## A preliminary investigation of the oxygen and hydrogen isotope hydrology of the greater Cape Town area and an assessment of the potential for using stable isotopes as tracers

Chris Harris\*, Bruce M Oom and Roger E Diamond

Department of Geological Sciences, University of Cape Town, Rondebosch 7700, South Africa

## Abstract

The oxygen and hydrogen isotope composition of rain-water, groundwater and mains supply water was determined with the aim of assessing the potential for applying these isotope systems to problems of urban hydrology in the greater Cape Town area. Water treatment plants supplying mains water to Cape Town produce water with a seasonal variation in hydrogen (H) and oxygen (O) isotope composition. In September 1996, at the end of the wet winter months, the treated water had  $\delta D$  and  $\delta^{18}O$  values that were 12 and 2‰ higher, respectively, than the values of April 1996 at the end of the previous summer. The  $\delta D$  and  $\delta^{18}O$  values of natural springs on the slopes of Table Mountain show a good correlation, with a line of best fit that is parallel to that of the global meteoric water line, but enriched in deuterium. Groundwater from the shallow Culemborg-Black River aquifer and the extensive Cape Flats aquifer have  $\delta D$  and  $\delta^{18}O$  values which plot closer to the global meteoric water line. These relatively minor differences in isotope composition between the springs and groundwater appear to be due to differences in the isotope composition of ambient rain-water.

The observed differences in  $\delta D$  and  $\delta^{18}O$  values between mains water and groundwater in the greater Cape Town area are not significant in winter, but towards the end of summer are of the order of 10 and 1.6%, respectively. We suggest that O- and H-isotope data would effectively discriminate between mains water and groundwater for most of the greater Cape Town area in the summer and autumn months.

## Introduction

Hydrogen and oxygen isotope studies have potentially important applications to urban hydrology. Where differences in isotope ratios exist between potential sources in an urban region (e.g. groundwater, piped mains water, rain-water, swimming-pool water) stable isotope ratios can be used to monitor the origin of water. Hydrogen and oxygen isotope ratios are highly conservative tracers for monitoring the origins of water. Because oxygen and hydrogen are the major constituents of water, it is practically impossible for their isotope ratios in water to change, except where there is substantial amounts of evaporation and/or mixing with significant proportions of water of different isotope ratio. In South Africa, Verhagen and Butler (1995) used O- and Hisotopes along with other environmental tracers to study groundwater in an urban/industrial area at Midrand, near Johannesburg. They found that leakages and waste water derived from the Rand Water mains system could be traced, as its isotope composition differed from most naturally recharged groundwaters. Some private boreholes in the Pretoria (Butler and Verhagen, 1997) area contain a significant component of mains water (up to 100%). There is also the possibility that pollution by sewage in groundwater could be traced using O- and H-isotopes because sewage might be expected to have isotope ratios similar to mains water. Water is not an abundant resource in South Africa, and for this reason alone, water supplies need to be effectively managed. In recent years, Cape Town has experienced a large increase in

population, mainly in informal settlements. There will be increasing pressure on water supplies in the years to come.

The aim of this paper is to evaluate the potential of O- and Hisotopes as hydrological tracers of the origin of groundwater in the Cape Town area. As we shall show, seasonality plays an important role in maximising potential differences between the different water reservoirs.

#### Geographical and geological outline

#### Geology of the Cape Town area

The oldest geological formations in the vicinity of Cape Town (Fig. 1) belong to the Malmesbury Group (Theron et al., 1992; Hartnady and Rogers, 1990). The Peninsula Granite batholith intruded these rocks at about 550 Ma (Burger and Coertze, 1973) and the approximately vertical contact between the Malmesbury Group and the granite lies just to the SW of the city centre (Fig. 2). The Cape Granite and the Malmesbury Group meta-sedimentary rocks are unconformably overlain by the quartzites of the Table Mountain Group. 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 (Fig. 1). Post-Palaeozoic erosion has removed the Table Mountain Group between False Bay and Table Bay to create the Cape Flats (Fig. 1) an area of low topography separating the Peninsula from the inland hills.

Sediments of the Cenozoic Sandveld Group overlie bedrock of much of the Cape Flats. Of special interest for this study 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

<sup>\*</sup> To whom all correspondence should be addressed.

<sup>(021) 650-2931;</sup> fax (021) 650-3783; e-mail kv@geology.uct.ac.za Received 12 March 1998; accepted in revised form 12 August 1998.



Figure 1 Sketch map of the Cape Peninsula and part of the Western Cape region showing the position of water treatment plants. The location of the Cape Flats and Culemborg-Black River aquifers is shown. Steenbras, Constantia Nek, Kloof Nek, Wemmershoek and Voëlvlei treatment plants are situated at or close to the reservoirs that supply them. Faure and Blackheath treatment plants were both supplied by the Theewaterskloof Reservoir near Villiersdorp at the time of sampling. Meteoric water sampling stations at UCT and Cape Town International Airport are also shown as are the general locations of well-points and boreholes sampled in the Cape Flats aquifer.



