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The potential for using stable isotopes for solving urban geohydrological problems in the Cape Town area

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Abstract

This thesis investigates the potential for using the stable isotopes of hydrogen and oxygen from surface water and shallow aquifer water in solving urban geohydrological problems in the Cape Town metropolitan region. Three different water groups were chosen for detailed analysis, namely groundwater, springwater and reservoir water destined to join the mains water supply system. The stable isotope composition of groundwater and springwater were assumed to be fairly constant throughout the year, and were thus sampled only once. The reservoir waters were subject to evaporation effects, which result in isotope fractionation. The reservoir waters were sampled at the end of summer (9th April 1996), and near the end of winter (14th August 1996), in order to identify any seasonal isotope variations in the reservoir water isotope values. Reservoir water was sampled before and after the mains water treatment process, to identify any effect water treatment had on the isotope composition of the water. The two effects of water treatment and seasonal variation were determined simultaneously. Chemical analyses (pH, electrical conductivity, alkalinity, major anions and cations) of many of the water samples were performed to investigate the potential for correlating isotope values with chemical concentrations, and for using chemical analyses to complement or supplement isotope studies.

Water treatment was found to be effecting the stable isotope composition of the reservoir waters in an unpredictable manner. Only treated waters therefore should be analyzed, as the isotope composition of the water entering the mains water supply system is of interest in urban hydrology. The stable isotope composition for the reservoir waters were significantly depleted in δD and $\delta^{18}O$ in August (end of the wet winter season) compared to samples taken in April (end of the dry summer season). The range in isotope values for the different water groups were as follows: springwaters δD -18‰ to -9‰ (mean -13‰), $\delta^{18}O$ -4.5‰ to -3.1‰ (mean -3.7‰); groundwaters δD -15‰ to -6‰ (mean -11‰), $\delta^{18}O$ -3.2‰ to -2.5‰ (mean -2.8‰); April treated waters δD -8‰ to +2‰ (mean -5‰), $\delta^{18}O$ -3.1‰ to -1.3‰ (mean -2.0‰) August treated waters δD -24‰ to -11‰ (mean -15‰), $\delta^{18}O$ -5.6‰ to -2.7‰ (mean -4.0‰). The calculated meteoric water line (MWL) for the groundwaters is $\delta D = 8.26\delta^{18}O + 12.50$ ($r^2 = 0.72$), and for the springwaters $\delta D = 6.54\delta^{18}O + 10.20$ ($r^2 = 0.77$). The April and August treated waters tend to lie on or near the unweighted SW Cape MWL ($\delta D = 6.15\delta^{18}O + 13.07$). The groundwaters were slightly less enriched in deuterium (δD

+12.50‰) relative to the SW Cape MWL while the springwaters are much less enriched in deuterium (δD +5.86‰) relative to the SW Cape MWL. The differences in the calculated MWL's for the different water groups from the SW Cape are ascribed to topographic and thus also microclimatic variations in the study area. The biggest isotope differences between mains waters and other waters occurred between the April treated samples and the groundwaters and springwaters, indicating that using stable isotopes to solve urban geohydrological problems would be most useful if applied at the end of summer, as differentiating water groups according to their stable isotope compositions becomes more effective as the isotope differences increase. However, the ranges for the isotope composition for each group of water overlap, therefore a water sample in the Cape Town area may not be conclusively identified from stable isotope determinations.

Groundwaters generally had the highest total dissolved solids (TDS), followed by springwaters, then mains waters. No statistically valid correlations were found to exist between stable isotope values of the waters and chemical parameters, such as pH, EC or any dissolved chemical constituent, therefore chemical parameters may not be used to confidently identify different groups of water.

A case study was undertaken to illustrate the use of stable isotope data in conjunction with chemical data in solving geohydrological problems. Water leaking out of a retaining wall was thought to be derived from either a nearby swimming pool, groundwater or mains water. It was necessary to identify the source of the leak before any repairs could be undertaken. Leaking water (δD +10‰, $\delta^{18}O$ +0.9‰) was shown to be derived from the nearby pool (δD +4‰, $\delta^{18}O$ +0.1‰). The heavier isotope values of the crack are ascribed to evaporation effects. The suggested evaporation is supported by EC values, with the crack EC (3610uS.cm^{-1}) higher than the pool EC (2210uS.cm^{-1}). The other possible sources, groundwater (δD -18‰, $\delta^{18}O$ -3.7‰) and mains water (δD -15‰, $\delta^{18}O$ -4.0‰) were eliminated due to their distinctly lower D content.

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Chapter 1. Introduction

Water is one of the most valuable resources available to mankind, and in the South African context, is very often in limited supply. In urban situations, up to 30% of the total mains waters are lost via leakage into the groundwater system. Identifying areas of such leakage in urban situations, and the contribution to the natural groundwater from leakages and waste water, therefore poses a specific and important urban geohydrological problem. The stable isotopes of H and O, which occur in a global fixed relative abundance, are an important tool in hydrological and geohydrological studies. Stable isotopes are more effective than chemical parameters as tracers in many instances, as they are highly conservative tracers, ie the stable isotope ratios are determined on water itself, and their ratios change very little due to interaction with other components in the water solution, or with the substrate the water has passes through at low temperatures. The chemical composition of a subsurface water sample generally cannot be used to accurately identify the sample source; rather, it records the nature and extent of mineral-water exchange reactions. The theory, development and application of stable isotopes as conservative tracers in hydrological and geohydrological studies is presented further in Chapter 2. Stable isotope science has been shown by Verhagen and Butler (1995) to have potentially useful applications in solving urban geohydrological problems in South Africa. In a study of an urban/industrial area at Midrand, Verhagen and Butler (1995) traced leakages and waste water derived from the local mains water supply, as its isotopic composition differed from the naturally charged groundwaters of the region, and found that point source concentrations of mains water in ground water were in the range of 10% to 100%.

In the present study, a similar approach to that of Verhagen and Butler (1995), was used in the Cape Town Metropolitan region, was used. The aim of the study involved attempting to group the groundwaters, springwaters and mainswaters in the Cape Town Metropolitan area according to their δD and $\delta^{18}O$ values. An attempt was made to explain any isotope variations and trends occurring, and to make recommendations regarding the use of stable isotopes in solving urban geohydrological studies in the Cape Town Metropolitan region. Chemical

analyses of many of the waters sampled were performed, in order to investigate if there are any correlations occurring between water chemistry and isotope compositions for different groups of waters. The potential use for using chemical compositions versus stable isotope values as tracers to solve urban geohydrological problems, or to supplement stable isotope studies, is also investigated.

Chapter 2. A brief review of oxygen and hydrogen isotope hydrology

2.1 Introduction

Stable isotope hydrology involves determining the oxygen ($^{18}O/^{16}O$) and hydrogen (D/H) isotope ratios of water, collectively forming part of a highly developed branch of the Earth sciences known as stable isotope geochemistry. Isotopes are atoms of the same element, but with differing atomic masses due to variations in the amount of neutrons in their nuclei. Stable isotopes are non-radiogenic, and non-radioactive, and when used in an Earth sciences context, apply to those isotopes occurring in fixed relative abundances. Stable isotope hydrology is of interest from both a scientific viewpoint (e.g. solving problems of fluid movement through geological formations), and an environmental hydrogeological viewpoint (pollution studies, water source determination, source utilisation potential), which are of interest to industry and the community.

2.2 Historical background

The discovery of radioactivity by M. Curie in the 1890's, and further work initiated by H. Becquerel, triggered research into atomic physics and chemistry at the start of the twentieth century. Many discoveries were made, and included F. Soddy's prediction that there must exist, for certain elements, different species with different atomic masses. These varieties in an elements atoms are called isotopes (Greek: *isos*, equal and *topos,* place, referring to the place in the periodic table.)

This prediction was verified by JJ Thompson, 1913, when he recorded atomic masses of ^{20}Ne and ^{22}Ne, using his 'positive ray' apparatus. The apparatus was modified by FW Aston, who confirmed Thompsons findings, as well as finding a third Ne isotope, ^{21}Ne. Aston named his improved device a mass spectrograph, and documented 212 of the 287 naturally occurring isotopes.

The development of modern stable isotope geochemistry is largely credited to the efforts, begun in the 1930's and 1940's, of Harold Urey and Alfred Nier. Urey developed much of the

theory behind stable isotope geochemistry, and Nier provided the design for the mass spectrometer, which allowed, with suitable modifications, the making of precise measurements necessary for accurate determinations of the isotope ratios of the lighter elements. Urey made many contributions to the field of stable isotope geochemistry, including the development of an oxygen isotope paleotemperature scale (Valley *et al.*, 1986). Stable isotope geochemistry has expanded in the last forty years into a wide range of specialities and sub-fields, including ocean paleotemperatures, high-temperature geothermometry, origins of natural waters, palaeoclimatology and glacier research.

2.3. Behaviour of stable isotopes

Isotopes of an element exhibit similar chemical behaviour, but due to mass differences, exhibit different physical properties. The differences in physical properties can lead to isotope fractionation during physical processes. Fractionation is any process that causes the isotope ratios in particular phases or regions to differ from one another. Isotope fractionation is recognised to occur via three possible mechanisms (Drever, 1988):

1. Equilibrium fractionation, which involves the exchange of isotopes of an element between different substances containing that element,

2.Kinetic fractionation, which is the differential distribution of isotopes during unidirectional non-equilibrium chemical reactions.

3. Physical fractionation, which is the separation of isotopes during physical processes such as evaporation, condensation, melting, freezing, sublimation and diffusion. The most important process in nature is vapour-liquid fractionation during evaporation and condensation.

The extent of isotopic fractionation between two phases is represented by the fractionation factor, α:

$$\alpha_{A\text{-}B} = R_A/R_B$$

where R_A and R_B are the isotopic ratios of an element in two phases, A and B.

Fractionation is greatest at the lowest temperatures, and varies according to the following

relationship.

$$\ln\alpha = k/T^2$$

where T is the temperature in Kelvin, and k is a constant specific to the pair of phases in which fractionation is occurring.

The vapour pressure of an element or compound is inversely proportional to its atomic mass, therefore lighter isotopes of an element or compound will preferentially evaporate or diffuse, while heavier isotopes will condense preferentially. Evaporation therefore produces a vapour enriched in the lighter isotopes relative to the source liquid, while the remaining liquid will be progressively enriched in the heavier isotopes as evaporation proceeds (Dansgaard, 1964).

2.4. Measurement of stable isotopes

The relative isotope abundance of an element in a sample is measured using a mass spectrometer, and is expressed as a deviation from the ratio in a standard. For oxygen and hydrogen isotopes in water, the international standard is a sample of sea-water, called the Standard Mean Ocean Water (SMOW) (Craig, 1961b). The deviation of the sample from the standard, δD or $\delta^{18}O$, is indicated in units per thousand, or per mil (‰).

For H: $\delta D = [(D/H)_{sample} - (D/H)_{SMOW}]/(D/H)_{SMOW} \times 1000$

For O: $\delta^{18}O = [(^{18}O/^{16}O)_{sample} - (^{18}O/^{16}O)_{SMOW}]/(^{18}O/^{16}O)_{SMOW} \times 1000$

Positive δ values imply that a sample is enriched in the heavy isotope (or depleted in the light isotope) relative to SMOW, whereas a negative δ value implies that the sample is depleted in the heavy isotope relative to the standard. It has been recommended that oxygen isotope ratios of all substances be expressed relative to VSMOW (Vienna Standard Mean Ocean Water) or VPDB (Vienna Peedee belemnite) on scales normalised so that $\delta^{18}O_{SLAP/VSMOW} = -55.5‰$ (Gonfiantini, 1984; Hut, 1987), where SLAP is Standard Light Antarctic Precipitation. For hydrogen, they recommended a scale normalised so that $\delta D_{SLAP/SMOW} = -428‰$. There is some dispute in stable isotope circles (eg. ISOGEOCHEM newsgroups) about the desirability of substituting SMOW by VSMOW (C. Harris pers.comm. 1996). All δD and $\delta^{18}O$ data in

the present study are expressed relative to SMOW, but are calculated according to the equations of Coplen (1988), which apply to the normalisation of oxygen and isotope data relative to VSMOW. Thus, in this thesis, SMOW is exactly equivalent to VSMOW.

2.5. Isotope hydrology

Geochemists have recognised and capitalised on the fact that water is composed of two elements that have stable isotopes with variable ratios, for example, the ratios D/H and $^{18}O/^{16}O$ provide two independent 'labels' or tracers of its origin (eg. Sheppard, 1986).

Sheppard (1986) has listed several defined principal water types. These are: ocean and seawater; meteoric water; connate water; formation water; metamorphic water; magmatic water; juvenile water, hydrothermal water and exotic water. Sea water used in this context often refers to inland seas. The purpose of this introduction is to focus on meteoric water, therefore descriptions of the other water types (metamorphic, magmatic, juvenile and exotic waters) will not be listed, as they are not relevant to this dissertation.

Meteoric waters are waters of any age that originated as precipitation: rain, snow, ice, river, lake and most low-temperature ground waters. They are derived from ocean water through the atmospheric circulation process (Sheppard, 1986).

The majority of present day meteoric waters have H- and O- isotopic compositions that vary in a systematic way (Craig, 1961b). The isotope compositions of meteoric water at a specific locality are related to several geographic parameters - temperature, altitude, distance from the coasts (continental effect), and intensity of precipitation (amount effect). The reasons for the fluctuations are described in the following paragraphs, and have been comprehensively documented in the literature (eg. Sheppard, 1986; Dansgaard, 1964). The resultant variations in isotope signatures allow stable isotopes to be used in environmental hydrogeological and hydrogeochemical studies, some examples of which will be discussed in later sections.

2.6.1 Temperature effect

Dansgaard (1964) showed that temperature is the major parameter that determines the isotope ratios of precipitation. The composition of precipitation depends not only on the temperature at which the oceanic water is evaporated, but also, the temperature of condensation at which clouds and rain or snow are formed. The fractionation factor (α) for evaporation and condensation is the same for both processes, therefore the temperature dependance is the same. The result is that lower temperatures yield isotopically lower precipitation values, as the isotopically heavier water molecules containing D and ^{18}O will condense at higher temperatures due to their lower vapour pressure, and as the temperature is lowered, increasing amounts of the isotopically lighter water molecules (containing H and ^{16}O) will condense, yielding a progressively lower isotope ratio for the condensed water body. As a consequence, the condensation temperature will also determine the isotope composition of the uncondensed vapour fraction, which will become progressively lower as the condensation temperature drops. Associated with the temperature effect is that, at lower temperatures, the cloud base is normally lower, therefore less evaporation will occur as the raindrop falls, and the subsequent degree of enrichment will be less.

2.6.2. Amount effect

Within a climatic area, the greater the amount of precipitation, the progressively lower (or more negative) are the δD and $\delta^{18}O$ values. The higher volume rain events are normally associated with lower temperatures. Dansgaard (1964) proposed two major explanations for the amount effect.

1. Lower ambient temperatures cause the formation of cloud condensate with lighter isotopic compositions, and lower temperatures cause increased rainfall..

2. Falling rain drops undergo evaporation, enriching the falling rain in D and ^{18}O. This enrichment effect is less severe when both ambient temperature is low, and when the amount of rainfall is high. The degree of evaporation is also dependant on humidity, and evaporation becomes progressively thermodynamically unfavoured as the relative humidity of the air mass increases.

Two effects are attributable purely to the amount of rainfall. Firstly, for any rain event, the more rain that falls, the more saturated the air below the cloud base becomes, therefore evaporation (and subsequent enrichment) becomes progressively thermodynamically unfavoured. Secondly, the first rain to fall will have the highest D- and ^{18}O- enrichment, and thereafter the isotope composition of the rain will become progressively lighter, in a model analogous to Rayleigh fractionation, resulting in an overall isotopically lower rainfall signature. Fontes (1981) has shown that in arid regions, groundwaters are dominantly charged by heavy rainfall events, whose isotope signatures are often quite different from those of minor precipitation events, and these differences may be attributed primarily to the amount effect.

2.6.3. Altitude effect

At higher elevations within a geographic area, the isotopic ratios for precipitation tend to become more negative (Siegenthaler and Oeschger, 1980). Several factors could contribute to this effect. Higher altitudes have lower temperatures, and therefore condensation temperature will be lower. Lower temperature also implies a higher relative humidity, and this, combined with the lower temperature, will result in less evaporation from falling raindrops. The higher relative humidity with altitude will tend to destabilize vapour masses and induce precipitation, resulting in a loss of heavy isotopes. The altitude effect has been used as an effective tool in tracing groundwater recharge (Payne and Yurtsever, 1974).

2.6.4. Continental effect

The greater the distance from the oceans and the trade wind belts (which are the main source of water vapour), the lower the isotope values will be for any precipitation (Sonntag *et al.*, 1979). This correlation is strengthened by increasing altitude with distance from the sea. The primary factor causing the continental effect is progressive rainout, resulting in the air mass becoming gradually lighter in its isotopic composition, and subsequent lighter resultant precipitation. The continental effect is often related to the temperature and altitude effects.

2.7. Meteoric water lines

Craig (1961b) published the results of about 400 riverine, lacustine and rainwater samples, and found that their stable isotope values fell along the line $\delta D = 8\delta^{18}O + 10$. The line provides a reasonably good fit for continental northern hemisphere data. Local differences between regional water lines are found around the world, with shallower gradients being found in tropical regions, oceanic regions and the southern hemisphere in general (Dansgaard 1964). Specific examples of local meteoric water lines include those found by Salati, *et al.*, (1980) for north-eastern Brazil ($\delta D = 6.4\delta^{18}O + 5.5$), and Dansgaard (1964) for most tropical islands ($\delta D = 4.6\delta^{18}O + 1.6$). For environmental studies, the meteoric water line is a convenient reference line for understanding and tracing local groundwater origins and movements, therefore, in hydrogeochemical and geohydrological investigations, the local meteoric water lines need to be established. The local unweighted meteoric water line for the South Western Cape has been shown to be $\delta D = 6.15\delta^{18}O + 10.87$ (Diamond and Harris, 1996). Figure 2.1 shows the relationship between the global MWL (Craig, 1961(b)), the SW Cape MWL (Diamond and Harris, 1996), SMOW and a typical evaporation line.

