An evaluation of materials and methods for vapour measurement of the isotopic composition of pore water in deep, unsaturated zones

Dyan L. Pratt, Mengna Lu, S. Lee Barbour & M. Jim Hendry

To cite this article: Dyan L. Pratt, Mengna Lu, S. Lee Barbour & M. Jim Hendry (2016) An evaluation of materials and methods for vapour measurement of the isotopic composition of pore water in deep, unsaturated zones, Isotopes in Environmental and Health Studies, 52:4-5, 529-543, DOI: 10.1080/10256016.2016.1151423

To link to this article: http://dx.doi.org/10.1080/10256016.2016.1151423
An evaluation of materials and methods for vapour measurement of the isotopic composition of pore water in deep, unsaturated zones*

Dyan L. Pratt, Mengna Lu, S. Lee Barbour and M. Jim Hendry

Civil & Geological Engineering, University of Saskatchewan, Saskatoon, SK, Canada; Geological Sciences, University of Saskatchewan, Saskatoon, SK, Canada

ABSTRACT
The development of in situ vapour sampling methods to measure δ²H and δ¹⁸O in pore water of deep, unsaturated soil profiles, including mine tailings and waste rock, is required to improve our ability to track water migration through these deposits. To develop appropriate field sampling methods, a laboratory study was first undertaken to evaluate potential materials and sampling methods to collect and analyse vapour samples from unsaturated mine waste. Field methods were developed based on these findings and tested at two mine sites using either on-site analyses with a portable isotope laser spectrometer or sample collection and storage prior to laboratory analyses. The field sites included a series of deep (>50 m) multiport profiles within a coal waste rock dump and open wells installed in a sand tailings dyke at an oil sands mine. Laboratory results show that memory effects in sample bags and tubing require 3–5 pore volumes of vapour flushing prior to sample collection and sample storage times are limited to 24 h. Field sampling highlighted a number of challenges including the need to correct for sample humidity and in situ temperature. Best results were obtained when a portable laser spectrometer was used to measure vapour samples in situ.

ARTICLE HISTORY
Received 30 June 2015
Accepted 8 January 2016

KEYWORDS
Hydrogen-2; isotope hydrology; mine waste hydrology; oxygen-18; unsaturated soil; water vapour

1. Introduction
The stable isotopes of water (²H and ¹⁸O) are valuable conservative tracers used to determine the origin, transit time, flow paths and mixing of waters in both the saturated and unsaturated zones [1–4]. There are a number of readily available methods to measure ²H/H and ¹⁸O/¹⁶O ratios in groundwater samples using isotope-ratio mass spectrometry or cavity ring-down spectrometry. Unsaturated zones present a unique challenge for isotopic measurements since samples of pore water are difficult to collect and, consequently, analyses are most often conducted using core samples and the extraction of pore water for liquid analysis or the use of the vapour-equilibration method [5–8]. Pore water extraction
methods are destructive and include high-speed centrifugation [2,9], high pressure mechanical squeezing [7], cryogenic distillation [10,11] and azeotropic distillation [9,12]. Each of these methods involves a significant time component and expense per sample, as well as greater potential for evaporative isotopic fractionation throughout the handling and extraction process. Vapour-equilibration methods measure the isotopic composition of water vapour that has come to equilibrium with liquid water contained within the soil cores [13–15]; however, due to the single time stamp that soil coring provides, the ability to track seasonal variations at depths becomes impossible without coring for new samples. In situ vapour measurements could provide the ability to measure these tracers in a high-frequency manner to capture seasonal effects on the isotopic values and track the migration of recharge waters in the subsurface.

