GEOCHEMISTRY OF A PRISTINE FYNBOS ECOSYSTEM IN THE HAROLD PORTER NATIONAL BOTANICAL GARDENS AND KOGELBERG BIOSPHERE RESERVE

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ABSTRACT

Water, soil and rock samples were taken from the Harold Porter National Botanical Gardens and the Kogelberg Biosphere Reserve in order to investigate interactions between the various nutrient pools in a pristine fynbos ecosystem. Physical variables (pH, EC, temperature, DO, alkalinity) were measured in the field, and water samples were collected and analysed for chemical composition. Chemical composition and mineralogy of soil and rock samples from the Peninsula, Cedarberg and Goudini formations were determined to assess the influence of parent geology on soil chemistry. The surface water chemistry in the study area was remarkably homogeneous, with only major ions Na, Cl, Mg, Ca, Si and SO_4 exceeding concentrations of 1 ppm at any of the sample sites. Concentrations of other major ions Al, K, NH_4, NO_3 and Fe ranged between 0.1 and 0.7 ppm. The minor and trace elements B, Sb, Sr, Zn and Mn were present in concentrations greater than 1 ppb. Compared to the seawater chloride ratio, Na, Mg, K and SO_4 were depleted in the streams relative to Cl, showing that these elements are preferentially accumulated and are conserved within the fynbos ecosystem. In contrast, Ca/Cl ratio is elevated in streams, indicating an external source of Ca other than the seawater. This source may be windblown dust. The Fe content of soils appears to be lower than that of the parent bedrock, especially in the case of the iron-rich Goudini Formation. This indicates an as yet undetermined pathway for iron to leave the system, which may be through deeper anoxic groundwaters in the area. Only one site from the Oudebosch River headwaters showed significant deviation from other sites in several of the elemental trends, and also had no measurable DOC content, compared to the other sites which ranged from 10 to 16 mg/L DOC. These differences are probably the result of the different vegetation (afromontane forest as opposed to fynbos) and geological setting (clay rich, Cedarberg Formation soils). Soils contained higher concentrations of water-soluble ions than the streams, and organic carbon content ranges from 6 to 34 wt%. Organic O horizons and Melanic/Humic A horizons constituted the major soil types. Cation exchange capacities of the soil samples ranges between 31.3-93 $mmol_c/kg$, and about half

of the soil samples were determined to be acid saturated and fairly leached of ions, probably due to the high rainfall. The soil composition and mineralogy correlate well with that of the underlying bedrock, and was dominated by quartz, with some clays, micas, feldspars and hematite. The study was similar to one in the Cedarberg, which has the same geological setting and equal fynbos species richness. This is the first integrated geochemical study to characterise the pristine fynbos biome of the Harold Porter National Botanical Gardens and the Leopards Gorge River Catchment, and will allow rapid assessment of any future changes.

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CHAPTER 1: INTRODUCTION

1.1 Stream Chemistry

Rivers and streams are the major transport pathways for erosion products from continents to the oceans. Geochemists study these systems to attempt to estimate the fluxes of continental material supplied to the oceans and to calculate chemical and physical weathering rates. They also provide important information on CO_2 consumption through the weathering of continental rocks. Such studies also enable deductions to be made concerning the average chemical and isotopic composition of Earth's continental crust and the processes that govern elemental distribution between particulate and solution phases in rivers (Picouet *et al.,* 2002). However, stream chemistry and cycling of nutrients is complex due to interacting factors and inputs from atmospheric deposition, groundwater recharge, riparian vegetation, weathering of rocks and soil water (Figure 1.1). These factors all need to be considered before a complete understanding of stream chemistry can be reached, especially in the case of the unique fynbos biomes of south-western South Africa.

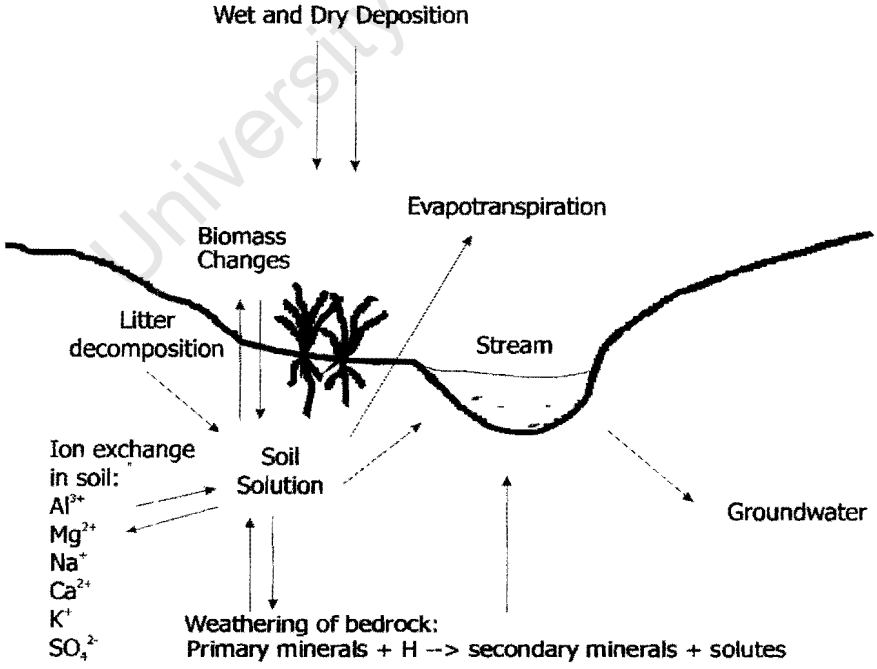


Figure 1.1. Typical inputs, outputs, and nutrient cycling within natural systems (adapted from Drever, 1997).

The Cape Floral Kingdom, situated in the Western Cape province of South Africa is one of the six floral kingdoms in the world, along with the Boreal, Patagonia, Paleotropical, Neotropical and Australian Kingdoms, and at 0.04% of the Earth's surface, is also the smallest (Gale, 1992). The fynbos (meaning "fine bush") biome is characteristic of this kingdom, and qualifies as an ecological hotspot in terms of loss of biodiversity (Myers *et al.,* 2000). There is thus a need to characterise the remaining pristine portions of this biome in terms of geochemistry and nutrient cycling in these globally unique environments. This reasoning spurred two projects, in two geographically separate, but ecologically similar locations, with this aim in mind. The first was done by Soderberg (2002) in the Cedarberg Wilderness Area and Olifants River Valley near Citrusdal (Figure 1.2), whereas this study will focus on the Kogelberg Biosphere Reserve about 200 km to the south (Figure 1.2). Both have similar geological setting, climate, and precipitation inputs, and have equal fynbos species richness

The 200 ha Harold Porter National Botanical Gardens (HPNBG) in Betty's Bay is situated on the southern coast of the Western Cape, and forms part of the core conservation area of the 100000 ha Kogelberg Biosphere Reserve (Jordaan, 1991). The core zone is defined as a biologically rich and undisturbed area that is rigorously protected by law (Johns and Johns, 2001). The Kogelberg area is bounded by the Atlantic Ocean and the Hottentots Holland Mountains, and is an excellent example of pristine mountain fynbos. The fynbos is especially well represented by the restios (reed like plants) (Haaksma and Linder, 2000) as well as the other typical families of sedges, ericas (heaths), proteas and geophytes (bulbous plants) that are so characteristic of the unique Cape Floral Kingdom (Jordaan, 1991; Johns and Johns, 2001). Almost 70% of the fynbos species are endemic, and as such are not found naturally anywhere else on earth. The Kogelberg itself is regarded as the floristic heartland of the fynbos biome (Burgers *et al.,* 1991), as it contains 1650 plant species and a fifth of all known fynbos species (Jordaan, 1991; Johns and Johns, 2001). Over and above its value as a botanical reserve, the Kogelberg is home to more species of mammals, reptiles and amphibians than the entire British Isles put together. To

date, invasion of the Kogelberg by alien vegetation is minimal (Jordaan, 1991), making it an excellent area of study on the natural processes occurring within the fynbos.

The Palmiet River is also partly sourced in the Kogelberg, and is considered the last pristine riverine system within the fynbos. Three of its four tributaries have their entire catchment restricted within the reserve, and the riparian vegetation of all three are perhaps in their most natural pristine state, which cannot be said of anywhere else in the southern fynbos (Jordaan, 1991). The Leopard's Gorge River running through the Harold Porter Botanical Gardens is also sourced from the same proclaimed mountain catchment areas, and is surrounded by pristine riparian vegetation. The dark brown colour of streams and rivers flowing through the region are indicative of high dissolved organic carbon (DOC) levels (usually above 10 mg/L; Drever, 1997). However, fynbos or heathland soils are typically nutrient-poor, especially with regards to Ca, P and Mg (Low, 1983). Thus, analyses of soil and streams flowing though the gardens should provide information on the contribution of fynbos to the stream chemistry and how they thrive on bedrock that is deficient of these nutrients.

The geochemistry of the Kogelberg Reserve is thus the result of interactions between the geology, unique vegetation, climate and other factors peculiar to this area. Although the Kogelberg is a proclaimed Biosphere Reserve, there is increasing pressure outside the core zones from agricultural expansion and coastal urban development (Johns and Johns, 2001). A dam was also proposed in the centre of the core reserve last decade (Jordaan, 1991). It is thus uncertain how long the Kogelberg can remain in its pristine condition. In this light, it is desirable to establish geochemical parameters and interactions while the area is still in as natural a state as possible, to safeguard against any possible future degradation.

1.2 Objectives

Aims for this study are to determine the composition and chemistry of bedrock, soil, and stream waters in order to understand better the geochemistry of the

fynbos ecosystem. Such a study would establish baseline geochemical parameters for this pristine system in the face of potential ecological degradation. It would also enable comparisons with previous studies in the area to determine if local variation in any parameters is present and would contribute towards a greater understanding of fynbos biomes and their unique ecology.

1.3 Study Area

The Kogelberg is situated in the winter rainfall region of the south-western Cape. The climate is controlled by the dynamic interaction of north and south meteorological systems. Cold fronts are brought from the south due to the circumpolar westerly system consisting of a succession of eastward moving low-pressure cells. To the north, there is sub tropical system of high-pressure cells positioned over the southern Atlantic Ocean, the southern Indian Ocean, and the interior plateau of southern Africa. Snowfall may occasionally occur on the higher mountain ranges in winter, but generally does not persist for more than a month (Le Maitre, 1984). Average rainfall varies between about 1000-1500 mm annually with peak rainfall occurring in June and coastal peaks receiving about twice as much as the valleys below them (Johns and Johns, 2001). The mean annual air temperature is 16°C, and mean annual maxima and minima are 22°C and 11°C, respectively (Le Maitre, 1984).

The vegetation is generally tall open shrubland dominated by *Leucadendron laureolum* (van Wilgen and Le Maitre, 1981) and is structured in such a way that the proteas form the taller emergent layer, the low ground cover is made up of herbaceous plants, and restios and ericas dominate the middle layer. Aspect also plays a role, with southern slopes receiving less sun and more moisture resulting in denser vegetation than the sunnier, drier northern slopes (Johns and Johns, 2002).

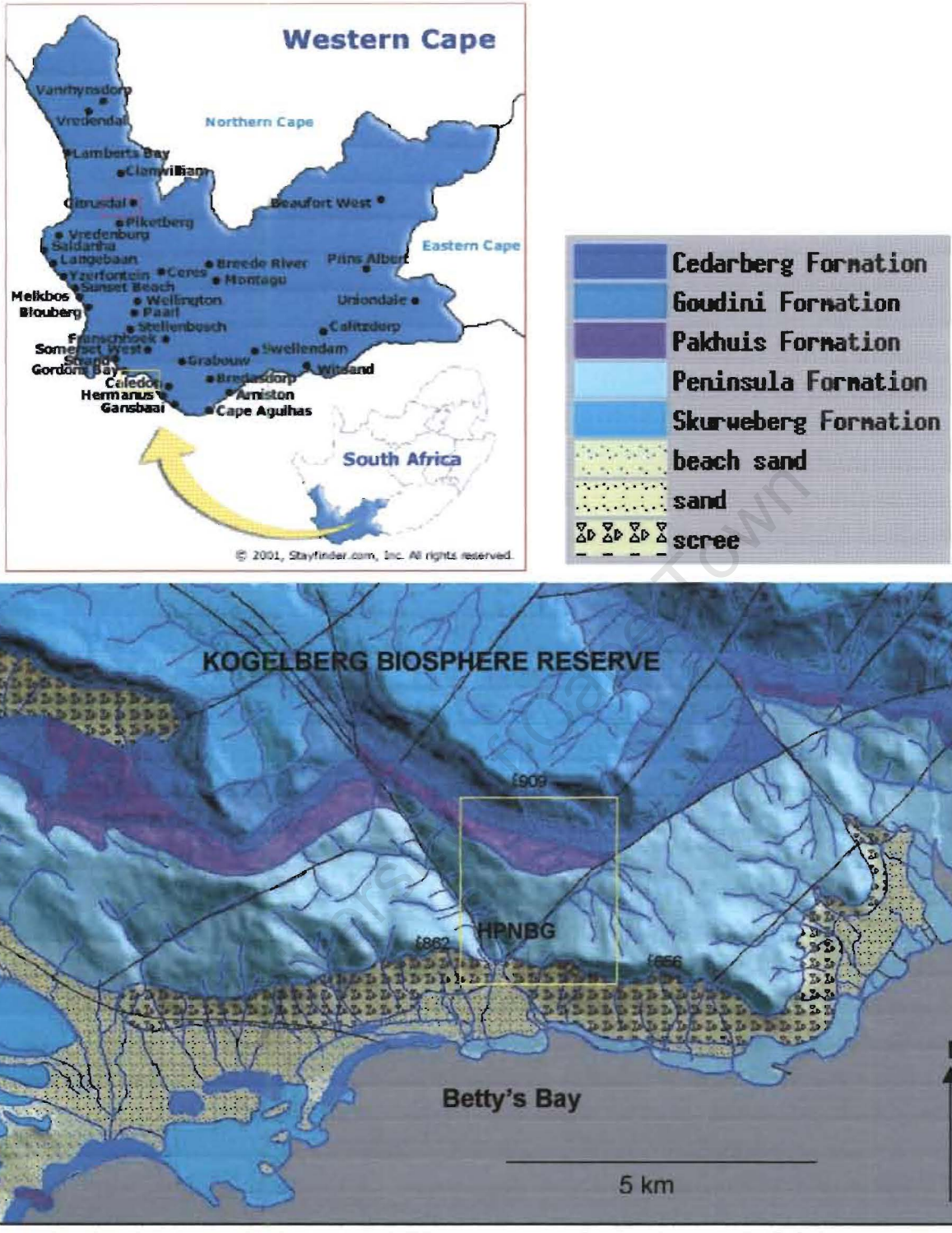


Figure 1.2. Location of the Kogelberg (outlined in yellow) and Citrusdal (outlined in pink) study areas and in the Western Cape, South Africa, along with bedrock geology. Location of the Harold Porter National Botanical Gardens is shown (HPNBG) Geological image is courtesy of Umvoto, and map of SA from Stayfinder.com.

The fractured bedrock and steep rocky slopes of the Kogelberg are the weathered remains of the massive mountain ranges that were uplifted Cape Fold Belt orogeny around 300 million years ago (Johns and Johns, 2001). The Cape Supergroup, consisting of the Table Mountain, Bokkeveld, and Witteberg Groups, dominates the underlying bedrock geology. The Table Mountain Group lies unconformably on the pre-Cape rocks (Van Eeden, 1972). Quartzitic sandstones are dominant in the Table Mountain and Witteberg groups whereas the Bokkeveld Group consists of alternate layers of shale and quartzitic sandstone in which the shale beds dominate. The Table Mountain Group is composed of the Peninsula, Pakhuis, and Cedarberg formations and the Nardouw Subgroup. The Cedarberg Formation is composed of shale and the Pakhuis Formation is formed from glacial tillite, grit and conglomerate. The two formations rarely exceed a thickness of 100 m, and the majority of the series is composed of the quartzitic sandstones of the Peninsula Formation and Nardouw Subgroup (Van Eeden, 1972). These hard, quartzitic sandstones are highly resistant to erosion, and the physiography of the Kogelberg tends to follow the underlying geological structure (Le Maitre, 1984).

The chiefly arenaceous bedrock composition of the area is poor in feldspars and micas (containing K, Na and Ca) and thus contains virtually no soluble material, except for quartz and small quantities of Fe (Day and King, 1995). These rocks thus contribute little carbonate buffering, and organic acids, such as the humates, can reduce the pH of surface waters to around 4 (Day *et al.,* 1998). However, stream chemistry is not only determined by the underlying rock and soil formations, but also by the uptake and release of chemicals by the local biota (Day *et al.*, 1998).

CHAPTER 2: MATERIALS AND METHODS

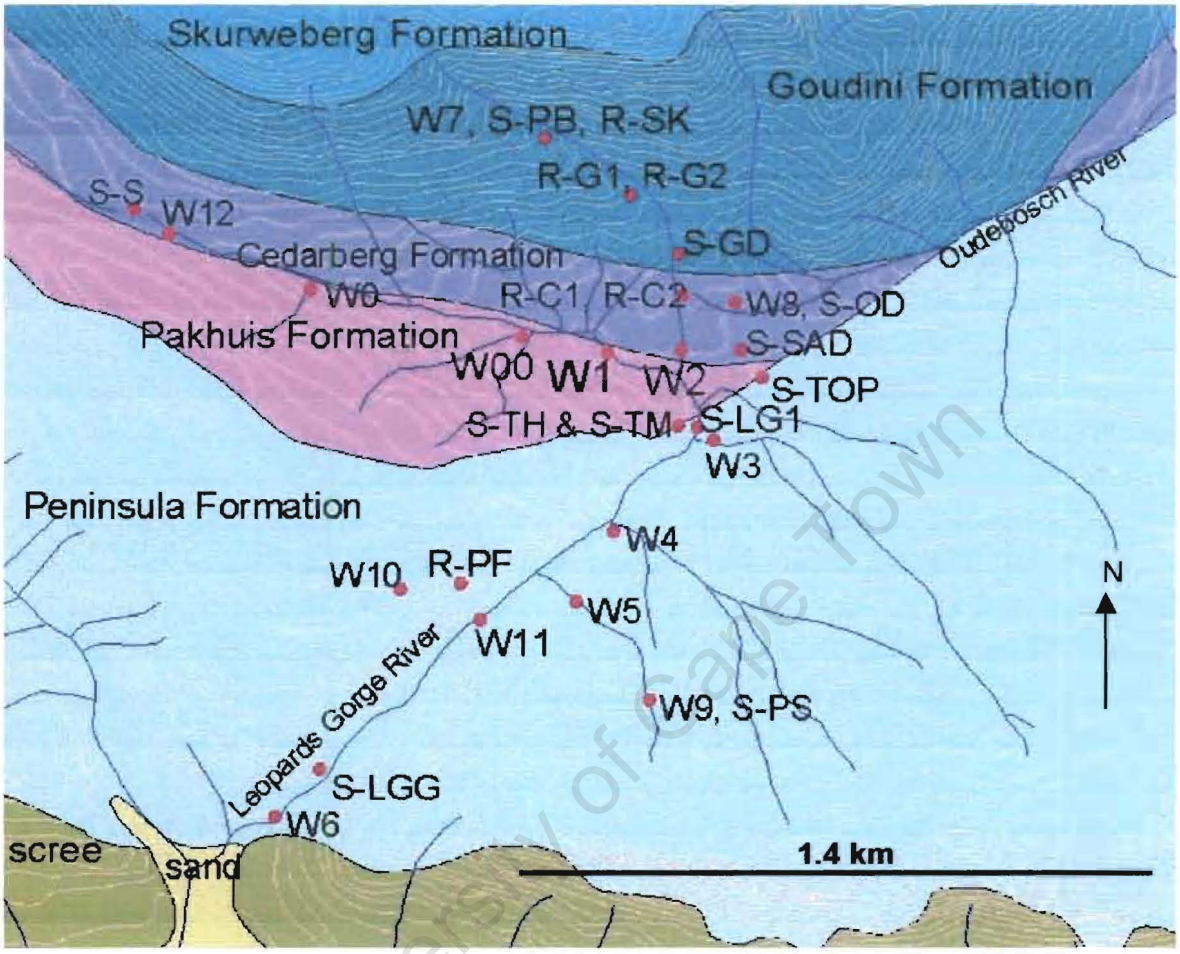


Figure 2.1. Locations of sample sites in the study area, with underlying bedrock geology and drainage Contours are in 20 m intervals. Water, soil and rock samples are prefaced with W, S and R respectively

2.1 Stream Water Sampling

Twenty-one water samples were taken from selected points along the course of the Leopard's Gorge River, including its tributaries and their sources (Figure 2.1). The sample sites were selected according the underlying geology, in order to detect any possible differences in stream chemistry caused by varying bedrock composition. Samples were also taken at progressive intervals along the course of the river to detect any cumulative changes in water chemistry. Some of the sites were sampled on multiple occasions to characterise any temporal variation

present, and ideally would have been done over the course of more than one season, but due to logistical reasons this was not possible. Field and laboratory titrations were also performed on several of the samples. Electrical conductivity (EC), pH, temperature and in some cases dissolved oxygen (DO) were measured in the field with portable equipment. pH was measured with a Radiometer portable pH meter, which was calibrated with buffers 4 and 7 at each sample site. Acid and base titrations to determine alkalinity were done with dilute HCl (0.0044M) and NaOH (0.0025M) solutions down to a pH of three and up to a pH of 10.3 to minimize error occurring from high DOC concentrations. Coordinates were taken from a portable Garmin GPS unit. Samples were taken back to the lab and stored at 4°C, and were filtered and acidified within 24 hours.

2.1.1 Major and Trace Element Chemistry

Concentrations of major cations and anions were measured with a Dionex ion exchange column. Trace elements were measured in the acidified samples with a Perkin Elmer Elan 6000 inductively-coupled plasma mass spectrometer (ICP-MS). Samples were diluted 1:10 with 5% nitric acid, and 50 μL of internal standard containing iridium, bismuth and indium was added. The samples were run in triplicate against the NIST 1640 standard.

2.1.2 DOC Analysis

Dissolved organic carbon analyses were done at the CSIR (Stellenbosch). The samples were acidified and purged with CO_2 free nitrogen. Upon resampling, potassium persulphate was added and UV digestion converted all organic carbon into CO_2 gas. This was measured, after it had passed through a membrane, solution containing phenolphthalein. Standards were prepared from potassium hydrogen phthalate.

Spectroscopic analyses in the UV/Vis range were done with an Aquamate thermospectronic spectrophotometer, using a quartz cuvette with a path length of 10 mm. Absorbencies were measured at 272, 280, 290, 300, 350, 400, 465, 500,

550, 600 and 665 nm. These were used to calculate the E4/E6 (Abs465 nm/Abs665 nm) and E3/E4 (Abs300 nm/Abs400 nm) ratios, which can be used to infer aromaticity and molecular weight of dissolved organic compounds.

2.2 Soil Sampling

Thirteen bulk soil samples were collected from the Harold Porter National Botanical Gardens (HPNBG) and Kogelberg Biosphere Reserve in August 2002. The sample sites were chosen at locations that progressed from the slopes of Platberg Mountain to within Leopard's Gorge below the waterfall. These samples were chosen to best represent any major variation that may occur within the study area, and thus soils were taken from sites on the Peninsula, Pakhuis, Cedarberg and Goudini Formations, to determine if the soils would differ significantly depending on their parent material (Figure 2.1). The samples were: **S-LGG** - 34.34643° S 18.93068° E, 74 m above sea level (a.s.l.) (Peninsula Formation); **S-PS** - 34.34447° S 18.94082° E, 414 m a.s.l. (Peninsula Formation); **S-LG1** - 34.33790° S 18.94249° E, 311 m a.s.l. (Peninsula Formation); **S-TP** - 34.33667° S 18.94450° E, 355 m a.s.l. (Peninsula Formation); **S-TM** - 34.33784° S 18.94187° E, 320 m a.s.l. (Pakhuis/Peninsula transition); **S-TH** - 34.33784° S 18.94187° E 320 m a.s.l. (Pakhuis/Peninsula transition); **S-SAD** - 34.33596° S 18.94383°. E, 347 m a.s.l. (Cedarberg Formation); **S-S** - 34.33190° S 18.92534°E, 472 m a.s.l. (Cedarberg Formation); **S-OD** - 34.33475° S 18.94371° E, 371m a.s.l (Cedarberg Formation); **S-S1** - 34.33597° S 18.93975° E, 330 m a.s.l (Cedarberg Formation); **S-GD** - 34.33344° S 18.94197°. E, 412 m a.s.l. (Goudini/Cedarberg transition) and **S-PB** - 34.33043° S 18.93797° E, 502 m a.s.l. (Goudini Formation with possible Skurweberg alluvium).

2.2.1 Grain Size Analysis

After air-drying, soil samples were sieved into greater and less than 2 mm fractions. A portion of the <2 mm fractions (about 30 g) was suspended in water overnight, and then ultrasonicated with a Virtis Virsonic ultrasonicator on low

power to break up soil aggregates. The sample was then wet-sieved through a 63 µm sieve to separate the soil into sand and mud fractions. The sand was dried and weighed. The mud (<63 µm) fraction, consisting of silt and clay in aqueous suspension, was then centrifuged at 5000 rpm for five minutes to reduce the volume. The resulting pellets were resuspended, and added to approximately 100 mL of dispersant (0.016 mM sodium hexametaphosphate) $(NaPO_3)_6$) before ultrasonication at high power. Silt was allowed to settle over time according to Stoke's Law (Non-affiliated Soil Analysis Work Committee, 1990), after which the still suspended clay fraction was decanted and isolated by centrifugation. The silt fraction was dried and weighed, and the weight of the clay fraction was inferred by difference. Suspensions of the clay fractions were further analysed by X-ray diffraction.

