TELLUS

The influence of below-cloud secondary effects on the stable isotope composition of hydrogen and oxygen in precipitation at Calgary, Alberta, Canada

By HAIDONG PENG[1], BERNHARD MAYER[2]*, STUART HARRIS[3] and H. ROY KROUSE[1],
[1]*Department of Physics and Astronomy, University of Calgary, Calgary, Alberta, Canada T2N 1N4,* [2]*Department of Geology and Geophysics, University of Calgary, Calgary, Alberta, Canada T2N 1N4,* [3]*Department of Geography, University of Calgary, Calgary, Alberta, Canada T2N 1N4*

ABSTRACT

Stable isotope compositions of hydrogen (δ^2H) and oxygen (δ^{18}O) for short-term precipitation samples ($n = 436$) collected at Calgary, Alberta, Canada, between January 1997 and December 2001 were determined. Linear regression between δ^2H and δ^{18}O values of snow and large amount rain samples (≥ 4 mm) yielded correlation equations δ^2H = $7.72 \times \delta^{18}$O + 5.02 and δ^2H = $7.50 \times \delta^{18}$O + 0.27, respectively. In contrast, correlation equations between δ^2H and δ^{18}O values for small amount rain samples (<4 mm) resulted in progressively lower slope and intercept values with decreasing precipitation. Correlations of isotope data with parameters such as local temperature, relative humidity, and precipitation amount provided evidence that small amount rain samples undergo secondary evaporation accompanied by mass dependent isotope fractionation during their descent from the cloud base to the ground. Hence, the isotope compositions of precipitation at Calgary, and likely also at other locations in the North American Great Plains region, are influenced by below-cloud secondary effects. Since about one-third of the precipitation events in the 5-yr observation period were rain samples accumulating less than 4 mm, below-cloud secondary effects resulted in a slight decrease of slope and intercept values of the local meteoric water line (δ^2H = $7.43 \times \delta^{18}$O − 2.79) calculated using amount-weighted monthly average δ^2H and δ^{18}O values compared to equations based on isotope data for snow and large amount rain events only. The correlation equation (δ^2H = $7.11 \times \delta^{18}$O − 11.60) calculated using δ^2H and δ^{18}O values of individual samples (non-amount weighted) yielded the lowest slope and intercept values caused by the significant influence of small amount rain samples.

1. Introduction

Isotope studies conducted throughout the last 50 yr have revealed that stable isotope compositions of hydrogen and oxygen in precipitation provide important information about moisture sources and atmospheric circulation patterns (e.g. Dansgaard, 1964; Friedman et al., 1964; Merlivat and Jouzel, 1979; Yurtsever and Gat, 1981; Rozanski et al., 1993; Gat, 1996; Hoffman et al., 2000; Bowen and Wilkinson, 2002; Peng et al., 2005). Furthermore, seasonal variations in stable isotope compositions of precipitation are of tremendous importance constituting the input function for hydrological studies using environmental isotopes (e.g. Salati et al., 1979; Schotterer et al., 1993; Kendall and Coplen, 2001). Realizing this enormous potential

for studying the hydrological cycle using stable isotope compositions, the International Atomic Energy Agency (IAEA) and the World Meteorological Organization (WMO) established the Global Network of Isotopes in Precipitation (GNIP) in 1961. In this network, the isotope compositions of precipitation from currently 379 active worldwide stations were reported based on amount-weighted monthly average δ^2H and δ^{18}O values (e.g. Rozanski et al., 1993; Gourcy et al., 2005).

Spatial and temporal variations in stable isotope abundance ratios of hydrogen (^{2}H^{1}H^{16}O/^{1}H$_2$^{16}O) and oxygen (^{1}H$_2$^{18}O/^{1}H$_2$^{16}O) are attributed to equilibrium exchange and kinetic isotope fractionation effects during moisture transfer from the surface oceans to the atmosphere, as described by the Craig and Gordon model (Craig and Gordon, 1965) and subsequent modifications, and by Rayleigh-type processes during progressive rainout of water vapour from air masses as they move towards lower temperature regions. Dansgaard (1964) described a series of relationships among the stable isotope abundance

*Corresponding author:
e-mail: bmayer@ucalgary.ca

ratios of hydrogen and oxygen in precipitation with parameters such as latitude, altitude, distance from the coast (continentality), and surface air temperature. During the last four decades, these relationships have been more thoroughly documented (latitude: e.g. Lorius and Merlivat, 1977; altitude: e.g. Rozanski and Sonntag, 1982; continentality: e.g. Friedman et al., 1992; seasonality: e.g. Smith et al., 1992, Peng et al., 2004). It is now well established that the evolution of the stable isotope compositions of an isolated moist air mass leaving its oceanic moisture source region and travelling towards continental or higher latitude regions characterized by lower temperatures can be described by a Rayleigh-type fractionation equation.