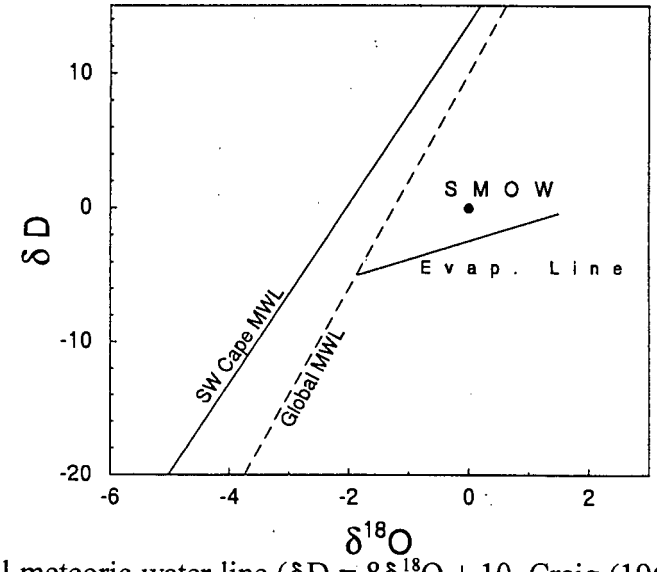


Figure 2.1. The global meteoric water line ($\delta D = 8\delta^{18}O + 10$, Craig (1961(b))); the SW Cape meteoric water line ($\delta D = 6.15\delta^{18}O + 10$, Diamond and Harris (1996)); SMOW ($\delta D = 0$; $\delta^{18}O = 0.0$)

2.8. Environmental uses of stable isotopes: practical applications for geohydrological studies

2.8.1. Hydrogeological studies

Hydrogeological and hydrogeochemical studies have often proven to be costly and time consuming when assessing the vulnerability of an aquifer to pollution, or pollution extent within the atmosphere. Walton *et al.* (1995), have shown that the use of stable and radioactive isotopes provide a relatively inexpensive and quick technique for identifying the vulnerability of an aquifer to pollution, for identifying pollution sources and the method of entry of the pollutant into the ground water system, and for estimating the percentage of end members in mixing.

Stable isotope tracers have the advantage of labelling the molecule itself, thus rendering the process of interaction with the aquifer almost irrelevant. Walton *et al.* (1993) illustrates how isotopes within their natural hydrogeological situation may supplement the data supplied by full hydrogeochemical and geohydrological surveys. The practical applications of the environmental isotopes of tritium, carbon-14, carbon-13, oxygen-18, deuterium and nitrogen in pollution studies are discussed. Of particular interest to this dissertation are uses of $\delta^{18}O$ and δD values in solving possible urban geohydrological problems, an example of which is outlined in the following paragraph.

2.8.1.1. Local urban applications

Verhagen and Butler (1995) used oxygen and hydrogen stable isotopes to study mixing of groundwater in an urban/industrial area at Midrand, near Johannesburg, South Africa. They found that leakages and waste water derived from the Rand Water Board mains system could be traced, as its isotope composition differed from most naturally charged ground waters. Secondly, in the same study, using boreholes as sampling points for ground water in the Pretoria region, they were able to use stable isotopes to suggest that significant amounts of groundwater recharge (10% to 100%) originated from mains water point sources, such as leakages. Estimating the percentages of end-members in a mixture is one of stable isotope

studies big advantages. Thirdly, the areas in which the leakage points were located could be identified. This has important economic and environmental significance, as mains leakages result in a waste of purified water, consequently costing the affected municipalities significant amounts of money, and leakage point determination often involves large scale excavations, which are expensive, time consuming and disruptive to the local environment, when compared to the cost of shallow borehole establishment and sampling. Water is not an abundant resource in South Africa, thus water supplies need to be effectively managed, therefore water conservation (leak elimination and waste reduction) as part of the water management strategy is crucial.

2.8.1.2. Agricultural applications

Sundara Sarma *et al.* (1993) used tritium and stable O isotopes to investigate the effects of land use and salinisation on perched water quality on farmland in western Rajasthan, India. Perched water refers to water which has collected above an aquiclude, resulting in a saturated groundwater zone. The ground below the aquiclude is generally unsaturated. Irrigation canal water and water from auger holes was collected and analyzed. An isotope mass balance relationship was used to determine the contribution of irrigation water to perched water, and results indicated that the salinity of the perched water was adversely affected by land-use practices involving agrochemicals.

Flo *et al.* (1994) investigated the influence of regional groundwater flow on-farm drain water quality in the western San Joaquin Valley, California, using stable isotopes as tracers. Irrigation, drainage and regional groundwater flows were found to be displacing shallow ground waters enriched in and salts. This displacement, combined with various geographical and chemical factors, was found to be adversely affecting Se levels. The suggestion was made that reducing the volume of water flowing out of the drainage channels should subsequently reduce Se loads in the groundwater and drain water.

2.8.1.3. Regional geohydrological applications

A major use of stable isotopes involves their use in providing qualitative and quantitative

information on the flow and circulation of water within the hydrological cycle. Numerous hydrogeological studies have been performed worldwide using environmental stable isotopes as the key experimental parameters. In the area of groundwater hydrology, isotopes often provide information on the source and area of recharge, the velocity of groundwater flow, and allow for the estimation of the aquifer parameters. The use of isotopes in such hydrological studies has been well documented in recent literature. Midgley and Scott (1994) used stable isotopes of water in rainfall and streams in the Jonkershoek Valley, Western Cape, South Africa to determine the relative amount of rainwater to streamflow during stormflow conditions, and concluded that the rapid response of streams in this area is mainly due to displaced groundwater.

Other studies include contributions to soil-water and ground water systems by various forms of precipitation. Maule *et al.* (1994) established the seasonal contributions of rain and snow to soil-water and groundwater systems in the Canadian Prairies region, on the basis of their physical states and the abundance of D and ^{18}O. Results of modelling based on the isotopic data indicated that the relative contributions of different precipitation types to the ground and soil-waters,(such as snow and rain), was not dependant on their relative amounts as precipitation. Maule *et al.* (1994) managed to evaluate their findings in terms of implications for climatic changes.

Bowen (1989) carried out investigations at Vanathavillu, Sri-Lanka, using isotope hydrology to establish information about the type, origin and age of groundwater of the multi-aquifer system present. He obtained valuable results in clarifying geohydrological phenomena, and obtaining data on recharge, infiltration rates and isotopic characteristics of the groundwater.

In the lakes region of southern Turkey, Gunyakti et al (1993) used tritium and oxygen isotopes to establish the relationship between various possible inputs into the lakes of the region. Stable isotopes were used to examine the relationships between precipitation, groundwater, and coastal springs. The results indicates that groundwater recharge was occurring predominantly from precipitation runoff from nearby mountains, and that coastal spring waters are charged from different sources.

Many groundwater resources need to be utilised fully for social and economic development. An investigation of groundwater of the El-Qusier-Safaga area on the Red Sea coastal zone was performed by Awad *et al.* (1996). δD and $\delta^{18}O$ data was used to clarify the interaction between different aquifers, and to identify the source of recharge, thus determining if groundwater from the region could be used on a sustainable basis. Hydrogeochemical investigation of the waters allowed for evaluation of the groundwater quality for various social and economic purposes.

Verhagen and Weizu (1995) evaluated groundwater as a potential irrigation supply source in the Ulan Buh desert of Inner Mongolia using environmental isotope and hydrochemical data. The Yellow River and runoff from the Lang Shan mountains were eliminated as recharge sources of regional significance. Results show that widespread diffuse recharge was occurring in the shallow phreatic aquifer of the region, and recharge of the deeper confined aquifer was occurring by replacement of palaeo-water by recent recharge through the phreatic aquifer. The confined aquifer was identified as a renewable resource, and suitable for desert irrigation of the area.

2.9. Conclusion

The development of stable isotope geochemistry during the twentieth century has resulted in the development of an effective and useful tool for Earth scientists. Stable isotopes behave predictably, and according to a combination of different effects (temperature of condensation, amount of precipitation, altitude of condensation and continental effects), meteoric waters with varying stable isotope compositions of D/H and $^{18}O/^{16}O$ are formed. In the case of H and O, their is a linear relationship between their relative abundances in meteoric waters. This relationship is represented in the form of meteoric water lines, which need to be established for any area of study. The establishment of meteoric water lines, and the use of relatively simple mass balance considerations, allow coupled H and O isotope studies of natural waters to identify, or place constraints on, the source(s) of waters. Stable isotopes have great application as groundwater tracers, as they are conservative properties of the groundwaters of interest, therefore their ratios do not generally change as a result of interaction with the substrate through which they pass, provided temperatures are low. Some applications involve

pollution monitoring, groundwater monitoring, identifying different sources and their relative contributions to water reservoirs, as well as evaluating the suitability of groundwater resources for various anthropogenic activities. They are a relatively cheap tool to use, (with one analysis presently costing about R20), thus their continued use as tracers is expected.

Table 3.1: Geological units of the Cape Peninsula.

Group	Formation	Period
Sandveld Group	Witzand* Langebaan Velddrif Springfontyn* Varswater Elandsfontyn*	Tertiary and Quaternary
False Bay Dolerites		Carboniferous to Jurassic (Reid *et al.* (1991))
Table Mountain Group	Pakhuis Peninsula Graafwater	Ordovician
Cape Granite Suite		
Malmesbury Group	Sea Point Bloubergstrand	Late precambrian

Note: * = not yet approved by the South African Committee for Stratigraphy (SACS).

The Peninsula Granites and the sedimentary Table Mountain Group (TMG) are separated by a unconformity. The oldest rocks of the TMG are the finely bedded sandstone and shales of the Graafwater Formation, which are overlain by the thicker bedded quartzitic sandstones of the Peninsula Formation. The summit of Table Mountain contains a thin remnant of the glacial deposits of the Pakhuis Formation, consisting of sandy tillite. The Table Mountain Group forms the basal part of the Cape Supergroup. The Malmesbury and Cape Granites, along with the lower parts of the TMG, have been intruded by a swarm of dolerite dykes, known as the False Bay Dolerites (Reid *et al.* 1991), which are known to be present over a wide area in False Bay, and off the Atlantic coastline.

The almost horizontal sandstones of the Peninsula Formation have been linked to the same formation capping the mountains on the eastern fringe of the Cape Flats. Post-Palaeozoic erosion has removed the sandstones between False Bay and Table Bay to create the Cape Flats.

Sediments of the Cenozoic Sandveld Group overlie bedrock of much of the Cape Flats, and

consist of the Middle Miocene Elands formation, the Early Pliocene Varswater Formation, the Pleistocene Springfontyn, Velddrif and Langebaan Formations, and the Recent Witzand Formation. The Elandsfontyn is represented by a fluvial sequence of gravelly quartzose sands with intercalated peats. The Elandsfontyn does not outcrop in the area, and is found in boreholes in the Noordhoek basin. The Varswater is a highly fossiliferous, phosphate bearing, muddy quartzose sand, underlying the coastal plain between Muizenberg and Swartklip, and is also only exposed in boreholes. Of great interest is the Springfontyn Formation, which is a chiefly aeolian formation of fine to medium quartzose sand, and is exposed over most of the central part of the Cape Flats. It forms the dominant part of the unconfined Cape Flats aquifer, and is the aquifer used for groundwater extraction near in the Atlantis area north of Cape Town. The Velddrif Formation is a patchy deposit of poorly consolidated intertidal and estuarine sediments, which is best exposed east immediately east and west of Swartklip. The Langebaan formation consists of cross-bedded, semi-consolidated aeolinites which overlie the Velddrif Formation. The Witzand Formation consists of unconsolidated, aeolian sand, which is often partly vegetated, and forms calcareous dunes. The Witzand Formation is seen, among other places, east of Swartklip, and at Fishhoek, Witsand Bay, Noordhoek and Hout Bay. The geology of the Cape Peninsula geological is presented in Figure 3.1.

3.3. Climate of the South Western Cape

This section has been adapted from South African Weather Bureau, The weather and climate of the south-western Cape, 1996. The South-Western Cape, incorporating the Cape Peninsula and adjoining districts, experiences a typical Mediterranean climate, with wet winters and dry summers. The geographical and topographical features influence the climate of the region, resulting in highly localised microclimates. The annual precipitation in the area averages at 600 mm per year, but is highly variable and controlled by topography. The mountains of the Cape Peninsula and the Hottentots Holland and Drakenstein ranges receive heavy orographic rains, with some areas, such as Newlands on the slopes of Table Mountain, receiving over 2000 mm per year.

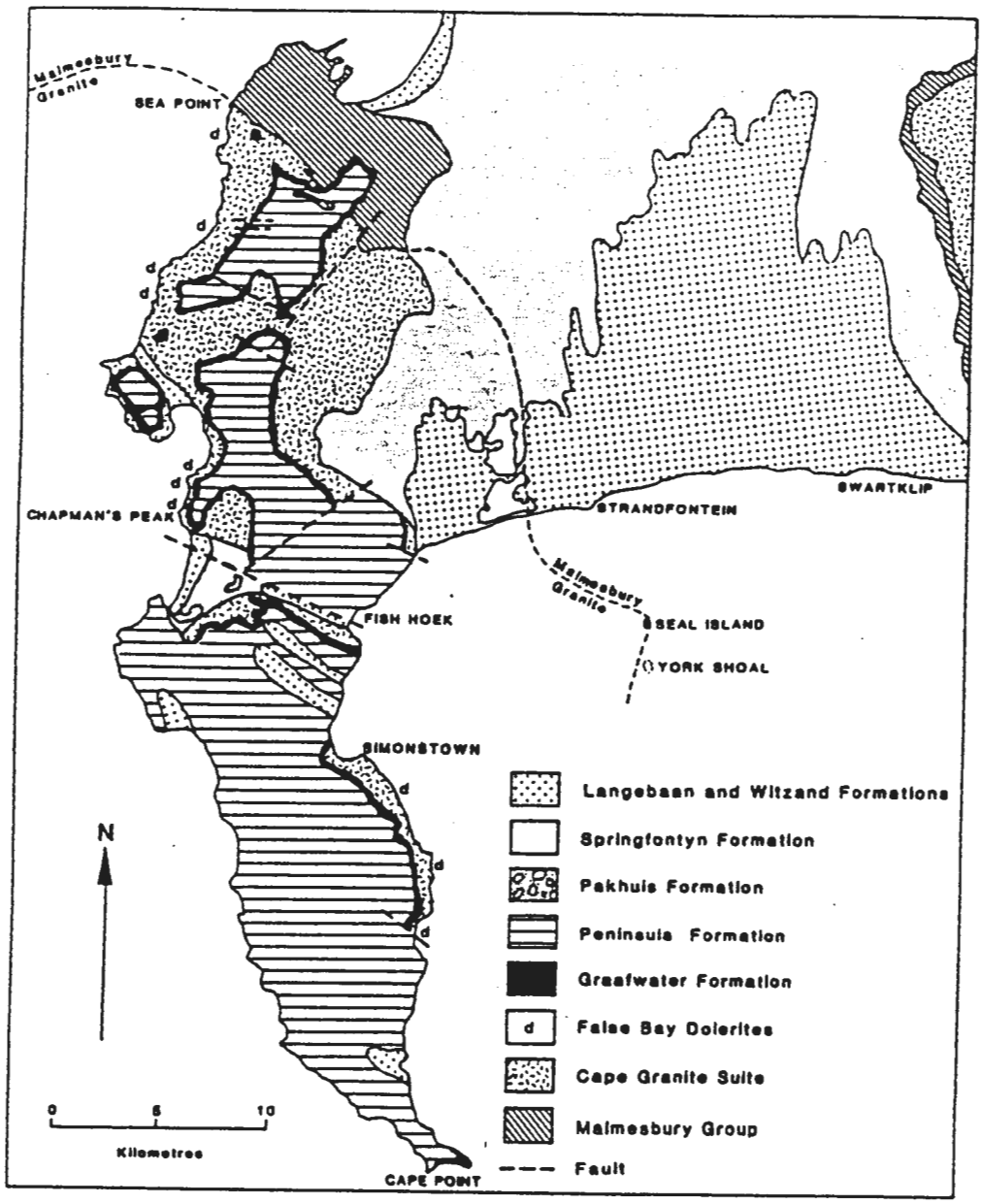


Figure 3.1. Geological map of the Cape Peninsula and Cape Flats (Theron, 1984).

The Cape Town southern suburbs receive on average 1300 mm rain per year, and this decreases to about 500 mm a year as one moves toward the flatter areas north and east of Cape Town. The rainy season is normally from May to September, often extending into October, with the majority of winter rain associated with frontal depressions. The summers are predominantly dry, with the variability of rainfall amounts in summer generally quite small. Heavy precipitation episodes may occur during summer in the mountain regions, but these are of generally short duration. The average monthly rainfalls for the University of Cape Town, along with the rainfall figures for the period from August 1995 to August 1996, are presented in Figure 3.2. The rainfall amounts vary over the South Western Cape, but the relative monthly distributions are quite similar over the region.

Coastal monthly temperatures do not deviate greatly from the annual mean, and are relatively low due to the moderating effect of the sea. As one moves into the interior, diurnal and annual temperature ranges become more considerable. Cape Town (33°50' S; 18°36' E; elevation 30m) has a mean January temperature of 21°C, and a mean July temperature of 13°C, whereas Ceres (33°22' S; 19°18' E; elevation 456m) has a mean January temperature of 22°C, and a mean July minimum of 9.1°C.

3.4. Geohydrology of the Cape Town region

This paragraph is based on a paper by Maclear (1995). The greater Cape Town Metropolitan Area lies on one of the most extensive sand aquifers in South Africa. The low lying sandy flats connecting the Table Mountain-Cape Peninsula range in the west to the Tygerberg-Stellenbosch ranges to the east cover an area of 765km^2, and were formed chiefly by river and wind erosion, and subsequent deposition. The thick unconsolidated quartz sand deposits of Cenozoic age underlie most of the Cape Flats from False Bay in the south to Table Bay in the north, and also occur along a narrow strip from Fishhoek to Noordhoek, around Hout Bay and in the Kraaifontein-Joostenbergs Vlakte area (Figure 3.3.) The generally shallow water table (av 3.75m below surface), and medium- to coarse grained nature of the saturated sands result in a primary aquifer of significant exploitation potential. Groundwater recharge in the Cape Town area is seasonal, occurring during the wet winter months, typically between May and September. The groundwater quality of the Cape Flats Aquifer Unit (CFAU) is

classified as fresh, with salinity ranging from 300-1000mg.l^{-1} TDS.

