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Evolution and Degradation Pathways of Landfill Leachate Doc and Detection of Groundwater Landfill-leachate Contamination Using Compound-specific Isotope Analysis

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EVOLUTION AND DEGRADATION PATHWAYS OF LANDFILL LEACHATE DOC AND DETECTION OF GROUNDWATER LANDFILL-LEACHATE CONTAMINATION USING COMPOUND-SPECIFIC ISOTOPE ANALYSIS

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Abstract

Dissolved organic carbon (DOC) is a complex, yet major component of leachate and groundwater contamination derived from municipal solid waste burial. Here I use a new analytical technique for the analysis of ^{13}C in specific compounds of DOC in leachate from the Trail Road Landfill (TRL) site, Ottawa, Ontario, in order to better characterize its biogeochemical and isotopic evolution during degradation; to determine methanogenesis pathways; and to identify characteristic tracers for recognizing potential of the leachate impact on the surrounding groundwater. This new operational system measures chromatographically-separated DOC compounds, and DOC compounds separated by DAX-8- resin, with a total inorganic/organic carbon analyzer (TCA) interfaced with a Thermo-Finnigan Delta^{Plus} continuous-flow isotope ratio mass spectrometer (CF-IRMS).

At the TRL site, with capacity of 8.8 million cubic meters and a footprint of approximately 65 hectares, waste emplacement has been undertaken in four stages since the 1980s. Samples were collected in 2003 through 2005 from the leachate pumping station (LPS), which drains the areas of youngest waste, from monitoring well M32, situated at the base of the earliest stage and from leachate from waste up to 28 years old, and from several nested multilevel monitoring wells situated in the periphery of the landfill site. The following results were obtained based on isotope analysis of leachate, of landfill gases, of various leachate DOC components, and of contaminated groundwater.

Leachate as a source of contamination has been characterized at different parts of the landfill as follows:

1. Elevated DOC and enriched $^{13}C_{DOC}$ values in old leachate from the older landfill (M32) (4770 mgl^{-1} and –21.6 ‰) in comparison with that of the younger leachate (LPS) (197 mgl^{-1} and –25.7 ‰) shows a fundamentally different biodegradation pathway and more advanced microbial processes in the degradation of dissolved organic mater (DOM) in the older part of the landfill. This resulted in the accumulation of simple fatty acids (acetate and propionate concentration of 1008 mgl^{-1} and 608 mgl^{-1}, respectively) at the older part of the landfill with more enriched ^{13}C values of acetic acid (-12.0 ‰) in comparison to that of young leachate at LPS (-16.9 ‰).

2. Deuterium excess provides a robust indicator of overall methane production, showing greater CH_4 production in the younger parts of landfill than the older parts. The CO_2 reduction pathway ($\alpha^{13}C_{CO2\text{-}CH4}$=1.06) dominants at the younger landfill, however, acetate fermentation is the more favored CH_4 production pathway at the older landfill. This can be confirmed with the less enriched $^{13}C_{DIC}$ (8.5 ‰) and a lower value for ^{2}H excess (9.8 ‰) at M32.

3. The higher ratio of humic/fulvic acids (HA/FA) in young leachate compared to the old leachate (0.18 and 0.05 for LPS and M32, respectively) is due to high concentrations of FA (4482 mgl^{-1}, 73% of the total DOC) and low concentrations of HA (21 mgl^{-1}, 0.3% of the total DOC) in old M32 leachate. Less aromatic carbon in M32 (3% and 5% for POC and HA, respectively) in comparison with that of young

leachate from the LPS (10% and 28% for POC and HA, respectively), estimated from ^{13}C-NMR spectra, is perhaps due to degradation of HA and transforming of aromatic carbon to low molecule weight dissolved organic carbon (LMW-DOC), which is consistent with the high concentration of acetic acid (AA) in this older leachate.

Although the elevated concentrations of leachate indicator parameters (like Cl and DOC) indicate that both shallow and deep aquifers have been contaminated at the TRL site, assessing the impact of landfill leachate on local groundwaters using geochemical parameters is often confounded by naturally elevated concentrations of these indicators. Here, environmental isotopes are used to provide a constraint in this assessment for leachate derived from the TRL site. The carbon geochemistry of different carbon pools (DIC, DOC, CH_4, CH_3COOH, humic substances (HS), particulate organic carbon (POC), particulate inorganic carbon (PIC)) and $\delta^{13}C$ were used to recognize leachate impact on the surrounding groundwater. Following are the results of this assessment:

1. The most unambiguous leachate indicator parameters remain dissolved methane and $\delta^{13}C_{DIC}$. In all proximal groundwaters, methane concentrations remain above detection and as high as 10 mgl^{-1}, close to the saturated equilibrium value for a 50% methane atmosphere in the unsaturated zone. The $\delta^{13}C$ value of methane demonstrates reactive loss of acetate in the leachate plume by methanogenic fermentation, with possible methane oxidation in the plume fringe. The enriched values of $^{13}C_{DIC}$ for the shallow and deep aquifers (averages of -6.4 ‰, -1.0 ‰ and -0.6 ‰ for the shallow, upper deep and lower deep aquifers, respectively) in

comparison to the upgradiant pristine groundwater with -15.2 ‰ also confirm that the leachate (+8.8‰ and +10.7‰ for leachate taken from M32 and LPS, respectively) has had an impact on these aquifers.

2. Continued reaction of DOC in groundwaters is confirmed by deviation of groundwater samples from the mixing lines on diagrams of DIC vs. $\delta^{13}C_{DIC}$ and DOC vs. $\delta^{13}C_{DOC}$, and by the absence of acetate. The calculated net reacted (lost) DOC (988 mgl^{-1}, 368 mgl^{-1}, and 272 mgl^{-1} for the shallow, upper deep and lower deep aquifers, respectively) correlates with net gains in DIC (185 mgl^{-1}, 117 mgl^{-1} and 85 mgl^{-1} for these aquifers, respectively) and is further evidence for continued reaction beyond the landfill. Acetate fermentation reactions resulted in enriched $^{13}C_{DIC}$ for the gained DIC. Howeve r, oxidation of DOC and/or methane oxidation resulted in negative shift in $\delta^{13}C_{DIC}$ for the gained DIC. The low amount of DIC associated with the low amount of Ca^{2+} suggests a mineralogical control through calcite precipitation.

3. Production of ^{13}C-depleted organic carbon, possibly through methanotrophic bacterial activity, seems to occur in the fringes of the advancing leachate plume. Evidence includes remarkably depleted $^{13}C_{DOC}$ at the lower part of the deep aquifer where values lower than –40‰ were measured. Further, the humic acid (HA) and fulvic acid (FA) components dominate the DOC of the leachate impacted groundwater (76 % to 87 % of total DOC content). The HA/FA ratio is below unity, which contrasts with un-impacted groundwaters where HA represents the major DOC component.

Keywords: Landfill leachate, carbon pools (DIC, DOC, CH_4), chromatographically separated DOC components (acetate, propionate, humic substances (HS)), environmental stable isotopes ($\delta^{13}C$, $\delta^{2}H$, and $\delta^{18}O$), compound specific isotopic analysis (CSIA), methane production, Trail Road Landfill (TRL).

Dedicated to my family on their help:

Samaneh, Alireza and Yahya

In the Name of GOD, the Compassionate and the Merciful

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General Introduction

Sanitary landfilling of municipal solid waste (MSW) is a worldwide method of waste disposal. Nowadays, waste disposal is an important issue in almost all countries and landfilling of MSW is the most widely used disposal method. While waste composting and recycling account for 30% and 78% of MSW management in the USA and Europe, respectively (Barlaz 2006), considerable amount of MSW is disposed in landfills all over the world. Although sanitary landfilling is a cost saving method (Castagnoli et al. 1990), generation of leachate and landfill gases (LFG), as sources of environmental contaminants, are two problems associated with this type of disposal. While surface water pollution represents a potential environmental impact from landfill leachate, groundwater pollution probably poses a greater environmental risk (Kjeldsen et al. 2002).

Landfill leachate is generated as rainfall percolating through the waste supports a range of biodegradation and leaching reactions resulting in elevated concentrations of dissolved metals; soluble biodegradation products of complex organic molecules; along with fines and colloids material (Reinhart and Grosh, 1998). Christensen et al. (2001), who reviewed the characteristics of leachate plumes downgradient of landfills, and Kjeldsen et al. (2002), who reviewed the present and long-term composition of municipal solid waste landfill leachates, suggested that pollutant transformation from the waste material to the percolating water is the result of a complex combination of physical, chemical, and biologically mediated processes within the waste material.

In general, leachate quality is highly variable and it is influenced by waste composition, environmental conditions in the landfill, waste landfilling technology, and by the length of time which has elapsed since waste placement at the landfill site (Kjeldsen et al., 2002;

Christensen et al., 2001). MSW contains various materials, which are biodegradable (e.g. food waste, wood, paper, trees, cardboard, etc.), poorly biodegradable (plastic, rubber, etc.) and inorganic solids (e.g. glass, metal, concrete, etc.). Cellulose and hemicellulose, the major biodegradable constituents in landfills, comprise 29 to 65% of the MSW (Barlaz 2006). The decomposition of these components of MSW (cellulose and hemicellulose) to CH_4 and CO_2 in landfills is well documented (Barlaz et al., 1989).

Dissolved organic mater (DOM) is one of the major groups of pollutants in MSW landfill leachate (Christensen et al., 2001). DOM in leachate is a bulk parameter covering a variety of organic degradation products and it contains a mixture of labile dissolved organic constituents, the composition of which is very dependent on landfill refuse of the respective site (Baedecker and Back, 1979a; Christensen et al., 1998; Hornibrook et al., 2000; Christensen et al., 2001). DOM in landfill leachate ranges from volatile fatty acids (e.g. acetic, propionic, and butyric) produced during the decomposition of lipids, proteins, and carbohydrates (Albaiges et al., 1986; Schultz and Kjeldsen, 1986) to refractory humic substances (HS) such as fulvic-like and humic-like compounds. Aromatic hydrocarbons (e.g. various xylenes, toluene, benzene and ethylbenzene) originating from petroleum products such as gasoline and fuel oils are common landfill contaminants (Schultz and Kjeldsen, 1986) and halogenated hydrocarbons (e.g. tetrachloroethylene, trichloroethylene, etc.) also have been found in high concentrations in the leachate (Kjeldsen et al. 2002).

Although organic compounds are removed from the waste pile as a result of dissolution by infiltrating rainwater, they decrease in concentration through decomposition as well (Qasim and Chiang, 1994, mentioned in Reinhart and Grosh,1998). Decay and dissolution of these

organic constituents through bacteria-meditated reactions, will generate different major carbon pools, such as dissolved inorganic carbon (DIC), dissolved organic carbon (DOC), and CH_4, within both the refuse pile and the leachate plume (Baedecker and Back, 1979b). As demonstrated in earlier research (Whiticar et al., 1986; Liu et al., 1992; Hackley et al., 1996; Hornibrook et al., 2000; Van Breukelen 2003; Van Breukelen et al., 2003 & 2004; North et al., 2004), the biogeochemical processes within the landfill environment and outgassing of CO_2 can produce characteristic ^{13}C signatures in the major carbon pools.

Leachate quality and the amount of CH_4 production depend on natural degradation of organic materials and the phase of decomposition of these materials within the landfill. The major phases of waste decomposition and stabilization are: 1) initial aerobic phase which is typical of young landfills (<1 year) and last for a few days because of lack of oxygen once the waste is covered. During this phase, DOM in landfill is degraded by aerobic bacteria as the oxygen content of the landfill is consumed; 2) anaerobic acid phase in which cellulose and hemicellulose materials, carbohydrates, proteins and fats are biodegraded by hydrolytic, fermentative, and acetogenic bacteria, resulting in an accumulation of carboxylic acids and volatile fatty acids (VFA); 3) the methane production phase in which the accumulated VFA are converted to CH_4 and CO_2. In some studies, this later phase is subdivided into two separate accelerated methane production and decelerated methane production (maturation) phases (Kjeldsen et al., 2002; Rooker 2000; Reinhart and Grosh, 1998).

In this study the Trail Road municipal Landfill (TRL) which is owned and operated by the City of Ottawa, Canada, has been investigated. The study was investigated to meet several objectives: 1) characterizing the geochemical composition of leachate; 2) isolating and

characterizing concentrations and $\delta^{13}C$ values of leachate DOC fractions to observe the isotopic evolution of these fractions during the degradation of organic carbon; 3) determining the methanogenesis pathways and estimating the rate of methane production; and 4) identifying characteristic tracers to recognize the potential of leachate impact on the surrounding groundwater. The investigation included developing a conceptual model of biodegradation at the site and studying the carbon geochemistry of different carbon pools (DIC, DOC, CH_4, CH_3COOH, and humic substances (HS)), environmental stable isotopes ($\delta^{13}C$, $\delta^{18}O$, and $\delta^{2}H$) and compound specific isotope analysis (CSIA) of leachate DOC fractions. New analytical methods now allow routine isotopic analysis of bulk DOC and the lighter weight components of DOC (Marschner et al., 2005; Mohammadzadeh et al., 2005; St-Jean 2003). This additional characterization of a major carbon pool provides additional insight into the geochemical pathways of methane production and DIC evolution in the landfill.

This thesis includes three manuscripts. The first manuscript is a technical contribution for the compound specific isotopic analysis (CSIA) of DOC components in landfill leachate. It explains; 1) the optimal setting for the HPLC parameters and the procedure of collecting DOC components, e.g. acetate, based on peak retention times with a programmable fraction collector; and 2) running of DOC components on the total carbon interface system for concentration and measurement of $\delta^{13}C$. In the second manuscript an attempt has been made to conceptualize the TRL site and to characterize the source of contamination, i.e. leachate. The extent of decomposition of organic material and the biodegradation pathways of dissolved carbon were evaluated at different areas, including the younger lined and older

unlined parts of the landfill, using geochemical characteristics and CSIA of the DOC components. In the third manuscript, the impact of landfill leachate on groundwater has been investigated using carbon geochemistry and environmental stable isotopes (^{13}C, ^{18}O and ^{2}H). The isotope signatures of the leachate carbon system are used to provide evidence of leachate contamination in marginally impacted groundwater.

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Compound Specific Isotopic Analysis (CSIA) of Landfill Leachate DOC Components

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Abstract

In an attempt to better characterize the biogeochemical evolution of dissolved organic carbon (DOC) in landfill leachates, and to interpret the origin of DOC in groundwater, we have developed a new analytical technique for the compound specific isotope (^{13}C) analysis (CSIA) of DOC. This is a new operational system that measures chromatographically-separated DOC compounds with a total inorganic/organic carbon analyzer (TCA) interfaced with an isotope ratio mass spectrometer (IRMS), and it represents a significant contribution to analytical technology.

Leachate samples were collected from the Trail Road Landfill (TRL) site located about 25 km to the west of the city of Ottawa, Canada. Measurements of Eh, pH, electrical conductivity, dissolved oxygen, total dissolved solids, and temperature were completed at the field site. High performance liquid chromatography (HPLC) was used to separate DOC components into fractions for separate analysis on TCA. The TCA is operated in-line with a Thermo-Finnigan Delta^{Plus} continuous-flow isotope ratio mass spectrometer (CF-IRMS) that oxidizes organic carbon to CO_2 for measurement of both concentration, by infrared absorption, and $\delta^{13}C$. DOC fraction collection was based on the detection of discrete peaks of individual compounds, allowing identification of key peaks, such as acetate, with recoveries of up to 100%. The difference in $\delta^{13}C$ values for leachate acetate (-10.7 to -16.9 ‰ VPDB) and the bulk DOC (-24.7 ‰ VPDB) can be used to distinguish landfill leachate derived DOC and identify biogeochemical reactions. The enrichment of ^{13}C in the acetate suggests that this biologically-derived compound has become a substrate for secondary biogeochemical reactions, likely methanogenesis.

Keywords: Landfill leachate, Dissolved Organic Carbon (DOC), Chromatographically separated DOC components, Compound Specific Isotopic Analysis (CSIA), Carbon-13, Acetate, Trail Road Landfill (TRL) site.

1. Introduction

The presence of dissolved organic components in landfill leachates is of some concern where such solutions may contaminate groundwaters. Their toxicity is not only dependent on the nature of dissolved organic matter (DOM), but also on concentration of dissolved organic carbon (DOC) and availability for DOC (Alkalay *et al.*, 1998). DOC is a complex component of groundwaters and leachate that includes high molecular weight humic and fulvic acids as well as lighter weight fatty acids such as acetate. DOC largely originates from biodegradation of solid organic wastes in the landfill. Even in a landfill that is decades old, the leachate may contain DOC at the level of thousands of milligrams per litre (Christensen *et al.*, 1998). Although natural DOC plays an important role in freshwater systems for the mobility of toxic heavy metals and other pollutants, DOC may itself be a groundwater contaminant (Christensen *et al.*, 1998; Drever, 1997).

Tracing the sources and biotransformations of DOC in groundwaters is aided by isotope analysis of DOC fractions (e.g. Wassenaar *et al.*, 1990). Traditional separations of DOC are methodological in nature, focusing on acid-base separations and hydrophobicity. Here we present a new method that characterizes DOC on the basis of concentrations and ^{13}C of discrete DOC compounds, mainly short chain fatty acids, separated by liquid chromatography. The method is applied to a methanogenic leachate from the Trail Road municipal Landfill (TRL).

2. Site description and sampling

The TRL is owned and operated by the City of Ottawa and is located in the former municipality of Nepean, about 25 km west of the city centre (Fig. 1). Site operation

commenced at the Nepean landfill site, just beside the TRL site in the early 1960's, and continued at the Nepean landfill for approximately 20 years. The landfill was extended in 1980 into the TRL site. At the present time the TRL accepts annually about 2.47 x 10^5 tons of residential, industrial, commercial and institutional refuse, plus construction and demolition waste from the City of Ottawa. Landfill leachate is the main source of groundwater pollution in this area. The previous physical and chemical hydrogeological studies show there is some leachate influence on groundwater beneath older stages of the TRL site, which has no bottom liner or leachate collection system (City of Ottawa, 2001, 2002; Golder Associates Ltd., 2001).

Sampling was done at three locations within the TRL site; at the leachate pumping station (LPS), in monitoring well M32 and at the leachate pond located on top of the landfill (Fig. 1). Samples were collected in amber glass bottles and stored at 4°C to limit any continued microbial activity. Samples taken back to the lab were filtered using 0.45 μm cellulose nitrate membrane filters (25 mmϕ circles, Cat. No. 7184002, Whatman International Ltd, Maidston, Germany) and were analyzed immediately in the laboratory. Samples were diluted with deinonized water (DIW) to get a sufficient volume for the TCA. Then, the leachate's DIC and DOC concentration and the $\delta^{13}C$ values of DIC and DOC were measured by TCA and IRMS, respectively. Field measurements of Eh, pH, electrical conductivity, dissolved oxygen, total dissolved solids, and temperature were performed using a flow-through cell. Table 1 shows the measured field parameters, DIC/DOC concentrations and stable isotopic composition ($\delta^{13}C$, $\delta^{18}O$, $\delta^{2}H$) of the leachate.

3. Methodology

3.1. Compound specific isotope analysis of DOC

A high performance liquid chromatograph (HPLC), a total inorganic/organic carbon analyzer (TCA), and subsequent continuous-flow isotope ratio mass spectrometry (CF-IRMS) were used to separate DOC components and to measure the concentrations and ^{13}C-isotopic compositions of each component in standards and leachate samples. Since the main aim of this work was to recover discrete organic fractions, the use of carrier solvents containing organic or inorganic carbon was precluded. After several experiments with different mobile phase systems (e.g., H_2SO_4, H_3PO_4, NaH_2PO_4) under different HPLC parameter conditions, the best separation was achieved on a reverse C-18 column using a dilute H_3PO_4 mobile phase. Samples were eluted using 5 mM H_3PO_4 (pH 3) with a flow rate of 3 to 8 ml min^{-1}, a UV detector wave length setting of 230 nm, and a column temperature of 60°C (see Table 2). A 5 mM H_3PO_4 mobile phase was flushed through the column for 10 minutes at 8 ml min^{-1} to remove any organic materials retained on the column between samples. After each multi-sample injection session, the column was cleaned with acetonitrile and DIW. A fraction collector was used to collect dissolved organic compound fractions based on time and on peak detection. Finally, the concentration and isotopic composition of DOC components were measured from the collected fractions on the TCA interfaced with CF-IRMS.

Quantitative DOC and DIC measurements were made with an OI Instruments Model 1010 Total Carbon Analyzer where organic carbon was converted to CO_2 by a wet oxidation method (St-Jean, 2001). Phosphoric acid (5% H_3PO_4) and sodium persulfate ($Na_2S_2O_8$) were used to convert DIC and organic materials to CO_2 respectively. DIC was removed from the

sample by acidification with H_3PO_4, and then DOC was reacted separately with $Na_2S_2O_8$; the procedure could not be reversed due to the volatility of DIC which could have caused an isotopic shift in the residual aliquot. Likewise, volatile organic species (VOS) could not be analyzed quantitatively by the TCA method.

The purged CO_2 following sample oxidation was measured by a non-dispersive infrared detector (NDIR) and was subsequently sent to a gas scrubber followed by the ConFlow III interface for $\delta^{13}C$ IRMS analysis of DIC and DOC (Table 2 & Fig. 2) (St-Jean 2001 and 2003). All concentrations in this paper are expressed in $mg \cdot l^{-1}$ of carbon. Isotope results are expressed in standard δ-‰ notation against the international VPDB standard (Vienna PeeDee Belemnite).

The combination of HPLC for separation, TCA for quantifying the DOC components, and IRMS for measuring the $\delta^{13}C$ values is ideal for the sensitive determination of dissolved organic materials in leachate and leachate-polluted groundwater.

3.2. Verification with standard solutions

Initial standardization using some simple short-chain organic acid standards was preformed prior to analysis of samples (Marschner *et al.*, 2005). This initial experimentation was done in order to optimize the HPLC parameters and to test the integrity of fraction recovery both quantitatively and isotopically after separation by HPLC. The reproducibility of the retention times was determined by several successive injections of a standard "cocktail" solution (contains: formic acid (FA), acetic acid (AA), propionic acid (PA), and butyric acid (BA)). After optimization of the chromatographic parameters, the column resolved the four separate

and sharp peaks of the standard cocktail. Figure 3 shows a typical HPLC chromatogram and the attribute table of these standards.

Standard DOC components, classified by their column retention times, were collected by a programmable fraction collector. Windows in the Fraction Collector (FC) were determined by: 1) the HPLC's time event, 2) the attribute and peak table of the out coming chromatogram, 3) the flow rate of the mobile phase, and 4) the travel time of the mobile phase between the UV detector and the FC's tubes. Finally, after adding some DIW to obtain the required volume, the collected DOC fractions were run on the TCA/CF-IRMS system for concentration and $\delta^{13}C$ measurement.

The results of two different runs are summarized in Table 3. Sample blanks, the carrier itself, were analyzed before starting to collect fractions and concentration of each DOC component was corrected by subtracting the blank concentration. The reproducibility (accuracy) of the analytical results for $\delta^{13}C$ in the acetic acid (-36.6 ‰ VPDB), its fraction (–36.5/-37.0 ‰ VPDB) and for the concentration of acetic acid are satisfactory (1019 $mg \cdot l^{-1} \cong 1000\ mg \cdot l^{-1}$). However, as noted in Table 3, in order to ensure that we will not have any contributions from the adjacent peak of the other acids, the accuracy of acetic acid fraction for the assigned windows in the fraction collector is not exactly 1000 $mg \cdot l^{-1}$. Since the $\delta^{13}C$ values are the target, the tail of the chromatogram was not significant to the results and therefore not collected. Dilution of samples is another reason for this discrepancy. As shown in Table 3, the recovered concentration of the standard DOC components and their $\delta^{13}C$ in both runs are similar. This indicates the high precision of the measurements. The accuracy of the technique was discussed at the end of section 4 using carbon mass balance.

3.3.Identification and analysis of acetate in leachate

Acetic acid (CH_3COOH), a simple short-chain fatty acid, is a low molecular weight molecule that can be produced during the oxidation of complex organic molecules in anoxic environments such as landfill leachate by fermentive bacteria. Typically, municipal landfill leachate has a pH range of 4.5 – 9.0 (Christensen *et al.*, 2001). In this pH range, which for the landfill leachate exceeds the pKa of acetic acid, at 4.7, most acetic acid will be present as a deprotonated ion, acetate (CH_3COO^-). This form of acetic acid has a different retention time than the acetic acid in the HPLC system. CH_3COO^- was converted to CH_3COOH by acidification with concentrated (85%) phosphoric acid (H_3PO_4). The CH_3COOH peak was easily detected by the UV detector and can be identified on the HPLC chromatogram (Fig. 4). For the leachate and the standard acetic acid, all the HPLC parameters except for time events, were assigned the same values as applied for the standard DOC components (see Table 2). Acetic acid in the leachate sample was identified by retention time (Rt) on the basis of the Rt determined for commercial acetic acid (Fig. 4).

Quantification of leachate acetate concentration was done by running acidified leachate samples on the HPLC under the same conditions as were applied for a series of standards. The concentrations were determined by measuring the area under the curve (AUC) and comparing the results with the calibration curves. Verifications were performed by spiking leachate samples with the acetic acid standard solution (50% leachate and 50% 100 $mg \cdot l^{-1}$ acetic acid). The concentration of acetic acid in this spiked solution based on our calibration curve, was 70.9 $mg \cdot l^{-1}$ within 15% of calculated value of 61.3 $mg \cdot l^{-1}$ from the average of leachate (23.5 +/- 1.63 $mg \cdot l^{-1}$) and the standard solution (100 $mg \cdot l^{-1}$).

3.4.DOC and $\delta^{13}C$ of the leachate acetic acid based on peak retention times

As noted earlier, the HPLC parameters for the leachate, with the exception of the time events, were assigned the same values as were applied for the standard DOC components. In order to attain separate and sharp peaks for the leachate, the time event was changed to isochratic condition with 3 ml min^{-1} flow rate (Table 2). Figure 4 shows the acidified leachate HPLC chromatogram which contains two peaks. The first peak is the solute front, present due to acidifying the leachate by H_3PO_4. The second peak, with the peak retention time of 11.5 minutes, represents elution of the acetic acid. For acetic acid, the HPLC eluent was collected three times between 10.5 and 13.5 minutes of the run time. The collected fraction was diluted by a factor of 2 to bring up to volume for the TCA, then, run on the TCA/CF-IRMS system for the concentration and $\delta^{13}C$ measurements. The results are summarized in Table 3.