Although Rayleigh fractionation describes many aspects of the evolution of the isotopic composition of precipitation at the cloud base, it does not always adequately describe the variations of δ^2H and $\delta^{18}O$ values of precipitation collected at the ground (Araguas-Araguas et al., 2000; Gat, 2000). For instance, this model does not account for below-cloud secondary processes. Partial evaporation of raindrops during their descent through the under-saturated atmosphere beneath the cloud base (secondary evaporation) accompanied by mass dependent isotope fractionation may have a significant influence on the δ^2H and $\delta^{18}O$ values of both precipitation and water vapour in the atmosphere, especially in areas with arid or semi-arid climate. During this process, the light isotopes ^1H and ^{16}O are preferentially evaporated, causing an enrichment of the heavy isotopes ^2H and ^{18}O in the remaining raindrops. This results in increasing δ^2H and $\delta^{18}O$ values and, as a result of kinetic isotope effects, in a decrease in the slope and intercept of linear correlation lines between δ^2H and $\delta^{18}O$ values. It is not well documented to which extent this effect influences the isotopic composition of precipitation in Northern America. Kendall and Coplen (2001) suggested that correlations between δ^2H and $\delta^{18}O$ values of river water yielding slopes of less than 6 may be caused by precipitation significantly affected by secondary evaporation in semi-arid regions of the western USA. The same authors note that there is a lack of isotopic data for short-term precipitation samples in the literature that makes it difficult to test their hypothesis. However, understanding the influence of secondary evaporation effects between cloud base and ground on the isotopic composition of precipitation particularly in semi-arid regions is of enormous importance for the field of isotope hydrology in these regions.

For a 10-yr observation period (1992–2001), Peng et al. (2004) reported a significant discrepancy between local meteoric water lines calculated for Calgary (Alberta, Canada) based on amount-weighted monthly average δ^2H and $\delta^{18}O$ values ($\delta^2H = 7.68$ $\delta^{18}O - 0.21$, $r^2 = 0.96$, $n = 104$) and that based on data for individual precipitation samples ($\delta^2H = 7.10 \times \delta^{18}O - 13.64$, $r^2 = 0.95$, $n = 839$). This could not be explained by a simple Rayleigh-type isotope fractionation. It was speculated that below-cloud secondary effects were responsible for the observed discrepancy (Peng et al., 2004). Therefore, the objective of this study was to better characterize the influence of below-cloud

secondary effects on the stable isotope composition of local precipitation under the semi-arid climate conditions of Calgary, Alberta, Canada.

2. Study area and sampling procedures

Calgary (51.01°N, 114.01°W, 1049 m asl) is located on the eastern side of the Canadian Cordillera in southern Alberta, Canada. This area is characterized by a dry continental climate with long cold winters and short warm summers. Moist and unstable maritime air masses originating at the Pacific Ocean are the source of most precipitation at Calgary (Peng et al., 2004). The average annual precipitation at Calgary is 401 mm with circa 70% occurring between May and August. The average annual air temperature is circa +1°C with monthly averages varying between −19.5 °C in February and +17.7 °C in July, respectively (Environment Canada, 1960–2001).

For this study, short-term precipitation (rain, sleet and snow) samples were collected twice daily at the Weather Station of the University of Calgary (Alberta, Canada) from January 1997 to December 2001. One sample was collected from 08:00 to 15:00 and the second either from 15:00 to 08:00 of the next day or from 15:00 on Friday to 08:00 on Monday of the following week. The samplers were either a MSC (Meteorological Service of Canada) Rain Gauge or a Nipher Gauge for snow. The precipitation amount and δ^2H and $\delta^{18}O$ values were determined for each sample.

3. Methods

Determination of hydrogen isotope abundance ratios was performed using H_2 generated by reduction of water over hot zinc metal at 490 °C (Coleman et al., 1982) or by chromium reduction (Gehre et al., 1996). Isotope analysis was carried out with a dual inlet isotope ratio mass spectrometer. Oxygen isotope abundance ratios measurements were performed on CO_2 equilibrated with water samples at 25 °C (Epstein and Mayeda, 1953) using dual inlet isotope ratio mass spectrometry.

