 21.**

Table 21 : Total sulphur and organic carbon analysis for Suikerbosrand soils

Soil Sample No.	Total S (%)	Organic C (%)
1	0.042	3.13
2	0.036	1.17
3	0.029	2.56
4	0.010	2.66
5	0.029	5.80
6	0.027	1.11
7	0.026	2.74
8	0.026	1.27
9	0.044	4.67
10	0.038	3.36
11	0.016	2.46
13	0.032	1.88
12	0.044	4.06
14	0.042	4.44
15	0.055	3.92
16	0.034	4.02
17	0.052	1.86
Mean	**0.034**	**3.01**

The relative sulphate retention capacities were estimated. The soils showed an average breakthrough of five pore volumes indicating the soils to have a relatively low sulphate retention capacity when compared to soils of the Vaal Dam catchment.

Most of the catchment consists of a soil covering which has a relatively low sulphate retention capacity when compared to the soils of the Vaal Dam catchment (Fey and Guy, 1993) - this corresponds to those areas with the thinnest soils. The thickest soils which also have the highest sulphate retention capacities were found in pockets in the drainage channels of the catchment.

If one assumes that the soil has a bulk density of 1.5 kg.ha^{-1} and a depth of 150 mm, the average total S concentration translates into an amount of 24 862.5 kg. Most of this sulphur will be associated with soil organic matter.

This overall average texture of the soils is a loamy sand, which is indicative of rapid infiltration and low water retention.

6. CATCHMENT BUDGET

The wet deposition as well as the dry deposition from the rock plots (54% of catchment) have been measured. The dry deposition for the grassland sections of the catchment (46%) are calculated as follows : -

6.1 Estimation of Dry Deposition for Grassland Part of Catchment

Using the measured SO_2 concentration and a deposition velocity of 0.3 $cm.sec^{-1}$ (Period B) and 1.3 $mm.sec^{-1}$ (Shepherd, 1974), which is the estimated rate for grasslands, the deposition due to gaseous absorption would be 32.2, 8.1, 21.7 and 75.0 $kg.ha^{-1}$ for periods A, B and C respectively.

This estimate, however, does not take into account the dry deposition due to particulates. The bulk sampler, being an inert collector gives primarily an estimate of particulate deposition. These have been estimated to be 3.03, 2.39 and 3.13 $kg.ha^{-1}$ for periods A, B and C respectively.

6.2 Mass Sulphate Balance for Catchment

Table 22 : Summary of sulphate inputs and outputs ($kg.ha^{-1}$)

Period	Inputs of Sulphate ($kg.ha^{-1}$)				Total	Output of Sulphate ($kg.ha^{-1}$)
	Wet Deposition	Dry Deposition				
		Rock Runoff (54%)	Grassland (46%)			
			SO_2	Particulate		
A (Oct 92 - Mar 93)	11.8	3.2	14.8	1.4	31.2	2.83
B (Apr 93 - Sep 93)	0.8	3.1	3.7	1.0	8.6	0.0
C (Oct 93 - Mar 94)	27.5	9.2	6.9	1.4	45.0	6.59
Totals	40.1	15.5	25.4	3.8	84.8	10.42

The total sulphate inputs for Periods A and B, which make up one annual cycle, was 39.8 $kg.ha^{-1}$ (27.2 $kg.ha^{-1}$ dry deposition and 12.6 $kg.ha^{-1}$ wet deposition). The proportion of dry and wet deposition to the total sulphate inputs was therefore 68% dry deposition and 32% wet deposition indicating the variability between years with a lower than average rainfall and those with an above average rainfall (the average annual rainfall at Suikerbosrand was approximately 700 mm).

The total sulphate deposition into the catchment for periods B and C which again comprises a complete annual cycle, was 53.6 $kg.ha^{-1}$ (25.3 $kg.ha^{-1}$ dry deposition and 28.3 $kg.ha^{-1}$ wet deposition). Thus, over Periods B and C, approximately 47% of the inputs were dry deposition and 53% wet deposition.

Approximately 7% of the total inputs of sulphate were exported from the catchment in Periods A and B. In Periods B and C, approximately 14% of the total sulphate inputs were exported. Thus, during periods A and B, approximately 93% of the deposited sulphate was retained in the catchment and in periods B and C, approximately 86% of the sulphate was retained.

7. DISCUSSION AND CONCLUSIONS

In terms of the original objectives, that the catchment should be a small undisturbed catchment, the Suikerbosrand was in many ways ideal. It was located in a remote part of the Suikerbosrand Nature Reserve and was almost completely undisturbed. In this way it was one of only a few suitable catchments in the region, as most upland catchments are disturbed to a certain degree, particularly if located in unprotected areas. The project almost floundered at an early stage due to the lack of available sites. We also were looking for a catchment with a sensitive geology and soils (low sulphate retention capacity) where the effects of atmospheric deposition could be more clearly seen and the processes simpler to understand than a catchment with a relatively high sulphate retention capacity. The original intention was to use the selected catchment as a large deposition sampler.

The catchment did, however, not have soils typical of the Vaal Dam catchment, the soils being thin and of a loamy sand type. A characteristic of small upland catchments in the headwaters of streams is, however, the relatively shallow soils and higher sensitivity to atmospheric deposition than larger, lowland catchments. It is therefore an anachronism to expect a small upland catchment to be representative of the whole of the Vaal Dam catchment. The catchment is probably one of the most, if not the most sensitive to atmospheric deposition in the region.

The geology of the catchment was quartz / sandstone which is a relatively inert geology with little or no sulphur (<0.5%). Approximately 54% of the catchment was exposed rock with grassland and exposed soil comprising 36% and 10% respectively.

The stream at the catchment was seasonal in nature, only flowing on 14 occasions after significant rainfall events of at least 20 mm. Over the two-year study period 14 flow events were recorded. The average runoff rate over the two-year study period was approximately 8.7%.

The catchment soils were found to be very thin (average depth 15 cm), and of a loamy sand type which had a relatively low sulphate retention capacity compared to other soil types of the Vaal Dam catchment.

The methods employed on this project varied between well-established technologies (wet and bulk deposition sampling) to techniques developed specifically to meet the objectives of this project (rock runoff sampling). Various techniques to estimate dry deposition were used with varying degrees of success and included ambient sulphur dioxide measurements, surface runoff plots, mist sampling and grass stem collars. Wind speed and direction was also recorded close to the catchment (on top of Heidelberg microwave tower) using an anemometer.

It was felt that wherever possible, natural surfaces should be used, as the study was catchment-based needing 'real' estimates of dry deposition.

The wet deposition samplers proved to be the most reliable pieces of equipment in that they operated over the whole two-year period without any breakdown with most rainfall events being sampled. The only occasions when samples were not collected were due to operator error.

The bulk samplers used were reliable within their design constraints. As bulk samples had to be collected, the collecting bottles were exposed to the atmosphere at all times leading to losses due to evaporation and possible contamination (birds etc.). They are, however, one of the few inexpensive readily available methods to measure particulate dry deposition.

The sulphur dioxide measurements were made close to the catchment using a simple apparatus whereby air was bubbled through a dilute solution of hydrogen peroxide solution. This method gave a reliable estimation of ambient SO_2 over two and three day periods. This sampling period was sufficient for the purposes of this study.

The technique of estimating the sulphate in solution by titration, however, proved to be the weakness of this method, as contamination by ammonia resulted in negative concentrations being extrapolated. The technique was therefore changed to allow for the direct determination of sulphate in the solutions which proved to be much more reliable than titration. The original purpose of using the sulphur dioxide samplers was to provide an inexpensive method of measuring the ambient SO_2 levels within the financial constraints of the project. In hindsight, it would have been more cost-effective to use an automatic SO_2 sampler in terms of man-hours, analyses and servicing. The data would also have been more amenable to comparison with wind speed and direction data.

The dew sampling exercise, which was primarily focused on determining the occurrence of dew formation, revealed the incidences of dew formation to be low, and not warranting detailed investigations.

The surface runoff plots were originally installed to test the reliability of the weir. The design and location was, however, inadequate for this task as the capacity of the collecting drums was often exceeded. At the time of installation it was not known what the runoff of rainfall patterns would be.

The plots were later modified during Period B to increase their capacity, but this was insufficient to measure all runoff as the rainfall was substantially higher in period C than Period A. The quality of the surface runoff was, however, analyzed and the ratio of the sulphate concentration in the runoff to sulphate concentration in the rainfall estimated.

The stem collar experiments which were designed to measure the throughfall of rainwater on clumps of grass gave consistent results when not destroyed by the wildlife of the reserve (baboons developed an attraction for the resin used).

Earlier in the project, plastic guttering was used to measure the throughfall of rainwater through bushes in the catchment. This was, however, not successful and was abandoned at an early stage.

The V-notch weir constructed in the catchment proved to be adequately designed and overflowed on only one occasion during Period A (October 1992 - March 1993). There was concern at one stage as to the rate of leakage from the weir which was estimated and found to be less than three per cent. All weirs do in fact leak. The weir was reinforced during the Period B (May - September 1993) to ensure no significant leaks occurred. As the flows were often of short duration, with large proportions of the flow passing the weir within a few hours, any losses were minimal.

The flows tended to be intense and of short duration (average duration of approximately 130 hours). This itself created many difficulties in the sampling programme. The original proposal envisaged sampling a perennial stream over the whole study period with an intensive sampling of 20 flood events.

This study was in many ways unique, both nationally and internationally, in that it is the first of its kind to be made in southern Africa, it is the first that has been undertaken in an area of high evaporation (and hence low runoff), and is the only study of its kind to be undertaken on a seasonal stream.

The rainfall patterns at the catchment were typical of the highveld region of South Africa, being highly variable and unpredictable (almost twice as much rainfall was recorded in Period C (843.5 mm) as compared to Period A (491.5 mm). The only predictability of the rainfall was that little or no rainfall was likely to fall during the dry winter months.

Even though the rainwater samples were collected at the nearby Ranger's house, this made little or no difference to the calculated wet deposition values for the main catchment as the quality of the rainfall was not significantly different between the two sites. The volume of rainfall collected was also very similar at the two sites (568 mm at the Ranger's house in Periods A and B, and 916 mm in Periods B and C), being less than 10% higher at the Ranger's house over the study period.

The wet deposition of sulphate in the catchment amounted to an annual deposition rate of 12.7 kg.ha^{-1} (Periods A and B) and 28.4 kg.ha^{-1} (Periods B and C). This is comparable to other sites in the Eastern Transvaal Highveld of between 15 and 24 kg.ha^{-1} (Tyson *et al.* 1988).

The mean ambient sulphur dioxide concentrations were 10.9 and 7.3 μg.m^{-3} for Periods A and B, and B and C respectively. These were within the ranges reported for the Eastern Transvaal Highveld of between 8.8 and 41.3 μg.m^{-3} (Turner, 1988). The relatively low concentrations recorded during Periods B and C (one annual cycle) could be explained by the higher than average rainfall experienced during that time, as the rainfall scours SO_2 from the atmosphere. It is not known whether the maximum daily SO_2 levels were exceeded as samples were collected over two or three day periods. At no time during the study did the SO_2 levels exceed the Department of National Health and Population Development's maximum limit of 130 μg.m^{-3}.

If the measured concentrations of ambient SO_2 were either an over- or under-estimate by as much as 20%, this would only have an effective 10% variation on the total estimated dry deposition load, as the SO_2 calculations were only used in the estimation of dry deposition to the 46% of the catchment covered with grassland and exposed soil.

The rock runoff plots were a particularly successful method of estimating total deposition and by subtraction of the wet deposition, the net amount of dry deposition. At least 94% of the total runoff was collected which did not take into account any evaporation that may have occurred before sample collection.

The total sulphate runoff of the rock plots was 23.3 kg.ha^{-1} (Periods A and B) and 49.5

kg.ha^{-1} (Periods B and C). The corresponding net dry deposition rates, with the proportions of the totals in brackets, were 11.8 kg.ha^{-1} (51%) and 22.8 kg.ha^{-1} (46%). The net dry deposition rate increased proportionally to the amount of wet deposition (no rainfall would result in no runoff collected).

The surface plots gave an estimate of total deposition to be approximately 4 times the amount of wet deposition in Period B and 1.5 times the wet deposition in Period C (annual average of 2.8). This estimate assumes that the sulphate concentration of the surface runoff is the same as that of the rainwater entering the soil and consequently that there is little or no sulphate retention in the top layer of the soil. This is unlikely to be the case and the estimate given is likely to be an underestimate.

The bulk sampler gave estimates of the total deposition of 19.4 kg.ha^{-1} and 28.5 kg.ha^{-1} for periods A and B, and B and C respectively. The estimate of dry deposition for these two annual cycles was approximately 38% and 20% of the wet deposition measured at the same site. The bulk sampler gave primarily an estimate of particulate deposition which is only a portion of the total dry deposition. The comparison between this method and other methods of estimating dry deposition will be discussed later.

The stem collars gave estimates of dry deposition of 7.0 and 15.5 kg.ha^{-1} for periods B and C respectively. It is, however, difficult to extrapolate these figures to the whole catchment on the basis of the individual clumps of grass which were selected. Attempts to estimate the sulphate deposition on open ground between the clumps of grass were not successful because baboons in the Reserve sought out and ate the sulphate absorbing resin thereby destroying many of the stem collars in the process. Nevertheless, this method holds promise for estimating the dry deposition on vegetation. If the method could be modified to take into account the spaces between clumps of grass, using a substrate that had the same physical surface characteristics as the catchment soil, then a complete estimate of the dry deposition to 45% of the catchment could be made.

The incidences of dew formation at Suikerbosrand were very infrequent with only six occurrences over a three month period, when dew formation was most likely. The sulphate concentrations of the dew, however, indicate a high degree of absorption of SO_2 gas.

The total inputs of sulphate over the study periods were 31.2 kg.ha^{-1} in Period A, 8.6 kg.ha^{-1} in Period B and 45.0 kg.ha^{-1} in Period C.

Comparing the five methods of estimating dry deposition, the bulk sampler gave the lowest estimation of total deposition, as it only measures the rate of particulate deposition. The other methods or combinations of methods gave estimates of 27.53 (SO_2 + 'Bulk'), and 16.4 $kg.ha^{-1}$ (Surface Runoff) for the 46% of the catchment that was covered by grasses and bare soil in Period B and C, and 22.82 $kg.ha^{-1}$ for the rock surface area of the catchment (54%). The combination of the SO_2 deposition rates and the bulk sampling was considered to be the best estimate of dry deposition for the 46% of the catchment covered by grasses and bare soil. As already stated, it is felt that the surface runoff estimates were underestimates and the leaf stem collar estimates were incomplete in that only grass clumps were measured and no estimate of the deposition between clumps of grass was made.

The two annual period (Periods A and B, and Periods B and C) gave different proportions of dry deposition to total deposition. These varied between 68% of total sulphate deposition as dry (32% wet) in Periods A and B, and 48% of the total as dry (52% wet) in Periods B and C. The relative proportions of dry deposition in the two wet periods (A and C) are dependent on the amount of rainfall which was considerably higher in Period C (843.5 mm) than in Period A (491.5 mm).

The water chemistry revealed the stream to be poorly buffered, with a pH of between 4.2 and 6.4. The Ca : Mg ratio was 2.3 : 1, which is itself an indication of an acid system. The low pH and ANC values of less than 180 $\mu eq.l^{-1}$ indicate the stream to have a high sensitivity to acidic inputs.

The episodic flow events which occurred at Suikerbosrand, should be described as form flow. The peaks in flow when the flow rate exceeded 0.02 $m^3.sec^{-1}$ caused a dilution effect on most of the chemical variables. Acidity (as measured by pH) was seen to be lowest at the time of peak in flow and aluminium at its highest (the solubility of aluminium increases with increasing acidity (as pH drops below 7.0)).

Potassium was unlike the other base cations as the highest concentrations were found at the onset of flow with no apparent dilution effect. This could be due to acidity causing increased mobilisation, although the transformation of the potassium ion in the soil is a complex process (Dixon and Weed, 1989).

It is assumed that most of the sulphate in the catchment has been deposited from the atmosphere as there are few 'natural' sources of sulphate in the catchment. There is evidence of sulphate in the rock, although this was estimated to be less than 0.5% of the total rock volume. It was beyond the financial resources of the project to precisely determine the sulphate content of the catchment rock. This, however, should be done as the assessment of sulphate content was based on visual inspection.

Table 23 : Comparison of Suikerbosrand with other poorly buffered catchments in the Region

Variable	Catchment					
	Suikerbosrand	Verlorenvallei	Sterkspruit	Sibabe	Ngogu	Mahai
pH	4.2 - 6.4	6.9	6.5	6.5	6.6	6.5
Na $mg.l^{-1}$	0.6	3	3	3	3	3
K $mg.l^{-1}$	1.1	3	2	1	1	1
Ca $mg.l^{-1}$	1.6	1	2	3	2	2
Mg $mg.l^{-1}$	0.7	1	2	2	1	2
Cl mg.l-1	1.6	9	11	5	5	5
SO_4 $mg.l^{-1}$	9.1	<2	<2	9	4	<2
NO_3 $mg.l^{-1}$	2.5	<0.2	<0.2	<0.2	<0.2	<0.2

A comparison of the average pH and stream concentrations of the Suikerbosrand catchment with other calibrated catchments in the northern hemisphere is shown below in **Table 24**.

The Suikerbosrand catchment had a similar pH to the other catchments. Even though range of pH was given for Suikerbosrand, the pH on a volume-weighted basis was in the 4 - 5 range. The levels of sodium were lower at Suikerbosrand than the other catchments and the levels of potassium higher. The levels of sulphate and nitrate were higher in comparison to the average values for the four other catchments.

An important consideration in the comparison between these catchments is that the Suikerbosrand catchment has only a temporary stream which flows in response to storm events. The effective runoff is 8.7% as compared to 55% in the Lake Gardsjon sub-catchments (Anderson and Olsson, 1985).

Table 24 : Comparison of Suikerbosrand with calibrated catchments in the northern hemisphere

Variable	Catchment				
	Suikerbosrand (South Africa)	Birkeness (Norway)	L Gardsjon (Sweden)	Hubbards Brook (USA)	Sudbury (Canada)
pH	4.2 - 6.3*	4.5	4.2	4.9	4.7
Na $mg.l^{-1}$	0.6	2.8	6.5	0.9	2.1
K $mg.l^{-1}$	1.1	0.3	0.6	0.2	0.5
Ca $mg.l^{-1}$	1.6	1.3	1.5	1.7	5.7
Mg $mg.l^{-1}$	0.7	0.5	1.4	0.4	1.3
Cl mg.l-1	1.6	4.4	11.0	0.5	5.7
SO_4 $mg.l^{-1}$	3.0	2.4	1.5	2.1	5.7
NO_3 $mg.l^{-1}$	0.6	0.1	0.1	0.4	-

This has the effect of a relative concentration of chemical variables, which may explain the higher levels of sulphate in particular.

Over the two annual cycles (Periods A and B, and Period B and C) approximately 93% and 86% of the estimated sulphate inputs into the catchment were retained in the catchment storage, or more correctly, not exported. The question is then whether this sulphate is retained in the catchment or recirculated into the atmosphere as dust, particulate aerosols?

The retention of sulphate in the catchment is both physical and chemical in nature. The periodic drying out of the catchment during the dry winter months and in between rainstorm events did not allow the catchment to be flushed out during the study periods.

The sulphate concentrations observed during the fourteen flow events were seen to be relatively constant when compared to the other water quality variables (**Tables 16** and **17**). The load of sulphate leaving the catchment appears to be more dependent on the actual volume of water leaving the catchment than the load of other variables. This relatively constant concentration suggests that the catchment is in fact saturated with sulphate.

Herold and Gorgens (1991) observed that at least 70% of the sulphate deposited in the Vaal Dam catchment was not exported.

To fully understand the accumulation processes involved, historic rainfall records should be examined, the runoff percentages calculated and the precise relationship between the levels of sulphate and runoff determined. This could not be addressed during this study due to time and financial constraints. There are a number of hydrogeochemical models that could be applied or modified for use on the Suikerbosrand catchment. These include the Birkeness and MAGIC models.

The retention time of water in the soils was not addressed. This should be examined if meaningful calculations of the water budget for the catchment over time are to be made.

The calculated amount of sulphate in the soils of the catchment is 24 862.5 kg. The inputs of sulphate on an annualized basis were 1 294.5 kg in Periods A and B, and 1 746.6 kg for Periods B and C. The nett inputs of sulphate that were retained in the soils were 1202.5 kg and 1499.9 kg respectively. The sulphate in the soils of the catchment therefore represents between 17 and 21 years accumulation. Current levels of atmospheric deposition have been steady since the mid 80's thus the sulphate in the catchment probably represents the net accumulation over at least the last 30 years. The Suikerbosrand catchment has been exposed to atmospheric deposition of sulphur compounds for many years due to its close proximity to major centers such as Johannesburg. Suikerbosrand is thus likely to be closer to a steady state with atmospheric deposition than any other small catchment in the region.

The load of salts leaving the catchment showed sulphate and nitrate to be the two most important variables of atmospheric origin. In Periods A and C the relative proportions of sulphate were 30% and 44% respectively. This was higher than observed in the Vaal Dam (Herold and Gorgens, 1991) where sulphate made up 10% of the anionic composition.

The relative proportions of nitrate were 14% and 9% for Periods A and C.

The proportion of base cations that have been leached from the catchment due to acidification has not been estimated, primarily because no historic records were available.

The contribution of the Suikerbosrand catchment to the runoff of the Vaal Dam catchment was, however, less than 0.002% based on a Mean Annual Runoff for the Vaal Dam catchment of 2 099 x10^6 m^3. It is considered unlikely that there are many similar catchments to Suikerbosrand in the catchment of the Vaal Dam and so the Suikerbosrand catchment should be considered an extreme case. The proportions of sulphate and nitrate in the runoff of upland catchments in the region would be between the levels found at Suikerbosrand and the levels found in the Vaal Dam itself.

This study has revealed many interesting aspects of the fate of atmospheric deposition in a small upland catchment. Many of the issues raised could not be dealt with in great detail due to time and financial considerations. However, it is envisaged that considerable development of the information gained in this study will take place. International review of the findings will be useful in many aspects. However, the study is unique in many ways and the specific expertise needed may not be available.

7.1 Conclusions

The main conclusions of the study are as follows : -

1. The Suikerbosrand catchment is a highly sensitive catchment to the effect of atmospheric deposition - it is probably one of the most sensitive catchments in the region.

2. The deposition rates of sulphate at the catchment are within the reported ranges for the region.

3. The calculated proportion of dry deposition as a percentage of total deposition varied between 68% and 48% on an annualized basis (1992 - 1993 and 1993 - 1994).

4. The catchment appears to be nitrogen saturated and excess nitrate is a significant load.

5. Large proportions of deposited sulphate were retained in the catchment during the study period (93% - Periods A and B, and 86% - Period B and C).

6. Sulphate was the most common chemical variable in terms of the Total Dissolved Solids load of the catchment. Sulphate contributed between 30% and 44% of the total salt load.

7. Nitrate contributed between 5% and 14% of the total salt load.

8. RECOMMENDATIONS

1. The influence of the catchment soils should be examined in more detail.

2. The nitrogen balance of the catchment and the process involved should be investigated.

3. Other upland catchments along a pollution gradient should be compared to the Suikerbosrand catchment to be able to assess the potential impacts of atmospheric deposition in the region.

4. The feasibility of using or modifying existing hydro-geochemistry models, such as the Birkeness or MAGIC models, which have been developed in Europe, should be investigated.

5. The hydrology of the catchment should be examined in detail using an appropriate small catchment model, to determine the retention time of water in the catchment.

6. A dry deposition model should be calibrated using the Suikerbosrand data and compared with recent estimates of dry deposition on the highveld which were calculated using an inferential model.

