ردیابی آلودگی آبهای زیرزمینی در محل دفن زباله ها با استفاده از فنآوری ایزوتوپهای پایدار ($\delta^{18}O$، $\delta^{2}H$ و $\delta^{13}C$)

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چکیده

در این مقاله، تاثیر شیرابه زباله ها بر روی سفره های آبهای زیرزمینی شهر اتاوا - پایتخت کانادا - با استفاده از ایزوتوپهای پایدار ($\delta^{18}O$، $\delta^{2}H$ و $\delta^{13}C$) مورد ارزیابی قرار گرفته و این فنآوری، آلودگی آبهای زیرزمینی توسط شیرابه زباله ها را تایید مینماید. مقادیر عددی بالای $^{13}C_{DIC}$ آبهای زیرزمینی (به ترتیب -۶,۵‰ و -۱,۰‰ برای سفره های کم عمق و عمیق) درمقایسه با $^{13}C_{DIC}$ آبهای زیرزمینی در بالادست محل دفن زباله ها (-۱۵,۲‰) تاییدی بر تاثیر شیرابه زباله ها (+۸,۸‰ تا +۱۰,۷‰) بر روی آبهای زیرزمینی منطقه می باشد. عدم انطباق آبهای زیرزمینی بر روی خطوط اختلاط در دیاگرامهای ترکیبی DIC با $\delta^{13}C_{DIC}$ و DOC با $\delta^{13}C_{DOC}$، نشان دهنده واکنشهای بیوشیمیایی مرتبط با کربن ارگانیکی محلول (DOC) می باشد که به نوبه خود بر روی غلظت DOC، غلظت کربن غیرارگانیکی محلول (DIC) و ایزوتوپ کربن ۱۳ تاثیر می گذارد. بنابراین علاوه بر اختلاط شیرابه زباله ها با آبهای زیرزمینی، واکنشهای بیوشیمیایی نیز بر کیفیت آبهای زیرزمینی تاثیر گذاشته است.

واژگان کلیدی: شیرابه زباله ها، ایزوتوپ پایدار ($\delta^{18}O$، $\delta^{2}H$ و $\delta^{13}C$)، کربن ارگانیکی محلول (DOC)،کربن غیرارگانیکی محلول (DIC)

Tracing Groundwater Contamination at Landfill Sites Using Stable Isotope Technique ($\delta^{18}O$, $\delta^{2}H$ and $\delta^{13}C$)

Abstract

In this paper, the stable isotope ($\delta^{18}O$, $\delta^{2}H$ and $\delta^{13}C$) was used to recognize groundwater contamination at Ottawa landfill site. The enriched $^{13}C_{DIC}$ (averages of 6.4 ‰, -1.0 ‰ for the shallow, deep aquifers, respectively) in comparison to the upgradient pristine groundwater (-15.2 ‰) confirm the leachate (+8.8‰ and +10.7‰) impact on these aquifers. Biochemical reaction of DOC in groundwaters is confirmed by deviation of groundwater samples from the mixing lines on DIC vs. $\delta^{13}C_{DIC}$ and DOC vs. $\delta^{13}C_{DOC}$ diagrams. Therefore, mixing and the reaction are two important processes which effected on groundwater quality at landfill site.

Keywords: Landfill leachate, stable isotopes ($\delta^{18}O$, $\delta^{2}H$ and $\delta^{13}C$), dissolved organic carbon (DOC), dissolved inorganic carbon (DIC)

Introduction

Leachate contains a mixture of dissolved organic constituents which can decay and dissolve through bacteria-mediated reactions resulted in generating different major carbon pools, such as DIC, DOC, and CH_4. The biogeochemical processes and outgassing of CO_2 can produce characteristic ^{13}C signatures in the major carbon pools and also generate ^2H enriched of water in landfill leachate (Baedecker and Back, 1979; Hackley et. al., 1996; Christensen et al., 2001; Van Breukelen et al., 2004; North et al., 2004; Mohammadzadeh and Clark, 2008). The objective of this paper is to investigate groundwater contamination at Trail Road Landfill (TRL) site, located approximately 25 km west of the Ottawa City, using stable isotope signatures.

