



## Research papers

Comparison of atmospheric water vapour  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  estimated using evaporation pan, rainfall equilibrium and continuous measurementsJagoda Crawford<sup>a,\*</sup>, Cecilia S. Azcurra<sup>b</sup>, Catherine E. Hughes<sup>a</sup>, John J. Gibson<sup>c,d</sup>, Stephen D. Parkes<sup>a</sup><sup>a</sup> ANSTO, Locked Bag 2001, Kirrawee DC, NSW 2232, Australia<sup>b</sup> School of Civil and Environmental Engineering, University of New South Wales, NSW 2052, Australia<sup>c</sup> InnoTech Alberta, 3-4476 Markham Street, Victoria, BC V8Z 7X8, Canada<sup>d</sup> Department of Geography, University of Victoria, P.O. Box 1700 STN CSC, Victoria, BC V8W 2Y2, Canada

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## ABSTRACT

For a period of 16 months in Sydney, Australia, the variations of  $^2\text{H}/^1\text{H}$  and  $^{18}\text{O}/^{16}\text{O}$  in atmospheric vapour ( $\delta^2\text{H}_\text{A}$  and  $\delta^{18}\text{O}_\text{A}$ ) were estimated using an evaporation pan method as well as using the isotopic precipitation-equilibrium approach. These calculations were then compared with  $\delta^2\text{H}_\text{A}$  values measured at 10 m above ground surface using a Fourier Transform Infrared Spectrometer (FTIR). As pan isotopic composition was available on a weekly time scale, the evaporation rates were measured daily, and the atmospheric variables were available hourly, the weekly time scale was used to calculate the arithmetic averages of the atmospheric variables that were used in the estimation of the pan-derived  $\delta^2\text{H}_\text{A}$ .

Good agreement ( $r = 0.7$ ,  $P\text{-value} = 0.00$ ) was found between the pan-derived and the FTIR measured  $\delta^2\text{H}_\text{A}$  for weekly intervals, although individual differences ranged from  $-25.0$  to  $20.4\%$ , with the absolute difference averaging  $8.0\%$ . A sensitivity analysis showed that the determination of  $\delta^2\text{H}_\text{A}$  is most sensitive to air temperature, relative humidity and the isotopic composition of the pan water.

While the precipitation-equilibrium approach only appears to be representative of atmospheric conditions close to times of precipitation events, the pan-derived isotopic composition of atmospheric vapour was found to be closer to the FTIR averages over longer periods including intervals with no precipitation. Overall, this means that the pan method is far more effective for uninterrupted estimation of  $\delta^2\text{H}_\text{A}$  and  $\delta^{18}\text{O}_\text{A}$  of atmospheric water vapour, as required for water budget studies, than the precipitation-equilibrium method, and it is more cost effective and robust than continuous measurement.

## 1. Introduction

Losses of water due to evaporation from surface waters can be an important component of the terrestrial hydrological cycle, particularly for arid and semi-arid regions (Skrzypek et al., 2015). Measurements of the parameters required to determine the evaporative flux is often time consuming and costly, especially for catchment scale studies. An alternative technique is to use the natural variations in  $^2\text{H}/^1\text{H}$  or  $^{18}\text{O}/^{16}\text{O}$  to quantify evaporative loss (e.g. van den Akker et al., 2011; Gibson and Reid, 2014; Jasechko et al., 2014; Skrzypek et al., 2015; Gibson et al., 2016). However, one of the parameters required is the isotopic composition of the evaporating moisture, which is difficult to measure; hence generally the Craig and Gordon model (1965) is used to estimate its value (Gibson et al., 2008a). Additionally, one of the parameters

required by the Craig and Gordon model is the isotopic composition of the atmospheric moisture into which the evaporation is occurring ( $\delta_\text{A}$ ). Over the continent,  $\delta_\text{A}$  can have considerable temporal and spatial variations (Horita et al., 2008; Purushothaman et al., 2014) due to (i) air masses of different origins and rainout histories, (ii) variation in the degree of day time vertical mixing which can cause the mixing of air close to the surface with air from the free atmosphere (Tsujimura et al., 2007) and (iii) moisture originating from evapotranspiration over land, which can also have a diurnal variation (e.g. Lee et al., 2006). While diurnal variations in  $\delta_\text{A}$  are observed, Lee et al. (2006) found that the variation through the weather cycle was higher. This parameter ( $\delta_\text{A}$ ) can be either determined from direct measurements or estimated. Direct measurements include cryogenic traps (e.g. Gibson et al., 1999; Vallet-Coulomb et al., 2010; Devi et al., 2015) or using laser

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spectroscopy (e.g. Welp et al., 2008). Galewsky et al. (2016) present an overview of techniques used to determine the isotopic composition of water vapour, including discrete water vapour sampling, cavity-enhanced spectroscopy and remote sensing.

The alternative to direct measurements is to estimate  $\delta_A$  either by liquid-vapour equilibrium calculations based on knowledge of the isotopic composition of local rainfall, or using evaporation pans. The isotopic composition of water vapour at ground level has been shown to be close to equilibrium with precipitation in most cases over the continents (from studies over Europe and the USA; Araguás-Araguás et al., 2000). However, estimation of  $\delta_A$  from precipitation records may not be suitable where the time period under consideration includes extended rain-free periods (Gibson et al., 1999), e.g. in arid climates (Gibson et al., 2008a; Tsujimura et al., 2007), or locations where local evaporation recycling affects vapour composition (e.g. lakes; Gat et al., 1994; Devi et al., 2015). An alternative is to use evaporation pans to derive the value of  $\delta_A$  in the vicinity of the pan, which is then assumed to be representative for predicating evaporative enrichment of downwind water bodies in the surrounding region. Evaporation pans have been widely used to determine irrigation schedules, but more recently have been used to determine hydroclimatic trends worldwide (Roderick et al., 2009). In Australia, Jovanovic et al. (2008) reported on a long-term pan evaporation trend using high quality pan data from 60 stations. Interestingly, as an evaporation pan network is already in operation across Australia, and a large number of these locations record the required meteorological conditions (Jovanovic et al., 2008), the potential exists to operationalize sampling of isotopes in pans and precipitation to permit calculation of  $\delta_A$  across the continent with little additional cost.

Gibson et al. (1999) have detailed evaporation pan-based models for determining  $\delta_A$  for three water balance situations: (1) a drying pan with no inflow, (2) a drying pan with precipitation input, and (3) a pan maintained at constant volume by the addition of water and precipitation. Previously, Welhan and Fritz (1977) and Allison and Leaney (1982) had shown that constant volume evaporation pans can be reliable methods for determining  $\delta_A$  of atmospheric moisture. More recent studies using evaporation pans include Wang et al. (2009), Vallet-Coulomb et al. (2010), van den Akker et al. (2011), and Devi et al. (2015).

To evaluate the evaporation pan technique for the determination of  $\delta_A$ , comparisons between pan-derived  $\delta_A$  and cryogenically trapped moisture have been published by a number of authors (e.g. Gibson et al., 1999; Vallet-Coulomb et al., 2010; Devi et al., 2015). Generally, most studies report higher  $\delta^2\text{H}$  measured from the vapour traps than in pan-derived  $\delta_A$ . For example, Devi et al. (2015) reported average differences between  $\delta^2\text{H}$  values measured in vapour traps and pan-derived  $\delta^2\text{H}$  values of 19.50 and 25.85‰ for two separate sites, with vapour trap values being more  $\delta^2\text{H}$  enriched. For  $\delta^{18}\text{O}$ , the differences were smaller: −0.14 and +0.27‰. They attributed these differences to diurnal changes in air mass movement. Devi et al. (2015) also reported that  $\delta_A$  derived under the assumption of isotopic equilibrium with the precipitation was consistent with the pan-derived values of  $\delta_A$ .

Many of the noted evaporation pan studies were of shorter duration (weeks) and estimates from pans were most commonly compared to vapour trap results. Two of the most recent studies were carried out in a Mediterranean wetland (Vallet-Coulomb et al., 2010) and in Roorkee (India; Devi et al., 2015). Here, we present results from a 16-month study for an east Australian site. Previous studies in Australia include a 50-day experimental trial using custom-designed constant feed pans reported by Allison and Leaney (1982) that showed good agreement between measured and modelled pan enrichment. We use a similar model applicable for standard class-A pan operation to determine  $\delta_A$  and compare results with measurements using an FTIR optic spectrometer (see Haverd et al. 2011), which were available at hourly time intervals. Early results from this study were presented in Azcurra et al. (2011). The aim of this study was to evaluate the pan method for the

determination of the isotopic composition of atmospheric water vapour by (1) using a longer time period to determine the atmospheric  $\delta_A$  using the pan method, than has been used in previous studies, (2) comparison of the pan method determined  $\delta_A$ , with FTIR measurement, for which no previous studies have been reported, (3) comparison of results with indirect estimates obtained from the assumption of an isotopic equilibrium between precipitation and atmospheric vapour, and (4) an application in an Australian setting.

