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ORIGINAL PAPER

Tracing the Seepage of Subsurface Sinkhole Vent Waters into Lake Huron Using Radium and Stable Isotopes of Oxygen and Hydrogen

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Abstract Exchange of water between groundwater and surface water could alter water quality of the surface waters and thereby impact its ecosystem. Discharges of anoxic groundwater, with high concentrations of sulfate and chloride and low concentrations of nitrate and oxygen, from three sinkhole vents (El Cajon, Middle Island and Isolated) in Lake Huron have been recently documented. In this investigation, we collected and analyzed a suite of water samples from these three sinkhole vents and lake water samples from Lake Huron for Ra, radon-222, stable isotopes of oxygen and hydrogen, and other ancillary parameters. These measurements are among the first of their kind in this unique environment. The activities of Ra are found to be one to two orders of magnitude higher than that of the lake water. Isotopic signatures of some of the bottom lake water samples indicate evidences for micro-seeps at distances farther from these three vents. A plot of δD versus $\delta^{18}O$ indicates that there are deviations from the Global Meteoric Line that can be attributed to mixing of different water masses and/or due to some subsurface chemical reactions. Using the Ra isotopic ratios, we estimated the transit times of the vent waters from the bottom to the top of the vent (i.e., sediment–water interface) to be 4–37 days. More systematic studies on the distribution of the radioactive and stable isotope studies are needed to evaluate the prevalence of micro-seeps in Lake Huron and other Great Lakes system.

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1 Introduction

Exchange between groundwater and surface waters (such as lakes, coastal ocean and rivers) is ubiquitous throughout the Earth. The major factors that drive the exchange of groundwater with another reservoir are the changes in the hydraulic gradient of the groundwater system, (primarily caused by recharge from precipitation and withdrawal from these reservoirs), and salinity or density gradients, if any. Additional factors that affect the exchange of water include aquifer geometry and heterogeneity which will affect the complex groundwater flowpaths. Such exchanges of water can alter the biogeochemical cycling of chemical species and thereby affect the recipient ecosystem. Generally, nutrient concentrations in groundwater are significantly higher than that of surface waters in lakes, and thus, excessive fluxes of nutrients from groundwater discharge could lead to the formation and sustenance of harmful algal blooms, eventually affecting the water quality of surface waters (e.g., Hagerthey and Kerfoot 1998).

Groundwater discharges are often diffuse and hence are difficult to characterize and quantify. Naturally occurring radioactive tracers, such as radium isotopes and ^{222}Rn, provide time- and space-integrated views of the discharge, and the timescale of integration is dependent upon the residence time/removal time/mean-life of the tracers (e.g., Moore 1996; Church 1996; Cable et al. 1996; Burnett et al. 2006). A large body of literature exists on the quantification of submarine groundwater discharge (SGD) using natural ^{226}Ra and ^{222}Rn in coastal marine waters (see an excellent review paper by Burnett et al. 2006), but limited data are available in freshwater system (e.g., Kraemer and Curwick 1991; Kraemer 2005). Utility of radium as a tracer in freshwater lakes is very limited, primarily due to its geochemical behavior.

The stable isotopic composition of oxygen (δ^{18}O) and hydrogen (δD) of waters provides insight into the sources and mixing of water masses as well as interaction of water with the rocks and minerals through which they pass (e.g., Long et al. 1988; McIntosh and Walter 2006; Raidla et al. 2011). Most of the δ^{18}O and δD data of meteoric water fall on the Global Meteoric Line (GML) and is given by: $\delta\text{D}\ (‰) = (8.1 \pm 0.1)\ \delta^{18}\text{O}\ (‰) + (11 \pm 1)$ for the continental stations in the Northern hemisphere (Daansgaard 1964). However, deviation from this line has been reported for groundwater and is utilized to quantify mixing of water masses with different δD and δ^{18}O isotopic composition and interaction of water with minerals (e.g., Long et al. 1988; McIntosh and Walter 2006; Raidla et al. 2011).

One of the least understood sources of water to the Great Lakes is the submarine outflow across the sediment–water interface into the lake (Grannemann et al. 2000). When meteoric water seeps through and reaches aquifers in terrestrial uplands adjacent to lacustrine systems, it is anticipated that there will be discharge of groundwater to the lake due to changes in the hydraulic head. In general, there is a variable time lag between aquifer recharge through precipitation and groundwater discharge to coastal waters (Michael et al. 2005). In areas where the aquifers lying adjacent to the lake have water tables above the lake level, the discharge of groundwater will likely occur throughout the

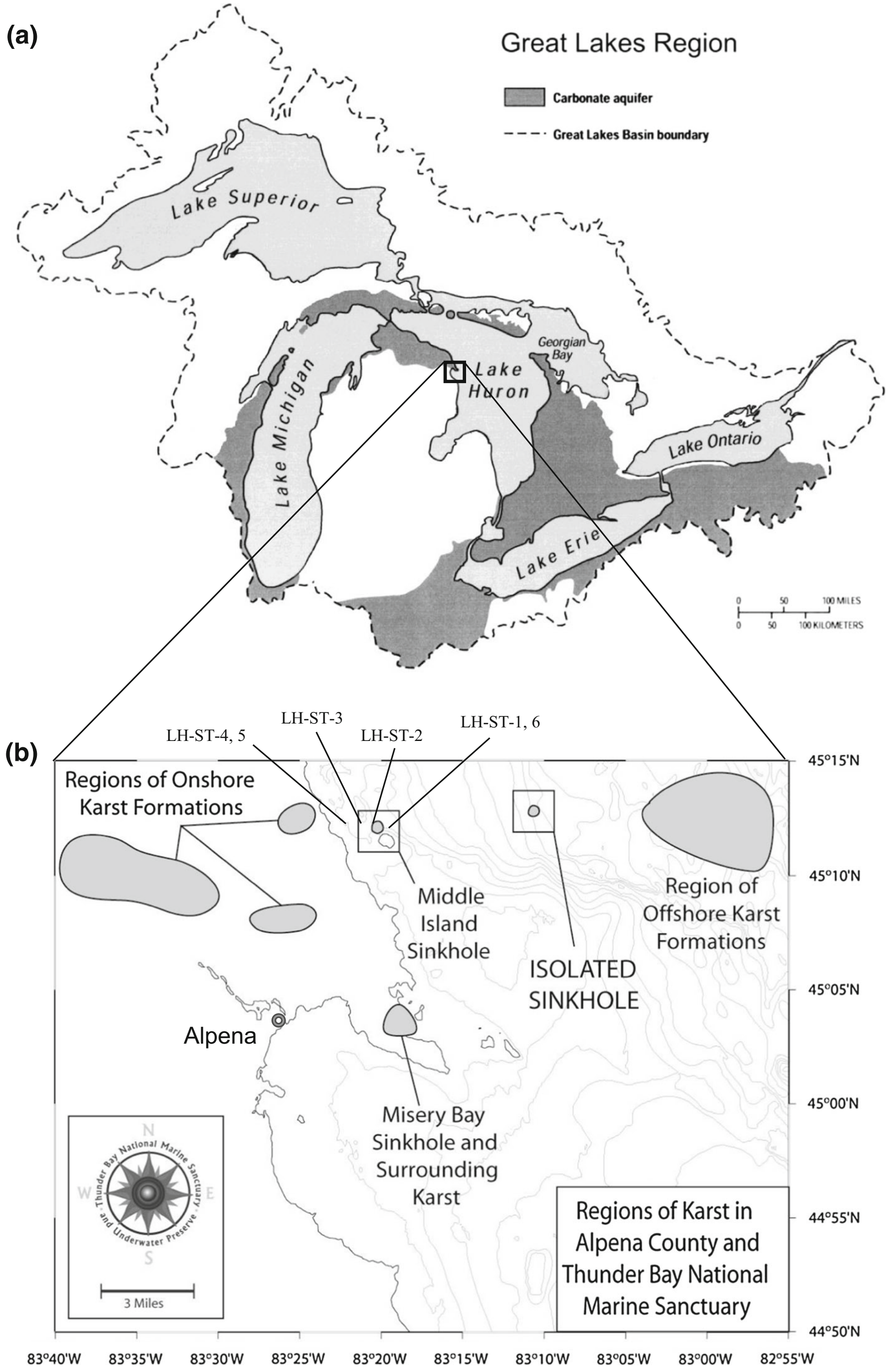


Fig. 1 Location of three sinkhole vents in Lake Huron

year, similar to what has been observed at the interface between the coastal ocean and the continents (Michael et al. 2005).

The discovery of sinkhole vents in Lake Huron (sinkholes around the Alpena, Michigan area are present at several onshore locations as well) during an archeological expedition in 2001 (Coleman 2002) revealed a new source of SGD to the lakes. These anoxic, highly reducing, high-sulfate and high-chloride waters with chemical signatures strikingly different from ambient lake waters has been shown to affect the ecology of the waters adjoining the vents (Biddanda et al. 2006, 2009); e.g., via the presence of massive purple, green and whitish bacterial mats observed in the Middle Island and El Cajon sinkholes (Fig. 1). The purple mats occurring along the ridges and on the lake floor were composed of filamentous cyanobacteria. Underlying the lake floor mats was a thick layer of black, sulfidic, organic-rich sediment whose stable isotopic signatures attest to their planktonic origin (Nold et al. 2013). The deep sinkhole (Isolated sinkhole) is below the photic zone (<90 m water depth), and biological activity at the groundwater/lake water interface is dominated by chemosynthesis. While these systems are easily accessible, they are analogues to systems in other extreme environments, such as deep-sea marine vents and sites beneath the Antarctic Ice Shelf (Domack et al. 2005).