#### Figure 2

The area close to Cape Town city centre showing the sample sites for natural springs, and monitoring wells in the Culemborg-Black River aquifer (see inset). The locations of the two river samples and the canal sample are also shown as is the course of the Liesbeeck River. The contact between the Malmesbury Group and the Peninsula granite which is approximately vertical is indicated. The Table Mountain Group lies unconformably above the Malmesbury Group and the Peninsula granite. The unconformity dips gently to the south, being at an altitude of ~430 m above Cape town and ~260 m at Constantia Nek. The position of the rain-water collection site at UCT is also shown.

the unconfined Cape Flats aquifer, and is the aquifer used for groundwater extraction at Atlantis area and in the area around Mitchells Plain (Fig. 1).

## Physiographical description and climate

The Peninsula and particularly the Cape Flats areas (Fig. 1) are densely populated, except in the high-lying areas of the Peninsula which attain a maximum altitude of 1 086 m on Table Mountain. It is bordered to the east by the Cape Flats, of which the highest dunes rise 65 m above sea level (m a.s.l.). On weathering, the resistant sandstones of the Table Mountain Group have given rise to steep cliffs on the Peninsula, as compared with the rolling hilly landscape characterising granite and Malmesbury rock terrain to the east of the Cape Flats.

The SW Cape, incorporating the Cape Peninsula and adjoining districts, experiences a typical Mediterranean climate, with wet winters and dry summers (SAWB, 1996). The geographical and topographical features influence the climate of the region, resulting in highly localised microclimates. The annual precipitation in the area averages 600 mm/yr, but is highly variable and controlled by topography. The mountains of the Cape Peninsula and the Hottentotsholland and Drakenstein ranges receive heavy orographic rains, with some areas, such as Newlands on the slopes of Table Mountain, receiving over 2 000 mm/yr. Figure 3 shows the monthly rainfall at UCT during the period of this study.

## Hydrogeology

#### The Cape Flats aquifer unit

The low-lying unconsolidated sands which connect the Peninsula to the Tygerberg and Stellenbosch hills to the east were formed by river and wind erosion and deposition. The water table in the area is shallow (average 3.75 m below surface) and the coarsegrained nature of the sands leads to a primary aquifer of significant exploitation potential (Maclear, 1995). Water from this aquifer is fresh (Maclear, 1995) and is presently used for irrigation of sports fields and gardens in the Mitchells Plain area. We have analysed samples of groundwater from well-points and boreholes in several localities in the aquifer: Atlantis in the north, Table View, Mitchells Plain to the south, and Constantia, Kirstenhof and Lakeside to the south-west (Fig. 1). The depth of the boreholes from which water was pumped ranged from about 6 m in Table View, to 22 m in the Mitchells Plain area.

## The Culemborg-Black River aquifer

The Culemborg-Black River aquifer is a freshwater aquifer created by reclamation of land immediately to the east of the Cape Town central business area. The water table was determined to be at an average depth of 0 to 3 m above mean sea level (m a.m.s.l.) at approximately 1.5 m below ground level (HKS, 1995). Ground-water flow is generally towards Table Bay, but is locally influenced by the existing and historic drainage patterns of the Black and Salt Rivers (HKS, 1995). Recharge is from the slopes of Devil's Peak to the south. Direct recharge from rain is important during the wet winter months and this may include leakage from storm drains in the area. No use of groundwater from this aquifer has been reported (HKS, 1995).



#### Figure 3

Plot of δD, δ<sup>18</sup>O and amount of rain vs. month for rainfall collected at UCT from June 1995 to May 1997 (Diamond, 1997 and Diamond and Harris, 1997). The average monthly temperature data are also plotted for Kirstenbosch Botanical Gardens 5 km SW of UCT (source: Weather Bureau)

#### Natural springs on the slopes of Table Mountain

Numerous springs exist on the slopes of Table Mountain, of which a selection were sampled. One of these is hosted in Table Mountain Sandstone (Hout Bay manganese mine), the remainder are either in rock of the Malmesbury Group or Cape Granite (or Quaternary cover) on the lower slopes of the mountain. Rates of flow vary enormously from less than 1  $\ell$ /min in the case of the Cable Way and the Hout Bay manganese mine to flow rates that are large enough to be exploited as a source of municipal drinking water (Albion Spring). Some of the springs are ephemeral (Klipper, Hout Bay manganese mine, Rhodes Memorial and Foresters) and no April 1997 sample could be taken because the springs were dry.

