

# High Resolution Pore Water $\delta^2\text{H}$ and $\delta^{18}\text{O}$ Measurements by $\text{H}_2\text{O}_{(\text{liquid})}$ – $\text{H}_2\text{O}_{(\text{vapor})}$ Equilibration Laser Spectroscopy

L.I. WASSENAAR,<sup>\*,†,‡</sup> M.J. HENDRY,<sup>†</sup>  
V.L. CHOSTNER,<sup>†</sup> AND G.P. LIS<sup>§</sup>

Department of Geological Sciences, University of  
Saskatchewan, Saskatoon, SK, Canada, S7N 5E2, and  
Environment Canada, 11 Innovation Blvd. Saskatoon, SK,  
Canada, S7N 3H5

Received July 24, 2008. Revised manuscript received  
October 3, 2008. Accepted October 8, 2008.

A new  $\text{H}_2\text{O}_{(\text{liquid})}$ – $\text{H}_2\text{O}_{(\text{vapor})}$  pore water equilibration and laser spectroscopy method provides a fast way to obtain accurate high resolution  $\delta\text{D}$  and  $\delta^{18}\text{O}$  profiles from single core samples from saturated and unsaturated geologic media. The precision and accuracy of the  $\text{H}_2\text{O}_{(\text{liquid})}$ – $\text{H}_2\text{O}_{(\text{vapor})}$  equilibration method was comparable to or better than conventional IRMS-based methods, and it can be conducted on geologic cores that contain volumetric water contents as low as 5%. Significant advantages of the  $\text{H}_2\text{O}_{(\text{liquid})}$ – $\text{H}_2\text{O}_{(\text{vapor})}$  pore water equilibration method and laser isotopic analysis method include dual hydrogen- and oxygen-isotope assays on single small core samples, low consumable and instrumentation costs, and the potential for field-based hydrogeologic profiling. A single core is sufficient to obtain detailed vertical isotopic depth profiles in geologic, soil, and lacustrine pore water, dramatically reducing the cost of obtaining pore water by conventional wells or physical water extraction methods. In addition, other inherent problems like contamination of wells by leakage and drilling fluids can be eliminated.

## Introduction

The  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values of pore water extracted from saturated and unsaturated geologic, soil, and lacustrine cores have been used for decades as natural hydrologic tracers to study paleoclimate, soil vapor fluxes, and in determining the origin and movement of pore water in water resource evaluation, groundwater contamination, and nuclear waste storage studies (1–8). To obtain high-resolution vertical profiles of  $\delta^{18}\text{O}$  and  $\delta\text{D}$  from pore water requires the installation of numerous individual wells or suction lysimeters to obtain water directly (9), or by continuous geologic coring followed by physical extraction of  $\text{H}_2\text{O}$  from the core matrix using methods such as high speed centrifugation (2, 7, 8), mechanical squeezing (3), cryogenic microdistillation (4–6), or azeotropic distillation (2, 7, 10, 11). All physical pore water extractions are followed by stable isotopic assays on  $\text{H}_2\text{O}$ , done separately for  $\delta^{18}\text{O}$  and  $\delta\text{D}$  (12). Physical pore water extraction methods are generally laborious, and most have great potential for isotopic fractionation caused by multistep

extraction procedures that can result in incomplete  $\text{H}_2\text{O}$  recovery or evaporative loss during handling. Conversely, the cost of installing numerous wells or suction lysimeters to obtain high resolution depth profiles is often cost prohibitive, and has the potential for contamination from overlying pore water leakage or from introduced drilling fluids.

Over the past decade, several techniques have been developed as alternatives to physical pore water  $\text{H}_2\text{O}$  extractions and installation of wells. One successful approach involves using a radial diffusive reservoir mixing method applied to sections of core (1, 12, 13), although the method is laborious and impractical for routine analysis of large numbers of samples. Faster and easier techniques have been proposed that directly equilibrate the pore water in core samples with helium– $\text{CO}_2$  or a He– $\text{H}_2$  catalyst mixtures or a headspace vapor equilibration, but still require subsequent analyses via purified  $\text{CO}_2$  and  $\text{H}_2$  assays by isotope-ratio mass spectrometry (IRMS) (13–15). In the case of direct  $\text{CO}_2$ – $\text{H}_2\text{O}$  or  $\text{H}_2$ – $\text{H}_2\text{O}$  equilibration methods, separate core samples and isotopic assays are needed for  $\delta\text{D}$  and for  $\delta^{18}\text{O}$  measurements by continuous-flow or dual inlet IRMS (13, 14).