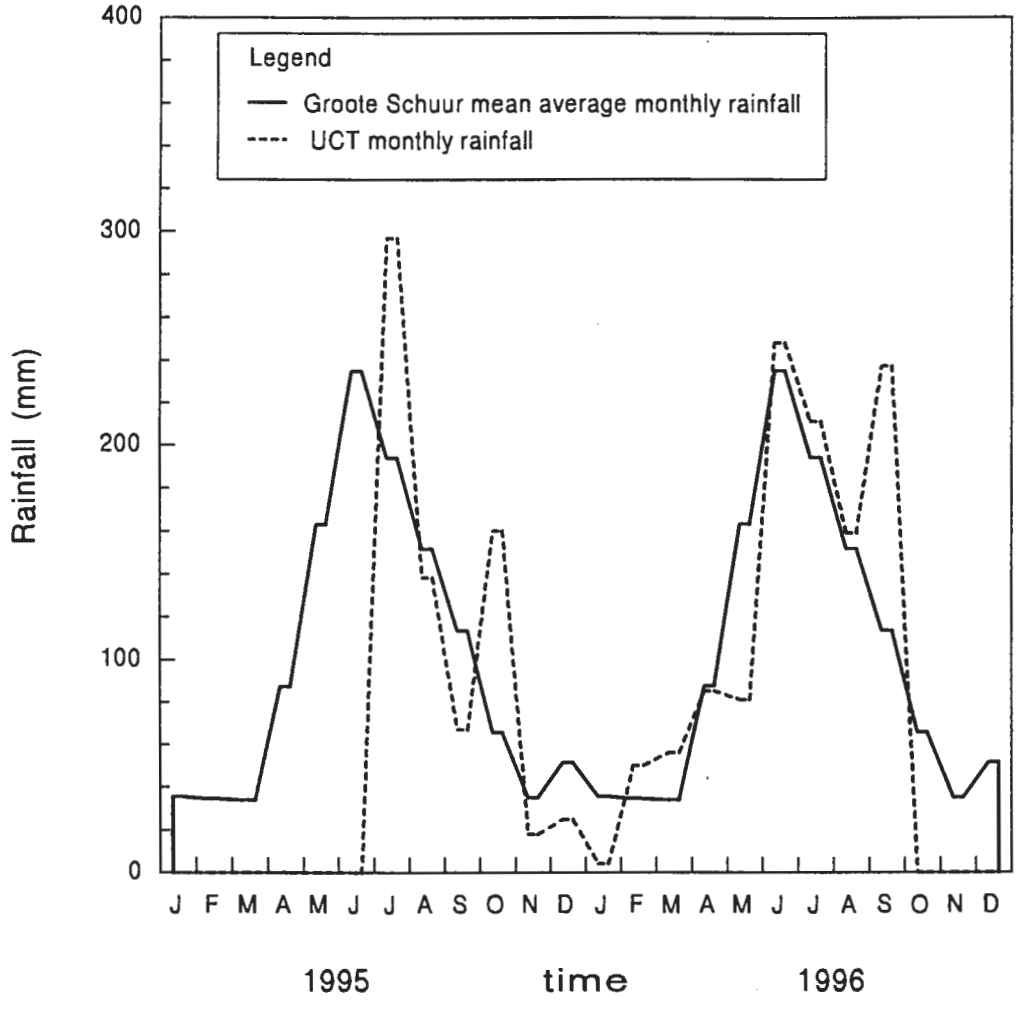


Figure 3.2. The mean average monthly rainfall for Groote Schuur, Cape Town, and the monthly rainfall for UCT from June 1995 to October 1996 (Diamond, 1997). (No data for UCT was collected prior to June 1995 and after October 1996.)

Sandstones are composed predominantly of quartz grains, with pores constituting 10-50% of the rock volume. The pores are generally interconnected, thereby providing high infiltration efficiencies. Sandstone aquifers thus normally have high storage capacities and rapid water throughflow, but cementation of the sandstone will reduce pore space and hydraulic conductivity. Although Table Mountain is composed predominantly of Table Mountain

Sandstone, it will not exhibit the characteristics of a typical sandstone aquifer unit because porosity has been reduced by metamorphism. Table Mountain is highly cemented, but has developed extensive jointing which provides channels for water flow. The sides of Table Mountain have several small ephemeral springs which flow during the wet winter months, and emerge from the finely bedded sandstones and shales of the Graafwater Formation. Water moving down through the permeable Peninsula Formation probably strikes the less permeable Graafwater Formation, and under conditions of high groundwater flow, the lower hydraulic conductivity of Graafwater Formation compared to the Peninsula Formation results in the Graafwater Formation exhibiting aquitard characteristics. As a result, excess water moves laterally along the contact between the two formations, and along cracks and fissures in the Graafwater Formation, to be discharged as ephemeral springs.

Some large permanent springs are present on the east face of Table Mountain, at the boundary between the low porosity Cape Granite and the fractured sandstone and shale of the Graafwater Formation, for example Albion Spring, which has a yield of 4 500 m^3 per day.

The Cape Town Metropolitan region is supplied with mains water from several reservoir sources. The treatment plants treating water for Cape Town are Kloof Nek, Constantia Nek, Blackheath, Faure, Steenbras, Voelvlei and Wemmershoek. The Blackheath and Faure treatment plants are supplied with water from Teewaterskloof dam, while the other treatment plants have their own associated reservoirs or dams of the same names. Each reservoir has its own associated catchment area. Mains water is imported into the Cape Town Metropolitan region according to the available supply and demand. The position of the treatment plants relative to Cape Town is shown in Figure 3.4.

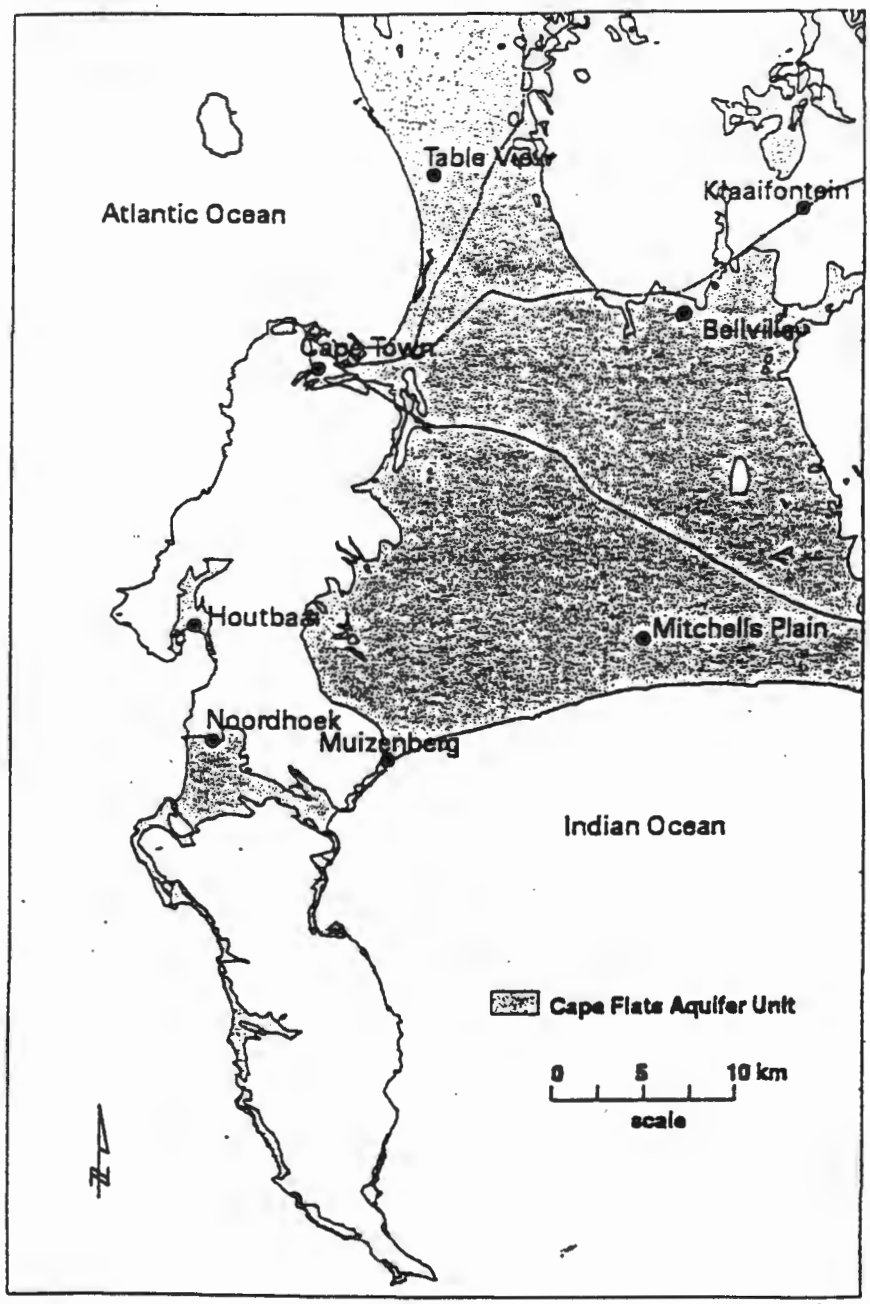


Figure 3.3. Regional extent of the Cape Flats Aquifer Unit (Maclear, 1995).

Chapter 4. Sampling and analytical methods

This chapter consists of an explanation of the sampling rationale, followed by the methods of analysis used in producing the chemical and stable isotope data.

4.1. Sampling

4.1.1. Sampling rationale

Water sampling consisted of obtaining selected samples from the several different groups of groundwaters found in the Cape Town area, namely reservoir waters, groundwaters and springwaters, in order to investigate isotopic differences and/or similarities between the different groups. If any significant isotope differences were established, then recommendations regarding the potential for using stable isotope geochemistry in solving urban geohydrological problems could be made. Water samples were collected from the water treatment plants at the reservoirs which supply the Cape Town metropolitan area with water, in order to establish if the waters piped into the Cape Town mains water supply were isotopically different to the groundwaters and spring waters of Cape Town. Samples were collected at the end of the dry summer season (09 April 1996), and after the wet winter season (14 August 1996), in order to establish if any seasonal isotopic variations exist. Samples were collected before and after water treatment in April (1996), in order to establish if any isotope fractionation occurred during the water treatment process.

Groundwaters and springwaters in the Cape Town area were sampled near the end of the wet winter season, in early September. It was expected that dominant recharge of the groundwaters of the region would occur during the wet winter season, over the four month period extending from May through to August. Limited recharge is expected to occur during the dry summer months, as discussed in the Section 3.4. The groundwaters will not be subject to evaporation effects after infiltration has occurred, and during the dry summer months, therefore it was assumed that the isotope composition of the groundwaters could, for the purposes of the study, be regarded as being constant throughout the year.

4.1.2. Sampling locations

Reservoir samples were collected from the following treatment plants supplying the greater Cape Town municipality: Kloof Nek, Constantia Nek, Blackheath (Kuilsrivier), Faure, Steenbras, Wemmershoek and Voelvlei. The positions of the reservoirs sampled, relative to Cape Town, are shown in Figure 3.4.

Natural springs in the Cape Town area were identified from a geological map of the city (Geological Survey, 1984). Most springs identified on the geological map were sampled, along with water from any other springs which could be found. The springs were located at various heights on the eastern and northern slopes of Table Mountain, except for the Hout Bay spring, which is located on the Western side. The altitudes and estimated yields of the springs at the time of sampling are shown in Table 6.4. The geographical co-ordinates for the springs are given in Table 4.1., and the locations of the springs are shown graphically in Figure 4.1.

Table 4.1. Geographical co-ordinates of the springs sampled.

Spring	Longitude (East)	Latitude (South)	Altitude (m)	Yield ($l.min^{-1}$)
Kirstenbosch	18°25'50"	33°59'15"	150	10-100
Klipper	18°27'05"	33°57'40"	100	10-100
Newlands	18°27'30"	33°58'20"	30	>1000
Main spring	18°24'22"	33°56'35"	120	>1000
Cable Way	18°24'10"	33°56'50"	310	1-10
Forries	18°27'35"	33°58'10"	40	100-1000
Fey	18°26'20"	33°59'55"	80	10-100
Rhodes Memorial	18°27'00"	33°57'05"	140	100-1000
Rugby	18°25'05"	33°57'00"	210	10-100
Albion	18°27'45"	33°58'00"	30	>1000
Glencoe	18°24'35"	33°57'05"	250	10-100
Hof	18°24'40"	33°56'20"	190	100-1000

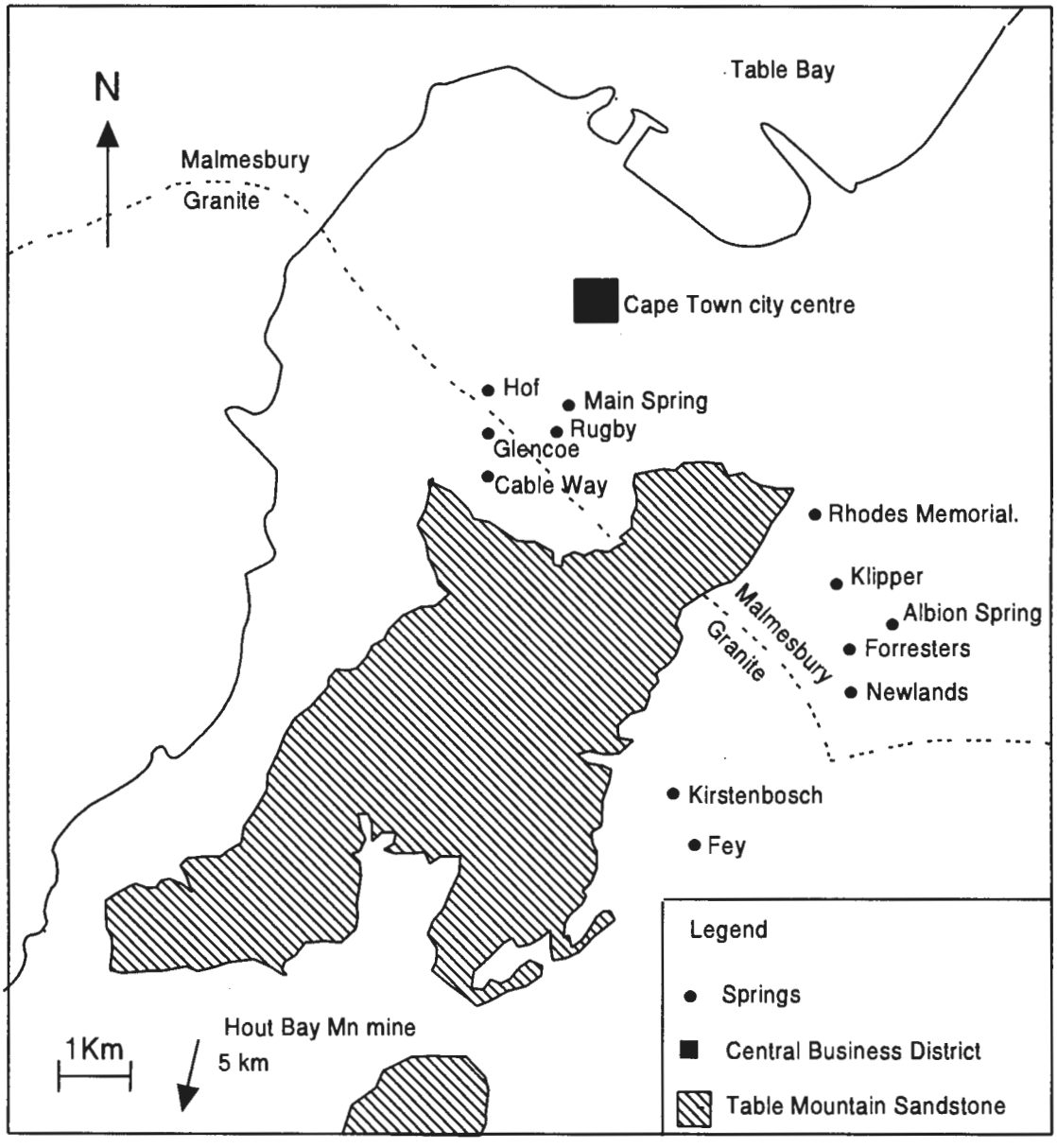
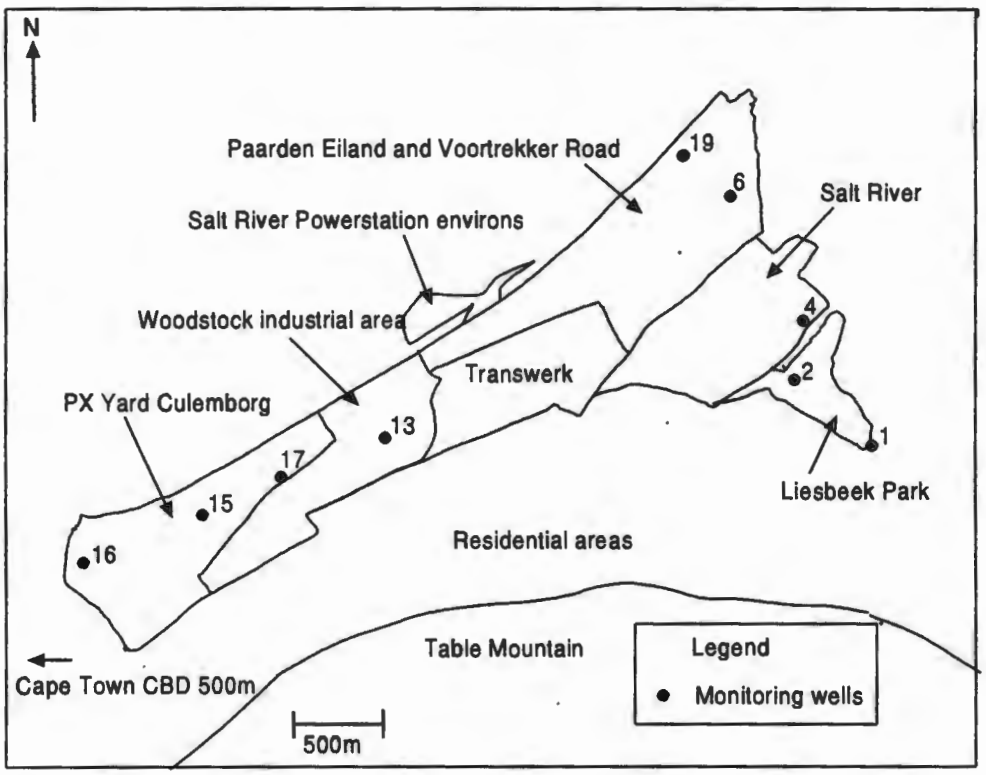


Figure 4.1. The locations of the natural springs sampled in Cape Town.

Groundwaters in the industrial areas immediately north and north-east of Table Mountain were sampled from several shallow monitoring wells, which have been established by a local engineering company as part of contract work with the Cape Town municipality. The area seemed deficient in boreholes and monitoring well, so a more comprehensive sampling of the groundwaters of the region was not undertaken. Political instability, and vandalisation of many boreholes prevented groundwater sampling in the Cape Flats region. The positions of the monitoring wells sampled are shown in Figure 4.2.

4.1.3. Sample collection

Duplicate samples from all sample points were collected in plastic sample bottles (Haynes and Matthews 100ml flat medical type). The bottles were totally filled and sealed immediately to prevent any isotope fractionation. All samples were stored in a cool, dark room.



