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Geochemistry of the fynbos ecosystem in a Table Mountain Group sub-catchment of the Olifants River, Western Cape, South Africa

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Abbreviations

AMU – Atomic Mass Unit
AAS – Atomic Absorption Spectrometry
CBE – Charge Balance Error
CEC – Cation Exchange Capacity
CFR – Cape Floristic Region
DOC – Dissolved Organic Carbon
EC – Electrical Conductivity
ECEC – Effective Cation Exchange Capacity
IAP – Ion Activity Product
IC – Ion Chromatography
ICP-MS – Inductively Coupled Plasma Mass Spectrometry
SAR – Sodium Adsorption Ratio
SI – Saturation Index
SPE – Saturated Paste Extract
TMG – Table Mountain Group
UCT – University of Cape Town
XRD – X-Ray Diffraction
XRF – X-Ray Fluorescence

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Abstract

The water chemistry along the path of the hydrologic cycle gives clues to the complex interactions among water and the bedrock, soil, vegetation and atmosphere. Recharge waters originate as rainfall where they interact with various types of aerosols. Rainwater then filters through soil and is influenced by chemical weathering and the uptake and release of elements by vegetation. The recharge exits the soil as surface water, evapotranspiration, or percolates into the bedrock. This study gives a first-order estimation of the chemical composition of the recharge, discharge, and ground waters, along with the bedrock, soil, and vegetation of the Olifants River Valley around Citrusdal. The valley occurs in a synclinal fold with the main aquifers, the Table Mountain Group (TMG) sandstones of the Peninsula Formation and the Nardouw Subgroup, folded beneath the central valley. The Peninsula aquifer is recharged in the east towards the Cedarberg Mountains and discharged at up to 43°C in the west. The headwater catchments support fynbos vegetation communities, part of the Cape Floral Kingdom, which is globally significant as one of 6 floral kingdoms in the world, and one of 25 recently identified biodiversity hotspots (Myers et al., 2000). Groundwater data for this study comes from two boreholes, one cold spring, and one warm spring. Ten surface water samples were taken to study discharge, and 14 rainwater samples for recharge (3 from Citrusdal, 11 from Cape Town). Alkalinity and acidity titrations were performed in the field to complement pH values in characterizing the acid-base status of the waters. Major ions were determined by ion chromatography, and trace elements by ICP-MS.

The recharge (pH 4.8-5.8) carries roughly a seawater signature, with some deviation from rainout of wind-blown dust. Rainwater composition in the study area is similar to that in Cape Town, which is much closer to the coast (about 5 km at the sampling point), and about 170 km south of the study area. Discharge is acidic in the study area (pH 4.9-5.8), and varies from clear to light brown (DOC <3 mg/l). TMG discharge is commonly acidic, particularly from the Peninsula Formation, where there is minimal buffering from weathering of the quartz arenite sandstones. In addition, it is difficult for organic acids to adsorb to the sandy soils (<7 wt% clay), allowing them to pass through the soil with the discharge. TMG ground waters studied have low ionic strength (0.2-1 mM) and electrical conductivity (2.5-12 mS/m). The low pH helps to keep trace metals in solution, particularly iron and manganese, which tend to precipitate in the presence of oxygen near the surface. The presence of metals in solution contributes to the ability of the ground waters studied to buffer the addition of hydroxyl ion (Base Neutralizing Capacity) in the acidity titration.

The size of the major elemental reservoirs and the fluxes among them are approximated from chemical analyses of the bedrock, soil, vegetation, and waters of the ecosystem. These estimates are used in a simplified box model to discuss the element dynamics within the fynbos ecosystem of a headwater catchment underlain by the Peninsula Formation. The data support the idea that soil and vegetation act as a filter, selectively retaining elements from the water, particularly K and Mn, but also including Ca, Mg, Fe, and Al. The properties of the ecosystem that allow for this retention of elements could be disrupted by humans as industry and individuals continue to increase their output of harmful chemicals.

1 Introduction

This project is an investigation of some of the chemical properties of fynbos ecosystems, focusing on chemical evolution of water as it passes from one part of the ecosystem to another. An ecosystems-based approach (e.g., Likens *et al.*, 1977) is attempted as a first step towards a more complete understanding of the ecosystem, which can help to guide future research. The Boontjies River catchment in the Olifants River basin east of Citrusdal in the Western Cape is studied as an example of the important and locally pervasive lithology-vegetation combination of Table Mountain Group (TMG) sandstones and mountain fynbos vegetation. The catchment also exhibits changes in land use from its near pristine headwaters to the main valley, which is used for agriculture.

For the purposes of this project, a fynbos ecosystem is defined as an ecosystem that supports vegetation of the fynbos biome. An ecosystem is a conceptual grouping of interdependent components that support some form of life, and can be defined at any scale. The concept of an ecosystem is important for understanding the mechanisms behind phenomena such as species richness.

Chemical elements are transferred from one component of an ecosystem to another, as well as into and out of the ecosystem as a whole. Conceptually, dividing a natural system into chemically distinct units (Fig. 1) and analyzing them as a whole should provide useful information about the functioning of the system, and the processes involved. The size of these elemental reservoirs and the fluxes among them will be approximated in this study from chemical analyses of the bedrock, soil, vegetation, and waters of the ecosystem.

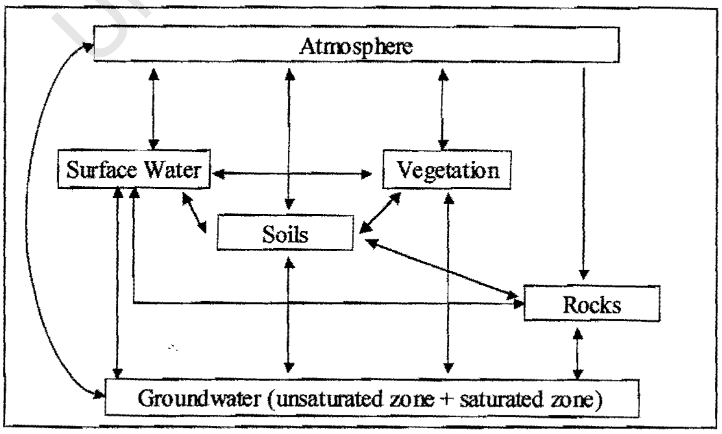

Figure 1: Simplified model of major chemical reservoirs and their interactions.

The fynbos biome is part (47% by area, Richardson *et al.*, 1995) of the Cape Floristic Region (CFR), also know as the Cape Floral Kingdom, which covers the Southwestern Cape of South Africa, and is one of six floral kingdoms in the world (Table 1). Fynbos communities are globally significant as part of the CFR biodiversity "hotspot" (Myers *et al.*, 2000). These ecosystems are known to have low overall nutrient concentrations due mainly to the pure sandstone parent material (Specht and Moll, 1983; Kruger, 1979). The CFR is underlain by bedrock of the Cape Supergroup, which is made up of sandstone, siltstone, shale, glacial formations, and granite. Fynbos communities are underlain predominately by Table Mountain Group sandstones (part of the Cape Supergroup), which are made up mostly of quartz, to a maximum of 99 wt% in the Peninsula Formation.

Table 1: Floral kingdoms of the world (Gale, 1992).

Floral kingdom	Percentage of Earth's land
Boreal Kingdom	42
Paleotropical Kingdom	35
Neotropical Kingdom	14
Australian Kingdom	8
Patagonia Kingdom	1
Cape Floral Kingdom (Cape Floristic Region)	0.04

Loss of the Cape Floristic Region's biodiversity is of global concern as it is recognized as an ecological hotspot for having high species density and endemism (uniqueness), particularly with regard to plant species, but also including vertebrates and invertebrates. A total of 25 hotspots are currently identified in this way, with 15 occurring in tropical forest habitats, and 5 in Mediterranean-type ecosystems. The CFR ranks 5th among the 25 hotspots for density of endemic plants with 31.6 species/100 km^2, and 15th for endemic vertebrates (Table 2). Also, the CFR currently has 1406 plant species listed in the Red Data Book, a list of endangered species compiled by the International Union for the Conservation of Nature, giving it the highest know concentration of endangered plant species (Cowling and Heijnis, 2001). The study area in particular has 216 Red Data Book species in the mountainous portions and 17 in the valleys (Hall and Veldhuis, 1985).

Table 2: Summary of some species data for the five Mediterranean-type ecosystem hotspots from Meyers *et al.* (2000). The number in brackets is the corresponding hotspot ranking, out of 25 total hotspots, except where indicated.

	Endemic plant species per 100 km^2	Endemic vertebrate species per 100 km^2	Remaining primary vegetation, as a % of original extent	Plant Species	Endemic Plants (% of global plants, 300,000)	% Plants that are endemic	Vertebrate species	Endemic Vertebrates	% Vertebrates that are endemic
Cape Floristic Region	31.6 (5)	0.3 (15)	24.3 % (6)	8200	5682 (1.9%)	69% (6)	562	53	9% (23)
Central Chile	1.8 (23)	0.06 (24)	30.0 % (1)	3429	1605 (0.5%)	47% (13)	335	61	18% (18)
South West Australia	13 (17)	0.3 (15)	10.8 % (15)	5469	4331 (1.4%)	79% (3)	456	100	22% (16)
Mediterranean Basin	11.8 (15)	0.2 (18)	4.7 % (24)	25000	13000 (4.3%)	52% (9)	770	235	31% (13)
California Floristic Region	2.7 (21)	0.09 (23)	24.7 % (5)	4426	2125 (0.7%)	48% (12)	584	71	12% (20)

The CFR is somewhat naturally protected in that many of its most diverse communities occur on land that is not feasible to cultivate either because of the low nutrient status of the soil or the rough terrain and high relief. But these communities aren't protected from other threats including the intrusion of alien plants and atmospheric deposition of pollutants. Invasive aliens disrupt the ecosystem's water cycle through increased evapotranspiration, possibly lowering the overall water table if enough aliens take root. Large alien trees also disrupt the natural fire cycle that fynbos communities depend on by making the fires too hot, and therefore dangerous rather than regenerative.

Comparisons have been made between the species richness of fynbos and that of tropical rainforests. Both have generally very high biodiversity and grow on nutrient deficient soils. Rainforests, however, differ in having much more litter, higher rates of nutrient cycling, and much more biomass than fynbos. For fynbos, in general, the lack of nutrients combined with regular fire disturbances have compartmentalized ecosystems allowing adaptations to take hold, and ultimately have caused species to fill specific roles in the various communities (Richardson *et al.*, 1995).

Why is biodiversity important? This is a necessary question that goes unasked at some levels of environmental advocacy. According to Gibbs (2001), there are three broad categories of justification for preserving biodiversity.

1 - "*A hedge against disease and famine*" – Biodiversity, or species richness gives depth to an ecosystem and our food supply, so that if a component of either is destroyed, another component can function in its place. Depth reduces the impact of disease.

2 - *"Ecosystem services"* – We are still figuring out what all the pieces of our ecosystem do. And they may do things that are very important to our survival. Until we have that knowledge, it is unwise to destroy them.

3 - *"A duty of stewardship"* – This is a romanticized argument that appeals to the majesty of nature. A species has the general right to continue to exist by virtue of its place in nature. This argument is weak in terms convincing policy makers and economists of the value of species richness. But it does seem to motivate many scientists in the field.

In addition to these justifications, the water table argument above has been a major force in describing the need for protection of fynbos communities and the eradication of invasive species. It is possible that this could fit into the "ecosystem services" category by stating it differently, that fynbos has been adapted to the local climate and is designed to work with the water table rather than just feed off it. That is, most fynbos plants have developed 'demand-side' water saving measures that allow them to survive under low-water conditions. Alien vegetation often require much more water, and can out-compete the fynbos for the available supply. Why are large, water-guzzling aliens trees able to succeed in the supposedly harsh fynbos environment? It seems as though they are filling a niche in the habitat. One possibility is that their deep roots can reach the water table more easily. A main factor is the susceptibility to fire in the indigenous community relative to the invading species. Frequent fires in fynbos provide vacant pockets in which the invading trees can become established. Once established, the successfully invaded community may be more resilient to burning, and hence more permanent, disrupting the lack of equilibrium to which fynbos has adapted (Richardson and Cowling, 1992).

There have been numerous previous studies on the major nutrient (C,N,P,S) dynamics of the fynbos ecosystem (e.g., Richardson *et al.*, 1995; Groves, 1983), but few studies on the alkali metals, alkaline earths and trace metals. Metals can play an important role as micronutrients for vegetation and in controlling pH and redox conditions in the soil. Characterizing the chemical nature of the various components of these systems is an important step in understanding the dynamics of this floristically significant area.

Water chemistry is an effective tool for monitoring the functioning of an ecosystem. Water is the working fluid of an ecosystem. It reacts with particles and gases in the atmosphere, vegetation, soils, and rocks, and transports the elements from one reservoir to another. The capacity of water to take up and deliver the necessary elements is an important defining parameter for an ecosystem. Human blood must be buffered to maintain a pH of between 7.3 and 7.5. If the pH falls below 7.3, the blood cannot take up CO_2 produced by the cells; and if it rises above 7.7, CO_2 cannot be released to the lungs (Ball, 1999, p. 226). Similarly, the components of an ecosystem have developed a certain way of interacting, and small changes in the water chemistry could have major effects on the functioning of other parts of the ecosystem.

Degradation of both surface and ground water quality is a major concern for the study area. Ground water is the major source of municipal water for the town of Citrusdal, as well as for farmers and smaller towns throughout the Olifants River basin. Surface water is also drawn for home use and, along with groundwater, is widely used for irrigation of crops in the valley. The main causes of water quality degradation in this rural setting are agricultural runoff and irrigation. In addition, the Table Mountain Group aquifers are currently being assessed to meet the increasing water requirements of the Western Cape.

Chemicals are placed on and around the crops as fertilizers and insecticides, get washed off and are mobilized into the ground or surface water reservoirs. One main concern is that the chemicals will overload the water systems with nutrients, creating an imbalance that could reduce the dissolved oxygen available to aquatic life. This phenomenon is seen on a large scale at the mouth of the Mississippi River in the Gulf of Mexico where a large path of coastline has been termed the "Dead Zone" as all the creatures that could move out of the area have, and those that couldn't move have died due to lack of oxygen. Also of concern are chemicals at concentrations that are directly toxic to parts of the ecosystem. These can, again, cause an imbalance in the system that will reduce the ability of the ecosystem to function well. Even trace amounts of toxic chemicals in the water can cause problems as they accumulate in biota (e.g. plants and fish) and reach toxic levels further up the food chain.

Irrigation can cause many problems if not managed correctly. In general, all forms of irrigation lose large amounts of water to evaporation. Whether it is sprayed or left to stand in a canal or trough, much of the water that is meant for the plants ends up in the atmosphere. Most chemical constituents, being non-volatile, remain in the soil. If left to build up over time, these constituents can make the soil infertile. And it is likely that they will make their way into the water cycle again, this time at levels that could harm humans, animals, and plants.

Atmospheric deposition is another point where water chemistry can be greatly affected by anthropogenic influence. Atmospheric deposition can take many different forms and have a range of effects on the ecosystem into which it falls. Rainwater can become very acidic from the dissolution of nitrogen and sulfur oxides into atmospheric water droplets. The oxides can be released in large quantities through the burning of fossil fuels in automobiles and industry. This phenomenon was seen dramatically in northern Europe and North America, but has not been documented in less industrially influenced regions like South Africa. The potential effects of acid rain, however, are sufficiently dramatic to warrant investigation. Poorly buffered systems like the CFR are particularly susceptible to acid rain. Another atmospheric pollutant to worry about is lead, which mainly originates in leaded gasoline, released in trace amounts in car exhaust. Though very little lead makes it into the atmosphere, it quickly accumulates in the soil once it has fallen, and is very difficult to remove. Lead is mentioned here for its known human toxicity, and for its widespread use in South Africa's gasoline.

1.1 Study objectives

The project has three main objectives:

1 – To determine the general chemical composition of the rainwater, surface water, groundwater, vegetation, soils, and bedrock of the Olifants River Valley around Citrusdal.
2 – To evaluate the source and pathways of elements by constructing a simplified box model that depicts the major chemical reservoirs and transfers in the ecosystem.
3 – To discuss the potential effects of changing human influence on the health of the ecosystem.

Chemical composition – Water samples from rain, surface water, springs, and boreholes are analyzed for major ions and trace elements. The samples were chosen to represent the major chemically distinct reservoirs in the study area. Given the floristic importance of the CFR, discussed above, it is relevant to study the chemistry of the various components of this system. A proper physiological study of the CFR vegetation is not attempted here, but the vegetation, soil, and bedrock are characterized chemically. Bedrock samples from the Peninsula Formation, Nardouw Sub-group, and Bokkeveld Series, and associated soils are analyzed for major and trace elements. Minor and trace elements are determined in vegetation samples from the same localities. It is hoped that these data will help in future studies of the physiology of CFR vegetation, particularly mountain fynbos.

Element sources and pathways – The Elandskloof catchment will be used as a starting point for the elemental box-model as it is chemically simple relative to other parts of the Boontjies River sub-catchment that have been impacted more heavily by agriculture and are underlain by various geologic formations.

Potential impacts – As South Africa's industry and population grows, there will be changes in anthropogenic influence on the environment, such as chemical inputs and water use. The impacts of various changes (e.g. acid rain and a lowered water table) on the study area and fynbos ecosystems in general will be discussed.

1.2 Study Area

The study area for the project is the portion of the Olifants River Valley around the town of Citrusdal, about 170 km north north-east of Cape Town (Fig. 3). Specifically, the samples (excluding the downstream Olifants River samples, the warm baths and rainwater collected at UCT) are from the Boontjies River sub-catchment to the east of Citrusdal, which includes the tributaries Boschkloof to the east and north, and Elandskloof to the east and south. The Olifants River headwaters are in the Agter Witzenberg mountains. It is dammed at Clanwilliam, where it continues to flow north to combine with the Doring River, before it turns west and empties into the Atlantic Ocean. The total catchment area for the Olifants River (including the Doring) is 2888 km^2 and runs through the Olifants River Valley, with large-scale commercial farming. The 763 m^2 of catchment upstream of Citrusdal (subcatchments E10A, B, C, and D; Umvoto Africa cc, 2000) consists mostly of mountains and small-scale farming.

The Olifants River Valley is a dramatic synclinal fold with peaks rising to over 1800 m on the eastern side. The synclinal structure (Fig. 2) is made up of sandstone and shale formations of the Cape Supergroup. The stratigraphy consists of Peninsula Formation (sandstone), Pakhuis Formation (diamictite/mudstone), Cedarberg Formation (siltstone/shale), Nardouw Sub-group (sandstone), Bokkeveld Series (siltstone/shale), and alluvium; all but the Bokkeveld Series are part of the Table Mountain Group. The Peninsula Formation (1000-1500 m) is the thickest in the sequence and is the principal aquifer. The Peninsula Formation and Nardouw Sub-group aquifers are recharged in the eastern mountains. The recharge waters flow into the syncline and exit at springs both on the eastern (17°C) and western (up to 43°C) sides of the valley (Meyer, 2002). Waters that flow from TMG sandstone naturally have low pH values (< 5.5), as well as very low alkalinity and ionic strength (< 1 mM). Surface waters of fynbos ecosystems often have a dark brown color from dissolved organic matter. This coloring is intermittent and not dramatic in the study area. Boreholes are extensively used by farmers as well as the municipality to augment the take-off from the rivers.

The headwaters of the Boontjies River catchment are sourced from the quartz arenite sandstones of the Peninsula Formation, and are the most pristine parts of the study area. The Boschkloof catchment forms part of the Cedarberg Wilderness Area, a recreational park that is known for its natural, unaltered state. The entire Elandskloof catchment, and portions of Boschkloof are underlain only by Peninsula sandstone (Fig. 4). The tributaries flow down the eastern arm of the syncline towards the main valley, and cut across successively younger formations along the way. Overlying the Peninsula Formation are the thin, easily weathered siltstones and shales of the Cedarberg Formation. The Nardouw Sub-group contains a series of sandstone formations (Goudini, Skurweberg, and Rietvlei) that are less pure than Peninsula Formation, and support both natural fynbos vegetation and agriculture. The Bokkeveld Series includes shales and siltstones that are overlain by alluvium for much of its extent.

The climate in the entire southwestern Cape is highly seasonal with mild wet winters, and hot dry summers. Citrusdal is an extreme example of this, with around 90% of its rainfall coming in the winter months (Taylor, 1977). This seasonality affects rates of weathering, recycling of biomass, as well as the general inflow and outflow of elements to and from a given system. Additionally, the mountains to the east of Citrusdal can receive more than twice as much rainfall as the main valley since most of the rain comes from storms that travel from the west, which release their moisture as they rise over the mountains (up to 1800 m). A recent model lists 1410 mm as the maximum mean annual rainfall in the area, occurring in the maximum altitudes, compared to 250-500 mm in the valleys (Hay and Hartnady, 2002). Also, mist often collects in the parts of the mountains that are protected from the sun for much of the day. These high altitude areas are the headwaters for the Boontjies sub-catchment.

Table 3: Description of study area in terms of geology and land use.

Geological unit	Pristine description and extent	Impacted description and extent
Peninsula Formation	High relief outcrops with mountain fynbos communities	Small amounts of agriculture towards the main Olifants River valley
Cedarberg Formation	Grassy, smooth hillslopes	Agriculture in all but the higher elevation areas
Nardouw Sub-Group	Knobbly outcrops with mountain fynbos communities	Much of the flat areas affected by agriculture
Bokkeveld Series	Small hills in the main Olifants River valley, surrounded by alluvium	All but the occasional small hills are overlain by alluvial sand and farmed

The vegetation around Citrusdal varies from pristine fynbos in the mountains to the east to cultivation in the main valley. The main Olifants River valley is dominated by cultivated fields, mainly citrus trees, as it supports a large amount of commercial farming. The non-cultivated land is dominated by alien trees and grasses, with a few patches of indigenous vegetation. What is left of the natural vegetation in the main valley is confined to the small hills of the Bokkeveld Series siltstones and shales, where the vegetation is much lower (<0.5 m) and more sparse than the natural vegetation in the mountains, with many geophytes and succulents. These differences could be attributed to the lower rainfall and different parent material for the soils in the main valley. In the mountains to the east of Citrusdal farming is also done where it is feasible, but because of the steep slopes, shallow soils, and large amount of rock cover, a much larger percentage of the headwater areas are still relatively pristine. In Elandskloof, for example, about 10% of the catchment's aerial extent is impacted by farming, houses, and roads, with all of this impact in the lower, flatter part of the catchment. These mountains include part of the Cedarberg Wilderness Area, which is the most un-altered part of the study area. The folded sandstones of the Nardouw Sub-group and Peninsula Formation form deep valleys, the bases of which are used for light agriculture. The natural vegetation in the mountain areas is fynbos. Taylor (1996) describes 26 vegetation communities of the Cedarberg Wilderness Area, which lie just to the east of the study area and have similar parent material and climate as most of the soil samples. The communities are divided into 15 communities of well-drained habitats, 7 of poorly-drained habitats, and 4 of fire-protected habitats. The mountains of the Boontjies sub-catchment seem to exhibit many of the same natural vegetation communities. Specifically, Taylor's communities of colluvial rock slopes (No.'s 13, 14, 15), high-altitude rock slopes (No. 16), and seepages (No. 24), are represented in the Boontjies River headwaters. The Elandskloof sub-catchment is dominated by large *Protea* shrubs in some areas, and *Restios* in others. The Boschkloof headwaters seem to be similar. The entire study area is classified as part of the fynbos biome by Cowling and Heijnis (2001), who divide the CFR into Broad Habitat Units (BHUs) for conservation management. The mountains in the east form part of the Cedarberg BHU, and the main valley forms part of the Olifants River BHU.

Soils that support fynbos are usually sandy, shallow, and acidic (Richardson *et al.*, 1995). This is mainly due to the parent material and climate. The pure sandstone parent material and lack of water in the summer months combine to reduce the biomass available for cycling into and out of the soil. Due to the sandy nature of the parent material and high relief, the soils should also be generally poorly developed with coarse grains. Most fynbos soils are well-drained, but those that see prolonged periods of wetness support a different set of fynbos strata, as evidenced by Taylor's communities described above.

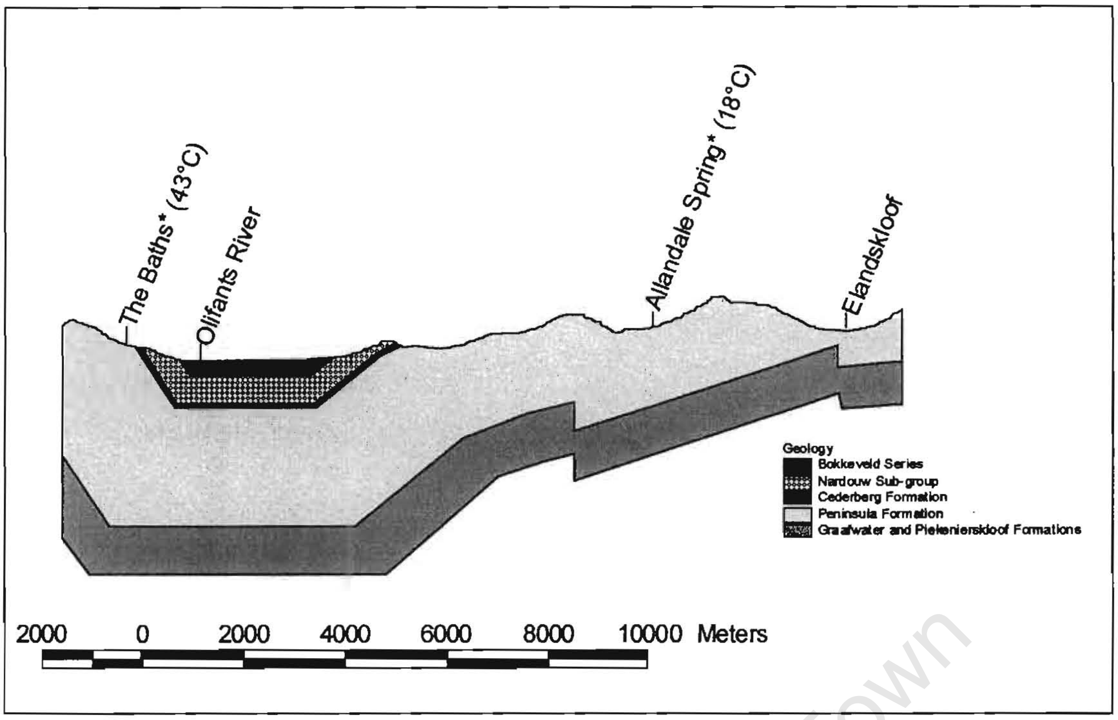

Figure 2: Profile (as indicated on Fig. 4) of the Olifants River Valley 15km south of Citrusdal.
Vertical and horizontal scale is the same. As can be seen on the aerial map, 'The Baths' and 'Alandale Spring' as marked on the profile are actually about 1.5 km south and 1 km north of the profile along a contour, respectively. Geology is estimated from Hartnady *et al.* (2000).

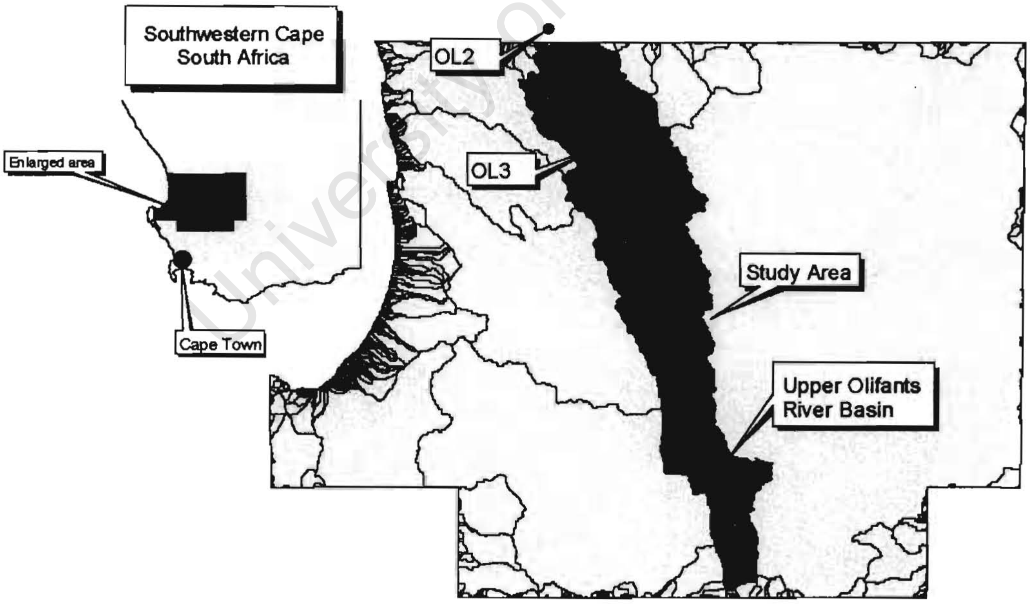

Figure 3: Location of study area. The inset shows the southwestern portion of South Africa, with the location of the enlarged area. In the enlarged map, river basins are outlined with the Upper Olifants catchment and the study area around Citrusdal highlighted.

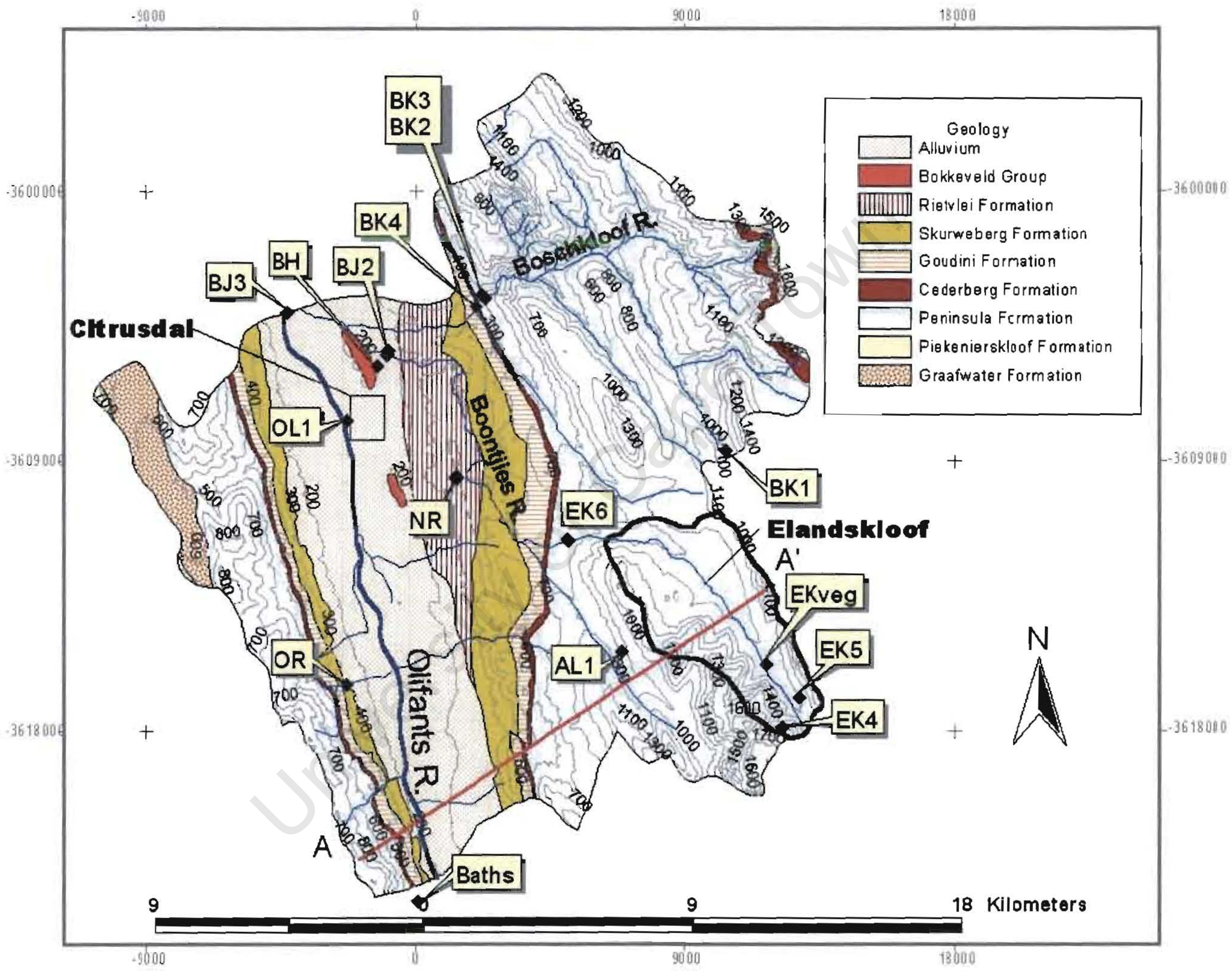

Figure 4: Geology of the Olifants River Valley around Citrusdal, showing the Boschkloof (BK1/2/3/4), Elandskloof (EK4/5/6), and Boontjies (BJ1/2/3) rivers. Geology adapted from Garlick (1999). Map grid is meters from the equator (vertical) and meters from 19°E. Contour heights are in meters, with an interval of 100 m.

2 Methods

2.1 *Summary*

Ten surface water samples were taken to study discharge, and 14 rainwater samples for recharge (3 from Citrusdal, 11 from Cape Town). Alkalinity (HCl) and acidity (NaOH) titrations were performed in the field to complement pH values in characterizing the acid-base status of the waters. Titrations were performed on unfiltered samples, and Gran function analysis was used to interpret the data. Major ions were determined by ion chromatography (IC), and trace elements by inductively couple plasma mass spectrometry (ICP-MS).

All water samples were collected in plastic bottles, refrigerated within 24hrs, and filtered (0.45 μm) within 48 hrs. Rainwater samples were collected for up to 30 min on a 50 cm diameter, 2 cm deep plastic tray, and poured into a bottle. All materials were pre-washed with acid and de-ionized water, and washed with the sample.

Seven soil samples were analyzed for soil pH (1:2.5, H2O and KCl), exchangeable acidity (KCl, titration), exchangeable cations (KCl, Atomic Absorption Spectrometry - AAS), soluble elements (saturated paste extract; IC, ICP-MS), grain size, and mineralogy (X-ray Diffraction - XRD). The seven soil and three bedrock samples (Peninsula sandstone, Nardouw sandstone (Rietvlei Formation), and Bokkeveld shale) were analyzed for major and trace element composition by X-ray Fluorescence (XRF).

Fourteen vegetation samples from areas underlain by Peninsula, Nardouw, and Bokkeveld bedrock were analyzed for elements detectable by ICP-MS after dry-ashing at 450°C in porcelain crucibles and acid (HNO3 and HF) dissolution (Vassileva *et al.*, 2001; Jones and Case, 1990). Notable exclusions from the elements analyzed are C, N, P, Na, S and Sn.

2.2 *Field Samples*

Specific groundwater, surface water, soil, vegetation and rock samples were chosen to address the project's objectives. A broad sample base was proposed to gain an initial understanding of the chemistry in each of the ecosystem's major reservoirs. To make the sampling more efficient, the study area was conceptually divided into sections relating to bedrock geology and land use/land cover. The geology relates to the chemical budget of the ecosystem by providing parent material for soils and inorganic constituents to ground and surface water as well as vegetation indirectly. Land use and land cover relates to the chemical budget through issues such as agricultural runoff, irrigation, evapotranspiration, and nutrient cycling. Specifically, it is interesting to identify water, soil, and vegetation samples that have had chemical inputs only from the weathering of the very pure (>98% SiO_2) Peninsula Formation sandstone and the atmosphere. The Elandskloof and Boschkloof headwaters are completely underlain by Peninsula sandstone, and are therefore a focus of the sampling.

2.2.1 *Water Samples*

Rainwater samples were collected both from the study area and from Cape Town. Two storm events (4 samples), both originating in the west, were sampled in the study area on 29-May-01 (CDrain), 19-Aug-01 (BathsRain). Six storm events (11 samples) were collected the roof of the geological sciences building at UCT, about 170km SW of the study area. The Cape Town samples were taken to complement the Citrusdal samples as it was more convenient to collect and analyze the Cape Town samples. It is expected that the Cape Town samples, due to a more urban setting, may have higher total concentration of certain elements (e.g. lead) than the Citrusdal samples. However, for elements where the concentrations from the two locations are found to compare well, the Cape Town samples can be used as a proxy for Citrusdal rain.

Surface water sampling points were chosen to roughly represent various chemically distinct areas. First, typical headwaters of the eastern tributaries (EK4, EK5, BK1), were selected as streams fed only by water coming from Peninsula sandstone. At the base of the Elandskloof and Boschkloof catchments, samples were collected (EK6, BK3) to identify the output of each catchment so that changes could be detected as the waters interact with different geological formations downstream (BJ1, BJ2, BJ3). The Olifants River was sampled over large distances starting just upstream of Citrusdal (OL1), 50 km downstream at Clanwilliam dam (OL3), and at the confluence with the Doring River 45 km further. The tributaries on the west side of the Olifants River, many of which are fed by warm springs, were not the focus of this project, and are represented by only one sample (OR1).

Two boreholes were sampled at the Boschkloof farm 7 km east of Citrusdal. The first (BK2) taps Peninsula sandstone with a total depth of 294 m and is artesian with flows between 5 and 8 L/s. The geology of the second borehole (BK4) is thought to be tapping Nardouw sandstone at the contact with Cedarberg shale, and is 348 m deep with artesian flows less than 1 L/s (Hartnady and Hay, 2002; BK2 and BK4 of the present study refer to BK4 and BK5 of this reference, respectively). BK4 is nicknamed the "bacteria borehole" for the abundance of bacteria colonies through the entire depth. Also, orange debris floats up with the water in small pieces (about 5 mm x 5 mm).