In this first isotopic study (radium, radon and stable isotopes of oxygen and hydrogen) of the vent waters from sinkholes in Lake Huron, we collected and analyzed a suite of water samples from three sinkhole vents. These three sites represent a shallow water vent (<5 m, El Cajon; ~9 m long and 5 m wide), a mid-depth vent (23.0 m, Middle Island; ~125 m long and 100 m wide), and a deep-water vent (~95 m, Isolated sinkhole, ~55 m long and 40 m wide). We also collected samples from adjoining ambient lake water for a suite of anions, stable isotopes of oxygen and hydrogen, Ra, ^{222}Rn and other ancillary parameters. For the first time, we report very high activities of Ra isotopes and distinctly different stable isotopic composition of oxygen and hydrogen in sinkhole waters compared to surface Lake Huron waters. This study was designed to address the following questions: (1) How do the activities of Ra isotopes vary in three sinkhole vents compared to those in Lake Huron water? (2) How does the δD and δ^{18}O isotope composition in the sinkhole waters compare with those in the Lake Huron waters and the groundwater samples from the central Michigan Basin? Is there any evidence for chemical reactions dominant in the vent waters as reflected in the values and relationship between δD and δ^{18}O? (3) Is there any isotopic evidence for other sinkhole vents and/or micro-seeps as evidenced by commonly occurring cyanobacteria species in different places at the bottom of Lake Huron? and (4) Can we constrain the temporal scales involved in the vertical movement of sinkhole vent waters based on the abundance and distribution of Ra isotopes?

2 Materials and Methods

2.1 Study Area

The Great Lakes were shaped about 11,000 years ago when the last glaciers receded from North America. Lake Huron, the third largest of the lakes, is contained within a basin underlain by 400-million-year-old Paleozoic limestone bedrock that formed when shallow seas covered these continental areas (Gardner 1974; Grannemann et al. 2000). The gradual dissolution of this limestone has led to caves, cracks, and fissures called karst formations. When underground caves collapsed, they formed sinkholes. Some of these sinkholes can be found on land, but interestingly, others are located under the modern-day surface waters of Lake Huron (Biddanda et al. 2009). In these submerged sinkholes, dense groundwater rich in sulfur but poor in oxygen continuously flows through cracks and underwater springs onto the floor of Lake Huron (Ruberg et al. 2008). Because the groundwater is likely modified by the limestone, shale, and marine evaporate layers through which it flows, it has significantly different physicochemical properties than the surrounding lake water (Nold et al. 2010). Along its flow path, the groundwater nourishes colorful benthic microbial mats not found anywhere else in the Great Lakes (Biddanda et al. 2012).

2.2 Sampling Location

Water samples were collected from three sinkhole vents and lake water samples from the surrounding areas during summer in 2008 and 2009 (Fig. 1). Sinkholes are commonly found around Alpena, Michigan, (Fig. 1) at several onshore locations as well as nearshore. The three sinkholes that were sampled are: (1) El Cajon (Misery Bay); (2) Middle Island sinkhole; and (3) Isolated sinkhole.

2.3 In Situ Field Measurements

Vertical arrays of temperature sensors were deployed at half meter intervals at several locations in and around the area of active SGD within the “Alcove” in the Middle Island sinkhole (Fig. 2) between August 2008 and May 2009. Hourly time series measurements were made between August of 2009 and May 2010. The sensors all had an accuracy of 0.5 °C or less.

2.4 Water Sampling and Analysis

Water samples were mainly collected during three separate sampling trips in June, July, and September of 2008. Water samples (10–25 L) from the sinkhole vents were collected

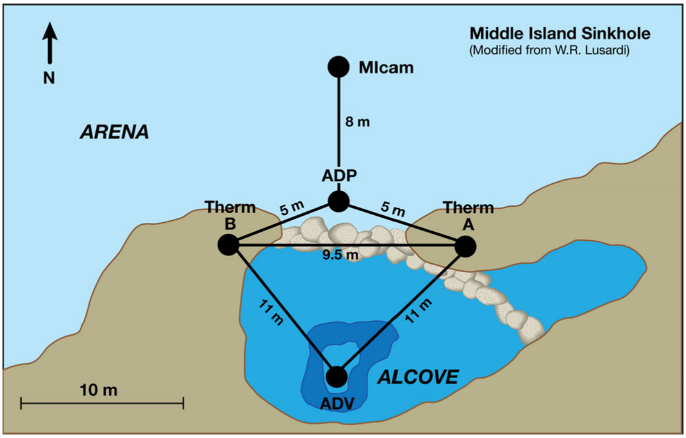


Fig. 2 Temperature sensor deployment at the Alcove, Middle Island sinkhole. The Alcove is the main source of groundwater at this sinkhole. Groundwater fills the Alcove and overflows through a shallow sill onto the wider Arena and spreads out on the bottom

for dissolved ^{223}Ra, ^{224}Ra, ^{226}Ra, and ^{228}Ra analysis, either through submersible pump or with the help of divers. The water samples were filtered at <1 L/min through two columns containing 10 g each of dry MnO_2-impregnated acrylic fiber (Mn fiber) to quantitatively extract dissolved Ra. Although anoxic waters containing H_2S could leach (and possibly reduce) some of the MnO_2 from the fiber making the fiber extraction method less effective, we did not observe any bleaching of the fiber during filtration and the surface area of the fiber retained its original color. Furthermore, we utilized two separate filter cartridges and combined the fiber from both cartridges for ashing, as suggested by Todd et al. (1988).

For the measurements of ^{223}Ra, ^{224}Ra and ^{228}Ra activities in lake water, about 600 L (as measured by a mechanical flow meter) of unfiltered water was pumped using a peristaltic pump and fed directly into one inline polypropylene pre-filter (1-µm nominal pore-size) followed in series by one inline MnO_2 fiber cartridge (polypropylene) at a flow rate of ~5–8 L/min. Although the removal of Ra onto MnO_2 fiber cartridges at high flow rates is not quantitative (Baskaran et al. 1993), reliable activity ratios of Ra (^{223}Ra/^{226}Ra, ^{224}Ra/^{228}Ra and ^{228}Ra/^{226}Ra) were obtained from this method and used in conjunction with a separate aliquot used for ^{226}Ra determination (Baskaran et al. 1993). After filtration, the MnO_2 fiber cartridge was placed in a ziplock bag, sealed, labeled and brought back to the laboratory. The cartridge was cut down its length, and the MnO_2 fiber was removed from the plastic core. For the quantitative analysis of ^{223}Ra, ^{224}Ra, ^{226}Ra, and ^{228}Ra, 60–100 L of filtered water sample was collected and were filtered through two columns of MnO_2 fiber column containing 10 g MnO_2 fiber in each cartridge at a flow rate of 0.75 L min. Specific activity of ^{226}Ra was determined from this sample, and the specific activities of ^{223}Ra, ^{224}Ra, and ^{228}Ra in the lake water samples were obtained from the ^{223}Ra/^{226}Ra, ^{224}Ra/^{226}Ra, and ^{228}Ra/^{226}Ra ratios and specific activity of ^{226}Ra.

The fibers, both polypropylene and acrylic coated with MnO_2, were placed in a crucible and ashed in a furnace for 8 h at 550 °C for polypropylene and 20–24 h at 850 °C for acrylic fibers. The ash was allowed to cool, quantitatively transferred to a 10-mL gamma-counting vial, weighed, and sealed. The first counting was usually conducted within 3 days after sampling. The second counting was conducted after a minimum of 3 weeks (^{222}Rn and its daughter products to reach secular equilibrium with ^{226}Ra). The radium isotopes were analyzed in a high-resolution well-type gamma detector, using the 352 keV (^{214}Pb) and 609 keV (^{214}Bi) peak energies for ^{226}Ra, and 338 keV (^{228}Ac), 911 keV (^{228}Ac) peak energies for ^{228}Ra, 269.5 keV peak energy for ^{223}Ra, and 238.6 keV (^{212}Pb) peak energy for ^{224}Ra (Krishnaswami et al. 1991).

The gamma ray detector was calibrated with standard reference materials RGU-Th for ^{228}Ra (via ^{228}Ac at 338 keV and 911 keV) and RGU-1 for ^{226}Ra (via ^{214}Pb at 352 keV and ^{214}Bi at 609 keV). Typical resolution (full width at half maximum) was ~1.3 keV at 46 keV and ~2.2 keV at 1.33 MeV. The peak/Compton ratio for ^{60}Co (1332 keV) was 45.0:1. Peak analysis was performed with the software peak analysis that came with the InSpector (Canberra Company). Typically, the samples were counted for 24 h.

Radon-222 measurements were conducted on samples collected via the ROV and in situ pumping system. Typically, 500-mL subsamples were drawn into an airtight syringe to which 100-mL He headspace was added. Samples were equilibrated by shaking the He transferred to a standard Lucas cell for counting (Mathieu et al. 1988; Key et al. 1979). Transfer efficiencies were determined by repeated serial extraction and vary according as the head space ratio, 52 % in the case of 500:100 mL ratio.

