ISOTOPIC ANALYSIS OF AMMONIUM (^{15}N), NITRATE (^{18}O & ^{15}N) AND DISSOLVED CARBON (^{13}C) IN LANDFILL LEACHATE PLUME

Hossein Mohammadzadeh
(University of Ottawa, Ottawa, ON., Canada and Ferdowsi University of Mashhad, Mashhad, Iran)
Ian Clark (University of Ottawa, Ottawa, ON., Canada),
Ramon Aravena (University of Waterloo, Waterloo, ON., Canada),
Annie Bourbonnais, Ivy Liu, Paul Middlestead (University of Ottawa, Ottawa, ON., Canada)

ABSTRACT: Environmental stable isotopes (δ^{15}N, δ^{13}C, δ^{18}O and δ^{2}H) are used to understand the biogeochemical pathways that affect carbon and nitrogen pools at the Trail Road Landfill (TRL) leachate plume, located at about 25 km West of Ottawa City. Samples of leachate and leachate-polluted groundwater were collected at TRL site from 2003 to 2005. A variety of analytical techniques (ion-selective combination electrode, simultaneous distillation and titration, ion chromatography, denitrifier method, diffusion sampler, gas extraction line, elemental analyser (EA), total inorganic/organic carbon (TIC/TOC) analyzer and isotope ratio mass spectrometry (IRMS)) were used to determine the concentrations and isotopic compositions of ammonium, nitrate and dissolved carbon in leachate and leachate-polluted groundwater. Landfill leachate has high NH_4^+ concentrations (average of 418 mg/L, 189 mg/L and 313 mg/L for leachate from leachate pumping station (LPS), leachate pipes (LP) and M32, respectively). The shallow groundwater underneath and near the landfill border, which has relative high NH_4^+ concentration up to 54 mg/L, was clearly impacted by landfill leachate. However in the deep aquifer the NH_4^+ concentration are low mainly reflecting background concentrations. Based on these data, the deep aquifer has not been impacted by leachate. However, the enriched $\delta^{13}C_{DIC}$ values of groundwater (-5.0 ‰ VPDB and -1.9 ‰ VPDB for the shallow and deep aquifers respectively) in comparison with the $\delta^{13}C_{DIC}$ value of upstream pristine groundwater (-15.0 ‰ VPDB) showed the deep aquifer is impacted by leachate plume. Therefore, the NH_4^+ is partly attenuated by nitrification and denitrification in the fringes of the plume. Low $NO3^-$ concentrations in leachate taken from LPS and M32 (lower than 2 mg/L) and groundwater (lower than 1 mg/L) show that natural attenuation is occurring through denitrification which take place in anoxic conditions. This is confirmed by the enriched δ^{15}N values of nitrate (13.5‰ for the leachate and -7.6‰ to -0.6‰ for the groundwater, respectively), the measured excess N_2 from diffusion sampler (0.2 mg/L to 4.7 mg/L) and δ^{15}N of dissolved N_2 (-1.8‰ to 3.1‰). In addition, the deviation of groundwater samples from the mixing lines on the cross plot of DIC vs. $\delta^{13}C_{DIC}$ and DOC vs. $\delta^{13}C_{DOC}$ confirm that DOC is consumed through a diverse array of biogeochemical reactions, including denitrification, within the aquifers. The significantly enriched δ^{13}C values of acetate from leachate (-14.5 ‰ VPDB) above the δ^{13}C of leachate bulk DOC (-25.7 ‰ VPDB), also indicate DOC consumption by redox reactions.

INTRODUCTION AND STUDY SITE

Both ammonium (NH_4^+) and nitrate (NO_3^-) are common contaminants found in shallow groundwater (Smith et al., 1991; Korom 1992; Kellman et al., 2003) and are known pollutants recognized by the U.S. Environmental Protection Agency (EPA), Health Canada and Environmental Canada. Although there are multiple anthropogenic sources of ammonium and nitrate such as agricultural fertilizer and septic systems, it also can enter groundwater reservoirs from landfill leachate (Christensen et al., 2001; North et al., 2004). Nitrate contamination of surface- and groundwater is a major concern in the region surrounding Trail Road Landfill (TRL) site, an active landfill located at about 25 km West of Ottawa City (Figure 1). Operation commenced in the early 1960s and currently the landfill site accepts about 247009 tons annually residential, industrial, commercial & institutional, and construction & demolition waste throughout the city of Ottawa. The TRL site was selected to evaluate the fate of the NH_4^+ and NO_3^- and its ^{15}N evolution in groundwater plumes. Several groundwater and leachate samples were collected in 2003, 2004 and 2005 for chemical (nitrogen species, DOC, DIC) and isotope analysis