CBD = Central Business District.

Figure 4.2. The locations of the monitoring wells sampled in the Cape Town industrial areas.

4.1.3.1. Reservoir water

Both treated and untreated water samples were collected immediately before and after the water treatment process, and as close to the source as possible to minimize fractionation by evaporation. The reservoir samples collected on 14 August were collected from identical locations, and in an identical manner, as the samples collected on 8 April. Only the treated reservoir samples were collected in August. The untreated water samples were taken from taps on the water pipes transferring water out of the reservoir into the treatment plant. The treated water samples were taken from sample taps designed for representative sampling of the treated water.

4.1.3.2. Springwater

Samples were collected as close to the source as possible in order to minimize fractionation by evaporation. Samples were kept in cool dark places to minimise any possible algae growth. The springs were sampled on 10 September 1996. No organic activity was observed in any of the samples.

4.1.3.3. Groundwaters

Groundwaters from the monitoring wells were sampled with a dedicated Teflon baler on 6 September 1996. The depth to the water table varied from 1m to 5m. The boreholes were purged manually to remove any meteoric water which had accumulated in the boreholes as a result of surface runoff or direct entry. Electrical conductivity (EC) was used as a measure of the source of the water in the borehole, as the recent meteoric waters generally had a different EC to the background aquifer waters. Electrical conductivity in the aquifer was continually monitored using a Corning digital multimeter; once the EC stabilised, it was assumed that the monitoring well was effectively purged, and any water seeping into the well was background aquifer water.

4.2. Analytical methods

4.2.1. Sample pretreatment

The samples to be used for pH, conductivity and alkalinity required no pretreatment. The samples used for anion analysis, and for elemental analysis by inductively coupled plasma-atomic emission spectroscopy (ICP-AES), were filtered through a 0.45μm filter (Millepore, type HAWP) before analysis.

4.2.2. pH determination

The pH was determined using a Crison micro pH 2001 pH meter, which contains a standard hydrogen electrode coupled to a reference calomel electrode. The meter was calibrated relative to pH 4.00 and pH 7.02 before any determinations were made. The pH was determined as soon as the samples were returned to the laboratory, which varied from one to five hours after sampling. However, for pH to be most reliable and useful, values should be determined at the wellhead. (American Public Health Association, 1985, pg. 429-437.)

4.2.3. Conductivity

Conductivity was measured using a Crison micro CM 2201 conductivity meter, and is expressed in siemens per unit distance, at a specific temperature. (American Public Health Association, 1985, pg. 76-80)

4.2.4. Alkalinity

Alkalinity was determined using a Radiometer Copenhagen TTT85 Titrator, coupled to a Radiometer Copenhagen ABU80 Autoburrete. The samples were titrated to an endpoint of pH 4.5, using 0.025M HCl. (American Public Health Association, 1985, pg. 63)

4.2.5. Fluoride determination

Fluoride concentrations were determined using a Corning Ion Analyzer 255, which utilizes an ion selective fluoride electrode. A three point calibration, using F^- concentrations of 10 ppm, 1 ppm and 0.1 ppm was performed before any determinations were made.(American Public Health Association, 1985, pg. 357) The calibration was repeated each hour to compensate for electrode drift, resulting from memory effects. (Fluoride Electrode. Operating Instructions/Technical Specifications, 1984.)

4.2.6. Anion analysis

Major anions (SO_4^{2-}, NO_3^-, Cl^-) for the water samples were determined using high performance ion chromatography (HPIC). The samples were diluted if necessary to reduce their EC to below 100$\mu S.cm^{-1}$. The diluted sub-samples were analyzed for anions using a Dionex DX300 series-suppressed ion chromatography system, coupled with A1450 chromatography software. An HPIC-AS4A separator column, fitted with an HPIC-AG4A guard column, was flushed with a sodium carbonate/bicarbonate eluent (1.80mM Na_2CO_3; 1.70 mM $NaHCO_3$)at a flow rate of 2.0 $ml.min^{-1}$. A MicroMembrane (AMMS) anion suppressor was used.

4.2.7. Elemental analysis

Total elemental concentrations of Na, K, Ca, Mg, Fe, Cu, Si and Al were analyzed by inductively coupled plasma-atomic emission spectroscopy (ICP-AES), using a Joby Yvon 70C instrument in the Department of Chemistry, UCT. The instrumental detection limits for yhe ICP operating plasma conditions are detailed in Table 4.2.

The instrumental detection limits for the elements analyzed under the ICP operating plasma conditions, are determined using the following equation.

$Dl = k\sigma_b$

k = multiple of standard deviation = 3

σ_b = standard deviation of the blank for the element under study

Dl = detection limit for the instrument operating conditions

The literature detection limits for ICP analysis on standard solutions (Potts, 1996) are included for comparison in Table 4.2. The standard deviation is calculated after 9 analytical duplicates.

Table 4.2. Literature and calculated detection limits for ICP-AES elemental analysis.

Element.	Literature Detection limit (ppm)	σ_b	Real detection limit (ppm)
Si	0.012	0.002	0.006
Fe	0.0062	0.001	0.003
Mg	0.00015	0.002	0.006
Al	0.045	0.004	0.012
Cu	0.0054	0.000	0.000
Ca	0.00019	0.018	0.054
Na	0.069	0.002	0.006
K	0.06	0.003	0.012

4.2.8. Assessment of analytical accuracy for chemical analyses

For most chemical analyses, a single measurement was taken. As a result, a statistical evaluation of the validity of the data could not be performed. Secondly, results were not validated against control laboratory methods, therefore an Analysis of Variance could not be performed. The reliability of the data was therefore appraised in terms of a charge balance, in which the total positive molar charge concentration was compared to the total negative molar charge concentration, and the charge difference expressed as a percentage:

Charge difference (%) =100(Σcations - Σanions)/(Σcations + Σanions).

Chemical analyses were performed on 37 water samples. A charge difference less than or

equal to 10% (positive or negative) was assumed to indicate a reliable set of analyses. Of the 37 analyses performed, 30 have charge balances less than 10%, four have charge balance differences between 10% and 15%, and 3 have charge balances greater than 15%. The highest charge difference belonged to the Kirstenbosch spring sample (21.49%). A full list of charge difference is included in Table 5.1. A possible reason for many of the disparities observed in some of the charge difference concentrations could be ascribed to the very low concentrations of dissolved constituents in some of the samples, which may lead to analytical uncertainty.

4.2.9. Stable isotope analyses

4.2.9.1. Break seal tube preparation

Pyrex break-seal tubes (6mm outside diameter, medium walled, 20 cm long and sealed at one end) were baked in a furnace at 500°C for 2 hours to expel any water which could have been trapped within the glass matrix. The tubes were stored in an oven at 110°C to prevent any adsorption of water onto the glass surface, before being removed from the oven and allowed to cool just prior to use.

4.2.9.2. Oxygen isotope determination

For the original description of this method, see Socki *et al.* (1993). The method is based on the original methodology developed by Epstein and Mayeda (1953). A 7ml vacutainer disposable test tube was placed onto the line via a hypodermic needle and then evacuated. Approximately 0.5 atm of CO_2 was loaded into the vacutainer from a tank of medical grade CO_2. The vacutainer was removed from the line and injected with ± 2ml of sample water. The vacutainer was then fixed to an automatic shaker and submerged in a 25°C bath for at least 1.5 hours, to allow for isotope equilibration between the H_2O and CO_2.

The vacutainer was placed onto the line with the hypodermic needle just piercing the rubber seal and not penetrating the vacutainer itself, and the air in the needle pumped out. Care was taken to attach the vacutainer to the preparation line rapidly after removal from the waterbath,

in order to prevent re-equilibration of the CO_2 below 25°C. The contents of the vacutainer were frozen with liquid N_2 for a period of four minutes, to ensure complete freezing of the H_2O and CO_2. The needle was then fully inserted into the vacutainer, and the line was evacuated, allowing any non-condensible gases to be evacuated out of the system. The contents of the vacutainer were kept frozen with liquid N_2 during this evacuation stage.

The line was closed off from the pump, and the liquid N_2 trap was removed from around the vacutainer and replaced with a slush of frozen propan-2-ol. This vaporised the CO_2, which expanded into the line, where it was re-frozen into a cold finger with liquid nitrogen. The non-condensible gases were then pumped out and the vacutainer was then closed off from the line. The liquid nitrogen was removed from the cold finger and immediately replaced with the propan-2-ol slush. The CO_2 was allowed to warm up and expand into the line, and then refrozen with liquid N_2 into a second cold finger attached to a pressure transducer. The second cold finger was shut off from the line and heated to room temperature in order to measure the voltage which can be used to calculate the number of micromoles of CO_2 and hence the yield. The yield was required to estimate whether or not there had been any leakage of CO_2 from the vacutainer. Assuming approximately the same amount of CO_2 had been let into the vacutainer, the yields should all be similar. The second cold finger was re-opened to the line and liquid nitrogen was placed around a break-seal tube in order to freeze in the CO_2. The break-seal tube containing the frozen CO_2 was then sealed under vacuum with an oxygen-propane torch.

4.2.9.3. Hydrogen isotope determination

Immediately prior to use, the break-seal tubes were loaded with 6 grains of analytical reagent desiccated zinc, supplied by Finnegan MAT. A break-seal tube was then placed onto the line and evacuated. Two µl of sample water was collected in a 2µl capillary tube, dropped into the loaded break-seal tube onto the Zn and attached to a closed portion of the evacuation line, whereupon the lower portion of the break-seal tube was immediately immersed in liquid nitrogen for 4 minutes. Once the water had frozen, the evacuation line was opened, and the non-condensible gases were then pumped out. The break seal tube was then sealed under vacuum using an oxygen-propane blow-torch.

Just prior to analysis, the break-seal tube was put in a furnace at 450°C for 30 minutes, in order to completely reduce the sealed water with the Zn reagent, to produce ZnO and H_2 gas. The method is based on the production of H_2 from H_2O by the Zn reduction method of Coleman *et al.* (1982).

4.2.9.4. Isotope measurement

All isotope data was measured using a Finnegan MAT 252 mass spectrometer. For oxygen, the fractionation factor between CO_2 and water was assumed to be 1.0412 (Coplen, 1988). For all isotope analyses, the internal isotope reference water standard (CTMP) was used to convert the raw data tp SMOW scale. CTMP has been calibrated using the IAEA (International Atomic Energy Agency) standards SMOW and SLAP (Standard Light Antarctic Precipitation), and independently analyzed. The average deviation from the mean of duplicate runs of CTMP is 0.90‰ for hydrogen (n=14) and 0.13 for oxygen (n=7) (Diamond and Harris, 1996). These correspond to values of 2σ of 1.1‰ and 0.18‰ respectively. SMOW is the same as VSMOW. All D/H analyses were duplicated, as were the analyses of CTMP for oxygen. The standards VSMOW and SLAP were analyzed to determine the degree of compression of raw data. The raw $\delta^{18}O$ values obtained were converted to the SMOW scale using equations 2 and 3 of Coplen (1988), and the δD values were converted to SMOW scale according to equations 13 and 14 of Coplen (1988). The co-efficient Z was calculated according to equation 15 of Coplen (1988). The H_3^+ contribution was corrected for using software provided with the Finnegan MAT 252 mass spectrometer. CTMP was used to correct for drift in the reference gases during the mass spectrometer runs. In this thesis, SMOW is equivalent to VSMOW of Coplen (1988) (see section 2.4)..

4.2.9.5. Analytical problems with the Zn reduction method

A large number of water samples prepared for hydrogen isotope analysis at an early stage of the experimental work resulted in clearly erroneous values. The normalised δD values ranged from -60‰ to -200‰, which were clearly out of the range expected, even though the yield of H_2 was correct. No agreement of data for duplicates was obtained either, resulting in about 60 δD determinations being disregarded. A problem with the Zn reagent was suspected.

Coleman et al. (1982) reported that the choice of Zn reagent was critical, and that incomplete reaction with the Zn lead to isotopic fractionation of the samples. Kendall and Coplen (1985) reported that problems inherent with Zn reduction could include surface inhomogeneity of the zinc, and exchange of the H with both the Zn and the glass walls of the reaction vessel. It is postulated that problems with the Zn reagent arose from the loading of the break seal tubes with Zn shot, and storing them in the oven at 110°C just before use. At elevated temperatures, the Zn could have oxidised to form ZnO, which resulted in armouring of the Zn surface and subsequent surface inhomogeneities of the reagent. This could have lead to isotope fractionation of the H during the reaction stage due to incomplete reduction of the water.

Kendall and Coplen (1985) recommended treating the Zn by cleaning with 3M HNO_3, rinsing in water and then acetone, outgassing under vacuum at 250°C, and then storing it in a desiccator. It was decided though to use a new batch of Zn, which had been stored under vacuum. Also, the Zn shot was loaded into the breakseal tubes just before use, and not stored in the oven at 110°C. After using fresh Zn reagent, and loading the Zn shot just before use, very good replication of data, in the δD ‰ range expected, was obtained.

4.2.9.6. Isotope analytical appraisal

The stable isotope laboratory in the Department of Geological Sciences, headed by Dr Chris Harris of University of Cape Town (UCT), South Africa, recently participated in an international ring test, to assess the D/H performance of mass spectrometers in various laboratories (Brand, 1996). The performance of the Finnigan Mat 252 in use at UCT is shown in Table 4.3, which lists the values obtained by the UCT instrument, compared with the mean values and standard deviations obtained for the results from all participating laboratories. A total of 38 laboratories participated in the study. The mean values and standard deviations tabulated below are calculated from the values returned from laboratories operating with mass spectrometers currently on the market.

Table 4.3. International performance appraisal for the UCT mass spectrometer (δD values)

	Gas B (‰) (relative to Gas A)	Gas C (‰) (relative to gas A)

UCT Finnigan MAT 252 (Instrument 6)	-406.53	-697.72
Mean Values (N= 17)	-408.03	-700.01
Std. Dev.	2.90	4.79

It is seen that the values for gases B and C, determined by the UCT Finnegan Mat 252, fall within the standard deviations calculated for results returned by other modern instruments.

Chapter 5. Results

This chapter reports the stable isotope data (δD and $\delta^{18}O$) that was determined for all the water samples collected. In addition, chemical analysis on all the spring waters, ground waters, and the reservoir waters collected on 14 August 1996, was performed. The waters were analyzed for pH, electrical conductivity (EC), cation elements (Na, K, Ca, Mg, Fe, Cu, Al, Si), and anions (HCO_3^-, F^-, Cl^-, Br^-, NO_3^-, SO_4^{2-}).

5.1. Stable isotope results

A comprehensive list of the stable isotope values obtained by the author during the course of the study for the water samples analyzed is presented in Table 5.1.

Table 5.1(a). Combined stable isotope data for the reservoir waters and groundwater.

Sample	δD(Mean Deviation*)	$\delta^{18}O$
Summer Reservoirs 09-04-1996		
Constantia Nek	-7(0.2)	-2.9
Blackheath R	-3(1.1)	-2.3
Blackheath T	-2(0.1)	-2.0
Faure R	2(1.1)	-1.3
Faure T	-5(1.2)	-2.7
Steenbras R	-5(0.8)	-2.6
Steenbras T	-4(1.0)	-2.1
Wemmershoek R	-8(3.0)	-3.1
Wemmershoek T	-11(1.3)	-2.9
Voelvlei R	+1(0.3)	-2.3
Voelvlei T	-5(1.1)	-1.5
Winter Reservoirs 14-08-1996		
Constantia Nek T	-13(0.2)	-3.9
Kloof Nek T	-16(0.2)	-4.7
Blackheat T	-25(1.1)	-5.6
Steenbras T	-11(1.4)	-2.9
Wemmershoek T	-16(0.2)	-4.4
Voelvlei T	-11(2.4)	-2.7
Groundwaters		
MW1	-10(0.6)	-2.8
MW2	-9(0.0)	-2.5
MW4	-6(0.7)	-2.5
MW6	-11(0.9)	-2.9
MW13	-14(1.0)	-3.0
MW15	-15(0.7)	-3.2
MW16	-10(2.2)	-2.8
MW17	-11	-2.5
MW19	-14(0.1)	-3.2

* Mean deviation = a-(a-b)/2, where a and b are the duplicate values; no mean deviation indicates that duplicates were not obtained for the specific sample

R = raw or untreated water, T = treated water

Table 5.1(b). Combined stable isotope data for the springwaters and the urban hydrological case study.

