

Pan-derived isotopic composition of atmospheric water vapour and its variability in northern Canada

J.J. Gibson^{a,*}, T.W.D. Edwards^b, T.D. Prowse^c

^aDepartment of Geography and Wetlands Research Centre, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1

^bDepartment of Earth Sciences, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1

^cNational Hydrology Research Centre, 11 Innovation Boulevard, Saskatoon, Saskatchewan, Canada S7N 3H5

Received 6 May 1997; accepted 19 January 1999

Abstract

Isotope mass balance of evaporation pans is a practical method for detecting and quantifying temporal variations in the isotopic composition of atmospheric moisture (δ_A), as demonstrated during summer in continental arctic and subarctic regions of Canada. Variability of δ_A , an atmospheric characteristic determined by air-mass origin and history, is a potentially useful tracer of synoptic atmospheric variations, and is an important control on isotopic behaviour of open-water bodies during surface–atmosphere exchange and evaporation. Flux-weighted δ_A estimation using class A evaporation pans may be a practical alternative to precipitation or direct vapour sampling in dry climates, and is well-suited to short-term isotope mass balance investigations of shallow lakes. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Environmental isotopes; Water balance; Evaporation; Tracers; Climate variability

1. Introduction

Various studies have investigated the potential for using naturally occurring variations in $^2\text{H}/^1\text{H}$ or $^{18}\text{O}/^{16}\text{O}$ ratios to estimate water balance parameters, including lake evaporation (Dinçer, 1968; Gat, 1970, 1981; Zuber, 1983; Gibson et al., 1993) and ground-water–lake exchange (Krabbenhoft et al., 1990). Widespread application of the technique to quantify evaporation has been limited, however, by practical difficulties associated with measuring or estimating the isotopic composition of evaporating moisture flux, either directly by sampling or indirectly using

boundary-layer mass transfer models. Studies based on the latter approach have frequently employed the linear resistance model of Craig and Gordon (1965) whereby the isotopic composition of evaporating moisture δ_E (assuming no resistance to transport of isotopic species in the liquid phase) is approximated as

$$\delta_E = \frac{(\delta_L - h\delta_A - \varepsilon)}{(1 - h + \varepsilon_K)} \quad (1)$$

which requires estimates of “free air” relative humidity (expressed as a fraction) normalized to the saturation vapour pressure at the temperature of the air–water interface h , the isotopic composition of “free air” atmospheric moisture δ_A , the isotopic composition of evaporating liquid δ_L , and the total isotopic

* Corresponding author. Fax: + 1-519-746-0658.

E-mail address: jjgibson@fes.uwaterloo.ca (J.J. Gibson)

Table 1
Summary of principle studies using pans to derive isotope exchange parameters

Study	Setting	Pan characteristics				Comments
		Type	Depth/volume (initial)	Method		
Gat (1970)	<i>L. Tiberias</i> , Israel	Class-A pans ^a Small pans	68–80 mm 70–85 mm	Drying Drying	Calc. ϵ_K by Eq. (6) using direct sampling of δ_A and measured h	
Welhan and Fritz (1977)	<i>Perch L.</i> Ontario, Canada	Class-A pans ^a Small pans	not given 10–30 mm, 1 L	Drying Drying	Best fit m and δ_A using Eq. (6), also calc. ϵ_K as in Gat (1970)	
Allison et al. (1979)	<i>Perch L.</i> Ontario, Canada	Class-A pans ^a Small dishes	20–40 L 1 L	Drying Drying	Best fit m and δ_A using Eq. (6)	
Allison and Leaney (1982)	Australia	Rectangular pans	10–30 mm, 54–162 L	Constant volume	Best fit m and δ_A using Eq. (10)	
This study	Northwest Territories, Canada	Class-A pans Class-A pans ^a Small pans	191 mm, 220 L 191 mm, 220 L 1 L	Constant volume Drying Drying	Calc. δ_A by Eqs. (10),(7), and (6), respectively using measured h	

^a Denotes class-A pans not operated by the standard method.

enrichment factor $\varepsilon = \varepsilon^* + \varepsilon_K$, that accounts for both equilibrium ε^* and kinetic ε_K enrichment¹.

Of these parameters, several can be measured or calculated routinely including: (1) h , determined from standard meteorological and water surface-temperature observations; (2) δ_L , measured directly from water samples; (3) ε^* , well-known for both oxygen and hydrogen as a function of temperature (see Gonfiantini, 1986); and (4) ε_K , understood from theoretical and experimental studies to be approximated by $C_K(1 - h)$ where $C_K = (D/D_i)^n - 1$. D and D_i are the molecular diffusion coefficients of the common ($^1\text{H}^1\text{H}^{16}\text{O}$) and heavy isotopic species ($^1\text{H}^1\text{H}^{18}\text{O}$ or $^1\text{H}^2\text{H}^{16}\text{O}$), respectively, and n is a turbulence parameter such that $n = 1/2$ for average turbulent flow, $n = 2/3$ for laminar flow and $n = 1$ for static transport (Gonfiantini, 1986; see also Vogt, 1976; Merlivat, 1978a,b; Merlivat and Coantic, 1975; Brutsaert, 1975).

The isotopic composition of atmospheric moisture δ_A , as with evaporating moisture δ_E , has proven more difficult to assess in natural situations due to logistical complications, namely: collection of vapour in suitable volumes for mass spectrometric analysis without inducing artificial isotopic fractionation, and spatial and temporal weighting of data for mass balance calculations, given the transient nature of atmospheric processes (and δ_A) in relation to isotopic changes in the liquid phase δ_L . Although specific measures could be employed to overcome such problems, including the use of sampling towers or balloons to characterize vertical isotopic gradients, or anemometer-gauged flow-control systems to obtain flux-weighted moisture sampling, the benefits of using tracers over conventional micrometeorological methods will decrease as instrumentation is increased. Several alternate methods of estimating δ_A are discussed in the following.

Where lakes are large in volume and therefore have sufficient isotopic inertia to minimize short-term fluctuations in atmospheric parameters, or where balances

are computed over extended periods, it may be sufficient to assume that δ_A is in isotopic equilibrium with local precipitation (i.e. $\delta_A = \delta_P - \varepsilon^*$, where δ_P is the isotopic composition of precipitation, and ε^* is approximated using mean air temperature records). In this case, δ_P may be estimated from weighted sampling of precipitation over a selected time interval, or alternatively, as the intersection of the local evaporation line (LEL) and meteoric water line (MWL) in $\delta^{18}\text{O}$ versus $\delta^2\text{H}$ space (see Gibson et al., 1993). The ‘‘precipitation equilibrium’’ approach has been applied to study natural lakes using isotopic and hydrologic steady-state models (e.g., Zuber, 1983; Gibson et al., 1993), although it may only be valid where the slope of a local evaporation trend can be shown to be independent of h parameter². The principal problem in assuming $\delta_A = \delta_P - \varepsilon^*$, as observed by Krabbenhoft et al. (1990) in a continental environment with numerous lakes, is that $\delta_P - \delta_A$ may exceed ε^* during mid-summer, due to buildup of evaporating moisture δ_E (i.e. terrestrial recycling of moisture) in the local atmospheric pool. This effect has also been noted for the Great Lakes Region (Gat et al., 1994), the Amazon Basin (Gat and Matsui, 1991) and elsewhere. In general, precipitation equilibrium is not a valid assumption for isotope balance studies on time-scales of weeks or months, particularly if such intervals include extended rain-free periods.

Isotope mass balance of evaporation pans has been used in several studies to derive δ_A on time-scales ranging from days to months, and has also been applied with limited success to independently estimate ε_K and h (Table 1). The principle convenience of pans is that both the isotope and water balance are explicitly known and liquid components can be sampled readily in order to estimate δ_E as a residual (as described later). Substitution of δ_E obtained from a pan into Eq. (1) then yields a local estimate of δ_A that can be applied in computing the mass balance of a nearby lake.

In general, use of pans has been viewed with

¹ δ values express isotopic ratios as deviations in per mil (‰) from the Vienna-SMOW (Standard Mean Ocean Water), such that $\delta_{\text{sample}} = 1000((R_{\text{sample}}/R_{\text{smow}}) - 1)$, where R is $^{18}\text{O}/^{16}\text{O}$ or $^2\text{H}/^1\text{H}$. $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values cited herein are normalized to -55.5‰ and -428‰ , respectively, for SLAP (Standard Light Arctic Precipitation) (see Coplen, 1996). ε values represent instantaneous isotopic separations in per mil between co-existing liquid and vapour, such that $\varepsilon_{\text{liquid-vapour}} = 1000((R_{\text{liquid}}/R_{\text{vapour}}) - 1) \approx (\delta_{\text{liquid}} - \delta_{\text{vapour}})$.

² While the LEL slope is generally dependent on h (Gonfiantini, 1986), if steady-state conditions are assumed, $\delta_A = \delta_P - \varepsilon^*$ and $\delta_l = \delta_P$, it is evident from theoretical considerations that the LEL will lie along the locus of steady-state compositions $\delta_S(h)$ such that the slope is independent of h (see Eqs. (7) and (8) in Gat and Bowser, 1991; see also Horita, 1990).

skepticism due to their dubious representation of natural evaporation conditions (Brutsaert, 1982) and, in the case of isotope balance applications, due to their over-sensitivity to short-term atmospheric fluctuations (Gonfiantini, 1986). The latter phenomenon is at least partly explained by the small pans used in most studies (<100 L, see Table 1), especially when pans were allowed to evaporate to near dryness and thus became hypersensitive to changes in boundary layer conditions, small inputs of precipitation, and fluctuations in δ_A and h in the latter stages of pan experiments. However, as noted by Allison and Leaney (1982), atmospheric variations can be damped effectively using pans of sufficient volume. The fact that pan evaporation is not equivalent to natural lake evaporation may not be very important for isotope balance purposes, providing that mass transfer mechanisms (e.g. the turbulence parameter n) for pans and lakes is similar and adjustments are made for differences in water temperature. As shown, pans are simply used to characterize changes in the isotopic composition of the atmosphere.

