O- AND H-ISOTOPE RECORD OF CAPE TOWN RAINFALL FROM 1996 TO 2008, AND ITS APPLICATION TO RECHARGE STUDIES OF TABLE MOUNTAIN GROUNDWATER, SOUTH AFRICA

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ABSTRACT

The O- and H-isotope composition of rainfall collected over a variety of time periods at the University of Cape Town (UCT) between 1996 and 2008 has been determined. A continuous record of monthly rainfall from 1996 to 2008 has a range in δD and $\delta^{18}O$ values from -57 to +18‰ and -8.1 to +3.5‰, respectively. These data show limited but discernable temperature and amount effects. Daily rainfall between June 2000 to September 2001 ranges in δD and $\delta^{18}O$ from -57 to + 27‰, and, -9.0 to +6.4‰ respectively, showing only a marginally greater temperature and amount effect than the monthly data. Rainfall collected at < hourly intervals during two storms in July and August 2000 showed changes in δD and $\delta^{18}O$ value of 26 and 3.3‰, respectively in as little as 30 minutes during the passage of a cold front. Unusual events such as snow and hail in the area have much lower δD and $\delta^{18}O$ values (-60 and -10.9‰). The deuterium excess values were significantly higher in the storm samples (average 20.0) and the hail and snow samples (average 30.1) than in the monthly rain samples (average 12.4).

The UCT monthly samples define a meteoric water line whose equation is $\delta = 6.41*\delta^{18}O + 8.66$ ($r = 0.88$). The daily and hail/snow samples show a better correlation ($r = 0.93$) due to the greater spread of values, with an equations of the line of best fit of $\delta D = 6.64\delta^{18}O + 11.89$. Rain water collected during two storms in July and August show an excellent correlation between δD and $\delta^{18}O$ ($r = 0.97$) with an equation of best fit of $\delta D = 7.89\ \delta^{18}O + 19.35$. There has been no systematic change in annual amount, mean temperature or weighted mean isotope composition from 1996 to 2008, but 1996 (16.1°C) was, on average, 1.3°C colder than 1997 to 2008 (ave. 17.3°C). Annual rainfall at UCT has varied from ~1000 mm (1997) to 1700 mm (2001), and the weighted mean annual δD and $\delta^{18}O$ values calculated from the monthly samples varies from -16 to -7‰ and -3.8 to -2.6‰, respectively. The years 2005 and 2006 showed a significantly lower deuterium excess (~6) compared to typical values of about 16, which suggests that these years experienced less frontal rain. This difference in isotope composition of rainfall is detectable in the isotope composition of water collected from springs on the lower slopes of Table Mountain and suggests that the Table Mountain aquifer(s) are recharged by approximately 50% within three years.

Introduction

Stable isotopes have been a mainstay analytical tool in the Earth sciences for over forty years (e.g. Valley and Cole, 2001), as well as contributing to studies on tracing of groundwater (e.g. Hitchon and Friedman, 1969), movement of water in soils (Zimmerman et al., 1967), weathering processes (Sheppard and Gilg, 1996), reservoir recharge studies (e.g. Dincer, 1968), mine hydrology (e.g. Mazor et al., 1977), and urban hydrology (Butler and Verhagen, 1977). In recent years as climate change has taken centre stage in the global scientific research community, the importance of stable isotopes in constraining past and present climatic conditions has been further highlighted. (e.g. Rozanski et al., 1997; Fricke and O'Neil, 1999). Although stable isotopes (principally of oxygen and hydrogen) have long been used to reconstruct palaeoclimatic conditions (e.g. Epstein et al., 1965; Johnsen et al., 1972; Emiliani and Shackleton, 1974), their role in evaluating recent global climate change is only now being fully appreciated. In conjunction with the rise in scientific research on climate change has been the associated quest for

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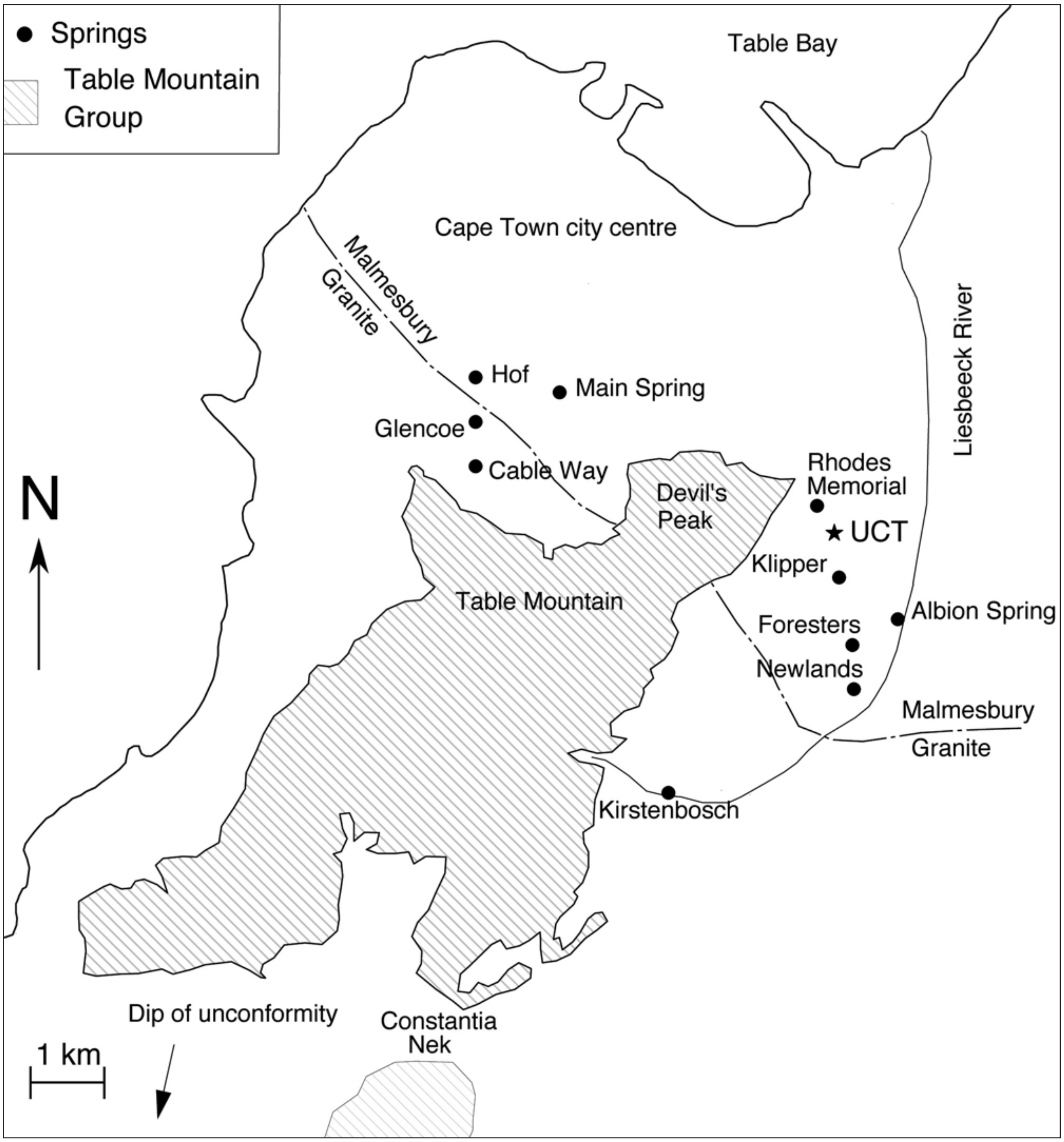

Figure 1. *Sketch map of Cape Town and Table Mountain showing the location of UCT and the springs sampled. The local geology is also shown with the high ground consisting of Table Mountain Group sandstone overlying the Malmesbury group in the north, and the Peninsular granite to the south. The contact between the Malmesbury and the granite is approximately vertical.*

additional sources of sustainable water and a greater understanding of how ground water recharge takes place.

Oxygen and hydrogen are the major elements present in water and as such they are the most conservative of all tracers. The oxygen and hydrogen isotope composition of rain water varies in a semi-predictable way, and this provides the basis for O- and H-isotope hydrology (e.g. Clark and Fritz, 1997). Craig (1961) showed that there was a remarkable correlation between δD and $\delta^{18}O$ in precipitation waters world-wide with a best-fit line corresponding to $\delta D = 8\delta^{18}O + 10$. This line is known as the global meteoric water line where the term 'meteoric water' is used to distinguish 'meteorological' such as rain, snow and hail water from connate and juvenile water. Although most precipitation world-wide lies close to the global meteoric water line, different areas have their own distinctive local meteoric water lines. Variations in the equation for the meteoric water line at a specific locality are a function of five main factors including:

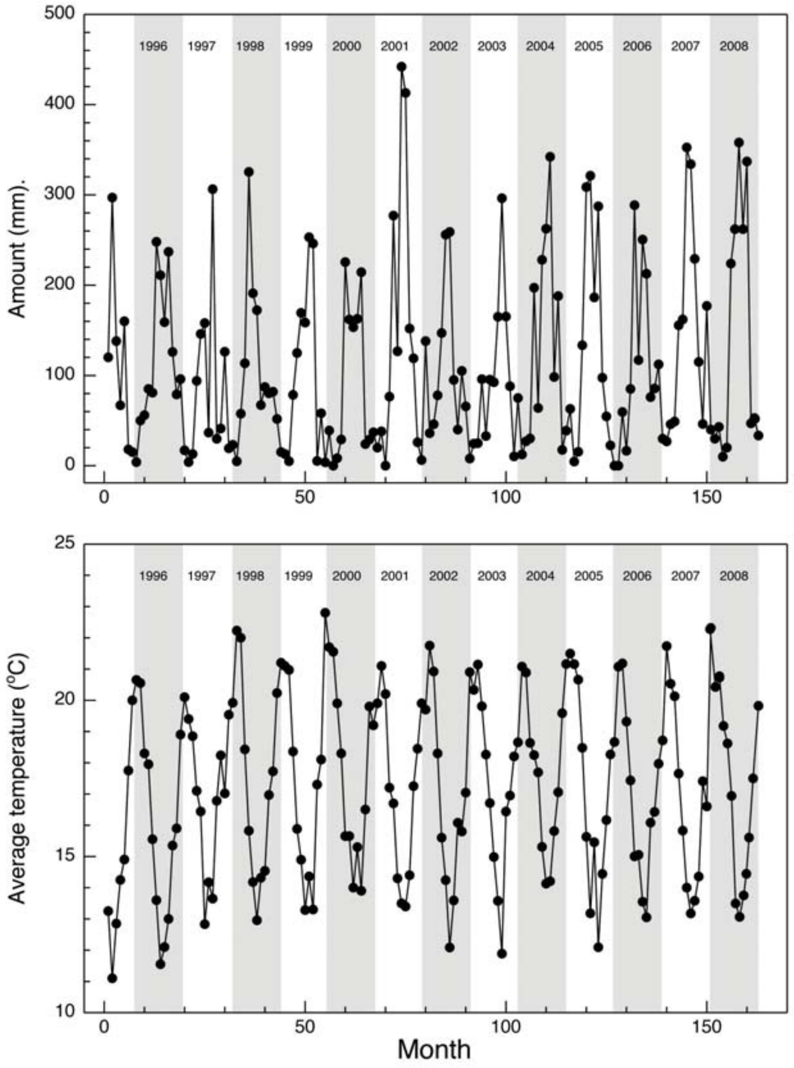

Figure 2. *Plot of the monthly amount of rain (mm) and average temperature vs. month, for the UCT monthly samples. Month 1 = June 1995 and month 163 = December 2008.*

(1) climate (temperature);
(2) altitude;
(3) the amount of precipitation;
(4) continentality; and
(5) source region of evaporation to form clouds (Dansgaard, 1964; Rozanski et al., 1993). Because of the subtle influence of these geographical factors on the equation of the meteoric water line at specific localities, it is essential to know the ambient oxygen and hydrogen isotope composition of meteoric water at these specific localities.