Here we propose a new method that uses either saturated or unsaturated geologic core samples and pore water  $\text{H}_2\text{O}_{(\text{liquid})}$ – $\text{H}_2\text{O}_{(\text{vapor})}$  equilibration, followed by dual stable isotopic analysis using newly available, laser based off-axis integrated cavity output spectroscopy (OA-ICOS). This technique enables direct and rapid measurement of  $\delta^{18}\text{O}$  and  $\delta\text{D}$  of pore water on a single core subsamples. Significant advantages of the proposed laser spectroscopy pore water  $\text{H}_2\text{O}_{(\text{liquid})}$ – $\text{H}_2\text{O}_{(\text{vapor})}$  equilibration technique are that pore water samples can be measured with minimal handling and exposure to evaporation. Separate assays using  $\text{CO}_2$  or  $\text{H}_2$  gas as the analyte are not required because laser spectroscopy measures the isotopologues of  $\text{H}_2\text{O}$  on vapor directly with no complicating isobaric interferences from air or other gases like  $\text{CO}_2$  or  $\text{CH}_4$ . Hence, no sample pretreatment or analysis gas cleanup is required (e.g., purification of  $\text{CO}_2$  or  $\text{H}_2$  as required for IRMS). These benefits greatly reduce sample handling and processing, and furthermore, they improve sample throughput and reliability by allowing dual-isotopic analysis on the same core or pore water sample. Additionally, the OA-ICOS laser instrumentation is comparatively low cost compared to IRMS, is field laboratory portable, uses no consumables, and is easy to operate. This may eventually allow investigators to obtain detailed pore water isotopic depth profiles onsite without having to collect and ship samples to conventional stable isotope laboratories for analysis.

## Materials and Methods

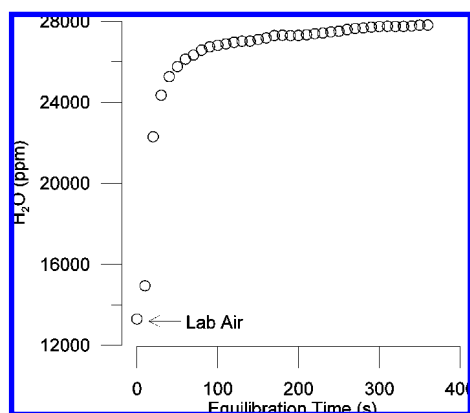
The principle of the proposed  $\text{H}_2\text{O}_{(\text{liquid})}$ – $\text{H}_2\text{O}_{(\text{vapor})}$  pore water equilibration method lies in the fact that pore water in geologic core samples placed in an isothermal closed-system container will quickly reach liquid–vapor and isotopic equilibrium with the surrounding enclosed headspace at 100% relative humidity (RH) conditions. By carefully controlling the temperature and time of the equilibration and by measuring the stable isotopic composition of headspace  $\text{H}_2\text{O}$  vapor (and its concentration) in the sample and a reference water sample headspace, the  $\delta^{18}\text{O}$  and  $\delta\text{D}$  of the pore water can be determined directly. While the approach is conceptually similar to direct  $\text{CO}_2/\text{H}_2$ -pore water equilibration (13), here dual-isotope assays were conducted directly on the  $\text{H}_2\text{O}$  vapor in equilibrium with liquid water or pore

\* Corresponding author e-mail: len.wassenaar@ec.gc.ca.

<sup>†</sup> University of Saskatchewan.

<sup>‡</sup> Environment Canada.

<sup>§</sup> Current Address: University of Bristol, U.K.



**FIGURE 1.** Time need to reach H<sub>2</sub>O liquid–vapor equilibrium is ~300s at 22 °C in headspace sampling bags. Time zero is the switch from laboratory air flushing to sealing the sample bags to reach H<sub>2</sub>O liquid–vapor equilibrium.

water by using a tunable diode laser based on OA-ICOS technology (16). Prior to field testing, the time frame required for full H<sub>2</sub>O<sub>(liquid)</sub>–H<sub>2</sub>O<sub>(vapor)</sub> equilibration using both pure standard waters and artificial cores, and to assess the expected accuracy and repeatability of the method, needed to be determined. Once these tests were completed, a routine sample H<sub>2</sub>O<sub>(liquid)</sub>–H<sub>2</sub>O<sub>(vapor)</sub> equilibration and analysis protocol was established for both cores and standards. Finally, the H<sub>2</sub>O<sub>(liquid)</sub>–H<sub>2</sub>O<sub>(vapor)</sub> pore water equilibration and laser spectroscopy method was field validated using continuous cores taken in 2008 at sites where long-term  $\delta^{18}\text{O}$  and  $\delta\text{D}$  data were available from monitoring wells, and where the pore waters spanned a large isotopic range of isotopic values (17).

**Laboratory Testing.** The first technical challenge was how to facilitate a practical closed system sample equilibration vessel that would allow subsequent headspace sampling of fully equilibrated geologic cores. This required a resealable (to enable core emplacement), inflatable and leak-tight (to avoid evaporation and isotope fractionation), and collapsible (to facilitate headspace withdrawal) gas sampling bag in which standard waters, artificial cores, and field cores could be placed and inflated with a dry air headspace. We initially investigated the possibility of using Tedlar and metalized Mylar gas sampling bags which are well-known to be gas impermeable (at least on the time scale of days), but unfortunately, neither of these specialized materials were available in a resealable bag format that could accept and reseal core materials, and were expensive for large sizes (>\$150 USD per bag). We considered using sheets of metalized Mylar or Tedlar and constructing custom heat sealable sample bags, but the cost of these materials was prohibitive for routine use or for numerous samples (>\$80 per bag) and would also require destructive puncturing for headspace inflation and sample withdrawal. We opted to use disposable food industry 945 mL-thick plastic freezer bags (Ziploc brand Double Guard freezer bags with Double Zipper Seal). The benefit of the Ziploc bags is that they are extremely low cost (\$10 USD/ 100 bags), disposable, and provided good gas seals. The primary disadvantage of these consumer bags was that ~30% of the bags did not properly seal. However, these faulty bags could be readily screened out by inflating, sealing and squeezing, and checking for leaks. Further, by double bagging all samples with two good Ziploc bags, we found the effective failure rate could be lowered to about 5%.