## 2. Theory

The isotopic composition of the evaporating moisture ( $\delta_E$ ), assuming zero resistance in the liquid phase, can be estimated using the Craig and Gordon (1965) linear resistance model:

$$\delta_E = \frac{\left(\frac{\delta_L - \varepsilon^+}{\alpha^+}\right) - h\delta_A - \varepsilon_k}{(1 - h + 10^{-3}\varepsilon_k)} \quad (1)$$

where  $\alpha^+$  is the liquid-vapour equilibrium isotopic fractionation factor determined using mean temperature (Gibson et al., 2008a) and  $\varepsilon^+ = 10^3(\alpha^+ - 1)$ . Gibson et al. (2016) indicated that the water surface temperature should ideally be used in the calculation. The other parameters required are: the isotopic composition of the pan water undergoing evaporation ( $\delta_L$ ), the isotopic composition of ambient vapour ( $\delta_A$ ), the relative humidity above the air/water interface  $h$  (normalised to the temperature at water surface and divided by 100), and the kinetic enrichment factor  $\varepsilon_k$ . The value of  $\delta_L$  can be measured directly from water sampling, and the relative humidity can be determined indirectly ( $h$  requires the relative humidity of the air  $h_{air}$  along with the temperatures of pan surface water  $T_{pan}$  and the temperature of air  $T_{air}$ ).

The kinetic fractionation factor, as described in Gat (1996), was based on wind tunnel experiments (e.g. Vogt, 1976; Merlivat 1978):

$$\varepsilon_k = nC_k^0\theta(1 - h) \quad (2)$$

where  $C_k^0$  is 25.0‰ and 28.5‰ for deuterium and oxygen-18, respectively,  $n$  is the turbulence parameter,  $n = 0.5$  is used for open water bodies (average turbulent flow; Gibson et al., 1999),  $n = 2/3$  for laminar flow and  $n = 1$  for static transport such as soil water (Barnes and Allison, 1988), and  $\theta = (1 - h')/(1 - h)$  is an advection term to account for the potential influence of humidity build-up,  $h'$  being the adjusted humidity of the downwind atmosphere following admixture of evaporating moisture. In this study  $\theta = 1$  was used, as this has been suggested suitable for small water bodies (Gat, 1996). Further, a number of values of  $n$  were considered in this application and it was found that when  $n$  was set to 0.5, as used by Vallet-Coulomb et al. (2010) and Devi et al. (2015), the estimated results corresponded more closely to the measured values.

The value of  $\delta_A$  in Eq. (1) needs to be determined. This can be either measured directly, or determined from local precipitation or evaporation pan experiments. Gibson et al. (1999) has detailed the equations required to estimate  $\delta_A$  using three methods; drying pan, drying pan with precipitation input and constant-volume pan.

### 2.1. Precipitation derived $\delta_a$

Using the precipitation equilibrium assumption (Gibson et al., 2008a)

$$\delta_{A\_Precip} = \frac{(\delta_{Precip} - \varepsilon^+)}{\alpha^+} \quad (3)$$

where  $\delta_{Precip}$  is the isotopic composition of precipitation,  $\alpha^+$  is the liquid-vapour equilibrium isotopic fractionation factor using mean air temperature (Gibson et al., 2008a) and  $\varepsilon^+ = 10^3(\alpha^+ - 1)$ .

## 2.2. Evaporation pan models

For a well-mixed evaporation pan with a constant density of water and no leak or overflow, the water and isotope mass balances are given by (Gibson et al., 1999):

$$\frac{dV}{dt} = I - E \quad (4)$$

and

$$\frac{d(V\delta_L)}{dt} = I\delta_I - E\delta_E \quad (5)$$

where  $V$  is the volume of the reservoir,  $dV/dt$  is the change in volume over the time period,  $I$  is the volume of input waters,  $E$  is the evaporation volume, and  $\delta_L$ ,  $\delta_I$  and  $\delta_E$  are the isotopic compositions of the evaporation pan, inflow and evaporated water, respectively.

Combining Eqs. (5) and (1) produces:

$$V \frac{d\delta_L}{dt} + \delta_L \frac{dV}{dt} = I\delta_I - E \left( \frac{\left( \frac{\delta_L - \epsilon^+}{\alpha^+} \right) - h\delta_A - \epsilon_k}{(1 - h + 10^{-3}\epsilon_k)} \right) \quad (6)$$

Solutions to Eq. (6) exist for three water balance scenarios (Gibson et al., 1999):

1. when there are no inputs to the pan and the change in pan water volume is only due to evaporation ( $I = 0$  and  $E > 0$ ; referred to as the ‘drying pan’ scenario);
2. when input waters to the pan do not total the amount of evaporation so that there is a change in volume (either  $I < E$  or  $E < I$ ; the ‘drying pan with input’ scenario); and
3. when the pan receives the same amount of water as has been evaporated ( $I = E$ ; the ‘constant volume pan’ scenario).

### 2.2.1. Constant volume pan

For hydraulic steady state conditions (i.e. where  $dV/dt = 0$ ), Eq. (6) simplifies to (Gonfiantini 1986; Gibson et al., 2016):

$$\frac{d\delta_L}{dt} = -[(1 + mx)\delta_L - \delta_I - x\delta^*] \left( \frac{I}{V} \right) \quad (7)$$

where  $x = E/I$  is the fraction of water lost by evaporation (for a constant volume pan, where outflow is negligible  $x = 1$ , as  $I = E$  in the case where a pan is topped daily to a constant volume; Gibson et al., 1999). Integrating Eq. (7) with respect to time (Gonfiantini 1986), gives:

$$\delta_L(t) = \delta_s - (\delta_s - \delta_0)e^{-(1+mx)\left(\frac{t}{V}\right)} \quad (8)$$

where  $\delta_0$  is the initial isotopic composition and (Gibson et al., 2016):

$$m = \frac{h - 10^{-3}\left(\frac{\epsilon^+}{\alpha^+} + \epsilon_k\right)}{1 - h + 10^{-3}\epsilon_k} \quad (9)$$

is the temporal enrichment slope, and  $\delta^*$ , the limiting isotopic composition of the water body (as  $V$  approaches zero; Gibson et al., 2016) is given by:

$$\delta^* = \frac{h\delta_A + \epsilon_k + \frac{\epsilon^+}{\alpha^+}}{h - 10^{-3}\left(\epsilon_k + \frac{\epsilon^+}{\alpha^+}\right)} \quad (10)$$

Finally, the steady-state isotopic composition,  $\delta_s$  is given by (Gonfiantini, 1986; Gat, 1996):

$$\delta_s = \frac{xm\delta^* + \delta_I}{1 + mx} \quad (11)$$

Gibson et al. (1999) points out that if we consider a class-A evaporation pan which is kept at a constant volume (by adding feed water daily) and is also subject to precipitation ( $P$ ), the value of “ $I$ ” in Eq. (8)

can be calculated as  $I = P + I_+$  and  $\delta_I = (P\delta_{Precip} + I_+\delta_+)/I$  (where  $I_+$  is the volume of feed water added, and  $\delta_+$  is the isotopic composition of the feed water). Bailing of water, after a precipitation event, to reset the volume to the constant volume will not change the isotopic composition of the pan (assuming that there was no overflow).

Parameters in this section are listed in the [Supplementary data](#) file.

## 3. Methods and data

### 3.1. Study site

The study site is located at the Australian Nuclear Science and Technology Organisation (ANSTO), at Lucas Heights (34°03'S, 150°59'E). Lucas Heights is 30 km southwest of Sydney and 18 km from the nearest coast to the east. Being at the southern edge of the Sydney metropolitan area, surface land use in the area is a mixture of suburban (mainly to the east and north) and natural bushland vegetation (mainly to the south – See [Supplementary Fig. S1](#)). The site is located on the top of a plateau. Locally the topography is complex, with changes in elevation of 150 m within 1 km of the site (Crawford et al., 2011; Chambers et al., 2011).