Since 1961, the International Atomic Energy Agency (IAEA) in conjunction with the World Meteorological Organisation (WMO) has been collecting and collating stable isotope data for precipitation on a monthly basis as part of an ongoing world-wide monitoring project. The data have been summarised in a number of reports (e.g. Rozanski, et al., 1993) and are available from the IAEA website (IAEA/WMO, 2006). Southern African stations for which analyses have been reported between the 1960's and 1980's were those at Cape Town, Pretoria, Windhoek and Harare. In Cape Town, the oxygen and hydrogen isotope composition of monthly rainfall was collected from an IAEA monitoring site at Cape Town International (formerly D.F. Malan) Airport from 1962 to 2006, but the coverage is not continuous. Rainfall data for the University of Cape Town (UCT) over a two year period were discussed by Diamond and Harris (1997). Other rain data for the Western Cape region may be

Table 1. O- and H-isotope composition, amount and average monthly temperature data for UCT monthly samples

Month	Year	Month	δD	δ^{18}O	Amount (mm)	Max T (°C)	Min T (°C)	Ave T (°C)
June	1995	1	-6	-3.81	120	17.6	8.9	13.3
July	1995	2	-5	-2.92	297	15.1	7.1	11.1
August	1995	3	-16	-4.92	138	17.1	8.6	12.9
September	1995	4	-2	-2.35	67	18.4	10.1	14.3
October	1995	5	-6	-3.12	160	19.2	10.6	14.9
November	1995	6	-25	-4.6	18	22.2	13.3	17.8
December	1995	7	-57	-8.1	15	24.4	15.6	20.0
January	1996	8	7	1.2	4	24.8	16.5	20.7
February	1996	9	-31	-4.9	50	25.3	15.8	20.6
March	1996	10	-21	-5.4	56	23.3	13.3	18.3
April	1996	11	1	-2.1	85	23.2	12.7	18.0
May	1996	12	-15	-5	81	20.9	10.2	15.6
June	1996	13	-7	-3.5	248	18	9.2	13.6
July	1996	14	-19	-5.9	211	15.9	7.2	11.6
August	1996	15	-22	-4.97	159	16.5	7.7	12.1
September	1996	16	-11	-2.98	237	16.6	9.4	13.0
October	1996	17	-2	-1.87	126	19.3	11.4	15.4
November	1996	18	-16	-3.35	79	19.5	12.3	15.9
December	1996	19	-15	-2.57	96	22.9	14.9	18.9
January	1997	20	-11	-1.39	17	24.2	16	20.1
February	1997	21	-1	-0.43	4	23.2	15.6	19.4
March	1997	22	4	-1.37	13	23.5	14.2	18.9
April	1997	23	-11	-3.41	94	21.4	12.8	17.1
May	1997	24	-24	-5	146	20.7	12.2	16.4
June	1997	25	-19	-4.72	158	16.0	9.7	12.8
July	1997	26	-2	-2.13	37	17.8	10.5	14.2
August	1997	27	-6	-2.24	306	16.7	10.6	13.6
September	1997	28	-5	-1.83	30	21.0	12.6	16.8
October	1997	29	-5	-2.15	41	22.9	13.5	18.2
November	1997	30	-15	-3.25	126	20.7	13.3	17.0
December	1997	31	4	-0.61	19	24.6	14.4	19.5
January	1998	32	-2	-1.57	23	24.4	15.5	19.9
February	1998	33	4	-0.91	5	26.7	17.8	22.2
March	1998	34	-5	-1.69	58	24.0	20.0	22.0
April	1998	35	-5	-1.55	114	22.7	14.6	18.4
May	1998	36	-24	-4.15	326	19.3	12.3	15.8
June	1998	37	-5	-2.11	191	17.9	10.4	14.2
July	1998	38	-9	-2.58	172	16.3	9.6	13.0
August	1998	39	-15	-3.27	67	18.6	10.1	14.3
September	1998	40	-4	-0.95	87	18.0	11.1	14.5
October	1998	41	-8	-2.26	80	21.0	13.0	17.0
November	1998	42	-5	-2.38	82	21.6	13.9	17.7
December	1998	43	-16	-2.59	52	24.4	16.0	20.2
January	1999	44	5	0.14	15	25.2	17.2	21.2
February	1999	45	7	-0.47	13	25.8	16.4	21.1
March	1999	46	3	-1.14	5	26.0	15.9	21.0
April	1999	47	-24	-5.44	79	23.5	13.2	18.4
May	1999	48	-7	-2.8	125	19.8	12.0	15.9
June	1999	49	-15	-3.69	169	19.4	10.4	14.9
July	1999	50	-11	-3.06	159	18.0	8.6	13.3
August	1999	51	-18	-4.66	253	19.0	9.7	14.4
September	1999	52	-17	-4.7	246	17.2	8.6	13.3
October	1999	53	7	-0.65	5	21.9	12.7	17.3
November	1999	54	2	-1.6	58	23.1	13.1	18.1
December	1999	55	-2	-1.3	4	27.9	17.7	22.8

Table 1. O- and H-isotope composition, amount and average monthly temperature data for UCT monthly samples continued

Month	**Year**	**Month**	δD	$\delta^{18}O$	**Amount (mm)**	**Max T (°C)**	**Min T (°C)**	**Ave T (°C)**
January	2000	56	-5	-2.39	39	26.2	17.2	21.7
February	2000	57			0	25.9	17.2	21.6
March	2000	58	-32	-5.59	8	24.0	15.8	19.9
April	2000	59	3	-1.23	29	23.2	13.4	18.3
May	2000	60	-4	-4.24	226	20.0	11.3	15.7
June	2000	61	-15	-3.13	162	19.3	12.0	15.7
July	2000	62	-14	-4.71	154	17.9	10.1	14.0
August	2000	63	-8	-2.65	163	19.5	11.1	15.3
September	2000	64	-3	-1.98	214	17.8	10.0	13.9
October	2000	65	-1	-1.16	24	21.5	11.6	16.5
November	2000	66	-11	-2.54	29	25.2	14.4	19.8
December	2000	67	-2	-1.64	37	23.5	14.8	19.2
January	2001	68	-13	-3.45	20	24.7	15.1	19.9
February	2001	69	-2	-1.2	38	26.0	16.2	21.1
March	2001	70			0	25.9	14.5	20.2
April	2001	71	-21	-4.73	77	21.7	12.7	17.2
May	2001	72	-6	-3.24	277	21.4	12.0	16.7
June	2001	73	-5	-3.06	127	18.3	10.4	14.3
July	2001	74	-19	-4.77	442	16.8	10.2	13.5
August	2001	75	-18	-4.48	413	16.6	10.2	13.4
September	2001	76	-4	-2.66	152	18.3	10.5	14.4
October	2001	77	3	-1.5	119	21.5	13.0	17.3
November	2001	78	-18	-2.68	26	23.0	13.9	18.5
December	2001	79	7	-0.28	6	24.8	15.0	19.9
January	2002	80	-17	-5.5	138	24.5	14.9	19.7
February	2002	81	0	-2.4	36	27.2	16.3	21.8
March	2002	82	2	-2.06	46	26.9	14.9	20.9
April	2002	83	0	-4.14	78	23.1	13.5	18.3
May	2002	84	0	-2.65	147	19.9	11.3	15.6
June	2002	85	-3	-2.26	256	16.7	11.78	14.2
July	2002	86		-3.39	259	15.53	8.65	12.1
August	2002	87	-36	-6.43	95	18.03	9.15	13.6
September	2002	88	-14	-2.99	40	20.28	11.88	16.1
October	2002	89	-15	-3.85	105	20.53	11.07	15.8
November	2002	90	-9	-3.31	66	22.60	11.48	17.0
December	2002	91	18	3.47	8	25.81	16.00	20.9
January	2003	92	18	3.3	25	25.67	14.99	20.3
February	2003	93	11	0.28	25	26.30	15.99	21.1
March	2003	94	-22	-5.6	96	24.7	14.92	19.8
April	2003	95	-3	-2.3	33	22.75	13.78	18.3
May	2003	96	-7	-2.7	95	20.94	12.48	16.7
June	2003	97	-5	-2.9	93	20.00	9.74	15.0
July	2003	98	-16	-2.71	165	18.47	8.68	13.6
August	2003	99	-23	-5.04	296	16.05	7.73	11.9
September	2003	100	-12	-2.76	165	22.72	10.15	16.4
October	2003	101	-4	-2.18	88	22.00	11.90	17.0
November	2003	102	9	-0.66	10	23.33	13.07	18.2
December	2003	103	-1	-1.45	75	22.94	14.37	18.7
January	2004	104	-18	-3.55	13	25.79	16.37	21.1
February	2004	105	-10	-2.87	27	24.85	16.93	20.9
March	2004	106	-8	-2.75	30	23.34	13.93	18.6
April	2004	107	-15	-3.54	197	22.72	13.90	18.2
May	2004	108	-6	-2.79	64	22.08	13.30	17.7
June	2004	109	-21	-4.65	228	19.13	11.48	15.3
July	2004	110	-14	-3.47	263	18.25	10.00	14.1

Table 1. O- and H-isotope composition, amount and average monthly temperature data for UCT monthly samples continued

Month	Year	Month	δD	$\delta^{18}O$	Amount (mm)	Max T (°C)	Min T (°C)	Ave T (°C)
August	2004	111	-10	-2.67	342	17.16	11.25	14.2
September	2004	112	-10	-2.38	98	19.55	12.08	15.8
October	2004	113	-31	-5.67	188	21.52	12.59	17.1
November	2004	114	-4	-1.51	18	24.06	15.11	19.6
December	2004	115	5	-0.5	39	25.83	16.49	21.2
January	2005	116	-7	-1.94	63	25.88	17.11	21.5
February	2005	117	-4	-1.4	5	25.95	16.36	21.2
March	2005	118	0	-1.16	15	25.53	15.79	20.7
April	2005	119	-37	-5.37	134	22.16	14.80	18.5
May	2005	120	-26	-3.22	309	19.14	12.12	15.6
June	2005	121	-14	-3.15	321	16.50	9.86	13.2
July	2005	122	-14	-1.67	187	19.61	11.30	15.5
August	2005	123	-15	-3.13	287	15.20	8.99	12.1
September	2005	124	-6	-2.4	98	18.12	10.77	14.4
October	2005	125	1		55	20.81	11.52	16.2
November	2005	126	4	0.97	23	23.18	13.35	18.3
December	2005	127			0	23.27	14.05	18.7
January	2006	128			0	25.51	16.65	21.1
February	2006	129	-3	-1.71	60	25.68	16.68	21.2
March	2006	130	-4	-1.5	17	24.25	14.38	19.3
April	2006	131	-18	-3.83	85	21.41	13.46	17.4
May	2006	132	-18	-3.4	289	18.54	11.47	15.0
June	2006	133	-13	-3.02	117	19.29	10.81	15.1
July	2006	134	-11	-2.74	251	17.43	9.67	13.6
August	2006	135	-14	-2.91	213	16.89	9.21	13.1
September	2006	136	-15	-2.6	76	20.90	11.26	16.1
October	2006	137	-7	-2.18	86	21.23	11.62	16.4
November	2006	138	-24	-4.38	112	22.72	13.21	18.0
December	2006	139	-9	-2.42	30	23.48	13.95	18.7
January	2007	140	11	1.27	27	26.01	17.46	21.7
February	2007	141	0	-3.03	46	25.40	15.66	20.5
March	2007	142	-3	-2.82	49	25.30	14.96	20.1
April	2007	143	-2	-2.72	156	22.94	12.36	17.7
May	2007	144	-14	-3.36	162	20.70	10.95	15.8
June	2007	145	-22	-4.62	353	17.69	10.31	14.0
July	2007	146	-15	-3.66	334	16.85	9.51	13.2
August	2007	147	-21	-4.06	229	17.40	9.76	13.6
September	2007	148	-2	-1.84	115	18.37	10.35	14.4
October	2007	149	0	-3.58	46	22.37	12.45	17.4
November	2007	150	-4	-1.66	177	20.87	12.34	16.6
December	2007	151	11	1.52	40	25.00	19.63	22.3
January	2008	152	-1	-2.40	30	24.68	16.12	20.40
February	2008	153	14	-1.22	43	25.21	16.38	20.80
March	2008	154	-7	-2.23	10	23.28	15.06	19.17
April	2008	155	-7	-2.66	20	23.30	13.98	18.64
May	2008	156	1	-1.78	224	20.41	13.56	16.99
June	2008	157	-13	-3.27	262	16.87	10.11	13.49
July	2008	158	-15	-4.66	358	16.63	9.46	13.05
August	2008	159	-25	-4.03	262	17.89	9.66	13.78
September	2008	160	-16	-3.07	337	16.98	11.79	14.39
October	2008	161	-1	-1.87	47	20.31	10.82	15.57
November	2008	162	-16	-3.61	52	22.35	12.48	17.41
December	2008	163	-2	-0.94	38	24.01	15.60	19.81

Notes: Temperature data courtesy of Kirstenbosch Botanical Gardens, ~ 3 km from UCT. Average temperature = (average monthly maximum + average monthly minimum)/2.

Table 2. Average annual amount, temperature and average and weighted δD and $\delta^{18}O$ values for UCT monthly samples

Year	Amount (mm)	Ave δD	Ave $\delta^{18}O$	Weighted ave δD	Weighted ave $\delta^{18}O$	Max T (°C)	Min T T (°C)	ave T (°C)	d
1996	1432.0	-12.6	-3.45	-13.0	-3.83	20.52	11.72	16.12	17.6
1997	991.7	-7.6	-2.38	-11.8	-3.20	21.06	12.96	17.01	13.8
1998	1256.3	-7.8	-2.17	-11.4	-2.65	21.24	13.68	17.44	9.8
1999	1130.9	-5.9	-2.45	-13.8	-3.83	22.24	12.95	17.63	16.9
2000	1084.6	-8.4	-2.84	-7.7	-3.12	22.00	13.24	17.62	17.2
2001	1696.5	-8.7	-2.91	-12.3	-3.76	21.58	12.81	17.19	17.8
2002	1273.7	-6.7	-2.96	-7.1	-3.48	21.76	12.58	17.17	20.8
2003	1166.0	-4.6	-2.06	-12.3	-3.22	22.16	12.32	17.25	13.4
2004	1506.2	-11.8	-3.03	-15.1	-3.53	22.02	13.62	17.82	13.2
2005	1495.1	-10.7	-2.25	-16.9	-2.87	21.28	13.00	17.14	6.1
2006	1333.7	-12.4	-2.78	-14.2	-2.57	21.44	12.70	17.07	6.3
2007	1693.4	-6.5	-2.73	-12.4	-3.34	21.57	12.98	17.28	14.4
2008	1683.0	-7.5	-2.77	-12.6	-3.25	20.99	12.96	16.96	13.4

Notes: d = deuterium excess (δD-8*$\delta^{18}O$).