Site characterization and analytical methods

There are both a shallow and a deep aquifer at TRL area. Several individual and nested piezometers representing more than 200 monitoring wells were installed by City of Ottawa to sample the groundwater. The nested piezometers were screened at different depths including the shallow aquifer, the upper deep aquifer, and the lower deep aquifer. (Dillon Consulting Ltd., 2006). Leachate samples were taken from M32 monitoring well and groundwater samples were taken from multilevel monitoring wells located down-gradient and up-gradient of the TRL site. The detailed description of sampling procedures and analytical techniques is given by Mohammadzadeh et al. (2005) and Mohammadzadeh and Clark. (2008).

Discussion and conclusions

All results are tabulated in Table 1. Review of the available geochemical data from M57 and M120, as reference groundwater, shows no evidence of leachate influence at these locations.

The presence alone of methane at some locations (M4-1, M4-2, M37-2, M23-1, and M23-2) is evidence of leachate impact on groundwater. Further evidence is provided by ^{13}C of DIC and that of CH_4. In comparison with pristine groundwater, samples from the shallow aquifer show variable concentrations of methane. Associated $\delta^{13}C_{CH4}$ values range from -60 ‰, indicating biogenic production, to -32‰ indicating subsequent oxidation. DIC also carries evidence for leachate impact, with high and variable concentrations as compared to pristine groundwater, with $\delta^{13}C_{DIC}$ values that show variable additions of ^{13}C-depleted DIC generated through the oxidation of methane. The deep aquifer monitored further from the landfill (M23 and M16), also has been affected by the landfill leachate. Similarly, the $\delta^{13}C_{DIC}$ in the upper (M37-2 and M23-2) and lower (M23-1 and M16-1) part of the deep aquifer shows variable degrees of both leachate impact on groundwater and subsequent methane oxidation. The $\delta^{13}C_{DIC}$ values at the lower part of the deep aquifer (M23-1 and M16-1) are enriched, 11.8 ‰ and -8.0 ‰, respectively, and the enriched values of $\delta^{13}C_{CH4}$ at M16-1 clearly provide evidence for methane oxidation at this point.

No methane and a low amount of DOC are present in up-gradient (M57) and down-gradient (M120) background groundwater. Concentrations of DOC and CH_4 in M32 (5130 mgl^{-1} and 1.6 mgl^{-1}, respectively) signify the input of the leachate plume from the unlined parts of landfill, and decrease in the groundwater flow direction. The high concentration of these species in M77 is due to the impacts of the adjacent Nepean landfill leachate on this part of the aquifer. Also decreasing along the flow direction is the $\delta^{13}C$ value of DIC, from the enriched value for the landfill site at M32 through M16-1, M114, M77-1, M77-2, M93 and M64. This reflects both dilution with background DIC ($\delta^{13}C$ of –17‰) plus contributions from the oxidation of dissolved organics and methane.

None of the average data obtained from samples taken from these aquifers plot on the mixing lines generated for the DIC and DOC vs. $\delta^{13}C$ diagrams (Figure not shown here), indicating reactive evolution in addition to simple dilution. Moreover, while DIC shows largely an increase in $\delta^{13}C$, DOC experiences a marked depletion in ^{13}C with evolution.

The groundwaters samples from both the shallow and upper deep aquifers plot on or below the OMWL on $\delta^{2}H$ - $\delta^{18}O$ diagram (Figure is not shown here). The absence of a deuterium excess in these waters reflects both dilution and lack of significant methane production. Shifts in $\delta^{2}H$ due to methanogenesis is strictly occurs in unsaturated zones with the landfill where high organic carbon loads coupled with low water to gas and solids ratios imparts a significant enrichment of ^{2}H on the residual water.