7. The sulphate content of the rock in the catchment as well as the weathering rate should be examined.

8. The potential for re-circulation of sulphate into the atmosphere should be investigated.

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APPENDIX

Raw Data Tables

Table A1: Daily Rainfall at Suikerbosrand 1992/94

Oct. 1992	mm	Nov. 1992	mm	Dec. 1992	mm	Jan. 1993	mm	Feb. 1993	mm	March 1993	mm	April 1993	mm	May 1993	mm	June 1993	mm
1	5.5	1		1		1		1		1	42.5	1		1		1	
2		2	10.0	2		2		2		2	9.0	2		2		2	
3		3	7.0	3		3		3		3	1.0	3		3		3	
4		4	2.0	4		4	2.5	4	14.5	4	34.5	4		4		4	
5		5	4.5	5		5		5	0.5	5		5		5		5	
6		6		6		6		6		6		6		6	3.5	6	
7		7		7		7		7		7		7		7		7	
8		8	54.5	8	17.0	8		8	29.5	8		8		8		8	
9		9	3.5	9	5.5	9	14.5	9	3.5	9		9		9		9	
10		10	4.0	10	1.5	10		10		10		10		10		10	
11	2.0	11		11		11		11		11		11	26.5	11		11	
12		12	7.5	12		12		12	8.5	12		12	12.0	12		12	
13		13	23.5	13		13		13	1.0	13		13		13		13	
14		14	1.0	14		14		14	2.5	14	1.5	14		14		14	
15		15	0.5	15		15		15	0.5	15	2.5	15		15		15	
16		16		16		16		16		16		16		16		16	
17		17		17	7.0	17		17	0.5	17		17		17		17	
18		18		18	2.0	18		18	2.0	18		18		18	1.5	18	
19		19	11.0	19		19		19		19	4.5	19		19		19	
20		20		20		20		20		20		20		20		20	
21		21		21	23.0	21		21		21		21		21		21	
22		22		22	3.0	22		22	3.5	22	4.5	22		22		22	
23		23	6.0	23	3.5	23	12.5	23	23.5	23		23		23		23	
24		24	3.0	24		24		24	1.0	24		24		24		24	
25		25		25		25		25		25		25		25		25	
26		26		26		26	1.0	26		26		26	0.5	26		26	
27		27		27		27		27		27		27		27		27	
28	8.5	28		28		28	0.5	28		28	3.5	28		28		28	
29		29		29		29	8.0			29	4.0	29		29		29	
30		30	2.5	30	4.0	30	30.0			30		30		30		30	
31	1.0			31		31				31				31			
Total Rainfall	17.0		140.5		66.5		69.0		91.0		107.5		39.0		5.0		0.0

Table A1 Continued

July 1993	mm	August 1993	mm	Sept. 1993	mm	Oct. 1993	mm	Nov. 1993	mm	Dec. 1993	mm	Jan. 1994	mm	Feb. 1994	mm	March 1994	mm
1		1		1		1	21.0	1		1		1	0.5	1	1.5	1	
2		2		2		2	7.5	2	8.5	2		2		2	30.0	2	2
3		3		3		3	0.5	3		3	14.0	3		3	1.0	3	
4		4		4		4		4		4	13.0	4		4		4	
5		5		5		5	15.5	5	12.0	5		5		5	26.0	5	
6		6		6		6	61.5	6		6		6		6	17.0	6	
7		7		7		7	23.5	7		7	7.0	7		7	10.0	7	
8		8		8		8	33.0	8		8	4.0	8		8	12.0	8	14
9		9		9		9		9		9	1.0	9		9	1.5	9	4.0
10		10	0.5	10		10		10		10		10	25.0	10	0.5	10	0.5
11		11		11		11	20.0	11	11.0	11		11	6.0	11		11	
12		12	0.5	12		12	22.5	12	13.5	12	7.5	12	1.0	12	8.0	12	2
13		13		13		13		13		13		13	2.0	13	0.5	13	
14		14		14		14	22.0	14		14		14		14		14	3.5
15		15		15		15	4.0	15		15	6.5	15		15		15	2
16		16		16		16	0.5	16		16	15.5	16		16	0.5	16	
17		17		17		17	4.5	17	0.5	17		17	25.0	17	1.0	17	
18		18		18		18		18		18		18	0.5	18		18	
19		19		19		19	0.5	19		19		19		19		19	
20		20		20		20		20	3.0	20	18.5	20	3.0	20		20	
21		21		21		21	0.5	21		21		21	10.0	21		21	
22		22		22		22		22	17	22	2.5	22	8.5	22	6.0	22	2
23		23		23		23		23	3	23		23	11.0	23		23	
24		24		24	3.5	24	3.5	24		24		24	12.5	24	10.0	24	
25		25		25	0.5	25	31.0	25	0.5	25		25	8.0	25		25	
26		26		26		26	4.5	26	2.5	26	2.5	26		26		26	3
27		27		27		27	7.5	27		27		27		27		27	3.5
28		28		28		28		28	38.5	28	4.0	28		28		28	46.5
29		29		29		29		29	0.5	29	22.5	29				29	
30		30		30	12.0	30		30		30	1.0	30				30	0.5
31		31				31				31		31	0.5			31	11.0
Total Rainfall	0.0		1.0		16.0		280.5		110.5		119.5		113.0		125.5		94.5

Table A2: Wet Deposition Analysis at Ranger's house (1992-1994)

Date	Rainfall (mm)	Variable (ppm)								
		pH	NO_3^-	Cl^-	SO_4^{2-}	Na^+	K^+	Ca^{2+}	Mg^{2+}	NH_4^+
1.10.92	5.5	4.2	6.8	0.8	6.9		0.5	1.8	0.4	2.5
11.10.92	2.0	5.4	6.9	1.1	8.8	0.8	0.5	3.7	0.7	
28.10.92	8.5	5.7	3.2	0.5	2.8	2.1	0.3	1.8	0.4	
1.11.92	1.0	4.3	1.9	0.8	1.6	0.2	0.4	1.4	0.2	0.1
2.11.92	11.0	4.4	1.4	0.2	1.9	1.8	0.1	1.2	0.1	
4.11.92	5.5	4.9	3.0	0.3	2.7		0.1	1.3	0.2	0.1
9.11.92	56.0	4.7	1.1	0.2	2.6		0.1	1.8	0.5	
11.11.92	4.0	4.3	3.1	0.4	2.0		0.2	2.8	0.6	
13.11.92	18.5	4.8	1.9	0.4	2.0	1.2		1.1	0.1	
20.11.92	25.0	4.8	2.0	0.4	2.6	1.9	0.1	0.9	0.1	
24.11.92	8.5	5.3	2.1	0.4	1.9	0.6	0.1	2.4	0.5	
1.12.92	2.5	3.7	10.0	0.6	12.1	0.7	0.2	3.4	0.5	0.3
8.12.92	20.5	4.3	3.0	0.5	6.2		0.2	3.4	0.6	
8.12.92	2.0	4.0	2.8	0.2	3.6		1.8	0.5		
12.12.92	1.5	4.5	1.0	0.1	1.4	0.3		1.2	0.1	
17.12.92	7.0	4.3	1.7	0.3	2.8		0.1	1.0	0.1	
22.12.92	24.5	4.5	2.3	0.3	2.3		0.2	0.9	0.1	
31.12.92	4.0	4.0	3.0	1.0	5.8	0.1	0.5	1.0	0.1	
9.01.93	14.5	4.2	2.7	0.3	3.5	0.8	0.1	1.0	0.1	
23.01.93	11.0	4.2	1.7	0.4	3.1		0.1	0.6		0.0
28.01.93	1.5	5.0	3.7	1.7	5.9		0.3	2.3	0.2	
29.01.93	8.5	4.3	2.1	0.4	3.1		0.2	1.2	0.1	
31.01.93	29.5	4.7	1.0	0.1	1.7	1.2	9.1	0.9	0.1	
4.02.93	15.0	4.5	0.9	0.3	1.5			1.0	0.1	0.1
8.02.93	33.0	4.5	0.7	0.2	1.8		0.1	0.9		
9.02.93	8.5	4.0	1.4	0.2	4.1	6.5	0.1	0.8		
18.02.93	2.0	4.5	3.3	0.5	3.5	0.4	0.1	0.9	0.3	
23.02.93	28.0	4.2	1.8	0.2	2.6		0.4	0.2		
1.03.93	43.0	5.3	0.1	0.1	0.3	0.7		0.3	0.1	
04.03.93	35.5	6.6	1.1	0.2	2.2	0.2	0.2	0.4	0.1	

Table A2: Cont.

Date	Rainfall (mm)	Variable (ppm)								
		pH	NO_3^-	Cl^-	SO_4^{2-}	Na^+	K^+	Ca^+	Mg^+	NH_4^+
30.03.93	4.0	3.8	1.9	0.2	3.7	0.1	0.1	0.3	0.1	
11.04.93	38.5	4.3	0.6	0.1	1.2		0.1	0.3	0.1	
11.05.93	3.5	6.8	2.1	0.7	5.0	0.3	1.5	0.7	0.3	
18.05.93	1.5	4.0	2.5	1.1	7.1	0.4	0.6	0.3	0.1	
10.08.93	0.5	6.4	4.1	1.0	5.5	0.4	1.8	2.9	0.5	
12.08.93	0.5	5.7	16.5	3.8	0.8	1.1	3.6	5.1	1.2	
25.09.93	4.0	5.4	5.2	2.2	0.7	2.5	4.1	0.9	0.1	
1.10.93	36.0	4.1	2.0	0.4	3.9		0.2	0.3	0.1	0.2
2.10.93	7.5	4.7	1.7	0.3	3.8		0.2			0.2
5.10.93	5.0	3.7	5.0	0.4	6.8		0.2	0.6	0.1	
6.10.93	43.5	4.1	1.2	0.3	3.0		0.1			0.1
7.10.93	61.5	5.0	1.2	0.8	3.1		0.1			0.1
8.10.93	23.0	4.4	1.9	0.1	2.9					0.1
12.10.93	42.5	4.1	1.7	0.3	2.4	0.1	0.2			0.1
14.10.93	11.5	3.7	3.3	0.5	5.4	0.1	0.1	0.1	0.1	
15.10.93	13.0	3.8	2.6	0.8	4.0		0.1	0.1		0.1
17.10.93	0.5	3.8	4.0	0.6	5.0	0.1	0.2	0.4	0.1	
18.10.93	4.5	3.8	3.9	0.8	5.2	0.1	0.2	0.1	0.1	
19.10.93	0.5	3.7	4.1	0.6	6.0	0.2	0.2	0.1	0.1	6.2
26.10.93	35.5	4.3	1.1	0.2	1.4					0.1
27.10.93	7.5	3.8	5.0	0.3	3.4		0.1	0.2	0.1	
28.10.93	0.5	4.0	2.3	0.1	3.6		0.1	0.4	0.1	0.2
3.11.93	8.5	4.8	2.6	0.2	3.6		0.1	0.4	0.1	0.2
6.11.93	12.0	4.2	2.3	0.2	2.5			0.1		0.1
11.11.93	7.5	4.6	1.8	0.2	2.1			0.2		
11.11.93	3.5	5.5	2.9	0.2	3.5		0.2	0.3	0.1	
12.11.93	9.0	4.7	0.2	2.9	3.6					
13.11.93	4.5	7.3	0.2	2.4	3.2	0.1	0.6	0.1	0.1	2.7
20.11.93	3.0	3.9		1.8	10.6			0.3	0.1	2.8
23.11.93	18.5	4.4		1.7	10.6			0.2		

Table A2: Cont.

Date	Rainfall (mm)	Variable (ppm)								
		pH	NO_3^-	Cl^-	SO_4^{2-}	Na^+	K^+	Ca^+	Mg^+	NH_4^+
24.11.93	0.5	4.2	0.6	3.5	6.8		0.1	0.6	0.1	0.2
27.11.93	2.5	3.4	6.6	0.7	12.2			0.9	0.2	0.4
29.11.93	39.0	3.8	0.9	2.9	3.5	0.2		0.3		0.2
4.12.93	13.0	4.0	5.6	0.4	2.9			0.2	0.1	0.1
8.12.93	9.0	4.1	1.4	0.2	2.0	0.1		0.4	0.1	0.1
9.12.93	3.0	4.2	1.6	0.4	2.0		0.2	0.4		0.1
12.12.93	0.5	4.5	0.6	0.1	1.1		0.2	0.5	0.1	0.1
13.12.93	6.0	4.0		0.2	1.0	0.1	0.1	0.4	0.1	0.2
16.12.93	15.0	5.6	2.0	0.3	3.3	0.3	0.4	0.4	0.1	1.7
17.12.93	7.0	6.0	1.1	0.2	2.1	0.1	0.3	0.2		1.7
21.12.93	18.5	5.6	2.6	0.2	2.3	0.2	0.6	0.3	0.1	1.7
22.12.93	1.0	5.0	0.7	0.2	0.9	0.3	0.6	0.2		
23.12.93	1.5	6.1	0.7	0.3	1.1	0.1	0.7	0.3		
26.12.93	2.5	6.3	0.6	0.2	1.1	0.1	0.6	0.2	0.1	
29.12.93	4.0	5.4	1.1	0.2	3.7	0.1	0.6	0.2		
30.12.93	22.5	6.0	0.8	0.1	1.6	0.2	0.6	0.2	0.1	
10.01.94	18.5	3.7	6.1	0.7	6.6	0.4	0.6	0.7	0.2	
11.01.94	7.5	2.3	1.9	0.3	4.9	0.2	0.6	0.2	0.1	
12.01.94	5.5	4.2	2.4	0.6	4.6	0.3	0.6	0.4	0.1	
13.01.94	2.5	4.8	0.5	0.5	1.1		0.5	0.2		
18.01.94	25.0	3.8	3.0	0.3	5.7	0.1	0.5	0.2	0.1	
19.01.94	0.5	6.0	3.6	0.8	4.9	0.5	2.1	1.3		2.7
22.01.94	10.0	4.6	0.5	0.2	1.7		0.5	0.5	0.2	0.2
22.01.94	8.5	4.6	0.7	0.5	1.5	0.1	0.6	1.0	0.3	0.2
23.01.94	5.5	3.9	1.8	0.5	3.9		0.3	0.9	0.2	0.7
24.01.94	9.0	4.1	1.1	0.1	2.8		0.8	0.6	0.1	
25.01.94	13.0	4.3	0.4		1.7		0.5	0.9	0.2	
26.01.94	4.0	4.3	0.4	0.1	1.8		0.2	0.8	0.2	
1.02.94	0.5	6.1	3.3	1.9	4.0	0.1	8.9	0.9	0.4	2.4
3.02.94	30.5	4.2	1.2	0.1	2.2		0.5	0.4	0.1	0.3

Table A2: Cont.

Date	Rainfall (mm)	Variable (ppm)								
		pH	NO_3^-	Cl^-	SO_4^{2-}	Na^+	K^+	Ca^+	Mg^+	NH_4^+
5.02.94	18.5	4.0	1.1	0.2	3.0		0.2	0.5	0.1	0.2
6.02.94	9.5	4.0	0.4	0.1	1.1		0.4	0.7	0.2	
7.02.94	10.5	4.0	0.9	0.1	4.9		0.6	0.9	0.2	0.4
8.02.94	13.0	4.0	1.4	0.2	3.5		1.0	0.6	0.2	0.3
9.02.94	9.0	4.4	0.3	0.1	1.9		1.2	1.9	0.3	
10.02.94	2.0	4.0	1.6	0.3	4.9		0.5	0.9	0.2	0.3
13.02.94	8.0	4.0	2.4	0.2	4.0		0.3	0.4	0.1	0.5
17.02.94	1.5	3.6	14.3	0.3	11.8	0.1	5.0	0.5	0.1	
23.02.94	6.0	4.0	3.2	0.3	5.1	0.2	0.3	0.4	0.1	
24.02.94	10.0	6.5	2.2	0.4	4.1	0.2	1.9	0.2	0.1	3.8
3.03.94	2.0	3.7	8.6	0.5	7.6	0.2	0.4	0.6	0.2	1.5
8.03.94	13.0	5.0	1.4	0.2	2.5		0.6	0.9	0.1	
10.03.94	4.0	4.5	1.8	0.2	2.2	0.1	0.3	0.3	0.1	1.3
14.03.94	1.5	4.4	1.9	0.4	4.5	0.2	0.5	0.7	0.1	1.5
15.03.94	4.5	4.1	1.7	0.1	4.1		0.3	0.3	0.1	1.3
22.03.94	1.5	5.3	7.7	0.5	8.9	0.2	0.6	2.8	0.5	2.1
26.03.94	3.0	6.5	9.1	0.9	12.4	0.7	6.2	1.2	0.7	6.6
28.03.94	3.5	4.2	1.8	0.3	2.6	0.1	0.3	0.5	0.1	1.4
29.03.94	46.5	5.0	0.5	0.1	1.2	0.1	0.3	0.3	0.1	
31.03.94	1.0	4.5	2.5	0.3	3.1	0.1	0.4	0.5	0.1	1.5
31.03.94	10.5	5.7	0.9	0.2	2.7	0.1	0.5	0.4	0.1	1.8

* note samples not collected on 14,15,19,22,29 and 29 March 1993

Table A3: Wet Deposition Analysis (μeq.l^{-1})

Date	Variable (μeq.l^{-1})								
	H^+	NO_3^-	Cl^-	SO_4^{2-}	Na^+	K^+	Ca^{2+}	Mg^{2+}	NH_4^+
1.10.92	61.2	109.7	22.6	143.7	0.0	12.8	89.8	32.9	136.4
11.10.92	3.6	111.3	31.0	183.2	34.8	12.8	184.6	57.6	0.0
28.10.92	2.1	51.6	14.1	58.3	91.4	7.7	89.8	32.9	0.0
1.11.92	48.6	30.6	22.6	33.3	8.7	10.2	69.9	16.5	3.3
2.11.92	40.4	22.6	5.6	39.6	78.3	2.6	59.9	8.2	0.0
4.11.92	11.7	48.4	8.5	56.2	0.0	2.6	64.9	16.5	2.8
9.11.92	22.2	17.7	5.6	54.1	0.0	2.6	89.8	41.1	0.0
11.11.92	52.1	50.0	11.3	41.6	0.0	5.1	139.7	49.4	0.0
13.11.92	16.1	30.6	11.3	41.6	52.2	0.0	54.9	8.2	0.0
20.11.92	16.8	32.3	11.3	54.1	82.7	2.6	44.9	8.2	0.0
24.11.92	4.9	33.9	11.3	39.6	26.1	2.6	119.8	41.1	0.0
1.12.92	202.6	161.3	16.9	251.9	30.5	5.1	169.7	41.1	18.8
8.12.92	52.1	48.4	14.1	129.1	0.0	5.1	169.7	49.4	0.0
8.12.92	99.2	45.2	5.6	75.0	0.0	46.0	25.0	0.0	0.0
12.12.92	30.0	16.1	2.8	29.1	13.1	0.0	59.9	8.2	0.0
17.12.92	55.8	27.4	8.5	58.3	0.0	2.6	49.9	8.2	0.0
22.12.92	32.1	37.1	8.5	47.9	0.0	5.1	44.9	8.2	0.0
31.12.92	103.9	48.4	28.2	120.8	4.4	12.8	49.9	8.2	0.0
9.01.93	65.6	43.6	8.5	72.9	34.8	2.6	49.9	8.2	0.0
23.01.93	64.1	27.4	11.3	64.5	0.0	2.6	29.9	0.0	2.2
28.01.93	10.6	59.7	48.0	122.8	0.0	7.7	114.8	16.5	0.0
29.01.93	54.5	33.9	11.3	64.5	0.0	5.1	59.9	8.2	0.0
31.01.93	18.9	16.1	2.8	35.4	52.2	232.8	44.9	8.2	0.0
4.02.93	35.2	14.5	8.5	31.2	0.0	0.0	49.9	8.2	3.3
8.02.93	29.3	11.3	5.6	37.5	0.0	2.6	44.9	0.0	0.0
9.02.93	111.3	22.6	5.6	85.4	282.8	2.6	39.9	0.0	0.0
18.02.93	32.1	53.2	14.1	72.9	17.4	2.6	44.9	24.7	0.0
23.02.93	61.2	29.0	5.6	54.1	0.0	10.2	10.0	0.0	0.0
1.03.93	5.0	1.6	2.8	6.2	30.5	0.0	15.0	8.2	0.0
04.03.93	0.3	17.7	5.6	45.8	8.7	5.1	20.0	8.2	0.0

Table A3: Cont.

Date	Variable (μeq.l⁻¹)								
	H^+	NO_3^-	Cl^-	SO_4^{2-}	Na^+	K^+	Ca^{2+}	Mg^{2+}	NH_4^+
30.03.93	164.7	30.6	5.6	77.0	4.4	2.6	15.0	8.2	0.0
11.04.93	53.3	9.7	2.8	25.0	0.0	2.6	15.0	8.2	0.0
11.05.93	0.2	33.9	19.7	104.1	13.1	38.4	34.9	24.7	0.0
18.05.93	97.0	40.3	31.0	147.8	17.4	15.3	15.0	8.2	0.0
10.08.93	0.4	66.1	28.2	114.5	17.4	46.0	144.7	41.1	0.0
12.08.93	2.0	266.1	107.2	16.7	47.9	92.1	254.5	98.7	0.0
25.09.93	4.2	83.9	62.1	14.6	108.8	104.9	44.9	8.2	0.0
1.10.93	86.4	32.3	11.3	81.2	0.0	5.1	15.0	8.2	8.3
2.10.93	18.9	27.4	8.5	79.1	0.0	5.1	0.0	0.0	11.1
5.10.93	184.7	80.7	11.3	141.6	0.0	5.1	29.9	8.2	0.0
6.10.93	78.8	19.4	8.5	62.5	0.0	2.6	0.0	0.0	7.2
7.10.93	9.3	19.4	22.6	64.5	0.0	2.6	0.0	0.0	6.1
8.10.93	42.3	30.6	2.8	60.4	0.0	0.0	0.0	0.0	7.2
12.10.93	77.0	27.4	8.5	50.0	4.4	5.1	0.0	0.0	6.7
14.10.93	217.1	53.2	14.1	112.4	4.4	2.6	5.0	8.2	0.0
15.10.93	157.2	41.9	22.6	83.3	0.0	2.6	5.0	0.0	6.7
17.10.93	153.7	64.5	16.9	104.1	4.4	5.1	20.0	8.2	0.0
18.10.93	160.9	62.9	22.6	108.3	4.4	5.1	5.0	8.2	0.0
19.10.93	212.1	66.1	16.9	124.9	8.7	5.1	5.0	8.2	345.9
26.10.93	49.7	17.7	5.6	29.1	0.0	0.0	0.0	0.0	7.8
27.10.93	146.8	80.7	8.5	70.8	0.0	2.6	10.0	8.2	0.0
28.10.93	103.9	37.1	2.8	75.0	0.0	2.6	20.0	8.2	12.8
3.11.93	15.4	41.9	5.6	75.0	0.0	2.6	20.0	8.2	10.0
6.11.93	65.6	37.1	5.6	52.1	0.0	0.0	5.0	0.0	6.7
11.11.93	24.4	29.0	5.6	43.7	0.0	0.0	10.0	0.0	0.0
11.11.93	2.9	46.8	5.6	72.9	0.0	5.1	15.0	8.2	0.0
12.11.93	19.3	3.2	81.8	75.0	0.0	0.0	0.0	0.0	0.0
13.11.93	0.0	3.2	67.7	66.6	4.4	15.3	5.0	8.2	148.6
20.11.93	133.8	0.0	50.8	220.7	0.0	0.0	15.0	8.2	154.7
23.11.93	36.9	0.0	48.0	220.7	0.0	0.0	10.0	0.0	0.0

Table A3: Cont.

Date	Variable ($\mu eq.l^{-1}$)								
	H^+	NO_3^-	Cl^-	SO_4^{2-}	Na^+	K^+	Ca^{2+}	Mg^{2+}	NH_4^+
24.11.93	68.6	9.7	98.7	141.6	0.0	2.6	29.9	8.2	12.2
27.11.93	360.2	106.5	19.7	254.0	0.0	0.0	44.9	16.5	22.2
29.11.93	153.7	14.5	81.8	72.9	8.7	0.0	15.0	0.0	12.8
4.12.93	103.9	90.3	11.3	60.4	0.0	0.0	10.0	8.2	6.7
8.12.93	75.3	22.6	5.6	41.6	4.4	0.0	20.0	8.2	7.8
9.12.93	70.2	25.8	11.3	41.6	0.0	5.1	20.0	0.0	5.5
12.12.93	32.1	9.7	2.8	22.9	0.0	5.1	25.0	8.2	5.5
13.12.93	90.5	0.0	5.6	20.8	4.4	2.6	20.0	8.2	10.5
16.12.93	2.3	32.3	8.5	68.7	13.1	10.2	20.0	8.2	94.2
17.12.93	1.1	17.7	5.6	43.7	4.4	7.7	10.0	0.0	92.0
21.12.93	2.7	41.9	5.6	47.9	8.7	15.3	15.0	8.2	91.5
22.12.93	10.9	11.3	5.6	18.7	13.1	15.3	10.0	0.0	0.0
23.12.93	0.8	11.3	9.0	22.9	4.4	17.9	15.0	0.0	0.0
26.12.93	0.5	9.7	5.6	22.9	4.4	15.3	10.0	8.2	0.0
29.12.93	4.2	17.7	5.6	77.0	4.4	15.3	10.0	0.0	0.0
30.12.93	0.9	12.9	2.8	33.3	8.7	15.3	10.0	8.2	0.0
10.01.94	189.1	98.4	19.7	137.4	17.4	15.3	34.9	16.5	0.0
11.01.94	5088.4	30.6	8.5	102.0	8.7	15.3	10.0	8.2	0.0
12.01.94	64.1	38.7	16.9	95.8	13.1	15.3	20.0	8.2	0.0
13.01.94	14.3	8.1	14.1	22.9	0.0	12.8	10.0	0.0	0.0
18.01.94	168.5	48.4	8.5	118.7	4.4	12.8	10.0	8.2	0.0
19.01.94	0.9	58.1	22.6	102.0	21.8	53.7	64.9	0.0	0.0
22.01.94	28.0	8.1	5.6	35.4	0.0	12.8	25.0	16.5	12.2
22.01.94	28.0	11.3	14.1	31.2	4.4	15.3	49.9	24.7	11.6
23.01.94	113.9	29.0	14.1	81.2	0.0	7.7	44.9	16.5	37.1
24.01.94	86.4	17.7	2.8	58.3	0.0	20.5	29.9	8.2	0.0
25.01.94	48.6	6.5	0.0	35.4	0.0	12.8	44.9	16.5	0.0
26.01.94	48.6	6.5	2.8	37.5	0.0	5.1	39.9	16.5	0.0
1.02.94	0.7	53.2	53.6	83.3	4.4	227.7	44.9	32.9	131.4
3.02.94	61.2	19.4	2.8	45.8	0.0	12.8	20.0	8.2	16.1

Table A3: Cont.