Sample	δD(Mean Deviation*)	$\delta^{18}O$
Spring Waters		
Rhodes Mem.	-13	-3.8
Hof spring	-11	-3.4
Rugby spring	-18(0.4)	-4.0
Main spring	-19(0.4)	-4.0
Albion spring	-9	-3.2
Newlands	-12	-3.4
Glencoe	-15	-4.1
Cable Way	-18(2.5)	-4.5
Forries	-12(1.1)	-3.2
Kirstenbosch	-15	-3.7
Fey	-11(0.2)	-3.1
Klipper	-12	-3.4
Hout Bay Mn Mine	-10	-3.7
Case Study		
Mieke mains	-15(0.8)	-4.0
Mieke crack	+10(0.0)	+0.9
Mieke groundwater	-18(0.3)	-3.7
Mieke pool	+4(1.0)	+0.1

* Mean deviation = a-(a-b)/2, where a and b are the duplicate values; no mean deviation indicates that duplicates were not obtained for the specific sample

R = raw or untreated water, T = treated water

5.1.1. Stable isotope data for the April reservoir samples

The reservoir water samples which have not passed through the water treatment process (untreated waters), collected on 09 April 1996, range in δD values from 2‰ for Faure to -8‰ for Wemmershoek. This represents a range in δD of 10‰ for the untreated waters. The $\delta^{18}O$

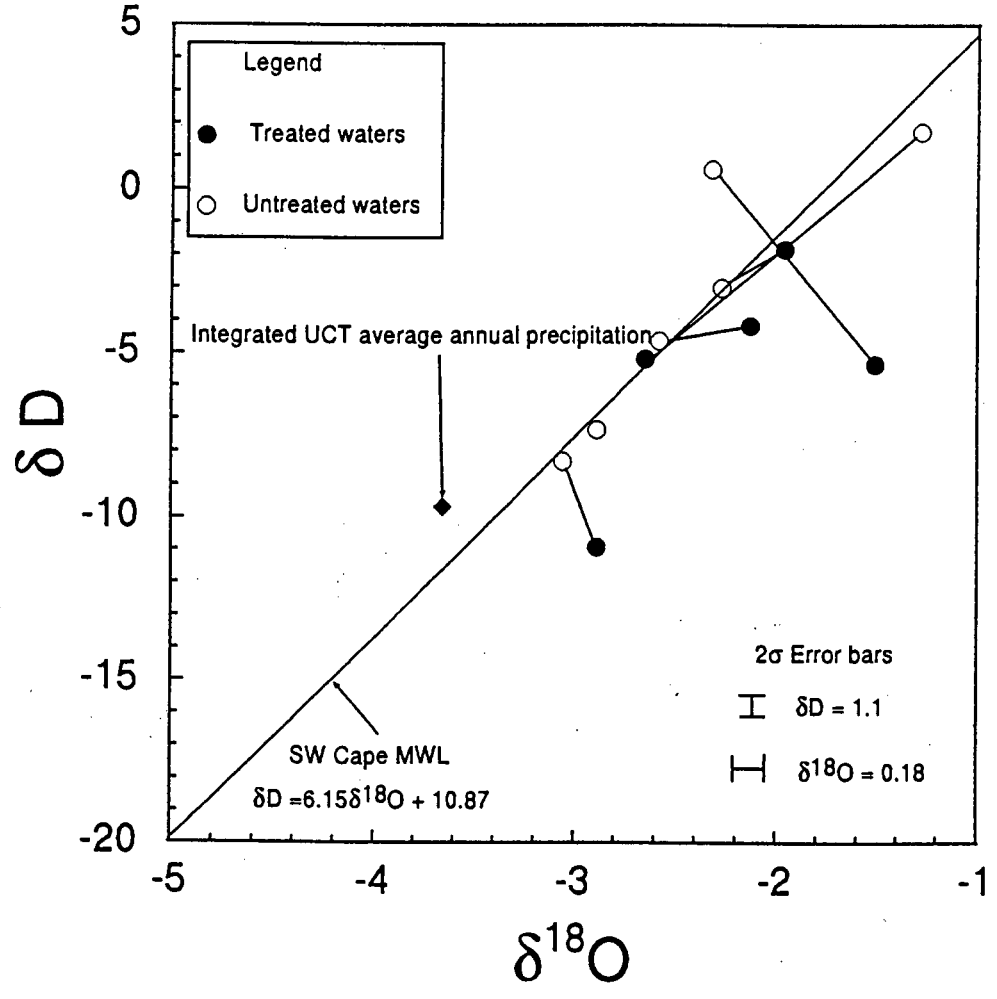


Figure 5.1. Stable isotope data for the treated and untreated April reservoir samples. (Integrated UCT average precipitation and unweighted SW Cape MWL from Diamond and Harris, 1996).

values range of from -1.3‰ for Faure to -3.1‰ for Wemmershoek, representing a range in $\delta^{18}O$ of 1.8‰. The calculated meteoric water line for the untreated April samples is $\delta D = 5.8\delta^{18}O + 10.42$ ($r^2 = 0.80$). The reservoir samples which have passed through the water treatment process, collected on 09 April 1996, range in δD isotope values from -2‰ for Blackheath to -11‰ for Wemmershoek, representing a δD range of 9‰. The $\delta^{18}O$ values for the treated waters range from -1.5‰ for Voelvlei to -2.9‰ for Wemmershoek, representing a range in $\delta^{18}O$ values of 1.4‰. The calculated meteoric water line for the treated April waters is $\delta D = 3.85\delta^{18}O + 3.074$ ($r^2 = 0.40$). Figure 5.1 graphically represents the change in stable isotope values after treatment for waters from the different reservoirs. In Figure 5.1, tie lines are shown leading from the untreated water to the treated water at each reservoir. The untreated sample point (δD -7‰; $\delta^{18}O$ -2.9‰), which does not have a corresponding treated sample point, belongs to the Constantia Nek reservoir, which was not treating any water at the time of sampling. The untreated water samples for Blackheath (δD -3‰; $\delta^{18}O$ -2.3‰), Steenbras (δD -5‰; $\delta^{18}O$ -2.6‰), Wemmershoek (δD -8‰; $\delta^{18}O$ -3.1‰), and Voelvlei (δD 1‰; $\delta^{18}O$ -2.3‰) all lie within 2σ errors (δD 1.1‰, $\delta^{18}O$ 0.18‰) of the SW Cape MWL. It is noted that water treatment affects the isotope values, in each case enriching the water samples in ^{18}O, but having a variable and seemingly unsystematic effect on the δD values. After treatment, the Blackheath $\delta^{18}O$ values become heavier by 0.3‰, the Faure $\delta^{18}O$ values by 1.4‰, the Steenbras $\delta^{18}O$ values by 0.5‰, the Wemmershoek $\delta^{18}O$ values by 0.2‰, and the Voelvlei $\delta^{18}O$ values by 0.8‰. However, the δD values for Blackheath and Steenbras both become heavier by 1‰, while the δD values for Faure, Wemmershoek and Voelvlei become lighter by -7‰, -3‰ and -6‰ respectively. The untreated waters tend to lie on or close to the SW Cape MWL (Figure 5.1), but the treated waters tend to deviate from the SW Cape MWL

5.1.2. Stable isotope data for the treated winter reservoir samples

Stable isotope values for the untreated August water samples was not obtained, as it was shown by the author that water treatment causes stable isotope fractionation, and that for use of stable isotopes in urban geohydrological applications, one would require the stable isotope values for the waters entering the municipal supply system, ie the stable isotope values for

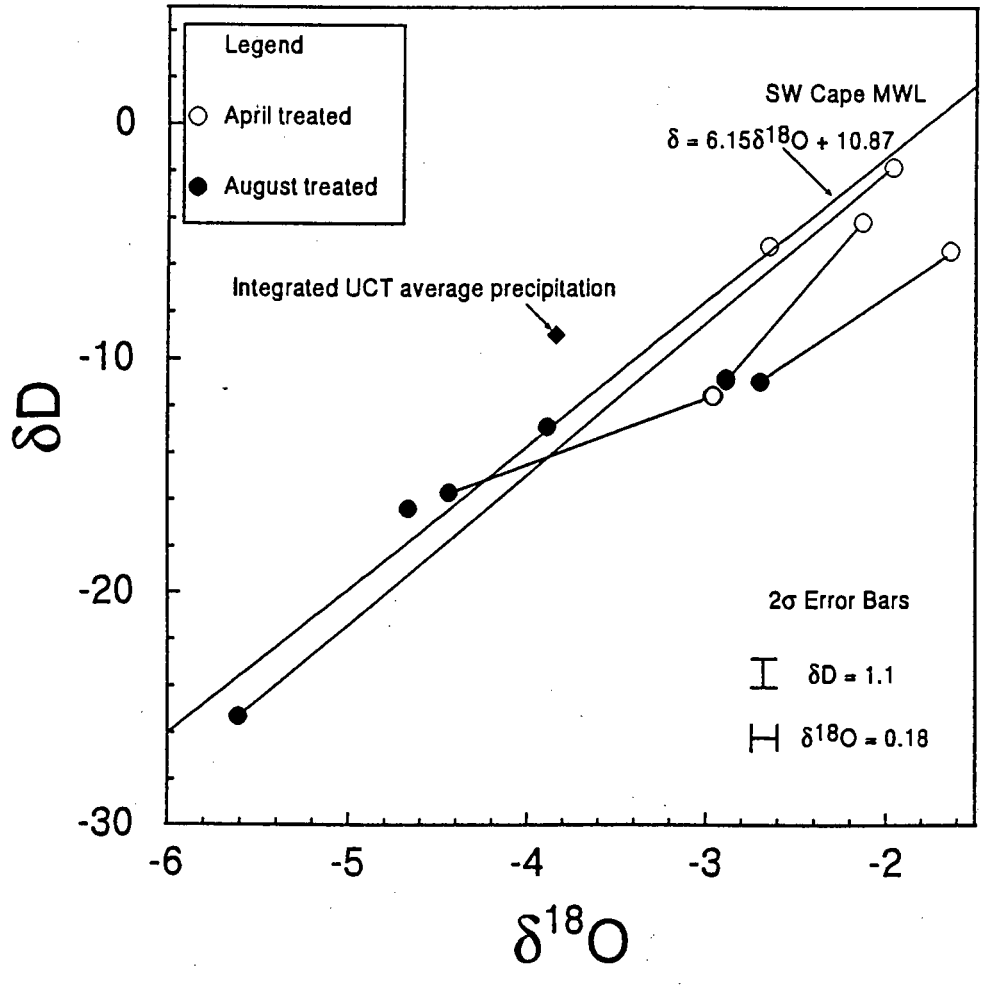


Figure 5.2. Stable isotope data for the treated April and August reservoir samples. (Unweighted SW Cape MWL for Diamond and Harris, 1996).

the treated waters. The data discussed in this section is from processed (treated) water only. The treated August reservoir samples range in δD values from -11‰ for Steenbras to -25‰ at Blackheath, representing a δD range of 14‰. The $\delta^{18}O$ values for the treated August reservoir samples range from -2.7‰ for Voelvlei, to -5.6‰ for Blackheath, representing a $\delta^{18}O$ range of 2.9‰. The range in both δD and $\delta^{18}O$ values has increased from April to August, with the δD range increasing from 9‰ to 14‰, and the $\delta^{18}O$ range increasing from 1.4‰ to 2.9‰. A comparison between the treated winter (August) reservoir samples and the treated summer reservoir data is shown in Figure 5.2. The tie lines in Figure 5.2 connect the treated summer water samples to the treated winter water samples for the same reservoirs. It is seen that δD and $\delta^{18}O$ values for the August (end of winter) values are lower than the values for the corresponding values determined for the April (end of summer) reservoirs, with depletion of the heavier isotopes normally occurring along a trend approximately parallel to the SW Cape MWL. The Blackheath values for the treated waters decrease from (δD -2‰; $\delta^{18}O$ -2.0‰) in April to (δD -25‰; $\delta^{18}O$ -5.6) in August, Steenbras decreases from (δD -4; $\delta^{18}O$ -2.1‰) to (δD -11‰, $\delta^{18}O$ -2.9‰), Wemmershoek decreases from (δD -11‰, $\delta^{18}O$ -2.9‰) to (δD -16, $\delta^{18}O$ -4.4), and Voelvlei decreases from (δD -5; $\delta^{18}O$ -1.5) to (δD -11; $\delta^{18}O$ -2.7). The average depletion between April and August in δD was 10‰, and in $\delta^{18}O$ was 2.0‰. The calculated best fit MWL for the treated August reservoir samples is $\delta D = 5.14\delta^{18}O + 5.86$ ($r^2 = 0.88$). The MWL's for all isotope data were calculated using classical unweighted regression with a computed y-intercept. It is noted in Figure 5.2, that the April isotope values for Faure (δD -5.2; $\delta^{18}O$ -1.28) are unconnected by a tie line to a corresponding August value, and the August isotope values for Constantia Nek (δD -12.89; $\delta^{18}O$ -3.89) and Kloof Nek (δD -16.39; $\delta^{18}O$ -4.67), are unconnected by tie lines to corresponding April values. This occurs as Faure was not treating water at the time of sampling in August, and Kloof Nek and Constantia Nek were not treating water during the April sampling period.

5.1.3. Stable isotope data for groundwaters from the Cape Flats aquifer

The groundwaters sampled from the monitoring wells are all obtained from the unconsolidated quartz sands of the Cape Flats Aquifer Unit (CFAU). The δD values for the groundwaters

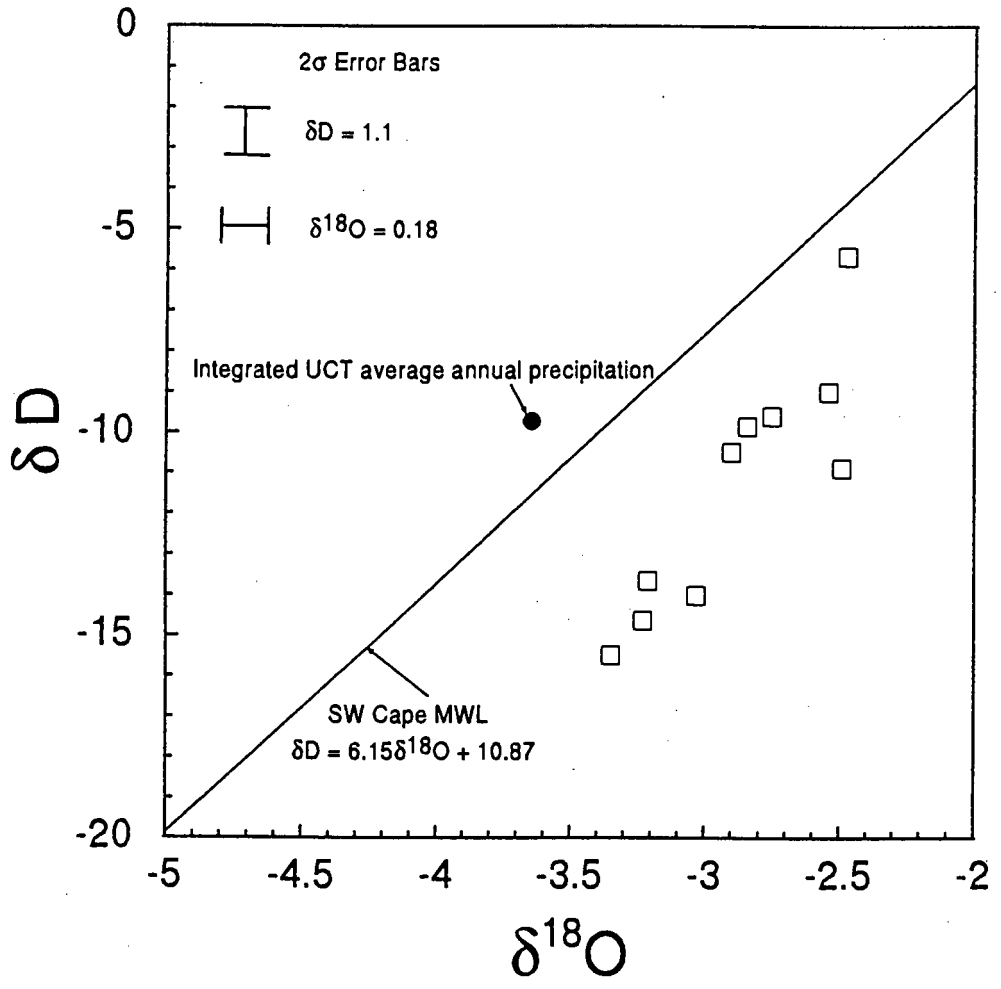


Figure 5.3. Stable isotope data for groundwaters from the Cape Flats Aquifer. (Integrated UCT average precipitation and unweighted SW Cape MWL from Diamond and Harris, 1996).

range from -6‰ at MW 4 to -15‰ at MW 15, representing a range in δD of 9‰. The $\delta^{18}O$ values range from -2.5‰ at MW 4 to -3.2‰ at MW 15, representing a $\delta^{18}O$ range of 0.7‰. The calculated best fit MWL for the groundwaters is $\delta D = 8.26\delta^{18}O + 12.51$ ($r^2 = 0.72$). The groundwater stable isotope results are presented in Figure 5.3.

5.1.4. Stable isotope data for natural springs on the slopes of Table Mountain

The stable isotope data for the springwaters sampled, presented in Figure 5.4, are divided into stable isotope data for ephemeral springs, and stable isotope data for permanent springs. The ephemeral springs are Rhodes Memorial, Cable Way, Forresters, Klipper Road and Hout Bay Mn Mine, and the permanent springs are Hof, Rugby, Main Spring, Albion Spring, Newlands, Glencoe, Kirstenbosch and Fey. The ephemeral group have a δD values ranging from -18‰ for the Cable Way spring, to -10‰ for the spring near Hout Bay, representing an overall δD range of 8‰. The $\delta^{18}O$ values for the ephemeral springs range from -4.5‰ for the Cable Way spring to -3.4‰ for Klipper spring, representing a range in $\delta^{18}O$ values of 1.1‰. The permanent springs have δD values ranging from -18‰ for Main Spring, to -9‰ for Albion Spring, covering a δD range of 9‰, and $\delta^{18}O$ values ranging from -4.0‰ for Main Spring, to -3.1‰ for Fey spring, representing a $\delta^{18}O$ range of 0.9‰. The calculated MWL for the spring data is $\delta D = 6.54\delta^{18}O + 10.21$ ($r^2 = 0.77$).

5.1.5. Graphical comparison of the different water groups

The isotope data for the treated April and August water samples, along with the groundwater and springwater, is shown in Figure 5.5. The different groups of water samples have been circled to graphically illustrate their differences and similarities.

5.2. Chemical analysis of the water samples

Chemical analysis was performed on the springwaters, groundwaters and the reservoir waters sampled in August. It was decided not to perform chemical analyses of reservoir waters sampled in April, as the municipal water treatment process is directed at producing water of

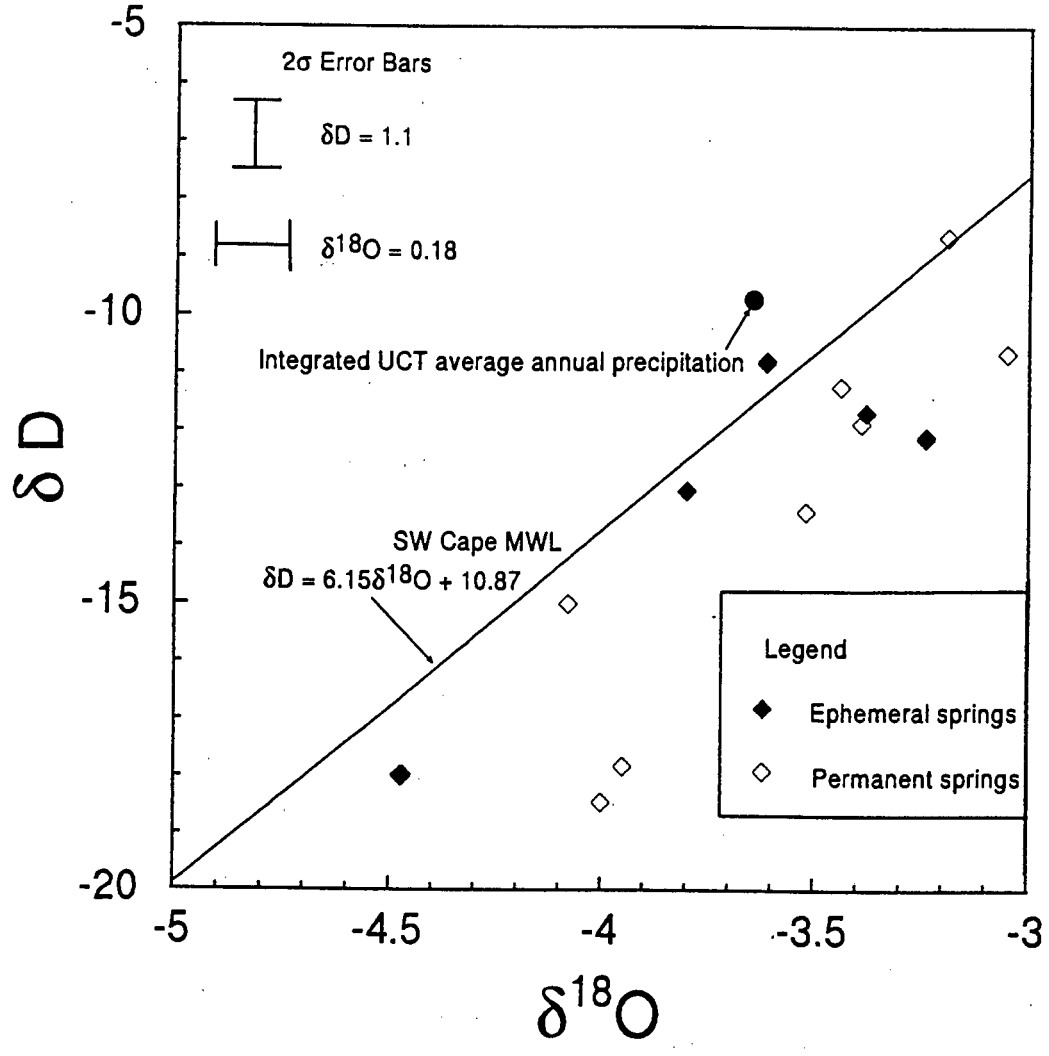


Figure 5.4. Stable isotope data for the natural springwaters from the slopes of Table Mountain. (Integrated UCT average precipitation and unweighted SW Cape MWL from Diamond and Harris, 1996).