Water samples were collected for stable isotope analysis in 2-mL glass vials using a peristaltic pump. The vials were filled until overflowing, tightly sealed without any headspace and shipped to the University of California—Davis Stable Isotope Analysis Laboratory for δD and $\delta^{18}O$ analyses. Analysis of $^{18}O/^{16}O$ and D/H isotope ratios was conducted using a Laser Water Isotope Analyzer V2 (Los Gatos Research, Inc., Mountain View, CA, USA). The samples were injected six times with the first three injections being discarded and the last three injections being used for isotope ratio calculations. The sample isotope ratios were standardized with working standards which were calibrated against IAEA-standard reference materials. The precision of this analysis is normally <0.8 ‰ for δD and <0.1 ‰ for $\delta^{18}O$. All the stable isotope results are reported as the difference between the isotope ratio of the sample and that of a standard and expressed in per mil (=per thousand) units as follows:

$$\delta\text{D or } \delta^{18}\text{O } (‰) = ((R_{\text{sample}}/R_{\text{standard}}) - 1) \times 10^3$$

where R is the $^2H/^1H$ or $^{18}O/^{16}O$ ratio and the standard is the Vienna Standard Mean Ocean Water (VSMOW).

Total dissolved solids (TDS) were calculated by evaporating a known amount of water sample in a Teflon beaker to leave a residue that was subsequently weighed with a precision analytical balance capable of 0.1 mg accuracy. Depth profiles were taken using a YSI 6600 sonde equipped with a YSI 6560 temperature/conductivity sensor, YSI 6150 ROX optical dissolved oxygen sensor, and 6565 pH/ORP sensor (Ruberg et al. 2008).

Water samples for chloride, sulfate, and nitrate measurements were collected by filtering the sample through a 0.45-μm Nuclepore filter and were analyzed by a modified ion chromatography method (APHA 1998) on a Dionex DX-500 ion chromatography system (Biddanda et al. 2006). Water samples for nutrient analyses were collected by either pumping up bottom water from within the sinkholes through tygon tubing attached to the umbilical cable of the ROV, or from discrete Niskin bottles for water samples collected to characterize background lake water conditions. All samples collected for nutrient analysis were processed immediately upon collection. Sample aliquots for dissolved nutrients were filtered through a 0.2-μm Nylon filter into polycarbonate tubes and frozen until analysis (Johengen et al. 1995). Sample aliquots for total phosphorus, 50 mL of raw lake water, were directly collected in acid-cleaned Pyrex tubes and stored in the dark at 4 °C until digested, usually within 1 week of collection. Nutrient concentrations were determined using standard automated colorimetric (APHA 1998) procedures on a Technicon Auto Analyzer II according to methods detailed in Davis and Simmons (1979). Ammonium was determined by the phenate method based on the indophenol blue reaction. Nitrate was determined by the cadmium reduction method based on the azo dye reaction. Total phosphorus (TP) was determined by persulfate digestion after the method of Menzel and Corwin (1965), followed by analysis for soluble reactive phosphorus (SRP).

2.5 Laboratory Analysis for Ra Absorption

About 1 g of sediment (1.9 dpm/g) from Detroit River (note: Detroit River is a connecting channel between Lake Huron and Lake Erie) was equilibrated with 30 mL of water of different salinities (0, 1, 5, 10, 25 and 35 ‰) after the addition of diluted uraninite solution with ^{226}Ra activity of 607 dpm (pH was adjusted with NH_3OH to the same as the freshwater prior to addition). The mixture was subjected to shaking in a wrist action shaker for ~24 h. The solution and solid were separated by vacuum filtration through a #42

Whatman filter paper. The solution was quantitatively passed through MnO_2 fiber five times to quantitatively extract Ra from solution on to the fiber. The fiber was then ashed and used for the determination of ^{226}Ra activities (Baskaran et al. 1993). The filter paper was ashed, and the ash was quantitatively transferred into a counting vial and activity of ^{226}Ra was determined.

3 Results

3.1 In Situ and Field Measurements

Hourly in situ observations made in the Alcove (Fig. 2) showed that the groundwater maintained a constant temperature of about 9.1 °C, while the temperature of the ambient lake water varied seasonally from 0 °C to over 20 °C. The temperature data also showed that the interface between the groundwater and the overlying lake water was at a depth of between 17.5 and 18.0 m, and that this depth remained constant throughout the year (Fig. 3). Horizontal current speeds measured in the Alcove averaged about 0.06 m/s with little variation over time.

The area through which the groundwater discharged from the Alcove to the arena is roughly triangular with a cross-sectional area of about 2.85 m^2. Current velocities measured in the bottom meter of the flow at the station acoustic Doppler current profiler (ADP) showed that the water traveled down the slope into the arena throughout the year with an average velocity of about 0.08 m/s. The measured velocities at this station were highly variable and probably reflect different degrees of mixing with the ambient lake water. Using average horizontal velocity of water discharged out of the Alcove into the arena of 0.06 m/s, the estimated discharge of groundwater from the vent is 0.171 m^3/s (or 5.40×10^6 m^3/year). Details on the vertical depth profile of conductivity and temperature in the near-bottom environment over the Isolated sinkhole taken by the M-Rover's CTD during 2003 are given in Biddanda et al. (2006).

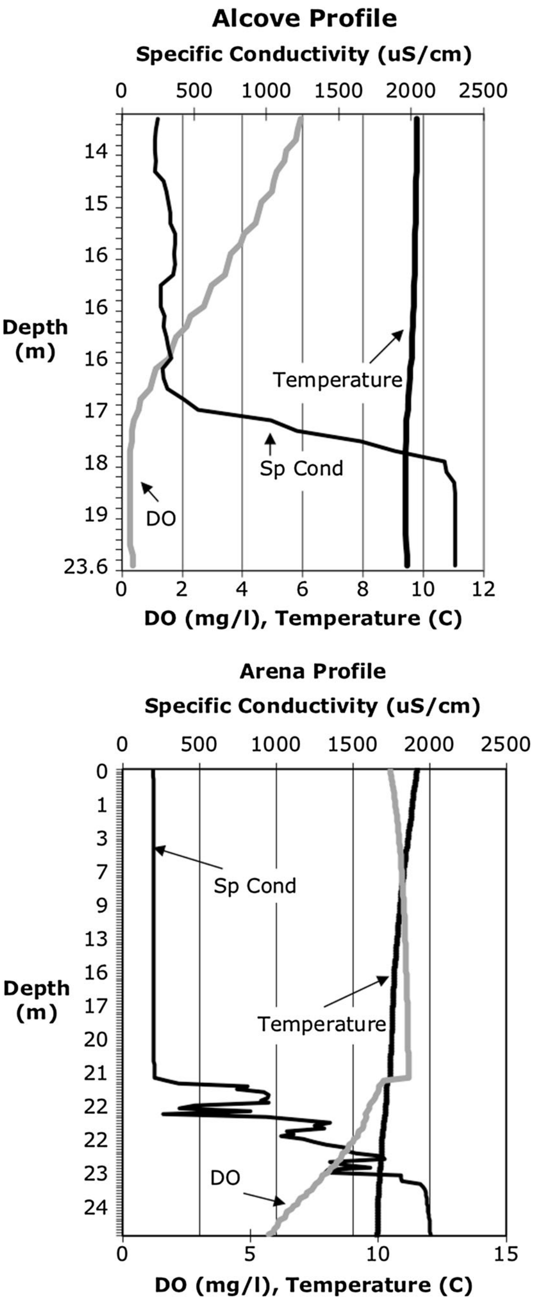
3.2 Sources and Variations in the Amount of Water Discharge from Sinkhole Vents

Field observations have indicated that there are temporal variations of the amount of water discharge in Middle Island sinkhole vent (Hawley, unpublished data), and no data are available from the other two vents. The discharge of groundwater venting in the karst sinkholes could be driven by hydrological and climatic conditions. The fluctuations in the amount of discharge could also control the concentrations of chemical species, life forms and biogeochemical processes in these ecosystems. Recharge of the Michigan basin from meteoric water in areas where the bedrocks are above the lake level is likely the driving agent for the discharge of water through the sinkhole vents.

3.3 Comparison of the Geochemical and Geophysical Parameters of the Vent and Lake Water

The temperature, specific conductance, pH, and concentrations of dissolved oxygen, chloride, and sulfate are given in Tables 1 and 2. The temperature of the vent waters during our sampling ranged between 4.2 and 10.0 °C in all three vents, with the lowest

Fig. 3 Vertical profiles of DO, temperature, conductivity in Alcove and Arena in the Middle Island sinkhole



temperature found in Isolated sinkhole vent. These measured variations in temperature of the vent waters in Isolated sinkhole are attributed to likely variations in the fractional amount of dilution of vent water with that of lake water. The temperature in the surface waters adjoining Isolated and Middle Island sinkholes varied between 9.6 and 24.6 °C, similar to the earlier observations reported (Ruberg et al. 2005; Biddanda et al. 2006). Vent

Table 1 Location, depth, dissolved oxygen (DO), total dissolved solids (TDS), conductivity, total phosphorus, ammonia, and other standard parameters on water samples collected from the sinkhole vents in Lake Huron