### Sampling and analytical methods

#### Sampling rationale

Water was sampled from various different sources in the Cape Town area, namely water from the water treatment plants providing mains water to the area, shallow groundwater from boreholes (up to 22 m in depth) and natural springs. Samples were also taken from the Liesbeeck River and a canal in the Culemborg area. The major aim was to establish what O- and H-isotope differences exist between these different water sources, and the magnitude of any seasonal variations. Apart from the Cape Flats aquifer wellpoints and boreholes, samples were taken at the end of summer (April 1996 or 1997) and at the end of winter (August or September 1996). At the start of this project, in April 1996, samples of treated and untreated mains water were collected in order to establish if any isotope fractionation occurred during the

Water treatment plants	April 1997		August 1996	
	δD	δ <sup>18</sup> Ο	δD	δ18(
Constantia Nek R	-7	-2.9		
Constantia Nek T			-13	-3.9
Blackheath R	-3	-2.3		
Blackheath T	-2	-2.0	-25	-5.0
Faure R	-5	-2.7		
Faure T	+2	-1.3		
Steenbras R	-5	-2.6		
Steenbras T	-4	-2.1	-11	-2.9
Wemmershoek R	-8	-3.1		
Wemmershoek T	-11	-2.9	-16	-4.4
Voëlvlei R	+1	-2.3		
Voëlvlei T	-5	-1.5	-11	-2.7
Groundwaters	April 1997		September 1	
Culemborg-Black Rive	r aquifer			
MW1	-4	-2.5	-10	-2.8
MW2	-4	-1.5	-9	-2.
MW4	-3	-1.1	-6	-2.5
MW6	-6	-2.0	-11	-2.9
MW13	-11	-2.6	-14	-3.0
MW15	-12	-2.7	-15	-3.2
MW16			-10	-2.8
MW17	-5	-2.0	-11	-2.5
MW19	-12	-2.5	-14	-3.2
Cape Flats aquifer*				
Atlantis	-14	-3.6		
Lentegeur 2	-15	-3.7		
Lentegeur 3	-14	-3.5		
Portland 1	-12	-3.3		
Portland 2	-14	-3.2		
Portland 3	-16	-3.3		
Table View 1	-19	-3.7		
Table View 2	-18	-3.6		
Table View 3	-21	-4.2		
Constantia	-14	-3.0		
Kirstenhof	-13	-3.1		
	10			

Notes: R = raw/untreated water samples, T = treated water samples. Lentegeur and Portland samples collected from sports fields in Mitchells Plain. \*Samples collected in August 1996 (Atlantis), December 1995 (Table View 1 and 2), May 1997 (Constantia) June 1997 (Lakeside, Table View 3, Kirstenhof). treatment process. Groundwater from the boreholes in the Cape Flats aquifer was sampled at various times of the year, between December 1995 and June 1997.

#### Sample locations and sampling methods

Samples of water were collected from the following treatment plants supplying the Cape Town area: Kloof Nek, Constantia Nek, Blackheath, Faure, Steenbras, Wemmershoek and Voëlvlei. All except Faure and Blackheath are situated close to, and are supplied by, reservoirs in the area (Fig. 1). Faure and Blackheath were supplied by Theewaterskloof Reservoir near Villiersdorp (Fig. 1) at the time of sampling (City Engineer's Dept., 1997). The springs in the Cape Town area were identified either from the geological map of the area (Geological Survey, 1984), or from local knowledge. 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 (Fig. 2). The altitude and estimated yield of the springs at the time of sampling are shown in Table 1.

Groundwater from the Culemborg-Black River aquifer (Fig. 2) was sampled from several shallow monitoring wells which have been established by a local engineering company (Fig. 2). The depth to the water table varied from 1 to 5 m. Water was sampled using a dedicated teflon baler and the boreholes were purged manually using the baler to remove 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 rain-water had a much lower EC compared to the aquifer water. Electrical conductivity in the borehole was continually monitored during purging; once the EC stabilised, it was assumed that the monitoring well was effectively purged, and any water present in the well was effectively "pure" aquifer water. Water from the boreholes in the Cape Flats aquifer was taken after pumping the well for several minutes.

Water samples were collected and stored in previously unused 100 m $\ell$  plastic bottles ("medical flats") which were totally filled and sealed immediately to prevent any evaporation. All samples were stored in a cool, dark room, and most samples were analysed within about 2 weeks of collection.

## Analytical methods

The CO<sub>2</sub> equilibration method of Socki et al. (1992) employing disposable preevacuated 7 ml glass vials was used for oxygen isotopes. About 0.5 atmosphere of medical grade CO<sub>2</sub> was equilibrated with about 2 ml water for 2h at 25°C. A variant of the Zn closed tube reduction method (Coleman et al., 1982) was used to reduce the water to H<sub>2</sub>. Approximately 2 mg of water contained in a microcapilliary tube was dropped into a pyrex tube containing a few grains of "Indiana" Zn. The tube was attached to the vacuum line, frozen in liquid N<sub>2</sub>, evacuated and then sealed using a torch. Once a large enough batch of samples had been prepared they were placed in a furnace at 450°C to reduce the water to H<sub>2</sub>. Isotope ratios of CO<sub>2</sub> and H<sub>2</sub> were measured using a Finnegan MAT252 mass spectrometer, and the fractionation factor between CO<sub>2</sub> and water at 25°C was assumed to be 1.0412 (Coplen 1993). Data are reported in the familiar  $\delta$  notation where  $\delta = ((R_{sample}/R_{standard})-1)*1000$ , and  $R = {}^{18}O/{}^{16}O$  or D/H. The average difference between duplicates of our internal water standard (CTMP) over the course of this research was 0.48‰ for H (n = 23) and 0.10‰ for O (n = 18). These correspond to 2 $\sigma$  values of 0.74‰ and 0.14‰, respectively. The standards V-SMOW and SLAP were analysed to determine the degree of compression of raw data and the equations of Coplen (1988) were used to convert raw data to the SMOW scale. Our internal water standard (CTMP) which has been calibrated against V-SMOW and SLAP, and independently analysed, was run with each batch of samples and used to correct for drift in the reference gases. Electrical conductivity (EC) was measured using a Crison micro CM2201 conductivity meter.