This study presents results from a series of evaporation-pan experiments conducted over several years as part of an intensive investigation of both isotopic (Gibson et al., 1996a) and non-isotopic (Gibson et al., 1996b) approaches to quantifying evaporation from surface waters in the Canadian arctic and subarctic. The study was prompted by the need for an efficient and reliable alternative to vapour sampling for characterizing temporal changes in δ_A . Allison and Leaney (1982) showed that isotope mass balance of constant-volume pans can be a reliable method for estimating exchange parameters for periods of several weeks or months, and may be more effective than direct vapour sampling for monitoring the net transfer process, as pans can be operated continuously and provide flux-weighted estimates of δ_A . Results of the present study suggest that standard class-A pans are appropriate for this purpose and also that class-A pans, if allowed to partially dry, can be used in a similar fashion providing that drying is limited to less than about 50% of the original volume. Systematic inter-comparison of constant-volume and drying pans, comparisons with direct vapour sampling, description of the general character of derived atmospheric moisture δ_A values, including spatial and temporal variability, and assessment of the transport

parameter C_K are presented. In addition to site-specific information, the experiments allow for evaluation of the degree of isotopic disequilibrium between precipitation and atmospheric vapour over larger spatial scales, which has broader implications for the use of simplified models to describe regional water balance.

2. Theory

Assuming constant density of water, the water-mass and isotope-mass balance for a well-mixed reservoir (lake or pan) over a specified time interval, dt , may be written respectively as:

$$\frac{dV}{dt} = I - Q - E \quad (2)$$

$$\frac{d(V\delta_L)}{dt} = I\delta_I - Q\delta_Q - E\delta_E \quad (3)$$

where V is the volume of the reservoir, dV is the change in volume, I , Q , and E are the rates of inflow, outflow, and evaporation, and δ_L , δ_I , δ_Q and δ_E are the mean isotopic compositions of the reservoir, inflow, outflow, and evaporative fluxes, respectively. Substituting δ_E from Eq. (1) into Eq. (3), and noting that the isotopic composition of outflow is identical to that of the reservoir (i.e. $\delta_Q = \delta_L$) yields:

$$V\frac{d\delta_L}{dt} + \delta_L\frac{dV}{dt} = \delta_I I - \delta_L Q + \left(\frac{\delta_L - h\delta_A - \varepsilon}{1 - h + \varepsilon_K}\right)E \quad (4)$$

which is a general form of the isotope balance equation that is valid for all well-mixed reservoirs.

Solutions of the isotope balance equations are considered for several water balance situations: (1) a drying pan with no inflow, (2) a drying pan during periods with precipitation, and (3) a pan maintained at constant volume by addition of water or precipitation. Details of the derivations employed can be found in Gonfiantini (1986).

2.1. Drying pan

For the simple case of a drying pan with no inflow or outflow, the volume V and isotopic changes in the reservoir $d\delta_L$ are controlled only by the evaporation rate E . Denoting the initial reservoir volume as V_0 , and

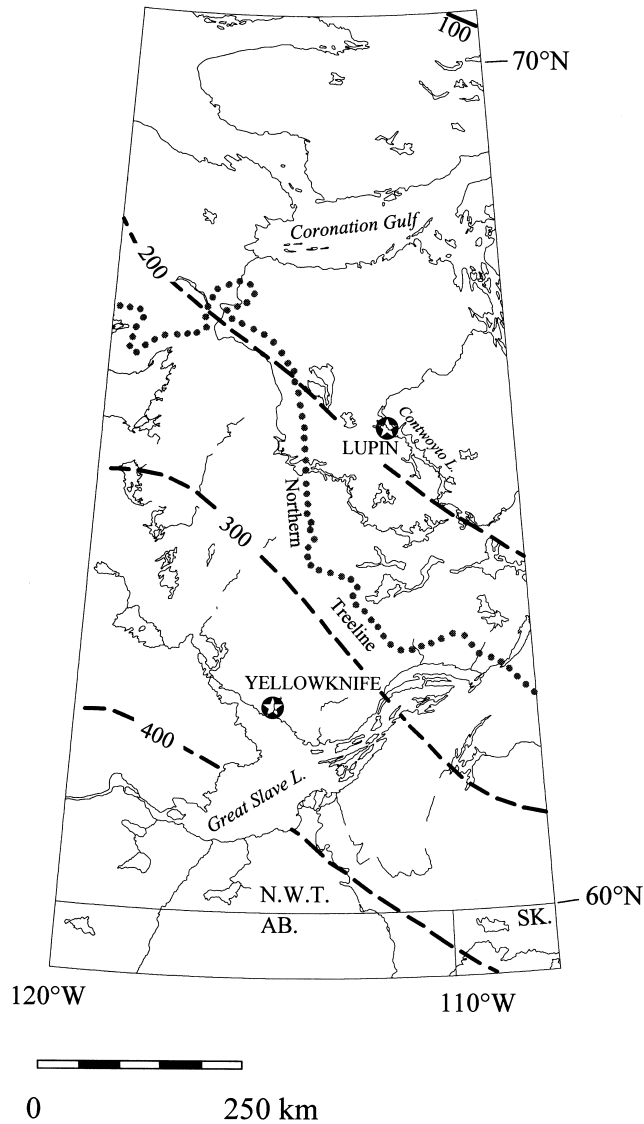


Fig. 1. Study locations. in the central Northwest Territories. Contours are mean small lake evaporation (mm a^{-1}) from denHartog and Ferguson (1978).

defining $f = V/V_0$ as the residual volume of water in the reservoir, Eq. (3) can be rearranged to yield an expression describing changes in isotopic composition with f as:

$$\frac{d\delta_L}{d \ln f} = \delta_E - \delta_L \quad (5)$$

Then, substituting Eq. (1) into Eq. (5) and

integrating with respect to f yields:

$$\delta_L = \delta^* - (\delta^* - \delta_0)f^m \quad (6)$$

where $m = (h - \varepsilon)/(1 - h + \varepsilon_K)$ as defined by Welhan and Fritz (1977) and Allison and Leaney (1982), δ_0 is the initial isotopic composition of the reservoir, and $\delta^* = (h\delta_A + \varepsilon)/(h - \varepsilon)$ is the limiting isotopic composition under local atmospheric conditions as defined by Gat (1981).

2.2. Drying pan with precipitation input

As precipitation may occur during the course of a drying-pan experiment, it is necessary to describe a new balance scenario whereby f and δ_L are modified by the addition of precipitation P of isotopic composition δ_P . In this situation, the isotope mass balance becomes:

$$\delta_L = \delta_S - (\delta_S - \delta_0)f^{-(1+mx)/(1-x)} \quad (7)$$

where $\delta_S = (\delta_I + mx\delta^*)/(1 + mx)$ is the steady-state isotopic composition that the reservoir liquid approaches (i.e. $\delta_L \rightarrow \delta_S$ as f approaches 0) and $x = E/I$ is the ratio of evaporation to inflow. Note that in this scenario inflow is composed entirely of precipitation such that $I = P$ and $\delta_I = \delta_P$. As expected, for the case where $I \rightarrow 0$, δ_S approaches δ^* and Eq. (7) reduces to Eq. (6). Similarly, in the case where $E \rightarrow 0$, δ_S approaches δ_I such that the reservoir acquires the isotopic composition of precipitation input.

2.3. Constant-volume pan

Where reservoir volume is constant ($dV/dt = 0$) and outflow is negligible ($I = E$) Eq. (3) reduces to:

$$\frac{d\delta_L}{dt} = (\delta_I - \delta_E) \frac{E}{V} \quad (8)$$

Substitution of Eq. (1) into Eq. (8) according to Allison and Leaney (1982) and others then yields:

$$\frac{d\delta_L}{dt} = [\delta_I + m\delta^* - \delta_L(1 + m)] \frac{E}{V} \quad (9)$$

And integrating Eq. (9) with respect to t over the limits yields:

$$\delta_L = \delta_S - (\delta_S - \delta_0)\exp[-(1 + m)(E/V)t] \quad (10)$$

which applies for the case of pan topped daily to constant volume (e.g. $I = E$). Note that for a class-A pan topped daily to constant volume but subject to periodic rainfall, $I = P + I_+$ and $\delta_I = (P\delta_P + I_+\delta_+)/I$ where I_+ is the volume added, P is precipitation, and δ_+ is the isotopic composition of the water source used to top the pan. Providing that the pan does not overflow, bailing of water to reset the volume will not change the isotopic composition of the pan. In the case of overflow an additional outflow parameter

would be required such that Eq. (9) becomes:

$$\delta_L = \delta_S - (\delta_S - \delta_0)\exp[-(1 + mx)(I/V)t] \quad (11)$$

For the latter situation, which was not observed during this study, it would be necessary to estimate the outflow $Q = (1 - x)I$ from records of precipitation depth and knowledge of pan overflow capacity.

3. Methodology

3.1. Class-A pans

Evaporation pan experiments were conducted at two sites in the Northwest Territories, Canada, as part of detailed hydrological studies to characterize evaporation in this remote region (Fig. 1). Primary investigations were undertaken near the Lupin gold mine (65°45'N, 111°15'W), located in the continental arctic, in a region characterized by tundra vegetation, low topographic relief, poorly integrated drainage and numerous, small shallow lakes.