Sample code and collection date	Depth (m)	Location	DO (mM)	pH	Temp (°C)	TDS (mg/L)	Conduct. (mS/cm)	SO_4^{2-} (mM)	Cl^- (mM)	TP (SRP) Mean (range) (μM)	NH_4 Mean (range) (μM)
El Cajon											
Sample-1 (June 19, 2008)	NM	45°05.20 N 83°19.09 W	NM	NM	NM	NM	NM	NM		NM [0.04(0.02–0.08)]	1.79 (1.21–2.64)
Sample-2 (June 2006)	NM	NM	NM	NM	NM	NM	NM	12.7	0.82	NM	NM
Vent (September 19, 2008)	<1 m	45°05.20 N 83°19.09 W	0.0	7.3	10.0	1601	2400	13.6	1.30	NM	NM
Middle Island											
Surface water (June 18, 2008)	<1 m	45°11.92 N 83°19.65 W	0.34	8.3	9–18	NM	200	0.28	0.37	NM [0.02(0.02–0.03)]	0.36 (0.26–0.49)
Lake water (June 19, 2008)	23.0	As above	0.11	7.4	11.0	74	217	NM	NM	NM [0.06(0.03–0.09)]	0.44
Vent water (June 19, 2008)	23.0	As above	0.00	7.2	9.0	1192	2300	17.6	1.13	NM	NM
Vent water (June, 2006)	23.0	As above	NM	NM	NM	NM	NM	9.49	0.59	NM	NM
Isolated sinkhole											
Isolated-1 (September 6, 2008)	93.7	45°10.73 N 83°09.19 W	0.04	NM	7.0	NM	1827	4.69	2.14	NM [0.06(0.01–0.14)]	2.57 (1.97–2.94)
Isolated-2 (September 7, 2008)	93.7	As above	0.11	NM	6.4	NM	2864	10.1	4.37	NM [0.06]	7.31
IS-VO-B1 (June 12, 2009)	94.3	As above	0.12	7.8	8.6	1085	2500	13.2	6.29	0.25 [0.09]	7.35
IS-VO-B2 (June 12, 2009)	94.3	As above	0.04	7.7	4.3	NM	1600	9.44	–	0.05 [0.01]	1.17
IS-VO-B3 (June 12, 2009)	94.3	As above	NM	NM	6.1	2506	2500^+	NM	5.53	0.20 [0.08]	6.93
IS-VO-B4	91.1	As above	NM	NM	4.1	2204	NM	12.7	6.05	0.22 [0.01]	4.44

Table 1 continued

Sample code and collection date	Depth (m)	Location	DO (mM)	pH	Temp (°C)	TDS (mg/L)	Conduct. (mS/cm)	SO_4^{2-} (mM)	Cl^- (mM)	TP (SRP) Mean (range) (μM)	NH_4 Mean (range) (μM)
IS-VO-R1	91.1	As above	0.16	7.7	7.6	2246	2620	12.3	5.67	0.20 [0.08]	6.50
June 12, 2009 IS-VO-R2 (June 12, 2009)	0.02	As above	0.02	7.8	9.3	2712	2820	NM	NM	0.35 [0.12]	7.14
IS-40 M cont. (June 12, 2009)	40.0	As above	0.43	8.2	4.2	56	210	NM	NM	0.05 [0.01]	0.38

NM not measured; concentrations of Si (μM, mean and range in parenthesis) are: 212 (196–231), 25 (23–27), 69 (65–75) and 159 [130–175 (μM)] in sample-1 (El Cajon), Middle Island (surface and Lake Floor), and Isolated sinkhole (Isolated 2), respectively; concentrations of NO_3^- (mM) in VO-B1, VO-B2, VO-B3, VO-B4, VO-R1, VO-R2 are 0.0008, 0.0047, 0.0010, 0.0048, 0.0011, 0.0008, 0.0048, respectively

Table 2 Location, conductivity, temperature and total dissolved solid (TDS) in vertical profiles[a] from Lake Huron (LH)

Area	Location	Depth (m)	Conductivity (μS/cm)	pH	Temp (°C)	TDS (mg/L)
Surface water	Collection: July 30, Aug. 1 2009					
LH-ST-1-S	45°11.93 N; 83°19.69 W	<1	91	NM	21.2	NM
LH-ST-1-M	45°11.93 N; 83°19.69 W	8.2	180	NM	23.6	NM
LH-ST-1-D	45°11.93 N; 83°19.69 W	16.9	273	NM	19.6	66
LH-ST-2-S	45°12.04 N; 83°20.41 W	<1	NM	NM	NM	NM
LH-ST-2-M	45°12.04 N; 83°20.41 W	6.4	NM	NM	NM	NM
LH-ST-2-D	45°12.04 N; 83°20.41 W	15.1	207	NM	24.0	108
LH-ST-3-M	45°12.10 N; 83°21.12 W	10.4	188	NM	24.6	NM
LH-ST-3-D	45°12.10 N; 83°21.12 W	19.0	967	NM	19.6	597
LH-ST-4-D	45°12.19 N; 83°21.99 W	9.4	200	8.3	22.2	145
LH-ST-5-S	45°12.13 N; 83°22.89 W	<1	NM	NM	NM	NM
LH-ST-6-M	45°11.92 N; 83°19.65 W	16.4	NM	NM	NM	NM
LH-ST-6-D	45°11.92 N; 83°19.65 W	22.0	NM	NM	NM	1767
SH-surface water	NM	<1	NM	NM	NM	NM

NM not measured

[a] *S* surface (upper 1 m), *M* mid-depth, *D* bottom (within ~1 m from sediment–water interface)

water temperatures found in Lake Huron are comparable to the 594-m-deep Crater Lake vent waters in Oregon where temperatures are reported to be 4.7–9.5 °C with bacterial mats at the bottom of the lake (Dymond et al. 1989). The pH of the vent waters is less basic (pH of 7.2–7.4) than the ambient lake water (8.3). Dissolved oxygen concentrations in the sinkhole vents are significantly lower, 0–0.16 mM (mean: 0.06 mM) compared to the concentrations in the surface lake waters (0.3–0.5 mM, Table 1), indicating that the sinkhole water is anoxic.

The total dissolved solid concentrations in the vent waters (1085–2712 mg/L) are one to two orders of magnitude higher than that of the lake waters (56–74 mg/L, Tables 1, 2). The specific conductivity in the vent waters are significantly higher (1600–2864 micro Siemens/cm) compared to the lake water (200 micro Siemens/cm; Table 1). The sulfate concentrations (4.7–17.6 mM) in sinkhole waters are about two orders of magnitude higher than the surface waters (0.28 mM, Table 1), indicating discharge of highly sulfidic waters into the lake. The chloride concentration in the vent waters (0.6–6.3 mM) is significantly higher than the surface lake waters (<0.4 mM, Table 1). While the concentrations of sulfate in sinkhole fluids are high, the concentrations of DOC and DO are significantly lower (Table 1, Biddanda et al. 2009). The total P concentrations varied between 0.05 and 0.35 μM in the vent waters and are higher than that in the surface lake water (Table 1). The ammonia concentration in the vent water (1.2–7.1 μM) is about an order of magnitude higher than that of the lake water (~0.4 μM, Table 1). The concentrations of Si varied between 23 and 231 μM in the vent waters. The nitrate concentrations in the vent waters are very low. Thus, the vents are characterized as high-sulfate, low-oxygen waters with high chloride and low nitrate. Filamentous cyanobacteria is found to thrive in this environment by producing energy from anoxygenic photosynthesis, where H_2S is used rather than oxygen as an electron source (Biddanda et al. 2009). A similar cyanobacterial community has been reported in sulfate-rich Lake Cadagno in Switzerland (Hebting et al. 2006).

3.4 Isotopes of Oxygen, Hydrogen and ^{226}Ra Distribution

The δ^{18}O and δD isotopic composition of water samples from Lake Huron and three sinkhole vents (El Cajon, Middle Island, and Isolated sinkhole) are given in Table 3. The δ^{18}O values in lake water varied between −6.6 and −7.6 ‰ (mean: −7.2 ‰, $n = 10$), while the corresponding δD values ranged between −53.1 and −60.5 ‰, with a mean value of −55.2 ‰ ($n = 10$, Table 3, LH-ST-2-D and LH-ST-6-D are excluded from this range and average calculated, discussion below). This can be compared to the earlier published values of −7.45 ‰ for δ^{18}O and −55.2 ‰ for δD in Lake Huron water samples (Long et al. 1988) and the predicted value for the east-central Michigan basin (43.62°N and 190 m amsl) of −7.3 to −8.6 ‰ for δ^{18}O and −50.6 to −60.4 ‰ for δD based on the relationship between δ^{18}O and δD and temperature, precipitation, latitude, and altitude (Yurtsever and Gat 1981; Long et al. 1988). When meteoric water undergoes evaporation, it leads to heavier values of δ^{18}O and δD.

In the El Cajon sinkhole vent, the δ^{18}O values on two samples collected 2 years apart (analyzed at two different laboratories) show consistent value, −12.2 and −12.5 ‰ for δ^{18}O (Table 3) while the measured δD value, −83.6 ‰, is highly depleted. The vent waters in Middle Island sinkhole also show similar values, −11.4 and −11.2 ‰ for δ^{18}O and −80.1 ‰ for δD (Table 3) again suggesting similar δ^{18}O values. Note that a relatively large range of δ^{18}O values (−7 to −18.5) and δD (−56 to −137 ‰) from over 350 domestic wells including near-surface saline groundwater in the east-central Michigan basin has been reported (Long et al. 1988). There is a correlation between Cl^- concentration and δ^{18}O in the sinkhole waters (Fig. 4, $r = 0.73$, $n = 10$). When water undergoes evaporation, it is enriched in ^{18}O, and the Cl^{-1} concentration also will increase, and hence this correlation is likely due to the effect of evaporation.