Table 4: Sample locations and descriptions.

Sample	Location[a]	Geology[b]	Land Use[c]	Land Cover	Slope, Aspect	Elevation (m)	Sample Type[d]
EK4	Headwaters of Elandskloof catchment	Peninsula	Natural	Mountain fynbos, 1-2m *Protea nitida*	Midslope, E	1200	W
EK5					Footslope, W	1000	W,S
EKveg					Midslope,E	860	V
EK6	Near base of Elandskloof sub-catchment	Peninsula	Citrus Farming	Thick grass	Valley bottom	560	W,S
BJ1	After confluence of Elandskloof and Boontjies Rivers	Nardouw	Farming	Thick aliens	Valley bottom	500	W
BJ2	Main valley, near Boontjies River	Bokkeveld/ Alluvium	Farming	Thick grass...no strong evidence of crops or current livestock.	Valley bottom	180	W,S,R
BJ3	Boontjies River before confluence with Olifants			Large aliens		150	W
NR	Along road towards main valley from Elandskloof	Nardouw (Rietvlei)	Natural	Mountain fynbos – heavy *Restios*, etc.	Midslope, W	390	W,S,R,V
BK1	Headwaters of Boschkloof catchment	Peninsula	Natural	Mountain fynbos - Community ??	Footslope, N	1010	W,S
BK2	Near base of Boschkloof catchment	Peninsula	Natural	Mountain fynbos – sparse grass and shrubs	Footslope, N	350	W,S,R
BK3					Valley bottom	350	W
BK4		Nardouw (Goudini)	Natural	Large reeds, edge of agricultural field	Valley bottom	350	W
BH	East side of Bokkeveld hill on edge of Citrusdal town	Bokkeveld	Natural	Sparse small shrubs and succulents	Valley bottom	200	R,V
OL1	Olifants River at Citrusdal bridge	Bokkeveld/ Alluvium	Farming	Heavy reeds in and along River	Valley bottom	155	W
OL3	Olifants River at Clanwilliam Dam		Farming	Light grass		145	W
OL2	Olifants River at confluence with Doring River		Wine farms	Heavy reeds and trees in and along River		100	W
Baths	"The Baths" hot springs resort 17km S of Citrusdal	Peninsula	Natural	Large trees	Midslope, E	300	W
OR	Olifants Rus hot springs resort 8km S of Citrusdal	Peninsula	Natural	Large trees, grass	Footslope, E	240	W
UCT	Roof of UCT's Geological Sciences building	-	-	Tarred roofing with some loose particles	-	110	W

a – Sample locations are plotted on Fig. 4, except OL2 and OL3 on Fig. 3.
b – The underlying geological formation
c – The major distinction here is between land that shows signs of being used for agriculture, and "natural" land that does not.
d – W=water, S=soil, R=rock (outcrop), V=vegetation

Two springs were sampled. Allandale Spring (AL1) is on the east side of the Olifants River valley about 5 km south of the main road leading east from Citrusdal (R303) on Allandale farm. The spring is at the base of a mountain covered in 1-2 m high fynbos. It's about 200 m from the Boontjies River, and seasonally shifts vertically on the hill slope within about a 20 m range. A concrete v-notch weir was constructed by Umvoto Africa in 1998. The road to Allandale Spring requires four-wheel drive. The other spring sampled is "The Baths" hot spring on the west side of the Olifants 17 km south of Citrusdal. The spring is easily accessible as the resort has cleared a path to the fracture where water flows from Peninsula sandstone at about 29 L/s with a temperature of 43° C (Meyer, 2002).

2.2.2 *Soil and Bedrock Samples*

Of the seven soil samples collected, six are from the topsoil (EK5, EK6, BK1, BK2a, BJ2, NR) , and one from the subsoil (BK2b). Five have Peninsula Formation sandstone as parent material (EK5, EK6, BK1, BK2a&b), one is underlain by the Rietvlei Formation of the Nardouw Sub-Group (NR), and the last by alluvium/Bokkeveld shales (BJ2). The sample names correspond to water samples taken nearby.

Each of the soil samples could be described as well-drained. There are, however, examples of soil patches near the headwaters of the Elandskloof River that are poorly drained. Taylor (1996) divides 22 of his 26 communities into those of well-drained habitats (Communities 5-19), and those of poorly drained habitats (Communities 20-26). This reflects the importance of drainage on the development of vegetation, and therefore also reflects the importance of drainage on soil development. Drainage of soils depends mainly on relief, water table depth, and porosity.

Three bedrock samples were chosen from the Peninsula Formation, Nardouw Sub-Group (Rietvlei Formation), and Bokkeveld Group. The Peninsula Formation specimen came from the base of the BK2 soil profile (Fig. 5). In each case, the visually least weathered surface specimen was chosen in close proximity to water, soil, and vegetation sampling points.

2.2.3 *Vegetation Samples*

Vegetation samples were taken from roughly 25 m^2 plots at four locations in the study area. A random sampling of was attempted at each location in an effort to obtain a representative sample of the major communities. That is, in each plot, except the Bokkeveld shale plot, specimen from the major recognized species or groups (e.g. restio, herb, woody shrub, succulent) were clipped, and the spatial coverage of each species or group estimated visually. Trees and large shrubs were sampled by taking a small branch with leaves. Random vegetation sampling is described as the ideal method as it can reduce the analyst's bias and allow for statistical tests. However, a true random sampling is very difficult, especially without formal training (Goldsmith *et al.*, 1986). For the purposes of this first-order study of the bulk chemistry of the vegetation, this semi-random sampling should work. That is, although various data are presented here, the analysis should be regarded as semi-quantitative only. The data should provide an idea of which elements are stored in the vegetation and their relative magnitudes. These findings are important for characterization of the biomass as a major chemical reservoir in an ecosystem. If the goal was to rigorously define differences in the chemistry of two communities, or between indigenous and alien species, a much more careful sampling procedure would be needed.

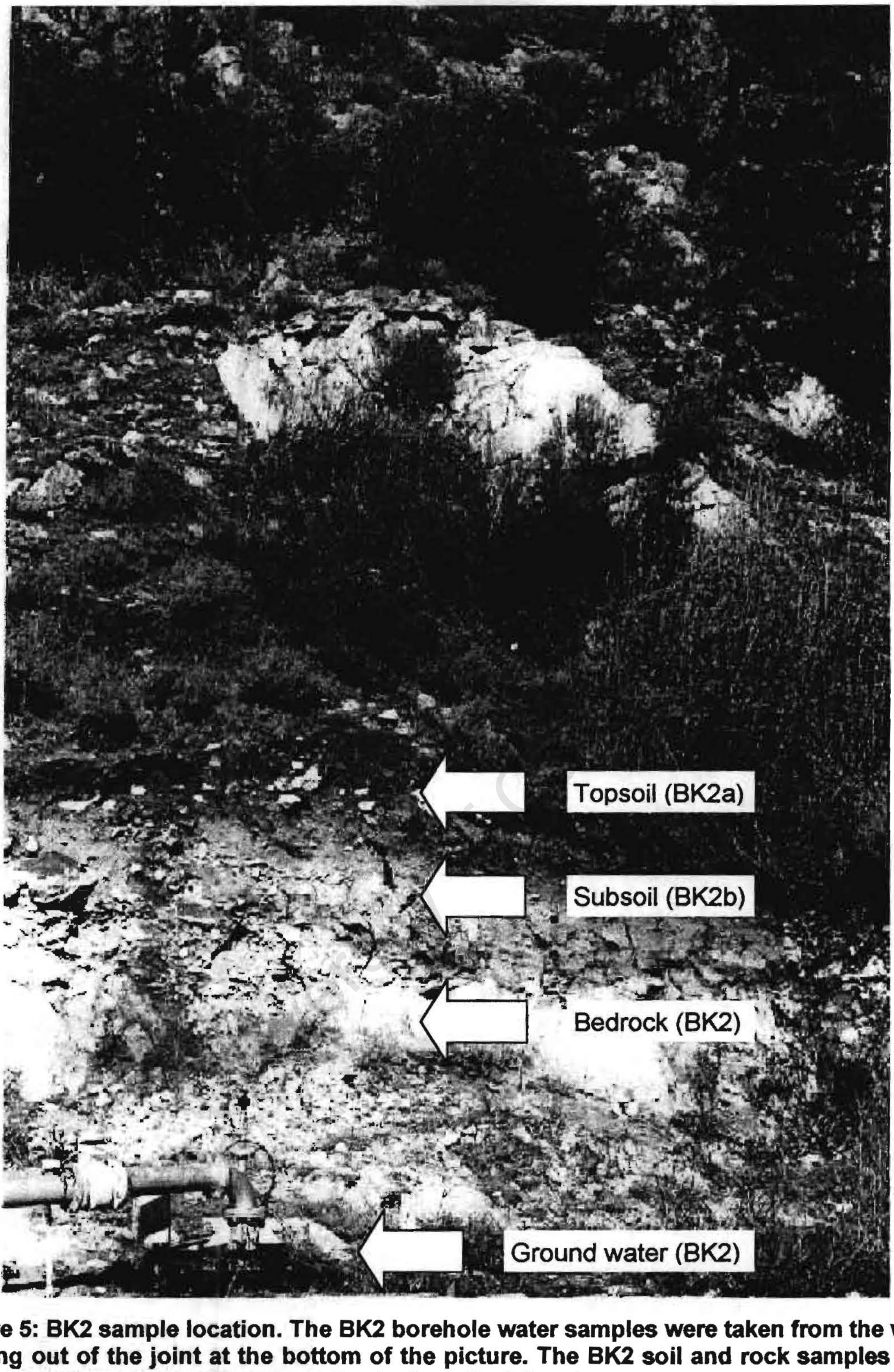

Figure 5: BK2 sample location. The BK2 borehole water samples were taken from the water flowing out of the joint at the bottom of the picture. The BK2 soil and rock samples were taken from the same profile, about 5 m to the left of the picture.

2.3 *Water Analysis*

In the field water samples were analyzed for pH, Electrical Conductivity (EC), and alkalinity. In the lab, major ions were measured via IC, major and trace elements via ICP-MS, hardness by titration, and DOC was measured by an external laboratory.

2.3.1 *pH and Electrical Conductivity*

Measurement of hydrogen ion activity is an essential element in the chemical analysis of waters. It also involves many uncertainties and is difficult to measure accurately in poorly buffered waters (Lahav *et al.*, 2001). Most of the samples in this study are very dilute (EC range <5-120 µS/cm) and poorly buffered. Measurement of pH was done with a Radiometer PHM201 which has a glass combination electrode. Stability is indicated on the meter's display with an "S-T-A-B" readout. However, drift of the pH reading often occurred after stability was indicated. To deal with this, the stability of a pH reading was operationally defined in the following two ways:

1. For sub-sample readings, the general procedure was to swirl the solution well, stop, and let the meter come to show stability. A stable pH reading was taken to be when the reading didn't change after swirling the solution.
2. For in situ readings, stability was not easily reached especially in faster-flowing streams. This is consistent with a "streaming effect" noted in the literature, which suggests that more slowly flowing water or a sub-sample should be measured (APHA, 1995). This was addressed in two ways.
    a. For waters that were flowing very quickly everywhere, the movement of the pH reading was monitored until it varied within about 0.05 units, and the average was taken.
    b. For waters with both fast flowing areas and slower flowing pools, the stable measurement of the pool was averaged with the value for the faster flowing areas as determined in a. above.

The memory effect was experienced in the pH measurement of the rainwater samples. That is, after placing the electrode in strongly buffered standard solutions for calibration, the meter takes a very long time to stabilize in the poorly buffered solution.

Electrical conductivity is a measure of the charged species in a given solution. It is defined as the inverse of the resistance measured across a set distance between electrodes. EC was measured in this study with a portable meter (CIBA-Corning Check-mate 90) that measures the electrical resistance across 1 cm. Care must be taken when comparing EC values as resistance across 1 m is often reported.

2.3.2 Alkalinity and Acidity Titrations

As a major goal of this project is to gain information regarding the acid/base equilibrium in the ecosystem, potentiometric titrations were performed with both acid and base as titrant. The acidimetric titration gives a measure of alkalinity or acid neutralizing capacity (ANC). The alkalimetric titration gives a measure of the acidity or base neutralizing capacity (BNC). Putting the two titration curves together gives a picture of the entire carbonate equilibrium spectrum for the system. The shape of this composite curve gives clues to the species present when it is compared to the theoretical carbonate curve.

ANC (alkalinity) and BNC (acidity) are conservative capacity parameters of a system defined as the amount of acid and base that a system can take up, respectively (Stumm and Morgan, 1996). BNC can be divided into free (mineral, H) and weak (CO_2) components that combine to form total BNC. Both ANC and BNC have been defined in the past by the pre-defined titration endpoints 4.5 and 8.3. This is now recognized as being potentially inaccurate, as the theoretical endpoints do not necessarily correspond to the points at which all H^+ or OH^- added stays in solution (i.e. equivalence points; Wilde *et al.*, 1998; Stumm an Morgan, 1996).

The titrations were performed on a 100 ml sub-sample directly after collection with a couple noted exceptions not exceeding 45 minutes after collection. The sample was left open to the atmosphere, but attempts were made to keep carbonate equilibrium as close as possible to in situ conditions. That is, the titration vessel was held in a bucket of sample water to maintain the temperature, and movements of the sample were kept smooth to reduce unnecessary release or dissolution of carbon dioxide. This is a critical property of the titration as seen by Stumm & Morgan (1996) distinguishing between open and closed systems during titration. To address this, many reported procedures include continuous or initial scrubbing of the sample with an inert gas, like nitrogen, to remove any dissolved carbon dioxide gas (e.g. Molvaersmyr and Lund, 1983). This technique has the advantage of a more well defined carbonate system as you know exactly what's happening to the dissolved CO_2, and the sample can be transported to the lab before analysis. The drawback is that it loses information with respect to the original sample from changes to the temperature and the carbonate system.

Titrant additions were made with a digital pipette (Eppendorf Digital Pipette 4710) and restricted to a discrete set of volumes between 100 and 1000 μL to allow for error calculations. Acidimetric titrations were performed with dilute HCl (0.01-0.005 M) to below pH 3.5 (Cantrell *et al.*, 1990; Sullivan *et al.*, 1989). Alkalimetric titrations were performed with dilute NaOH (0.0025 M) to a pH of at least 9 (Molvaersmyr and Lund, 1983). A maximum acceptable pH change for a single titrant addition was taken as 0.3 units, though an average change of about 0.15 units was attempted in order to obtain a high-resolution curve. Additionally, titrant additions were chosen for smaller pH changes within 0.2 units of the traditionally used carbonate end-points of pH 4.5 and 8.3.

2.3.3 *Dissolved Organic Carbon*

DOC was measured by CSIR Environmentek, an external laboratory in Stellenbosch, South Africa, about 80 km from UCT. Filtered (0.45 μm) samples were submitted to the lab. In the lab, samples are acidified and purged with CO_2-free nitrogen. All organic carbon is converted to CO_2 after the addition of potassium persulphate and UV digestion. The CO_2 dissolves into a phenolphthalein solution, changing the solution's color, which is measured against potassium hydrogen phthalate standards.

2.3.4 *Collection and Preservation*

Two bottles were filled at each sampling point, and taken to the lab where they were filtered within 48 hrs. Borehole samples (BK2 and BK4) were sampled from artesian flow at the top of the borehole. One bottle was acidified with several drops of distilled 33% HNO_3 to keep metals in solution. The other was left un-acidified for analysis on IC and for DOC. All samples were kept in a dark refrigerator below 4°C.

2.3.5 *Lab Analysis*

The constituents Cl^-, F^-, NO_2^-, NO_3^-, Br^-, SO_4^{2-}, Na^+, Li^+, PO_4^+, K^+, Ca^{2+}, and Mg^{2+} were determined by ion chromatography (Dionex, see Appendix A for specifications). A small amount of calcium and magnesium ions were present in the MQ (double distilled) water that was used in calibrating the IC unit. So the actual concentration of these two ions in the standards was higher than the theoretical concentration calculated from the original stock standards. This was corrected by assuming the following:

1 – The calibration curve plotted as Response (conductance) vs. Theoretical Concentration (ppm) should go through the origin.
2 – The calibration curve is linear.
3 – The concentrations of calcium and magnesium ions in the MQ water has remained constant from the time the stock standards were made in March 2001, to the time of analysis when the standard dilutions were made in June, August, and November 2001.

Using these assumptions, the horizontal shift required to place the x-intercept of the Response vs. Theoretical Concentration linear regression curve was taken as the MQ concentration. The concentrations of the standard dilutions were then corrected according to their respective dilutions. In effect, this is basically a horizontal shift of the linear regression curve.

Inductively coupled plasma mass spectrometry (ICP-MS) was used to analyze for the total concentrations of the following elements: Li, Be, B, Mg, Al, Si, K, Ca, Sc, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Br, Se, Rb, Sr, Y, Zr, Mo, Ag, Cd, Sn, Cs, Ba, La, Ce, Nd, W, Tl, Pb, Th, U, Sb. This wide selection of elements was chosen in an effort to discover any patterns in the chemistry of the water samples. ICP-MS is especially useful for its low detection limits for heavier elements. The model used was Perkin Elmer / Sciex Elan 6000, see Appendix A for further specifications.

Hardness determinations were made as a check of the calcium and magnesium determinations by IC and ICP-MS. The EDTA molybdo-silicate method (APHA, 1995) was used with a diluted EDTA for less uncertainty as the water samples had very low concentrations of calcium and magnesium.

Due to the very low ionic strength of the water samples analyzed, pre-concentration by evaporation was attempted on three samples (AL1, EK4, BK1) and a blank of de-ionized water. The samples were evaporated by a heat lamp (about 60°C) from one plastic bottle into another through a teflon connection. The receiving bottle was constantly cooled by a flowing water bath to allow the distillate to condense. Both the distillate and concentrate solutions were analyzed on ICP-MS.

2.4 *Soil Analysis*

Samples were collected with a metal trowel and sealed in plastic bags. They were air-dried uncovered on a lab bench and stored in plastic bottles until further analysis. Various physical and chemical properties of the soils were determined as described below. For major and trace element composition by XRF, the soil samples were processed in the same way as the bedrock samples.

2.4.1 *Grain Size*

A basic grain size analysis was performed to divide the soils into gravel, sand, silt, and clay (Table 5). Gravel was separated first by a 2 mm sieve. In this analysis, the >2 mm portion of the sample is not considered part of the soil, following the convention of the International Society of Soil Science (vanLoon and Duffy, 2000). The sand was then separated by washing a small amount (about 10g) of the <2 mm fraction through a 0.063 mm sieve. Though many particle size definitions (e.g. Soil Classification Working Group, 1991) take 0.053 mm as the smallest sand particle, 0.063 mm is the boundary for the geological Wentworth-Udden scale (Kearey, 1996).

The suspension of water and particles that passed through the 0.063 mm sieve contained both the clay and silt fractions. Approximately 50 ml sodium hexametaphosphate $(NaPO_3)_6$, “Calgon”, was added to each sample to disperse the clay particles. Using Stoke’s Law for idealized settling time, the clay fraction was poured off at the correct time based on a settling rate for the smallest silt particle (0.002 mm) of 46 min. per centimeter of water height. In pouring off the suspended clay fraction, up to 100 ml of the suspension had to remain with the silt fraction in order not to mix silt with the clay. The result being that the silt fraction is increased some amount by the clay left behind. This is unfortunate as the heaviest clay particles would have been at the bottom of the suspension near the settled silt. In retrospect a better method would have been to carefully pipette the suspension out rather than pouring. The sand and silt fractions were dried in an oven (60-70°C) to a constant weight.

Table 5: Grain size definitions and separation techniques.

Grain size	Particle size range (mm)	Separation Technique
Gravel	>2	Dry sieve
Sand	0.063-2	Wet sieve
Silt	0.002-0.063	Wet sieve, settle
Clay	<0.002	Wet sieve, pour off

2.4.2 Soil pH

Soil pH was determined in an aqueous suspension with a ratio of 1 part soil to 2.5 parts aqueous phase. Distilled water and 1M KCl were used as aqueous phases in separate runs. The pH was determined from a glass combination electrode (Radiometer PHM201) after stirring the suspension, letting it sit for 50 min, stirring again, and letting sit for 10 min (McLean, 1986).

2.4.3 Exchangeable Cations and Acidity

Exchangeable acidity was determined by titration of filtrate from a suspension of soil and 1M KCl in a ratio of 1:10. The filtrate was titrated to the phenolphthalein endpoint with 0.01M NaOH. The exchangeable Ca, Mg, and Na ions, those adsorbed to the surfaces of soil particles, were displaced by K^+ ions in the same suspension used for exchangeable acidity above. These ions were then determined by Atomic Absorption Spectrometry (specifications in Appendix A).

2.4.4 Saturated Paste Extract

An aqueous saturated paste was created for each sample in an attempt to reconstruct the natural soil solution, which is impractical to sample directly. Saturation is preferred over other soil to water ratios (1:1, 1:10) as it is a better estimate of in situ conditions. The soluble salts were measured collectively through electrical conductivity by submerging an EC probe (CIBA-CORNING Check-mate 90) in the saturated paste prior to extraction of the soil solution.

The soil solution was vacuum extracted from the paste through a Whatman filter (No.1) and then a 0.45 μm membrane filter via a syringe. This filtered extract was analyzed for major ions by Ion Chromatography (IC), and total elemental concentrations via Inductively Couple Plasma Mass Spectrometry (ICP-MS) (Appendix A). Simple geochemical modeling was done on the software program PHREEQC using the concentration data using the concentration data obtained by IC and ICP-MS.

2.4.5 *Organic Carbon*

Soil organic carbon was determined with the Walkley-Black Procedure. A small amount of oven-dried soil (0.5-1 g) is weighed out and oxidized by sulfuric acid and potassium dichromate. The excess potassium dichromate is titrated with iron (II) ammonium sulfate to determine the amount used in the oxidation procedure. The dark violet-brown endpoint is determined visually, but is rapid and distinctive.

2.4.6 *Phosphate Sorption*

In an attempt to estimate the partition coefficient for phosphate (PO_4^{3-}) in each of the soils, 2.5 g of soil was shaken for 24 hrs with a standard of known phosphate concentration (0, 0.5, 1, 2, 3, or 5 mg P/mL). The supernatant was then treated with ammonium molybdate and ascorbic acid, and absorbance was measured on a spectrophotometer at 880 nm.

2.4.7 *Mineralogy*

The mineral composition of the soils was determined using X-ray diffraction (Appendix A). Bulk (<2 mm) soil samples were ground by hand to a fine powder, and pressed as a dry powder in a sample holder. Clay fractions were prepared on glass slides by two methods: pipetting of a suspension, and smearing an even layer of clay particles directly on the slide. Both bulk and clay samples were analyzed with a continuous scan with the take-off angle (°2Θ) ranges of 5-54 for bulk, and 3-30 for clay. A copper x-ray source was used.

The peaks indicated by the system software were manually identified as being caused by specific minerals based on correlating the angle of diffraction to the theoretical angles calculated from each mineral's d-spacing. This method is only meant to provide a qualitative description of which minerals are present in the samples.

2.5 *Bedrock Analysis*

Prior to analysis, the outside portions of each specimen were split off and discarded to reveal the freshest part of each rock. Thin sections were produced for each specimen, and about 80 g was crushed to a fine powder in a carbon-steel Sieb Mill. This powder was used to produce fusion and pressed discs for major and trace element XRF analysis. The fusion discs were made by first weighing 6 g of sample in a platinum crucible and drying at 105°C to determine moisture content. Then the samples were roasted at 850°C to remove any organic material and determine loss on ignition. A flux is added to the roasted sample, and the disc produced by the lab. Pressed discs were made using a carbon-steel piston set to compress 6g of sample mixed with a binder ("4% Mowiol 13/8/99") encased in powder-form boric acid.

2.6 *Vegetation Analysis*

The samples were clipped and stored loosely in open plastic bags until arrival at the laboratory 24-48hrs later. In the laboratory, the samples were washed with a brush and running tap water before being photographed and laid out to air-dry for 14 days. The air-dried vegetation was then cut into small pieces and placed in beakers, weighed, and placed in an oven at 60°C. In some cases a sub sample was taken at this stage as the original specimen was too large. After obtaining a constant oven-dry weight, a portion of each sample was hand-ground in a quartz agate mortar and pestle. This step helps to homogenize the sample so that the very small amount taken for final analysis can be representative of the original. However, due to the difficulty of hand-grinding the vegetation to a fine enough powder, complete powdering and homogenization of the samples was done during the mineralization step described below.

The steps in preparing a vegetation sample for analysis include homogenization, mineralization, and dissolution (Hoenig, 2001; Vassileva *et al.*, 2001; Hoenig, 1998; Jones and Case, 1990). In this case, homogenization and mineralization overlapped, with the mineralization performed by dry ashing in open porcelain crucibles at 450°C. The samples were left to roast in the oven for up to 8 hrs, and after 4 hrs they were checked. At this point each sample was further ground to a powder in its crucible to allow for complete oxidation of organic matter. Dissolution was performed following the same procedure used to prepare powdered rock samples for analysis on an ICP-MS, which includes a combination of HNO_3 and HF.

3 Results

3.1 *Water Analyses*

All samples have generally low pH, EC, hardness, and DOC (Table 7). The rainwater pH ranges from 4.6 to 5.8, with a mean of 5.1 for 9 samples. Surface water from the eastern tributaries at Citrusdal show a similar pH range of 4.5-5.8 with a mean of 4.9 (Table 6). The mean pH of all TMG waters in this study is 5.0. This includes the groundwater and surface water samples, but excludes samples OL3 and OL2 as they were taken from 50 and 70 km downstream of Citrusdal, respectively. OL3 and OL2 have higher EC and hardness values (138 and 769 μS/cm EC, 190 and 1497 μmol/L hardness, respectively) than the Citrusdal samples, where the highest values are 132 μS/cm and 159 μmol/L (OR1). The Nardouw Sub-group borehole EC and hardness values are similar to OR1, with all other samples having lower values. Looking at all samples, EC and hardness values increase from rainwater to surface and ground waters. DOC ranges from 1.0 to 2.1 mg/L in the TMG waters and has its highest values in the eastern tributaries.

Table 6: Statistics for general parameters of water samples.

		pH	EC (μS/cm)	Hardness (μmol/l)	DOC (mg/l)
Rainwater	Mean	5.1	16	15	n.a.
	Standard deviation	5.1	14	13	
	C.V.	106%	86%	83%	
	N	9	14	5	
Boonjties River sub-catchment	Mean	4.9	35	38	1.3
	Standard deviation	4.9	11	15	0.57
	C.V.	92%	31%	40%	43%
	N	8	8	8	8
All TMG surface and groundwaters (excluding OL2, OL3)	Mean	4.9	52	66	1.2
	Standard deviation	5.0	34	48	0.6
	C.V.	75%	65%	74%	49%
	N	14	14	14	11

n.a. – not analyzed; C.V. – Coefficient of Variation; N – number of samples

Table 7: General parameters for all water samples.

Sample	Date Collected (2001)	Category	Description	PH	Sample Temp (°C)	EC (µS/cm)	Hardness (µmol/l)	DOC (mg/l)
CDrain	29 May	Rainwater	Citrusdal rainwater	5.4	n.a.	26	25	n.a.
ORrain	19 Aug			n.a.	n.a.	46	n.a.	n.a.
BathsRaina	19 Aug			5.2	n.a.	15	n.a.	n.a.
BathsRainb	19 Aug			5.5	13.0	4	13	n.a.
UCTrain1	25 Jun		Cape Town rainwater	n.a.	n.a.	n.a.	n.a.	n.a.
UCTrain2	3 Jul			5.6	n.a.	5	n.a.	n.a.
UCTrain3	18 Jul			n.a.	n.a.	19	n.a.	n.a.
UCTrain4	16 Aug			5.3	n.a.	35	32	n.a.
UCTrain5	16 Aug			4.6	n.a.	14	n.a.	n.a.
UCTrain6	17 Aug			4.8	n.a.	35	n.a.	n.a.
UCTrain7	17 Aug			5.8	15.0	3	3	n.a.
UCTrain8	17 Aug			5.4	n.a.	14	n.a.	n.a.
UCTrain9	29 Aug			n.a.	n.a.	5	4	n.a.
UCTrain10	29 Aug			n.a.	n.a.	5	n.a.	n.a.
UCTrain11	29 Aug			n.a.	n.a.	4	n.a.	n.a.
AL1	29 May	Spring and groundwater	Peninsula Fm. cold spring	4.7	17.5	25	19	< 1.0
BK2	30 May		Peninsula Fm. borehole	5.0	28.0	61	75	n.a.
Baths	19 Aug		Peninsula Fm. warm spring	5.0	43.0	73	134	n.a.
BK4	30 May		Nardouw Sub-group borehole	4.8	22.5	116	149	n.a.
OR1	19 Aug		Warm stream near the Baths	5.2	20.0	132	159	< 1.0
BK1	30 May	Surface water	Surface waters from Boonjties River sub-catchment	4.6	9.0	39	40	1.0
BK3	30 May			5.8	13.0	49	52	1.0
EK4	28 May			5.0	13.5	19	17	1.0
EK5	28 May			4.9	13.0	21	17	< 1.0
EK6	29 May			4.5	12.0	30	33	1.4
BJ1	29 May			5.6	13.0	36	41	2.1
BJ2	29 May			5.2	13.5	41	44	2.1
BJ3	30 May			5.2	14.0	46	60	1.5
OL1	30 May		Olifants River at Citrusdal	5.2	14.0	48	80	1.5
OL3	31 May		Olifants River at Clanwilliam	6.2	17.0	138	190	1.8
OL2	31 May		Olifants River at Trawal	7.5	13.0	769	1497	3.7

n.a. – not analyzed

Table 8: Molar concentration^{a} of major ions and charge balance for 30 water samples.

Sample	Date Collected (2001)	Category	Description	Na$^+$	Mg^{2+}	Ca^{2+}	K$^+$	NH$_4^+$	Li$^+$	H$^+$	ΣCations (ueq/L)	Cl$^-$	SO$_4^{2-}$	Br$^-$	F$^-$	PO$_4^{3-}$	NO$_2^-$	NO$_3^-$	^{b}ANC	^{c}A$^-$	ΣAnions (ueq/L)	CBE (%)	Ionic Strength
CDrain	29-May	Rainwater	Citrusdal rainwater	152	11	9	24	n.d.	n.d.	4	220	143	8	n.d.	n.d.	n.d.	n.d.	0.3	^{d}9	n.d.	168	13.3	0.22
ORrain	19-Aug			22	59	31	5	3	n.d.	^{d}8	219	326	27	2	n.d.	0.2	n.d.	1	^{d}9	n.d.	392	-28.3	0.41
BathsRaina	19-Aug			75	8	2	6	0.5	n.d.	7	109	82	11	n.d.	n.d.	n.d.	0.6	0.7	^{d}9	n.d.	114	-2.3	0.09
BathsRainb	19-Aug			13	5	5	4	1	n.d.	3	41	16	2	2	n.d.	n.d.	0.4	0.3	10	n.d.	32	11.6	0.08
UCTrain1	25-Jun		Cape Town rainwater	73	3	7	7	8	n.d.	^{d}8	118	34	19	2	n.d.	n.d.	0.6	0.8	^{d}9	n.d.	84	16.8	0.12
UCTrain2	3-Jul			66	1	3	13	2	n.d.	2	90	32	8	2	n.d.	n.d.	0.4	0.5	^{d}9	n.d.	58	21.6	0.08
UCTrain3	18-Jul			146	12	6	8	4	n.d.	^{d}8	204	152	9	2	n.d.	n.d.	n.d.	0.4	^{d}9	n.d.	180	6.3	0.21
UCTrain4	16-Aug			244	25	4	8	2	n.d.	5	316	288	17	2	n.d.	n.d.	n.d.	0.5	25	n.d.	349	-5.0	0.37
UCTrain5	16-Aug			111	10	2	5	2	n.d.	25	166	107	10	2	n.d.	0.3	0.5	0.6	n.d.	n.d.	129	12.3	0.16
UCTrain6	17-Aug			270	27	5	13	4	n.d.	16	367	306	21	2	n.d.	n.d.	n.d.	0.8	n.d.	n.d.	350	2.4	0.40
UCTrain7	17-Aug			40	1	0.4	3	0.7	n.d.	2	49	11	3	n.d.	n.d.	n.d.	0.4	0.3	^{d}9	n.d.	26	30.1	0.04
UCTrain8	17-Aug			107	9	1	8	4	n.d.	4	144	95	8	2	n.d.	n.d.	0.4	0.5	^{d}9	n.d.	123	7.6	0.15
UCTrain9	29-Aug			35	2	0.7	19	0.9	n.d.	^{d}8	70	36	5	2	n.d.	0.2	0.6	0.6	^{d}9	n.d.	59	8.4	0.06
UCTrain10	29-Aug			42	2	0.7	5	0.9	n.d.	^{d}8	64	21	3	n.d.	n.d.	n.d.	0.4	0.5	^{d}9	n.d.	38	25.5	0.05
UCTrain11	29-Aug			16	2	0.6	3	0.5	n.d.	^{d}8	34	18	3	2	n.d.	n.d.	0.4	0.5	^{d}9	n.d.	36	-2.9	0.03
AL1	29-May	Spring and groundwater	Peninsula Fm. cold spring	155	17	2	6	n.d.	0.7	22	222	156	4	2	n.d.	n.d.	n.d.	n.d.	n.d.	5	171	13.1	0.22
BK2	30-May		Peninsula Fm. borehole	308	39	22	30	n.d.	n.d.	11	470	301	9	3	n.d.	0.03	n.d.	0.6	83	n.d.	405	7.5	0.51
Baths	19-Aug		Peninsula Fm. warm spring	353	^{e}83	^{e}66	56	n.d.	n.d.	9	716	448	16	0.6	6	n.d.	n.d.	2	165	n.d.	654	4.5	1.05
BK4	30-May		Nardouw Sub-group borehole	641	97	34	33	n.d.	1	15	952	797	15	n.d.	n.d.	n.d.	n.d.	4	121	n.d.	953	0.0	1.09
OR1	19-Aug		Warm stream near the Baths	956	120	35	41	n.d.	n.d.	7	1313	1108	35	1	6	n.d.	n.d.	3	62	5	1255	2.2	1.47
BK1	30-May	Surface water	Surface waters from Boonjties River sub-catchment	223	30	8	7	2	n.d.	26	332	258	5	0.01	n.d.	n.d.	n.d.	1	4	10	284	7.7	0.34
BK3	30-May			249	38	10	14	5	n.d.	2	365	316	8	0.6	0.3	0.2	n.d.	0.5	23	10	367	-0.2	0.42
EK4	28-May			109	13	5	7	n.d.	n.d.	11	161	136	3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	10	153	2.6	0.17
EK5	28-May			118	14	2	3	n.d.	n.d.	12	165	131	4	n.d.	n.d.	n.d.	n.d.	n.d.	21	5	164	0.1	0.17
EK6	29-May			187	24	7	9	n.d.	n.d.	35	291	199	6	n.d.	n.d.	n.d.	n.d.	0.2	12	14	237	10.4	0.28
BJ1	29-May			206	31	8	9	n.d.	n.d.	2	295	240	7	n.d.	n.d.	n.d.	n.d.	0.2	18	21	293	0.3	0.34
BJ2	29-May			227	34	8	10	n.d.	n.d.	7	327	258	7	n.d.	n.d.	n.d.	n.d.	0.1	7	21	299	4.4	0.36
BJ3	30-May			256	41	11	12	n.d.	n.d.	7	379	302	12	n.d.	n.d.	n.d.	n.d.	0.1	9	15	350	4.1	0.43
OL1	30-May		Olifants River at Citrusdal	251	51	18	15	n.d.	1	7	413	284	16	0.8	0.2	0.1	n.d.	0.1	38	15	371	5.4	0.48
OL3	31-May		Olifants River at Clanwilliam	686	^{e}137	^{e}78	39	n.d.	n.d.	0.7	1154	852	45	0.9	3	0.04	n.d.	0.6	80	18	1046	4.9	1.36
OL2	31-May		Olifants River at Trawal	4310	^{e}962	^{e}801	112	n.d.	n.d.	0.03	7945	4857	553	2	n.d.	n.d.	n.d.	0.7	1223	37	7227	4.7	8.82

a – Units are μmol/L except for Σanions and cations (μeq/L), and charge balance error (CBE, %)
b – acid neutralizing capacity.
c – A$^-$ is the dissociated weak acid concentration estimated from DOC (see text).
d – Average of all rain waters
e – taken from IC analysis (see text)

3.1.1 Major ion composition of water samples

Rainwater samples are dominated by Na^+, Cl^-, Mg^{2+} and SO_4^{2-} ions (Table 8), with ion to chloride ratios similar to seawater (Table 10). The rainwater samples collected near Citrusdal are similar to those collected in Cape Town both in terms of relative and absolute concentrations. For example, Cl^- concentrations range from 16 to 326 μmol/L in Citrusdal, and 11 to 306 μmol/L in Cape Town (Fig. 6). Of the eight storms sampled at Cape Town, four were sampled sequentially and show a decline in Cl^- concentration as more rain falls (Aug 16, 17, 19, 29). The one exception to this is the second collection on 17 Aug. This sample was collected during a very hard downpour, while the other two for that day were collected during lighter rain (Table 9).