Date	Variable ($\mu eq.l^{-1}$)								
	H^+	NO_3^-	Cl^-	SO_4^{2-}	Na^+	K^+	Ca^{2+}	Mg^{2+}	NH_4^+
5.02.94	92.6	17.7	5.6	62.5	0.0	5.1	25.0	8.2	12.2
6.02.94	106.3	6.5	2.8	22.9	0.0	10.2	34.9	16.5	0.0
7.02.94	97.0	14.5	2.8	102.0	0.0	15.3	44.9	16.5	21.1
8.02.94	94.8	22.6	5.6	72.9	0.0	25.6	29.9	16.5	16.6
9.02.94	41.4	4.8	2.8	39.6	0.0	30.7	94.8	24.7	0.0
10.02.94	103.9	25.8	8.5	102.0	0.0	12.8	44.9	16.5	0.0
13.02.94	99.2	38.7	5.6	83.3	0.0	7.7	20.0	8.2	0.0
17.02.94	279.6	230.7	8.5	245.7	4.4	127.9	25.0	8.2	0.0
23.02.94	97.0	51.6	8.5	106.2	8.7	7.7	20.0	8.2	0.0
24.02.94	0.3	35.5	11.3	85.4	8.7	48.6	10.0	8.2	207.9
3.03.94	212.1	138.7	14.1	158.2	8.7	10.2	29.9	16.5	82.1
8.03.94	10.4	22.6	5.6	52.1	0.0	15.3	44.9	8.2	0.0
10.03.94	30.0	29.0	5.6	45.8	4.4	7.7	15.0	8.2	72.6
14.03.94	41.4	30.6	11.3	93.7	8.7	12.8	34.9	8.2	81.5
15.03.94	71.9	27.4	2.8	85.4	0.0	7.7	15.0	8.2	74.3
22.03.94	4.7	124.2	14.1	185.3	8.7	15.3	139.7	41.1	116.4
26.03.94	0.3	146.8	25.4	258.2	30.5	158.6	59.9	57.6	365.9
28.03.94	70.2	29.0	8.5	54.1	4.4	7.7	25.0	8.2	74.8
29.03.94	10.6	8.1	2.8	25.0	4.4	7.7	15.0	8.2	0.0
31.03.94	34.4	40.3	8.5	64.5	4.4	10.2	25.0	8.2	82.6
31.03.94	1.9	14.5	5.6	56.2	4.4	12.8	20.0	8.2	99.8

Table A4: **Comparison of rainwater samples at the Suikerbosrand catchment and Ranger's House**

Suikerbosrand Catchment					
Variable	**Date**				
	16.12.93	**17.12.93**	**11.1.94**	**13.01.94**	**18.01.94**
NO_3^-	2	1.1	3.2	0.5	3.7
Cl^-	0.3	0.2	0.5	0.5	0.3
SO_4^{2-}	3.3	2.1	7.4	1.1	6.8
Na^+	0.3	0.1	0.2	0	0.3
K^-	0.4	0.3	0.7	0.5	0.5
Ca^{2-}	0.4	0.2	0.3	0.2	0.3
Mg^{2-}	0.1	0	0.1	0	0.1
Rainfall	15	7	7.5	2.5	25

Ranger's House					
Variable	**Date**				
	16.12.93	**17.12.93**	**11.1.94**	**13.01.94**	**18.01.94**
NO_3^-	2.1	1.2	4.6	0.9	3
Cl^-	0.4	0.2	0.6	0.3	0.3
SO_4^{2-}	3.8	2.2	5.9	2.2	5.7
Na^+	0.1	0.9	0.3	0.1	0.1
K^-	0.3	0.3	0.7	0.5	0.5
Ca^{2-}	0.3	0.4	0.6	0.3	0.2
Mg^{2-}	0.1	0.1	0.2	0.1	0.1
Rainfall	7.5	9.5	5	5	21

Table A5 : Sulphur dioxide concentrations at the Ranger's House

Period A (October 1992 - March 1993)								
Month	**Day**	**SO_2 Conc $\mu g.m^{-3}$**	**Month**	**Day**	**SO_2 Conc $\mu g.m^{-3}$**	**Month**	**Day**	**SO_2 Conc $\mu g.m^{-3}$**
Oct 92	2	3	Dec 92	4	5	Feb 93	1	4
	5	26		7	5		3	15
	7	22		9	8		5	13
	9	27		11	5		8	1
	12	0		14	1		10	32
	14	14		16	12		12	7
	16	33		18	56		15	6
	19	0		21	3		18	5
	21	6		23	62		22	1
	23	5		25	9		24	56
	26	0		29	11		26	40
	28	0		31	5	Mar 93	1	51
	30	0	Jan 93	2	6		3	50
Nov 92	2	0		4	7		6	32
	4	12		6	5		8	27
	6	2		8	11		9	4
	9	9		11	12		12	10
	11	20		13	23		16	163
	13	15		16	11		22	16
	16	55		18	29		23	22
	18	8		22	10		26	10
	20	15		25	7		28	24
	23	2		27	73		30	24
	25	8		29	13		31	47
	27	21						
	30	13						

Period B (April 1993 - September 1993)								
Month	Day	SO_2 Conc $\mu g.m^{-3}$	Month	Day	SO_2 Conc $\mu g.m^{-3}$	Month	Day	SO_2 Conc $\mu g.m^{-3}$
Apr 93	2	98	Jun 93	2	0	Aug 93	3	47
	5	2		5	15		4	14
	7	18		7	34		6	40
	9	12		10	27		10	10
	12	12		14	35		12	14
	14	6		16	69		13	27
	17	8		21	142		16	63
	19	10		27	28		18	37
	21	25	Jul 93	3	66		20	47
	26	12		5	59		23	30
	28	55		8	28		25	10
May 93	1	14		10	4		27	44
	3	43		11	70		30	13
	5	18		16	35	Sep 93	1	24
	8	0		18	7		4	67
	10	0		20	62		6	24
	12	0		22	41		8	57
	15	0		25	0		10	37
	17	0		27	28		13	40
	19	0		29	19		15	26
	21	0		31	50		18	10
	24	70					20	0
	27	54					22	10
	29	3					24	22
	31	2					27	21

Period C (October 1993 - March 1994)								
Month	**Day**	**SO_2 Conc $\mu g.m^{-3}$**	**Month**	**Day**	**SO_2 Conc $\mu g.m^{-3}$**	**Month**	**Day**	**SO_2 Conc $\mu g.m^{-3}$**
Oct 93	1	4	Dec 93	1	48	Feb 94	2	8
	4	12		3	22		4	2
	6	6		6	14		7	4
	8	14		8	18		9	10
	11	3		10	25		11	24
	13	10		13	40		14	15
	15	9		15	44		16	14
	18	1		17	26		18	9
	20	16		20	18		21	10
	22	5		22	18		23	16
	25	7		24	14		25	15
	27	2		27	23		28	0
	29	25		29	14	Mar 94	2	27
Nov 93	1	18		31	19		4	48
	3	12	Jan 94	3	8		7	13
	5	22		5	21		9	7
	8	15		7	43		11	43
	10	3		10	12		14	16
	12	7		12	13		16	2
	15	14		14	26		18	31
	17	41		17	20		21	12
	19	20		19	17		23	20
	22	13		21	14		25	31
	24	11		24	8		28	14
	26	45		26	12		30	5
	29	24		28	38		31	0
				31	10			

Table A6: Rock Plot Runoff of Sulphate

Date	Volume (l)	SO_4 Conc. mg.l^{-1}	Factor	kg.ha^{-1}
Start 08.11.92				
13.11.92	9.00	4.60	1.62	0.69
17.11.92	2.54	4.32	1.67	0.18
20.11.92	4.66	7.23	1.67	0.59
24.11.92	3.12	9.02	1.67	0.50
01.12.92	2.85	13	1.67	0.66
08.12.92	1.15	24.3	1.67	0.47
15.12.92	21.89	6.11	1.67	2.39
22.12.92	13.17	4.69	1.67	1.07
23.12.92	0.07	17.76	1.67	0.02
24.12.92	0.87	17.30	1.67	0.29
31.12.92	1.89	17.70	1.67	0.57
05.01.93	1.79	11.74	1.75	0.37
08.01.93	0.29	2.59	0.27	0.05
10.01.93	5.27	7.95	1.65	0.70
23.01.93	3.45	12.36	1.67	0.73
02.02.93	16.75	4.25	1.60	1.17
24.02.93	10.62	5.51	1.67	1.01
02.03.93	14.04	2.22	1.67	0.51
04.03.93	18.50	3.26	1.67	1.03
16.03.93	2.70	15.64	1.67	0.72
23.03.93	4.55	15.08	1.67	1.17
30.03.93	4.12	10.90	1.67	0.80
13.04.93	20.00	3.82	1.77	1.39
04.05.93	1.38	18.49	1.77	0.44
11.05.93	2.15	10.59	1.67	0.38
18.05.93	1.59	19.84	1.67	0.52
02.08.93	1.80	43.77	2.22	0.49
15.09.93	1.76	23.62	2.22	0.25

Table A6: Cont.

Date	Volume (l)	SO_4 Conc. mg.l^{-1}	Factor	kg.ha^{-1}
25.09.93	1.76	57.06	1.67	1.51
01.10.93	16.05	7.46	1.65	1.99
02.10.93	3.16	11.11	1.67	0.61
06.10.93	0.00	0.00	0.00	0.00
07.10.93	14.24	5.62	1.67	1.39
08.10.93	7.04	4.88	1.67	0.59
12.10.93	19.83	4.25	1.67	1.49
14.10.93	4.97	8.03	1.67	0.67
15.10.93	5.60	8.45	1.67	0.87
17.10.93	0.00	0.00	0.00	0.00
19.10.93	1.60	10.54	1.67	0.29
26.10.93	19.82	3.27	1.67	1.12
28.10.93	3.95	7.29	1.67	0.49
03.11.93	3.19	6.82	1.67	0.37
06.11.93	5.36	5.19	1.67	0.49
11.11.93	4.81	5.46	1.67	0.46
13.11.93	6.09	5.61	1.67	0.62
20.11.93	1.26	15.17	1.75	0.34
23.11.93	9.33	5.14	1.67	0.85
30.11.93	19.37	6.77	1.67	2.21
04.12.93	12.41	5.73	1.67	1.20
08.12.93	4.01	7.29	1.67	0.50
16.12.93	7.86	6.94	1.67	0.93
17.12.93	2.72	5.23	1.67	0.25
21.12.93	7.95	4.19	1.67	0.54
23.12.93	0.73	13.07	1.67	0.16
29.12.93	14.32	4.80	1.67	1.19
04.01.94	0.30	0.00	1.67	0.00
11.01.94	12.62	10.65	1.60	2.15
12.01.94	0.39	21.00	1.67	0.15

Table A6: Cont.

Date	Volume (l)	SO_4 Conc. mg.l^{-1}	Factor	kg.ha^{-1}
13.01.94	0.75	12.79	1.75	0.18
18.01.94	9.05	9.83	1.67	1.45
20.01.94	0.02	32.89	1.71	0.01
23.01.94	10.07	6.66	1.67	1.03
24.01.94	0.00	0.00	0.00	0.00
25.01.94	11.26	7.32	1.67	1.57
26.01.94	0.01	15.17	1.67	0.00
30.01.93	0.00	0.00	0.00	0.00
03.02.94	12.75	3.75	1.70	0.81
06.02.94	15.80	5.31	1.75	1.58
08.02.94	13.54	6.96	1.67	1.70
09.02.94	2.24	4.87	1.67	0.21
11.02.94	0.70	232.42	1.65	1.94
14.02.94	3.80	8.61	1.67	0.57
23.02.94	2.57	14.78	2.16	0.60
24.02.94	0.65	12.82	1.67	0.15
04.03.94	0.43	22.61	1.67	0.16
09.03.94	6.78	5.84	1.67	0.66
15.03.94	2.49	11.50	1.66	0.48
22.03.94	2.02	16.64	1.77	0.61
29.03.94	23.62	3.87	1.67	1.55
01.04.94	5.91	4.55	1.66	0.44

Table A7: Bulk deposition at Ranger's house

Date	SO4 conc. (mg.l^{-1})	Rainfall (mm)	Bulk dep. (kg.ha^{-1})	Wet conc (mgl^{-1})	Wet dep. (kg.ha^{-1})
01.10.9	3.20	5.5	0.18	6.90	0.38
11.10.92	18.60	1.5	0.28	8.80	0.13
28.10.92	5.60	7.0	0.39	2.80	0.20
31.10.92	0.70		0.05		0.00
01.11.92	0.50	7.0	0.04	1.60	0.11
02.11.92	0.50	12.0	0.06	1.90	0.23
04.11.92	3.10	5.0	0.16	2.70	0.14
09.11.92	2.30	72.5	1.67	2.60	1.89
11.11.92	1.00	5.0	0.05	2.00	0.10
13.11.92	1.50	19.0	0.29	2.00	0.38
19.11.92	2.80	12.0	0.34	2.60	0.31
24.11.92	1.30	11.5	0.15	1.90	0.22
30.11.92	1.40		0.10		0.00
01.12.92	9.80	7.0	0.69	12.10	0.85
08.12.92	54.90	5.0	2.75	6.20	0.31
08.12.92	3.50	16.0	0.56	3.60	0.58
12.12.92	1.10	34.0	0.37	1.40	0.48
17.12.92	2.30	11.0	0.25	2.80	0.31
22.12.92	0.60	15.0	0.09	2.30	0.35
31.12.92	4.00	4.0	0.16	5.80	0.23
01.01.93	0.60		0.04		0.00
09.01.93	1.30	17.0	0.22	3.50	0.60
23.01.93	0.70	16.5	0.12	3.10	0.51
28.01.93	5.00	3.0	0.15	5.90	0.18
29.01.93	2.70	5.5	0.15	3.1	0.17
31.01.93	1.60	14.5	0.23	1.70	0.25
01.02.93	0.70		0.05		0.00
04.02.93	2.30	11.5	0.26	1.50	0.17
08.02.93	2.70	55.0	1.49	1.80	0.99
09.02.93	4.10	12.0	0.49	4.10	0.49
18.02.93	4.70	6.0	0.28	3.50	0.21
23.02.93	2.30	85.0	1.96	2.60	2.21
01.03.93	0.70	50.0	0.35	0.30	0.15

Date	SO4 conc. (mg.l^{-1})	Rainfall (mm)	Bulk dep. (kg.ha^{-1})	Wet conc (mgl^{-1})	Wet dep. (kg.ha^{-1})
01.03.93R	0.50		0.04		0.00
30.03.93	5.60	8.0	0.45	3.70	0.30
31.03.93	0.20		0.01		0.00
11.04.93R	1.10	27.0	0.30	1.20	0.32
01.05.93	3.60		0.25		0.00
11.05.93	4.60	2.0	0.09	5.00	0.10
18.05.93R	9.80	1.5	0.15	7.10	0.11
20.07.93R	15.5		1.10		0.00
03.08.93C	4.00		0.28		0.00
10.08.93C	0.00	0.5	0.0	5.50	0.03
12.08.93C	0.00	0.5	0.0	0.80	0.00
06.09.93C	0.00		0.0		0.00
25.09.93C	0.00	2.5	0.0	0.70	0.02
01.10.93	3.30	28.5	0.94	3.90	1.11
01.10.93R	0.10		0.01		0.00
02.10.93	4.10	6.5	0.27	3.80	0.25
05.10.93	8.50	2.5	0.21	6.80	0.17
06.10.93	1.80	39.0	0.70	3.00	1.17
07.10.93	1.20	28.0	0.34	3.10	0.87
08.10.93	2.50	30.0	0.75	2.90	0.87
12.10.93	1.10	40.0	0.44	2.40	0.96
14.10.93	5.50	13.0	0.72	5.40	0.70
15.10.93	4.20	18.0	0.76	4.00	0.72
17.10.93	7.30	5.0	0.37	5.20	0.26
18.10.93	7.00	2.0	0.14	6.00	0.12
19.10.93	30.52	0.5	0.15	6.00	0.03
26.10.93	1.50	35.5	0.53	1.40	0.50
27.10.93	2.94	9.0	0.26	3.40	0.31
02.11.93R	1.09		0.08		0.00
03.11.93	2.48	7.0	0.17	3.60	0.25
06.11.93	2.31	9.0	0.21	2.50	0.23
11.11.93	1.88	10.5	0.20	2.10	0.22
12.11.93	0.73	9.0	0.07	2.60	0.23
13.11.93	1.32	9.0	0.12	3.20	0.29

Date	SO4 conc. (mg.l^{-1})	Rainfall (mm)	Bulk dep. (kg.ha^{-1})	Wet conc (mgl^{-1})	Wet dep. (kg.ha^{-1})
20.11.93	7.27	5.5	0.40	10.60	0.58
23.11.93	1.59	23.0	0.37	10.60	2.44
24.11.93	3.37	1.0	0.03	6.80	0.07
27.11.93	14.59	3.0	0.44	12.20	0.37
29.11.93	2.81	24.5	0.69	3.50	0.86
02.12.93R	0.83		0.06		0.00
04.12.93	3.63	24.0	0.87	2.90	0.70
08.12.93	5.83	8.5	0.50	2.00	0.17
09.12.93	2.84	3.0	0.09	2.00	0.06
12.12.93	3.50	1.5	0.05	1.10	0.02
13.12.93	3.87	4.0	0.15	1.00	0.04
16.12.93	4.26	7.5	0.32	3.30	0.25
17.12.93	2.01	9.5	0.19	2.10	0.20
21.12.93	2.53	19.0	0.48	2.30	0.44
22.12.93	4.26	1.0	0.04	0.90	0.01
23.12.93	1.79	2.0	0.04	1.10	0.02
26.12.93	1.76	3.0	0.05	1.10	0.03
29.12.93	3.96	8.0	0.32	3.70	0.30
29.12.93	1.49	39.0	0.58	1.60	0.62
30.12.93	1.49	2.0	0.03	1.60	0.03
01.01.94R	0.00		0.00		0.00
10.01.94	7.59	10.5	0.80	0.60	0.69
11.01.94	4.84	7.0	0.34	4.90	0.34
11.01.94	7.74	5.0	0.39	4.60	0.23
13.01.94	4.84	5.0	0.24	1.10	0.06
18.01.94	5.95	21.0	1.25	5.70	1.20
19.01.94	4.84	5.5	0.27	4.90	0.27
22.01.94	2.04	16.0	0.33	1.70	0.27
22.01.94	1.73	7.0	0.12	1.50	0.11
23.01.94	4.15	5.5	0.23	3.90	0.21
24.01.94	4.29	6.0	0.26	2.80	0.17
25.01.94	1.61	11.0	0.18	1.70	0.19
26.01.94	3.49	2.5	0.09	1.80	0.05
01.02.94	8.37	1.5	0.13	4.00	0.06

Date	SO4 conc. (mg.l^{-1})	Rainfall (mm)	Bulk dep. (kg.ha^{-1})	Wet conc (mgl^{-1})	Wet dep. (kg.ha^{-1})
03.02.94	2.56	48.5	1.14	2.20	1.07
05.02.94	3.39	22.5	0.76	3.00	0.68
06.02.94	1.38	8.0	0.11	1.10	0.09
07.02.94	3.56	3.5	0.12	4.90	0.17
08.02.94	3.84	13.0	0.50	3.50	0.46
09.02.94	2.18	7.5	0.16	1.90	014
10.02.94	5.19	2.5	0.13	4.90	0.12
13.02.94	4.46	8.0	0.36	4.00	032
17.02.94	23.40	1.5	0.35	11.80	0.18
23.02.94	5.80	6.0	0.35	5.10	0.31
24.02.94	3.64	10.0	0.36	4.10	0.41
01.03.94	0.80		0.06		0.00
03.03.94	8.76	1.5	0.13	7.60	0.11
08.03.94	3.15	17.0	0.54	2.50	0.43
10.03.94	2.47	2.0	0.05	2.20	0.04
14.03.94	6.26	1.5	0.09	4.50	0.07
15.03.94	4.32	4.5	0.19	4.10	0.18
22.03.94	21.91	1.5	0.33	8.90	0.13
26.03.94	18.36	3.0	0.55	12.40	0.37
28.03.94	6.17	6.0	0.37	2.60	0.16
29.03.94	1.64	45.0	0.74	1.20	0.54
31.03.94	5.80	1.0	0.06	3.10	0.03
31.03.94	2.44	11.0	0.27	2.70	0.30
01.04.94R	0.18		0.0127		

Note: C = Contaminated, R = Rinse

Table A8 : Full metal analysis (ICP)

Sample: B28 (ppm)		**Variable**	**Sample: B5 (ppm)**	
4.74		pH	6.26	
Dissolved	**Acid-soluble**		**Dissolved**	**Acid-soluble**
<0.001	<0.001	Be	<0.001	<0.001
<0.017	0.039	B	0.007	0.143
0.237	0.340	Al	0.033	0.182
<0.001	<0.001	Ti	<0.001	<0.001
<0.003	<0.003	Va	<0.003	<0.003
<0.003	<0.003	Cr	<0.003	<0.003
0.213	0.290	Mn	0.284	0.365
0.003	0.089	Fe	<0.003	0.349
<0.005	<0.005	Co	0.007	0.010
<0.004	0.013	Ni	<0.005	0.011
<0.004	<0.004	Cu	<0.004	<0.004
0.048	0.034	Zn	0.031	0.024
<0.050	<0.050	Ag	<0.050	<0.050
0.015	0.025	Si	0.021	<0.029
<0.001	<0.001	Zr	<0.001	<0.001
<0.006	<0.006	Mo	<0.006	<0.006
<0.001	<0.001	Cd	<0.001	<0.001
<0.002	<0.002	Ba	<0.002	<0.002
<0.020	<0.020	Hg	<0.020	<0.020
<0.020	<0.020	Pb	<0.020	<0.020

APPENDIX
continued

Rainfall, Flows and Sulphate Concentrations

(Only as hard copies)

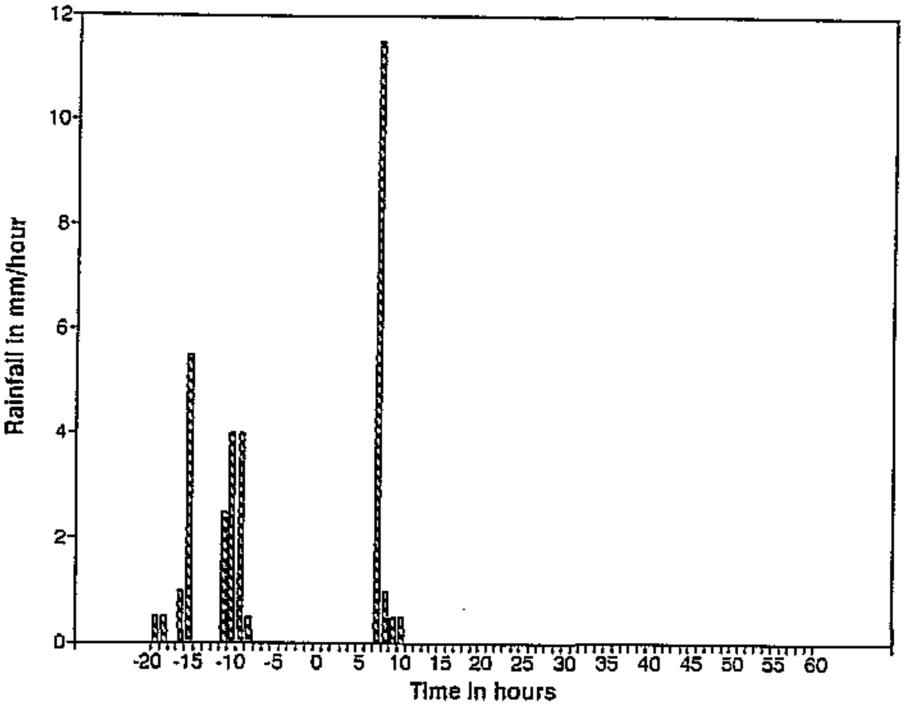


Figure A1a: Rainfall - Flow A2 - 32 mm

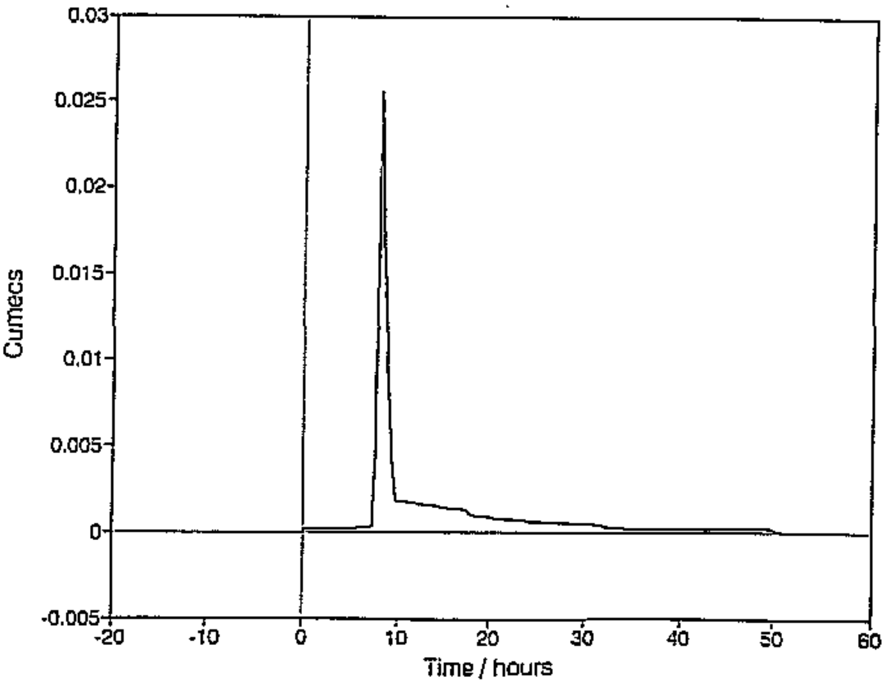


Figure A1b: Flow A2 (11 - 13 Nov 92)