For sample equilibration, the Ziploc bags containing core or water were inflated to ~900 cc (less gas volume if bags contained more core) with dry air to create a sample equilibration and headspace sampling volume. Dry air may

be used to avoid atmospheric moisture contamination. However, contamination by using atmospheric air as the headspace gas may be negligible depending on the amount of water in the sample. For example, during our experiments our laboratory air contained approximately 11 000–12 000 ppmV H<sub>2</sub>O (4–5 mg/ 500 CC), and the headspace in fully H<sub>2</sub>O<sub>(liquid)</sub>–H<sub>2</sub>O<sub>(vapor)</sub> equilibrated sampling bags (using 20 mL of H<sub>2</sub>O) at 100% RH at 22 °C contained 28 000–29 000 ppmV H<sub>2</sub>O. Our core pore water and liquid water samples contained a target mass of ~20 mL (20 000 mg) of H<sub>2</sub>O. Thus the potential for atmospheric H<sub>2</sub>O contamination from air is extremely low on a mass balance basis (<~0.03%) and would not adversely impact the resultant isotopic assays. Nevertheless, dry air was used in our experiments.

For liquid water samples (e.g., isotopic calibration standards) 20 mL of isotopically known laboratory standard waters were placed into a 945 mL Ziploc bag. The bag was inflated with ~900 mL of dry air and immediately “zipper” sealed. The sample bag was then rechecked for leaks by gently squeezing. As a precaution against slow undetectable leakage, this bag was placed inside a second sealed Ziploc bag and then placed on a laboratory bench at isothermal (22.5±0.1 °C) conditions to avoid transient, temperature dependent, liquid–vapor isotope fractionation of the equilibrated samples.

Geologic and artificial core sample weights were targeted to achieve the same ~20 mL of pore water content using previously determined gravimetric moisture content information (~100 g of saturated geologic core on average). Core materials were carefully (to avoid compromising the zipper edge) placed into a 945 mL Ziploc bag. The bag was inflated with dry air to ~900 mL, immediately resealed, and checked for leakage. Core samples were then double bagged and placed on the same isothermal laboratory bench as the liquid water standards.

Because laser based OA-ICOS does not make use of a calibrated reference isotopic gas and experiences isotopic drift (16), laboratory working standards must be prepared and systematically measured along with the core samples via the Principle of Identical Treatment (18). Two laboratory water standards of known isotopic composition were prepared and treated identically to the cores and were used to allow for normalization of results and drift correction (16) using a repeating sequence of standard A, three samples, standard B.

**Off-Axis Laser Spectroscopy.** For H<sub>2</sub>O vapor stable isotopic analyses, two different OA-ICOS analyzers obtained from Los Gatos Research Inc. ([www.lgrinc.com](http://www.lgrinc.com); California) were used. The first instrument was the LGR model 908–0008 (liquid water analyzer), which was adapted by the factory to facilitate manual injections of 50 mL, 100% RH water vapor samples. Vapor samples could be taken manually from gas sampling bags by puncturing with a 50 mL syringe (Hamilton model 1050) and injected into a heated (70 °C) septum port. The vapor was then expanded statically into the analyzer chamber for stable isotopic analysis. Because of potential intersample memory effects (16), five manual injections (250 mL total) of 100% RH samples were required and the last three results were averaged. Between manual injections the needle puncture hole in the sampling bag was immediately covered with Scotch tape to prevent headspace leakage.

The second instrument used was a LGR model 908–0004 (water vapor isotope analyzer). This instrument enabled continuous-flow headspace sampling of H<sub>2</sub>O vapor directly from the gas sampling bags. This instrument measured H<sub>2</sub>O concentration and the H<sub>2</sub>O isotopologues at 10 s integration intervals. The instrument was connected to a 1 m long by 6.4 mm (1/4”) stainless steel tube attached to a female Luer-lok adaptor. A 21G stainless steel disposable needle was attached to the end of this fitting. For the liquid water standards and