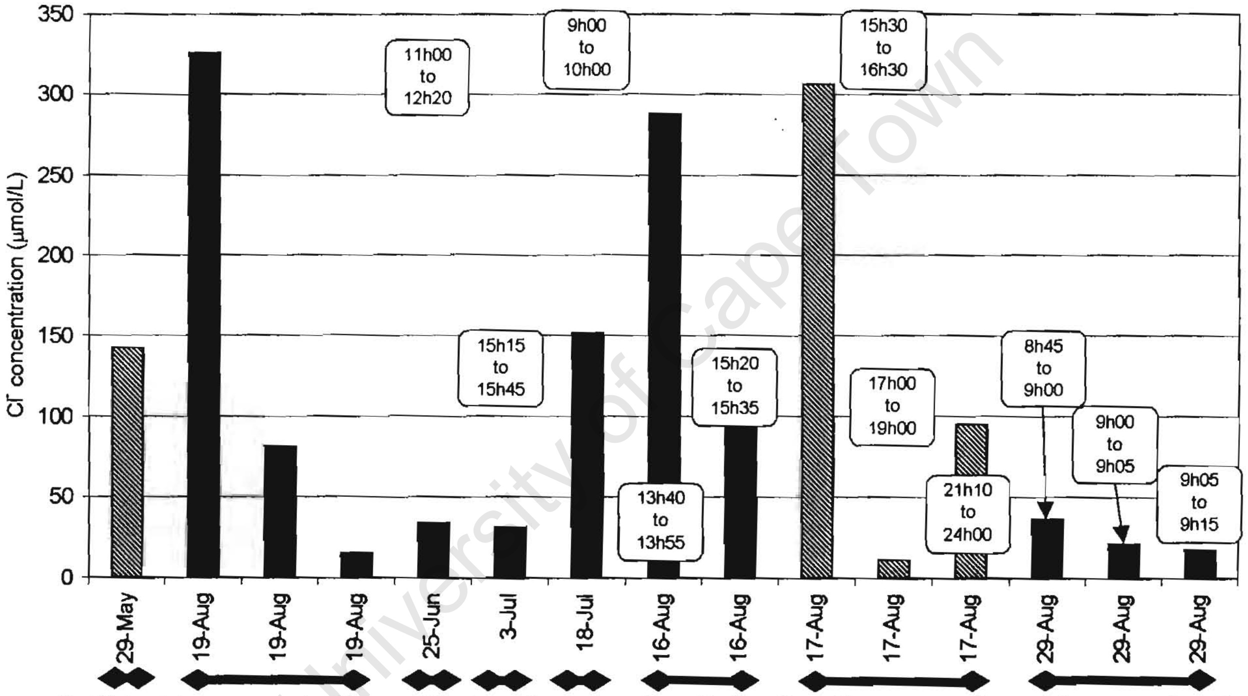

Figure 6: Chloride concentrations of rainwater samples. Collection times are shown for samples that were taken from the same storm.

Table 9: Rain collection volumes, rates, and electrical conductivities (EC's). BathsRainB1 is a sample that became part of the BathsRainB composite sample.

Sample	Storm Description	Collection Date&Time	EC (uS/cm)	Collection Duration (min)	Amount Collected (mL)	Rainfall rate (mm/hr)
UCTrain3		18-Jul	19.3	30	750	5.3
UCTrain4		16-Aug	35.1	80	1000	2.7
UCTrain5		16-Aug	14.3	25	600	5.1
UCTrain7	Intermittant rates and wind directions	17-Aug	2.8	25	1000	8.5
UCTrain8		17-Aug	13.9	15	250	3.5
ORrain	From the West, over Piekenierskloof mountains	19-Aug	45.5	60	50	0.2
BathsRainA		19-Aug	14.8	120	200	0.4
BathsRainB		19-Aug	4.1	170	1500	1.9
BathsRainB1		19-Aug	7.4	40	400	2.1
UCTrain9	Major downpour, from the South	29-Aug	4.9	15	1000	14.1
UCTrain10		29-Aug	4.8	5	250	10.6
UCTrain11		29-Aug	3.9	10	500	10.6

The relative concentrations of ions remains similar from rain water to surface water, spring, and borehole samples (Fig. 8). Na^+ and Cl^- remain the dominant ions, and the waters retain a rough seawater signature (Table 10). Notable enrichments in ion-Cl^- ratio with respect to seawater, are ANC (4.5 to 58), K^+ (1.9 to 4.6, excluding the Ope cold spring sample), Ca^{2+} (1.7 to 3.8, excluding the Ope cold spring sample), and F^- (22 to 35). The only consistently depleted ion is SO_4^{2-} (0.37 to 0.70, excluding rain water).

While the relative concentrations remain similar across the water samples, the absolute concentrations change, as indicated by an increase in ionic strength from 0.1 mM in rainwater to 1 mM in groundwater. This increase in dissolved constituents is particularly evident in comparing the rainwater to the pristine Peninsula Formation (Ope) headwater samples (BK1, EK4, EK5) and the Ope groundwater samples (AL1, BK2, Baths; Fig. 7). The Nardouw Sub-group (Sn) borehole sample (BK4) has a higher ionic strength than any of the Ope samples.

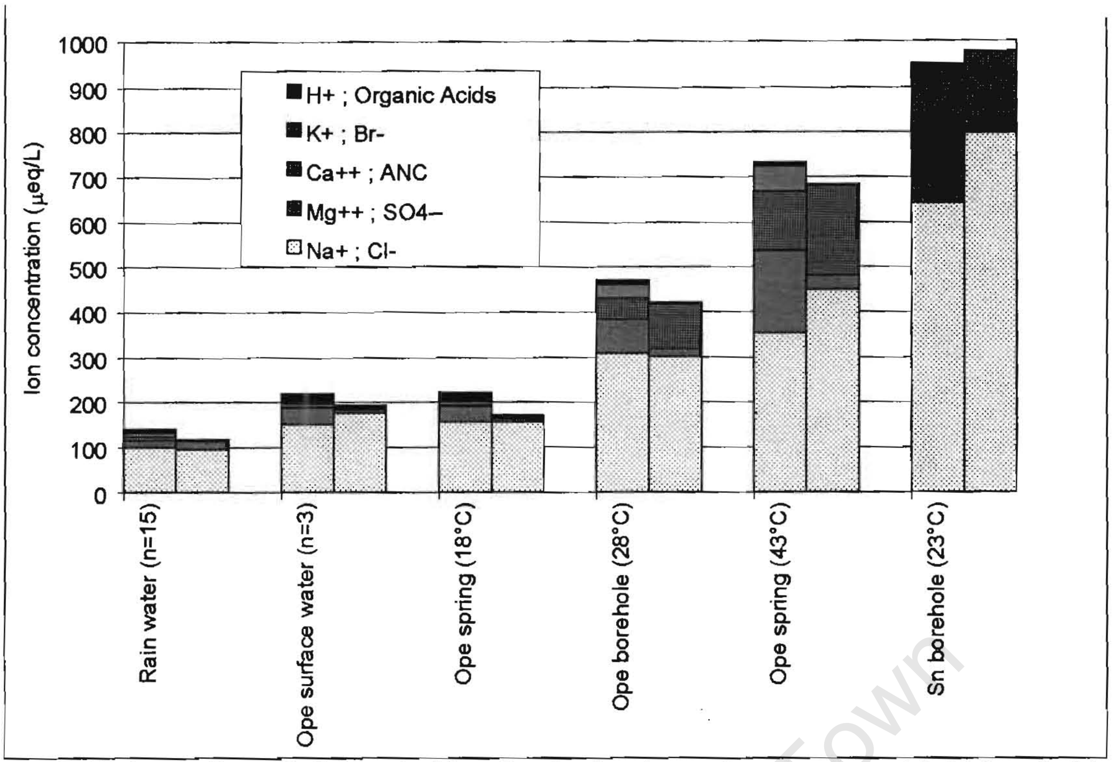

Figure 7: Major cations (left hand side of paired columns) and anions (right hand side of paired columns) for rainwater (n=14), Peninsula (Ope) surface water (n=3; BK1, EK4, EK5), Ope springs (18°C-AL1, 43°C-Baths), Ope groundwater (BK2), and Nardouw (Sn) groundwater (BK4).
ANC – Acid Neutralizing Capacity. Exit temperature of springs and boreholes is given in parentheses.

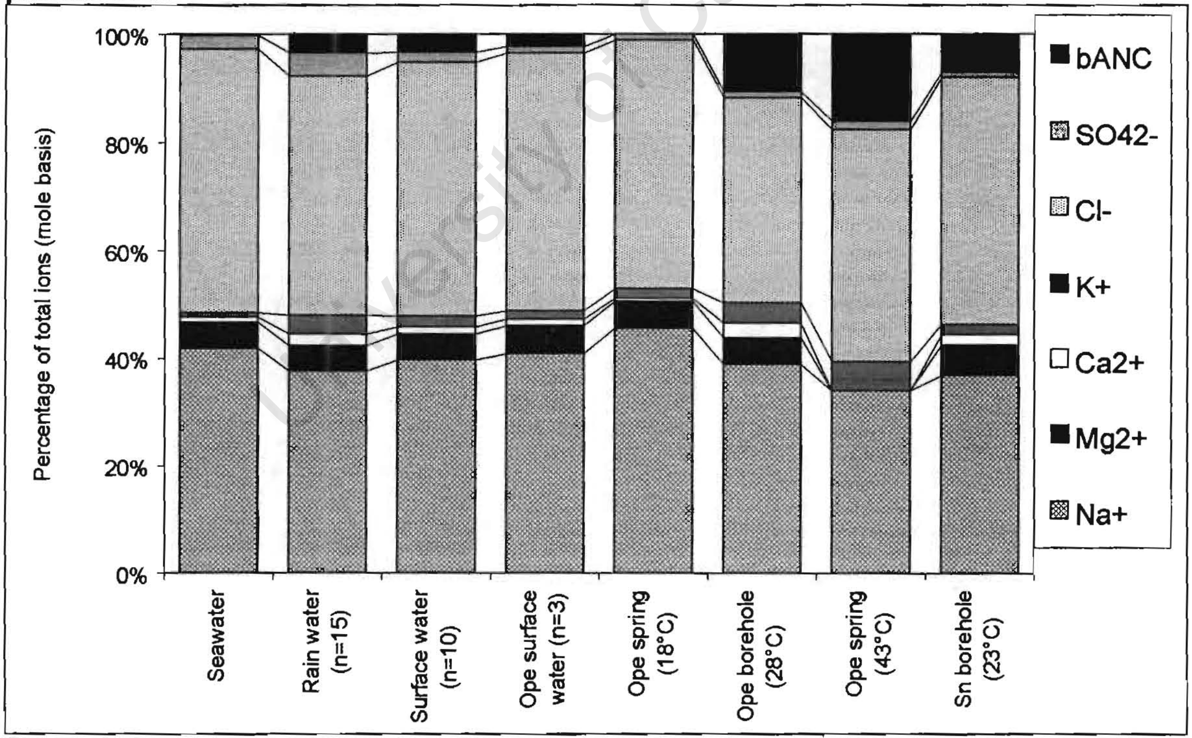

Figure 8: Percentage of total ions for seawater, rainwater (n=14), Peninsula (Ope) surface water (n=3; BK1, EK4, EK5), Ope springs (18°C-AL1, 43°C-Baths), Ope groundwater (BK2), and Nardouw (Sn) groundwater (BK4).
ANC – Acid Neutralizing Capacity. Exit temperature of springs and boreholes is given in parentheses.

Table 10: Ion-Cl^- ratio for water samples compared to Ion-Cl^- ratio for seawater. ANC is represented as HCO_3^-.

Ion	Rainwater (n=14)	Surface water (n=10)	Ope surface water (n=3)	Ope spring (18°C)	Ope borehole (28°C)	Ope spring (43°C)	Sn borehole (23°C)
Na^+	1.2	0.99	1.0	1.0	1.1	1.0	1.0
Mg^{2+}	0.92	1.4	1.4	1.1	1.2	1.3	1.3
Ca^{2+}	1.7	2.9	3.8	0.77	1.8	1.6	1.8
K^+	4.6	2.7	3.6	1.1	2.4	2.2	1.9
Cl^-	1	1	1	1	1	1	1
SO_4^{2-}	1.9	0.64	0.48	0.55	0.54	0.51	0.54
Br^{--}	8.7	1.0	1.3	n.d.	n.d.	n.d.	n.d.
F^-	n.d.	22	35	n.d.	n.d.	n.d.	n.d.
HCO_3^-	22	31	58	n.d.	19	15	20

n.d. – not detected

3.1.2 Minor and trace constituents of water samples

Minor and trace element concentrations follow a similar trend to the major ions, with absolute concentrations increasing from rain water to surface and ground waters. The highest concentrations are found in the Peninsula Formation (Ope) warm bath sample (Baths), the stream near the warm baths (OR1), the Ope borehole (BK2), the Nardouw Sub-group borehole (BK4), and the Olifants River sample from 70 km downstream of Citrusdal (OL2). The Baths has the highest concentration of Al (9450 nmol/L), As (180 nmol/L), Pb (38 nmol/L), Rb (294 nmol/L), Si (1498 μmol/L), and Zn (3281 nmol/L). Theoretically, Si should increase with increasing temperature, and this is seen in the samples (Fig. 9). BK2 and the Baths have the highest Cu concentrations (394 and 256 nmol/L, respectively), which are about a factor of 5 higher than the next highest sample. The OL2 sample contains the largest concentration of Sr (3621 nmol/L). Fe is highest in OR1 (19697 nmol/L), with the next highest concentrations being an order of magnitude lower, and occurring in surface water samples (up to 1960 nmol/L, OL2). BK4 has the highest Mn concentration (1221 nmol/L) followed by the Baths (896 nmol/L), with an anomalously high surface water value at OL3 (1049 nmol/L). B is an order of magnitude higher in OR1 and OL2 than in the other samples.

Table 11: Concentrations (nmol/L, except Si) of minor and trace elements for water samples, determined by ICP-MS.

Sample	Date Collected (2001)	Category	Description	Al	As	B	Ba	Cr	Cu	Fe	Mn	Pb	Rb	Se	Si (µmol/L)	Sr	Zn
CDrain	29-May	Rainwater	Citrusdal rainwater	198	1	157	13	24	67	169	41	8	6	1	n.d.	33	980
BathsRaina	19-Aug			77	1	191	18	42	23	98	20	7	2	2	n.d.	17	125
BathsRainb	19-Aug			27	n.d.	n.d.	25	15	n.d.	158	1	4	0	n.d.	0.03	6	17
UCTrain1	25-Jun		Cape Town rainwater	105	2	n.d.	23	10	26	162	111	11	1	1	1.00	25	148
UCTrain2	3-Jul			168	0	n.d.	39	14	61	293	78	23	1	n.d.	0.36	6	142
UCTrain3	18-Jul			120	1	132	21	5	55	102	162	4	1	2	n.d.	25	116
UCTrain4	16-Aug			45	2	292	7	24	11	127	10	16	1	3	0.04	43	46
UCTrain5	16-Aug			54	1	38	9	86	2	54	3	18	1	1	n.d.	17	51
UCTrain6	17-Aug			97	2	419	27	7	47	113	50	8	2	4	0.20	51	185
UCTrain7	17-Aug			18	n.d.	n.d.	14	26	7	61	1	14	0	n.d.	n.d.	3	19
UCTrain8	17-Aug			34	1	46	24	n.d.	14	161	10	16	1	1	n.d.	16	43
UCTrain9	29-Aug			22	0	n.d.	6	n.d.	5	n.d.	3	8	0	0	n.d.	5	25
UCTrain10	29-Aug			9	0	n.d.	4	19	6	23	1	8	0	0	n.d.	5	26
UCTrain11	29-Aug			12	0	n.d.	10	21	4	n.d.	0	6	0	0	n.d.	5	20
AL1	29-May	Spring and groundwater	Peninsula Fm. cold spring	504	2	203	18	n.d.	4	157	57	2	2	1	103	16	38
BK2	30-May		Peninsula Fm. borehole	70	6	662	21	25	394	143	39	2	48	1	207	55	386
Baths	19-Aug		Peninsula Fm. warm spring	9454	180	1755	450	59	256	668	896	38	294	14	1498	112	3281
BK4	30-May		Nardouw Sub-group borehole	552	3	1059	114	25	10	640	1221	2	43	4	202	234	160
OR1	19-Aug		Warm stream near the Baths	8093	9	14491	2496	399	41	19697	470	15	62	61	253	183	262
BK1	30-May	Surface water	Surface waters from Boonjties River sub-catchment	1654	1	269	42	19	1	241	157	1	2	2	33	76	138
BK3	30-May			1162	2	528	30	2	18	840	262	9	13	3	118	51	74
EK4	28-May			1385	4	159	6	25	n.d.	281	43	1	1	n.d.	26	24	39
EK5	28-May			1095	1	218	7	3	n.d.	14	42	1	0	2	31	19	16
EK6	29-May			1152	2	294	19	2	3	819	306	1	5	n.d.	81	39	57
BJ1	29-May			1279	2	296	25	n.d.	5	993	216	1	5	1	73	54	78
BJ2	29-May			2194	3	270	30	n.d.	3	1110	107	0	5	1	74	57	53
BJ3	30-May			1802	3	320	45	n.d.	3	1045	197	0	7	1	86	75	48
OL1	30-May		Olifants River at Citrusdal	1761	2	437	61	2	1	1139	156	0	9	n.d.	74	108	34
OL3	31-May		Olifants River at Clanwilliam	294	6	1701	77	17	14	1498	1049	1	18	6	93	202	128
OL2	31-May		Olifants River at Trawal	963	23	12209	281	48	34	1960	48	2	14	39	55	3621	69

n.d. – not detected

Table 12: Mean minor and trace element concentrations (nmol/L, except Si) for water sample groupings.

Sample Group	Al	As	B	Ba	Cr	Cu	Fe	Mn	Pb	Rb	Se	Si (µmol/L)	Sr	Zn
Rain water (n=14)	70	1	182	17	24	25	127	35	11	1	1	0	18	139
Surface water (n=10)	1340	5	1518	57	15	9	904	235	2	7	7	68	393	67
Ope surface water (n=3)	1378	2	215	18	16	1	178	80	1	1	2	30	40	64
Ope spring (18°C)	504	2	203	18	n.d.	4	157	57	2	2	1	103	16	38
Ope borehole (28°C)	70	6	662	21	25	394	143	39	2	48	1	207	55	386
Ope spring (43°C)	9454	180	1755	450	59	256	668	896	38	294	14	1498	112	3281
Sn borehole (23°C)	552	3	1059	114	25	10	640	1221	2	43	4	202	234	160

Ope is Peninsula Formation, and Sn is Nardouw Sub-group.

n.d. – not detected

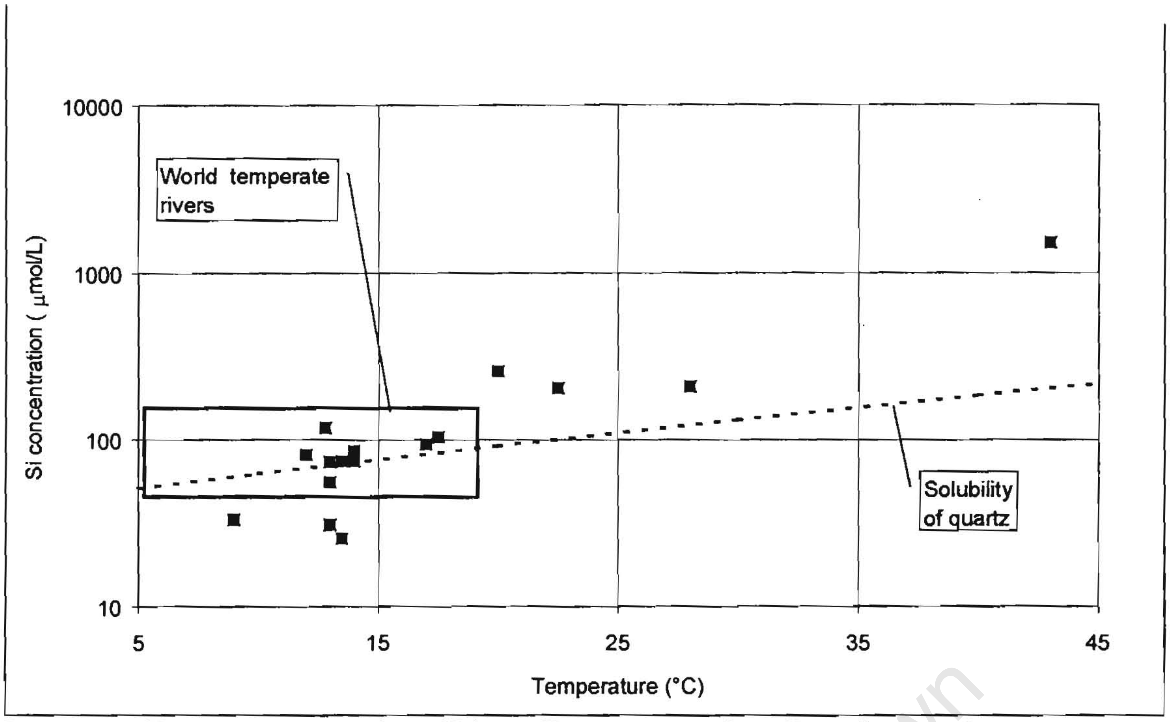

Figure 9: Si concentration (μmol/L) vs Temperature for all surface and ground water samples.
World temperate rivers (Berner and Berner, 1996) and theoretical solubility of quartz at pH of 7 are presented for reference.

3.1.3 *Acid and Base Neutralizing Capacity*

The alkalimetric and acidimetric titrations (Fig. 11) are used to estimate Acid Neutralizing Capacity (ANC) and Base Neutralizing Capacity (BNC) of a sample, respectively. Gran (1952) defined three functions that rearrange the data from a titration curve in different ways. The first two functions are valid for the pH ranges covered in the titrations of this study.

$$F_1 = (V_0 + V) \times 10^{-pH}$$
$$F_2 = (V_0 + V) \times 10^{pH}$$

Where, V_0 is the original sample volume
V is the cumulative amount of titrant added

These functions are plotted against the moles of H^+ that have been added to the solution (Fig. 10). The linear portions of these functions are fitted with a line by linear regression whose intercept with the horizontal axis indicates either strong or total acid concentration in the sample. Subsequent alterations (e.g., Johansson, 1970) to the Gran functions have been made to improve the definition of the "linear" portions of the functions. The various functions tended to give similar results for the titration data in this study. For simplicity, the original Gran functions were used in this analysis. The original functions continue to be used in the literature (e.g., Stumm and Morgan 1996; Johnson and Sigg, 1985).

An additional caveat of the Gran plots relates to DOC. The slope of one of the altered Gran functions (Johansson, 1970) is inversely proportional to an average dissociation constant for weak acids in the solution (Table 13).

$$y = \frac{1}{K_a} \times (V_e - V)$$

with,

$$y = V \times [H^+] + \frac{V_0 + V}{C_B} \times [H^+]^2$$

V = volume of base titrant added
V_e = volume of base titrant added to the equivalence point
C_B = concentration of base titrant
K_a = dissociation constant of the weak acid

This y is plotted against cumulative titrant volume. As with the other Gran functions, the a line is fitted to the linear portion of the plot. The slope of this function is the inverse of the average K_a of the weak acids in the solution.

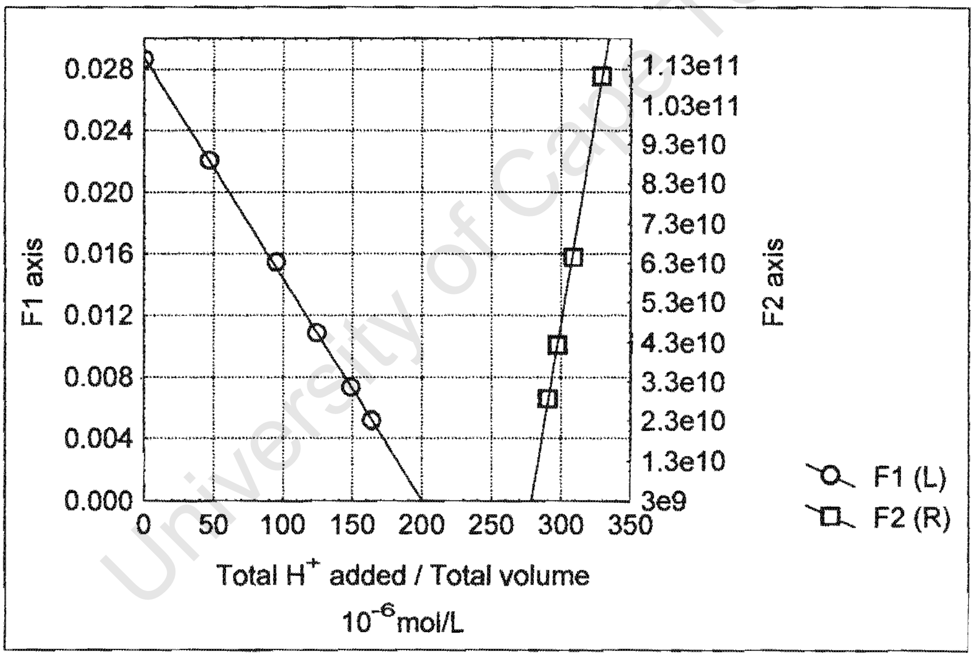

Figure 10: Gran plots for composite (acidimetric combined with alkalimetric) titration data from Peninsula cold spring AL1.
199 μmol HCl was added in the acid titration, giving ANC = -1 μeq/L, BNC = 74, Mineral Acidity = 1, and Weak acidity = 72.

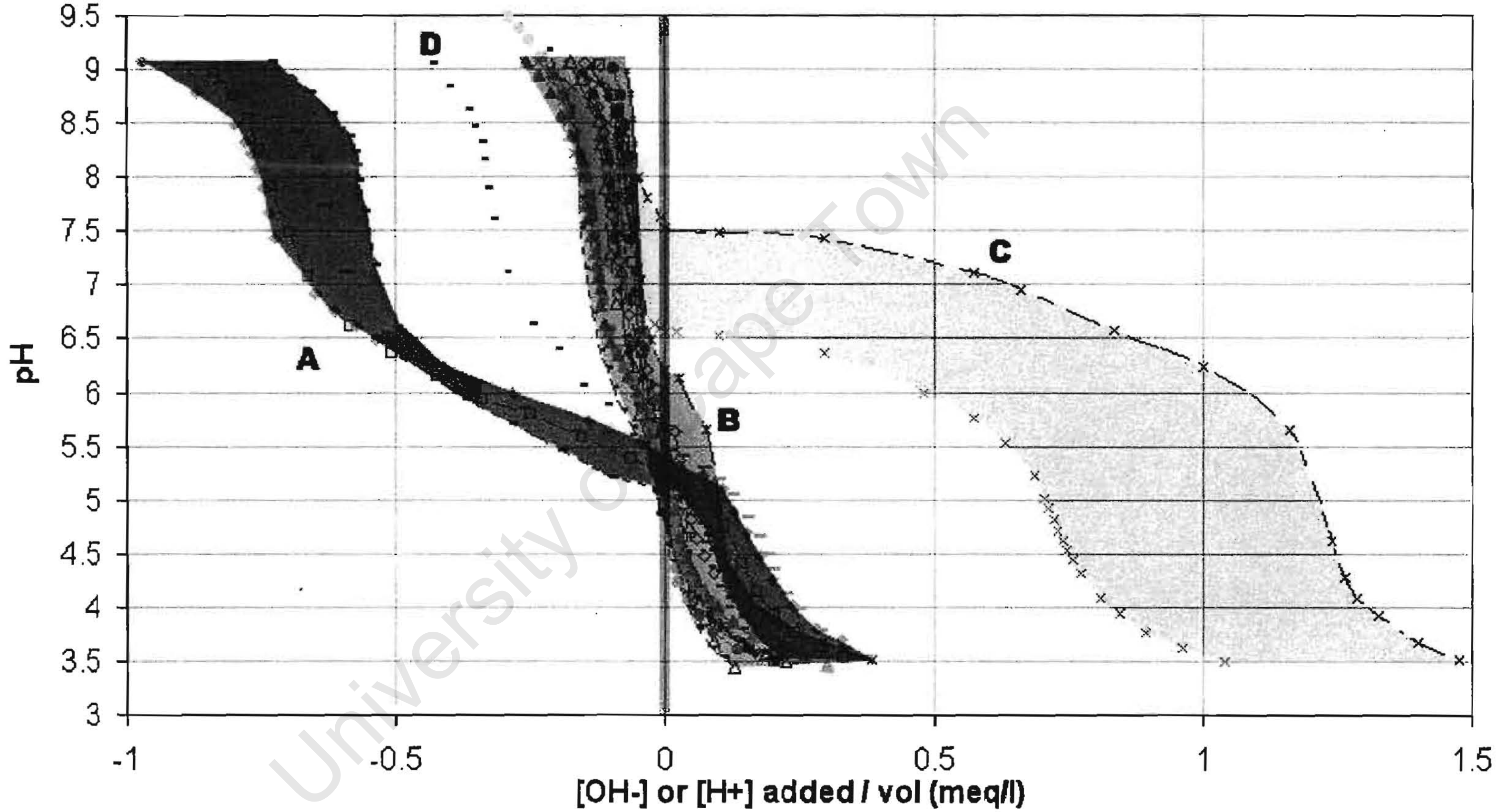

Figure 11: Composite (alkalinity + acidity) titration curves.
A - Groundwater and the warm spring; B - Rain and surface water; C - Olifants River water below confluence with the Doring (about 70 km N of Citrusdal); and D - Stream fed by warm spring discharge. Positive and negative titrant values correspond to the addition of HCl and NaOH, respectively.

Table 13: Acid-base data from alkalimetric and acidimetric field titrations.

Sample	Collection Date (2001)	ANC	BNC	Weak Acids	pKa
BathsRainA	19-Aug	10	92	92	6.9
UCTrain4	16-Aug	25	171	171	6.9
UCTrain5	16-Aug	-17	202	186	7
UCTrain6	17-Aug	-14	51	65	6.9
BK1	30-May	4	159	159	7.1
BK3	30-May	23	108	108	6.2
EK4	28-May	-0	55	55	6.7
EK5	28-May	-21	67	46	6.7
EK6	29-May	12	107	107	6.9
BJ1	29-May	18	71	71	6.9
BJ2	29-May	7	104	104	6.9
BJ3	30-May	9	102	102	6.9
AL1filtered	29-May	-1	78	77	6.7
AL1	29-May	-1	74	72	6.7
BK2	30-May	83	520	520	6.9
BK4	30-May	121	739	739	6.8
BathsA	19-Aug	178	623	623	6.8
BathsB	20-Aug	151	741	741	6.7
OR1	19-Aug	62	328	328	7
OL1	30-May	38	107	107	7.3
OL3	31-May	80	59	59	6.6
OL2	31-May	1223	60	60	6.8

Acid and base neutralizing capacity (ANC and BNC) and **weak acids are in µeq/L. pKa is the average distribution coefficient for a presumed monoprotic weak acid, following Johansson (1970).**

3.1.4 Analysis of concentrated water samples

Three low ionic strength water samples (EK4, AL1, BK1), and a de-ionized water blank were concentrated by evaporation. The original sample, concentrate and distillate were analyzed by ICP-MS. The original motivation for pre-concentrating dilute water samples was to bring elements of interest (e.g. elements that are toxic to plants or animals at low concentrations) into detectable range.

The large amount of uncertainty introduced through the procedure is reflected in the inconsistencies between concentrations in the original sample and those calculated from analysis of the concentrate. For elements detectable in the original sample, the concentration in the original sample should be equal to those calculated from analysis of the concentrate, giving a 1:1 correlation (Fig. 12). The three samples used in this experiment have a fairly good correlation (r >0.99, Table 14), while the blank has a weaker correlation (r = 0.75). This result is a bit misleading as the range of concentrations is large in the three samples (0.001 to 3524 ppb), which can make large absolute differences in concentration less significant in the context of such a large range. The range of concentrations in the blank is comparatively small (0.001 to 24 ppb).

A less misleading way of comparing the original to the concentrate value is through a ratio of the concentrate value to the original value (C/O; Table 14). This ratio would be equal to 1 if the two methods gave the same result. This set of results shows much more variability between the original and concentrate values than does the correlation coefficient. Also, while the blank has the poorest agreement between original and concentrate, it is not that different from the three samples. This indicates that the smaller concentration range of the blank could be linked to its weaker correlation coefficient described above.

Table 14: Comparison of elemental concentration calculated from analysis of the pre-concentrated sample ('concentrate') to that from analysis of the original sample ('original'). C.V. is the Coefficient of Variation. R is the correlation coefficient.

Sample	Concentration (ppb)		R	N	Concentrate/Original		
	Min	Max			Mean C/O	Standard Deviation	C.V.
AL1	0.002	3524	0.9997	31	1.0	0.5	50%
BK1	0.001	1082	0.9962	31	1.4	1.6	113%
EK4	0.001	719	0.9928	31	0.8	0.6	84%
Blank	0.001	24	0.7531	18	1.6	2.4	148%

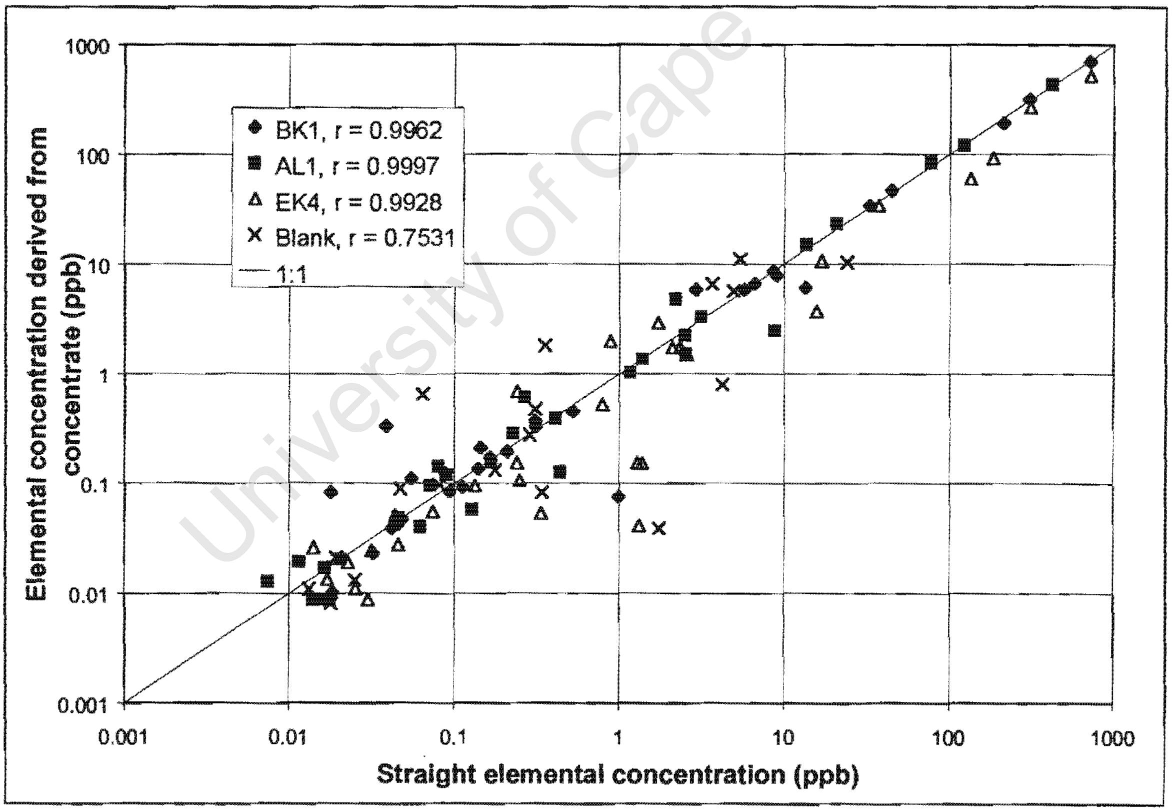

Figure 12: Elemental concentrations from analysis of the concentrate (vertical axis) vs those from analysis of the original sample (horizontal axis), for three low ionic strength samples and a blank of de-ionized water. Note that log scales are used.

A few elements were measurable in the concentrate that were not detectable in the original sample (Table 15). Notably, Cr was found to be present in the spring water sample, arsenic in the blank, and Se in a headwater sample as well as the blank. These data should be viewed with caution as the concentrations involved are very low, and therefore subject to contamination. For example, in the blank, Cu, B and Si are calculated as being present at concentrations that could have been detected in the original sample. This could indicate contamination from the Boro-Silicate glassware used at times in the procedure.

Table 15: Concentrations (ppb) derived from concentrated samples for elements that were not detectable in the original sample. Blank cells indicate that the element was detectable in both the original sample and the concentrate.

	Blank	AL1	BK1	EK4
Dilution Factor	11	9.0	14	23
Li	7	d	36	d
Be	1	d	20	d
B	244	d	d	d
Si	3357	d	d	d
Sc	16	d	d	d
Cr	d	109	d	d
Cu	225	d	d	303
Ga	19	d	d	d
As	32	d	d	d
Se	7	d	d	76
Zr	29	2	d	20
Mo	d	31	7	d
Cd	4	d	15	9
Cs	2	6	1	d
La	3	d	d	d
Ce	3	d	d	d
Nd	n.d	8	d	d
W	n.d.c.	d	10	d
Tl	n.d.	d	3	d
Th	n.d.	d	d	3
U	1	d	d	5

d – detectable in both the original and concentrate; n.d. – not detectable in either the original or concentrate; n.d.c. – detectable in the original, but not the concentrate

3.2 *Soil and bedrock Analyses*

The seven soil samples collected are summarized in Table 16. More information about the localities, including motivation for choosing the sampling points, is available in the Methods chapter (Table 4). Six of the samples are from the topsoil, and one from the subsoil (BK2b). Five are underlain by Peninsula Formation sandstone (EK5, EK6, BK1, BK2a&b), one by Nardouw (NR), and the last by alluvium/Bokkeveld shales (BJ2).