A variety of techniques have been utilized to collect and analyse the isotopic composition of soil pore water from soil vapour samples in unsaturated soil profiles. Thoma et al. [16] pumped soil air (water vapour) from depths up to 25 m onto a molecular sieve. The water from the sieve was then extracted via cryogenic distillation and analysed for the $\delta^{2}H$ concentration and in the laboratory and compared to soil core data. They found close agreement between $\delta^{2}H$ of the water vapour collected on the molecular sieve and $\delta^{2}H$ from the core sample. Saxena and Dressie [17] also used the molecular sieve technique to sample soil vapour for the $\delta^{18}O$ concentration to estimate groundwater recharge processes at shallow depths (<4 m). Their results were in close agreement with those obtained from soil cores in which the pore water was extracted via cryogenic distillation. Neither of these studies measured both $\delta^{2}H$ and $\delta^{18}O$. The first attempt at measuring both isotopes concurrently via soil vapour extraction was undertaken by Allison et al. [18]. In this study, soil air was collected in glass jars and the water extracted using a dry ice/alcohol bath. The results were compared to results obtained using soil cores in which the pore water was extracted via cryogenic distillation. Although the $\delta^{2}H$ and $\delta^{18}O$ results did not show close agreement, they did yield similar depth profiles [18]. They determined that condensation of the sample as it passes through the sampling line and into the sampling container caused rapid isotopic exchange that altered the measured values in the vapour. To overcome this problem, they recommended that the sampling line and flask be kept at a temperature above the temperature at the depth being sampled. Izbicki et al. [19] used a technique similar to that used in [18] to sample soil vapour in glass bulbs and compared these profiles to drill core water extracted via azeotropic distillation. The results from the vapour samples were in agreement with comparable core data in which the pore water was extracted via cryogenic distillation when analysed at the same time of year [19].

More recently, the portability of isotope laser spectrometer instruments has resulted in an increased interest in real-time measurement of vapour samples [20–26]. The early adopters of this concept deployed portable instruments to measure the stable isotopic signature of atmospheric water vapour [22,23]. To date, there are few studies employing real-time sampling and analyses of soil pore vapour stable isotopic signatures. Rothfuss et al. [21] evaluated the use of gas permeable polypropylene tubing for vapour sampling under laboratory conditions. They embedded the tubing within sand of varying water contents and pumped dry air through the tubing at a rate of 25 ml/min, sampling the water vapour using a cavity ring-down spectroscope (L1102-i-Analyzer, Picarro, Santa Clara, CA, USA). Their lab-based study demonstrated that the method works at varying temperatures and water contents with the measured vapour showing isotopic enrichment (equilibrium
fractionation) that could be linearly corrected at all tested temperatures [21]. Volkmann and Weiler [20] demonstrated a similar protocol with drive tips custom fabricated to contain gas permeable tubing driven into soil vertically. To control condensation and fractionation effects, a nitrogen gas system was employed to dilute the water vapour at the source. Their results produced comparable profiles to those obtained from soil cores [20]. These studies suggest that sampling and analyses of $^2$H and $^{18}$O in water vapour can be used to determine the isotopic composition of pore water in shallow or deep unsaturated zones.

Tracking water movement is of particular value in mining waste such as waste rock where the unsaturated zone can be hundreds of metres thick. Current monitoring installations within these deposits often include gas monitoring from open standpipe wells or monitoring ports to multiport systems such as the Waterloo Multiport Systems (WMS) (Solinst Canada Ltd.). The great depths of sampling points in these dumps requires the impact of temperature variations (e.g. condensation), water vapour adsorption and fractionation associated with exchanges with the tubing (e.g. sampling memory effects) to be considered.

The three key elements of a field sampling protocol for these installations include: (1) the method of pore-air sampling (e.g. pumps and tubing), (2) the method of sample storage (e.g. sample bags/bottles) and (3) the method of sample analyses (e.g. on-site or laboratory based analyses systems). In this study, the performance of various tubing and sample storage elements in regard to water vapour adsorption and fractionation (i.e. sampling memory effects) were characterized. We also undertook a preliminary comparison of results obtained from on-site, real-time analyses of samples pumped from monitoring wells, to those obtained for samples collected and transported to a laboratory for analyses. These field samples were collected from unsaturated waste rock or coarse textured tailings at two different mine sites.

2. Methodology

The first phase of this study evaluated potential sampling protocols and materials under controlled laboratory conditions, while the second phase carried out a preliminary evaluation of on-site isotope analyses vs. transportation and laboratory analyses of the collected samples. The field samples were collected at two mine sites equipped with WMS and standpipe piezometers. A Picarro L1102-i (Picarro, Santa Clara, CA, USA) was used for the first phase and an L2120-i for the second. For both portions of this study, standard water samples were prepared using the liquid-equilibration method by adding 10 ml of standard water into a Ziploc bag and inflating with dry air [5]. These standards were measured after every four samples to correct for instrument drift and to normalize the results to the Vienna Standard Mean Ocean Water scale with an accuracy of the laboratory standard waters of $\pm 1$ ‰ for $\delta^{18}$O and $\pm 2$ ‰ for $\delta^2$H determined via repetitive measurement.