2.2.2 Soil pH

Soil pH was measured in 1:2.5 soil/water mass ratio suspensions. Air-dried soil samples (<2 mm fraction) were weighed and 10 g of each sample was added to 25 mL of Milli-Q water (pH-H_2O) or 25 mL of 1M KCl solution (pH-KCl). The resulting suspensions were then mixed with a glass rod rapidly for five seconds, then left to stand for 50 minutes, stirred again, and finally left to stand for another 10 minutes. pH measurements were then made ten minutes later with a calibrated Radiometer pH meter. Readings were taken with the electrodes positioned in the supernatant both after 30 seconds as well as after the meter had stabilised. The results were reported as either pH(H_20) or pH(KCl).

2.2.3 Cation Exchange Capacity and Extractable Acidity

Extractable cations were determined by two methods, using both KCl and ammonium acetate solutions. Using a KCl solution is a simple and easy method, although it is unable to quantify any exchangeable potassium present in the soil. For this reason, an ammonium acetate solution was additionally used, both to compare the results between the two methods, and to estimate the proportion of

exchangeable potassium present. To determine the CEC by KCl, 25 mL of a 1M KCl solution was added to approximately 2.5 g of bulk <2mm soil sample in 50 mL centrifuge tubes. These were capped and placed horizontally on a reciprocating shaker for about four minutes. The solutions were then centrifuged for three minutes at 4000 rpm, after which the pH of the supernatant was recorded, and the solutions were then filtered into storage containers. Ten millilitres of the supernatant was pipetted into a small conical flask for extractable acidity titrations with 0.0025M NaOH. Although the method recommends the use of 0.01M NaOH, lab tests showed that this higher concentration resulted in very small titrant volumes used (<1 mL). Four drops of phenolphthalein were used as indicator, and the solutions were titrated to a stable pink endpoint (i.e. so that the colour did not revert upon standing). The remaining filtrate was then used for Ca, Mg and Na determination by flame atomic absorption spectrophotometry (FAAS) at the Department of Chemical Engineering at UCT. Detection limits of the method are about 0.01ppm for Ca and between 0.003 to 1 ppm for Mg (Baker and Suhr, 1982).

A 1M-ammonium acetate solution adjusted to pH 7 was used for the additional determination of exchangeable potassium. Fifty millilitres of this solution (cooled to approximately 20°C) were added to five grams of <2 mm bulk soil sample in 250 mL plastic bottles. The bottles were then placed on a reciprocating shaker for 30 minutes. The resulting mixtures were filtered under suction into storage containers, for later FAAS analysis of the major base cations. The solutions were refrigerated to prevent bacterial growth.

2.2.4 Organic Carbon Content by the Walkley-Black Method

The organic carbon content of the soil samples was determined by the Walkley-Black method as described by the Non-affiliated Soil Analysis Work Committee (1990). Organic material in soil can be oxidised by potassium dichromate ($K_2Cr_2O_7$) and sulphuric acid (H_2SO_4) according to the following reaction:

$$2Cr_2O_7^{2-} + 3C + 16H^+ = 4Cr^{3+} + 3CO_2 + 8H_2O$$

The soil samples (about 2 g of the <2 mm fraction) were ground with an agate mortar and pestle, and between 0.1 to 0.4 g were transferred to an Erlenmeyer flask, along with 10 mL of 0.167M dichromate. Because some fine organic material passed through the 2 mm sieve and survived grinding, it was necessary to physically remove small roots and other organic detritus that exceeded 2 mm. The mixture was then swirled to disperse the soil, and 20 mL of concentrated sulphuric acid was rapidly added while swirling, continuing for about a minute and then left to cool for 30 minutes. After cooling, 150 mL of Milli-Q water was added along with 10 mL concentrated orthophosphoric acid and 1 mL indicator (barium diphenylamine sulphonate). This solution is then titrated to endpoint (an emerald green colour) with 0.5M iron (II) ammonium sulphate, and the volume recorded. In the case of one sample (S-S), the very high organic carbon content caused more than 75% reduction of the dichromate solution after the addition of the sulphuric acid (even with a sample mass of only 0.1 g). The method suggests repeating the analysis with less sample if this occurs, however it was decided not to reduce the mass to below 0.1 g in case larger errors were introduced. Rather, the dichromate volume was doubled to 20 mL for this sample. A 20 mL dichromate blank was also run. Results were then reported as percentage organic carbon (of the <2 mm fraction). An example of the calculations used to determine percentage organic carbon is given in the appendix.

2.2.5 XRD and XRF Analysis

The mineralogy of soil and rock samples was determined using a Philips X-Ray diffractometer using a copper K α tube (λ=1.542 Å) at 40 kV and 20 mA. The <2 mm soil fractions and rock samples were ground up in an agate mortar and pestle before running. Clay sample suspensions (from grain size analysis) were analysed on slides. The bulk ground up powders were analysed through to 2θ=110°, whereas the clay samples were run until 2θ=40°.

A low diffusion technique was used to determine major elemental composition by XRF (Willis, 1999). Rock samples were split, crushed and finally ground in a sieb mill whereas soil samples were ground up using an agate mortar and pestle. The exception to this was the S-S soil sample, which dried to extremely hard accretions, and it was thus necessary to use the sieb mill to obtain the appropriate grain size for analysis. All samples (approximately 2 g) were then dried at 110°C for at least four hours and weighed, after which they were roasted at 850°C overnight and reweighed. Six grams of flux (lithium tetraborate; dried overnight at 450°C) was used to dilute 0.7 g of sample (both accurate to four decimal places). The resulting mixture was stored briefly in a desiccator, before fusion discs were prepared using a Claisse Fluxy. Analyte intensities were determined with a molybdenum/scandium x-ray tube and an X'Unique Philips XRF Spectrometer.

2.2.6 Saturated Paste Extracts

Saturated pastes were prepared from seven soil samples from sites that were chosen to be representative of the different geological units in the area. These were: S-PS and S-TH (Peninsula Formation), S-S1 (Pakhuis Formation), S-OD and S-S (Cedarberg Formation), S-GD (Goudini Formation) and S-PB (Goudini/Skurweberg transition). An amount of between 170 and 250 g of soil (depending on soil density) of each air-dried sample was placed into a plastic container, using the method described by the Non-affiliated Soil Analysis Work Committee (1990). Milli-Q water was gradually added while mixing with a wooden spatula. The paste is considered saturated when all the pores are filled with water, and has the following characteristics: the surface is shiny, the paste flows slightly when the container is tilted, free water does not collect when a small trench is drawn on the surface, and it does not cling to the surface of the spatula unless the soil is clayey. Each sample was then slightly over saturated with a few mL's of water to counteract the effects of evaporation overnight. The saturated pastes were then extracted under vacuum and stored at 4°C the following day. The extracts were analysed for pH and electrical conductivity (EC), as well as

major, minor and trace elements. The latter was done as outlined in Section 2.1.2, except that up to 6x (IC) and 100 and 1000x (ICP-MS) dilutions were necessary to optimise the detection ranges of the instruments.

2.3 Rock Samples

Rock specimens from each representative geological formation in the study area were sampled. In order of altitude, from highest to lowest, these were from the Skurweberg-Goudini transition (R-SK - 34.33043° S 18.93797° E), Goudini (R-G, R-G(2), 33.33194° S 18.94056° E), Cedarberg (R-C1, R-C2, 34.3345° S 18.94207° E), Pakhuis/Cedarberg transition (R-PK, 34.33597° S 18.93975° E) and Peninsula Formation (R-PF, 34.34172° S 18.93513° E). Thin sections were made of each and studied by light microscopy. Portions of each specimen were also powdered and analysed by XRD and XRF (Section 2.2.5).

CHAPTER 3: RESULTS

3.1 Surface Waters

Surface water analyses were carried out both in the field and in the lab. Estimates of error and uncertainty are given in Appendix B

3.1.1 Physico-chemical Variables

Physico-chemical variables measured in the field and in the lab (pH, EC, dissolved oxygen (DO) and temperature) are listed in Table 3.1. Values are given both for in-stream measurements and for measurements taken in an Erlenmeyer flask (in the field). Ranges were 110.8-159.6 µS/cm (EC), 3.64-4.65 (pH), 11.2-15.5°C (temp) and 5.6-8.6 mg/L (DO). Measurements on the 26/8 were not done in the field due to the lack of a meter. Due to relief high gradients of streams sampled, DO levels approached saturation in most cases, and was therefore not considered useful in further sampling. Composite acid and base titration curves from field titrations are shown in Figure 3.1. Raw titration data is listed in Appendix A.

Table 3.1. pH, electrical conductivity (EC), temperature and dissolved oxygen (DO) of surface waters .

	In Stream				In Flask			
Site (Date)	pH	EC (µS/cm)	Temp	DO (mg/l)	pH	EC (µS/cm)	Temp	DO (mg/L)
W11 (19/8)	4.06	124.0	12.7	6.7	4.16	124.0	12.7	8.6
W12 (19/8)	4.01	128.5	11.2	6.5	4.05	128.8	12.6	5.6
W0 (19/8)	3.98	116.3	12.6	7.9				
W00(19/8)	3.97	116.1	13.5	7.8				
W1 (19/8)	4.05	118.8	11.9	7.9				
W2 (19/8)	4.08	115.8	11.4	8.0				
W3 (19/8)	3.89	129.9	13.4	7.8				
W4 (19/8)	4.00	125.7	14.4	7.4				
W5 (19/8)	3.66	142.1	14.8	7.3				
W6 (19/8)	3.87	134.0	13.2	7.8	3.99	135.1	13.2	
W7 (26/8)(lab)					4.18	110.8		
W6 (26/8)(lab)					4.38	128.4		
W3 (26/8) (lab)					4.14	131.2		
W8 (26/8) (lab)					4.65	138.5		
W11 (5/9)	3.84	120.1	12.0		4.06	133.4	12.7	
W9 (5/9)					4.14	159.6	13.9	
W4 (5/9)	3.92	130.1	14.7		4.02	126.0	14.4	
W3 (5/9)	3.65	120.0	14.1		3.64	121.5	14.1	
W5 (5/9)	3.71	141.9	15.2		3.86	150.5	15.5	
W10 (5/9)	3.66	132.9	11.5		3.87	121.2	13.2	
W6 (5/9)	3.74	133.0	12.7		3.86	121.1	13.2	

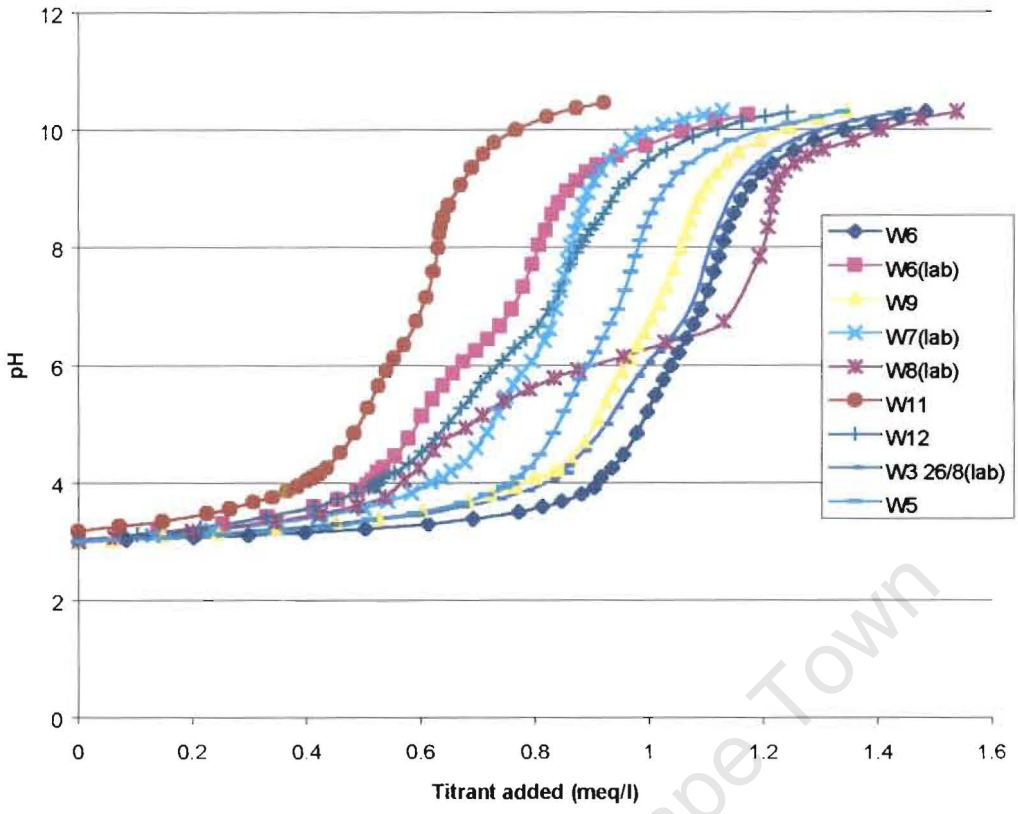


Figure 3.1. Composite acid and base titration curves for surface water samples

Alkalinities were calculated using the USGS web-based alkalinity calculator (theoretical carbonate titration curve 1) at http://oregon.usgs.gov/alk/. This method uses the theoretical equation for a carbonate titration and finds the carbonate and bicarbonate endpoints separately using a non-linear least-squares fitting technique. The site uses Powell's method to find the best-fit values for alkalinity. Mean titrant volume error is given where the method did not fit the data well, indicating something other than carbonate or bicarbonate being neutralised (Table 3.2).

Table 3.2. Alkalinities of samples from field and lab titration data.

Sample	Alkalinity		Titrant error (mL)
	meq/l	$CaCO_3$ (mg/L)	
W6(field)	-0.04	-1.8	3.6
W6(lab)	-0.02	-1	
W12	-0.02	-1.1	
W9	-0.01	-0.5	2.75
W7	-0.01	-0.5	4
W8	0	-0.01	6.82
W11	-0.01	-0.5	2.37
W3	-0.01	-0.5	
W5	-0.03	-1.5	5.15

3.1.2 Dissolved Organic Carbon

Surface water samples contain between 10 mg/L (W7) and 16 mg/L (W10 and W12), with the exception of W8, which had DOC below the detection limit of the instrument (1 mg/L) (Figure 3.2).

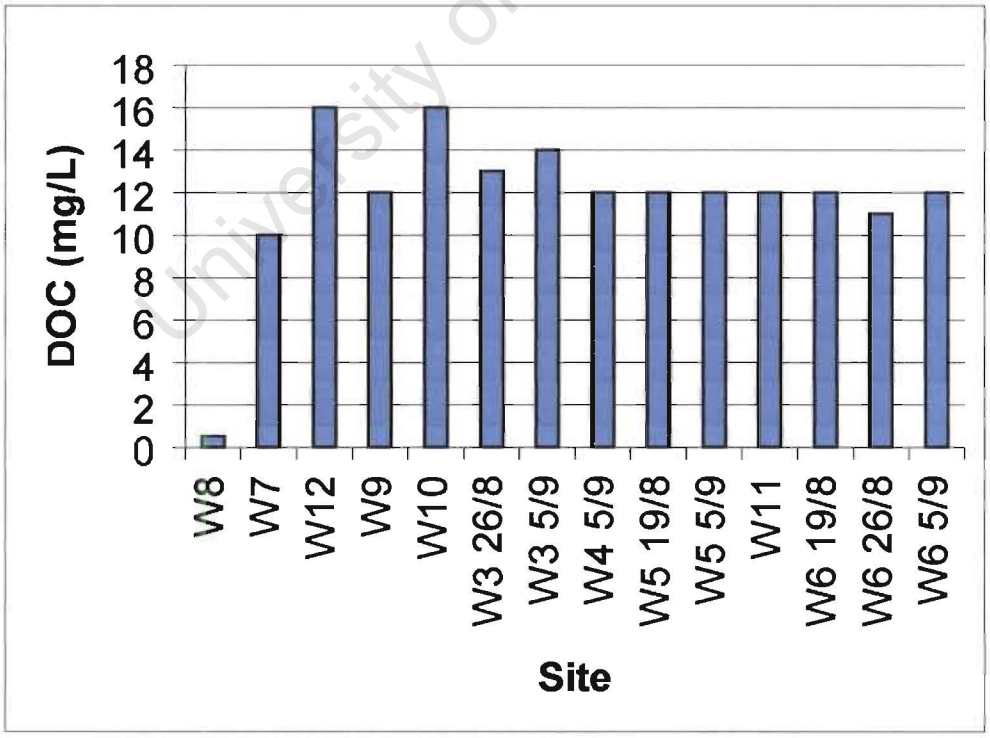


Figure 3.2. DOC content in surface waters (in mg/L)

3.1.2 Major Ions in Stream Waters

Major elements and ions determined by ICP-MS, IC and FAAS are given in Tables 3.3 to 3.7. Elements that are known to have poor resolution in IC or ICP-MS (Ca, Mg, Fe) were repeated with FAAS. Major ions such as Na and K were also done on FAAS to determine whether any differences in concentration arose from the removal of organics (DOC) in water samples by a polyvinylpyrrolidone (PVP) cartridge before IC analysis. PVP is known to strongly adsorb humic substances, and there existed the possibility that significant concentrations of cations or anions may be complexed with this organic matter and thus removed before analysis.

Table 3.7 presents best data for reproducible ions, averaging duplicates and using measurements that correlated for two or more analytical methods, or using the method that had the least analytical uncertainty for the ion in question (see Appendix B).

Table 3.3: Concentrations of major ions in surface water samples by ICP-MS (in ppm). Numbers in parentheses indicate a second run on the instrument. Dates are given for sites where samples were taken on more than one occasion.

	Ion (ppm)						
Sample	Na	Mg	Al	Si	K	Ca	Fe
TRIP BLANK 5/9	*n.d.*	0.01	0.04	*n.d.*	*n.d.*	*n.d.*	*n.d.*
TRIP BLANK 19/8	0.00	0.00	0.03	*n.d.*	0.05	0.05	*n.d.*
W12	14.38	1.38	0.20	0.40	0.34	0.52	0.05
W10	15.69	1.54	0.20	0.38	0.19	0.60	0.03
W10 (2)	11.95	1.65	0.19	0.53	0.26	0.68	0.05
W7	13.63	1.35	0.14	0.55	0.15	0.52	0.03
W7 (2)	11.89	1.52	0.14	0.69	0.20	0.61	0.04
W8	18.28	1.68	0.32	1.01	6.61	0.33	0.00
W8 (2)	17.03	2.10	0.28	1.18	0.35	0.41	0.01
W9	20.79	2.02	0.30	0.31	0.13	0.90	0.09
W6 5/9	14.60	1.42	0.23	0.36	0.14	0.51	0.08
W6 26/8	15.62	1.54	0.22	0.46	0.16	0.62	0.08
W6 19/8	15.66	1.55	0.23	0.43	0.55	0.60	0.10
W6 19/8 (2)	12.25	1.60	0.21	0.60	0.21	0.75	0.11
W11	15.26	1.53	0.23	0.55	0.19	0.57	0.09
W11 (2)	12.12	1.59	0.24	0.55	0.22	0.67	0.82
W3 26/8	15.41	1.53	0.19	0.16	0.13	0.65	0.04
W3 5/9	13.70	1.35	0.18	0.16	0.10	0.46	0.05
W3 5/9 (2)	12.20	1.42	0.21	0.29	0.20	0.98	0.05
W4	15.24	1.48	0.17	0.38	0.13	0.52	0.03
W5 19/8	17.59	1.74	0.25	0.42	0.16	0.64	0.07
W5 5/9	18.30	1.78	0.25	0.43	0.09	0.66	0.06
W5 5/9 (2)	13.48	1.84	0.23	0.55	0.12	0.72	0.07

n.d = not detected

Table 3.4. Trace ions in surface waters as measured by ICP-MS (in ppb). Numbers in parentheses indicate a second run on the instrument.

Sample	Ion (ppb)					
	B	Mn	Zn	Sr	Sb	Pb
TRIP BLANK 5/9	*n.d.*	*n.d.*	*n.d.*	0.09	0.60	*n.d.*
TRIP BLANK 19/8	*n.d.*	0.03	3.30	0.09	0.73	0.21
W12	6.46	2.35	3.83	12.57	2.80	4.29
W10	3.78	0.59	*n.d.*	14.99	3.94	*n.d.*
W10 (2)	9.67	0.64	1.57	11.40	*n.a.*	0.44
W7	*n.d.*	0.58	*n.d.*	11.71	3.45	*n.d.*
W7 (2)	12.80	0.76	2.85	10.54	*n.a.*	0.75
W8	1.43	5.05	13.88	9.78	3.23	0.58
W8 (2)	10.46	5.19	21.08	8.48	*n.a.*	0.60
W9	4.65	2.40	4.09	17.20	2.96	*n.d.*
W6 5/9	14.24	5.22	8.70	12.90	3.31	0.09
W6 26/8	10.03	7.78	4.76	14.08	3.44	0.43
W6 19/8	11.95	6.42	8.92	14.74	3.14	3.57
W6 19/8 (2)	11.20	7.05	3.03	11.34	*n.a.*	0.91
W11	10.14	1.75	41.97	14.05	3.15	0.19
W11 (2)	10.70	1.73	39.37	11.31	*n.a.*	1.12
W3 26/8	5.05	1.47	9.73	15.02	5.39	0.66
W3 5/9	5.46	0.77	3.39	12.65	2.71	0.21
W3 5/9 (2)	13.90	1.65	10.00	12.40	*n.a.*	1.56
W4	2.13	1.19	12.25	14.31	3.11	0.09
W5 19/8	8.68	2.69	15.12	16.56	3.09	0.82
W5 5/9	8.18	1.55	*n.d.*	16.83	3.48	*n.d.*
W5 5/9 (2)	10.68	1.72	1.23	13.49	*n.a.*	0.40

n.d = not detected

n.a. = not analysed

Table 3.5: Major ion concentrations in surface water samples as measured by FAAS (in ppm). Numbers in parentheses are duplicate measurements for that sample.

Sample	Ion (ppm)				
	Ca	Mg	Na	K	Fe
W12	0.95	1.37	13.13	0.38	0.12
W10	0.86	1.46	13.11	0.51	<0.06
W7	0.86	1.26	12.18	0.23	0.08
W8	0.56	1.58	16.56	0.32	<0.06
W9	1.23	2.15	17.38	0.20	0.13
W6 19/8	0.89	1.53	14.19	0.39 (0.37)	0.12 (0.12)
W6 26/8	1.15	1.46	13.67	0.20	0.21
W6 5/9	0.93 (0.91)	1.36	12.98	0.23	0.09
W11	0.84	1.45	15.88	0.20	0.12
W3 26/8	1.93	1.46	13.61	1.00	0.29
W3 5/9	0.93	1.42	15.41	0.12	<0.06
W4 5/9	1.09	1.5 (1.49)	13.99	0.18	0.08
W5 19/8	1.00	1.81	15.69	0.17	0.06
W5 5/9	0.97	1.75	15.44 (15.48)	0.26	0.12

Table 3.6. Major cations and anions as determined by IC, along with the charge balance error (CBE). Numbers in parentheses indicate a second or third run on the instrument.

Sample	Cations (ppm)					Anions (ppm)					CBE
	Na	NH_4	K	Mg	Ca	Cl	Br	NO_2	NO_3	SO_4	(m_{eq}/L)
Tblank 1	0.07	0.00	0.03	-0.22	0.03	0.00	0.00	0.15	0.00	0.00	
W12	12.49	0.17	0.39	1.73	0.72	23.87	0.34	0.00	0.00	3.78	2.1
W10	11.97	0.12	0.28	2.01	0.79	25.22	0.00	0.00	0.00	2.67	2.6
W7	11.44	0.00	0.22	1.66	0.68	22.11	0.04	0.00	0.00	2.54	1.0
W7 (2)	11.25	0.18	0.24	1.67	0.70	12.96	0.00	0.00	0.03	1.97	-24.0
W7 (3)	11.46	0.09	0.22	2.23	1.08	21.56	0.00	0.00	0.02	2.45	-5.4
W8	16.44	0.00	0.38	2.14	0.72	32.50	0.00	0.00	0.02	3.12	3.0
W9	17.29	0.73	0.22	2.09	1.04	33.95	0.00	0.00	0.00	2.46	-0.1
W6 19/8	13.15	0.00	0.43	2.08	0.74	27.53	0.00	0.00	0.03	3.88	5.0
W6 19/8 (2)	13.85	0.31	0.47	2.04	1.06	26.32	0.05	0.00	0.00	2.50	-2.8
W6 19/8 (3)	10.19	0.12	0.36	2.12	1.29	26.15	0.00	0.00	0.00	2.46	6.8
W6 26/8	13.33	0.00	0.24	1.86	1.03	26.97	0.00	0.00	0.04	2.74	2.4
W6 5/9	12.70	0.21	0.22	2.14	0.79	25.37	0.00	0.00	0.00	2.37	-0.7
W11	12.88	0.00	0.25	2.00	0.75	*n.a.*	*n.a.*	*n.a.*	*n.a.*	*n.a.*	*n.a.*
W11 (2)	12.72	0.51	0.28	1.59	1.55	23.87	0.00	0.00	0.02	2.33	-4.3
W11 (2) dup	14.81	0.20	0.67	*n.a.*	0.66	24.12	0.00	0.00	0.04	2.36	2.4
W11 (3)	13.28	0.26	0.24	2.28	1.20	23.39	0.00	0.00	0.04	2.38	-8.0
W3 26/8	13.16	0.00	0.18	1.92	1.00	26.47	0.00	0.00	0.02	1.93	0.7
W3 5/9	11.30	0.12	0.19	1.66	0.69	24.33	0.00	0.00	0.00	2.24	4.8
W4 5/9	13.49	0.00	0.47	2.15	0.93	27.26	0.00	0.00	0.08	2.67	0.9
W5 19/8	15.35	0.00	0.22	2.54	1.11	30.46	0.00	0.00	0.12	2.96	-0.1
W5 19/8 (2)	15.87	0.21	0.24	2.06	0.88	21.54	0.00	0.00	0.10	1.76	-17.0
W5 19/8 (3)	16.05	0.13	0.30	2.73	1.60	29.03	0.00	0.00	0.10	2.22	-7.6
W5 5/9	15.32	0.00	0.19	2.17	0.93	30.95	0.00	0.00	0.00	2.55	2.2

n.a. = not analysed

Table 3.7. Average concentrations of major and trace ions averaging duplicates and best-fit analytical techniques.