The grain size composition the <2 mm fraction of soil samples from the study area are reported in Table 17. Sand is the dominant grain size, ranging between 75 and 95 wt%. Samples EK5, EK6, BK1, and NR contain around 90 wt% sand, while sample BJ2 contains 95%. The BK2 samples have the lowest sand content, with 79 wt% in the topsoil (BK2a), and 75 wt% in the subsoil (BK2b). All soils are classified as loamy sands except for one sandy loam (BK2), and one sand (BJ2). The standard Munsell colors for the dry and wet samples are given in Table 18.

Table 16: Description of soil samples.

Sample	Collection depth (cm)	Total soil depth (cm)	Location	Geology	Land Use	Land Cover	Slope, Aspect
EK5	0 - 20	<100	Headwaters of Elandskloof catchment	Peninsula	Natural	Mountain fynbos, 1-2m *Protea nitida*	Footslope,W
EK6	0 - 20	<100	Near base of Elandskloof catchment	Peninsula	Citrus Farming	Thick grass	Valley bottom
BJ2	0 - 20	??	Main valley, near Boontjies River	Bokkeveld/ Alluvium	Farming	Thick grass...no strong evidence of crops or current livestock.	Valley bottom
NR	0 - 20	<100	Along road towards main valley from Elandskloof	Nardouw	Natural	Mountain fynbos – heavy *Restios*, etc.	Midslope,W
BK1	0 - 20	<100	Headwaters of Boschkloof catchment	Peninsula	Natural	Mountain fynbos – fewer *proteas* than EK	Footslope,N
BK2a	0 - 20	150	Near base of Boschkloof catchment	Peninsula	Natural	Mountain fynbos – sparse grass and shrubs	Footslope,N
BK2b	50-70	150					

Table 17: Particle size distribution

Sample	Gravel	Sand	Silt	Clay	Texture Class
	% of air dry sample	% of <2mm fraction			
BJ2	1.7	95	3	2	Sand
BK1	1.4	90	4	6	loamy sand
BK2a	18.7	79	19	3	loamy sand
BK2b	5.2	75	18	6	sandy loam
EK5	12.4	89	5	6	loamy sand
EK6	10.1	87	9	5	loamy sand
NR	6.9	89	4	7	loamy sand

Table 18: Munsell color codes (Hue Value/Chroma) and descriptions (Munsell Color, 1992).

Sample	Munsell Dry		Munsell Wet	
BJ2	2.5YR 5/2	greyish brown	2.5YR 3/1	v. dark grey
BK1	10YR 5/3	brown	10YR 3/3	dark brown
BK2a	10YR 4/1	dark grey	10YR 2/2	v. dark brown
BK2b	7.5YR 4/1	dark grey	10YR 2/1	Black
EK5	10YR 4/3	brown	10YR 2/2	v. dark brown
EK6	7.5YR 4/3	brown	7.5YR 2.5/3	v. dark brown
NR	10YR 6/3	pale brown	10YR 4/4	dark yellowish brown

The pH(H_20) range is between 5.1 and 5.9 with the exception of the one subsoil sample, BK2b (Table 19). The BK2 profile is more acidic in the subsoil. The pH(KCl) follows a similar pattern ranging between 0.8 and 1.6 pH units below pH(H_20). This indicates that the colloids in each soil suspension have a net negative charge. The pH of the supernatant from the KCl suspension used to measure exchangeable acidity and cations is slightly higher than that of the unseparated suspension. Exchangeable acidity is defined as the sum of titratable acids that are displaced by K^+ from a 1M KCl solution. Titratable acids include H^+ and Al species, and generally tends to follow pH. The exchangeable cations, and effective cation exchange capacity (ECEC), for the topsoil samples are highest in the soil of the Elandskloof sub-catchment headwater area (EK5) and lowest in the Nardouw soil (NR). In the BK2 profile, the topsoil has nearly 5 times as much exchangeable Ca and Mg than the subsoil, while their Na values are similar. Acid saturation is the percentage of the ECEC contributed by H^+ and Al species. It is highest for the BK2 subsoil, as would be expected given that it has the highest exchangeable acidity. The ECEC and acid saturation values have been calculated using corrected Ca, Mg, and Na concentrations. That is, the soluble portions of these elements (SPE, Table 20) were subtracted from the exchangeable concentration since the method does not distinguish between the exchangeable and soluble portions.

Table 19: General soil analysis results. (* - pH of the supernatant)

		BJ2	BK1	BK2a	BK2b	EK5	EK6	NR
Organic Carbon (wt%)		0.7	0.9	1.2	1.0	1.5	1.8	0.1
pH(H2O)		5.1	5.2	5.3	4.7	5.9	5.8	5.6
pH(KCl)		4.1	4.1	4.2	3.9	4.3	4.4	4.1
pH(KCl)_super*		4.3	4.4	4.4	4.0	4.5	4.6	4.3
Exchangeable Acidity (meq/kg)		1.1	2.0	0.9	5.5	1.3	0.7	0.7
% Acid Saturation		7.8	16	3.5	36	3.6	2.8	6.9
Ca^{2+}	Exchangeable Cations (meq/kg soil)	5.4	3.4	12.6	2.7	21.0	13.7	3.1
Na^{+}		6.6	6.5	8.7	8.1	6.8	7.0	6.0
Mg^{2+}		2.6	1.2	7.1	1.8	8.3	5.8	1.2
ECEC		14	13	26	16	36	26	10

3.2.1 *Saturated Paste Extracts (SPE)*

The EC of the SPE shows high soluble salt content in the BK2 soil profile as well as in soils BJ2, EK5, and EK6 (Table 20). This is supported by the major ion concentrations, which are generally lowest in the NR and BK1 samples. The total soluble N values for BJ2, EK5, EK6, BK1, and BK2a range between 121 and 302 μmol/L, while there are smaller amounts of total soluble N in BK2b and NR (45 and 67 μmol/L, respectively). ICP-MS data (Table 21) show higher concentrations of Fe for NR, as expected from the parent material, Nardouw, containing more impurities than the Peninsula Formation. Mn concentrations are higher than Fe concentrations for all soils underlain by Peninsula Formation (BK1, BK2a, BK2b, EK5, and EK6), and Mn is lower for the other two samples (NR and BJ2). Al concentration is at least three times higher in BJ2, BK1, and NR than in BK2a, EK5, and EK6; and Al is almost twice as high in the subsoil sample (BK2b) than in the associated topsoil sample (BK2a).

Lead isotopes Pb-206, Pb-207, and Pb-208 were measured in the SPE on the ICP-MS as the ratios Pb-206/Pb-207 and Pb-208/Pb-207 are commonly used to identify the environmental source of lead. The peak intensity (Table 22) was used to calculate the ratios, which show a larger range in Pb-208/Pb-207 (2.41-2.48) than in Pb-206/Pb-207 (1.10-1.14).

Simple geochemical modeling of the soil solutions for BK2a&b in PHREEQC (Parkhurst *et al.*, 2002) returns the chemical speciation of the solution along with saturation indices. With the input set to equilibrate the solution with a $CO_{2(g)}$ concentration of 10^{-2} ppm, the topsoil sample BK2a is supersaturated with respect to the Fe-bearing minerals hematite and geothite, as well as the Mn-bearing minerals manganite, pyrochoite, and pyrolusite. It is just about at equilibrium with quartz (SI = 0.29), and is undersaturated with the other mineral phases considered in the model. Under the same conditions, the corresponding subsurface sample BK2b shows the same pattern. The full phase equilibrium information for the two samples is given in Appendix C.

Table 20: Saturated Paste Extract general data and major ion concentrations. Ca^{2+}, Na^+, and Mg^{2+} are presented in both μmol/L and meq/kg soil for comparison with the exchangeable cations in Table 19.

		BJ2	BK1	BK2a	BK2b	EK5	EK6	NR
Water/Soil		0.32	0.31	0.24	0.24	0.30	0.28	0.22
EC (uS/cm)		1826	580	2440	1838	793	932	377
SAR[a]		1.2	1.5	2.3	2.5	1.5	1.1	3.2
CBE (%)[b]		79	41	73	15	42	43	12
Ca^{2+}	meq/kg soil	0.4	0.1	0.5	0.3	0.2	0.2	0.1
Na^+		0.7	0.3	1.8	1.6	0.5	0.3	0.2
Mg^{2+}		0.4	0.2	0.6	0.6	0.2	0.2	0.0
Br^-	μmol/L	n.d.	1	n.d.	15	1	n.d.	n.d.
Ca^{2+}		705	227	1055	735	353	365	191
Cl^-		2493	633	7634	8629	1192	889	861
F^-		106	108	156	128	542	91	65
K^+		1691	226	809	322	386	333	249
Mg^{2+}		622	246	1299	1238	405	417	41
Na^+		2277	1025	7502	6917	1633	1231	1055
NH_4^+		92	55	49	29	114	54	60
NO_2^-		123	10	121	n.d.	n.d.	188	n.d.
NO_3^-		21	80	132	14	7	60	7
Total N		236	145	302	42	121	302	67
PO_4^{3-}		n.d.	n.d.	n.d.	n.d.	n.d.	9	n.d.
SO_4^-		733	46	989	890	250	209	172

a – Sodium Adsorption Ratio; b – Charge Balance Error (see Appendix B)

Table 21: Saturated Paste Extract minor and trace element data (nmol/L), mean of 3 ICP-MS Analyses of the same sample.

	BJ2	BK1	BK2a	BK2b	EK5	EK6	NR
Al	92851	107517	33346	59802	23828	18558	102132
As	42	101	68	84	29	29	28
B	31041	54691	21837	37406	11589	12866	21472
Ba	397	2134	569	733	585	652	420
Cr	37	251	110	220	66	14	71
Cu	530	1102	855	848	688	392	512
Fe	13885	17700	4067	3837	9828	3923	28351
Mn	10709	45784	30233	3405	65940	20548	16930
Pb-208	23	65	23	37	16	9	15
Rb	903	1415	187	102	606	396	204
Se	59	605	186	273	131	78	73
Si	187434	574718	379258	560095	237810	198716	237405
Sr	823	3787	2895	2057	1521	1923	446
Zn	2189	4912	2041	5031	2250	1131	1445
Zr	112	63	246	111	15	49	54

Table 22: Lead isotope response (peak intensity) from ICP-MS used to calculate relative abundances.

	Pb-206	Pb-207	Pb-208
BJ2	3471	3056	7526
BK1	14990	13254	32827
BK2a	3258	2877	7011
BK2b	5036	4480	10895
EK5	4352	3816	9301
EK6	2759	2440	5932
NR	5115	4637	11164

3.2.2 Mineralogy

X-ray diffractograms and peak lists for the bulk (< 2 mm) and clay (< 2 μm) fractions of BK2a&b are in Appendix D. The mineralogy as indicated by the x-ray diffraction patterns of the bulk samples of the soils are almost entirely made up of quartz. Other, minor peaks are similar in the samples, and indicate the presence of kaolinite group minerals with possibly some mica. The clay fraction is dominated by kaolinite group minerals for both samples. It also includes peaks from quartz and an X-ray amorphous hump from about 4.00 to 3.87 Å.

3.2.3 Major and Trace Elements

The concentrations of major elements of the seven soil and three rock samples are shown in Table 23. The Peninsula Formation bedrock sample has the highest SiO_2 content (98.8 wt%). The Nardouw Sub-group (Rietvlei Formation) sample has a much lower content (85.3%), and the soils range from 90.2 to 95.6 wt% SiO_2. Al_2O_3 is highest in the Bokkeveld Series bedrock sample (18.2 wt%), and lowest in the Peninsula bedrock (0.5 wt%), while the soils have concentrations ranging from 2.0 to 4.3 wt%. Interestingly, while the Bokkeveld and Nardouw bedrock samples have the highest overall Al_2O_3 content, their associated soils have the lowest content of all the samples. K_2O content tends to follow Al_2O_3, with Bokkeveld and Nardouw bedrock having the highest content (3.5 and 1.9 wt%, respectively), Peninsula bedrock having the lowest (0.1 wt%), and the soils having moderate values (0.1 to 0.4 wt%).

Among the trace elements (Table 24), Mn is notable as the sample with the highest Mn content (EK5S, 594 ppm) is derived from parent material, Peninsula bedrock, which has the lowest Mn content (33 ppm). Zr shows a similar pattern, with the highest overall concentration occurring in Peninsula soil (EK6S, 370 ppm), and the lowest in Peninsula bedrock (40 ppm). Cu concentrations all fall in the range 12 to 59 ppm, with Peninsula bedrock and Peninsula soil having the minimum and maximum values, respectively.

Table 23: Major element analysis (oxide wt%) of soil and bedrock samples, by XRF.

Sample	BK2R	EK5S	EK6S	BK1S	BK2BS	BK2AS	NR1R	NRS	BHR	BJ2S
Type	Rock	Soils					Rock	Soil	Rock	Soil
Geology	Peninsula Formation						Nardouw Sub-group		Bokkeveld Series/ Alluvium	
SiO_2	98.80	90.33	90.69	92.62	90.17	90.67	85.31	95.38	60.48	95.63
TiO_2	0.03	0.30	0.28	0.31	0.35	0.36	0.26	0.33	0.95	0.16
Al_2O_3	0.46	2.14	2.24	2.03	4.29	3.20	9.17	1.87	18.16	1.00
Fe_2O_3	0.30	2.10	1.97	1.32	0.69	0.97	0.53	0.72	7.21	0.73
MnO	0.00	0.07	0.04	0.01	0.01	0.02	0.00	0.01	0.03	0.01
MgO	<0.08	<0.02	<0.04	<0.03	0.01	0.02	0.05	<0.05	2.18	<0.07
CaO	<0.07	<0.02	<0.06	<0.05	<0.06	<0.06	<0.06	<0.06	0.23	<0.05
Na_2O	<0.09	<0.03	<0.02	<0.06	<0.02	<0.01	<0.04	<0.04	1.27	<0.08
K_2O	0.09	0.35	0.12	0.19	0.37	0.32	1.93	0.24	3.47	0.10
P_2O_5	0.01	0.06	0.07	0.03	0.09	0.08	0.02	0.02	0.18	0.03
H_2O-	0.03	0.24	0.27	0.23	0.40	0.27	0.20	0.12	1.04	0.18
LOI	0.11	3.59	3.63	2.30	3.08	3.28	1.96	0.93	4.77	1.95
Total	99.83	99.17	99.32	99.04	99.48	99.18	99.42	99.61	99.98	99.79

LOI – Loss on Ignition (850°C)

Table 24: Trace element concentrations (ppm) for bedrock and soil samples from the Peninsula Formation (BK, EK), Nardouw Sub-group (NR), Bokkeveld shale (BH), and alluvium (BJ2), by XRF.

	BK2R	EK5S	EK6S	BK1S	BK2AS	BK2BS	NR1R	NRS	BHR	BJ2S
Type	Rock	Soils					Rock	Soil	Rock	Soil
Geology	Peninsula Formation						Nardouw Sub-group		Bokkeveld Series/ Alluvium	
Ba	26	107	60	54	123	135	311	74	638	31
Co	<1.2	<1.5	<1.5	2.1	2.1	3.1	1.9	<1.3	15	<1.3
Cr	11	29	31	25	37	33	38	24	118	31
Cu	12	54	46	59	21	50	20	58	47	21
Mn	33	594	342	80	152	62	52	76	274	70
Mo	0.88	1.3	1.8	1.6	1.6	1.2	<0.62	1.1	<0.74	1.6
Nb	10	7	7	9	19	10	5.4	7.8	19	3.7
Ni	3.0	7.6	7.6	6.4	8.5	8.9	6.7	5.7	53	7.0
Pb	<1.8	6.6	5.8	6.0	12	12	28	8.9	19	3.1
Rb	1.5	20	8.8	11	17	19	61	10	167	4.6
S	32	179	196	127	225	405	183	43	45	199
Sc	0.4	1.67	1.95	1.67	3.5	4.4	5.38	1.58	22	1.16
Sr	4.1	18	14	9.3	41	23	13	6.4	63	6.8
Th	<1.4	3.4	6.1	4.0	7.3	7.5	4.4	3.6	14	1.5
U	<1.3	<1.4	1.5	<1.4	2.6	3.1	<1.4	<1.3	4.7	<1.3
V	2.3	23	23	20	28	28	22	13	176	11
Y	2.2	12	11	12	19	22	9.1	10	40	7.7
Zn	0.62	4.7	7.3	3.1	9.1	4.9	5.3	2.4	130	3.7
Zr	40	258	370	313	224	199	164	339	194	155

3.3 *Vegetation*

As described in the Methods chapter, vegetation samples were taken from four 25 m^2 plots: two underlain by Peninsula bedrock (Ope), one by Nardouw (Sn), and one by Bokkeveld (Db). A total of 31 samples were cut into small pieces, dried at 105°C, and roasted at 450°C. From this total, 14 were chosen to be analyzed for minor and trace elements by ICP-MS after dissolution via HNO_3 and HF. Of the 14 analyzed samples, 7 are Ope, 6 Sn, and 1 Db. All 14 samples are from the above-ground portion of the plant. There are 2 *Protea* leaf samples, 1 *Protea* branch, 4 non-*Protea* tree branch, 2 *Restio*, 2 shrub, 2 non-woody, and 1 succulent sample (Table 25).

Table 25: Contributions of each specimen to the calculation of a weighted average "bulk" composition for vegetation from each of the three substrates sampled.

Sample Name	Description	Ope	Sn	Db
Ope leaf (*Protea*)	*Protea nitida* leaves	2.0%		
Sn leaf (*Protea*)	*Protea laurifolia* leaves		0.1%	
Sn branch (*Protea*)	*Protea laurifolia* branch		2.9%	
Ope branch (rockwood)	*Heeria argentea* branch	23%		
Sn branch (gum)	*Eucalyptus* branch		5%	
Ope branch (myrtle)	*Metrosideros angustifolia* branch	23%		
Sn branch (pine)	*Pinus* branch		5%	
Ope *Restio*	Composite of above-ground portion of *Restios*	33%		
Ope *Restio* (leaf)	Above-ground portion of an individual *Restio* leaf			
Sn shrub	Bulk composite of above-ground portion of shrubs (small, non-proteoids with woody branches)		61%	
Ope shrub		14%		
Ope non-woody	Bulk composite of above-ground portion of non-woody plants (e.g. grasses, geophytes)	7.0%		
Sn non-woody			26%	
Db succulent	Above-ground portion of an individual succulent, *Euphorbia mauritanica*			100%

Ope - Peninsula Formation, Sn - Nardouw Sub-group, Db - Bokkeveld Series

3.3.1 *Mineralization and dissolution*

In the dry ashing procedure used for the mineralization, or isolation of the inorganic portion of the sample, it is key to avoid excessive flaming or explosion (Hoenig, 2001). This will result in loss of some of the inorganic fraction of the sample. To avoid this, the temperature in the muffle oven was raised slowly. However, some evidence for flaming (prominent dark marks on the inside of the crucible above the level of the plant material) of the samples was present after 4 hrs of roasting at 450°C (Table 26). The final product of this procedure was a grayish white ash that weighed less than 4% of the original sample (Table 27).

Table 26: Degree of flaming evidence at the middle of the mineralization procedure. 34 samples were roasted at 450 °C.

Degree of flaming	No. of Samples
None	6
Very minor	11
Minor	6
Moderate	5
Slightly major	4
Major	2

Table 27: Ash % for 34 mineralized samples grouped by vegetation type.

Vegetation type	Ash (wt% of dry matter)			Number of samples
	Mean	Max	Min	
Herb	3.40%	6.00%	1.55%	4
Leaf	3.23%	6.24%	0.82%	9
Leaf - alien	3.29%	4.33%	2.09%	3
Restio	3.91%	7.71%	1.77%	5
Root	2.05%	2.27%	1.83%	2
Shrub	3.45%	5.84%	1.25%	4
Succulent	1.97%	1.97%	1.97%	1
Wood	5.26%	11.20%	1.21%	9
Wood - alien	2.88%	5.21%	1.21%	4
Total	3.81%	11.20%	0.82%	34

3.3.2 Composition

The chemical composition of "bulk" vegetation samples (Table 29) was calculated by combining the analytical results for individual samples through an estimate of the mass distribution of the original field plot. For example, the contribution of each of the 7 Ope samples analyzed was calculated (Table 25) based on a visual estimation in the field of the aerial extent and biomass of each sample. There is obviously a high-degree of error in this method, and as mentioned before, the results should be regarded as semi-quantitative. There were three steps at which a sub sample was chosen in this procedure. While it is generally desirable to minimize the instances of selecting a representative sample, the initial specimen selection is most likely the largest source of error in determining the total elemental composition of vegetation on a given plot of land. For each element there is a fairly high amount of variation in its absolute and relative concentration among the samples. This is true even when comparing plants from the same substrate (Figs. 13 and 14).

Sample	Al	B	Ba	Br	Ca	Ce	Co	Cr	Cu	Fe	Ga	K	Li	Mg	Mn	Ni	Pb	Rb	Si	Sr	Zn	Zr
Ope leaf (*Protea*)	90	13	28	1.3	2630	0.2	0.1	ND	3	69	0.8	4496	3	1176	397	0.5	0.2	4	105	51	3	0.1
Sn leaf (*Protea*)	68	17	32	2.0	2079	0.2	0.1	ND	2	51	0.9	2840	1	1191	75	0.2	0.5	2	16	33	2	0.2
Sn branch (*Protea*)	117	6	49	ND	905	0.3	0.3	ND	3	93	1.4	2278	3	705	96	0.4	1.9	2	19	22	21	0.3
Ope branch	97	9	46	ND	2055	0.2	0.2	ND	5	104	1.4	4312	3	3259	272	1.1	0.6	4	60	42	15	0.2
Sn branch (gum)	24	8	25	ND	2664	0.1	0.0	ND	6	64	0.7	2866	3	992	33	0.5	0.2	4	3	40	11	0.0
Ope branch	187	6	60	ND	2429	0.3	0.3	ND	4	376	1.8	1358	1	1004	684	1.5	0.5	6	8	72	6	0.5
Sn branch (pine)	383	6	3	ND	1228	0.2	0.0	ND	2	74	0.1	1710	1	715	39	0.4	3.3	4	3	16	33	0.2
Ope *Restio*	164	2	10	0.3	1792	0.1	0.1	0.4	2	83	0.4	2990	11	1630	912	0.4	0.3	8	13	20	6	0.1
Ope *Restio* (leaf)	123	2	4	0.3	978	0.1	0.1	0.6	2	88	0.2	6766	1	1021	1164	0.7	0.2	23	57	11	9	0.0
Sn shrub	247	25	39	2.2	2934	0.7	0.2	1.2	7	157	1.5	12354	1	2385	259	1.9	2.0	5	249	40	40	0.5
Ope shrub	200	10	30	ND	2177	0.9	0.1	0.3	4	131	1.2	6979	5	1218	470	0.6	0.4	9	74	44	7	0.3
Ope non-woody	432	8	32	ND	2099	1.3	0.1	2.5	4	328	1.2	8572	2	1579	222	0.4	1.1	8	103	38	16	0.8
Sn non-woody	120	1	5	0.5	399	0.1	0.4	0.0	3	81	0.2	4585	2	243	95	0.5	0.6	2	2	3	11	0.2
Db succulent	95	10	11	5.9	3021	0.2	0.8	3.1	5	91	0.4	18298	8	3141	41	1.2	0.2	4	28	51	19	ND

Table 28: Elemental concentrations (ppm) for vegetation samples (ashed at 450°C and analyzed by ICP-MS) from Peninsula Formation (Ope), Nardouw Sub-group (Sn), and Bokkeveld shale (Db) derived soils.
ND – not detected

Table 29: Weighted mean concentration (ppm), by ICP-MS, for vegetation from the three substrates sampled. Ope - Peninsula Formation, Sn - Nardouw Sub-Group, Db - Bokkeveld Series.

	Ope	Sn	Db
Al	175	206	95
Fe	177	126	91
K	3851	9025	18298
Mg	1790	1625	3141
Si	38	153	28
Ba	34	28	11
Ca	2085	2116	3021
Co	0.1	0.2	0.8
Cr	n.d.	0.7	3.1
Cu	3.5	5.9	5.3
Mn	600	189	41
Mo	0.1	0.1	0.1
Ni	0.8	1.4	1.2
Pb	0.5	1.6	0.2
Rb	6.5	3.9	3.7
Sc	0.03	0.0002	n.d.
Sr	42	29	51
Th	n.d.	0.1	0.02
U	n.d.	0.01	0.003
V	0.2	0.1	n.d.
Y	0.1	0.1	0.1
Zn	9.0	30	19
Zr	0.3	0.4	n.d.

n.d. – not detected

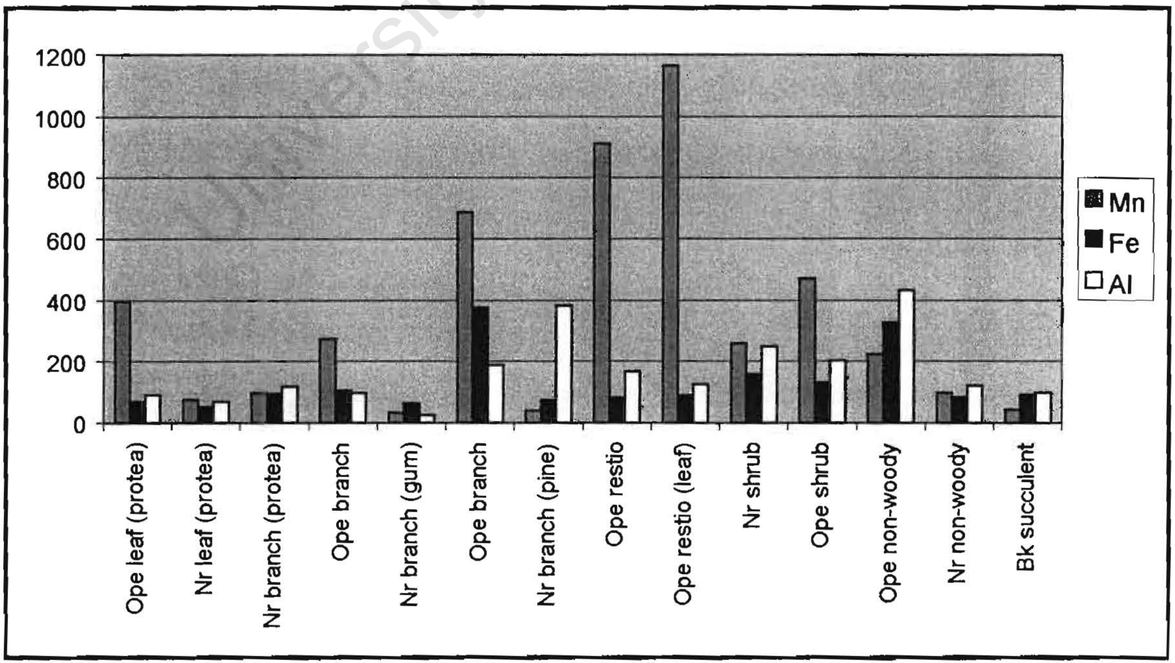

Figure 13: Mn, Fe, and Al concentrations (ppm) for vegetation samples. Ope - Peninsula Formation, Sn - Nardouw Sub-group, Db - Bokkeveld Series.

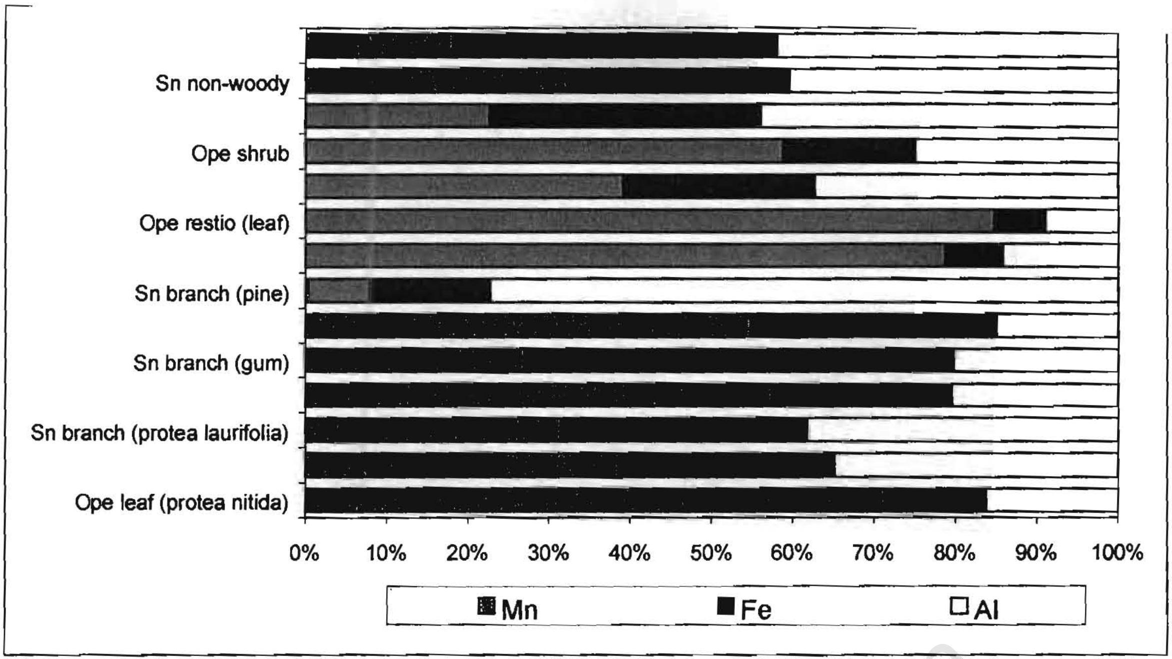

Figure 14: Mn, Fe, and Al concentrations (% of the sum of Mn, Fe, and Al) for vegetation samples. Ope - Peninsula Formation, Sn - Nardouw Sub-group, Db - Bokkeveld Series.

3.4 Data Quality

All measurements have an associated uncertainty which can be estimated by making replicate measurements and analyzing a standard by the same procedure. This uncertainty is caused by both systematic and random errors. Systematic errors can be quantified for measurements made on calibrated equipment (e.g. volumetric flasks and burettes). Random errors make up the balance of the uncertainty in a measurement. The information available for assessing uncertainty in the quantitative measurements of this study is summarized in Table 30.

Table 30: Summary of uncertainty information for quantitative techniques.

Technique	Measured uncertainty		Types of errors	
	Precision	Accuracy	Systematic	Random
IC	Duplicates and triplicates of samples and standards	Seawater and NIST standard, blank		Contamination
ICP-MS	Duplicates and triplicates of samples and standards	NIST standard	Dilution	Contamination, unknown interefences (e.g. residual organic carbon in vegetation)
Hardness (EDTA)	Duplicates and triplicates of samples and standards	IC Cation std, blanks	Buret reading	Contamination
ANC/BNC	Duplicates	Blanks	Pipeting, volume measurements, titrant concentration	CO_2 contamination and degassing
Grain Size			Weighing	Variation from ideal grain shape in settling; decanting suspended clay fraction
XRF			Weighing	
Soil Organic Carbon	Duplicates	Blanks	Buret reading	Unoxidized organic carbon after H_2SO_4 addition
DOC			Filtration, dilution	
Concentration of water samples	Concentrate vs original sample;		Volume measurements	Spillage, concentrate left in bottle

All weighing data should be taken as accurate within 0.05g. This is an estimate from experience with the scales used, as they read out to 0.01g (Appendix A). Temperature was measured in the field and lab with a glass mercury thermometer, and should be taken as accurate to 0.5°C.

ICP-MS data are generally considered to be accurate to sub-parts per billion levels with exceptions for interferences associated with the argon plasma. For this reason, the K, Ca, and Fe values should be considered less accurate, although K and Ca still compare fairly well with standard values (Table 32). Triplicate analyses were done on the soil SPE's and a standard reference material in the same run, and show good agreement between analyses for nearly all analyzed elements. Relative standard deviations in machine response (peak intensity, measured in counts per second) vary by element, but are generally less than 5% (Table 33).

IC data are considered accurate to sub-parts per million levels. Using seawater as a standard, at the time of analysis the lab reported overall relative bias of -3.4% Na, 2.0% K, 18% Mg, -56% Ca, -2.9% Cl, -15% SO4, and -246% Br. Variability in the measurements is quantified with range divided by mean concentration among replicate analyses (Table 34). Ca and Mg cations are not very well estimated at low concentrations on the IC, and should be taken as accurate within about 10%, depending on concentration. This is evidenced by the range/mean and the comparison of hardness data shown below. The sample concentrations fall within the standards for AAS, and relative standard deviations of instrument response range from 0.1% to 0.9% for Ca and Mg, and 1.3% to 8.7% for Na.

The pH meter reports values to the second decimal place. However, values are taken to be accurate to within 0.05 pH unit due to possible drift from calibration. The pH reading in a soil suspension changes substantially with time since the suspension is mixed, and is therefore dependent on the time at which the reading is taken. Alkalinity titrations for rainwater samples are fairly reproducible within a given rain storm (Fig. 15). Variation in the composite titration curves comes in the acidity portion, and indicates variable weak and strong acid concentration.

Soil organic carbon was determined titrimetrically with the Walkley-Black procedure. Variability in the replicate analyses is shown by the maximum and minimum values in replicate analyses (Table 31). Systematic errors can account for 4.3% of the variability, arising from buret reading, endpoint recognition, soil weight, and molarity of the ammonium ferrous sulfate reagent.

Table 31: Soil organic carbon replicate analyses.

Sample	Organic Carbon (wt %)			Number of analyses
	Mean	Max	Min	
NR	0.13	0.15	0.11	3
BJ2	0.68	0.83	0.54	2
BK2a	1.2	1.19	1.12	2
BK2b	0.95	1.05	0.85	2
EK6	1.8	2.07	1.54	2
EK5	1.4	1.52	1.29	2
BK1	0.91	0.94	0.87	2

Table 32: Range divided by mean concentration for triplicate analyses of soil SPE's analysed by ICP-MS (a-standard reference material NIST-1640).

Sample ID	BJ2	BJ2old	BK1	BK2a	BK2b	EK5	EK6	NR	NIST-1640[a]
Ag	0.64	0.61	0.20	0.06	0.27	1.63	1.07	0.56	0.02
Al	0.02	0.03	0.02	0.01	0.02	0.02	0.04	0.02	0.10
As	0.23	0.13	0.01	0.12	0.05	0.09	0.02	0.13	0.04
B	0.05	0.07	0.07	0.12	0.12	0.12	0.07	0.08	0.10
Ba	0.04	0.03	0.04	0.05	0.06	0.05	0.02	0.07	0.01
Be	1.91	0.63	0.40	0.12	0.07	3.00	23.36	0.38	0.07
Ca	0.11	0.12	0.06	0.13	0.12	0.12	0.11	0.11	0.09
Cd	0.13	0.22	0.03	0.23	0.06	0.17	0.26	0.22	0.03
Ce	0.01	0.04	0.13	0.02	0.02	0.12	0.05	0.05	0.05
Co	0.04	0.05	0.02	0.02	0.02	0.02	0.01	0.02	0.01
Cr	2.06	1.33	0.38	0.37	0.65	0.18	3.26	0.29	0.06
Cs	0.02	0.04	0.02	0.21	0.10	0.03	0.08	0.10	0.04
Cu	0.01	0.01	0.03	0.01	0.01	0.02	0.01	0.01	0.01
Fe	0.05	0.03	0.04	0.14	0.24	0.04	0.14	0.05	0.54
Ga	0.08	0.04	0.00	0.14	0.12	0.06	0.07	0.09	0.17
K	0.06	0.08	0.09	0.07	0.07	0.07	0.08	0.07	0.09
La	0.02	0.07	0.05	0.02	0.04	0.03	0.23	0.14	0.03
Li	0.47	0.27	0.17	0.08	0.16	0.35	0.19	0.11	0.05
Mg	0.02	0.04	0.06	0.05	0.05	0.04	0.06	0.01	0.02
Mn	0.03	0.08	0.05	0.05	0.02	0.06	0.07	0.05	0.01
Mo	0.07	0.05	0.04	0.12	0.07	0.04	0.04	0.13	0.01
Nd	0.01	0.04	0.10	0.05	0.06	0.07	0.09	0.04	0.02
Ni	0.06	0.16	0.06	0.02	0.12	0.08	0.09	0.02	0.02
Pb-206	0.02	0.01	0.01	0.04	0.09	0.01	0.05	0.05	0.03
Pb-207	0.02	0.06	0.02	0.05	0.09	0.03	0.02	0.03	0.04
Pb-208	0.03	0.00	0.05	0.03	0.08	0.01	0.01	0.03	0.03
Rb	0.02	0.03	0.01	0.04	0.03	0.03	0.05	0.01	0.04
Sc	0.27	0.28	0.07	0.26	0.13	0.40	0.21	0.27	0.25
Se	0.30	0.28	0.09	0.15	0.15	0.09	0.01	0.23	0.13
Si	0.06	0.02	0.01	0.02	0.02	0.03	0.01	0.04	0.10
Sr	0.03	0.03	0.03	0.01	0.01	0.02	0.01	0.03	0.04
Th	0.08	0.06	0.07	0.14	0.06	0.17	0.12	0.04	1.25
Tl	0.04	0.01	0.01	0.03	0.10	0.03	0.05	0.12	0.21
U	0.04	0.03	0.02	0.02	0.07	0.10	0.06	0.03	0.04
V	0.11	0.03	0.24	0.09	0.03	0.31	0.34	0.11	0.07
W	10.88	4.16	0.53	0.55	-146.78	0.41	6.33	2.22	0.93
Y	0.04	0.02	0.05	0.02	0.03	0.09	0.01	1.11	0.05
Zn	0.03	0.05	0.03	0.03	0.03	0.03	0.04	0.05	0.03
Zr	0.03	0.03	0.14	0.04	0.02	0.10	0.02	0.09	0.14

Table 33: Mean relative standard deviation (%) in peak intensity[a] (counts per second) for soil SPE analyses via ICP-MS.