2.1. Phase 1: laboratory characterization of sample collection materials

This study evaluated a variety of tubing and sample bags with a focus on defining the fractionation associated with losses to the tubing or bags during water vapour sampling (i.e. sampling memory effects). A reservoir of water vapour equilibrated with a water standard
of known isotopic composition was created using Extra Large Ziploc Freezer bags (7.5 L volume). This water vapour reservoir was renewed daily by placing 20–30 ml of laboratory standard water (Birsay, BIR (−180 ‰ δ²H, −23 ‰ δ¹⁸O) or Saskatoon, SKT (−130 ‰ δ²H, −16 ‰ δ¹⁸O) as described by [5,27]) within the bag and inflating the bag with dry air. Once inflated, the bags were shaken and allowed to equilibrate for 30 min prior to experiment initiation.

Three types of tubing commonly installed in multiport systems were evaluated for memory loss effects: stainless steel (SS) (Sandvik Materials Technology), high-density polyethylene (HDPE) (Cole-Parmer) and nylon (Tectran). The tubing was attached to the vapour reservoir using a 24-ga hypodermic needle, which was connected to the vapour inlet of the Picarro L1102-i. The Picarro was used as the vacuum source, and pore volumes were calculated based on elapsed time, flow rate of the Picarro and tubing dimensions (I.D. and length). Each type of tubing was tested using vapour equilibrated with BIR and SKT standard waters, and the δ²H and δ¹⁸O values of the vapour were analysed over multiple pore volumes until a stable reading was obtained. To reset the tubing between tests, dry air was pumped through each tube until the water concentration reading on the Picarro was less than 200 ppmv. Additional testing details were reported by Lu [28].

To evaluate sampling bag memory losses, Flexfoil gas sample bags (SKC, Inc.), a commonly used gas sampling bag, were flushed with known quantities (500 ml per flush) of standard sample vapour from the vapour chambers using a 100 ml syringe and needle. δ²H and δ¹⁸O were measured following each flush; the bags were then evacuated and the procedure was repeated until a stable reading was obtained. The bags were flushed with a minimum of 6 pore volumes (3000 ml) of dry air to reset the initial conditions within the bag following each test.

Fractionation caused by vapour loss during sample storage time was also assessed for each water standard. Flexfoil bags (n = 6) were flushed 5 times with the sample vapour and were then filled with vapour from a standard water and stored in a Coleman™ cooler. A bag was sacrificed for isotopic analysis at 8, 24, 48, 72, 96 and 120 h.

The effects of changing relative humidity (RH) values in the water vapour as cold vapour samples in the soil profile warm up prior to analyses was also evaluated. Standard water vapour samples were injected into Flexfoil bags, Isojars (Isotech Laboratories) and Ziploc™ bags and mixed with dry air at specific ratios from 20 to 100 % RH and analysed for δ¹³H and δ¹⁸O to establish a correction for RH conditions and to compare different container types.

2.2. Phase 2: comparison of on-site and laboratory analyses of field samples

The field sampling campaign was undertaken in two different mine wastes and sampling systems: Waterloo multiport gas sampling profiles installed at depths between ground surface and 180 m at 4 locations in waste rock at a steelmaking coal mining operation in the Elk Valley, British Columbia; and standpipe piezometers (n = 24) in a sand tailings dyke (depths between 1 and 40 m) at an oil sands mine near Fort McMurray, Alberta. The waste rock is a relatively coarse sand and gravel with more cobbles in the upper 13 m of the profile [28], while the oil sand tailings are predominantly fine to medium sand with fines (clay and silt) and some residual bitumen [29]. WMS systems were constructed using HDPE monitoring tubes at specified zones below ground separated by a
bentonite seal. At each sampling zone, the HDPE tube was screened with a 50-mm stainless steel mesh filter. These systems are generally used for water sampling in saturated zones, or for gas chemistry sampling in unsaturated zones. Multiport sampling was performed in two ways: direct connection of the laser analyzer to the sampling tube in the field and collecting vapour samples in Flexfoil bags for laboratory analysis on the Picarro L2120i, with each method being performed immediately after each other. For direct connection of the Picarro, measurements were not taken until the values had stabilized on the instrument within ±0.5‰ for δ²H and ±0.2‰ for δ¹⁸O. This could take upwards of 10 min once initial tubing memory had been flushed. Temperature measurements for the WMS were also performed on its corresponding thermistor string. Flushing volumes and storage times identified in the laboratory testing programme were used to define the field sampling protocols.