	Ion (ppm)							Ion (ppb)					Ion (ppm)			
Sample	**Na**	**Mg**	**Al**	**Si**	**K**	**Ca**	**Fe**	**B**	**Mn**	**Zn**	**Sr**	**Sb**	**NH4**	**Cl**	**NO3**	**SO4**
W12	13.3	1.4	0.2	0.4	0.4	0.8	0.1	6.5	2.4	3.8	12.6	2.8	0.2	23.9	0.00	3.8
W11	13.8	1.5	0.2	0.6	0.2	0.9	0.1	10.4	1.7	40.7	12.7	3.2	0.3	23.8	0.03	2.4
W6 19/8	13.8	1.6	0.2	0.5	0.4	0.9	0.1	11.6	6.7	6.0	13.0	3.1	0.1	26.7	0.01	2.5
W6 26/8	14.2	1.5	0.2	0.5	0.2	1.1	0.2	10.0	7.8	4.8	14.1	3.4	0.0	27.0	0.04	2.7
W6 5/9	13.4	1.4	0.2	0.4	0.2	0.9	0.1	14.2	5.2	8.7	12.9	3.3	0.0	25.4	0.00	2.4
W8	17.1	1.6	0.3	1.1	0.3	0.6	<0.06	10.5	5.1	17.5	9.1	3.2	0.0	32.5	0.02	3.1
W7	12.0	1.4	0.1	0.6	0.2	0.8	0.1	12.8	0.7	2.9	11.1	3.5	0.0	21.8	0.02	2.5
W9	17.3	2.1	0.3	0.3	0.2	1.1	0.1	4.7	2.4	4.1	17.2	3.0	0.7	34.0	0.00	2.5
W3 26/8	13.4	1.5	0.2	0.2	0.2	1.5	0.3	5.1	1.5	9.7	15.0	5.4	0.0	26.5	0.02	1.9
W3 5/9	13.2	1.4	0.2	0.2	0.2	0.8	<0.06	9.7	1.2	6.7	12.5	2.7	0.1	24.3	0.00	2.2
W4	14.4	1.5	0.2	0.4	0.2	1.0	0.1	2.1	1.2	12.3	14.3	3.1	0.0	27.3	0.08	2.7
W5 19/8	15.7	1.8	0.3	0.4	0.2	1.0	0.1	8.7	2.7	15.1	16.6	3.1	0.0	29.7	0.11	2.3
W5 5/9	15.6	1.7	0.2	0.5	0.2	1.0	0.1	9.4	1.6	1.2	15.2	3.5	0.0	31.0	0.00	2.6
W10	12.3	1.5	0.2	0.5	0.2	0.8	<0.06	6.7	0.6	1.6	13.2	3.9	0.1	25.2	0.00	2.7

3.1.3 Spectroscopic Analyses of Water Samples

Samples were scanned over a range of wavelengths, and E3/E4 and E4/E6 ratios calculated. Absorbance values at each wavelength as well as the E-ratios are presented below in Table 3.8. Samples W8 to W3 5/9dup (upper table) are from the Kogelberg, whereas samples OK1 to BK3 (lower table) are from the Cedarberg in the Citrusdal area (K. Soderberg, pers. comm., 2002).

Table 3.8. Absorbencies at different wavelengths for surface water samples. E-ratios are calculated from 300/400 nm (E3/E4) and 465/665 nm (E4/E6).

Site	Wavelength (nm)											E-Ratios	
	272	280	290	300	350	400	465	500	550	600	665	E4/E6	E3/E4
W8	0.030	0.031	0.027	0.024	0.009	0.005	0.002	0.002	0.000	0.000	0	-	4.80
W7	0.599	0.555	0.494	0.437	0.228	0.104	0.044	0.028	0.015	0.007	0.001	44.00	4.20
W12	0.961	0.887	0.788	0.697	0.363	0.166	0.073	0.048	0.026	0.014	0.006	12.17	4.20
SPS	0.771	0.713	0.635	0.565	0.302	0.146	0.066	0.046	0.026	0.015	0.005	13.20	3.87
W10	1.013	0.939	0.837	0.744	0.395	0.183	0.080	0.053	0.029	0.016	0.005	16.00	4.07
W3 26/8	0.807	0.746	0.663	0.588	0.313	0.145	0.063	0.042	0.023	0.012	0.005	12.60	4.06
W3 5/9	0.933	0.864	0.770	0.685	0.365	0.170	0.074	0.049	0.027	0.014	0.005	14.80	4.03
W4	0.808	0.750	0.670	0.598	0.326	0.159	0.076	0.053	0.032	0.019	0.008	9.50	3.76
W5 5/9	0.853	0.793	0.710	0.635	0.348	0.172	0.084	0.060	0.037	0.023	0.010	8.40	3.69
W11	0.764	0.708	0.631	0.561	0.297	0.139	0.061	0.041	0.023	0.012	0.003	20.33	4.04
W6 19/8	0.783	0.726	0.646	0.574	0.306	0.145	0.065	0.045	0.026	0.014	0.006	10.83	3.96
W6 5/9	0.810	0.751	0.668	0.594	0.314	0.146	0.063	0.042	0.023	0.013	0.004	15.75	4.07
W3 5/9dup	0.944	0.875	0.780	0.694	0.369	0.171	0.075	0.049	0.026	0.013	0.006	12.50	4.06
OK1	0.264	0.264	0.266	0.263	0.081	0.032	0.011	0.006	0.001	0	0	-	8.22
BK1	0.031	0.032	0.027	0.024	0.008	0.003	0.001	0	0	0	0	-	8.00
BJ3	0.069	0.067	0.058	0.051	0.021	0.009	0.003	0.001	0	0	0	-	5.67
EK6	0.044	0.045	0.039	0.034	0.014	0.006	0.003	0.001	0	0	0	-	5.67
BJ2	0.075	0.072	0.062	0.054	0.024	0.010	0.003	0.001	0	0	0	-	5.40
OL1	0.098	0.092	0.080	0.069	0.031	0.014	0.005	0.003	0.001	0	0	-	4.93
EK4	0.029	0.030	0.026	0.022	0.009	0.005	0.002	0.001	0	0	0	-	4.40
BK3	0.068	0.067	0.058	0.050	0.026	0.016	0.010	0.007	0.006	0.005	0.003	3.33	3.13

3.2 Soils

Twelve samples were taken and seven were selected for further analysis, as they were thought to be representative of the various geological units present in the study area. The S-PS sample was taken from the Peninsula Formation, S-OD and S-S from the Cedarberg, S-S1 close to a Pakhuis outcrop, S-GD between the Cedarberg and Goudini and S-PB between the Goudini and the Skurweburg sandstones of the Nardouw Subgroup. The S-GD sample was initially separated

into a lower and upper horizon to determine any differences in mineralogy occurring at depth below the soil surface.

3.2.1 Soil Site Descriptions

A brief description of each sampling site, including factors such as slope, aspect, and characteristics of the soil sample sites is given below. Coordinates and altitudes of each site are listed in Section 2.2. Soil forms are not described here, as they were considered debatable, and are therefore discussed in Section 4.2.1.

S-LG1 - This sample was taken from a west facing vertical exposure (±1 m in height), about 2 m away from the Leopard's Gorge stream flow. The exposure is probably the result of erosion during flood events. The soil was dark grey in colour, well bound by roots, damp and appeared to have low clay content. The soil profile had no apparent layering or structure. The profile (±45 cm) appeared to lie directly on bedrock (or large boulder), which was sandstone. Some white quartz grains were observed, with a few larger pebbles present in the soil as well. Soil surface was densely vegetated with indigenous fynbos (restios, ericas, some proteas, *Brunia spp*). However, the leaf litter layer was thin (<0.5 cm).

S-TP –This sample was taken from a shallow slope (east facing) near the TOP of an intervalley ridge, probably still Peninsula sandstone, but about 50-100 m away from the contact with the Cedarberg Formation. Soil colour was dark grey with scattered quartz grains, but had fewer roots and the soil was poorly sorted compared to S-LG1. No layering was apparent. The soil profile was thin and could only be sampled down to a depth of about 15 cm before hitting bedrock. Vegetation density was less than at S-LG1, mainly restios and some larger proteas.

S-SAD –This site is located on the saddle between the watersheds of the Leopard's Gorge and Oudebosch Rivers. The saddle is underlain by the Cedarberg shale/Pakhuis tillite formations. Soil was dark in colour, but more

brown tinged than the previous samples, and displayed a slight layering. The surface layer was dark, muddier than previous samples down to about 15 cm; at the base was a coarser, lighter coloured layer of rounded quartz grains (1-2 mm). Both layers were quite water saturated compared to the previous sites. Average density vegetation was present.

S-LGG –This sample site is located at the bottom of Leopard's Gorge, next to the gate through to the falls. The vegetation was 2-3 m high, with some trees and ferns as opposed to fynbos. The vegetation may contain elements of indigenous afromontane forest. There was substantially more leaf litter than all other sites and a thin organic topsoil/ leaf litter layer about 1 cm thick. Soil was sampled down to about 15 cm, and was dark grey but not as damp as previous samples. Again, quartzite pebbles were present in the soil.

S-TM – A sample was taken from an active termite mound on a fairly steep (about 15 degrees), northeast-facing slope, about 20 m above and 50 m west from the S-LG1 site, and on the other side of the river. The soil was well cemented and no leaf litter was apparent. Soil colour was dark grey to black.

S-TH – A sample was taken from a soil profile adjacent to S-TM. Slope and elevation details are the same as for S-TM. Soil was similar in physical character to S-LG1 and S-TP, well bound by roots but sandy. Some restio samples were taken.

S-S – This sample was taken from the TOP of the saddle above the headwaters of the Leopards Gorge River on a shallow southerly slope (± 5 degrees). Sparse clumps of restios were present, but no vegetation within about a 1m radius of the sample site. The soil was very moist under a dryer top layer, very spongy with possibly quite a high clay content. No layering, some root material present. The site appeared to have been under water recently and had begun to dry out.

S-OD – A soil sample adjacent to (and about 1m above) the headwaters of the Oudebosch River was taken, as this soil was assumed to be derived from Cedarberg Shale. The Oudebosch River flows into the Palmiet, and as such is not connected to the Leopards Gorge River. However, the Oudebosch headwaters are located only a few hundred meters away from the tributaries of the Leopards Gorge River, and both flow through common geological units. This site was well vegetated by indigenous afromontane forest on a North facing slope of approximately ten degrees. The soil appeared to be much more clayey in nature than many of the samples, and was dark brown and loamy. It contained roots, but not the dense root mat that was common to most samples vegetated by fynbos. The 20 cm depth of the hole dug revealed neither layering nor bedrock. The leaf litter layer was substantial.

S-S1 – The streambed near this site appeared to be running along the Pakhuis/Cedarberg contact. The sample site was approximately 1 m above the stream flow on the Cedarberg Formation side, and was densely vegetated (plants up to 2 m high) mainly by Restios, Ericas, Proteas and *Brunia spp*. The slope was estimated to be about five degrees or less to the South. Soil was taken from a 15-20 cm hole, which revealed no layering. Soil colour was dark grey, sandy and speckled with white quartz pebbles, and was similar in appearance to the Peninsula Formation derived soils within Leopards Gorge. Root mats were also in evidence in the soil.

S-PB – A soil sample was taken from within the gorge leading up to Platberg in an area that was thought to represent the Skurweburg Formation of the Nardouw Subgroup. The slope was steep (25-30 degrees) and had a north-eastern aspect. Dense vegetation was present. The soil was sandy, with a thin surface humic layer (± 2 cm) and soil profile was very shallow (10-15 cm), situated on parent rock.

S-GD – Below the Skurweburg Formation in the Nardouw Subgroup occurs the Goudini Formation. Soil was taken from a site situated directly on parent Goudini rock, but also close (~50 m) to a Cedarberg outcrop, and may thus have been on the transition between the two formations. Shale-like bands were visible within the sandstone layers. The slope is South facing, and approximately eight degrees. Vegetation was mainly restioid, and the soil depth above the parent rock was about 20 cm. Some pebbles were present at the base of the soil, but otherwise the transition between soil and rock was abrupt. No other layering was visible. The soil was moist, and slightly more clayey than the S-PB sample. This sample was separated into upper and lower portions, with each processed separately, in order to characterise any differences associated with soil depth.

S-PS – This soil sample was taken from a seep two thirds of the way up the north-western facing slope of Leopards Gorge. The bedrock here is the arenaceous sandstone of the Peninsula Formation. The soil was water saturated, with dense vegetation situated above (mainly restios), and small, white quartz pebbles were present. Depth sampled was approximately 15 cm, and no layering was evident.

Fractions of soil greater and less than two mm and results of grain size analyses are given in Table 3.9. None of the soils had positive reactions to field tests for carbonates. Soil colour (from Munsell soil colour charts), percentage organic carbon and pH (in KCl and H_2O) are given in Table 3.10.

Table 3.9. Size fractions of the different samples. Sand is >63 µm whereas silt and clay were separated based on settling time for >2 µm particles (silt). Percentage sand silt and clay are given as percentages of the <2 mm fraction.

Sample	%>2 mm	%<2 mm	%Sand	%Silt	%Clay
S-TH	5.35	94.65	94.22	4.88	0.90
S-OD	24.94	75.06	76.40	10.04	13.56
S-S	19.82	80.18	84.60	3.24	12.16
S-PB	22.71	77.29	83.53	8.95	7.51
S-S1	9.03	90.97	84.49	6.99	8.52
S-GD low	9.31	90.69	65.48	13.13	21.39
S-GD upper	21.02	78.98	90.03	5.83	4.13
S-PS	13.79	86.21	93.01	2.53	4.46

Table 3.10. Physico-chemical soil variables including soil colour, percentage organic carbon, pH (H_2O), pH (KCl) and delta pH of the <2 mm fraction. pH readings are the mean of the readings at 30 s and after the pH meter had stabilised. Numbers in parentheses indicate readings for duplicate soil samples.

	Munsell Soil Colour		$\%C_{org}$	pH (H_2O) Mean	pH (KCl) Mean	Delta pH
Sample	Dry	Wet				
S-TH	3/2 2.5Y	2.5/1 2.5Y	15.1 (19.3)	4.20	3.13	-1.08
S-OD	3/2 10YR	3/1 2.5Y	10.60	5.40 (5.41)	3.91 (3.92)	-1.49
S-S	2.5/1.5 Y	2.5/1.5Y	35.6 (33)	3.59	2.41	-1.18
S-PB	4/1 2.5Y	2.5/1 2.5Y	7.20	5.63	4.10	-1.54
S-S1	3/1 2.5Y	2.5/1 2.5Y	6.90	4.79	3.05	-1.74
S-GD low	5/1 2.5Y	3/1 2.5Y	6.80	4.60	3.22	-1.38
S-PS	3/2 2.5Y	2.5/1 2.5Y	23.50	4.5 (4.6)	3.11 (3.11)	-1.39

3.2.2 Mineralogy

Mineralogy of powdered bulk samples and clay suspensions as determined by XRD is given in Figures 3.3 and 3.4, respectively. The mineralogy of most samples was dominated by quartz, with clay subordinate minerals (kaolinite and some smectite) and micas. Hematite was also present in some of the samples.

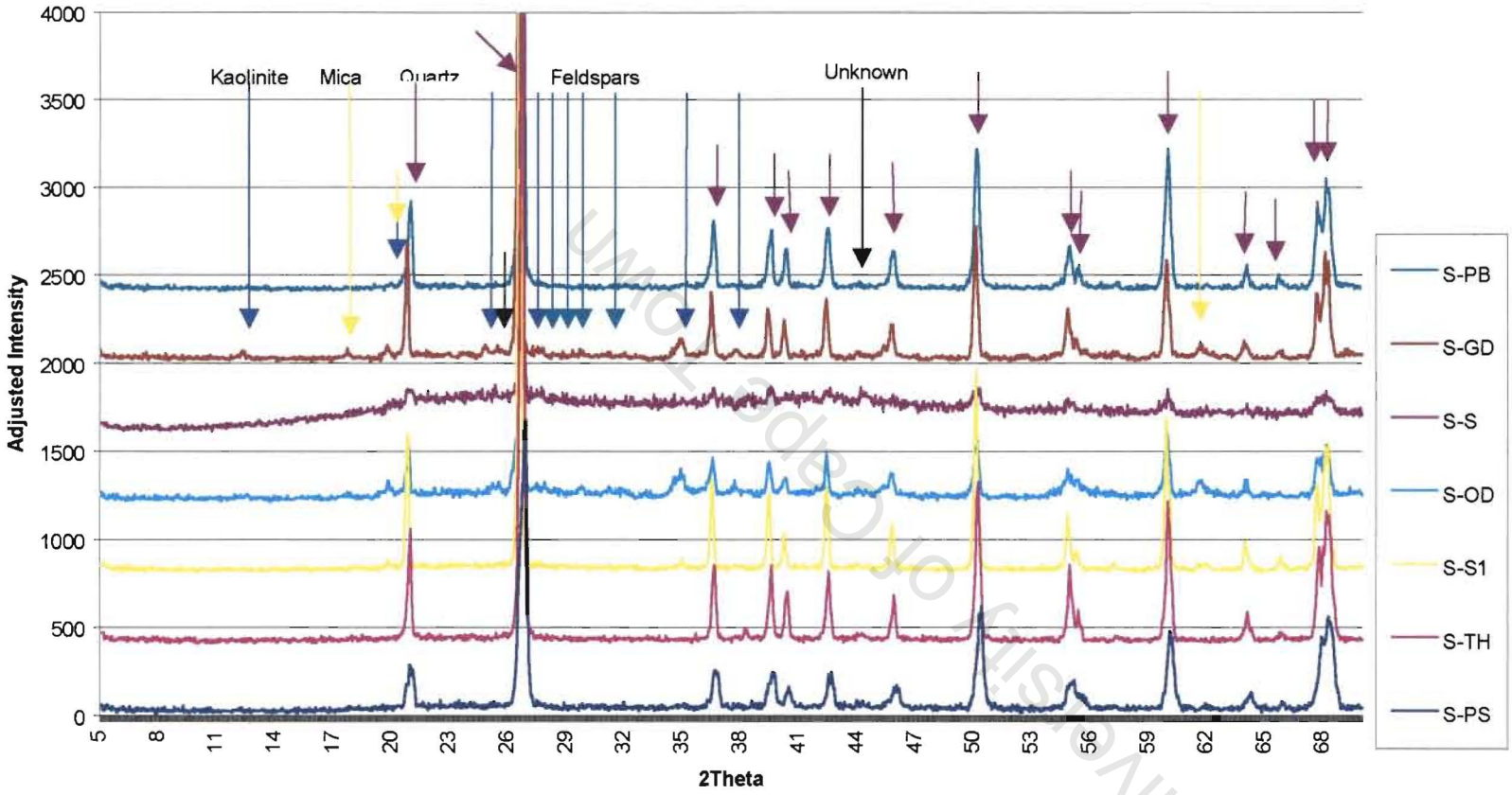


Figure 3.3. XRD patterns of bulk soil samples (<2mm)

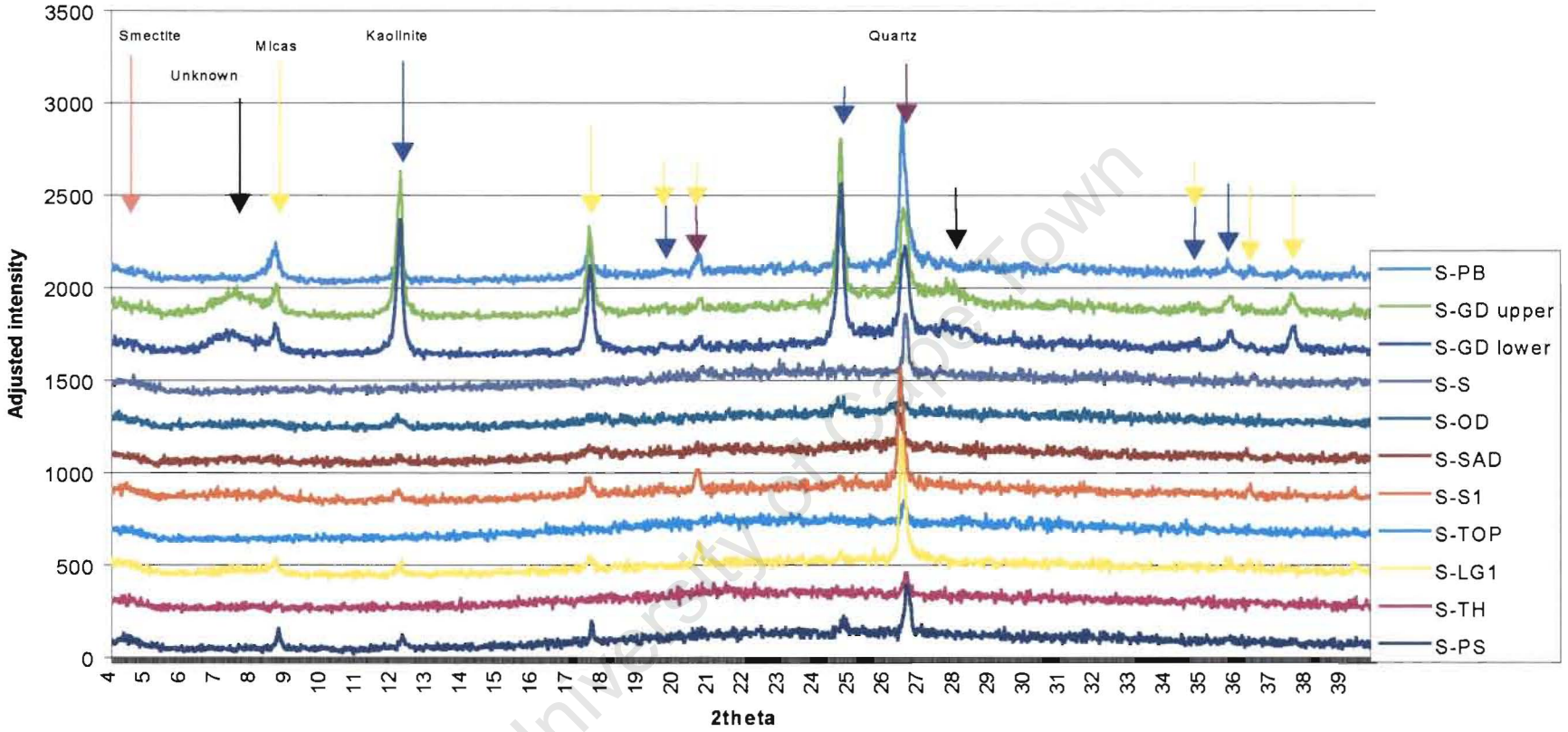


Figure 3.4: XRD patterns of the clay size fraction of the soil samples.

3.2.3 CEC and exchangeable cations

Exchangeable soil base cations (Na, Mg, Ca and K) from the KCl and ammonium acetate methods were measured by FAAS. The KCl method cannot determine exchangeable K, and extractable acidity titrations could only be done by the same method. Results (in meq/kg) are listed in Table 3.11.The S-PB and S-S samples had the highest ECEC. The S-GD, S-OD, and S-S samples are acid saturated soils, whereas the remaining samples are base saturated.

Table 3.11. Extractable base cations from soils by ammonium acetate and KCl methods, effective CEC and percent acid and base saturation. Results are in meq/kg soil.

	Exchangeable Base Cations					Extractable	% Acid	% Base
Sample	Ca	Mg	Na	K	ECEC	Acidity	Saturation	Saturation
S-GD NH4	8.6	9.7	5.4	0.7	24.3			
S-OD NH4	8.0	12.0	7.0	7.6	34.5			
S-PB NH4	58.4	26.5	8.5	3.4	96.7			
S-PS NH4	13.3	15.0	5.9	1.6	35.7			
S-S1 NH4	9.9	12.7	6.3	1.2	30.1			
S-S NH4	17.1	28.1	10.4	1.9	57.5			
S-TH NH4	31.3	27.0	9.2	3.6	71.1			
S-GD KCl	9.0	13.0	9.3		31.3	109.0	77.7	22.3
S-OD KCl	10.2	15.1	7.2		32.5	68.9	67.9	32.1
S-PB KCl	47.8	29.9	7.9		85.6	11.5	11.8	88.2
S-PS KCl	14.9	18.4	6.7		39.9	28.3	41.5	58.5
S-S1 KCl	16.3	17.6	8.3		42.2	23.0	35.3	64.7
S-S KCl	26.4	45.2	9.5		81.1	119.0	59.5	40.5
S-TH KCl	46.2	37.8	8.9		93.0	15.5	14.3	85.7

3.2.4 Saturated Paste Extracts

pH, EC and concentrations of major, minor and trace elements in saturated paste extracts (measured by ICP-MS and IC) are presented in Tables 3.12 to 3.17. The dominant cation was determined to be Na in all samples and Cl the dominant anion.

Table 3.12. pH, EC (in µS/cm) as well as major and minor ion concentrations by ICP-MS in saturated paste extracts of soils (mg/kg soil). Numbers in parentheses indicate a second run on the instrument, whereas samples marked "dup" are duplicates of saturated pastes.