Sample ID	BJ2	BJ2old	BK1	BK2a	BK2b	EK5	EK6	NR	NIST-1640[b]
Ag	37.3	18.2	10.1	12.6	17.1	95.8	11.5	18.6	1.1
Al	1.8	1.5	1.2	1.1	1.2	2.7	1.1	1.9	3.0
As	3.2	6.9	1.8	4.5	3.3	5.7	6.2	5.8	2.4
B	3.6	2.4	1.9	3.4	2.3	3.3	2.5	1.1	2.7
Ba	1.8	1.7	3.8	1.5	3.4	0.6	2.4	2.0	1.3
Be	212.4	52.4	42.8	52.2	13.9	1134.0	381.2	36.7	1.4
Ca	1.3	0.7	1.2	1.1	1.2	0.9	1.3	0.8	1.7
Cd	21.3	10.8	5.3	17.8	3.5	12.9	8.4	7.9	1.8
Ce	2.6	3.9	9.8	2.6	1.2	7.2	5.2	5.6	3.8
Co	1.5	3.9	0.6	3.5	0.7	1.9	2.5	1.6	1.5
Cr	30.2	12.1	8.7	15.8	6.1	16.4	61.8	13.1	1.2
Cs	6.7	3.7	3.4	10.4	6.3	5.1	7.1	5.6	5.6
Cu	1.3	0.8	1.3	0.8	0.8	1.7	0.7	0.8	1.2
Fe	1.3	1.6	2.8	11.1	2.8	2.6	3.2	1.3	9.9
Ga	3.8	4.2	2.0	4.3	1.9	3.5	1.9	1.8	1.8
K	1.6	1.3	1.1	1.2	2.0	1.3	1.2	0.8	2.5
La	2.4	10.1	8.6	3.5	1.3	4.5	7.2	17.0	4.1
Li	21.7	11.8	7.0	24.8	16.1	12.5	17.7	6.8	3.1
Mg	1.3	1.3	1.2	1.2	0.9	1.4	1.0	0.9	1.1
Mn	1.5	1.1	0.5	1.5	0.7	0.8	1.0	1.1	0.6
Mo	3.7	3.6	1.0	2.8	1.4	3.4	1.7	4.3	1.4
Nd	3.3	3.0	11.5	4.7	3.0	4.7	3.2	12.6	4.1
Ni	3.2	3.8	1.5	1.3	1.2	3.6	3.6	2.8	1.9
Pb-206	5.0	3.1	2.4	3.8	2.1	2.7	3.9	2.4	1.7
Pb-207	4.5	3.8	2.7	3.3	2.3	2.6	3.6	4.6	0.5
Pb-208	2.5	4.3	5.0	2.4	2.5	1.4	1.9	1.8	0.7
Rb	1.6	1.5	1.0	1.3	1.8	1.5	1.0	0.9	2.1
Sc	5.8	4.5	2.2	3.0	3.1	4.1	3.0	5.0	6.8
Se	40.6	20.2	3.9	8.6	7.8	13.7	11.6	6.8	8.8
Si	1.7	1.6	1.5	1.2	1.4	1.7	1.7	1.7	1.1
Sr	0.9	1.1	1.4	1.2	1.4	1.1	1.3	1.1	1.6
Th	1.1	3.4	2.8	3.4	2.9	5.3	1.9	3.9	5.5
Tl	11.2	4.0	4.5	9.2	8.0	4.7	5.1	9.6	14.3
U	2.0	3.5	2.4	1.9	2.1	2.3	1.4	7.4	1.3
V	1.5	0.5	11.8	2.2	1.5	2.7	1.0	1.9	1.6
W	36.7	16.5	4.8	4.5	74.9	5.6	20.2	50.3	6.8
Y	2.7	3.7	3.9	4.8	1.8	4.7	2.5	42.1	5.5
Zn	1.2	1.1	0.8	1.3	1.2	1.4	1.7	1.0	1.3
Zr	1.5	2.0	7.2	1.3	1.6	7.6	1.8	3.8	11.1

a – Each concentration reported by ICP-MS is based on a peak intensity, which is estimated from continuous measurement by the detector in the mass spectrometer
b – Standard reference material NIST-1640

Table 34: Range divided by mean concentration for duplicate analyses of anions and cations via IC.

Sample	Runs	F^-	Cl^-	NO_2^-	Br^-	NO_3^-	PO_4^{3-}	SO_4^{2-}
ORrain	2	n.d.	0.065	n.d.	n.d.	0.044	2.0	0.035
OL1	2	2.0	0.016	n.d.	2.0	2.0	2.0	0.25
OL2	2	n.d.	0.012	n.d.	0.12	0.25	n.d.	0.009
AL1	2	n.d.	0.009	n.d.	0.04	n.d.	n.d.	0.10
BK1	5	n.d.	0.097	n.d.	5.0	3.3	n.d.	0.69
BK2	2	n.d.	0.032	n.d.	2.0	2.0	2.0	0.057

Sample	Runs	Li^+	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}
AL1	2	2.0	0.039	n.d.	0.041	0.11	0.70
BJ1	2	n.d.	0.023	n.d.	0.030	0.027	0.24
BJ2	2	n.d.	0.013	n.d.	0.074	0.38	1.1
BJ3	2	n.d.	0.002	n.d.	0	0.021	0.14
BK1	4	n.d.	0.076	4.0	0.25	0.33	0.75
BK2	2	n.d.	0.048	n.d.	0.025	0.15	0.048
CDrain	2	n.d.	0.011	n.d.	0.075	0.58	0.59
EK4	2	n.d.	0.11	n.d.	0.038	0.040	0.16
EK5	2	n.d.	0.011	n.d.	0.29	0.099	0.11
EK6	2	n.d.	0.023	n.d.	0.057	0.040	0.018
OL1	3	3.0	0.085	n.d.	0.067	0.25	0.65
OL2	2	n.d.	0.001	n.d.	0.011	0.006	0.023
ORrain	2	n.d.	0.62	0.46	0.27	0.067	0.10
Baths	2	n.d.	0.13	n.d.	0.005	0.19	0.23

n.d. – not detected

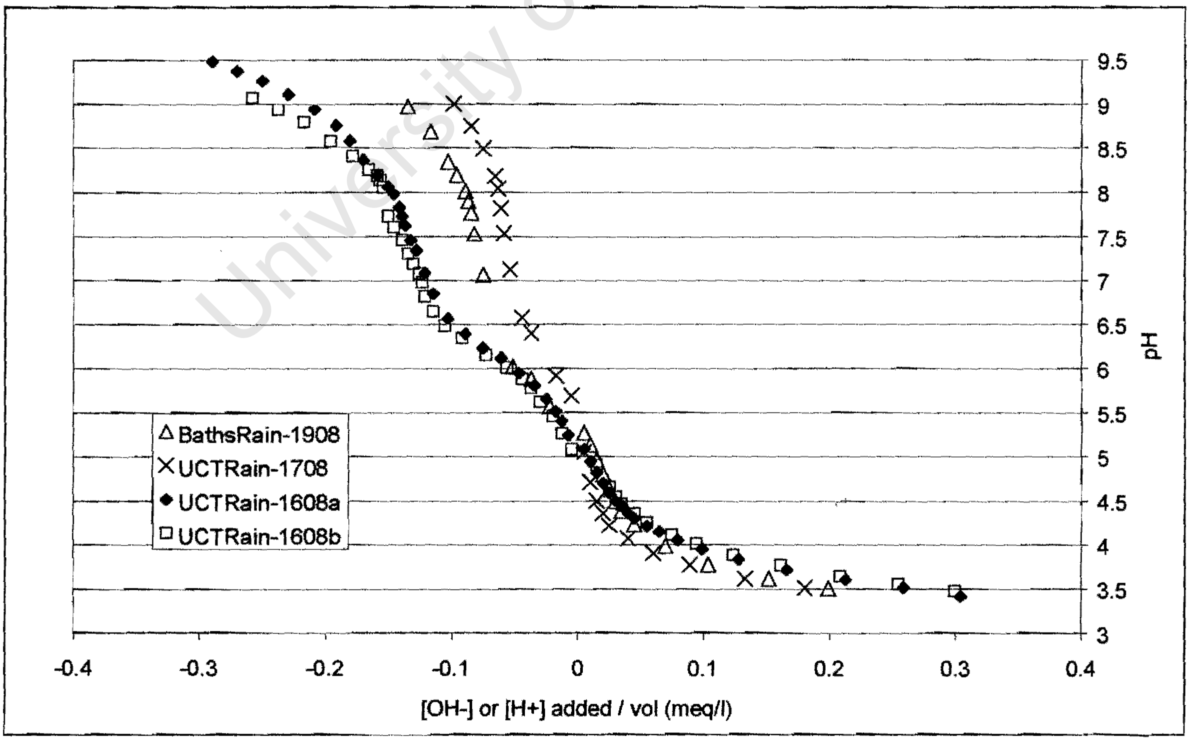

Figure 15: Composite titration curves for 3 UCT samples, and 1 Citrusdal sample.

Table 36: Hardness (Ca + Mg) values for three techniques. The 'Best technique' column lists the technique that was closest to the EDTA titration value.

SampleID	EDTA Titration	IC	ICP-MS	Best technique
UCTrain-170801b	3	32	2	ICP-MS
UCTrain-290801a	4	38	3	ICP-MS
BathsRain-190801b	14	70	10	ICP-MS
EK4-280501	17	46	17	ICP-MS
EK5-280501	17	52	16	ICP-MS
AL1-290501	19	40	19	ICP-MS
CDrain-290501	25	32	20	ICP-MS
UCTrain-160801ab	32	95	28	ICP-MS
EK6-290501	33	65	30	ICP-MS
BK1-300501	40	78	37	ICP-MS
BJ1-290501	41	54	39	ICP-MS
BJ2-290501	44	63	41	ICP-MS
BK3-300501	52	73	48	ICP-MS
BJ3-300501	60	73	52	ICP-MS
BK2-300501	75	107	61	ICP-MS
OL1-300501	80	102	69	ICP-MS
Baths-190801	134	148	248	IC
BK4-300501	149	203	130	ICP-MS
OR1-190801	159	188	155	ICP-MS
OL3-310501	190	236	130	IC
OL2-310501	1497	1764	1191	IC

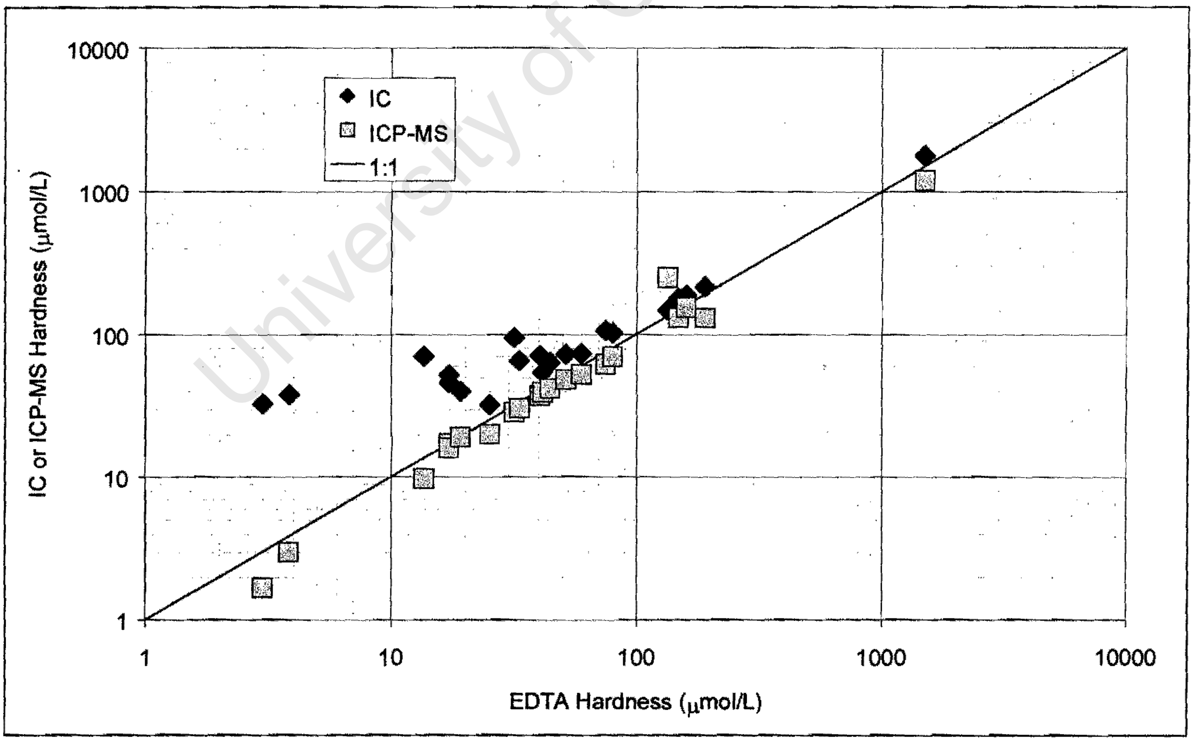

Figure 16: Hardness (Ca + Mg) by IC and ICP-MS compared with hardness by titration (EDTA).

4 Discussion

The objectives of this study are to determine the chemical composition of the major reservoirs in a fynbos ecosystem, evaluate the source and pathways of elements in this system, and discuss the potential influence of human activities. The first objective was covered in the results. The second will form the main part of this discussion, followed by a short section on the possible impacts of human activities.

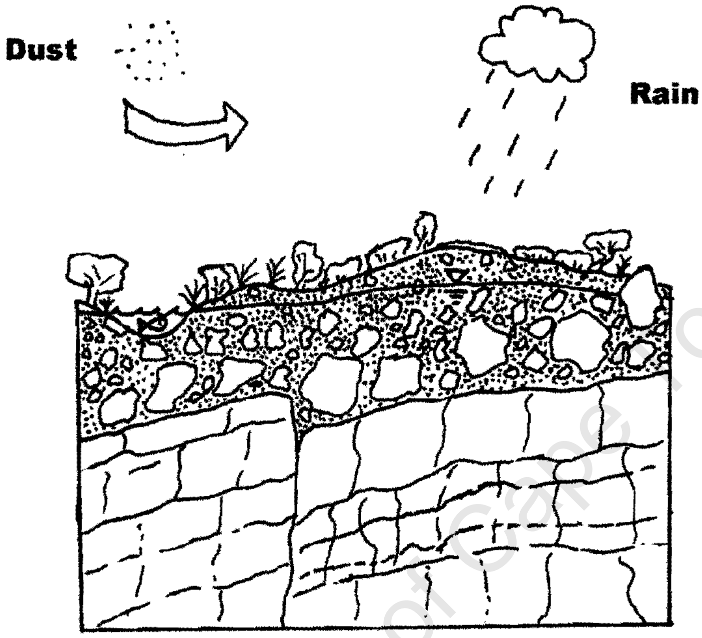

Figure 17: Cross-section of an ecosystem, showing atmospheric deposition and the six ecosystem reservoirs: vegetation, soil (bound and available), ground water, surface water, and bedrock.

The atmosphere, vegetation, soil, bedrock, groundwater, and surface water make up the major chemical reservoirs of an ecosystem (Fig. 17). Elements are transferred into and out of the ecosystem, as well as from one reservoir to another by interaction with water. Bedrock acts as a source of elements through weathering, while the soil and vegetation act as a filter, retaining certain elements and allowing others to pass through. The uptake or release of elements by processes in the ecosystem should be reflected by changes in the chemistry of the waters of the system.

The chemical composition of each reservoir is discussed below, starting with rain and the transfer of elements by atmospheric deposition. Rain water is followed as it filters through the vegetation and soil while it mixes with ground water and interacts with bedrock, before exiting the system as ground or surface water outflow. This path is particularly relevant to a headwater catchment on Peninsula Formation sandstone where many of the biologically important elements (e.g., K, Ca, and Mg) retained in the vegetation and soils will have come entirely from the atmosphere. It should be noted that other types of systems may have other significant inputs and outputs. A section on the interactions among the reservoirs follows the individual reservoir discussions.

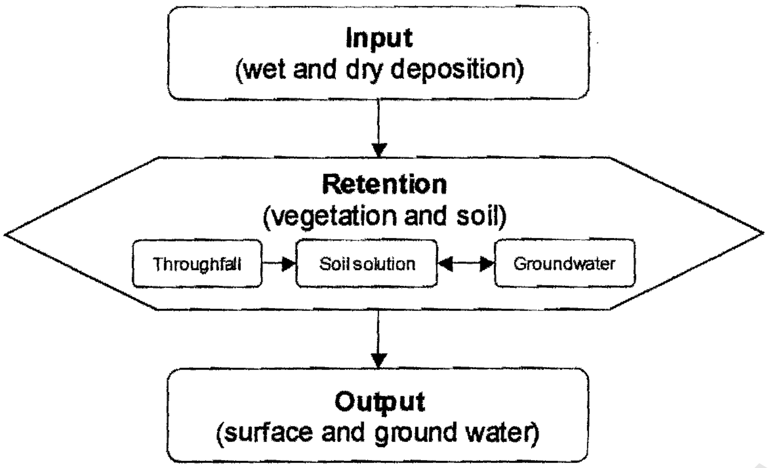

Figure 18: Flow of elements through a headwater catchment.

4.1 *Atmospheric deposition*

The atmosphere plays a major role in the movement of elements into and out of terrestrial ecosystems. Atmospheric fluxes are important in describing the chemical dynamics of these systems. The transfer of particles, gases, and aqueous species from the atmosphere into terrestrial ecosystems occurs by both wet and dry deposition Two parameters are needed to estimate wet and dry deposition in the elemental mass balance of an ecosystem:

1 - concentration of the element in the deposited material (Mass/Volume)

2 - net depositional flux (Volume/Time)

However, there are many difficulties with estimating these parameters by any combination of measurement and modeling.For wet deposition, parameter 1 is the concentration in rainfall, and parameter 2 is the total rainfall volume over a given time period. Dry deposition is essentially the same, but without the rain.

4.1.1 *Wet and dry deposition*

Wet deposition is the removal of gases, liquids and aerosols from the atmosphere through precipitation. Soluble gas phase species diffuse into a water droplet to become part of the solution that eventually falls. For aerosols there is a distinction made between those removed by virtue of being involved in the condensation of the water droplet, rainout, and those that became part of the droplet by impaction while the droplet was falling, washout (Berner and Berner, 1996). The washout process creates variation in the concentration of dissolved salts in the rainwater. This is especially true near the sea, where many of the aerosols are evaporated sea-salts that are very soluble, and therefore can quickly become part of the rain droplet solution as it falls.

Seawater is the primary source for rain water in the present study as the major ions are Cl^- and Na^+, followed by Mg^{2+}, SO_4^{2-}, and Ca^{2+}. The ion:chloride ratios of the samples normalized to those of seawater (Fig. 19; Table 10) suggest that there is a source other than seawater for Ca^{2+} (enrichment coefficient of 1.7), K^+ (4.6), SO_4^{2-} (1.9), Br^- (8.7), and HCO_3^- (22). The surface water samples are more enriched in Ca^{2+} (2.9-3.8) than rain water, while less enriched in K^+ (2.7). This could reflect a release of Ca^{2+} from ion exchange in the soil, and an uptake of K^+ by the soil and vegetation. While enriched in the rain water, SO_4^{2-} is depleted to a similar degree in all surface and ground water samples (0.48-0.64), reflecting its retention in the vegetation and soil. The retention in the soil can be seen by the high S content in the Ope soils (179-405 ppm) compared to Ope bedrock (32 ppm; Table 24).

A separate study of a mountain fynbos catchment (van Wyk et al., 1992) also measured surface water and deposition chemistry, though the deposition data are not directly comparable to the present study (Fig 19) as they include dry deposition as well as wet. It is interesting to see that in this study (Fig. 20) the enrichment coefficients of ions in the stream water follows that for total deposition closely. This indicates that atmospheric deposition is the primary source for the ions analyzed in the stream water. All ions have a smaller enrichment coefficient in stream water except for Mg, which has nearly the same enrichment coefficient in stream water as in total deposition. This reflects the preferential retention of Na, Ca, K, F, and bicarbonate in the soil and vegetation.

The chloride concentrations are in the "Marine and Coastal Rain" range (Table 3.4 in Berner and Berner, 1996) for nearly all rain water samples in the present study. This makes sense as the storms came from the direction of the ocean and the collection sites are within 5 km (UCT), and 80 km (Citrusdal) of the coast. Weaver *et al.* (1999) studied the rainfall chemistry in the Agter-Witzenberg Mountains, which form part of the headwaters for Olifants River drainage basin, about 50 km south of Citrusdal. They used cumulative collectors to obtain a sample of all the rain from May 1995 to May 1996. Confidence was placed only in the isotope and chloride values from these samples (Weaver, pers. comm., 2001). Their mean chloride concentration from 5 stations, 8 samples, is 134 μeq/L, which is somewhat

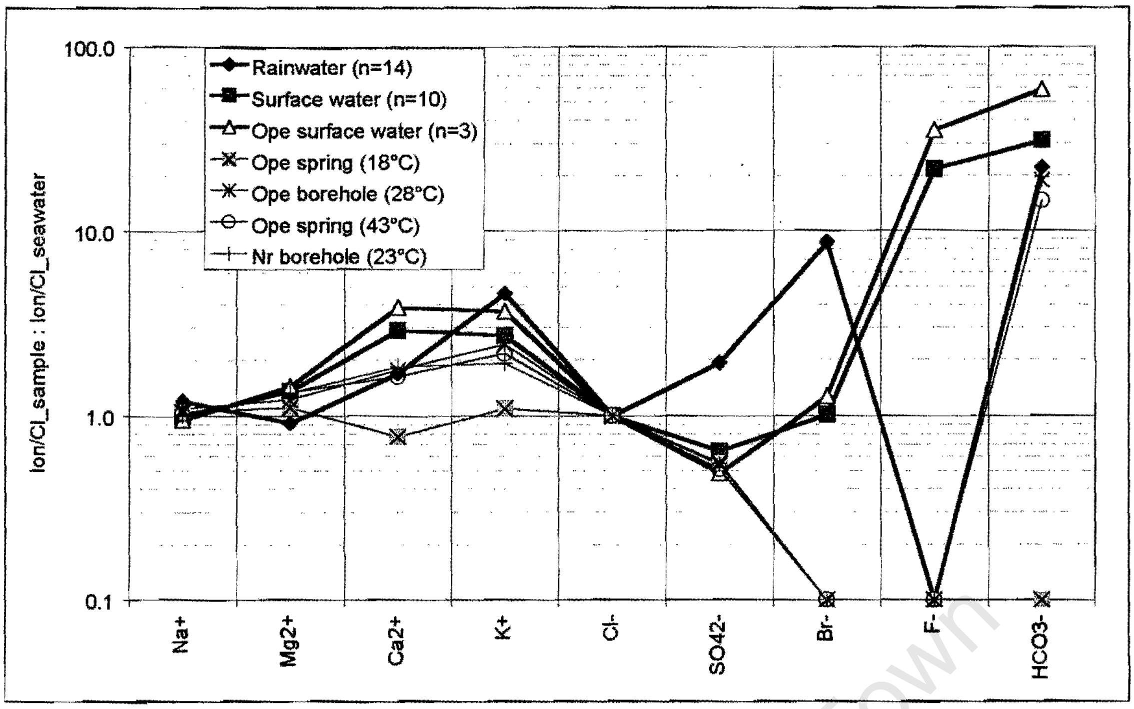

Figure 19: Ion to chloride ratios normalized to seawater for water samples in the present study.
Values of 0.1 indicate that the ion was not detected.

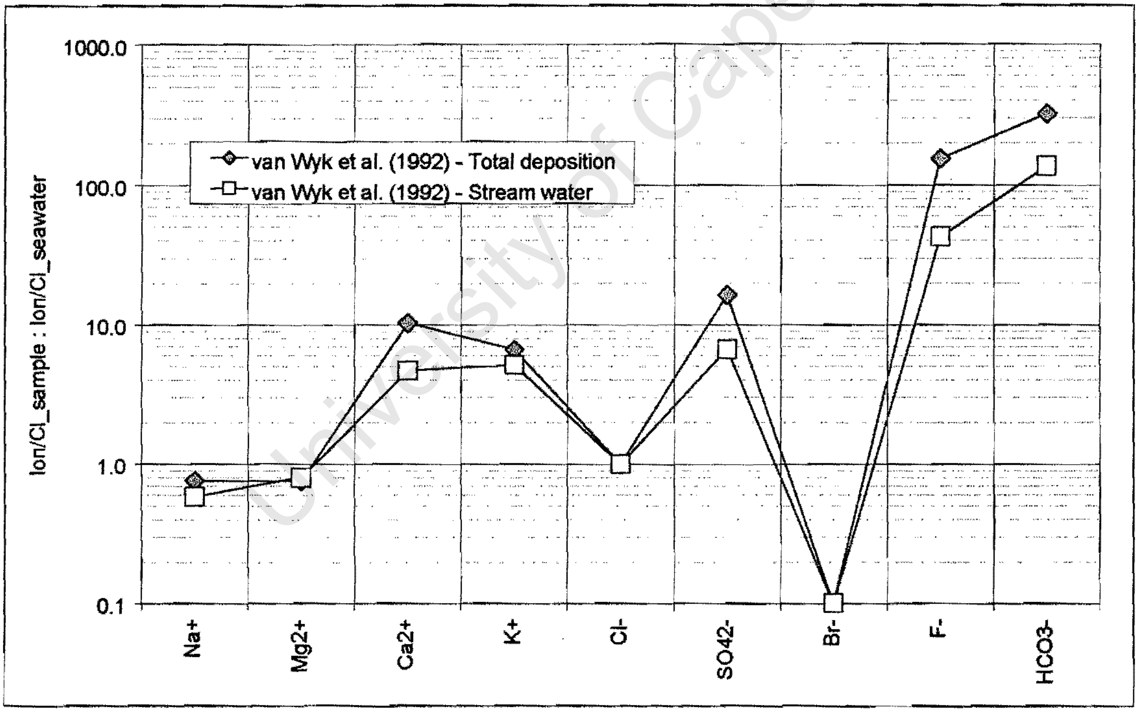

Figure 20: Ion to chloride ratios normalized to seawater for Swartboskloof (Stellebosch; van Wyk et al., 1992). Values of 0.1 indicate that the ion was not detected.

higher than our mean chloride concentration of 111 µeq/L (standard deviation 111 µeq/L; Table 8) for 14 samples. van Wyk *et al.* (1992) also studied bulk atmospheric deposition in a mountain fynbos community, and observed a mean concentration of 112 µeq/L over the period January 1986 to December 1988. Comparing these two studies with data from the present study indicates the potential for 15-30% greater chloride input.

Dry deposition is the transfer of gas or solid phase substances without precipitation. It is affected by atmospheric and meteorological conditions, surface type and conditions, and physical and chemical properties of the gas or particle (Pryor and Barthelmie, 2000). The simplest mechanism is that of gravity, which only governs the deposition of particles larger than 20 μm (Berner and Berner, 1996). The other pathway is driven by turbulence and slowing down near the surface. The particle or gas is transported by eddies until it reaches a thin area near the surface where turbulence is absent, allowing it to be trapped by the surface (Pryor and Barthelmie, 2000).

Some measurements of wet, dry, and total deposition have been made in fynbos ecosystems and similar areas around the world. For example, Schlesinger *et al.* (1982) studied the wet and dry deposition of various nutrients to a California chaparral system. They found that contribution of dryfall to the total deposition outweighed the wetfall contribution for Ca, K, Mg, and N, but not for Na and S (Fig. 21). This is taken to indicate that there is a strong terrestrial influence on the total deposition of Ca, K, and N (particularly NO_3^-). Given the prolonged periods of soil drying the winter-rainfall climate, soil particles are mobilized as dust, and could affect the total deposition of Ca, K, and NO_3^-.

Schlesinger *et al.* (1982) suggested that the source of NO_3^- may not be local as the NH_4^+ to NO_3^- molar ratio in nearby surface soils is 11.5, compared to an average of 0.25 in the total deposition. Stock and Lewis (1986) found a smaller difference in NH_4^+/NO_3^- between total deposition (1) and that for soils (0.5), in a coastal fynbos site about 110 km south of Citrusdal. They also used this finding to indicate a possible distal source for N. For Citrusdal, the Saturated Paste Extracts (SPE's) of the soils yield a mean NH_4^+/NO_3^- of 4, compared to that for rain water from Citrusdal and Cape Town of 3. Following Stock and Lewis, this result could indicate a non-local source for N in the rain. However, given the myriad of factors contributing to the speciation of N in the soil and atmosphere, a rain water ratio of 3 could not be deemed significantly different from a soil value of 4. Although, the atmospheric ratio of NH_4^+ to NO_3^- has been found to be relatively constant at a weather station in Pretoria, ranging between 0.8 and 1.8 over a year (Heaton, 1987).

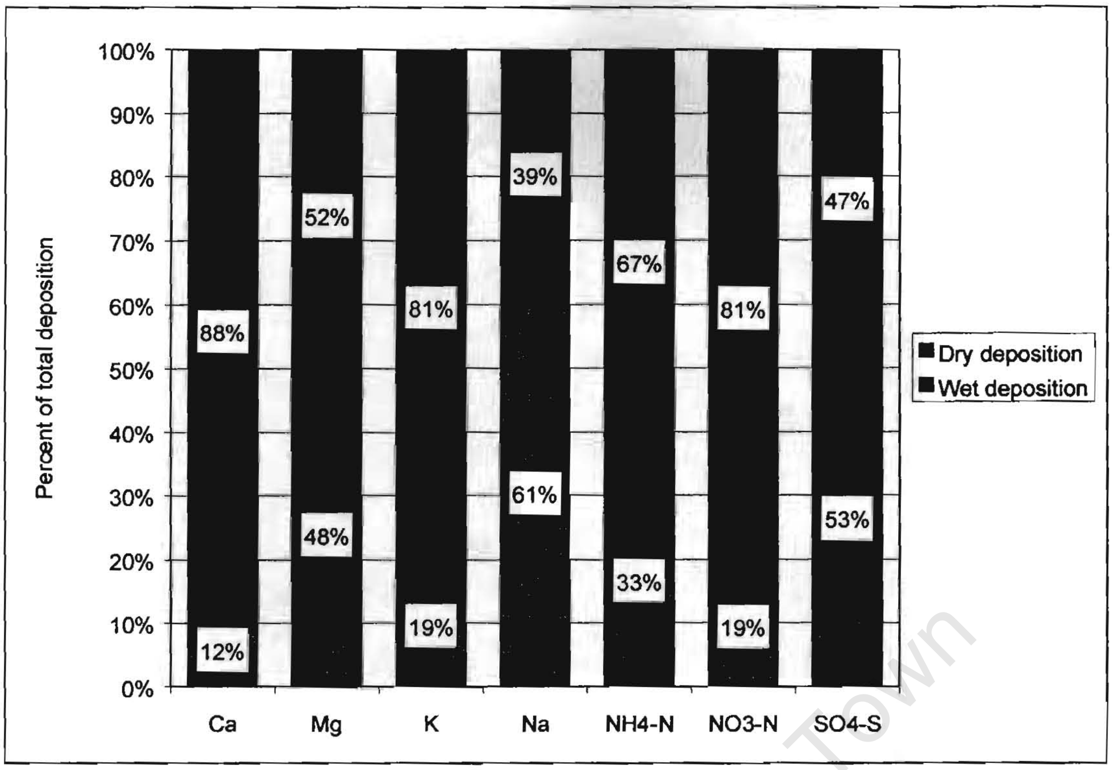

Figure 21: Wet and dry contributions to total deposition for various nutrients in California chapparal of the Santa Ynez Mountains (Schlesinger *et al.*, 1982).

Annual inputs of elements can be calculated using the composition of wet and dry deposition, along with mean annual rainfall. This is useful, again, for the Elandskloof catchment described above, where many of the elements collected in the soil, water, and biomass must have originated from outside of the catchment. In order to obtain total deposition values for Elandskloof, the relationships of Schlesinger *et al.* (1982) between wet and dry deposition are taken to be analogous. Thus, dry deposition is calculated for each element by multiplying the wet deposition values by the corresponding dry to wet ratio ("Dry/wet" column, Table 37). Cl, Fe, Mn, Al, and Si were not analyzed by Schlesinger *et al.* Thus, Cl is taken to have the same dry to wet ratio as Na, while the dry to wet ratio for Fe, Mn, Al, and Si is taken as the average of K and Ca due to their terrestrial influence. This method of calculating dry deposition seems to underestimate the total deposition of Si, comparing 0.41 kg/ha Si in the present study with the 9.1 kg/ha measured by van Wyk *et al.* (1992). Total deposition of Na, Cl, Ca, and NH_4-N is also lower than the values of van Wyk *et al.*, while SO_4-S and K are higher in the present study, and NO_3-N deposition is about equal in the two studies. Schlesinger *et al.* found much lower values of Na, K, Ca, and Mg, with comparable total N and S deposition.

Table 37: Deposition data for the present study (wet, dry, and total), another mountain fynbos study, and California chapparal.

	Wet deposition		Dry Deposition		Total Deposition (kg/ha/yr)		
	mg/kg/yr	kg/ha/yr	kg/ha/yr	Dry/wet[b]	Elandskloof (present study)	Swartboskloof[a]	California chapparal[b]
Na	2.5	15	9.8	0.65	25	48	7.3
Cl	3.8	23	15	0.65	38	96	n.a.
K	0.34	2.0	8.4	4.2	10	5.0	0.68
Ca	0.094	0.60	4.6	7.6	5.2	13	2.2
Mg	0.22	1.3	1.4	1.1	2.7	5.0	1.2
Fe	0.0071	0.043	0.25	5.9	0.30	n.a.	n.a.
Mn	0.0019	0.011	0.065	5.9	0.076	n.a.	n.a.
Al	0.0019	0.011	0.065	5.9	0.076	n.a.	n.a.
Si	0.0092	0.060	0.35	5.9	0.41	9.1	n.a.
NH4-N	0.029	0.17	0.34	2.0	0.51	2.0	0.60
NO3-N	0.0071	0.040	0.17	4.3	0.21	0.23	1.6
SO4-S	0.83	5.0	4.4	0.89	9.4	2.0	3.6

n.a. – not analyzed
a – van Wyk *et al.*, 1992; b – Schlesinger *et al.*, 1982

4.1.2 Deposition of aerosols

Deposition is a continuous process, and therefore best estimated by a continuous collector. Though complicated by removal processes, a river catchment can be taken as a large continuous atmospheric deposition collector. In the current study, wet and dry deposition are combined in considering the source of clay minerals. The catchment under consideration here, Elandskloof, is entirely underlain by the quartzite sandstones of the Peninsula Formation, which contains about 0.5 wt% Al_2O_3 (Table 23). The clay minerals in the soil (~6 wt% of <2 mm fraction) are predominantly kaolinite, a secondary alumino-silicate mineral. The presence of kaolinite in the soil's clay fraction along with the observation of wind-blown dust events (Section 4.1.4) suggest that an aeolian source of the clay particles is possible. As the minerals of the Peninsula sandstone were not identified in this study, it remains a possibility that some of the kaolinite could have been derived from the weathering of the small amount of Al_2O_3 in the bedrock. While it is beyond the scope of this study to identify the exact source of the minerals, it is hypothesized that atmospheric deposition is the most likely source for minerals in the soil that are not likely to have been derived from weathering of Peninsula sandstone. To evaluate this hypothesis would require a more detailed study of the chemistry of the clay minerals, Peninsula sandstone, and aeolian dust.

The closest data for clay mineralogy of aeolian dust in South Africa is that for dust off the coast of southern Namibia at about latitude 27°S. These particles were found to be made up of about 58% illite, 24% chlorite, and 18% kaolinite (Pye, 1987, after Chester *et al.* 1972). This composition is different to the clay fractions of the soils in the present study, which are dominated by kaolinite, suggesting a different source than the dust analyzed off the coast of southern Namibia. Clay mineralogy has been used to identify the source of loess deposits (Kohfeld and Harrison, 2001), and could be backed up with isotope signatures of the deposited particles and possible source particles. Some lead isotope data for the soils is discussed below.

4.1.3 Lead isotopes and the origin of clay minerals

Lead isotope ratios in the SPE should give some insight into the source of the lead as its isotopes are relatively heavy (204, 206, 207, and 208 amu), which prevents mass fractionation. This means that different sources of lead would have distinct isotope ratios. The ratios looked at here are Pb-206/Pb-207 and Pb-208/Pb-207 (Fig. 22). Potential sources of lead in any given surface system are mineral weathering and the atmosphere. Atmospheric sources include dust and pollution from leaded fuel and industrial effluent.