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($\square^{15}N_{NH4+}$, $\square^{15}N_{NO3-}$, $\square^{18}O_{NO3-}$, $\square^{13}C_{DIC}$ and $\square^{13}C_{DOC}$) on ammonium (NH_4^+), nitrate (NO_3^-) and dissolved carbon (DIC and DOC). Leachate samples were taken from leachate pumping station (LPS), leachate pipes (LP) and M32, samples from this well represent leachate sample, and groundwater samples were colleted from multilevel monitoring wells at TRL site. In addition to water samples, gas-diffusion samplers were installed within several multilevel monitoring wells and LP at TRL site in July 2005 to collect nitrogen gas (N_2). The gas-diffusion samples were retrieved after two weeks and were analysed for nitrogen gas concentrations and its isotope values ($^{15}N_{N2}$). The main objectives of this work were to determine the landfill leachate impacts on marginally groundwater using a multiisotope approach and to evaluate the fate of the NH_4^+ and NO_3 and their impact in the groundwater.

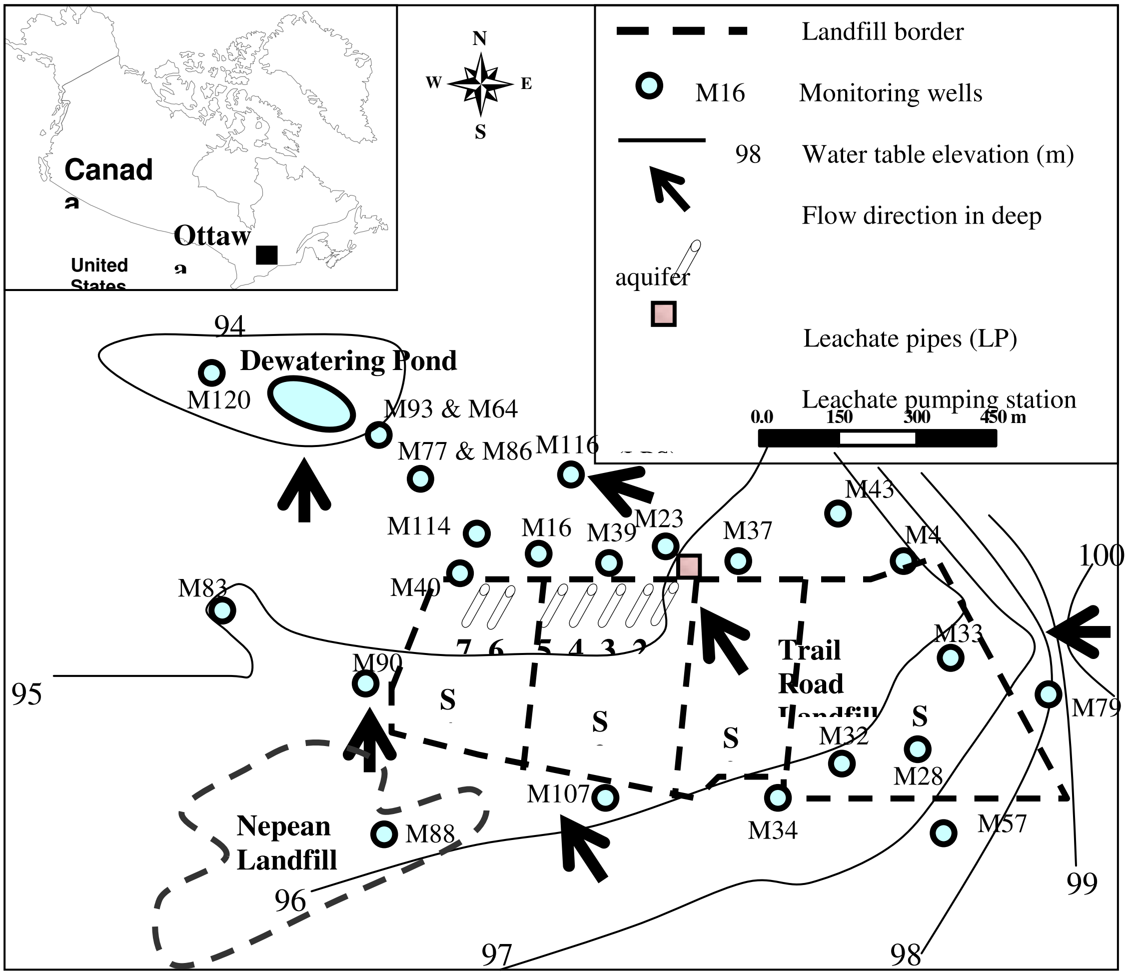

FIGURE 1: Plan view of study area and flow direction in deep aquifer.