#### Results

### Rain-water

Most of the rain in the Cape Town region falls in the months of June to September, that is in the months experiencing the lowest average temperatures. Figure 3 shows the variation of average monthly temperature, monthly rainfall and weighted  $\delta D$  and  $\delta^{18}O$  values for UCT from June 1995 to May 1997. During November 1995 to April 1996 when rainfall was very low, the  $\delta D$  and  $\delta^{18}O$  values were highly variable. For the same months in 1996/7 there is a greater correspondence between high  $\delta D$  and  $\delta^{18}O$  values of rain-water with higher average ambient temperature (the "temperature effect" of Dansgaard, 1964).

Longer-term weighted monthly oxygen and hydrogen isotope data for rain-water are available for Cape Town International Airport (IAEA, 1997; Station 6881600 "Malan" (The name of this monitoring station changed from DF Malan Airport to Cape Town International Airport in 1995. In this paper it will be referred to as Cape Town Airport)) for the years 1961 to 1975 (with numerous gaps in the data). If the year is split into summer (September to March) and winter (April to August), the average summer  $\delta D$  and  $\delta^{18}$ O values are -9.9 and -2.78‰ respectively (n = 5), and the average winter  $\delta D$  and  $\delta^{18}$ O values are -15.7 and -3.78‰ respectively (n = 6). These data indicate that there are likely to be seasonal differences in the isotope composition of recharge to groundwater and reservoirs which are not obvious from the UCT 1995 to 1997 data.

The IAEA Cape Town Airport and UCT data are plotted on Fig. 4 where (as is to be expected) it can be seen that they show a high degree of correspondence. The weighted annual values for  $\delta D$  are almost identical within error (Airport = -12.7; UCT = -11.9‰) but UCT has a significantly lower weighted annual  $\delta^{18}$ O value (-3.74‰) than Cape Town Airport (-3.31‰). It should also be noted that the data form an array parallel to the global meteoric water line of Craig (1961), with samples having a higher deuterium excess (defined by Dansgaard, 1964, as being d =  $\delta D - 8\delta^{18}$ O).

#### Water treatment plants (summer)

It is evident from Table 1 and Fig. 5 that water treatment affects the isotope values, in each case enriching the water samples slightly in <sup>18</sup>O, but having a variable and seemingly unsystematic effect on the  $\delta D$  values. Figure 5 shows clearly that the treated waters are offset to slightly higher  $\delta^{18}O$  values. Excluding Constantia Nek, for which no treated sample could be collected in April, the mean  $\delta D$  values for raw and treated water are both



#### Figure 4

Plot of  $\delta D$  vs.  $\delta^{18}O$  for meteoric water collected at UCT and Cape Town International Airport. The global meteoric water line (MWL) of Craig (1961) is shown for reference in this and the following diagrams ( $\delta D = 8\delta^{18}O + 10$ ). The crosses represent the weighted annual  $\delta D$  and  $\delta^{18}O$ values of Cape Town International Airport (Data from IAEA, 1997) and UCT.



Figure 5

Plot of  $\delta D$  vs.  $\delta^{18}O$  for treated and untreated water collected at treatment plants. Mean values, weighted according to throughput of water, for treated samples collected in April and August 1996 are shown.

TABLE 2   O- AND H-ISOTOPE COMPOSITION OF SPRING WATERS AND RIVER SAMPLES								
		April 1997 September		April 1997		ber 1996		
Spring waters	Alt.(m)	Yield	δD	δ18Ο	δD	δ <sup>18</sup> Ο		
Rhodes Mem.	140	10-100			-13	-3.8		
Hof spring	190	>1000	-11	-3.0	-11	-3.4		
Main spring	120	>1000	-13	-3.6	-19	-4.0		
Albion spring	30	>1000	-9	-2.9	-9	-3.2		
Newlands	35	>1000	-11	-3.1	-12	-3.4		
Glencoe	250	10-100	-14	-3.8	-15	-4.1		
Cable way	310	1-10	-14	-3.9	-18	-4.5		
Foresters	40	10-100			-12	-3.2		
Kirstenbosch	150	10-100	-12	-3.1	-15	-3.7		
Fey	80	10-100	-11	-3.5	-11	-3.1		
Klipper	100	10-100			-12	-3.4		
Hout Bay	280	1-10			-10	-3.7		
Rivers								
Liesbeeck 1	10		-10	-3.0	-9	-2.4		
Liesbeeck 2	65		-10	-3.6	-13.4	-3.5		
Canal (MW19)	10		-1	-0.2	-7	-2.8		
Notes: Rhodes Memorial Foresters, Klipper and Hout Bay springs are enhemeral and								

Notes: Rhodes Memorial, Foresters, Klipper and Hout Bay springs are ephemeral and were not flowing in April 1997. The yield is an estimate of the amount of water in  $\ell/min$  at the time the sample was taken.