At Trail Road Landfill (TRL) site, both the shallow and deep aquifers have been impacted by leachate infiltrating from the unlined portions of the landfill site. The concentrations and $\delta^{13}C$ of dissolved methane, the concentration and $\delta^{13}C$ of DIC, provide evidence for landfill leachate impact. Bulk DOC concentrations and $\delta^{13}C_{DOC}$ in groundwaters are affected by a combination of dilution and continued reaction. Consumption of DOC via acetate fermentation and oxidation of DOC within the aquifers is documented by: 1) deviation of groundwater samples from mixing lines, drawn for DIC vs. $\delta^{13}C_{DIC}$ and DOC vs. $\delta^{13}C_{DOC}$; 2) correlation between net reacted (lost) DOC and the net gains in for shallow and deep aquifers.

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Table 1: Geochemical and isotopic data for the groundwater samples collected at TRL site. All concentrations in mg l^{-1} and isotopic values in ‰ VPDB (for ^{13}C) and in ‰ VSMOW (for ^{18}O and ^{2}H), if not stated.

	Sample ID	Date	H_2O		DIC		DOC		CH_4		CO_2		$\alpha^{13}C_{CO2-CH4}$
			$\delta^{18}O$	$\delta^{2}H$	mg l^{-1}	$\delta^{13}C_{DIC}$	mg l^{-1}	$\delta^{13}C_{DOC}$	mg l^{-1}	$\delta^{13}C_{CH4}$	$\delta^{13}C_{CO2}$	$\delta^{18}O_{CO2}$	
Reference	M57	July 22, 2005	-13.6	-96.9	48	-13.4	0.9	-26.8	0.00	-50.8	-17.9	-0.4	1.035
	M57	July 9, 2004	-13.4	-96.3	58	-17.1	1.21	-31.1	0.00	bl	bl		
	Average		**-13.5**	**-96.6**	**53**	**-15.2**	**0.9**	**-28.9**	**0.00**	**-50.8**	**-17.9**	**-0.4**	**1.0**
	M120	July 21, 2005	-9.8	-78.2	59	-13.3	0.6	-26.9	0.00	-47.4	-17.2	11.5	1.032
	M120	July 9, 2004	-9.6	-75.4	45	-14.8	1.32	-41.1	0.00	bl	bl		
	M120	Nov 14, 2003	-9.4	-74.4	47	-14.3	0.5	-22.1	0.00				
	Average		**-9.6**	**-76.0**	**50**	**-14.1**	**0.5**	**-30.0**	**0.00**	**-47.4**	**-17.2**	**11.5**	**1.0**
	M79	Nov 14, 2003	-11.3	-80.1	104	-16.5	8.7	-27.3	0.01				
Pond	DWP-SE	July 21, 2005	-10.8	-77.9	72	-4.3	1.4		0.21	-9.9	-12.0	-8.6	0.998
	DWP-SE	July 9, 2004	-10.9	-66.1	85	-7.3	2.5	-41.6	0.27	-44.5	-13.7		1.032
	DWP-SE	Nov 14, 2003	-11.0	-82.1	102	-6.9	1.8	-21.1	0.07				
	DWP-NW	Nov 14, 2003	-10.6	-81.0	89	-8.2	1.6	-23.9	0.02				
	Average		**-10.9**	**-76.8**	**87**	**-6.7**	**1.8**	**-28.9**	**0.14**	**-27.2**	**-12.8**	**-8.6**	**1.0**
Shallow Aquifer	M16-3	July 8, 2004	-12.8	-87.5	68	-17.5	2.0	-32.4	0.00	-74.8	bl		
	M37-3	July 20, 2005	-11.6	-77.4	247	6.1	30.8	-26.9	0.26	-32.5	-4.2	8.0	1.029
	M37-3	July 8, 2004	-11.5	-78.0	417	3.9	76.8	-25.2	0.63	-43.5	-2.1		1.043
	M37-3	Nov 6, 2003	-11.3	-80.2	178	-8.8	39.2	-26.1	0.02				
	M23-3	July 8, 2004	-12.6	-86.9	49	-20.8	2.6	-28.8	0.00	-61.8	bl		
	M43	July 8, 2004	-12.2	-85.9	332	18.8	18.5	-18.8	6.28	-57.9	18.0		1.081
	M4-2	July 22, 2005	-11.8	-85.3	151	-11.9	3.9	-26.5	7.27	-69.0	-15.2	9.2	1.058
	M4-2	July 7, 2004	-12.0	-83.5	194	-14.8	5.5	-30.1	9.99	-59.0	-15.4		1.046
	M4-2	Nov 6, 2003	-11.9	-86.6	165	-6.1	6.1	-29.9	4.53				
	M33-1	July 7, 2004	-11.3	-79.3	339	1.6	20.2	-25.6	3.04	-49.6	-0.8		1.051
	M116-3	Nov 7, 2003	-13.2	-98.3	47	-13.6	2.6	-34.1	0.00				
	M86	Nov 7, 2003	-11.7	-82.4	53	-14.0	1.8	-31.4	0.00				
	Average		**-12.0**	**-84.3**	**187**	**-6.4**	**17.5**	**-28.0**	**2.67**	**-56.0**	**-3.3**	**8.6**	**1.051**