	S-PS	S-TH	S-TH (2)	S-TH (dup)	S-S1	S-OD	S-OD (2)	S-OD (dup)	S-S	S-GD	S-GD (2)	S-GD (dup)	S-PB
pH	**4.37**	**4.5**		**3.97**	**4.37**	**5.9**		**4.77**	**3.55**	**4.05**		**3.98**	**6.7**
EC	**285**	**625**		**580**	**350**	**549**		**526**	**450**	**545**		**429**	**310**
Li	0.05	0.89	0.72	0.02	0.06	11.80	8.03	0.02	0.04	18.44	21.87	0.03	0.06
Na	122.42	252.81	156.58	237.18	190.44	198.69	90.18	204.36	150.37	160.60	137.16	109.63	132.38
Mg	24.22	48.29	34.57	91.63	16.80	42.98	26.24	43.49	48.50	52.22	56.44	36.72	16.04
Al	2.60	10.17	8.28	59.33	9.15	2.91	2.26	4.74	2.14	7.06	5.45	7.21	1.06
Si	3.28	3.93	*n.d.*	0.70	8.26	17.31	17.07	24.95	3.76	4.07	1.11	5.82	6.92
K	42.90	68.37	13.21	67.44	21.61	48.53	40.40	45.20	13.73	19.46	17.67	9.35	57.61
Ca	16.21	42.77	30.55	1307.64	13.84	17.79	12.38	22.06	30.58	28.67	27.41	37.72	18.44
B	0.14	0.20	0.15	*n.d.*	0.62	2.15	2.02	1.74	6.36	0.36	0.22	0.48	0.19
Ti	*n.a.*	*n.a.*	0.09	0.10	*n.a.*	*n.a.*	0.05	0.04	*n.a.*	*n.a.*	0.07	0.09	*n.a.*
Mn	0.01	0.27	0.22	0.14	0.04	1.61	1.45	1.42	0.06	0.09	0.08	0.05	0.02
Fe	0.42	0.94	*n.d.*	*n.d.*	4.03	0.34	*n.d.*	0.67	0.21	1.02	0.28	0.96	0.50
Ni	*n.d.*	0.01	0.02	0.09	0.01	0.02	0.04	0.16	0.00	0.00	0.04	0.07	0.00
Zn	0.11	0.90	0.76	0.38	0.17	0.24	0.23	0.25	0.24	1.04	0.97	0.49	0.40
Sr	0.19	0.49	0.45	0.60	0.18	0.32	0.29	0.27	0.37	0.48	0.42	0.44	0.21
Sb	*n.a.*	*n.a.*	0.01	0.01	*n.a.*	*n.a.*	0.00	0.01	*n.a.*	*n.a.*	0.00	0.01	*n.a.*
Ba	0.04	0.09	0.12	0.11	0.10	0.21	0.27	0.20	0.05	0.24	0.25	0.25	0.04
Hg	*n.d.*	*n.d.*	0.02	0.02	0.00	*n.d.*	0.03	0.04	*n.d.*	*n.d.*	0.02	0.03	*n.d.*

n.d. = not detected

n.a. = not analysed

Table 3.13. Major and minor element concentrations (mg/kg soil) in saturated paste extracts, averaging duplicates and using analytical techniques that gave best data.

Sample	Li	Na	Mg	Al	Si	K	Ca	B	Ti	Mn	Fe	Zn	Sr	Ba
S-PS	0.1	120.8	44.9	2.6	3.3	45.8	37.5	0.1	-	0.0	0.4	0.1	0.2	0.0
S-TH	0.0	259.9	94.2	9.3	2.3	75.9	82.5	0.2	0.2	0.2	0.3	0.7	0.5	0.1
S-S1	0.1	198.1	61.4	9.2	8.3	25.2	41.3	0.6	0.1	0.0	4.0	0.2	0.2	0.1
S-OD	0.0	235.7	75.8	3.3	19.8	45.7	33.2	2.0	-	1.5	0.3	0.2	0.3	0.2
S-S	0.1	164.8	95.7	2.1	3.8	17.8	86.2	6.4	-	0.1	0.2	0.2	0.4	0.1
S-GD	0.1	152.8	83.7	6.6	3.7	19.5	49.4	0.4	0.1	0.1	0.7	0.7	0.4	0.3
S-PB	0.1	135.8	59.5	1.1	6.9	34.4	49.9	0.2	-	0.0	0.5	0.4	0.2	0.0

Table 3.14. Trace elements in saturated paste extracts of soils by ICP-MS (in µg/kg soil). Numbers in parentheses indicate a second run on the instrument, whereas samples marked "dup" are duplicates of saturated pastes.

	S-PS	TH	S-TH (dup)	S-TH (2)	S-S1	S-OD	S-OD (2)	S-OD (dup)	S-S	S-GD	S-GD (2)	S-GD (dup)	S-PB
V	17.50	55.0	40.7	*n.d.*	119.7	17.47	*n.d.*	13.76	23.36	24.84	*n.d.*	31.24	14.31
Cr	3.61	16.59	16.13	*n.d.*	12.08	3.41	34.01	*n.d.*	8.03	15.81	*n.d.*	22.73	5.16
Co	3.15	4.16	1.49	3.97	3.23	36.96	33.67	32.11	2.54	3.93	2.41	3.01	1.81
Cu	6.13	29.27	33.77	113.2	42.66	22.03	10.65	111.8	11.14	23.76	*n.d.*	94.3	18.76
Ga	1.95	4.40	2.60	3.03	4.76	7.78	4.33	4.30	2.09	9.28	2.53	5.93	1.82
As	3.71	6.37	6.68	*n.d.*	5.14	10.92	*n.d.*	12.25	18.03	5.82	*n.d.*	10.87	3.96
Se	12.81	15.06	2.94	*n.d.*	14.10	43.7	47.7	41.95	13.75	65.8	80.4	39.34	5.63
Rb	50.1	71.7	53.2	90.2	40.34	161.9	145.5	124.5	9.16	5.30	6.79	4.38	38.30
Zr	10.09	6.17	1.07	10.49	11.74	2.57	5.01	2.13	2.48	7.60	5.55	7.43	1.47
Mo	2.41	7.21	3.96	7.02	16.68	1.63	1.49	2.46	0.65	4.50	4.10	2.61	34.15
Ag	4.50	4.36	0.44	101.6	4.59	3.42	36.79	1.11	4.47	4.34	109.2	1.16	13.01
Cd	1.20	21.53	32.18	27.59	20.68	1.51	2.94	16.31	6.85	30.75	36.66	139.5	2.07
W	7.62	37.81	43.1	63.0	7.24	0.225	12.69	51.9	1.44	2.01	9.57	78.2	4.57
Pb	5.68	14.61	14.97	1.18	20.82	2.70	0.66	*n.d.*	3.56	16.00	1.00	110.2	21.30

n.d. = not detected

Table 3.15. Trace elements in saturated paste extracts of soils by ICP-MS (in µg/kg soil) averaging duplicates and using analytical techniques that gave best data.

Sample	V	Co	Cu	Ga	Se	Rb	Zr	Mo	Cd	W
S-PS	17.5	3.2	6.1	2.0	12.8	50.1	10.1	2.4	1.2	7.6
S-TH	47.9	3.2	31.5	3.3	9.0	71.7	5.9	6.1	27.1	48.0
S-S1	119.7	3.23	42.7	4.8	14.1	14.1	11.7	16.7	20.7	7.2
S-OD	15.6	34.2	48.2	5.5	44.5	144.0	3.2	1.9	6.9	21.6
S-S	23.4	2.5	11.1	2.1	13.8	9.2	2.5	0.7	6.9	1.4
S-GD	28.0	3.1	59.0	5.9	61.8	5.5	6.9	3.7	69.0	29.9
S-PB	14.3	1.8	18.8	1.8	5.6	38.3	1.5	34.2	2.1	4.6

Table 3.16. Major cations and anions in saturated paste extracts as measured by IC, in mg/kg soil. Numbers in parentheses indicate a second run on the instrument, whereas samples marked "dup" are duplicates of saturated pastes.

	S-PS	S-TH	S-TH(2)	S-TH dup	S-S1	S-OD	S-OD dup	S-S	S-S(2)	S-GD	S-GD(2)	S-GD dup	S-PB
Br	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	11.8	0.0	0.0
Ca	58.7	123.3	59.4	156.2	68.8	43.1	70.8	121.2	106.9	57.4	no data	96.1	81.4
Cl	232.2	488.2	258.1	614.0	278.4	293.3	584.8	349.4	471.1	368.1	488.3	342.8	176.9
F	11.8	9.3	11.4	17.9	0.0	2.5	7.7	1.4	0.0	11.2	26.5	19.9	0.0
K	48.7	80.8	51.3	86.9	28.8	33.5	60.7	19.8	19.9	19.5	no data	13.3	11.2
Li	0.8	0.9	0.2	0.0	0.0	6.8	0.0	0.1	0.1	18.5	no data	0.0	0.1
Mg	65.5	106.9	61.6	143.4	61.4	60.7	101.4	122.0	116.5	104.5	no data	121.7	103.0
Na	119.2	285.4	139.6	264.0	205.8	114.0	251.0	169.8	174.2	160.6	no data	243.7	139.2
NH_4	7.7	26.6	15.5	15.1	20.8	26.2	32.9	35.6	21.7	0.0	no data	20.7	17.5
NO_2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	72.3	66.0	143.5	0.0
NO_3	1.3	5.7	1.5	1.6	1.2	9.0	78.0	57.5	87.8	4.3	3.1	0.5	1.8
PO_4	0.4	0.0	0.0	0.0	0.0	0.0	0.0	84.1	19.5	0.0	0.0	0.0	0.0
SO_4	152.0	207.8	142.7	242.5	150.5	43.5	83.2	278.6	280.3	169.1	171.5	228.2	124.6

Table 3.17. Ion concentrations (mg/kg soil) of SPE, averaging duplicates and using analytical techniques that gave best data.

Sample	Cl	F	NH_4	NO_2	NO_3	PO_4	SO_4
S-PS	232.2	11.8	7.7	0.0	1.3	0.4	152.0
S-TH	453.4	12.8	19.0	0.0	2.9	0.0	197.7
S-S1	278.4	0.0	20.8	0.0	1.2	0.0	150.5
S-OD	439.0	5.1	29.6	0.0	43.5	0.0	63.3
S-S	410.2	0.7	28.6	0.0	72.6	51.8	279.4
S-GD	355.5	19.2	10.3	93.9	2.6	0.0	189.6
S-PB	176.9	0.0	17.5	0.0	1.8	0.0	124.6

3.2.5 XRF Data

Bulk soils were analysed for major oxide composition by XRF. Composition incorporating H_2O- and loss-on-ignition (LOI), as well as composition recalculated on a volatile free basis is presented in Tables 3.18 and 3.19.

Table 3.18. Major oxide composition of soil samples by XRF, with H_2O- and LOI.

Sample	S-PS	S-TH	S-S1	S-OD	S-S	S-GD	S-PB
SiO_2	59.66	73.75	81.02	57.01	6.42	77.07	83.03
TiO_2	0.19	0.10	0.42	0.61	0.15	0.60	0.59
Al_2O_3	0.95	0.33	1.25	9.65	0.85	6.47	1.10
Fe_2O_3	0.09	0.06	0.16	1.91	0.08	0.47	0.05
MnO	0.00	0.00	0.00	0.01	0.00	0.00	0.00
MgO	0.07	0.04	0.05	0.44	0.11	0.11	0.03
CaO	0.14	0.12	0.02	0.01	0.20	<0.03	0.20
Na_2O	0.00	0.04	<0.04	0.04	0.03	0.03	<.001
K_2O	0.16	0.04	0.24	1.48	0.02	1.25	0.19
P_2O_5	0.03	0.02	0.02	0.14	0.02	0.03	0.02
SO_3	0.06	0.02	<0.022	<0.022	0.04	<0.031	<.001
NiO	0.00	0.01	<0.001	0.00	0.00	0.00	0.00
Cr_2O_3	0.00	0.00	0.00	0.01	0.00	0.00	0.00
H_2O-	3.96	2.38	2.44	7.11	12.15	1.41	1.77
LOI	33.89	22.20	13.71	20.79	79.32	12.06	12.88
Total	99.22	99.12	99.33	99.20	99.38	99.49	99.87

Table 3.19. Major oxide composition of soil samples by XRF recalculated on a volatile (H_2O- and LOI) free basis.

Sample	S-PS	S-TH	S-S1	S-OD	S-S	S-GD	S-PB
SiO_2	96.46	98.07	96.75	79.32	80.59	89.14	97.31
TiO_2	0.30	0.13	0.51	0.85	1.83	0.70	0.70
Al_2O_3	1.54	0.44	1.49	13.42	10.65	7.48	1.29
Fe_2O_3	0.15	0.08	0.19	2.66	0.97	0.54	0.06
MnO	0.00	0.00	0.00	0.02	0.01	0.00	0.00
MgO	0.12	0.06	0.06	0.61	1.40	0.13	0.03
CaO	0.23	0.16	0.02	0.01	2.51	<0.03	0.23
Na_2O	0.00	0.05	<0.04	0.05	0.39	0.03	<.001
K_2O	0.26	0.05	0.28	2.06	0.31	1.44	0.22
P_2O_5	0.05	0.02	0.02	0.19	0.20	0.03	0.03
SO_3	0.10	0.03	<0.022	<0.022	0.45	<0.031	<.001
NiO	0.00	0.02	<0.001	0.00	0.05	0.00	0.00
Cr_2O_3	0.00	0.00	0.00	0.01	0.03	0.00	0.00
Total	99.22	99.12	99.33	99.20	99.38	99.49	99.87

3.3 Rock Sample Analyses

Rock samples were studied in thin section as well as analysed for major oxide composition by XRF (Table 3.20) and mineralogy by XRD (Figure 3.5).

3.3.1 Petrography of Bedrock Samples

R-SK

This sandstone sample was taken from high up on the slopes of Platberg Mountain, near the transition between the Skurweburg and Goudini formations of the Nardouw Subgroup. It was uncertain whether the boulder from which the sample was taken was in place, or a large fragment from upslope. Quartz is the dominant mineral (~98%), with major opaque iron oxide minerals (probably; ~1%). The quartz grains (~0.3 mm) appeared fused and solution sutures were evident. Iron oxide minerals were concentrated on the edges (or solution fronts)

of quartz grains. Small amounts of feldspars, apatite and a number of zircons were also observed.

R-G(2)

Outcrops of Goudini sandstone were evident lower down on the slopes of Platberg Mountain, and samples were taken from two outcrop exposures (about 10 m apart). R-G(2) was an extraordinarily dark purple, suggesting iron oxides in higher concentrations than the light yellow R-SK sample. Composition was about 80% quartz, and about 15% opaque iron oxides. Again, the quartz grains were fused and angular (~0.2 mm), and the crystals exhibited undulose extinction. Iron oxide minerals were concentrated in the pore spaces between the quartz grains. Small amounts of mica, including biotite, were visible.

R-G1

This rock specimen is pink with white patches. The quartz grains in thin section (~95%) were not as fused as those in the previous two samples, and about 0.2 mm in size. Once again, iron oxide opaques were the other major component (~4%) and were focused on the edges of quartz grains. There appeared to be more biotite than in R-G(2), as well as some muscovite. A clear band (the white patch on the sample) in the centre of the slide had far fewer opaques and was more micaceous than the darker, opaque dominant sections.

R-C1

Two samples were taken from the Cedarberg Shale, but this formation appeared to be more of a siltstone than true shale. The quartz was again dominant but not as much as in the sandstones (~68%), and the grains were much finer (<0.1mm), indicating a lower energy deposition environment. In contrast to the previous sandstone samples, clay and mica minerals (e.g. muscovite) were second most abundant at around 25-30%. Iron oxides were also present, but only at around 2%. These also occurred mainly together with the quartz.

R-C2

This sample had dark streaks in it, which in thin section appeared to be bands of clay minerals, perhaps associated with organic matter. Otherwise, this sample was very similar in composition to R-C1.

R-PK

This sample was taken from an in-stream exposure at the Pakhuis/Cedarberg Formation contact. In thin section, the quartz was mostly very fine grained (<0.05 mm), but had layers of alternating coarser and finer grained material that could be representative of varves (seasonal glacial depositions). Quartz made up about 65% of the sample, with the rest chiefly clays and micas (30%), along with some feldspars and iron oxides. There were also fine lineaments of dark material cross cutting the coarse and fine layers at about 60° to the bedding plane. This is perhaps a result of incipient cleavage from shear deformation across the fine-grained rock at some stage.

R-PF

A sample of Peninsula Formation bedrock was taken from an outcrop on the path near the Leopards Gorge waterfall. The composition of this formation is chiefly quartz (~99%) with virtually no other minerals present.

3.3.2 XRF Data

Weight percent compositions of rock and soil samples determined by XRF are given in Table 3.20. All samples were dominated by SiO_2 Other significant components were aluminium, iron and potassium oxides. Titanium, calcium and magnesium oxides were present in small amounts, with all other oxides less than one percent.

Table 3.20. Major composition of rock samples as determined by XRF, incorporating H_2O- and loss-on-ignition (LOI), and recalculated on a volatile free basis.

Sample	R-SK	R-G1	R-G(2)	R-C1	R-C2	R-PK	R-PF
SiO_2	95.78	89.93	68.47	75.94	60.28	63.21	98.60
TiO_2	0.70	0.29	0.23	1.04	1.33	1.12	0.05
Al_2O_3	1.28	2.49	1.05	14.11	23.55	22.10	0.07
Fe_2O_3	0.88	2.77	29.13	1.17	1.93	1.23	<0.01
MnO	0.01	0.01	0.02	0.01	0.01	0.01	0.00
MgO	<0.01	<0.01	<0.02	0.49	1.11	0.94	<0.03
CaO	<0.07	<0.06	<0.07	<0.07	<0.07	<0.07	<0.06
Na_2O	<.001	0.13	<0.02	0.11	0.13	0.11	<0.04
K_2O	0.08	0.60	0.21	2.97	6.20	6.80	0.01
P_2O_5	0.02	0.02	0.04	0.03	0.03	0.05	0.01
SO_3	<0.037	<0.03	<0.022	<0.031	<0.031	<0.029	<0.038
NiO	0.00	0.01	0.00	0.00	0.00	<.001	<0.001
Cr_2O_3	0.00	0.01	0.00	0.01	0.02	0.01	0.00
H_2O-	0.07	0.30	0.07	0.18	0.44	0.30	0.03
LOI	0.28	2.88	0.46	3.52	4.74	4.05	0.28
Total	99.10	99.42	99.69	99.57	99.77	99.94	99.04
Majors recalculated on a volatile free basis							
Sample	R-SK	R-G1	R-G(2)	R-C1	R-C2	R-PK	R-PF
SiO_2	96.12	92.90	68.83	78.87	63.58	66.09	98.90
TiO_2	0.70	0.30	0.24	1.09	1.40	1.17	0.05
Al_2O_3	1.28	2.57	1.06	14.65	24.84	23.11	0.07
Fe_2O_3	0.88	2.86	29.28	1.22	2.04	1.29	<0.01
MnO	0.01	0.01	0.02	0.01	0.01	0.01	0.00
MgO	<0.01	<0.01	<0.02	0.51	1.17	0.98	<0.03
CaO	<0.07	<0.06	<0.07	<0.07	<0.07	<0.07	<0.06
Na_2O	<.001	0.13	<0.02	0.11	0.13	0.12	<0.04
K_2O	0.08	0.62	0.21	3.08	6.54	7.11	0.01
P_2O_5	0.02	0.02	0.04	0.03	0.03	0.05	0.01
SO_3	<0.037	<0.03	<0.022	<0.031	<0.031	<0.029	<0.038
NiO	0.00	0.01	0.00	0.00	0.00	<.001	<0.01
Cr_2O_3	0.00	0.01	0.01	0.01	0.02	0.02	0.00
Total	99.10	99.42	99.69	99.57	99.77	99.94	99.04

3.3.3 XRD Data

Rock samples powdered and analysed by X-ray diffractometry to determine mineralogy. The principal mineral is quartz in all samples with accessory minerals mica, kaolinite, hematite and some feldspars (Figure 3.5).

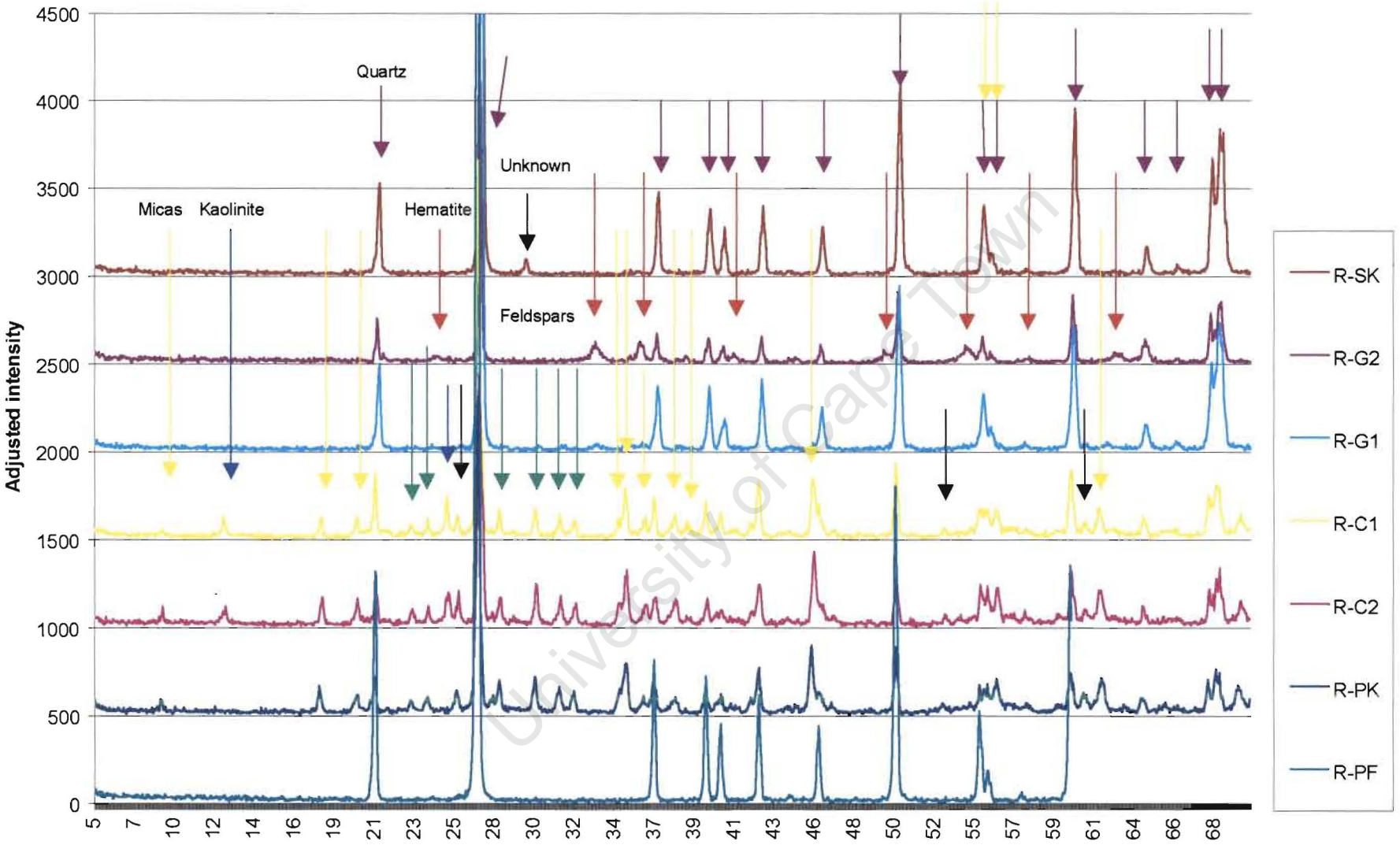


Figure 3.5: XRD patterns of rock samples from the study area.

CHAPTER 4: DISCUSSION

4.1 Stream Water Chemistry

The chemistry of the various streams sampled in this proclaimed mountain catchment area (MCA) is remarkably homogeneous on the whole, given that they flow or arise on geological formations with significantly different chemistry. The one sample that appears to differ significantly in some trends is the W8 sample from the headwaters of the Oudebosch River, in the Oudebosch Forest. The waters are also exceptionally pure, with very low EC (< 160 µS/cm) (Table 3.1) in all cases. This is somewhat higher than EC of headwaters of the Palmiet River (<80 µS/cm) (Gale, 1992). The Palmiet River headwaters make an excellent comparison to the streams studied in the area, as it arises in the Kogelberg ~70 km to the north, in similar geology and terrain dominated by mountain fynbos. pH was < 4.5 at all sites (except W8) which, along with the low temperatures (<15°C), makes the Leopards Gorge River and its tributaries cool, acid, blackwater mountain streams typical of the south-western Cape (Gale, 1992; Koch *et al.*, 1994). Of the major dissolved ions, only Na, Mg, Cl and SO_4 were present in all samples in concentrations exceeding 1 ppm, and varied within 5, 0.7, 13.8 and 1.9 ppm respectively in all the measured samples (Table 3.7). Dissolved silica and calcium exceeded 1 ppm in one and six samples, respectively. Other ions present were Al, K, Fe, NH_4 and NO_3 (Table 3.7). Of the trace elements that were reproducible by ICP-MS, only B, Zn, Sr, Sb and Mn were present in concentrations greater than 1 ppb (Table 3.7). All samples from the study area had zero or negative alkalinity in meq/L or as $CaCO_3$ in mg/L (Table 3.2). Gale (1992) similarly reported zero alkalinity in the headwaters of the Palmiet River, and this is typical of surface waters flowing over the highly leached Table Mountain Group (TMG) sandstones in the coastal southern Cape regions (Koch *et al.*, 1994; Lahav *et al.*, 2001). Stream pH is also low in these areas, with values for the Palmiet headwaters ranging between 4.0 and 4.5 (Gale, 1992), which is very similar to the values obtained in this study. The in situ pH, compared to measurements taken in glassware in the field, was consistently

lower. This was probably due to equilibrium effects and the pH instability in flowing water, as well as carbon dioxide degassing in samples after collection. The low pH, combined with the negative alkalinity of the samples from the Kogelberg and HPNBG study area implies something other than bicarbonate being neutralised, or the presence of strong mineral acidity (Rounds, 2001). The combination of organic acids, in the form of DOC, together with the lack of carbonate buffering from the bedrock and silicic acid from quartz weathering, are the most probable causes of the low pH of stream waters.