#### Figure 6

Plot of δD vs. δ<sup>18</sup>O for spring waters collected from the flanks of Table Mountain. Samples collected in September 1996 and April 1997 are distinguished and the δ<sup>18</sup>O values are plotted against altitude (m a.s.l.) in the inset diagram.

-4‰, and the mean  $\delta^{18}$ O values for raw and treated waters are - 2.6 and -2.0‰ respectively. On average there is, therefore, a 0.6‰ shift to higher  $\delta^{18}$ O values during the treatment process.

The  $\delta D$  and  $\delta^{18}$ O values of untreated water collected in April 1996 form an array which is offset from the global meteoric water line (Fig. 5), whereas the treated waters collected at the same time lie much closer to the meteoric water line. It is, therefore, evident that the water treatment process increases the  $\delta^{18}$ O value of the water.

#### Water treatment plants (winter)

Because of the small differences between treated and untreated waters, it was decided to collect and analyse only treated water in August 1996, which is any case a more useful parameter to the urban hydrologist. The range in  $\delta D$  and  $\delta^{18}O$  values is from -11‰ (Steenbras and Voëlvlei) to -25‰ (Blackheath), and from -2.7‰ (Voëlvlei), to -5.6‰ (Blackheath) respectively. Two important features of the data are:

- The range in both δD and δ<sup>18</sup>O values is somewhat larger for August compared to April (Fig. 5).
- The  $\delta D$  and  $\delta^{18}O$  values for the August (end of winter) samples have significantly lower  $\delta D$  and  $\delta^{18}O$  values than those of April (end of summer), with most of the data plotting above the global meteoric water line (Fig. 5).

The average difference between  $\delta D$  and  $\delta^{18}O$  values of April and August treated samples is 10‰ and 2.0‰ respectively.

TABLE 3   AVERAGE O- AND H-ISOTOPE COMPOSITION OF MAIN WATER TYPES						
Water type	δD	δ¹ <sup>8</sup> O				
Treated water (April 1996)*	-4.3	-1.97				
Treated water (September 1996)*	-16.3	-4.02				
Table Mountain springs (April 1997)	-11.9	-3.36				
Table Mountain springs (September 1996)**	-13.8	-3.68				
Culemborg-Black River aquifer (April 1997)	-7.1	-2.11				
Culemborg-Black River aquifer (September 1996)	-10.4	-2.90				
Cape Flats aquifer	-15.4	-3.41				
Notos	•					

\* Value weighted according to output of treated water.

\*\* Only permanent springs were included in the average so the April and September values are directly comparable.

#### Springs on the slopes of Table Mountain

The stable isotope data for the spring waters sampled are shown on Fig. 6. In most cases the samples collected in September 1996 have slightly lower  $\delta D$  and  $\delta^{18}O$  values than the samples collected in April 1997 (Table 2) but the differences are slight. The data plotted in Fig. 6 give the impression that there is a significant seasonal variation in  $\delta D$  and  $\delta^{18}O$  values of the springs. This is misleading because some of the springs with the lowest  $\delta D$  and  $\delta^{18}O$  values are ephemeral and were not sampled in April 1977. The springs show a good correlation between  $\delta D$  and  $\delta^{18}O$  values and the data (Fig. 6) form an array which is enriched in deuterium relative to the global meteoric water line of Craig (1961). The inset to this diagram shows that there is a negative correlation between  $\delta^{18}O$  value and altitude which can be ascribed to the well known "altitude effect" (Dansgaard, 1964).

## Groundwater from the Cape Flats and Culemborg-Black River aquifers

Groundwater samples from the Cape Flats aquifer (Maclear, 1995) have lower  $\delta D$  and  $\delta^{18}O$  values than the samples collected from the Culemborg-Black River aquifer in either September 1996 or April 1997 (Fig. 7). The Culemborg-Black River aquifer samples show some seasonal variation in O- and H-isotope ratio (Fig. 7, Table 3). This could be related to evapo-transpiration and/ or recharge by rain-water because these samples were from boreholes of only about 3 to 5 m depth. By contrast, the Cape Flats aquifer samples are from boreholes between 6 and 22 m depth and are therefore less susceptible to seasonal changes (compare data for samples taken during different months in Table 1). The groundwater data form an array (Fig. 7) which is much closer to the global meteoric water line than either the spring or water treatment plant data.