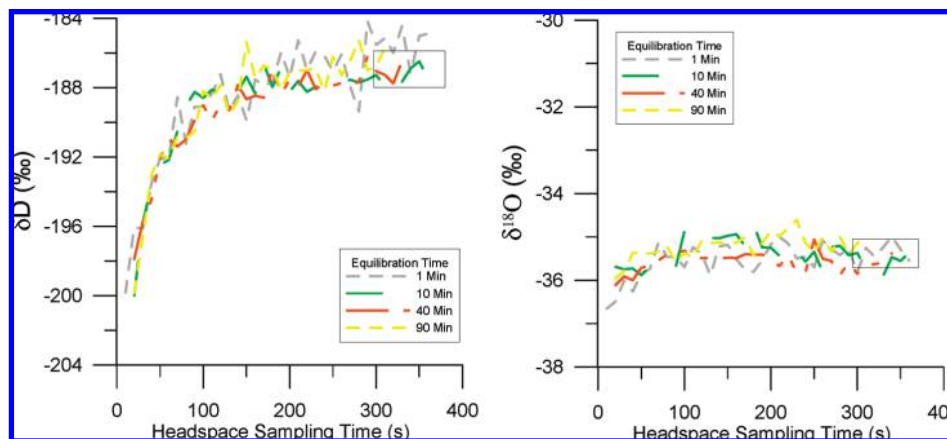


FIGURE 2. Continuous-flow (10 s integration), 100% RH headspace sampling using OA-ICOS for  $\delta D$  and  $\delta^{18}O$  for pure water samples equilibrated with dry air for experimental liquid–vapor equilibration times ranging from 1 to 90 min. Water-vapor equilibration times of 10–20 min at 22 °C, and headspace sampling times acquisition >300 s (using only last five integrations) were sufficient to obtain acceptable precision for  $\delta D$  and  $\delta^{18}O$ .  $T = 0$  is defined as the time when the sample headspace sampling begins, switching from atmospheric air flow. Repeatability for sample equilibration times between 10 and 90 min and headspace sampling >300 s (open box) was  $-187 \pm 0.7\text{‰}$  for  $\delta D$  and  $-35.3 \pm 0.3\text{‰}$  for  $\delta^{18}O$  ( $n = 25$ ).

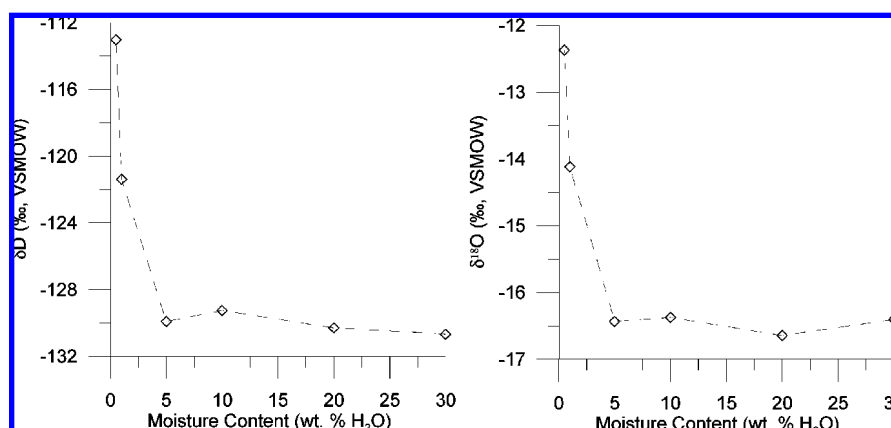


FIGURE 3. Plot of  $\delta D$  and  $\delta^{18}O$  in sampling bag headspace versus pore water moisture content for silica sand test samples. Acceptable results were obtained above 5% moisture content, suitable for saturated geologic media and most soils.

TABLE 1. Repeatability of Hydrogen and Oxygen Isotopic Results from Triplicate Dried and Re-Wetted Clay Rich Core Samples and Lab Standard Waters (BIR and SK-T); Repeatability was  $\pm 0.7\text{‰}$  ( $n = 3$ ) for  $\delta D$  and  $\pm 0.02\text{‰}$  for  $\delta^{18}O$  ( $n = 3$ ), Respectively

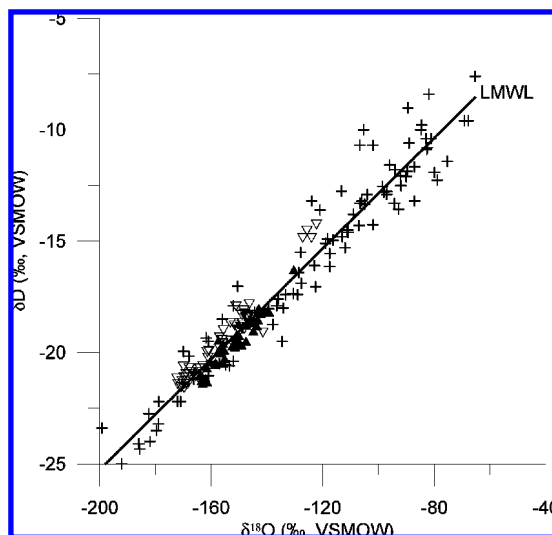
sample/std	uncorrected $\delta D$ (raw)	$\delta^{18}O$ (raw)	corrected	$\delta^{18}O$ (std/corr)
BIR std	-231.2	-41.8	-179.8	-23.1
BIR std	-230.9	-41.8	-179.8	-23.1
BIR std	-231.0	-42.1	-179.8	-23.1
BV2 9.9 m	-184.5	-35.0	-133.4	-15.7
BV2 9.9 m	-184.3	-35.0	-133.3	-15.8
BV2 9.9 m	-183.6	-35.0	-132.5	-15.8
SK-T std	-185.6	-35.2	-135.0	-16.2
SK-T std	-186.5	-35.7	-135.0	-16.2