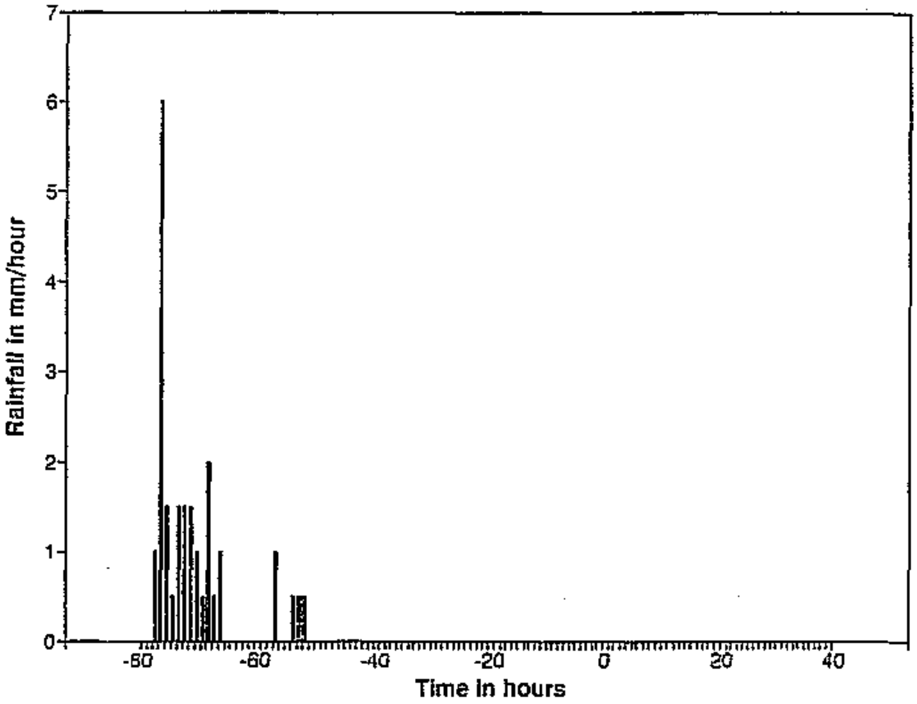


Figure A2a: Rainfall - Flow A3 - 21 mm

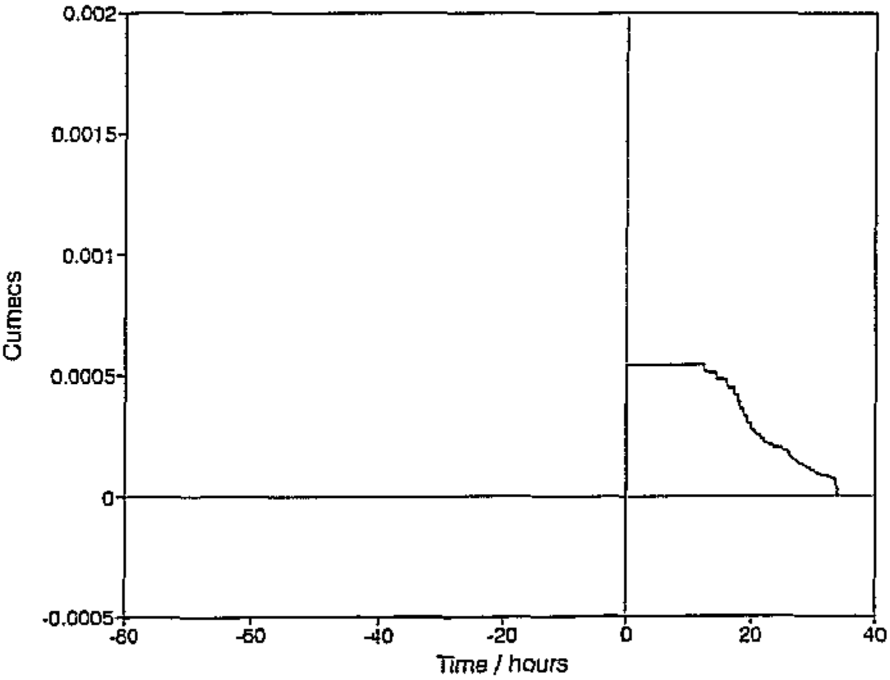


Figure A2b: Flow A3 (12 Dec 92)

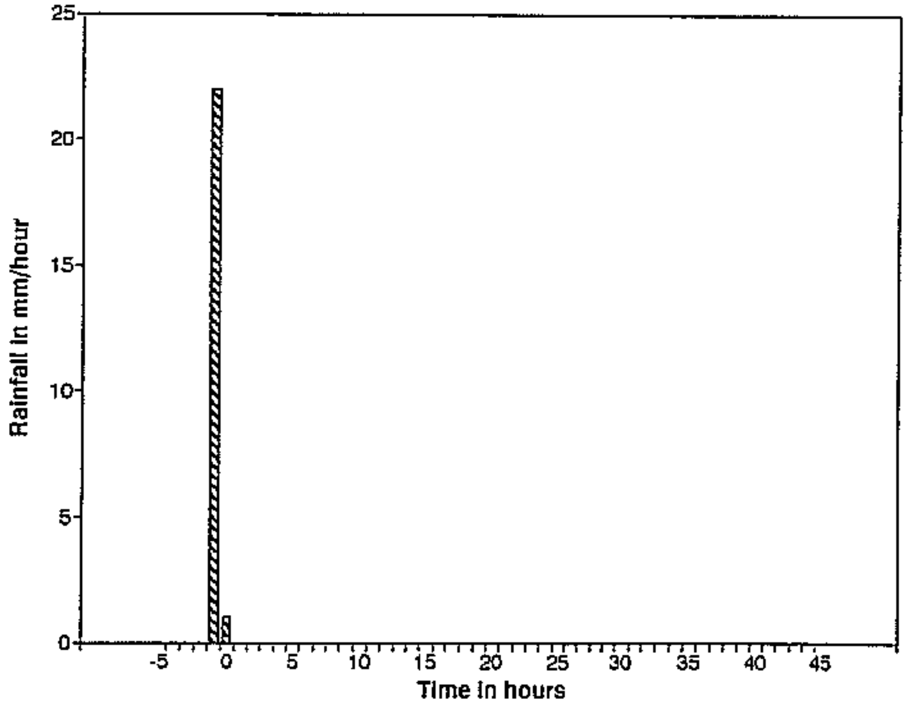


Figure A3a: Rainfall - Flow A4 - 23 mm

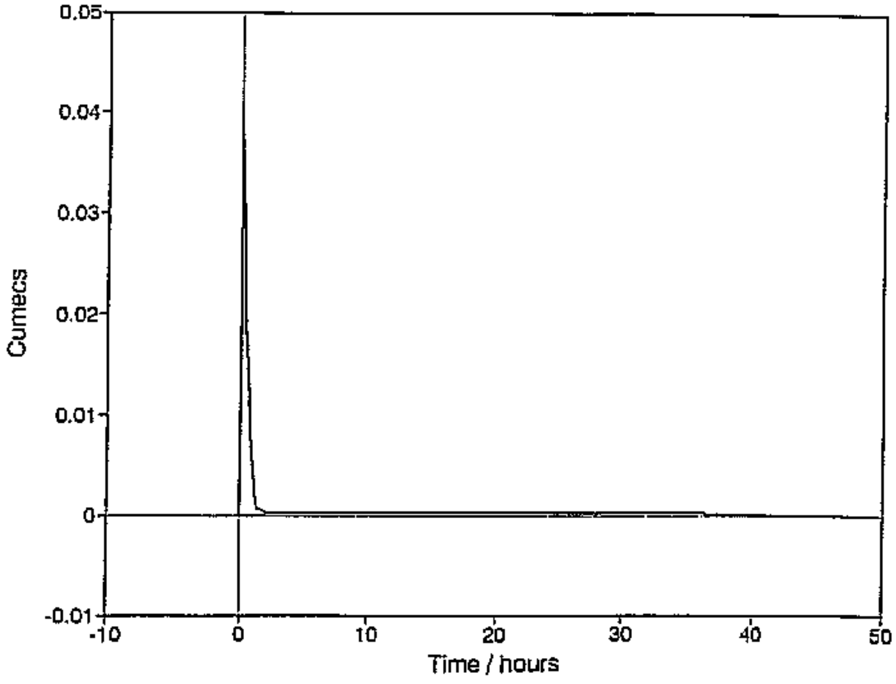


Figure A3b: Flow A4 (21 - 23 Dec 92)

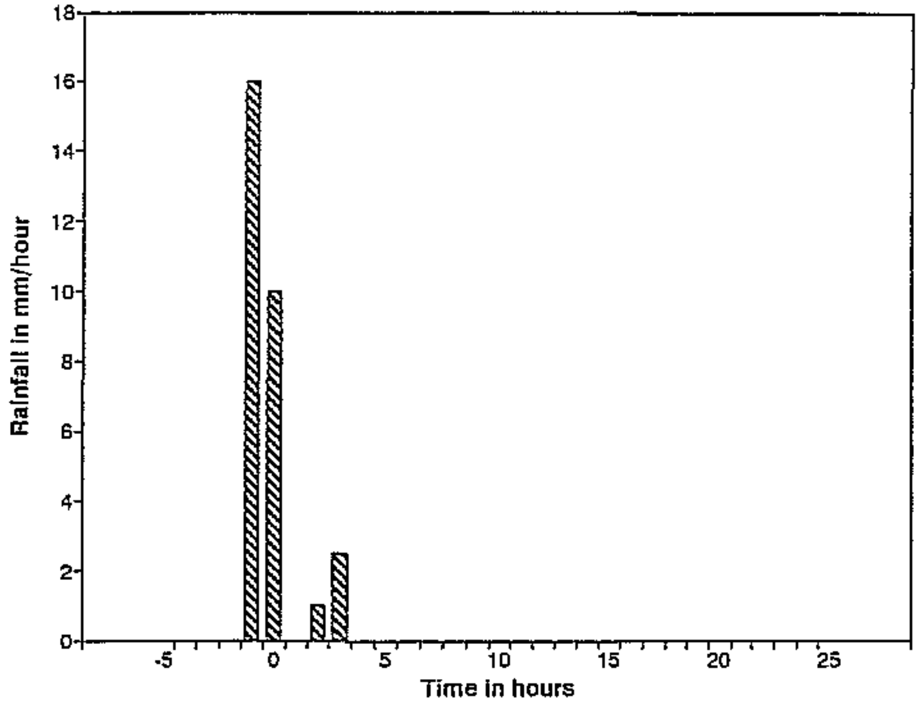


Figure A4a: Rainfall - Flow A5 - 29.5 mm

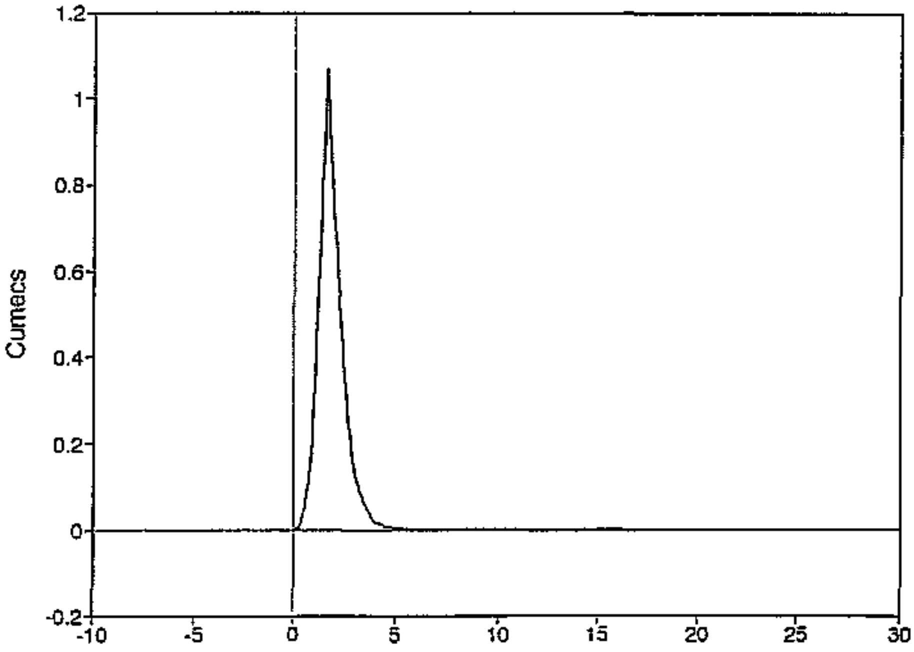


Figure A4b: Flow A5 (30 - 31 Jan 93)

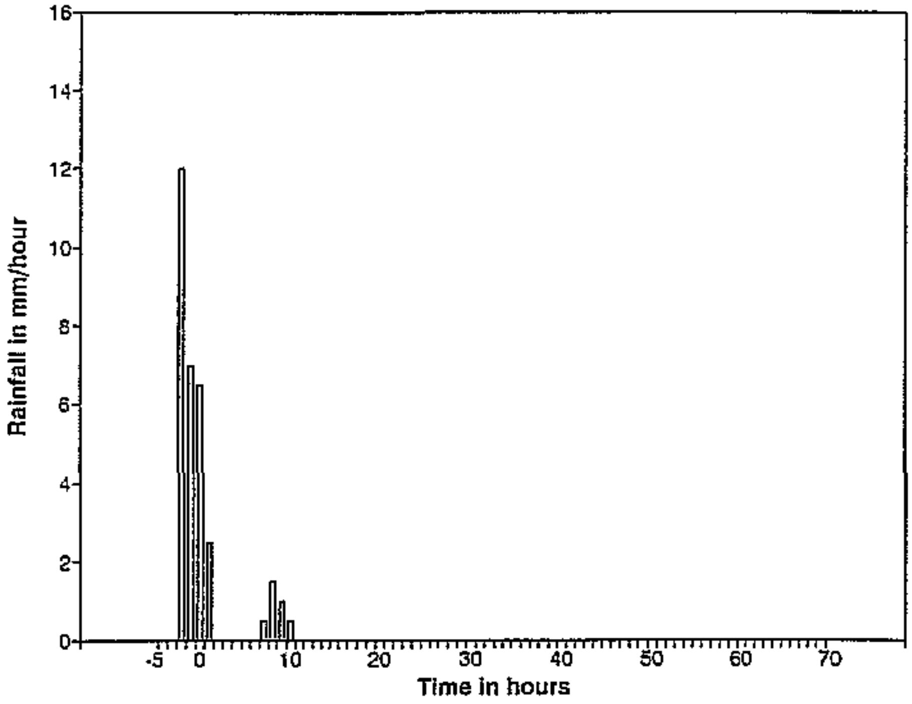


Figure A5a: Rainfall - Flow A6 - 31.5 mm

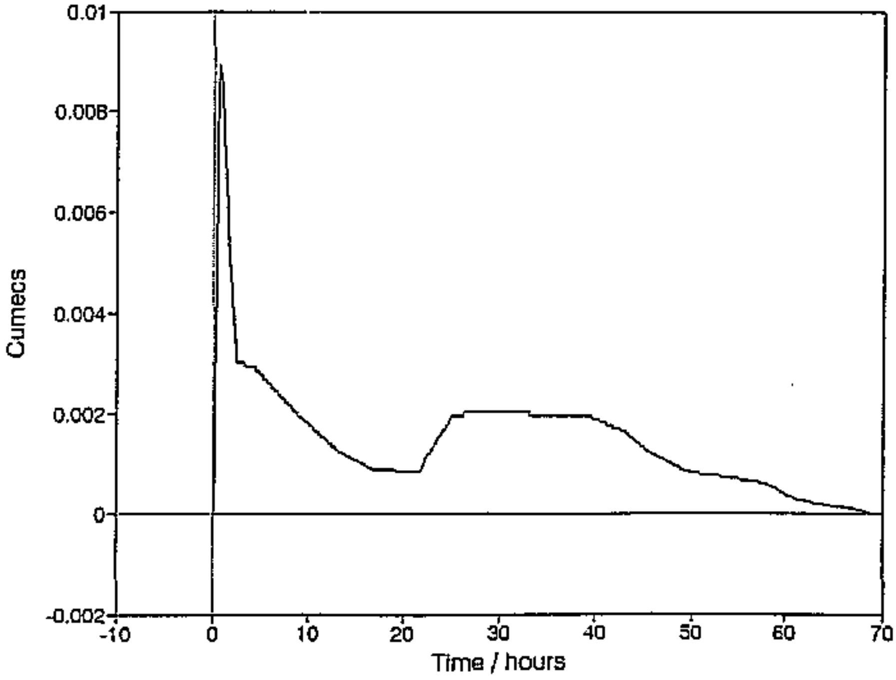


Figure A5b: Flow A6 (8 - 11 Feb 93)

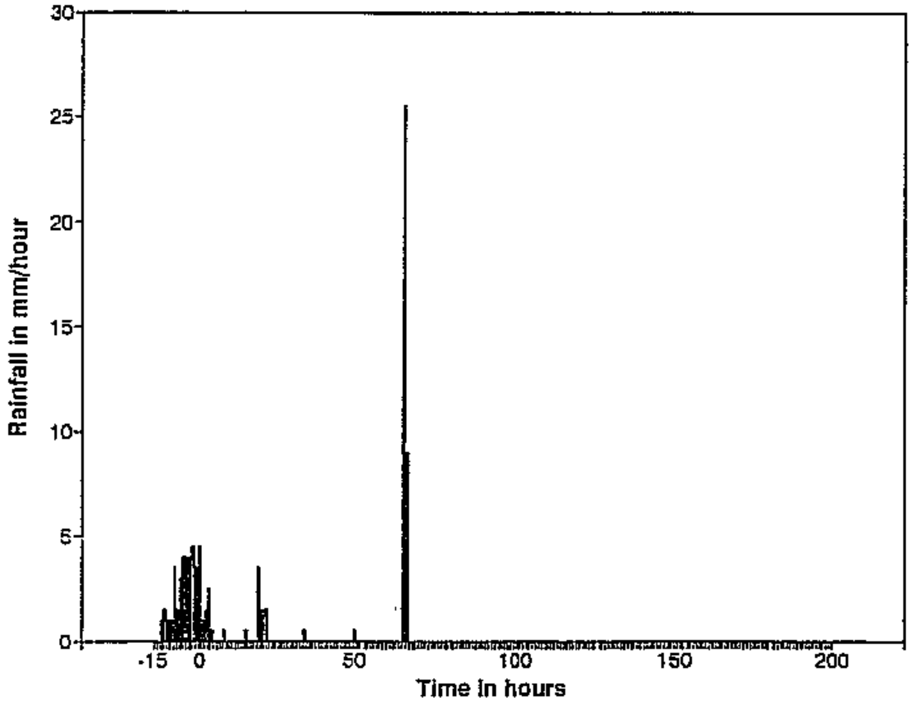


Figure A6a: Rainfall - Flow A7 - 87 mm

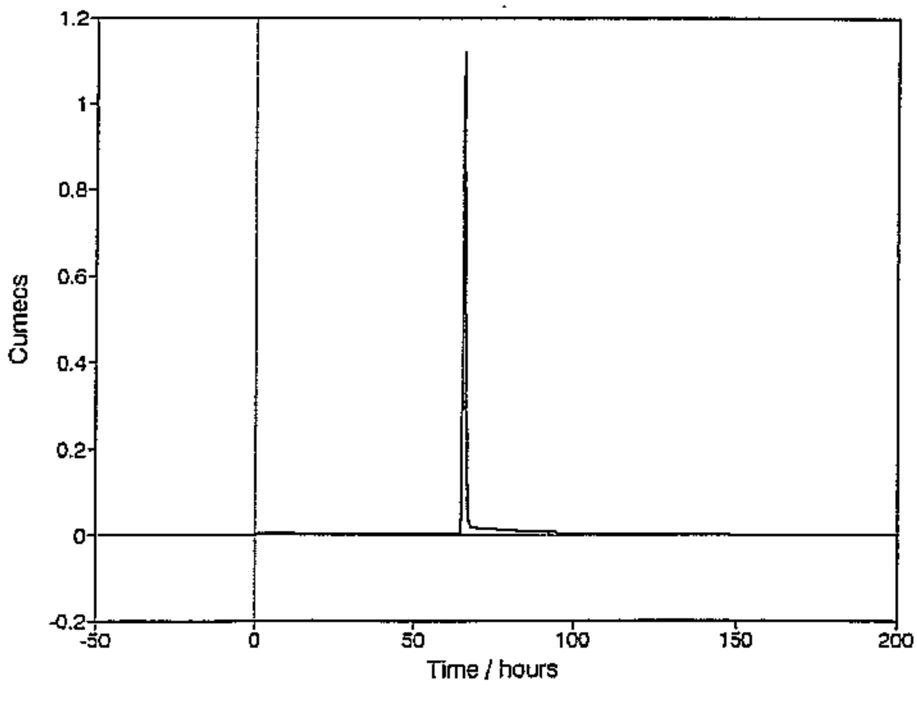


Figure A6b: Flow A7 (1 - 9 Mar 93)