## Rivers

The Liesbeeck River shows a small seasonal variation (based on a very small number of samples, Fig. 8) but also changes in isotope composition as it flows from Kirstenbosch towards the sea. The samples of the Liesbeeck River from Kirstenbosch (LR2, Fig. 2) plot within the field for the springs, whereas the down-



Figure 7

Plot of  $\delta D$  vs.  $\delta^{i8}O$  for groundwater sampled from monitoring wells in the Culembourg-Black River aquifer and from boreholes in the Cape Flats aquifer

stream river samples collected at Hartleyvale (LR1, Fig. 2) plot within the Culemborg-Black River groundwater field. These data indicate that the river water is fed by local groundwater (at least at the time of sampling). Samples were taken from one of the canals within the Culemborg area (adjacent to borehole MW19), which is very close to sea level. The April 1997 canal sample has an isotope composition very close to sea-water which suggests that the canal may be tidal at that point. Note also that some of the groundwater samples appear to lie on a mixing line between "typical groundwater values" and that of the canal indicating possible sea-water infiltration into some of the monitoring wells in the Culemborg area.



Plot of  $\delta D$  vs.  $\delta^{18}O$  for river and canal samples with global MWL and fields for groundwater from Figs. 6 and 7 for reference.



Plot of electrical conductivity (EC) in S/cm vs.  $\delta^{18}$ O for analysed water types. The expected position of sea-water is also shown.

#### Electrical conductivity (EC)

The EC of the reservoir samples is uniformly low with the treated water having slightly higher EC values (130 to 200  $\mu$ S/cm) than the untreated water (24 to 94 µS/cm). The springs on Table Mountain also show low EC values ranging from 22 to 33 µS/cm. Groundwater from the Cape Flats aquifer has EC values from 181 to 1134 µS/cm indicating a higher concentration of dissolved salts. The samples from the Culemborg-Black River aquifer show a large range in EC from 366 to 47 600 µS/cm indicating generally much higher dissolved salt content than the Cape Flats aquifer samples. Figure 9 shows that there is very little correlation between the  $\delta^{18}O$ value and EC for any of the groups of water samples analysed (nor is there any correlation between  $\delta D$ and EC). The most important feature to note is that there is no correlation between  $\delta^{18}$ O value and EC for the Culemborg-Black River aquifer samples.

This lack of correlation means that the large range in EC (and hence total dissolved salt content) of these groundwaters is not generally due to mixing of groundwater of meteoric origin with sea-water. The dissolved salts in these groundwaters must, therefore, largely come from the substrate either in the form of salt of marine origin, or (possibly, given that the area has been a dumping site for coal waste, ash and furnace waste, HKS, 1995) dumped chemicals. Two samples (MW2 and MW4 collected in April 1997) provide an exception and on the basis of the stable isotope data possibly contain about a 50% sea-water component, though their EC is approximately equivalent to that of sea-water (Fig. 9). The combination of stable isotope and EC data strongly suggests that the canal sample taken in April 1997 is of almost entirely marine origin (Fig. 9).

## Discussion

# Changes in isotope ratio caused by water treatment

It has been shown above that the  $\delta^{18}O$  values for treated water samples are on average about 0.6‰ higher than those of the raw water. The treatment at the different plants varies somewhat; most include a settlement period, most have aluminium sulphate  $(Al_2(SO_4)_2)$  added to the water, all have lime (Ca(OH)<sub>2</sub>) added to the water and some have CO<sub>2</sub> added to the water (City Engineer's Dept., 1997). In theory, the shift in  $\delta^{\scriptscriptstyle 18}\!O$  value could be caused by the various additives, because the O in these materials will have a much higher  $\delta^{18}O$  value than the water (particularly sulphate and carbonate which have very high values of ∆mineral-water at low tempartures, Friedman and O'Neil, ). However, in no case is more than 150 mg/l sulphate + lime added to the water. Addition of such a small amount of material, even if it had an extremely high  $\delta^{18}O$ values of 40‰, will only increase the  $\delta^{18}$ O value of the water by < 0.01‰. The cause of the shift in  $\delta^{18}O$ value must, therefore, be related to evaporation during the settling process.

#### Summer vs. winter treated water

As shown above, the treated water has higher values of  $\delta D$  and  $\delta^{\scriptscriptstyle 18}O$  at the end of summer in comparison with the end of winter and this is likely to be related to two effects. Firstly, meteoric water inflow will have lower  $\delta D$  and  $\delta^{18}O$  in winter compared to summer (see discussion of rain-water data above) Secondly, evaporation, which leads to increases in isotope ratio, will be more effective in summer because of higher temperatures, strong south-easterly winds and low rainfall (Fig. 3). The first effect is limited by the fact that the amount of rain in summer is considerably less than in winter (see data for UCT, Fig. 3). In the Western Cape, reservoirs tend to be filled to capacity at the end of the winter period. Thereafter, the rate of removal of water into the mains system, and by evaporation, exceeds the rate of inflow of meteoric water (including groundwater) and the level of the reservoir drops, typically reaching a minimum level at the end of April.

During 1996, when the samples were collected, Steenbras Dam was at 64.8% of its maximum capacity in April, and rose to 100% capacity in August, while Voëlvlei was at 64.5% capacity in August, and rose to 95.4% in August. The differences in stable isotope ratio for the April and August treated samples must obviously be related to how full each reservoir was at the time of sampling. This in turn depends on:

- Removal of water for drinking (which does not fractionate the stable isotopes).
- Evaporation of water from the surface of the reservoirs which will increase the δD and δ<sup>18</sup>O values in the water remaining.
- · Inflow of meteoric water and recharge by groundwater.