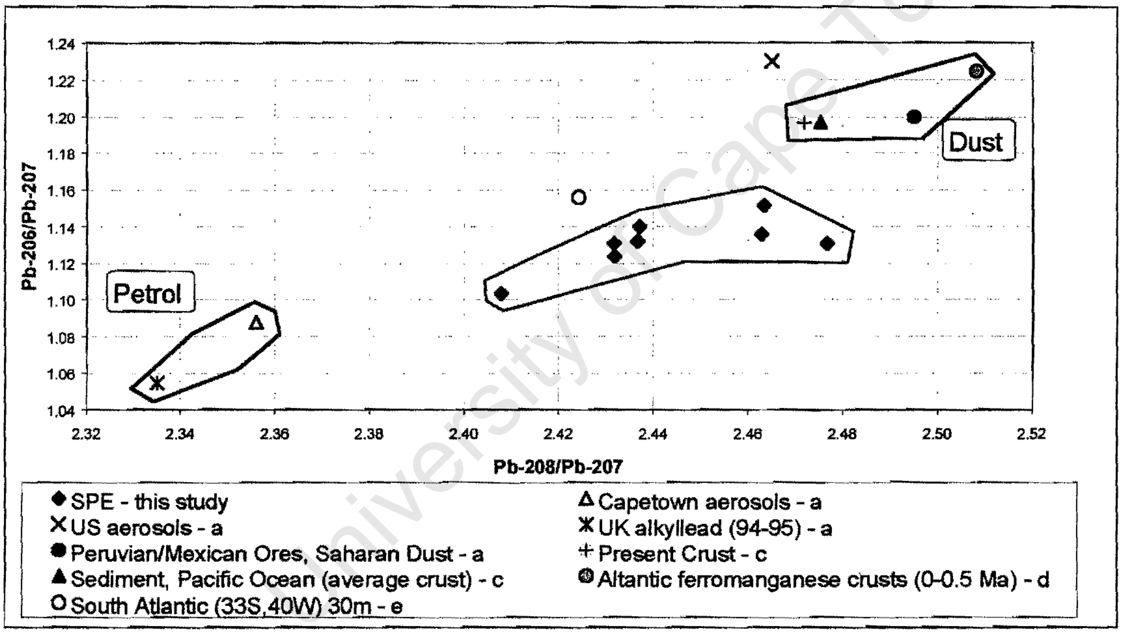

Figure 22: Pb isotope ratios for saturated paste extracts and literature values for recent leaded petrol, present crust, and aerosols (a - Bollhofer and Rosman, 2000; b - Veron *et al.*, 1999; c – Faure, 1986; d - O'Nions *et al.*, 1998; e - Alleman *et al.*, 2001b).

There is a general distinction between mean isotope ratios of lead currently found near the surface of the earth's crust, and that used in leaded fuel. This is of interest for determining the fate of lead in the environment, given that it is known to have toxic effects on humans. Lead from the earth's surface has been shown to be more radiogenic (enriched in Pb-206) than that in petrol (Véron *et al.*, 1999).

Véron *et al.* (1999) identified a change in the lead isotopic ratio Pb-206/Pb-207 of aerosols in France from 1.108 in 1983 to 1.148 in 1994, and used this as an indication of an increase in more radiogenic (more Pb-206) lead inputs to the atmosphere relative to less radiogenic lead such as that found in leaded fuel. These values cover the range of ratios found in the SPE's of soil samples from the current study, which show Pb-206/Pb-207 and Pb-208/Pb-207 ratios of 1.10-1.15 and 2.41-2.48, respectively.

The wide range in these Pb ratios suggest a mixing of the two sources of soluble lead in the seven soil samples, petrol and crustal dust ("Cape Town aerosols" in the bottom left and "Present Crust" values in the upper right; Fig. 22). The samples fall along a trend that would represent the mixing of lead deposited as aerosols originating from the combustion of leaded petrol, and lead from a crustal source such as aeolian dust.

This variability could also reflect some sort of error in the analysis. Error could arise from contamination of the samples or the analysis itself. The analysis was done on an ICP-MS, which specializes in low concentrations of heavy elements. The samples were not prepared in a clean lab, and were therefore exposed to ambient levels of lead in the lab air. This suggests that contamination is the more likely source of any major errors in the values. If contamination did occur in the lab, it would reveal itself only if the contaminating lead had an isotopic ratio different from that of the samples. The samples were all treated the same, and should therefore still exhibit the observed variability in isotopic ratios if the influence of contamination was uniform.

4.1.4 Evidence for washout of aerosols

A dust source for the kaolinite is supported by an observation of dust washout in Cape Town on 20 May 2002 when a "Berg Wind" event was experienced. ENE winds brought high temperatures and dust that created an extensive brown haze, initially reducing visibility. Visibility improved a couple of days later, after a front with moderate to heavy rains came through. During an event like this, and continuously on a smaller scale, some fraction of the particles blown over the catchment gets deposited, wet or dry. The deposited particles remain in the soil for a certain time period (residence time), which is influenced by the physical and chemical properties of both the soil and the particles, as well as the rainfall amounts and intensities.

The washout of dust particles should add certain terrestrial elements such as Ca, Al, and Si to the rainwater. This would change the ratio of the enriched element to chloride with respect to the same ratio in seawater (Table 10). It is assumed that all Al and Si dissolved in rain water is derived from aerosols, while there is an initial concentration of Ca which is augmented by aerosols (Sugawara, 1967). Thus, there should be a correlation between the enrichment of Ca and the concentration of Al and Si in rainwater, which is roughly seen in the data (Fig. 23)

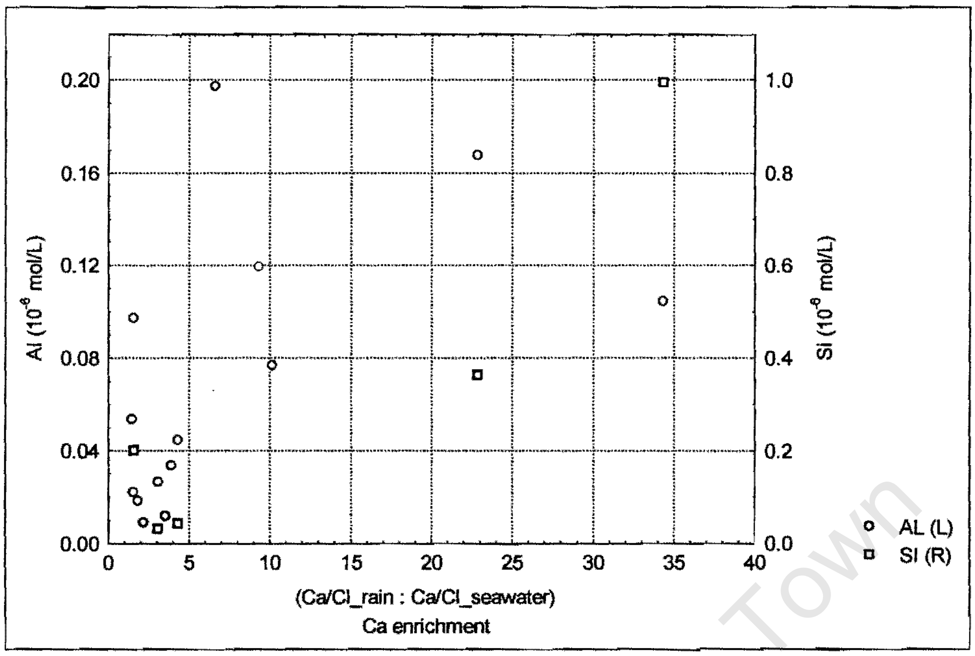

Figure 23: Al and Si vs Ca enrichment for rain water samples.

Evidence for the washout process, whether the aerosols are terrestrial or marine, can be seen by comparing rough estimates of rainfall rate with EC measurements (Fig. 24). As described above, washout introduces aerosols into rain water droplets, some of which will dissolve to form ions. Increased ion concentration increases the EC of the rain water. With a higher rainfall rate, more rain water will interact with a given concentration of aerosols, leading to a lower concentration of washout-induced ions, hence a lower EC. This is observed in both Cape Town and Citrusdal, as the Cape Town rainfall events show higher rainfall rates over the same EC range. This could be an indication of a higher concentration or higher solubility of aerosols in Cape Town than in Citrusdal, which is reasonable considering that Cape Town is on the coast where aerosols are heavily influenced by sea spray, and Citrusdal is about 80 km inland. It is important to consider that washout is likely to increase the EC of rain water more towards the beginning of a rain storm. However, this does not affect the interpretation as the Citrusdal rain storm was sampled sequentially from the beginning, and would have much higher EC values if the aerosols in Citrusdal were of the same type and concentration as those in Cape Town.

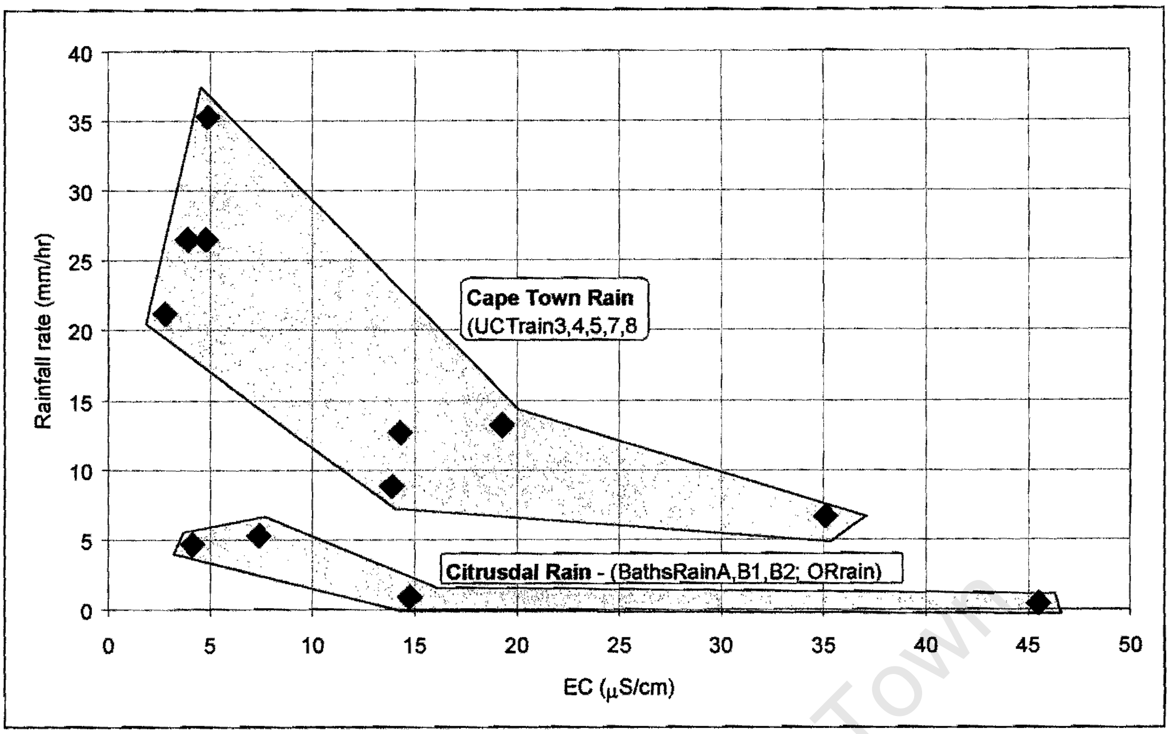

Figure 24: Rainfall rate vs. EC for Cape Town (8 measurements, 4 rain storm events) and Citrusdal (4 measurements, 1 rain storm event).

4.1.5 *The general estimation of wet and dry deposition*

The low concentrations of cations and anions in rainwater makes them difficult to measure accurately. This difficulty results, in part, from the analytical precision, which is lower at low concentrations (Appendix B). For wet chemistry and ion chromatography, concentrations are measured against standards in a calibration curve. Rainwater concentrations will most likely be near the lower limit of this curve. This can become a problem if a given species, e.g. Ca^{2+}, is present in even very small amounts in the de-ionized water used to make the standards. In this case one must ensure that the lowest standard concentration is lower than the concentration in the rainwater.

Rainwater can also be easily contaminated. Electrical conductivities of rain waters in this study were low (median of 9.4 μS/cm), making measured concentrations sensitive to any extra dust or sweat from the analyst's brow. To help alleviate this, one should collect large sample volumes in addition to the usual contamination precautions.

The major constituents of wet deposition are Na^+, Cl^-, SO_4^{2-}, Mg^{2+}, Ca^{2+}, and K^+. Other important species are NH_4^+, NO_3^-, and H^+. Bicarbonate alkalinity is usually a minor constituent (Table 8). If one wanted to detect the presence of trace elements, the sample could be pre-concentrated. Also, the condition of electro neutrality in natural waters allows the use of charge balance to estimate analytical errors and contamination, assuming all major species have been measured (Appendix B).

Dry deposition is more difficult to estimate than wet, both in bulk deposition rates and composition. The systems in the lower atmosphere are very dynamic. Diurnal and seasonal effects on the atmospheric and surface conditions must be taken into account. The aerosols of dry deposition are taken and kept aloft by wind, and in non-industrial inland areas their composition would be dominated by the common terrestrial elements K, Na, Ca, and Mg (Berner and Berner, 1986). Aerosols that originate as mineral dust far outweigh those from anthropogenic sources (Buseck and Schwartz, 2002), though both types can play important roles in the atmosphere.

The composition of suspended aerosols is not necessarily the same as that of particles that actually get deposited on surfaces. There is differentiation of the particles based on surface conditions such as wind speed, vegetation cover, and the relative 'wetness' of a surface. The exact surface conditions are often difficult to quantify. For this reason, NOAA developed the 'Inferential Model' that uses more easily estimated parameters to model dry deposition rates. This method divides the vegetation into layers and takes into account various parameters on stomatal and leaf boundary layer resistances. It seems to agree well with other estimation methods (Meyers *et al.*, 1998).

4.2 The vegetation reservoir

Vegetation retains elements preferentially for its physiological requirements. It takes up elements in either aqueous or gaseous forms from the atmosphere and the soil. The elements C, H, O, N, Ca, K, Al, Mg, Fe, P, and S form the bulk of plant biomass (Fig. 25), of which Ca, K, Al, Mg, and Fe were analyzed in this study. Of the potential minor and micro nutrients that were analyzed in this study, there seems to be a general concentration order that can be divided into three categories (Tables 38 and 39).

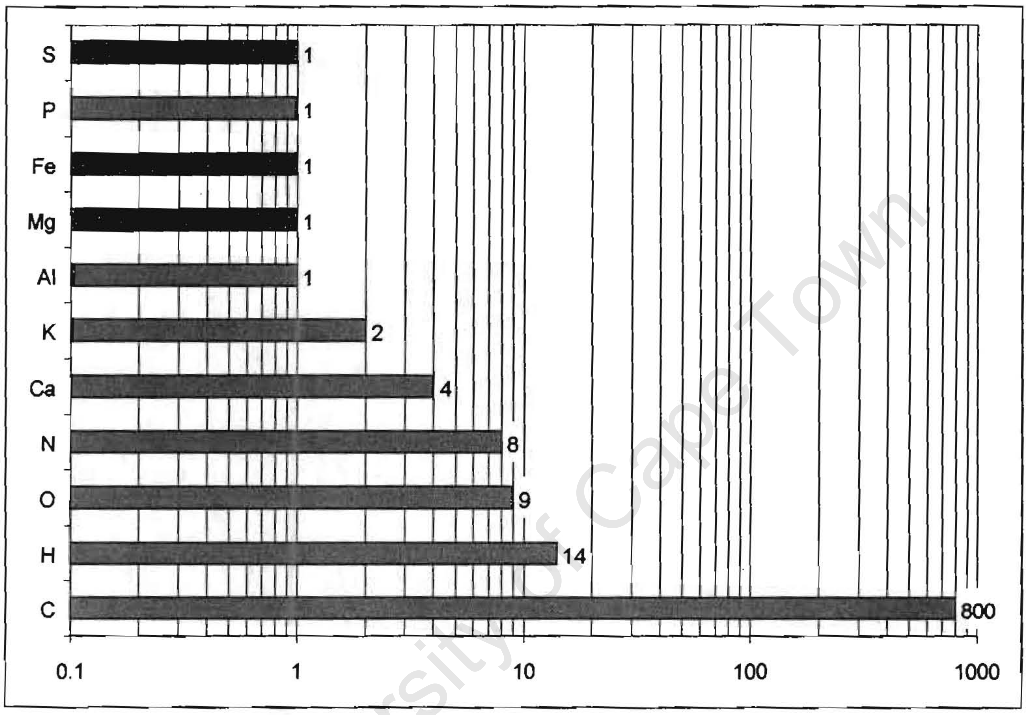

Figure 25: Approximate stoichiometry for generic biomass (Drever, 1997, p. 238)

Table 38: General categories for elements in vegetation. Minor (except P and S), micro, and trace elements were analyzed in this study.

Category	**Elements**
Major	C, N, H, O
Minor	Ca, K, Al, Mg, Fe, P, S
Micro	Mn, Si, Sr, Ba, Zn, Cu, Rb, Ni
Trace	Co, Cr, Mo, Pb, Sc, Th, U, V, Y, Zr

Table 39: General concentration categories for minor and micro nutrients analyzed in plant material in the present study.

Category	Concentration Range (ppm)	Elements and relative abundance
1	1000 – 18000	K > Ca, Mg
2	50 – 600	Mn > Fe, Al
3	1 – 50	Si, Sr > Ba, Zn > Cu, Rb, Ni

There are few studies of the bulk chemical properties of mountain fynbos. The one study of plant chemistry near the current study area (Cedarberg Mountains), von Willert *et al.* (1989), used a different method of analysis than the current study. Specifically, plant leaves were dried, ground, and then elements were extracted by boiling the ground samples in water for 30 min. This differs from the current study in which the dried, ground plant materials were roasted and the resulting ash totally digested for analysis. However, since the plant communities, climate, and soils are similar for the two sets of samples, it is interesting to compare the K and Ca concentrations (Table 40). The Na and Cl concentrations of von Willert *et al.* are difficult to interpret as the contribution from the water used to extract the elements is unknown, and their concentrations would have changed in the boiling procedure. Na and Cl are most likely present in soluble forms on the vegetation, as they are not usually involved in the production of biomass (Drever, 1997). Another study of mountain fynbos on sandstone (about 150 km S of Citrusdal) measured Na and Cl concentrations of 600 and 2100 ppm, respectively (van Wilgen and le Maitre, 1981), using a dry ashing and dissolution method similar to the method used in the present study. Na and Cl were not measured in the present study, so the concentrations of van Wilgen and le Maitre will be used to approximate the Na and Cl content of the vegetation samples.

Table 40: Comparison of K and Ca concentrations (mg/kg dry matter) for vegetation samples from the Cedarberg Mountains (von Willert *et al.*, 1989), and just to the southwest of the Cedarberg Mountains (this study).

Sample		**K**		**Ca**		**Na**	**Cl**
This study (S)	**von Willert *et al.* (1989) (V)**	**S**	**V**	**S**	**V**	**V**	**V**
Sn leaf (*Protea*)	Proteoid: *Protea laurifolia* (mean of 4)	2640	2500	2079	150	2100	900
Ope *Restio* (leaf)	Restioid: *Cannomois acuminata*	2990	8200	1792	880	13000	16000
Ope + Sn shrub	Ericoid (mean of 4)	9670	7900	2560	1500	5900	3800
Ope + Sn non-woody	Herb (*Salvia* spec.) + Geophyte (*Dilatris corymbosa*)	6580	13000	1250	1400	750	5300

4.2.1 Estimating the size of the vegetation reservoir

In considering the vegetation as a chemical reservoir the concentration values on a dry weight basis are often converted to mass or moles of a given element on a spatial basis (e.g. kg/ha). This calculation requires an estimate of the density of organic matter for which the elemental concentration was calculated. The chemical reservoir of vegetation corresponds to phytomass, which is often divided into above-ground (aerial) and below-ground phytomass. The above and below ground fractions are further divided into living (biomass) and dead (necromass) biomass (e.g. van Wyk *et al.*, 1992). Values from the literature suggest that the above-ground phytomass of mountain fynbos communities depends largely on the stand age, or the years since the community was last burned, as fynbos communities are naturally subjected to periodic fires (Fig. 26). It has also been found that necromass as a percentage of phytomass decreases along an elevational gradient in the fynbos (Rutherford, 1978).

Phytomass was not measured in the current study, so it is necessary to make an estimate based on similar study areas in the literature. This estimate, while very rough, will allow for an order-of-magnitude comparison of elemental totals in phytomass with those in the other ecosystem reservoirs. Rutherford (1978) studied biomass in four plant communities near Robertson in the Western Cape, and found phytomass values of 11400 and 14500 kg/ha for tall and low fynbos, respectively. The Cedarberg area is mentioned by Rutherford as having analogous vegetation gradients to those in the mountains near Robertson. The Elandskloof headwater catchment can therefore be considered a mixture of Rutherford's tall and low fynbos communities, allowing Rutherford's values to be used to estimate phytomass in Elandskloof. Another control can come from comparing soil organic carbon to phytomass values, as a soil with high organic carbon content should be able to sustain more phytomass than a soil with low organic carbon. For example, the Kogelberg Biosphere Reserve on the southern coast of the Western Cape visually contains much more biomass than Elandskloof in communities on soils derived from the similar parent material. The soils in the Kogelberg have around 3-5 times higher organic carbon content than analogous soils in Elandskloof (A. Smit, pers. comm., 2002). Using the one phytomass value for the Kogelberg of around 15000 kg/ha, Elandskloof phytomass could fall between 3000 and 5000 kg/ha. This is just a speculative correlation, and these values are probably on the low side. From these loose constraints, a round figure of 10000 kg/ha can be used as a very rough estimate of mean phytomass in Elandskloof. Using this value, a reservoir inventory can be produced (Table 41). The mean biomass elemental totals compare well with other studies of mountain fynbos chemistry, with K and Mg slightly higher than values from Zachariashoek, Bakkerskloof, and Kogelberg. Total phytomass concentrations are towards the low end of the literature values, reflecting the low phytomass chosen for Elandskloof.

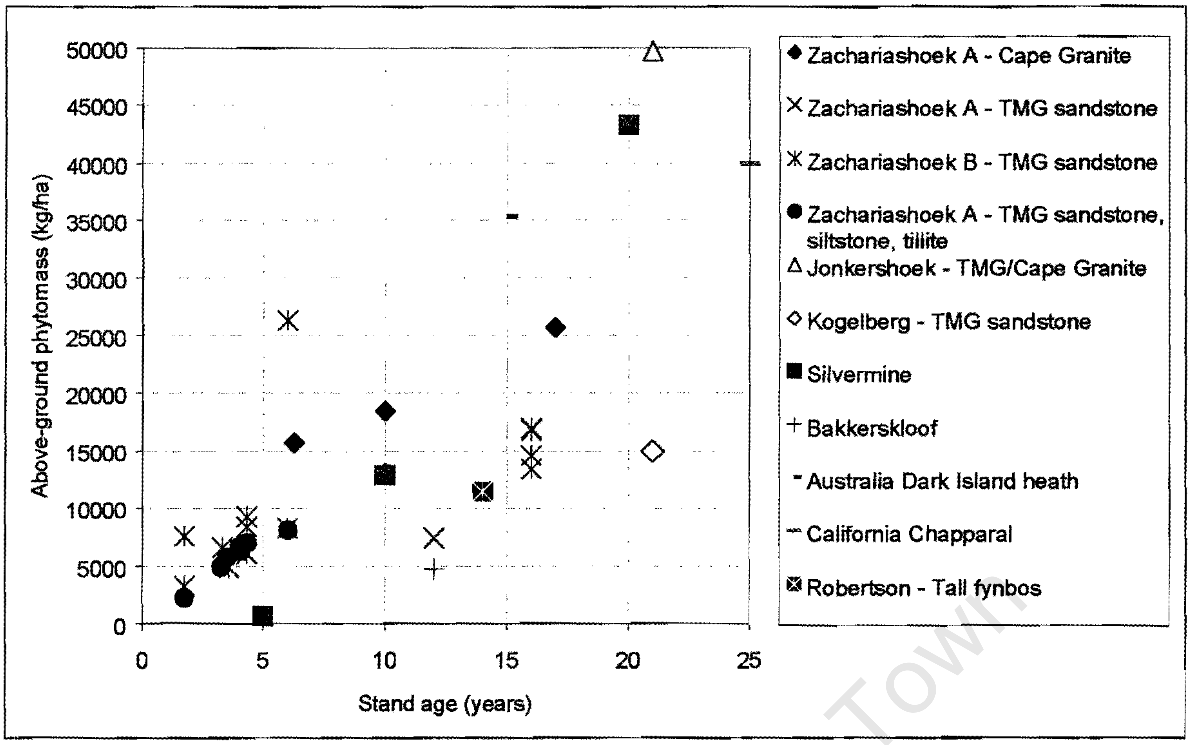

Figure 26: Above-ground biomass vs. stand age (years since last burn) for 3 mountain fynbos communities. Zachariashoek.
A – Kruger, 1977; Zachariashoek B, Jonkershoek – Mitchell, 1987; Silvermine – Kathan, 1981

Table 41: Concentration on a mass and spatial basis for vegetation from Elandskloof, and some literature values.

Element	Mean biomass (mg/kg)							Total phytomass (kg/ha)			
	Present study (Elandskloof)	Zachariashoek[a] (sandstone)	Bakkerskloof[a] (sandstone)	Kogelberg[a] (sandstone)	Kogelberg[b] (sandstone)	Australian Heath[b]	California Chapparal[b]	**Present study (Elandskloof)**	Swartboskloof[c] (granite & sandstone)	Jonkershoek[a] (granite)	Zachariashoek[a] (sandstone)
Na	**[a]600**	1160	1050	n.a.	n.a.	n.a.	n.a.	**6**	n.a.	38	6.7
Cl	**[a]2100**	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	**21**	n.a.	61	21
K	**3900**	3640	3540	2570	2900	5120	9400	**39**	112	72	21
Ca	**2100**	1970	1520	2600	2200	3460	9143	**21**	119	69	15
Mg	**1800**	792	702	1340	1300	1540	1671	**18**	34	14	5
Fe	**177**	n.a.	n.a.	n.a.	n.a.	101	205	**1.8**	n.a.	n.a.	n.a.
Mn	**600**	n.a.	n.a.	n.a.	n.a.	58	108	**6.0**	n.a.	n.a.	n.a.
Al	**175**	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	**1.8**	n.a.	n.a.	n.a.
Si	**38**	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	**0.38**	n.a.	n.a.	n.a.

n.a. – not analyzed

a - van Wilgen and le Maitre, 1981; .b – Specht and Moll, 1983; c – van Wyk *et al.*, 1992

4.3 The soil and bedrock reservoirs

Soil is defined as the less than 2 mm fraction of the material above bedrock. It contains organic and mineral fractions, both of which are involved in the preferential retention of elements. Water passes through the soil as part of the surface water-groundwater system after falling as rain, and is the medium for most chemical and biological activities in the soil (Schwab, 2000). The physical and chemical properties of the soil and soil solution determine the speed with which water travels through the pore spaces. The wetness of the soil affects the transport of elements as plants take up elements when they are dissolved in water, water drives weathering reactions, and prolonged wetting affects the availability of gases in the soil.

The soils in the present study are sandy with less than 7% clay (in the <2 mm fraction), and organic carbon content of between 0.7 and 1.8 wt%. The low clay content is corroborated by other studies of similar soils (Table 42). Similar organic carbon contents (0.9-1.8 wt%) have also been found on mountain fynbos soils (van Wyk *et al.*, 1992; van Reenen *et al.*, 1992). However, higher organic carbon levels could be found in fynbos soils that support more phytomass, receive more rainfall, or sit in flat areas. Chemically, the soils are expected to have low pH, low cation exchange capacity, and low but variable organic carbon. Specifically, the mountain soils near Citrusdal have had CEC's between 20-40 meq/kg soil and pH's between 4.5 and 6.5 (Taylor, 1996). Quartz is obviously expected to be the main mineral of the bulk soil. The soil is the largest reservoir of carbon, nitrogen, and phosphorus in fynbos ecosystems (Stock & Alsopp, 1992).

Table 42: Clay content of soils derived from TMG sandstone.

Clay content (wt% of <2mm fraction)	No. Samples	Parent material	Reference
3 – 7	5	Ope, Sn	Present study (Table 17)
7	52	Quartzitic "fynbos" soils	Campbell 1985
8.0	3	Ope	van Wyk *et al.* 1992
2 – 8	5	Ope	Lambrechts *et al.* 1986

Bedrock acts as a source of elements for the soil above it, and transfers those elements through weathering. In the study area the bedrock reservoirs are the Peninsula Formation sandstone (Ope), Cedarberg Formation shale, Nardouw Sub-group sandstone (Sn), and Bokkeveld Series siltstone/shale (Db). Ope and Sn cover the largest aerial extent and support the fynbos ecosystems of interest. Major element composition of Ope and Sn are similar in comparison to Db, but the three samples are distinct (Fig. 27). Ope and Sn weather to form sandy soils like those sampled in this study, and Db would form more clayey soils.

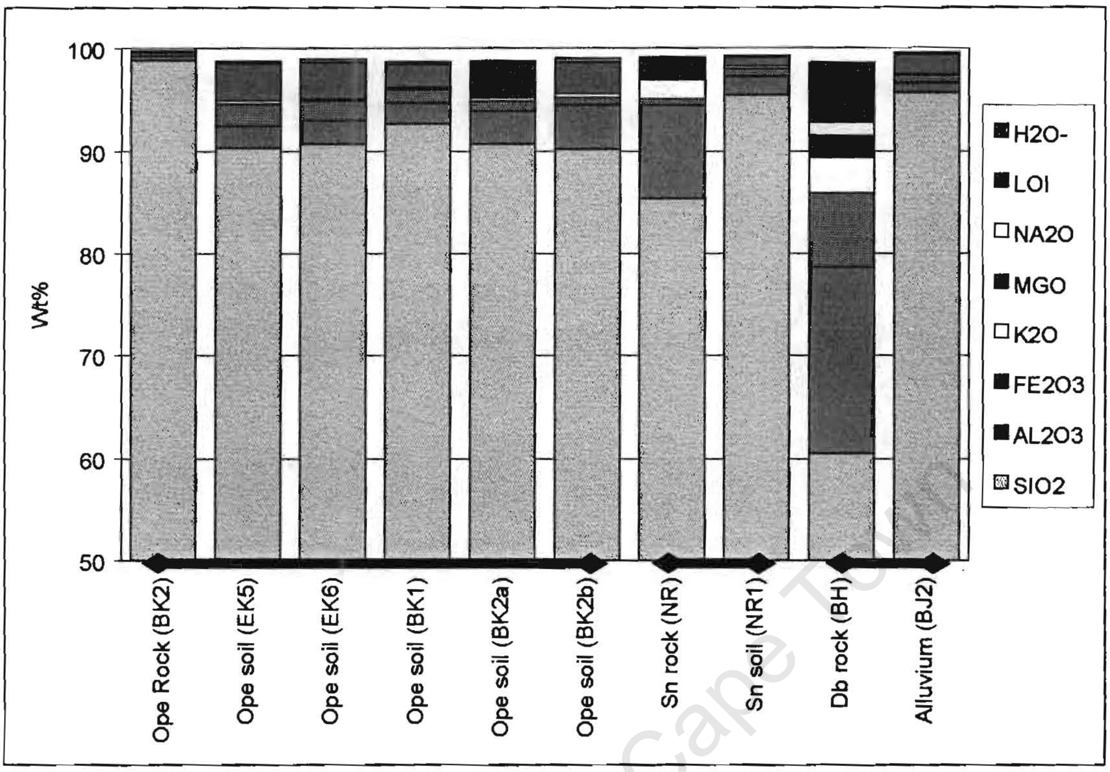

Figure 27: Major components of bedrock and soil samples (wt%) by XRF. Note that the scale starts at 50 wt%. LOI is Loss on Ignition (850°C); H2O- is weight loss at 450°C.

Elements can enter the soil via weathering, decomposition, rainfall, or anthropogenic inputs. They are subsequently concentrated in different parts of the regolith through processes such as leaching into groundwater and uptake by the vegetation. For example, in the BK2 profile, one explanation for there being more Zn in the SPE of the subsoil than in the topsoil (5.0 vs 2.0 μmol/L) is that Zn is a micronutrient, and would therefore be removed from the topsoil by plants. The same pattern is seen in Al, with 60 μmol/L in the subsoil, and 33 μmol/L in the topsoil. Mn, however, shows the opposite trend. While being an important micro nutrient for the vegetation, soluble Mn is nearly an order of magnitude higher in the BK2 topsoil (30 μmol/L) than in the subsoil (3.4 μmol/L). Part of the explanation for this could be that the sandy soils allow water to percolate through quickly, leading to longer periods of wetting in the subsoil above bedrock, and hence, periods of a less oxic environment in the subsoil. Mn is highly immobile under oxidizing conditions, and will only leach down the soil profile with percolating water as Mn^{2+}. Mn concentrations are therefore higher in the more oxidizing topsoil than in the subsoil.

The major mineral composition of the soil broadly reflects the mineral composition of the parent material, but includes minerals that either precipitated from the soil solution or were deposited in the soil from the atmosphere. For example, Peninsula Formation (Ope) soils contain mostly quartz, but are influenced by the precipitation or deposition of Al and Fe (Fig. 5) as these elements are present in higher concentration than in the parent material. This is expected as SiO_2 is more soluble than Al_2O_3 and Fe_2O_3 under the conditions of the soil. The Nardouw (Sn) soil and alluvium have similar major element compositions to the Ope soils, even though the underlying bedrock in each case contains more varied major elements. That is, the Ope soils have retained elements to greater concentrations than in the bedrock, while the Sn soil analyzed has released elements relative to its underlying bedrock. For the Sn soil this may indicate a high degree of leaching, with virtually all of the K from the parent material weathered out, and only residual Al and Fe left to supplement the quartz. The alluvium sample is underlain by Bokkeveld (Db), but is likely to have a distal source of sandstone, giving it a highly leached composition similar to the Sn soil.

Also related to leaching, the BK2 profile has a much greater acidity in the subsoil than in the topsoil (5.55 vs 0.93 meq/kg soil). This could be correlated to the higher Al content as there is more total Al in BK2b than BK2a. But this correlation does not hold looking at the other samples. Perhaps there is some sort of buffering of weak carbonic and organic acids from the excess Mn-oxides in the topsoil mentioned above.

4.3.1 *Estimating the size of the soil and bedrock reservoirs*

As with vegetation, it is useful to convert values from a mass basis to a spatial basis when considering the soil and bedrock as chemical reservoirs. This requires estimates of porosity (ϕ), grain density (ρ, g/cm^3), and mean depth (d). Although these parameters were not measured in this project they can be estimated to get a general feel for the magnitude of the values on a spatial basis:

$$M = C \times A \times d \times \rho \times (1 - \phi)$$

with, M = amount of an element on a spatial basis (kg/ha or mol/ha)
C = mean concentration of an element for the specified area on a dry mass basis (g/kg or mmol/kg)
A = area for which the calculation is based (m^2)

Taking the Elandskloof headwater catchment as an example and assuming the following,

C = the concentration in the soil sample EK5
A = 10000 m^2 (1 ha)

$d = 0.5$ m
$\rho = 2.65$ g/cm^3 , mean particle density for quartz (Deer *et al.* 1992)
$\phi = 0.3$, estimate

the weight or moles of each element analyzed can be calculated. This calculation only gives an idea of the magnitude of the soil reservoir for each element, and is subject to a large amount of error. The error comes from variability (in all dimensions) in the soil chemistry, porosity, and soil depth. More accurate values would require a soil survey that covers the parts of the catchment where distinct soil properties are expected (e.g. different slope, aspect, and elevation). In addition to considering the total elemental reserve in the soil, it is relevant to separate the portion of the soil reservoir that is available to be taken up by plants.

The soluble fraction is the part of the soil reservoir that is most readily available to be dissolved into the soil solution, a form that allows an element to be taken up by plants. The soluble fraction is also most easily flushed out of the soil during a rain storm. Compounds in the exchangeable fraction can also become part of the soil solution, but not as easily as the soluble compounds. The soluble and exchangeable amounts of an element are, together, considered to be available to plants, and this can be calculated by using the SPE concentration in the above equation. For Na, Ca, and Mg, the KCl-exchangeable amounts can be taken to represent the available portion as the soluble portion will become part of the KCl solution in the procedure. Exchangeable K was not measured in this study, but could increase the available K value significantly for TMG sandstone soils. For example, Specht and Moll (1983) reported exchangeable K as having a higher concentration than exchangeable Ca, Mg, and Na for mountain fynbos sandstone soils of the Kogelberg (Table 43), which is about 20-40 times larger than the soluble K measured in the SPE's of the present study. The large amount of exchangeable K could be reflected in the total soil concentrations of the present study, which is 2900 ppm for K (EK5) while Na, Ca, and Mg are below the detection limit (< 100 ppm, Table 44).

Table 43: Exchangeable cations from fynbos soils of the present study and Kogelberg.

Element	Exchangeable concentration (meq/kg)	
	Kogelberg mountain fynbos TMG sandstone surface soils (Specht and Moll, 1983)	Mountain fynbos TMG sandstone surface soils (EK5, EK6, BK1, BK2a, NR) of the present study
Ca	6.9	13
Mg	2.7	5.6
Na	2.9	7.2
K	8.7	?

The bedrock reservoir is by far the largest reservoir in the ecosystem, although only the surfaces of the bedrock in contact with groundwater actually interacts with the surface ecosystem. Again, it is difficult to quantify the total size of the bedrock reservoir, but it can be estimated using the same equation used for the soil reservoir. For Elandskloof, the mean thickness (d) of the Peninsula Formation is about 1000 m (Fig. 2). Particle density can also be taken as 2.65 g/cm^3. The porosity of a fractured aquifer is difficult to estimate, but a generic value of 10% can be used as a starting point. This aquifer can supply elements from anywhere in its body to the surface ecosystem through the movement of ground water. Thus, the entire formation can be taken as the bedrock reservoir for Elandskloof.

Table 44: Concentrations and inventories for the soil and bedrock reservoirs.