MATERIALS AND METHODS

Samples of different volumes were collected in amber glass and plastic bottles. To measure the ammonium concentrations and the $\delta^{15}N$ of ammonium, one litter samples were collected using plastic bottles. Samples to measure concentrations and $\delta^{15}N$ of nitrate were collected in 30 ml plastic bottles. In order to measure dissolved inorganic/organic carbon (DIC and DOC) 40 ml samples were collected using amber glass bottles. Samples were freezing at -20°C for ammonium and nitrate analysis in order to limit bacterial activity. For DIC and DOC analysis, samples were stored in the fridge at 4°C. Samples were filtered with 0.45 µm filters to remove particles. All measurements of electromotive potential (Eh), pH, electrical conductivity (EC), dissolved oxygen (DO), and temperature (T) were performed in the field, using appropriate meters and a flow-through cell, before the installation of diffusion samplers within some selected monitoring wells. Since the silica tubing of the diffusion sampler is only permeable to gases in the solution, it allows dissolved gases to diffuse into the diffusion sampler and then reach equilibrium. After leaving for 3 weeks below the water table for equilibration, the diffusion samplers were taken out of the wells and sealed at both joins between the open ends of copper tubing and silica tubing with refrigerator clamps. This sealing has to be done under water as quickly as possible to avoid atmospheric air to diffuse into the samplers and contaminate the sampling gases. Since only gas can diffuse into the samplers, they were taken back to the lab and attached to gas extraction line directly without going through water vapour absorption process.

δ^{15}N analysis of both ammonium and nitrate in water and δ^{13}C analysis of DOC were done at the geochemistry and the G.G. Hatch Isotope Laboratories of department of Earth Sciences at University of Ottawa. To measure ammonium concentrations, an Ion-Selective Electrode (ØTM 390 Ph/Temp/mv/ISE Meter; Beckman Instruments, Inc.) was used for low concentrations samples whereas simultaneous distillation and titration were used for high concentrations samples. Ion chromatography (IC model DIONEX-DX-100) was used to measure nitrite and nitrate concentrations. For determination of ammonium δ^{15}N, collected homogeneous powder of ammonium sulfate salt ($(NH_4)_2SO_4$) after distillation were weighed into tin capsules and then flash combusted at 1800 ^{o}C in an elemental analyzer (EA). Resulting gases were carried via helium through an EA to purify and separate the N_2. N_2 gas was carried from the EA into an isotope ratio mass spectrometer (IRMS) for isotope analysis (δ^{15}N). For the determination of the isotopic composition of nitrate (δ^{18}O and δ^{15}N), the so called "denitrifier method" has been applied (Sigman et al, 2001, Casciotti et al., 2002). During isotopic analysis, NO_3^- of water samples is transformed to N_2O gas by bacteria that lack an active N_2O reductase enzyme. The N_2O gas is then frozen into trap for 15 min, released and run in continuous flow via GasBench peripheral interfaced to an Isotope Ratio Mass Spectrometer (Delta XP Thermo Finnigan). CF-IRMS was used to measure the N_2 concentration and δ^{15}N of N_2 from the gas-diffusion samplers. The δ^{13}C values of both DIC and DOC were characterized using a total inorganic/organic carbon (TIC/TOC) analyzer interfaced to a Delta^{plus} continuous-flow-IRMS. The procedures for δ^{13}C analysis of DIC, DOC and acetate are explained in details in Mohammadzadeh et. al., 2005.