The ^{226}Ra activities in Lake Huron water varied between 3.0 and 13.8 dpm/100 L (mean: 6.6 dpm/100 L, $n = 10$). Although the δ^{18}O values in sinkhole waters are similar, the ^{226}Ra activities vary widely (Table 3); in the case of Middle Island sinkhole, the ^{226}Ra activity differs by a factor of 2 (161 and 345 dpm/100 L). The variations in ^{226}Ra activity could be due to either varying amount and extent of mixing of groundwater with subsurface brines or varying extent of precipitation of $RaSO_4$ and/or $BaSO_4$ during the transit or precipitation at the sediment–water interface. It also could be due to dilution with lake water. The eight samples in the Isolated sinkhole waters form two different clusters with different trends: IS-VO-B1 to IS-VO-B4 samples form one group and the rest form another group (Fig. 5a). The Isolated-1, 2, IS-VO-R1, and IS-VO-R2 samples are isotopically similar to El Cajon and Middle Island sinkhole waters, with the δ^{18}O values ranging between −10.2 and −12.5 ‰ (mean: −11.6 ‰, $n = 6$) and δD values ranging between −74.9 and −83.6 ‰ (mean: 80.6 ‰, $n = 6$), while the ^{226}Ra activity varied between 161 and 430 dpm/100 L (mean: 305 dpm/100 L, $n = 8$) and is about an order of magnitude lower than the value reported for the hydrothermal vent water at 350 °C in the Galapagos Rise spreading center, ~3900 dpm/100 L (Turekian and Cochran 1986). In IS-VO-B1 to IS-VO-B4 samples, the δ^{18}O and δD values are isotopically anomalous, with the heaviest values of δ^{18}O (−1.5 to −4.7 ‰, mean: −2.9 ‰, $n = 4$) and δD (−42.8 to −55.1 ‰, mean: −48.5 ‰, $n = 4$) found. However, the ^{226}Ra activities varied between 5.0 and 310 dpm/100 L. It is not clear what is causing the two low ^{226}Ra values (IS-VO-B2 and IS-VO-B4) in the vent waters, 5.0 and 6.7 dpm/100 L, although both δ^{18}O and δD are highly enriched (Table 3). It could be due to sulfate precipitation along with Ra in the sampling container. Further work needs to be conducted to assess the factors that cause the

Table 3 Activities of ^{223}Ra, ^{224}Ra, ^{226}Ra and ^{228}Ra and δD and δ^{18}O of water samples in and around three sinkhole vents from Lake Huron

Sample code	Depth (m)	^{223}Ra (dpm 100 L^{-1})	^{224}Ra (dpm 100 L^{-1})	^{226}Ra (dpm 100 L^{-1})	^{228}Ra (dpm 100 L^{-1})	^{222}Rn (dpm/L)	δD (‰)	δ^{18}O (‰)
El Cajon								
Sample 1 (2008)	<1	29.8 ± 12.4	18.0 ± 2.9	234.9 ± 2.3	25.1 ± 1.9	NM	−83.6	−12.2
Sample 2 (2006)[a]	<1	NM	NM	165.0 ± 15.6	BD	NM	NM	−12.5
Middle Island								
Surface water	<1	BD	7.9 ± 2.0	6.0 ± 0.7	2.4 ± 0.9	NM	−53.7	−6.9
Vent water (2008)	23.0	147.7 ± 4.1	16.7 ± 3.9	344.6 ± 2.8	39.0 ± 2.1	NM	−80.1	−11.4
Vent water (2006)[a]	23.0	NM	NM	160.9 ± 5.7	BD		NM	−11.2
Isolated sinkhole vent								
Isolated 1	93.7	23.2 ± 3.8	36.9 ± 8.2	394.1 ± 4.0	79.9 ± 3.7	302	−74.9	−10.2
Isolated 2	93.7	26.7 ± 1.8	57.9 ± 2.2	429.8 ± 3.3	91.2 ± 2.8	736	−83.0	−11.7
IS-VO-B1	94.3	23.2 ± 3.8	36.9 ± 8.2	310.4 ± 3.7	61.2 ± 3.1	872	−55.1	−3.5
IS-VO-B2	94.2	BD	BD	5.0 ± 0.7	BD	NM	−48.8	−4.7
IS-VO-B3	94.3	18.0 ± 4.0	21.9 ± 9.2	298.5 ± 3.2	54.7 ± 2.7	946	−47.1	−1.5
IS-VO-B4	91.1	BD	BD	6.7 ± 1.9	5.8 ± 2.7	870	−42.8	−1.9
IS-VO-R1	94.3	14.3 ± 3.6	22.6 ± 11.4	324.9 ± 3.3	64.5 ± 2.8	904	−79.3	−11.4
IS-VO-R2	94.4	40.4 ± 5.9	40.0 ± 16.6	383.3 ± 3.9	73.0 ± 3.3	969	−82.4	−11.9
IS-40 M-CONT	40.0	BD	BD	1.7 ± 0.2	BD	NM	−55.8	−7.1
Alpena on land								
Library Well (2006)	NM	NM	NM	235.1 ± 5.6	BD	1100	NM	−12.9
Lake water—profiles[a]								
LH-ST-1-S	<1	BD	7.49 ± 2.5	4.2 ± 0.4	1.3 ± 0.3	NM	−54.3	−7.2
LH-ST-1-M	8.2	BD	0.93 ± 0.6	5.3 ± 0.6	5.3 ± 1.1	NM	−54.4	−7.2
LH-ST-1-D	16.9	2.20 ± 1.1	4.72 ± 1.8	13.8 ± 0.6	4.8 ± 0.8	NM	−56.2	−7.5
LH-ST-2-S	<1	BD	BD	10.1 ± 0.6	5.0 ± 0.9	NM	−53.1	−7.6
LH-ST-2-M	6.4	BD	2.96 ± 2.0	3.0 ± 0.4	1.4 ± 0.6	NM	−54.0	−7.5
LH-ST-2-D	15.1	BD	BD	8.0 ± 1.0	22.5 ± 1.7	NM	−53.6	−7.5

Table 3 continued

Sample code	Depth (m)	^{223}Ra (dpm 100 L^{-1})	^{224}Ra (dpm 100 L^{-1})	^{226}Ra (dpm 100 L^{-1})	^{228}Ra (dpm 100 L^{-1})	^{222}Rn (dpm/L)	δD (‰)	δ^{18}O (‰)
LH-ST-3-M	10.4	BD	BD	5.4 ± 0.8	BD	NM	−57.6	−6.6
LH-ST-3-D	19.0	BD	BD	183.3 ± 2.0	BD	NM	−68.6	−8.9
LH-ST-4-D	9.4	BD	BD	5.4 ± 0.7	3.1 ± 0.7	NM	−54.9	−6.8
LH-ST-5-S	<1	BD	BD	9.0 ± 0.8	4.1 ± 1.0	NM	NM	NM
LH-ST-6-M	16.4	BD	BD	5.0 ± 0.4	0.9 ± 0.3	NM	−60.5	−7.6
LH-ST-6-D	22.0	BD	BD	112.2 ± 1.8	11.3 ± 1.2	NM	−74.6	−10.4
LH Surface Water	<1	NM	NM	14.0 ± 6.0	BD	NM	NM	−8.0

NM not measured, *BD* below detection limit

[a] *S* surface (upper 1 m), *M* mid-depth, *D* bottom (within ~1 m from sediment–water interface)

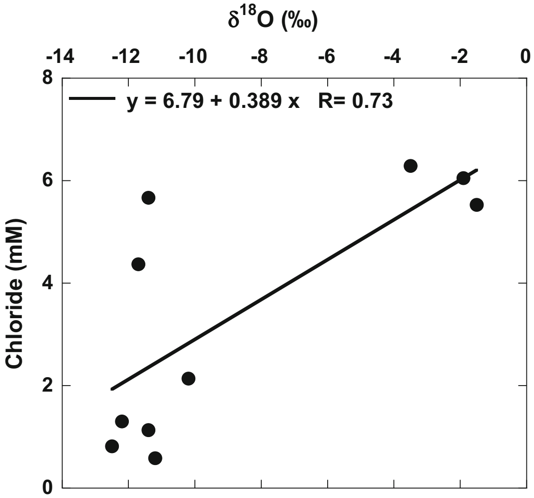


Fig. 4 Concentrations of chloride versus $\delta^{18}O$ in sinkhole waters

variability in the ^{226}Ra activities. There is a correlation between Cl^- and ^{226}Ra activity in the sinkhole vent waters, and the increase in radium content with Cl^- can result from their solubilization through formation of chloride complexes (Fig. 5a, Langmuir and Reise 1985; Herczeg et al. 1988; Krishnaswami et al. 1991).

The $\delta^{18}O$ and δD values in two bottom lake water samples are strikingly different: LH-ST-2-D and LH-ST-6-D at 15.1, 22.0 m depths, respectively, have $\delta^{18}O$ and δD values in between the lake water and the sinkhole vent waters (LH-ST-2-D: −8.9 ‰ for $\delta^{18}O$ and −68.6 ‰ for δD; LH-ST-6-D: −10.4 ‰ for $\delta^{18}O$ and −74.6 ‰ for δD). The ST-6 site is close to the Middle Island sinkhole, and hence there is a possibility that this water is a mixture of lake water and vent water. However, the activity of ^{226}Ra in Lake waters at 1–3 m from the vent was not enriched, suggesting the impact of the vent is local. On the other hand, there is no reported vent near ST-2 (Table 1), and thus, it appears that there could be other micro-seep fluxes of groundwater discharge that is not as prominent as the three sinkholes. Wide distribution of sinkhole-derived cyanobacteria have been reported in Lake Huron and were attributed to vertical transport of benthic mats by upward buoyancy from microbially produced gases released from the sediment and may then be dispersed by prevailing currents (Biddanda et al. 2009). Our tracer study indicates vent-like isotopic signatures are found far away from the vents, and we hypothesize that there may be micro-seeps present throughout Lake Huron and possibly other Great Lakes system wherever karstic sinkholes are found.