4. Results and Discussion

The aim of this work is the integration of compound-specific isotope and concentration data with other geochemical and isotope parameters to obtain insights to the origin and biogeochemical reactions taking place in the DOC of groundwater. Relevant data are summarized in Table 1. The DOC concentration of the TRL pumping station leachate varies between 300 $mg \cdot l^{-1}$, in August 2002, and 202 $mg \cdot l^{-1}$ in April 2003, reflecting the amount of dilution from precipitation during different seasons. This variation in seasonal contributions is demonstrated by the strong shift in stable isotopes of the leachate water ($\delta^{18}O$ and $\delta^{2}H$,

Table 1), which vary from –8.4‰ for $\delta^{18}O$ in August to –15.6‰ in April. The average DOC concentration and $\delta^{13}C$ value of the leachate are 249 $mg \cdot l^{-1}$ and -25 ‰ VPDB (Table 1).

By contrast, the samples from M32, a monitoring well completed at the base of the unlined Stage 1 landfill, has DOC concentrations varying between 4871 and 5125 $mg \cdot l^{-1}$ for two sampling dates, and little to no change in the stable isotope ratios of water. This site is clearly less affected by seasonal dilution and can be considered a leachate sampling site. The $\delta^{13}C$ of the DOC is also remarkable, in that it varies from –28.8‰ (November, 2003) to –17.5‰ (July, 2004) between the two seasons. This remarkable shift suggests a considerable turnover of DOC likely due to variable rates of biological activity.

In order to assess the retention time distribution of the DOC components in leachate, the fractions were collected by: 1) five-minute intervals, and 2) peak retention times using the programmable fraction collector. Data from the analysis of leachate from LPS and from M32 are summarized in Table 3. For the LPS data, the 5 to 10 minute fractions, which resulted in the highest peak in the HPLC chromatogram, had the highest DOC concentration of 86 $mg \cdot l^{-1}$, and a $\delta^{13}C$ value of -21.1 ‰ VPDB. The DOC concentrations of the subsequent 5-minute fractions were lower than that of 5 to 10 minute fractions. Each equal time interval had a specific amount of DOC and $\delta^{13}C$, which may be used for tracing leachate derived DOC. Peak separation was then attempted as a more effective means to identify and isotopically characterize the specific compounds.

The acetate peak in leachate was identified by injecting acidified leachate at pH 2.3 in the HPLC under optimized conditions. Note that at this pH, humic acids become largely insoluble, and so this component of the DOC was precipitated from solution prior to

injection into the HPLC. The concentration of acetate peak, determined by the area under the curve measurement, was 23 ±1 $mg \cdot l^{-1}$ for the LPS leachate, and by running the collected acetate fraction on the TCA/CF-IRMS system was 24 ±1 $mg \cdot l^{-1}$ (Table 3). The $\delta^{13}C$ value of acetate in the leachate is variable between collection sites and sample dates, ranging between –10.7‰ and –17.0‰ VPDB, which is significantly enriched in ^{13}C above the precursor DOC of the leachate (-24.7 ‰ VPDB). This difference of $\delta^{13}C$ values implies that microbial processes are involved in the degradation of the acetate fraction leading to the enrichment of ^{13}C in leachate's acetate. As acetate is a product of anaerobic degradation of vegetation (typically represented as carbohydrate, CH_2O), and subsequently used in methanogenic reactions, one can begin to trace the loosing of carbon in such systems.

The $\delta^{13}C$ values for M32 acetate and bulk DOC show a pattern of enrichment between the two sample dates that is reflected by other parameters as well. The $\delta^{13}C$ of DIC experiences an enrichment of close to 4‰ over this period. Similarly, the $\delta^{13}C$ of methane (–50.8‰) is highly enriched in the later sample as compared with biogenic methane from other landfills, which is generally in the range of <–60‰ (Clark and Fritz, 1997). Enrichment trends in acetate, bulk DOC and other carbon components are evidence of substrate consumption, which results in a Rayleigh type enrichment in ^{13}C. While preliminary, these data reflect a series of biogeochemical reactions that vary in rate through time.

In order to assess the efficiency of HPLC fraction collection and preservation of isotope signals during separations, experimental data were compared with theoretical values in a carbon mass balance. First, the mass balance was performed based on the following equation

using $\delta^{13}C$ and the recovered carbon concentration of each of the four standard DOC component fractions (FA, AA, PA, and BA) and their mixture:

$$\delta^{13}C_{Cocktail} \times C_{Cocktail} = (\delta^{13}C_{FA} \times C_{FA}) + (\delta^{13}C_{AA} \times C_{AA}) + (\delta^{13}C_{PA} \times C_{PA}) + (\delta^{13}C_{BA} \times C_{BA})$$

Where, $\delta^{13}C$ is the per mil (‰) value of each component and C is the carbon concentration.

For calculating the mass balance of the leachate acetate, the same equation was applied for the M32 leachate sample. Relevant data are summarized in Table 4. Calculated errors are approximately 7% and 6% for the standards and leachate data, respectively (Table 4). Comparison of the recovered mass of carbon and $\delta^{13}C$ with initial data also shows the high efficiency of HPLC fraction collection. Consequently, the accuracy of chromatographically-separated DOC compounds and the measured concentration and $\delta^{13}C$ values of these DOC fractions using a TCA interfaced with IRMS is high and this technique can be used to: 1) distinguish landfill-derived DOC, 2) identify metabolic pathways, and 3) identify biogeochemical reactions in leachate contaminated aquifers.

5. Conclusion

HPLC, the TCA, and the IRMS are important analytical instruments for characterizing dissolved organic matter in groundwater. We show that they can be interfaced sequentially in series for the quantitative and ^{13}C-isotopic analyses of discrete organic compounds in naturally-occurring waters. This new methodology generates reproducible (precise) results, which prove that chromatographically-separated organic fractions can be used for compound-specific isotopic analysis (CSIA). Such analyses complement routine isotopic

characterization of DOC components using methodological separations such as on acid and base solubilities and hydrophobicity. Further, it provides access to low concentration samples using reasonable sample sizes.

Optimal setting for the HPLC parameters and the reproducibility of the peak retention times were determined by several successive injections of a standard solution containing formic acid, acetic acid, propionic acid, and butyric acid (1000 $mg \cdot l^{-1}$ each). Standard DOC components, acetate peak, and 5 minute time intervals of the TRL leachate chromatogram, classified by time and peak retention times, were collected with a programmable fraction collector and later run on the TCA/CF-IRMS system for concentration and measurement of $\delta^{13}C$. Each peak in the leachate chromatogram is related to a specific DOC compound (e.g., acetic acid). While time interval fractions can be used, peak separation and collection is the preferable method for quantification of DOC components and their subsequent isotope analysis.

The significant difference of $\delta^{13}C$ values of the leachate's acetate (-10.7 to -16.9 ‰ VPDB) versus $\delta^{13}C$ value of the leachate (-24.7 ‰ VPDB) provides insights into cycling of carbon and biogeochemical reactions of DOC in this preliminary case study of a landfill leachate. Further applications will include other groundwaters and waste waters contaminated by elevated levels of DOC, as well as the analysis of natural DOC in methanogenic and other groundwaters.

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Table 1: Field parameters, DIC, DOC concentrations and stable isotope values of Trail Road Landfill (TRL) leachate. The sampling locations are shown on Figure 1 (^{13}C isotope values in ‰ VPDB and both ^{18}O and ^{2}H isotope values in ‰VSMOW).

Sample Location	Sample #	Date of Sampling	Field Measurements					
			T(°C)	pH	Eh (mv)	EC (µm/cm)	TDS(mg/l)	DO (mg/l)
Leachate Pumping Station (LPS)	L1	6-Nov-03	15.4	6.69	169	5120		3.03
		11-Apr-03	17.6	6.77	306	6090	3080	
Stage 4 Leachate Pond	L2	11-Apr-03	10.3	6.07	376	4786	2630	
			Lab. Measurements					
			DIC (mgl^{-1})	DOC (mgl^{-1})	$\delta^{13}C_{DOC}$ (‰)	$\delta^{13}C_{DIC}$ (‰)	$\delta^{18}O$ (‰)	$\delta^{2}H$ (‰)
Leachate Pumping Station (LPS)	L1	6-Nov-03	509	245	-24.6	9.9	-12.4	-73.2
		11-Apr-03	832	202	-24.4		-15.4	-92.4
		10-Aug-02	647	300	-25.0	15.4	-8.4	-42.3
Stage 4 Leachate Pond	L2	11-Apr-03	42	10	-24.8		-15.6	-116.5
Monitoring well on landfill	M32	6-Nov-03	200	4871	-28.8	7.0	-9.8	-68.4
		12-Jul-04	339	5125	-17.5	10.7	-10.0	-70.4

Note: A large percentage of Stage 4's pond was precipitation, even snow and ice was seen in pond

Table 2: HPLC, TCA and Delta^{Plus} IRMS operating conditions.

HPLC	**TCA**
Column: C18 column 25 * 0.94 cm (Preparative column) Pre-column: Cartridge precolumn Mobile phase: 5 mM H_3PO_4 pH 3.00 UV Wave length: 230 nm Sample loop: 1.00 ml Injection volume: 1 ml Temperature: 60 °C Solvent flow rate: Gradient and Isocratic time events • Gradient program for standards: 0:00 – 19:00 min 3 ml min^{-1} 19:00 – 20:00 min transition 3 to 8 ml min^{-1} 20:00 – 26:00 min 8 ml min^{-1} 26:00 – 27:00 min transition 8 to 3 ml min^{-1} 27:00 – 40:00 min 3 ml min^{-1} • Isocratic program for leachate samples and acetic acid: 0.00 – 32:00 min 2 ml min^{-1} Fractions collector procedures: 1. Set HPLC optimized conditions 2. Set fraction windows in FC 3. Prepare samples and standards 4. Prepare suitable time events, method and sequence 5. Run Powerstreem 6. Inject samples 7. Run FC 8. Load injected samples in HPLC column 9. Run UV detector of HPLC	Model: 1010 TCA TIC reagent: 300 µl 5% H_3PO_4 • Reaction time: 2:00 min • Detection time: 1:00 min • Reaction temperature: 90°C TOC reagent: 1300 l of 100 gl^{-1} $Na_2S_2O_8$ • Reaction time: 3:00 min • Detection time: 1:30 min • Reaction temperature: 97°C Rinse: 25 ml DIW Rinse per sample: 2 Rinse temperature: 85 °C Standby temperature: 85 °C Sample loop (calibrated): 1.00 ml Carrier gas: N_2 & He Calibration standards: • 0 ppmC DIW (H_2O) • 5 ppmC Citric acid ($C_6H_8O_7CH_2O$) • 10 ppmC KHP • 20 ppmC Sucrose ($C_{12}H_{22}O_{11}$) **Delta^{Plus} IRMS** Model: ConFlow interface: III Carrier gas: He Flow rate: 110 ml min^{-1}

Table 3: DOC concentrations and $\delta^{13}C$ values of standards and leachate fractions based on peak retention times and 5 minute time intervals in the chromatogram.

Sample ID		HPLC				TCA and IRMS	
		Fraction Collector window (min)	Flow rate (ml min^{-1})	Number of injections	Total collected volume (ml)	Recovered Carbon (mgl^{-1})	$d^{13}C_{VPDB}$ (‰)
Standards							
Acetic acid 1000 mgl^{-1}		10:30 – 13:30	2	2	12	1019	-36.6
Cocktail first run	Formic acid fraction	05:00 – 07:00	3	1	6	1014	-19.0
	Acetic acid fraction	07:00 – 09:00	3	1	6	822	-36.5
	Propionic acid fraction	14:30 – 18:30	3	1	12	932	-27.9
	Butyric acid fraction	29:00 – 40:00	3	1	33	894	-28.0
Cocktail second run	Formic acid fraction	05:00 – 07:00	3	1	6	938	-18.8
	Acetic acid fraction	07:00 – 09:00	3	1	6	855	-37.0
	Propionic acid fraction	14:30 – 18:30	3	1	12	884	-28.9
	Butyric acid fraction	29:00 – 40:00	3	1	33	897	-26.4
Cocktail (containing FA, AA, PA and BA in a concentration of 1000 mgl^{-1})					# 1	3859	-27.9
					# 2	3709	-28.2
					# 3	3960	-28.3
Leachate samples							
Acetic acid in LPS #1		10:30 – 13:30	2	3	18	24	-16.9
Acetic acid in LPS #2		10:30 – 13:30	2	3	18	23	-17.0
Acetic acid in LPS #3		10:30 – 13:30	2	3	18	25	-16.8
Acetic acid in LPS + AA 1000 mgl^{-1}		10:30 – 13:30	2	1	6	542	-36.4
Acetic acid in M32* #1		10:30 – 14:00	2	1	7	1666	-10.7
Acetic acid in M32 #2		10:30 – 14:00	2	1	7	1755	-10.8
Propionic acid in M32 #1		20:30 – 29:30	2	1	18	961	-19.3
Propionic acid in M32 #2		20:30 – 29:30	2	1	18	1313	-20.6
Acetic acid + Propionic acid in M32			2	1	25	2518	-14.8
5 minutes time interval fractions in LPS chromatogram							
Fraction # 1		00:00 – 05:00	na	na	na	na	na
Fraction # 2		05:00 – 10:00	2	1	10	86	-21.1
Fraction # 3		10:00 – 15:00	2	1	10	61	-25.1
Fraction # 4		15:00 – 20:00	2	1	10	45	-25.4
Fraction # 5		20:00 – 25:00	2	1	10	39	-24.7

* Samples taken from M32 monitoring well represnt leachate

Table 4: Mass balance data for the standards and leachate fractions (^{13}C isotope values in ‰VPDB).

Parameter		Standards					Leachate in M32			
		Formic A	Acetic A	Propionic A	Butyric A	Cocktail	Acetic A Peak #1	Unknown Peak #2	Propionic A Peak #3	Whole chromatogram (Peak # 1,2,3)
Initial Carbon	Mass (mg)	1.00	1.00	1.00	1.00	4.00				
	$\delta^{13}C_{VPDB}$	-18.7	-37.6	-28.7	-27.5	-27.9				
Recovered Carbon	Mass (mg)	0.970	0.832	0.902	0.890	3.859	1.665	0.060	0.96	2.59
	$\delta^{13}C_{VPDB}$	-18.9	-36.8	-28.4	-27.2	-27.9	-10.7	-18.8	-19.3	-15.4
$\delta^{13}C*M_C$		-18.17	-31.27	-25.92	-24.46	-107.73	-17.80	-1.12	-18.51	-39.91
Sum		-99.82					-37.43			
Error (%)		7.34					6.22			

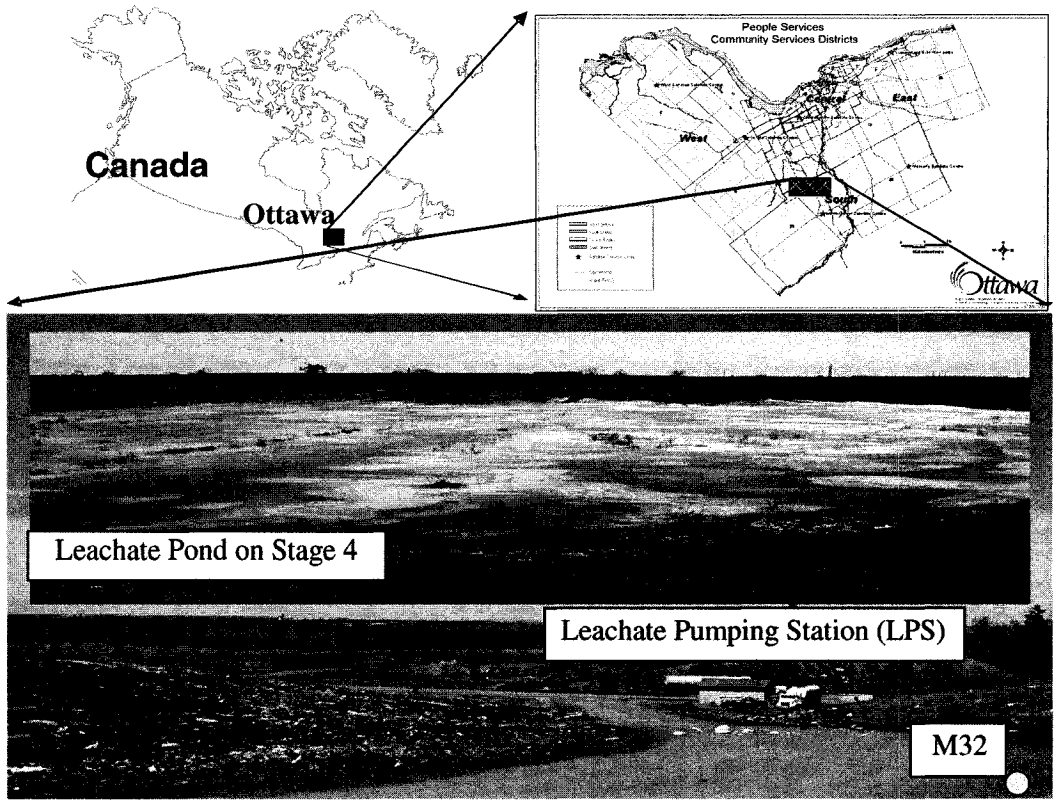


Figure 1: Trail Road Landfill (TRL) site, the leachate pumping station and the leachate pond of the TRL Site.

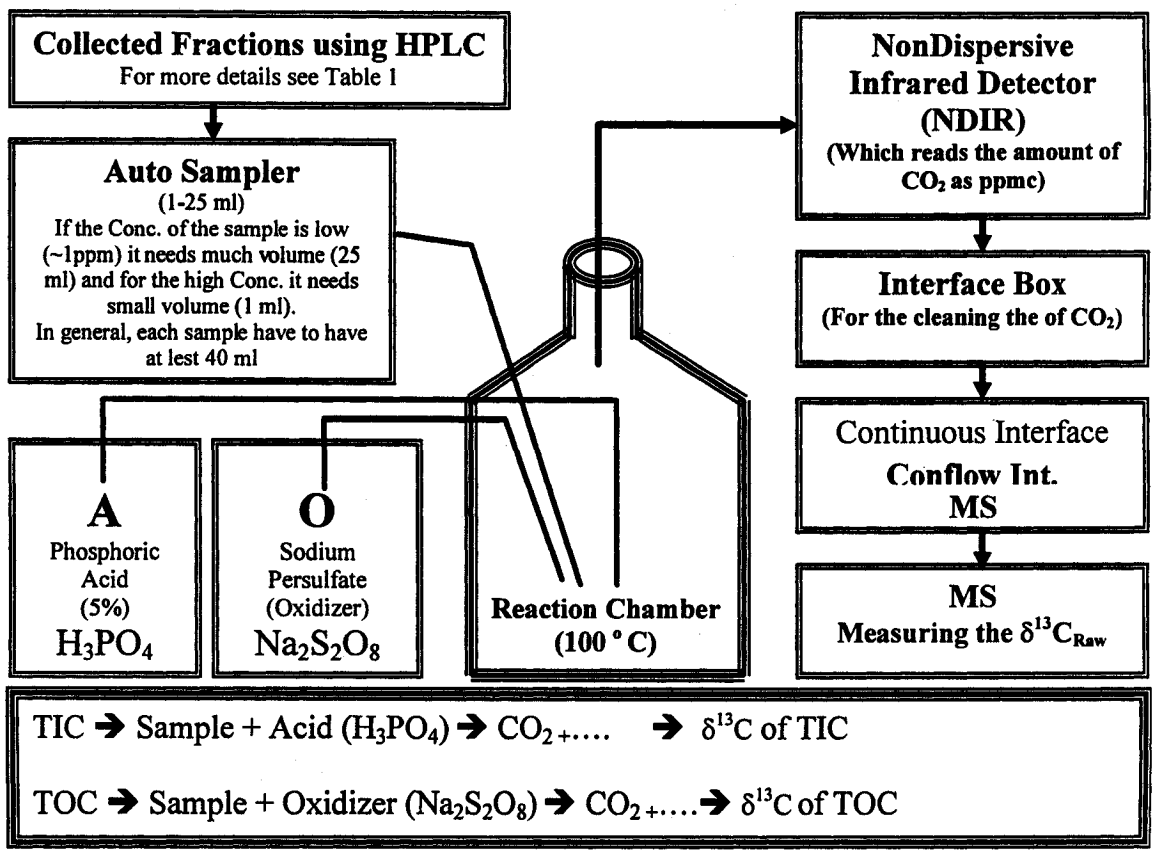
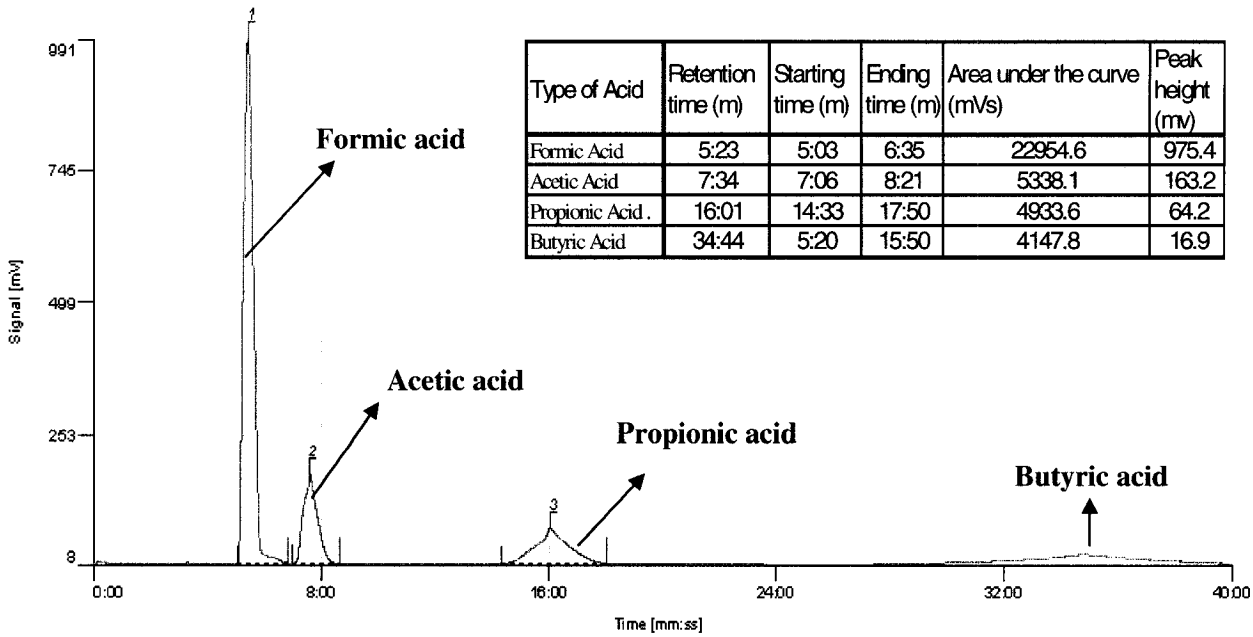


Figure 2: Schematic illustration of TCA and CF-IRMS interface.



Type of Acid	Retention time (m)	Starting time (m)	Ending time (m)	Area under the curve (mVs)	Peak height (mv)
Formic Acid	5:23	5:03	6:35	22954.6	975.4
Acetic Acid	7:34	7:06	8:21	5338.1	163.2
Propionic Acid.	16:01	14:33	17:50	4933.6	64.2
Butyric Acid	34:44	5:20	15:50	4147.8	16.9

Figure 3: A typical HPLC chromatogram and its attribute table of a standard solution containing formic acid, acetic acid, propionic acid and butyric acid in a concentration of 1000 mgl^{-1} each. The experimental parameters are shown in Table 2.

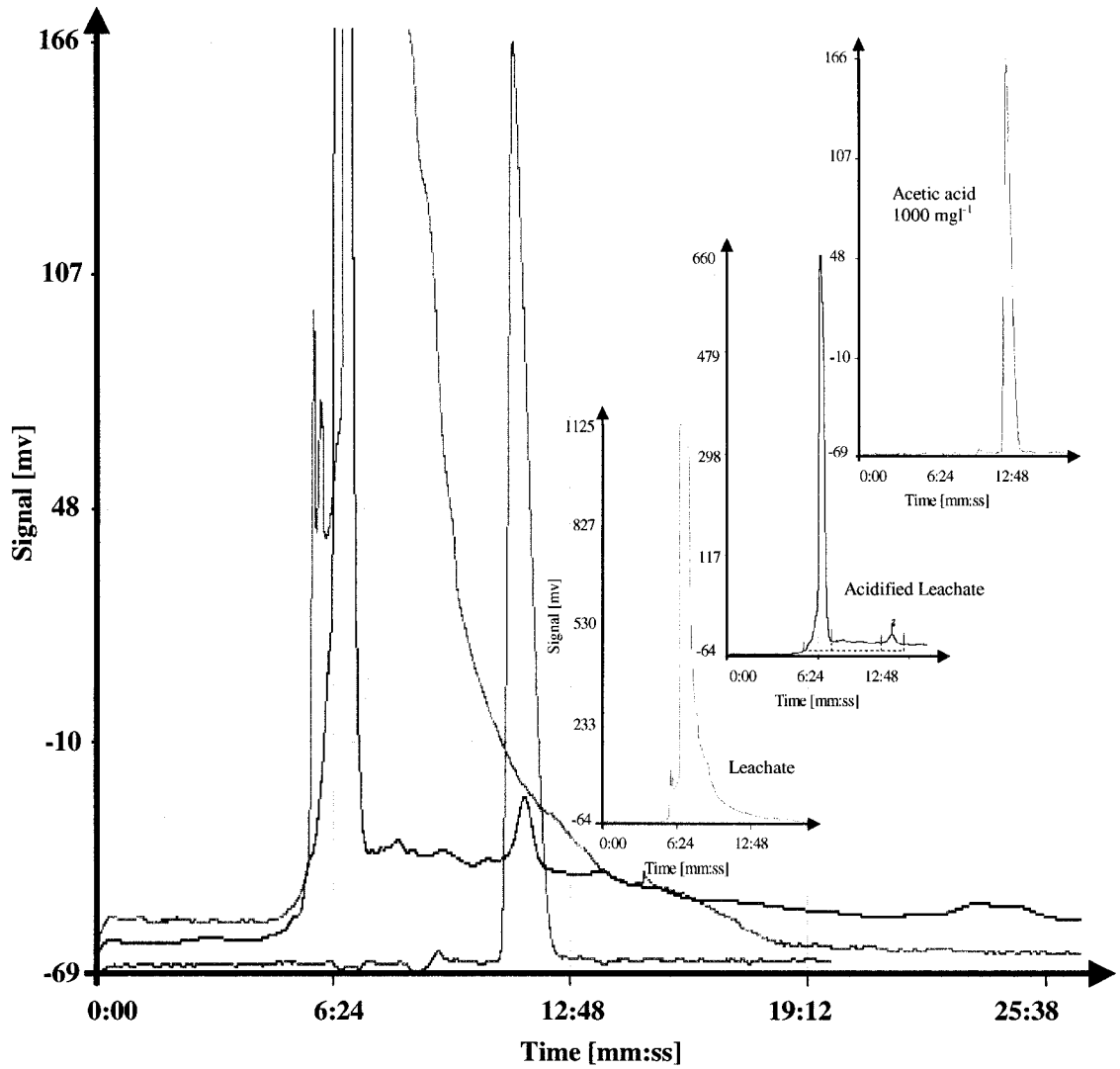


Figure 4: The HPLC chromatograms of leachate, acidified leachate and 1000 mgl^{-1} acetic acid. The acetate peak appears after acidifying the leachate using concentrated (85%) phosphoric acid. Four drops of H_3PO_4 added to 20 ml leachate sample reduces the pH of the leachate to 2.2.