The conventional delta notation is used to express the stable isotope ratios of hydrogen and oxygen in the precipitation samples:

$$\delta(\%o) = \frac{R_{sample} - R_{standard}}{R_{standard}} \times 1000, \qquad (1)$$

where R_{sample} and $R_{standard}$ represent the $^2H/^1H$ or $^{18}O/^{16}O$ abundance ratios in sample and standards, respectively. The standard for both hydrogen and oxygen isotope measurements is V-SMOW established and distributed by the International Atomic Energy Agency (IAEA) in Vienna, Austria. Normalization of δ^2H and $\delta^{18}O$ measurements was achieved by using the IAEA reference materials V-SMOW, GISP and SLAP, so that the δ^2H value of SLAP is −428‰ and its $\delta^{18}O$ value is −55.5‰ (Coplen, 1996). The uncertainty of the measurement was determined by repeated analysis of international reference materials

and lab internal standards ($n = 10$). The analytical uncertainty of δ^2H measurements was better than $\pm 1.5‰$, whereas that of $\delta^{18}O$ measurements was better than $\pm 0.2‰$.

Air temperature and relative humidity 1 m above ground were measured at the Weather Station of the University of Calgary at 1-min intervals. Average air temperature (T) and average relative humidity (h) values during each sample collection period for the respective precipitation events were calculated as follows:

$$T = \frac{\sum_{i=1}^{m} T_i}{m}, \qquad (2)$$

$$h = \frac{\sum_{i=1}^{m} h_i}{m}, \qquad (3)$$

where m is the total number of minutes of each sample-collection period. T_i and h_i are the air temperature and relative humidity values measured each minute, respectively.

4. Results

Table 1 summarizes number of precipitation events, precipitation amounts, and slope and intercept values for linear correlation equations between δ^2H and $\delta^{18}O$ values. Data are subdivided into different categories. In the 5-yr observation period, the average annual precipitation amount accumulated during 436 individual precipitation events was 364 mm yr^{-1}. Whereas 43.6% of the samples ($n = 190$) fell as snow, the average accumulation as snowfall totalled only 78 mm per annum or 21% of the annual precipitation. The remainder (286 mm yr^{-1} represented by 246 sampling events) fell as rain. Of the 246 rain samples, 75 (30% of all rain samples) accumulated less than 1 mm, 77 samples (31%) were characterized by accumulations between 1 and 4 mm, with the remaining 94 samples (38%) accumulating more than 4 mm of precipitation.

Table 1. Number of samples, total precipitation amounts, and δ^2H–$\delta^{18}O$ correlation parameters for snow and rain (different amount ranges) collected at Calgary between January 1997 and December 2001

Samples	Number of samples	Total amount (mm)	Slope	δ^2H–$\delta^{18}O$ intercept ‰	r^2
Total Samples	436	1820.7	7.11	−11.60	0.96
Snow	190	391.6	7.72	5.02	0.94
Rain	246	1429.1	6.76	−15.71	0.90
0–1 mm	75	23.1	6.44	−25.53	0.98
1–2 mm	38	53.3	6.72	−18.32	0.97
2–3 mm	20	52.6	7.33	−6.70	0.94
3–4 mm	19	67.8	7.47	−3.70	0.91
4–60 mm	94	1232.3	7.50	0.27	0.89

Between 1997 and 2001, the local meteoricwater line for precipitation in Calgary based on amount-weighted monthly average δ^2H and $\delta^{18}O$ values was:

$$\delta^2H = 7.43 \times \delta^{18}O - 2.79 \ (r^2 = 0.97, \ n = 56). \qquad (4)$$

The correlation equation based on δ^2H and $\delta^{18}O$ values of individual precipitation samples yielded the following, significantly different equation:

$$\delta^2H = 7.11 \times \delta^{18}O - 11.60 \ (r^2 = 0.96, \ n = 436). \qquad (5)$$

To reveal the causes for the discrepancy between eqs. (4) and (5), correlation equations were calculated separately for snow and rain samples based on the δ^2H and $\delta^{18}O$ values of the individual precipitation samples (Table 1). Snow samples were governed by the equation: $\delta^2H = 7.72 \times \delta^{18}O + 5.02$ ($r^2 = 0.94$, $n = 190$) displaying higher slope and intercept values than eq. (4). In contrast, the equation for rain samples was $\delta^2H = 6.76 \times \delta^{18}O - 15.71$ ($r^2 = 0.90$, $n = 246$), having lower slope and intercept values than eq. (5). Further subdivision of the rain samples revealed that the slope and intercept values of the correlation equations between δ^2H and $\delta^{18}O$ values of individual rain events were dependent upon precipitation amount (Table 1). Linear correlation of δ^2H and $\delta^{18}O$ values for rain events accumulating ≥ 4 mm resulted in slope and intercept values similar to those of snow samples and those of eq. (4): $\delta^2H = 7.50 \times \delta^{18}O + 0.27$ ($r^2 = 0.89$, $n = 94$). With decreasing precipitation amounts, the slopes of the correlation equations decreased from 7.5 (3–4 mm) to 6.4 (<1 mm) with a simultaneous decrease of the intercept to values as low as $-25.5‰$. This indicates that the discrepancy between eqs. (4) and (5) is related to the isotope composition of small amount rain samples.