Two class-A pans (220 L capacity) were operated during the 1992 and 1993 thaw seasons along the shore of a 6-ha lake. The pans were installed by standard methods and topped daily with water from a nearby lake to maintain constant volume (190.5 mm), as controlled using shielded point gauges within each pan. Although evaporation reduced pan volumes by up to 4 mm (2%) daily, this effect was considered to have a minor influence on dV/dt such that Eq. (10) could be applied without substantial introduction of error. Samples (30 mL) were collected for isotopic analysis from the class-A pans and the source water at regular intervals, typically between five and seven days. Grab-samples of precipitation were also collected for isotopic analysis. Instrumentation installed at the site included sensors for detailed analysis of mass balance, energy balance, and mass transfer from the adjacent lake (Gibson et al., 1996b). Relative humidity, air and pan temperatures, and other meteorological variables were measured at 10-s intervals and hourly-averages were recorded.

Secondary investigations were conducted near Yellowknife, N.W.T. (62°27'N, 114°22'W), in a region hydrologically similar to Lupin but characterized by subarctic forest vegetation. During 1992, a constant-volume class-A pan was operated as part of

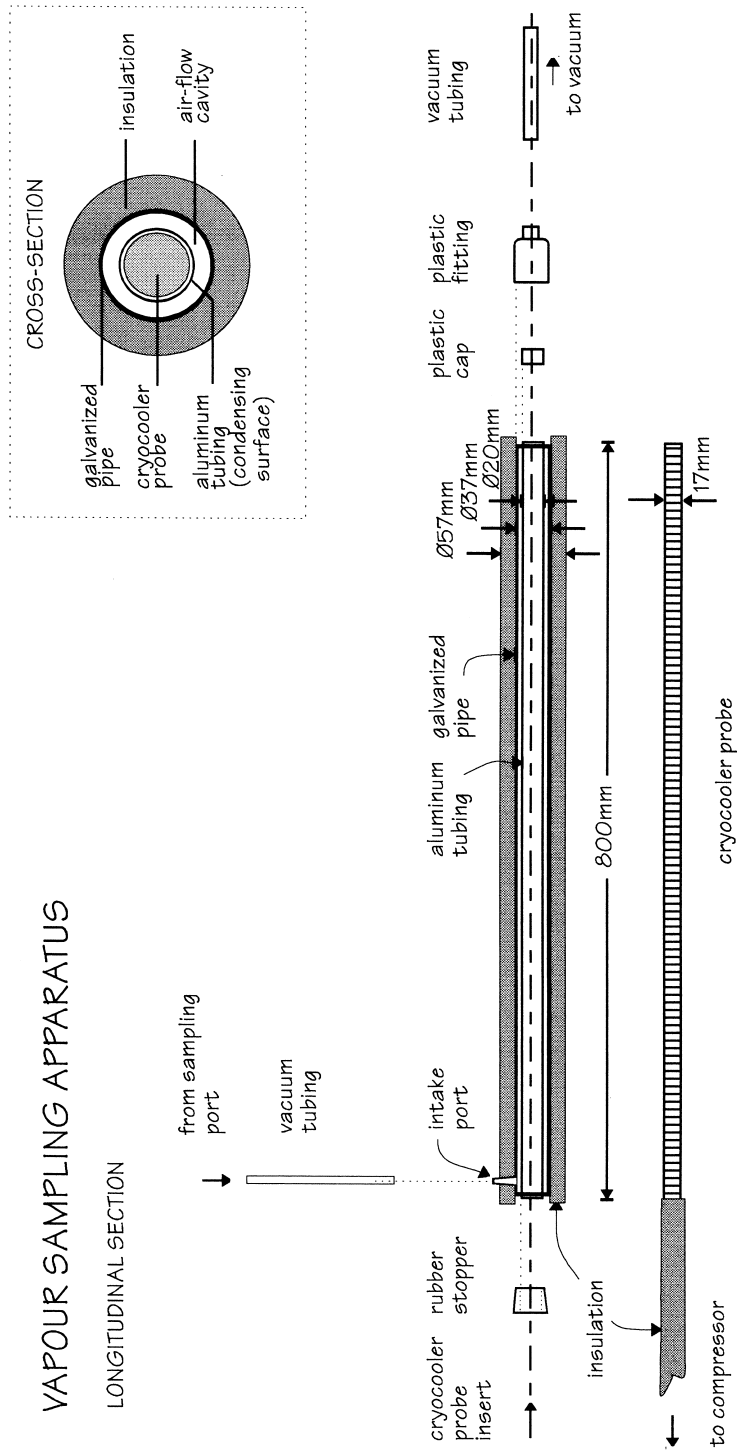


Fig. 2. Concentric tube cryogenic vapour trap.

standard Environment Canada weather observations at the Yellowknife airport, and two class-A pans, one allowed to partially dry and one maintained at constant volume, were operated on the shore of a nearby lake. Pans were sampled at weekly intervals and grab-samples of precipitation were collected during selected rainfall events (see Taal, 1994). During subsequent years (1993 and 1994), a single drying class-A pan was monitored at the lake site concurrent with a micrometeorological study. During this period, precipitation was collected in a non-evaporating rain gauge and allowed to accumulate over individual pan sampling intervals. Humidity, air temperature, and pan temperatures were recorded both at the local airport and at the lake site.

3.2. Small pans

Several 1-L drying-pan experiments were also carried out at Yellowknife during 1992. Small volumes were used to investigate short-term oscillations in δ_A (diurnal to several days) and to demonstrate the smoothing effect of using larger-volume class-A pans. Pans were fabricated from plastic buckets, 20–30 cm in diameter and 5 cm deep with flexible rims, which allowed water to be easily transferred to volumetric cylinders for accurate determination of residual volume f at intervals during the drying experiments. Between three and seven samples were collected for isotopic analysis during the course of individual experiments which typically lasted from one to seven days.

3.3. Vapour sampling

Over a 50-d period during 1993, atmospheric water vapour was collected daily at the Lupin site at a single location about 1 km from the nearest lake. This activity was undertaken to compare results from the evaporation pan and more commonly employed vapour trap technique. As a result of practical considerations, it was not possible to use conventional Horibe-type vapour traps which require constant replenishment of acetone/dry ice coolants (see Schoch-Fischer et al., 1984). Instead, an electrically powered cryogenic cooler (NESLAB™ CC-100II, Probe F) was used as a cold source to condense moisture within a custom-designed vapour trap (Fig. 2). Using a vacuum pump, air was drawn through the annulus of a 800 mm-long cylindrical trap between

aluminum tubing (cooled to -80°C) and an insulated steel jacket. Polypropylene tubing was connected to the intake port of the trap and was fixed to a 6.9-m sampling tower. Air was drawn through the trap at a constant rate of $0.75 \text{ m}^3 \text{ h}^{-1}$. Over a 2- to 5-h period each day, samples of 5 to 55 g of frost were collected on the aluminum tubing and then transferred to bottles by disassembling the unit. Atmospheric water vapour was extracted with an efficiency estimated at between 96 and 99% (Gibson, 1996). As such, it is expected that some isotopic fractionation may have occurred due to incomplete removal of water vapour. Correction factors of Schoch-Fischer et al. (1984) for -50°C were used as a conservative estimate of the isotopic fractionation effect, which amounts to about 0.43‰ for oxygen and 5.1‰ for deuterium (the collected water being enriched as compared to the atmospheric vapour). Although these estimates were not explicitly verified in trials using a vapour of known isotopic composition, the vapour trap results are nonetheless useful for displaying the fundamental difference between vapour trap and pan-derived moisture compositions, and provide a better understanding of atmospheric moisture variations near the ground surface.

3.4. Lake and groundwater sampling

Samples for isotopic analysis were collected at regular intervals from nine local lakes at Lupin ($n = 304$). Supra-permafrost groundwaters ($n = 115$) were also collected at regular intervals throughout the study via a network of 14 piezometer nests within a detailed study basin (see Gibson et al., 1996b). Water was also extracted from unsaturated zone soil cores by azeotropic distillation in order to characterize the isotopic composition of potential sources of boundary-layer evaporate.

For all isotopic analyses, laboratory reported analytical uncertainty is estimated at $\pm 0.2\%$ for oxygen and $\pm 2\%$ for hydrogen.

4. Results and discussion

From the algebraic derivations presented earlier, it is evident that δ_A can be calculated from records of isotopic changes in the liquid δ_L provided that pan water balance, h , pan T , δ_I , $\varepsilon^*(T)$ and $\varepsilon_K(h, C_K)$ are known. Herein, constant values for C_K of 14.2‰ for

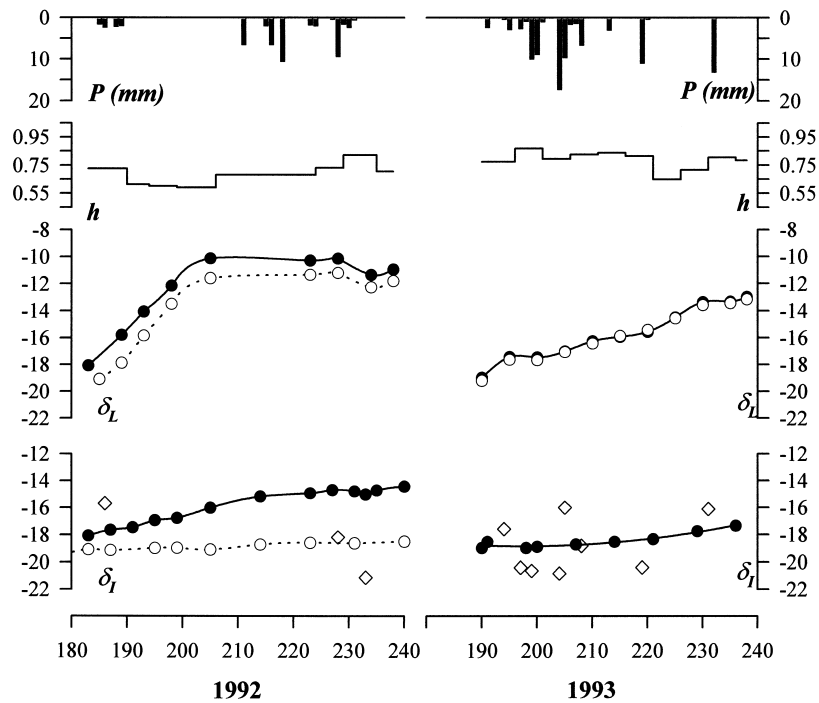


Fig. 3. Constant volume class-A pan experimental data from the Lupin site. Time-series of daily precipitation P , mean time-step relative humidity h , $\delta^{18}\text{O}$ of pan water δ_L , and $\delta^{18}\text{O}$ of input waters δ_I , including precipitation δ_p (diamonds) and source water δ_s (circles). Solid and open circles denote separate pans. Note that identical input δ_I for both pans in 1993, produced nearly identical $d\delta_L/dt$ for each pan. Similar trends were observed for $\delta^2\text{H}$ (not shown).