Degradation Pathways of Dissolved Carbon in Landfill Leachate traced with compound-specific ^{13}C analysis of DOC

Abstract

The composition of carbon pools and quantity of landfill leachate, which considerably impact the rate of carbon lost via methane and leachate production, are subject to seasonal variations and are greatly influenced by the length of time that has elapsed since waste placement. In this study, the carbon geochemistry of different carbon pools (DIC, DOC, CH_4, CH_3COOH, and humic substances (HS)), environmental stable isotopes ($\delta^{13}C$, $\delta^{18}O$, and $\delta^{2}H$) and compound specific isotope analysis (CSIA) of leachate DOC fractions are used to characterize the carbon composition of leachate from the Trail Road Landfill (TRL) site receiving municipal solid waste (MSW). The objectives were to identify characteristic tracers for recognizing potential of the leachate impact on the surrounding groundwater; to isolate and characterize (concentrations and $\delta^{13}C$ values of) leachate DOC fractions to observe the isotopic evolution of these fractions during the degradation of organic carbon; and to determine the methanogenesis pathways.

A variety of analytical techniques have been applied to measure leachate parameters and to interpret the leachate at the TRL site: ion chromatography (IC), inductively coupled plasma atomic emission spectroscopy (ICP-AES), gas chromatography (GC), DAX-8 resin adsorption chromatography, elemental analyser (EA), high performance liquid chromatography (HPLC), total carbon analyzer (TCA), isotope ratio mass spectrometry (IRMS) and NMR (nuclear magnetic resonance).

At TRL, waste materials contain more than 50% paper and wood waste, the major contributors to the cellulose and hemicellulose concentrations. These organics are biodegraded to dissolved organic maters (DOM) and eventually to CH_4 and CO_2. Our isotope analysis on leachate, landfill gases and various leachate DOC components indicate that: 1) microbial processes are more advanced in the degradation of DOM in the leachate collected from the older parts of the landfill site (M32), which is more than 28 years old; 2) simple fatty acids (e.g. acetic, propionic, etc.) accumulate in the leachate

from older part of the landfill; 3) the acetate fermentation CH_4 production pathway dominants in older parts of the landfill. While, in the younger part of the landfill (LPS), CO_2 reduction pathway ($\alpha^{13}C_{CO2\text{-}CH4}$=1.06) is the more favoured CH_4 production pathway; 4) fulvic acid (FA) is the main fraction of leachate DOC and the enriched ^{13}C value of FA and of LMW DOC as well as of the bulk DOC with increasing age of the landfill is due to more advanced degradation in the older part of the landfill.

A huge shift in humic/fulvic acid (HA/FA) ratios between young and old leachate (0.18 and 0.05 for LPS and M32, respectively) is because of high concentrations of FA (4482 mgl^{-1}, 73% of the total DOC) and low concentrations of HA (21 mgl^{-1}, 0.3% of the total DOC) in old M32 leachate. Perhaps the lower concentration of aromatic carbon group, in M32, estimated from ^{13}C-NMR spectra of HA and particulate organic carbon (POC) is due to degradation of HA under anaerobic conditions and transformation of aromatic carbon to LMW-DOC. The depleted $\delta^{13}C_{HA}$ (-28.1‰) and enriched $^{13}C_{LMW\text{-}DOC}$ (-8.0‰), in the older leachate from M32, can be explained by this disproportion reaction in which the ^{13}C would go preferentially to the oxidized molecules.

Keywords: Trail Road Landfill (TRL), leachate, carbon pools (DIC, DOC and CH_4), environmental stable isotopes ($\delta^{13}C$, $\delta^{2}H$, and $\delta^{18}O$), acetate and propionate, humic substances (HS), methane production

1. Introduction

Landfill leachate is a significant source of groundwater contamination. It is created as rainfall percolating through the waste supports a range of biodegradation and leaching reactions resulting in dissolved metals; soluble biodegradation products of complex organic molecules; along with fines and colloids material (Reinhart and Grosh, 1998). Kjeldsen et al. (2002), who reviewed the present and long-term composition of municipal solid waste (MSW) landfill leachate, and Christensen et al. (2001) suggested that pollutant transformation from the waste material to the percolating water is the results of a complex combination of physical, chemical, and biologically mediated processes within the waste material.

Leachate quality is highly variable and its composition varies significantly among landfills. As inferred from other studies (Reinhart and Grosh, 1998; Rooker, 2000; Christensen et al., 2001; Kjeldsen et al., 2002), leachate quality depends on: 1) waste composition and depth of waste, 2) waste age and the degree of waste stabilization, 3) the availability of moisture and oxygen, 4) landfilling technology (landfill design and operation), 5) codisposal with sewage sludge and MSW incinerator ash, 6) climate, 7) site hydrology and water infiltration, 8) and leachate sampling methods and sample handling routines.

Dissolved organic carbon (DOC) is one of the major groups of pollutants in MSW landfill leachate (Christensen et al., 2001). DOC in leachate is a bulk parameter covering a variety of organic degradation products and it contains a mixture of labile dissolved organic constituents, the composition of which is very dependent on landfill refuse of the respective

site (Baedecker and Back, 1979a, 1979b; Christensen et al., 1998; Hornibrook et al., 2000; Christensen et al., 2001). To date, a huge range of different types of organic compounds have been identified in landfill leachates (Kjeldsen et al., 2002; Christensen et al., 2001; Reinhart and Grosh, 1998).

DOC in landfill leachate ranges from small volatile fatty acids (e.g. acetic, propionic, and butyric) produced during the decomposition of lipids, proteins, and carbohydrates (Albaiges et al., 1986; Schultz and Kjeldsen, 1986) to refractory humic substances (HS) such as fulvic-like and humic-like compounds. Aromatic hydrocarbons (e.g. various xylenes, toluene, benzene and ethylbenzene) from petroleum products such as gasoline and fuel oils which are common landfill contaminants (Schultz and Kjeldsen, 1986) and halogenated hydrocarbons (e.g. tetrachloroethylene, trichloroethylene, chlorinated aliphatic compounds, phenols, pesticides, phthalates etc.) have also been found in leachate (Christensen et al., 2001; Kjeldsen et al. 2002). However, we are not interested in these xenobiotic organic compounds (XOCs) in this paper, which focuses on the more ubiquitous DOC, which can affect leachate composition and act as substrate for the microbial redox processes. Here we try to characterize the composition of DOC, including volatile fatty acids (acetic and propionic acids) and refractory humic substances (HS) such as fulvic acid and humic acid compounds.

HS is one of the important fractions of the DOC content of the landfill leachate (Kang et al., 2002; Kjeldsen et al., 2002; Christensen et al., 2001; Christensen et al., 1998). In general, HS can be either derived from any organic material, including plant and animal debris, microfauna, and biowastes (Kang et al., 2002) or formed from polymerization of reactive monomers into high molecular weight (HMW) polymers (Stevenson 1985; Aiken et al.,

1985; Thurman, 1985). Tipping (2002) mentioned that the humification can also be governed by a collection of undirected chemical and microbially mediated reactions.

HS are composed of C, O, H, N and S in varying proportions and they are defined as a category of naturally occurring and biogenic organic substances which can be characterized as HMW, refractory, heterogeneous, and as being light yellow to black in color (Stevenson, 1985). In terms of their solubility, HS can be divided into three major fractions; humin, humic acid (HA), and fulvic acid (FA). Humin is not soluble in water at any pH and HA is not soluble in water under acidic conditions and precipitates from solution at pH less than 2, while FA is the fraction of HS that is soluble in water under all pH values. Low molecular weight (LMW) compounds (hydrophilic fraction) make up the rest of DOC which includes cellulose, protein, and organic acids such as carboxylic, acetic, amino acids (Stevenson, 1985). Because of differences in vegetation, decompositional history, climate etc., the properties of HA and FA vary from one location to another (Stevenson, 1994).

Ubiquitous in terrestrial and aquatic environments and heterogeneous in terms of elemental composition, chemical functionality, and molecular size distribution, HS significantly affects the behaviour of some pollutants in aquatic environments. Although HS are resistant to microbial degradation and are generally considered recalcitrant under anaerobic conditions (Kjeldsen et al., 2002; Drever, 1997), recent studies (Lovley et al., 1996 and 1998; Scott et al., 1998) demonstrated that HS can be dynamically involved in the transfer of electrons in anaerobic environments and can act as electron acceptors to support anaerobic oxidation of organic compounds.

Most studies conducted on DOC fractions of landfill leachate use isolation methods to investigate temporal and spatial variations (Kang et al., 2002; Christensen et al., 1998; Casitagnoil et al., 1990; Artoila-Fortuny and Fuller, 1982). A few studies have been conducted on the chemical structure of leachate DOC fractions (e.g. Stevenson, 1994; Gobbels and Puttmann, 1997) and on the characterization of the acid-precipitated and acid-soluble fractions of landfill leachate DOC (Nanny and Ratasuk, 2002). Less is known regarding the isotopic composition of these fractions and the evolution of ^{13}C isotope over degradation process (e.g., Gron et al.,1996).

New analytical methods now allow routine isotopic analysis of bulk DOC and the lighter weight components of DOC (Marschner et al., 2005; Mohammadzadeh et al., 2005a; St-Jean 2003). This additional characterization of major and minor carbon pools provides additional insight into the geochemical pathways during methane production and DIC evolution in the landfill. This approach is applied here for leachate from the Trail Road Landfill (TRL) site. The objective of this research is to isolate and characterize the concentrations and the $\delta^{13}C$ values of the principal DOC fractions of leachate, and to observe the isotopic evolution of these fractions during the degradation of organic carbon. This will determine the methanogenic pathways involved in DOC degradation and quantify methane production in the landfill. This characterization of DOC can then be used to identify isotope signatures that provide evidence of leachate in marginally impacted groundwater.

2. TRL site description and sampling locations

The TRL is owned and operated by the City of Ottawa and is located approximately 25 km west of the city (Figure 1). The landfill has capacity of 8.8 million cubic meters and landfilling has been undertaken in four stages with a footprint of approximately 65 hectares (ha) situated in the 150 ha of the landfill property. The landfill area is surrounded by light industry and farmland. It is situated on a northwest-southeast ridge of glacio-fluvial sands and gravels. This ridge extends out to the Jock River, and is locally confined in places by marine clay. The TRL and the adjacent old Nepean landfill (NL) sites are located on the east and the west side of this ridge, respectively (Golder Associates Ltd., 2001, 2002).

Figure 2 shows the site operation of the TRL and the NL site, which commenced at the NL site in the early 1960's, and continued at the NL for approximately 20 years. Landfilling commenced at the TRL site in 1980 when the site was operated by the former Regional Municipality of Ottawa-Carleton (RMOC). The waste generation rates are approximately 0.34 tonnes/capita/annum (t/c/a) for residential, 0.28 t/c/a for industrial, commercial and institutional (IC&I), and 0.16 t/c/a construction and demolition (C&D) (City of Ottawa, 2002).

The TRL currently receives municipal solid waste from throughout the City of Ottawa, annually about 3.0×10^5 tonnes of residential, IC&I and C&D wastes. This tonnage includes all material received at the site (i.e., recyclable, compost and fill material). For instance, out of 3.0×10^5 tonnes of waste materials received at the site in 2005, about 1.7×10^5 tonnes were landfilled. The balance included materials that were composted (residential and

commercial leaf and yard waste), stockpiled (including diverted waste such as appliances and tires) for re-use, recycling or used on-site as daily cover (fill). Table 1 summarized the results of waste characterization of three samples obtained from three locations from stages 1 and 2, representative of the upper, middle and lower strata of the refuse (City of Ottawa, 2002). This waste was placed between 1980 and 1990 when not much waste recycled. Paper, wood and plastic, the main carbon-bearing materials in the landfill, formed more than 50% of the waste materials. It is assumed that the waste composition in stages 1 and 2 is different than the waste composition in stages 3 and 4.

The TRL is divided into stages 1 through 4. Stages 1 and 2 of the TRL (26 ha and ~12, respectively) and NL were covered with a low permeability geomembrane consisting of 40 millimeter thick very low density polyethylene (VLDPE) geomembrane in 1988, 1991, 1993 respectively. These parts of the landfill were designed for natural attenuation with no bottom liners and no leachate collection systems. The last two stages of the TRL, Stages 3 and 4 (17.4 ha and 12.4 ha, respectively), are both equipped with a composite bottom liner of clay (60 cm) and HDPE geomembrane liner (80 mil) with an overlying geotextile fabric. These stages are also equipped with a leachate recirculation, evacuation and collection system. Stage 3 was covered with an interim cover in 2003. Stage 4 is the only stage of the landfill that is currently active (Figure 2). Figure 3 illustrates the layout of the landfill, showing a cross section of the low permeable cover with the leachate and gas collection systems (City of Ottawa, 2002; Dillon Consulting Limited, 2005 and 2006).

Sampling focused on the two principal areas – the lined Stages 3 and 4 which have a leachate collection system installed, and the unlined Stages 1 and 2. For the lined sites, leachate

samples were taken from the leachate pumping station (LPS), from inclined leachate pipes (LP) installed along the north edge of Stages 3 and 4 (referred to as manholes in related reports). Leachate from the unlined Stages 1 and 2 was sampled from M32, the only monitoring well where leachate from these unlined stages was available (Figure 1).

The LPS integrates leachate generated throughout Stages 3 and 4 while samples taken from the LP are more characteristics for local sources (Figure 1). LPS leachate was collected from Stages 3 and 4 by means of a gravity drainage system beneath the waste material and lead to a collector header that feeds the LPS. After pumping the leachate to a collector manhole, a portion of the leachate from the collector manhole is recirculated to Stage 4 of the TRL and the remainder is trucked to the Robert O. Pickard Environmental Centre (ROPEC) for treatment (Dillon Consulting Ltd., 2005). Although M32 is a local leachate source, it is an important on-site monitoring well that captures pure undiluted leachate at the base of the unlined landfill of Stage 1.

Landfill gas (LFG) was collected from Stages 1, 2 and 3 and at the NL through vertical extraction wells and collector pipes (Figure 3) (Golder Associates Ltd., 2003; Dillon Consulting Ltd., 2004, 2005 & 2006). These gases are directed to a central collection building north of Stage 3 where the gas is flared (Figure 1). A study conducted by Earth Tech (2004) indicates that gases at the TRL site (from Stages 1, 2 and 3) are migrating to the south of these stages, as measured in gas-monitoring wells installed along the south border of the TRL site in 2003 through 2005. Data show gases to be an average of 39% CH_4 by volume within the monitoring wells located at south border of Stages 2 and 3 in 2005 (Figure 4). Installation in 2005 of an air injection system (12 air injection wells, approximately 100

m apart) along the south side of Stages 2 and 3 affected the measured concentrations of the landfill gases (Figure 5).

As Figure 4 shows, the CH_4 concentrations in the period of May-July 2005 (before installation of an air injection system) are higher than that of the period of August-December 2005 (after installation of an air injection system). Table 2 tabulates the measured landfill gases (CH_4, CO_2 and O_2) from three monitoring wells located at south border of Stages 2 and 3, for the period of May to December in 2005. The average of 23 measurements of these gases in October 2005, within monitoring wells located on top of Stage 2, is presented. The concentrations of CH_4 and CO_2 at these monitoring wells in 2005, before operation of air injection system, were 39% and 30% by volume, respectively.

3. Sampling, field measurements and analytical techniques

3.1.Field measurements and sampling

The leachate sampling program was restricted to LPS, LP and are available monitoring well (M32) on top of the landfill (Figure 1). Leachate samples from LPS (41 samples) were taken weekly in 2005. Leachate samples from LP (9 samples) and M32 (3 samples) were taken in 2004 and 2005. Two samples were also taken from the LPS and M32 in 2003. Gas measurements were conducted at the gas flare station (GFS) and available gas monitoring wells by Dillon Consulting Ltd. on and around the TRL site in 2004 through 2005 (Figure 1).

Electromotive potential (Eh), pH, electrical conductivity (EC), dissolved oxygen (DO), and temperature (T) were measured in the field using appropriate meters and an in-line flow-through cell to preclude uptake of atmospheric O_2 during measurement. Total inorganic/organic carbon (DIC and DOC) samples were collected using 40 ml amber glass bottles with septum caps. For inorganic anions and cations and the δ^2H and $\delta^{18}O$ of the water, 30 ml samples were collected for each analysis using plastic bottles. About 0.1 ml ultra pure nitric acid ($HNO3^-$), as preservative, was added to the cations bottle. Gas samples were collected in 125ml Wheaton glass bottles with headspace to measure the methane concentration and isotope values in methane and CO_2. For the separation and measurement of humic substances (HA, FA, LMW DOC and acetate fractions), 4L samples were collected in amber glass bottles from the LPS, from LP and M32.

Since DOC concentrations may change during storage of the samples due to bacterial activity, all samples were immediately transported to the laboratory for processing. Samples were filtered with 0.45 μm membranes to remove bacteria, suspended solids and particulate carbon, stored at 4°C to stabilize the samples prior to analysis and to limit any continued microbial activity and were analyzed within 2 weeks. 4L samples for analysis of HS were filtered using 0.7 μm glass-microfiber filters (Whatman cat No. 1825047) and acidified to pH lower than 2 with concentrated HCl (% 38).

3.2. General hydrochemical parameters

Ion chromatography (IC model DIONEX - DX – 100) and Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES model VISTA-PRO, CCD Simultaneous ICP-

OES) were used to measure the samples' inorganic anions and cation concentrations. Prior to cation analysis, the samples were filtered by means of 0.45 μm cellulose nitrate membrane filters (25 mmϕ circles, Cat. No. 7184002, Whatman International Ltd, Maidston, Germany) and were acidified using 0.1 ml ultra pure HNO_3^-.

3.3.Isotope measurements (^2H and ^{18}O) of water

One ml of each water sample was pipetted into 12 ml glass Exetainers with septum caps to determine both $\delta^{18}O$ and δ^2H of the water using the Gasbench and a DeltaPlus XP isotope ratio mass spectrometer (ThermoFinnigan, Germany). To measure the $\delta^{18}O$ of the water, samples and the internal standards both were flushed with a gas mixture of 2% CO_2 in helium using the Gasbench. Exetainer vials were left for a minimum of 18 hours to equilibrate the CO_2 of the headspace with oxygen in the water at 25°C. For the deuterium of water, Pt catalyst rods were added to the samples and internal standards in the Exetainer vials before being flushed with a gas mixture of 2% H_2 in helium using the Gasbench. Exetainers were left for a minimum of 1.5 hours to equilibrate H_2 of the headspace with the dissolved H_2 in the water at 25°C. Analytical precision for the $\delta^{18}O$ and the δ^2H of the water were ±0.15 and ±2.0 ‰, respectively. Since samples were suspected to contain sulphur (S), which could have affected the results, copper wool was added to samples and refrigerated for a few days before analysing for ^{18}O and ^2H.

3.4.DAX-8 resin column separation for humic substances

Humic substances were isolated from leachate according to a procedure modified from the method described by Thurman (1981) and Hendry and Wassenaar, (2005). The isolation of

HS was done by acid precipitation of humic acids (HA), the isolation of FA on DAX-8 and characterizing the LMW DOC (hydrophilic compounds) by HPLC. All filtered and acidified 4L samples were filtered again with 0.7 μm glass-microfiber filters to separate HA. The fulvic acids (FA) of the samples were separated from the LMW DOC fraction using Supelite DAX-8 adsorbsent resin (Supleco XAD-8-20278, specific surface area: 160 A, particle size: 40-60 mesh, pore volume: 0.79 mL/g, density: 1.09 g/ml for true wet and 1.23 g/ml for skeletal; purchased from Sigma-Aldrich Co, 1998) via passing through the chromatography column by gravity flow, modified from the method of Thurman and Malcolm (1981).

During resin preparation, the DAX resin was immersed in 50°C water for 24 hours before use. The resin slurry was then poured slowly into the column and backwashed for approximately 30 minutes to remove air bubbles and remove resin fines. To adsorb the FA to the resin, samples were loaded with a flow rate of 5 bed volumes per hour (Table 3). The "bed volume" is equal to the volume of resin in the column [$\pi \times$ (½ inside diameter)$^2 \times$ length of the bed] after the column has been filled, backwashed, and the water level has been adjusted to 2.5 cm above the top of the resin bed. The adsorbed FA on the DAX-8 resin was eluted with 0.1 N NaOH, and acidified to pH < 2 to minimize the alteration of samples at high pH 9 (Aiken et al., 1992; Hendry and Wassenaar, , 2005). Between samples, the DAX-8 resins were cleaned with sequential rinses of 0.1 N HCl and DIW until neutral pH was obtained. Figure 6 illustrates the schematic of FA separation using the chromatography column. After passing the samples through the column resin and before using 0.1 N NaOH to elute the adsorbed FA, the glass reservoir was rinsed using DIW.

All collected samples were analyzed in a total carbon analyzer (TCA) linked to a stable isotope-ratio mass spectrometer (IRMS). Data are summarized in Table 4. In order to assess the efficiency of DAX-resin column for collection of HS fractions, experimental data were examined in a carbon mass balance. The mass balance was performed based on the following equation using measured $\delta^{13}C$ and the recovered carbon concentration of each of the three collected HS fractions (HA, FA and LMW DOC fraction) and total DOC:

$$\begin{aligned} \delta^{13}C_{DOC} \times C_{DOC} = & \left(\delta^{13}C_{HA} \times C_{HA}\right) \\ & + \left(\delta^{13}C_{FA} \times C_{FA}\right) \\ & + \left(\delta^{13}C_{LMW\ DOC} \times C_{LMW\ DOC}\right) \end{aligned} \quad (1)$$

Here C is the carbon concentration and $\delta^{13}C$ is the carbon isotope ratio in permil (‰) of each component. Calculated errors are less than 7.2%, demonstrating acceptable accuracy of HS separation and isotope analysis procedures.

3.5.TCA and HPLC measurements for the CSIA of carbon compounds

A total inorganic/organic carbon analyzer (TCA) interfaced with a continuous-flow isotope ratio mass spectrometry (CF-IRMS) was used to measure the concentration and ^{13}C-isotopic composition of DIC and DOC in leachate samples. Quantitative DOC and DIC measurements were made with an OI Instruments Model 1010 Total Carbon Analyzer where inorganic carbon is converted to CO_2 using 5% H_3PO_4, then purged with He gas for analysis. Subsequently, organic carbon is converted to CO_2 by wet oxidation using sodium persulfite ($Na_2S_2O_8$). The purged CO_2 following the two steps of sample acidification and oxidation was measured by a non-dispersive infrared detector (NDIR) and passed through the ConFlow

III interface for $\delta^{13}C$ IRMS analysis of DIC and DOC (St-Jean, 2003). The DIC and DOC concentrations and their $\delta^{13}C$ values were measured based on standard calibration curves.

Propionic and acetic acids were analysed individually by injection of acidified (~pH 2) aliquots for HPLC separation (Mohammadzadeh et al., 2005). Note that at this pH, high molecular weight DOC, e.g. humic acids, become largely insoluble (Hendry and Wassenaar, 2005) and were precipitated from solution prior to injection into the HPLC. The $\delta^{13}C$ and DOC of 40 ml aliquots of total DOC, the FA and LMW DOC fractions, and also of the collected HPLC fractions were then measured with the OI Instruments TCA linked to the IRMS.

3.6. CH_4 concentrations and ^{13}C isotope measurements of headspace gases (CH_4 and CO_2)

Gas samples were collected in 120 ml glass bottles leaving a 40 ml headspace (at ambient atmosphere pressure) to measure the concentration of the methane gas and the isotope values of the methane and of CO_2. Methane from the leachate partitions into the headspace of the bottle due to its low solubility. A maximum of 0.2 ml of standard and headspace gas of each sample was injected into a gas chromatograph (GC model SRI 8610C, SRI instruments, Inc.) using a 250 µl needle to measure the methane concentration. Total concentration of the dissolved methane ($m_{g\text{-}CH4}$) in leachate samples (in mol L^{-1}) was calculated from the measurement of the headspace methane (in mol) using Henry's constant for methane solubility ($K_{H\text{-}CH4}$ =0.0014 mol/L/atm, at 25 °C) together with water and headspace volumes.

Headspace samples were analysed for $\delta^{13}C_{CH4}$ and $\delta^{13}C_{CO2}$ using a gas chromatography (GC) combustion system (GCC III) interfaced with a Thermo-Finnigan Delta^{Plus} continuous-flow isotope ratio mass spectrometer (CF-IRMS). The analytical precision for the $\delta^{13}C$ was +/-0.2 to +/-0.3 ‰.

3.7.Elemental and isotope ratio analyzes of Humic Acid (HA)

The percent carbon and ^{13}C in solid (precipitated) humic acid samples were analysed with a Vario EL III elemental analyser (EA) by flash combustion with oxygen at 1800 °C, followed by advection with a helium carrier gas through a TCD (thermal conductivity detector) to the mass spectrometer. The routine analytical precision (2 sigma) is ±0.1% for concentration and ±0.15 ‰ for ^{13}C. Figure 7 illustrates the isolation procedures and $\delta^{13}C$ measurements for the humic acids, fulvic acid and LMW DOC fractions from leachate. All measurements were performed in the geochemistry and the G.G. Hatch stable isotope laboratories at the University of Ottawa.