bl = blow detection limit

Table 1: Continued.

	Sample ID	Date	H_2O		DIC		DOC		CH_4		CO_2		$\alpha^{13}C_{CH4-CO2}$
			$\delta^{18}O$	$\delta^{2}H$	mg l^{-1}	$\delta^{13}C_{DIC}$	mg l^{-1}	$\delta^{13}C_{DOC}$	mg l^{-1}	$\delta^{13}C_{CH4}$	$\delta^{13}C_{CO2}$	$\delta^{18}O_{CO2}$	
Upper Deep Aquifer	M114-2	July 21, 2005	-11.7	-84.0	38	-13.6	1.3	-26.7	0.00	-59.6	-17.9	7.5	1.044
	M114-2	July 9, 2004			49	-19.4	1.7	-30.3	2.16	-50.4			
	M107-2	July 22, 2005	-10.8	-79.2	83	-16.8	3.7	-27.9	0.00	-57.1	-21.3	-8.3	1.038
	M34	July 22, 2005	-11.7	-85.2	214	4.7	3.6	-38.1	0.68	-39.7	-2.2	4.9	1.039
	M64	July 21, 2005	-11.7	-83.7	111	-1.5	3.4	-29.0	1.85	-41.8	-8.0	-8.0	1.035
	M64	July 9, 2004	-11.8	-83.0	143	-7.6	4.8	-35.3	3.61	-43.6	-11.1		1.034
	M64	Nov 14, 2003	-11.7	-82.0	151	-1.7	3.2	-33.9	1.21				
	M77-2	July 21, 2005	-11.2	-80.9	129	-3.6	1.7	-27.3	0.25	-32.5	-9.3	10.0	1.024
	M77-2	July 9, 2004	-11.4	-79.6	166	-9.5	2.9	-22.0	0.34	-37.7	-10.4		1.028
	M77-2	Nov 7, 2003	-11.4	-83.7	164	-5.9	1.7	-39.6	0.23				
	M40-4	July 20, 2005	-11.1	-84.4	157	-3.9	1.6	-29.1	0.74	-39.8	-9.8	-6.7	1.031
	M23-2	July 8, 2004	-12.0	-84.7	79	15.7	4.3	-31.8	3.40	-58.3	8.3		1.071
	M16 -2	July 21, 2005	-12.8	-90.7	17	-12.6	0.7	-26.5	0.00	-59.3	-16.3	1.7	1.046
	M16 -2	July 8, 2004			22	-21.3	0.9	-29.1	4.94		-21.5		
	M39-4	July 20, 2005	-11.9	-84.2	124	1.8	1.9	-27.8	5.37		-5.3	7.1	
	M39-4	Nov 7, 2003	-11.5	-84.2	143	2.5	5.0	-18.0	2.37	-57.1			
	M39-7	July 20, 2005	-11.7	-84.1	110	-1.6	2.6	-27.3	1.16	-31.3	-8.5	7.3	1.023
	M37-2	July 20, 2005	-11.9	-83.4	107	-0.6	4.6	-26.2	5.08	-61.2	-7.7	5.5	1.057
	M37-2	July 8, 2004	-12.0	-85.4	94	-4.4	7.7	-18.2	2.79	-61.3	-11.3		1.053
	M37-2	Nov 6, 2003	-11.8	-87.5	99	-2.4	8.0	-31.8	1.02				
	M4-1	July 20, 2005	-12.2	-89.6	132	18.3	8.5	-26.9	5.79	-71.2	7.2	6.0	1.084
	M4-1	July 7, 2004	-12.3	-85.7	129	14.9	7.0	-23.3	9.88	-71.4	6.5		1.084