3.5 Activities and Activity Ratios of Ra Isotopes and Rn-222

The activity of ^{223}Ra in lake and vent waters varied between below detection limit to 2.2 dpm/100 L and below detection limit to 148 dpm/100 L (mean: 32.8 dpm/100 L, $n = 10$), respectively (Table 3). Activities of ^{224}Ra in lake water and vent water varied between below detection limit and 7.5 dpm/100 L (mean: 2.6 dpm/100 L, $n = 12$) and below detection limit and 57.9 (mean: 25.3 dpm/100 L, $n = 10$), respectively (Table 3). The corresponding values for ^{228}Ra varied between below detection limit and 22.5 dpm/100 L (mean: 4.1 dpm/100 L, $n = 15$) and below detection limit and 91.2 dpm/100 L (mean:

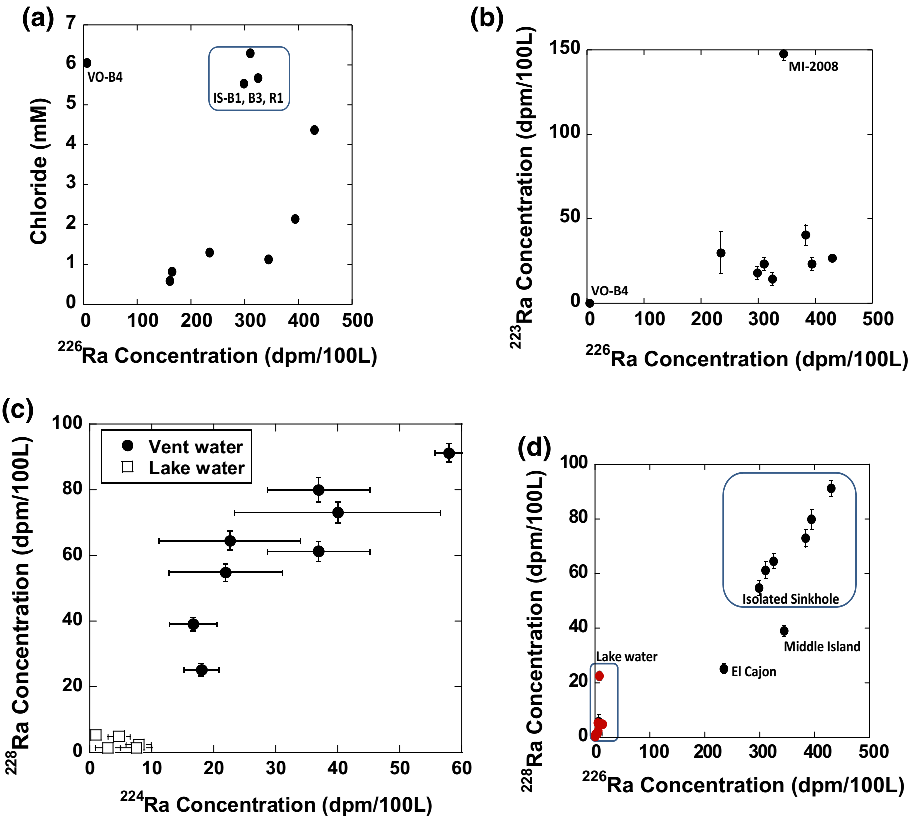


Fig. 5 **a** Concentrations of chloride versus ^{226}Ra; **b** concentration of ^{223}Ra versus ^{226}Ra; **c** concentrations of ^{228}Ra versus ^{224}Ra and **d** concentrations of ^{228}Ra versus ^{226}Ra in all the waters (Lake Huron and sinkhole)

45.1 dpm/100 L, $n = 11$), respectively. From these data, it is evident that the activities of ^{223}Ra, ^{224}Ra, and ^{228}Ra in the vent waters are one to two orders of magnitude higher than those in the lake waters. There are two anomalous values in the lake water which are not included in the calculation of the average value for the lake water or the vent water: LH-ST-6-D water had δ^{18}O and δD values closer to the range of values reported for the vent waters, and it is likely that there is seepage at the sediment–water interface. LH-ST-3-D sample had very high concentration, although the oxygen and hydrogen isotopic ratios appear to be a mixture of vent and lake water. The vent water samples, IS-VO-B2 and IS-VO-B4, had very low ^{226}Ra and ^{228}Ra values, but the δ^{18}O and δD values do not reflect the range of values obtained for the lake water. These data are not included in the calculation of average values. Although the ^{223}Ra/^{226}Ra activity ratio in the host rock is expected to be constant, it varies widely in the waters, and there is no correlation between activities of ^{223}Ra and ^{226}Ra activities in the waters (Fig. 5b). Also, there is no correlation between activities of ^{224}Ra and ^{228}Ra (Fig. 5c), although both are derived from the same parent, ^{232}Th. This lack of correlation is attributed to the different half-lives and the differences in the sources of ^{232}Th and ^{228}Th. The ^{228}Ra activity is plotted against ^{226}Ra activity in Fig. 5d, indicating that they form distinct groups (lake water, Middle Island Sinkhole and

Isolated sinkhole). The ^{222}Rn activities in the Isolated sinkhole varied between 302 and 969 dpm/L (Table 3), and this range is commonly found in the groundwater samples, where the ^{222}Rn concentration is expected to be 2–4 orders of magnitude higher than that of surface waters. Constant degassing of ^{222}Rn from surface waters results in lower concentrations, while higher concentrations are found in groundwater from the recoil supply from host minerals.

The activity ratios of ^{226}Ra/^{228}Ra, ^{224}Ra/^{223}Ra, ^{223}Ra/^{226}Ra, and ^{224}Ra/^{228}Ra in lake and vent waters vary widely (Table 4). The measured ^{226}Ra/^{228}Ra activity ratios in Lake Huron varied between 0.4 and 9.9 (mean: 3.1, $n = 10$, calculated from data given in Table 4). The corresponding values in the vent waters varied between 1.2 and 9.4 (mean: 5.5, $n = 9$, Table 4). Note that the ^{226}Ra/^{228}Ra activity ratios in El Cajon and Middle Island vent waters have similar values, 9.4 and 8.8, respectively, while the corresponding values in Isolated sinkhole is distinctly different, varying between 1.2 and 5.5 (mean: 4.5, $n = 7$).

3.6 K_d Values of Radium in Freshwater

The K_d values obtained from the laboratory experiment are plotted in Fig. 6. The K_d values in freshwater is generally lower than that in the seawater, but much lower than the K_d values for Pu, Th, Pb, Be and other particle-reactive radionuclides (Jweda et al. 2008). The variations in K_d is likely due to the differences in the nature of inorganic complexes that are formed with Ra. Note that the Ra activities in groundwater are often an order of

Table 4 Activity ratios of ^{226}Ra, ^{228}Ra, ^{223}Ra and ^{224}Ra in sinkhole vent and Lake Huron water

Area	^{226}Ra/^{228}Ra AR	^{224}Ra/^{228}Ra AR	^{224}Ra/^{223}Ra AR	^{223}Ra/^{226}Ra (×10) AR
El Cajon Sample-1 (2008)	9.36 ± 0.71	0.72 ± 0.13	0.60 ± 0.27	1.27 ± 0.53
Middle Island surface water	2.5 ± 1.0	3.3 ± 1.5	–	–
Vent water	8.8 ± 0.5	0.43 ± 0.10	0.11 ± 0.03	4.29 ± 0.12
Isolated 1	4.93 ± 0.23	0.46 ± 0.10	1.59 ± 0.44	0.59 ± 0.10
Isolated 2	4.71 ± 0.15	0.63 ± 0.03	2.17 ± 0.17	0.62 ± 0.04
IS-VO-B1	5.07 ± 0.26	0.60 ± 0.14	1.59 ± 0.44	0.75 ± 0.12
IS-VO-B3	5.46 ± 0.28	0.40 ± 0.17	1.22 ± 0.58	0.60 ± 0.13
IS-VO-B4	1.16 ± 0.63	–	–	–
IS-VO-R1	5.04 ± 0.22	0.35 ± 0.18	1.58 ± 0.89	0.44 ± 0.11
IS-VO-R2	5.25 ± 0.24	0.55 ± 0.23	0.99 ± 0.44	1.05 ± 0.15
LH-ST-1-S	3.23 ± 0.81	5.76 ± 2.34	–	–
LH-ST-1-M	1.00 ± 0.24	0.18 ± 0.12	–	–
LH-ST-1-D	2.88 ± 0.50	0.98 ± 0.41	2.15 ± 1.35	1.6 ± 0.8
LH-ST-2-S	2.02 ± 0.38	–	–	–
LH-ST-2-M	2.14 ± 0.96	2.11 ± 1.69	–	–
LH-ST-2-D	0.36 ± 0.05	–	–	–
LH-ST-4-D	1.74 ± 0.45	–	–	–
LH-ST-5-S	2.20 ± 0.57	–	–	–
LH-ST-6-M	5.56 ± 1.90	–	–	–
LH-ST-6-D	9.93 ± 1.07	–	–	–

LH Lake Huron water

magnitude higher than that of the surface waters. More studies are needed to address how the partitioning of Ra takes place in the presence of different organic and inorganic complexes.

4 Discussion

The sinkhole vents are characterized as high-chloride and high-sulfate, low-nitrate and low-DO waters. A comparison of the specific conductivity, ORP, and concentrations of chloride and sulfate in Alpena deep well with those in El Cajon spring and Middle Island vent waters indicates that the vent waters have similar values as that of the groundwater (Table 5). Low values of DO could lead to higher microbial activity over metazoans in the vicinity of the sinkhole vents as well as limited degradation of organic matter, possibly resulting in higher accumulation of organic matter. Thus, the sinkholes could serve as a major sink for organic carbon leading to high benthic productivity. In earlier studies, presence of massive purple filamentous cyanobacteria, green, and whitish mats in Middle Island and El Cajon sinkholes have been reported (Ruberg et al. 2008). Under the Lake floor mats, thick layer of organic-rich, black, sulfidic sediments have been observed (Biddanda et al. 2009).