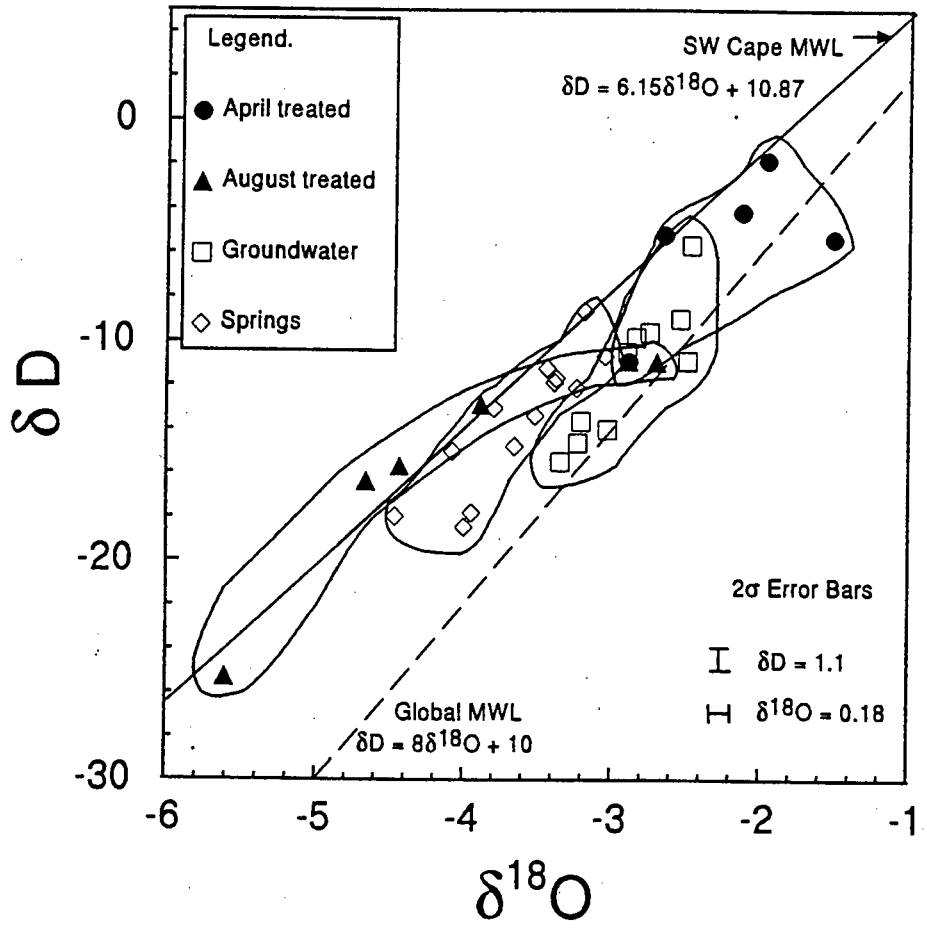


Figure 5.5. Stable isotope data for the April and August treated reservoir samples, along with the groundwater and springwater samples. (Integrated UCT average precipitation and unweighted SW Cape MWL from Diamond and Harris, 1996).

a specific chemical quality which is maintained throughout the year. As such, no geochemical difference was expected between the treated reservoir water in April, and the treated reservoir water in August (Cape Town Municipal Services Division, pers.com., 1996). A complete table of all the aqueous chemical data obtained is presented in Table 5.2., in which the data has been grouped according to the water sample source (spring water, ground water, reservoir water), and in each group in order of ascending electrical conductivity.

5.2.1. Correlations between stable isotope data and geochemical parameters

A statistical analysis was performed to test for correlations between δD and $\delta^{18}O$ values and all measured chemical parameters of the water groups, and $\delta^{18}O$ and all measured chemical parameters of the water groups. Separate Pearson-Product Moment Correlations were performed for each group of samples. Correlations statistically significant at the 95% confidence level ($p < 0.05000$) were checked against two dimensional scatterplots to graphically check the statistically valid correlations. A complete list of Pearsons r^2 coefficients for the three different sample groups is presented in Table 5.3. It was noted that, apart from the expected correlations between δD and $\delta^{18}O$ values, the only other significant correlation occurred in the groundwater samples, between δD and Mg ($r^2 = 0.68$). A graphical inspection of the associated scatterplot between the groundwater δD values and Mg concentrations (Figure 5.6) revealed that the correlatiion is not valid, as outliers in the Mg data set were adversely influencing the best fit line, thereby giving a "false" correlation. The correlation between δD and Mg were therefore rejected. It was expected that no correlations would occur between chemical and isotopic data, as isotope values are influenced by processes occurring before the water enters the geohydrological system, whereas the chemical parameters are strongly influenced by interaction of the waters with the matrix they are in direct contact with. In Figure 5.7, a plot of $\delta^{18}O$ against EC (which is empirically related to total dissolved solids [TDS] [McBride, 1991]) reveals no correlation between stable isotope values and EC (or TDS by association).

Table 5.2. Combined aqueous geochemical data. (All values in ppm unless specified).

Sample	Number	pH	EC (uS/cm)	Si	Fe	Mg	Al	Ca	Na	K	HCO3 (pH 4.5)	F	Cl	Br	NO3	SO4	Charge Balance (%)
Wem R 14-08	9	6	24	1	0.1	0.3	0.1	1	3	0.5	5	0.02	6			1	20
Blackheath R 14-08	5	6	33	1	0.1	0.5	0.1	1	3	0.6	6	0.02	8			1	5
Steenbras R 14-08	7	5	73	1	0.2	1.1	0.2	2	6	0.8	4	0.02	18		0.4	4	2
Kloof Nek R 14-08	3	5	82	0	0.2	1.3	0.3	2	6	0.7	0	0.02	19			3	0
Wem T 14-08	10	9	84	2	0.1	0.7	0.1	12	3	0.6	40	0.03	6			4	7
Voelvlei R 14-08	11	7	93	1	0.3	2.4	0.4	2	7	1.2	15	0.03	18			3	5
Con Nek R 14-08	1	5	94	1	0.2	1.6	0.3	1	8	1.0	1	0.02	23		0.2	4	-0
Blackheath T 14-08	6	9	129	2	0.1	0.9	0.1	18	4	0.7	46	0.02	8			15	7
Voelvlei T 14-08	12	8	130	1	0.1	2.9	0.1	7	7	1.1	18	0.04	21		0.8	13	-1
Steenbras T 14-08	8	8	163	2	0.1	1.6	0.1	18	7	1.0	43	0.02	18			18	1
Kloof Nek T 14-08	4	9	181	1	0.1	1.5	0.2	17	9	0.8	40	0.02	22			25	-9
Con Nek T 14-08	2	9	199	1	0.1	1.6	0.1	18	11	1.0	34	0.03	23			33	-4
MW 17	20	8	480	6	0.1	4.3	0.1	82	11	4.3	188	0.41	23		11.7	26	14
MW 6	16	7	703	8	0.1	6.5	0.1	64	12	4.6	163	0.54	27			56	8
MW 15	18	8	732	9	0.1	13.2	0.1	122	16	6.7	202	0.35	32		47.8	115	12
MW 16	19	8	1375	7	0.1	10.5	0.1	105	148	15.2	270	0.22	219			71	7
MW 1	13	6	1467	10	0.1	25.8	0.1	44	144	16.3	212	0.12	305	2	26.1	9	-1
MW 13	17	7	1763	10	0.1	21.0	0.1	158	185	20.8	479	0.48	229		18.0	198	2
MW 19	21	7	4090	12	0.1	75.3	0.1	198	582	34.5	730	0.46	1013		25.5	312	-4
MW 4	15	7	32700	10	0.1	871.0	0.2	445	7748	355.0	1316	0.57	11946	42		2590	3
MW 2	14	7	45700	8	0.1	928.0	0.2	608	10805	667.0	899	0.28	16666			3574	-3
Kirstenbosch	31	6	107	6	0.1	2.1	0.1	1	9	2.7	10	0.02	26	0	0.4	3	21
Klipper	33	5	131	2	0.1	2.9	0.1	3	11	2.4	7	0.02	31		1.0	9	2
Newlands	27	5	133	4	0.1	3.0	0.1	2	10	2.4	10	0.02	30		3.5	4	13
Main Spr.	25	6	152	3	0.1	2.8	0.1	2	13	2.4	35	0.02	38		1.2	5	-12
Cable Way	29	7	156	5	0.1	2.9	0.1	1	14	2.9	8	0.01	40			5	9
Forries	30	5	157	4	0.1	3.5	0.1	2	11	2.4	8	0.01	34		6.2	4	9
Fey	32	6	166	4	0.1	3.2	0.1	7	11	3.8	26	0.05	31			9	8
Rhodes Mem	22	5	186	1	0.1	3.4	0.1	2	15	2.3	5	0.02	42		4.0	8	-10
Rugby	24	9	191	1	0.1	1.7	0.1	16	8	2.1	35	0.03	20			26	-6
Albion	26	6	215	6	0.1	5.4	0.1	4	15	2.6	33	0.01	41		2.6	7	7
Hout Bay	35	6	239	1	0.1	4.7	0.1	2	25	3.1	5	0.02	80			10	-17
Glencoe	28	6	413	3	0.1	6.4	0.2	2	41	4.0	9	0.01	102			8	-6
Hof	23	7	734	4	0.1	11.5	0.2	7	86	5.1	48	0.04	174			46	-7
Mieke O/w.	37	6	2210	13	0.4	34.3	0.3	13	356	5.4	19	0.11	689			125	-5
Mieke Mains		9	155								0						
Mieke Creek		9	3610														
Mieke Pool		8	3300														

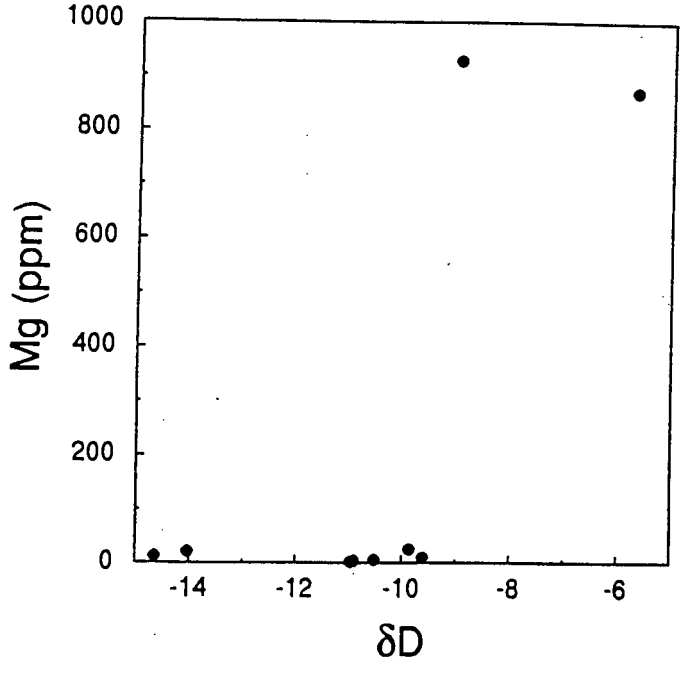


Figure 5.6. X-Y plot of all groundwater δD values and Mg concentrations.

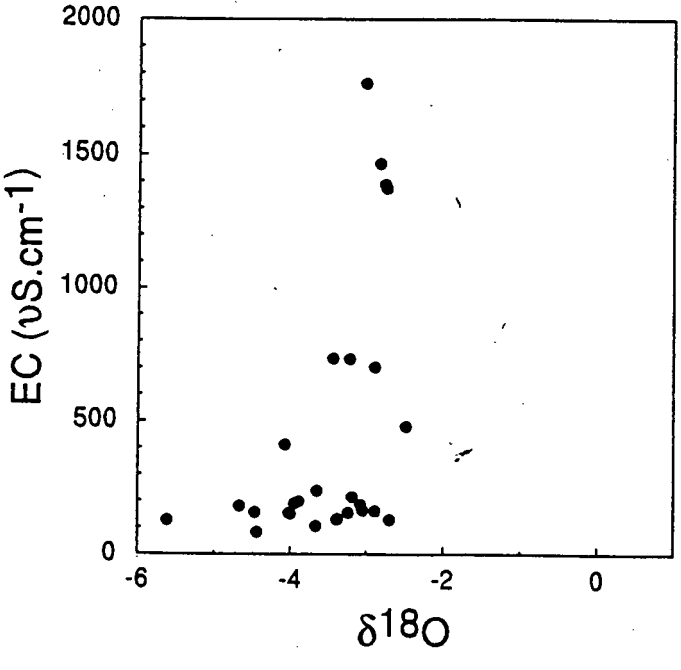


Figure 5.7. X-Y plot of $\delta^{18}O$ values and EC for all samples.

Table 5.3. R^2 values, obtained from Pearson-Moment correlation calculations.

Variable	Treated Reservoir Waters.		Groundwaters.		Springwaters.	
	δD	$\delta^{18}O$	δD	$\delta^{18}O$	δD	$\delta^{18}O$
δD	1.00	0.93*	1.00	0.85*	1.00	0.81*
$\delta^{18}O$	0.93*	1.00	0.85*	1.00	0.81*	1.00
pH	-0.60	-0.79	-0.32	-0.11	-0.34	-0.37
EC	0.26	0.16	0.62	0.58	0.19	-0.03
Si	-0.35	-0.14	-0.29	-0.56	0.20	0.07
Fe	0.06	-0.08	0.63	0.53	0.11	-0.21
Mg	0.65	0.78	0.68*	0.60	0.40	0.12
Al	-0.46	-0.57	0.64	0.63	0.04	-0.14
Ca	-0.37	-0.45	0.48	0.46	-0.13	0.02
Na	0.54	0.40	0.63	0.59	0.20	-0.03
K	0.71	0.79	0.55	0.56	0.26	-0.01
HCO_3^+	-0.57	-0.65	0.52	0.37	-0.04	0.03
F^-	0.50	0.53	-0.01	-0.03	0.18	0.34
Cl^-	0.63	0.57	0.63	0.59	0.22	-0.06
SO_4^{2+}	0.17	0.05	0.60	0.57	0.06	0.01

Note: * values indicate statistically significant correlations ($p<0.05$).

5.2.2. Water grouping using chemical parameters

The water groups were divided into reservoir waters, groundwaters, and spring waters. The chemical concentration average distributions for each group are presented in Figure 5.8. Only the chemical constituents which are consistently present in all three sample groups, in concentrations greater than 1 ppm, are represented. It is noted that a log scale is used to represent the ppm concentrations, in order to accommodate the wide range of values present. Table 5.4 presents the average compositions and relative standard deviations (RSD) for the three water groups.

Table 5.4. Average chemical and isotope compositions and relative standard deviations for the different water groups. (All concentrations in ppm unless stated.)

Parameter	April Reservoirs	August Reservoirs	Groundwaters*	Springs
	Mean (RSD%)	Mean (RSD%)	Mean (RSD%)	Mean (RSD%)
δD (‰)	-6 (60.72)	-15 (35.5)	-12 (30.3)	-14 (27.1)
$\delta^{18}O$ (‰)	-2.6 (45.80)	-4.0 (27.5)	-2.9 (13.1)	-3.5 (13.3)
pH	8.8 (6.85)	8.7 (6.6)	7.19 (6.5)	6.19 (17.6)
EC ($\mu S.cm^{-1}$)	140 (23.670	147 (28.7)	1602.5 (72.6)	229 (52.4)
Si		1.5 (30.6)	9.34 (23.9)	3.31 (49.6)
Mg		1.54 (49.3)	23.86 (96.9)	4.12 (62.4)
Ca		15.01 (29.4)	98.23 (61.7)	3.98 (103.5)
Na		6.75 (43.4)	181.77 (109.5)	20.67 (103.3)
K		0.87 (20.7)	13.47 (127.5)	2.95 (29.5)
HCO_3^{-1}		36.78 (27.7)	351.4 (82.8)	18.41 (80.6)
Cl^{-1}		16.23 (45.9)	317.19 (112.6)	53.12 (80.9)
SO_4^{2+}		17.87 (56.6)	113.77 (87.9)	11.01 (107.8)

*: The values for MW 2 and MW 4 were omitted from these calculations, due to their exceptionally high dissolved constituent concentrations.

RSD = Relative standard deviation

An inspection of the average chemical concentration distributions (Figures 5.8) between the three different chemical groups reveals that trends occur in the relative distribution of chemical constituent concentrations in each group is occurring. It is seen that the reservoir waters generally have the lowest concentrations of chemical species, the springwaters have concentrations intermediate between the reservoir waters and the groundwaters, and the groundwaters have the highest chemical species concentrations. However, an inspection of the values of Table 5.4, above, reveals that most average concentration values for each water

group have high associated RSD's, which indicate substantial variations in the chemical composition between individual group members. As such, caution should be exercised when classifying waters in the Cape Town area according to their chemical composition. The average pH has the lowest associated RSD's. However, Ca, Na, K and Cl^- differ in relative amounts in all three different water groups by a factor of at least three, and this would serve to highlight their potential for use as parameters for differentiating the water groups, and their subsequent use in determining which water group an unknown water sample belongs to.