Local meteorological conditions are monitored every 15 min from a 50 m instrumented tower. Wind speed and wind direction are measured at 10 and 49 m above ground level (a.g.l.). For this investigation the 10 m a.g.l. measurements were used. In the cooler months of the year the wind direction is predominantly from the south-west and in the warmer month predominantly from the east. Thus in the cooler month of the year the air masses arriving at Lucas Heights have a longer overland history, whereas in the warmer months of the year there is a more recent oceanic fetch. Temperature and relative humidity from 2 m a.g.l. was used.

When using the pan method to estimate the isotopic composition of the vapour, the information required include: (1) the isotopic composition of the pan water, rainfall and feed water used to top up the pan; (2) the pan temperature, atmospheric temperature, relative humidity and the amount of rainfall and feed water added. Further, for evaluation of the method, the measured isotopic composition of the vapour (using a Fourier Transform InfraRed Spectrometer, FTIR) is used. The methods used to obtain these variables are detailed in the following sections.

### 3.2. Direct observations

Meteorological data were available from the Lucas Heights weather station operated by ANSTO. The data consisted of manual measurements of daily pan evaporation to 9 am and daily precipitation amount to 9 am (BOM Station 066078) with estimated accuracy of  $\pm 0.05$  mm, and automated measurements (BOM Station 066023) of the following: rainfall (tipping bucket rain gauge measurements) at a frequency of 15 min (greater of  $\pm 0.25$  mm or  $\pm 2\%$ ), air temperature at 2 m at a frequency of 15 min ( $\pm 0.05^\circ\text{C}$ ), relative humidity at 2 m ( $\pm 0.05$ ), and wind speed ( $\pm 0.05$  m/s) and direction ( $\pm 0.05^\circ$ ) at 10 m. For the analysis, the average hourly measurements were used.

### 3.3. Sampling

#### 3.3.1. Evaporation pan operation and sampling

The evaporation pan has the standard dimensions of a Class A pan, with 1.2 m diameter and a depth of 0.25 m deep, located on a wooden platform (Jovanovic et al., 2008).

Water from the evaporation pan of the Lucas Heights weather station has been sampled at weekly intervals for isotope analysis since October 2006, as part of an ongoing project. Potable feed water at the site has also been sampled at weekly intervals, along with precipitation collected over the same time intervals.

The evaporation pan is topped up (or bailed if necessary) at 9 am

each day with water from the local potable supply to maintain a volume depth of 170 mm. The volumes of potable water added to the pan and pan water removed from the pan were manually measured and recorded. Duplicate 30 mL samples of the pan and potable feed waters were taken for isotopic analysis at regular intervals of between six and eight days (typically seven). If pan water had significant algal growth or was noticeably turbid, the pan was emptied and cleaned, and filled to 170 mm with water from the potable supply.

In addition to the stable isotope data from the water samples, the temperature of the water was also recorded. As it was assumed that the pan water was well-mixed, a single bulk temperature measurement was taken at hourly intervals with an Odyssey Submersible Temperature Logger, suspended in the pan water. However, in this study pan water temperature was routinely measured at mid-depth rather than at the water surface. An assessment was undertaken over a 4-day period where the temperature was measured both at the surface and at the bottom of the pan. The main difference between the two temperatures was that during periods of warming, the surface temperature increased before the temperature at the bottom of the pan. The average percentage difference was 1.3% (0.35 °C) and only 64 measurements (out of the 382 measurements) had a difference of more than 2%, with the maximum difference being 7.6% (2 °C). Therefore, the overall impact of this was minor.

A weekly time step was used for the purpose of pan modelling.

### 3.3.2. Precipitation sampling

Precipitation was sampled in a collector previously described by Hughes and Crawford (2013), where precipitation was accumulated over the time interval between pan samples from the weather station. The collector consisted of a high density polyethylene (HDPE) plastic container, fitted with a plastic funnel and venting tube. Similar to the simple collector described by Gröning et al. (2012), the collector featured a submerged tube that connects the tip of the funnel directly to the bottom of the collection container to prevent evaporation of the sample and exchange with ambient vapour. A 5 m long venting tube allows the air pressure in the bottle to equilibrate with outside atmospheric pressure while reducing the risk of diffusion.

This collection method was found to be comparable to collection in a container with a 1 cm layer of paraffin oil for events greater than 2 mm, and better than composite samples from daily rain gauge samples (Hughes and Crawford 2013). However it was noted that enrichment of samples could occur for precipitation volumes less than 5 mm depending on temperature and the time between precipitation and sample collection.

Several time intervals consisted of composite precipitation samples as significant forecast precipitation necessitated the early change-over of the precipitation collector in case of overflow.

### 3.3.3. Atmospheric vapour isotopes

A low-resolution Fourier Transform InfraRed (FTIR) spectrometer deployed at the Lucas Heights weather station was used to collect in-situ measurements of  $\delta^2\text{H}$  in ambient vapour. The instrumentation used was similar to that described by Haverd et al. (2011). During the monitoring periods, the FTIR sampled air through heated sampling lines from a height of 10 m. The FTIR collects spectra continuously at a rate of approximately 2 Hz, however, at this sampling rate the precision of the measurements was very poor. Averaging scans over 1 h produced a measurement precision (1 $\sigma$ ) of < 0.5‰ at mixing ratios between 5000 and 30000 ppm.

For comparison with pan-derived  $\delta_A$ , mean FTIR measured vapour was compiled for the same time steps used in the evaporation pan modelling. However, as there were a number of gaps in the measured  $\delta^2\text{H}_{\text{A,FTIR}}$ , for comparison purposes the average of the available FTIR data in each period was used. A test was also undertaken where if less than 24 measurements were missing; linear interpolation was used to fill the gaps, following which the average of the interpolated and

available FTIR data in each period was used. This resulted in no improvement of the results; hence the data without the interpolation is used in the remainder of the document. Further, the percentage of time for which the  $\delta^2\text{H}_{\text{A,FTIR}}$  values were available was calculated (Supplementary data file column E) and analysis was carried out, and once again the percentage of time for which the FTIR data was available had no significant impact on the results.

Comparing FTIR data at an elevation of 10 m with ground level pan-derived  $\delta_A$  can be justified by reference to Radon-222 measurements available at 2 m and 50 m above surface level at the site (Chambers et al., 2011). Radon-222 is a naturally occurring radioactive gas emitted from soil/rocks, and provides a measure of the extent of vertical mixing. At Lucas Heights, Radon-222 measurements indicate strong vertical mixing between 10 am and 6 pm, corresponding to the period of the largest evaporation rates (Parlange and Katul, 1992). Hence it is expected that the vertical gradient of the isotopic composition of the vapour will not be significant, due to the significant vertical mixing.

Direct measurements of  $\delta^2\text{H}$  of ambient vapour were only available between June 2009 and October 2010, hence this is the period used for this analysis. A more detailed description of the operation of the FTIR can be found in Griffith et al. (2006). In this application calibration was undertaken by vaporising liquid water of known isotopic composition (with varying mixing ratios) and then analysing it using the FTIR. At the time of this study spectral interference for  $^{18}\text{O}$  on the relatively low resolution FTIR resulted in an unacceptable level of uncertainty for  $\delta^{18}\text{O}$ .

### 3.4. Laboratory analysis

$\delta^2\text{H}$  and  $\delta^{18}\text{O}$  were determined for 184 samples of pan water, precipitation and feed water collected at weekly intervals. Results are expressed in per mille (‰) and reported relative to VSMOW. Isotope analyses were conducted at the ANSTO Environmental Isotope Laboratories (N = 169) and the Alberta Research Council (N = 15).

At the Alberta Research Council laboratory (ARC), samples were analysed using a Delta V Advantage dual-inlet mass spectrometer with an HDevice peripheral for  $\delta^2\text{H}$ , and a GasBench II peripheral for  $\delta^{18}\text{O}$ . At ANSTO, samples were analysed using a Picarro L1115-i Cavity Ring-Down Spectroscopy (CRDS) method.