for cores, the sampling bag containing headspace-equilibrated core or water was punctured with the needle and the instrument dynamically sampled  $H_2O$  vapor in the headspace by low speed suction into the laser analyzer chamber. The rate of headspace sampling was controlled by the sample inlet orifice diameter with a gas sampling flow rate fixed at 150 mL/min using a constricting orifice. During continuous flow headspace sampling the 945 mL sample bag slowly deflated over a period of about 6–7 min.

The main functional difference between the two laser analyzers was that the continuous-flow instrument was better optimized for vapor isotopes by using a dynamic flow higher gas pressure optical cavity and a significantly longer optical path length (D. Baer, Los Gatos Research Inc., personal communication). The liquid analyzer required manual injections and repeated sample bag punctures, which was accordingly slower than continuous flow headspace sampling using the vapor analyzer. The total time for analysis per sample was approximately 15 min using the manual injection method (five injections), and approximately 9 min using the continuous flow  $H_2O$  vapor analyzer method. For routine sampling, a regular sequence of calibrated standard waters and core samples was required as described above and previously (16), and hence, approximately 50 core samples could be reliably processed per day.

**Field Testing.** For field validation of the  $H_2O$ (liquid)– $H_2O$ (vapor) method, continuous core samples (0.08 m diameter) were collected at two thick, clay-rich till aquitards near Birsay, Saskatchewan, Canada in December 2007 (King site; 1.5–15.3 m depth) and April 2008 (Luck Lake site; 1.5–13.4 m depth). The hydrogeology of the King and the Luck Lake sites were studied by Hendry and Wassenaar (17) and Remenda (19). Over the past decade, stable isotopes of water samples were analyzed between four and seven occasions from 12 wells completed between 1.2 and 19 m below ground at the King site and on two occasions from five





**FIGURE 4.** Cross plot of  $\delta D$  and  $\delta^{18}O$  data obtained from King and Luck Lake cores via pore water  $H_2O_{(liquid)}-H_2O_{(vapor)}$  equilibration compared the local meteoric water line for nearby Saskatoon, Canada (1990–2007; Environment Canada).  $\nabla$ , Luck Lake site,  $\blacktriangle$ , King site, and crosses denote local precipitation data.

wells completed between 8 and 45 m below ground at Luck Lake. In the current study,  $\delta D$  and  $\delta^{18}O$  measurements were performed on core samples collected from the King site ( $n = 43$ ) using the  $H_2O_{(liquid)}-H_2O_{(vapor)}$  equilibration method (manual injections only) and on 35 (manual injections) and 20 (continuous flow) core samples from Luck Lake. The Luck Lake core allowed a comparison of manual and continuous flow methods, and all sites were compared to  $\delta D$  and  $\delta^{18}O$  measurements from well water samples and the local meteoric water line. This allowed us to validate the  $H_2O_{(liquid)}-H_2O_{(vapor)}$  equilibration method data against conventional measurements obtained from wells at both sites.

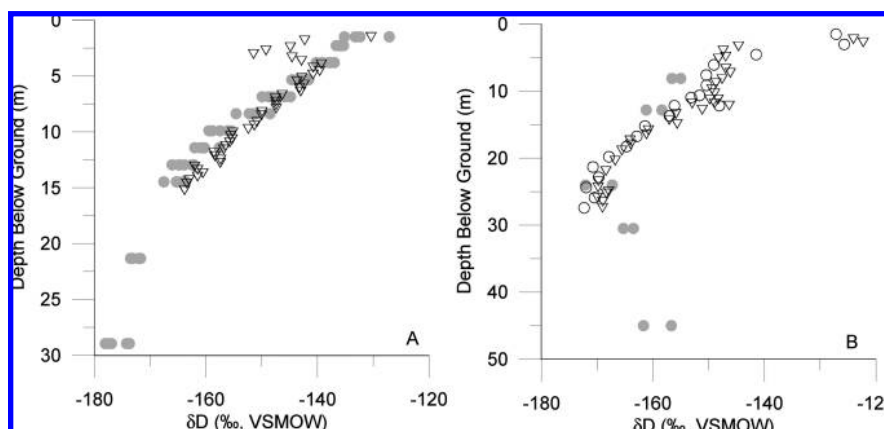
## Results and Discussion

**Liquid and Pore Water–Vapor Equilibration.** The minimum time required to achieve full  $H_2O_{(liquid)}-H_2O_{(vapor)}$  isotopic equilibrium in the sample bag headspace depended on whether the sample was pure liquid water (e.g., calibration standards), or pore water within geologic core material (sand, silt, or clay). For geologic and artificial cores, the sample equilibration time was dependent on whether intact cores

were used (e.g., clay, rock), if the core was broken into smaller pieces, or was unconsolidated (e.g., soil, sand).