RESULTS AND DISCUSSION

Nitrogen and carbon concentrations and corresponding isotopic values are shown in Table 1. The concentrations data collected in 2003 through 2005 shows a high load of NH4$^+$ in the landfill leachate from LPS, LP and M32 ranging between 336 and 552 mg/L, 79 and 270 mg/L, 90 and 510 mg/L, respectively. The shallow groundwater underneath and near the landfill border is clearly impacted by the landfill leachate with NH_4^+ concentrations as high as 54 mg/L. However, much lower NH_4^+ concentrations with values less than 6 mg/L were observed in the deeper aquifer. This means, the deep aquifer has not been impacted by landfill leachate. However, the enriched $\delta^{13}C_{DIC}$ values of groundwater (average of -5.0 ‰ VPDB and -1.9 ‰ VPDB for the shallow and deep aquifers respectively) in comparison with the $\delta^{13}C_{DIC}$ value of upstream pristine groundwater (-15.0 ‰ VPDB) indicated that both sallow and deep aquifers are impacted by leachate (+12.3 ‰ VPDB). Therefore, the NH_4^+ is partly attenuated by nitrification and denitrification in the fringes of the plume. Leachates from LPS and M32 generally have nitrate concentrations below 2 mg/L. However, leachate collected from beneath the landfill, LP, have the highest nitrate concentrations (97 mg/L). Groundwater collected from wells in both shallow and deep aquifers generally have low nitrate concentrations, except M37-3 shallow well which has the highest nitrate concentration (70 mg/L). The high NH_4^+ concentration in LP (average amount of 189 mg/L, n = 9) and in M32 (average amount of 313 mg/L, n=3) in comparison to groundwater samples shows that leachate environment is free of oxygen (anoxic condition). Low NO_3^- concentrations in leachate taken from LPS and M32 is due to low nitrification of the NH_4^+ and natural attenuation of nitrate through denitrification which take place under this sufficiently anoxic environment (e.g., Hiscock et al., 1991; Smith et al., 1991; Chen et. al., 2005).

TABLE 1: Ammonium (NH_4^+), nitrate (NO_3^-), DIC and DOC concentrations and corresponding isotope values ($\delta^{15}N_{NH4+}$, $\delta^{15}N_{NO3-}$, $\delta^{18}O_{NO3-}$ and δ13C) of the leachate and groundwater at TRL site. All isotope data in ‰.