In-house standards, established by runs with VSMOW2 and SLAP2 at ANSTO (AILS-001:  $\delta^2\text{H} = +32.5\text{‰}$ ,  $\delta^{18}\text{O} = +7.47\text{‰}$ ; AILS-004:  $\delta^2\text{H} = -174.0\text{‰}$ ,  $\delta^{18}\text{O} = -22.19\text{‰}$ ) and ARC (Std1:  $\delta^2\text{H} = +17.4\text{‰}$ ,  $\delta^{18}\text{O} = +4.69\text{‰}$ ; Std2:  $\delta^2\text{H} = -170.8\text{‰}$ ,  $\delta^{18}\text{O} = -22.41\text{‰}$ ), were run as samples to allow the results to properly be reported vs VSMOW (Nelson, 2000). Results are accurate to  $\pm 1\text{‰}$  for  $\delta^2\text{H}$  and  $\pm 0.2\text{‰}$  for  $\delta^{18}\text{O}$  for ARC and  $\pm 1.0\text{‰}$  for  $\delta^2\text{H}$  and  $\pm 0.15\text{‰}$  for  $\delta^{18}\text{O}$  for ANSTO. The data are reported relative to VSMOW on scales normalized such that  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  values of SLAP are  $-55.5$  and  $-428\text{‰}$  relative to VSMOW.

Data were checked for outliers and as a result two feedwater data points were rejected; because feedwater isotope composition varies slowly over time, the composition was estimated by interpolation.

### 3.5. Data combined to determine an evaporation pan-derived $\delta_A$

In this study, a constant volume pan was used for the determination of  $\delta_A$ . Given atmospheric temperature and humidity, pan temperature, precipitation amount, feed water amount, and the isotopic compositions of the feed water, precipitation and water body, the value of  $\delta_A$  can be determined by nonlinear least squares methods where the difference between the measured  $\delta_L$  and that predicted by Eq. (8) (Section 2.2) is minimised.

The meteorological variables were available on an hourly basis, whereas pan evaporation amount was available on daily basis and the isotopic composition of pan water, feed water and precipitation were available on weekly basis. As a result a weekly time step was used in Eq.

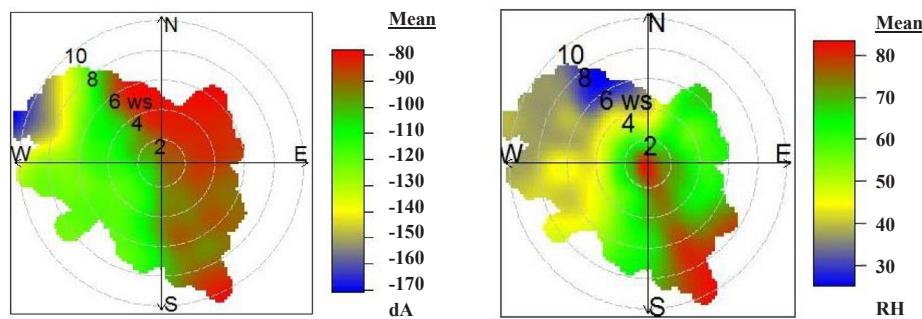


Fig. 1. Distribution of vapour  $\delta^2\text{H}_{\text{A\_FTIR}}$  (left) and relative humidity (right) with wind speed (labelled concentric circles) and direction.

(8) for the determination of  $\delta_A$  using the arithmetic average values of the meteorological variables.

#### 4. Results and discussion

This results and discussion section compares the results of three different methods of estimating the isotopic composition of atmospheric water vapour over 16 months:

- direct measurements of  $\delta^2\text{H}$  by Fourier Transform Infrared Spectrometer ( $\delta^2\text{H}_{\text{A\_FTIR}}$ );
- estimates of  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  using the pan method ( $\delta^2\text{H}_{\text{A\_pan}}$ ,  $\delta^{18}\text{O}_{\text{A\_pan}}$ );
- estimates of  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  using precipitation equilibrium ( $\delta^2\text{H}_{\text{A\_precip}}$ ,  $\delta^{18}\text{O}_{\text{A\_precip}}$ ).

##### 4.1. Measured $\delta^2\text{H}$ of vapour

Measured  $\delta^2\text{H}$  in the vapour ( $\delta^2\text{H}_{\text{A\_FTIR}}$ ) ranged between  $-199.71$  and  $-47.20\text{‰}$ , and systematic variations with wind speed and direction were noted (Fig. 1-left). Overall, more negative values of  $\delta^2\text{H}$  in vapour occurred when the wind direction was from the northwest, especially at higher wind speeds. This pattern is interpreted to arise in situations where the air mass has travelled long distances over the continent and undergone significant rainout, as well as addition of moisture derived from evaporative recycling. These air masses typically show lower atmospheric relative humidity (Fig. 1-right). In contrast, air masses arriving from the northeast and southeast, along fetches characterized by more recent oceanic passage, tend to have higher relative humidity and typically have higher  $\delta^2\text{H}$ . Analysis of seasonal trends in wind speed and direction at the study site (Fig. 2) reveal that westerly wind setup is more common during May to August (late autumn/winter), leading to more negative values of  $\delta^2\text{H}$  in precipitation and atmospheric moisture at this time.

Consistent with the findings of Lee et al. (2006), seasonal isotopic variations (Fig. 3a) were more pronounced than diurnal variations (Fig. 3b) including both summer (Fig. 3c) and winter periods (Fig. 3d). Little diurnal variation was observed at this site; a similar trend was also observed by Cai et al. (2015) which was attributed to low impact of atmospheric vapour from local evapotranspiration on the isotopic composition.

#### 4.2. Derived $\delta^2\text{H}$ and $\delta^{18}\text{O}$ of vapour

##### 4.2.1. Arithmetic averages

The statistics for the  $\delta_A$  estimates using the three methods (measured using the FTIR, and derived using the pan and equilibrium with precipitation) are presented in Table 1. A high degree of correlation was seen between  $\delta^2\text{H}_{\text{A\_pan}}$  and  $\delta^{18}\text{O}_{\text{A\_pan}}$  ( $r = 0.93$ , P-value of 0.00). This correlation is higher than that reported by Gibson et al. (1999; with  $r > 0.60$ ) and Devi et al. (2015; with  $r > 0.66$ ). Precipitation-derived

$\delta^2\text{H}$  values of atmospheric moisture ( $\delta^2\text{H}_{\text{A\_precip}}$ ) ranged between  $-158.7$  and  $-64.2\text{‰}$ , and the  $\delta^{18}\text{O}_{\text{A\_precip}}$  values ranged between  $-21.26$  and  $-9.82\text{‰}$ , with an  $r$  value of 0.94. The lowest values of  $\delta^2\text{H}_{\text{A\_precip}}$  corresponded to a 9 mm precipitation event that will be discussed later on.

Fig. 4 presents the bi-variate plots of  $\delta^2\text{H}$  versus  $\delta^{18}\text{O}$  for the measured isotopic values of precipitation ( $\delta_{\text{precip}}$ ) and the pan water ( $\delta_L$ ), as well as the estimated isotopic values of atmospheric moisture ( $\delta_{\text{A\_precip}}$  and  $\delta_{\text{A\_pan}}$ ). The local meteoric water line (LMWL) is also shown ( $\delta^2\text{H} = 7.84\delta^{18}\text{O} + 14$ ;  $r^2 = 0.94$ ) which is derived using the weekly precipitation isotopic values collected over the period of this study. This is close to the LMWL developed by Hughes and Crawford (2013;  $\delta^2\text{H} = 7.74\delta^{18}\text{O} + 13.6$ ). The isotopic composition of the pan water ( $\delta_L$ ) plots on an evaporation line (LEL) of reduced slope ( $\delta^2\text{H} = 4.64\delta^{18}\text{O} + 0.42$ ;  $r^2 = 0.97$ ), consistent with previous surface water studies in the region (i.e. Gibson et al. 2008b; Meredith et al., 2009). The precipitation-equilibrium estimates of atmospheric vapour ( $\delta_{\text{A\_precip}}$ ) plot on or slightly below the LMWL, whereas the  $\delta_{\text{A\_pan}}$  values are scattered more evenly around the LMWL on a line with a lower slope (4.11, which is close to the LEL). This was also found in previous studies (e.g. Gibson et al., 1999; Devi et al., 2015). This is likely due to use of relative humidity at 2 m height rather than directly above the evaporation pan (as detailed in section 4.5; relative humidity has a significant impact on the determined  $\delta_{\text{A\_pan}}$  values).