The WMS tubes were constructed from HDPE tubing. As a result, 4–5 pore volumes of vapour were flushed with an SKC Grab Air Sample Pump™ (SKC, Inc.) prior to direct analysis or bag sample collection. Flow rates were kept low (30–1000 ml/min, with 30 corresponding to the Picarro pumping rate, and 1000 to the SKC Grab Air Sample Pump) as suggested by previous studies [16] to maintain a zone of influence (less than 10 L of vapour) representative of gases at the elevation of the WMS. The sample bags were also flushed with 1.5 L of vapour (3 fill volumes) prior to sample collection. In the case of the standpipe piezometers, HDPE tubing was lowered down the standpipe to 10 cm above the phreatic surface or base of the riser if the well was dry. The top of the riser was then sealed from the atmosphere, and five pore volumes of vapour were flushed through the tubing prior to vapour collection in Flexfoil bags. The bags were placed in a cooler and analysed in the laboratory at the end of the day (i.e. <8 h after sample collection). For standpipes where a water sample could also be collected, the water was sampled and analysed using the vapour-equilibration method [5]. It is important to note that, in general, the ground temperatures were relatively constant and lower than atmospheric air temperature and, therefore, the potential for vapour condensation in the sample tubing was low. It would have been preferable to inject dry air during sample to eliminate the potential for condensation [20]; however, the configuration of the WMS did not allow dry air to be injected during sampling.

2.3. Correction methods

The procedure used to obtain the pore water composition associated with the field vapour samples included the following steps:

- the isotopic composition of the vapour sample was corrected for RH effects (δ⁵H) based on the method of Schmidt et al. [30];
- the ratio between the known standard water value and the measured vapour value was calculated (Δ₁);
- the theoretical ratio of the vapour and liquid composition of the standard samples (Δ₂) was calculated for laboratory temperatures based on equilibrium fractionation using equilibrium fractionation factors from Majoube [31];
- the theoretical equilibrium fractionation of a standard water at the in situ temperature was calculated and ratio was then calculated against the measured vapour value (Δ₃);
the in situ pore water isotope composition was then calculated using the sample vapour measurements (corrected for RH) and Equation (1).

\[
\delta_{\text{corrected}} = \delta_{\text{SH}} + \Delta_1 + (\Delta_2 - \Delta_3).
\] (1)

3. Results and discussion

3.1. Sample tubing memory effects

The measured isotopic composition and water concentration of the vapour passing through the three different types of sample tubing with BIR and SKT standards are presented in Figure 1. The isotopic values in Figure 1 were normalized using

\[
\frac{C}{C_0} = \frac{C - C_{\text{min}}}{C_{\text{max}} - C_{\text{min}}},
\] (2)

where \(C/C_0\) is the normalized isotope value, \(C\) is measured \(\delta\) value and \(C_{\text{min}}\) and \(C_{\text{max}}\) are the minimum (initial atmospheric air in tubing) and maximum (standardized water vapour) \(\delta\) values. The results are presented in terms of pore volume, calculated as the volume of vapour that passed through the tubing based on the inner diameter and length of each tube and the flow rate. Measurements were recorded until the normalized concentration \((C/C_0)\) equalled one. In some instances never reached one due to tube permeability (nylon).

The results indicate that HDPE tubing has the least effect on memory compared to SS and nylon tubing, with consistent values being obtained after 1–1.5 pore volumes of vapour. SS tubing also produced stable readings after three pore volumes. Nylon never reached a stable standard value indicating that this tubing type is inadequate for sample collection due to its high gas permeability.

The results were slightly different for the two different water standards. In the case of HDPE tubing, there was little difference in the normalized values or water vapour breakthrough curves between the two standard vapour sources. However, the SS tubing exhibited a quicker response time for the more enriched standard water (SKT); similar enriched effects were also observed by Schmidt et al. [30]. The reason for the slightly delayed response for more depleted water (BIR standard) for the HDPE tubing in Figure 1 is not known but is likely due to the greater impact of isotopic fractionation due to adsorption on water that is already more depleted.