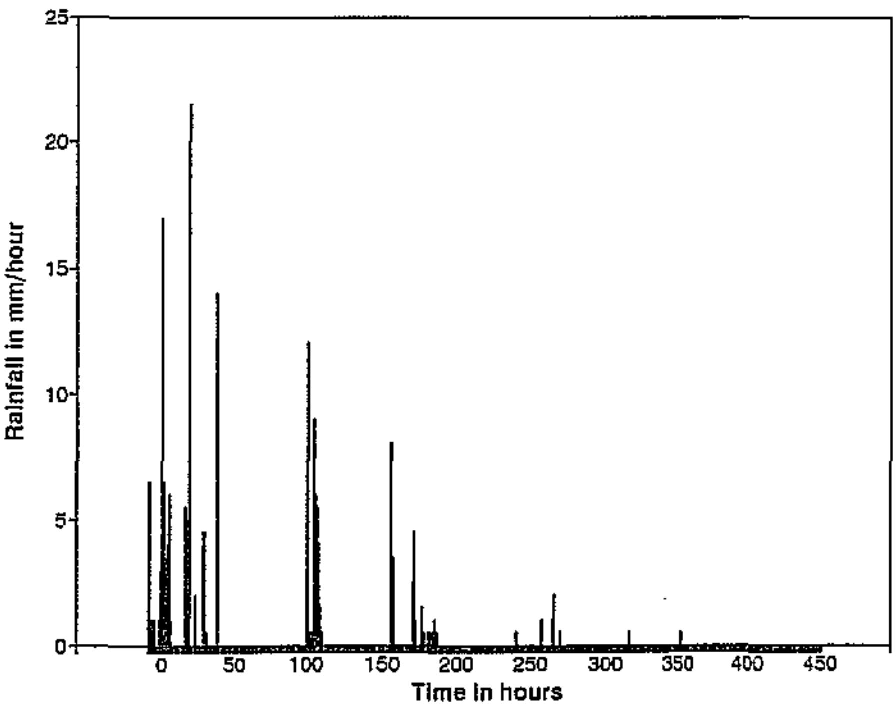


Figure A7a: Rainfall - Flow C8 - 187.5 mm

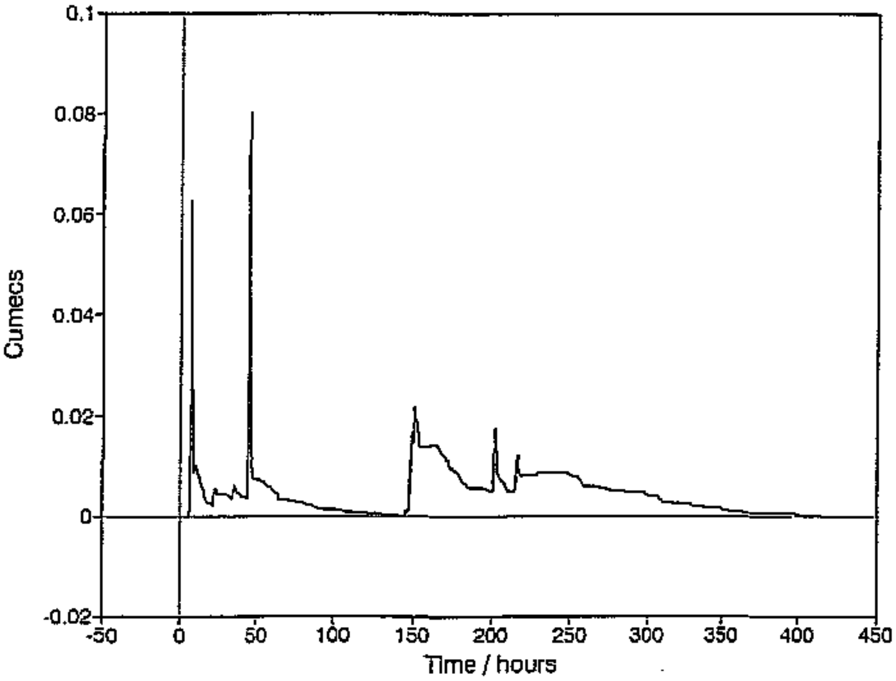


Figure A7b: Flow C8 (6 - 23 Oct 93)

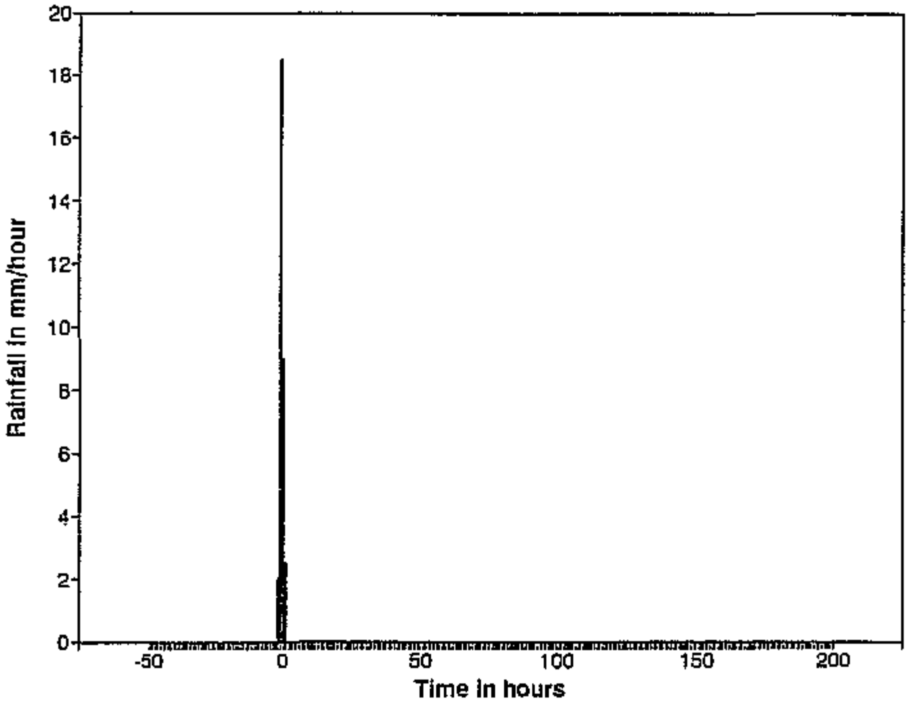


Figure A8a: Rainfall - Flow C9 - 32 mm

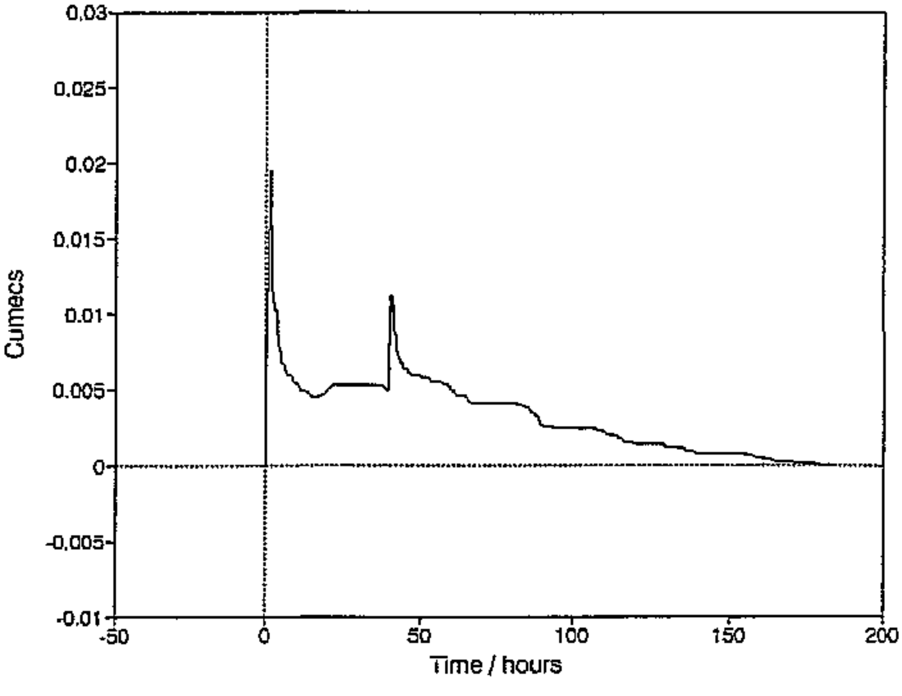


Figure A8b: Flow C9 (25 Oct- 2 Nov 93)

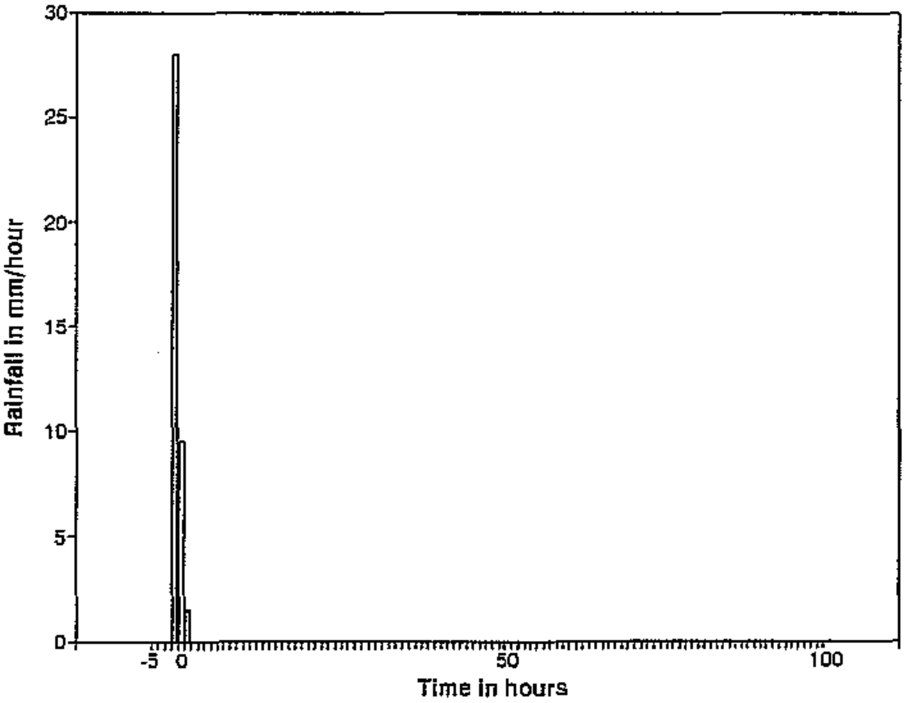


Figure A9a: Rainfall - Flow C10 - 39 mm

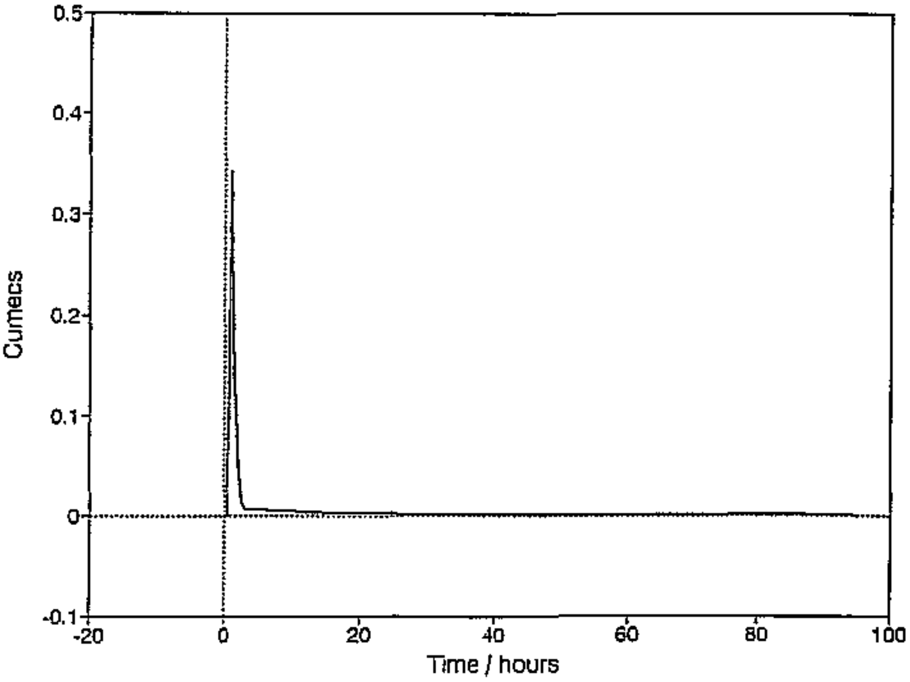


Figure A9b: Flow C10 (28 Nov - 2 Dec 93)

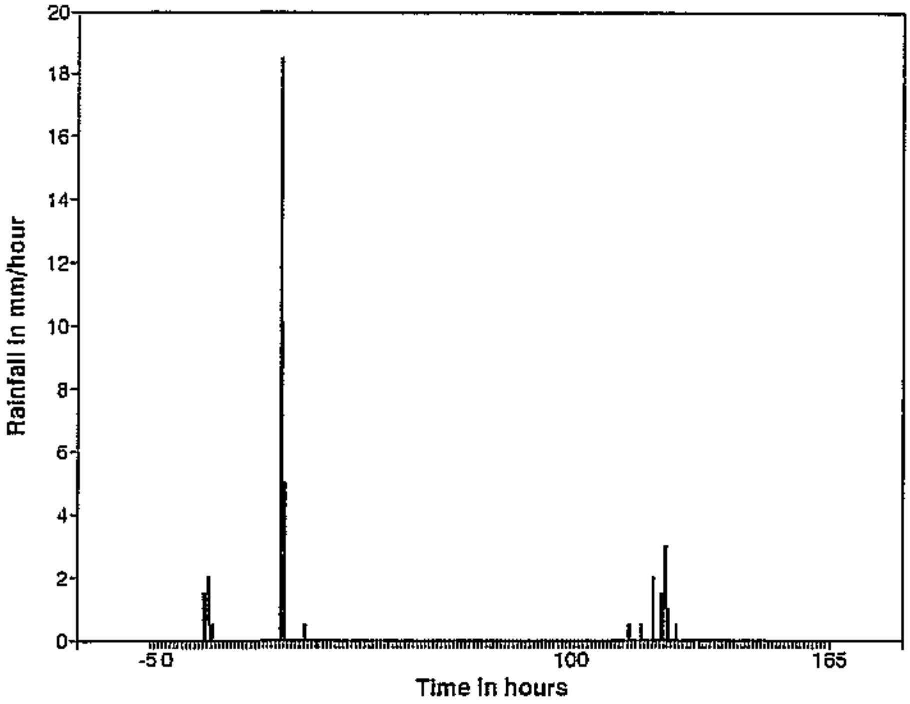


Figure A10a: Rainfall - Flow C11 - 37 mm

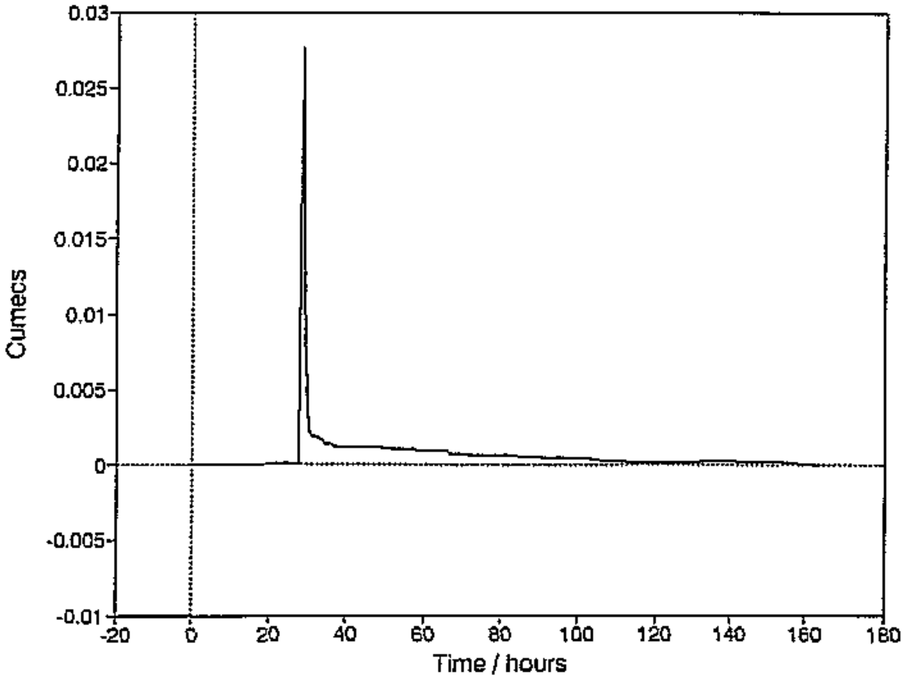


Figure A10b: Flow C11 (2 - 9 Dec 93)

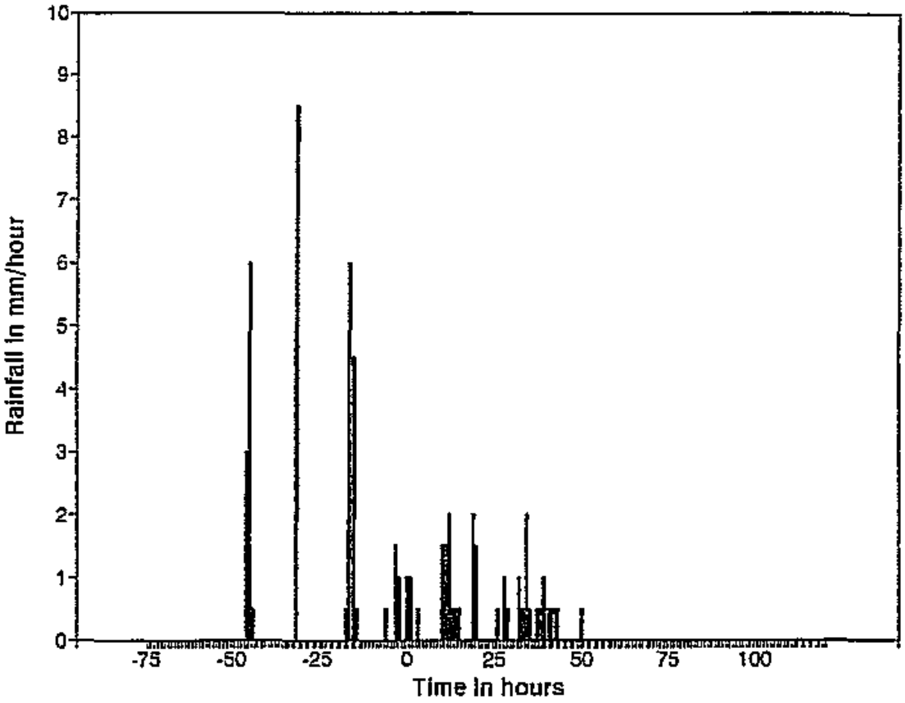


Figure A11a: Rainfall - Flow C12 - 58.5 mm

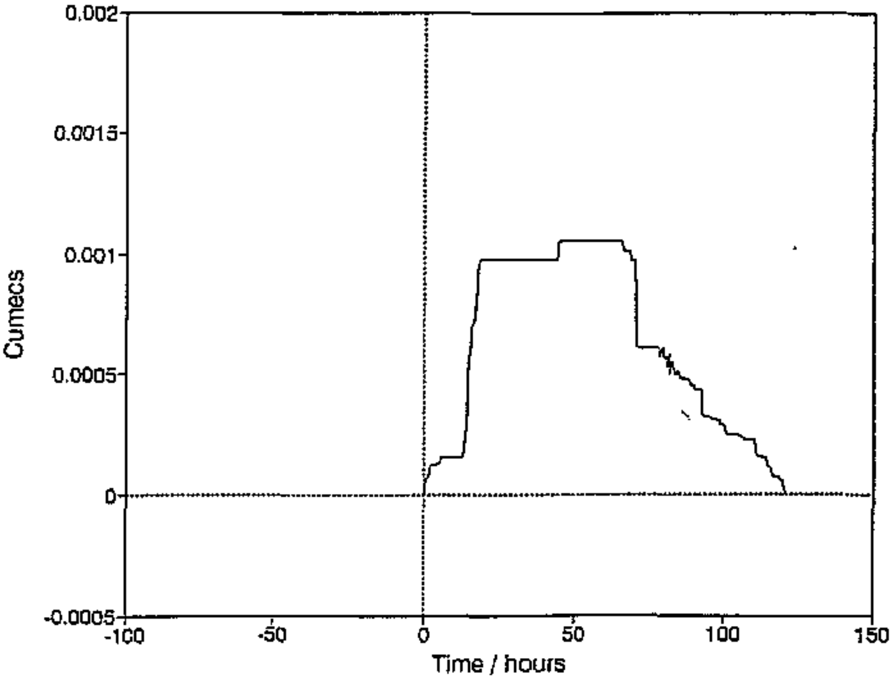


Figure A11b: Flow C12 (23 - 28 Jan 94)

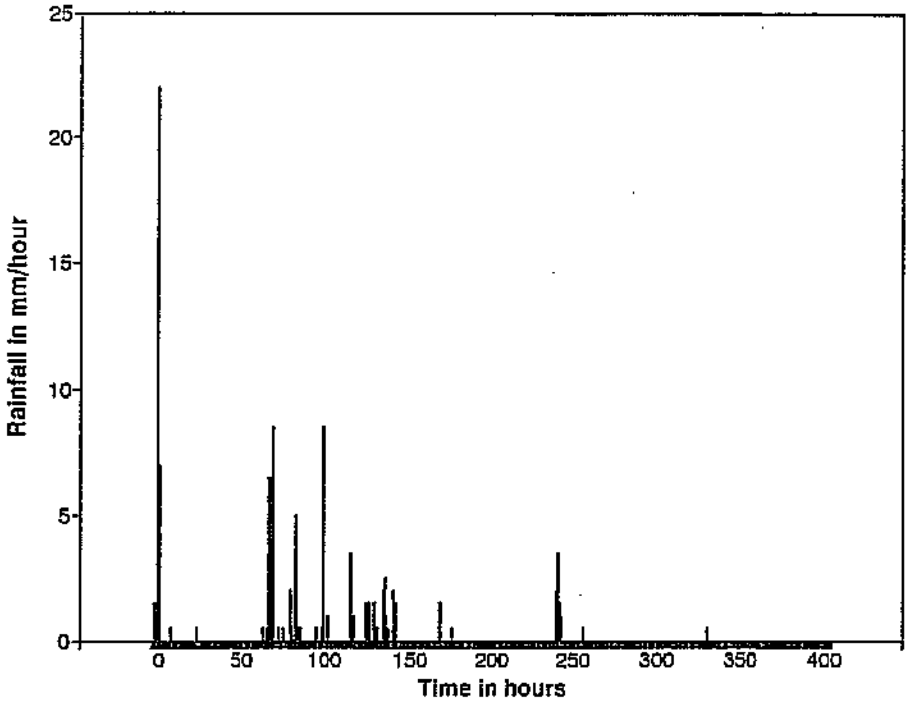


Figure A12a: Rainfall - Flow C13 - 107.5 mm

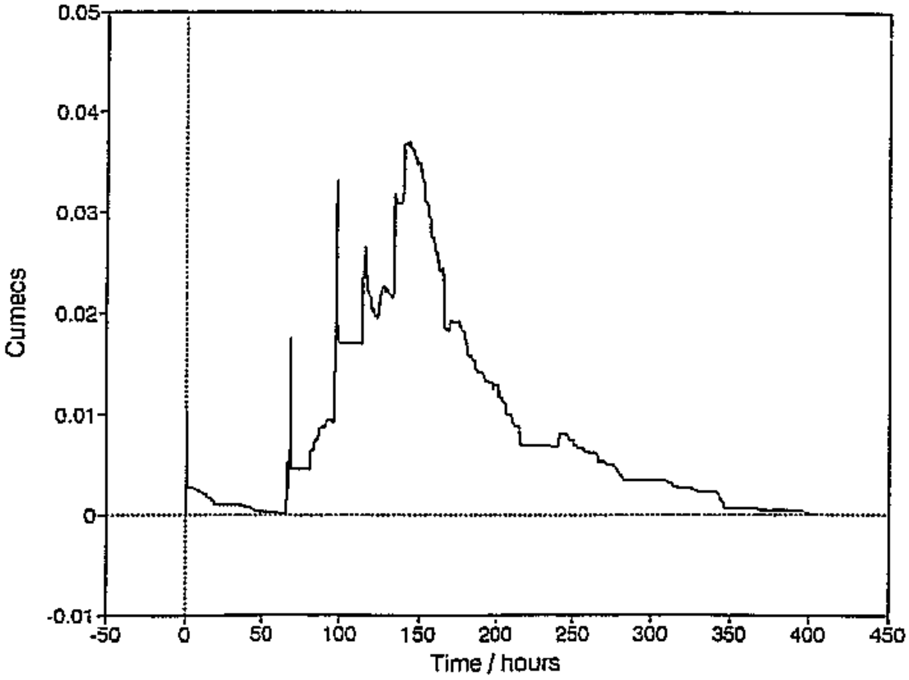


Figure A12b: Flow C13 (2 - 19 Feb 94)