4.1 Fluid and Chemical Fluxes from Sinkhole Vents to Lake Huron

From the water discharged out of the Alcove with a cross-sectional area of 2.85 m^2 and horizontal water velocity of 0.06 m/s, the annual estimated volume discharged is 5.4×10^6 m^3/year. Over the hydrological residence time of water (22 years) in Lake Huron, this corresponds to 1.2×10^8 m^3, which is 3.4×10^{-3} % total water volume of Lake Huron, 3.54×10^{12} m^3. An annual flux estimate for SO_4^{-2}, Cl^{-1}, NH_4, and ^{226}Ra from Alcove vent are: 6.3×10^4 mol (total in the lake: 1.0×10^9 mol) for SO_4^{-2}; 1.8×10^7 mol (total in the lake: 1.3×10^{12} mol) for chloride; 2.7×10^4 mol (total in the lake: 1.3×10^{10} mol) for ammonium and 1.6×10^{10} dpm (total in the lake: 2.3×10^{14} dpm) for ^{226}Ra. This estimate is only from one vent, and we do not know whether there are a large number of other vents present in the lake. However, as presented in the Results section, some of the isotopic signatures of the bottom waters indicate possible presence of diffusive fluxes from waters that have similar stable oxygen and hydrogen isotopic signatures and ^{226}Ra activities. It is likely that these estimates are grossly underestimates and

Table 5 Comparison of water chemistry of sinkhole vents, groundwater in Alpena, and Lake Huron

Parameter	Alpena deep well	El Cajon spring	Middle Island vent	Lake Huron end member
Temp (°C)	12.4	10.3	9.1	18.3
pH	7.3	6.8	7.1	8.5
Sp. cond. (mS/cm)	2.3	2.4	2.3	0.2
ORP (mV)	−134	−71	−120	106
DO (mg/L)	3.2	0.9	0.4	10.3
Cl (mg/L)	38	29	21	6
SO_4 (mg/L)	1106	1220	912	13
DOC (mg/L)	1.02	1.59	2.45	1.73

the loading of these chemical species from the sinkhole vents will not affect the biogeochemical cycling of major and minor ionic species in Lake Huron. However, if a large number of vents are present, it could have an impact, although more systematic study could only yield information on how common such vents are in Lake Huron.

4.2 Variations in the Concentrations and Activity Ratios of Radium and δ^{18}O and δD Isotopic Composition

What are the processes that lead to distinctly different δ^{18}O and δD isotopic composition and ^{226}Ra activity (and other Ra isotopes, Table 3) in the sinkhole waters than what is found in the meteoric water? When meteoric water infiltrates through the subsurface limestone, the chemistry of the precipitation is modified by the carbonate equilibrium reactions resulting in substantial chemical and isotopic change of the infiltrating water. The values of δ^{18}O, δD, and ^{226}Ra of the groundwater evolve with time, depending on the extent of rock-water interactions, evaporation, and mixing with other aquifers. If mixing were occurring between brines and non-brine groundwater, a linear relationship between these two end members is expected. In this region, shallow groundwater (<100 m) has been observed to have high salinity, with total dissolved solids ranging between 0.1 and 53 g/L, and the salinity was hypothesized to be the result of advection/diffusion of brines into the overlying meteoric water, and the salinity distribution was attributed to slow flushing of water in the argillaceous sediments by recent meteoric water (Long et al. 1988). In the east-central Michigan basin, the groundwater is reported to have a wide range in δ^{18}O (6.9 to −18.5 ‰) and δD (−47 to −137 ‰) values, with the values falling along the GML. Some of our values fall off the GML, suggesting either chemical processes that have altered the meteoric signature or mixing of waters with highly enriched δ^{18}O and δD values with waters that have ‘meteoric water’-type signature (Fig. 7). Note that the groundwaters with highly enriched δ^{18}O and δD values, and hence presumably less mixed, do fall along the GMWL (Long et al. 1988).

Based on the δ^{18}O and δD composition (Fig. 7), the water samples can be grouped into four categories: (1) values that represent the Lake Huron water; (2) values that represent sinkhole vents; (3) waters that have undergone extensive chemical reactions for which the δ^{18}O and δD values deviate from the GML; and (4) values that represent mixing of these

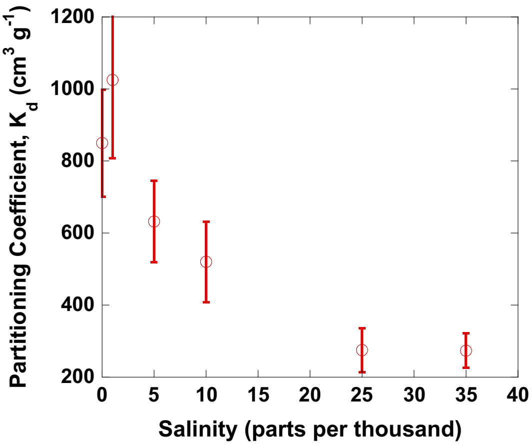
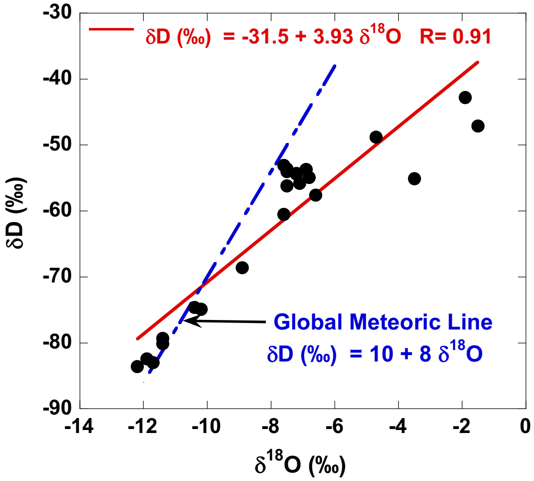


Fig. 6 Partitioning coefficient of ^{226}Ra as a function of salinity. The K_d values in freshwater is generally lower than that in the seawater, but much lower than the K_d values for Pu, Th, Pb, Be and other particle-reactive radionuclides

two end members. The Middle Island surface water sample is lake water, based on both $\delta^{18}O$ and δD values. However, the deep vent waters are composed of water falling on the 'normal' GMWL and apparently come from a marine carbonate rock ($^{228}Ra/^{226}Ra$ activity ratio of 0.1–0.2, typical for a uranium-rich and thorium-poor carbonate). In the case of Isolated sinkhole, IS-VO-B1 through B4, based on their $\delta^{18}O$ and δD isotope ratios, seem to be an evaporated water (Fig. 7) with enriched $\delta^{18}O$ relative to δD values typical for evaporated seawater; the $^{228}Ra/^{226}Ra$ activity ratio suggests that the water came from a marine carbonate reservoir, except for IS-VO-B4, one of the unusually low radium samples. Furthermore, the Isolated sinkhole seems to contain types of water coming from a limestone/carbonate aquifer: Isolated 1 and 2, IS-VO-R1 and R2, which seem to be meteoric water and IS-VO-B1 to IS-VO-B4 seem to contain large fraction of some original Michigan Basin formation water, based on their heavy ^{18}O values. The Isolated sinkhole samples seem to have high TDS values. It is also possible that these samples may represent meteoric water that dissolved NaCl evaporites somewhere along the flow path, but did not mix with heavy ^{18}O evaporated from formation water (Fig. 7).

Short-lived Ra isotopes (^{223}Ra $T_{1/2} = 11.435$ days; ^{224}Ra $T_{1/2} = 3.66$ days) have been widely used to quantify coastal water mixing and residence time of Ra (and thereby water) (e.g., Zhang et al. 2011). The variations in the activity ratios is attributed to the variations in the concentrations and locations of ^{238}U and ^{232}Th in the mineral grains from which Ra isotopes are eventually released either by congruent dissolution or by recoil from their parents (^{232}Th, ^{230}Th, ^{228}Th, ^{227}Th for ^{228}Ra, ^{226}Ra, ^{224}Ra, ^{223}Ra, respectively), release from the recoil of Ra atoms from the decay of Th atom sorbed on mineral grains, and recoil efficiency of Ra isotopes (^{226}Ra and ^{223}Ra are the third α decay products from ^{238}U and ^{235}U, respectively) and ^{232}Th (^{228}Ra and ^{224}Ra is the first and second α decay product from ^{232}Th, respectively). It is possible that the source water for El Cajon and Middle Island sinkholes are the same, with similar $^{226}Ra/^{228}Ra$ ratios and proximity, while the Isolated sinkhole farther offshore have different origin, with different water history and varying ^{238}U and ^{232}Th concentrations. The $^{223}Ra/^{226}Ra$ activity ratios varied between 0.03 and 0.66 (mean: 0.30, $n = 5$), and this can be compared to the constant value of $^{235}U/^{238}U$ (both of these reach Ra after 3 α decays) activity ratio of 0.046. A large variation of this ratio, 0.18–1.21, in subsurface brines and 0.002–0.005 in geothermal brines have been reported and this is attributed to faster replenishment of short-lived isotope after their

Fig. 7 δ D versus $\delta^{18}O$ in all the water samples (Lake Huron + sinkhole vent). The *dotted line* indicates the Global Meteoric Line (Daansgaard 1964)



removal (Krishnaswami et al. 1991) and slow weathering and leaching of Ra from solid phases occurring over longer timescales (Hammond et al. 1988). The ^{224}Ra/^{228}Ra activity ratios in the lake waters varied between 0.08 and 10.0 ($n = 5$), although in a majority of the samples, the ^{224}Ra is below our detection limit of the methodology used.