	Soil Soluble		Soil Exchangeable		Soil Total		Bedrock	
	mg/kg	kg/ha	mg/kg	kg/ha	mg/kg	kg/ha	mg/kg	kg/ha
Na	11	100	156	1447	< 100	< 928	< 334	< 8000000
Cl	13	120	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
K	4.5	42	n.a.	n.a.	2900	27000	800	19000000
Ca	4.3	40	421	3905	< 100	< 928	< 500	< 12000000
Mg	3.0	28	100	928	< 100	< 928	< 500	< 12000000
Fe	0.17	1.6	n.a.	n.a.	14660	136000	2100	50000000
Mn	1.1	10	n.a.	n.a.	529	4900	39	1000000
Al	0.19	1.8	n.a.	n.a.	11300	100000	2430	58000000
Si	2.0	19	n.a.	n.a.	422000	3900000	462000	11000000000

"<" indicates that the element is below the detection limit shown

4.3.2 *Soil Classification*

In terms of soil form, it is impossible to classify completely the five locations for which only topsoil was taken. From the literature, the quartzite-derived soils (EK5, EK6, BK1, BK2a&b) are typically of the Mispah, Houwhoek, Lamotte, Champagne, Hutton, Clovelly, Constantia, or Fernwood forms. For the one potentially shale-derived soil, BJ2, the list is Hutton, Clovelly, Avalon, Glenrosa, Swartland, Sterkspruit, Estcourt, and Kroonstad. These lists can be narrowed based on slope, rainfall, and iron oxide content (Lambrechts 1979; Campbell 1985; Table 45).

Table 45: Sample color and classification possibilities

Sample	Horizon	Form
BJ2	Orthic A	Clovelly, Hutton, Swartland
BK1	Orthic A	Houwhoek, Lamotte, Clovelly, Hutton
BK2a	Orthic A	developing into Groenkop or Houwhoek
BK2b	developing Podzol?	developing into Groenkop or Houwhoek
EK5	Orthic A	Mispah, Houwhoek, Lamotte
EK6	Orthic A	Lamotte, Fernwood
NR	Orthic A	Lamotte, Clovelly, Constantia, Hutton

The BK2 profile (Fig. 5) shows a poorly developed soil derived from blocky boulders of Peninsula Formation sandstone. The boulders look disordered, indicating that they could have tumbled a short distance as scree to their present position on the footslope. They have since been filled in by very fine grained material either washed down the slope or accumulated in a low velocity bend during flood events.

The soil profile seems to be young in terms of weathering, but could be developing a Podzol B Horizon subsoil above the C Horizon of boulders. This is supported by the subsoil being non-plastic and darker than topsoil when wet. One of the Podzol B variants is described as "a soft, very dark grey to black horizon with little sesquioxic hardening, often wet" (Soil Classification Working Group, 1991). The development of a Podzol B under an Orthic A and above a saprolite would place the soil in the Groenkop form. The development of a leached E horizon between the A and B would place the soil in the Houwhoek form.

4.4 The ground and surface water reservoirs

The ground and surface water reservoirs of a system are closely linked. Surface waters are fed by discharge from the water table, flow from the unsaturated zone, and direct surface runoff during rainfall events. Ground water is the result of a mixture between precipitation and soil pore water ("throughfall" and " soil solution" in Fig. 18). Surface water is more influenced by the soil chemistry than is ground water as it is constant contact with the soil solution, while ground water is predominantly in contact with bedrock and has a much larger volume in which to dilute the effects of the soil.

The alkalinity and acidity titrations (Fig. 10) confirm the low buffering capacity anticipated in the ground and surface waters from the nearly pure SiO_2 composition (>98 wt%) of the quartzite bedrock. Compared to other regional surface water, such as the samples downstream of the study area (Fig. 10c), the Upper Olifants River headwaters and TMG ground waters have extremely low alkalinity, nearly as low as the rain waters analyzed (Fig. 10a and b). Weathering of the bedrock does add slightly to the alkalinity, or Acid Neutralizing Capacity, which is highest in the warm spring sample after the water has traveled tens of kilometers over thousands of years (Meyer, 2002). This is related to the redox chemistry of Fe and Mn, which are minor (2100 ppm) and trace (39 ppm) elements in the bedrock, respectively (Tables 23 and 24). The solubility of Fe and Mn is controlled by pH and redox potential (pe) of the groundwater. Low pH and pe levels of TMG ground waters allow for high solubility of Fe and Mn, which decreases with increased pH and pe. Outcrops of Peninsula Formation and Nardouw Sub-group sandstones are often stained orange and black from the oxidation of the trace amounts of Fe and Mn that flow in groundwater as reduced species, and precipitate out upon oxidation when they reach the surface.

The carbonate system dominates weak acidity in most natural waters. The total carbonate concentration is controlled by equilibrium of the solution with the pCO_2 of the surrounding air. The pCO_2 of the atmosphere is $10^{-3.5}$ atm. It can be much higher in soils where degradation of organic material is taking place. The species involved are:

$[H_2CO_3^*]$
$[HCO_3^-]$
$[OH^-]$
$[CO_3^{2-}]$

Speciation depends on the pH of the solution (e.g. Stumm and Morgan 1996, p.157). This system acts as a weak acid in that $H_2CO_3^*$ and HCO_3^- can dissociate to donate H^+ to the solution. At equilibrium with atmospheric CO_2, rainwater has a pH of 5.6. At this pH the carbonate system could contribute 21 ueq/L to total acidity. Organic acids can also be present in rainwater (Stumm and Morgan 1996, p.209), including formic, acetic, oxalic, and benzoic acids. They arise as products of the oxidation of organic aerosols and gases, and have been found generally to only occasionally exceed a few μeq/L.

The size of the ground water reservoir can be estimated by assuming that it fills all of the pore space and fractures of the bedrock. The concentration of groundwater underlying the Elandskloof headwater catchment are estimated from the Peninsula Formation borehole (BK2) and Allandale spring (AL1) sample. The size of the surface water reservoir is seasonal, but a basic figure can be obtained from maps and aerial photographs. For Elandskloof the surface water concentration are estimated from the samples EK4, EK5, and EK6 (Table 46).

Table 46: Concentrations and inventories for elements in the surface and ground water reservoirs.

	Surface Water		Ground Water	
	mg/kg	kg/ha	mg/kg	kg/ha
Na	3.4	0.0026	5.3	5300
Cl	6.2	0.0048	8.1	8100
K	0.24	0.00019	0.70	700
Ca	0.17	0.00013	0.48	480
Mg	0.41	0.00032	0.68	680
Fe	0.021	0.000016	0.0084	10
Mn	0.0072	0.0000056	0.0027	2.7
Al	0.033	0.000026	0.0078	10
Si	1.3	0.0010	4.4	4400

4.5 Synthesis

4.5.1 Estimates of reservoir size

The rough estimates of reservoir sizes, as well as fluxes into and out of the system are shown in Table 47. This exercise is meant to identify the magnitude of each reservoir with respect to some elements of interest, and to provide a basis for comparing these elements within the reservoirs. Using estimates of physical and hydrological parameters for each reservoir (described above and listed in Table 48), the magnitudes range from 10^{-6} kg/ha Mn in surface water to 10^{10} kg/ha Si in bedrock.

Table 47: Concentrations in the various chemical reservoirs, and basic inputs and outputs to the system.

	Wet deposition	Dry deposition	Phytomass	Soil total	Soil soluble	Soil exchangeable	Bedrock	Surface Water	Ground Water	Surface water removal	Net change
	kg/ha/yr		kg/ha							kg/ha/yr	
Na	15	9.8	6.0[a]	< 930	100	1400	< 8000000	0.0026	5300	4.3	20
Cl	23	15	21[a]	n.a.	120	n.a.	n.a.	0.0048	8100	7.1	31
K	2.0	8.4	39	27000	42	n.a.	19000000	0.00019	700	0.35	10
Ca	0.60	4.6	21	< 930	40	3900	< 12000000	0.00013	480	0.26	4.9
Mg	1.3	1.4	18	< 930	28	930	< 12000000	0.00032	680	0.58	2.2
Fe	0.043	0.25	1.8	140000	1.6	n.a.	50000000	0.000016	10	0.046	0.25
Mn	0.011	0.065	6.0	4900	10	n.a.	1000000	0.0000056	2.7	0.017	0.059
Al	0.011	0.065	1.8	100000	1.8	n.a.	58000000	0.000026	10	0.031	0.045
Si	0.060	0.35	0.38	3900000	19	n.a.	11000000000	0.0010	4400	2.3	-1.9

a – value taken from van Wilgen and le Maitre, 1981, see text

"<" – value is less than the detection limit shown

Table 48: Estimated parameters for Elandskloof headwater catchment reservoir calculations.

Parameter	Estimate	Unit	Description
Mean annual precipitation	600	mm	Hay and Hartnady, 2002
Mean annual runoff	100	mm	Hay and Hartnady, 2002
Phytomass	10000	kg/ha	Estimate, see discussion above
Soil porosity	0.3	-	Estimate
Soil particle density	2.65	g/cm^3	Deer *et al.*,1999
Soil thickness	0.5	m	Estimate from outcrop and slope observations
Bedrock effective porosity	0.1	-	Estimate
Bedrock particle density	2.65	g/cm^3	Deer *et al.* 1999
Bedrock thickness	1000	m	Hartnady *et al.*, 2000
Catchment size	27	km^2	Estimate from GIS
Mean stream depth	0.1	m	Estimate from observations
Mean stream width	1	m	Estimate from observations
Total length of streams	21	km	Estimate from GIS

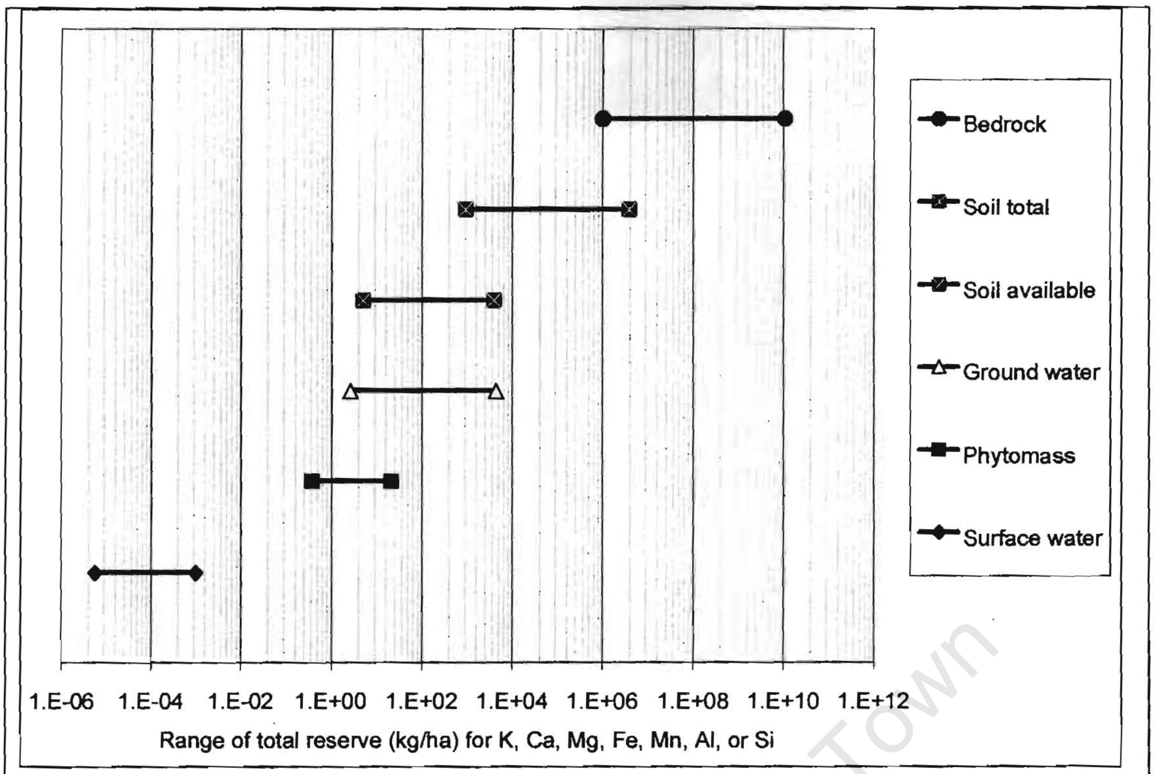

Figure 28: Ranges of total elemental content (kg/ha) for K, Ca, Mg, Fe, Mn, Al and Si in each of the 6 ecosystem reservoirs.

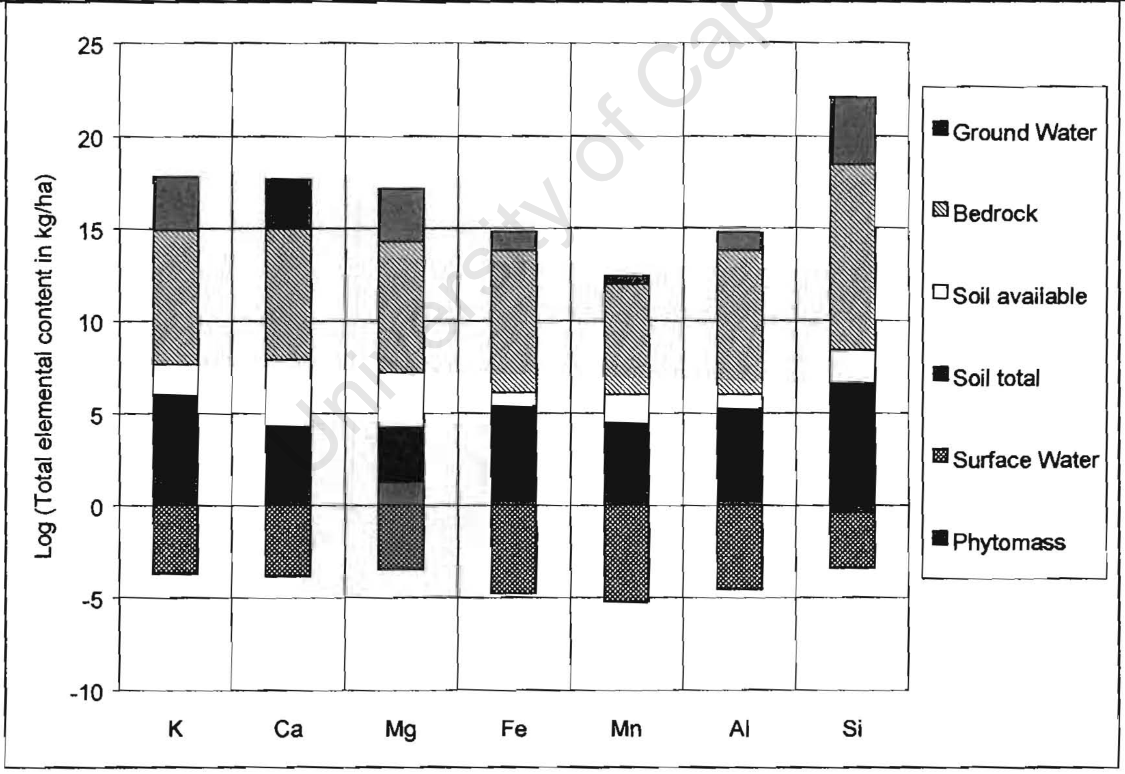

Figure 29: Log of total elemental content (kg/ha) for K, Ca, Mg, Fe, Mn, Al and Si in each of the 6 ecosystem reservoirs.

4.5.2 *Retention of elements*

The flow of elements through an ecosystem (Fig. 18), and specifically the retention of elements in the soil and vegetation, is difficult to quantify. For a headwater catchment, the situation is somewhat simplified as the only inputs are from the atmosphere and groundwater. Major outputs are surface and ground water, with less significant outputs being volatilization and removal by wind. Considering the major inputs and outputs, retention of an element could be calculated by:

$$A = V_a C_a + C_{gw}(V_{gw,in} - V_{gw,out}) - V_{sw,out} C_{sw,out}$$

where, A = elemental retention rate (mol/ha/year)
V = volume (L/year)
C = elemental concentration (mol/ha)
Subscript a = atmosphere
Subscript gw = groundwater
Subscript sw = surface water

The flow of groundwater into and out of the system is particularly difficult to measure. Thus, it is often assumed that the ground water is at steady state, with the amount entering the system balanced by the same amount leaving as ground water (e.g. van Wyk *et al.*, 1992; Likens *et al.*, 1977). This allows retention to be calculated as atmospheric inputs less surface water exports (Table 47, last column "Net Change"), giving the absolute retention of an element in the ecosystem. The rough estimates used in this calculation show that, among the elements considered, Si is the only element lost from the ecosystem. Cl, Na, and K have the highest retention rates (31, 20, and 10 kg/ha/yr, respectively) followed by Mg, Ca, Fe, Mn, and Al. Cl is normally considered a conservative ion as it is generally not part of biological processes. It may be retained here due to the lack of other anions (HCO_3^- is low, and SO_4^{2-} is taken up by plants) to maintain electro neutrality in the soil solution.

While absolute retention of elements in the vegetation and soil is based on gross estimates of physical parameters, relative retention of the elements can be discussed without those estimates. For example, comparing the total reserve of Fe, Mn, and Al in the phytomass, soil available, and groundwater reservoirs (Table 47) shows that Mn is retained in phytomass and soil available to a greater degree than Fe and Al. That is, total mass of Fe and Al are both on the order of 5 times larger than total mass of Mn in the groundwater, but are both about 5 times smaller than total mass of Mn in the phytomass and soil available reservoirs. Fe and Al concentrations, on a dry weight basis, are lower in phytomass than in the total soil and bedrock for Ope, Sn, and Db samples (Figs. 30 and 31); while the corresponding Mn concentrations are of a similar range to the soil and bedrock concentrations. However, the soil soluble (SPE) concentrations show a similar relationship to the phytomass concentrations between Mn and both Fe and Al. Fe, Al, and Mn are concentrated by vegetation from the water soluble fraction of the soil in the same relative proportions, but Mn is retained in the phytomass more efficiently than Fe and Al.

To help identify relative changes in composition among the reservoirs, elemental concentrations are normalized to Cl, which is assumed to be a conservative tracer (Fig. 32). That is, Cl is not involved in biological processes and is very soluble in water. Thus, there is no significant mechanism that would preferentially remove Cl from the system. The concentration of other elements which may be required by biological processes (e.g. K), or may become insoluble under certain conditions in the soil or groundwater (e.g. Al), can be gauged against Cl concentration. This comparison gives clues to the movement of elements in the system. Na is also fairly conservative, and therefore shows only minor enrichment in the soil soluble fraction (SPE) and depletion in the phytomass relative to surface, ground, and rain waters, which differ very little from each other. K is more active than Na, showing enrichment in the phytomass relative to all other reservoirs. Surface water is depleted in K relative to rain water as it is in constant contact with soils, and therefore subject to ion exchange and uptake for biological requirements in both the soil and vegetation. This fits with the conceptual model of the soil and vegetation acting as a filter, preferentially retaining elements that are supplied by the bedrock and atmosphere via the circulating water (Fig. 18). Groundwater plots closer to rain water as it has more time and higher temperatures in which to accumulate K, than does surface water. With Ca, and to a lesser extent Mg, the trend reverses, with phytomass being relatively less enriched and the SPE slightly more enriched. Ground water plots above both rain and surface water for Ca. While K, Ca, and Mg are all retained in the soil and vegetation to some extent, K seems to be retained in the vegetation more efficiently than Ca, with Mg somewhere in between, which could reflect their relative biological importance.

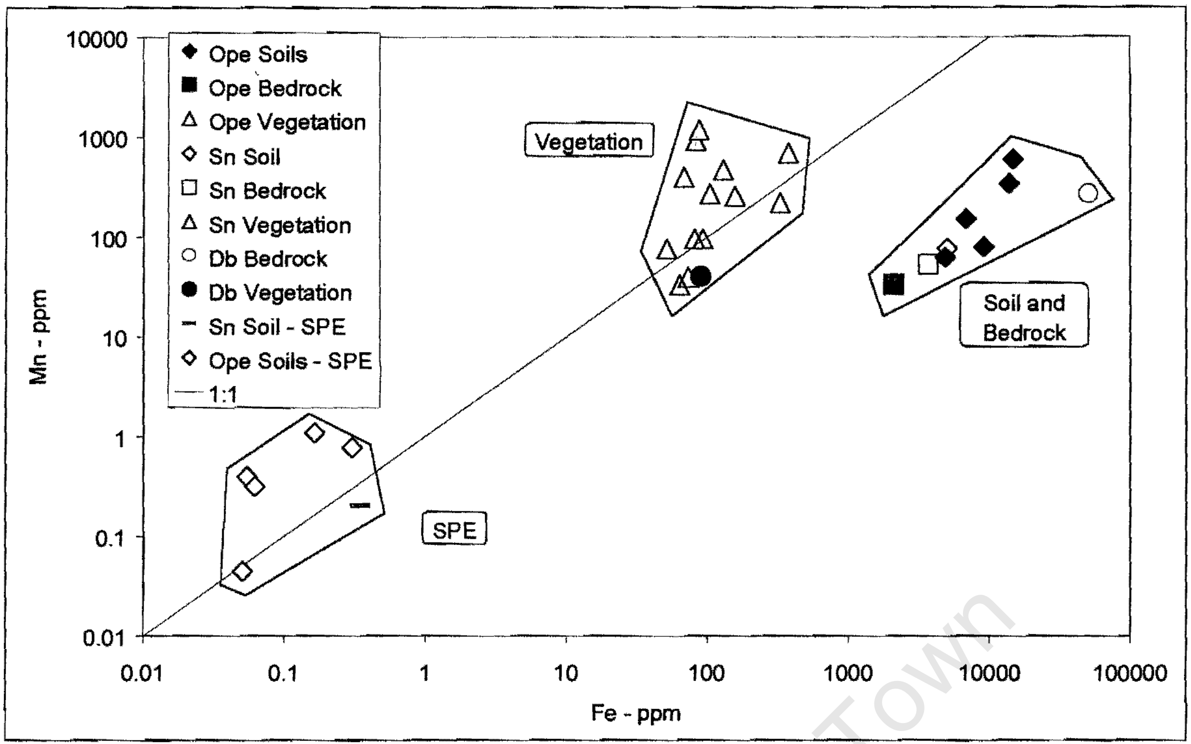

Figure 30: Mn vs Fe for all soil, bedrock, and vegetation samples. Ope - Peninsula Formation, Sn - Nardouw Sub-Group, Db - Bokkeveld Series.

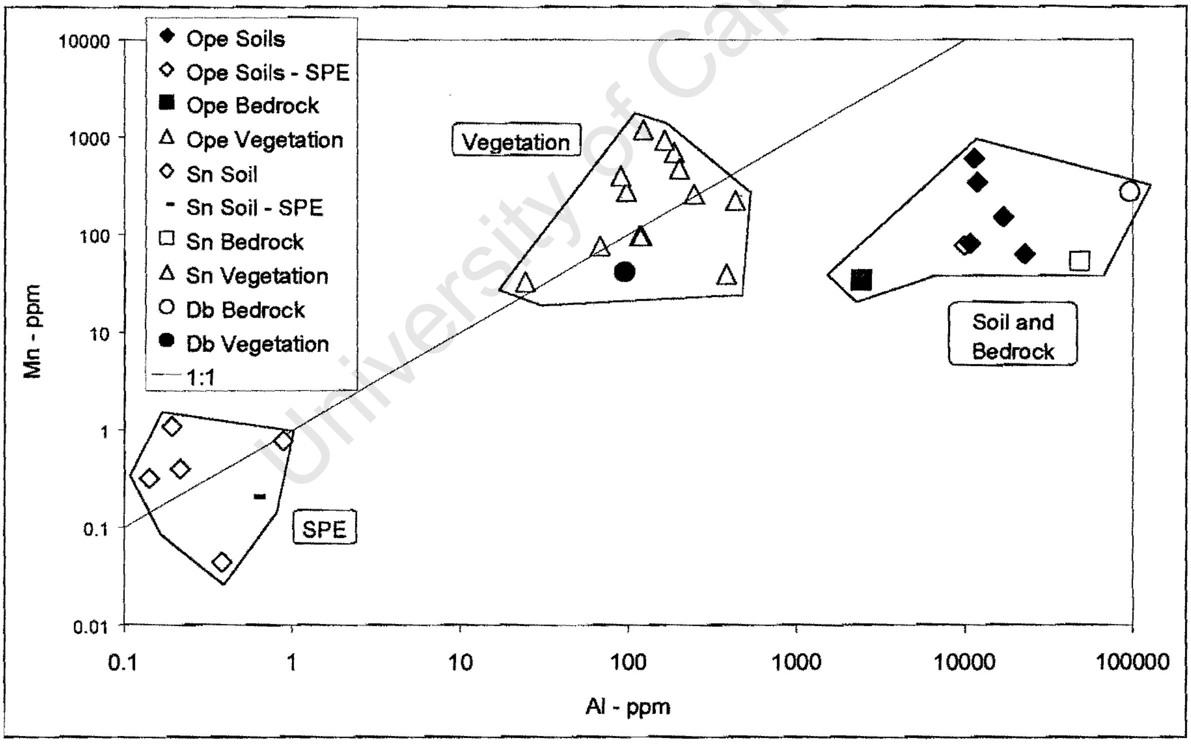

Figure 31: Mn vs. Al for all soil, bedrock, and vegetation samples. Ope - Peninsula Formation, Sn - Nardouw Sub-Group, Db - Bokkeveld Series.

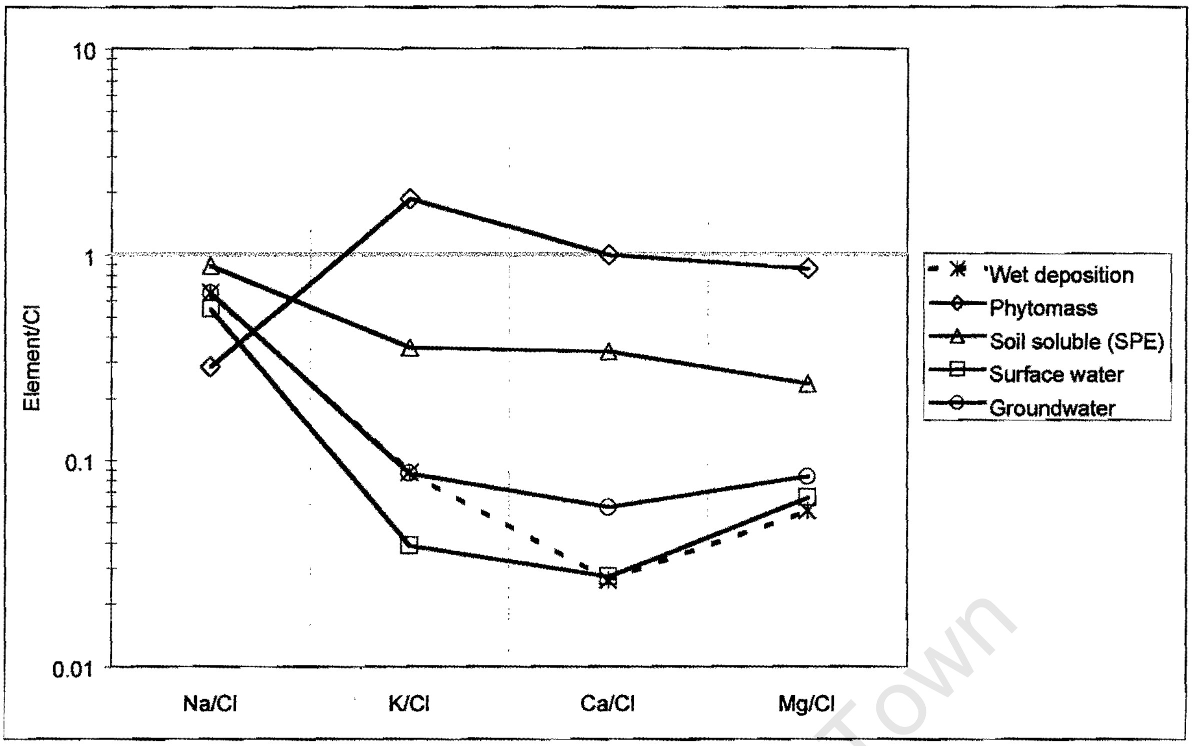

Figure 32: Concentrations normalized to Cl on a mass basis for the ecosystem reservoirs. The "Bedrock", "Soil Total", and "Soil exchangeable" reservoirs are excluded as no estimate of total Cl could be made.

4.5.3 *Accumulation time calculation*

Accumulation time for a particular element is calculated from reservoir size and net change over a given time period for that element. If C is the concentration of an element on a mass basis, and M the reservoir mass on a spatial basis (e.g. kg/ha), accumulation time, T, is given by:

$T = C^*M/(Cout-Cin)$
with, T in years
C in (kg of element)/(kg of reservoir material on a dry weight basis)
M in kg/ha
Cin,out in kg/ha/yr

In this project the only input and output values are for the entire headwater catchment system -- Cin is the atmospheric deposition, and Cout is the surface water flow from the catchment (EK6). Thus, the only accumulation time that can be calculated is that for the entire system, not individual reservoirs. As mentioned above, ground water is assumed to be at steady state. That is, the concentration of a given element in the ground water that enters the soil and bedrock underlying the Elandskloof catchment is assumed to be equal to the concentration in the waters that exit the system in the subsurface.

Using this method for the elements considered, Na, Cl, K, Ca, Mg, Fe, Mn, and Al are accumulating, and Si is being lost from the system (Table 47). The accumulating elements are likely to be accumulating in all of the reservoirs except bedrock and, for some elements, the bound fraction of the soil. That is, in fynbos soils, Na, Cl, K, Ca, and Mg are stored primarily in the available (exchangeable + soluble) fraction, while Fe, Mn, and Al can accumulate in the bound portion of the soil in addition to the available fraction, depending on pH and redox conditions.

The mean accumulation times (Table 49) for the accumulating elements show that Na and Cl are cycled through the system the fastest (about 300 yrs), followed by Ca and Mg (830 yrs), K (2,800 yrs), Mn (83,000 yrs), Fe (560,000 yrs), and Al (2,200,000 yrs). Na and Cl are generally not essential for biological processes, leading to their relatively short accumulation times. Ca, Mg, and K have longer accumulation times as they are biologically essential and adsorbed by the soil/vegetation efficiently, with K being retained preferentially among the three. Mn, Fe, and Al are strongly retained by the soil, with Mn cycling fastest, which can also be seen in its higher concentrations in the SPE and phytomass. Interestingly, the Mn concentration in the surface water is an order of magnitude lower than that of Al and Fe. The Si value is negative to indicate that it is being lost from the system, and the large value (2,100,000) shows that the removal rate (1.9 kg/ha/yr) is very small relative to the very large reservoir of Si in the soil (3,900,000 kg/ha), which reflects the slow rate of quartz weathering.

Table 49: Mean accumulation time in the system and relative sizes[a] of the soil, ground water, and phytomass reservoirs.

	Mean accumulation time[b] (years)	Accumulating fraction[c]		
		Soil[d]	Ground water	Phytomass
Na	330	21%	79%	0.089%
Cl	270	1.5%	98%	0.25%
K	2800	97%	2.5%	0.14%
Ca	900	89%	11%	0.48%
Mg	760	57%	42%	1.1%
Fe	560000	100%	0.0071%	0.0013%
Mn	83000	100%	0.055%	0.12%
Al	2200000	100%	0.010%	0.0017%
Si	-2100000[e]	100%	0.11%	0.000010%

a – Percentage of the sum of soil, ground water, and phytomass for a given element.

b – $\frac{\sum(phytomass, soil, waters)}{Input - Output}$**, with phytomass, soil, and waters in kg/ha; and input and output in kg/ha/yr ("Net Change" in Table 46)**

c – On a kg/ha basis, the bedrock and surface water are the largest and smallest reservoirs, respectively, for all elements considered.

d – The exchangeable concentration is used for Na, Ca, and Mg; the total concentration is used for K, Fe, Mn, Al, and Si; and the soluble concentration is used for Cl.

e – The negative sign reflects that Si is being lost from the system. The 'residence time' value can be considered the number of years it would take to remove all of the Si from the phytomass, soil, and waters.

4.5.4 *Changes in the reservoirs over time*

Each ecosystem reservoir has changes in its chemical composition over time. Some changes are seasonal, due mainly to changing amounts of rainfall, and some changes occur on longer time scales. An example of seasonal changes in chemical composition is that of soluble elements in the soil. The lack of rain in the summer months, and more specifically the dominance of evapotranspiration, allows for the accumulation of soluble salts in the soils. In winter salts are washed out of the soils. It is a bit more complicated since, even in summer, many mountain areas receive considerable moisture from morning mist, possibly reducing the accumulation. There is a hint of seasonality in the SPE data because six samples (EK5, EK6, BK1, BK2a&b, and BJ2) were collected at the end of the summer (May 2001), and one sample (NR) was collected towards the end of winter (August 2001). The NR soil would normally be expected to have higher salt concentrations than soils derived from Peninsula Formation sandstones due to more impurities in the parent material. However, the SPE data show the reverse. Salt concentrations in the soils derived from Peninsula Formation sandstones are higher than the NR soil, suggesting that seasonal flushing could be affecting the chemical composition of the soil reservoir.

The most dramatic non-seasonal change is from periodic fires that occur about every 12-20 years. Fire would remove large amounts of the elements retained in vegetation and some from the soils through volatilization in the smoke, and removal of the ash by wind and surface runoff. The effects of fire on elemental budgets in mountain fynbos was studied in Swartboskloof, a mountain fynbos catchment west of Stellenbosch (van Wyk *et al.*, 1992). It was found that the catchment lost significant amounts of all elements determined due to fire (Table 50). Over the long term, the effect of fire would probably even out as one catchment will receive output from another. However, these catchments will never be at equilibrium with respect to vegetation, always building up biomass for the next fire, which is an interesting aspect of fire-dependent systems. This also emphasizes the importance of the soil reservoir, which is very large compared to the phytomass and its size is not significantly effected by fires.

Table 50: Accumulation or loss of elements (kg/ha/yr) with and without fire in a mountain fynbos catchment (van Wyk *et al.*, 1992).

Species	Net gain/loss without fire	Net gain/loss with fire
K^+	- 0.776	- 3.675
Ca^{2+}	+ 4.811	+ 2.163
Mg^{2+}	- 1.753	- 2.510
Total P	+ 0.970	+ 0.638
Total N	+ 3.407	- 2.927

4.5.5 *Potential human impacts on fynbos ecosystems*

Modern humans increase pressures on every ecosystem they interact with. They alter the natural workings of an ecosystem by changing the vegetation and use of the land, and adding chemicals to the system either directly or indirectly. Examples of direct addition of chemicals to an ecosystem include the disposal of waste, the use of fertilizers on the soil and insecticides on the vegetation and soil, and release of chemicals into the atmosphere. The most significant anthropogenic additions of chemicals to an ecosystem through the atmosphere are from industrial, automobile, and household combustion of hydrocarbons. Indirect addition of chemicals includes the accumulation of salts in the soil from irrigation.

The Western Cape of South Africa industrial, automobile, and household exhausts all contribute to atmospheric pollution in the region. Currently the pollution levels are low outside of the greater Cape Town area, which is the largest city and the industrial base of the region. South Africa's energy is derived from coal combustion, which is most intense in the Gauteng Province, 1500 km from Cape Town. In Gauteng industrial pollution adds significant amounts of NO_x to the atmosphere, which can transform into HNO_3 in the rain water, leading to acid rain (Heaton, 1987; Zunckel, 1999). The other main component of acid rain globally is H_2SO_4, which is also important for South Africa, though less significant than in other parts of the world as South Africa's coal has a low S content. Increasing population forces the energy industry to expand, potentially increasing the problems of local air pollution in the Western Cape.

Industry-induced acid rain could have a pH of less than 4.0 (e.g Berner and Berner, 1996, p. 129). If this low pH fell on a fynbos ecosystem the primary effect would be the increased dissolution of elements from the soil and removal in surface or ground water, including all of the elements considered in the ecosystem reservoirs above. This would decrease the nutrients available to the vegetation, disrupting the physiological mechanisms developed specifically for the TMG sandstone soils. The effects of this disruption are unknown, but could include an increased invasion of plant species that can deal with the decreased nutrient status by tapping further into the soils with root systems that are more extensive than those of fynbos. However, fynbos vegetation is particularly adapted to low nutrient, acidic soils, so it is possible that some species could adapt to the new conditions. Another consideration with fynbos is its high biodiversity, which increases the possibility of there being species that can survive when conditions change.

Fynbos soils are naturally acidic, and the surface water that has filtered through them can reach a pH of 4 (e.g. Campbell, 1985), but this low pH is due to the presence of organic acids, which are much weaker than the nitric and sulfuric acid of acid rain. The weaker organic acids could potentially take up H^+ introduced from the strong acids, buffering the pH to an extent. This theory has been tested in other parts of the world susceptible to the effects of acid rain, and it was found that organic acids add minimal buffering capacity, and fail to significantly abate the drop in pH from the addition of strong acids (Hruska *et al.*, 1997; Mattsson *et al.*, 1995; Roila *et al.*, 1994). Hruska *et al.* added H_2SO_4 and $NaHCO_3$ separately to an organic rich (DOC 48.9 mg/l, total organic acids 344 μeq/L, dissociated organic acids 174 μeq/L) stream, and found that about 80% of the additions remained unbuffered. The streams in the present study have a maximum DOC of around 3.0 mg/L, though other fynbos streams have DOC values greater than 10 mg/L (A. Smit, pers. comm., 2002; Koch, 1994). The chemical structure of humic and fulvic acids is not understood completely, but they can contain multiple phenolic (OH) and carboxylic (COOH) functional groups, particularly humic acids, which could complicate their behavior on the addition of H^+ to the system (vanLoon and Duffy, 2000; Schlesinger, 1997). The character of the dissolved organic matter in fynbos streams is not well studied, but it is unlikely that they would be able to buffer significant additions of strong acid.