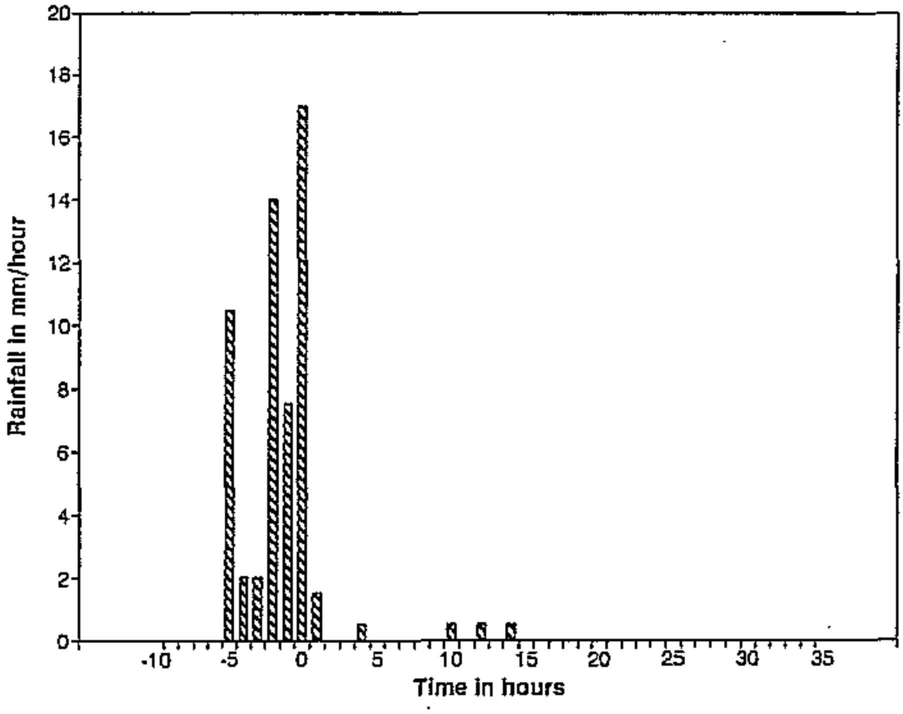


Figure A13a: Rainfall - Flow C14 - 42 mm

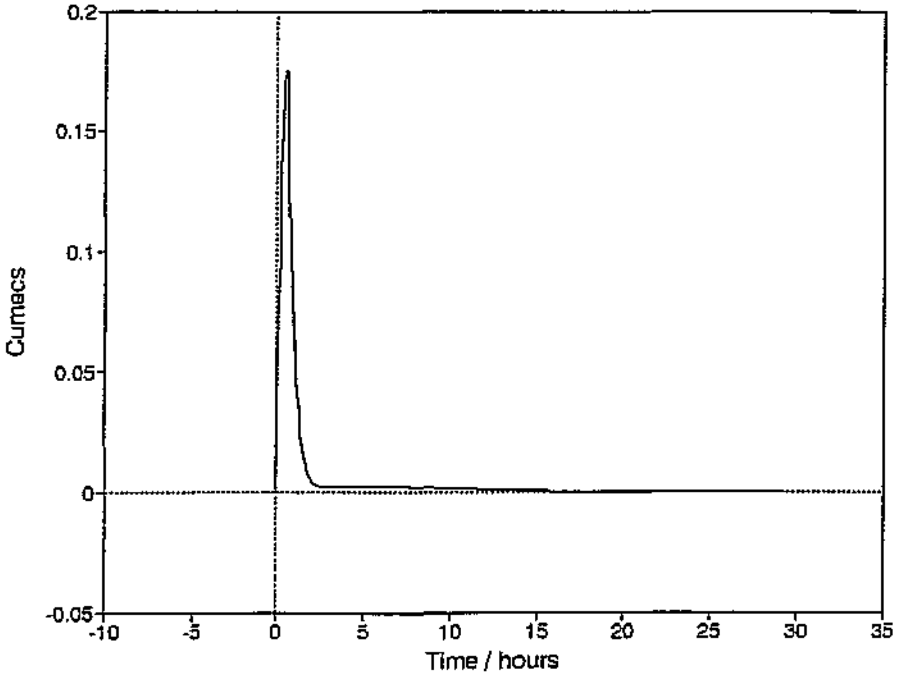


Figure A13b: Flow C14 (28 - 30 Mar 94)

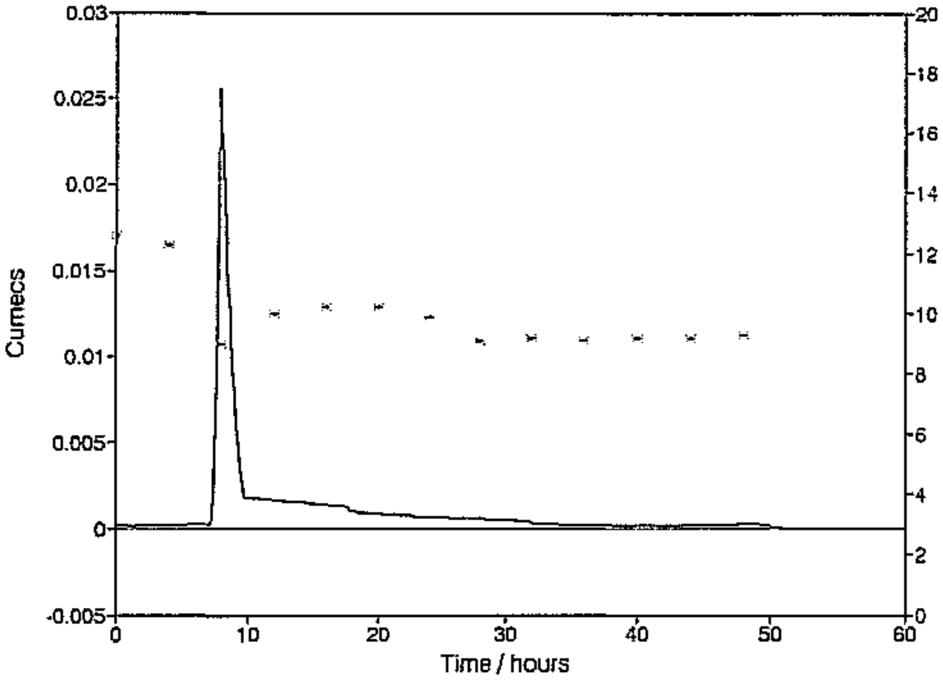


Figure A14: Sulphate Levels and Flow - Flow A2 (11 - 13 Nov 92)

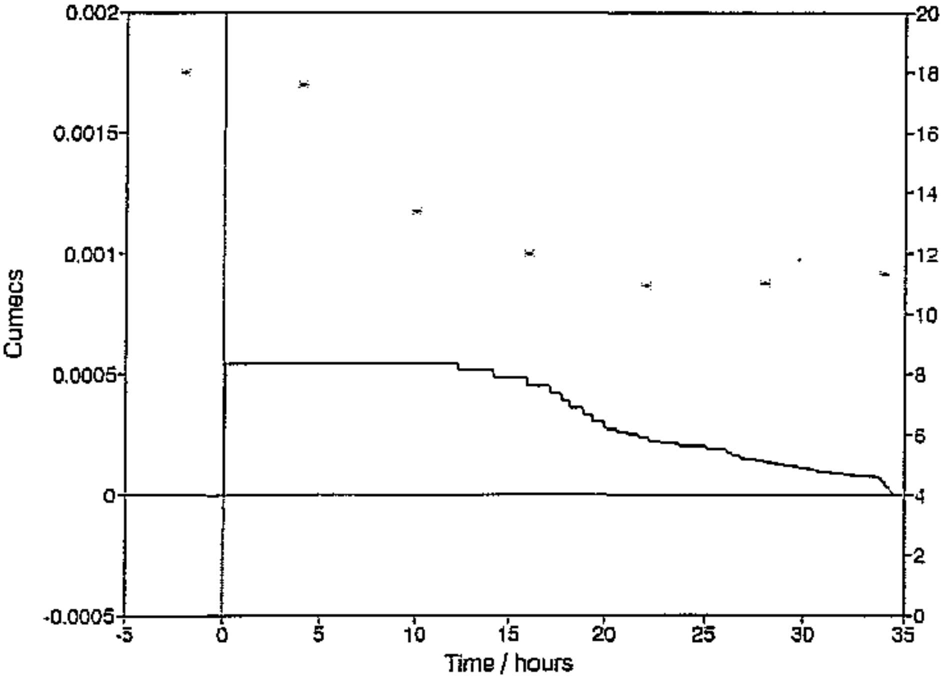


Figure A15: Sulphate Levels and Flow - Flow A3 (12 Dec 92)

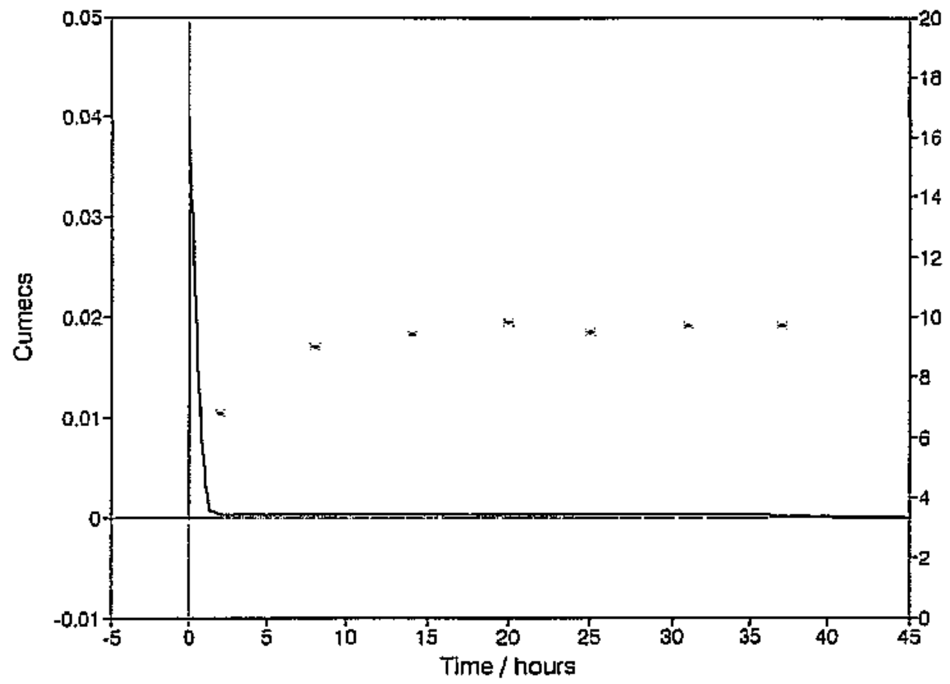


Figure A16: Sulphate Levels and Flow - Flow A4 (21 - 23 Dec 92)

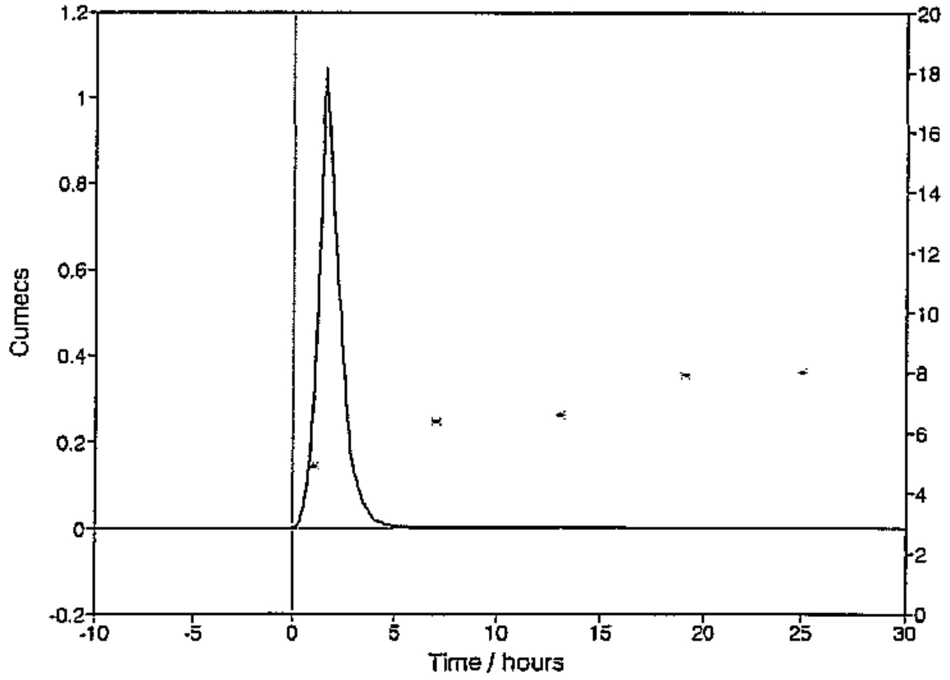


Figure A17: Sulphate Levels and Flow - Flow A5 (12 Dec 92)

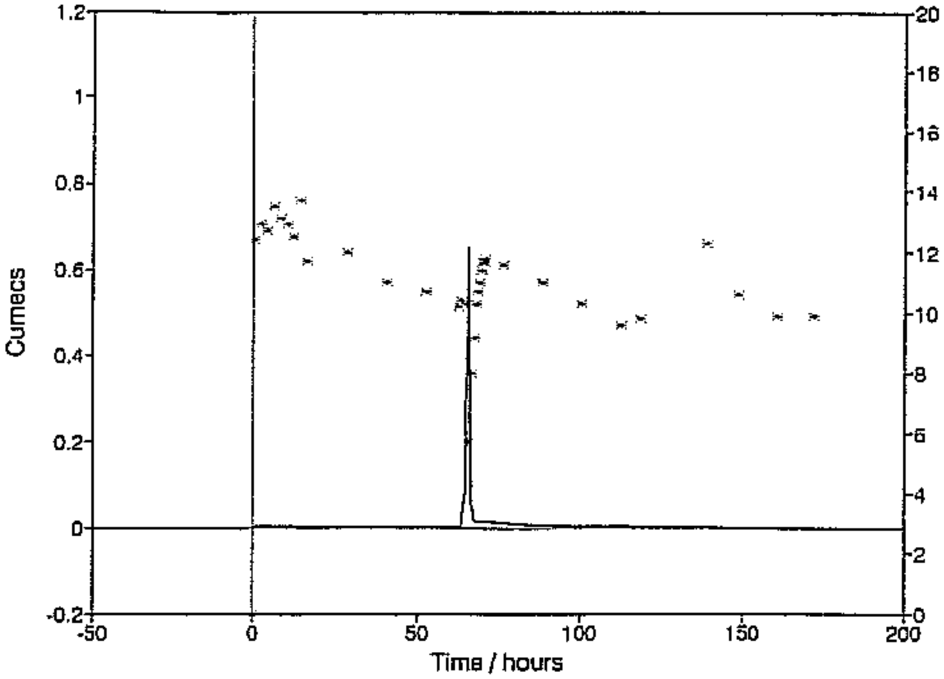


Figure A18: Sulphate Levels and Flow - Flow A7 (1 - 9 Mar 93)

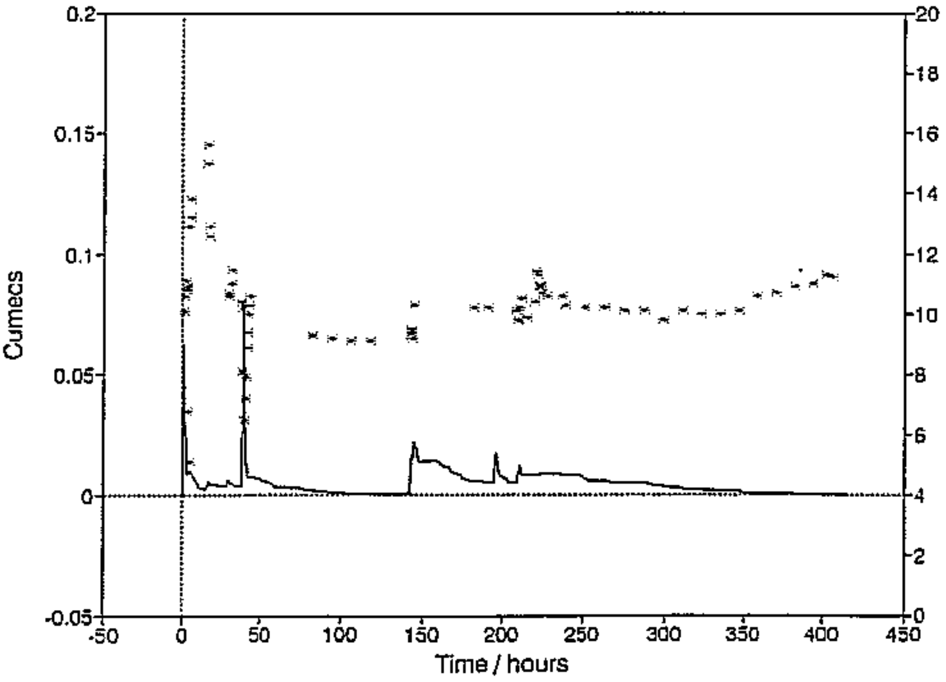


Figure A19: Sulphate Levels and Flow - Flow C8 (6 - 23 Oct 93)

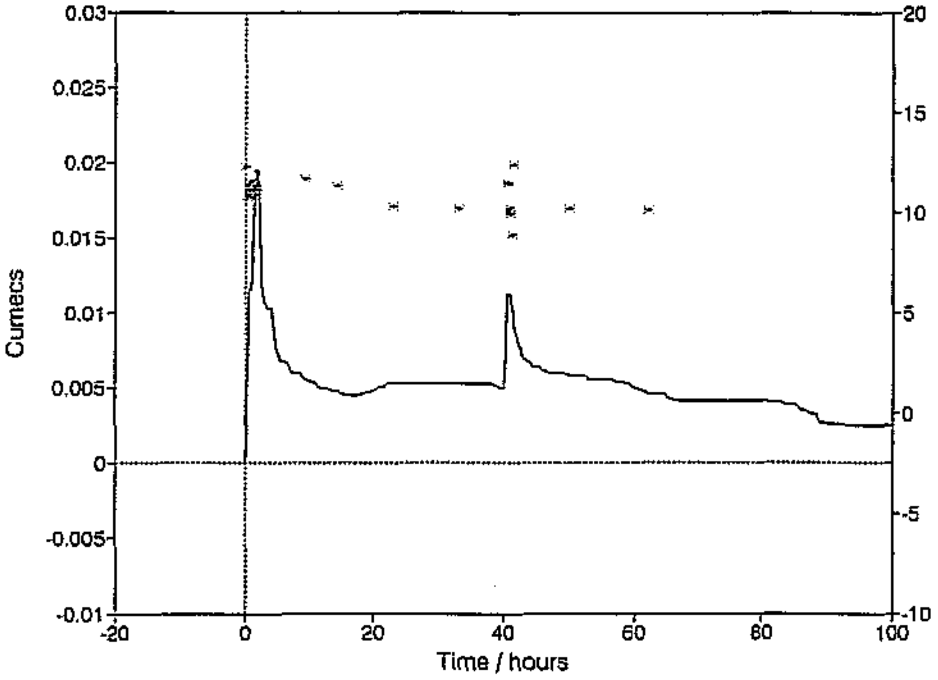


Figure A20: Sulphate Levels and Flow - Flow C9 (25 Oct - 2 Nov 93)

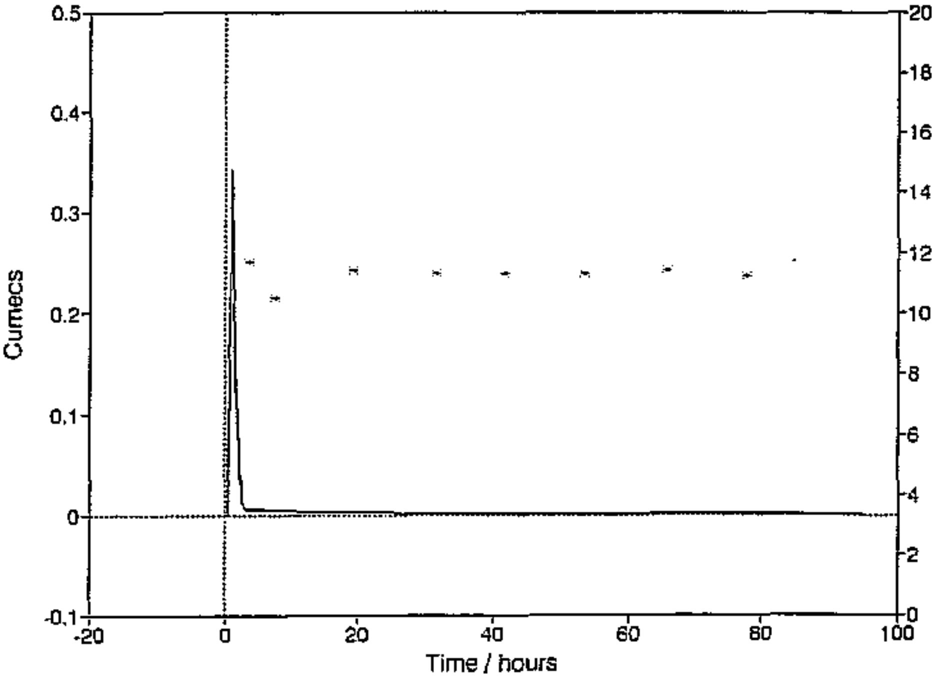


Figure A21: Sulphate Levels and Flow - Flow C10 (28 Nov - 2 Dec 93)

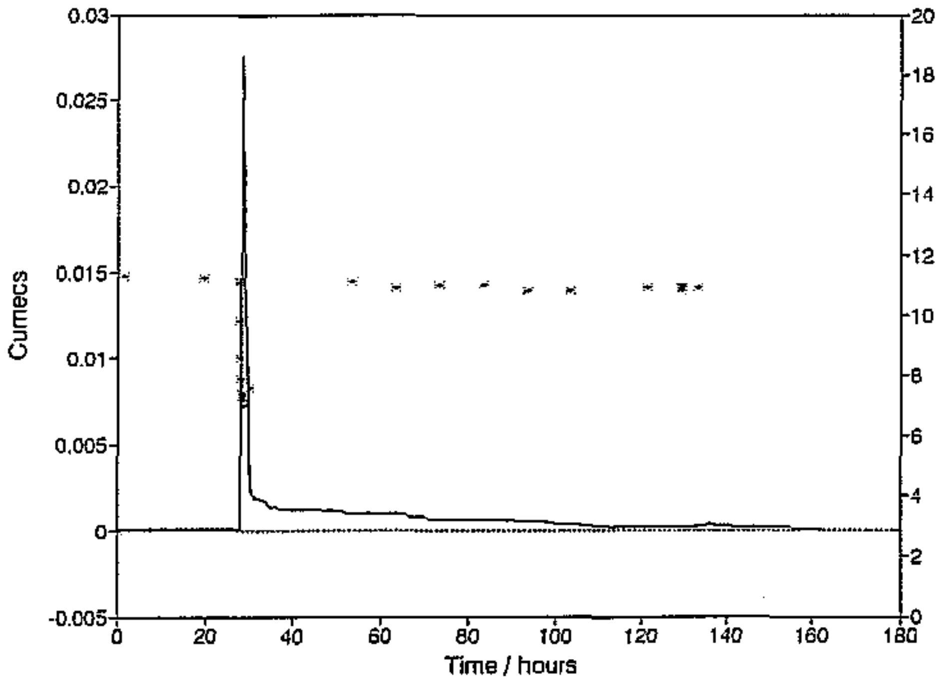


Figure A22: Sulphate Levels and Flow - Flow C11 (2 - 9 Dec 93)

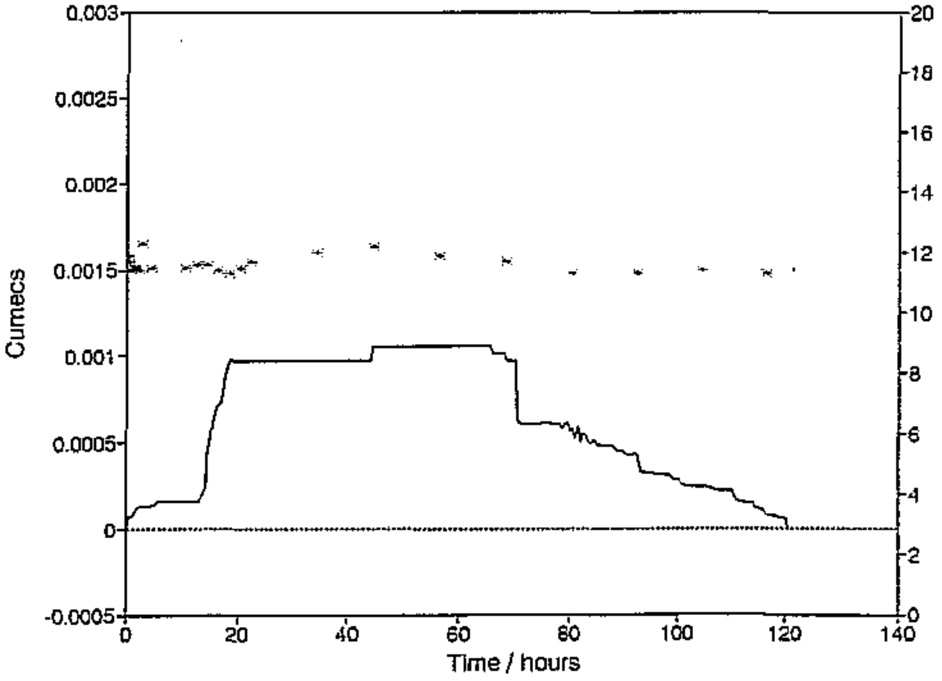


Figure A23: Sulphate Levels and Flow - Flow C12 (23 - 28 Jan 94)