We further investigated whether the decreasing slope and intercept values of the δ^2H–$\delta^{18}O$ correlation with decreasing rain amounts had any relationship to temperature and/or relative humidity at the collection site. Table 2 summarizes mean δ^2H and $\delta^{18}O$ values and slopes and intercept values for linear correlation equations for δ^2H and $\delta^{18}O$ values of individual rain samples in four different amount categories collected at different ground temperature ranges. In all precipitation amount categories, the highest δ^2H and $\delta^{18}O$ values were observed at the highest temperatures (>10 °C) and the lowest values were observed at the lowest temperatures (<5°C) displaying the well-known 'temperature effect' (e.g. Dansgaard, 1964). However, within each of the four amount range categories, the slope and intercept values of the δ^2H and $\delta^{18}O$ correlation equations were not significantly different for different temperatures (see mean values and standard deviations in Table 2).

The influence of relative humidity on the slope and intercept values of the correlation equations for δ^2H and $\delta^{18}O$ values of individual precipitation samples is shown in Fig. 1. Correlation equations for δ^2H and $\delta^{18}O$ values of snow and rain samples, the latter subdivided in different amount and temperature categories, were calculated for different ranges of relative humidity.

Table 2. Isotope compositions of rain samples collected at Calgary between 1997 and 2001. The data are placed into four categories based on precipitation amounts and further subdivided in three temperature ranges

Amount ranges (mm)	Temperature ranges (°C)	Number of samples	δ^2H ‰	$\delta^{18}O$ ‰	δ^2H–$\delta^{18}O$	
					Slope	Intercept ‰
0–1	$T<5$	21	−127.0	−15.9	6.58	−23.21
	$5<T<10$	25	−118.3	−14.9	6.35	−23.97
	$T>10$	29	−105.1	−12.4	6.47	−24.34
				Mean	6.47	−23.84
				SD	0.12	0.58
1–2	$T<5$	12	−126.3	−16.4	6.48	−23.20
	$5<T<10$	11	−116.6	−15.0	6.44	−23.67
	$T>10$	15	−110.3	−13.1	6.74	−23.52
				Mean	6.55	−23.46
				SD	0.16	0.24
2–4	$T<5$	7	−142.3	−17.5	6.85	0.37
	$5<T<10$	15	−120.3	−15.0	7.44	0.10
	$T>10$	17	−106.6	−13.1	7.31	−2.73
				Mean	7.20	−0.75
				SD	0.31	1.71
4–60	$T<5$	31	−110.5	−13.1	7.36	0.18
	$5<T<10$	32	−101.7	−12.0	7.55	2.11
	$T>10$	31	−99.4	−11.2	7.47	0.25
				Mean	7.46	0.85
				SD	0.10	1.09

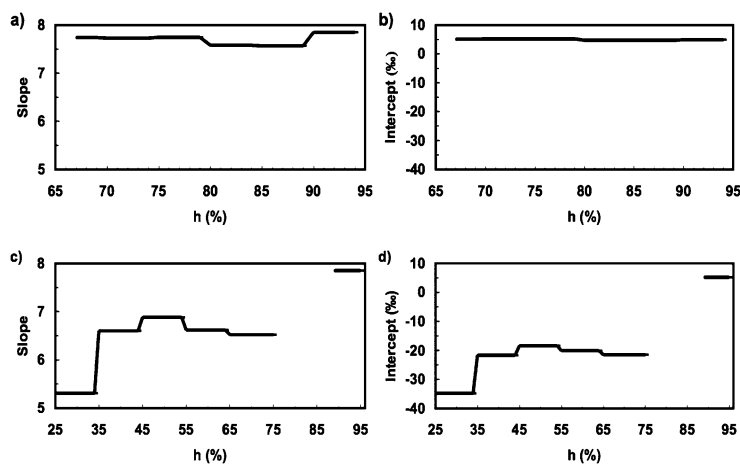*Fig. 1.* Slope and intercept values for δ^2H–$\delta^{18}O$ correlation equations versus relative humidity values for snow (a and b) and rain samples (c and d) collected between 1997 and 2001 at Calgary.