oxygen-18 and 12.5‰ for deuterium are employed based on experimental D/D_i values of Merlivat (1978a), which are also consistent with those of Vogt (1976), and $n = 1/2$ characteristic of turbulent flow conditions, a value shown by Merlivat (1978b) to be a good approximation for aerodynamically rough surfaces characterized by surface roughness Reynolds numbers > 1 . Analysis of aerodynamic profile data at the Lupin site confirmed that this criterion is met over periods of days or longer for a typical small lake of 6 ha (Gibson et al., 1996b). Indeed, such conditions are most commonly observed for natural water surfaces (Gonfiantini, 1986). Values of ε^* are taken from Majoube (1971) for both oxygen and hydrogen, as calculated by the formulae presented in Gonfiantini (1986).

4.1. Class-A pan experiments

Class-A pan experimental data and time-series of

$\delta^{18}\text{O}$ are shown in Figs. 3 and 4 for Lupin and Yellowknife, respectively. Similar trends were observed for $\delta^2\text{H}$ but are not shown. Lupin class-A pans rapidly enriched by 8‰ in $\delta^{18}\text{O}$ over July 1992 (Day 183 to 205) from an initial value of -18.1 ‰ to a maximum of -10.1 ‰ (Fig. 3), and then remained relatively constant between -10.1 and -11.0 ‰ for the remainder of the observation period (Day 205 to 238). Rapid enrichment during the early season occurred as cumulative evaporation progressed and pan water slowly readjusted to new water balance and atmospheric conditions, characterized by low relative humidity and precipitation. Further enrichment in $\delta^{18}\text{O}$ during the subsequent period was limited by high relative humidity, increased precipitation input, and lower evaporation. The relative constancy of $\delta^{18}\text{O}$ values during this time suggests that the pan water was close to isotopic steady-state for a constant volume reservoir given the prevailing atmospheric conditions. A noticeable decline in pan water $\delta^{18}\text{O}$ of 1.2‰

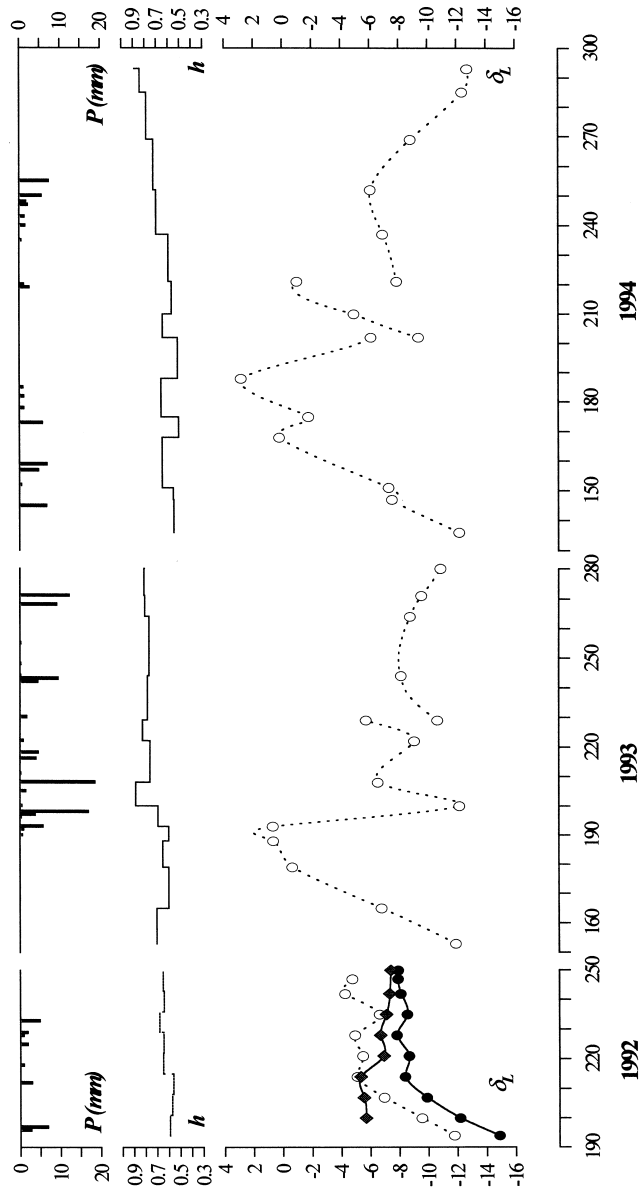


Fig. 4. Class-A pan experimental data for the Yellowknife site. Time-series of daily precipitation P , mean time-step relative humidity h , and the $\delta^{18}\text{O}$ composition of pan water δ_L . Open circles denote drying pan runs at Pocket Lake where uninterrupted intervals are joined by dotted lines. Solid and grey diamonds denote constant volume pan runs at Pocket Lake (constant source water $\delta_+ = -14.9\text{‰}$) and the Yellowknife airport (constant source water $\delta_+ = -12.7\text{‰}$), respectively. Similar trends were observed for $\delta^2\text{H}$ (not shown). 1992 data from Taal (1994).

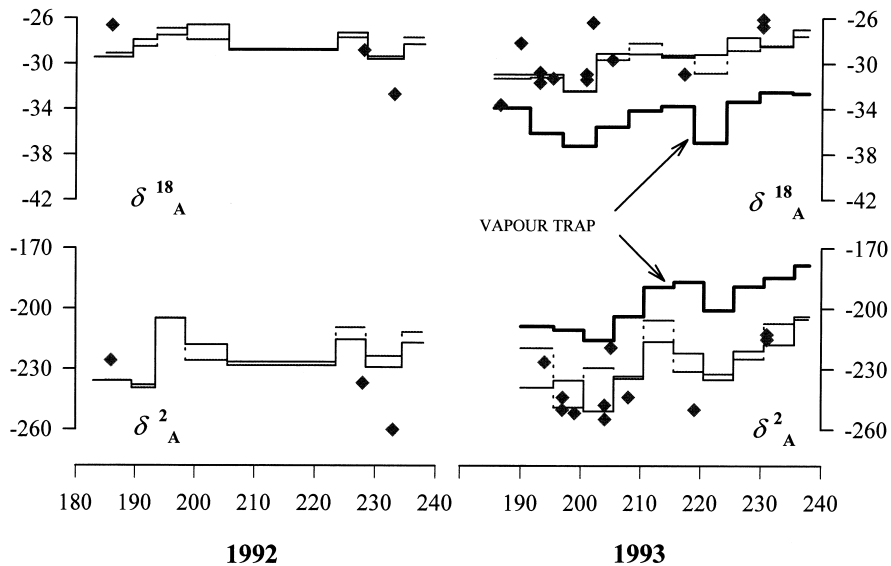


Fig. 5. Lupin, NWT.: Time-series of step-wise δ_A values derived from class-A pans (lines), moisture collected daily in a vapour trap δ_{VT} (bold lines), and point values of δ_A based on the assumption of isotopic equilibrium with grab-sampled precipitation (diamonds). See text for discussion.

occurred in the late season during a cold-air intrusion, associated with reduced air temperatures, higher relative humidity, diminished evaporation rates and input of isotopically depleted snowfall. The systematic offset between $\delta^{18}\text{O}$ of water in two adjacent pans, maintained throughout 1992, is expected considering that pans were topped daily with different source waters (Fig. 3). Isotopic enrichment in the pan was evidently influenced by temporal changes in the isotopic composition of ambient moisture δ_A (Fig. 5), as determined by solving the pan isotope-mass balance in Eq. (10) for individual time-steps assuming $n = 1/2$.

Very different ^{18}O -enrichment trends, consistent with higher relative humidity, higher precipitation, and lower daily evaporation rates, were observed in the constant-volume class-A pans during 1993. Pan water gradually enriched by 6‰ over July and August 1993 (Day 190 to 238) from an initial value of -19.2‰ to a maximum of -13.3‰ (Fig. 3). As pans were topped with identical source water during this year, nearly identical enrichment trends occurred despite the pans being several hundred metres apart on opposite shores of the 6-ha study lake. Gradual and continuous enrichment observed for 1993 relative to

1992 is strongly related to differences in residence times ($\approx V/E$), as E was about equal to V for 1992, and only about 50% of V for 1993, which inhibited attainment of isotopic steady-state in the latter year. Also, temporal changes in the isotopic composition of ambient moisture apparently influenced pan enrichment trends during 1993 (as calculated by Eq. (10)) and predicted trends in δ_A are consistent between the pans (Fig. 5).