When the same test was repeated with 50 % RH vapour the results were similar (Supplemental Figure S1) although there was a slightly longer time lag time when compared to 100 % RH. This is consistent with findings reported by Schmidt et al. [30], who found that a drop in water concentration caused a longer lag time. This is assumed to be due to the amount of water required to fill adsorption sites on the tubing wall.

3.2. Sample bag memory effects and storage

Memory effects for the sampling bags were also evaluated using the two water standards at two different RH conditions. The results for both 100 % RH (a) and 50 % RH (b) are shown in Figure 2. For 100 % RH conditions (\(\text{H}_2\text{O} \geq 22,000 \text{ ppmv}\)), the first 2 bag flushes deviated from the standard, but stabilized at 3 flushes and beyond. It was also observed that \(\delta^{2}\text{H}\)
Figure 1. (a) SKT standard – tubing memory effects characterized by normalized isotope values vs. pore volume and (b) BIR standard – tubing memory effects characterized by normalized isotope values vs. pore volume.
was more affected by bag memory than $\delta^{18}O$ for the first two flushes. In the case of the 50 % RH ($H_2O \approx 12,000$ ppmv) samples, a similar effect was noted and is likely due to the requirement for additional water vapour required to satisfy all of the moisture adsorption sites. For both standard waters, the bags exhibited similar moisture adsorption (results not shown).

Sample storage time was assessed for the Flexfoil bags. Flexfoil™ reports a 48-h stability of gases such as hydrogen, $H_2S$, carbonyl sulphide and others, but does not report on the stability of stable isotopes of water in vapour form. Changes in the measured isotopic composition of the water vapour stored within the Flexfoil bags are shown in Figure 3. It

![Figure 2](image)

**Figure 2.** (a) 100 % RH; (b) 50 % RH storage bag memory effects characterized by isotopic vapour composition for repeated flushing of Flexfoil storage bag (Birsay BIR and Saskatoon tap water SKT standards). *Bands (±) are shown for BIR and SKT reference standards for both $\delta^2H$ (±1 ‰) and $\delta^{18}O$ (±2 ‰).
highlights that although the $\delta^{18}$O values may remain stable over many days, the $\delta^2$H values begin to drift within 24–48 h, with both values closest to the standard value at 8 h. If the cause of the memory effect within tubing or bags is the result of water adsorption, then it seems reasonable that there would be a greater impact of adsorption on $\delta^2$H relative to $\delta^{18}$O, as shown in Figures 2 and 3, where the effect of adsorption is to produce fractionation similar to that observed for a natural evaporation line.

3.3. Humidity effects

The water concentration within the vapour samples tested in this programme ranged from 5000 to 25,000 ppmv H$_2$O (20–100 % RH) as shown in Figure 4. The pattern of measured isotopic composition vs. RH is markedly different for $\delta^2$H and $\delta^{18}$O; however, the shape of the relationships for the two standard waters is similar and consistent between storage containers.

The change in $\delta^2$H with increasing water vapour concentration is initially non-linear but stabilizes at water vapour concentrations greater than 10,000 ppmv H$_2$O and trends towards the standard reference water value regardless of water concentration. The more depleted water standard (BIR) showed more scatter. The $\delta^{18}$O curves tend to be more bilinear across the humidity range for both SKT and BIR reference samples with a distinct change in slope around the 10,000 ppmv value, similar to findings in [30]. It is of note that the manufacturer suggests that the analyses should be correct at water concentrations above 2500 ppmv. The Isojars and Flexfoil bags produced similar results while more scatter was observed for Ziploc™ bags. This variation is less apparent for the BIR samples, but is more pronounced with the SKT reference standard. The Flexfoil bag not only performs well in all of the tests, but it is also preferable from an operational standpoint due to its larger volume (1000 ml vs. 600 ml) and flexibility. Laser instruments are not able to handle pressure spikes during analysis and due to the fixed volume of the Isojar, it is difficult to pull a sample directly from the jar without putting it under

Figure 3. Flexfoil™ bag stability of vapour sample storage time.
vacuum, making them not ideal for vapour collection. Ziploc bags also produced similar results but in practice, are more prone to tears and leakage.