For snow samples, the slope and intercept values of the regression line were nearly constant at 7.72 ± 0.12 and 5.20 ± 0.19‰, respectively, independent of the relative humidity measured at the ground level (Figs 1a and b). For rain samples, it was observed that the relative humidity was usually less than 75% during small-amount events (<4 mm), and higher, typically >88%, during large-amount rain events (≥4 mm) (Fig. 1c and d). This

indicates that heavy showers or continuous rain events lead to a gradual saturation of the air column below the cloud base from which the precipitation originates. For rain samples collected at relative humidities >88%, δ^2H–$\delta^{18}O$ correlations yielded a slope of 7.5 and an intercept value of 0.27‰ (Fig. 1c and d), similar to values observed for snow samples. For rain samples collected at relative humidities between 35 and 75%, the slope of
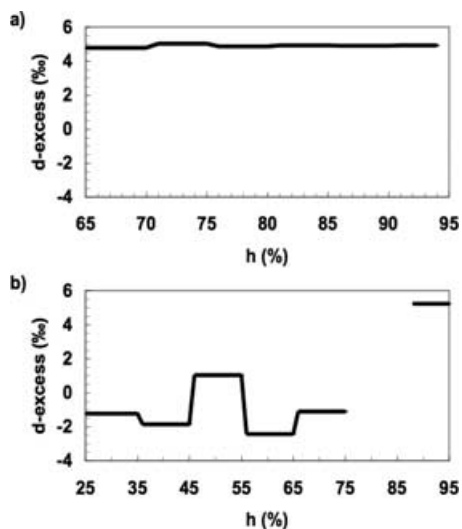
Fig. 2. d-excess values versus relative humidities for snow (a) and rain samples (b) collected between 1997 and 2001 at Calgary.

the δ^2H–δ^{18}O correlation was 6.7 ± 0.1 and the intercept value was −20.5 ± 1.5‰ (Figs 1c and d). At relative humidities of less than 35%, the δ^2H–δ^{18}O regression line displayed the lowest slope, 5.3 (Fig. 1c), and the lowest intercept value, −35.1‰ (Fig. 1d).

Deuterium-excess, defined by Dansgaard (1964) as $d = \delta^2$H–$8 \times \delta^{18}$O, is a measurement of the deviation of a set of data points from a line with slope 8 in the δ^2H–δ^{18}O diagram. Snow samples collected between 1997 and 2001 at Calgary were characterized by a d-excess value of 4.9 ± 0.1‰ independent of relative humidity (Fig. 2a). In contrast, rain samples collected at different relative humidities at the ground level displayed significant differences in d-excess values. Large amount rain samples collected at humidities >88% had a *d*-excess value of 5.2 ± 1.1‰ (Fig. 2b), similar to that of snow samples. In contrast, rain samples collected at humidities of less than 75% displayed significantly lower d-excess values ranging from +1.1 to −2.7‰ (Fig. 2b).

5. Discussion

The data indicate that slope, intercept and d-excess values derived from linear correlations of δ^2H–δ^{18}O values of snow and large amount (>4 mm) rain samples collected at Calgary are significantly different from those derived for small amount rain samples (Fig. 3). The slope and intercept values for the correlation equation for snow samples were 7.72 ± 0.12 and +5.0 ± 0.2‰, respectively, and the d-excess value was 4.9‰ independent of temperature and relative humidity at the collection site. According to Moser and Stichler (1980), snow may be subject to sublimation during its descent from the cloud base to the ground, but this process does not significantly alter the iso-
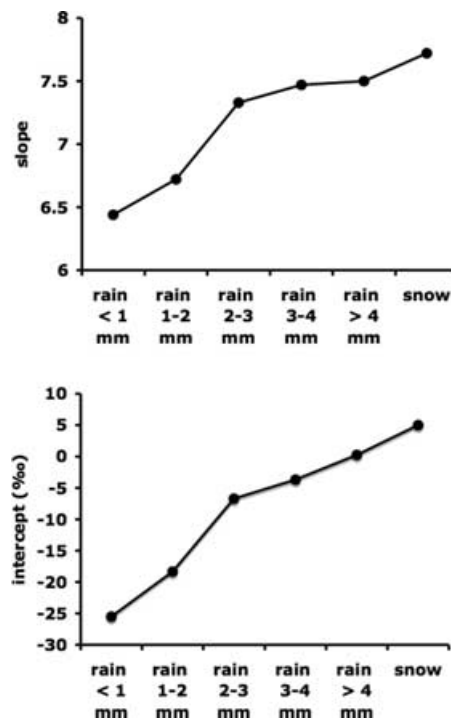

Fig. 3. Slope and intercept values for linear regressions of δ^2H and δ^{18}O values for snow and rain events (subdivided in different amount categories) collected between 1997 and 2001 at Calgary.

tope composition of the snow. Hence snow, during its descent towards the ground, retains its isotopic characteristics (δ^2H, δ^{18}O and d-excess) obtained during condensation in the cloud (= condensate sample).