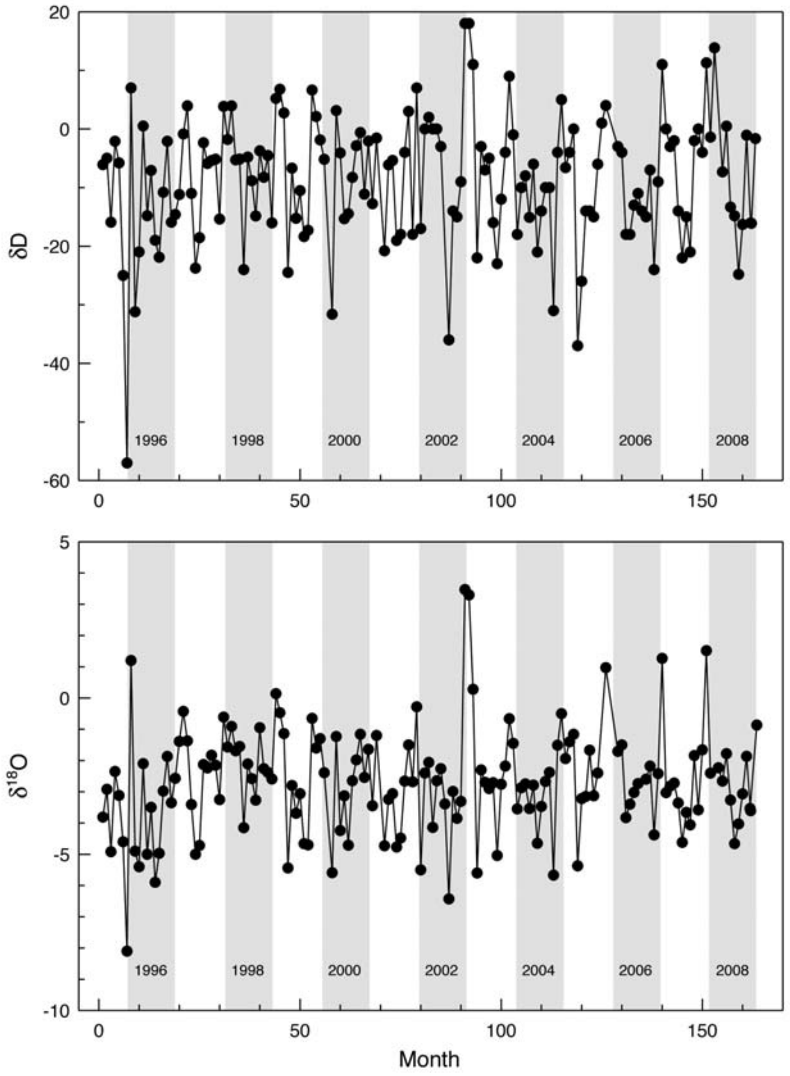

Figure 3. *Plot of δD and $\delta^{18}O$ vs. month for the UCT monthly samples.*

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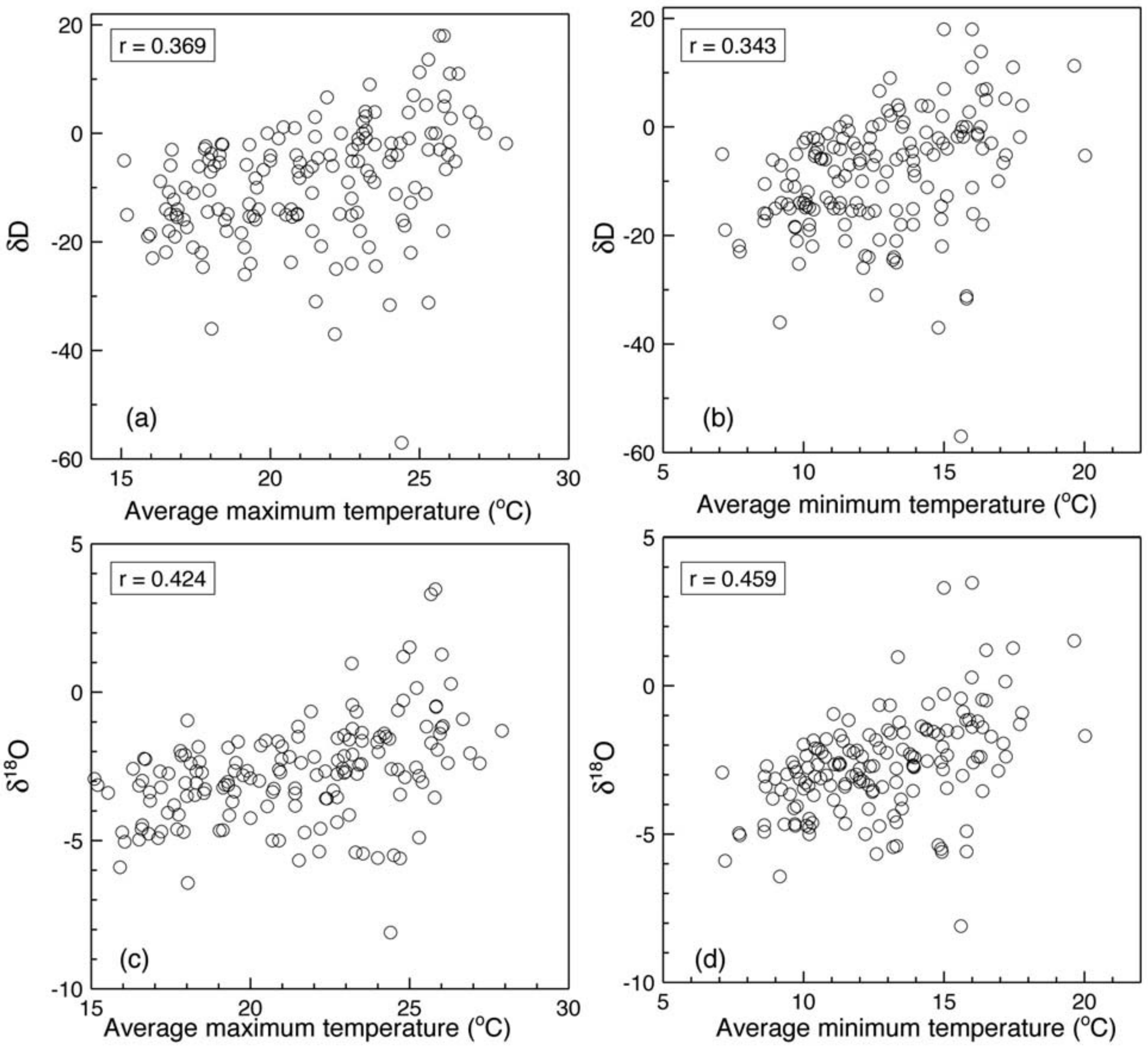

Figure 4. *Plot of δD and δ^{18}O vs (**a**) average monthly maximum and minimum temperature.*

found in Weaver and Talma (2005), Weaver et al. (1999) and Midgley and Scott (1994). The O- and H-isotope composition of rain in the Western Cape has been discussed by Diamond and Harris (1997) and by Harris et al. (1999). Diamond and Harris (1997) calculated the line of best fit through the rain data from the Western Cape ('local meteoric water line') to have the equation $\delta D = 6.2*\delta^{18}O + 10.6$.

In this paper we report a 12 year record of monthly hydrogen and oxygen isotope data for meteoric waters collected at UCT. We also report a 15 month record of the isotope composition of rainfall collected on a daily basis and data for samples collected during two winter storm events as well as data for hail/snow at the University of Cape Town (UCT) and elsewhere in the Western Cape. Included in this is a re-evaluation of the local meteoric water line, and a determination of the weighted (i.e. the mean value weighted by amount of precipitation) annual meteoric water δD and δ^{18}O values. These values presumably approximate those of groundwater recharge in the area more closely than the arithmetic means because rain events of minor amount often have extreme isotope composition.

Long-term data on the composition of rain is essential for an increasingly number of studies in the Earth and life sciences. The use of 'environmental' isotopes (including O- and H-) in hydrological studies in southern Africa has been reviewed by Verhagen (1984). One such application in the Cape Town region is the impending water shortage, which is being

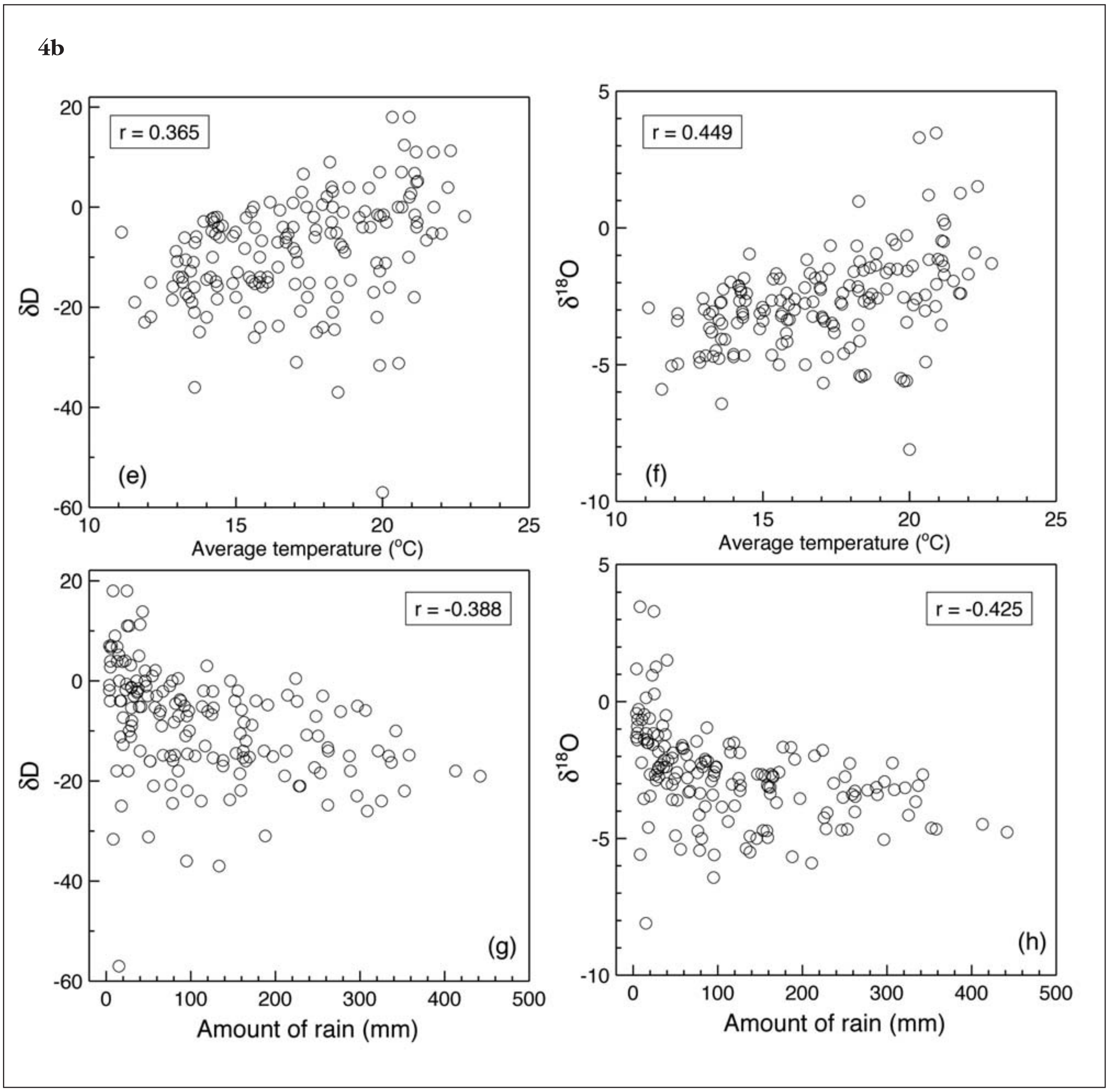

Figure 4. *Plot of δD and $\delta^{18}O$ vs (**b**) average monthly temperature, and amount of rain for UCT monthly samples. Correlation coefficients (r) are given for each plot.*

addressed by assessing the viability of the Table Mountain Group (TMG) as a source of water. This requires an assessment of the ability of TMG aquifers to withstand significant water abstraction. In the final part of this paper, the long-term variation in isotope composition of rainfall is used to estimate the recharge rate and volume of stored water of the TMG in Table Mountain. We hope that publication of this dataset will encourage similar long-term studies elsewhere in South Africa.