4.1.1 Major Element Chemistry of Stream Waters

The major element composition of river water (Ca, Mg, Na, K, SO_4, Cl, and Si) reveals the nature of weathering and a variety of other natural and anthropogenic processes on a basin-wide scale. The major element chemistry of river water can also provide important insight into global biogeochemical cycles of elements in the continent–ocean–atmosphere system (Chen *et al.,* 2002). The main source of ions in waters of the south-western Cape appears to be rain, mist, snow or dry deposition inputs (Day and King, 1995). Due to the area's close proximity to the ocean, sea salts are a major source of dissolved material in precipitation. Seawater droplets become transferred to the atmosphere by wave action, turbulence and evaporation until a solid aerosol particle is left. Generally, Na, Cl, Mg and K decrease in concentration, and the ionic ratio Na/Cl increases, with distance inland from the coast (Ward and Robinson, 1990). It is thus of value to plot the major elements against chloride as a conservative tracer, as it is unlikely that there would be a chloride sink, or source in this system other than sea spray. In this way, it is possible to discuss the inputs of major elements. The purity of these waters can be partly explained by looking at the composition of the bedrock in the area (Table 3.20). Rock samples taken are dominated by quartz (SiO_2), and the geological formations contain very little easily weathered minerals that would provide a source of major elements to soils, and ultimately to streams. Even so, it might be expected that concentrations of certain elements would be elevated when stream waters flow through soils derived from bedrock containing

more of that element. For example, the Cedarberg Formation contains an order of magnitude more potassium oxide than the other formations analysed in the study area, and thus the stream waters at W8 and W12 (which lie on Pakhuis/Cedarberg) should have higher concentrations of soluble K. Although the K concentrations are slightly elevated at these sites, they are certainly not an order of magnitude higher, and a similarly elevated K concentration was recorded downstream at W6, which is on pure Peninsula bedrock. This example can be applied to most elements that might be expected to show variations in accordance with underlying bedrock composition. The homogeneity among the various water samples can be explained partly by the geology, relief, and the residence time of groundwater in the area.

Although the Cedarberg and Pakhuis formations do occur in the Kogelberg, they are relatively minor compared to the dominant sandstones of the Peninsula Formation and the Nardouw Subgroup. The major peaks are all sandstone with the more erodable shales of the Cedarberg Formation forming flatter plateaus, saddles and gorges (Johns and Johns, 2001). The bulk of precipitation recharge thus falls on sandstone at the higher elevations where it enters the groundwater through the intricate network of joints, fractures, fissures and cavities characteristic of the Table Mountain Group (TMG). These factors govern the infiltration, storage and transmission of groundwater though its fractured arenaceous units. Due to this fractured nature, groundwater recharge is generally favourable in high rainfall regions like the Kogelberg, and precipitation infiltration rates of up to 15% aren't unrealistic (Meyer 2001). Thus, the TMG has abundant springs; three kinds of which can be distinguished: fault and major structure controlled (generally deep circulating springs), lithologically controlled (relatively shallow circulating springs), and springs seeping from numerous small fractures and joints (very evident shortly after rainfall events) (Meyer, 2001). Most springs in the Kogelberg observed during this study can be categorised as shallow seeps Groundwater residence time is in the study area would be shorter than for deeper springs (days or weeks compared to hundreds or thousands of years). During the high rainfall winter season surface waters will be fed

predominantly by surface runoff that has a seawater signature. Even during the drier months, perennial streams will be fed by waters from shallow aquifers that still have a seawater signature from short residence time and lack of easily weathered material in the predominant Peninsula and Skurweburg formations. Thus, time appears to be a limiting factor in this regard. This would appear to be supported by the fact that concentrations of Si in stream waters are well below the solubility of quartz at 14°C (Langmuir, 1997) (Figure 4.1). This would be caused by the continuous removal of dissolution products, and lack of residence time in slow moving aquifers, which would cause dissolved Si to approach equilibrium concentrations more closely.

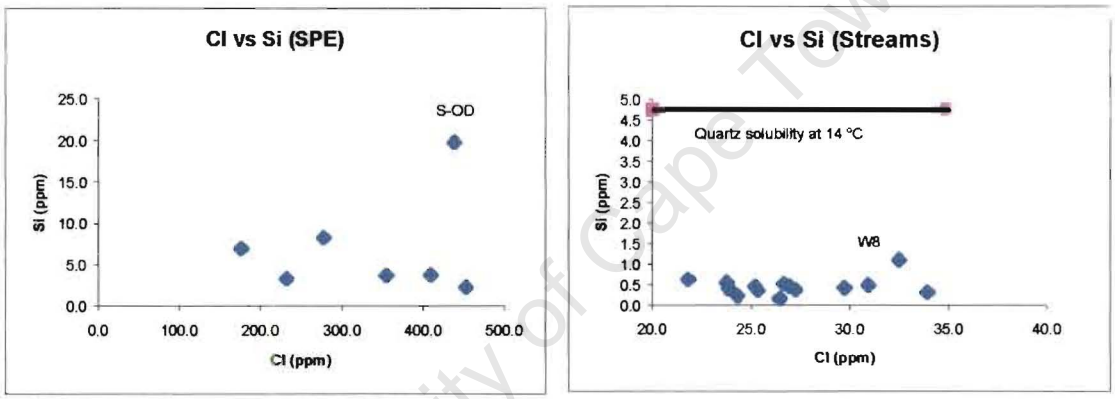


Figure 4.1 Silica against Cl for stream waters and saturated paste extracts (SPE). Quartz solubility at 14°C is also illustrated. Samples falling off the trend are noted.

Most Si in natural waters occurs mainly as monosilicic acid H_4SiO_4, and is from the weathering of quartz and aluminosilicate minerals (Langmuir, 1997). The Cedarberg Formation contains a higher proportion of such minerals (e.g. kaolinite) (Table 3.20 and Figure 3.5) and this is probably the reason why the S-OD and W8 samples (both soil and water), which are situated on this formation, are elevated in dissolved Si, but are still not saturated. There is also the possibility that the undersaturation is caused by Si retention by fynbos vegetation, although this needs further study to be confirmed.

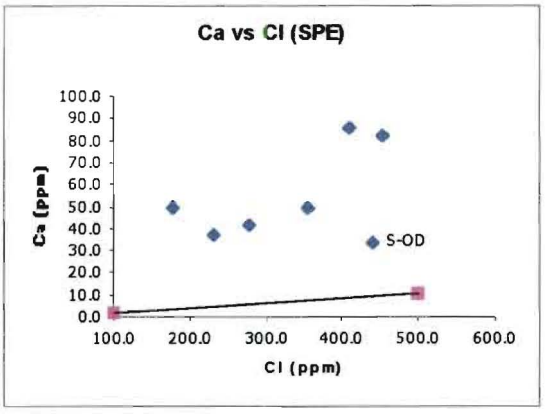
Although the Department of Water Affairs and Forestry (DWAF) has no groundwater data for the study area, the water data obtained in this study can be compared to that from other sites on the TMG. Chemical components and

parameters of sampled TMG groundwater around the Worcester area are given in Table 4.1. The quality of groundwater in the TMG is generally excellent (from a consumption point of view) with electrical conductivities (EC) usually ranging between 50 and 700 µS/cm. The groundwater normally has the same signature as the precipitation (Meyer, 2001). The waters from the study area have EC in the same range as those TMG sites sampled in Table 4.1. Levels of F, Si and SO_4 are lower in the study area whereas Na, Cl, Mg, Ca and K fall within the ranges for the TMG (Table 4.1).

Table 4.1. Physico-chemical parameters of TMG groundwater sampled in boreholes (A, B and C) near Worcester, Western Cape (after Meyer, 2001), and global mean concentrations in rivers.

Parameter	Unit	A	B	C	Global Mean River Water (Langmuir, 1997)
EC	µS/cm	50	360	78	
TDS	mg/L	21.0	203.0	51.0	120
pH		6.95	7.4	6.4	
Na	mg/L	3.9	25.0	7.17	6.3
K	mg/L	0.31	2.3	1.93	2.3
Ca	mg/L	0.7	28.0	3.37	15
Mg	mg/L	1.4	6.0	1.72	4.1
Cl	mg/L	7.4	60.0	12.48	7.8
SO_4	mg/L	4.2	22.0	1.73	11
TAL (as $CaCO_3$)	mg/L	2.4	48.0	12.83	
F	mg/L	0.09	0.2	n.d.	
$NO_3 + NO_2$ (as N)	mg/L	n.d.	0.09	n.d.	
PO_4 (as P)	mg/L	0.03	0.009	0.16	
Si	mg/L	5.77	10.5	n.d.	13 (as SiO_2)
NH_4 (as N)	mg/L	0.01	0.04	n.d.	
Fe	mg/L	n.d.	n.d.	n.d.	0.67

n.d. = not determined
TDS = Total dissolved solids
TAL = Total alkalinity



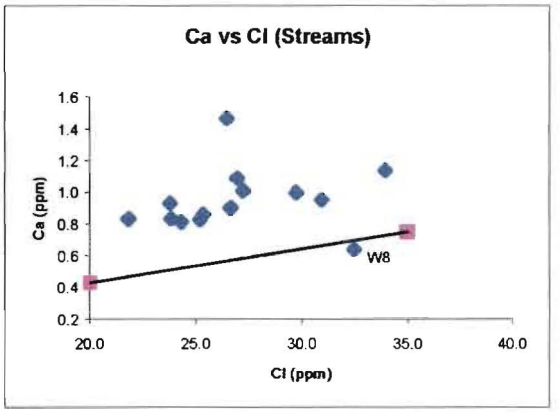


Figure 4.2. Plots of Ca vs. Cl for both SPE and streams. The seawater signature line is shown linking squares. Samples that do not conform to the trends are labelled.

Ca is elevated relative to chloride compared to the seawater ratio in both stream water and SPE (Figure 4.2). There is thus an output of Ca in the system, which needs to be balanced by an additional source apart from the bedrock, which contained <0.07 wt% Ca in all samples (Table 3.20). Calcium, which is an essential element in plants (Ugolini and Spaltenstein, 1992), would appear to be returned to the soils through litter mass, which in the Kogelberg is more rich in Ca than any other base cation (i.e. Na, Mg, K) per hectare. Compared to the data for above-ground live biomass, it appears that Ca is least conserved from live biomass to fynbos litter mass compared to Mg and K (Van Wilgen and Le Maitre, 1981) and suggests a preferential accumulation of Mg and K in fynbos. Van Wyk *et al.* (1992) also determined a net Ca gain in a mountain fynbos catchment, even after fire, but the study area in Stellenbosch may have been on Cape granite, which contains more Ca rich minerals than TMG sandstones. The additional source of Ca is possibly wind blown dust, which is often enriched in this component compared to other ions (Berner and Berner, 1996), but the source of such dust is uncertain, perhaps being transported from the Karoo during Berg wind events, and deposited over the Kogelberg.

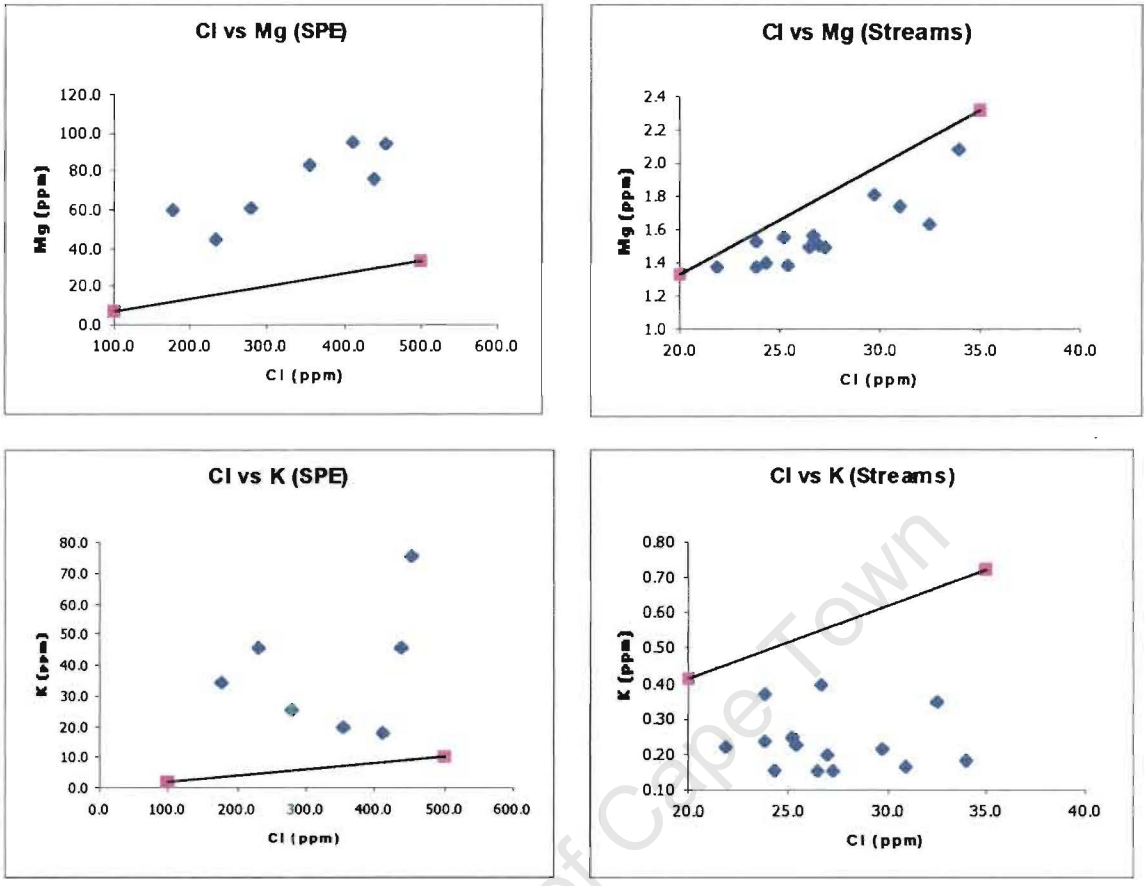


Figure 4.3. Concentrations of K and Mg in SPE and streams relative to Cl. The seawater ratio is shown as a solid line.

In contrast to Ca, Mg and K are elevated relative to Cl in the soils compared to the seawater ratio, but depleted in the streams (Figure 4.3). Both are also essential elements in plants (Ugolini and Spaltenstein, 1992), and are chiefly derived in soils and stream waters from mineral weathering (Drever, 1997). Both Mg and K are present in small amounts in the bedrock of the study area (MgO and K_2O up to 1.17 and 7.11 wt%, respectively; Table 3.20), and are also contributed by precipitation inputs. The stream depletion of these ions would imply that the available Mg and K from the bedrock (which are present in higher concentrations than Ca; Table 3.20) are being concentrated by the fynbos, and recycled sufficiently well that the output from the streams is reduced compared to Ca.

Sodium, another essential plant element, appears to behave similarly to Mg and K in that it is slightly depleted in the streams relative to chloride, but the trend in the soils follows the seawater signature (Figure 4.4).

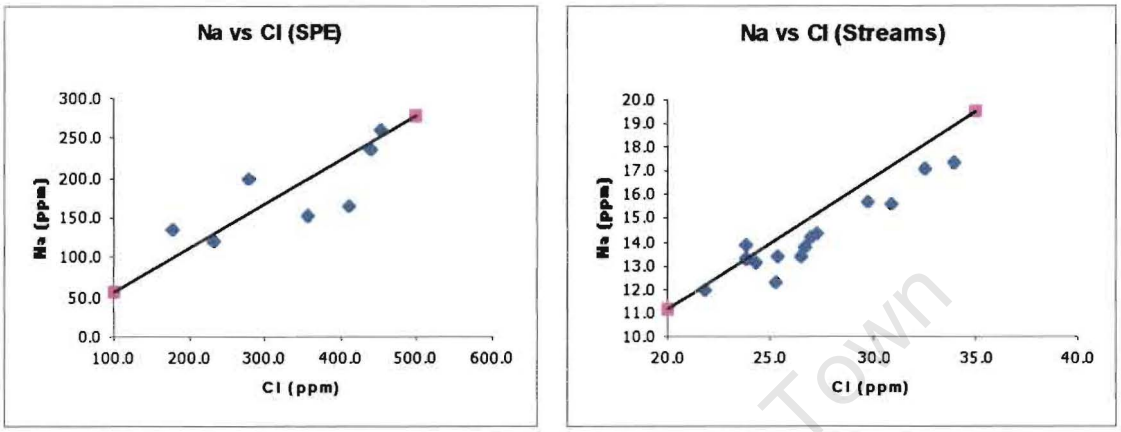


Figure 4.4. Sodium relative to Cl in SPE and streams, compared to the seawater signature.

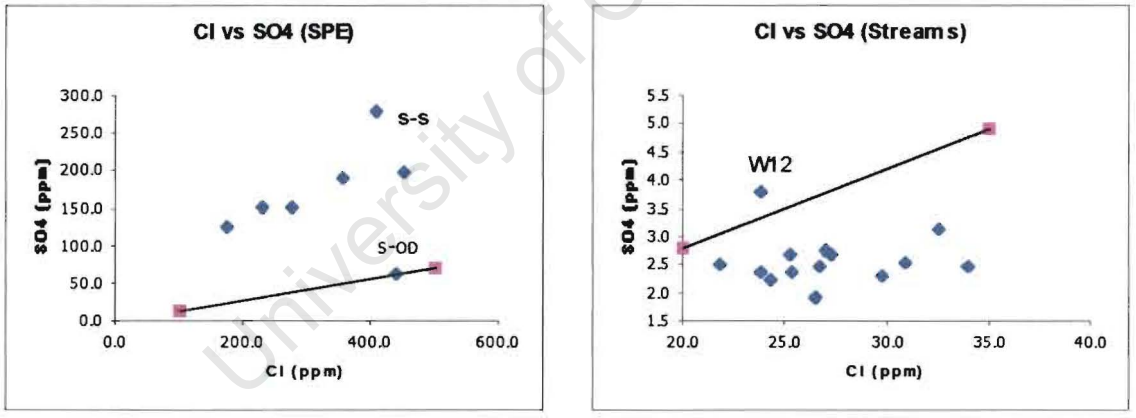


Figure 4.5. Sulphate against Cl in SPE and streams, compared to the seawater signature.

Plots of sulphate against Cl in SPE and streams (Figure 4.5) show that SO_4 levels are elevated in the soils relative to the seawater signature (except for S-OD) and depleted in the stream output (except for W12) similar to Na, Mg and K. The S-OD soil sample is on the seawater signature line, indicating that the soil in the afromontane Oudebosch Forest does not significantly accumulate SO_4 compared to the other sites sampled. This may be because of the different

element composition of the vegetation compared to the fynbos. The W12 (stream) and S-S (soil) samples are significantly elevated in SO_4 relative to Cl compared to other sample sites. These two samples are in close proximity and come from a bog like environment with high amounts of DOC in the water and organic C in the soil. Close relationships have been established between total sulphur and organic carbon in soil, and over 90% of soil sulphur is derived from organic residues. Portions of these residues are decomposed by soil organisms to SO_4 (Murphy, 1980). Thus, the elevated SO_4 at W12 and S-S is probably related to the high organic matter content present at these sites (Table 3.10). Additionally, slow flow combined with evaporation may be increasing the higher concentrations in this area. Gale (1992) found similar concentration ranges of up to 4 ppm in the headwaters of the Palmiet River.

Small amounts of nitrate and ammonium, but no nitrite, were measured in stream samples. Ammonium tended to increase in the samples over time, as consecutive runs on the IC showed elevated concentrations over the first run. This is most likely a by-product of microbial processes within the sample, even though it was refrigerated; it was unacidified for IC analysis. No phosphate was recorded in any of the surface water samples, confirming the typical nutrient poor status of blackwater mountain streams in the western Cape. Nitrate and ammonium were similar to concentration ranges in the Palmiet headwaters (Gale, 1992) but the low nitrite (<60 ppb) and phosphate (<50 ppb) measured by that study probably would have been below the detection limits of the IC, and were therefore not observed in this study.

4.1.2 Trace Elements

Apart from the major elements, only boron, manganese, zinc, strontium, antimony and lead were present in surface waters in concentrations exceeding 1 ppb. Data for elements below 1 ppb was discarded because of poor reproducibility. Strontium and antimony are present in relatively narrow concentration ranges compared to zinc and boron, which is probably because the

latter are essential micronutrients in organic systems (Davies, 1980; Knezek and Ellis, 1980).

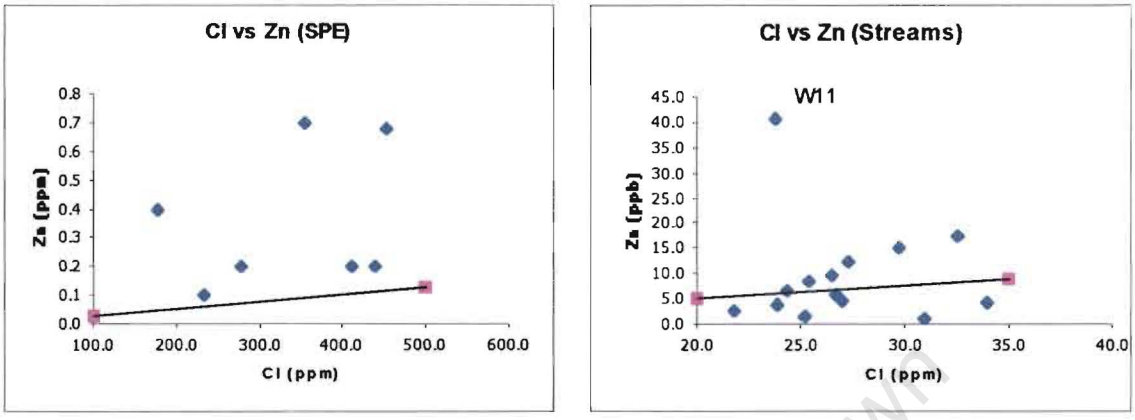


Figure 4.6. Zinc relative to Cl in SPE and streams, compared to the seawater signature (solid line).

Zinc is elevated relative to Cl in soil water compared to the seawater ratio, but the stream output appears to conform better to the seawater ratio (Figure 4.6). There is some scatter in the SPE but there does appear to be a trend to increase dissolved Zn with increasing Cl in stream waters. Increasing ionic strengths do increase the tendencies of ions to move into solution (Stumm and Morgan, 1996), which is probably the case here. The W11 sample (just upstream of the Leopards Gorge waterfall) shows an anomalous spike in Zn, and does not conform to the trend shown by the other samples. It is uncertain why this may be, as the sample taken downstream at W6 on the same day did not show a similar spike. It is possible that a small local variation in Zn occurred on the ppb scale, as Zn is a plant micronutrient and complexes readily with dissolved organic matter (DOM). Local changes in pH or availability of other ions influencing Zn solubility (Cu, Al, Fe) (Knezek and Ellis, 1980) may be causative agents.

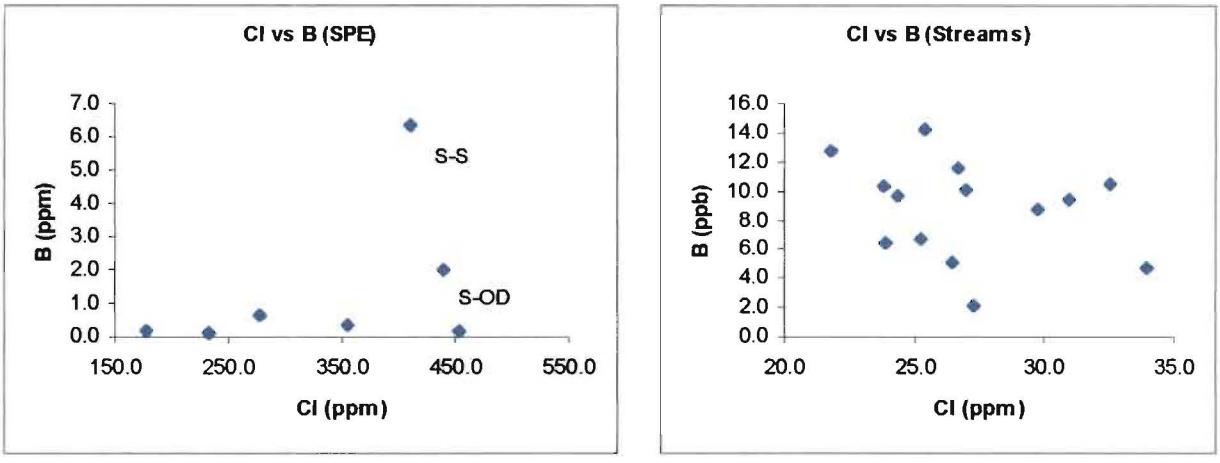


Figure 4.7. Boron plotted against Cl in both SPE and streams.

Boron does not appear to show any trends in soil or streams (Figure 4.7), but B is present in higher concentrations in soils derived from shales (such as the Cedarberg Formation), loess and alluvium, and tends to increase with soil organic matter (Fleming, 1980). This would explain the higher values for B in S-OD (shale soil) and S-S (35% organic C content) in SPE.

An understanding of the processes controlling trace metal cycling in natural waters is vital in determining and anticipating anthropogenic impacts on the hydrosphere (Stumm and Morgan, 1996). The pristine nature of the waters in the Kogelberg should enable an immediate assessment of any pollution impacts, because the existing levels or trace metals are so low. Soderberg (2002) found small amounts of anthropogenic Pb in the Citrusdal area, but this can probably be ascribed to heightened agricultural and other anthropogenic activity in that area compared to the Kogelberg.