Table 5 and Table 6 show the measured field parameters, the concentrations and the stable isotopic compositions ($\delta^{13}C$, $\delta^{18}O$ and $\delta^{2}H$) of the leachate samples in 2005, 2004 and 2003. All concentrations cited in this paper are expressed in mgl^{-1} and isotope results are expressed in standard δ-‰ notation against the international VPDB standard (Vienna PeeDee Belemnite) for ^{13}C and the international V-SMOW standard (Vienna-Standard Mean Ocean Water) for ^{2}H and ^{18}O (Craig, 1953, 1957; Coplen, 1994).

3.8. ^{13}C-Nuclear Magnetic Resonance (NMR) spectra for the HA and POC

High resolution solid-state ^{13}C-NMR spectra were obtained for humic acid (HA) and particulate organic carbon (POC, i.e. acidified original precipitated materials) of the leachate samples. These spectra can be use to determine the type of carbon present in the organic substances and the relative abundances of functional groups in the sample (Wershaw, 1985). The regions between 0–95 ppm and 95–160 ppm represent the aliphatic carbon and aromatic carbon, respectively. The phenolic and carboxylic carbon can be distinguished between 160–185 ppm regions. Finally, the region 185–220 ppm represents carbonyl carbon.

NMR spectra were acquired on a Bruker ASX 200 NMR spectrometer operating at 50.32 MHz for ^{13}C and 200.09 MHz for ^{1}H. Samples were packed in 7 mm O.D. zirconia rotors and capped with commercial kel-F fluorinated polymer caps. The proton 90 degree pulse was 4.25 μsec and the decoupling field was 59 kHz. The contact time, relaxation delay and acquisition time were set at 2 msec, 2 sec, respectively. 1024 points were collected using a spectral width of 18, 939 kHz. The data were zero filled to 16K data points and treated with 40 Hz of exponential line broadening prior to Fourier transformation. The number of scans collected for each sample varied from 34,000 to 128,000 depending on the quantity of sample and/or the amount of carbon present. Data collection time ranged from 19.2 hours to 3 days.

4. Results and discussion

4.1.Leachate geochemistry and redox conditions

In general, leachate quality is influenced by the composition of the waste, environmental conditions in the landfill (humidity, O_2 availabitity) and by time (Kjeldsen et al., 2002). MSW contains various materials, including readily biodegradable compounds (food waste, wood, paper, cardboard, yard waste), poorly biodegradable (plastic, rubber, etc.) and solids (e.g. glass, metal, concrete, etc.). Cellulose and humicellulose, the major biodegradable polymers in landfills, comprise 29 to 65% of MSW (Barlaz 2006). The decomposition of these components to CH_4 and CO_2 in landfills is well documented (Barlaz et al., 1989). At TRL, waste materials contain more than 50% paper, wood and plastic (Table 1).

The major phases of waste decomposition are: 1) an initial aerobic phase typical of young landfills (<1 year) which lasts for days to weeks due to the restricted access to oxygen once the waste is covered. During this phase, organics are aerobically degraded by aerobic bacteria and the oxygen content of the landfill is quickly consumed resulting in anaerobic conditions; 2) anaerobic acid phase in which cellulose and hemicellulose materials, carbohydrates, proteins and fats are biodegraded by hydrolytic, fermentative, and acetogenic bacteria, resulting in an accumulation of carboxylic acids, volatile fatty acids and CO_2; and 3) the methane production phase in which the accumulated carboxylic acids are converted to CH_4 and CO_2 (Kjeldsen et al., 2002; Rooker, 2000; Reinhart and Grosh, 1998).

As illustrated in Figure 2, Stages 1 and 2 were opened in 1980 and were closed and capped in 1988 and 1991, respectively. The emplacement of waste materials in Stage 3 commenced in 1991 and lasted for 12 years. Stage 4 is the only currently active stage and has been active

since 1999. As refuse is buried over many years, it is anticipated that the different stages of the TRL site will be in different phases of decomposition and perhaps different redox environments exist at different areas of the landfill. The Leachate Pumping Station (LPS) drains leachate from both Stage 3 (14 years old) and Stage 4 (active). Therefore, samples taken from LPS represent a mixture of young leachate and the leachate from waste with up to 14 year old. The Leachate Pipes (LP) beneath Stage 4 are associated with recent emplacement of solid waste, and so leachate from these points is young. By contrast with the LPS and LP leachates, M32 captures older leachate from waste with an average age of 28 years from the water table at the base of the unlined landfill (Stage 1). Sampling these different sources of leachate allow us to characterise and compare young and old leachate, and the phase of waste decomposition and stabilization (Table 5 and Table 6).

A general description of leachate geochemistry in LPS and M32 provides a distinction between early stage leachate in LPS and late stage or more mature leachate in M32. A review of the inorganic geochemistry of the two different leachates from LPS and M32 shows that the LPS leachate is dominated by low TDS (2200 mg/L) Na – Cl facies reflecting a first stage dissolution of soluble salts with high dilution from infiltration of ambient precipitation. The older and capped landfill produces leachate at M32 with higher TDS (5300 mg/L) dominated by a Ca (Na) – Cl geochemical facies. Both have slightly acidic pH levels (6.7 to 6.8) and redox conditions favouring ferrous iron, ammonium and methane, and only minor sulphate.

The organic geochemistry of these two leachates are strongly contrasted with the older and more concentrated M32 leachate having almost 5000 mgl^{-1} DOC while the younger and more

dilute LPS had only 200 mgl^{-1} DOC. Normalized to Cl^- to compensate for dilution, M32 still shows a much higher concentration of DOC. Both have close to 300 mgl^{-1} dissolved inorganic carbon (DIC) and high ammonium concentrations (>300 mg-N/L).

As illustrated in Figure 5, prior to air injection in 2005, no O_2 gas was recorded in either the M34 or GM12 gas monitoring wells located south of the Stages 2 and 3 air injection system, indicating that anaerobic conditions dominate in the unperturbed unsaturated zone of the landfill (Figure 8). Anaerobic conditions may be sustained by not only the O_2-consuming reactions with landfilled organic waste, but also by oxidation of methane diffusing and convecting to the surface which will preclude downward diffusion of oxygen into the waste (P. Kjeldsen, personal communication).

Figure 9 shows the p*e* – pH diagram for principal redox pairs (Table 7) in leachate from TRL site. The stability line of each redox pair on p*e* – pH diagrams was drawn using calculated activity of ions and measured partial pressure of required gases (Table 8). Most data plot near 170 mV (pe = 16.9 Eh = 3), close to the Eh found for an acid phase leachate (Thornton et al., 2000). Further, these data plot at a considerably higher Eh than would be expected for methanogenenic waters. Ruling out instrumental error during measurement, this may reflect heterogeneous redox conditions in the landfill, where micro-methanogenic zones exist in both the saturated and unsaturated zones. The presence of low but persistent amounts of higher electromotive potential electron acceptors such as NO_3^-, NO_2^- and SO_4^{2-} are consistent with a heterogeneous distribution of redox conditions resulting in disequilibrium in the bulk leachate. The platinum electrode redox probe is likely to be more responsive to the ionic redox pairs including dissolved iron and nitrogen species.

Despite the high platinum electrode data, evidence suggests a very significant methane production throughout the site and that most of the landfill profile is under very low redox conditions. Estimates for a high methane production rate, considerably greater than the measured rates of gas production at the GFS can be made from the deuterium excess of the leachate.

4.2. Deuterium excess in leachate and methanogenesis

The stable isotope composition of leachate water (δ^2H and $\delta^{18}O$) provides a means of estimating the production of methane and CO_2 during degradation of organics. Leachate water exchanges ^2H with methane, which preferentially takes the light hydrogen (^1H) and with CO_2, which has heavy oxygen (^{18}O). Figure 10 shows the δ^2H - $\delta^{18}O$ diagram of different samples of leachate. The $\delta^{18}O$ values of the leachate samples varies with season of sampling (-15.4 to -8.4 ‰ VSMOW). This variation in the TRL leachate is due to seasonal variations in $\delta^{18}O$ of precipitation, reflecting a rapid movement of water through the pile with minimal storage in the waste.

Despite shifts in leachate $\delta^{18}O$ due to strong seasonal variation contributions and the short residence time of water in the landfill, the ^2H of the leachate is always significantly enriched, with average deuterium excess (d-excess) of 21‰, 15‰ and 10‰ VSMOW (for the LPS, LP and M32, respectively) (Table 6 and Figure 10). Deuterium excess shows the enrichment of ^2H over global meteoric water line. Such deuterium enrichments have often been observed in landfill leachates, and are attributed to fractionation during methanogenesis, where the

light hydrogen isotope (^1H) is preferentially partitioned into methane, while ^2H is enriched in H_2O (Daniels et al., 1980; Siegel et al., 1990; Liu et al., 1992; Hackley et al., 1996, 1999).

For isothermal conditions and constant hydrogen isotope fractionation between water and methane, ^2H enrichment must be proportional to methane production. The degree of ^2H enrichment above the local meteoric water line can then be expected to reflect the extent of the methanogenic reaction per given volume of leachate discharged from the landfill. This is evident from the correlations of d-excess with methane and leachate production.

The measured d-excess in leachate samples has a negative correlation with leachate production (Figure 11), suggesting that methane production remains relatively unchanged during the seasonal increases in flow through the waste. This demonstrates that methane production is independent of leachate production (discharge), where increased leachate production is due dilutes d-excess. Variability in methane production as measured in the gas flare station may be due to other factors such as changes in the degree of methane captured by the gas collection system. Evidence for the inefficiency of this system is found in the gas monitoring wells installed beyond the landfill in the surrounding phreatic zone (Figure 1).

4.3. Characterization of the bulk DOC and DIC

A first step in evaluating organic carbon degradation and methanogenic pathways is the isotopic characterization of dissolved organic and inorganic carbon in the young and mature leachates (Table 6). For the young leachates, the average concentration of DOC are relatively

low reflecting dilution in the uncapped setting, and with $\delta^{13}C$ values close to typical biomass precursors (–26‰):

LPS – DOC =197 mgl^{-1}, $\delta^{13}C$ = –25.7‰

LP – DOC =117 mgl^{-1}, $\delta^{13}C$ = –26.0 ‰

By contrast, M32 has much higher DOC which is substantially enriched in ^{13}C:

M32 – 4770 mgl^{-1}, $\delta^{13}C$ = -21.6 ‰

The strong variability in DOC concentration at LPS reflects the impact of dilution by precipitation, but may also be affected by changes in biogeochemical reactions, as suggested by the off-set from dissolved inorganic carbon (DIC) (Figure 12c). Variation from dilution is demonstrated by the strong shift in $\delta^{18}O$ of the leachate (Table 6, Figure 10, and Figure 12b) and by the good correlation between $\delta^{18}O$ and leachate volume (Figure 11). This effect of significant seasonal dilution of the leachate and strong seasonal shift in $\delta^{18}O$ underlines the rapid movement of infiltration water through the waste.

The much greater concentration together with the enriched $^{13}C_{DOC}$ value for the bulk DOC of the older leachate at M32 (–21.6 ‰) in comparison with that of the young leachate at LPS (–25.7 ‰) and LP (–26.0 ‰) indicates that microbial processes are more advanced in the degradation of dissolved organic materials in older part of the landfill site (Stage 1).

The average concentration of DIC in the different leachate sources are less variable taken from LPS = 349 mgl^{-1}, LP = 494 mgl^{-1}, and M32 = 290 mgl^{-1}, but also affected by seasonal dilution (Figure 12c). For all, however, the $^{13}C_{DIC}$ is highly enriched (+10.7 ‰ ± 4.2, n=41

for the LPS, and +4.7 ± 3.8, n=8 for the LP and +8.5 ‰ ± 1.0, n=3 for M32), due to carbon isotope fractionation during methanogenesis (discussed below). Together with the deuterium excess discussed above, these are the two unequivocal benchmarks for the impact of methanogenesis on the residual leachate. Figure 13 shows a strong positive correlation between ^{2}H excess and $\delta^{13}C_{DIC}$ in LPS.

A competing mode of production of DIC in leachate is through the aerobic oxidation of organic carbon by O_2 advected into the pile during high precipitation events. This is demonstrated by the negative correlations between leachate production at LPS and $\delta^{13}C_{DIC}$ (Figure 11). Here, depleted $^{13}C_{DIC}$ values are generated from organic matter oxidized with O_2 in the fringes of the landfill (Figure 8), according to the following quantitative reaction:

$$CH_2O + O_2 \rightarrow CO_2 + H_2O \qquad (2)$$

The impact on $\delta^{13}C$ of DIC can be determined if we assume that TRL precipitation contains 15 ppm (~0.5 mmoles O_2) dissolved oxygen O_2 and excess organics. Percolated precipitation can generate 5.6 ppm C inorganic carbon with an $\delta^{13}C$ isotope value of -26 ‰. Mixing with leachate having DIC of 349 mgl^{-1} and $\delta^{13}C_{DIC}$ of +10.7 ‰, the resulting $\delta^{13}C_{DIC}$ value of the mixture is provided by isotope mass balance (Equation 3),

$$\delta^{13}C_{Total-DIC} \times C_{Total-DIC} = \left(\delta^{13}C_{Leachate-DIC} \times C_{Leachate-DIC}\right) + \left(\delta^{13}C_{Precipitation-DIC} \times C_{Precipitation-DIC}\right) \qquad (3)$$

By taking into account the large amount of precipitation in wet seasons (increases by factor of 6), the final $\delta^{13}C_{DIC}$ value of the mixture would be about 7.4 ‰. Therefore, minimized infiltration and recirculation of generated leachate reduces aerobic decomposition of the organic waste material and enhances CH_4 production for conversion to energy in terms of electricity by co-generation (Barlaz, 2006).

4.4. Major components of the DOC system

The similar enrichments in ^2H (d-excess) and $^{13}C_{DIC}$ for both the older (M32) and younger (LPS) leachates suggests similar rates of methane production per volume of leachate. However, examination of the organic components of DOC in each reflects quite different methanogenic pathways. These differences are explored in this section.

The organic load of landfill leachate contains a variety of DOC components, which are poorly characterized (Christensen et al., 2001; Kjeldsen et al., 2002). Degradable complex DOC components are transformed into simpler organics through a series of hydrolysis and disproportionation reactions. Figure 14 illustrates the hydrolysis of the polymers (HMW molecules) followed by the fermentation of monomers (e.g. sugars, fatty acids and glycerol and amino acids) to carboxylic acids and simple fatty acids (e.g. propionate, butyrate, etc.) which eventually degraded to CH_4, CO_2 and H_2O through bacteria mediated reactions (e.g. acetogenesis and methanogenesis), as adapted from Clark et al. (2004); Christensen et al. (2000); Bogner et al. (1996). In order to develop a model for the degradation of the DOC with evolution of the isotopes in these components and the methane production pathways,

the various DOC components are quantified and analysed by compound-specific isotope analysis (CSIA).

Here, the leachate DOC fractions investigated include acetic acid (AA) and propionic acid (PA) as well as refractory humic substances (HS) such as fulvic acid (FA) and humic acid (HA). These are important reactants and products in the degradation of organic carbon. AA and PA are produced during fermentation of carboxylic acids. AA and PA are eventually converted to CH_4 during acetoclastic methanogenesis. Separation techniques for these different DOC fractions are described in section 3.5.

The concentration of AA (between 218 and 1755 mgl^{-1}) and PA (between 29 and 1313 mgl^{-1}), two simple short-chain fatty acids with low molecular weight, are the dominant components of DOC in M32 (Table 6 and Figure 15). Methanogenesis in the older leachate samples is characterized by the production of these compounds through fermentation reactions (Figure 14).

By contrast, the concentration of AA in young leachate at LPS is only about 24 mgl^{-1} (σ = 1.0, n=3) and there was no measurable PA. The high amount of AA and PA in older leachate from M32 (1008 mgl^{-1} and 608 mgl^{-1}, respectively) in comparison with that of younger leachate from LPS (24 mgl^{-1} and 0.0 mgl^{-1}), clearly shows a fundamentally different biodegradation pathway in this older part of the landfill site (Stage 1). This also can be confirmed by the high amount of bulk DOC in M32 (4770 mgl^{-1}) and more enriched values of $^{13}C_{DOC}$ for the precursor DOC of the older leachate at M32 (–21.6 ‰) in comparison with that of the young leachate at LPS (–25.7 ‰) and LP (–26.0 ‰).

HS in landfill leachates represents more than 60% of the total organic carbon (Artiola-Fortuny and Fuller , 1982). They are important components reflecting the rate of biological degradation of landfill leachate contaminants (Chian et al., 1976), for their role in transporting pollutants along the flow paths (Artinger et al., 2000), and for facilitating electron transfers in anaerobic environments (Lovley et al., 1996 and 1998; Scott et al., 1998). HA can make up 10 % of DOC in landfill leachate (Christensen et al., 1998). Concentrations and isotopic ratios of the HS and the LMW DOC fractions are tabulated in Table 9. The percentages of the DOC present as FA and LMW DOC were estimated using the measured data (Table 9) and the distribution of HA, FA and the LMW DOC fractions of landfill leachate DOC is shown in Figure 16.

In both young (LP and LPS) and older (M32) leachate, FA is the major fraction of the HS (69% to 74 % of total DOC content of leachate). The HA fraction in young leachate comprised from 6% to 18% of the leachate DOC. However, it is quite low (0.3% of the leachate DOC) in older leachate from M32. The LMW DOC fraction, which comprised from 13% to 20% of total DOC for the young leachate, is slightly higher (27% of the total leachate DOC) in older leachate. Thus, the HMW DOC or hydrophobic acids (HA and FA) dominated the DOC of the leachate and it represents 73.5 % to 87.1 % of total DOC content of both young and older leachates (Figure 16).

These concentrations are similar to those found by Gron et al. (2000), but higher than the values found by Artiola-Fortuny and Fuller (1982) (60%), and by Harmsen (1983) (33%). Artinger et al. (2000) and Wassenaar et al. (1990) also indicated that the hydrophobic

fraction (HA and FA) could be dominant component in the DOC pool. Concentrations of the FA and LMW fractions are generally attributed to biological transformation of HMW DOC compounds into LMW DOC compounds or simpler hydrophilic acids (e.g., Thurman, 1985), and so the concentrations of HA and the HA/FA ratio can reflect on the extent of these reactions for varying ages of leachate and waste (e.g. Artiola-Fortuny and Fuller, 1982; Castagnoli et al., 1990), and upon the HS present in the source (Gron et al., 1996).

At the TRL site, the calculated humic/fulvic acid (HA/FA) ratios for all leachate samples are below unity (Table 9) which for some researchers reflects aging of the landfill leachate (e.g., Castagnoli et al., 1990; Chian and DeWalle, 1976). The ratio in younger leachate from LPS (0.18) is approximately 3.6 times greater that than of the older leachate from M32 (0.05). This huge shift in HA/FA ratio between LPS and M32 is essentially due to high concentrations of FA in old M32 leachate (4482 mgl^{-1}), whereas there is not much difference in concentration of HA between LPS (28 mgl^{-1}) and M32 (21 mgl^{-1}). HA forms just about 0.3% of the total DOC at M32 (Figure 16). Consequently, we speculate that this fundamental difference between leachate from M32, which is more than 28 years old, and young leachate, from both LPS and LP, is due to an emphasis on disproportionation reactions of complex organics in the older site.

The ^{13}C-NMR spectra for HA and POC provide further characterization of the DOC components. These spectra show three major types of carbon (aliphatic, aromatic, and carboxylic carbons) (Figure 17). In some spectra, the minor peak of phenolic is also observed. As described by Aravena et al. (2004), the relative abundance of these major carbon groups (aromatic, aliphatic, carboxyl and carbonyl) in humic acid (HA) and

particulate organic carbon (POC) of leachate samples from TRL site were estimated by measuring peak areas in ^{13}C-NMR spectra (Table 10). While there is not much difference between other carbon groups, the aromatic carbon group is much less in M32 (3% and 5% for POC and HA, respectively) in comparison with that of young leachate from LPS (10% and 28% for POC and HA, respectively). This reflects degradation of HA (dominated by aromatics) and their transformation to LOM-DOC, and is consistent with the high concentration of AA in this older leachate.

Stable ^{13}C isotope data further clarify the dominant reaction pathways of HMW DOC. In disproportion reactions, the ^{13}C would go preferentially to the oxidized molecules, i.e. CO_2, while ^{12}C would preferentially remain in the reduced organic molecules, i.e. HA (Figure 16). This is confirmed by the depleted $^{13}C_{HA}$ (-28.1‰) and the enriched $^{13}C_{LMW\text{-}DOC}$ of M32 (-8.0‰) which is discussed in the next section.

4.5.CSIA of DOC components

The average $\delta^{13}C$ values of bulk DOC (-26‰ and -21‰ for the young and older leachate, respectively) reflect the average isotopic composition of the dissolved organic carbon material. Decomposition of this material generally results in enriched ^{13}C values (Van Breukelen et al., 2003) due to greater selectivity by bacteria for metabolizing material with the weaker ^{12}C bonds. A more enriched ^{13}C value of bulk DOC of the older leachate at M32 (-21 ‰) reflects more advanced reactions. Bacterially mediated fermentation of carbohydrate and methylated organics, produce acetate and other fatty acids, as well as inorganic carbon and hydrogen according the following equations (Klass 1984):

$$6CH_2O \rightarrow CH_3CH_2CH_2COOH + 2CO_2 + 2H_2 \quad (4)$$

DOM *Butyric acid*

$$CH_3CH_2CH_2COOH + 2H_2O \rightarrow CH_3CH_2COOH + CO_2 + 3H_2 \quad (5)$$

Butyric acid *Propionic acid*

$$CH_3CH_2COOH + 2H_2O \rightarrow CH_3COOH + CO_2 + 3H_2 \quad (6)$$

Propionic acid *Acetic acid*

Crbon isotope fractionation effects during these fermentation reactions are not known. However, the example of acetoclastic methanogenesis, which fractionates ^{13}C between the methyl and carboxyl groups enriches the CO_2 by some 50‰ over methane, suggests that the DIC produced during carbohydrate fermentation will be enriched in ^{13}C over the complementary organic acids. However, unless the residual methyl groups become exceedingly depleted in ^{13}C, the product CO_2 cannot be highly enriched in ^{13}C. Acetate in the LPS and M32 has $\delta^{13}C$ values enriched in ^{13}C (–17 and –12‰) with respect to DOC precursors (~ –26‰) showing that this is not the case.

The production of hydrogen during these reactions provides substrate for subsequent methanogenesis:

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \qquad \Delta G°r = -130.58 \quad (7)$$

or homoacetogenesis reactions:

$$2CO_2 + 4H_2 \rightarrow CH_3COOH + 2H_2O \qquad \Delta G°r = -78 \text{ kJ} \quad (8)$$

which can subsequently support acetoclastic methanogenesis:

$$CH_3COOH \rightarrow CO_2 + CH_4 \qquad \Delta G°r = -52.58 \quad (9)$$

Fermentative reactions are essential precursors or parallel processes for methanogenesis, as they operate under anaerobic conditions to generate the hydrogen substrate required for methane production. This is then accomplished by either CO_2 reduction or the acetate fermentation pathway. However, CO_2 reduction (7) must compete with acetogenesis (reaction (8)) for H_2, and while more energetically favourable acetogenesis requires less H_2 for each mole of CO_2 sequestered.

Isotope fractionation associated with CO_2 reduction has been estimated by Whiticar et al. (1986) to be $\alpha^{13}C_{CH_4\text{-}CO_2} = 0.935$, thus imparting a depletion greater than about 65‰ on the $\delta^{13}C$ of methane, whereas methane from acetate fermentation is less than about 50‰ depleted from $\delta^{13}C$ of CO_2. Homoacetogenesis, by contrast consumes twice as much DIC per mole of H_2 substrate and can be expected to impart an even greater enrichment in ^{13}C on the residual DIC. Further, the acetate from reaction (8) should experience significant enrichment due to formation from a ^{13}C-enriched DIC substrate.

In order to better understand methane production in the young and old leachates, the evolution of ^{13}C in these components during transformation is a useful tracer. Isotopic analysis of isolated DOC compounds was undertaken by compound specific isotope analysis – CSIA.

Acetate - From Table 6, the $\delta^{13}C$ values for acetate in M32 leachate are remarkably enriched, ranging from -13.7 to -10.7 ‰ (average of -12.0, n=4). PA is less enriched, ranging from -20.6 to -18.5 ‰ (average of -19.3, n=4). The $\delta^{13}C$ value of the minor acetate in young

leachate at LPS is considerably less enriched in ^{13}C than in M32, with $\delta^{13}C$ = -16.9 ‰ (σ = 0.1, n=3) and there was no propionic acid measured in LPS. These isotope values are very important to understanding methanogenic pathways which are discussed in the next section.

Low Molecular Weight DOC - As illustrated in Figure 16, the isotopic values of LMW DOC and its HPLC fractions, which were collected on the basis of HPLC peak retention times between 8 and 12.5 minutes (following elution of acetate), are depleted (-27.1‰ and -34.8‰, respectively) in young leachate from LPS. By contrast, a very significant enrichment was observed for the ^{13}C value of LMW DOC of the older M32 leachate (-8.0‰ and -13.0‰,), as compared to the $\delta^{13}C$ value of bulk DOC (-18.4‰). This is consistent with the enrichment trend for $\delta^{13}C$ for acetate.

Fulvic and Humic Acid – The $\delta^{13}C$ values for these high molecular weight compounds show the same contrasts between the young LPS and older M32 leachates as observed for the low molecular weight compounds. For the young (LPS) leachate, the $\delta^{13}C$ value of FA (the major fraction of HS) is -26.2‰. This is slightly higher than the $\delta^{13}C$ value of corresponding LMW DOC (-27.1‰), but is lower by about 3.3‰ compared to the equivalent $\delta^{13}C$ value of HA (-22.9‰). In the older leachate (M32), by contrast, the $\delta^{13}C$ value of FA (-20.3‰) is significantly enriched compared to the HA (-28.1‰). Like the LPS leachate, the $\delta^{13}C_{FA}$ is close to that of the bulk DOC (-18.4‰).