Local climate

Cape Town is situated at approximately 18°25'E and 33°55'S. Table Mountain and the Cape Peninsula are to the south of Cape Town (Figure 1), and UCT is situated on the eastern slopes of Table Mountain, which is the highest point on the Peninsula at 1086 m above sea level. Local topography of the Peninsula consists of steep, elevated sandstone cliffs, the level Cape Flats and rolling hilly landscape comprised of the Late Proterozoic Malmesbury Group and Cambrian Cape Granite Suite. The annual rainfall in Cape Town is 600 mm on average (South African Weather Service, 2006) and most occurs from May to September. The annual rainfall at UCT is much higher and ranged from 992 to 1697 mm between 1996 and 2008. Temperature is very variable locally; and averages 13°C in winter and 21°C in summer (IAEA/WMO 2006). The long term (1974 to 2001)

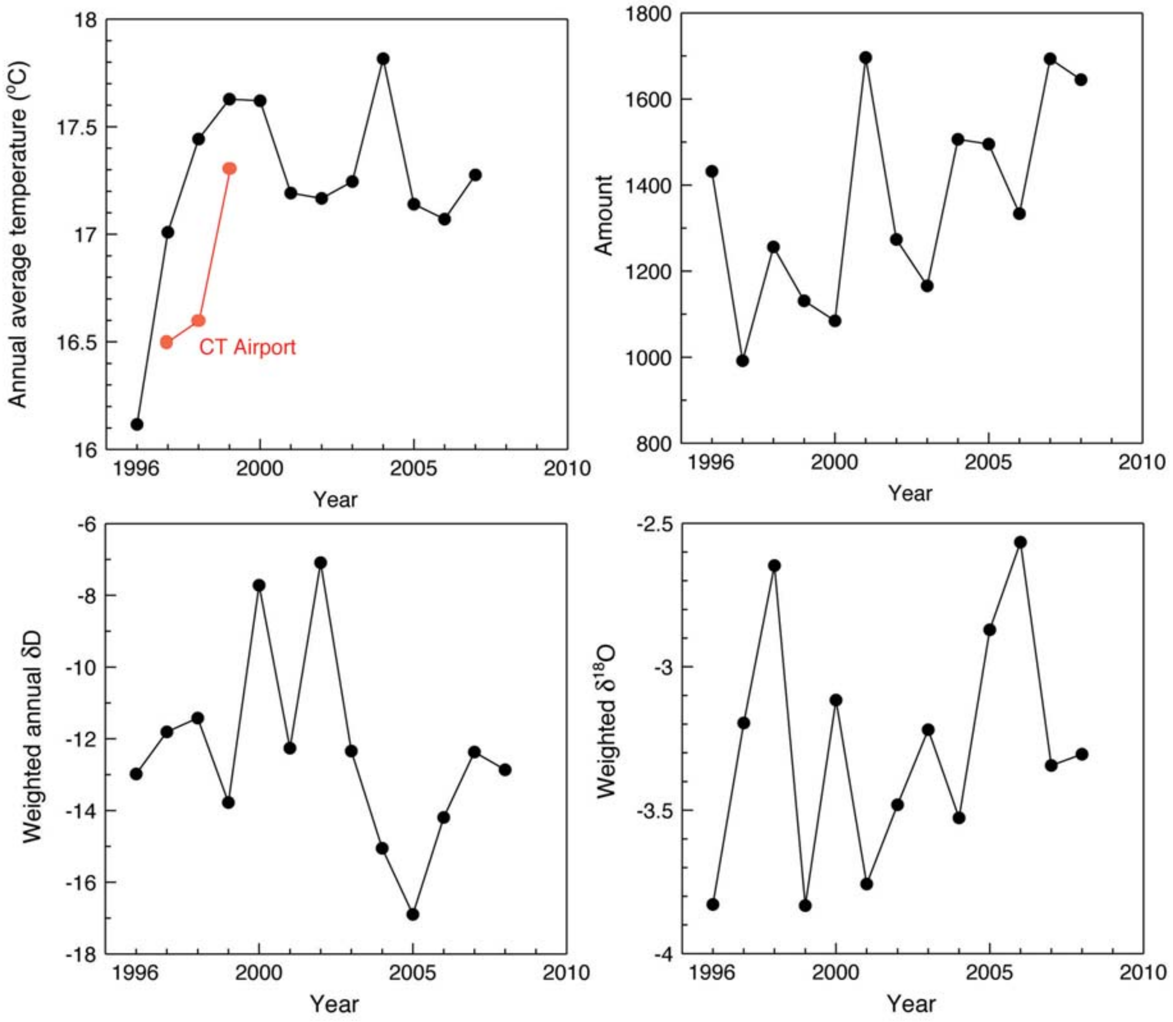

Figure 5. *Annual average temperature, amount and δD and δ^{18}O value weighted by amount vs. year calculated from UCT monthly samples. Temperature data for Cape Town International Airport for 1996 to 1998 from IAEA/WMO (2006).*

average temperature for Cape Town Airport (IAEA/WMO 2006) is 16.3°C, whereas at Kirstenbosch (Figure 1) from 1996 to 2008 it was 17.2°C. The wind blows predominantly from northerly and southerly directions in winter, and southerly to southeasterly directions in summer.

Average monthly temperatures from June 1995 to December 2008 are plotted in Figure 2, and annual average maximum, minimum and average temperatures for 1996 to 2008 are given in Table 2. These data are from the Kirstenbosch Botanical Gardens about 3 km south of UCT. The average temperature for each year ranges from 16.12 to 17.82°C, with 2004 being the hottest year. Also shown on Figure 2 is the monthly rainfall amount collected at UCT during the same period. The maximum monthly rainfall each year was typically between 300 and 350 mm, with 2001 having >400 mm in both July and August. The annual rainfall amount ranges from 992 to 1697 mm per year (Table 2). Note the strong seasonal variation in both temperature and amount, with low rainfall in the hot summer moths and high rainfall in the winter months. The only systematic change in the Kirstenbosch temperature record (Figure 2) is an increase in the average temperature of the coldest month of about 3°C from 1995 to 2000 (there is no corresponding increase in the average temperature of the hottest month). From 2000 to 2009, there has been no systematic variation in temperature. There is no systematic change in the amount of rain over the last 12 years.

Sample types, sampling and analytical method

Five types of samples were collected as part of this study:

1. Monthly rain samples (June 1995 to December 2008);
2. Daily rain samples (June 2000 to September 2001);
3. Hail at UCT and snow in the mountains some 150 km east of Cape Town;
4. Storm events (two storms in the winter of 2000); and
5. Spring samples in the Cape Town area (Figure 1).

Monthly and daily rain water samples were collected in a standard rain gauge and transferred at 8 am each morning (after rainfall occurred), to a larger screw-top glass container. At the end of each month, two samples were taken from the integrated rainfall sample for that month and the rest discarded. For the daily rain samples, a second rain gauge was used with the samples again transferred at 8 am each morning into individual bottles. Bottles used for storing of both the monthly and daily samples were either 100 ml plastic or 50 ml glass bottles. Where a sample is given a date, this is the date of collection. Thus, a sample collected on June 2nd would include all the rain that fell from 8 am on June 1st to 8 am on June 2nd. The monthly samples include all rain from 8 am on the last day of the previous month to 8 am on the last day of the month.

Temperature readings supplied by Kirstenbosch Botanical Garden were made at 8 am each day, hence the maximum temperature is for the day before and the minimum temperature for the day in which the reading was taken. The time interval for daily rain water collection and temperature readings was, therefore, the same. Kirstenbosch and UCT are 3 km apart and at

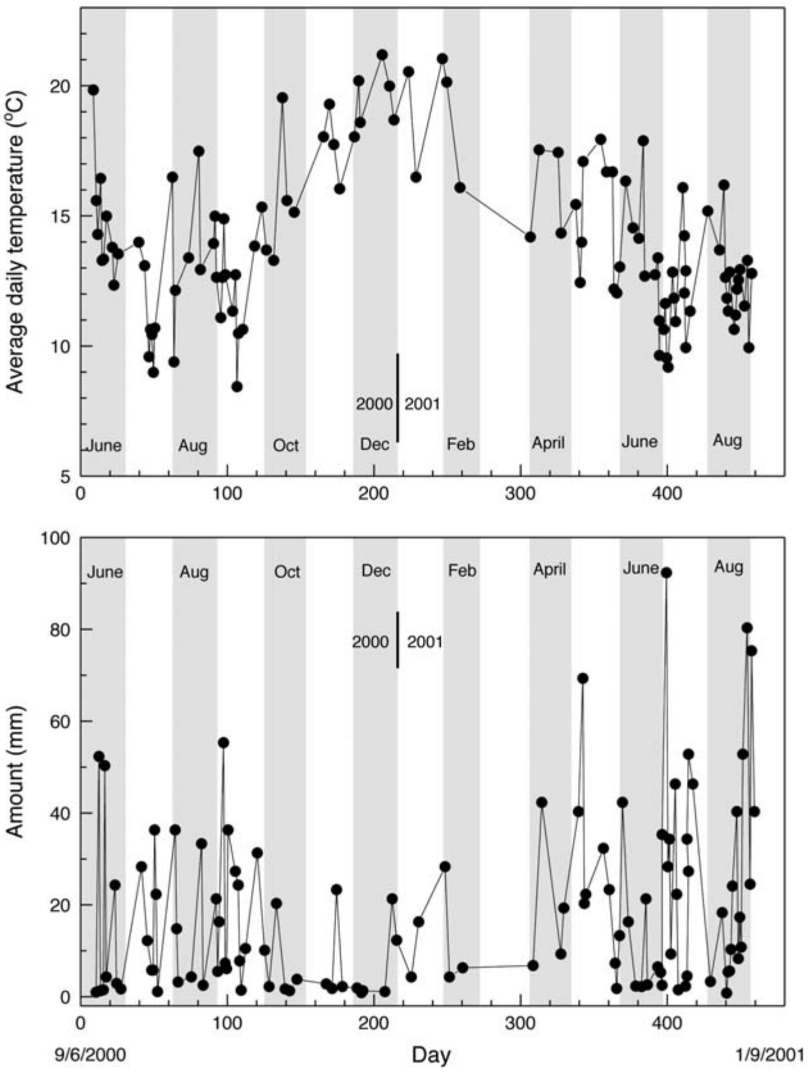

Figure 6. *Plot of average temperature and amount of rain vs. day for the UCT daily samples. Day 1 = June 9th 2000 and day 471 = September 1st 2000*

Table 3. O- and H-isotope composition of daily rainfall at UCT

Month	Date	Day#	δD	$\delta^{18}O$	Amount (mm)	Max T (°C)	Min T (°C)	Ave T (°C)
2000								
June	9	9	21	6.44	0.7	23.7	15.9	19.8
June	11	11	-32	-5.23	52	19.4	11.7	15.6
June	12	12	7	-0.60	1	13.8	11.5	14.3
June	14	14	7	-0.37	1.2	21.0	11.8	16.4
June	15	15	-5	-1.94	50	15.0	11.5	13.3
June	16	16	-20	-4.88	4	15.0	11.6	13.3
June	18	18	-8	-2.67		15.4	14.5	15.0
June	22	22	-13	-2.65	24	16.0	11.5	13.8
June	23	23	-15	-3.76	2.6	15.6	9.0	12.3
June	26	26	8	-0.97	1.4	18.6	8.4	13.5
July	10	40	-8	-2.66	28	14.9	13.0	14.0
July	14	44	-42	-6.73	11.9	14.6	11.5	13.1
July	17	47	9	-2.05	5.5	12.7	6.4	9.6
July	18	48	6	-1.42	5.5	11.6	9.6	10.6
July	19	49	-8	-3.74	36	14.4	6.4	10.4
July	20	50	-11	-4.65	22	11.4	6.5	9.0
July	21	51	-8	-4.12	0.8	14.0	7.3	10.7
August	2	63	-23	-4.95	36	21.5	11.4	16.5
August	3	64	-14	-4.62	14.5	19.2	9.5	9.4
August	4	65	-7	-3.10	2.9	13.6	10.6	12.1
August	14	74	8	-0.41	4	17.2	9.5	13.4
August	21	81	4	-1.16	33	22.0	12.9	17.5
August	22	82	2	-1.61	2.2	16.0	9.8	12.9
August	30	91	4	-1.02	21	15.8	12.0	13.9
August	31	92	-10	-2.25	5.2	17.4	12.5	15.0
September	1	93	-1	-1.05	16	15.3	9.9	12.6
September	4	96	-8	-2.58	55	14.1	8.0	11.1
September	5	97	8	-1.69	7	13.8	11.4	12.6
September	6	98	3	-1.62	5.8	16.8	12.9	14.9
September	7	99	4	-1.36	36	16.4	9.0	12.7
September	11	104	3	-1.89	27	14.6	8.0	11.3
September	13	106	-7	-3.26	24	17.6	7.8	12.7
September	14	107	-6	-4.15	7.5	12.5	4.3	8.4
September	15	108	-23	-5.37	1.1	13.3	7.6	10.5
September	18	111	-6	-4.46	10.2	13.9	7.3	10.6
September	27	119	1	-1.53	31	17.7	9.9	13.8
October	2	124	-14	-3.14	9.8	19.7	10.9	15.3
October	5	127	8	-0.48	1.9	18.1	9.2	13.7
October	10	132	0	-1.34	20	17.7	8.8	13.3
October	16	138	27		1.4	24.7	14.3	19.5
October	19	141	-7		1	19.9	11.2	15.6
October	24	146	4	-0.85	3.5	20.8	9.4	15.1
November	13	166	-40	-5.24	2.5	23.0	13.0	18.0
November	17	170	3	0.27	1.5	23.0	15.5	19.3
November	20	173	-9	-2.73	23	22.9	12.5	17.7
November	24	177	5	-0.34	1.9	22.8	9.2	16.0
December	4	187	3	0.15	1.6	22.3	13.7	18.0
December	7	190	-1		0.6	24.4	15.9	20.2
December	8	191	-7		1	22.1	15.0	18.6
December	23	206	14		0.8	25.2	17.1	21.2
December	28	211	0	-1.73	21	23.6	16.3	20.0
December	31	214	-14	-2.71	12	22.1	15.2	18.7

approximately the same altitude, hence the temperature conditions at both locations would have been very similar.

All samples were analysed as soon as possible after collection. For oxygen, the CO_2 equilibration method of Socki et al. (1992) employing disposable pre-evacuated 7 ml glass vials was used. For hydrogen, 2 mg of water contained in a microcapilliary tube was dropped into a Pyrex tube containing a few grains of Indiana Zn (Schimmelman and DeNiro 1993). The tube was attached to the vacuum line, frozen in liquid nitrogen, 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_2. Isotope ratios of CO_2 and H_2 were measured using either a Finnegan MAT252 or Delta XP mass spectrometer, and the fractionation factor between CO_2 and water at 25°C was assumed to be 1.0412 (Coplen, 1993). Data are reported in the familiar δ notation where $\delta = (R_{sample}/R_{standard} - 1)*1000$, and $R = {}^{18}O/{}^{16}O$ or D/H.