Three class-A pans were operated near Yellowknife during 1992, and are referred to as the “airport” and “lakeshore” constant-volume pans, and the “lakeshore” drying pan, to distinguish their locations and configurations. Overall, the seasonal pattern of enrichment in $\delta^{18}\text{O}$ of the lakeshore constant-volume pan was similar to that observed for constant-volume pans at Lupin, and was also strongly influenced by variations in h , precipitation input, and differences in the isotopic composition of source water (Fig. 4). The only exception was for the airport pan which did not undergo substantial changes in its isotopic composition as it was operated for approximately one month prior to the beginning of sampling, such that pan water had already enriched to $\delta^{18}\text{O}$ values representative of isotopic steady-state. Interestingly, a 1.7‰ drop in the

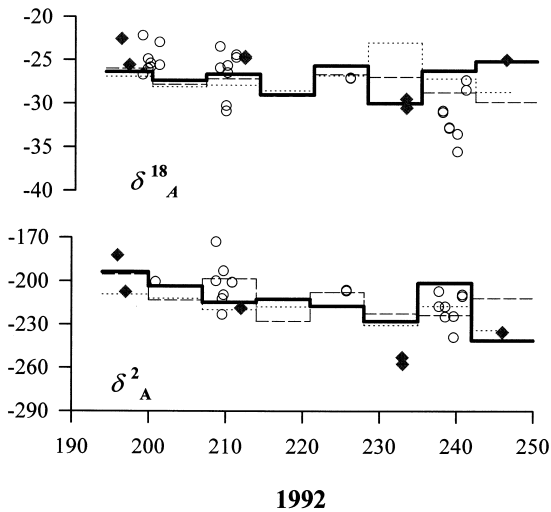


Fig. 6. Yellowknife, NWT.: Time-series of step-wise δ_A values derived from class-A pans, including lakeshore constant-volume pan (bold line), lakeshore drying pan (dotted line) and airport constant-volume pan located 5.5 km away (dashed line). Also shown are point values of δ_A based on the assumption of isotopic equilibrium with grab-sampled precipitation (diamonds), and δ_A values derived from three 1-L drying pans over 5- to 24-h time steps (open circles). See text for discussion.

$\delta^{18}\text{O}$ of drying-pan water occurred in late-August 1992 in response to input of precipitation associated with the same cold-air intrusion noted for Lupin. This event did not affect the constant-volume pans as significantly due to their large volume (220 L) relative to the drying pan at this time (28 L). Isotope mass balance calculations based on Eqs. (6), (7), and (10) revealed that pan water was also influenced by significant temporal variations in δ_A (Fig. 6).

During 1993 and 1994, only drying pans were deployed at the Yellowknife lake site as daily addition of source water was logistically difficult. To span the complete ice-free period of the adjacent lake, drying pans were replenished with source water once during 1992 and twice during 1993. $\delta^{18}\text{O}$ of uninterrupted drying runs are joined by dashed lines in Fig. 4. Overall, similar enrichment trends were observed as described for 1992, although $\delta^{18}\text{O}$ values reached maxima of +0.7‰ (1992) and +2.8‰ (1993) during extended dry periods. Once again, reduction in f over time, variations in h , precipitation input (Fig. 4) and evidently δ_A (Fig. 7) were the primary controls on $\delta^{18}\text{O}$ of pan water.

Pan-water enrichment trends for Yellowknife and Lupin are also shown in $\delta^{18}\text{O}$ versus $\delta^2\text{H}$ space (Fig. 8) in relation to the Meteoric Water Line (MWL) of Craig (1961), Local Evaporation Lines (LEL) for each site based on multi-year time-series sampling of local

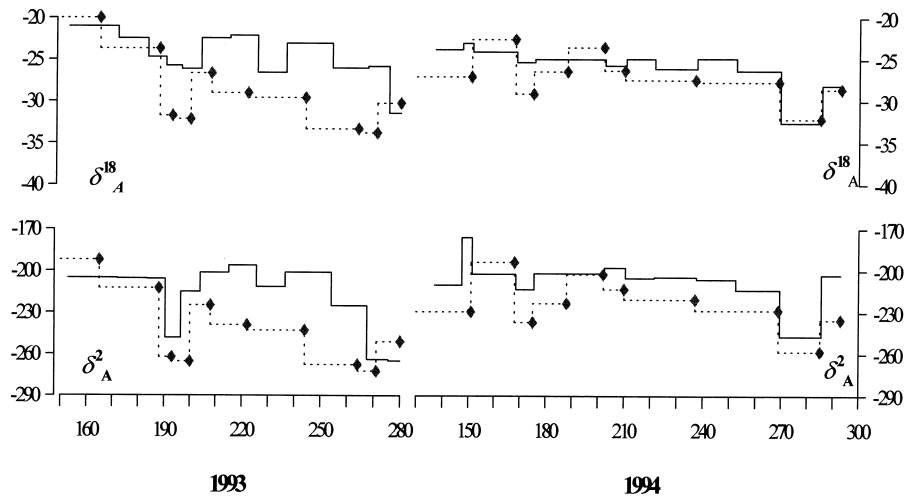


Fig. 7. Time-series of 1993 and 1994 interval δ_A values derived from class-A drying pans at Pocket Lake (solid line), and interval δ_A values based on integrated sampling of precipitation δ_p (dashed line-diamonds). See text for discussion.

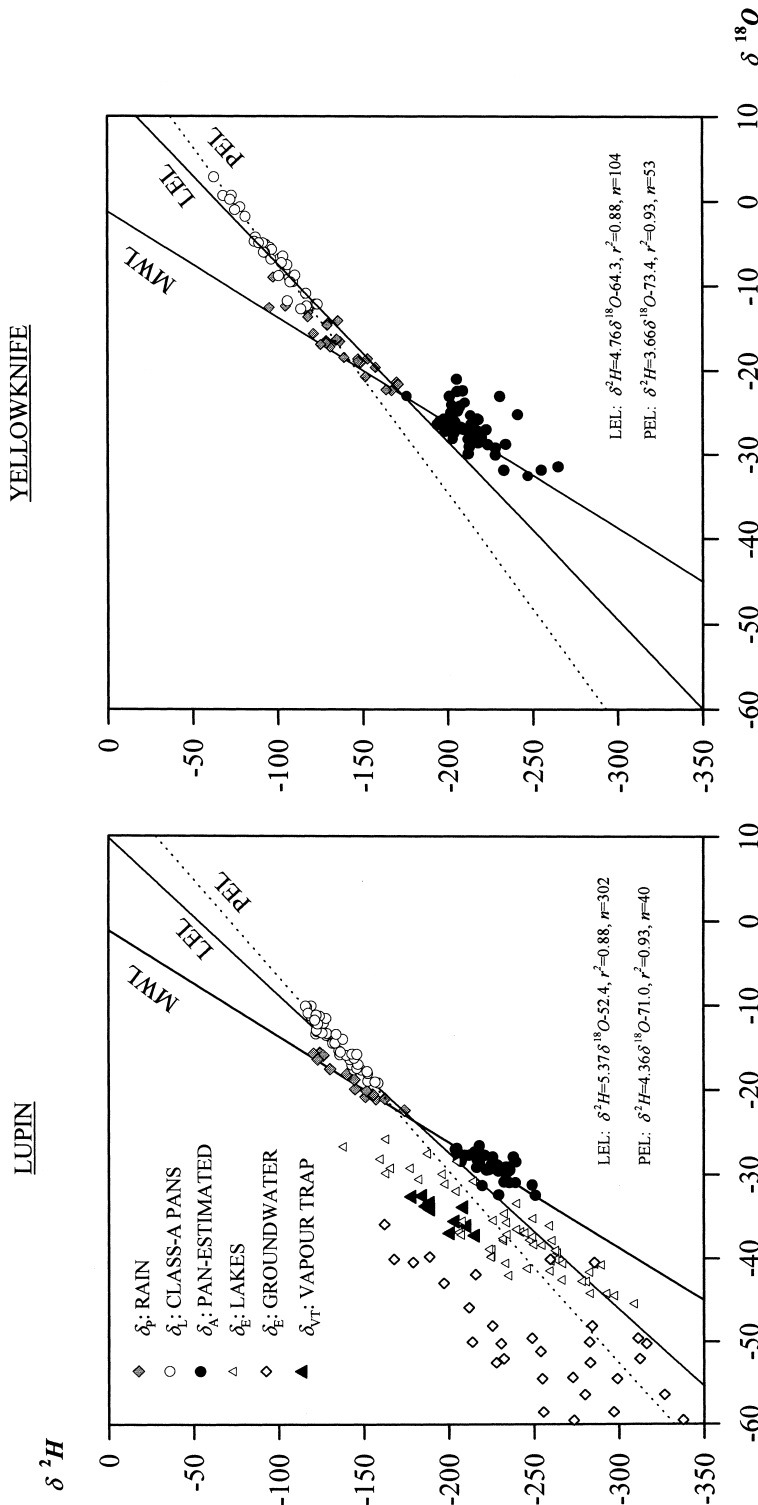


Fig. 8. Plots of $\delta^{18}O$ versus δ^2H for measured and estimated waters and vapours at Lupin and Yellowknife, N.W.T. Shown are rainfall samples collected during the course of evaporation pan experiments δ_p , class-A pan waters δ_L , and pan-derived atmospheric moisture δ_A , daily vapour trap water δ_{VT} , and calculated lake evaporate δ_E (assuming turbulent transport, $n = 1/2$) and active-layer groundwater evaporate δ_E (assuming static transport, $n = 1$) is also shown. Note that MWL is the Meteoric Water Line of Craig (1961), Local Evaporation Line (LEL) is based on multi-year time-series sampling of local lakes at each site, and Pan Evaporation Line (PEL) is based on all class-A pan water samples.

lakes, and precipitation sampled during the course of the pan experiments (Gibson, 1996). Pan Evaporation Lines (PEL) at both sites are characterized by slightly lower slopes than the LELs, which is a consequence both of lower humidity during the course of pan experiments relative to the total thaw season, and differences in the isotopic composition of the replenishment sources for each, as pans were topped with mixtures of lake water and summer rainfall, while lakes are naturally fed by contributions of summer rainfall, spring snowmelt, and related surface and sub-surface runoff. The isotopically depleted character of the snowpack at Lupin, for example ($-24.1 \pm 2.4\%$ in $\delta^{18}\text{O}$ and $-176 \pm 19\%$ in $\delta^2\text{H}$ based on a 250-point depth-integrated snow survey conducted during the late winter of 1993), is a dominant early-season source of input to lakes, and enhances the slope of the LEL relative to the PEL. The influence of δ_I and other water balance parameters on local evaporation trends was discussed by Horita (1990).