	M4-1	Nov 6, 2003	-12.3	-89.5	127	14.4	5.0	-34.9	3.42				
	M28	July 22, 2005	-11.7	-82.3	198	22.0	13.1	-25.7	6.04	-53.4	11.1	-9.6	1.068
	M28	Nov 6, 2003	-11.5	-83.2	264	22.8	23.8	-37.3	0.94				
	M90	Nov 14, 2003	-11.9	-84.8	86	7.0	2.8	-33.4	3.09				
	M83-2	Nov 14, 2003	-10.7	-80.6	136	-24.2	4.0	-31.7	0.22				
	Average		-11.7	-84.2	121	-1.0	4.8	-29.2	2.47	-51.5	-7.1	1.4	1.048
Lower Deep Aquifer	M93	July 21, 2005	-11.9	-85.7	60	-3.3	1.6	-27.0	1.81	-62.3	-10.1	4.5	1.056
	M93	July 9, 2004	-12.1	-83.8	71	-5.1	2.0	-33.9	3.23	-54.4	-11.3		1.046
	M77-1	July 21, 2005	-11.9	-85.1	87	10.0	3.5	-26.8	3.65	-71.6	2.6	7.7	1.080
	M77-1	July 9, 2004	-11.9	-83.2	105	9.5	5.2	-30.5	5.16	-59.8	2.6		1.066
	M77-1	Nov 7, 2003	-11.7	-87.4	117	9.5	4.0	-34.9	1.85				
	M114-1	July 21, 2005	-11.9	-87.6	80	-6.6	1.2	-28.9	0.95	-58.2	-12.0	5.7	1.049
	M114-1	July 9, 2004	-12.1	-83.2	71	-11.2	1.3	-41.9	1.04	-55.9	-16.6		1.042
	M16 -1	July 21, 2005	-11.6	-86.9	149	-1.9	3.0	-27.3	0.49	-21.5	-7.9	9.2	1.014
	M16 -1	July 8, 2004	-11.7	-80.1	181	-8.0	3.8	-23.9	0.94	-36.6	-10.1		1.028
	M40-1	July 20, 2005	-11.7	-84.4	139	-4.0	2.1	-27.7	0.19		-10.2	6.4	
	M39-1	July 20, 2005	-11.9	-84.4	118	3.4	2.9	-25.9	4.14		-4.9	-9.4	
	M39-1	Nov 7, 2003	-11.7	-84.6	155	3.4	3.7	-36.3	3.07	-52.2			
	M23-1	July 20, 2005	-12.0	-84.7	68	13.5	2.8	-27.1	6.20	-67.3	4.9	7.6	1.077
	M23-1	July 8, 2004	-12.0	-81.7	86	11.8	4.0	-37.8	5.65	-55.9	5.3		1.065
	M107-1	July 22, 2005	-11.6	-83.6	26	-10.8	1.0	-27.3	0.01	3.6	-17.4	-9.0	0.979
	M37-1	July 20, 2005	-12.1	-86.4	28	-8.6	0.6	-27.6	0.32	-63.3	-15.1	3.5	1.051
	M37-1	July 8, 2004	-12.2	-84.6	30	-17.5	0.8	-42.0	0.16	-63.7	-18.9		1.048
	M37-1	Nov 6, 2003	-12.1	-89.5	34	-8.5	0.8	-54.2	0.19				
	M83-1	Nov 14, 2003	-11.6	-84.0	170	9.3	12.5	-32.1	4.72				
	M116-1	Nov 7, 2003	-10.8	-80.0	59	2.1	3.3	-33.0	1.41				
	Average		-11.8	-84.5	92	-0.6	3.0	-32.3	2.26	-51.4	-7.9	2.9	1.046