Table 3. O- and H-isotope composition of daily rainfall at UCT continued

Month	Date	Day#	δD	$\delta^{18}O$	Amount (mm)	Max T (°C)	Min T (°C)	Ave T (°C)
2001								
January	10	224	-1	-1.63	4	24.3	16.7	20.5
January	15	229	-14	-4.05	16	20.4	12.5	16.5
February	2	247	-4	-1.42	28	25.6	16.4	21.0
February	5	250	-1	-0.37	4	25.3	14.9	20.1
February	14	259	-8	-2.27	6	19.1	13.0	16.1
April	3	307	4	-2.92	6.5	18.3	10.0	14.2
April	7	313	-30	-5.58	42	20.7	11.0	17.5
April	22	326	-8	-2.76	9	22.7	12.1	17.4
April	24	328	-9	-4.25	19	18.1	10.5	14.3
May	4	338	-36	-6.35	40	20.2	10.6	15.4
May	7	341	-12	-4.42	69	14.3	10.5	12.4
May	8	342	1	-1.90	20	15.9	12.0	14.0
May	9	343	-7	-1.54	22	21.5	12.6	17.1
May	20	355	1	-1.22	32	15.7	13.8	17.9
May	25	359	4	-1.80	23	20.8	12.5	16.7
May	29	363	-5	-2.86	7	21.6	11.7	16.7
May	30	364	-10	-3.82	1.5	15.0	9.3	12.2
June	1	366	-13	-3.73	13	15.6	8.4	12.0
June	3	368	-8	-2.77	42	13.7	11.5	13.0
June	7	372	-18	-3.65	16	19.6	13.0	16.3
June	11	377	0	-0.89	2	17.8	11.2	14.5
June	15	381	2	-0.91	1.9	16.6	11.6	14.1
June	18	384	-13	-3.52	21	22.6	13.1	17.9
June	19	385	-12	-2.54	2.3	16.7	8.6	12.7
June	26	392	0	-1.56	6.2	15.6	9.8	12.7
June	28	394	2	-1.95	5	18.1	8.6	13.4
June	29	395	4	-1.49	2.2	12.5	6.7	9.6
June	30	395	-14	-4.65	35	19.0	6.2	10.9
July	3	398	-19	-4.24	92	19.7	11.5	10.6
July	4	399	-50	-8.01	28	13.6	9.6	11.6
July	5	400	-48	-8.96	34	12.6	6.4	9.5
July	6	401	-33	-7.38	9	12.8	5.5	9.2
July	9	404	6	-1.49	46	14.5	11.1	12.8
July	10	405	-8	-2.91	22	13.5	10.1	11.8
July	11	406	-4	-1.94	1.2	14.3	7.5	10.9
July	16	411	6	-0.05	2	20.1	12.0	16.1
July	17	412	-2	-1.17	4.2	15.9	12.5	14.2
July	18	413	-4	-2.46	27	14.8	10.9	12.9
July	19	412	-23	-4.93	34	13.6	10.4	12.0
July	20	413	-41	-7.14	52.5	12.8	7.0	9.9
July	23	416	-2	-2.36	46	15.0	7.6	11.3
August	2	428	10	-0.12	3	17.7	12.6	15.2
August	10	436	-19	-3.12	18	16.4	10.9	13.7
August	13	439	8	0.04	0.5	22.1	10.2	16.2
August	14	440	-8	-3.55	5.1	16.4	8.8	12.6
August	15	441	-10		5.3	15.6	8.0	11.8
August	16	442	-3	-3.18	10	13.6	9.0	11.3
August	17	443	-3	-1.82	23.8	13.8	11.8	12.8
August	20	446	-5	-2.14	40	13.6	7.6	10.6
August	21	447	3	-2.70	8	13.4	8.9	11.2
August	22	448	-15	-4.28	17	13.9	10.4	12.2
August	23	449	3	-1.24	10.5	13.6	11.4	12.5
August	24	450	-10	-2.69	52.5	14.6	11.2	12.9
August	27	453	-15	-3.70	80	13.4	9.6	11.5
August	29	455	-14	-3.71	24.2	16.6	9.9	13.3
August	30	456	-57		75	12.7	7.1	9.9
September	1	458	-4		40	15.7	9.8	12.8

Notes: Record started on June 1st 2000. Day = calendar date, Day# = day numbered sequentially from June 1st 2000. Where days are missing, it did not rain. The $\delta^{18}O$ values was not determined on very small quantities of rain (<1.5 mm). Temperature data courtesy of Kirstenbosch Botanical Gardens, ~ 3 km from UCT. Average temperature = (average monthly maximum + average monthly minimum)/2.

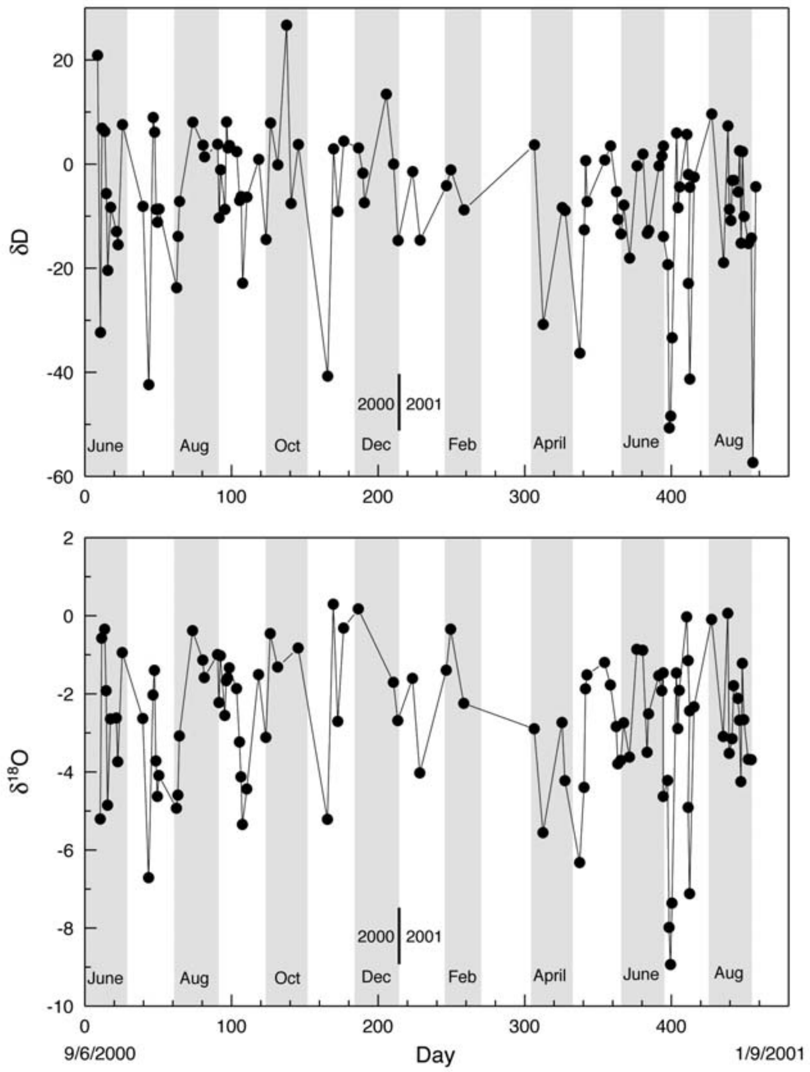

Figure 7. *Plot of δD and $\delta^{18}O$ vs. day for the UCT daily samples.*

The long-term average difference between duplicates of our internal water standards (CTMP, CTMP2, CTMP3) over the course of this research was 1.4‰ for hydrogen and 0.10‰ for oxygen. This suggests that the errors are of the order of 1.0‰ for δD and 0.05‰ for $\delta^{18}O$. The standards V-SMOW and SLAP (and calibrated secondary standards) were analysed to determine the degree of compression of raw data and the equations of Coplen et al. (1993) were used to convert raw data to the SMOW scale. Our internal water standards (CTMP1, CTMP2 and CTMP3), which have been calibrated against V-SMOW and SLAP, and independently analysed, were run with each batch of samples and used to correct for drift in the reference gases. Since 2007, Evian bottled water (δD -73‰, $\delta^{18}O$ -10.11‰; Spangenberg and Vennemann, 2008) was analysed routinely with each batch of samples as an additional analytical check.

Results

Monthly samples

Data for the monthly samples from UCT are reported in Table 1. This represents a 163 month data set with a range in δD and $\delta^{18}O$ values from -57 to +18‰ and -8.1 to +3.5, respectively. Most δD and $\delta^{18}O$ values are between -20 and 0‰, and -5 and -1‰, respectively. The variation in δD and $\delta^{18}O$ with month is shown in Figure 3. Some of the variation is seasonal with higher values in summer months and lower values in winter months. There is no systematic variation in either δD or $\delta^{18}O$ over the 12 years of measurement. Figure 4 shows δD and $\delta^{18}O$ plotted against minimum, maximum

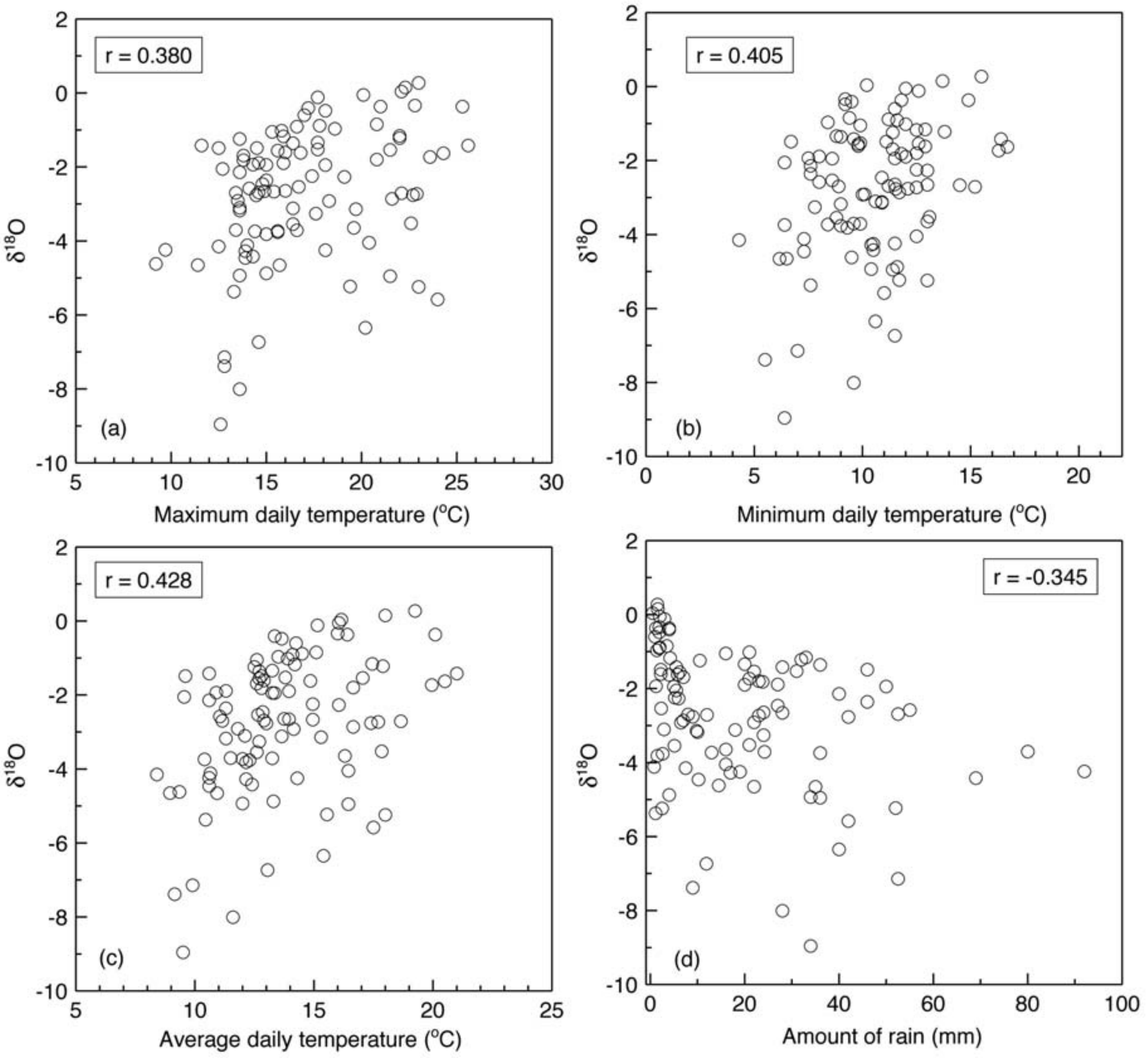

Figure 8. *Plot of $\delta^{18}O$ vs. maximum and minimum daily temperature, average daily temperature, and amount of rain for UCT daily samples. Correlation coefficients (r) are given for each plot.*

Table 4. Isotope composition of hail and snow samples.