4.2. Time-series of δ_A estimated from class-A pans

Temporal variations in the isotopic composition of atmospheric moisture δ_A are shown in Figs. 5–7 as calculated from isotope mass balance of class-A pans assuming $n = 1/2$. Note that $\delta^{18}\text{O}$ and $\delta^2\text{H}$ of atmospheric moisture δ_A are denoted by δ_A^{18} and δ_A^2 , respectively.

At Lupin, five- to seven-day mean δ_A^{18} ranged from -26.6 to -31.4% , with time-weighted mean values of -28.4% (1992) and -29.6% (1993). Likewise, δ_A^2 ranged from -205 to -250% , with time-weighted mean values of -225% (1992) and -232% (1993). Overall, the systematic covariance of δ_A^{18} and δ_A^2 ($r^2 > 0.70$) and excellent agreement of estimates derived from separate pans ($r^2 > 0.60$) reveals, first, that the method yields consistent and reproducible estimates of δ_A . Second, and equally important, the small differences observed between pans over most time-steps suggest that errors related to characterization of isotope balance parameters, including analytical uncertainty, are small despite the use of single water samples to characterize δ_0 and $\delta_L(t)$ for each time-step. Third, the systematic covariance between δ_A and vapour-trap moisture collected at a point within the boundary layer (see Fig. 5; $r^2 = 0.49$) and general agreement between pan-derived δ_A and estimates

based on isotopic equilibrium with sampled precipitation (Fig. 5), is compelling evidence that pans are tracing variations in ambient atmospheric conditions. The near-constant offset between pan-derived δ_A and vapour-trap moisture reveals that both vapours are dependent on some common atmospheric processes but are not identical. As discussed in the following, we attribute this to the presence of a mixture of ambient δ_A and upward fluxes of δ_E in the vapour-trap samples due to the proximity of the trap to the ground surface.

Similar systematic relationships were observed at the Yellowknife site. For individual time-steps, pan-derived δ_A^{18} ranged from -21.0 to -33.6% , with time-weighted mean values of -27.4% (1992), -24.9% (1993), and -25.9% (1994). Likewise, δ_A^2 ranged from -176 to -265% , with time-weighted means of -215% (1992), -217% (1993), and -209% (1994). Covariance between pan-derived δ_A^{18} and δ_A^2 is also pronounced, particularly for 1993 and 1994 ($r^2 > 0.76$; see Fig. 7), and good agreement was found between three separate pans during 1992 ($r^2 > 0.50$; Fig. 6). General agreement between pan-derived δ_A and estimates based on isotopic equilibrium with sampled precipitation (Figs. 6 and 7) is also convincing evidence that pans are tracing variations in ambient atmospheric conditions.

Altogether, the magnitude of temporal variability and the covariance between pan-derived δ_A^{18} and δ_A^2 are reasonable and anticipated for ambient moisture in the region, considering that both tracers are controlled primarily by variations in air-mass history. The precision of pan-derived estimates of δ_A and conformity to theoretically predicted values is clearly demonstrated in a plot of $\delta^{18}\text{O}$ versus $\delta^2\text{H}$ (Fig. 8). As predicted from theoretical considerations (i.e. Horita, 1990; Gat and Bowser, 1991): δ_A plots close to the MWL; is on average close to isotopic equilibrium with δ_P ; and, variability is consistent with that of δ_P .

Previous pan studies, wherein C_K was derived and δ_A was assumed to be well-characterized by vapour-trap sampling (e.g. Gat, 1970; Table 1), have proposed that C_K may also vary diurnally and daily in response to changes in mass-transfer mechanisms, with moderate variability predicted for ^{18}O (10–16%) and extreme variability predicted for ^2H (2.5–40%). The overall consistency and covariance of derived δ_A^{18} and δ_A^2 from the more extensive experiments presented

herein argues against enhanced sensitivity or unpredictable behaviour of ^2H inferred by Gat (1970) on time-scales of 5 days or more, and suggests that use of constant C_K values accurately describes mean evaporation conditions over such periods.

4.3. Comparison of pan types

During 1992, two class-A pans were operated simultaneously within several metres of each other on the shore of the 6-ha Lupin study lake in order to evaluate potential errors arising from application of the constant-volume class-A pan methodology at a point. Different source water δ_+ and pan temperature records were used in order to avoid systematic errors related to characterization of these components, although the same h and δ_P records were used (Fig. 3). For 5- to 10-day time steps, the uncertainty (1σ) in estimating δ_A at a point was found to be close to $\pm 0.6\%$ for oxygen and $\pm 4\%$ for hydrogen.

Several different pan types, including a constant-volume class-A pan, a drying class-A pan and three 1-L drying pans were operated during 1992 within several metres of each other on the shore of the small study lake near Yellowknife. This sub-study was undertaken to examine possible systematic errors related to pan type, and specifically, to evaluate the potential use of class-A drying pans in studies where daily maintenance was not possible or where automated constant-feed pans (e.g. Allison and Leaney, 1982) were not available. Overall, agreement between pan-derived δ_A for individual time steps was within $\pm 3\%$ for oxygen and $\pm 9\%$ for hydrogen; two or three times larger than observed for the Lupin class-A pans due to the non-constant-volume effect. Differences over individual intervals may be particularly high when pan volume is reduced to less than about 30 L ($f = 0.15$). Excellent agreement is observed in the case where $f > 0.50$ (Day 190 to 220) which provides a conservative, but logistically useful range of applicability for class-A drying pans in the present setting.

One-litre drying pans were found to be roughly consistent with the larger class-A pans but were apparently strongly sensitive to high-frequency oscillations in h and δ_A (Fig. 6). The estimated δ_A values are not directly comparable to the class-A pan estimates however, as they did not span entire time-steps

of the latter. Rapid fluctuations predicted in δ_A^{18} and δ_A^2 of up to 6‰ and 30‰, respectively over some 4- to 30-h periods are not inconsistent with daily variability observed in vapour trap moisture at Lupin (Fig. 8). While such methods are potentially interesting for the study of short-term atmospheric variability, they generally are more labour-intensive, require isotopic analysis of more water samples, and are prone to large errors in δ_A for small errors in measurement of precipitation depth. As concluded by previous workers (Welhan and Fritz, 1977; Gonfiantini, 1986) small drying pans are oversensitive to atmospheric conditions and provide information that is less hydrologically useful. On the contrary, class-A pans appear to have sufficient volume to damp high-frequency atmospheric oscillations and provide flux-weighted δ_A estimates over hydrologically useful periods of five or more days.

4.4. Spatial variability of δ_A

The experimental results also provide some insight into spatial variability of δ_A at several scales in the present setting, as concurrent experiments were conducted at distances ranging from: (1) several hundred metres (Lupin, 1993), (2) 5.5 km (Yellowknife airport and nearby lake, 1992) and, (3) 375 km (Lupin and Yellowknife, 1992, 1993).

Pan-derived δ_A estimates during 1993 at Lupin (Fig. 5) were very consistent ($\pm 0.7\%$ in δ_A^{18} and $\pm 11\%$ in δ_A^2) despite being operated on opposite sides of a 6-ha lake. Overall, agreement was better than observed for 1992 when pans were operated within several metres, however variability between individual intervals was slightly higher. Analysis of wind directional data revealed no strong relationship between wind direction (i.e. onshore or offshore relative to the individual pans) and agreement between δ_A estimates, suggesting that it may not be important where pans are operated relative to a lake this size. Other studies have also concluded that pan positioning relative to a lake may not be critical (Allison et al., 1979).

At Yellowknife, the airport and lakeshore constant-volume class-A pans were consistent to within $\pm 2\%$ in δ_A^{18} and $\pm 15\%$ in δ_A^2 , comparable to differences observed between the two lakeshore class-A pans situated within a few metres. The similarity of

Table 2

Comparison of mean δ_A derived from isotope mass balance of class-A pans and δ_A assuming isotopic equilibrium with precipitation (i.e. $\delta_A = \delta_P - \varepsilon^*$) at Lupin and Yellowknife, N.W.T. for the indicated years. Note that ε^* was calculated for each precipitation sample or weighted interval based on measured air temperatures near the ground. Columns 3 and 7 show Z^a averaged over the entire experiment for each year. Columns 4 and 8 indicate 1 standard deviation of Z for individual time intervals

Site	Year	^{18}O				^2H			
		1 Pan-derived δ_A (‰)	2 $\delta_P - \varepsilon^*$ (‰)	3 Z^a	4 1σ	5 Pan-derived δ_A (‰)	6 $\delta_P - \varepsilon^*$ (‰)	7 Z^a	8 1σ
Lupin	1992	-28.8	-29.4	0.94	0.08	-227	-241	0.85	0.05
	1993	-29.9	-29.2	1.07	0.15	-224	-235	0.88	0.14
Yellowknife	1992	-27.0	-26.1	1.09	0.03	-214	-225	0.88	0.15
	1993	-25.7	-29.0	0.69	0.33	-222	-243	0.78	0.24
	1994	-26.0	-27.0	0.90	0.17	-206	-224	0.81	0.17

^a Here $Z = (\delta_P - \delta_A^{\text{PAN}})/\varepsilon^*$ is the fraction of predicted equilibrium liquid–vapour separation.

atmospheric moisture between the nearby sites (Fig. 6), despite the open, well-drained upland location of the airport and the humid, forested location of the nearby lakeshore, is convincing evidence that pans are tracing “free-air” conditions as defined in the Craig and Gordon (1965) model, without substantial influence from local boundary-layer anomalies. Although the spatial scale of variability remains to be fully characterized, these results suggest that δ_A is relatively constant within about 5.5 km, and within this distance it may be sufficient to use pan-derived δ_A estimates from a single pan to characterize δ_E via Eq. (1) for several lakes.