Without a proper study of water balance in the reservoirs (e.g. Dincer, 1968) it is not possible to evaluate the relative effects of evaporation and inflow/recharge. However, the change in isotope ratio from winter to summer is effectively parallel to the meteoric water line which suggests that changing isotope composition of the water added to the reservoir is the dominant process, as opposed to evaporation which typically produces correlations between  $\delta D$  and  $\delta^{18}O$  values with a shallower gradient than the global meteoric water line (e.g. Welhan, 1987).

#### Spring- and groundwaters

The inset to Fig. 6 shows variation of  $\delta^{18}$ O values vs. the altitude of the springs and shows that there is a regular slight depletion of <sup>18</sup>O with altitude. A regression of  $\delta^{18}$ O against altitude resulted in an apparent altitude effect of -0.55‰  $\delta^{18}$ O/100 m increase in altitude (r<sup>2</sup> = 0.61). This is higher than the typical value of about -0.26‰  $\delta^{18}$ O per 100 m increase in altitude (Payne and Yurtsever, 1974). However, the correlation is not good, and the varied topography of the mountain (particularly the steep cliffs above the areas where most of the springs are located), makes it difficult to ascribe any observed isotope effect to a single factor such as altitude.

It can be seen in Fig. 10 that the spring-waters form an array which is enriched in deuterium relative to the global meteoric water line, whereas the Cape Flats groundwaters plot closer to the global meteoric water line. This is most likely to be related to the



Figure 10

Plot of δD vs. dd<sup>18</sup>O for all analysed water types. The crosses represent the weighted mean values of meteoric water at UCT and Cape Town International Airport.

difference in isotope composition of ambient rain-water. At UCT, on the slopes of Table Mountain (Fig. 2) rain-water has, on average, a higher deuterium excess than the rain-water falling on Cape Town International Airport in the Cape Flats region. The untreated mains water samples, which must be dominated by mountain rainfall, have a similar deuterium excess to the springs. The reasons for the difference between the Cape Flats and the Table Mountain/reservoir signature presumably relate to differences in microclimate caused by physiography.

## Applications to urban hydrology

For O- and H-isotopes to be useful in urban hydrology, it is necessary for water of different origins to have distinct isotopic compositions. Specifically, it is desirable for mains water to be distinct from shallow groundwater in isotope composition. It is evident from Fig.10 that this is not always the case. At the end of summer, mains water should have higher  $\delta D$  and  $\delta^{\rm 18}O$  values than groundwater whereas at the end of winter there should be little or no difference in these values. Table 3 summarises the average values for the different types of water analysed during this study. The optimum time of year to employ O- and H-isotopes as a tracer is, therefore, in summer and autumn. The differences in isotope composition which are of the order of 9‰ ( $\delta D$ ) and 1.6‰ ( $\delta^{18}O$ ) should enable mains water to be distinguished from groundwater, but would not allow reliable estimates to be made of the proportion of mains water contributing to a particular borehole. There is less isotope distinction between mains water and the shallow groundwater in the Culemborg area, but there is evidence that in summer, mixing with sea-water occurs. The degree of distinction

between mains water and groundwater will vary according to magnitude of the shift in isotope signature in the reservoirs. In April 1996 when the "end-of-summer" samples were taken from the treatment plants for this study, reservoirs were not at particularly low levels. At this time Steenbras and Voëlvlei were 64.8 and 64.5% full respectively. But the average minimum level for 1987 to 1996 is 48.6 and 58.5% respectively (pers. comm. City Engineers Dept., 1997). Low levels must be related to lack of rain-water input and groundwater recharge as well as evaporation and it is not obvious what the combined effect will be on isotope ratios of the reservoir water. If the evaporation signal is enhanced in times of drought, when tracing mains water leakage would be of greatest importance, it is possible that O- and H-isotopes might provide a much clearer distinction between mains water and groundwater than that observed during this research. Further studies of changes in  $\delta D$  and  $\delta^{18}O$  of local reservoir water would seem warranted.

## Conclusions

- Water from treatment plants contributing to Cape Town's mains water supply shows a seasonal variation in H- and O-isotope composition. The δD and δ<sup>18</sup>O values of treated water were found to be higher in April than September. The seasonal difference must be caused by a combination of seasonal changes in isotope composition of ambient meteoric water and evaporation from reservoirs.
- Groundwater in the low-lying Cape Flats aquifer is isotopically different from spring-water from the lower slopes of Table Mountain. This is related to differences in the weighted mean δD and δ<sup>18</sup>O values of ambient rain-water. The differences are subtle and while they are of scientific interest, are not diagnostic enough for most isotope hydrology applications.
- It ought to be possible to distinguish mains water and groundwater in the Cape Town area at the end of summer (March, April, May). Differences between mains water and groundwater signatures ought to be most pronounced during periods of drought, when identifying mains water leakage would be of prime importance.
- The study of the Culemborg-Black River aquifer groundwater illustrates how stable isotopes can be used to distinguish between water of marine origin and water containing salts dissolved from the substrate. Some of the samples have EC values equivalent to sea-water, yet on the basis of their stable isotope ratios must have a largely meteoric origin.