4.1.3 Dissolved Organic Carbon (DOC)

All natural waters contain dissolved organic compounds (Drever, 1997; Crum *et al.*, 1996, Schwarzenbach *et al.*, 1993). Dissolved organic carbon/material (DOC/DOM) is typically defined as the fraction that can pass through a 0.45µm filter as opposed to particulate organic carbon (POC), which cannot. Concentrations of DOC in the surface waters for this study were all above 10 mg/L (Figure 3.1), ranging up to 16 mg/L in the W12 and W10 samples. This is

consistent with the blackwater appearance of the streams in the study area. There is little doubt that the high DOC content is related to the soil organic carbon content, and that the soil water must be supplying large amounts of DOC in the form of humic substances to the surface streams in the Kogelberg and HPNBG. The return of nutrients to the soil (or directly to water in the case of riparian, or stream-bank vegetation) from litterfall via decomposition is an important link in plant nutrient cycling, and the carbon rich sclerophyllous leaves of fynbos (Mitchell *et al.*, 1986) almost certainly contribute the bulk of organic carbon to soil and stream water. Recent hydrochemical research in headwater catchments has emphasised the importance of the riparian zone as a relatively restricted part of the catchment that exerts a disproportionately large influence on stream water chemistry. The extent to which the riparian zone influences stream water chemistry is still under debate and the scale over which that influence operates is uncertain (Smart *et al.,* 2001). The stream sample lowest in DOC (W7) was completely overgrown with fynbos at the sample site. High DOC levels may therefore have been expected and riparian vegetation probably would have a large impact on the water chemistry (i.e. DOC) at this site were it not for the steep gradient and resulting short residence time of water through this section. There would appear to be a good inverse correlation between stream gradients (and thus flow rates) in the field and DOC concentration. The highest DOC values were recorded from the W12 sample, (which is the head waters for the main flow of the Leopards Gorge River), and W10 (which was a seep flowing across the path on the western side of Leopards Gorge). Both these sites had the shallowest slope and hence slowest flow rate (and therefore longest residence time in terms of contact with the soil) compared to all other sites, with the possible exception of S-PS. The W7 site had the steepest slope and thus probably had the fastest flow rate of all sites.

The DOC of the streams in the study area is approximately an order of magnitude higher than the mean for samples taken from the Cedarberg Mountains in the Citrusdal are by K. Soderberg (2002). This is probably indicative of the difference in biomass between the Kogelberg and Cedarberg areas, with

the Kogelberg having much denser vegetation on a scale also approaching an order of magnitude.

Humic substances generally show strong absorbance in the UV–Vis range (from 190 to 800 nm), especially in the UV region, because of the presence of aromatic chromophores and other organic compounds (Chen *et al.*, 2002). The absorbance curve is characterised by a featureless decrease with increasing wavelength, and gives virtually no structural information (Figure 4.8). Despite the differences in origin of fulvic acids (FA), and humic acids (HA), the absorbance curves overlap, perhaps due to their similar π electron distributions (Ghosh and Schnitzer, 1979). The UV absorbance at 260 nm is often used to determine the relative abundance of aromatic C=C content of natural organic matter (NOM) because π–π^* transitions in substituted benzenes or polyphenols occur in this wavelength region. Absorbance ratio at 465/665 nm, commonly referred to as the E4/E6 ratio, is independent of the concentration of the humic substances but is variable with the genesis of organic matter in different environments (Ghosh and Schnitzer, 1979, Chen *et al.*, 2002). The E4/E6 ratio for humic acids (HA) is usually <5.0; the ratio for fulvic acids (FA) ranges from 6.0 to 8.5 (Chen *et al.*, 2002).

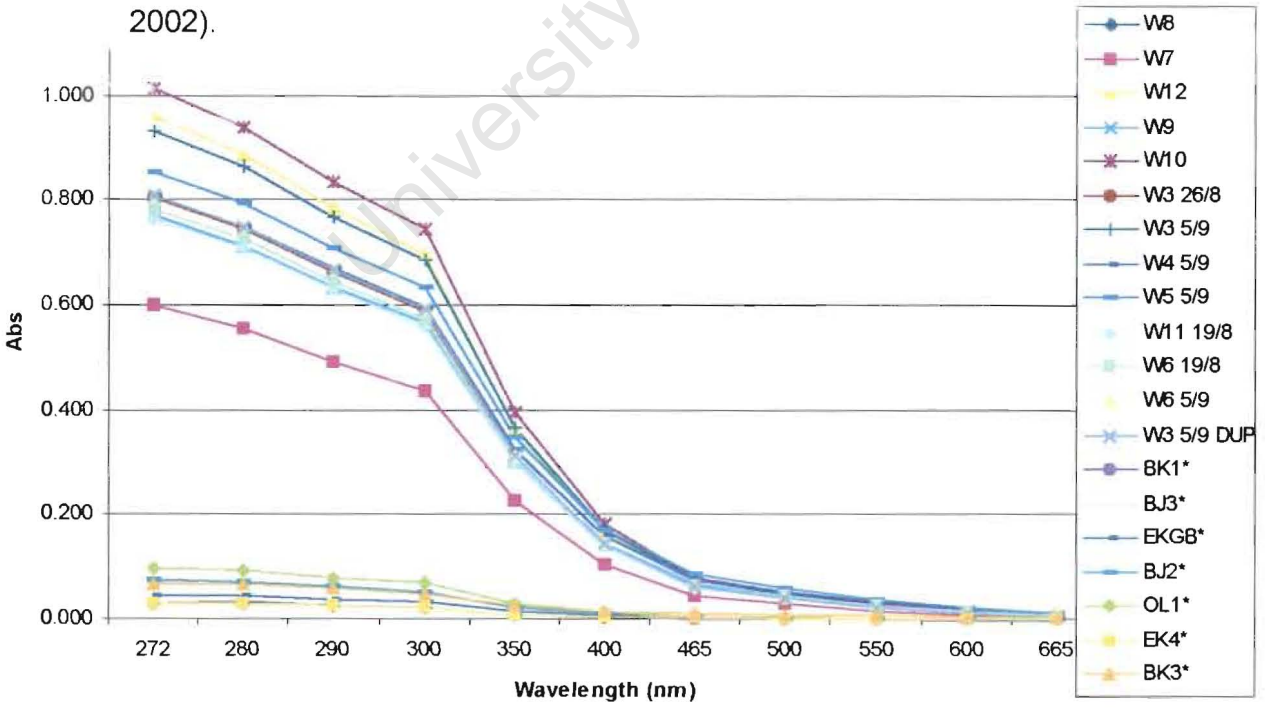
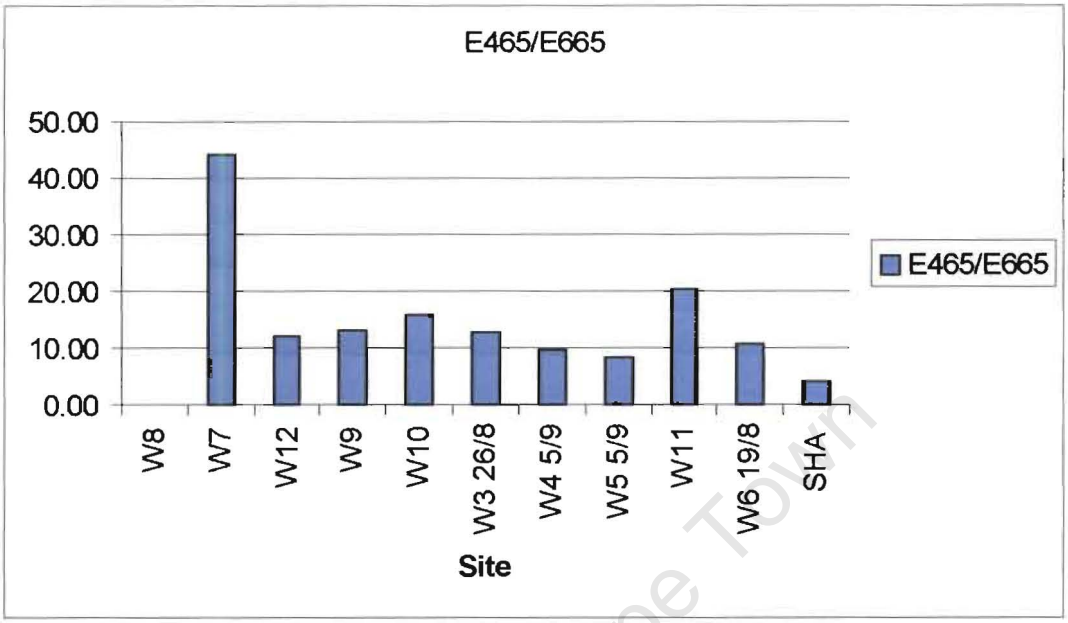


Figure 4.8. Absorbance plots of surface water samples from 272 nm to 665 nm. Samples labelled with a * are from the Cedarberg (Soderberg, 2002).

A



B

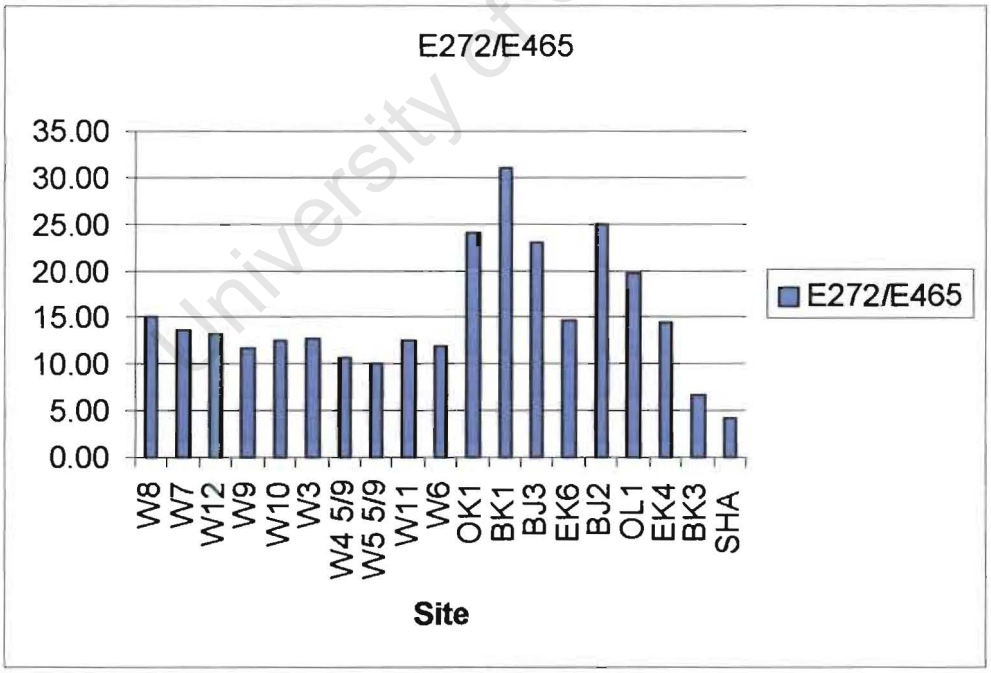


Figure 4.9 E4/E6 rations (A) and E272/E465 ratios (B) of DOC in surface water samples from the Kogelberg (OHW to LGB on the x-axis) and Cedarberg (OK1 to BK3 on the x-axis). SHA is soil humic acid described by Chen *et al.*, 2002.

All of the Kogelberg water samples except for W8 show higher absorbencies than the samples from the Cedarberg. This is probably related to the higher DOC concentrations in the Kogelberg. As mentioned above the E4/E6 ratios above are useful for discriminating between humic and fulvic acids. Unfortunately, absorbance at 665 nm was zero or negative for Cedarberg samples, possibly because the DOC concentration was too low for effective characterisation by absorbance at that wavelength. Thus, a comparison between the Cedarberg and Kogelberg areas was not possible for this ratio. The ratios for the Kogelberg samples are all >5 (Figure 4.9 A), and greater than that obtained for soil humic acid (SHA) by Chen *et al.* (2002), suggesting that the major component of the DOC is fulvic acid in nature. This is corroborated by the fact that no precipitation (of humic acids) or change in colour was observed in the samples upon acidification to pH <1.5. This is only a tentative characterisation, as the absorbencies at 665 nm are very low (<0.01) and the ratio is thus sensitive to very small changes in absorbance at this wavelength. However, it is consistent with mean DOC composition of surface waters in the USA, where 45% of the DOC is fulvic acid and only 5% is humic acid (Drever, 1997). Chen *et al.* (2002) used the ratio 265/465 nm in a similar fashion as the E465/E665 ration to detect trends in DOC. Although measurements at 265 nm were not done in this study, Figure 4.9 (B) illustrates ratios for E272/E465, which should be very comparable. These ratios appear to be much more consistent in the Kogelberg samples than in the Cedarberg samples, which may reflect the larger watershed sampled in the Cedarberg study. Again, both Kogelberg and Cedarberg samples have ratios higher than that of soil humic acid (Chen *et al.*, 2002), suggesting a fulvic acid character. The W8 sample is anomalous in this case, as it did not have measurable DOC content, and had low absorbance at 272 and 465 nm. The correlation between Abs 272 nm and DOC is exceptionally good (0.9915) (Figure 4.10). This also implies that the DOC in all the samples is of a similar nature, thus giving the comparable E4/E6 and E272/E465 ratios.

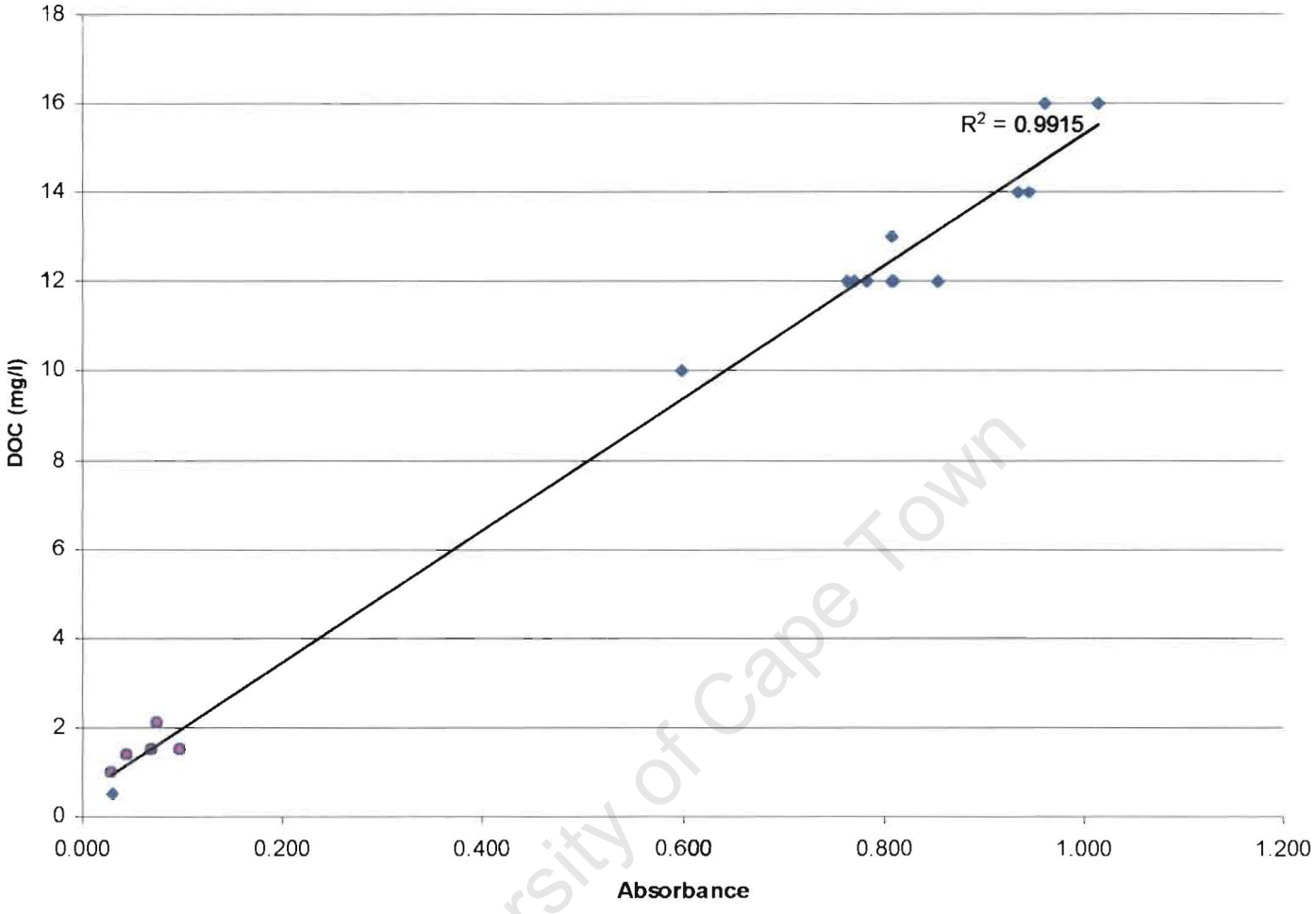


Figure 4.10. Correlation between DOC concentration (in mg/L) and specific absorbance at 272 nm. Kogelberg samples are shown as diamonds, and Cedarberg samples are shown as circles.

4.2 Soils

4.2.1 Soil Types

Previous studies determined that soils present in the Kogelberg were of the Mispah or Clovelly form (Le Maitre, 1984). The soils of the Kogelberg were reported as generally grey to very dark grey (2.5 YR 6/1 to 2.5YR 3/1) and to vary from a shallow sandy A horizon over fractured rock (Mispah form) to a more

developed Clovelly form (according to the S.A. Binomial System; Mavicar *et al.*, 1977) with a coarse sandy A horizon and a yellow apedal B horizon over rock. In some cases, the Clovelly form appeared over an impermeable layer of clay, indicating a duplex soil possibly derived from overlying or presently neighbouring Bokkeveld shales at some period in the past (Le Maitre, 1984).

However, taking soil chemistry such as CEC and organic carbon into account, it would appear that at least one sample (S-S) is representative of an organic O horizon, having an average organic carbon content of about 34% (Table 3.10), which is far higher than the required 10% that would be required to classify it as such (Soil Classification Working Group, 1991). The S-S sample was also quite moist, being just above the seep where the W12 water sample was collected and it appears to be an incipient peat bog. Organic O horizons are indeed found on mountain slopes, and are normally black to dark brown (which was the case) and the predominant state of decomposition of plant litter varies from finely divided to fibrous. This type of horizon is not widely distributed in South Africa (and S-S was certainly unique in the study area), and has not been well studied (Soil Classification Working Group, 1991). The classification is therefore somewhat tentative.

It is quite difficult to qualify the remaining samples with certainty. Mispah soils have orthic surface horizons (not melanic, vertic, humic or organic) situated on parent bedrock (R horizon). Although all soil samples except S-OD and S-S were sampled down to parent bedrock (which was mostly at a soil profile depth of about 20cm), it is possible to classify these as humic A horizons. This is because they all contain at least 1.8% organic carbon; do not overlie G or E horizons or podzol, plinthic, prismatcutanic or red structured B horizons, placic pans or other material with signs of wetness, and have less than 40 $mmol_c/kg$ exchangeable cations per one percent of organic carbon present. However, the organic carbon content of several samples is enough to classify them as organic O horizons. The Humic A horizon is characterised by low base status, and is a freely drained topsoil horizon with an accumulation of organic matter in a cool moist climate (Soil Classification Working Group, 1991), as indeed most of the soils in the

study area appear to be. However, the soils also do fulfil some of the requirements for melanic A horizons in terms of structure and colour. It is thus tempting to resolve these discrepancies by classifying the horizons as orthic A in that they do not fully satisfy the requirements for any of the other categories.

4.2.2 Soil Mineralogy

Soil mineralogy, from the diffractograms in Figures 3.3 and 3.4, is mostly dominated by quartz, as would be expected in soils lying chiefly on TMG sandstones. Accessory minerals such as micas (especially muscovite) and kaolinite are also present. This appears to be the trend for most of the soil samples, with only the amounts varying. For example, the clay rich samples S-OD and S-GD have strong kaolinite peaks representative of the underlying Cedarberg Formation, which is also rich in kaolinitic clay. Small smectite peaks are also visible, but are probably less significant than the kaolinite. The S-S sample has fewer minerals present, but displays a clear amorphous hump in the XRD diffractograms (~ 17-29 2θ), probably due to the very high concentration of organic carbon, and indeed, this trend is mirrored in most of the soil samples, albeit to a lesser degree. The soils are compared to bedrock composition (major oxides) in the figures below. All of the figures are plotted from at least 60%, due to the high quartz concentrations present.

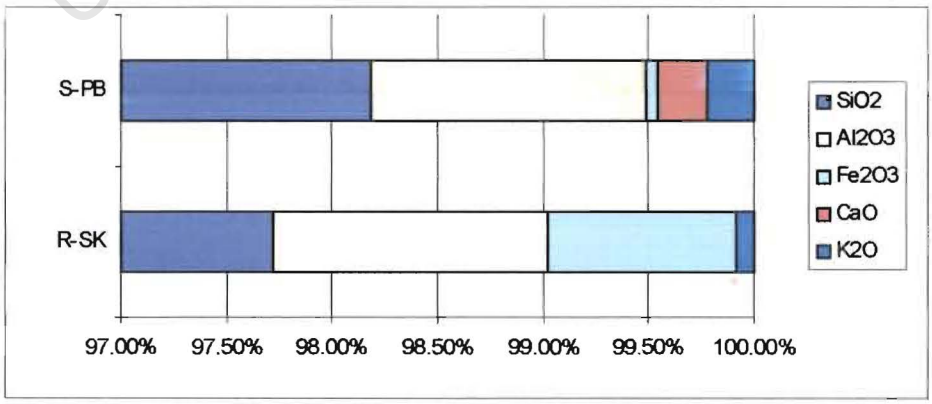


Figure 4.11. Comparison of major oxide content between the S-PB soil (top) and R-SK bedrock (bottom).

The S-PB soil is similar in silicon and aluminium oxide content, but is preferentially concentrating calcium and potassium oxides compared to the bedrock (Figure 4.7), which is either Goudini Formation or alluvium from the Skurweburg Formation above. The additional Ca probably comes from leaf litter and perhaps atmospheric deposition. Interestingly, iron is depleted in the soil relative to the bedrock, which raises the question: is iron leaving the system? Moreover, if Fe is leaving the system, through what pathway? Weathering of the Goudini Formation may not release soluble ions in the same proportions that they occur in the bedrock. Iron may be removed more rapidly from the bedrock, leaving the less soluble siliceous material behind as a barrier to further Fe removal. Some may be taken up in the fynbos, as Fe is an essential soil nutrient (Ugolini and Spaltenstein, 1992). The highly oxygenated (and thus oxidising) state of the surface waters is not favourable for Fe transport. The stream waters contain <0.3 ppm Fe (Table 3.7), which accounts for some of the output. Iron is known to have significant interactions with humic substances in the dissolved and particulate fractions of surface waters, sediments and soils (Tipping *et al.*, 2002), and some of the Fe in the streams of the Kogelberg is probably complexed with fulvic acids. Iron may be mobilised from bedrock in the acidic soils under slightly reducing conditions in the soil water and transported to surface waters where it will precipitate out in the oxidising stream environment. Thus, if iron is moving through this pathway, Fe-oxide coatings might be expected on in-stream rocks or at spring seep sites and Fe-rich sediments in the streams of the study area. However, distinctive light-orange Fe-oxide coatings were not observed in streambed sediments adjacent Goudini outcrops. There is also the possibility that the anoxic and consequently more reducing conditions required to keep Fe in solution may be found in deeper groundwaters than those noted in the study area. The extensive jointing and fracturing in the sandstones of the Kogelberg could recharge aquifers with longer residence times, but without extensive further study, it is impossible to say with certainty.

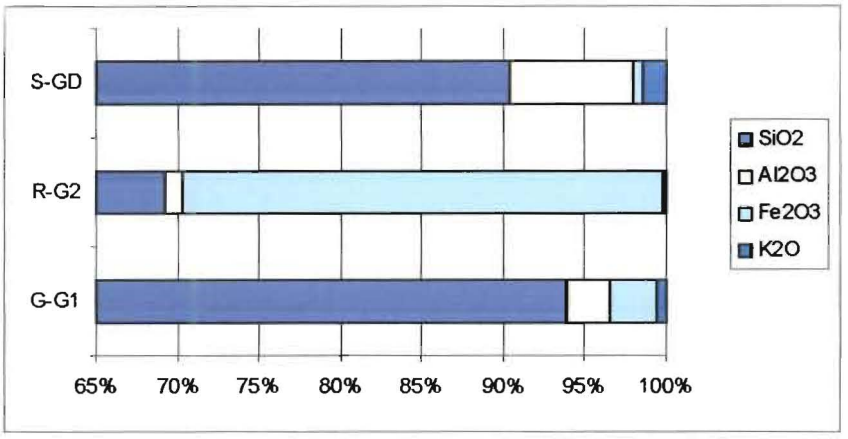


Figure 4.12. Comparison of Goudini bedrock samples (R-G1 and R-G(2)) to the GDS soil sample lying on the same formation.

The Goudini Formation was determined to be much richer in iron oxides that any other formation analysed in the study area. There is certainly variation within the formation as well, from 30 wt% iron oxide content in the R-G(2) sample to just over three percent in R-G1. The S-GD sample does appear to relate well to the bedrock composition, given the ranges of mineral concentrations present. However, the soil sample was collected close to (or perhaps even on) the contact with the Cedarberg Formation. Some bands of softer shale like rock were seen at the site, and this might account for the increased aluminium and potassium oxide content. S-GD was also high in clay content, which may be largely derived from the softer, kaolinite rich Cedarberg Formation. There is very little calcium oxide present in the soil sample, which may be partly explained by the vegetation, which was dominated by restios. Compared to proteoid and ericoid plants, restios have an order of magnitude less calcium present in the leaf litter (Mitchell *et al.*, 1986). Once again, iron is depleted in the soil relative to the bedrock, especially compared to Al-oxide, and in greater proportions compared to the S-PB site.