It is apparent from comparisons between Yellowknife and Lupin, however, that pan-derived δ_E cannot be extrapolated to distances as large as 375 km. Although δ_A at the sites was not markedly dissimilar (within 1.2‰ in δ_A^{18} and 6‰ in δ_A^2 for 1992 and 4.8‰ in δ_A^{18} and 12‰ in δ_A^2 for 1993), Yellowknife vapour was consistently enriched relative to Lupin vapour, and both sites had distinct temporal patterns, attributable to differences in relative contributions of Pacific and Arctic air-mass sources and steep climatic gradients across northern treeline (see Bryson and Hare, 1974).

4.5. Test of $\delta_A - \delta_P$ equilibrium

In Figs. 5–7 and Table 2, pan-derived δ_A estimates are compared to estimates assuming $\delta_A = \delta_P - \varepsilon^*$. This is a common first-approximation employed in many isotope mass-balance studies (i.e. Horita,

1990; Gat, 1980, 1981; Gat and Bowser, 1991; Gibson et al., 1993), and is generally expected to occur in the case where precipitation forms in equilibrium with in-cloud moisture and falls to the ground through saturated air (Gat, 1980). Very good temporal agreement was observed, particularly during 1993 at Lupin and during 1992 and 1994 at Yellowknife. Overall, estimates are found to be consistent to within 5‰ for δ_A^{18} and 21‰ for δ_A^2 , although $\delta_P - \delta_A^{\text{PAN}}$ tended to be less than ε^* for most years (i.e., $Z < 1$; see Table 2). This is expected considering that precipitation occurred only sporadically over the course of the pan experiments, typically during times of high humidity, whereas pans recorded continuously such that pan-derived δ_A estimates also reflect interim periods characterized by lower humidity and enriched δ_A . Interestingly, $\delta_P - \delta_A^{\text{PAN}}$ tended to be less than ε^* , contrary to mid-summer observations by Krabbenhoft et al. (1990), who used vapour traps located near the ground to characterize δ_A for a site in Wisconsin having numerous lakes. Likewise, if we assume that δ_A is well-characterized by moisture collected in the vapour trap (Fig. 5), we also obtain values of $\delta_P - \delta_A$ greater than about $1.4\varepsilon^*$ ($Z = 1.4$) for the 1993 mid-summer period at Lupin. As noted also by Krabbenhoft et al. (1990) this is evidently due to the presence of local evaporate in the vapour-trap moisture. As we have shown in Fig. 6 and revisit in the following, vapour trap moisture δ_{VT} is not likely representative of the “free air” described in Eq. (1) that controls pan or lake water isotopic enrichment.

Despite good agreement overall, substantial

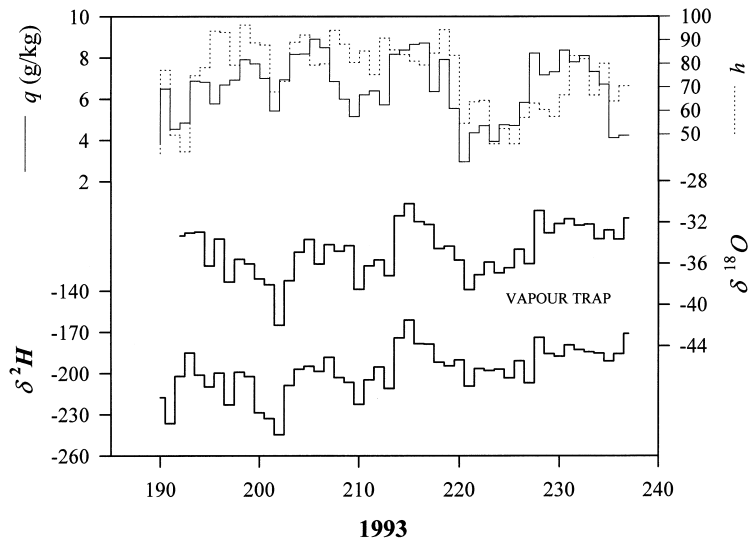


Fig. 9. Time-series of humidity h , specific humidity q , and $\delta^{18}\text{O}$ and $\delta^2\text{H}$ of vapour trap moisture δ_{VT} for daily sample collection periods (approx. 0900–1200 hours daily). See text for discussion.

differences in δ_{A} are predicted by the two methods during early July to late September 1993 (Day 190 to 270) at Yellowknife. Although further study is required, apparent differences may indicate error in the pan computation or more complex relationships between precipitation and atmospheric moisture. Nevertheless, precipitation equilibrium relationships are potentially useful for independent verification of pan-derived δ_{A} using information that is required anyway for the latter technique.

4.6. Direct moisture sampling at Lupin

Many previous studies, as noted, have relied solely on point-sampling of moisture within the boundary layer to estimate δ_{A} . At Lupin during 1993, moisture was collected daily in a vapour trap at 6 m above the tundra surface on a topographic high about 1 km from the nearest lake and 6.9 m above the elevation of the evaporation pan stations. Time-series plots of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ are shown in Fig. 9, along with humidity h and specific humidity q (g kg^{-1}) of the air measured during the hours of collection. In addition, five-day mean values of δ_{VT} are shown in Fig. 5 in relation to pan-derived δ_{A} .

From Fig. 9, several general trends are apparent: (1) a distinct positive correlation exists between $\delta^{18}\text{O}$ and

$\delta^2\text{H}$ ($r^2 = 0.80$); (2) variability of δ_{VT} is substantial and day-to-day differences range from near-zero to as high as 6‰ ($\delta^{18}\text{O}$) and 30‰ ($\delta^2\text{H}$) and; (3) δ_{VT} variations are weakly correlated to changes in specific humidity q within the boundary layer ($r^2 = 0.2$).

On a plot of $\delta^{18}\text{O}$ vs. $\delta^2\text{H}$ (see Lupin, Fig. 8), daily values of δ_{VT} are shown in relation to pan-derived δ_{A} , rainfall δ_{P} , and the MWL, LEL and PEL. Vapour trap moisture δ_{VT} is shown to lie above the MWL, and is enriched in $\delta^{18}\text{O}$ and depleted in $\delta^2\text{H}$ relative to pan-derived δ_{A} . This separation between pan-derived δ_{A} and δ_{VT} is systematic, and is clearly not primarily the result of incomplete vapour trapping which would produce enrichment in both in $\delta^{18}\text{O}$ and $\delta^2\text{H}$. Rather, it likely reflects a substantial component of recycled terrestrial moisture within vapour trap moisture δ_{VT} . Possible sources of recycled moisture were considered and their isotopic compositions were modelled. δ_{E} values were calculated using pan-derived δ_{A} and Eq. (1) assuming static transport for groundwater ($n = 1$, typical for evaporation through the unsaturated zone, e.g. see Allison et al., 1983) and turbulent transport for lakes $n = 1/2$. The relatively large scatter in δ_{E} predicted for lakes and groundwater (Fig. 8) is due mainly to the effect of diurnal, daily, and longer-term fluctuations in relative humidity. As shown in Fig. 8, δ_{VT} lies in a distinct grouping intermediate between

δ_E calculated for vapour from active-layer groundwater and both δ_E for local lakes and pan-derived δ_A .

From these comparisons, it is evident that δ_{VT} is more consistent with a mixture of δ_E^{GW} plus δ_A or δ_E^{LAKES} than with δ_A alone, which in theory should plot near the MWL. Considering that the vapour trap was operated over the tundra surface and at a distance from local lakes, and given the well-developed unsaturated zone within the active-layer at Lupin during 1993 (Gibson et al., 1996a), δ_{VT} most likely reflects a mixture of δ_E^{GW} , transpired moisture (likely similar to local groundwater) and ambient moisture δ_A . In addition, it is possible that δ_{VT} records contributions of re-evaporated rainfall intercepted by the tundra vegetation canopy, and re-evaporated surface dewfall and hoar-frost accumulation, as sampling was conducted during the late morning hours. These moisture sources, broadly consistent with the range of observed rainfall δ_P (Fig. 8), would produce δ_E consistent with that observed for δ_{VT} assuming turbulent transport. Quantitative evaluation of the relative contributions of upward and ambient moisture in δ_{VT} is difficult with this single-point sampling method. It is evident, however, that vapour traps positioned close to the ground surface do not provide representative estimates of δ_A in the present setting.

5. Concluding comments

Reliable and consistent characterization of δ_A and its temporal variability are important prerequisites to wider application of isotope mass balance methods, and in particular to the development and use of high-resolution time-variant models. The experimental results demonstrate that δ_A can be readily obtained from careful monitoring of the isotope and mass budgets of conventional evaporation pans. This conclusion is reinforced by successful use of pan-derived δ_A values in isotope-mass balance analysis of the study lake at Lupin (reported previously by Gibson et al., 1996a), which yielded evaporation rates in close agreement (within $\pm 10\%$) with results based on both Bowen ratio energy balance and aerodynamic profile calculations. Our present analysis further confirms that class-A pans operated over five- to seven-day time-steps provide highly suitable temporal resolution of δ_A for use in isotope mass

balance methods in the continental subarctic and low-arctic of northern Canada.

The results also suggest that grab-sampled moisture collected at points within the boundary layer may be dominated by evaporate or varying mixtures of evaporate and ambient moisture and is therefore not characteristic of δ_A as described in the Craig and Gordon model. Use of vapour trap samples to characterize δ_A is a likely source of error in previous investigations, especially those relying on hydrogen-isotope data. Perhaps not surprisingly, the isotopic composition of atmospheric moisture was found to be as fundamentally variable as relative humidity, and must therefore be explicitly considered in computation of short-term isotope balances of lakes.