Type	**Location**	**Date**	**δD**	**$\delta^{18}O$**	**d**
Snow	N1 highway, Matroosberg	15/7/2000	-55	-10.66	30.3
Snow	N1 highway, Matroosberg	15/7/2000	-60	-10.89	27.1
Snow	Gydo Pass	July 2000	-21	-6.85	33.8
*Snow	Theronsberg Pass	July 1996	-59	-10.5	25.0
*Snow	Waaihoek	July 1996	-30	-6.6	22.8
Hail	UCT	19/7/2000	-40	-8.65	29.2
Hail	UCT	August 2004	-31	-8.36	35.9
Hail	UCT	October 2008	-30	-8.27	36.2
Hail	Pinelands	31/8/08	-39	-7.83	23.6
*Hail	UCT	July 1995	-51	-11.6	41.8
*Hail	UCT	July 1996	-32	-7.2	25.6
*Hail	UCT	July 1996	-30	-7.5	30.0

*1995-6 data from Diamond and Harris (1997); d = deuterium excess

Table 5. Individual storm events sampled at UCT

Sample/time	δD	$\delta^{18}O$	Amount (mm)	Temp (oC)	Air pressure (Pa)	d
Series 1 July 14/15 2000						
11:45 July 14	-28	-5.67	2.9	12.1	978.2	17.0
13:15 July 14	-38	-6.56	1	12.4	977.9	14.6
13:50 July 14	-29	-5.81	0.7	11.5	977.3	17.2
15:00 July 14	-30	-6.19	1	10.7	978.0	20.0
15:30 July 14	-56	-9.39	4.5	9.5	978.8	19.3
16:00 July 14	-54	-9.50	2.3	9.0	979.3	22.1
17:15 July 14	-58	-8.83	1.2	8.3	980.6	12.8
20:15 July 14	-22	-5.90	4.6	8.0	982.5	25.6
21:00 July 14	-16	-5.15	2.3	8.4	982.4	25.4
21:40 July 14	-36	-7.69	3.5	7.1	983.4	25.1
24:00 July 14	-33	-7.15	6	7.6	983.6	24.1
11:40 July 15	-27	-6.37	8.4	8.9	988.8	24.0
14:10 July 15	-18	-5.72	5.6	7.5	990.8	27.5
Series 2 August 4 2000						
00:35	-6	-3.19	3.5	11.9	1001.8	20.0
01:35	-2	-2.74	7.5	11.9	1001.8	19.7
02:20	-10	-3.41	10.0	11.9	1002.2	17.7
02:45	-8	-3.49	0.5	11.8	1002.1	19.8
03:30	-6	-3.07	4.0	12.0	1001.6	18.9
04:00	-5	-2.70	3.0	12.1	1001.7	16.2
04:30	-9	-3.27	10.0	12.2	1001.7	17.0
04:45	-15	-3.74	2.8	12.2	1001.7	15.5

Sample/time refers to time samples was taken; d = deuterium excess.

and average monthly temperature, and in all cases there is a relatively weak positive correlation (r = 0.316 to 0.450). There is a weak negative correlation (Figure 4b) between the amount of rain and both δD (r = -0.39), and $\delta^{18}O$ (r = -0.422). High δD and $\delta^{18}O$ values are confined to months with very low rainfall (< 50 mm).

The monthly samples (Table 1) were used to calculate the annual amount and the average and weighted average (δ values weighted by amount) δD and $\delta^{18}O$ values for the years 1996 to 2008 (Table 2). Average δD and $\delta^{18}O$ are typically more variable and less negative than the weighted average δD and $\delta^{18}O$values. Weighted average δD and $\delta^{18}O$ range from -17 to -7 and -3.8 to -2.6, respectively. Weighted averages reflect recharge values better than arithmetic means, because they represent the isotope composition of all rainfall in a particular year. Figure 5 shows the average annual temperature and amount vs. year. It can be seen that although 1996 was significantly colder than subsequent years, there is no systematic change with time. There is, however, a general increase in amount of rain from 1996 to 2008, with the years 2004 to 2008 being significantly wetter than the years 1996 to 2000. There is no systematic change in weighted δD and $\delta^{18}O$ values with year, but an interesting feature of the data is the lack of correspondence between δD and $\delta^{18}O$ values. The correlation coefficient (r) between average δD and average $\delta^{18}O$ value = 0.554, but there is no correlation at all between weighted annual δD and $\delta^{18}O$ values (r = -0.081).

The deuterium excess (d = δD to $8^*\delta^{18}O$; Dansgaard, 1964) has been calculated using a slope of 8 as parameter of deviation from the global meteoric water line (GWML), although the local MWL has a lower slope (6.41, see below). This parameter has been generally related to the evaporation processes operating in the major source regions of the cloud vapour (the subtropical oceans) e.g. Rozanski et al. (1993). The deuterium excess is a useful way of describing the variation of water composition on a δD vs. $\delta^{18}O$ plot. An alternative would have been the $\delta D/\delta^{18}O$ ratio, but this parameter has not been widely used in isotope hydrology. The deuterium excess averages 12.4 for the monthly rain data (Table 1).

Daily samples

Daily rainfall was collected at 8 am from June 9th 2000 until September 1st 2001 (a period of 471 days) with rain falling on 108 of those days. Isotope data together with temperature and amount are reported in Table 3, and Figure 6 shows the amount and the average daily temperature for those days on which rain fell. High temperatures and low rainfall correspond to summer months, and Figure 7 shows the δD and $\delta^{18}O$ values of rain throughout that period. Figure 8 shows $\delta^{18}O$ vs. average max, min and average daily temperature and amount of rain. The patterns and correlation coefficients are similar to the same plots for monthly samples. There is no correlation between either δD or $\delta^{18}O$ and the number preceding days without rain.

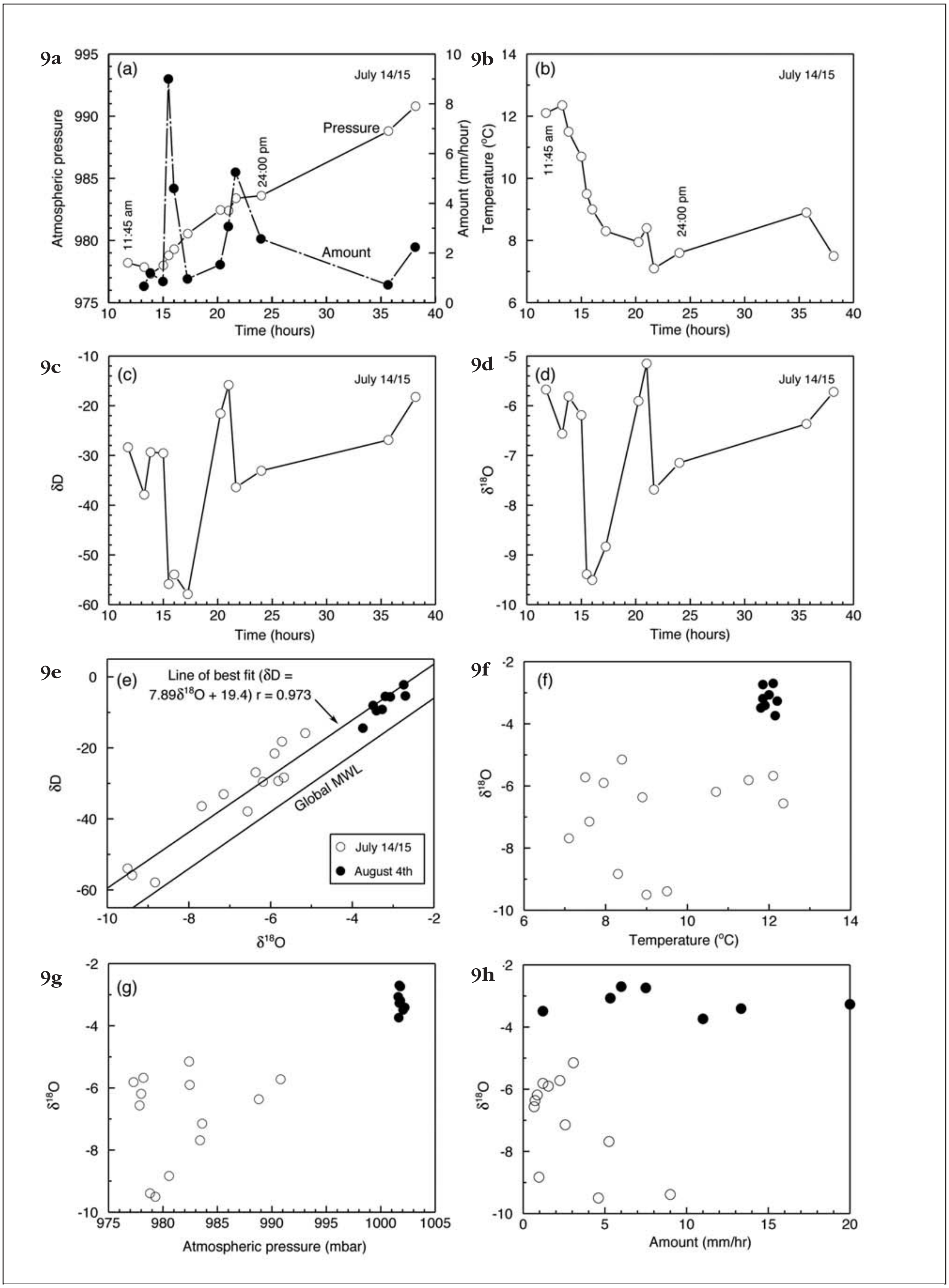

Figure 9. *(**a**) Pressure and amount of rain (in mm/hour), (**b**) Temperature, (**c**) δD and (**d**) δ^{18}O vs. time (hours) for the July 14/15 storm event. Time 10 = 10.00 am. (**e**) Plot of δD vs. δ^{18}O, and δ^{18}O vs. (**f**) temperature, (**g**) atmospheric pressure, and (**h**) amount of rain for the July 14/15 and August 4th 2000 storm events at UCT.*

Table 6. O- and H-isotope composition of springs sampled

Sample	Altitude	δD	$\delta^{18}O$	δD	$\delta^{18}O$	δD	$\delta^{18}O$	δD	$\delta^{18}O$
Year	**(m)**	**September 1996**		**April 1997**		**September 1999**		**October 2008**	
Rhodes Memorial	140	-13	-3.80			-11	-3.63	-15	-3.38
Hof	190	-11	-3.44			-13	-3.71	-13	-2.89
Main Spring	120	-17	-4.00	-13	-3.56	-18	-4.05	-16	-3.46
Albion Spring	30	-9	-3.19	-9	-2.87	-12	-3.10	-13	-3.01
Newlands	40	-12	-3.38	-11	-3.06	-12	-3.36	-11	-2.96
Glencoe	250	-15	-4.08	-14	-3.77	-17	-4.21	-15	-3.66
Cable Way	310	-18	-4.47	-14	-3.93	-15	-4.46	-17	-3.83
Foresters	45	-12	-3.24			-11	-3.39	-14	-3.08
Kirstenbosch	150	-15	-3.66	-12	-3.14		-3.41	-14	-2.98
Klipper Road	100	-12	-3.39			-11	-3.35	-12	-3.02

Hail and snow

A small number of hail/snow samples (Table 4) were collected when the opportunity arose. Five samples from 1995/6 are from Diamond and Harris (1997) but an additional four hail samples from UCT and Pinelands (~5 km from UCT), and three samples of snow from the Gydo Pass, and the N1 at Matroosberg (about 150 km from Cape Town) were analysed. The snow samples collected on 15/7/2000 resulted from the same storm event sampled at UCT (Table 5). The sample recording the lowest δD and $\delta^{18}O$ values of -60 and -10.9‰, respectively, is a snow sample from the N1 highway near Matroosberg Station. The snow and hail samples have deuterium excess values that range from 23 to 42, and an average of 30.1. This is significantly higher that the average for the monthly rain samples (d = 12.4).

Storm samples

Table 5 shows δD and $\delta^{18}O$ values for rain collected during two storms in July and August 2000. Also shown are the temperature and pressure at the time of collection and the amount of rain collected after each interval.

The first storm sampled arrived at Cape Town on the 13th of July 2000 and resulted in extensive cloud cover for 24 hours without any precipitation. On the morning of the 14th of July 2000 at approximately 10h00 it started raining. Rain continued falling all day, varying from heavy rain to drizzle, and finally ceased at 18h00. There was a period of two hours with no rain with patchy clouds, and the wind continued to blow northerly to north-easterly. At approximately 20h00 the rain resumed and fell heavily for the next four hours with sporadic lighting. Between 24h00 and 11h40 only 6 mm of rain fell. Between 11h40 and 14h00 heavy rain and hail fell for approximately half an hour with a midday temperature low. This, the first major winter storm of the year, resulted in extremely cold conditions, heavy rainfall and snow on the Ceres Mountains situated to the east of Cape Town. The variation of air pressure, temperature and isotope composition for the July 14/15 storm is shown in Figure 9 (a to d). The fairly regular increase in pressure with time contrasts with the rapid decrease in temperature from 12 to around 8° in <4 hours. This storm was the result of a low-pressure system situated in the South Atlantic Ocean and is typical of winter frontal activity in the region. Extremely large changes in δD and $\delta^{18}O$ were found to occur in a very short space of time (Table 5, Figure 9), with a decrease in δD of 26‰ and $\delta^{18}O$ of 3.3‰ in 30 minutes from 15.00 to 15.30. This was followed by a slightly more gradual rise in both δD and $\delta^{18}O$ values, and then another more rapid decrease in δD and $\delta^{18}O$ values occurred with a 20‰ decrease in δD and a 2.5‰ decrease in $\delta^{18}O$ in 40 minutes.