##### 4.2.2. Evaporation-flux-weighted $\delta^2\text{H}_{\text{A\_FTIR}}$ values

Given that daily pan evaporation rates were available; we compare the  $\delta_{\text{A\_pan}}$  values on a weekly basis against the weekly evaporation-flux-weighted  $\delta^2\text{H}_{\text{A\_FTIR}}$  values. This was achieved by first obtaining a daily arithmetic average value of  $\delta^2\text{H}_{\text{A\_FTIR}}$  and then converting this to a weekly evaporation-flux-weighted  $\delta^2\text{H}_{\text{A\_FTIR}}$  value by using the daily measured pan evaporation rates. The correlation between  $\delta^2\text{H}_{\text{A\_pan}}$  and the evaporation-flux-weighted  $\delta^2\text{H}_{\text{A\_FTIR}}$  values ( $r = 0.68$ ) was marginally lower than that for arithmetic averages shown in Fig. 5. The largest difference occurred between the following dates, 29/09/2009–06/10/2009 (24.9‰), 15/12/2009–22/12/2009 (23.0‰) and 20/07/2010–27/07/2010 (22.7‰), where 92%, 66% and 95% of the  $\delta^2\text{H}_{\text{A\_FTIR}}$  data was available. In these three cases the difference between  $\delta^2\text{H}_{\text{A\_FTIR}}$  and  $\delta^2\text{H}_{\text{A\_precip}}$  were low (9.0, 4.3 and 1.5‰, respectively). For these periods there were 43, 9 and 15 h during which rainfall occurred. The rainfall duration explains the difference for the first case; however the difference for the middle case could well be due to the lower percentage of the  $\delta^2\text{H}_{\text{A\_FTIR}}$  available data. During the period of missing data a large proportion of the wind was from the south-east sector, as opposed to predominantly from the north-east sector during the period of available data. As seen in Fig. 1, a large variation in  $\delta^2\text{H}_{\text{A\_FTIR}}$  can be seen between these quadrants mainly due to the distance from the site to the nearest ocean in each direction; larger values in the north-east quadrant and more variable and lower values in the south-east quadrant. For this period the  $\delta^2\text{H}_{\text{A\_pan}}$  value was  $-104.2\text{‰}$  as opposed to  $-81.6\text{‰}$  for the evaporation-flux-

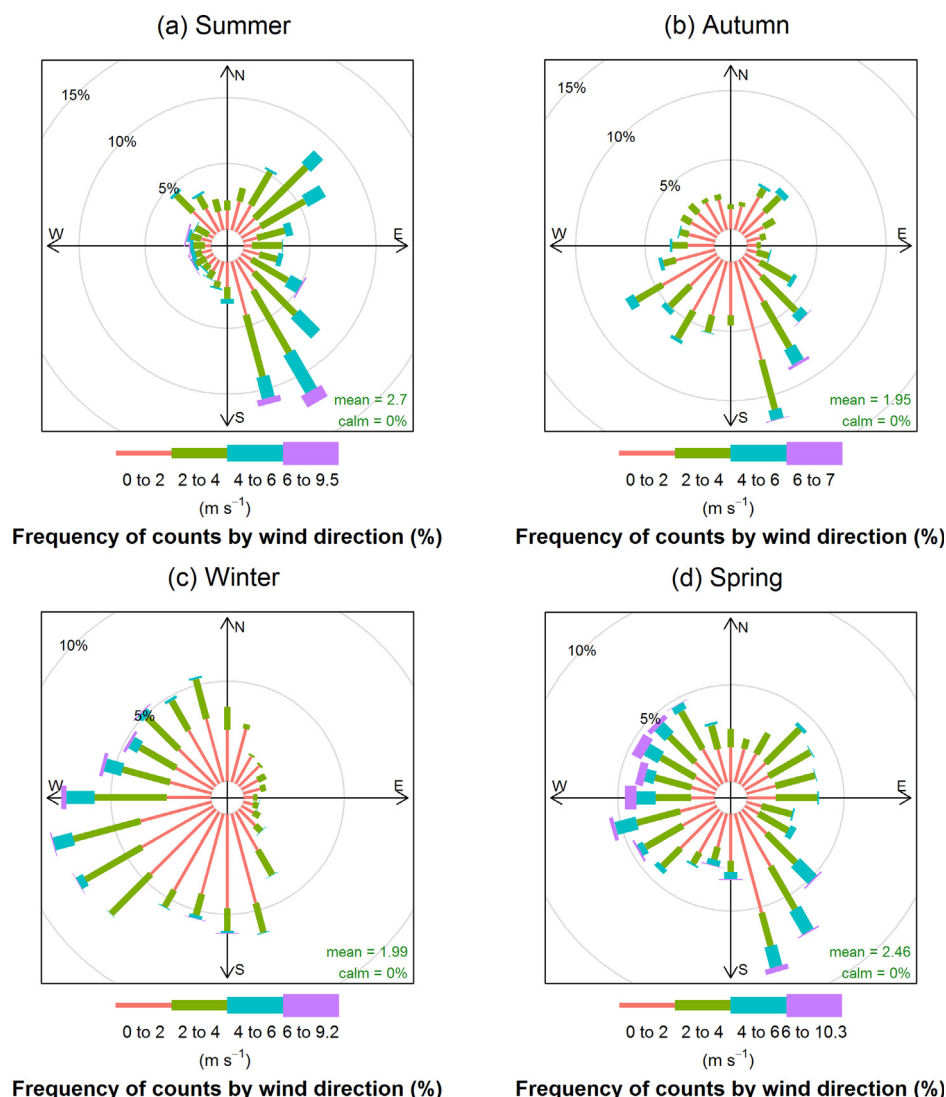


Fig. 2. Wind roses for Lucas Heights by time of year (summer D-J-F, autumn M-A-M, winter J-J-A, and spring S-O-N), for the period of this study.

weighted  $\delta^2\text{H}_{\text{A-FTIR}}$  value. For the last period rainfall had occurred on four out of the seven days, which could explain the reason for  $\delta^2\text{H}_{\text{A-FTIR}}$  being closer to  $\delta^2\text{H}_{\text{A-precip}}$  than  $\delta^2\text{H}_{\text{A-pan}}$ .

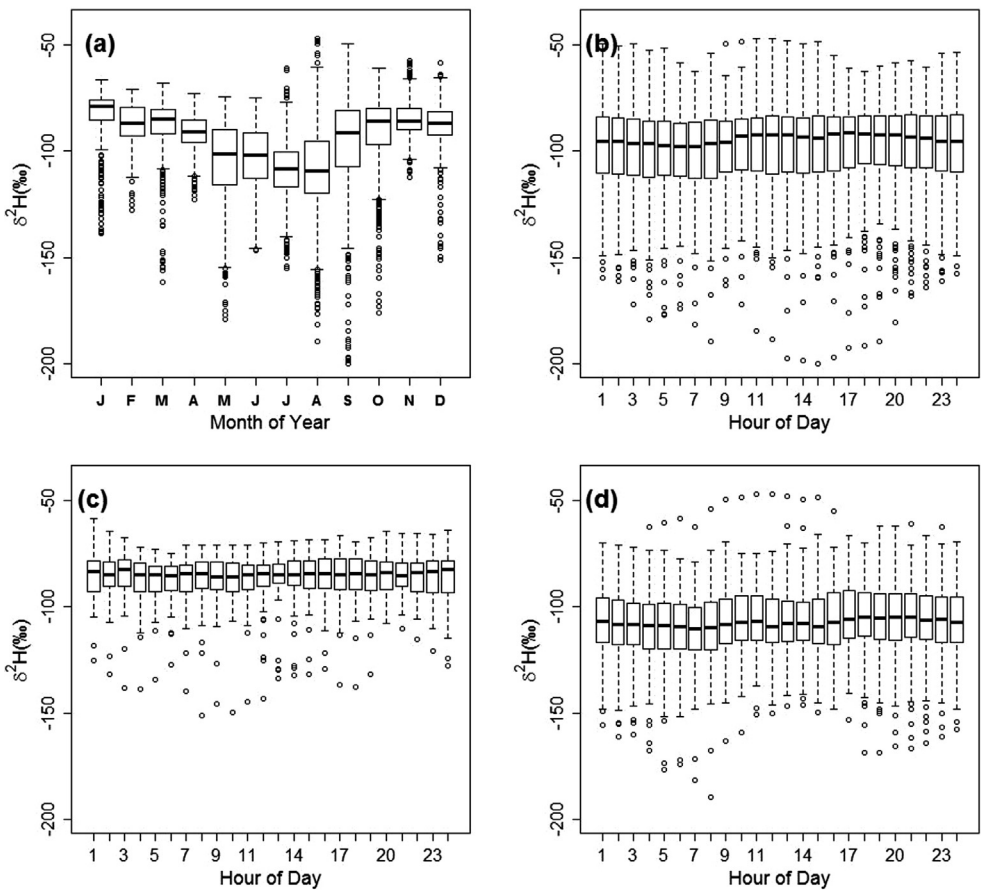
While the evaporation rate can vary on diurnal scales (given that for instance the relative humidity and temperature exhibit diurnal variations; see [Supplementary Fig. S2 a and b](#)), from [Fig. 3](#), the diurnal variation of  $\delta^2\text{H}_{\text{A-FTIR}}$  is low. This can also be seen in [Supplementary Fig. S2c](#), where small variations in the hourly average values are only seen for winter. This is an indication that the pan-derived estimations will not vary significantly if hourly evaporation rates were considered.