For pure water, the time to reach  $H_2O$ –vapor equilibrium (100% RH headspace at 22.5 °C) in the gas sampling bags was <5 min (Figure 1). Pure water samples were tested for equilibration over times ranging from 1 to 90 min (Figure 2). The data revealed that a  $H_2O$  and isotopic equilibration time of 10 min (22 °C), and dynamic instrumental headspace sampling acquisition times above 300 s (zero slope), yielded acceptable precisions for  $\delta D$  and  $\delta^{18}O$ . We defined acceptable precisions to be  $<\pm 2$  ‰ and  $<\pm 0.4$  ‰ for  $\delta D$  and  $\delta^{18}O$ , respectively, which is comparable to modern continuous flow IRMS methods. In Figure 2,  $t = 0$  was defined as when the continuous flow instrument was switched to the sample bag for headspace sampling from an atmospheric air flow. Repeatability for liquid–water sample equilibration times of between 10 and 90 min, with instrumental headspace sampling integration around 300 s, was  $-187 \pm 0.7$  ‰ for  $\delta D$  and  $-35.3 \pm 0.3$  ‰ for  $\delta^{18}O$  ( $n = 25$ ; open boxes in Figure 2). These precisions are similar to IRMS-based equilibration methods (14, 20), and better than those reported for physical water extractions (2, 11).

For geologic core materials, the time required to reach pore water–vapor equilibrium in the plastic sample bags must be determined experimentally for the specific type and volume of geologic medium used. For example, here we used intact low permeability clay rich core samples from the King site (17), which probably represents a worst case scenario, because the plasticity of the core did not allow samples to be easily broken into smaller pieces. Hence the time to reach  $H_2O$  liquid–vapor equilibrium for these samples was controlled by matrix diffusion. Intact clay rich cores ( $n = 3$ ;  $70 \times 50$  mm diameter) placed in Ziploc bags were sealed and inflated with air to 900 mL. The headspace vapor  $\delta D$  and  $\delta^{18}O$  were measured using 50 mL manual injections after 1, 3, 4, and 12 days. In all cases, samples of  $\delta^{18}O$  and  $\delta D$  reached a plateau after 3 days, but by day 12 showed clear evidence of evaporative isotopic enrichment. Thus, for core samples, the optimum holding time for equilibration in resealable Ziploc sample bags is about 3–4 days. This equilibration time frame, of course, would be considerably lower for sandy and high permeability cores where pore water to vapor phase equilibration is much faster and approaching that of liquid water ( $\sim 10$  min). This experiment, however, revealed one major drawback to the use of Ziploc bags - that water vapor leakage (and isotopic fractionation) through the seal and plastic is inevitable over a relatively short time. Thus, careful planning and timing of core sample collection, sample



**FIGURE 5.** Vertical depth profiles for  $\delta D$  from King Site (A) and Luck Lake (B) clay–silt field sites. Filled circles are piezometer data (1990–2007) (17, 19).  $\nabla$ ,  $\delta D$  data from core samples done by  $H_2O_{(liquid)}-H_2O_{(vapor)}$  equilibration and laser spectroscopy using the manual injection method.  $\circ$ ,  $\delta D$  data obtained from core samples done by  $H_2O_{(liquid)}-H_2O_{(vapor)}$  equilibration and the continuous-flow injection method. The fractured zone (extending from  $<5$ –15 m depth) at the sites contain seasonally dynamic water movement and water table fluctuations.

storage, and isotopic analysis will be required. Ideally, samples should be collected, immediately placed in Ziploc bags, inflated with air, and measured as soon as possible, with liquid water isotopic standards prepared in the same manner that are analyzed at the same time to allow for data normalization and instrumental drift correction. If longer storage times for cores are required it may be preferable to store sealed core samples in a 100% RH-controlled chamber until isotopic analyses can be undertaken.

Following all sample isotope measurement processing, the OA-ICOS laser instrument should either be left in vacuum mode, or thoroughly flushed with dry air, before being shut down to avoid condensation of H<sub>2</sub>O (from 100% RH samples) in the optical cavity and on the internal highly reflective mirrors.

**Moisture Content Effects.** A series of tests were conducted to determine the range of moisture contents (MC) that could be measured for stable isotopes before adverse isotopic effects were observed. For this test, oven-dried dry silica sand samples (60 g) were placed in plastic bags and were wetted with distilled water having a  $\delta D$  value of  $-131\text{‰}$  and a  $\delta^{18}O$  value of  $-16.7\text{‰}$ . Individual samples were wetted to MC of 30, 20, 10, 5, 1, and 0.5 weight % MC, respectively. Immediately after wetting, the sample bags were inflated with dry air, resealed, and allowed to equilibrate for 12 h. Two laboratory isotopic standard waters were prepared and processed at the same time. Sample analysis was performed using the continuous flow method, with isotopic laboratory standards analyzed after every two samples (16). Results were normalized to the standard waters and are shown in Figure 3. These test results revealed excellent accuracy and repeatability for samples between 30% and 5% MC ( $\delta^{18}O = -16.5 \pm 0.1$ ,  $\delta D = -130 \pm 0.6$ ;  $n = 4$ ). However, below 5% MC the hydrogen and oxygen isotope values data became markedly and progressively worse, despite the sample bags still having a 100% RH headspace. This suggested that inflation of the sample bags with dry air below 5% MC resulted in progressive evaporative enrichment, and suggested that this technique may not be appropriate for low water content dry sands or some consolidated shale.