Sample ID		**Date**	**NH_4**		**NO_2**	**NO_3^-**			**N_2**		**DIC**		**DOC**	
			mg/L	**$\delta^{15}N_{NH4}$**	**mg/L**	**mg/L**	**$\delta^{15}N_{NO3}$**	**$\delta^{18}O_{NO3}$**	**mg/L**	**$\delta^{15}N_{N2}$**	**mg/L**	**$\delta^{13}C_{DIC}$**	**mg/L**	**$\delta^{13}C_{DOC}$**
Reference	M120	July 21, 2005	0.0		0.2	2.8			0.2	0.7	59	-13.3	0.6	-26.9
		July 9, 2004	0.3	bl	0.2	1.6	-1.8	0.5			45	-14.8	1.3	-41.1
	M57	July 22, 2005	0.0		0.0	1.8			0.3	-1.6	48	-13.4	0.9	-26.8
		July 9, 2004	0.3	bl	0.0	1.8	-1.0	19.1			58	-17.1	1.2	-31.1
Leachate	M32	July 22, 2005	89.5		26.9	0.9			3.3	0.2	331	7.8	4310	0.0
		July 6, 2004	337.4	7.4	22.8	2.2	bl	bl			339	10.7	5130.0	-17.4
		July 7, 2003	510.5	6.3	na	na	na	na			200	7.0	4870.0	-28.8
	LP1	July 20, 2005	79.2		5.9	97.0			0.9	-1.0	258	0.9	23.87	-27.4
		July 7, 2004	120.6	9.2	0.0	0.0	bl	bl			399	1.0	115.6	-26.3
	LP2	July 7, 2004	221.6	9.1	1.2	29.2	13.5	2.1			414	3.4	107.7	-25.7
	LP3	July 6, 2004	144.8	9.8	2.8	0.0	bl	bl			424	-11.2	156.8	-26.4
	LP4	July 7, 2004	244.3	7.0	0.0	0.0	bl	bl			501	2.3	145.1	-26.3
	LP5	July 7, 2004	154.8	7.4	0.0	4.8	bl	bl			336	7.9	51.4	-26.5
	LP6	July 21, 2005	270.4		0.9	1.1					753	12.7	224.6	-27.0
		July 7, 2004	224.4	6.5	0.0	0.0	bl	bl			901	6.6	177.8	-23.4
	LP7	July 7, 2003	238.4	7.3	1.9	3.2	bl	bl			388	2.6	91.1	-25.4
	LPS	July 20, 2005	357.5		0.8	1.0			3.7	2.0	720	11.5	153	-26.4
		Aug , 2002	552.0	15.9	na	na	na	na			509	9.9	245.0	-24.6
		Apr , 2003	432.0	5.9	na	na	na	na			832	na	202.5	-24.4
		Nov 14, 2003	336.0	6.6	na	na	na	na			647	15.4	299.6	-25.0
Pond	DWP-SE	July 21, 2005	0.0		0.1	1.2			3.4	-1.8	72	-4.3	1.42	0.0
		July 9, 2004	0.5	bl	0.1	0.5	8.6	8.9			85	-7.3	2.5	-41.6
Shallow Aquifer	M16-3	July 8, 2004	0.8	8.5	0.0	0.8	-7.6	-8.6			68	-17.5	2.0	-32.4
	M37-3	July 20, 2005	17.5			69.8			4.3	3.1	247	6.1	30.75	-26.9
		July 8, 2004	16.8	8.2	0.3	0.8	bl	bl			417	3.9	76.8	-25.2
		July 6, 2004	15.5	9.7	na	na	na	na			178	-8.8	39.2	-26.1
	M23-3	July 8, 2004	0.2	bl	0.1	0.2	bl	bl			49	-20.8	2.6	-28.8
	M43	July 8, 2004	53.7	5.5	0.2	0.2	bl	bl			332	18.8	18.5	-18.8
	M4-2	July 22, 2005	17.2			0.2					151	-11.9	3.93	-26.5
		July 7, 2004	42.7	4.5	0.0	0.4	bl	bl			194	-14.8	5.5	-30.1
		July 6, 2004	30.2	6.7	na	na	na	na			165	-6.1	6.1	-29.9
	M33-1	July 7, 2004	29.6	4.9	0.2	0.2	bl	bl			339	1.6	20.2	-25.6
Deep Aquifer	M64	July 21, 2005	0.0								111	-1.5	3.44	-29.0
		July 9, 2004	0.6	bl	0.1	0.1	bl	bl			143	-7.6	4.8	-35.3
	M77-2	July 21, 2005	0.0						4.7	0.1	129	-3.6	1.7	-27.3
		July 9, 2004	1.1	bl	0.2	0.1	bl	bl			166	-9.5	2.9	-22.0
	M114-2	July 21, 2005	0.0			0.1			3.5	1.1	38	-13.6	1.32	-26.7
		July 9, 2004	0.4	bl	0.0	0.1	bl	bl			49	-19.4	1.7	-30.3
	M16 -2	July 21, 2005	0.4			1.0			2.2	0.1	17	-12.6	0.66	-26.5
		July 8, 2004	1.6	3.1	0.1	0.3	-0.6	-6.9			22	-21.3	0.9	-29.1
	M23-2	July 8, 2004	0.2	bl	0.1	0.0	bl	bl			79	15.7	4.3	-31.8
	M37-2	July 20, 2005	0.1		0.1	0.1			2.5	1.0	107	-0.6	4.55	-26.2
		July 8, 2004	0.8	bl	0.1	0.0	bl	bl			94	-4.4	7.7	-18.2
	M4-1	July 20, 2005	0.6		0.2	0.1					132	18.3	8.46	-26.9
		July 7, 2004	1.2	3.3	0.0	0.2	bl	bl			129	14.9	7.0	-23.3
	M93	July 21, 2005	0.0						2.3	1.4	60	-3.3	1.62	-27.0
		July 9, 2004	0.5	bl	0.1	0.2	bl	bl			71	-5.1	2.0	-33.9
	M77-1	July 21, 2005	0.0			0.2			1.5	-0.1	87	10.0	3.5	-26.8
		July 9, 2004	0.5	bl	0.0	0.2	bl	bl			105	9.5	5.2	-30.5
	M114-1	July 21, 2005	0.0			0.1					80	-6.6	1.18	-28.9
		July 9, 2004	0.6	bl	0.1	0.1	bl	bl			71	-11.2	1.3	-41.9
	M16 -1	July 21, 2005	0.0		0.3	0.1					149	-1.9	2.97	-27.3
		July 8, 2004	0.5	bl	0.0	0.1	bl	bl			181	-8.0	3.8	-23.9
	M23-1	July 8, 2004	0.4	bl	0.1	0.1	bl	bl			86	11.8	4.0	-37.8
	M37-1	July 20, 2005	0.0						2.2	0.5	28	-8.6	0.61	-27.6
		July 8, 2004	0.2	bl	0.0	0.1	bl	bl			30	-17.5	0.8	-42.0
	M34	July 22, 2005	6.0			0.1			-1.3	0.2	214	4.7	3.59	-38.1
	M28	July 22, 2005	3.4		0.2	0.5			-0.7	-0.5	198	22.0	13.08	-25.7