#### 4.3. Difference between measured and pan-derived $\delta^2\text{H}$ of vapour

When pan-derived ( $\delta^2\text{H}_{\text{A-pan}}$ ) and FTIR measured ( $\delta^2\text{H}_{\text{A-FTIR}}$ ) values of atmospheric moisture were compared, a significant correlation was seen ( $r = 0.7$ ,  $P\text{-value} = 0.00$ ; [Fig. 5a](#)).  $\delta^2\text{H}_{\text{A-pan}}$  varied between  $-121.7$  and  $-70.5\text{‰}$ , whereas average FTIR measurements over the same period varied between  $-123.3$  and  $-78.6\text{‰}$ . The difference ( $\delta^2\text{H}_{\text{A-pan}} - \delta^2\text{H}_{\text{A-FTIR}}$ ) spanned a range from  $-25.0$  to  $20.4\text{‰}$ , with a mean absolute difference of  $8.0\text{‰}$ . These results show a smaller difference between measured and estimated values than was reported in [Devi et al. \(2015\)](#). A more interesting result was that the  $\delta^2\text{H}_{\text{A-FTIR}}$  values were not consistently higher than the  $\delta^2\text{H}_{\text{A-pan}}$  values (as found in [Devi et al., 2015](#)); in fact the differences were almost evenly

distributed on either side of zero (with 33 weeks having a difference of less than zero and 30 weeks having a difference greater than zero). However, in [Devi et al. \(2015\)](#) the vapour trap measurements were carried out between 9:30 am and 3:30 pm, whereas in this study continuous hourly values of  $\delta^2\text{H}_{\text{A-FTIR}}$  were available and the value used for the comparison was the average over the period covering the pan calculation. For the current study site marginally higher values of  $\delta^2\text{H}_{\text{A-FTIR}}$  were seen in the daily measurement time-window used by [Devi et al. \(2015; Fig. 3a\)](#), which may account for some of this difference. Also, [Devi et al. \(2015\)](#) used daily calculations, whereas in this case weekly calculations were used, which might smooth out the results.

Humidity, rather than temperature, wind speed, or wind direction, was found to be the dominant control on the degree of match between  $\delta^2\text{H}_{\text{A-pan}}$  and  $\delta^2\text{H}_{\text{A-FTIR}}$ . Higher differences were seen at low and high relative humidity. When the relative humidity was above 85%,  $\delta^2\text{H}_{\text{A-pan}}$  was higher by more than 9‰ than  $\delta^2\text{H}_{\text{A-FTIR}}$  for seven cases and was lower only for two cases. This is consistent with reports by [Kumar and Nachiappan \(1999\)](#) who noted high uncertainty in the estimation of isotopic composition of evaporating moisture for relative humidity above 75%. Correlation between relative humidity and  $\delta^2\text{H}_{\text{A-pan}} - \delta^2\text{H}_{\text{A-FTIR}}$  was weak but significant ( $r = 0.32$ ;  $p\text{-value} = 0.01$ ). A correlation was seen between the difference and the standard deviation of either the air temperature or pan temperature



**Fig. 3.** Box plots showing distribution of  $\delta^2\text{H}$  in vapour at the Lucas Heights study site: (a) monthly, (b) diurnally all year and diurnally for (c) summer and (d) winter. Boxes represent the 25th and 75th percentiles, the median is represented by the line through the box, whiskers represent the 10th and 90th percentiles and the outlier events are also indicated.

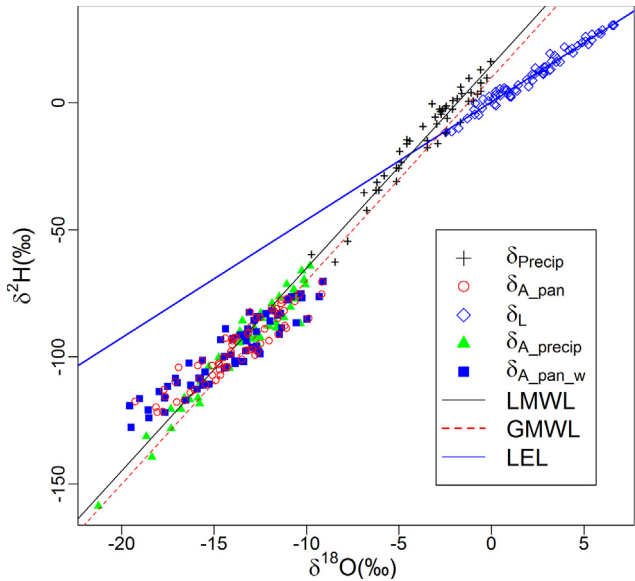
**Table 1**  
Statistics of  $\delta_A$  values (for  $\delta^2\text{H}$  in ‰) as measured by the FTIR and as derived by the pan method and equilibration with precipitation.

|                                         | Min    | Max   | Average | Standard Deviation |
|-----------------------------------------|--------|-------|---------|--------------------|
| $\delta^2\text{H}_{A\text{-FTIR}}$      | −123.3 | −78.6 | −97.2   | 12.3               |
| $\delta^2\text{H}_{A\text{-pan}}$       | −121.7 | −70.5 | −96.7   | 13.0               |
| $\delta^2\text{H}_{A\text{-precip}}$    | −158.7 | −64.2 | −95.8   | 20.1               |
| $\delta^{18}\text{O}_{A\text{-pan}}$    | −19.26 | −9.16 | −13.78  | 2.32               |
| $\delta^{18}\text{O}_{A\text{-precip}}$ | −21.26 | −9.82 | −13.49  | 2.60               |

( $r = -0.39$ ;  $p\text{-value} = 0.01$ ), which reflects the diurnal range. No significant relationship was seen between the rainfall amount and  $\delta^2\text{H}_{A\text{-pan}} - \delta^2\text{H}_{A\text{-FTIR}}$ .

The assumption of the Craig-Gordon model that there is no divergence, is not fully met for a pan, particularly under low humidity, when there is effectively a larger sink (and higher evaporation) as evaporating pan moisture disperses into the air. In addition, in this study wind speed was higher under lower humidity which would increase this effect. Under lower humidity conditions, the net effect would be for the pan method to estimate lower  $\delta_A$  values in comparison to those measured with the FTIR.