4.3 Timescale of the Fluid Transport Using Ra Isotopes as Tracers

The depths where the sinkhole waters originate below the sediment–water interface are unknown. The activities of Ra and their activity ratios in sinkhole waters are governed by their mode of supply (recoil [direct from mineral grains and Th sorbed on the coating of oxy-hydroxides on the mineral grains], congruent dissolution, and preferential leaching) and timescale of supply. Once the water reaches the vent, the timescale involved include: (1) the time it resides at the bottom of the vent (2) the transit time in the vent to reach the surface.

If we assume that all Ra in the sinkhole water are derived from recoil, the activity ratio of the two isotopes '*i*' and '*j*' is given by:

$$({}^{i}\mathrm{Ra}/{}^{j}\mathrm{Ra})_{\mathrm{T}} = \varepsilon({}^{i+4}\mathrm{Th}/{}^{j+4}\mathrm{Th})_{\mathrm{R}}[1-\exp(-\lambda_i T)]/[1-\exp(\lambda_j T)][\exp-(\lambda_i-\lambda_j)t] \tag{1}$$

where λ_i and λ_j refer to the decay constant of ^{i}Ra and ^{j}Ra, respectively, ε is the relative recoil efficiency, and ($^{i+4}$Th/$^{j+4}$Th)$_{\mathrm{R}}$ is the activity ratio of the parent nuclides of ^{i}Ra and ^{j}Ra, respectively; t is the transit time of the vent water from the bottom to the top of the vent; T is the time elapsed at the bottom of the vent during which Ra accumulates from recoil and chemical reaction. The ε values is different for different pairs [$\varepsilon = 1$ for ^{223}Ra/^{226}Ra, as both are third α decay product from their progenitors, ^{235}U and ^{238}U; $\varepsilon = 0.80$–1.82 for ^{228}Ra/^{226}Ra, depending on the extent of adsorption of the intermediate nuclides between ^{238}U and ^{226}Ra (Krishnaswami et al. 1982)].

In addition to the recoil input given by Eq. (1), if there is additional input from chemical processes acting on the host rock, assuming a constant rate of supply of ^{i}Ra and ^{j}Ra, after time '*T*', the activity ratio is given by:

$$({}^{i}\mathrm{Ra}/{}^{j}\mathrm{Ra})_{\mathrm{T}} = (\lambda_j/\lambda_i)({}^{i+4}\mathrm{Th}/{}^{j+4}\mathrm{Th})_{\mathrm{R}}[1-\exp(-\lambda_i T)]/[1-\exp(-\lambda_j T)][\exp-(\lambda_i-\lambda_j)t] \tag{2}$$

The total supply from recoil and chemical processes, the sum of Eqs. (1) and (2), is given by:

$$\begin{aligned}&({}^{i}\mathrm{Ra}/{}^{j}\mathrm{Ra})_{\mathrm{T}}\\&\quad= ({}^{i+4}\mathrm{Th}/{}^{j+4}\mathrm{Th})_{\mathrm{R}}\{[1-\exp(-\lambda_i T)]/[1-\exp(-\lambda_j T)]\}[\varepsilon+\lambda_j/\lambda_i][\exp-(\lambda_i-\lambda_j)t]\end{aligned} \tag{3}$$

Among the four Ra isotopes, the pairs that are useful to obtain timescales of mixing and transport are: ^{223}Ra/^{226}Ra, ^{224}Ra/^{228}Ra, and ^{228}Ra/^{226}Ra. For ^{223}Ra/^{226}Ra and ^{228}Ra/^{226}Ra ratios, if the recoil supply ratio is equal to the production ratio, then the ratio in the water will be the same as the host rock in ~8000 years. In the case of ^{224}Ra/^{228}Ra, it will be in about 30 years. With our current data set of the activities and activity ratios of radium of the vent water samples, without measuring the activity ratios at the bottom of the vent and host rocks, it is not possible to obtain a unique solution for T and t. However, one can estimate the timescale involved in the movement of vent water by making certain assumptions: If the source water has an initial activity ratio, (^{223}Ra/^{226}Ra)$_0$, at the bottom of the vent (=0.04608 which is assumed to be the activity ratio of the parent nuclide, ^{235}U/^{238}U), assuming that there is no exchange with the surrounding waters (either through supply via leaching, dissolution or recoil) and there is no removal (via precipitation and/or sorption on to the host minerals) along the vent during the vertical movement of the fluid, after a transit time of '*t*,' the change in the ^{223}Ra/^{226}Ra activity ratio is only caused by the radioactive decay of ^{223}Ra during transit. From the relationship between the (^{223}Ra/^{226}Ra)$_0$ and measured (^{223}Ra/^{226}Ra) ratio, the transit time '*t*' can be calculated from:

$$t = [1/(\lambda_3 - \lambda_6)]\ln[(^{223}\mathrm{Ra}/^{226}\mathrm{Ra})_m/(^{223}\mathrm{Ra}/^{226}\mathrm{Ra})_0] \quad (4)$$

The calculated transit times varied between 4 days (IS-VO-B3) and 37 days (Middle Island vent water) with difference between these two waters being 33 days. This implies that if Middle Island and Isolated sinkholes have the same initial ratio at the bottom of the vents, based on the decrease in the ^{223}Ra/^{226}Ra activity ratios due solely to radioactive decay, it takes 37 days to reach the sediment–water interface in Middle Island sinkhole. There are many caveats to this estimate that include no loss (sorption, precipitation, loss due to chemical reactions) or gain (recoil input, dissolution, leaching) of Ra as it migrates upward. It is also too simplistic, in that it assumes that the faster water reaches the sediment–water instantly. Finer time-resolution studies along with the collection of long sediment cores to determine the concentrations of Ra isotopes are needed to get a better handle on the time estimates given here.

4.4 Estimation of Vertical Diffusion Coefficient Using ^{224}Ra/^{228}Ra Activity Ratio

One can also estimate vertical diffusion coefficient using the gradient in the activity ratio of ^{224}Ra/^{228}Ra activity ratio between LH-ST-1-M (8.2 m, ^{224}Ra/^{228}Ra = 0.18 ± 0.12, Table 4) and ST-1-D (16.9 m, ^{224}Ra/^{228}Ra = 0.98 ± 0.41, Table 4). Assuming that the ^{224}Ra/^{228}Ra vertical ratios are governed by diapycnal processes (arising from differences in temperature) and the role of vertical advection is small compared to that of vertical diffusion, the (^{224}Ra/^{228}Ra) ratio at any depth is given by:

$$(^{224}\mathrm{Ra}/^{228}\mathrm{Ra})_z = (^{224}\mathrm{Ra}/^{228}\mathrm{Ra})_0 \exp[-z((\lambda_4 - \lambda_8)/k)^{1/2}] \quad (5)$$

where (^{224}Ra/^{228}Ra)$_z$ and (^{224}Ra/^{228}Ra)$_0$ are the activity ratios at some height z above the bottom, k is the diffusion coefficient, and λ_4 and λ_8 are the decay constants of ^{224}Ra and ^{228}Ra, respectively. The vertical diffusivity calculated using Eq. (5) is 5.0 m^2/d (0.58 cm^2/s; note that the errors in the measured ^{224}Ra/^{228}Ra is high and hence the error associated with this diffusivity constant is >50 %). This value is comparable to 0.18 cm^2/s reported for Lakes in Japan and Israel (Etemad-Shahidi and Imberger 2006). Note that of the three samples in one vertical profile in ST-1 from Lake Huron, we could only use the middle and deep waters of ST-1 to obtain vertical diffusivity, and we could not use the value of the surface water sample, and hence the diffusion coefficient obtained needs to be used with caution.

5 Conclusion

From the measurements of Ra, ^{222}Rn, stable isotopes of oxygen and hydrogen and other ancillary parameters, we draw the following conclusions: (1) The activities of $^{226.228,223,224}$Ra in waters derived from sinkhole vent waters are one to two orders of magnitude higher than that of Lake Huron waters, but about an order of magnitude lower than that of high-temperature hydrothermal waters reported in the oceans—suggesting that the chemistry of the waters control the activities of radium coming out of these vents; (2) Based on oxygen, hydrogen, and Ra isotopic composition of some of the bottom waters, it appears that there are effusive fluxes of water entering the lake at farther distances from the three vents identified so far and thus, we hypothesize that such micro-seeps may be common and widespread in Lake Huron, and possibly in other regions of all the lower four Great Lakes where subsurface karst formations are abundant; (3) A plot of δD versus $\delta^{18}O$ reveals that in some of the samples the $\delta^{18}O$ values are highly enriched compared to the δD values, possibly indicating evaporation and mixing of water masses with different isotopic composition and possibly subsurface chemical reactions with limestone resulting in the alternations of the values of $\delta^{18}O$; (4) Estimates of transit time from the bottom of the vent to the sediment–water interface ranged between 4 and 37 days, based on the measured $^{223}Ra/^{226}Ra$ activity ratios in vent waters; and (5) The model-derived vertical diffusivity based on the concentration gradient in the activity ratio of $^{224}Ra/^{228}Ra$ is estimated to be 0.58 cm^2/s, which is within the range of values reported in other lakes elsewhere.

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