The second storm that was sampled occurred in August 2000. Rain commenced just before midnight on the 3rd of August. Sample collection took place from midnight till 05h00. During this period heavy, steady rain fell without cessation. After 05h00, rain did not resume and the storm passed on. The storm data are reported in Table 5 and plotted on Figure 9. The temperature changed very little (from 11.8 to 12.2°C, and there was very little change in air pressure. Both temperature and air pressure in this second storm were significantly higher than in the first storm. This storm is typical of orographic rain caused by the movement of moist air over the Cape Peninsula. Although the second storm produced more rain, with 10 mm falling during a 45 minute period from 1.30 am and 10 mm falling in 30 minutes from 4.30 am, there is very limited variation and in δD and $\delta^{18}O$ value. The δD and $\delta^{18}O$ values range from -2 to -15‰, and -2.7 to -3.7‰, respectively, and are significantly higher than in the first storm.

The combined data for the two storms shows a good correlation between δD and $\delta^{18}O$ (r = 0.973, Figure 9e). There is no correlation between $\delta^{18}O$ (and therefore also δD) and either temperature or amount of rain (in mm/hr) for either of the storms. However, there is a generally positive correlation between $\delta^{18}O$ and pressure for the data set as a whole. The storm samples have and average deuterium excess of 20.0, which is significantly higher than the monthly rain samples (d = 12.4).

Meteoric water lines

The monthly UCT data are plotted on the classic δD vs. $\delta^{18}O$ diagram in Figure 10a and show a good positive correlation (r = 0.876). The line of best fit was calculated using the reduced major axis method (RMA or

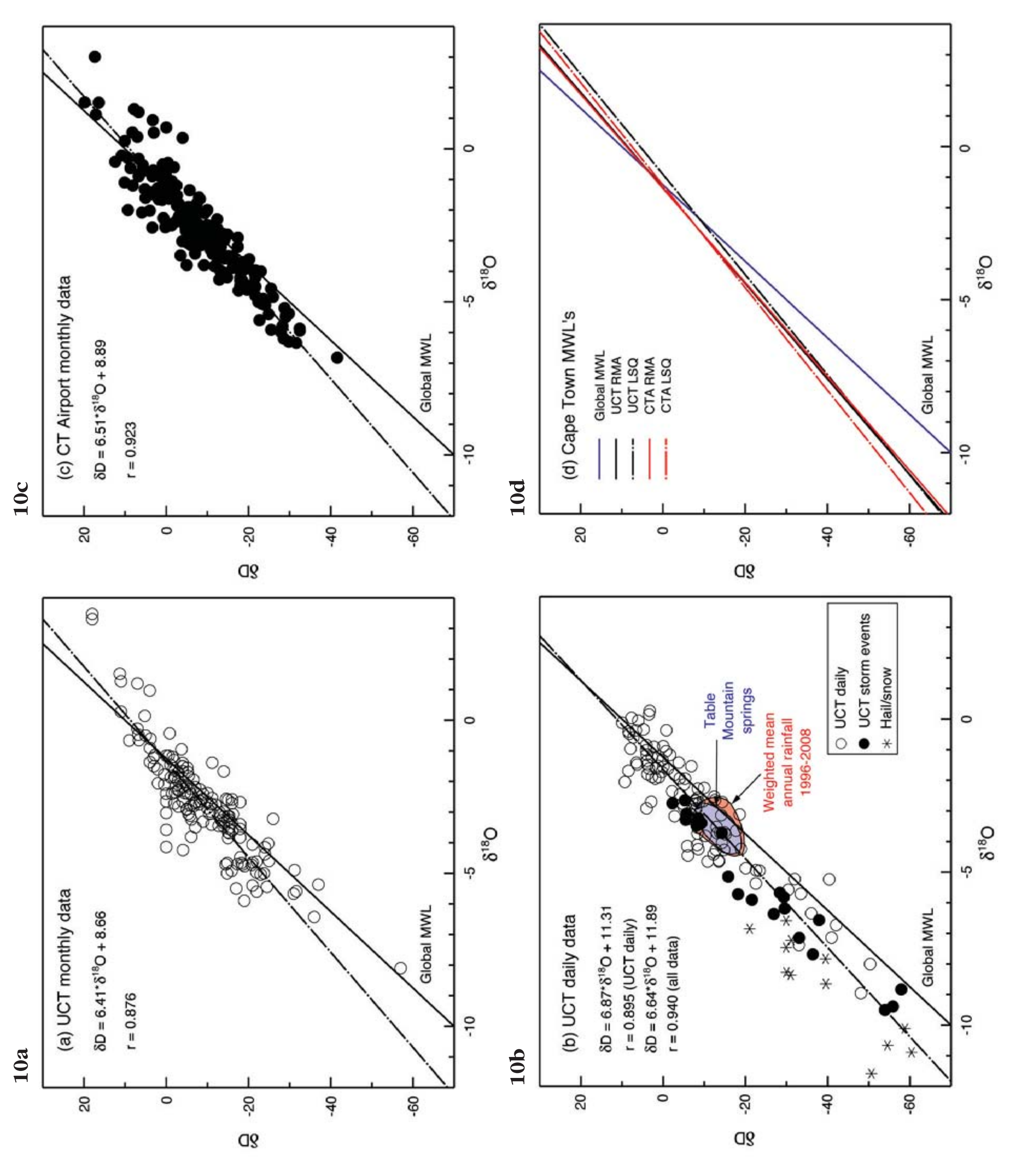

*Figure 10. Plot of δD vs. $\delta^{18}O$ for (**a**) UCT monthly samples and (**b**) UCT daily samples and hail/snow events. The equation of the Global Meteoric Water Line (MWL) is $\delta D = 8\delta^{18}O + 10$ (Craig 1961). The lines of best fit through the data (local meteoric line) were calculated using the reduced major axis method with the equations and correlation coefficients given. Also shown is the field for the Table Mountain spring data. (**c**) Plot of δD vs. $\delta^{18}O$ for Cape Town International Airport monthly samples 1961-2001 (IAEA/WMO 2006). (**d**) comparison of local MWL's (UCT and Cape Town Airport) calculated by different methods with the Global MWL.*

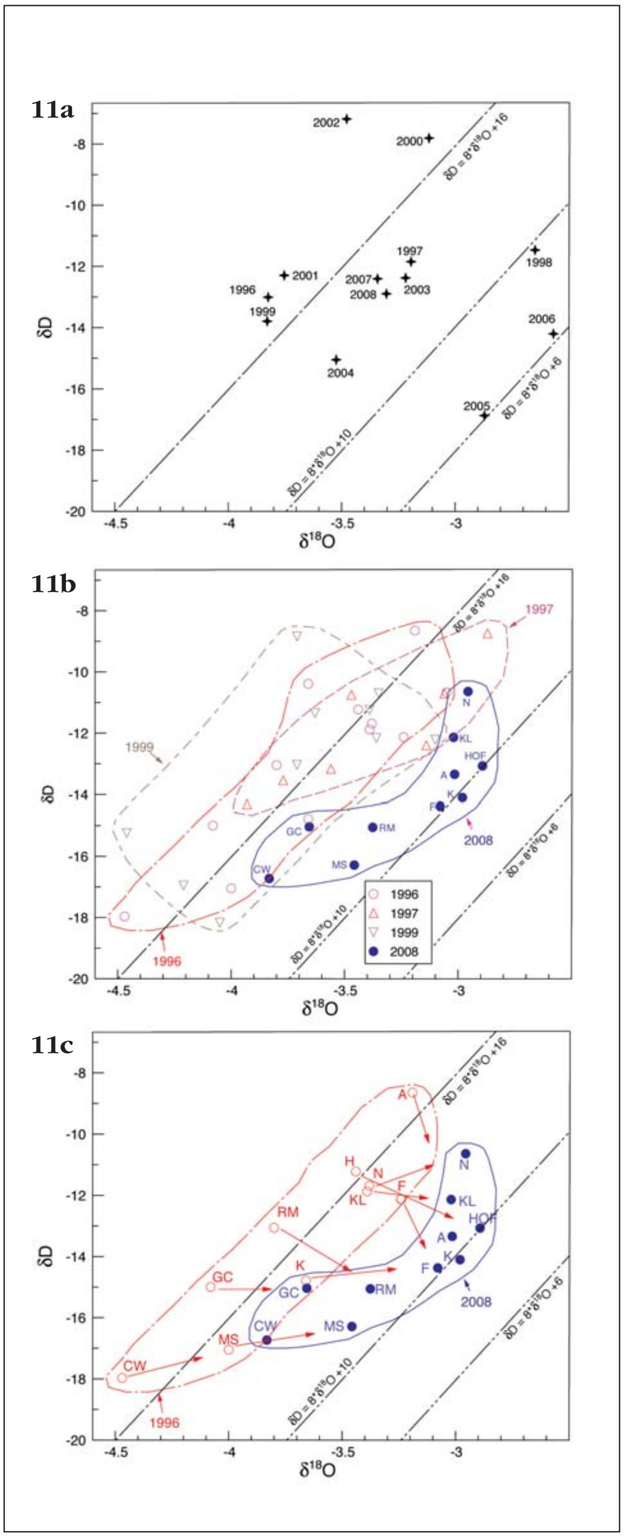

__Figure 11.__ *(__a__) Plot of δD vs. $\delta^{18}O$ for weighted average annual rainfall for UCT for the years 1996 to 2008 (__b__) Plot of δD vs. $\delta^{18}O$ for Table Mountain springs. Samples taken in 1996, 1997, 1999 and 2008 shown in different symbols. (__c__) The same plot with only 1996 and 2008 spring data plotted. Arrow indicates direction of change in spring composition between 1996 and 2008. RM = Rhodes Memorial, Hof = Hof, MS = Main Spring, A = Albion, N = Newlands, GC = Glen Coe, CW = Cable Way, F = Foresters, K = Kirstenbosch, KL = Klipper Road.*

orthogonal regression, Rock, 1988) and is less steep than the Global Meteoric water line of Craig (1961). The RMA is the preferred method of determining the line of best fit because it does not assume a dependence of X on Y (unlike least squares regression (LSQ)) and both X and Y are assumed to have errors. Where correlation coefficients are high, the least squares regression line and that calculated by RMA are very similar.

The equation of the line of best fit for the UCT monthly data is $\delta D = 6.41*\delta^{18}O + 8.66$ (LSQ for the same data set gives $\delta D = 5.55*\delta^{18}O +6.11$). This is very similar to the line of best fit through the Cape Town Airport dataset (IAEA/WMO 2006) where $\delta D = 6.51*\delta^{18}O +8.89$ (RMA) or $5.97*\delta^{18}O +7.52$ (Figure 10a,c). The daily samples, the storm samples and the hail/snow are plotted on a similar diagram in Figure 10b. The daily samples from UCT show a similar spread to the monthly samples, but there are more daily samples with significantly lower δD and $\delta^{18}O$ values than the UCT monthly data. The correlation coefficient for the daily rainfall data is slightly higher than monthly data (r = 0.895). The hail and snow samples all have lower δD and $\delta^{18}O$ values than found in all but a few of the monthly samples. As presented above, the storm data show a very strong correlation between δD and $\delta^{18}O$ (r = 0.973) and the line of best fit through the data from both storms is defined by the equation $\delta D = 7.89*\delta^{18}O+ 19.4$. The storm data for July 14/15 2000 overlap with the group of samples having low δD and $\delta^{18}O$ values on Figure 10b, whereas the August 3/4 2000 storm data have δD and $\delta^{18}O$ typical of the monthly rain data (Figure 10a). Inclusion of hail, snow and storm data improve the correlation of δD vs. $\delta^{18}O$ in Figure 10b (r = 0.94) and the line of best fit has the equation $\delta D = 6.64*\delta^{18}O + 11.89$ (calculated using the RMA method).

Springs

Springs issuing from the slopes below Table Mountain have been sampled sporadically over the study period (1996, 1997, 1999, 2008). The 1996 and 1997 data were reported by Harris et al. (1999) where more details (such as height, temperature and flow rate) springs can be found. They range in altitude from 30 to 310 m a.s.l. and the yield ranges from <10 litres/minute to >1000 litres/minute. The isotope data for the springs are plotted on Figure 10b and show a restricted range in composition relative to the daily rainfall data, with δD and $\delta^{18}O$ ranging from -18 to -9‰ and -4.5 to -3.0, respectively. The spring δD and $\delta^{18}O$ values coincide very closely with those of the weighted mean annual rainfall values (Figure 10b), which indicates that the weighted mean composition of rainfall is a good approximation to the isotope composition of recharge.