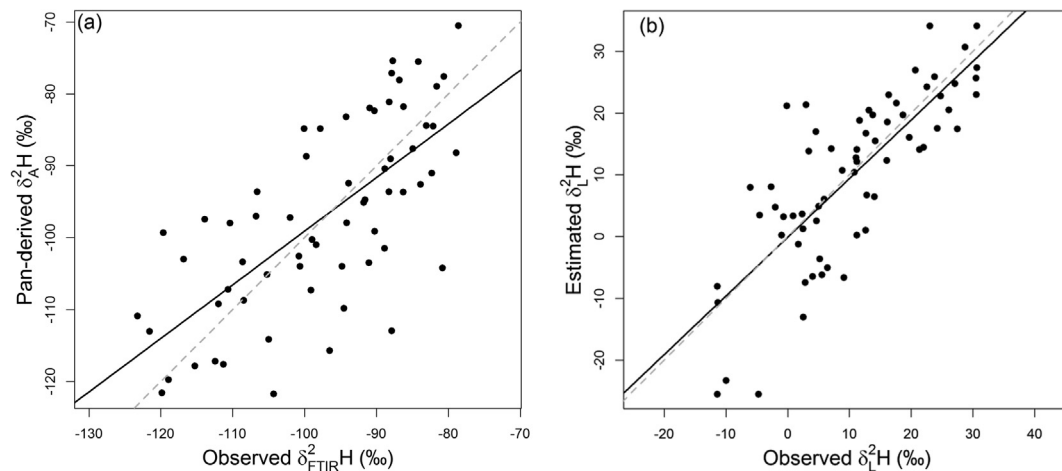
Conversely for high humidity the measured wind speed was lower and the evaporation rate was probably more consistently low, due to both less diurnal fluctuation in temperature; (i.e low temperature standard deviation), and lower humidity gradient between pan and air. For the equilibrium component this should cause no concern but instead the assumption of turbulent flow underpinning the choice of  $n$  for kinetic fractionation (Eq. (2)) may need to be adjusted – should it be more laminar and could this be parameterised as a function of humidity and wind speed for the pan model? This was tested by replacing  $n$  in Eq. (2) from 0.5 to 1 which resulted in a small improvement in the



**Fig. 4.** Plot of  $\delta^2\text{H}$  versus  $\delta^{18}\text{O}$  for the various compositions; the measured isotopic composition of pan water ( $\delta_L$ ) and precipitation ( $\delta_{\text{precip}}$ ) and the estimated values of atmospheric vapour ( $\delta_{A\text{-precip}}$ ,  $\delta_{A\text{-pan}}$  when using the arithmetic mean and  $\delta_{A\text{-pan}_w}$  when using the evaporation weighted mean values).

estimated  $\delta^2\text{H}_{A\text{-pan}}$ , with the difference ( $\delta^2\text{H}_{A\text{-pan}} - \delta^2\text{H}_{A\text{-FTIR}}$ ), when the relative humidity was above 80%, reducing to 9.8, 9.8, 13.8 and 12.1 from 10.3, 11.7, 14.6 and 12.4, respectively, when a value of 0.5 was used for  $n$ .

A further test was undertaken, where Eqs. (8)–(11) were used to determine the  $\delta^2\text{H}$  values of the pan water at the end of each week using



**Fig. 5.** (a) Pan-derived  $\delta^2\text{H}_{\text{A-pan}}$  versus average  $\delta^2\text{H}_{\text{A-FTIR}}$  for the same time interval. The solid line presents the trend line for the correlation of the values (with a slope of  $0.74 \pm 0.1$ , an intercept of  $-24.5 \pm 9.7$  and  $r = 0.69$ ) and the dashed line is the 1:1 line. (b) Estimated versus measured  $\delta^2\text{H}$  for the pan water. The solid line presents the trend line for the correlation of the values (with a slope of  $0.95 \pm 0.1$ , an intercept of  $-0.11 \pm 1.4$  and  $r = 0.79$ ) and the dashed line is the 1:1 line. The fitted lines are not statistically different to the 1:1 line.

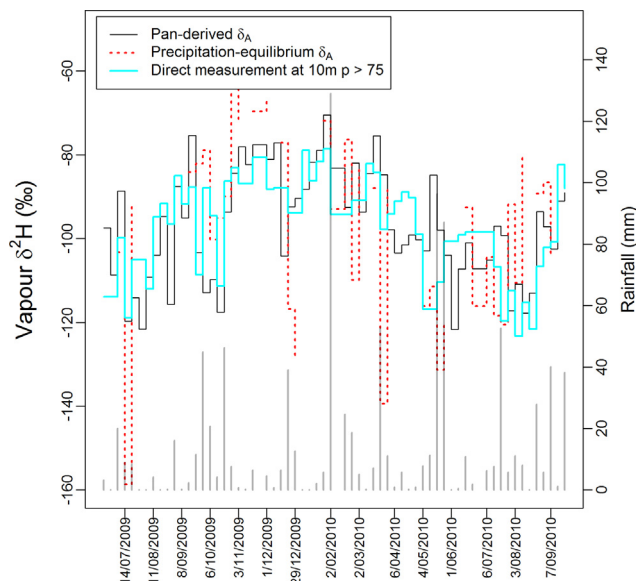
the measured  $\delta^2\text{H}_{\text{A-FTIR}}$  value for  $\delta_{\text{A}}$  in Eq. (10). The correlation coefficient between the measured and estimated  $\delta^2\text{H}$  values of the pan water was  $r = 0.76$ , P-value of 0.00 (Fig. 5b) with the largest differences, occurring under higher relative humidity. A strong and significant correlation ( $r = 0.99$ ) was seen between the differences of the measurements and estimates for  $\delta^2\text{H}$  values of pan water ( $\delta_{\text{L}} - \delta_{\text{L-estimated}}$ ) and  $\delta^2\text{H}$  values of atmospheric vapour ( $\delta^2\text{H}_{\text{A-pan}} - \delta^2\text{H}_{\text{A-FTIR}}$ ).

#### 4.4. Difference between measured and precipitation derived $\delta^2\text{H}$ of vapour

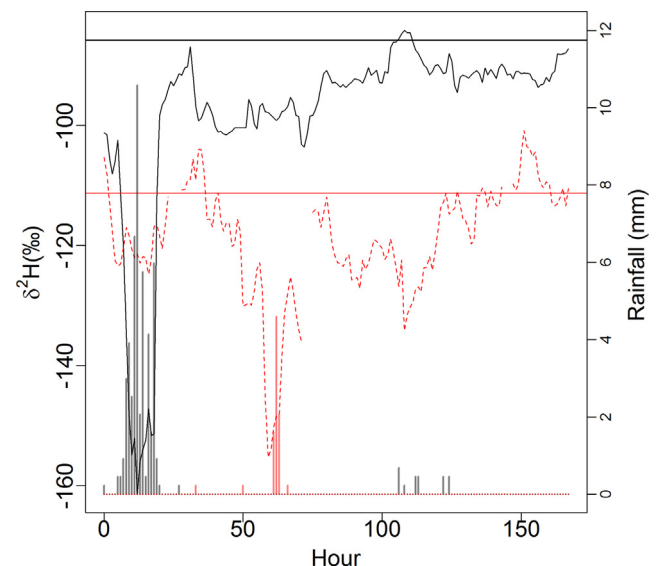
Precipitation-equilibrium estimates of the isotopic composition of the atmospheric vapour ( $\delta^2\text{H}_{\text{A-precip}}$ ) are more poorly correlated with  $\delta^2\text{H}_{\text{A-FTIR}}$  overall ( $r = 0.58$ , P-value = 0.00), than  $\delta^2\text{H}_{\text{A-pan}}$  is, due to a marked difference for a number of time intervals (Fig. 6). This difference was the largest for periods when less precipitation was recorded. However, these differences are considered to be predominantly due to the seven-day averaging time used in the calculations. The first interval with a large discrepancy between  $\delta^2\text{H}_{\text{A-precip}}$  and  $\delta^2\text{H}_{\text{A-FTIR}}$  was noted for the seven days ending on 21 July 2009. Average  $\delta^2\text{H}_{\text{A-FTIR}}$  for that

period was  $-119.2\text{‰}$  whereas the estimated  $\delta^2\text{H}_{\text{A-precip}}$  value was  $-158.7\text{‰}$ , a difference of  $39.5\text{‰}$ . The precipitation occurred over a six hour period on 17 July 2009, and had an  $\delta^2\text{H}$  value of  $-74.9\text{‰}$ . Over this period, the average  $\delta^2\text{H}_{\text{A-FTIR}}$  value was  $-140.7\text{‰}$ , which is closer to the estimated  $\delta^2\text{H}_{\text{A-precip}}$ . Thus, the precipitation derived isotopic composition of atmospheric vapour was more representative of conditions during the precipitation event than during the entire week.

For a second seven-day period ending on 6 April 2010,  $\delta^2\text{H}_{\text{A-precip}}$  was estimated to be  $-139.4\text{‰}$  while the seven-day average measured  $\delta^2\text{H}_{\text{A-FTIR}}$  was  $-97.9\text{‰}$ , however during the precipitation event the average measured  $\delta^2\text{H}_{\text{A-FTIR}}$  was  $-140.4\text{‰}$ , very close to the estimated value. This demonstrates that using the assumption that the isotopic composition of the atmospheric vapour is in equilibrium with the isotopic composition of precipitation is not valid after some time has passed since the end of the precipitation event. This is clearly demonstrated in Fig. 7, where prior to the precipitation event the measured



**Fig. 6.** Time series of  $\delta^2\text{H}_{\text{A-pan}}$ ,  $\delta^2\text{H}_{\text{A-FTIR}}$ , and  $\delta^2\text{H}_{\text{A-precip}}$ . The grey vertical bars represent the rainfall amount (mm).