Previous studies report different relationships between isotopic composition and ppmv range, from linear to non-linear, with either positive or negative correlations, depending on equipment and sample preparation methods. Previous works by Schmidt [30] and others [26,32,33] have shown that a machine-specific correction for RH is required for RH values less than 100 %. Those same studies also showed a positive correlation of both $\delta^2$H and $\delta^{18}$O with respect to varying water concentrations with this study sharing similar results above 10,000 ppmv. This exercise should be completed on each laser spectrometer used for vapour sampling to develop a machine-specific correction.

### 3.4. Field in situ analysis and bag sampling using methods from phase 1

Field sampling was undertaken at two mine sites using two different methods: (1) direct connection of the Picarro laser spectrometer to the WMS and (2) collection of soil vapour in Flexfoil bags for laboratory analysis within 8 h (WMS and standpipe piezometers). Bag vapour samples ($n = 16$) were collected from standpipe piezometers installed in an oil sands tailings dyke. Water samples ($n = 8$) were also collected in a number of these sites in wells that still contained water.

Results for in situ measurements and bag samples ($\delta^2$H, $\delta^{18}$O and H$_2$O ppmv) from the Waterloo multiport are shown in Figure 5. When comparing samples collected in bags vs. the direct attachment of the Picarro at each sampling port, on-site attachment of the laser spec provides some values that are in general agreement to those collected in the bag for some depths ($\pm 5$ ‰ $\delta^2$H and $\pm 1$ ‰ $\delta^{18}$O). In specific instances however, this is not the case; the results show that above 20 m and below 45 m, the variance between the two is greater ($\pm 30$ ‰ $\delta^2$H and $\pm 10$ ‰ $\delta^{18}$O).

Some of the differences between bag samples and those analysed directly in situ may correlate to the difference in H$_2$O ppmv measured for each one as shown in Figure 5. At

![Figure 4](image_url)
depths between 20 and 45 m, the water concentrations were similar, while at other depths such as those less than 15 m or greater than 45 m, water concentrations varied by as much as 50 % or more. An RH equivalent calculation for the measured vapour values with their corresponding measured in situ temperatures demonstrates that the equivalent RH at the shallower depths is much greater than 100 %, as shown in Supplemental Figure S2a. A back calculation of temperature from measured ppmv and the assumption that the subsurface is at 100 % RH indicate temperatures vary greatly from those measured in the top 20 m (Figure S2b). It is clear from the thermistor profile that the ground temperatures are nearly constant with elevation until about 15 m below ground where they go through a cooling and warming trend towards surface. It is likely that this caused fractionation within the sampling tube. The checks on in situ RH based on sampled ppmv and temperature as well as the check on temperature from measured ppmv both highlight disequilibrium between ground conditions and the vapour being sampled, making it difficult to isolate the cause. The inaccuracies above 20 m could be due to faulty temperature measurements on the thermistors, bypass flow through the dump, water content, pulling in saturated atmospheric air via excessive pumping (near surface), laser spectrometer failures, or unaccounted memory losses (i.e. bags not flushed enough with sample prior to collection). It is also possible that there is some sort of disequilibrium between the temperatures measured in the thermistor cable grouted into the borehole annulus and the unsaturated waste rock over these depths or that there was some convective air flow through the upper portion of the dump which has led to the presence of an air phase which is not yet in equilibrium with the surrounding matrix.

The deuterium excess profile obtained at the waste rock multiport location is shown in Supplemental Figure S3. This site location is expected to have relatively little surface

![Figure 5. Vapour and isotope measurement via direct connection of Picarro in situ as compared to bagged samples for WMS.](image-url)
evaporation relative to recharge rates and consequently $d$-excess values are expected to be relatively small. The levels of $d$-excess are relatively low (<−40 for corrected samples) with the smallest negative values, and most consistent depth pattern of $d$-excess, being associated with the corrected Picarro on-site measurements.

Results for both the WMS and standpipe piezometers as measured and corrected vapour to pore water composition were plotted against the Local Meteoric Water Line (LMWL) [34,35] for each location as shown in Figure 6. The figure includes the direct measurements from the vapour samples for the WMS as well as samples corrected for RH and in situ temperatures as described previously. For the sand tailings dyke (Figure 6(a)), the temperature and SH corrections move the sample results from below the LMWL back on to the LMWL with a more enriched isotope signature which, for ~40 % of the samples, overlaps with the water samples collected in the same wells. However, it is important to note in Figure 6(a) that the remaining RH and temperature corrected vapour samples plot along the LMWL but with much more depleted values than those observed in the water samples, typically the lowest $\delta$-values that might be expected in the profile since they are consistent with estimates of snow melt recharge. The reason for this additional depletion is not known.