In summary, $\delta^{13}C$ values of DOC components demonstrate different environments of anaerobic degradation between the two leachate generation systems. The younger LPS

system is characterized by considerably lower DOC and has lower concentrations of most isolated compounds. The older M32 leachate has more than 10 times greater DOC, with over 40 times more acetic acid and other light molecular weight compounds and some 30 times more fulvic acid. Only humic acid has a similarly low concentration in both leachates.

The much higher concentrations of these isolated compounds of DOC in M32 are accompanied by enrichment in ^{13}C. Moreover, the enrichment in ^{13}C is strongly biased to the lighter weight compounds, with acetic acid having a $\delta^{13}C$ value as high as –10.7‰. By contrast, fulvic acid and the light molecular weight compounds in the LPS leachate are depleted in ^{13}C. Only acetic acid in LPS is enriched above the $\delta^{13}C$ value for the bulk DOC, with a value of –16.8‰.

From before, evidence from the enriched ^{13}C of DIC and the d-excess parameter indicates greater methane generation in the young Stage 3 and 4 leachate from LPS than for the older M32 leachate. In general, it seems that biodegradation in the younger leachate system is characterized by rapid conversion of DOC to methane, which allows little accumulation of intermediate products. By contrast, biodegradation in M32 leachate is characterized by slower conversion of DOC to methane and an accumulation of low molecular weight compounds in the leachate.

4.6. Methanogenic pathways

The contrasting profiles of DOC compound concentrations and isotope values suggests different pathways for production of methane in the older, covered landfill from Stage 1 and

in the younger, uncapped landfill in Stages 3 and 4. Current research on CH_4 has focused on carbon isotope fractionation between coexisting methane and CO_2 to determine the methane origin and methanogenesis pathways (Barker et al., 1981; Balabane et al., 1987; Coleman and Risatti, 1981; Coleman et al., 1988; Aravena and Wassenaar, 1993; Aravena et al., 1995; Hornibrook et al., 2000).

A look at the isotope values for methane from the old and the young leachates (Table 6) sheds little light on their methanogenic pathway. Two measurements of $\delta^{13}C_{CH4}$ for the young leachate from LPS are –59.4 and –56.8‰, while three samples from the older leachate at M32 range from –68.4 to –50.8‰, averaging –59.6‰, which is virtually the same as for LPS. Nine samples from the LP sites vary between –64.4 to –22.7‰. Note that the enriched values likely reflect secondary oxidation in the vented system of the LPs, which this process selects the light species. This is strengthened by the depleted ^{13}C isotope of DIC found in those LP samples with ^{13}C enriched CH_4 due to contributions of DIC from methane.

If the deuterium excess, d, is taken as a measure of net methane production, then the young leachate from LPS, with d = 16.3‰, has produced considerably more methane per litre of leachate than M32 (d = 5.8‰). Similarly, the $\delta^{13}C$ of DIC can be taken as a measure of methane production. Considering the maximum measured values (to minimize the contributions from seasonal contributions of DIC in LPS from aerobic oxidation of organics, discussed above), LPS has a greater value than M32 (+17.4‰ vs +10.7‰). The LPS also has higher DIC than M32 from methane production, given that the overall reaction pathway results in a net production of DIC.

The efficiency of methane production can be measured by the degree of acetate accumulation. The synthesis of reactions (4) to (6) gives the overall reaction for anaerobic degradation of organic matter as:

$$6CH_2O \rightarrow CH_3COOH + 4CO_2 + 8H_2 \quad (10)$$

Consumption of the energetically rich hydrogen substrate by CO_2 reducers (reaction (7)) and of the acetate by acetoclasts (reaction (9)) results in the net reaction:

$$2CH_2O \rightarrow CH_4 + CO_2 \quad (11)$$

However, if ubiquitous acetogenic bacteria can out-compete the methanogens for available H_2 (reaction (8)), the result will be a net accumulation of acetate in solution, providing substrate for acetoclastic methane production (reaction (9)). This seems to be the case for the old leachate in M32, which has over 1 g/L carbon as acetate, while the young leachate in LPS has only minor acetate (24 mgl^{-1}).

Further evidence for homoacetogenesis in M32 is the enriched ^{13}C of acetate (–12.0‰) which reflects formation from ^{13}C-enriched DIC (reaction (8)). The $\delta^{13}C$ of the minor acetate in LPS is –17‰ indicating that CO_2 reducing bacteria must be the primary consumers of H_2. Also, the enrichment in ^{13}C for M32 acetate above the $\delta^{13}C$ of DOC (–18.4 ‰) suggests that this acetate has not evolved from the simple degradation of larger organic molecules, which

would be expected to impart a depletion of ^{13}C on the produced acetate due to release of ^{13}C-enriched DIC.

From this model of acetogenesis in M32, it follows that the propionic acid would also accumulate in M32, although at a lower concentration (600 mg/L) and with lower $\delta^{13}C$ (-19.3‰) through anaerobic degradation of organics. If the high concentration of acetate in this leachate followed from propionic acid fermentation (reaction (6)), the acetate would have a lower $\delta^{13}C$ value. By contrast, homoacetogenesis from the enriched DIC pool and H_2 would produce a higher $\delta^{13}C$ of acetate.

The $\delta^{13}C$ of methane can also be considered. For both M32 and LPS, this value is close to –60‰. In the case of M32, this is too low for significant production directly from acetate fermentation (reaction (9)) which should produce methane with $\delta^{13}C = \sim -37‰$, i.e. only 25‰ lighter than the acetate precursor ($\varepsilon^{13}C_{CH_4\text{-}CO_2} = -50‰$). However, if acetoclastic fermentation proceeds slowly, (reaction (9)), bacterial selectivity for the light molecules of the acetate pool would produce an enrichment on the residual acetate pool. Subsequent cleaving the methyl and carboxyl groups of these isotopically light acetates resulted in an additional depleted ^{13}C of methane.

In LPS, the methane is clearly produced by the combination of CO_2 reduction ($\varepsilon^{13}C_{CH_4\text{-}CO_2} <$ –65‰) which consumes the H_2 pool, and fermentation of residual acetate following the degradation reactions producing H_2 (reactions (4) to (6)). CO_2 reduction with the DIC in LPS

would produce methane with $\delta^{13}C < -55‰$, while acetoclastic methane would have $\delta^{13}C$ less than –42‰.

In general, as illustrated in Figure 14 and discussed above, acetate can accumulate through the enzyme mediated acetogenesis reaction (the fermentation of propionic acid by acetogenic bacteria - equation (6) and also through the homoacetogenesis reaction (8)) which these acetate can subsequently convert to methane through the acetoclastic methanogenesis (9). Based on the Michaelis-Menten equation (Hult 2005) or Monad type models for degradation of acetate and subsequent methane production (White and Rabinson, 2003; Miller 2003), if the other factors (i.e. pH, T, etc) that effect the rate of reaction are at optimal values, the acetate accumulates until a maximum rate of methane production (μ_M) is achieved. If the amount of the enzyme (E) is constant and the substrate (acetate) concentration is then gradually increased, the rate of methane production (9) will increase to a maximum. In this state, enzyme active sites are saturated with the acetate substrate. Increases in acetate will not only fail to increase the rate of methane production, but can also cause it to decrease.

5. Summary and conclusions

At the TRL site, refuse has been buried over many years. Therefore, the extent of decomposition of organic material and the biodegradation pathways of organics is diverse at different areas of the landfill. The LPS drains a mixture of young (active Stage 4) and 14 year old (Stage 3) leachate, plus leachate re-circulated through Stage 4. Monitoring well M32, the base of the unlined landfill (Stage 1), by contrast, captures leachate from older waste with a speculated average age of 28 years.

In this study, specific organic analysis and compound specific isotope analysis (CSIA) of DOC compounds of the young leachate (from LP and LPS) and older leachate (from M32) of the TRL site have been conducted on samples collected from 2003 through 2005. Carbon-13 has been used to trace the principal methanogenic pathways and to characterize compounds that can be used as tracers for leachate impacted groundwaters. While detailed sampling on several occasions over this period provides some indication of the variability of the chemical and isotopic compositions, it does not capture long-term trends in leachate evolution. Only through the availability of samples from the old (M32) and young (LPS) leachate sites, can temporal changes be assessed.

In general, the following conclusions can be made from the geochemical parameters, the carbon geochemistry of different carbon pools (DIC, DOC, CH_4, CH_3COOH, and humic substances (HS), the environmental stable isotopes ($\delta^{13}C$, $\delta^{18}O$, and $\delta^{2}H$) and CSIA of leachate DOC fractions of the leachate analysis:

1. The younger landfill is in a strongly methanogenic phase. Deuterium excess (21‰) provides a semi-quantitative indicator of overall methane production, showing greater CH_4 production than in the older landfill. Methanogenesis must be dominated by CO_2 reduction ($\alpha^{13}C_{CO2\text{-}CH4}$=1.06). This was confirmed by more enriched ^{13}C of DIC at LPS (10.7 ‰). However, the very minor accumulation of LMW fatty acid (propionate is below detection limit and acetate <30 mgl^{-1}) indicates that acetoclastic methanogenesis must also take place. Low concentrations of all DOC components with lower $\delta^{13}C$

values, indicate rapid conversion of DOC to methane at LPS, which allows little accumulation of intermediate products.

2. The high amount of DOC (4770 mgl^{-1}) and that of low fatty acids (acetate and propionate are 1008 mgl^{-1} and 608 mgl^{-1}, respectively) shows a fundamentally different biodegradation pathway in the older part of the landfill site (M32). Enriched values of $^{13}C_{DOC}$ for the bulk DOC of the older leachate at M32 (–21.6 ‰) in comparison with that of the young leachate at LPS (–25.7 ‰) indicate that microbial processes are more advanced in the degradation of dissolved organic matter in the older part of the landfill site (Stage 1). The older landfill has much lower methane production (d-excess < 10‰) and is in an acetate fermentation phase with accumulation of LMW fatty acids. It seems that the acetate fermentation pathway for CH_4 production dominates in older part of the landfill (M32) with minor methane produce via the CO_2 reduction pathway. Diminishing of the CO_2 reduction is perhaps due to the landfill being capped with less water infiltration and degradation of older organics with the supply of labile organics being exhausted. This can be confirmed by the less enriched $^{13}C_{DIC}$ (8.5 ‰) and low ^{2}H excess (10 ‰) at M32. Enriched ^{13}C in LMW DOC (-8.0 ‰), and particularly for acetate with a $\delta^{13}C$ value of -12.0 ‰ shows that acetate is being consumed and/or was formed from ^{13}C-enriched DIC.

3. Due to high concentrations of FA (4482 mgl^{-1}, 73% of the total DOC) and low concentration of HA (21 mgl^{-1}, 0.3% of the total DOC) in old M32 leachate, a large decrease in the HA/FA ratio between LPS and M32 was observed. Less aromatic carbon

in M32 (3% and 5% for POC and HA, respectively) in comparison with that of young leachate from the LPS (10% and 28% for POC and HA, respectively), is perhaps due to degradation of HA and transformation of aromatic carbon to LMW-DOC.

Although enrichment trends in the ^{13}C of the leachate acetate, the carbon pools (DOC, DIC and CH_4) and the $^{2}H_{H2O}$ of the leachate are evidence for substrate consumption, future investigations should concentrate on the detailed secondary processes. These include biodegradation and variations in the concentrations of redox sensitive species and isotopic data which can be used to identify the series of reactions which are occurring simultaneously within the landfill site at varying rates over time.

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Table 1: Waste characterization of three samples obtained from three locations, representative of the upper (1.0 – 2.5 m depth), middle (1.0 – 4.5 m depth) and lower (8.0 – 9.5 m depth) strata of the refuse (City of Ottawa, 2002).

	Weight (kg)				
	Upper	Middle	Lower	Average	%
Wood	72	138	56	89	8.9
Plastics	110	75	61	82	8.2
Paper	352	455	295	367	36.6
Metals	55	35	31	40	4.0
Glass	9	14	5	9	0.9
Textile	27	50	25	34	3.4
Fines(<2")	406	330	404	380	37.9
Total	1031	1097	878	1002	100
	Volume (m^3)				
	Upper	Middle	Lower	Average	%
Wood	0.31	0.31	0.17	0.26	10.7
Plastics	0.58	0.46	0.38	0.48	19.5
Paper	0.92	1.00	0.85	0.92	37.8
Metals	0.19	0.15	0.13	0.16	6.5
Glass	0.02	0.02	0.01	0.02	0.6
Textile	0.12	0.08	0.12	0.10	4.2
Fines(<2")	0.54	0.42	0.54	0.50	20.5
Total	2.67	2.44	2.20	2.43	100

Table 2: Landfill gases (CH_4, CO_2 and O_2) concentrations in M34, GM12 and M107 during the period of May to December 2005. The gas concentrations of Stage 2 are the average of 23 measurements within monitoring wells, located on top of Stage 2, in October 2005. All concentrations in % by volume.

Monitoring Wells	Parameters	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
M34	%CH_4	52.8	24.7	0.2	4.1	0.0	0.3	0.0	0.9
	%CO_2	40.4	23.3	1.5	5.5	0.7	0.5	0.6	1.7
	%O_2	0.4	9.7	19.9	17.0	20.4	19.7	19.4	20.2
GM12	%CH_4	48.0	35.4	4.0	1.2	1.2	0.2	0.2	0.8
	%CO_2	40.0	33.5	9.8	6.8	5.1	4.1	2.6	5.2
	%O_2	0.5	4.0	12.4	15.6	16.0	17.2	17.7	16.3
M107	%CH_4	41.5	39.2	20.8	8.5	33.6	20.7	0.0	0.0
	%CO_2	24.4	25.6	19.6	17.6	22.2	22.4	15.6	14.5
	%O_2	4.3	1.8	2.0	0.4	0.0	1.3	1.3	4.0
Stage 2	%CH_4						28.6		
	%CO_2						19.5		
	%O_2						9.0		

Table 3: Samples' loading rate and eluting rate of 0.1 N NaOH to collect the adsorbed fulvic acid in DAX-8 Resin.

Parameters	M57	M39-7	M37-2	M4-1	M37-3	M34	LP1A	LP6A	LPS	M32 **
	Loading rate of the samples in DAX-8 Resin									
t_1 (hh:mm:ss)	0:53:35	0:36:12	0:26:15	0:39:52	1:19:00	0:41:20	0:52:29	0:46:00	1:01:20	0:53:00
t_2 (hh:mm:ss)	1:30:00	0:57:15	0:59:20	0:59:40	2:26:00	1:10:00	1:30:00	1:01:10	1:45:00	
Q_1 (ml/h)	672	994	1371	908	456	871	686	818	587	566
Q_2 (ml/h)	667	1048	1011	1006	411	857	667	984	571	
	Eluting rate of 0.1 N NaOH to collect the adsorbed Fulvic Acid									
t_1 (hh:mm:ss)	1:23:00	1:18:00	0:35:30	1:26:23	1:24:00	1:25:30	1:00:00	1:19:30	0:58:00	0:55:00
t_2 (hh:mm:ss)	1:54:00	1:42:28	1:31:45	1:48:20	2:13:00	1:53:40	1:20:00	1:38:40	1:41:00	
Q_1 (ml/h)	434	462	1014	417	429	421	600	453	621	545
Q_2 (ml/h)	211	769	654	695	451	528	750	608	594	

t1 = Time at passing 3 bed volumes (600 ml)
t2 = Time at the end of experiment or 5 bed volumes (1000 ml)
Q1 (ml/h) = Flow rate by the end of 3rd bed volume (600 ml)
Q2 (ml/h) = Flow rate by the end of experiment or 5th bed volume (1000 ml)
** Due to hard filteration work, Just 500 ml of M32 has been passed through the resin

Table 4: Isotope mass balance data on measured fractions of humic substances (HA = humic acid; FA = fulvic acid; LMW DOC = low molecular weight DOC) for the leachate samples (^{13}C isotopic values in ‰ VPDB).

Parameter		LP1				LP6				LPS				M32			
		Total DOC	HA	FA	LMW DOC	Total DOC	HA	FA	LMW DOC	Total DOC	HA	FA	LMW DOC	Total DOC	HA	FA	LMW DOC
Recovered Carbon	Mass (mg)	0.046	0.003	0.034	0.009	0.329	0.059	0.226	0.044	0.219	0.028	0.160	0.031	6.126	0.021	4.483	1.622
	$\delta^{13}C_{VPDB}$	-27.3	-29.3	-26.2	-26.8	-26.7	-22.0	-26.4	-27.4	-25.7	-22.9	-26.2	-27.1	-18.4	-28.1	-20.3	-8.0
$\delta^{13}C*M_C$		-1.3	-0.1	-0.9	-0.2	-8.8	-1.3	-5.9	-1.2	-5.6	-0.6	-4.2	-0.8	-112.7	-0.6	-91.0	-13.0
Sum			-1.2				-8.4				-5.7				-104.6		
Error (%)		2.8				3.8				0.8				7.2			

Table 5: Field parameters and the concentrations of cations and anions for the TRL leachate. All concentrations in mgl^{-1}, if not stated.

Well #	Date	Field Parameters				Cations ($mg\ l^{-1}$)											Anions ($mg\ l^{-1}$)						
		T (°C)	pH*	Eh (mV)	DO	B	Ba	Ca	Fe	K	Mg	Mn	Na	NH_4^+	S**	Sr	F	Cl	NO2	Br	NO3	PO4	SO4
LPS	April 21, 2005	na	na	na	na	2.9	0.1	12	0.4	170	48	0.1	346		6	1.5	0.2	476	0.7	2.9	0.4	1.0	12
LPS	May 5, 2005	na	na	na	na	4.8	0.4	252	0.9	283	80	0.9	653		8	11.2	0.4	699	0.8	4.4	0.8	2.6	36
LPS	May 12, 2005	na	na	na	na	4.0	0.3	235	0.7	216	74	0.8	479		5	10.5	0.2	664	1.3	3.8	0.7	1.3	15
LPS	May 19, 2005	na	na	na	na	2.7	0.2	115	0.4	163	49	0.3	344		4	7.3	0.5	761	1.0	3.6	3.1	2.5	11
LPS	May 27, 2005	na	na	na	na	5.8	0.5	288	1.1	349	108	0.8	738		7	15.2	0.6	743	0.6	2.8	1.9	1.9	15
LPS	June 2, 2005	na	na	na	na	3.8	0.4	169	0.7	222	70	0.4	457		5	10.4	0.5	707	1.4	5.7	1.2	3.1	2
LPS	June 10, 2005	na	na	na	na	3.0	0.3	139	0.5	170	52	0.4	352		4	8.1	1.1	680	0.7	4.2	1.7	1.1	3
LPS	June 16, 2005	na	na	na	na	3.8	0.4	144	0.9	245	49	0.4	622		34	7.7	1.0	680	2.0	5.2	2.4	0.9	78
LPS	June 21, 2005	na	na	na	na	5.7	0.5	239	1.1	321	92	0.6	713		10	14.1	1.1	710	1.5	2.5	1.3	1.3	15
LPS	June 23, 2005	na	na	na	na	5.2	0.5	245	1.0	291	91	0.8	627		8	13.5	2.5	646	0.7	2.5	1.4	1.2	16
LPS	July 7, 2005	na	na	na	na	4.6	0.5	189	0.9	276	79	0.5	605		8	12.2	0.5	795	1.6	3.9	0.7	1.2	10
LPS	July 20, 2005	20.6	6.7	227	0.4	3.2	0.3	99	0.4	180	54	0.1	386	357	5	9.4	0.4	830	0.8	3.0	1.0	1.1	18
LPS	Nov.14/2003	15.4	6.7	169	3.0	4.5	<1	194	1.9	223	113	0.6	580	336	24			625					
Average		**18.0**	**6.7**	**198**	**1.7**	**4.3**	**0.4**	**192**	**0.9**	**245**	**76**	**0.5**	**546**	**347**	**10**	**10.9**	**0.8**	**712**	**1.1**	**3.8**	**1.5**	**1.6**	**20**
LP1	July 20, 2005	20.8	6.6	192	2.5	4.2	0.2	152	0.1	104	37	0.5	334	79	34	1.7	0.1	371	5.9	2.4	97.0	2.2	108
LP6	July 21, 2005	26.0	6.9	347	0.1	10.4	1.0	173	1.7	538	137	0.2	1200	270	10	23.4	0.5	1250	0.9	7.4	1.1	2.3	26
LP1	July.7/2004	17.5	6.6	201	1.2	3.7	0.2	163	10.3	108	38	0.8	379	121	59	1.9	0.9	524	0.0	3.6	0.0	3.5	181
LP2	July.7/2004	15.3	7.1	na	3.4	7.6	0.2	59	0.3	278	60	0.1	621	222	82	1.8	1.3	493	1.2	2.6	29.2	4.8	159
LP3	July.6/2004	23.0	6.8	232	0.2	2.7	0.1	52	0.2	145	33	0.1	351	145	74	4.3	0.9	495	2.8	1.3	0.0	1.2	280
LP4	July.7/2004	22.3	6.6	198	0.2	4.9	0.2	103	1.5	191	75	0.2	536	244	134	9.4	0.0	356	0.0	2.6	0.0	3.2	233
LP5	July.7/2004	15.5	6.4	226	1.7	1.0	0.2	363	12.6	92	62	1.2	173	155	265	25.6	0.0	154	0.0	0.0	4.8	3.7	701
LP6	July.7/2004	15.1	6.9	251	3.1	4.8	0.2	61	0.5	249	104	Its	568	224	7	10.0	1.0	706	0.0	1.7	0.0	4.3	4
LP7	July.7/2004	15.9	6.9	227	3.1	3.0	0.4	111	Ins	162	81	Its	382	238	108	18.1	0.8	369	1.9	3.6	3.2	4.0	286
Average		**19.0**	**6.7**	**234**	**1.7**	**4.7**	**0.3**	**137**	**3.4**	**208**	**70**	**0.5**	**505**	**189**	**86**	**10.7**	**0.6**	**524**	**1.4**	**2.8**	**15.0**	**3.2**	**220**
M32	July 22, 2005	22.0	7.2	244		1.2	18.4	2108	34.5	123	498	2.6	1068	89	9	4.4	0.0	935	26.9	0.0	0.9	54.6	10
M32	July.6/2004	na	7.2	na		0.9	11.0	858	2.5	85	249	0.9	604	337	8	2.8	0.5	748	22.8	2.8	2.2	7.2	2
M32	Nov.7/2003	8.0	6.3	195	3.2	2.0	32.6	3378	32.5	167	706	7.8	1565	511	16			1581					
Average		**15.0**	**6.8**	**219**	**3.2**	**1.4**	**20.7**	**2115**	**23.2**	**125**	**485**	**3.8**	**1079**	**312**	**11**	**3.6**	**0.3**	**1088**	**24.9**	**1.4**	**1.6**	**30.9**	**6**

* In order to take the averrage of pH log values, first pH convert to H^+ (H^+=10^-pH), then pH recalculated from the average values of H^+ (pH=-log(H^+))

** Total S in samples

Table 6: Average, minimum and maximum concentrations and isotopic data of carbon pools and ^{2}H and ^{18}O of water for the TRL leachate. All isotopic data in ‰ VPDB (for ^{13}C) and in ‰ VSMOW (for ^{18}O and ^{2}H).

	DIC		DOC		CH_4		CO_2	Acetic Acid (Propionic Acid)		H2O			
	mg l^{-1}	$\delta^{13}C_{DIC}$	mg l^{-1}	$\delta^{13}C_{DOC}$	mg l^{-1}	$\delta^{13}C_{CH4}$	$\delta^{13}C_{CO2}$	mg l^{-1}	$\delta^{13}C$	$\delta^{2}H_{H2O}$	$\delta^{18}O_{H2O}$	^{2}H Shift*	^{2}H Excess**
Leachate from LPS													
Minimum	17	-5.0	27	-27.2	0.8	-59.4	2.2	23 (bl)	-17.0	-92.4	-15.4	1.3	5.6
Maximum	832	17.4	437	-17.7	3.2	-56.8	7.6	25 (bl)	-16.8	-40.2	-8.4	35.6	39.6
Average	349	10.7	197	-25.7	2.0	-58.1	4.9	24 (bl)	-16.9	-65.2	-10.7	16.3	20.6
Sdv.	201	4.2	98	1.5				1	0.1	13.8	1.4	8.0	7.9
n	41	41	41	41	2	2	2	3	3	41	41	41	41
Leachate from LP													
Minimum	258	0.9	24	-27.4	0.0	-64.4	-13.6	-	-	-88.0	-12.3	5.4	10.3
Maximum	901	12.7	225	-23.4	4.8	-22.7	7.8	-	-	-62.7	-10.0	18.2	22.4
Average	494	4.7	117	-26.0	1.6	-42.4	-0.9	-	-	-72.3	-11.0	11.0	15.4
Sdv.	206	3.8	61	1.2	1.5	10.7	6.1	-	-	7.1	0.8	4.1	4.2
n	9	9	9	9	9	9	9	-	-	9	9	9	9
Leachate from M32													
Minimum	200	7.0	4310	-28.8	1.6	-68.4	0.1	218 (29)	-13.7 (-20.6)	-73.0	-10.4	5.3	9.3
Maximum	339	10.7	5130	-17.4	6.8	-50.8	6.6	1755 (1313)	-10.7 (-18.5)	-68.4	-9.8	6.4	10.3
Average	290	8.5	4770	-21.6	4.8	-59.6	2.7	1008 (608)	-12.0 (-19.3)	-70.6	-10.1	5.8	9.8
Sdv.	78	1.9	419	6	1.4	12.4	3.4	815 (629)	1.5 (0.9)	2.3	0.3	0.6	0.5
n	3	3	3	3	3	3	3	4	4 (4)	3	3	3	3

*Over local meteoric water line (LMWL) **Over global meteoric water line (GMWL)

bl = below detectoion limit

Table 7: The sequence of principal redox reactions in landfill leachate along with their calculated standard Gibbs free-energy (ΔG_0) and the equation of stability line for each redox pair. By the addition of oxidized organic material (CH_2O), theoretical redox potential (Eh) decreases and the $\delta^{13}C$ values of DIC decreases (after Christensen et al., 2001; Clark and Fritz, 1997; Drever, 1997).