Finally, the results suggest that isotopic sampling of conventionally-operated class-A evaporation pans may be a straightforward and cost-effective solution to the problem of documenting the shifting isotopic distribution in atmospheric moisture. The method could provide a continuously-weighted record of δ_A for use in isotope-climate research, including large time-intervals not preserved in precipitation archives, which may be of particular value at stations with infrequent precipitation. Such data could serve as a tool in hydrometeorological studies at various spatial and temporal scales (e.g. in regional studies like the Global Energy and Water Cycle Experiment GEWEX; see Edwards and Gibson, 1995) as well as being a source of data for validation of atmospheric general circulation models incorporating isotope water tracers (e.g. Jouzel et al., 1987; Jouzel et al., 1991; Hoffmann and Heimann, 1993), and a contribution to ongoing international efforts like GNIP (Global Network for Isotopes in Precipitation; see Schotterer et al., 1996).

Acknowledgements

Portions of this research were funded by Environment Canada (NHRI, Saskatoon), Indian and Northern Affairs Canada (Water Resources Division, Yellowknife, and Northern Scientific Training Program Grants), Canada-NWT Mineral Initiatives Program, CANMET, the Natural Sciences and Engineering Research Council of Canada, the Waterloo Centre for Groundwater Research (Ontario

Technology Fund), Echo Bay Mines Ltd., Royal Oak Mines Inc., Nanisivik Mines Limited, and the Metall Mining Corporation. We thank R. Reid, T. Carter, C. Spence, J. Whidden and H. Weatherly for field assistance and H. Wilson, D. Hohnstein and A. Gilbert for logistical support. This manuscript has benefitted from the comments of G. Hoffmann and one anonymous reviewer.

References

- Allison, G.B., Leaney, F.W., 1982. Estimation of isotopic exchange parameters using constant-feed pans. *J. Hydrol.* 55, 151–161.
- Allison, G.B., Brown, R.M., Fritz, P., 1979. Estimation of the isotopic composition of lake evaporate. *J. Hydrol.* 42, 109–127.
- Allison, G.B., Barnes, C.J., Hughes, M.W., 1983. The distribution of deuterium and ^{18}O in dry soils. *J. Hydrol.* 64, 377–397.
- Brutsaert, W., 1975. A theory for local evaporation (or heat transfer) from rough and smooth surfaces at ground level. *Water Resour. Res.* 11, 543–550.
- Brutsaert, W., 1982. *Evaporation into the Atmosphere*. Reidel, Dordrecht, Netherlands.
- Bryson, R.A., Hare, R.K., 1974. The climate of North America. In: Bryson, R.A., Hare, R.K. (Eds.). *Climates of North America*, Elsevier, New York, pp. 1–47.
- Coplen, T.B., 1996. New guidelines for reporting stable hydrogen, carbon, and oxygen isotope-ratio data. *Geochim. Cosmochim. Acta* 60, 3359–3360.
- Craig, H., 1961. Isotopic variations in meteoric waters. *Science* 133, 1833–1834.
- Craig, H., Gordon, L.I., 1965. Deuterium and oxygen-18 variations in the ocean and marine atmosphere. In: E. Tongiorgi (Ed.), *Stable Isotopes in Oceanographic Studies and Paleotemperatures*, Lab. Geologia Nucleare, Pisa, pp. 9–130.
- Diñçer, T., 1968. The use of oxygen-18 and deuterium concentrations in the water balance of lakes. *Water Resour. Res.* 4, 1289–1305.
- Edwards, T.W.D., Gibson, J.J., 1995. Comments on the use of isotopic tracers in GCIP-LSA-NC and MAGS. In: *Proc. International GEWEX Workshop on Cold-Season/Region Hydrometeorology*, Banff, May 1995, IGPO Pub. 15, pp. 120–123.
- Gat, J.R., 1970. Environmental isotope balance of Lake Tiberias. *Isotopes in Hydrology*, 1970. IAEA, Vienna, pp. 151–162.
- Gat, J.R., 1980. The isotopes of oxygen and hydrogen in precipitation. In: Fritz, P., Fontes, J.Ch. (Eds.). *Handbook of Environmental Isotope Geochemistry*, 1. Elsevier, New York, pp. 27–47.
- Gat, J.R., 1981. Lakes. *Stable Isotope Hydrology—Deuterium and Oxygen-18 in the Water Cycle*. In: J.R. Gat, R. Gonfiantini (Eds.). IAEA Technical Report Series No. 210, Vienna, pp. 203–221.
- Gat, J.R., Bowser, C.J., 1991. Heavy isotope enrichment in coupled evaporative systems. In: H.P. Taylor, J.R. O'Neil, I.R. Kaplan (Eds.), *Stable Isotope Geochemistry: A Tribute to Samuel Epstein*, Special Publication No. 3, The Geochemical Society, San Antonio, Texas, pp. 159–168.
- Gat, J.R., Matsui, E., 1991. Atmospheric water balance in the Amazon Basin: an isotopic evapotranspiration model. *J. Geophys. Res.* 96, 13 179–13 188.
- Gat, J.R., Bowser, C.J., Kendall, C., 1994. The contribution of evaporation from the Great Lakes to the continental atmosphere: estimate based on stable isotope data. *Geophys. Res. Lett.* 21, 557–560.
- Gibson, J.J., 1996. *Non-steady isotopic methods for estimating lake evaporation: development and validation in Arctic Canada*. Ph.D. Thesis, University of Waterloo, 238 pp.
- Gibson, J.J., Edwards, T.W.D., Bursey, G.G., Prowse, T.D., 1993. Estimating evaporation using stable isotopes: quantitative results and sensitivity analysis for two catchments in northern Canada. *Nordic Hydrol.* 24, 79–94.
- Gibson, J.J., Prowse, T.D., Edwards, T.W.D., 1996. Development and validation of an isotopic method for estimating lake evaporation. *Hydrol. Processes* 10, 1369–1382.
- Gibson, J.J., Prowse, T.D., Edwards, T.W.D., 1996. Evaporation from a small lake in the continental arctic using multiple methods. *Nordic Hydrol.* 27, 1–24.
- Gonfiantini, R., 1986. Environmental isotopes in lake studies. In: Fritz, P., Fontes, J.Ch. (Eds.). *Handbook of Environmental Isotope Geochemistry*, 3. Elsevier, New York, pp. 113–168.
- denHartog, G., Ferguson, H.L., 1978. Mean annual lake evaporation. Plate 17, *Hydrological Atlas of Canada*, Ottawa, Dept. Fisheries and Environment, Ottawa, Ontario, map.
- Hoffmann, G., Heimann, H., 1993. Water tracers in the ECHAM general circulation model. In: *Proc. International Symposium on Applications of Isotope Techniques in Studying Past and Current Environmental Changes in the Hydrosphere and the Atmosphere*, IAEA, Vienna, 19–23 April 1993, IAEA-SM-329/7, pp. 3–14.
- Horita, J., 1990. Stable isotope paleoclimatology of brine inclusions in halite: modeling and application to Searles Lake California. *Geochim. Cosmochim. Acta* 54, 2059–2073.
- Jouzel, J., Koster, R., Suozzo, R., Russell, G., White, J., Broecker, W., 1991. Simulations of the HDO and H_2^{18}O atmospheric cycles using the GISS general circulation model: Sensitivity experiments for present-day conditions. *J. Geophys. Res.* 96, 7495–7507.
- Jouzel, J., Russell, G., Suozzo, R., Koster, R., White, J., Broecker, W., 1987. Simulations of the HDO and H_2^{18}O atmospheric cycles using the GISS general circulation model: Seasonal cycle for present-day conditions, 92. *J. Geophys. Res.* 92, 14 739–14 760.
- Krabbenhoft, D.P., Bowser, C.J., Anderson, M.P., Valley, J.W., 1990. Estimating groundwater exchange with lakes I. The stable isotope mass balance method. *Water Resour. Res.* 26, 2445–2453.
- Majoube, M., 1971. Fractionnement en oxygène-18 et en deutérium entre l'eau et sa vapeur. *J. Chim. Phys.* 197, 1423–1436.
- Merlivat, L., 1978. Molecular diffusivities of H_2^{16}O , HD^{16}O and H_2^{18}O in gases. *J. Chem. Phys.* 69, 2864–2871.
- Merlivat, L., 1978. Dependence of bulk evaporation coefficients on air–water interfacial conditions as determined by the isotopic method. *J. Geophys. Res.* 83, 2977–2980.

- Merlivat, L., Coantic, M., 1975. Study of mass transfer at the air–water interface by an isotopic method. *J. Geophys. Res.* 80, 3455–3464.
- Schoch-Fischer, H., Rozanski, K., Jacob, H., Sonntag, C., Jouzel, J., Ostlund, G., Geyh, M.A., 1984. Hydrometeorological factors controlling the time variation of D, ^{18}O , and ^3H in atmospheric water vapour and precipitation in the northern westwind belt. Proceedings, Isotope Hydrology Symposium, 12–16 Sept. 1983, IAEA, Vienna, pp. 3–30.
- Schotterer, U., Oldfield, F., Fröhlich, K., 1996. Global Network for Isotopes in Precipitation. PAGES/IGBP, Druckerei Läderach, Bern.
- Taal, T.A., 1994. Comparative study of evaporative flux using stable isotopes at Pocket Lake, near Yellowknife, Northwest Territories. M.Sc. Thesis, University of Waterloo.
- Vogt, H.J., 1976. Isotopentrennung bei der Verdampfung von Wasser. Staatsexamensarbeit, Universität Heidelberg.
- Welhan, J.A., Fritz, P., 1977. Evaporation pan isotopic behaviour as an index of isotopic evaporation conditions. *Geochim. Cosmochim. Acta* 41, 682–686.
- Zuber, A., 1983. On the environmental isotope method for determining the water balance of some lakes. *J. Hydrol.* 61, 409–427.