A similar shift was obtained between the measured and corrected samples for WMS located in coal waste rock on the LMWL (Figure 6(b)). In general, the WMS samples measured directly in the field are closer to the LMWL and show less scatter than those collected in bags. There was no independent check on the isotopic composition of the vapour samples for the waste rock spoil as there was with the water samples (Figure 6(a)). However, analysis of the distribution of the isotopic composition of pore water from the waste rock using core samples had a range for $\delta^2$H from $-116$ to $-160$ ‰ and for $\delta^{18}$O

![Figure 6](image-url). (a) Vapour bag sampling and water sampling from standpipe piezometers at oil sands tailings dyke for the analysis of $\delta^2$H and $\delta^{18}$O, and (b) vapour sampling of Waterloo multiport at waste rock spoil, a comparison of direct connection of Picarro vs. vapour bag sampling.
from $-15$ to $-20\,\%$. It is also important to note that the average gravimetric water contents through the waste rock dump in the upper zone were quite low ($\sim 4\%$). At these low water content values, it would not be unexpected that there might have been isotope fractionation from the aqueous to water vapour in a similar manner as that noted in laboratory measurements by Wassenaar et al. [5]. This would also occur if there was ongoing convective or diffusive vapour migration across the upper surface of the dump, which enhanced vapour exchange with the atmosphere. Taken together, these observations suggest that during sampling there may have been some depletion of the vapour samples from these much deeper sampling depths. Since the applied correction produces similar results for each, for sites where access is simple, direct attachment of a laser spectrometer can provide rapid measurements of isotopic data, but in the event bag samples are required, comparable results are possible.

4. Conclusions

This study evaluated basic sampling parameters and equipment including sampling tubing and storage bag memory effects and their influence on the stable isotope values obtained for water vapour. Isotopic memory effects were determined for three tubing types as well as memory effects in Flexfoil™ bags. Stainless steel and HDPE tubing are suitable to use for in situ soil vapour collection and require flushing of a minimum of 3–5 pore volumes of sample vapour prior to sample collection to encompass any humidity changes at depth. For sites where direct connection of a laser spectrometer is impossible, Flexfoil bags for sample collection and transport for analysis within 24 h is an acceptable alternative. Flexfoil bags also demonstrated a memory effect and require 3–5 (500 ml ea.) flushes of sample vapour prior to final sample collection depending on the RH of the sample, with lower RH requiring more flushes (>5) to surpass the memory of the bag. Sample storage in Flexfoil bags should not exceed 48 h, and is preferable to analyse within 8–24 h. Also, of importance, is the humidity effect on the analyzer. Results reveal the need for each analyzer to be run through a specific set of humidity tests to form the correction parameters for the instrument for RH <$100\,\%$ vapour samples.

Preliminary results of the field based portion of this study suggest that the methods of establishing the natural, stable isotope of water profiles for pore water in thick unsaturated mine waste is challenging; however, direct attachment of a laser spectrometer or sampling vapour into Flexfoil bags for laboratory analysis can provide comparable results. In sand tailings, corrected bag sampling soil vapour produced results that plotted along the LMWL in a range consistent with water samples collected from nearby wells. However, a number of the vapour samples that plotted on the LMWL were isotopically depleted below the minimum values expected for these profiles. The cause of these shifts is not known. For coal waste rock spoils, direct connection of the Picarro to the Waterloo multiport provided a better vapour value than bag sampling. Further, it must be ensured that appropriate corrections for temperature and specific humidity be applied for analyses of vapour samples.

Disclosure statement

No potential conflict of interest was reported by the authors.
Funding
Support for the project was provided by NSERC-IRC, Syncrude Canada Limited and Teck Resources Limited.

ORCID
Dyan L. Pratt http://orcid.org/0000-0003-4706-3765

References
[17] Saxena RK, Dressie Z. Estimation of groundwater recharge and moisture movement in sandy formations by tracing natural oxygen-18 and injected tritium profiles in the unsaturated


[34] Baer TJ. An evaluation of the use of natural stable isotopes of water to track water movement through oil sands mine closure lanforms. Saskatoon: University of Saskatchewan; 2014.