**Core Sample Repeatability.** An assessment of the repeatability of isotopic measurements on individual core samples was done using cores taken from the King site. Subsamples of clay-rich core samples collected at 9.9 m depth were oven-dried for 24 h, ground using a mortar and pestle, and wetted to 30% MC using distilled water of known isotopic composition ( $\delta D = -131\text{‰}$ ,  $\delta^{18}O = -16.7\text{‰}$ ). The samples were immediately split into three separate plastic bags, inflated with dry air, and allowed to equilibrate for 12 h. The samples were normalized to the two laboratory standard waters prepared at the same time. The results are shown in Table 1 and showed excellent sample repeatability ( $\delta D -133 \pm 0.5\text{‰}$ ,  $\delta^{18}O -15.7 \pm 0.02\text{‰}$ ,  $n = 3$ ).

**Field Validation.** The relationship between  $\delta D$  and  $\delta^{18}O$  values of pore water obtained from clay-rich core samples at both field sites determined by the manual and continuous flow injection methods were compared to the local meteoric water line (LMWL) at Saskatoon, Saskatchewan (about 120 km north of the sites) in Figure 4. A least-squares regression of pore water  $\delta D$  and  $\delta^{18}O$  values yielded an identical slope to the LMWL, indicating that the pore water samples were not affected by evaporation during the equilibration procedure, and that our sample processing, laser analysis method, standardization and data normalization approach can be used with confidence.

The high-resolution vertical pore water profile of  $\delta D$  ( $\delta^{18}O$  not shown, but see Figure 4) from the King site using manual injections is presented in Figure 5A and compared with data from groundwater piezometers at the same site. These results showed excellent agreement with pore water  $\delta D$  values from

wells as reflected in the  $\delta D$  depth profile (Figure 5A). The high-resolution vertical pore water profile for  $\delta D$  from the Luck Lake site (comparing manual and continuous flow injection methods) are shown in Figure 5B. As was the case for the King site, these results were in good agreement with available well data, showing that either the manual injection or continuous flow technique can be used to determine pore water  $\delta^{18}O$  and  $\delta D$  values.

Because our core profiles extended from near ground surface through the unsaturated zone and below the water tables at both sites, we were able to obtain a far more detailed profile through the upper 8 m interval than from the piezometers. This detailed vertical profile obtained from core showed that there is significant and discrete spatial isotopic structure that must be related to the hydrogeology and recharge history of the site. Further, subtle variations in the high-resolution  $\delta D$  profiles, such as the slight increase in the  $\delta D$  at about 12 m depth at the Luck Lake site, likely reflect heterogeneity in the hydrogeologic media. These subtle variations of water history could not be previously identified using coarsely spaced piezometer data.

This study showed that assays of  $\delta D$  and  $\delta^{18}O$  by a H<sub>2</sub>O<sub>(liquid)</sub>-H<sub>2</sub>O<sub>(vapor)</sub> pore water equilibration method and laser spectroscopy provided a new way to obtain accurate high resolution  $\delta D$  and  $\delta^{18}O$  values of pore water from single samples of saturated and unsaturated geologic media having volumetric water contents as low as 5%. Our results showed that a single continuous core may be sufficient to obtain detailed vertical isotopic depth profiles for pore water from geologic, soil and lacustrine media, thereby dramatically reducing the cost of obtaining pore waters using wells or physical water extraction methods. In our study, the maximum depth of vertical profiling was limited by the availability of hollow stem auger and the drill rig used. The use of drill equipment would allow coring to greater depths and thus permit the extension of high-resolution profiles to greater depths. In addition, the use of cores and this technique minimizes other inherent problems with the use of wells such as contamination by leakage from shallower depths and drilling fluids. We anticipate this method will be improved in future hydrogeologic studies with advances in sample bags technologies and with experiments designed to reduce sample size. The precision and accuracy of the laser based pore water H<sub>2</sub>O<sub>(liquid)</sub>-H<sub>2</sub>O<sub>(vapor)</sub> equilibration method was comparable or better than conventional and IRMS-based direct equilibration methods. Significant advantages of the H<sub>2</sub>O<sub>(liquid)</sub>-H<sub>2</sub>O<sub>(vapor)</sub> pore equilibration method and coupled laser based analysis method include dual hydrogen and oxygen isotope assays obtained on a single core sample, low consumables and instrumentation costs compared to IRMS systems, and the potential of field-laboratory based experiments.