bl = blow detection limit and na = not available

In addition, low amount of nitrate (below 1 mg/L, except M37-3), associated with the existence of anaerobic conditions were observed in both shallow and deeper groundwater. Enriched isotope values of nitrate (13.5‰ for the leachate and -7.6‰ to -0.6‰ for the groundwater, respectively) also support the occurrence of denitrification since during this process, bacteria preferentially use lighter isotopes, leaving residual nitrate enriched in heavier isotopes (Clark et al, 1997). High concentrations and $\delta^{15}N$ values of ammonium in August 2002 and July 2004 in comparison to November 2003 show the seasonal variation of leachate due to precipitation, which can be confirmed by ^{2}H and ^{18}O isotopic data (data not shown). $\delta^{15}N$ values of ammonium in August 2002 and July 2004 in comparison to November 2003 show the seasonal variation of leachate due to precipitation, which can be confirmed by ^{2}H and ^{18}O isotopic data (data not shown).

Since biological reactions use preferentially $^{14}N_{NO3}^{-}$, the $\delta^{15}N$ of the nitrogen gas produced during the reduction of NO_3^- to N_2 (denitrification) will be depleted and an exponential enrichment occurs in the $\delta^{15}N_{NO3}^{-}$ of the residual nitrate reservoir (Clark et al. 1997). The measured N_2 from the gas-diffusion samplers were transformed from gaseous to aqueous phase by applying Henry's law. Excess N_2 range from 0.2 mg/L to 4.7 mg/L (Table 1), and are believed to be the product of denitrification. We have found that $\delta^{15}N$ of dissolved N_2 (a mixture of atmospheric and denitrification nitrogen) ranged from -1.8‰ to 3.1‰, which is deviated from the $\delta^{15}N$ of atmospheric N_2 equilibrated with water of 1‰. The wide range of $\delta^{15}N$-N_2 indicates that the groundwater system has a combination of denitrification at various stages (Kellman, 1998). The composition diagrams of DIC vs. $\delta^{13}C_{DIC}$ and DOC vs. $\delta^{13}C_{DOC}$ (diagrams not shown), show that the deviation of groundwater samples from the mixing lines, drawn based on $\delta^{13}C$ mass balance between the two leachate and the pristine groundwater end members, is due to biogeochemical redox reactions, like denitrification, within the aquifer. The significantly enriched $\delta^{13}C$ values of leachate acetate (-14.5 ‰ VPDB) above $\delta^{13}C$ of leachate bulk DOC (-25.7 ‰ VPDB) also indicate DOC consumption through redox reactions. A more detailed discussion on DIC and DOC in leachate and groundwaters at TRL site that incorporated isotopic data can be found in Mohammadzadeh et. al., 2004 and 2005.