**Fig. 7.** Hourly FTIR measured  $\delta^2\text{H}$  of atmospheric vapour over a seven day period ending on 6th of April 2010 (black) and ending on the 21st of July 2009 (red dashed). The straight horizontal lines of the corresponding colour represent the pan-derived values. Rainfall amount is shown as vertical bars with the corresponding colour. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

$\delta^2\text{H}_{\text{A-FTIR}}$  value was around  $-100.0\text{‰}$ , during the precipitation event the value went down to less than  $-150.0\text{‰}$ , and after the precipitation event it returned to above  $-100.0\text{‰}$ . Inspection of the  $\delta^2\text{H}_{\text{A-FTIR}}$  hourly time series shows that where precipitation leads to a distinct change in the  $\delta^2\text{H}_{\text{A-FTIR}}$ , this change generally only persists for a period of 6–36 h before the atmospheric vapour returns to a similar composition to that seen before the precipitation event.

While equilibrium with precipitation appears to accurately capture conditions during precipitation periods, it may be less appropriate than evaporation pans for predicting conditions over longer periods, especially during drier conditions. We find pan-derived  $\delta_{\text{A}}$  to be closer to measured values using FTIR over weekly periods. Due to the intrinsic temporal/flux weighting of pans, they appear to provide more representative records for nearby evaporation studies. In addition, at this study site, precipitation had occurred for only 7.6% of the study period and precipitation was above 5 mm/h for only 0.4% of the study period (on an hourly basis). This is an additional indication of the benefit of the pan-derived method.

#### 4.5. Sensitivity analysis to determine most important parameters

To determine which parameters are most significant in the determination of  $\delta^2\text{H}_{\text{A-pan}}$  and  $\delta^{18}\text{O}_{\text{A-pan}}$ , a sensitivity analysis was carried out by perturbing each measured value of the parameters by 10% (one parameter at a time). Following this the root-mean-square error (RMSE) between the pan-derived isotopic composition of atmospheric vapour as determined by the base case and the perturbed case was determined (where the measured values of the parameters were used in the base case). From the results in Table 2, it can be inferred that the most important parameter is relative humidity, followed by air temperature and pan temperature. An increase in relative humidity results in a higher estimate of both  $\delta^2\text{H}_{\text{A-pan}}$  and  $\delta^{18}\text{O}_{\text{A-pan}}$  values (and vice versa). On the other hand an increase in air temperature, which would result in lower relative humidity (under conditions of no change in specific humidity), results in lower estimates of both  $\delta^2\text{H}_{\text{A-pan}}$  and  $\delta^{18}\text{O}_{\text{A-pan}}$  values (and vice versa). The influence on the  $\delta^{18}\text{O}_{\text{A-pan}}$  values is proportionally greater than that on  $\delta^2\text{H}_{\text{A-pan}}$  values due to differences in the equilibrium vapour pressure of the two heavy isotopologues.

The importance of relative humidity in the Craig-Gordon model has previously been identified in a study by Kumar and Nachiappan (1999), where errors in the measured parameters were propagated to the estimate. They concluded that an error in the relative humidity would

**Table 2**

Root-mean-square errors of the pan-derived isotopic composition of atmospheric moisture between the base case and when each parameter was perturbed, in turn, by 10% (left) and then a more likely error on the right.

| 10% perturbation                                         |                                   |                                      | Likely Errors              |                                   |                                      |
|----------------------------------------------------------|-----------------------------------|--------------------------------------|----------------------------|-----------------------------------|--------------------------------------|
| Parameter                                                | RMSE<br>$\delta^2\text{H}$<br>(‰) | RMSE<br>$\delta^{18}\text{O}$<br>(‰) | Parameter                  | RMSE<br>$\delta^2\text{H}$<br>(‰) | RMSE<br>$\delta^{18}\text{O}$<br>(‰) |
| <i>Isotopic composition</i>                              |                                   |                                      |                            |                                   |                                      |
| $\delta^2\text{H}$ (1‰) and $\delta^{18}\text{O}$ (0.2‰) |                                   |                                      |                            |                                   |                                      |
| Pan water                                                | 1.44                              | 0.33                                 | Pan water                  | 1.15                              | 0.25                                 |
| Feed water                                               | 0.26                              | 0.06                                 | Feed water                 | 0.23                              | 0.05                                 |
| Precipitation                                            | 0.25                              | 0.05                                 | Precipitation              | 0.1                               | 0.02                                 |
| <i>Meteorological variables</i>                          |                                   |                                      |                            |                                   |                                      |
| Air Temp                                                 | 7.49                              | 1.89                                 | Air Temp (1 °C)            | 6.04                              | 1.51                                 |
| Pan Temp                                                 | 5.53                              | 1.7                                  | Pan Temp (1 °C)            | 5.23                              | 1.56                                 |
| RH                                                       | 8.51                              | 2.12                                 | RH (5%)                    | 6.57                              | 1.64                                 |
| <i>Pan volume</i>                                        |                                   |                                      |                            |                                   |                                      |
| Added                                                    | 0.1                               | 0.02                                 | Added (3 mm/week)          | 0.24                              | 0.04                                 |
| Precipitation                                            | 0.1                               | 0.01                                 | Precipitation (1 mm/event) | 0.56                              | 0.07                                 |
| Depth                                                    | 0.07                              | 0.01                                 | Depth (5 mm)               | 0.02                              | 0                                    |

result in errors in the estimated isotopic composition of the evaporating moisture. Furthermore, errors in the other parameters were more significant for relative humidity above 80%.

When only the isotopic composition of pan water, feed water and precipitation was considered, the isotopic composition of the pan water was the most important parameter, consistent with the finding of Vallet-Coulomb et al. (2010). Vallet-Coulomb et al. (2010) undertook sensitivity studies based on the accuracy of measurements of various parameters in the Craig-Gordon model. They found that the uncertainty in the measurement of the isotopic composition of the pan water was the most important and that the uncertainty in the estimation of the isotopic composition of the evaporating vapour was higher than the error in the estimation of the isotopic composition of atmospheric vapour (i.e.  $\delta_{\text{A}}$ ). Further, the importance of the relative humidity was also stressed, and diurnal variation in the relative humidity was a potential source of uncertainty.

When sensitivity to errors relating to measurement uncertainty are considered (Table 2: right) smaller errors are expected, aside from the amount of water added to the pan. However, these errors are still an order of magnitude smaller than the errors due to uncertainty in the meteorological variables.

#### 5. Conclusions

The isotopic composition of atmospheric vapour has been determined by using two methods: (1) the pan method and (2) equilibrium with local precipitation, and compared against measurements using the FTIR. A complication in the pan-derived  $\delta_{\text{A}}$  estimation procedure was that the pan isotopic composition was available on weekly time scales, the evaporation rate was available on daily time scales and the atmospheric variables were available on hourly time scales. As the weekly time scale had to be used for the pan calculations, in one set of estimates the arithmetic averages of the atmospheric variables were used. In this case good agreement was seen between the pan derived and the FTIR measured  $\delta^2\text{H}_{\text{A}}$ . The difference between pan derived and FTIR measured  $\delta^2\text{H}_{\text{A}}$  ranged from  $-25.0$  to  $20.4\text{‰}$  with the mean of the absolute difference being  $8.0\text{‰}$ . The cost of deployment of instruments such as the FTIR and their continuous maintenance is higher, while evaporation pans are more robust and require less maintenance.

While the precipitation-equilibrium approach produces good results close to the precipitation event, if average values are required over a longer period, the pan-derived isotopic composition of atmospheric vapour was closer to the average of the measured values over the same period. This means that because the pan method enables  $\delta_{\text{A}}$  to be estimated regardless of whether precipitation has occurred, it can provide a far more accurate continuous dataset than can be achieved using precipitation equilibrium, and at far less cost than continuous measurements. In addition at this study site precipitation had occurred for only 7.6% of the study period which is an additional indication of the benefit of the pan method.

Potential users of the pan method need to ensure accurate measurements of the atmospheric relative humidity and the isotopic composition of the pan water, and need to take caution with results for relative humidity above 80%.

#### Declaration of Competing Interest

None.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jhydrol.2019.06.056>.

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