The easily weathered and kaolinite rich Cedarberg Formation underlies both the S-OD and S-S sample sites. Titanium, iron, magnesium, aluminium and potassium oxides appear to be similar in both bedrock and soil, and in fact, S-OD bears a very strong resemblance to the R-C1 bedrock sample (Figure 4.13).

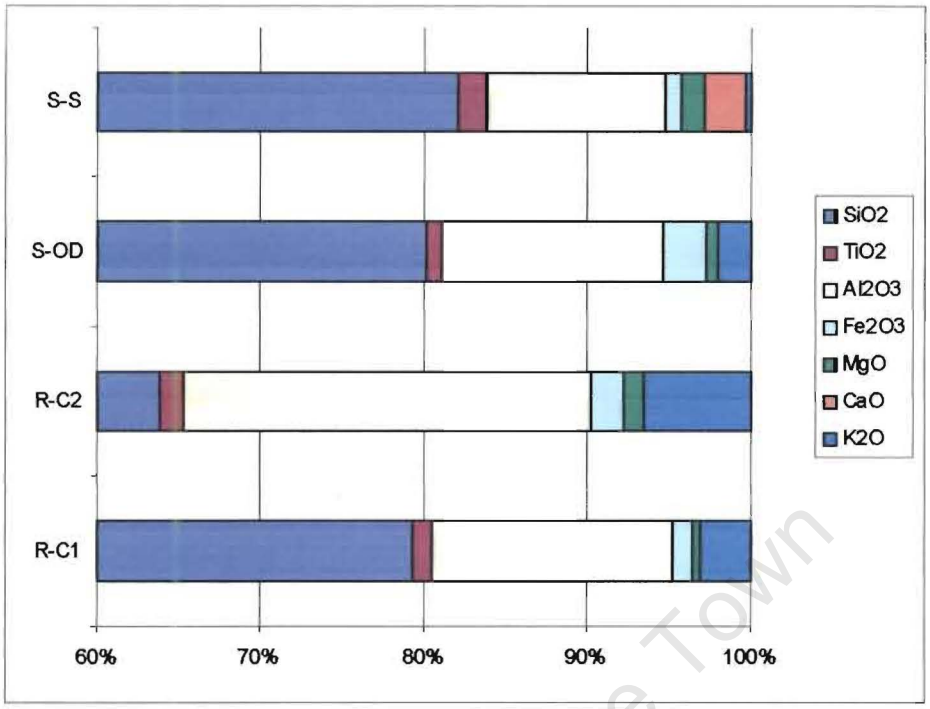


Figure 4.13. Comparisons of Cedarberg bedrock samples (R-C1, 2) to soils (S-S and S-OD) lying on that formation.

The S-S sample has significantly higher Ca, which is again probably from Ca-rich organic matter (the S-S sample has > 30 wt% organic carbon). The Al, Mg and K oxides are present in higher amounts in these samples than the other sandstone formations and their derived soils. These are most likely from the aluminosilicate clays in the bedrock.

The R-PK bedrock sample was thought to be a specimen from the Pakhuis Formation, and it was taken from the Cedarberg/Pakhuis contact, along which the stream appeared to be flowing. However, it seems that the R-PK sample is an organic-rich, basal Cedarberg member that has been encountered in borehole drilling (C. Hartnady, pers. comm., 2002). The major oxide composition of R-PK certainly bears more than a superficial resemblance to that of the CED samples (Figures 4.13 and 4.14).

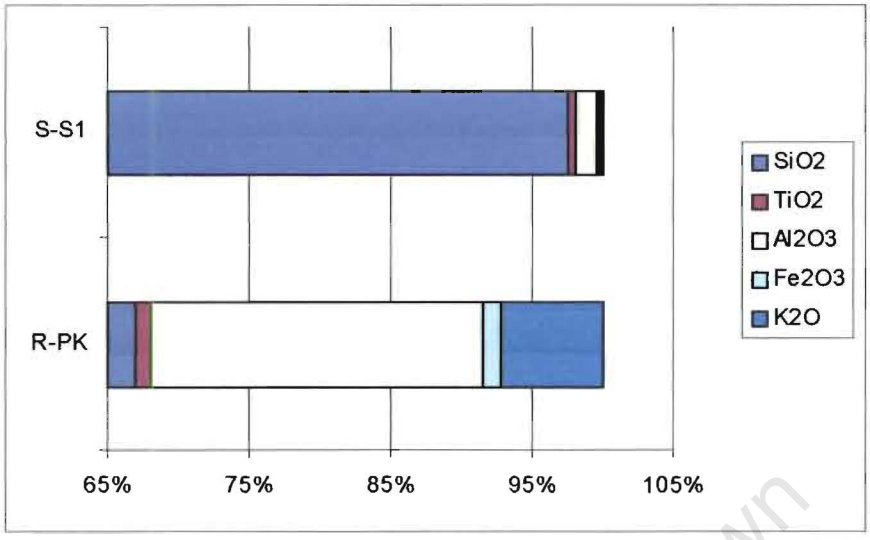


Figure 4.14. Major oxide compositions of the R-PK bedrock sample and the adjacent S-S1 soil sample.

The S-S1 soil sample, which was taken about 10 m away from the R-PK exposure, does not appear to be from weathering of the Cedarberg Formation (Figure 4.14). The small knoll upon which S-S1 was sited may be mostly derived from sandstone alluvium, most likely from the Goudini and Skurweburg formations of the Nardouw Subgroup. The highly siliceous nature of the S-S1 soil does suggest a sandstone parent material.

The Peninsula Formation is certainly the most arenaceous bedrock in the study area, at 99% SiO_2 (Figure 4.15). This does not seem to impact on the quality of fynbos vegetation on these slopes, and although the Peninsula derived soil sample (S-PS) is also very high in quartz content, there are higher concentrations of vital plant nutrients such as Mg, Ca and K oxides. The less soluble and hence less bioavailable oxides (Ti and Al oxides) in the bedrock also appear to be preferentially concentrated in the soil, which is expected.

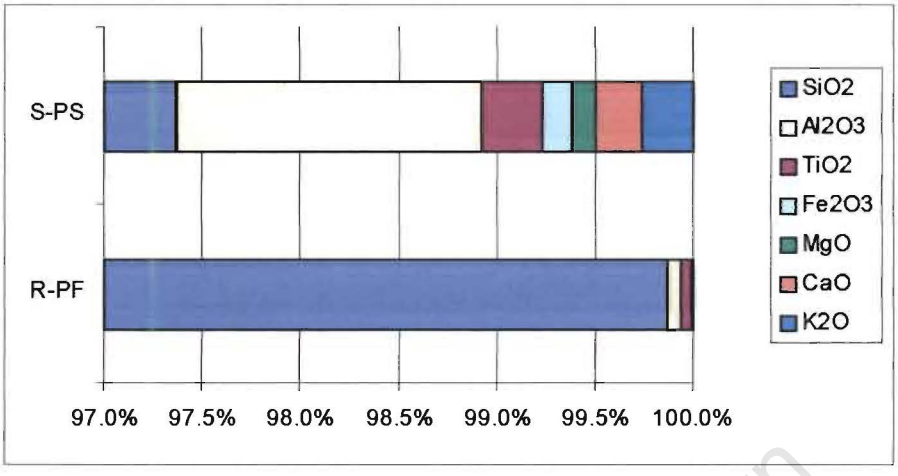


Figure 4.15. Major oxide composition of the R-PF bedrock sample and the S-PS soil from the Peninsula Formation.

The S-TH soil sample was taken close to the Pakhuis/Peninsula Formation contact. Unfortunately, no specimen of the Pakhuis was collected for comparison, but S-TH seems very similar in composition to the S-PS soil sample (Figures 4.16 and 4.15). The proximity of the sample site to the Peninsula Formation does suggest that this soil was derived from the Peninsula Formation.

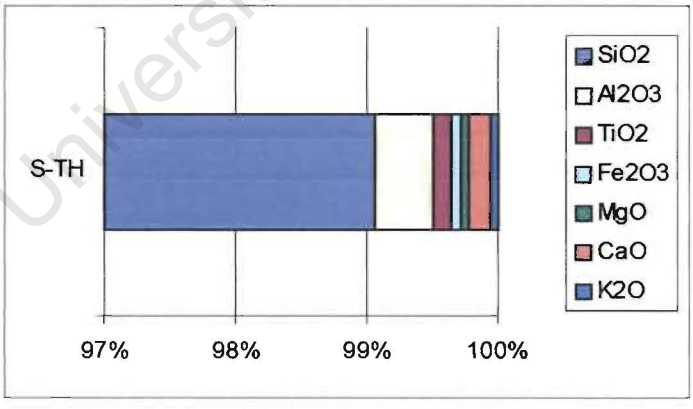


Figure 4.16. Major oxide composition of the S-TH soil sample.

4.2.3 CEC and Extractable Acidity

The amount of exchangeable cations obtained from the KCl and ammonium acetate methods are is in Table 3.9. The two datasets are reasonably comparable, although on average the KCl method produces higher concentrations of Ca, Mg and K. The KCl method cannot determine exchangeable K, however, it can be seen from the amounts of K produced from the ammonium acetate method that, except for the S-OD sample, K is relatively insignificant compared to the other base cations. The soils in the HPNBG show higher CEC (31.3 – 93.0 $mmol_c/kg$) than those reported by Le Maitre (1984) for Kogelberg soils (averaging about 4 $mmol_c/kg$), and are higher than would be expected from the base cation poor bedrock. The values compare better with those reported by Soderberg (2002) for TMG soils in the Cedarberg (~ 28 $mmol_c/kg$, without K), and with those for the Kogelberg by Specht and Moll (1983) (~21 $mmol_c/kg$, which included K). Specht and Moll (1983) also found that K was the exchangeable cation present in the highest concentrations, compared to this study, which found Ca and Mg to dominate. The vegetation type also appears to impact on the CEC, perhaps more so than the clay content. For example, the S-GD sample had the lowest CEC, even though it had high kaolinitic clay content. This can be partly explained by the restioid vegetation which was the only vegetation type noted at the site, and which has been determined to be the poorest in terms of Ca and Mg content in litter mass (Mitchell *et al.,* 1986). High organic carbon content is also known to increase CEC significantly, because of charged sites on the organic molecules (McBride, 1994), and in the case of the Kogelberg soils with large organic components this would certainly appear to be playing a role. Some of the soils in the study area also appear to have appreciable clay content (Table 3.7), which also contribute cation exchange sites, but the clays are mostly kaolinitic in nature, which contribute less CEC than expandable clays such as smectites (McBride, 1994). There does appear to be some smectite present in some of the soil samples (see section 4.2.2), but probably much smaller amounts than the kaolinite. The sum of

all these factors may account for the higher than expected amounts of exchangeable base cations. It is interesting to note that the clay content measured in this study is higher than what the geology might suggest. The, Goudini, Skurweburg and especially the Peninsula sandstone formations do not have enough feldspar or other easily weathered minerals to account for the clay content observed. The reason for the high clay content may partly be due to a bias during analysis, where some soil organic matter became included in the clay fraction during sieving. There is also the possibility of aeolian clay input, as was found in the Cedarberg (K. Soderberg, pers. comm., 2002).

Fires are known to be important pathways for the return of essential ions and nutrients to soil (Van Wilgen and Le Maitre, 1982) and it is possible that the base cation content of the soil may have been increased through this pathway. However, fires are not as common in the Kogelberg as in other parts of the south-western Cape, with the last fire in the HPNBG occurring in 1991 (T. Schaide, pers. comm., 2002). It is possible that this fire returned a large pool of nutrients to the soil, but it is difficult to speculate whether this would have been significant enough to persist after 11 years.

4.2.4 Soil Minor Elements

Minor elements detectable in soil saturated paste extracts were iron, titanium, manganese, zinc, strontium and barium (Table 3.13). The Fe content of the soils, as discussed in Section 4.2.2, appears to be lower than expected, given the higher concentrations present in some of bedrock formations, especially the Goudini Formation. The SPE of sample S-S1 has the highest Fe content of 4ppm, with all other samples below 1 ppm. Although Fe is not very reproducible on the ICP-MS, it is possible that the S-S1 site was more representative of Fe-rich Goudini colluvium, rather than the underlying Cedarberg Formation.

Titanium was present in all of the bedrock samples analysed, and again, some is present in all of the soil samples. Earth's crust is 0.19% Ti (Ugolini and Spaltenstein, 1992), and so it is not unexpected to have titanium present

throughout the study area. This metal is generally a residual element during weathering and is not really considered an essential micronutrient, or toxic to plants in normal circumstances (McBride, 1994), and thus further discussion would be of limited interest.

Manganese was present in the S-TH, S-OD, S-S and S-GD samples, with the S-OD sample having the highest concentration of Mn at 1.5 ppm, an order of magnitude more than the other samples. An essential soil micronutrient (Knezek and Ellis, 1980), the Mn content of soils is very variable, and is not closely related to bedrock composition, due to redox reactions rapidly cycling Mn between mobile and precipitated forms (McBride, 1994). This is supported by the fact that, in this case, although the S-OD sample clearly and consistently displayed elevated Mn compared to other samples in the SPE and volatile-free soil samples analysed by XRF, most bedrock samples contained similar levels of Mn. The difference may be more related to the different environment at S-OD, dominated by afromontane forest and not fynbos. The only stable form of Mn in soils, Mn^{2+}, tends to be more mobile in acid soils, which the soils in the study area are, and may therefore be more toxic in these conditions (McBride, 1994), but it is unlikely that the low concentrations present would be problematic to plant growth.

Zinc is an essential micronutrient in soils (Knezek and Ellis, 1980) and Zn concentrations in the SPE ranged from 0.1 to 0.7 ppm. The lowest concentration was found in the S-PS sample, which is not surprising given the highly arenaceous nature of the Peninsula Formation bedrock on which the S-PS sample was sited. However, it is interesting to note that the S-TH sample, which is also potentially derived from the same formation, contains 0.7 ppm Zn, and is thus on the high concentration end of the spectrum. The Zn content of the soils may therefore have more to do with the complexation of the Zn2+ ion with soil organic matter, as in acidic aerobic soils, Zn tends to bind with exchange sites on clays and organic matter (especially the humic and fulvic fractions; Knezek and Ellis, 1980), but still has medium mobility (McBride, 1994).

Strontium and barium rank under Mn, C and S in terms of crustal abundance at 0.009 and 0.006% respectively (Ugolini and Spaltenstein, 1992). Concentrations found in the SPE ranged between 0.2 and 0.5 ppm for Sr and 0 to 0.3 ppm for Ba. Neither are essential elements in plants, and Ba is considered rather immobile in soils because of high selectivity for this ion on clay and humus exchange sites (McBride, 1994).

4.2.5 Soil Trace Elements

Trace elements present in the soil saturated paste extracts (SPE) were vanadium, cobalt, copper, gallium, selenium, rubidium, zirconium, molybdenum, cadmium and tungsten (Table 3.15). Vanadium is not an essential element needed by plants (Ugolini and Spaltenstein, 1992), and concentrations of V ranged from 14.3 ppb in the S-PB sample to 119.7 ppb in the S-S1 sample. The solubility of V in soils tends to increase with increasing pH, and at low pH vanadate anions bond to silicates and oxides, and the vanadyl cation binds tightly to organic matter at low pH (McBride, 1994). Thus with the acidity and high organic content of the soils in the study area, V can be considered immobile, and not potentially toxic.

Cobalt is one of the 17 essential soil elements (Ugolini and Spaltenstein, 1992), and concentrations ranges in the study area were from 1.8 ppb in the S-PB sample to 34.2 ppb in the S-OD sample. The order of magnitude difference between the S-OD sample and the other sites may be related to soil redox state, and the fact that the S-OD soil had the highest pH of all samples. Co is more mobile in acidic soils, and tends to complex with organic matter with increasing pH (McBride, 1994). Consequently, the more acidic soils of the fynbos may be more leached of Co than the slightly less acidic soil of the afromontane forest at S-OD. However, the S-PB sample also had higher comparative pH and had the lowest Co of all samples. It is thus likely that multiple variables are controlling Co content and speciation in the soils of the study area.

Copper is also an essential micronutrient (Ugolini and Spaltenstein, 1992), but is also phytotoxic in high concentrations (McBride, 1994). Concentrations

found in SPE were 6.1 to 59 ppb. The Cu^{2+} ion, which is the most common form of Cu in soils, has very high affinity for organic matter, especially at neutral to alkaline pH (McBride, 1994). That would appear to be the case in the soils of the study area, as the amount of organic carbon appears to be negatively correlated with the amount of Zn coming into solution in the SPE (Figure 4.17). However, the acid and perhaps slightly reducing conditions of the soils in the field would probably tend to favour more mobility of Cu.

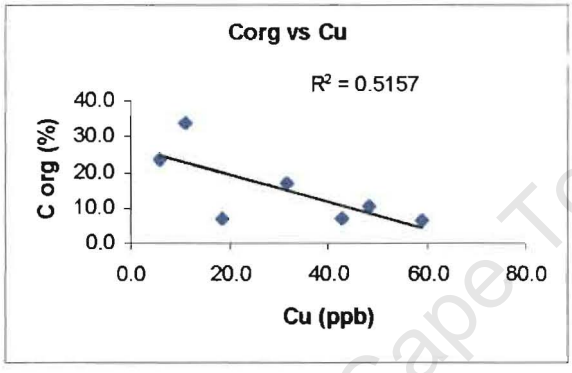


Figure 4.17. Relationship of copper in SPE to organic carbon content in soils

Gallium is present in very small concentrations in seawater (10-20 ppt) (Murray, 1992), and thus only small concentrations might be expected to enter the system over large amounts of time, and remain there, as Ga is not useful to plants (Ugolini and Spaltenstein, 1992). Consequently, Ga concentrations in SPE were also very low, between 1.8 and 5.9 ppb.

Selenium was present in SPE between 5.6 and 61.8 ppb. Selenium is also not considered to be an essential element in soils (Ugolini and Spaltenstein, 1992) The mobility of Se in acid, wet and humus-rich soils is very low, due to the formation of insoluble reduced forms. This would be expected for the soils in the study area, which were all acid, humus-rich and moist.

Rubidium concentrations ranged from 5.5 to 144 ppb in the SPE of soil samples from the study area. The S-TH and S-OD samples were the highest at 71.7 and 144 ppb respectively, and the same samples were the highest in K, which is consistent with the two ions' similar charge/ionic radius characteristics.

Rubidium is not considered an essential soil element (Ugolini and Spaltenstein, 1992).

Zirconium concentrations were found to vary between 1.5 and 11.7 ppb. A number of zircons were seen in thin section of some of the bedrock samples (noticeably S-PB), and Zr in the soils is most likely derived from these minerals.

Molybdenum was found in soil SPE between 0.7 and 34.2 ppb. The most common form of Mo in soils is the molybdate ion, which sorps to oxides and layer aluminosilicate clays at low pH. Molybdenum is thus very immobile in acid soils containing iron oxides (McBride, 1994), which is certainly the case in the study area. Molybdenum is also considered an essential element for plants in soils (Ugolini and Spaltenstein, 1992).

Cadmium concentrations ranged between 1.2 and 69 ppb in the soil sample SPE. Cadmium is an element of concern in soils due to its high toxicity and generally high bioavailability, even though worldwide mean concentration of Cd in soils is quite low. The Cd^{2+} ion does not adsorb strongly to humus, clays or oxides at pH below six (McBride, 1994). Thus in the well-drained acid soils of the Kogelberg, it would be expected that Cd would be mobile and potentially phytotoxic.

Tungsten was present in the soil SPE between 1.4 and 48 ppb. It is not considered an essential nutrient in soils (Ugolini and Spaltenstein, 1992). Thus the various inputs of tungsten, while probably only on the ppt level or less, may be accumulating in the soil due to its relative non-reactivity and that fact that it is not needed in organic systems.

4.2.6 Soil pH

Soil pH is one of the most limiting factors to plant growth (McBride, 1994). pH ranges in the Kogelberg are between 3.5 to 5.5 in H_2O and 2.5 to 4.5 in KCl. Soil pH in the study area is thus acidic, and is more acidic than that reported by Le Maitre (1984) for elsewhere in the same reserve (4.8-5.9 for pH (H_2O) and 3.7 to 4.5 for pH (KCl)). The S-S sample was extremely acidic and has the lowest pH in both ranges. This is probably due to the much higher organic carbon content

(34%) than the other samples. The organic acids are probably responsible for the low pH of all the soil samples, with carboxyl and other protonated functional groups donating H^+ ions into the soil solution (McBride, 1994). This, coupled with the lack of carbonate buffering in the system has caused the soils to be acidic, but does not seem to affect the growth of fynbos on these soils, which appear to have fully adapted to the local conditions. The shallowness of the soils is probably more of a factor in limiting the biomass than soil pH. A comparison of soil pH in KCl and in H_2O is illustrated in figure 4.18 below.

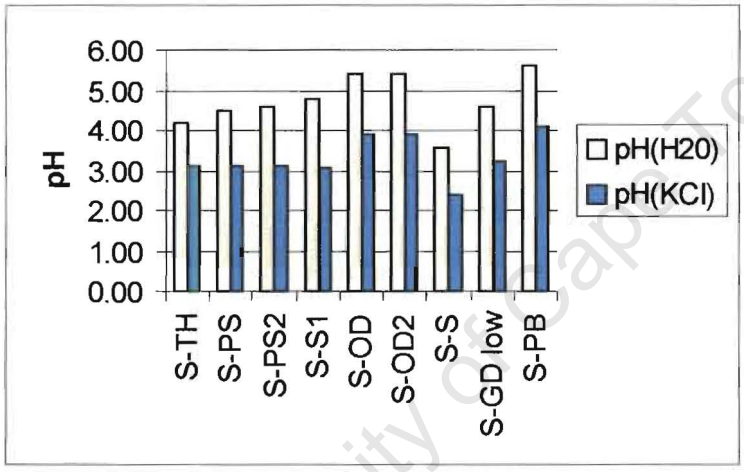


Figure 4.18. Soil pH in both H_2O and KCl.

Delta pH, which is pH(KCl)-pH(H_2O) is consistently negative, which is also indicative of cation exchange capacity. This is because in negatively charged soils, equilibrating the soil solution with KCl results in ion exchange, with K^+ substituting for H^+ ions on exchange sites. This increases the activity of H^+ in solution, causing the pH to be lower in KCl (Rowell, 1988)

4.2.7 Soil Organic Carbon

The organic carbon content of the soil samples was measure to be between six and 34 wt% (Table 3.10), with the S-S peat bog sample being the highest. These values are far higher than those obtained by Le Maitre (1984), who reported

values < 1 wt% for elsewhere in the Kogelberg. Considering the amount of DOC being exported to the streams and groundwater in the Kogelberg, a large pool of soil organic carbon in various stages of decomposition should be expected. Fynbos shrubs maintain positive carbon balances throughout the year, and have carbon-rich sclerophyllous leaves as a result (Stock *et al.*, 1992). In general, these leaves, have a low mineral content and a high content of organic polymers compared to other types of plants (Mitchell *et al.*, 1986) (Table 4.1) and this would appear to contribute the bulk of the organic carbon to the soil and thus to surface waters. These sclerophyllous plants may have adapted to low soil nutrient conditions by their conservation of nutrients and the concomitant production of poor quality litter, especially in terms of N and P, and it is generally accepted that periodic fires in the fynbos are probably the major means of nutrient release from litter rather than decomposition, which is extremely slow (Mitchell *et al.*, 1986).

Table 4.1. Organic and inorganic constituents (in mg/g) of the litter produced by proteoid, ericoid and restioid fynbos at Pella, SA (after Mitchell *et al.*, 1986).