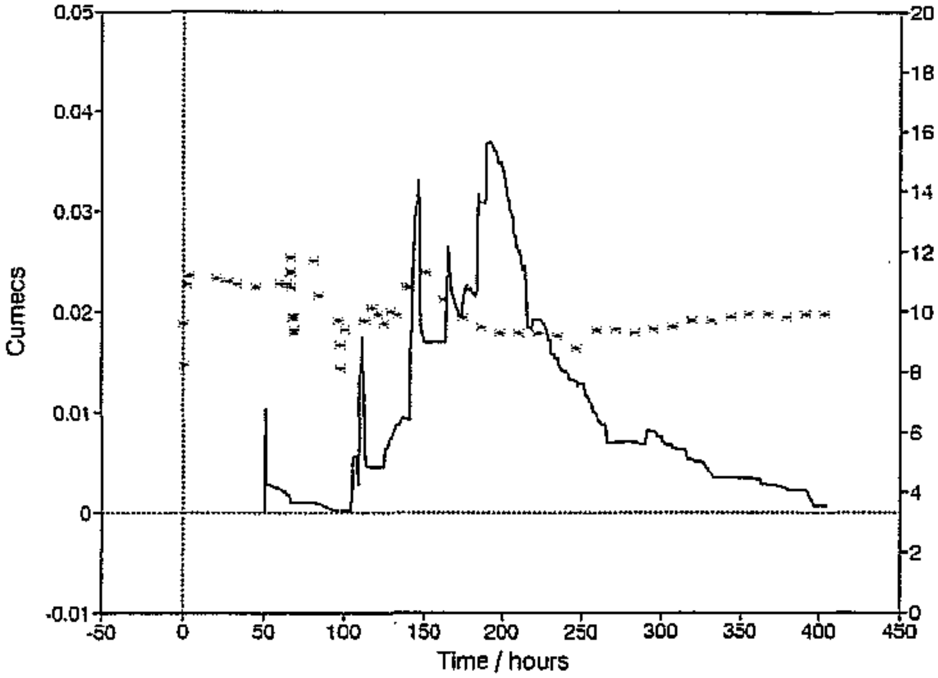


Figure A24: Sulphate Levels and Flow - Flow C13 (2 - 19 Feb 94)

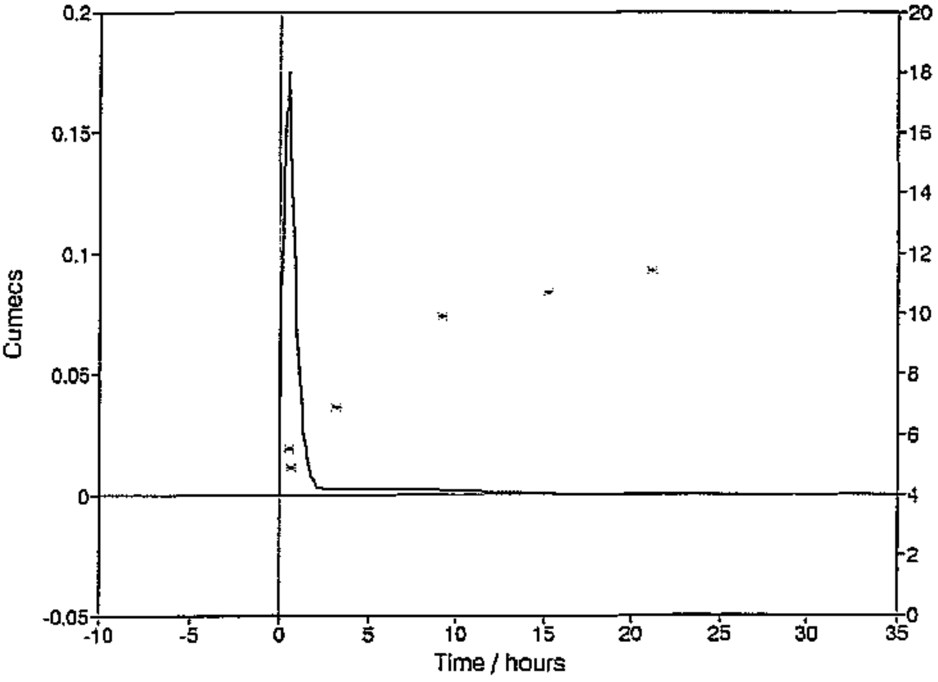
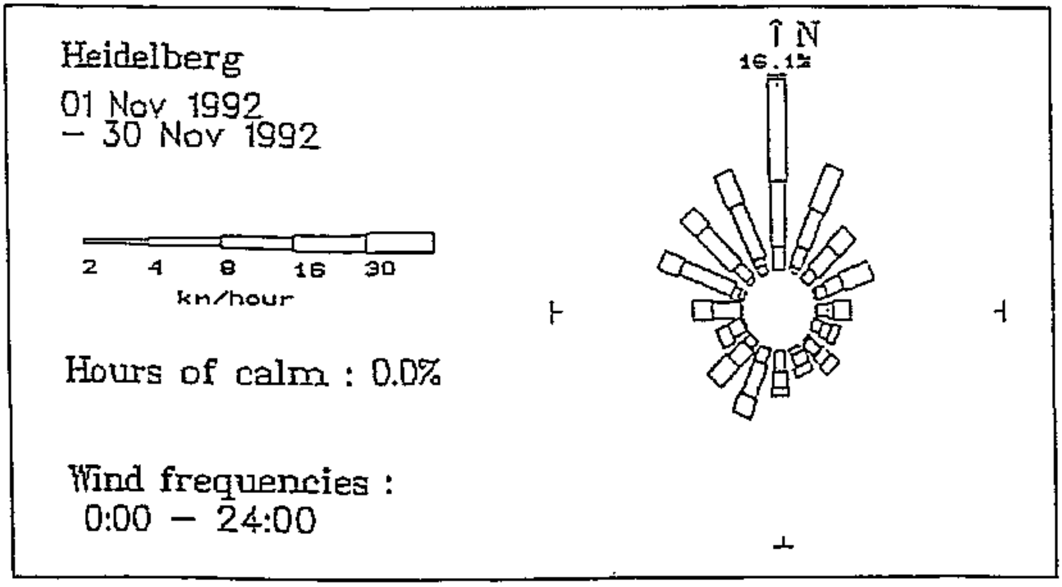
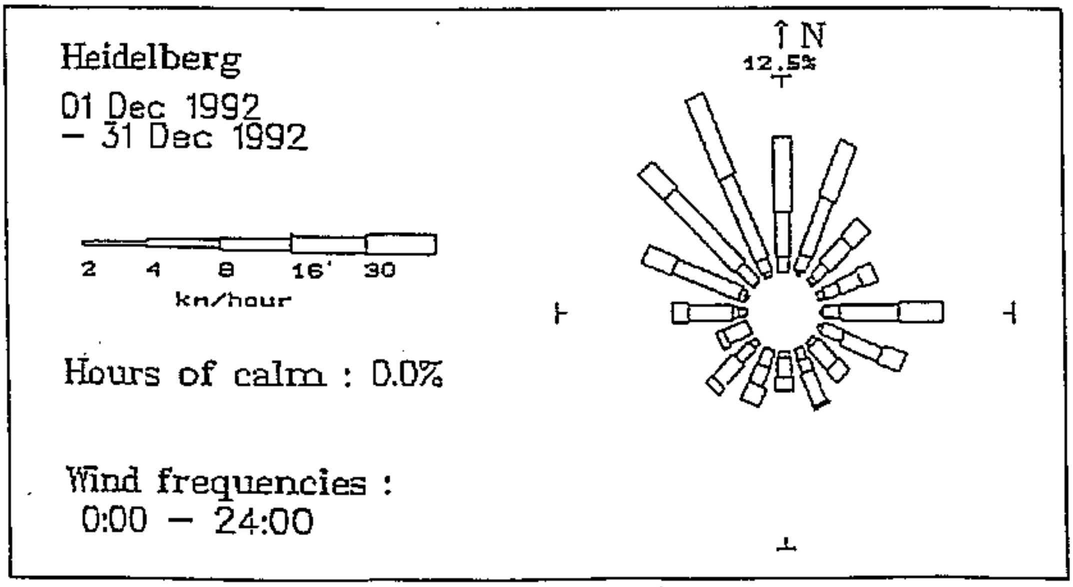
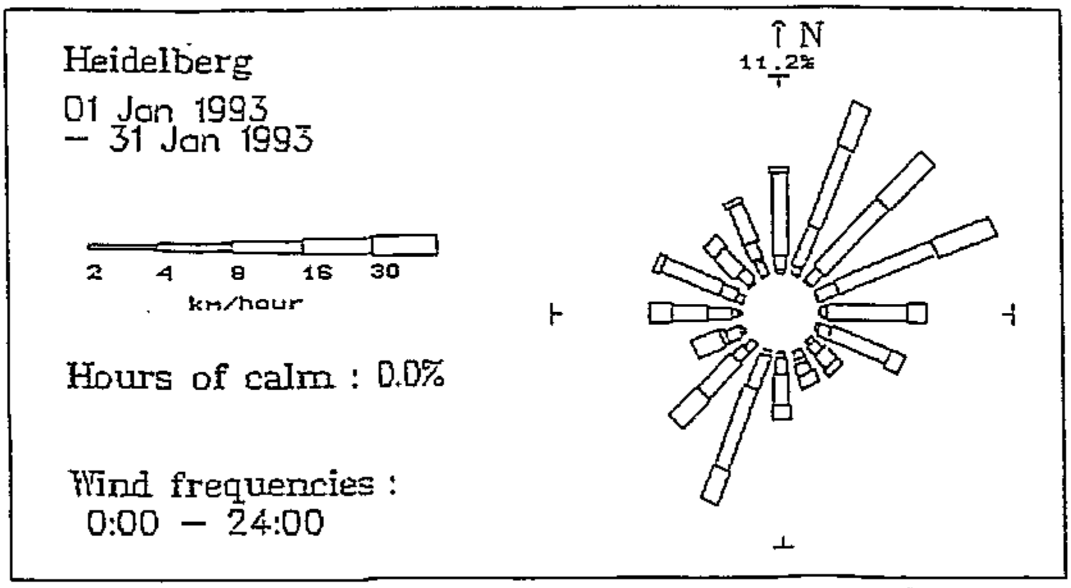


Figure A25: Sulphate Levels and Flow - Flow C14 (28 - 30 Mar 94)


Heidelberg
01 Nov 1992
– 30 Nov 1992
2 4 8 16 30
km/hour
Hours of calm : 0.0%
Wind frequencies :
0:00 – 24:00
N
16.1%


Heidelberg
01 Dec 1992
– 31 Dec 1992
2 4 8 16 30
km/hour
Hours of calm : 0.0%
Wind frequencies :
0:00 – 24:00
N
12.5%


Heidelberg
01 Jan 1993
– 31 Jan 1993
2 4 8 16 30
km/hour
Hours of calm : 0.0%
Wind frequencies :
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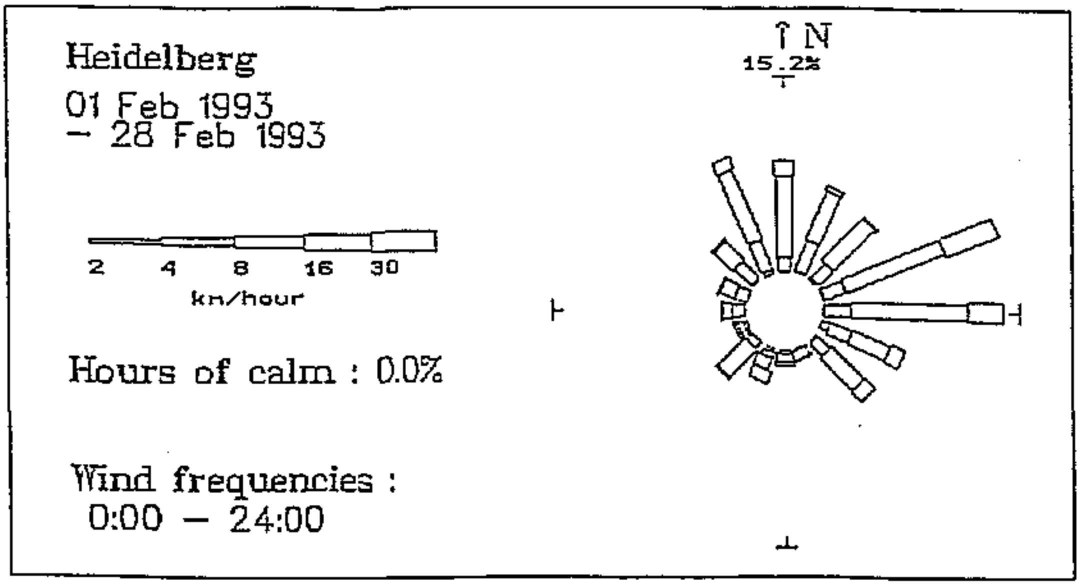
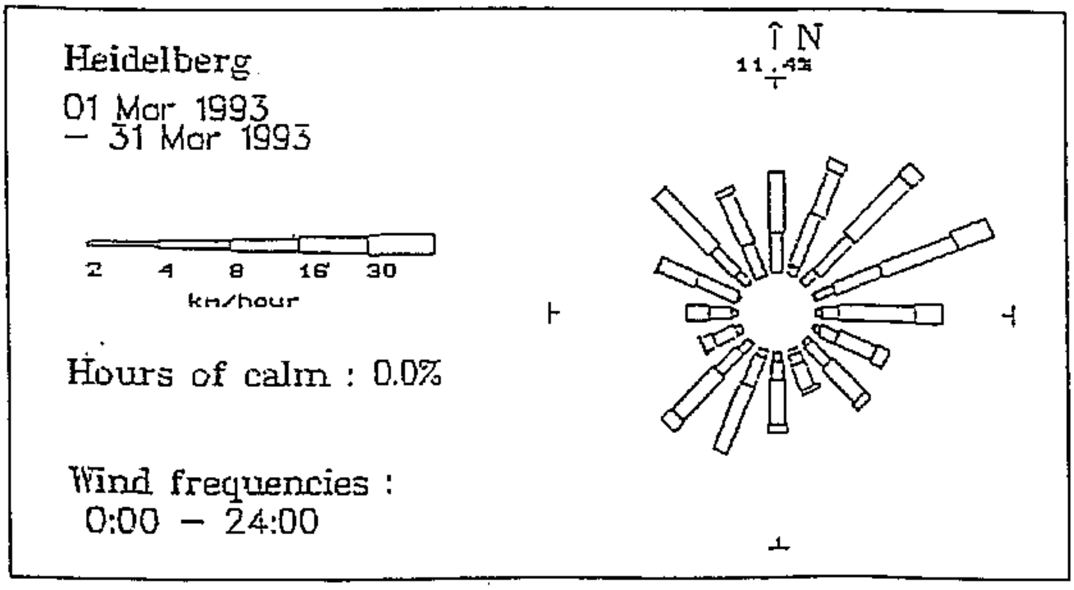
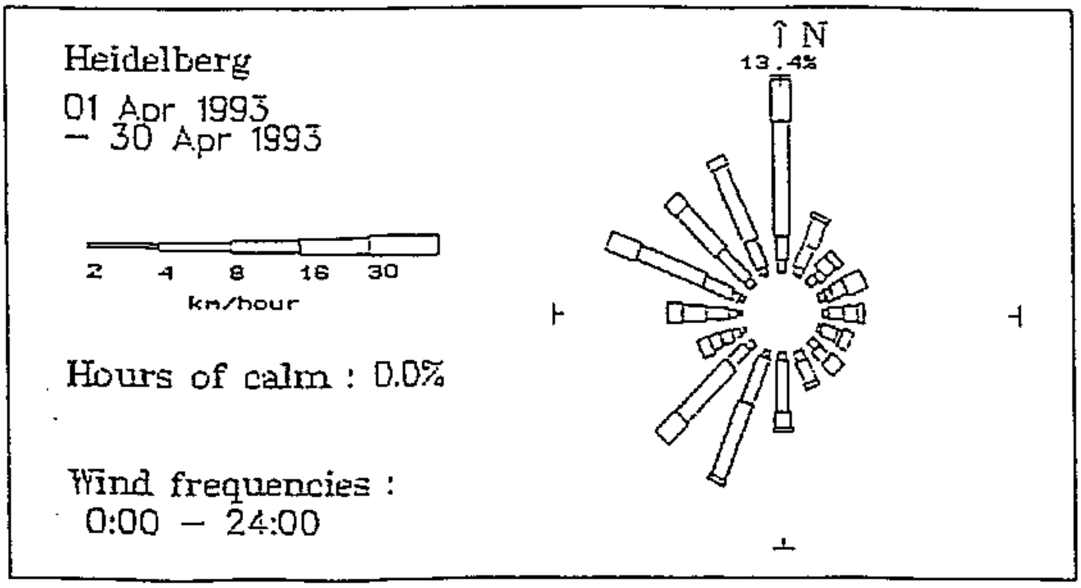
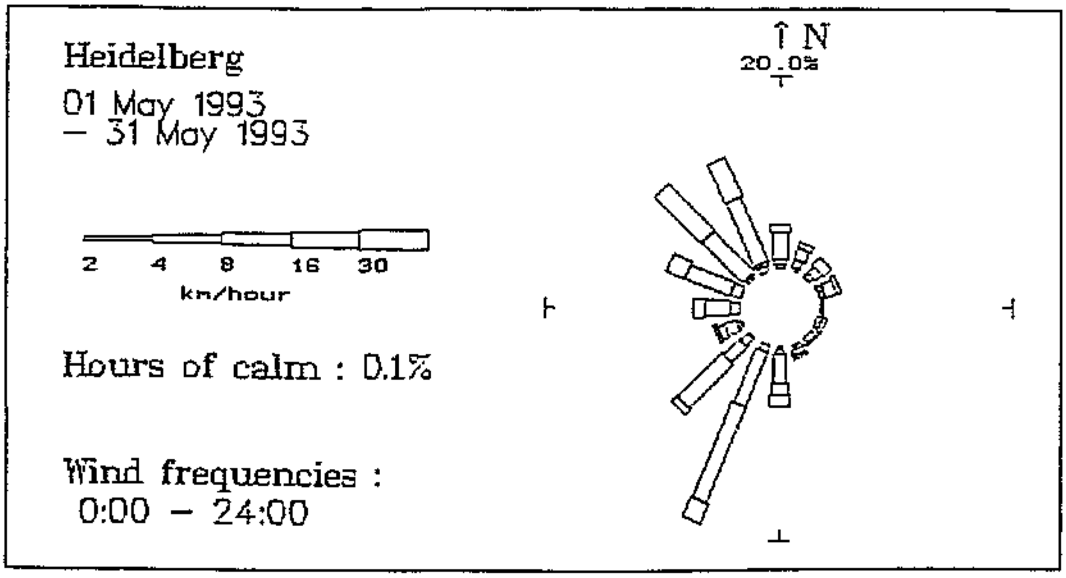
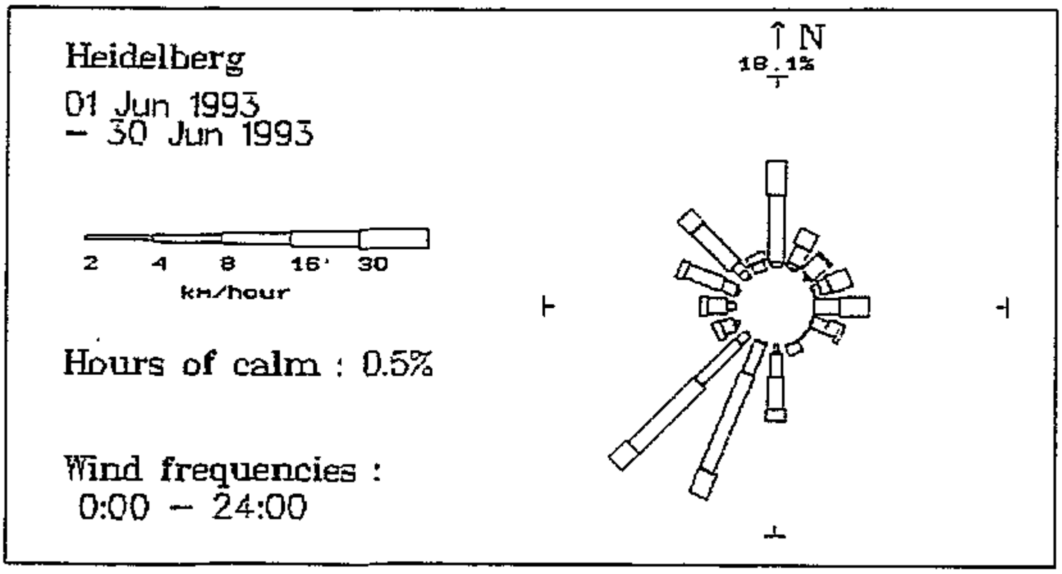
N
11.2%


Heidelberg
01 Feb 1993
– 28 Feb 1993
2
4
8
16
30
km/hour
Hours of calm : 0.0%
Wind frequencies :
0:00 – 24:00
N
15.2%


Heidelberg
01 Mar 1993
– 31 Mar 1993
2
4
8
16
30
km/hour
Hours of calm : 0.0%
Wind frequencies :
0:00 – 24:00
N
11.4%


Heidelberg
01 Apr 1993
– 30 Apr 1993
2
4
8
16
30
km/hour
Hours of calm : 0.0%
Wind frequencies :
0:00 – 24:00
N
13.4%


Heidelberg
01 May 1993
– 31 May 1993
2 4 8 16 30
km/hour
Hours of calm : 0.1%
Wind frequencies :
0:00 – 24:00
N
20.0%


Heidelberg
01 Jun 1993
– 30 Jun 1993
2 4 8 16 30
km/hour
Hours of calm : 0.5%
Wind frequencies :
0:00 – 24:00
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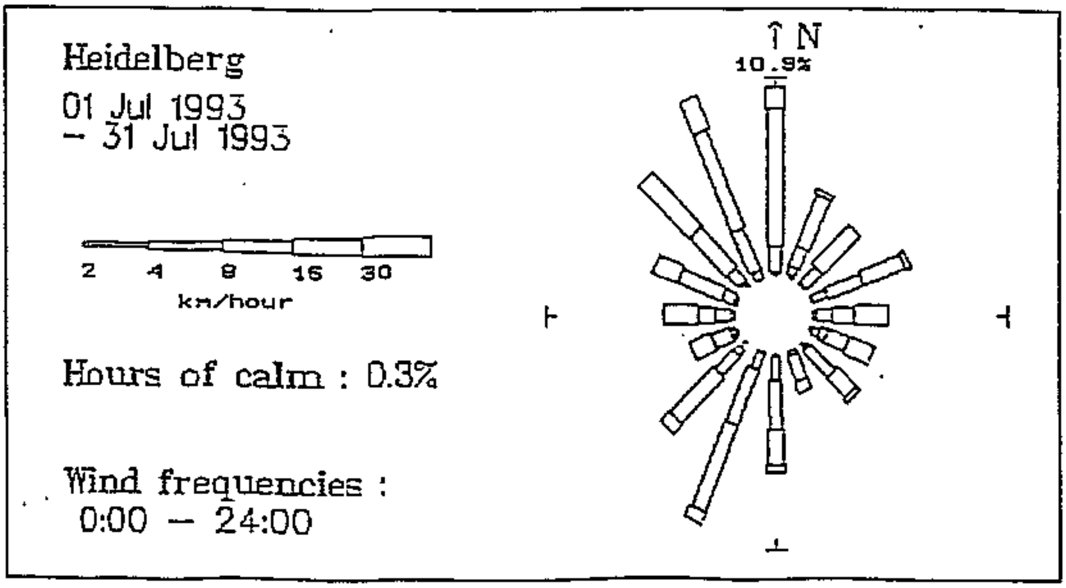
18.1%


Heidelberg
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– 31 Jul 1993
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km/hour
Hours of calm : 0.3%
Wind frequencies :
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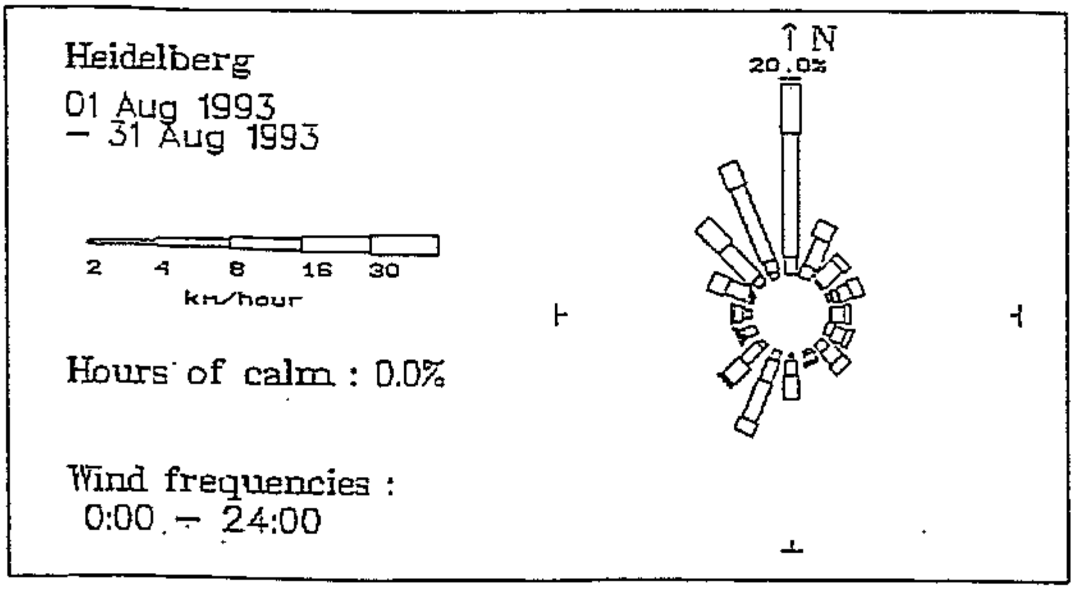
10.9%