## Acknowledgements

We are grateful to the FRD for financial support in the form of a core-grant to Chris Harris and studentships to Bruce Oom and Roger Diamond. We are indebted to the many people who helped us collect water samples. In particular we thank Gordon Maclear, Jon McStay and Martin Fey. The Cape Town City Engineer's Dept. provided much useful information and gave permission for us to take samples at water treatment plants. We are especially grateful to Fayrooza Rawoot for carefully producing most of the analyses. Balt Verhagen, Torsten Vennemann, Paul Dennis and Kevin Faure are thanked for their comments on the theses of Oom and Diamond and Gordon Maclear, Martin Fey, Balt Verhagen and an anonymous reviewer provided helpful comments on early versions of this paper.

#### References

- BURGER AJ and COERTZE FJ (1973) Radiometric age measurements on rocks from southern Africa to the end of 1971. *Geol. Surv. S. Afr., Bull.* 58.
- CITY ENGINEER'S DEPARTMENT (1997)Communication from the City Engineer's Department, Cape Town.
- COLEMAN MC, SHEPHERD TJ, DURHAM JJ, ROUSE JD and MOORE GR (1982) Reduction of water with zinc for hydrogen isotope analysis. *Anal. Chem.* **54** 993-995.
- COPLEN TB (1993) Normalization of oxygen and hydrogen isotope data. Chem. Geol. (Isot. Geosci. Sect.) 72 293-297.
- CRAIG H (1961) Isotopic variations in natural waters. *Science* 133 1702-1703.
- DANSGAARD W (1964) Stable isotopes in precipitation. *Tellus* 16 436-468.
- DIAMOND R (1997) Stable Isotopes of the Thermal Springs of the Cape Fold Belt. M.Sc. Thesis (Unpubl.), Univ. of Cape Town.
- DIAMOND RE and HARRIS C (1997) Oxygen and hydrogen isotope composition of Western Cape meteoric water. S. Afr. J. Sci. 93 371-374.
- DINCER T (1968) The use of oxygen 18 and deuterium concentrations in the water balance of lakes. *Water Resour. Res.* **4** 1289-1306.
- FRIEDMAN I and O'NEIL JR (1976) Compilation of stable isotope fractionation factors of geochemical interest. *Data of Geochemistry* (6th edn.), Geological Survey Professional Paper 440-KK.
- GEOLOGICAL SURVEY (1984) 1:50000 Geological Series. 3318CD Cape Town. Department of Mineral and Energy Affairs. Republic of South Africa.
- HARTNADY CJH and ROGERS J (1990) The scenery and geology of the Cape Peninsula. Guidebook Geocongress '90 Geological Society of South Africa M1.
- HKS (HILL, KAPLAN and SCOTT-LAW GIBB) (1995) Introductory Study - Environmental Contamination and Geotechnical Conditions. Culemborg - Black River, Cape Town. Unpublished Report to Cape Town City Council.
- IAEA (INTERNATIONAL ATOMIC ENERGY AGENCY) (1997) Station 6881600 "Malan" (Cape Town) South Africa, Global Network of Isotopes in Precipitation (GNIP), http://www.iaea.or.at/programs/ri/ gnip/gnipmain.htm
- MACLEAR LGA (1995) Cape Town Needs Groundwater: A Note on the Potential of the Cape Flats Aquifer Unit to Supply Groundwater for Domestic Use in the Cape Town Metropolitan Area. Geohydrology Directorate, Department of Water Affairs and Forestry, Cape Town. Technical report No. Gh3868.
- PAYNE BR and YURTSEVER Y (1974) Environmental isotopes as a hydrological tool in Nicaragua. *Isotope Techniques in Groundwater Hydrology*. 1 IAEA 193-202.
- SOCKI RA, KARLSSON HR and GIBSON EK (1992) Extraction technique for the determination of oxygen-18 in water using preevacuated glass vials. *Anal. Chem.* **64** 829-831
- SAWB (SOUTH AFRICAN WEATHER BUREAU) (1996) *The Weather and Climate of the Extreme South-western Cape.* Department of Environmental Affairs and Tourism, South Africa.
- THERON JN, GRESSE PG, SIEGFRIED HP and ROGERS J. (1992) *The Geology of the Cape Town Area.* Geological Survey, Republic of South Africa, Government Printers.
- VERHAGEN BT and BUTLER M (1995) Urban isotope geohydrology. Paper 36, Conference papers volume, Groundwater Recharge and Rural Water Supply. 26-28 September, Midrand, South Africa.
- BUTLER MJ and VERHAGEN BT (1997) Environmental isotopic tracing of water in the urban environment of Pretoria, South Africa. In: J Chilton et al. (eds.) Groundwater in the Urban Environment Vol. 1, Problems, Processes and Management. 101-106. Balkema.
- WELHAN JA (1987) Stable isotope hydrology. In: TK Kyser (ed.) Stable Isotope Geochemistry of Low Temperature Fluids, Min. Soc. Canada Short Course Handbook 13 129-161.