Reaction	**Process**	**ΔG_0 (kJ/mole)**	**Eh (mV)**	**$\delta^{13}C_{DIC}$**
O_2 reduction (respiration)	$CH_2O+O_2 \rightarrow CO_2+H_2O$ $(\frac{1}{2} O_2 + 2e^- + 2H^+ \Leftrightarrow H_2O)$ $pe = 20.78 - pH + \frac{1}{4}\log P_{O2}$	-502 -273		-15‰
NO_3^- reduction (denitrification)	$CH_2O+4/5NO_3^-+4/5H^+ \rightarrow CO_2+2/5N_2+7/5H_2O$ $(NO_3^- + 5e^- + 6H^+ \Leftrightarrow \frac{1}{2} N_2 + 3H_2O)$ $pe = 21.1 + 1/5 \log a_{NO3-} - 1/10\log P_{N2} - 6/5pH$	-509 -602		
Mn reduction	$CH_2O+2MnO_2+4H^+ \rightarrow CO_2+2Mn^{2+}+3H_2O$ $(MnO_2 + 2e^- + 4H^+ \Leftrightarrow Mn^{2+} + 2H_2O)$ $pe = 20.8 - \frac{1}{2} \log a_{Mn2+} - 2pH$	-502 -237		
Fe reduction	$CH_2O+4Fe(OH)_3+8H^+ \rightarrow CO_2+4Fe^{2+}+11H_2O$ $(Fe(OH)_3 + e^- + 3H^+ \Leftrightarrow Fe^{2+} + 3H_2O)$ $pe = 17.9 - \log a_{Fe2+} - 3pH$	-436 -102		
SO_4 reduction	$2CH_2O+SO_4^{2-}+H^+ \rightarrow 2CO_2+HS^-+2H_2O$ $2CH_2O+SO_4^{2-} \rightarrow H_2S+2HCO_3^-$ $(SO_4^{2-} + 8e^- + 9H^+ \Leftrightarrow HS^- + 4H_2O)$ $pe = 4.21 + 1/8\log (a_{SO42-}/a_{HS-}) - 9/8\ pH$	-247 -198 -192		
CO_2 reduction	$CO_2+4H_2 \rightarrow CH_4+2H_2O$ $HCO_3^-+4H_2 \rightarrow CH_4+2H_2O+OH^-$ $(CO_2 + 8e^- + 8H^+ \Leftrightarrow CH_4 + 2H_2O)$ $pe = 2.86 + 1/8\log (P_{CH4}/P_{CO2}) - pH$	-131 -95 -131		-26‰
Acetate Fermentation	$CH_3COOH \rightarrow CO_2+CH_4$	-48		
H_2O reduction	$H_2O + e^- \Leftrightarrow \frac{1}{2} H_2 + OH^-$ $pe = -\frac{1}{2}\log P_{H2} - pH$	80		

Table 8: Calculated parameters needed to plot the stability line of redox pairs on pe – pH diagram. All gas concentrations in atmosphere pressure.

	T (°C)	pH	Eh(mV)	pe*	α_{NO3-1}**	α_{Mn+2}	α_{Fe+2}	α_{SO4-2}	α_{HS-1}	P_{O2}	P_{N2}	P_{CH4}	P_{CO2}	P_{H2}	SI $_{cal}$***
LPS	18	6.7	198	3.4	1.8E-05	3.3E-06	5.3E-06	7.0E-05		0.09	0.2	0.48	0.2	1	0.1
LP	19	6.7	234	4.0	1.8E-04	2.7E-06	2.0E-05	7.6E-04	4.3E-04		0.05				0.1
M32	15	7.2	219	3.8	1.3E-05	7.5E-06	4.5E-05	7.0E-06	5.8E-04		0.18				1.2

* $pe = \frac{F}{2.303RT} \times Eh$, where F is Farady's constant (96.484 kJ/volt), R is the gas constant (8.314E-3 kJ/K.mol), and T is temperature in K

** $a_i = m_i \times \gamma_i \quad , \quad \gamma_i = \frac{-0.5 z_i^{\,2} \sqrt{I}}{1 + 0.33 a_i \sqrt{I}} + 0.3I \, , and \quad I = \frac{1}{2} \sum m_i \times z_i^2$

*** $SI_{Cal} = \log(\frac{IAP}{K_{sp-cal}}) = \log(a_{Ca^{2+}} \times a_{CO_3^{2-}}) + 8.48 = \log(a_{Ca^{2+}} \times \frac{a_{HCO_3^-} \times 10^{-10.33}}{10^{-pH}}) + 8.48$

Table 9: Distribution of the total dissolved organic carbon (DOC) into humic acids (HA), fulvic acids (FA), LMW DOC fraction, and the HPLC fractions of LMW DOC and the corresponding $\delta^{13}C$ values for the leachate samples. The ratio of humic/fulvic acids (HA/FA) have been calculated using HA and FA concentrations. (Some data reported in the literature for leachate are given for comparison).

	Total DOC		Humic Acid (HA)			Fulvic Acid (FA)			LMW DOC			HPLC Fractions of LMW DOC			HA/FA
	(mg L^{-1})*	$\delta^{13}C$ ‰	(mg L^{-1})	% of DOC	$\delta^{13}C$ ‰	(mg L^{-1})	% of DOC	$\delta^{13}C$ ‰	(mg L^{-1})	% of DOC	$\delta^{13}C$ ‰	(mg L^{-1})	% of LMW DOC	$\delta^{13}C$ ‰	
LP1	46.3	-27.3	2.9	6.3	-29.3	34.2	73.9	-26.2	9.2	19.9	-26.8	2.4	26.2	-29.2	0.09
LP6	329.3	-26.7	58.9	17.9	-22.0	225.5	68.5	-26.4	43.9	13.3	-27.4			-42.4	0.26
LPS	219.1	-25.7	28.2	12.9	-22.9	160.4	73.2	-26.2	30.5	13.9	-27.1	11.4	37.3	-34.8	0.18
M32	6125.8	-18.4	21.3	0.3	-28.1	4482.5	73.2	-20.3	1622.0	26.5	-8.0	226.4	14.0	-13.0	0.05
Literature (Nanny et al., 2002)			4 to 44 % of Total DOC			7 to 72 % of Total DOC									

* Sum of HA, FA and LMW DOC

Table 10: Relative abundances of major functional groups in humic acid (HA) and particulate organic carbon (POC) of leachate samples from TRL site as determined by solid-state ^{13}C-NMR.

Sample	Aliphatic C (%)	Aromatic C (%)	Carboxyl C (%)	carbonyl C (%)
	0–95 ppm	95–160 ppm	160–185 ppm	160–185 ppm
LP6-HA	58	20	19	3
LPS-HA	47	28	17	8
M32-HA	66	5	19	10
LP6-POC	48	17	19	16
LPS-POC	66	10	20	4
M32-POC	64	3	20	13

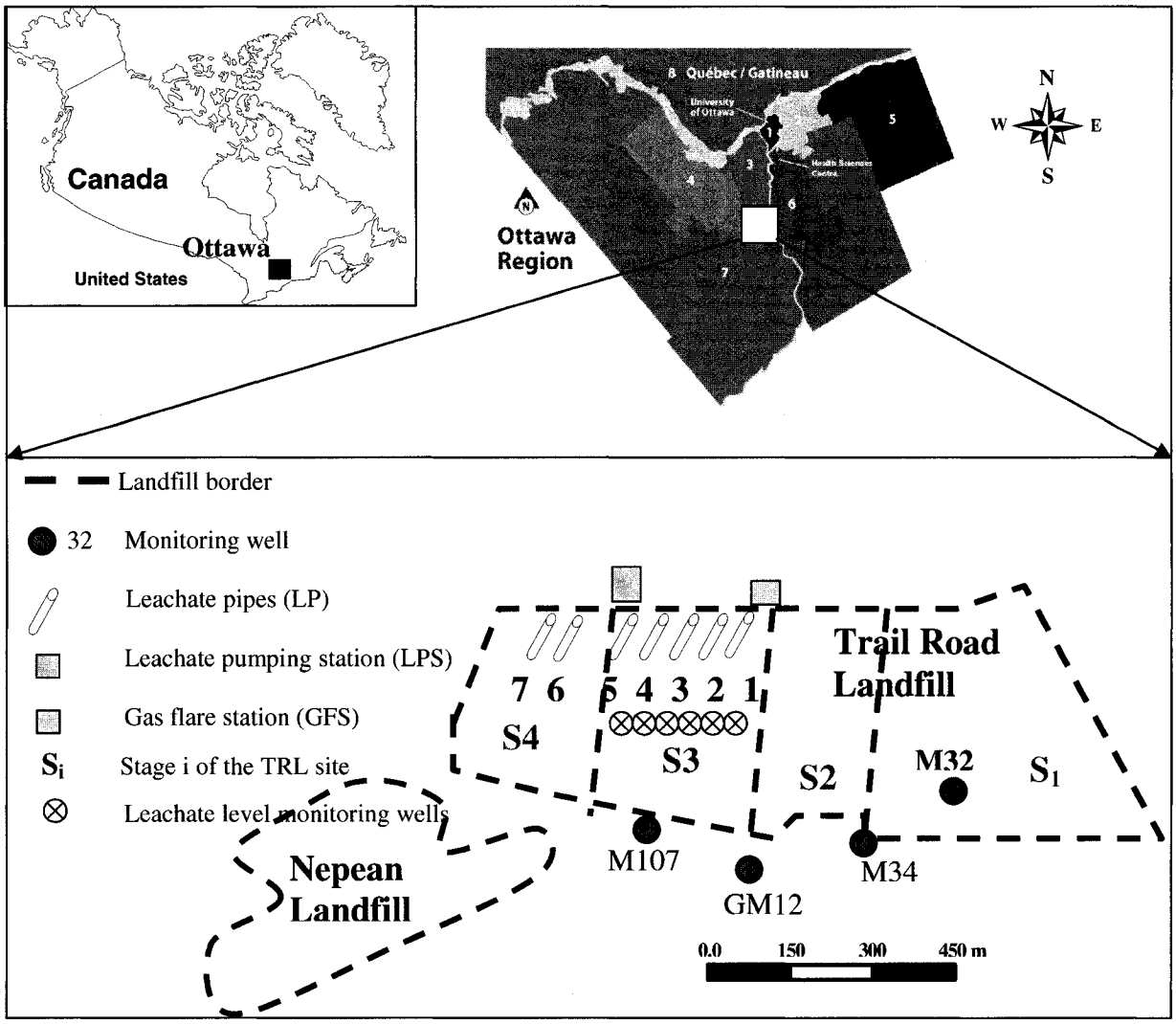


Figure 1: Plan view of study area and sampling location.

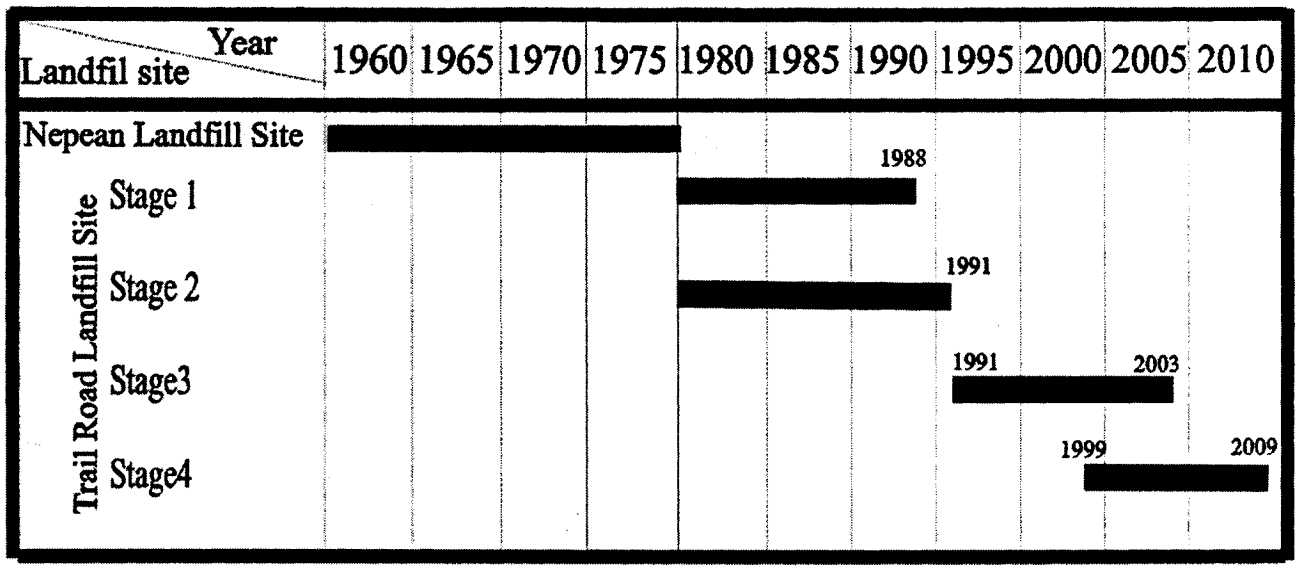


Figure 2: Site operation of TRL and the adjacent old Nepean landfill site.

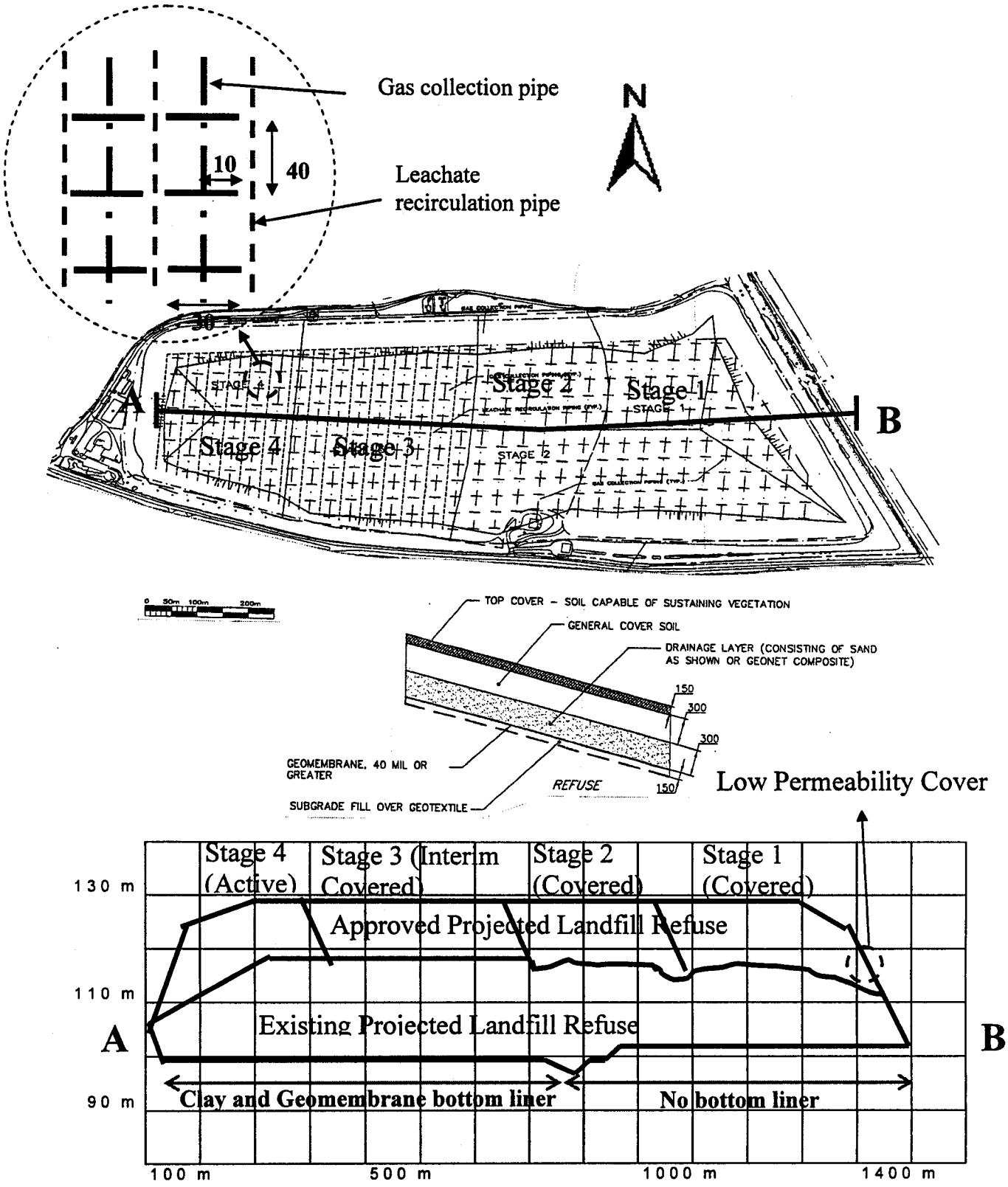


Figure 3: Schematic plan view of leachate recirculation and gas collection piping with a cross section to show vertical dimension and details of low permeability cover (City of Ottawa, 2002).

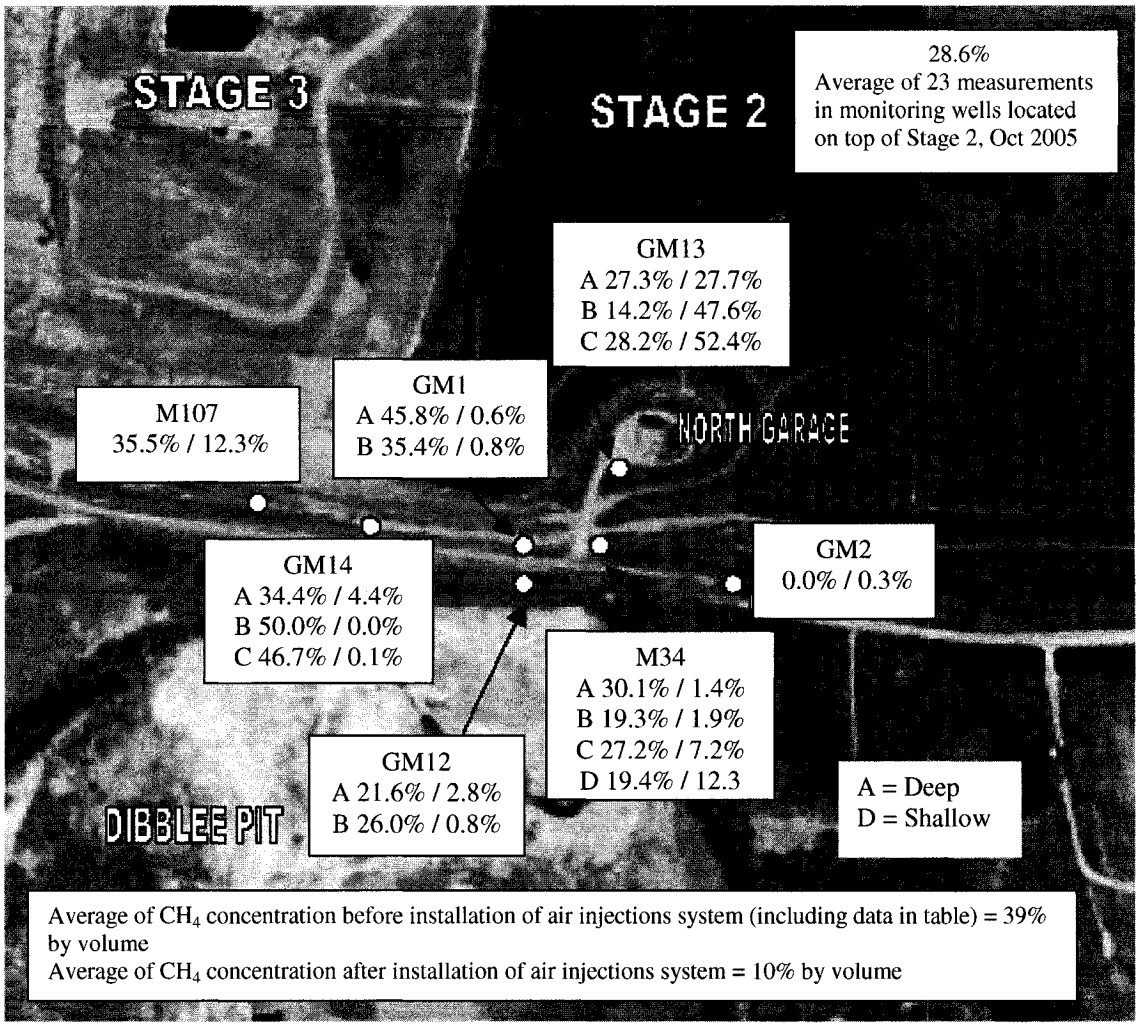


Figure 4: CH_4 concentrations for periods of January-July (before installation of an air injection system) and August-December (after installation of an air injection system) in 2005 (19.4 % / 6.4 % by volume). After Dillon Consulting Ltd., 2006.

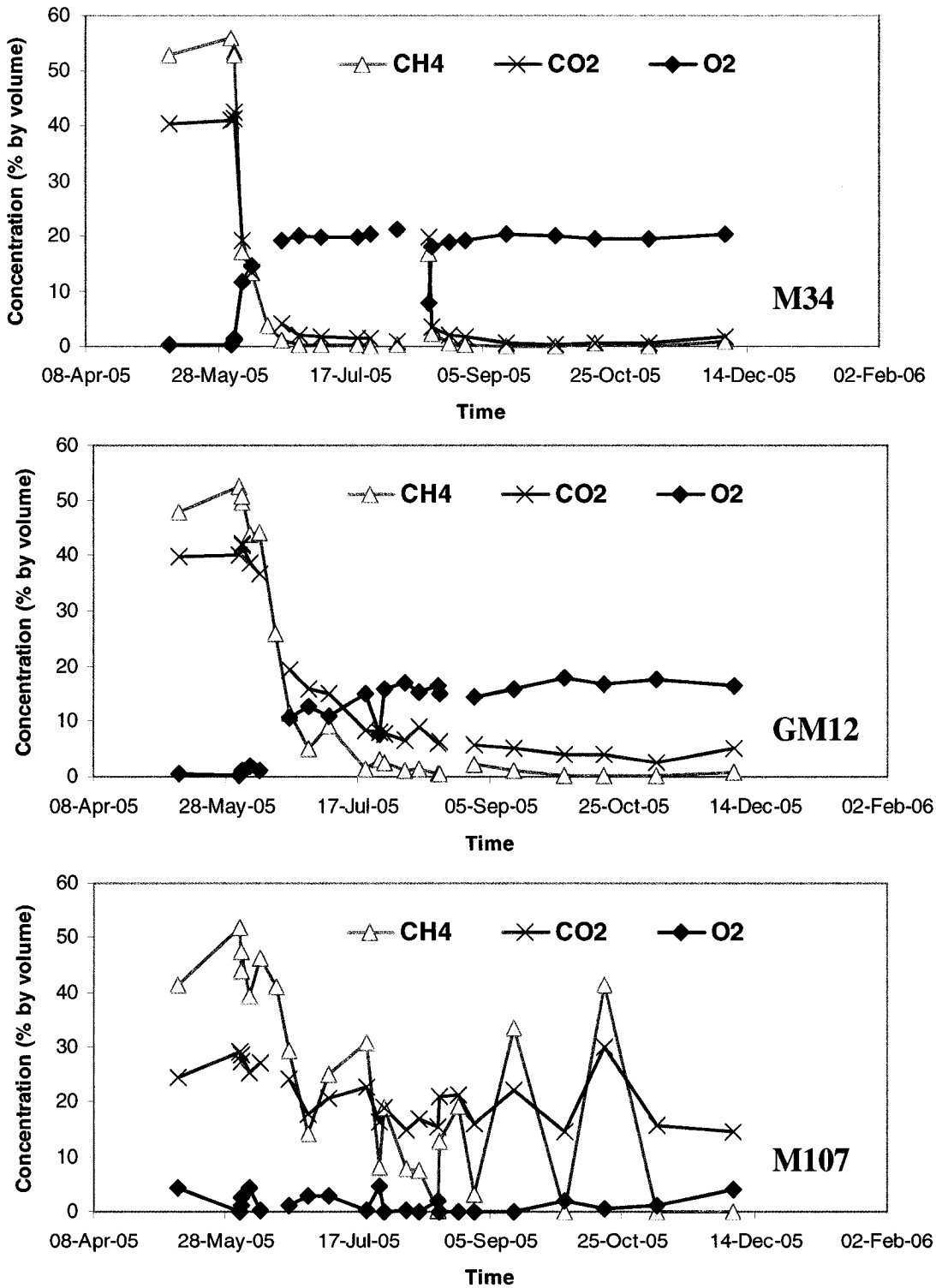


Figure 5: Variation of landfill gases (CH_4, CO_2 and O_2) in unsaturated zone (Data from Dillon Consulting Ltd., 2006).