The other main concern regarding the addition of chemicals to the systems is commercial agriculture's use of irrigation, fertilizers and pesticides. Irrigation can lead to salinization of the soil and groundwater, making the land infertile. This is a general problem in South Africa's semi-arid agricultural areas (Hoffman and Ashwell, 2001). Fertilizers upset the balance of any system by providing an excess of nutrients, leading to eutrophication. When the overgrowth of aquatic vegetation from eutrophication dies, the high demand for oxygen in the decomposition process deprives the rest of the aquatic ecosystem of oxygen. Pesticides include many substances that do not degrade under natural conditions, and can accumulate in vegetation to the point of becoming toxic to plants and animals.

Data from the lower Olifants River show increases in pH and all major ions (OL1, OL3, and OL2; Table 8). This is difficult to interpret as various controlling mechanisms are involved. Evaporation of river water and irrigation both concentrate the major ions, and it is therefore difficult to separate the two mechanisms. Comparing the Clanwilliam Dam sample (OL3) with the Citrusdal sample (OL1), Cl^- shows a 3-fold increase downstream, with more than a 4-fold increase for Ca^{2+}, and less than 3-fold for the other major ions. From Citrusdal to Clanwilliam the pH increases from 5.2 to 6.2 (Table 7). Further downstream at Trawal (OL2), pH increases to 7.5. In addition, Cl^- increases another 6-fold from Clanwilliam, with more than 10-fold increases in SO_4^{2-}, Ca^{2+}, K^+, and

ANC. Between Clanwilliam and Trawal is a canalized irrigation system to feed the wine and citrus farms. The OL2 sample is near the confluence with the Doring River, which drains a completely different geology than the Upper Olifants. Thus, this sample may be influenced by mixing with the Doring River water, which complicates the interpretation of its chemistry. The data do not show major increases in nitrate and phosphate concentrations, which would indicate influence from fertilizer application. However, increases in major ions relative to the conservative Cl^- increases indicate some possible impact of agriculture on the water quality.

It could be argued that the remaining fynbos ecosystems are in the mountains and protected areas, far upstream of the threats of irrigation, eutrophication, and pesticides. However, while the threat of water quality degradation is primarily in the lower Olifants, the pristine headwaters and the agricultural valleys are part of the same ecosystem. Problems in the valley will eventually cause problems in the headwaters.

5 Conclusion

In this project, some interesting chemical characteristics are determined for various components of the fynbos ecosystem in a sub-catchment of the Olifants River around Citrusdal. These components include atmospheric inputs, as well as the surface water, ground water, vegetation, soil, and bedrock chemical reservoirs. The analyses of these components are combined to look at the organization of elements in the ecosystem. As a synthesis, the main findings from each part of the project are summarized below.

The atmosphere supplies the ecosystem with elements through both wet and dry deposition. The wet deposition (rain water) collected both in Citrusdal and Cape Town is found to have originated as seawater, with the major ions being Na^+ and Cl^-. Relative to Cl^-, the rain water has more Ca^{2+}, K^+, and SO_4^{2-} than seawater. This is due to the dissolution of atmospheric particles and gases into the rain water through the processes of washout and rainout. The particles and gases are derived from both the land and sea. Those from the land include wind-blown dust, which carries clay minerals into the fynbos ecosystem. Mountain fynbos vegetation grows mainly on the sandstone formations of the Table Mountain Group, which have very low nutrient content to support vegetation, especially the quartz arenite Peninsula Formation. Thus, additions of clay minerals bring essential elements such as Al and K to the ecosystem.

Fynbos species are well-adapted to low-nutrient soils, but they do need some nutrients to survive. The benefit of wind-blown nutrient additions to fynbos ecosystems requires a dry region with higher nutrient content soils from which soil particles can be picked up and transported by the wind. The fynbos has this in the semi-arid Karoo to the northwest, but the future of this dust-source is unclear as global climate change is predicted to make some regions around the world drier and some wetter than they are today. Changes to the climate of southwestern South Africa could increase or decrease the wind-blown nutrient supply of fynbos, both of which could upset the balance of the ecosystem.

The soil is a crucial link in supplying the fynbos with nutrients. It preferentially retains elements from the cycling water that are necessary for biological processes through adsorption mainly to clay particles and organic matter. The sources for the elements in the water are atmospheric deposition and the weathering of bedrock. The soils derived from Peninsula Formation sandstone have a higher concentration of Al and Fe than their parent material, and the soil derived from Nardouw Sub-group (Rietvlei Formation) has a lower concentration of Al, Fe, and K than in the parent material. This indicates that the soils retain the elements they need to support the vegetation, and release the remainder.

The elements are then taken up and concentrated by vegetation from bioavailable forms (soluble and exchangeable) in the soil. In particular, K and Ca are concentrated as minor nutrients in fynbos. Also, Mn is taken up preferentially in the vegetation relative to the other minor nutrients of similar concentration, Fe and Al. Changes in atmospheric input due to land-use changes and increasing population could affect which elements are available in the soil for uptake by plants.

In the Elandskloof headwater sub-catchment, on a spatial basis, bedrock is the largest chemical reservoir for the elements considered (Na, Cl, K, Ca, Mg, Fe, Mn, Al, and Si) due to the great depth of the Peninsula Formation (~1000 m). However, only a very small portion of the bedrock is chemically connected to the ecosystem above via the ground water. Soil is the next largest reservoir, except for Na and Cl, for which ground water holds the greatest mass. Groundwater is followed by phytomass, and by far the smallest chemical reservoir in the ecosystem is surface water. When the periodic fires strike an ecosystem, it is important that the soil is such a large reservoir, as it remains relatively unaffected compared to the phytomass reservoir. The input to Elandskloof catchment from atmospheric deposition is larger than the output in surface water for all elements listed above except Si. With these input and output rates, the time it would take to accumulate elements in the vegetation, soil, and ground water reservoirs is about 300 yrs for Na and Cl, 800 yrs for Mg and Ca, 2800 yrs for K, 83,000 yrs for Mn, 560,000 yrs for Fe, and 2,200,000 yrs for Al. It would take about 2,100,000 yrs to completely deplete these reservoirs of Si.

Overall, this project gives a broad look at the geochemistry of fynbos. It is hoped that work from this project will spark further research into the chemical dynamics of fynbos ecosystems. The sources of wind-blown dust and the bioavailability of certain elements are of particular interest as they both may change with changes in climate and human influence in the region.

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Appendix A – Analytical Equipment Specifications

Ion Chromatograph

Anion column
  Sample loop: 50 uL
  Separator column: AS14 (4 mm)
  Guard column: AG14 (4mm)
  Eluant: 2.4 mM Na_2CO_3 + 1 mM $NaHO_3$
  Eluant flow rate: 1.2 mL/min
  Suppressor: ASRS-I-4mm
Cation column
  Sample loop: 25 uL
  Separator column: CS12 (4 mm)
  Guard column: CG12 (4mm)
  Eluant: 2.2 N H_2SO_4
  Eluant flow rate: 1.0 mL/min
  Suppressor: CSRS-ULTRA-4mm

Inductively Coupled Plasma Mass Spectrometer

Perkin Elmer / Sciex Elan 6000 inductively coupled plasma mass spectrometer
acid-resistant cross flow nebuliser
RytonTM Scott-type spraychamber and a
Perkin Elmer AS 90 autosampler.

The ICP-MS facility in the University of Cape Town's Department of Geological Sciences was used for the analyses presented. The following is taken from the ICP-MS facility's website (http://www.uct.ac.za/depts/geolsci/icpms/home/home.html):

> The centrepiece of the laboratory is a Perkin Elmer / Sciex Elan 6000 inductively coupled plasma mass spectrometer equipped with a acid-resistant cross flow nebuliser, a RytonTM Scott-type spraychamber and a Perkin Elmer AS 90 autosampler. For the analysis of solid samples, the Elan 6000 can be connected to a Cetac LSX-200 laser ablation module that uses a frequency-quadrupled Nd-YAG laser (266 nm wavelength radiation) and is equipped with a 54mm i.d. sample chamber, a ccd colour video camera and a colour monitor.

The facility incorporates a chemical lab where samples are dissolved by acid digestion and a sample preparation lab where samples are weighed out on a Mettler Toledo AG245 balance, standard solutions are made and samples are diluted for analysis. The facility has access to high purity Milli-Q water as well as high purity bottle-distilled acids through the Department of Geology's Radiogenic Isotope Facility. A variety of additional sample preparation facilities (e.g. mechanical splitter, chaw crusher, Sieb mills, furnaces, drying ovens, powder briquette press, fusion disk apparatus, thin section preparation) and analytical equipment (e.g. EMP, XRFS, TIMS, XRD, HPIC) are available in the department.

Atomic Absorption Spectrometer

Department of Chemical Engineering, UCT
Contact Helen Divey, 021-650-2378

X-Ray Diffractrometer

Manufacturer: Philips Analytical
Control unit: PW3710
Goniometer: PW1050 (Coupled Omega)
Generator: PW1830/00
Generator tension: 40 kV
Generator current: 25 mA
Divergence slit: Autom. Div. Slit 12 mm
Software: X'Pert Software for X-Ray Diffraction, v.1.2a 26Aug1999

Scales

SCALTEC SPO52
Denver Instruments Model 400

Appendix B - Charge Balance Error and Organic Acids

A useful calculation in determining the accuracy and completeness of water analyses is charge balance error (CBE), which is based on the principle that all waters must be electrically neutral. That is, the number of positive charges must equal the number of negative charges, and CBE is a widely accepted way to present deviation from the electroneutrality condition in water analyses (Freeze and Cherry, 1979).

$$CBE = \frac{\sum cations - \sum anions}{\sum cations + \sum anions} \times 100$$

With anions and cations in moles of charge per litre (e.g. μeq/L)

This deviation could be caused by two types of errors:

Type 1 – Bias in the analytical procedure

Type 2 – Ions not included in the calculation

Type 1 errors can be evaluated through an analysis of the systematic and random errors in the procedure, or through independent analysis of the water sample. Type 2 errors can be identified through multiple analyses of similar samples where Type 1 errors have been quantified.

An example of a Type 2 error is seen in the saturated paste extracts (SPE's) of the soil samples (Table 20). The large positive CBE's on the SPE's of all soil samples indicates that some constituent was not measured. This is alkalinity. In soils alkalinity can be a major contributor to the soil solution anions because of the high $CO_{2(g)}$ concentration (Schwab, 2000). Alkalinity is, therefore, an essential component to measure if one wants to study the acid-base relationships in the soil solution.

Freeze and Cherry warn that the CBE can be deceptive for determining the accuracy of a procedure, as random errors in the analysis could by chance result in a low charge balance error, falsely indicating accurate results. But Fritz (1994) points out that if an analysis consistently shows low CBE values for a number of samples, the potential deceptiveness of CBE diminishes. The implication is that CBE can be misleading for individual analyses, but, for a set of similar samples that have been analyzed by the same procedure, the average CBE should give a good indication of the overall bias of the procedure.

For interpretations of an average CBE that involve estimating the presence of unmeasured constituents, the requirement that samples are similar in composition is critical. For example, if water samples are analyzed by Ion Chromatography vary significantly in DOC content, then those samples with high DOC are likely to have a larger positive CBE from the presence of unmeasured weak acid anions. If the measurements are accurate and precise, the average CBE would be positive. If the measurements overestimate the cations, the average CBE would also be positive. Thus, to answer questions about a charge balance error indicating unmeasured cations or anions, the procedure must be verified independently of the charge balance and CBE for the individual sample must be considered. If a procedure is determined independently to be accurate, the CBE can indicate that some combination of anions or cations not included in the analysis may be present in the solution.

Three methods for estimating weak acid contributions to charge balance error are dissolved organic carbon, comparison of the titration curve to that of a theoretical solution, and Gran interpretations from the same titration curve. For natural waters containing large amounts of dissolved organic matter, Glover and Webb (1979) describe a procedure in which organic carbon content can be used to estimate weak acids assuming that the majority of weak acid activity is from humic and fulvic acids. They use the acidity of humic and fulvic acids (Schnitzer & Khan, 1972) to give an estimate of 40 µeq/l weak acids from 2 mg/l organic carbon, giving the formula:

$$WeakAcids[\mu eq / L] = 20 \times DOC[mg / L]$$

Oliver *et al.* (1983) go further by isolating humic and fulvic acids and relating their carboxyl group content to DOC. This allows the organic acid concentration in highly colored waters to be estimated.

$$OrganicAcids[\mu eq / L] = 10 \times DOC[mg / L]$$

This is an empirical formula based on the isolation and analysis of the fulvic and humic acids of 8 rivers and streams, 4 lakes, 5 wetlands, and 2 groundwaters of the USA and Canada. The procedure differs from that of Glover and Webb (1979) in that it specifically relates the active carboxyl groups of humic and fulvic acids to DOC, rather than the sum of weak acids. Hence, the factor of two difference in their estimation of weak and organic acids by the two methods.

Oliver's model has been widely used as a starting point for further research. For example, Hemond (1990) reviews and criticizes the various definitions of alkalinity. A new definition, CBALK, is defined from the charge balance in order to be "unambiguously defined and conservative with respect to both CO2 and organic acid addition." Titration alkalinity is left with the term Acid Neutralizing Capacity. A relationship is described between CBALK, Gran ANC and OrgT (Total Organic Carbon) as follows:

$$CBALK = GranANC + 4.6 \times OrgT$$

This is based on the model of Oliver *et al.* (1983). It is used to create a graphical method for the relationship between CBALK, pH, and organic acid concentration.

Another possibility for estimating organic acids is through the evaluation of acidimetric and alkalimetric titration curves. The USGS "Web-based Alkalinity Calculator" (USGS and Rounds (2001) provides Gran Function, Inflection Point, End-point, and Theoretical Carbonate interpretations of potentiometric acid titration data via a web-page submission program. For each of the interpretations it also tests whether or not the titration curve matches with the theoretical curve based on a simple carbonate system at the sample's temperature and pH. If the titration data does not fit this curve well the program returns a "mean titrant volume error" (MTVE). The MTVE is assumed to represent a measure of non-carbonate alkalinity in the sample. This does not, however, seem to show a correlation with CBE for the 10 water samples of the current study that showed deviation from the theoretical curve. Of 30 samples analyzed, the 10 that showed deviant titration curves had either positive or neutral CBE's.

Checking the accuracy of a procedure

Charge balance error on the water samples (Table 8) highlights the difficulty of accurate measurements at low concentrations, as the largest errors generally occur on the samples with the lowest ionic strength. There are, however, different views on this issue. Tchobanoglous and Schroeder (1985) present a way of checking the accuracy of a water analysis based on empirical data on the standard deviations of anions and cations at various concentrations. Using units of meq/L, the accuracy of the analysis is said to be "within the allowable limits" if the following condition is satisfied.

$$\left|\sum anions - \sum cations\right| \le 1.065 + 0.0155 \times \sum anions$$

Fritz (1994) presents 68 published (6 relevant journals from v1 to Jan1993) charge balance analyses and assesses their relative precision. Of the 68 summarized analyses compiled by Fritz, 34 pass this test based on mean CBE. Of the 31 individual samples in the present study, 29 pass the test (Fig. 33). It's possible that this test is not valid for Fritz's values for anions and cations, which are mean values derived from as few as 2 and as many as 56 individual samples.

There does not seem to be any correlation between the result of Tchobanoglous and Schroeder's test condition and ionic strength for Fritz's analyses. That is, the difference between the left and right sides of the test inequality shows a correlation coefficient (r) of -0.03 when compared with average ionic strength.

The US EPA Standard Methods (APHA, 1995) lists 6 procedures for measuring the "correctness" of analysis (section 1030 F). The most commonly used is the charge balance. But, as Fritz points out, the full analyses required for a charge balance are often either not performed or not presented. In the case of missing data, other checks using TDS and EC relationships can be used as an estimate of correctness.

For charge balance error, the Standard Methods use the same definition as Freeze and Cherry described above. But their interpretation of the results uses different criteria than Tchobanoglous and Schroeder (Table 51).

Table 51: Criteria for CBE interpretation (APHA, 1995).

Maximum Acceptable CBE (%)	Sum of the anions used to calculate CBE (meq/L)
0.2	Less than 3.0
2	Between 3.0 and 10.0
5	Greater than 10.0

These criteria make it more difficult to perform a "correct" analysis for samples that have a lower concentration of ions. It's also true that it is harder to measure the cations and anions in low ionic strength samples. So it is very difficult to create an acceptable charge balance for dilute samples. In the present study, 29 of the 31 water samples fail this test (Fig. 34). This approach is in contrast to that reported by Tchobanoglous and Schroeder, which is an empirical relationship that must be based on the theory that the analyses used to develop the criteria represent the best estimates of the various constituents at a given ionic strength.

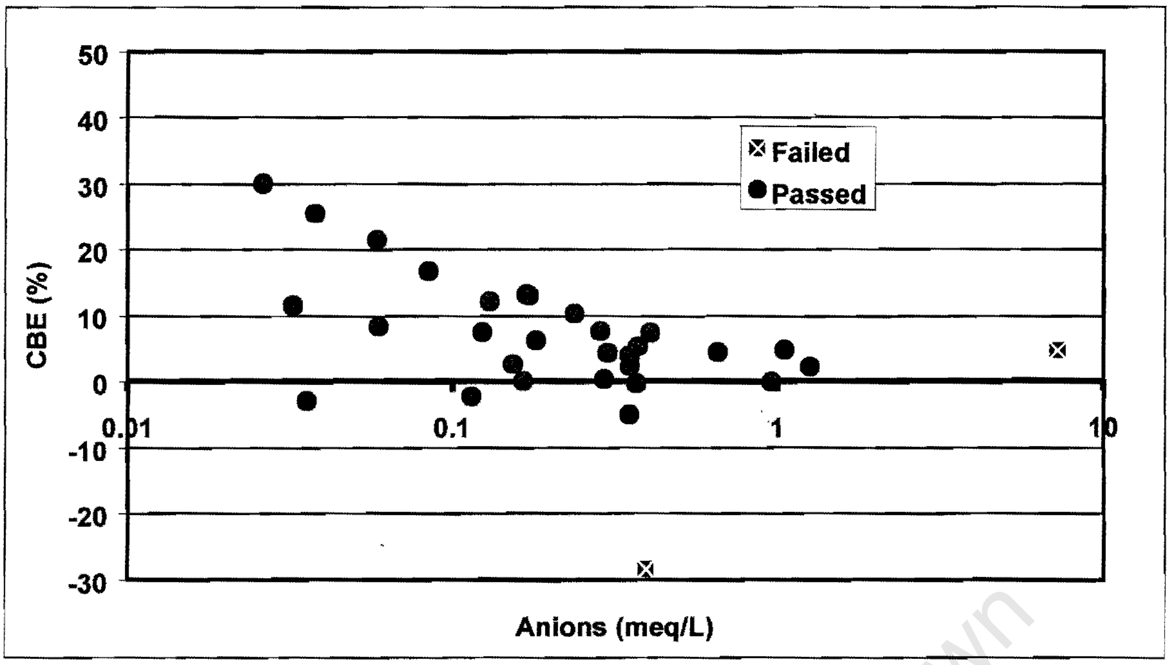

Figure 33: CBE vs. Total Anions for 31 water samples of the present study. Empirical criterion for validity of a sample's analyses from Tchobanoglous and Schroeder (1985).

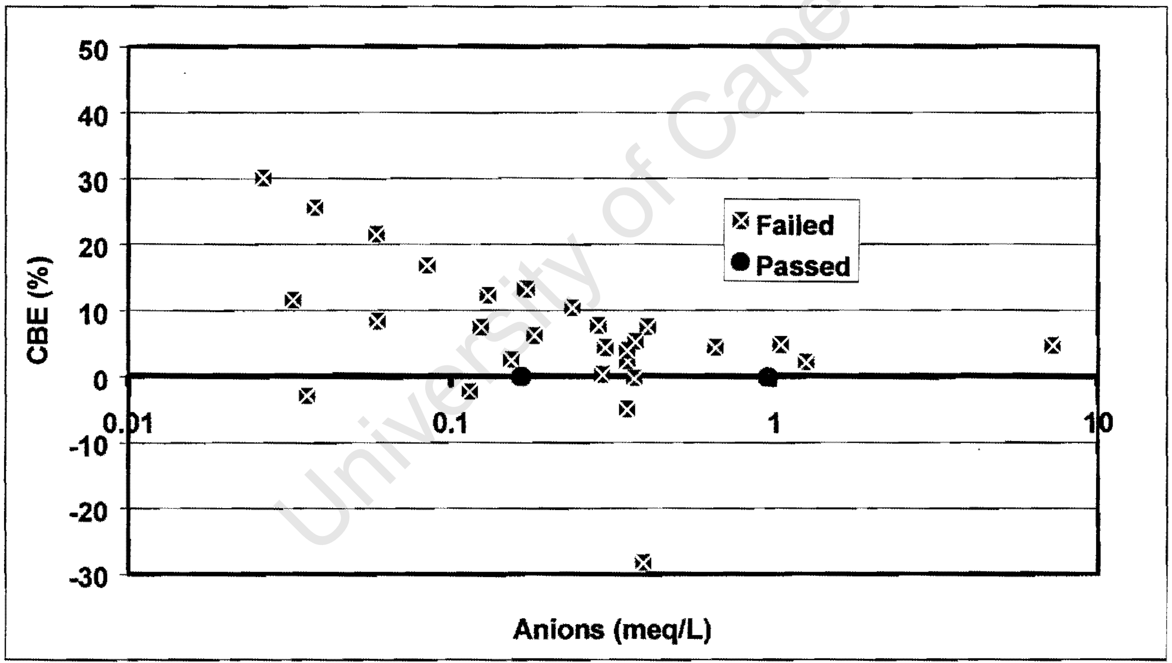

Figure 34: CBE vs Total Anions for 31 water samples of this study. CBE criterion from Standard Methods (APHA, 1995).

Appendix C – PHREEQC Data

BK2a Output

```
---------------------------Phase assemblage---------------------------

                                    Moles in assemblage
          Phase            SI log IAP  log KT   Initial      Final      Delta
          CO2(g)         -2.00  -20.16  -18.16  1.000e+01  9.998e+00 -1.921e-03

-------------------------Solution composition-------------------------
          Elements          Molality      Moles

          Amm             1.501e-04   1.501e-04
          C             1.921e-03   1.921e-03
          Ca             1.049e-03   1.049e-03
          Cl            7.650e-03   7.650e-03
          Cu             8.505e-07   8.505e-07
          F             1.580e-04   1.580e-04
          Fe             4.068e-06   4.068e-06
          K             8.190e-04   8.190e-04
          Mg             1.317e-03   1.317e-03
          Mn             3.024e-05   3.024e-05
          N             1.022e-02   1.022e-02
          Na             7.488e-03   7.488e-03
          S             9.897e-04   9.897e-04
          Si            1.782e-04   1.782e-04
          Sr            2.901e-06   2.901e-06
          Zn             2.036e-06   2.036e-06

-----------------------Description of solution-----------------------

                                  pH  =   6.908     Charge balance
                                  pe  =  12.695     Adjusted to redox equilibrium
                      Activity of water  =   0.999
                        Ionic strength  =   1.938e-02
                     Mass of water (kg)  =   1.000e+00
                 Total alkalinity (eq/kg)  =   1.536e-03
                     Total CO2 (mol/kg)  =   1.921e-03
                    Temperature (deg C)  =  20.000
                 Electrical balance (eq)  =  -6.733e-03
Percent error, 100*(Cat-|An|)/(Cat+|An|)  = -20.65
                             Iterations  =  23
                               Total H  = 1.110133e+02
                               Total O  = 5.554153e+01

-------------------------Saturation indices-------------------------

          Phase            SI log IAP  log KT

          Amm(g)          -8.29    3.02   11.31  Amm
          Anhydrite       -2.20   -6.54   -4.34  CaSO4
          Aragonite       -1.28   -9.58   -8.31  CaCO3
          Calcite       -1.13   -9.58   -8.45  CaCO3
          Celestite      -2.47   -9.10   -6.62  SrSO4
          CH4(g)       -132.35 -176.99  -44.64  CH4
          Chalcedony       -0.14   -3.75   -3.61  SiO2
```

```
Chrysotile      -8.28   24.55   32.83  Mg3Si2O5(OH)4
CO2(g)          -2.00  -20.16  -18.16  CO2
Dolomite        -2.09  -19.06  -16.97  CaMg(CO3)2
Fe(OH)3(a)        2.21   20.24   18.03  Fe(OH)3
FeS(ppt)      -134.99 -173.30  -38.32  FeS
Fluorite        -0.34  -11.00  -10.66  CaF2
Goethite         8.10   20.25   12.14  FeOOH
Gypsum          -1.96   -6.54   -4.58  CaSO4:2H2O
H2(g)          -39.16  -39.21   -0.05  H2
H2S(g)        -131.54 -173.95  -42.41  H2S
Hausmannite       3.94   66.23   62.29  Mn3O4
Hematite        17.83   40.49   22.66  Fe2O3
Jarosite-K      -0.36   30.25   30.60  KFe3(SO4)2(OH)6
Mackinawite   -134.25 -173.30  -39.05  FeS
Manganite         3.27   28.61   25.34  MnOOH
Melanterite    -14.21  -16.48   -2.27  FeSO4:7H2O
N2(g)            0.03   -3.11   -3.14  N2
O2(g)           -6.50   78.41   84.91  O2
Pyrite        -220.62 -308.04  -87.42  FeS2
Pyrochroite     -6.19    9.01   15.20  Mn(OH)2
Pyrolusite       6.02   48.21   42.19  MnO2:H2O
Quartz           0.29   -3.75   -4.04  SiO2
Rhodochrosite   -0.04  -11.16  -11.11  MnCO3
Sepiolite       -5.77   10.12   15.89  Mg2Si3O7.5OH:3H2O
Sepiolite(d)    -8.54   10.12   18.66  Mg2Si3O7.5OH:3H2O
Siderite        -8.66  -19.52  -10.86  FeCO3
SiO2(a)         -0.99   -3.75   -2.75  SiO2
Smithsonite     -2.42  -12.36   -9.95  ZnCO3
Sphalerite    -120.02 -166.15  -46.12  ZnS
Strontianite    -2.87  -12.14   -9.27  SrCO3
Sulfur         -98.28 -134.74  -36.46  S
Talc            -4.92   17.06   21.98  Mg3Si4O10(OH)2
Willemite       -3.89   11.85   15.75  Zn2SiO4
Zn(OH)2(e)      -3.70    7.80   11.50  Zn(OH)2
```

BK2b Output

```
---------------------------Phase assemblage---------------------------

                                      Moles in assemblage
      Phase         SI log IAP  log KT   Initial      Final      Delta

      CO2(g)      -2.00  -20.16  -18.16  1.000e+01  1.000e+01 -3.979e-04

-------------------------Solution composition-------------------------

      Elements        Molality      Moles

      Amm            8.891e-05   8.891e-05
      C              3.979e-04   3.979e-04
      Ca             7.365e-04   7.365e-04
      Cl             8.634e-03   8.634e-03
      Cu             8.503e-07   8.503e-07
      F              1.264e-04   1.264e-04
      Fe             3.834e-06   3.834e-06
      K              3.224e-04   3.224e-04
      Mg             1.239e-03   1.239e-03
```

```
        Mn              3.406e-06   3.406e-06
        N               6.644e-04   6.644e-04
        Na              6.921e-03   6.921e-03
        S               8.906e-04   8.906e-04
        Si              2.615e-04   2.615e-04
        Sr              2.056e-06   2.056e-06
        Zn              5.036e-06   5.036e-06

----------------------------Description of solution----------------------------

                                       pH  =   4.591      Charge balance
                                       pe  =  15.597      Adjusted to redox equilibrium
                        Activity of water  =   1.000
                           Ionic strength  =   1.364e-02
                       Mass of water (kg)  =   1.000e+00
                 Total alkalinity (eq/kg)  =  -2.838e-05
                       Total CO2 (mol/kg)  =   3.979e-04
                      Temperature (deg C)  =  20.000
                  Electrical balance (eq)  =   1.322e-04
 Percent error, 100*(Cat-|An|)/(Cat+|An|)  =   0.60
                               Iterations  =  16
                                  Total H  = 1.110136e+02
                                  Total O  = 5.551362e+01

------------------------------Saturation indices------------------------------

        Phase               SI log IAP  log KT

        Amm(g)          -10.83    0.48   11.31  Amm
        Anhydrite        -2.33   -6.67   -4.34  CaSO4
        Aragonite        -6.03  -14.34   -8.31  CaCO3
        Calcite          -5.88  -14.34   -8.45  CaCO3
        Celestite        -2.60   -9.22   -6.62  SrSO4
        CH4(g)         -137.04 -181.67  -44.64  CH4
        Chalcedony        0.03   -3.58   -3.61  SiO2
        Chrysotile      -21.83   11.00   32.83  Mg3Si2O5(OH)4
        CO2(g)           -2.00  -20.16  -18.16  CO2
        Dolomite        -11.47  -28.45  -16.97  CaMg(CO3)2
        Fe(OH)3(a)       -0.08   17.95   18.03  Fe(OH)3
        FeS(ppt)       -137.93 -176.24  -38.32  FeS
        Fluorite         -0.68  -11.34  -10.66  CaF2
        Goethite          5.81   17.95   12.14  FeOOH
        Gypsum           -2.09   -6.67   -4.58  CaSO4:2H2O
        H2(g)           -40.33  -40.38   -0.05  H2
        H2S(g)         -131.60 -174.01  -42.41  H2S
        Hausmannite     -11.44   50.85   62.29  Mn3O4
        Hematite         13.24   35.90   22.66  Fe2O3
        Jarosite-K       -0.71   29.90   30.60  KFe3(SO4)2(OH)6
        Mackinawite    -137.20 -176.24  -39.05  FeS
        Manganite        -1.66   23.68   25.34  MnOOH
        Melanterite     -12.47  -14.74   -2.27  FeSO4:7H2O
        N2(g)            -3.40   -6.54   -3.14  N2
        O2(g)            -4.16   80.75   84.91  O2
        Pyrite         -222.45 -309.88  -87.42  FeS2
        Pyrochroite     -11.71    3.49   15.20  Mn(OH)2
        Pyrolusite        1.67   43.87   42.19  MnO2:H2O
        Quartz            0.45   -3.58   -4.04  SiO2
        Rhodochrosite    -5.56  -16.67  -11.11  MnCO3
        Sepiolite       -14.53    1.37   15.89  Mg2Si3O7.5OH:3H2O
```

```
Sepiolite(d)   -17.29    1.37   18.66  Mg2Si3O7.5OH:3H2O
Siderite      -11.54  -22.40  -10.86  FeCO3
SiO2(a)         -0.83   -3.58   -2.75  SiO2
Smithsonite     -6.57  -16.51   -9.95  ZnCO3
Sphalerite    -124.23 -170.36  -46.12  ZnS
Strontianite    -7.62  -16.89   -9.27  SrCO3
Sulfur        -97.17 -133.63  -36.46  S
Talc          -18.14    3.84   21.98  Mg3Si4O10(OH)2
Willemite      -12.02    3.72   15.75  Zn2SiO4
Zn(OH)2(e)                    -7.85            3.65          11.50       Zn(OH)2
```

Appendix D: XRD Data

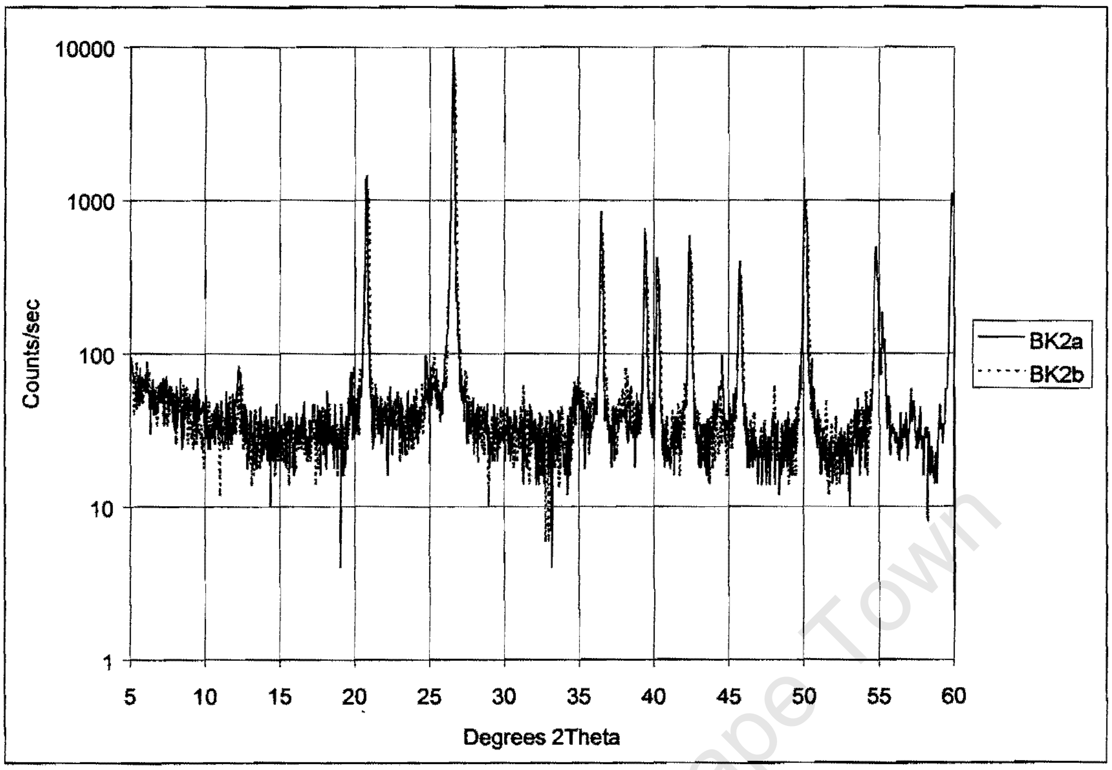

Figure D1: Bulk sample (<2mm) XRD scans

BK2a bulk		BK2b bulk	
deg2Theta	Rel. Int.	deg2Theta	Rel. Int.
12.3106	0	12.3547	0
19.7646	0	19.8891	1
20.7952	14	20.882	17
24.8065	1	25.2796	1
26.5836	100	26.6672	100
34.859	0	34.9284	0
36.4997	7	36.5645	9
39.4258	5	38.1506	0
40.2592	3	39.5033	5
42.4054	5	40.287	4
44.5925	1	42.4635	6
45.7525	3	45.83	4
50.0825	13	48.0361	0
54.8	4	50.146	15
55.3017	1		
57.2098	0		

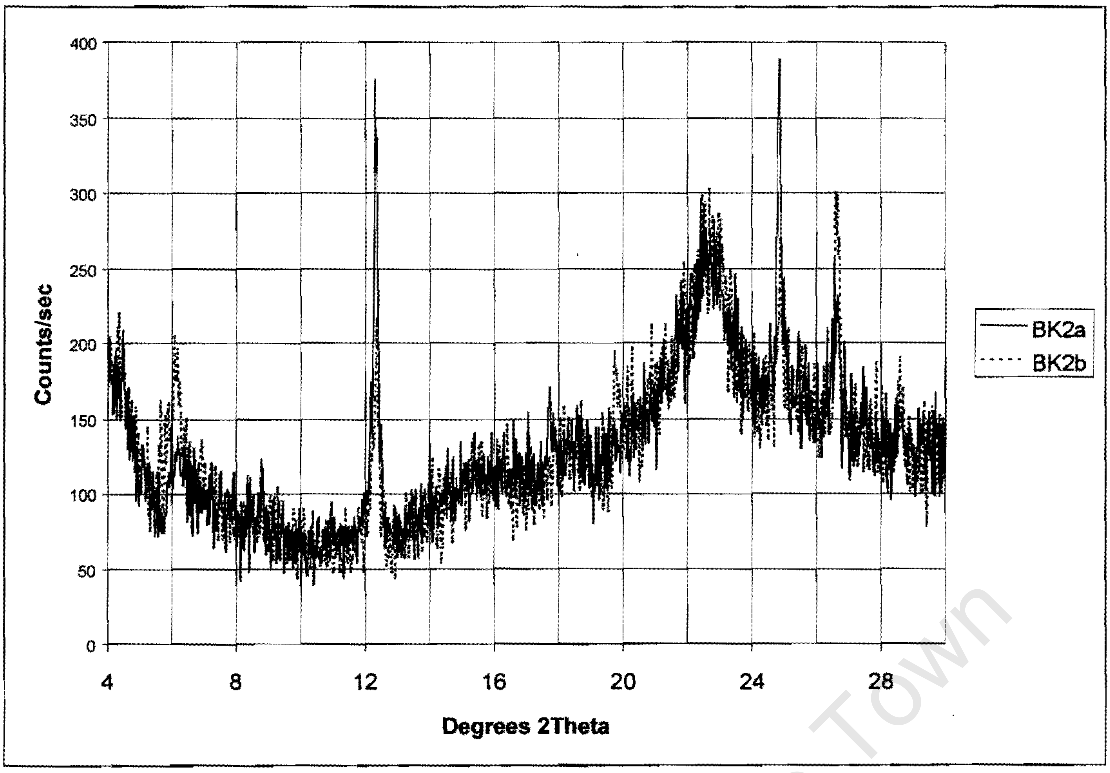

Figure D2: BK2 clay sample (drop by pipette) XRD scans

BK2a clay		BK2b clay	
deg2Theta	Rel. Int.	deg2Theta	Rel. Int.
4.5302	43	4.3776	64
6.0993	22	5.6601	51
8.7671	13	6.1532	65
12.3368	100	12.3531	97
17.7644	13	18.5386	11
21.792	29	19.7429	45
22.5328	49	22.9325	54
24.863	97	24.8628	52
26.6507	36	26.6159	100
28.0808	0	28.5977	20