Compound	Proteoid	Ericoid	Restioid
Carbon	508.3 ± 3.2	530.1 ± 9.5	494.0 ± 1.0
Fats and waxes	8.8 ± 2.1	7.6 ± 1.5	5.5 ± 0.5
Soluble carbohydrates	13.8 ± 2.0	18.8 ± 6.6	18.7 ± 2.3
Soluble phenolic compounds	22.0 ± 0.3	22.2 ± 1.0	20.8 ± 0.6
Holocellulose	119.8 ± 4.2	71.3 ± 17.2	319.5 ± 23.8
Lignin	359.5 ± 20.9	348.4 ± 9.9	173.3 ± 3.9
Calcium	11.0 ± 1.4	6.8 ± 2.1	0.8 ± 0.1
Magnesium	1.9 ± 0.3	1.5 ± 0.1	0.5 ± <0.1
Potassium	0.5 ± <0.1	0.7 ± 0.2	1.4 ± 0.2
Iron	0.9 ± 0.2	0.7 ± 0.1	0.2 ± <0.1
Phosphorus	0.3 ± 0.1	0.3 ± 0.1	0.1 ± <0.1
Nitrogen	5.7 ± 1.4	5.9 ± 0.9	4.3 ± 0.8

CHAPTER 5: CONCLUSIONS AND RECOMMENDATIONS

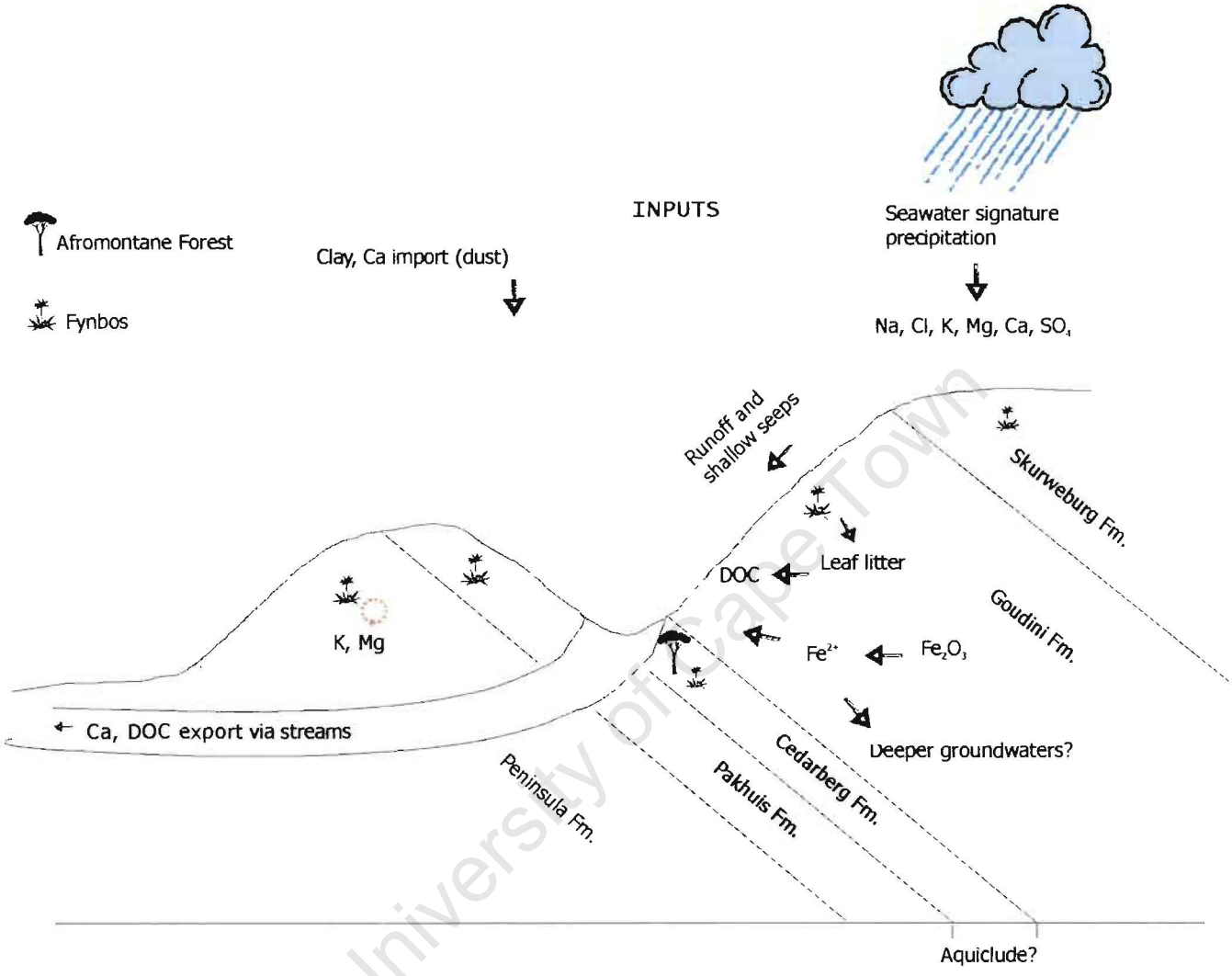


Figure 5.1. A schematic representation of the study area, with underlying geology, inputs and exports and cycling of selected components

In conclusion, the Kogelberg is a product of complex interactions on many different scales, including variables such as climate, geology and vegetation (Figure 5.1). The precipitation inputs into the system have a strong seawater signature. The slightly acidic pH of this precipitation is further lowered by interactions with soil organic matter from the fynbos biome, and is kept low (3.6-4.5) by the lack of carbonate buffering (and thus zero alkalinity) from the highly quartzitic sandstones. The arenaceous bedrock contributes little by way of

nutrients to soils or stream waters, resulting in the retention of the basic seawater signature, with Na, Mg, K and SO_4 slightly depleted relative to Cl. These ions thus appear to be preferentially conserved compared to Ca, which is slightly elevated in stream export relative to Cl. This is probably the result of two factors, firstly the elevated contribution of Ca by the mountain fynbos to soils and thus streams. The Kogelberg fynbos also appears to contribute more Ca than any other major cation to soils and surface waters, suggesting that this ion is not as effectively recycled as Mg and K. There is also some probable import of Ca through an aeolian pathway, which is, as yet, undetermined and merits further study. The small contributions of ions from the bedrock and other sources, and the retention of the dilute seawater signature from the precipitation recharge have given rise to very low EC stream waters (110-160µS) in this part of the Kogelberg. The only major elements and ions present in concentrations greater than 1 ppm at one or more sample sites were Na, Cl, Mg, Ca and SO_4. Other major elements and ions were Al, K, NH_4, NO_3 and Fe. The only trace elements present in concentrations greater than 1 ppb were B, Sb, Sr, Zn and Mn The stream waters of the Kogelberg and HPNBG thus appear to be typical cool, acid, black water streams of the mountainous south-western Cape with high DOC (up to 16 mg/L). From spectroscopic analysis, the DOC appears to be mainly fulvic acid as opposed to humic acid in character, which would fit with data from elsewhere in the world.

The soil types appear to be mostly melanic A horizons that have a strong relationship to the underlying bedrock of the Peninsula, Cedarberg and Goudini Formations. One sample was determined to be an organic O horizon, and was probably a young peat bog. All the soils are quartzitic in composition, reflecting their sandstone genesis, and tend to be leached and acidic, probably from the high rainfall in the area. Clay content of the soils was higher than expected and may also be influenced by aeolian inputs. Soil organic matter (SOM) was higher than previously reported values for the Kogelberg, and it appears that the fynbos is renewing a large pool of SOM that is gradually decomposed and dissolved to contribute high DOC concentrations to the shallow groundwaters and streams.

The organic acids also contribute acidity to lower the soil pH. Cation exchange capacities (CEC) were higher than previous studies indicated, and higher than the comparative study done in the Cedarberg. Again, the large soil organic matter component is probably contributing the bulk of exchange sites to soils, with some kaolinitic and smectitic clay making up the rest.

There appears to be removal of iron during weathering of bedrock, especially in the Goudini Formation. The weight percent of Fe-oxide in the Goudini bedrock samples range up to 30%, which was certainly not reflected in the soils on the same unit. This could be caused by a multitude of factors. Firstly, the soils sampled may not have been chiefly derived from the Goudini Formation, but rather from colluvium from the Skurweberg Formation upslope. Some Fe is leaving the system through the surface waters, some in solution and probably some complexed with the organic matter in solution as well. Iron is also taken up by plants as a micronutrient, which may account for some further removal from the soils. There also exists the possibility that iron is mobilised from the bedrock in the acidic soil solution, and being transported to deeper circulating aquifers with longer residence time than the groundwater seeps noted in the field. This is especially interesting considering the prevalence of iron-clogged boreholes in the same geology in the Klein Karoo area (M. Smith, pers. comm., 2002). For this reason, the mechanisms of Fe-oxide weathering, Fe transport and Fe cycling in the Goudini Formation merits extensive further study.

The only site that appeared to differ overall in terms of soil and water chemistry was the headwaters of the Oudebosch River at W8. This site had less than 1 mg/L DOC, which given that there was high organic carbon content in the soil, suggests binding of soil organic matter to clays derived from the Cedarberg bedrock. There were also other small anomalies in ionic concentrations compared to other sites. This site is part of a different catchment, which sources the Palmiet. It is also sourced in afromontane forest on Cedarberg shale, and is much less influenced by sandstones than the other sites.

To conclude, the combination of factors like soils, climate and geology have resulted in a unique preserve of pristine mountain fynbos and ultra-pure

surface waters. Most of the differences between the Kogelberg and the Cedarberg Wilderness Area appear to stem from the higher rainfall in the Kogelberg, which has resulted in much greater biomass. This biomass has increased the levels of organic matter in both soils and streams, and this is probably the most profound difference affecting the geochemistry of the Kogelberg area. The Cedarberg is perhaps also more affected by anthropogenic impacts such as farming. In the light of such anthropogenic impacts, it is vitally important to continue characterisation of pristine ecological areas with studies such as this one, in order to safeguard against, and rapidly assess any future degradation.

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Appendix A: Raw Titration Data

A1.Acid Titrations

Sample ID	**LGB(field)**
Collection Date & Time	2002/26/08 16:30pm
Analysis Date & Time	2002/26/08 16:30pm
Sample Size	100 ml
Method	pipette (epp)
Titrant	0.0043632 M HCl
Init pH	3.91
Temp (Deg. C)	13

pH	mL Acid	mL Acid (tot)
3.91	0	0
3.8	0.5	0.5
3.68	0.8	1.3
3.59	0.8	2.1
3.5	1	3.1
3.38	2	5.1
3.3	2	7.1
3.21	3	10.1
3.15	3	13.1
3.1	3	16.1
3.07	3	19.1
3.03	4	23.1
3	3	26.1

Sample ID	**HW**
Collection Date & Time	2002/19/08 10:30 am 2:30pm
Analysis Date & Time	2002/19/08 10:30 am 2:30pm
Sample Size	100 ml
Method	pipette (epp)
Titrant	0.004363 M HCl
Init pH	3.95
Temp (Deg. C)	13

pH	mL Acid	mL Acid (tot)
3.95	0	0
3.94	0.1	0.1
3.92	0.2	0.3
3.82	0.5	0.8
3.71	0.8	1.6
3.58	1	2.6
3.42	2	4.6
3.23	3	7.6
3.11	3	10.6
3.01	3	13.6

Sample ID	**LG2**
Analysis Date & Time	2002/19/08 10:30 am
Sample Size	100 ml
Method	pipette (epp)
Titrant	0.0043632 M HCl
Init pH	4.13
Temp	13

pH	mL Acid	mL Acid (tot)
4.13	0	0
4.1	0.1	0.1
4.08	0.1	0.2
4.03	0.2	0.4
3.93	0.4	0.8
3.86	0.4	1.2
3.75	0.6	1.8
3.67	0.8	2.6
3.56	1	3.6
3.48	1	4.6
3.34	2	6.6
3.26	2	8.6
3.18	2	10.6

Sample ID	**LGB(lab)**
Collection Date & Time	2002/19/08 6:00pm
Analysis Date & Time	2002/20/8 11:00am
Sample Size	100 ml
Method	pipette (epp)
Titrant	0.0043632 M HCl
Init pH	4.04
Temp	17

pH	mL Acid	mL Acid (tot)
4.04	0	0
3.96	0.2	0.2
3.87	0.4	0.6
3.71	0.8	1.4
3.59	1	2.4
3.42	2	4.4
3.29	2	6.4
3.16	3	9.4
3.03	4	13.4

Sample ID	**PS**
Collection Date & Time	2002/05/09 12:30pm
Analysis Date & Time	2002/05/09 12:30pm
Sample Size	100 ml
Method	pipette (epp)
Titrant	0.004363 M HCl
Init pH	4.16
Temp (Deg. C)	14

pH	mL Acid	mL Acid (tot)
4.16	0	0
4.21	0.2	0.2
4.09	0.5	0.7
3.94	0.8	1.5
3.8	1	2.5
3.68	1	3.5
3.52	2	5.5
3.4	2	7.5
3.32	2	9.5
3.22	3	12.5
3.15	3	15.5
3.09	3	18.5
3.03	3	21.5
3	2	23.5

Sample ID	**S3 (lab)**
Collection Date & Time	2002/08/26
Analysis Date & Time	2001/08/27
Sample Size	50 ml
Method	pipette (epp)
Titrant	0.004363 M HCl
Init pH	4.16
Temp (Deg. C)	17

pH	mL Acid	mL Acid (tot)
4.16	0	0
4.04	0.3	0.3
3.87	0.5	0.8
3.72	0.6	1.4
3.59	0.8	2.2
3.45	1	3.2
3.29	2	5.2
3.17	2	7.2
3.05	3	10.2
2.99	2	12.2

Sample ID	**S5 5/9**
Collection Date & Time	2002/09/05
Analysis Date & Time	2002/09/05
Sample Size	100 ml
Method	pipette (epp)
Titrant	0.004363 M HCl
Init pH	4.16
Temp (Deg. C)	13

pH	mL Acid	mL Acid (tot)
3.97	0	0
3.92	0.25	0.25
3.79	0.75	1
3.65	1	2
3.48	2	4
3.36	2	6
3.22	2	8
3.15	3	11
3.11	2	13
3.06	3	16
3.02	3	19
3	2	21

Sample ID	**OHW**
Collection Date & Time	2002/26/08 10:45 AM
Analysis Date & Time	2002/26/08 07:30 PM
Sample Size	50 ml
Method	pipette (epp)
Titrant	0.004363 M HCl
Init pH	4.72
Temp (Deg. C)	19

pH	mL Acid	mL Acid (tot)
4.72	0	0
4.55	0.2	0.2
4.25	0.3	0.5
4.05	0.3	0.8
3.76	0.4	1.2
3.61	0.6	1.8
3.47	0.8	2.6
3.35	1	3.6
3.18	2	5.6
3.07	2	7.6
3.02	1	8.6

Sample ID	**PBHW**
Collection Date & Time	2002/26/08 2:30pm
Analysis Date & Time	2002/26/08 2:30pm
Sample Size	100 ml
Method	pipette (epp)
Titrant	0.004363 M HCl
Init pH	4.2
Temp (Deg. C)	19

pH		ml Acid	
	4.2	0	0
	4.09	0.3	0.3
	4.01	0.5	0.8
	3.83	0.8	1.6
	3.68	1	2.6
	3.57	1	3.6
	3.42	2	5.6
	3.32	2	7.6
	3.19	3	10.6
	3.1	3	13.6
	3.01	4	17.6

A2. Base Titrations

Sample ID	**LGB (field)**	**Sample ID**	**LGB(lab)**
Collection Date & Time	2002/05/09 14:30pm	Collection Date & Time	2002/19/08 6:00pm
Analysis Date & Time	2002/05/09 14:45pm	Analysis Date & Time	2002/20/08 10:30am
Sample Size	100 ml	Sample Size	100 ml
Method	pipette (epp)	Method	pipette (epp)
Titrant	0.0025 M NAOH	Titrant	0.0025 M NAOH
Init pH	3.98	Init pH	4.19
Temp	15	Temp	19

pH	mL base	mL base (tot)	pH	mL base	mL base (tot)
3.98	0	0	4.19	0	0
4.09	0.5	0.5	4.18	0.4	0.4
4.25	0.8	1.3	4.26	0.4	0.8
4.47	0.8	2.1	4.45	0.8	1.6
4.84	1	3.1	4.76	1	2.6
5.21	0.8	3.9	5.14	1	3.6
5.49	0.6	4.5	5.42	0.8	4.4
5.75	0.6	5.1	5.66	0.8	5.2
5.99	0.6	5.7	5.86	0.8	6
6.21	0.6	6.3	6.06	0.8	6.8
6.45	0.6	6.9	6.25	1	7.8
6.69	0.6	7.5	6.44	1	8.8
6.94	0.6	8.1	6.67	1	9.8
7.26	0.6	8.7	6.95	1	10.8
7.58	0.5	9.2	7.33	1	11.8
7.84	0.4	9.6	7.71	0.8	12.6
8.11	0.4	10	8.04	0.6	13.2
8.34	0.4	10.4	8.29	0.6	13.8
8.57	0.5	10.9	8.56	0.6	14.4
8.8	0.6	11.5	8.75	0.6	15
9.03	0.8	12.3	8.95	0.8	15.8
9.26	1	13.3	9.12	0.9	16.7
9.42	1	14.3	9.28	1	17.7
9.64	2	16.3	9.4	1	18.7
9.81	2	18.3	9.55	2	20.7
9.99	3	21.3	9.72	3	23.7
10.1	3	24.3	9.96	4	27.7
10.21	3	27.3	10.13	4	31.7
10.3	3	30.3	10.25	4	35.7

Sample ID	**PS**
Collection Date & Time	2002/09/05
Analysis Date & Time	2002/09/05
Sample Size	100 ml
Method	pipette (epp)
Titrant	0.0025 M NAOH
Init pH	4.12
Temp	14

pH	mL base	mL base (tot)
4.12	0	0
4.22	0.5	0.5
4.4	0.8	1.3
4.68	1	2.3
5.08	1	3.3
5.38	0.6	3.9
5.65	0.6	4.5
5.89	0.6	5.1
6.11	0.6	5.7
6.34	0.6	6.3
6.56	0.6	6.9
6.79	0.6	7.5
7.04	0.6	8.1
7.33	0.6	8.7
7.64	0.6	9.3
7.98	0.6	9.9
8.23	0.4	10.3
8.46	0.4	10.7
8.68	0.4	11.1
8.88	0.5	11.6
9.07	0.6	12.2
9.26	0.8	13
9.46	1	14
9.62	1	15
9.82	2	17
10.04	3	20
10.2	3	23
10.32	3	26

Sample ID	**HW**
Collection Date & Time	2002/19/08 10:30 am 3:00pm
Analysis Date & Time	2002/19/08 10:30 am 3:00pm
Sample Size	100 ml
Method	pipette (epp)
Titrant	0.0025 M NAOH
Init pH	4
Temp	13

pH	mL base	mL base (tot)
4	0	0
4.07	0.5	0.5
4.17	0.8	1.3
4.33	1	2.3
4.52	1	3.3
4.75	1	4.3
5.02	1	5.3
5.26	1	6.3
5.46	0.8	7.1
5.7	0.8	7.9
5.86	0.8	8.7
6.08	1	9.7
6.29	1	10.7
6.46	1	11.7
6.65	1	12.7
6.95	1	13.7
7.25	1	14.7
7.71	1	15.7
7.9	0.6	16.3
8.02	0.3	16.6
8.09	0.3	16.9
8.2	0.4	17.3
8.3	0.4	17.7
8.39	0.4	18.1
8.57	0.8	18.9
8.77	0.8	19.7
9	0.8	20.5
9.16	1	21.5
9.46	2	23.5
9.65	2	25.5
9.87	3	28.5
10.01	3	31.5
10.14	3	34.5
10.22	3	37.5
10.29	3	40.5

Sample ID	**ODW (lab)**		**Sample ID**	**S5 5/9**	
Collection Date & Time	2002/26/08 10:45 am 3:00pm		Collection Date & Time	2002/05/09	
Analysis Date & Time	2002/26/08 8:00 pm 3:00pm		Analysis Date & Time	2002/05/09	
Sample Size	50 ml		Sample Size	100 ml	
Method	pipette (epp)		Method	pipette (epp)	
Titrant	0.0025 M NAOH		Titrant	0.0025 M NaOH	
Init pH	4.57		Init pH	3.98	
Temp	19		Temp	13	
pH	mL base	mL base (tot)	pH	mL base	mL base (tot)
4.57	0	0	3.98	0	0
4.73	0.4	0.4	4.09	0.5	0.5
4.94	0.4	0.8	4.25	0.8	1.3
5.15	0.6	1.4	4.47	0.8	2.1
5.39	0.8	2.2	4.84	1	3.1
5.59	1	3.2	5.21	0.8	3.9
5.78	1	4.2	5.49	0.6	4.5
5.92	1	5.2	5.75	0.6	5.1
6.15	2	7.2	5.99	0.6	5.7
6.38	2	9.2	6.21	0.6	6.3
6.74	3	12.2	6.45	0.6	6.9
7.85	2	14.2	6.69	0.6	7.5
8.34	0.5	14.7	6.94	0.6	8.1
8.68	0.2	14.9	7.26	0.6	8.7
8.9	0.1	15	7.58	0.5	9.2
9.04	0.1	15.1	7.84	0.4	9.6
9.16	0.2	15.3	8.11	0.4	10
9.29	0.4	15.7	8.34	0.4	10.4
9.42	0.6	16.3	8.57	0.5	10.9
9.54	0.8	17.1	8.8	0.6	11.5
9.66	1	18.1	9.03	0.8	12.3
9.82	2	20.1	9.26	1	13.3
10	2	22.1	9.42	1	14.3
10.18	3	25.1	9.64	2	16.3
10.3	3	28.1	9.81	2	18.3
			9.99	3	21.3
			10.1	3	24.3
			10.21	3	27.3
			10.3	3	30.3

Sample ID	S3 (lab)		Sample ID	PBHW (lab)	
Collection Date & Time	2002/08/26		Collection Date & Time	2002/26/08 2:00pm	
Analysis Date & Time	2002/08/26		Analysis Date & Time	2002/26/08 8:30pm	
Sample Size	50 ml		Sample Size	100 ml	
Method	pipette (epp)		Method	pipette (epp)	
Titrant	0.0025 M NaOH		Titrant	0.0025 M NAOH	
Init pH	4.28		Init pH	4.1	
Temp	18		Temp	19	
pH	mL base	mL base (tot)	pH	mL base	mL base (tot)
4.28	0.4	0	4.1	0	0
4.53	0.6	0.6	4.2	0.4	0.4
4.99	0.8	1.4	4.35	0.6	1
5.27	0.4	1.8	4.59	0.8	1.8
5.56	0.4	2.2	4.86	0.8	2.6
5.81	0.4	2.6	5.19	0.8	3.4
6.04	0.4	3	5.46	0.6	4
6.23	0.4	3.4	5.67	0.6	4.6
6.45	0.5	3.9	5.86	0.6	5.2
6.72	0.5	4.4	6.07	0.8	6
7.03	0.4	4.8	6.42	1	7
7.35	0.3	5.1	6.61	0.4	7.4
7.63	0.2	5.3	6.96	0.5	7.9
7.9	0.2	5.5	7.27	0.4	8.3
8.16	0.2	5.7	7.51	0.3	8.6
8.34	0.2	5.9	7.77	0.3	8.9
8.61	0.3	6.2	8.03	0.3	9.2
8.86	0.3	6.5	8.27	0.3	9.5
9.06	0.3	6.8	8.47	0.3	9.8
9.24	0.4	7.2	8.72	0.4	10.2
9.42	0.5	7.7	8.93	0.4	10.6
9.64	0.8	8.5	9.13	0.5	11.1
9.83	1	9.5	9.31	0.6	11.7
9.97	1	10.5	9.49	0.8	12.5
10.14	2	12.5	9.64	1	13.5
10.27	2	14.5	9.85	1	14.5
10.33	1	15.5	9.95	1	15.5
			10.08	2	17.5
			10.18	2	19.5
			10.25	2	21.5
			10.32	2	23.5

Sample ID	**LG2**
Collection Date & Time	2002/19/08 10:30 am
Analysis Date & Time	2002/19/08 10:30 am
Sample Size	100 ml
Method	pipette (epp)
Titrant	0.0025 M NAOH
Init pH	4.12
Temp	13

pH	mL base	mL base (tot)
4.12	0	0
4.15	0.2	0.2
4.25	0.5	0.7
4.51	1	1.7
4.84	1	2.7
5.27	1	3.7
5.65	0.8	4.5
5.91	0.6	5.1
6.12	0.6	5.7
6.35	0.8	6.5
6.75	1	7.5
7.15	0.8	8.3
7.59	0.6	8.9
7.99	0.4	9.3
8.24	0.1	9.4
8.36	0.1	9.5
8.51	0.2	9.7
8.72	0.5	10.2
9.06	1	11.2
9.35	1	12.2
9.59	1	13.2
9.78	1	14.2
10	2	16.2
10.22	3	19.2
10.37	3	22.2
10.46	3	25.2

APPENDIX B: DATA QUALITY AND ESTIMATES OF UNCERTAINTY

Estimates of analytical uncertainty for water sample analyses are given below in Table C1. There was insufficient sample to do more than one duplicate per element for AAS, and figures for that technique are from H. Divey (pers. comm., 2002). However, the duplicates done did support those estimates.

Table B1. Precision, relative bias and analytical uncertainty for selected elements and ions by the different analytical techniques (surface water samples).

Method	Analyte	Precision (%)	No of samples	No of duplicates	Rel Bias (%)	Analytical uncertainty (%)
IC	Na^+	13	14	5	-2	15
	K^+	13	14	5	-3	16
	Ca^{2+}	15	14	5	11	26
	Mg^{2+}	14	14	5	21	35
	Cl^-	2	14	5	-2	4
	SO4	8	14	5	-27	35
ICP-MS	B	93	14	7	-4	97
	Na	14	14	7	7	21
	Mg	4	14	7	6	10
	Al	11	14	7	19	30
	Si	20	14	7	-5	25
	K	80	14	7	-5	85
	Ca	37	14	7	-10	47
	Mn	27	14	7	-1	28
	Zn	44	14	7	18	62
	Sr	21	14	7	-1	22
	Sb	n.d	14	7	-5	5
FAAS	Na^+	2	14	1	3	5
	Mg^{2+}	2	14	1	3	5
	Ca^{2+}	2	14	1	3	5
	K^+	2	14	1	3	5
	Fe	2	14	1	3	5

Table B2. Precision, relative bias and analytical uncertainty for selected elements and ions by the different analytical techniques (saturated paste extracts).

Method	Analyte	Precision (%)	No of samples	No of duplicates	Rel. Bias (%)	Analytical uncertainty (%)
IC	Na+	12	7	3	-2	15
	K+	7	7	3	-3	10
	Ca2+	15	7	3	11	26
	Mg2+	1	7	3	21	22
	Cl-	23	7	3	-2	25
	F-	123	7	3	n.d	123
	NO2-	22	7	3	n.d	22
	NO3-	91	7	3	n.d	91
	PO43-	297	7	3	n.d	297
	SO4	3	7	3	-27	35
ICP-MS	B	10	7	3	-4	14
	Na	40	7	3	7	47
	Mg	20	7	3	6	26
	Al	5	7	3	19	24
	Si	11	7	3	-5	16
	K	138	7	3	-5	143
	Ca	30	7	3	-10	40
	Mn	5	7	3	-1	6
	Zn	8	7	3	18	26
	Sr	5	7	3	-1	6
	V	33	7	3	-2	35
	Cr	149	7	3	-1	150
	Co	9	7	3	1	10
	Cu	69	7	3	3	72
	Cd	31	7	3	-4	35
	W	29	7	3	n.d	32
	Rb	18	7	3	-2	20
	As	151	7	3	-3	154
	Ga	69	7	3	n.d	69
	Zr	50	7	3	n.d	50
	Mo	64	7	3	-3	67
	Ag	278	7	3	-11	289
	Pb	136	7	3	4	140
	Se	18	7	3	1	19
	Ba	16	7	3	-1	17
	Hg	6	7	3	n.d	6
	Fe	47	7	3	56	103
	Sb	1	7	3	-5	6