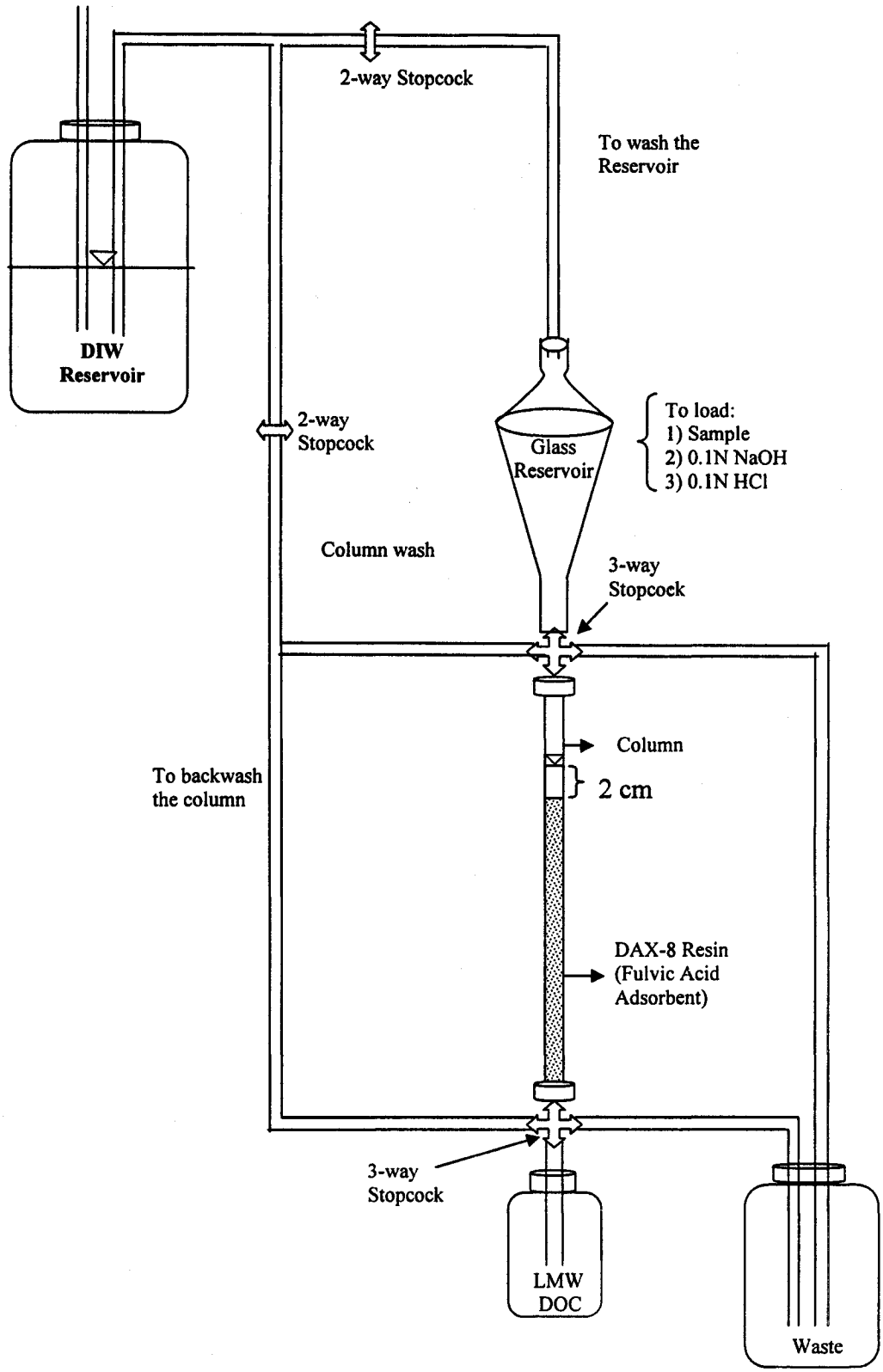


Figure 6: Schematic illustration of DAX-8 column to separate fulvic acid and LMW DOC fractions.

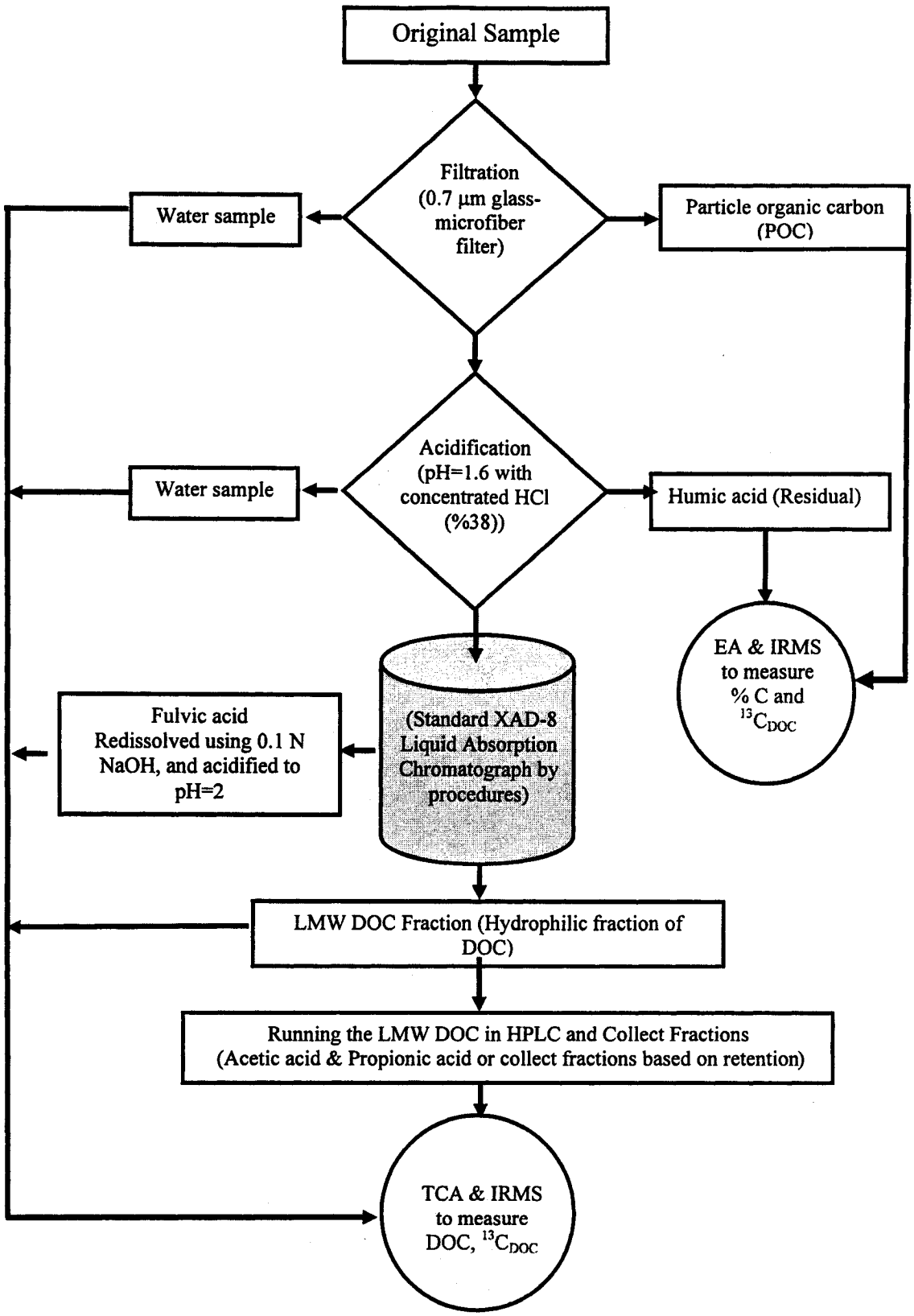


Figure 7: Isolation procedures and $\delta^{13}C$ measurements for the POC, humic acids, fulvic acid and LMW DOC fractions from leachate.

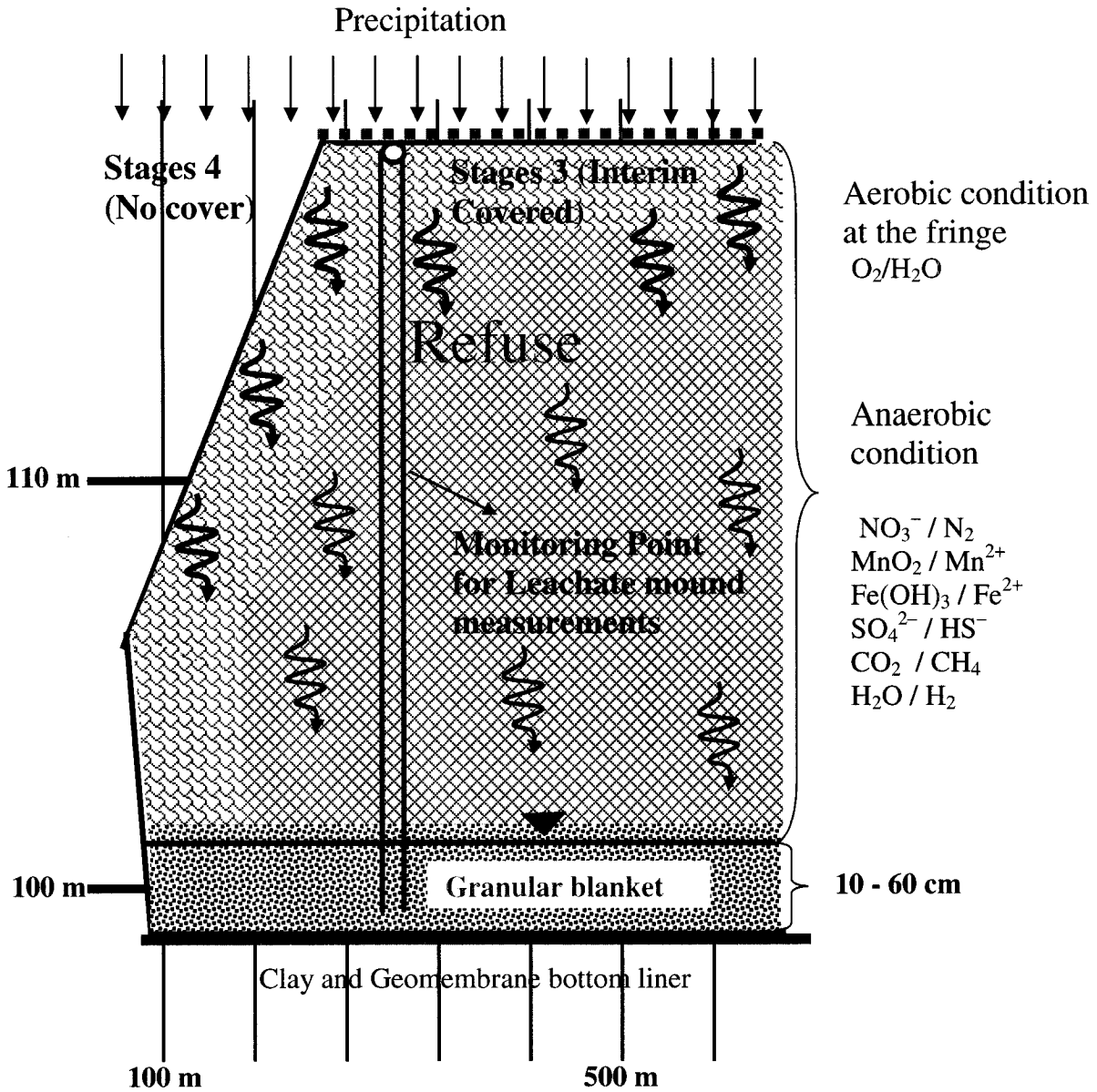


Figure 8: Schematic conceptual model for the hydrogeology of Stages 3 and 4 of the TRL site. The thickness of the aerobic fringe zone depends on the amount of precipitation and it changes by seasons.

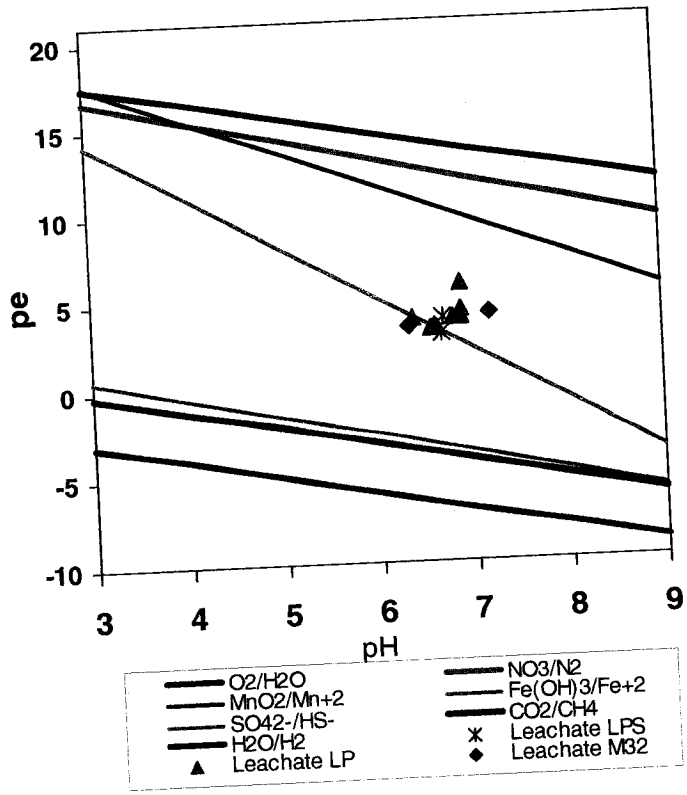


Figure 9: p*e* – pH diagram for principal redox buffering pairs in leachate from TRL site with plotted leachate samples. The stability lines were drawn based on equations in Table 7 and using calculated data in Table 8.

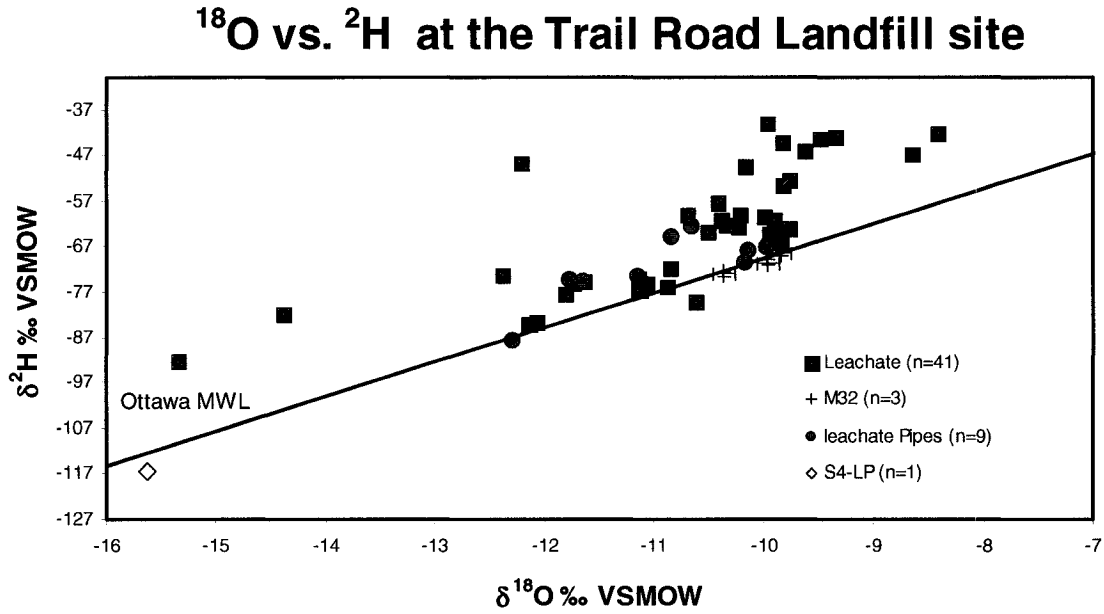


Figure 10: δ^2H and $\delta^{18}O$ of leachate water from the TRL site. The Ottawa meteoric water line (OMWL) is based on IAEA/WMO GNIP, 2004.

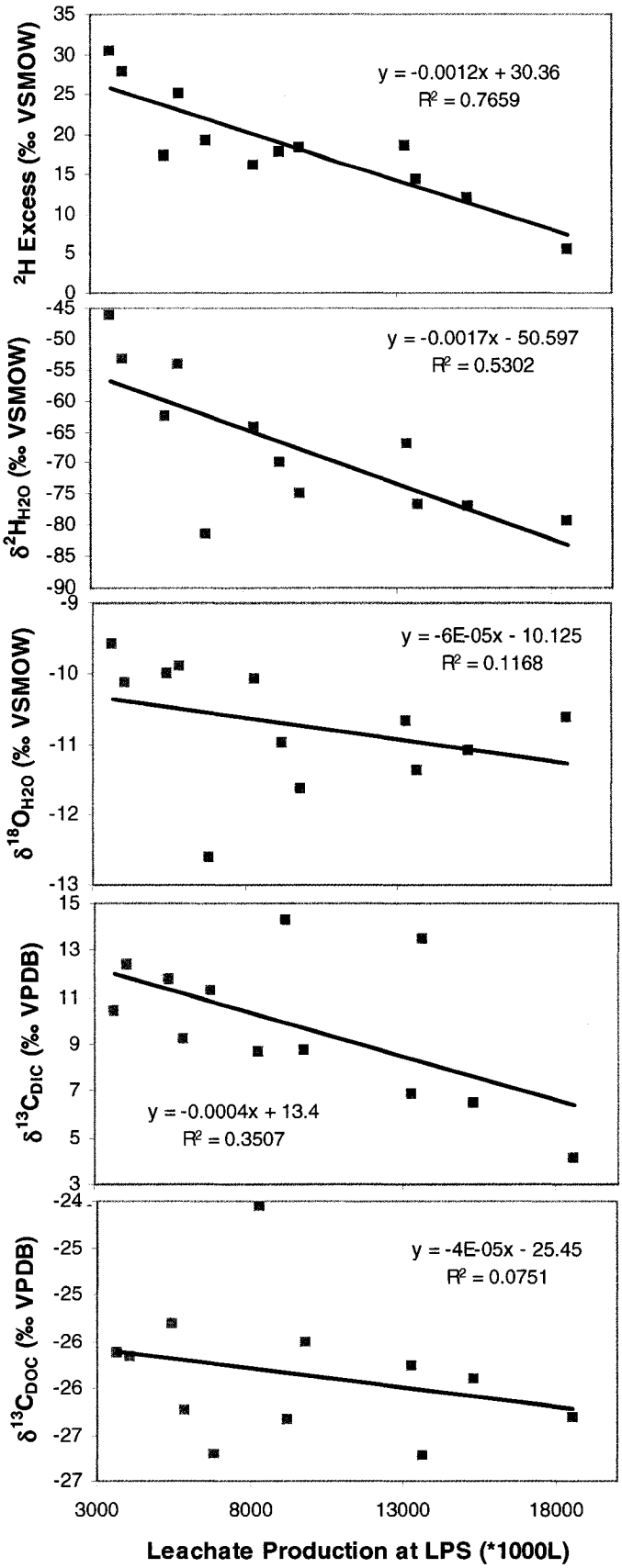


Figure 11: Correlation between leachate production at LPS with different isotopes (δ^2H_{H2O}, $\delta^{18}O_{H2O}$, $\delta^{13}C_{DIC}$, $\delta^{13}C_{DOC}$ values and ^2H excess).

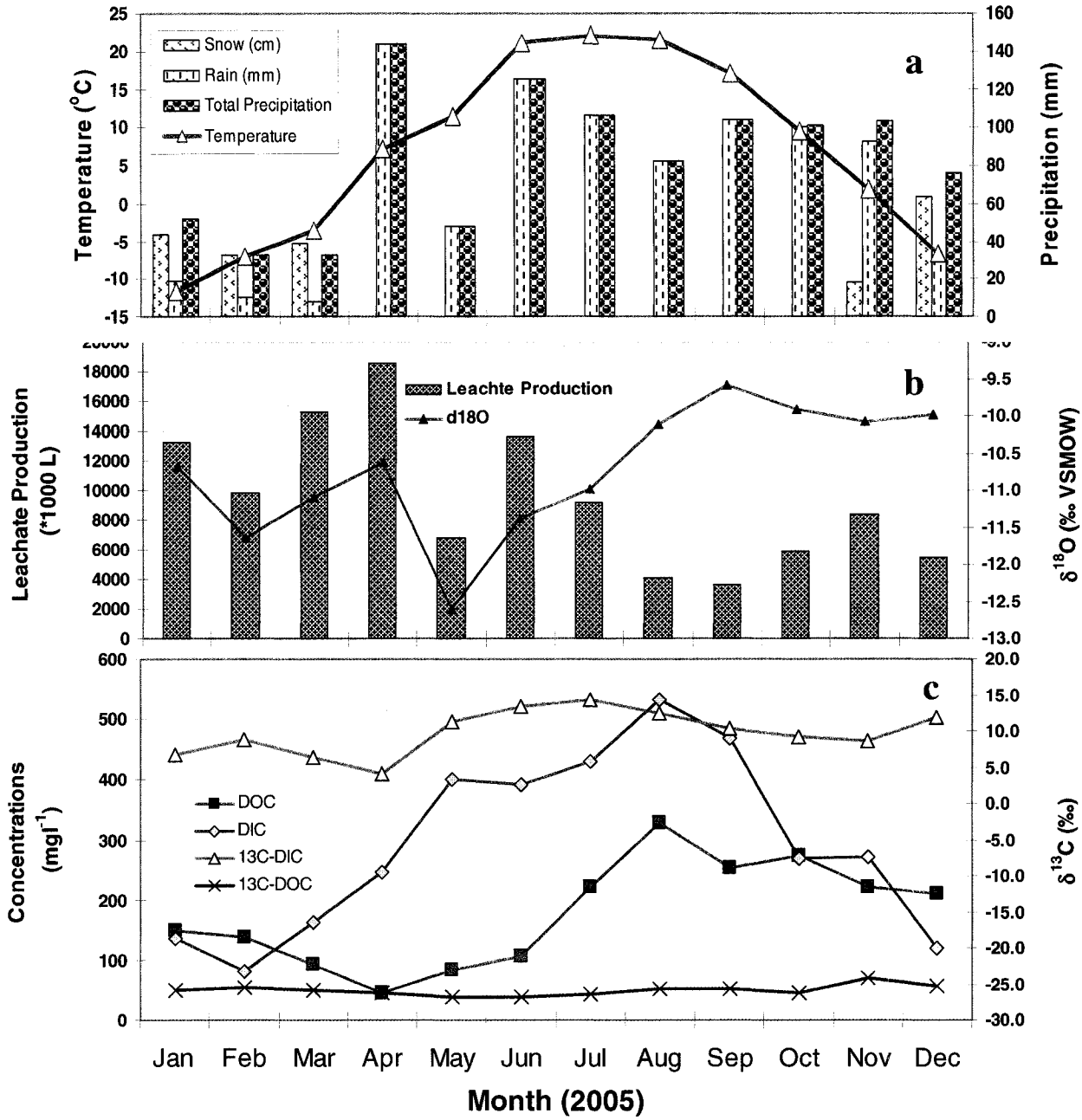


Figure 12: Variations of DIC, DOC and isotopic ($\delta^{13}C$) composition in leachate from LPS with time. The top histograms show the meteorological parameters (temperature and precipitation), the monthly production of the leachate at TRL site which was calibrated by inventories of truck loads (hauling leachate from LPS) and seasonal variation of $\delta^{18}O$.

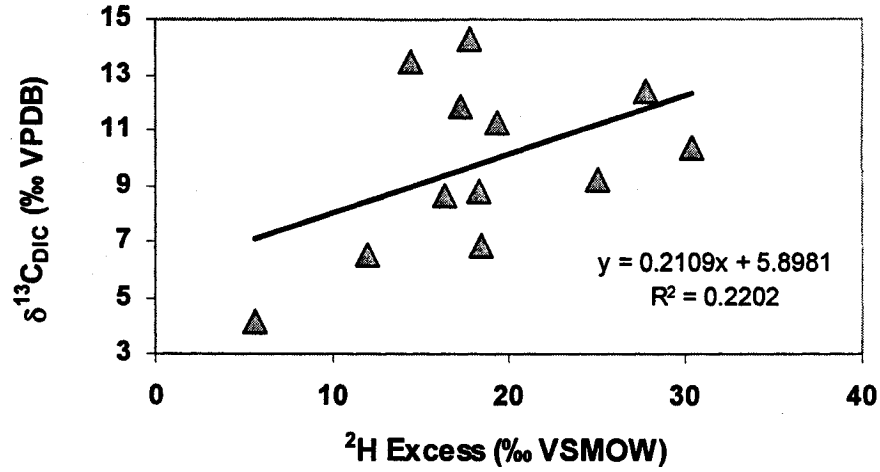
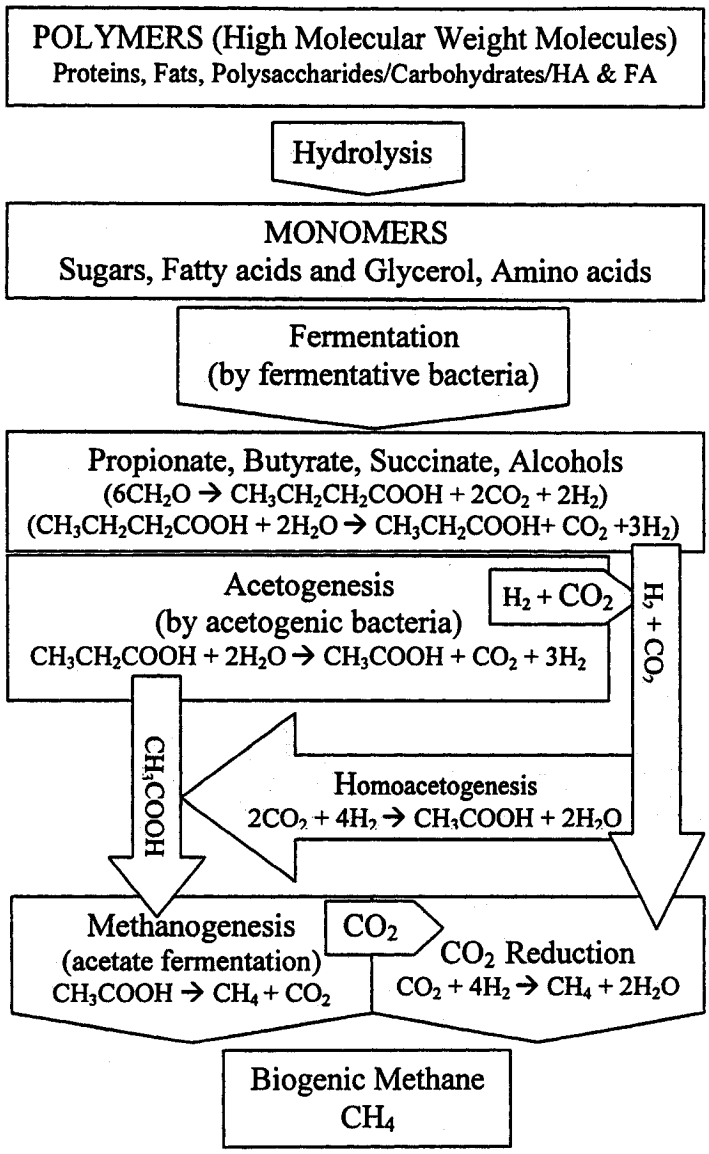


Figure 13: Correlation between ^{2}H excess with $\delta^{13}C_{DIC}$ values for leachate from LPS.