In contrast, slope, intercept and d-excess values derived from linear correlations of δ^2H–δ^{18}O values for rain samples were characterized by significant variations dependent upon precipitation amount and relative humidity at the collection site. For large amount rain samples (>4 mm), slope (7.5), intercept (0.3‰) and d-excess values (5.2‰) derived from δ^2H to δ^{18}O correlations were similar or only slightly lower compared to those for snow samples. However, the slope and intercept values of the correlation equations progressively decreased for rain samples accumulating less than 4 mm (Fig. 3). This suggests that small amount rain events at Calgary are affected by below-cloud secondary effects including partial evaporation of raindrops beneath the cloud base, often termed secondary evaporation. This process is accompanied by equilibrium and kinetic isotope fractionation effects (Dansgaard, 1964) during which the light isotopes ^{1}H and [16]O are relatively enriched in the vapour phase. Consequently, the heavy isotopes ^{2}H and [18]O are preferentially retained in the falling raindrops as they descend towards the Earth's surface (Miyake et al., 1968; Steward, 1975; Yapp, 1982; Jouzel, 1986). This results in increasing δ^2H and δ^{18}O values of the rain samples collected on the ground. In addition, the kinetic isotope effect during secondary evaporation is expected to cause a decrease of

the slope of the δ^2H–δ^{18}O correlation for the falling raindrops (e.g. Dansgaard, 1964; Steward, 1975). This effect becomes increasingly apparent as the ratio of water evaporated versus water remaining increases (reservoir effect), and hence is most apparent for smallest amount rain samples (Fig. 3).

We also note that secondary evaporation between cloud base and ground decreases d-excess values. The d-excess for snow samples and large amount rain samples (>4 mm) that are not significantly impacted by secondary evaporation effects was approximately 5‰, whereas small amount rain samples affected by secondary evaporation were characterized by d-excess values of less than 1‰ (Fig. 2b). Low relative humidity in the atmosphere enhances secondary evaporation of rain drops during their descent from cloud-base to ground. This resulted in lower d-excess values for small-amount rain samples (-1.1 ± 1.3‰) compared to those of in-cloud condensates, constituting one of several factors that can alter d-excess values.

During the 5-yr observation period (1997–2001), 89.2% (325 mm yr^{-1}) of the precipitation fell in the form of snow or large-amount (≥ 4 mm) rain samples in 284 individual precipitation events. These samples are hardly influenced by secondary evaporation between cloud base and ground. The remaining 152 samples were collected during small amount rain events accumulating less than 4 mm during the respective sampling periods. These samples appeared to be influenced by secondary evaporation in the semi-arid climate of Calgary. The small amount rain samples influence the calculated local meteoric water line based on amount-weighted monthly average values by lowering the slope and the intercept value somewhat (δ^2H = 7.43 × δ^{18}O – 2.79) compared to values derived by using snow and large amount rain samples only (δ^2H = 7.66 × δ^{18}O + 4.22). For amount-weighted monthly mean values, the deviations are rather small since small amount rain samples (<4 mm) contribute only 10.8% (39 mm yr^{-1}) of the annual precipitation. However, small amount rain samples (<4 mm) constituted 34.8% of all precipitation events during the observation period from 1997 to 2001. These samples are influenced by secondary evaporation resulting in significantly lower slope and intercept values for local meteoric water lines calculated based on δ^2H and δ^{18}O values of individual samples (see eq. 5: δ^2H = 7.11 × δ^{18}O – 11.60). We suggest that the difference between slope and intercept values derived from δ^2H to δ^{18}O correlations calculated using amount-weighted average values and values for individual samples can be used as an indicator for the extent of below-cloud secondary evaporation affecting rain events.

6. Conclusions

Close examination of the isotope composition of short-term precipitation samples collected at Calgary (Alberta, Canada) between 1997 and 2001 revealed that there is secondary evaporation in the semi-arid climate of Calgary. According to Peng et al. (2004), the local meteoric water line (LMWL) for Calgary based on 10-yr observation period is:

$$\delta^2\text{H} = 7.68 \times \delta^{18}\text{O} - 0.21 \qquad (6)$$

This study revealed that the slope of the δ^2H–δ^{18}O correlation equations for snow samples (7.72 ± 0.13) and large-amount rain samples (7.50 ± 0.08) was close to that of the LMWL. These samples showed no significant effect of secondary evaporation between cloud base and ground, and hence reflect the isotope compositions of in-cloud condensates. In contrast, linear correlation of δ^2H and δ^{18}O values for small-amount rain samples revealed increasingly lower slope and intercept values with decreasing rain amount and decreasing relative humidity. This suggests that equilibrium and kinetic isotope fractionation during secondary evaporation between cloud base and ground significantly alters the isotopic composition of small-amount rain samples at Calgary. As previously reported by Jacob and Sonntag (1991), the isotope composition of small amount rain samples collected at ground level may not necessarily represent that of the condensate at cloud base. Based on our observations at Calgary, we speculate that small-amount precipitation events in the semi-arid continental regions of the North American Great Plains are affected by secondary evaporation of raindrops during descent from the cloud base to the ground particularly at low relative humidities in the atmosphere.