In detail, there are subtle variations in the isotope composition of the spring waters. These are shown on a δD vs. $\delta^{18}O$ diagram in Figure 11 with an expanded scale, together with the weighted average annual

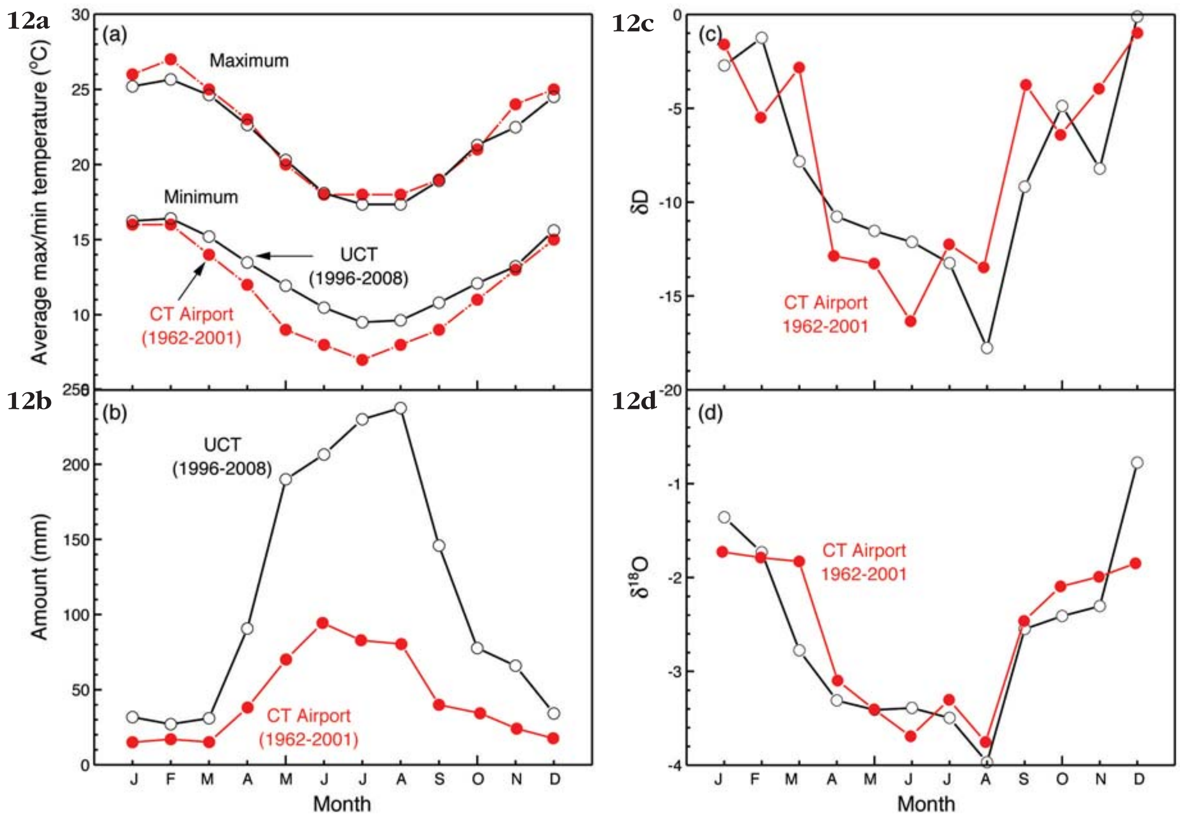

Figure 12. *(**a**) Average maximum and minimum monthly temperatures, and (**b**) average monthly rainfall (mm) for Cape Town International Airport (1962 to 2001) and UCT (1996 to 2008). (**c**) Plot of weighted average annual δD and (**d**) $\delta^{18}O$ for UCT (1996 to 2008) and Cape Town International Airport (IAEA/WMO, 2006) vs. month.*

composition of UCT rain (Table 2) for the years 1996 to 2008. The fields for the springs in 1996 to 1999 overlap quite well, and the deuterium excess is constant and relatively high (~16). The 2008 spring data show a significantly lower deuterium excess (average 11.7). The UCT monthly rainfall data have deuterium excess values calculated for the weighted mean annual rainfall data (Table 2) that range from 6.1 to 20.8. Significantly lower deuterium excess is seen in the years 2005 (d = 6.1) and 2006 (d = 6.3) and, to a lesser extent, 1998 (d = 9.8). All other years have a value of d >13.2. The deuterium excess for rainfall at Cape Town Airport has a similar range (9.3 to 16.4 from 1974 to 2001, with many missing years) (IAEA/WMO 2006).

Discussion

Correlation of rainfall isotope composition with climate conditions

As pointed out by Lawrence and White (1991), globally, there are two major climate factors that correlate with isotope ratios of rainwater. These are temperature and amount of precipitation, and the best correlation with temperature occurs in continental regions at high latitude whereas the correlation with amount is best in tropical regions (Lawrence and White, 1991). In more temperate latitudes (such as Cape Town), both factors can be seen from the data presented in Figures 4 and 8.

Although the plots of δD and $\delta^{18}O$ vs. amount and temperature show limited correlations, on average the winter months have rainfall with lower δD and $\delta^{18}O$ than the summer months. This is illustrated on Figure 12, which shows the inverse relationship between average monthly temperature and average monthly rainfall at UCT and Cape Town International Airport. Note that UCT receives considerably more rain on average than Cape Town Airport due to its proximity to Table Mountain. The average monthly δD and $\delta^{18}O$ values are highest in the summer months and the profiles (Figure 12 c, d) show a strong correspondence with the amount profile and an anti-correlation with the temperature profile. These data indicate a strong seasonal effect even though the temperature effect is not strongly developed (Figure 4). This could be a function of length of time interval in that the average temperature of a month might be controlled by numerous hot dry days with rain falling on only a few days.

For the monthly data, the average temperature might not reflect the temperature at the time the rain actually fell, and this might account for the lack of an obvious temperature effect. The temperature effect might become more apparent if the time interval for sampling is shortened, but daily samples do not show significantly better correlation between isotope composition and temperature (Figures 4 and 8). The lack of a strong relationship between isotope composition of rain and temperature is typical of low latitude localities (Rozanski et al., 1993).

If the year is divided into ‘summer’ (October-March) and ‘winter’ months (April-September), there are clear seasonal differences. From 1995/6 to 2007/8, the summer months have average δD and δ^{18}O values of -5 and -2.0 ‰ with an average monthly rainfall of 45 mm. The corresponding averages weighted according to amount of rain are -8 and -2.5‰. For the winter months from 1996 to 2008, the average δD and δ^{18}O values were -12 and -3.4‰ with an average monthly rainfall of 183 mm. The corresponding averages weighted according to amount of rain are -13 and -3.4‰. Hence, although there is no clear temperature effect apparent in the data, it is clear that winter rain has, on average, significantly lower δD and δ^{18}O values than summer rain. The amount effect is also not strong (Figure 4) apart from the observation that high d values only occur when the amount of rain is low.

Although our rainfall isotope record spans more than 12 years, the time interval is not sufficient to study the effects of climate change on isotope composition. The increase in temperature seen from 1995 to 2000 is consistent with global trends (e.g. Jones and Moberg, 2002), but since 2000, there is no indication of a systematic change in temperature at Kirstenbosch (Figure 2). There is no evidence for a systematic change in isotope composition from 1995 to 2000. At Cape Town Airport, the mean annual temperature for 1961 to 1999 is 16.3 ± 0.4°C, which is similar to the value obtained for 1996 at Kirstenbosch. Unfortunately there is very little overlap between the two temperature records. The average annual temperature for Cape Town Airport in 1999 was 17.3°C (Figure 5), which suggests that the higher temperatures observed at Kirstenbosch are not a local phenomenon.

Meteoric water lines

As described above, the equations for lines of best fit through rain data of various types (monthly, daily, special events) are very similar. The local meteoric water line equation based on the 12 year monthly rainfall data set is $\delta D = 6.41*\delta^{18}O + 8.66$. The equation calculated by least squares regression is $\delta D = 5.55*\delta^{18}O + 6.11$. The isotope composition of rain in the Western Cape has been discussed by Diamond and Harris (1997) and by Harris et al. (1999). Diamond and Harris (1997) calculated the line of best fit through rain data from the Western Cape to have the equation $\delta D = 6.2*\delta^{18}O + 10.6$. The IAEA has a measuring site at Cape Town International Airport (IAEA/WMO 2006; Rozkanski et al., 1993) and the O- and H-isotope data for pooled monthly samples from this location have a line of best fit is whose equation is $\delta D = 6.51*\delta^{18}O + 8.89$ ($\delta D = 5.97*\delta^{18}O + 7.52$ by LSQ regression). Thus the data set presented in this paper gives a local meteoric water line that is closely similar to those for the IAEA site at Cape Town Airport.

In most areas, world-wide, the local meteoric water line has a less steep gradient on a δD vs. δ^{18}O plot than the Global Meteoric Water Line (GMWL) (Kendall and Coplen, 2001; Sharp 2007). The GMWL approximates to the line of best-fit through a large number of local MWL’s with a range of intercepts. The LMWL equation proposed above is, therefore, normal.

Storm data

The two storms sampled show very different climatic behavior and isotope variation. The orographic rainfall of the August 4th storm series shows little variation in the isotope composition with time, and this is consistent with the lack of change in temperature. The fairly constant air pressure indicates that this is not a frontal system (Figure 9) despite the amount of rainfall per hour being variable and up to 20 mm/hour. For the July 14/15 storm, although temperature and, especially, pressure show systematic variation, the overall correlation between isotope composition and either parameter is not good. That is also true for the amount of rain (in mm/hour, Figure 9h) for the data as a whole. However, there is a strong inverse relationship between the amount of rain and isotope composition (Figures 9a,c,d). The overall lack of variation between isotope composition and pressure, temperature and amount can be attributed to the more complex processes of rain generation associated with frontal systems as opposed to pure orographic rain. For example, the temperature measured on the ground may not accurately reflect that of the rain where it is generated. There are insufficient data to make too many claims about the variation of isotope composition during the storms. What these data clearly show is that even at the scale of hourly sampling, there is no simple relationship between climate signal and isotope composition, as pointed out by Lawrence and White (1991) and Fricke and O’Neil (1999).

As shown above, MWL’s with similar gradient were obtained for the daily rainfall at UCT, the storm events and hail/snow. However, the intercept value for the MWL’s calculated for the storm, daily and hail/snow data being significantly higher (11.89, Figure 10b). The line of best fit through the storm data (Figure 9e) gives a significantly higher intercept of 19.4. The average d-excess of the storm samples is 20.0, with some samples from the July 14/15 storm having a d-excess as high as 27.5. These data suggest that frontal storms produce precipitation with higher d-excess than non-frontal rain. The snow and hail samples had even higher d-excess (average 30.1). A possible explanation for the low d-excess of rainfall in 2005 and 2006 is, therefore, that there was a lower proportion of frontal rain in these years than in the others. At present, we are unable to verify this hypothesis.

Recharge of the Table Mountain aquifer(s)

It was shown above that the isotope composition of rainfall in 2005 and 2006 (Figure 11a) is distinct from 1996 to 2004 and 2007 to 2008 rainfall due to its low deuterium excess (d ~6). Apart from 1998, which has a d of 10, all other years analysed, have d > 12 with five years (1996, 1999, 2000, 2001, 2002) having a d > 16. Although the lack of isotope data for the springs between 1999 and 2008 means that there is considerable uncertainty in the interpretation, it can be shown that recharge is relatively rapid.

Various interpretations of the data are possible, but the simplest is as follows. The 1996 and 2008 spring data are compared in Figure 11(b), and the direction of change of composition from the 1996 to the 2008 values indicated. With the exception of the Newlands and Klipper springs, the change of composition is towards the 2005 and 2006 rainfall composition, with a 'bulge' in the data towards these values. This bulge encompasses the Hof, Albion, Kirstenbosch and Foresters springs. If the 2008 spring data are interpreted as mixtures of 1996 spring water and 2005/6 rain water, the proportion of 2005/6 rain water can be estimated using the lever rule. If the spring water at the end of 2004 had a d-excess of 13, then the Hof, Albion, Forresters and Klipper springs in 2008, which are closest to the composition of 2005/6 water (Figure 11b), would contain about 50% 2005/6 rain water.

An alternative explanation could be that the springs had a d-excess of around 6 at the end of 2006 and have migrated back towards 2007 and 2008 compositions. It is not possible to distinguish between these models because of the lack of spring data between 1999 and 2008. The first model seems the most likely, both because it is simpler, but also because of the shape of 2008 data array is 'pulled towards' the 2005/6 data. This suggests that some of the springs are recharged faster than others.

Regardless of the exact interpretation, the comparison of rain and spring data indicate that recharge is relatively rapid and of the order, with 50% recharge possibly being effective within three years. At present, these estimates are crude with the major uncertainty in interpretation being due to the lack of data for spring water between 1999 and 2008. However, the potential for detailed studies to improve the understanding of recharge in TMG (and other) aquifers, is clear.

Conclusion

1. A continuous 12 year record of monthly rainfall δD and δ^{18}O values for UCT shows shows no strong temperature or amount effect, but does show seasonal variability.
2. There has been no systematic change in weighted mean annual δD and δ^{18}O during the last 12 years.
3. The line of best fit through the monthly rain fall data calculated using the reduced major axis method suggests a local meteoric water line (LMWL) with the equation $\delta D = 6.41\delta^{18}O + 8.66$. This is similar to the LMWL for Cape Town International Airport calculated using the same method from the GNIP database (IAEA/WMO, 2006). Daily samples and hail/snow samples show a wider range of values, and define a LMWL with a higher intercept term.
4. Two storm events were samples continuously. The frontal storm system showed changes in δD and δ^{18}O values of 26 and 3.2‰, respectively, within 30 minutes. The orographic rain showed very little change in isotope composition in four hours.
5. The rainfall sampled during the storms had a much higher deuterium excess (average d = 20.0) than the normal rain samples (average d = 12.4) and the snow/hail samples had the highest deuterium excess (average d = 30.1).
6. The monthly rainfall at UCT in 2005 and 2006 has lower deuterium excess (d) values (6.1 and 6.3) than the other years. One possible explanation is that these two years experienced less frontal rain. A similar change in d occurs between 1997 and 2008 in spring water on Table Mountain. These data enable crude estimates on the recharge rate to be made. More importantly, they indicate the value of long-term isotope records of rainfall and springwater in the interpretation of aquifer recharge.

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