CONCLUSIONS

Nitrogen and carbon concentrations and environmental stable isotopic values ($\delta^{15}N$, $\delta^{13}C$) clearly showed that the TRL leachate impacts on marginally groundwater and that denitrification is an important biogeochemical pathway at this landfill site. The average NH_4^+ concentrations of landfill leachate from LPS, LP and M32 are 418 mg/L, 189 mg/L and 313 mg/L, respectively. The shallow aquifers at TRL site is obviously impacted by the landfill with high NH_4^+ concentrations in groundwater (54 mg/L). Although the enriched $\delta^{13}C_{DIC}$ values of groundwater (-5.0 ‰ VPDB and -1.9 ‰ VPDB for the shallow and deep aquifers respectively) compare to the $\delta^{13}C_{DIC}$ value of upstream pristine groundwater (-15.0 ‰ VPDB) showed the deep aquifer is impacted by leachate plume, much lower NH_4^+ concentrations with values less than 6 mg/L were observed in the deeper aquifer. The NH_4^+ is partly attenuated by nitrification and denitrification in the fringes of the plume in deep aquifer. High NH_4^+ concentrations in leachate from LP and M32 compared to groundwater samples shows that leachate environment has anoxic condition. The low NO_3^- concentrations in leachate taken from LPS and M32 (lower than 2 mg/L) and groundwater (lower than 1 mg/L) is due to natural attenuation of nitrate through denitrification process that take place under this sufficiently anoxic environment. This can be confirmed by the enriched isotope values of nitrate (13.5‰ for the leachate and -7.6‰ to -0.6‰ for the groundwater, respectively). The measured excess N_2 from diffusion samplers ranged from 0.2 mg/L to 4.7 mg/L and is likely the product of denitrification. The wide range of $\delta^{15}N$ of dissolved N_2 (ranging from -1.8‰ to 3.1‰) indicates that the groundwater system has a combination of denitrification at various stages. The deviation of groundwater samples from the mixing lines on the cross plot of DIC vs. $\delta^{13}C_{DIC}$ and DOC vs. $\delta^{13}C_{DOC}$ confirm the consumption of DOC through biogeochemical redox reactions within the aquifer.

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REFERENCES

Casciotti, K. L., D. M. Sigman, M. Galanter-Hastings, J. K. Böhlke, and A. Hilkert. 2002. "Measurement of the Oxygen Isotopic Composition of Nitrate in Seawater and Freshwater Using the Denitrifier Method." *Analytical Chemistry.* 74:4905-4912.

Chen, D. J. Z., and K. T. B. MacQuarrie. 2005. "Correlation of □^{15}N and □^{18}O in NO_3^- During Denitrification in Groundwater." *Journal of Environmental Engineering and Science*. 4:221-226.

Christensen T.H., P. Kjeldsen, P. L. Bjerg, D. L. Jensen, J. B. Christensen, A. Baun, H. J. Albrechtsen and G. Heron. 2001. "Review Biogeochemistry of Landfill Leachate Plumes." *Applied Geochemistry.* 16:659-718.

Clark, I. D., and P. Fritz. 1997. *Environmental Isotopes in Hydrogeology*. Lewis Publishers, Boca Raton, FL.

Hiscock, K. M., J. W. Lloyd, and D. N. Lerner. 1991. "Review of Natural and Artificial Denitrification of Groundwater." *Wat. Res*. 25 (9):1099-1111.

Kellman, L. M, and C. Hillaire-Marcel. 1998. "Nitrate Cycling in Streams: Using Natural Abundance of NO3—□^{15}N to Measure in-Situ Denitrification." *Biogeochemistry.* 43:273-292.

Kellman, L. M., and C. Hillaire-Marcel. 2003. "Evaluation of nitrogen isotopes as indicators of nitrate contamination sources in an agricultural watershed." *Agriculture, Ecosystems and Environment.* 95:87-102.

Korom, S. F. 1992. "Natural Denitification in the Saturated Zone: A review." *Water Resources Research.* 28(6):1657-1668.

Mohammadzadeh, H., I. D. Clark, S. T. Gilles, and P. Middlestead. 2004. "Tracing Landfill Leachate Impacts on Groundwater Using DOC Geochemistry and d^{13}C Measurements." *4th International Conference on Groundwater Quality. GQ-2004*, pp.332-337. IAHS Publishers.

Mohammadzadeh, H., I. D. Clark, M. Marschner, and G. St-Jean. 2005. "Compound Specific Isotopic Analysis (CSIA) of Landfill Leachate DOC Components." *Chemical Geology.* 218:3-13.

North, J. C., R. D. Frew, and B. M. Peake. 2004. "The Use of Carbon and Nitrogen Isotope Ratios to Identify Landfill Leachate Contamination: Green Island Landfill, Dunedin, New Zealand." *Environmental International.* 30:631-637.

Sigman, D. M., K. L. Casciotti, M. Andreani, C. Barford, M. Galanter, and J. K. Böhlke. 2001. "A Bacterial Method for the Nitrogen Isotopic Analysis of Nitrate in Seawater and Freshwater." *Analytical Chemistry.* 73:4145-4153.

Smith, R. L., B. L. Howes, and J. H. Duff. 1991. "Denitrification in Nitrate-Contaminated Groundwater: Occurrence in Steep Vertical Geochemical Gradients." *Geochemical et Cosmochimica Acta.* 55:1815-1825.