Although 35% of all precipitation events at Calgary were influenced by the amount effect during the 5-yr observation period, these events contributed only 11% of the total precipitation volume. Therefore, the influence of secondary evaporation between cloud base and ground on slope and intercept values of the local meteoric water line calculated based on amount-weighted monthly mean δ^2H and δ^{18}O values (slope 7.43) is relatively small compared to those calculated for condensate samples (slope 7.66). Moreover, secondary evaporation between cloud base and ground influences the isotopic composition of small-amount precipitation events predominantly in the summer months, when runoff and groundwater recharge are typically low. Therefore, we submit that slope values of less than 7 for δ^2H–δ^{18}O correlations for surface waters (Kendall and Coplen, 2001; Ferguson et al., 2007) or groundwaters (Fritz et al., 1987; Rock and Mayer, 2007) in western North America indicate post-rainfall evaporation in the soils or water bodies of the respective watersheds.

7. Acknowledgments

References

Araguas-Araguas, L., Froehlich, K. and Rozanski, K. 2000. Deuterium and oxygen-18 isotope composition of precipitation and atmospheric moisture. *Hydrol. Proc.* **14**, 1341–1355.

Bowen, G. J. and Wilkinson, B. 2002. Spatial distribution of d^{18}O in meteoric precipitation. *Geology* **30**, 315–318.

Coleman, M. C., Shepherd, T. J., Durham, J. J., Rouse, J. D. and Moore, G. R. 1982. Reduction of water with zinc for hydrogen isotope analysis. *Anal. Chem.* **54**(6), 993–995.

Coplen, T. B. 1996. New guidelines for reporting stable hydrogen, carbon, and oxygen isotope-ratio data. *Geochimica et Cosmochimica Acta* **60**, 3359–3360.

Craig, H. and Gordon, L. I. 1965. Deuterium and oxygen-18 variations in the ocean and the marine atmosphere. In: *Stable Isotopes in Oceanographic Studies and Paleotemperatures* (eds E. Tongiorgi). Cons. Naz. delle Ric., Pisa, Italy, 9–130.

Dansgaard, W. 1964. Stable isotopes in precipitation. *Tellus* **16**(4), 436–468.

Environment Canada, Atmospheric Environment Service. 2002. In: *Monthly Meteorological Summary at Calgary, Alberta* (January 1960-December 2001). Environment Canada, Atmospheric Environment Service, Calgary, Canada.

Epstein, S. and Mayeda, T. 1953. Variations of ^{18}O content of water from natural sources. *Geochimica et Cosmochimica Acta* **4**, 213–224.

Ferguson, P. R., Weinrauch, N., Wassenaar, L. I., Mayer, B. and Veizer, J. 2007. Isotope constraints on water, carbon, and heat fluxes from the Great Plains region of North America. *Global Biogeochem. Cycles*, Paper #2006GB002702, in press.

Friedman, I., Redfield, A. C., Schoen, B. and Harris, J. 1964. The variation of the deuterium content of natural waters in the hydrologic cycle. *Rev. Geophys.* **2**, 1–124.

Friedman, I., Smith, G. I., Gleason, J. D., Warden, A. and Harris, J. M. 1992. Stable isotope composition of waters in southeastern California, 1. Modern precipitation. *J. Geophys. Res.* **97**(D5), 5795–5812.

Fritz, P., Drimmie, R. J., Frape, S. K. and O'Shea, K. 1987. The isotopic composition of precipitation and groundwater in Canada. IAEA-SM-299, 539–550.

Gat, J. R. 1996. Oxygen and hydrogen isotopes in the hydrologic cycle. *Ann. Rev. Earth Planet. Sci.* **24**, 225–262.

Gat, J. R. 2000. Atmospheric water balance—the isotopic perspective. *Hydrol. Proc.* **14**, 1357–1369.

Gehre, M., Hoefling, R., Kowski, P. and Strauch, G. 1996. Sample preparation device for quantitative hydrogen isotope analysis using chromium metal. *Anal. Chem.* **68**, 4414–4417.