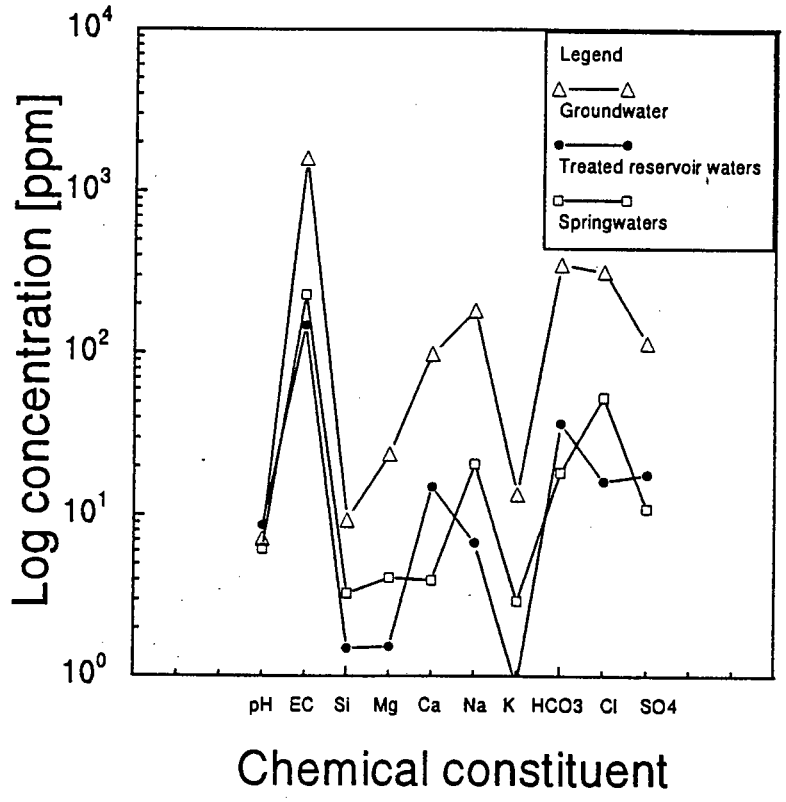


Figure 5.8. Average chemical concentration distributions for the different water groups (log of EC in $\mu S.cm^{-1}$).

Chapter 6. Discussion

This chapter discusses the reasons for the variations observed in stable isotope values for the different groups of waters, along with the potential use of using stable isotope and chemical compositions for classifying and identifying different water groups in urban isotope geohydrology. The correlations between stable isotope and chemical compositions are also discussed.

6.1. Treated *vs.* untreated summer reservoir data

The change in δD and $\delta^{18}O$ values for the water samples during the water treatment process is probably as a result of the treatment processes used, which vary from plant to plant. Different treatment plants use varying amounts of CO_2 during the process, which is obtained from different sources. This may result in equilibration of the waters with the CO_2 used, and possible isotope fractionation, though the ratio of CO_2 : water must be small. Some of the plants have settling stages, with the length of the settling stages dependant on water quality at the time. Water may be subjected to evaporative effects during the settling stages, as the settling tanks are generally open and exposed to the atmosphere. The settling tanks are shallower than the reservoirs, with a greater surface area per unit volume of water, therefore evaporation from the settling tanks may occur at a fast enough rate to effect significantly the stable isotope ratios of the waters. It is noted that reasons for isotope fractionation of the waters during the treatment process are not part of the authors study. It should be noted that the water which is to be integrated into the municipal supply network is important in hydrological studies, hence treated water should be analyzed for their isotopic composition rather than untreated water.

6.2. Summer *vs.* winter reservoir data

Variations in the slope values for each reservoir (from the SW Cape MWL) are a function of climate, geographic location and source region of evaporation (Dansgaard, 1964, Merlivat and Jouzel, 1979), and thus, due to the microclimate and locality variations of the different reservoirs and catchment areas (described in Section 3.3), it is possible that the isotope values

for water from each reservoir and associated catchment area could fall off the SW Cape MWL. The rainfall between April and August for 1996, as seen in Figure 3.1, was lower in May than the average, but typical during June, July and August. As a result, the reservoirs filled up considerably with unevaporated meteoric water derived from the high winter rainfall. Steenbras dam was at 64.8% of its maximum capacity in April, and rose to 100% capacity in August, while Voelvlei was at 64.5% capacity in August, and rose to 95.4% in August. In general, it could be expected that the stable isotope values for the reservoirs will become considerably lower during the wet winter season, and higher during the dry summer season. The depletion of the August reservoir waters in δD and $\delta^{18}O$, relative to the April reservoir waters is most probably explained due to Rayleigh fractionation as a result of the amount effect, which is expected due to the dominant winter rainfall of the study area. Conversely, the lower rainfall in summer is expected to have heavier stable isotope values than the higher winter rainfall (Diamond, 1997). Secondly, the cooler conditions and reduced evaporation during the winter period will contribute toward the lighter isotope values measured, as well as reduce the degree of deviation from the local MWL's.

6.2.1. Simple model Rayleigh fractionation for selected reservoirs

Simple Rayleigh fractionation calculations were performed, in order to determine the degree of evaporation in the Steenbras dam and Voelvlei based on the change between summer and winter $\delta^{18}O$ values, and to compare the calculated values with the reported values for the reservoir levels at the times of sampling. The calculations were based on the equation: $R_A/R_0 = F^{(\alpha-1)}$, where R_A is the isotopic ratio of oxygen in April (after evaporation); R_0 is the isotopic ratio of oxygen in August (assuming no evaporation - dam levels 100%); F is the fraction remaining of the original liquid volume, and α is the fractionation factor. For this exercise, it was assumed that the April values are typical evaporated values, and the August values are typical recharged values. Calculations were performed at 20°C and 30°C , using both $\delta^{18}O$ and δD to investigate the effect of temperature fluctuations on the degree of evaporation. Table 6.1a. lists the reported dam levels, and the calculated dam levels for April using $\delta^{18}O$, at 20°C and 30°C, where F represents the fraction of the dams maximum capacity. F was assumed to be 1 in August, indicating the dams were at 100% capacity. Table 6.1b lists the recalculated F values using δD.

Table 6.1a. Results of simple model Rayleigh Fractionation, using $\delta^{18}O$ (α values from Bottinga and Craig, 1968).

Reservoir	F reported	F calculated at 20°C	F calculated at 30°C
Steenbras	0.648	0.921	0.917
Voelvlei	0.645	0.883	0.874

Note: $\alpha_{\text{water vapour-water liquid, 20°C}} = 0.9905$; $\alpha_{\text{water vapour-water liquid, 30°C}} = 0.9918$; F = fraction remaining

Table 6.1b. Results of simple model Rayleigh Fractionation, using δD (α values from Merlivat *et al.*, 1971).

Reservoir	F reported	F calculated at 20°C	F calculated at 30°C
Steenbras	0.648	0.9136	0.9047
Voelvlei	0.645	0.9276	0.9201

Note: $\alpha_{\text{water vapour-water liquid, 20°C}}=0.9250$; $\alpha_{\text{water vapor-water liquid, 30°C}}=0.9323$; F = fraction remaining.

It is seen from Table 6.1a and Table 6.1b that the calculated F values for the two reservoirs are greater than the observed F, where F is the fraction of water left in the reservoir such that a greater value of F implies less evaporation. If one considers that water is being removed from the reservoirs to be integrated into mains water supplies, then one would expect $F_{\text{calculated}}$ to be greater than F_{observed}. The results indicate that, at 20°C, evaporation accounts for about a third of the water which is removed from the reservoirs. It is also noted that a 10°C rise in temperature results in F increasing by 0.004 for Steenbras dam, and by 0.009 for Voelvlei, using $\delta^{18}O$ calculations. This represents a total volume loss of less than 1% for a 10°C average increase in temperature. Implications for this are that the range of temperature fluctuations in the reservoir areas will not have a large effect on the amount of water evaporated from the reservoirs, compared t othe amount of water removed by abstraction. A comparison of the modelling results obtained using δD, compared with the modelling results obtained using $\delta^{18}O$, at 20°C, show a calculated F difference of 0.0074 (or 0.74% of the total dam volume) for Steenbras dam, while the results for Voelvlei show an F difference of 0.0446 (or 4.46% of the total dam volume). It is suggested that calculated F for the

systems of interest should be determined by averaging the values obtained from both $\delta^{18}O$ and δD calculations.

The calculated average integrated stable isotope values required for the reservoirs to be recharged, and to have the resulting observed stable isotope values, was determined by the following expression:

$\delta^{18}O_{F(2)} = F_1*(\delta^{18}O_{F(1)}) + (F_2 - F_1)*X$ (1),

where X is the average $\delta^{18}O$ recharge value; F_1 is the fraction of liquid in the reservoir before a recharge episode; F_2 is the fraction of liquid in the reservoir after a recharge episode; $\delta^{18}O_{F(1)}$ is the $\delta^{18}O$ value corresponding to F_1; $\delta^{18}O_{F(2)}$ is the $\delta^{18}O$ value corresponding to F_2. Therefore, for Voelvlei:

$F_1 = 0.65$; $\delta^{18}O_{F(1)} = -1.5$; $F_2 = 1.00$; $\delta^{18}O_{F(2)} = -2.7$,

therefore average recharge: $2.7 = 0.65*(-1.5) + (1.00-0.65)*X$.

Solving for X gives a recharge $\delta^{18}O$ value of -4.93. The δD recharge values were calculated using (1), except δD values were substituted for $\delta^{18}O$ values. The calculated δD and $\delta^{18}O$ recharge values are shown in Table 6.2. The calculated average $\delta^{18}O$ values was substituted into the SW Cape MWL equation ($\delta D = 6.15\delta^{18}O + 10.87$. Diamond and Harris, 1996), to give an indication of how the calculated recharge values corresponded with the SW Cape MWL. These values are included in Table 6.2. Only Steenbras and Voevlei are modelled, as reservoir level data was not readily available for the other reservoirs analysed.

Table 6.2. Calculated average isotope recharge values and the expected corresponding δD recharge values obtained by substitution into the SW Cape MWL (Diamond and Harris, 1996).

Reservoir	Recharge $\delta^{18}O$	Recharge δD	Expected δD
Steenbras	-4.50	-23.4	-16.81
Voelvlei	-4.93	-21.34	-19.45

It is seen from Table 6.2 that the calculated recharge δD values are lighter than the expected δD values. The Steenbras δD values differ by 6.59‰, and the Voelvlei δD values differ by 1.89‰. Both differences exceed the 2σ standard deviation of δD= 1.1‰ (Diamond and Harris, 1996). It is therefore recognised that the simple modelling performed above allows for a quick

approximation of the expected isotope values of a given system. However, many factors (such as relative humidity) were not accounted for in the calculations, therefore one should be cautious about expressing too much confidence in the theoretical isotope results. Simple modelling is useful in obtaining a fairly good estimate of how much water is lost through evaporation in the reservoirs, and the average recharge isotope values could possibly be extended to approximate the integrated rainfall isotope values in the reservoir catchment areas during the four month interval between sampling.

6.3. Groundwaters

The groundwaters lie on a calculated MWL of $\delta D = 8.26\delta^{18}O + 12.50$ ($r^2 = 0.71$). Figure 5.3 shows the groundwater data, compared with the SW Cape MWL ($\delta D = 6.15\delta^{18}O + 10.87$), as well as the integrated UCT average annual precipitation (δD -9.8‰; $\delta^{18}O$ -3.65‰). It is seen that the groundwater values lie to the right of the SW Cape MWL, and the integrated UCT average annual precipitation value. The UCT precipitation average was determined at an altitude of 120m above sea level, while the groundwater samples were all taken from monitoring wells with a surface altitude of 10m to 25m above sea level. If the altitude effect were to account for the variations observed, then the groundwater values should still lie on the SW Cape MWL, but with slightly lower isotope values. Sea water intrusion into the monitoring wells is not suspected, as the values for δD and $\delta^{18}O$ are not shifted substantially toward SMOW. The high EC values for MW2 and MW4, which could have suggested sea-water intrusion into the Cape Flats Aquifer Unit (CFAU) are explained by MW2 being situated in salt rich pleistocene estuarine silt, and MW4 being situated above a railways ash/slag dump, which would result in substantial contamination of the groundwater with dissolved salts. Stable isotope values for the winter (August) reservoir waters entering the Cape Town municipal supply system group closer to the SW Cape MWL than the groundwaters analyzed in this study, (the winter reservoir samples only are considered here, as groundwater sampling was performed in early September), therefore substantial contributions to the groundwaters from leaking mains water supply systems is not suspected. September is the wrong time of the year to search for contributions to the groundwaters from the mainswaters on two counts - firstly, the water table is high, with the groundwater being subject to very recent high recharge, and secondly, the groundwaters and reservoir waters at

the start of September have similar δD and $\delta^{18}O$ values. The stable isotope values for Steenbras (δD = -11; $\delta^{18}O$ = -2.9), and Voelvlei (δD = -11; $\delta^{18}O$ = -2.7), lie in the centre of the groundwater isotope value distribution (Figure 5.1), but contribution to these groundwaters from water originating either at Steenbras or Voelvlei is not suspected, as these reservoirs do not generally supply the Cape Town central area.

6.4. Springwaters

An inspection of Figure 5.4. reveals that the ephemeral springs appear to lie closer to the SW Cape MWL than most of the permanent springs. This could possibly be explained by the fact that, after prolonged periods of rainfall (such as after the winter rainfall period), the water table in the Table Mountain Aquifer system will have risen considerably. This would result in the water table intersecting the surface of Table Mountain in various places, resulting in ephemeral springs at these points, until such a time as the water table is lowered again. Water from these points will probably be very recent meteoric water, and would be expected to have stable isotope values which lie on or are close to the SW Cape MWL. Table 6.4 shows a comparison between the $\delta^{18}O$- and δD values and the spring altitudes.

Table 6.4. Yields, altitude above sea level, δD and $\delta^{18}O$ values for the sample springs.

Spring name	Yield ($l.min^{-1}$)	Altitude	δD (‰)	$\delta^{18}O$ (‰)
Albion Spring	>1000	30	-9	-3.2
Newlands	>1000	30	-12	-3.4
Forries	100-1000	40	-12	-3.2
Fey	10-100	80	-11	-3.1
Klipper Spring	10-100	100	-12	-3.4
Main Spring	>1000	120	-18	-4.0
Rhodes Memorial	10-1000	140	-13	-3.8
Kirstenbosch	10-100	150	-15	-3.7
Hof	100-1000	190	-11	-3.4

Table 6.4. (continued)

Spring name	Yield (l.min^{-1})	Altitude	δD (‰)	$\delta^{18}O$ (‰)
Rugby	10-100	210	-18	-4.0
Glencoe	10-100	250	-15	-4.1
Hout Bay	1-10	280	-10	-3.7
Cable Way	1-10	310	-18	-4.5
UCT rainfall (yearly		120	-10	-3.7

Figure 6.1. shows the distribution of the δD and $\delta^{18}O$ isotope ratios for the springs, as a function of the altitude of the springs. It is noted that there appears to be a regular slight depletion of ^{18}O with altitude. A regression of $\delta^{18}O$ against altitude resulted in an apparent altitude effect of -0.41‰ $\delta^{18}O$/100m increase in height ($r^2 = 0.72$). This is slightly higher than the typical value of about -0.26‰ $\delta^{18}O$\100m increase in height (Payne and Yurtsever, 1974), but less than the effect reported by Diamond and Harris (1996) of -0.74‰ $\delta^{18}O$\100m increase in height for Table Mountain. The value reported by Diamond and Harris (1996) was obtained from a study to investigate the altitude effect on Table Mountain, and is regarded as being the result of several effects, including rainout, and the samples taken being integrated rainfall from different periods of several days rain (Diamond and Harris, 1996). The variation in $\delta^{18}O$ with altitude for the springs could be as a result of groundwater recharge for the different springs occurring at different heights on Table Mountain, with the lower altitude effect than that reported by Diamond and Harris (1996) possibly due to mixing of waters in the Table Mountain aquifer system, which landed at different altitudes on Table Mountain, and during different rain events. This mixing effect would serve to moderate effects such as the altitude effect. However, the varied nature of the rain falling on Table Mountain, along with the varying topography of the mountain, make it difficult to confidently ascribe any observed effect to a single factor such as the altitude effect, therefore no reliable estimate of the altitude effect may be made from the springwater samples.

It is seen that most of the springs are depleted in D relative to the UCT average annual mean, but seven are enriched in ^{18}O, and five are depleted in ^{18}O, relative to the UCT weighted

annual mean (Figure 5.3, Figure 6.1). The most likely explanation for this phenomena is the same offered in section 5.1.3. (Groundwater), in that the Cape Town region experiences microclimatic differences, which are strongly influenced by Table Mountain, the direction the rain comes from, and altitude and amount effects. An example of the differences in stable isotope values which may occur during a single precipitation event in the Cape Town area have been shown by Diamond and Harris (1996), who collected precipitation samples from UCT (altitude 140m; δD +3‰; $\delta^{18}O$ -1.4‰) and Observatory (altitude 140; δD +13‰; $\delta^{18}O$ +0.2‰) on the same morning. The two sampling points are about four kilometres apart. The differences in the stable isotope values for the Observatory and UCT rainfall were ascribed by Diamond and Harris (1996) to topographical effects caused by Table Mountain, which induces precipitous rain on its steep southern and eastern slopes. UCT is situated on the eastern slopes of Table Mountain, and subsequently receives higher rainfall than Observatory. Due to the amount effect, the isotope values for the UCT rain are subsequently lower. The microclimatic differences would result in a lack of confidence in establishing a MWL for Cape Town which is rigidly applicable to all precipitation occurring in the city. Figure 5.4. shows that the springwater samples have a slight $\delta^{18}O$ enrichment relative to the SW Cape MWL, and lie on a MWL ($\delta D = 6.54\delta^{18}O + 10.20$, $r^2 = 0.77$) which is intermediate in gradient and deuterium excess between the SW Cape MWL ($\delta D = 6.15\delta^{18}O + 10.87$, Diamond and Harris, 1996) and the Global MWL ($\delta D = 8\delta^{18}O + 10$, Craig, 1961).

It should be noted that the author calculated the springwater MWL using a classical regression, which assumes one variable ($\delta^{18}O$) to be independent, and have no error. Different methods are available for calculating regression lines for two sets of independent variables, and these will result in slightly different equations for calculated MWL's. The slight variation in the springwater MWL from the SW Cape MWL is most probably ascribed to microclimatic variations in the spring recharge zones. All the springs sampled were cold springs, therefore deep circulation, and mixing with deeper groundwaters, is not suspected. This is reflected in the stable isotope values, which do not seem to show mixing with any waters which are significantly isotopically different from thr sample set. δD. The $\delta^{18}O$ value for the UCT weighted rainfall ($\delta^{18}O$ -3.65‰(2σ 0.18‰); altitude 120m) is lighter than the $\delta^{18}O$ values for Albion Spring, Newlands, Forries and Fey. This would possibly seem to indicate that the average recharge height is occurring on Table Mountain, but at an altitude lower than UCT.