## Acknowledgments

This research was supported by a Natural Sciences and Engineering Research Council of Canada (NSERC) IRC grant to M.J.H. and Environment Canada funding to L.I.W.

## Literature Cited

- van der Kamp, G.; van Stempvoort, D. R.; Wassenaar, L. I. The radial diffusion method 1. Using intact cores to determine isotopic composition, chemistry, and effective porosities for groundwater in aquitards. *Water Resour. Res.* **1996**, 32 (6), 1815–1822.
- Allison, G. B.; Hughes, M. W. The use of natural tracers as indicators of soil-water movement in a temperate semi-arid region. *J. Hydrol.* **1983**, 60, 157–173.
- Patterson, R. J.; Frape, S. K.; Dykes, L. S.; Mcleod, R. A. A coring and squeezing technique for the detailed study of subsurface water chemistry. *Can. J. Earth Sci.* **1977**, 15, 162–169.
- Stewart, G. L. Clay-water interaction, the behavior of 3H and 2H in adsorbed water, and the isotope effect. *Soil Sci. Soc. Am.* **1972**, 36, 421426.

- (5) Araguas-Araguas, L.; Rozanski, K.; Gonfiantini, R.; Louvat, D. Isotope effects accompanying vacuum extraction of soil water for stable isotope analyses. *J. Hydrol.* **1995**, *168*, 159–171.
- (6) Walker, G. R.; Woods, P. H.; Graham, A. B. Interlaboratory comparison of methods to determine the stable isotope composition of soil water. *Chem. Geol.* **1994**, *111*, 297–306.
- (7) Ingraham, N. L.; Shadel, C. A comparison of the toluene distillation and vacuum/heat methods for extracting soil water for stable isotopic analysis. *J. Hydrol.* **1992**, *140*, 371–387.
- (8) Gimmi, T.; Waber, H. N.; Gautschi, A.; Rubel, A. Stable water isotopes in pore water of Jurassic argillaceous rocks as tracers for solute transport over large spatial and temporal scales. *Water Res. Res.* **2007**, *43*, 4.
- (9) Freeze, R. A.; Cherry, J. A., *Groundwater*; Prentice Hall: Englewood Cliffs, NJ, 1979.
- (10) Hendry, M. J. Groundwater recharge through a heavy-textured soil. *J. Hydrol.* **1982**, *63*, 201–209.
- (11) Revesz, K. A.; Woods, P. H. A method to extract soil water for stable isotope analysis. *J. Hydrol.* **1990**, *115*, 397–406.
- (12) Altinier, M. V.; Savoye, S.; Michelot, J. L.; Beaucaire, C.; Massault, M.; Tessier, D.; Waber, H. N. The isotopic composition of porewater from Tournemire argillite (France): An inter-comparison study. *Phys. Chem. Earth* **2007**, *32* (1–7), 209–218.
- (13) Koehler, G.; Wassenaar, L. I.; Hendry, M. J. An automated technique for measuring  $\delta D$  and  $\delta^{18}O$  values of porewater by direct  $CO_2$  and  $H_2$  equilibration. *Anal. Chem.* **2000**, *72* (22), 5659–5664.
- (14) Kelln, C. J.; Wassenaar, L. I.; Hendry, M. J. Stable isotopes ( $\delta^{18}O$ ,  $\delta^2H$ ) of pore waters in clay-rich aquitards: A comparison and evaluation of measurement techniques. *Ground Water Monit. Rem.* **2001**, *21* (2), 108–116.
- (15) Rubel, A. P.; Sonntag, C.; Lippmann, J.; Pearson, F. J.; Gautschi, A. A. Solute transport in formations of very low permeability: Profiles of stable isotope and dissolved noble gas contents of pore water in the Opalinus Clay, Mont Terri, Switzerland. *Geochim. Cosmochim. Acta* **2002**, *66* (8), 1311–1321.
- (16) Lis, G. P.; Wassenaar, L. I.; Hendry, M. J. High-precision laser spectroscopy D/H and  $18O/^{16}O$  measurements of microliter natural water samples. *Anal. Chem.* **2008**, *80* (1), 287–293.
- (17) Hendry, M. J.; Wassenaar, L. I. Implications of the transport of  $\delta D$  and  $\delta^{18}O$  in porewaters on groundwater flow and the timing of geologic events in a thick aquitard system. *Water Resour. Res.* **1999**, *35* (6), 1751–1760.
- (18) Werner, R. A.; Brand, W. A. Referencing strategies and techniques in stable isotope ratio analysis. *Rapid Commun. Mass Spectrom.* **2001**, *15* (7), 501–519.
- (19) Remenda, V. H. Origin and migration of natural groundwater tracers in thick clay tills of Saskatchewan and the Lake Agassiz clay plain. Ph.D. Thesis, University of Waterloo, Waterloo, Ontario, Canada, 1993.
- (20) Morrison, J.; Brockwell, T.; Merren, T.; Fourel, F.; Phillips, A. M. On-line high-precision stable hydrogen isotopic analyses on nanoliter water samples. *Anal. Chem.* **2001**, *73* (15), 3570–3575.

ES802065S