Heidelberg
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– 31 Aug 1993
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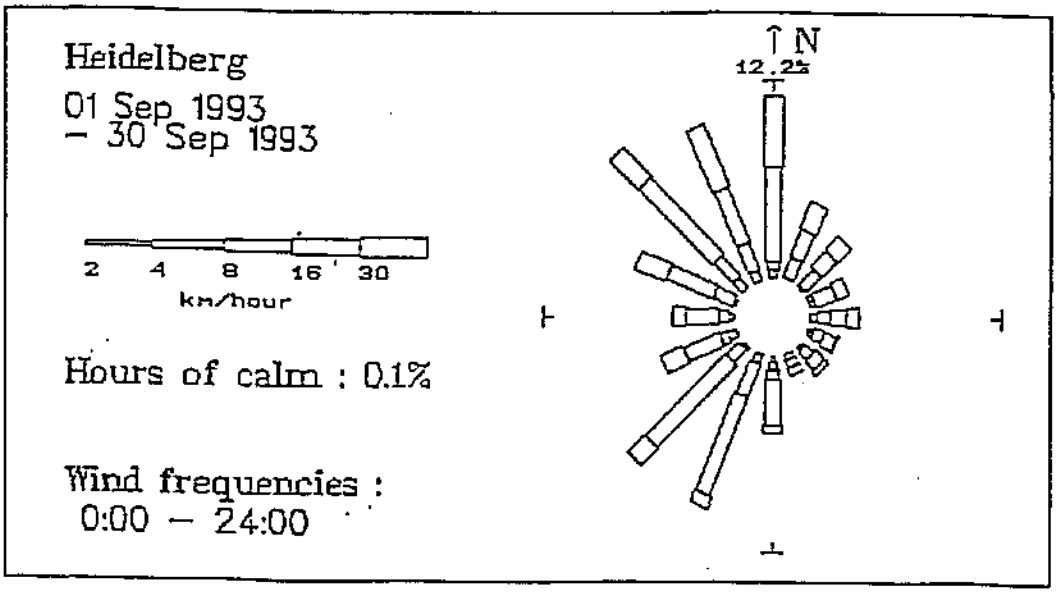
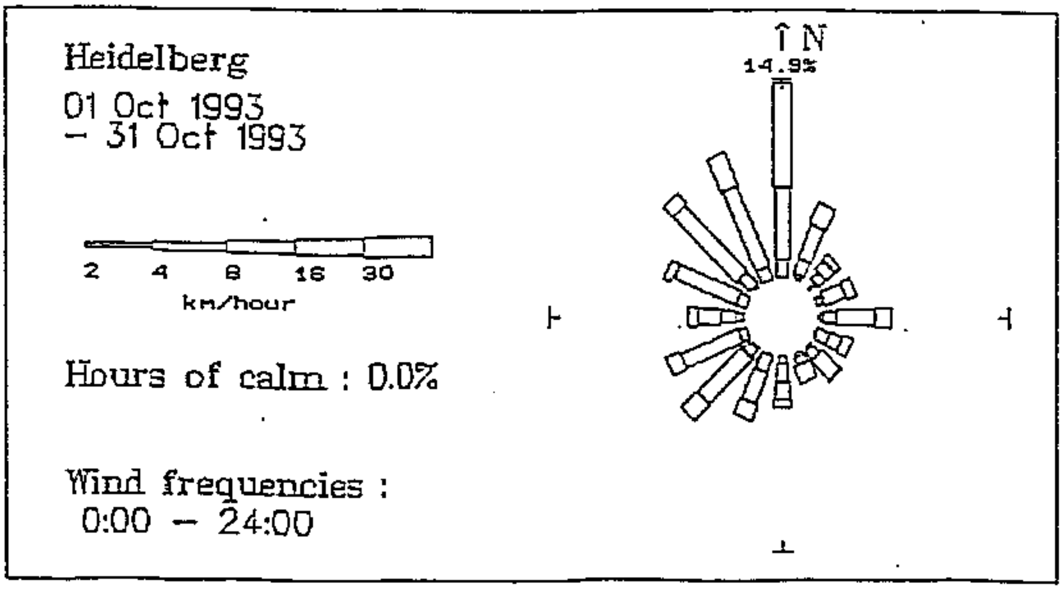
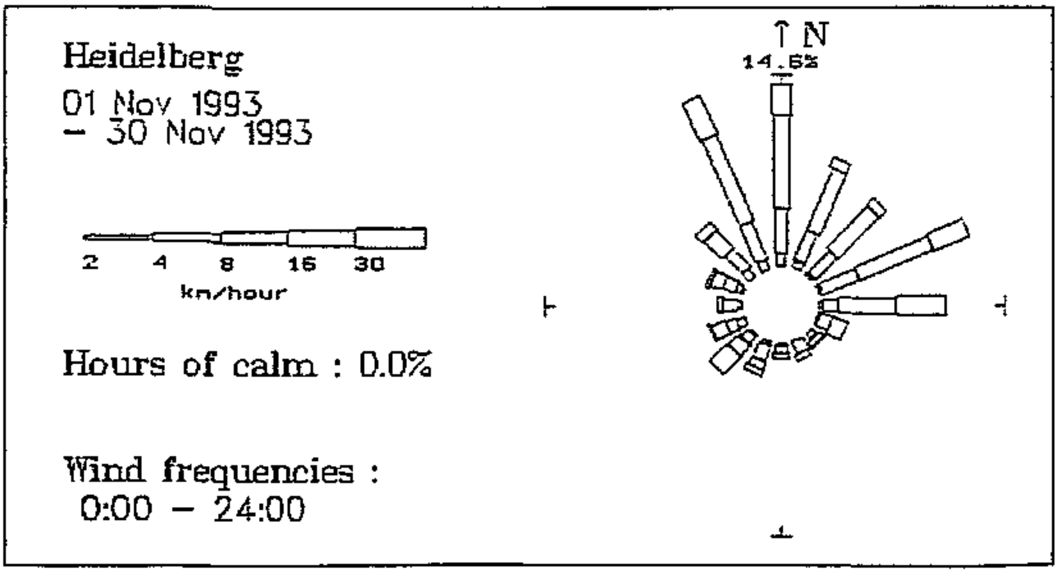
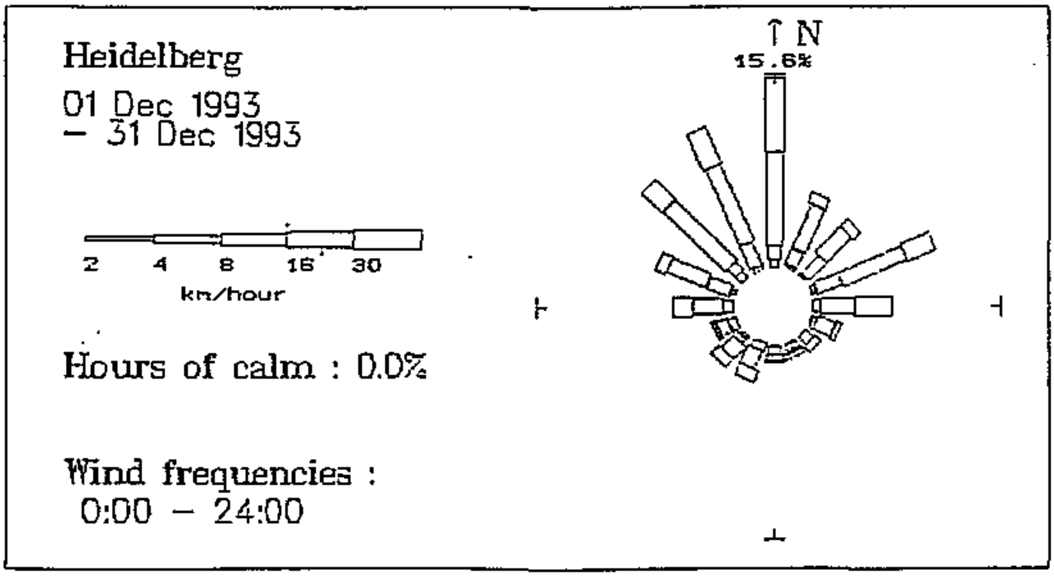
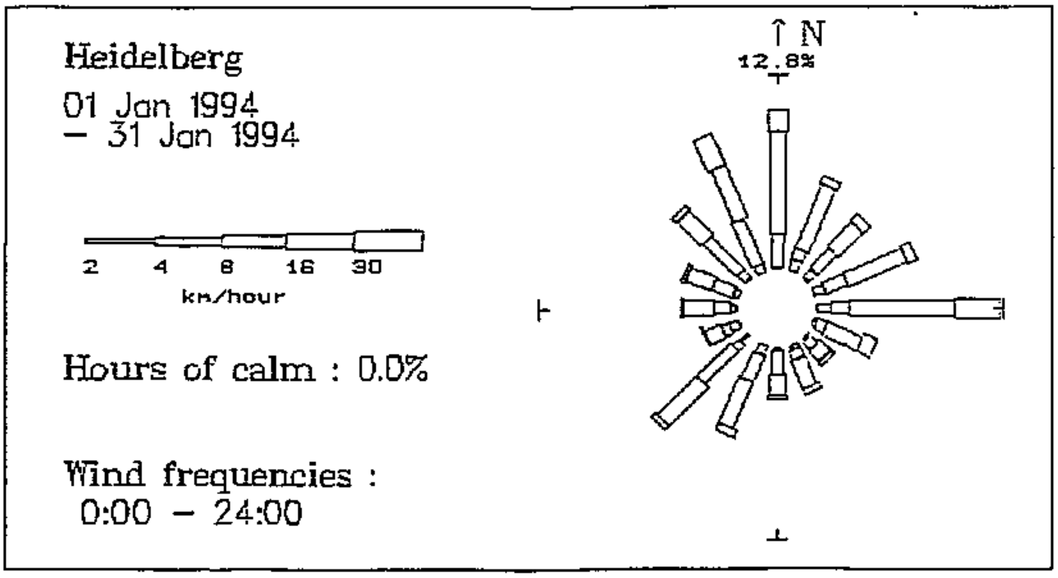
km/hour
Hours of calm : 0.0%
Wind frequencies :
0:00 – 24:00
N
20.0%

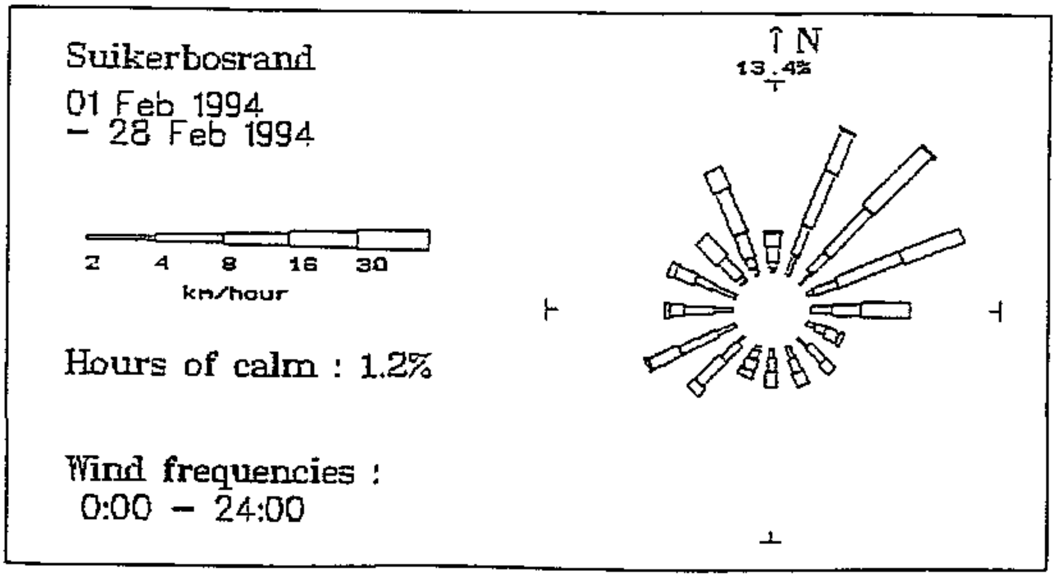

Heidelberg
01 Sep 1993
– 30 Sep 1993
2 4 8 16 30
km/hour
Hours of calm : 0.1%
Wind frequencies :
0:00 – 24:00
N
12.2%

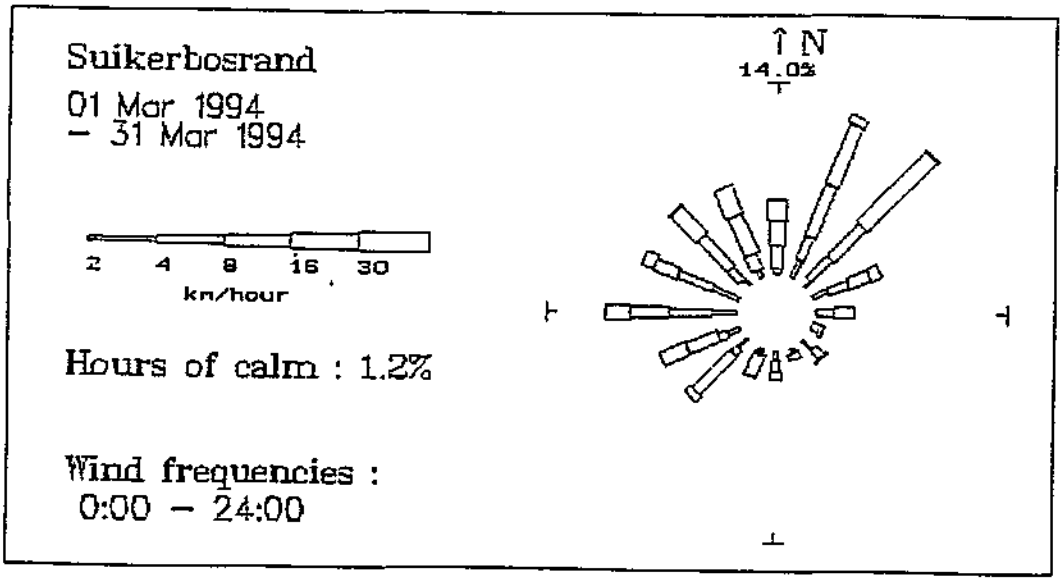

Heidelberg
01 Oct 1993
– 31 Oct 1993
2 4 8 16 30
km/hour
Hours of calm : 0.0%
Wind frequencies :
0:00 – 24:00
N
14.9%


Heidelberg
01 Nov 1993
– 30 Nov 1993
2 4 8 16 30
km/hour
Hours of calm : 0.0%
Wind frequencies :
0:00 – 24:00
N
14.6%


Heidelberg
01 Dec 1993
– 31 Dec 1993
2 4 8 16 30
km/hour
Hours of calm : 0.0%
Wind frequencies :
0:00 – 24:00
N
15.6%


Heidelberg
01 Jan 1994
– 31 Jan 1994
2 4 8 16 30
km/hour
Hours of calm : 0.0%
Wind frequencies :
0:00 – 24:00
N
12.8%


Suikerbosrand
01 Feb 1994
– 28 Feb 1994
2 4 8 16 30
km/hour
Hours of calm : 1.2%
Wind frequencies :
0:00 – 24:00
↑ N
13.4%


Suikerbosrand
01 Mar 1994
– 31 Mar 1994
2 4 8 16 30
km/hour
Hours of calm : 1.2%
Wind frequencies :
0:00 – 24:00
↑ N
14.0%

APPENDIX
continued

Soil Survey Report

CATCHMENT SOIL SURVEY AND ANALYSIS REPORT FOR A STUDY CATCHMENT AT SUIKERBOSRAND

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CATCHMENT SOIL SURVEY AND ANALYSIS REPORT FOR A STUDY CATCHMENT AT SUIKERBOSRAND

AIM : The objective of this study was to firstly : -

1. compile a soils map of a 31 ha catchment in the Suikerbosrand range,
2. classify the catchment into zones of uniform classification and depth and,
3. obtain representative samples of the soil-types for laboratory analysis.
4. Secondly, to analyze composite samples with respect to their sulphate and,
5. soil water retention capacities.
6. Thirdly, a prediction of the probable effect of sulphate buffering, by the soil, of an annual loading, was envisaged.

METHODS :

1. Fieldwork

On the 23rd, 24th and 25th of November 1992, a detailed soil survey of the study catchment was carried out. This involved the identification of soil types (based on the taxonomical soil classification system for South Africa) and depth classes based on a fine network of auger points.

Samples were taken at each point and similar soils mixed into composites for laboratory analysis. Zones representing these similar soil-type/depth class/% rock combinations were delineated to produce a soils map of the catchment.

Results

Three soil-types were identified in the catchment:

1. Most of the catchment has a very shallow soil covering comprising of loamy sand orthic A-horizon associated with a substantial percentage of exposed rock, the Mispah 1 100 form/family.
2. The Oakleaf soils generally have a thin A-horizon overlying a red, non-luvic neocutanic B. A neocutanic B is one which occurs in unconsolidated material, usually transported, which has undergone a small degree of pedogenesis.

3. The deepest soils were classified as orthic A-horizon over a yellow-brown apedal B (Clovelly form/family combination). The B horizon in this case has a very weak structure and a loamy sand texture.

2. Analysis

Five composite samples were selected as typical of the range of soils in the catchment. These included two Mispahs, two Oakleafs and one Clovelly. Particle size (Table 1) and sulphate retention breakthrough (Table 2) analyses were carried out on them. The pH (1M KCl) of all samples were measured to ensure the applicability of the selected samples. The results supported the representation (Table 3).

While particle size analysis and pH measurement are standard procedures, elaboration on the techniques used to determine the sulphate retention breakthrough curves is called for.

This experiment involved a leaching and loading procedure using prepared soil columns. The columns were firstly leached using distilled water to remove all excess salts. The endpoint of this part of the experiment is when the leachates' electrical conductivity value showed no change between successive pore volumes. Thereafter a dilute solution of H_2SO_4 was drained through the columns and the ECs measured as before. The breakthrough point is that point where the attenuating capacity of the soil for sulphate is reached and corresponds to a sharp increase in EC.

Results

The catchment for the most part shows an average breakthrough index of approximately five pore volumes. A small area of the catchment has a breakthrough at two pore volumes. The overall average texture of a loamy sand is indicative of rapid infiltration of low water retention.

Table 1 : Particle size analyses

Sample No.	% Clay	% Silt	% Sand
12-24	9.18	12.15	78.87
35/36/39	12.31	14.72	72.97
46A	12.41	10.89	76.7
46B	17.17	11.54	71.29
47/48A	9.78	9.26	80.96
47/48B	11.03	9.45	79.52
53/54A	9.95	11.79	78.26
53/54B	9.13	7.57	83.3

Table 2: pH (1 M KCl)

Sample No.	pH (KCl)
4-11	3.94
12-24	4.02
17/33A	3.9
17/33B	4.22
31.45	4.3
35/36/39	3.94
46A	4.3
46B	4.19
47/48A	4.01
47/48B	4.18
30/51/52	4.06
53/54A	3.9
53/54B	4.25
56/57/58	3.78
59/60/61	4.58
1, 2, 3, 7A	4.01
1, 2, 3, 7B	4.24

3. Interpretation

Table 3 : Sulphate retention EC breakthrough values

Pore volume	Control (6AB)	12-24	35/36/39	46AB	47/48AB	53/54AB
1	7.96	10.06	13.4	11.4	8.33	10.05
2	6.88	9.46	12.33	12.93	8.02	9.21
3	6.44	8.46	11.7	20	7.41	8.68
4	6.71	13.5	11.8	27.2	7.4	8.57
5	7.82	9.3	14.1	30.6	7.8	8.61
6	9.95	12.46	18.5	32.5	14.7	9.95
7	10.1	17.8	22.8	34.1	19.7	14.4
8	13.1	22.2	26.1	34.3	24.1	19.6
9	16.2	25.6	28.5	34.8	27.2	24.7
10	19.3	27.8	30	35	29.3	28.6
11	22.7	29.5	31.1	35.2	30.8	31.1
12	26.1	30.6	32	35.4	32	33.1
13	28.4	31.5	32.5	-	32.6	34.3
14	29.9	32.5	32.8	-	33.1	35.4
15	30.9	32.1	33.7	-	33.6	35.7
16	31.6	33.2	33.5	-	33.9	36.5
17	32	33.3	33.7	-	34.3	37
18	32.4	33.6	33.7	-	34.7	37
19	32.6	33.7	-	-	34.6	37.4
20	32.8	33.7	-	-	34.8	37.6
21	32.9	33.8	-	-	34.8	37.9
22	33.1	-	-	-	35	38.1
23	33.1	-	-	-	35	38
24	33.3	-	-	-	-	-
25	33.3	-	-	-	-	-

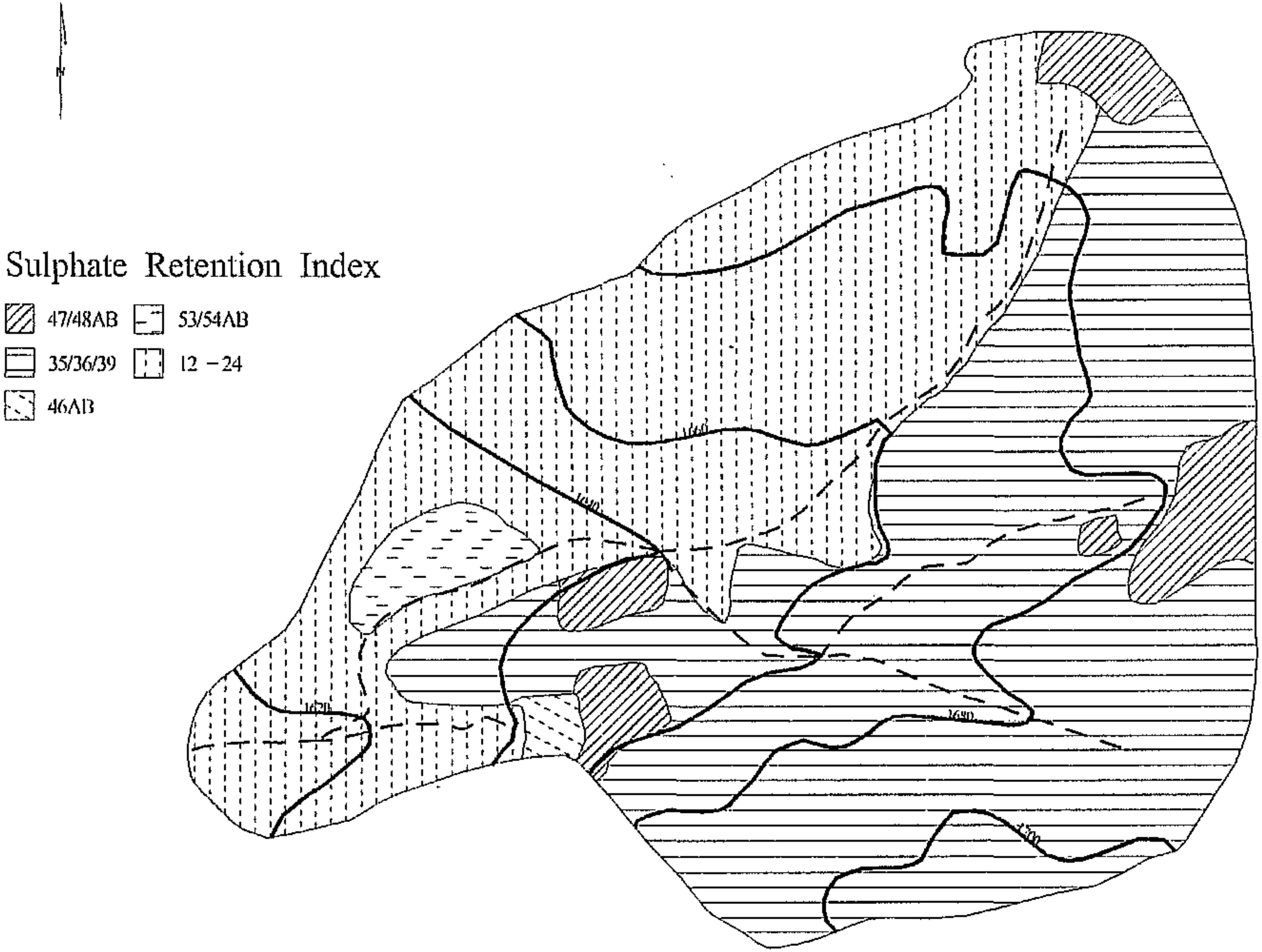

Fig S2: Map of Sulphate Retention Capacity