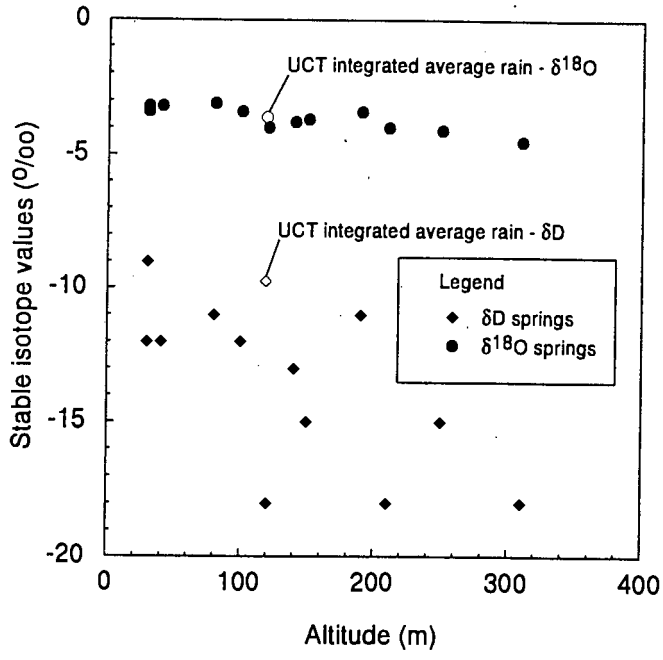


Figure 6.1. Plot of altitude vs δD and $\delta^{18}O$ for the springwater samples.

6.5. The use of geochemical parameters for identifying different water groups

Figure 5.7 indicated that there is no significant correlation between EC and either δD or $\delta^{18}O$ values for either the reservoir waters, groundwaters or spring waters, while Table 5.4 indicated no statistically valid correlation between any of the chemical constituents of the waters and either δD or $\delta^{18}O$ values. It was noted that the groundwaters generally had the highest concentrations of dissolved salts, followed by the springwaters, and finally the reservoir waters. Calcium, Na, K and Cl would be the best chemical parameters for differentiating between water from the different groups on a non-stable isotope basis. However, the dissolved salt concentrations of the waters of interest is highly variable, represented by the large standard variations evident for most chemical parameters (Ground water EC's range from 480μS.cm^{-1} to 45700μS.cm^{-1}, σ = 72.57%), therefore classifying waters in the Cape Town region on the basis of dissolved chemical constituents is not advised. Possibly the best chemical parameter for identifying different waters would be pH, as the treated reservoir waters have an average pH of 8.7 (σ = 6.55%), the groundwaters have a pH average of 7.19 (σ = 6.54), and the spring waters have an average pH of 6.19 (σ= 17.6).

However, the chemical parameters, and pH, are non-conservative properties of water, as they are not properties of the water molecule itself, and are subject to change according to the matrix they are in contact with. Secondly, if different waters mix, the resultant chemical properties of the mixed waters are not purely intermediate between the properties of the original waters. For example, an equal volumes of water of pH 5 and pH 9 mixing will rarely result in water of pH 7, but the resultant pH will be dependant on other factors such as alkalinity. Stable isotope compositions of recent meteoric groundwaters are highly conservative, not changing significantly once the water is protected from evaporation, and are properties of the water molecule. Consequently, stable isotope compositions are a good conservative parameter to monitor the mixing of different water masses. Differences in isotopic compositionreflect differences in ground water groups, where the waters are derived from, what physical processes they have been subjected to before entering closed water systems, and to what degree the water of interest has mixed with waters from other sources.

6.6. A case study using stable isotopes in an urban environment

An application of using the stable isotopes of H and O to solve a hydrological problem was performed by the author during the course of the study. It involved a crack in a retaining wall below a swimming pool, from which water was leaking. The origen of the leaking water was unknown.It was decided to use stable isotopes, along with other geochemical parameters, to determine if the leaking water was coming from the swimming pool, groundwater or mains water. The δD and $\delta^{18}O$ values, and pH and EC for the pool, mains water from the area, the crack water and tap water were determined, and are presented in Table 6.5.

Table 6.5. Stable isotope and geochemical data for the hydrological case study.

Water source	δD (‰)	$\delta^{18}O$ (‰)	EC ($\mu S.cm^{-1}$)	pH
Mieke Crack	+10	+0.9	3610	8.76
Mieke Swimming pool	+4	+0.1	3300	8.06
Mieke Groundwater	-18	-3.7	2210	6.45
Mieke Tap water	-15	-4.0	155	9.12

An inspection of Table 6.4. indicates that the crack water is enriched in D and ^{18}O (δD 10‰; $\delta^{18}O$ 0.9‰). The only possible water source that is enriched in the heavier isotopes is the swimming pool (δD +4‰; $\delta^{18}O$ +0.1‰). The crack water has a higher EC (3610 $\mu S.cm^{-1}$) than the groundwater (2210$\mu S.cm^{-1}$) and the pool water (3300$\mu S.cm^{-1}$), and a much higher EC than the tap water (155$\mu S.cm^{-1}$). On the basis of EC, the crack water could have been derived from either the groundwater or pool water, and subjected to evaporative effects before being sampled. The pH value of the crack water (pH 8.76) is intermediate between the tap water pH of 9.12, and the pool pH of 8.06, thus, on the basis of pH, the crackwater could have come from either tapwater or poolwater. The only definitive parameters, which allow a confident determination of the crack water source are the δD and $\delta^{18}O$ values. However, chemical parameters such as pH and EC may often be useful in supplementing a small scale stable isotope study, as is illustrated in the above example. Figure 6.2 shows the stable isotope data for the discussed case study. The enriched isotope values and higher EC for the crack water compared to the pool water suggest the crack water has been subject to evaporation. The cost of such a preliminary isotope study is a few hundred rand, compared with the possibility of many thousands of rand for mistakingly excavating for a suspected mains water leak, or trying to fix a pool which may not be leaking.

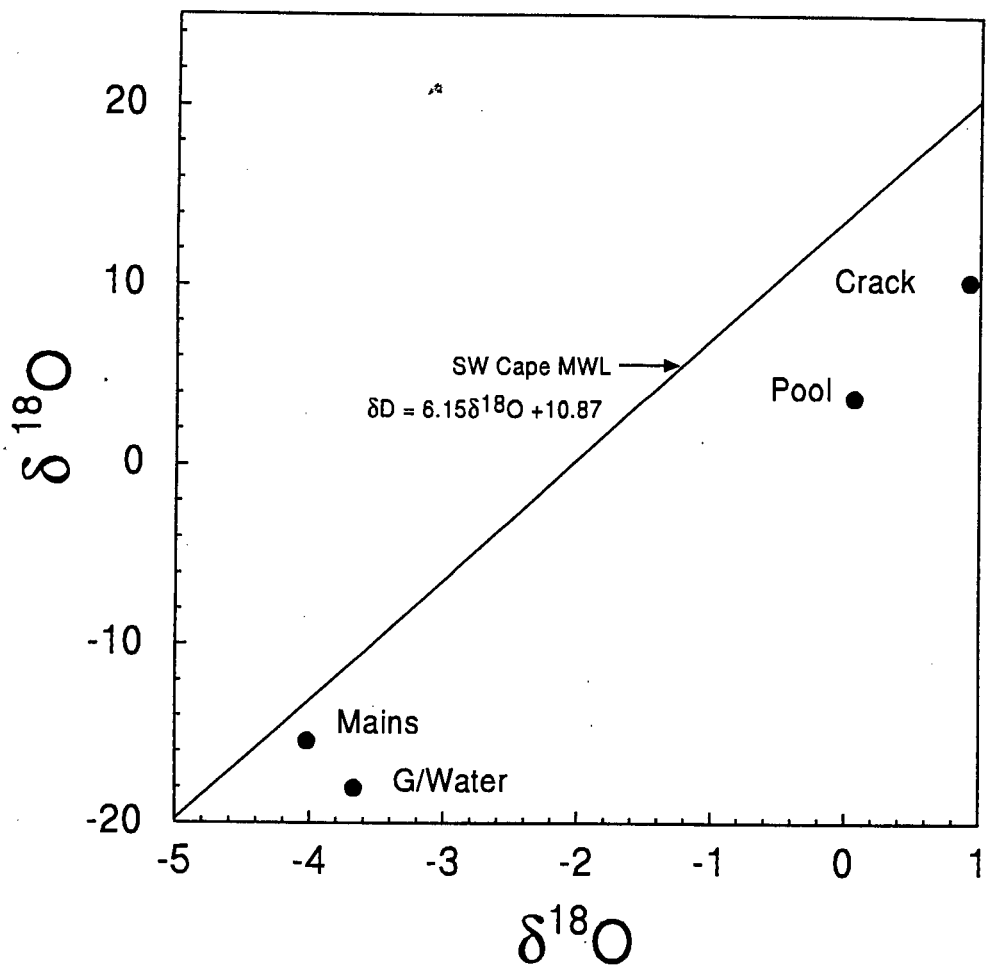


Figure 6.2. Stable isotope data for the hydrological case study.

Chapter 7. Conclusions and recommendations

The waters in the Cape Town region have been grouped according to their sources, and have been divided into either groundwaters, springwaters or reservoir (mains) waters. Surface waters have been excluded from the study, as the rivers in the Cape Town area are few and small, and flow primarily as a result of base flow contribution during summer, and surface runoff contribution during winter. An equation of best fit was established for the springwaters and the groundwaters, and meteoric water lines (MWL) were established for the reservoir water groups. The calculated MWL or equation of best fit for each water group, along with the SW Cape and Global MWL, are shown in Table 7.1 below.

Table 7.1. Calculated meteoric water lines for water groups in the south western Cape.

Water Group	MWL or Equation of Best Fit	r^2
SW Cape rain (Diamond 1997)	$\delta D = 6.15(2\sigma\ 1.1)\delta^{18}O + 10.87(2\sigma\ 0.18)$	
April reservoir water*	$\delta D = 3.85\delta^{18}O + 3.07$	0.40
August reservoir water*	$\delta D = 5.14\delta^{18}O + 5.86$	0.87
Springwaters	$\delta D = 6.54\delta^{18}O + 10.20$	0.77
Groundwaters	$\delta D = 8.26\delta^{18}O + 12.50$	0.72

Note: * indicates reservoir water that has been treated.

It is seen from Table 7.1. that, apart from the April reservoir waters, the other water groups display fairly good correlations between δD and $\delta^{18}O$ compositions. The differences in meteoric water lines from the SW Cape MWL are ascribed primarily to microclimatic variations in the SW Cape, which occur as a result of the varied topographical conditions which are present in the area. Other effects could be due to evaporation, different periods of recharge and a time lapse between recharge and sampling.

An analysis of the distribution of isotope values for the different water groups indicates that the April treated reservoir waters, the August treated reservoir waters, the spring waters and the groundwaters may be grouped according to their combined δD and $\delta^{18}O$ values (Figure 5.3). The average δD and $\delta^{18}O$ values for each group are shown below in Table 7.2, and graphically in Figure 7.1.

Table 7.2. Average stable isotope values for the different water groups.

Water Group	Average δD (range) (‰)	Average $\delta^{18}O$ (range) (‰)
April treated	-5 (9)	-2.0 (1.4)
August treated	-15 (14)	-4.0 (2.9)
Groundwaters	-11 (9)	-2.8 (0.7)
Springwaters	-13 (8)	-3.7 (0.9)

Note: 2σ for δD = 1.1; 2σ for $\delta^{18}O$ = 0.18 (Diamond and Harris, 1996).

: Range = (the lowest group value - the highest group value).

It is seen that the average values for the different groups, for both δD and $\delta^{18}O$, differ in all cases by an amount greater than the standard deviation. However, an inspection of the ranges of values which occur reveal that there is a definite overlap in stable isotope values between members of different groups. This statement is reinforced visually by an inspection of Figure 7.1, which graphically illustrates the overlap between the different groups. The differences between the different groups of waters are therefore not great enough to conclusively identify the waters from the different sources on the basis of their stable isotope values alone. The largest difference in stable isotope values occurs between the April treated reservoir values (δD -5; $\delta^{18}O$ -2.0), and the other groups. It is recognised that sampling of springwaters and groundwaters should have been performed in April as well, in order to identify seasonal variations in the groundwater and springwater isotope values. However, low seasonal variations in the springwater and groundwater isotope ratios were expected, as dominant recharge of the waters occurs during the wet winter months form May to September. This has the resulting implications of one being able to distinguish groundwater and springwater from reservoir (mains) water during the last months of

summer, before any periods of significant winter rain in the reservoir catchment areas, as the reservoirs stable isotope values should be sufficiently heavier than the groundwaters and springwaters due to evaporation effects.

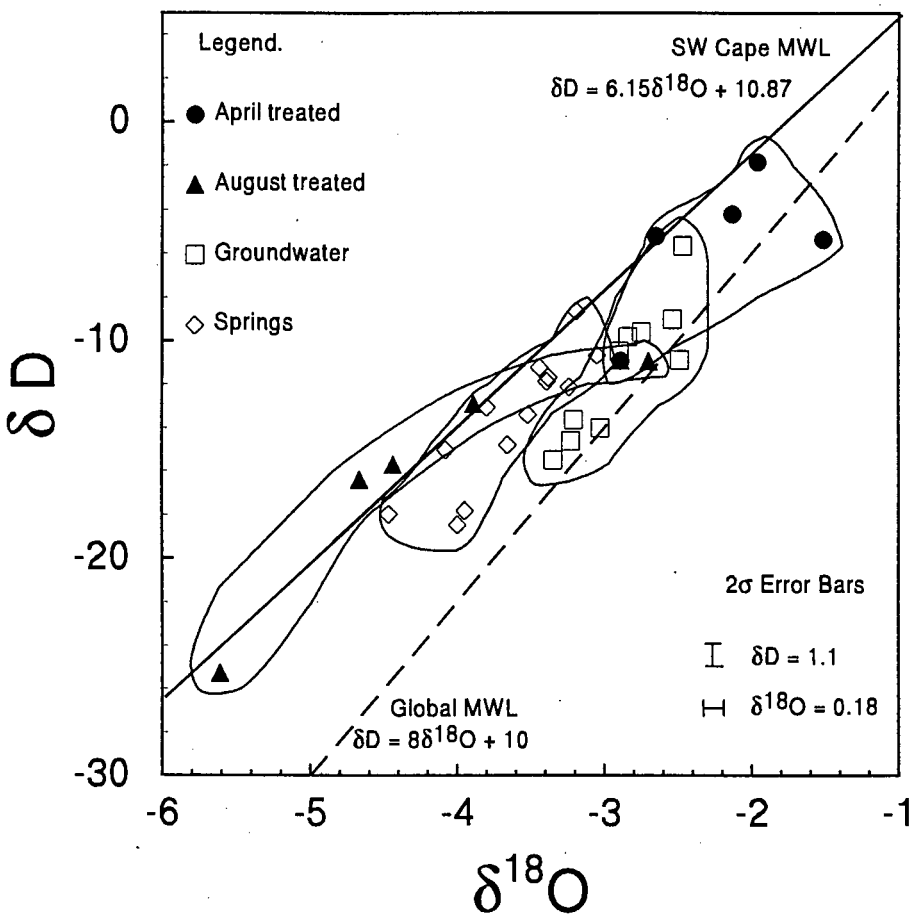


Figure 7.1. The grouped stable isotope values for the treated April and August reservoir waters, the springwaters and the groundwaters.(Unweighted SW Cape MWL from Diamond and Harris, 1996; Global MWL from Craig, 1961(b))

An investigation into the correlation between stable isotope values (δD, $\delta^{18}O$) and other geochemical parameters of the waters (pH, EC, cationic elements and anions) revealed no

statistically relevant correlations between any of the geochemical correlations and the stable isotope values. This was expected, as the stable isotope values of meteoric waters are determined before infiltration into the ground water system, whereas most of the geochemical parameters are determined by interaction of the infiltrated meteoric water with subsurface components. Some water-rock interaction may occurr and change the δD and $\delta^{18}O$ compositions of the water, but this is unlikely at low temperatures. However, it was recognised that certain geochemical parameters would be effective in identifying which group waters of interest belonged to. The geochemical parameters which showed the greatest relative difference between group variation were Ca, Na, K and Cl, and it is recommended that if waters in the Cape Town area are to be identified according to geochemical parameters, then they should be analyzed for these four elements.

A small scale hydrological investigation using stable isotopes (δD, $\delta^{18}O$) and two geochemical parameters (EC and pH) was performed during the course of the author's study. Stable isotope values for the waters of interest conclusively determined the source of a water leakage, and was confirmed using EC and pH. The geochemical parameters could have been used in conjunction with each other to predict where the water was coming from, but the non-conservative nature of most geochemical parameters introduces uncertainty into such a study. The highly conservative nature of the stable isotopes of H and O allows great confidence in the results obtained, as the stable isotope compositions are not significantly influenced by interaction of the water with any substrate that it has contact with, considering the ambient temperatures of the system of interest. Economically, stable isotope values may be more expensive to determine than other geochemical parameters for aqueous systems, but the certainty of the results obtained may translate into high savings later.

It is recognised that the stable isotopes of H and O have a limited role in solving larger urban geohydrological problems in the Cape Town area after the seasonal winter rainfall period. It is suspected, on the basis of the results obtained, that there is potential for using stable isotopes for solving suspected urban geohydrological problems at the end of the dry summer season, when differences between incoming mains water and natural ground and spring waters would be most

apparent. The author recommends that an investigation into the stable isotope characteristics of groundwaters and springwaters be determined at other times of the year (in November and February), in order to determine with certainty the potential for using stable isotopes in solving urban geohydrological problems in Cape Town at different times of the year. The differences in stable isotope values for natural groundwaters and mains water could be maximised by using water from selected reservoirs,such as Voelvlei, as the greater the difference in the isotope values between the mains water and groundwater will enable easier identification of any contribution to groundwaters from mains water. The small scale case study, which involved solving an urban geohydrological problem having three possible water sources, illustrated the potential that stable isotope applications may have in certain situations, as well as the usefulness of combining selected chemical analyses with a stable isotope investigation. It is recommended that each possible hydrological and geohydrological problem be independently assessed, and that the use of selected chemical analyses in solving geohydrological problems should not be discounted.

7.1. Final recommendations

1) Using stable isotopes to solve urban geohydrological problems will be most effective at the end of the Cape Town summer (March to April). This recommendation is based on the assumption that spring and groundwaters do not vary seasonally. It would be important in a more detailed study to locally assess all sources of water.

2) Due to the overlap in stable isotope values for the different groups of water in the Cape Town area, selected chemical analyses should be used in conjunction with isotope studies.

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