Gourcy, L. L., Groening, M. and Aggarwal, P. K. 2005. Stable oxygen and hydrogen isotopes in precipitation. In: *Isotopes in the Water Cycle* (eds P. K. Aggarwal, J. R. Gat and K. F. O. Froehlich). Springer, Dordrecht, 39–51.

Hoffman, G., Jouzel, J. and Masson, V. 2000. Stable water isotopes in atmospheric general circulation models. *Hydrol. Proc.* **14**, 1385–1406.

Jacob, H. and Sonntag, C. 1991. An 8-year record of the seasonal variation of ^{2}H and ^{18}O in atmospheric water vapor and precipitation in Heidelberg, Germany. *Tellus* **43B**, 291–300.

Jouzel, J. 1986. Isotopes in cloud physics: multiphase and multistage condensation process. In: *Handbook of Environmental Isotope Geo-*

chemistry Vol. 2: The Terrestrial Environment (eds P. Fritz and J. Ch. Fontes). Elsevier, Amsterdam, 61–105.

Kendall, C. and Coplen, T. B. 2001. Distribution of oxygen-18 and deuterium in river waters across the United States. *Hydrol. Proc.* **15**, 1363–1393.

Lorius, C. and Merlivat, L. 1977. Distribution of mean surface stable isotope values in East Antarctica: observed changes with depth in the coastal area. In: *Isotopes and Impurities in Snow and Ice*, IAHS Publication **118**, 127–137.

Merlivat, L. and Jouzel, J. 1979. Global climatic interpretation of the deuterium-oxygen 18 relationship for precipitation. *J. Geophys. Res.* **84**, 5029–5033.

Miyake, Y., Matsubaya, O. and Nishihara, C. 1968. An isotopic study on meteoric precipitation. *Papers Meteorol. Geophys.* **19**, 243–266.

Moser, H. and Stichler, W. 1980. Environmental isotopes in ice and snow. In: *Handbook of Environmental Isotope Geochemistry, 1. The Terrestrial Environment* (eds P. Fritz and J. Ch. Fontes). Elsevier, Amsterdam, 141–178.

Peng, H., Mayer, B., Harris, S. and Krouse, H. R. 2004. A 10-year record of stable isotope compositions of hydrogen and oxygen in precipitation at Calgary, Alberta, Canada. *Tellus* **56B**, 147–159.

Peng, H., Mayer, B., Norman, A.-L. and Krouse, H. R. 2005. Modelling of hydrogen and oxygen isotope compositions for local precipitation. *Tellus* **57B**, 273–282.

Rock, L. and Mayer, B. 2007. Isotope hydrology of the Oldman River basin, southern Alberta, Canada. *Hydrological Processes*, in press (published on-line on December 7, 2006). DOI: 10.1002/hyp.6545.

Rozanski, K. and Sonntag, C. 1982. Vertical distribution of deuterium in atmospheric water vapour. *Tellus* **34**, 135–141.

Rozanski, K., Araguas-Araguas, L. and Gonfiantini, R. 1993. Isotopic patterns in modern global precipitation. In: *Climate Change in Continental Isotopic Records, Geophysics Monograph No. 78* (eds P. K. Swart, K. C. Lohmann, J. McKenzie and S. Savin). American Geophysical Union, Washington, 1–36.

Salati, E., Dall'Olio, A., Matsui, E. and Gat, J. R. 1979. Recycling of water in the Amazon basin: an isotopic study. *Water Resourc. Res.* **15**, 1250–1258.

Schotterer, U., Froehlich, K. and Stichler, W. 1993. Temporal variation of ^{18}O and deuterium excess in precipitation, river and spring water in alpine regions of Switzerland. In: *Isotope Techniques in the Study of Past and Current Environmental Changes in the Hydrosphere and the Atmosphere, Proceedings of Symposium*. IAEA, Vienna, 19–23.

Smith, G. I., Friedman, I., Gleason, J. D. and Warden, A. 1992. Stable isotope composition of waters in southeastern California: 2. Groundwaters and their relation to modern precipitation. *J. Geophys. Res.* **97**(D5), 5813–5823.

Steward, M. K. 1975. Stable isotope fractionation due to evaporation and isotopic exchange of falling water drops: Applications to the atmospheric processes and evaporation of lakes. *J. Geophys. Res.* **80**, 1133–1146.

Yapp, C. J. 1982. A model for the relationships between precipitation D/H ratios and precipitation intensity. *J. Geophys. Res.* **87**, 9614–9620.

Yurtsever, Y. and Gat, J. R. 1981. Atmospheric waters. In: *Stable Isotope Hydrology: Deuterium and Oxygen-18 in the Water Cycle. Technical Report Series No. 210*, International Atomic Energy Agency, Vienna, 103–142.