	LPS	M32
$\delta^{13}C_{DOC}$ (‰)	-25.7	-18.4
$\delta^{13}C_{HA}$ (‰)	-22.9	-28.1
$\delta^{13}C_{FA}$ (‰)	-26.2	-20.3
$\delta^{13}C_{LMW}$ (‰)	-27.1	-8.0
$\alpha^{13}C_{DOC-AA}$	1.028	1.021
$\delta^{13}C_{PA}$ (‰)	-	-19.3
$\delta^{13}C_{AA}$ (‰)	-16.9	-12.0
$\alpha^{13}C_{CO2-CH4}$	1.067	1.061
$\delta^{13}C_{CO2}$ (‰)	+4.9	+2.7
$\delta^{13}C_{CH4}$ (‰)	-58.1	-59.6

Figure 14: The general pathways of CH_4 generation and evolution of the $\delta^{13}C$ values for the DOC components during DOC degradation at anaerobic conditions (after Clark et al., 2004; Christensen et al., 2000; Bogner et al., 1996) in both young leachate (LPS) and older leachate (M32) at TRL site (DOC = total dissolved organic carbon, HA = humic acid, FA = fulvic acid, LMW = low molecular weight DOC, PA = propionic acid and AA = acetic acid). All isotopic data in ‰ VPDB.

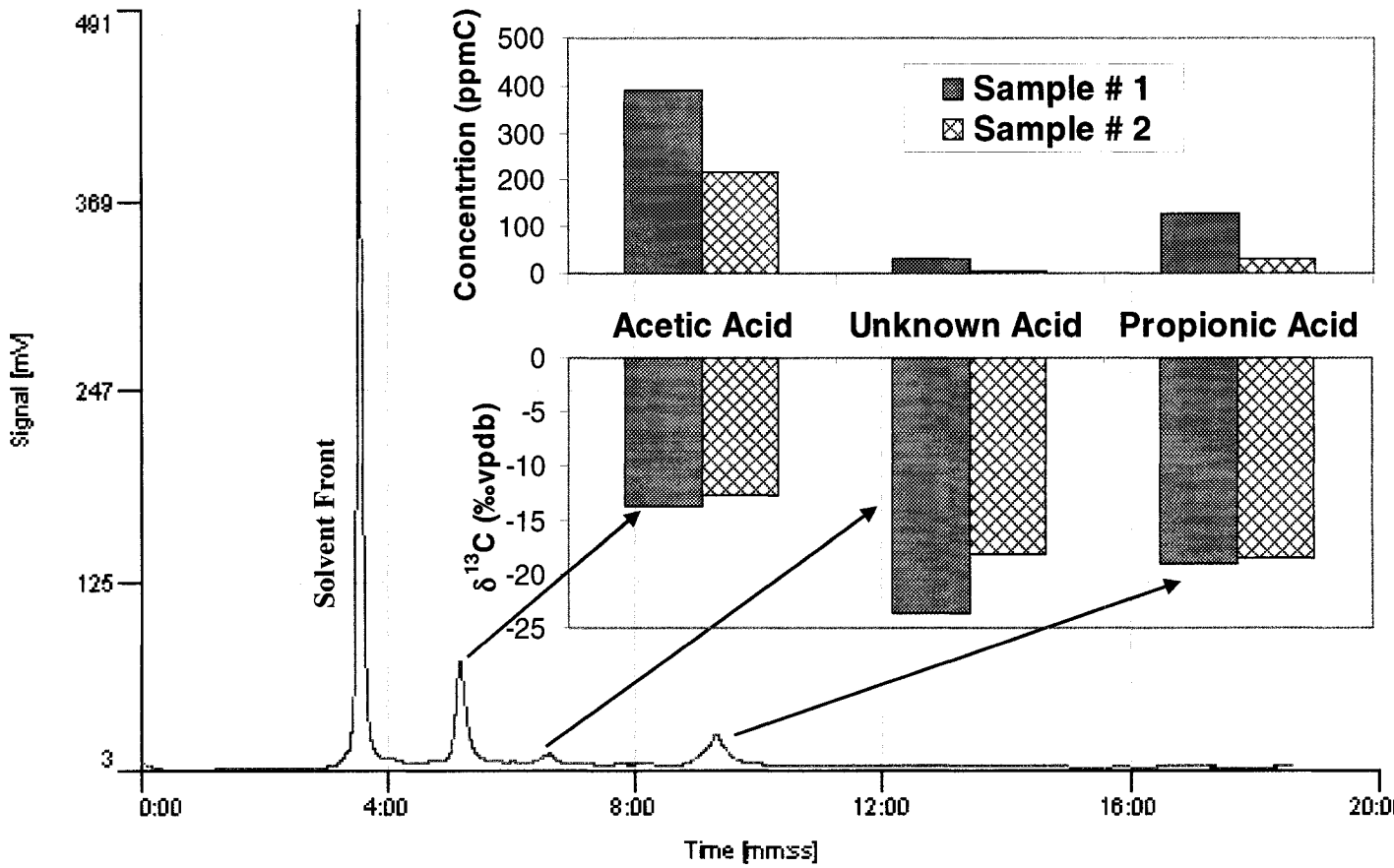


Figure 15: The HPLC chromatogram and the results of collected fractions of acidified samples from M32. For the details of experimental parameters refer to Mohammadzadeh et al., 2005.

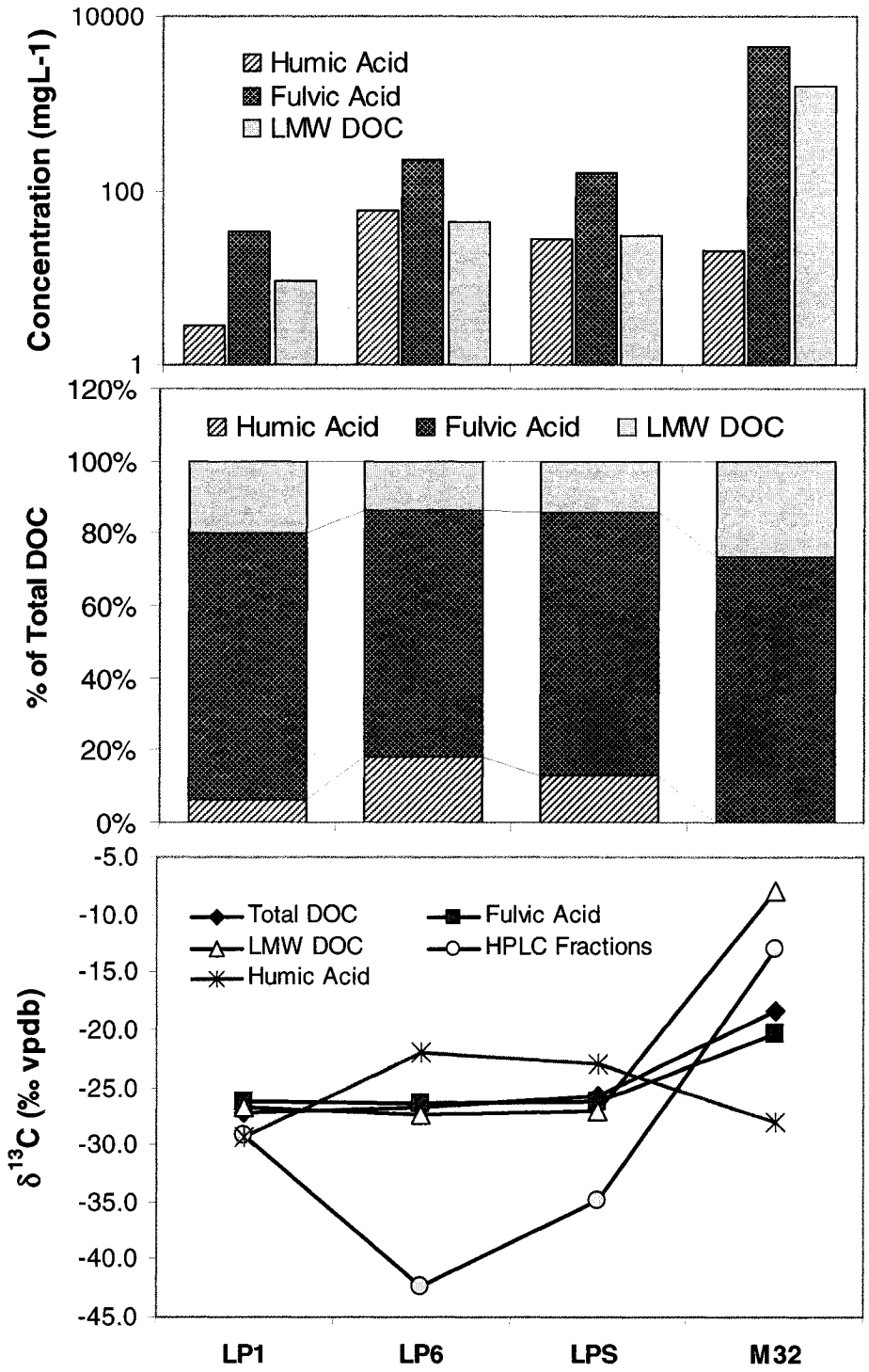


Figure 16: Concentrations and the distribution of humic substances and variations of the $\delta^{13}C$ values of DOC fractions in leachate samples.

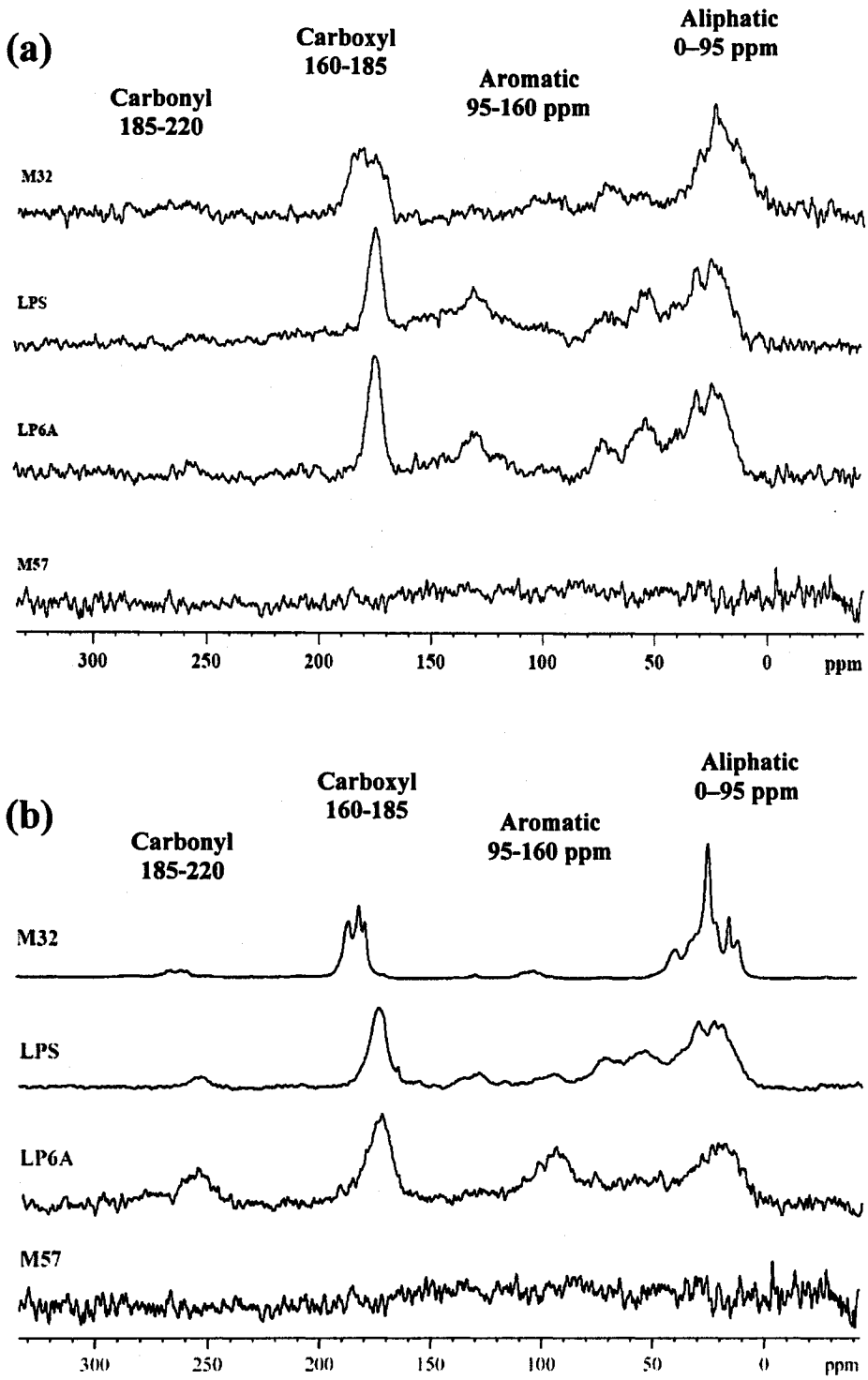


Figure 17: ^{13}C-NMR spectra for HA (a) and POC (b) of leachate samples from M32 and LPS.

Tracing landfill leachate impact on groundwater using carbon geochemistry and environmental isotopes (^{13}C, ^{18}O and ^{2}H)

Abstract

Assessing the impact of landfill leachate on local groundwaters using geochemical parameters is often confounded by naturally elevated concentrations of indicator compounds like Cl and DOC. Here, environmental isotopes are used to provide a constraint in this assessment, for leachate derived from the Trail Road Landfill, Ottawa, Ontario. The carbon geochemistry of different carbon pools (DIC, DOC, CH_4, CH_3COOH, humic substances (HS), and particulate organic carbon (POC) and particulate inorganic carbon (PIC)) and $\delta^{13}C$ were used to recognize leachate impact on the surrounding groundwater.

The most unambiguous leachate indicator parameters remain dissolved methane and $\delta^{13}C_{DIC}$. In all proximal groundwaters, methane concentrations remain above detection and as high as 10 mgl^{-1}, close to the saturated equilibrium value for a 50% methane atmosphere in the unsaturated zone. The $\delta^{13}C$ value of methane demonstrates reactive loss of acetate in the leachate plume by methanogenic fermentation, and methane oxidation in the plume fringe. The enriched $^{13}C_{DIC}$ for the shallow and deep aquifers (averages of -6.4 ‰, -1.0 ‰ and -0.6 ‰ for the shallow, upper deep and lower deep aquifers, respectively) in comparison to the upgradient pristine groundwater with -15.2 ‰ also confirm that the leachate (+8.8‰ and +10.7‰ for leachate taken from M32 and LPS, respectively) has had an impact on these aquifers. The low amount of DIC associated with the low amount of Ca^{2+} suggests a mineralogical control through calcite precipitation.

Continued reaction of DOC in groundwaters is confirmed by deviation of groundwater samples from the mixing lines on diagrams of DIC vs. $\delta^{13}C_{DIC}$ and DOC vs. $\delta^{13}C_{DOC}$, and by the absence of acetate. The calculated net reacted (lost) DOC (988 mgl^{-1}, 368 mgl^{-1}, and 272 mgl^{-1} for the shallow, upper deep and lower deep aquifers, respectively) correlated with net gains in DIC (185 mgl^{-1}, 117 mgl^{-1}

and 85 mgl^{-1} for these aquifers, respectively) is further evidence for continued reaction beyond the landfill.

Production of ^{13}C-depleted organic carbon, possibly through methanotrophic bacterial activity, seems to occur in the fringes of the advancing leachate plume. Evidence includes remarkably depleted $^{13}C_{DOC}$ in the lower part of the deep aquifer where values lower than –40‰ were measured. Further, the humic acid (HA) and fulvic acid (FA) components dominate the DOC of the leachate impacted groundwater (76 % to 87 % of total DOC content). The HA/FA ratio is below unity, which contrasts with un-impacted groundwaters where HA represents the major DOC component.

Keywords: Trail Road Landfill (TRL) leachate, carbon pools (DIC, DOC and CH_4), environmental stable isotopes ($\delta^{13}C$, $\delta^{2}H$, and $\delta^{18}O$), groundwater, acetate fermentation.

1. Introduction

Leakage of landfill leachate pollutants from unlined landfill sites over time is a source of groundwater contamination and may pose a threat to groundwater resources. Nonetheless, many of the geochemical components of leachate may also be found naturally in groundwaters, or have been derived from other sources. Leachate contains a mixture of labile dissolved organic constituents, the composition of which is very dependent on landfill refuse of the respective site (Baedecker and Back, 1979a; Christensen et al., 1998; Hornibrook et al., 2000; Christensen et al., 2001). Decay and dissolution of these organic constituents through bacteria-mediated reactions will generate different major carbon pools, such as DIC, DOC, and CH_4, within both the refuse pile and the leachate plume (Baedecker and Back, 1979b).

As demonstrated in earlier research (Liu et al., 1992; Hackley et. al., 1996; Clark and Fritz, 1997; Hornibrook et al., 2000; Van Breukelen 2003; Van Breukelen et al., 2003 & 2004; North et al., 2004 & 2006), the biogeochemical processes associated with refuse decomposition within the landfill environment and outgassing of CO_2 not only can produce characteristic ^{13}C signatures in the major carbon pools, but also generate ^{2}H enriched of water in landfill leachate.

Hackley et al. (1996, 1999) has conducted extensive research on isotopic compositions characteristic of landfill leachates and gases. In comparison to pristine groundwater, landfill leachate and leachate-impacted groundwater contain elevated ^{13}C in CO_2 and DIC due to production of ^{13}C-depleted CH_4, providing a tool to trace the origin of carbon pools and a

means to distinguish CH_4 from different sources (Schoell 1988; Whiticar et al., 1986; Coleman and Risatti, 1981; Coleman et al., 1988; Liu et al., 1992; Desrocher and Lollar, 1998). This $\delta^{13}C$ technique has been applied to identify the source of methane in non-landfill leachate-impacted groundwater systems (Barker and Fritz, 1981; Whiticar et al., 1986; Schoell 1988; Zhang et al., 1998; Desrocher and Lollar, 1998) and also contaminated groundwater systems related to anthropogenic landfill CH_4 (Baedecker and Back, 1979a, 1979b; Bonger et al., 1996; Fritz et al., 1994; Hackley et al., 1996; Desrocher and Lollar, 1998; North et al., 2006). Most of the research on CH_4 has focused on ^{13}C and ^{2}H and the carbon isotope fractionation (α_C) between coexisting carbon species to determine the methane origin, whether biogenic or thermocatalytic, in groundwater systems (Barker and Fritz, 1981; Balabane et al., 1987; Coleman et al., 1988; Aravena and Wassenaar, 1993; Aravena et al., 1995; Hornibrook et al., 2000).

In landfill leachate environments, the bacterial breakdown of organic waste contributes high concentrations of low molecular weight fatty acids to the dissolved organic carbon pool (Baedecker and Back, 1979a). New analytical methods now allow routine isotopic analysis of bulk DOC and the lighter weight components of DOC (Marschner et al., 2005; Mohammadzadeh et al., 2005a; St-Jean 2003). This additional characterization of a major carbon pool provides additional insight to the geochemical pathways of methane production and DIC evolution in the landfill and groundwater. This approach is applied here for leachate and groundwater samples collected from a leachate pumping station (LPS), from leachate pipes (LP) and from several nested monitoring wells on and around the Trail Road Landfill (TRL) site. The objective of this work is to identify unambiguous isotope signatures in the

leachate carbon system that provide evidence of leachate contamination in marginally impacted groundwaters.

2. Site setting and hydrostratigraphy

The TRL is owned and operated by the City of Ottawa and is located approximately 25 km west of the city (Figure 1). It is situated on a Northwest-Southeast ridge of glacio-fluvial sand deposit which is extended out to the Jock River, and locally confined by clay. The sequence of sediments are glacial outwash sand and gravel, then clay overlain by sand. The clay layer is discontinuous with windows in some parts of the study area. The TRL and the adjacent old Nepean landfill (NL) sites are located on the east and the west side of this ridge, respectively (Figure 2).

The TRL is divided into Stages 1 through 4 (Figure 1). Only Stages 1 and 2 of the TRL and NL, which are covered with a low permeability geomembrane consisting of 40 millimeter low density polyethylene (LDPE) liner in 1988, 1991, 1993, respectively, were based on natural attenuation landfill designs with no bottom liners and no leachate collection system. The last two stages of TRL, Stages 3 and 4, are both equipped with a composite bottom liner of clay (60 cm) and a high density polyethylene (HDPE) geomembrane liner (80 mil) with overlying geotextile fabric. These stages are also equipped with a leachate collection system including recirculation and evacuation to a leachate pumping station (LPS). Stage 3 was covered with an interim cover in 2003. Stage 4 is the only stage of the landfill which is active and it is currently in operation (City of Ottawa, 2002; Dillon Consulting Ltd., 2005 and 2006).

Based on the geological history of the study area, monitoring well logs, and observations, there are both a shallow and a deep aquifer in this area, separated by a discontinuous clay aquitard (Figure 2, Figure 3 and Figure 4). The deep aquifer is confined where it is overlain by the clay-confining unit (northern and western portions of the site) and it is unconfined below the southern half of Stages 1, 2 and under most of Stages 3 and 4. The thickness of the deep aquifer varies from several metres to 25 m in the centre of the sand and gravel ridge hosting the landfills. Prior to the excavation of the dewatering pong (DWP), in windows where the clay is absent, the shallow aquifer is contiguous with the deep aquifer (Figure 3a). The excavation of dewatering ponds in the late 1980s in a sand and gravel deposit located northwest of the landfill site (Figure 1) reversed the natural upward hydraulic gradient from the deep aquifer to the shallow aquifer (Figure 3b). The dewatering ponds have lowered the water table of the deep aquifer making the shallow aquifer perched in some locations. Over the clay aquitard, shallow groundwater flows northward and follows the general slope of the underlying clay which varies approximately 20 m in elevation over the study area. In the deep aquifer, flow is toward the Jock river and the DWP located northwest of the TRL site. Several individual and nested piezometers representing more than 200 monitoring wells were installed by City of Ottawa to sample the groundwater (Figure 1). The nested piezometers were screened at different depths including the shallow aquifer, the upper deep aquifer, and the lower deep aquifer. (Golder Associates Ltd., 2001, 2002, 2003; City of Ottawa 2002; Dillon Consulting Ltd., 2004, 2005, 2006).

Both shallow and deep aquifers at the TRL site are highly permeable. In the shallow aquifer, the geological material tends to be more consistent than that of the deep aquifer, which varies

from fine to medium sand to silty sand. In the deep aquifer, the materials vary from fine silty sands to cobbles with more coarse materials at the base (more gravel) and it contains a complex sequence of coarse sands and gravels overlying bedrock (City of Ottawa 2002).

3. Sampling and analytical methods

3.1.Sampling

As discussed in previous chapters, leachate samples were taken from the LPS, leachate pipes (LP) and from the M32 monitoring well. In this paper focus was also placed on monitoring wells selected to represent shallow and deep groundwater, as well as some background sites (Figure 1). Samples were taken from multilevel monitoring wells located down-gradient and up-gradient of the TRL site in 2003 through 2005. Geochemical parameters measured in the field included electromotive potential (Eh), pH, dissolved oxygen (DO), and temperature (T) using appropriate meters and an in-line flow-through cell.

To measure concentrations and ^{13}C of dissolved inorganic and organic carbon (DIC and DOC), 40 ml samples were collected using amber glass bottles. To measure inorganic anions and inorganic cations and the $\delta^{2}H$ and $\delta^{18}O$ of the water, 30 ml samples were collected using plastic bottles. About 0.1 ml ultra pure nitric acid ($HNO3^{-}$), as preservative, was added to the cations bottle. Samples with headspace were collected to measure the methane concentration and isotope values of methane and CO_2 in the saturated zone (groundwater samples) using 125ml Wheaton glass bottles. To isolate and measure dissolved organic carbon fractions

(humic and fulvic acids, light molecular weight DOC and fatty acid fractions), 4L samples within amber glass containers were collected from selected monitoring wells in July 2005.

Since DOC concentrations can change during storage due to bacterial activities, all samples were immediately transported to the geochemistry and isotope laboratories. Samples (filtered with 0.45 μm membranes – to remove bacteria and suspended solids) were stored at 4°C prior to analysis to limit microbial activity and were analyzed within 2 weeks. The suspended solids from each 4L amber glass were analysed for total carbon (TC) contents and $\delta^{13}C$. 4L samples for analysing the organic compounds were filtered using 0.7 μm glass-microfiber filters (Whatman cat No. 1825047) and acidified to below pH 2 with concentrated HCl.

3.2. Analytical methods

A detailed description of analytical techniques is given in the previous chapter and by Mohammadzadeh et al. (2005a). A variety of analytical techniques were used to analyze dissolved and precipitated organic and inorganic compounds, including ion chromatography (IC), inductively coupled plasma atomic emission spectroscopy (ICP-AES), gas chromatography (GC), DAX-resin adsorption chromatography, elemental analyser (EA), high performance liquid chromatography (HPLC), total carbon analyzer (TCA) and isotope ratio mass spectrometry (IRMS). In order to eliminate cross contamination, column work (DAX-resin and HPLC work) started with loading upgradient reference groundwater sample (M57) followed by leachate-contaminated groundwaters (M39-7, M37-2, M4-1, M37-3, M34), then leachate samples (LP1, LP6, LPS, M32). All measurements were performed in the geochemistry and G.G. stable isotope laboratories at the University of Ottawa. The

results of field parameters, cations and anions, and calculated parameters (electron activity (*pe*), ionic strength (*I*) and calcite saturation index (SI_{cal})), for all groundwater samples (collected 2003 through 2005), and the results of isotopic analysis are summarised in Table 1 and Table 2, respectively.

4. Results and discussion

In the following, the characteristics of background uncontaminated groundwater (reference groundwater) and of the contaminant source (leachate) are described. Then, the impact of leachate on the surrounding aquifers and leachate interaction with groundwater will be discussed using some key leachate indicators (chloride (Cl), bromide (Br), ammonia (NH_4) and DOC), redox conditions, carbon geochemistry, and ^{13}C isotope characteristics of DIC and DOC components.

4.1. Characteristics of the background uncontaminated groundwater

To characterize the reference groundwater, three monitoring wells: M57 and M79 located upgradient (UG) and M120 located downgradient (DG) of the landfill site (Figure 1) were sampled in 2003 through 2005. Review of the available geochemical data shows no evidence of leachate influence at these locations. As tabulated in Table 1 and Table 2, there is no evidence for the high concentrations of leachate indicator parameters (methane, chloride (Cl), bromide (Br), ammonium (NH_4) and DOC) in reference groundwater from both M57 (UG) and M120 (DG). Nor is there an enriched $^{13}C_{DIC}$ which is an important leachate indicator parameter. The concentrations of redox sensitive elements (Fe (II), Mn, methane and ammonium (NH_4)) are below detection limit and there is little DOC (0.5 to 0.9 mgl^{-1}) or

NH_4 (0.1 mgl^{-1}). The pH of groundwater from both M57 and M120 is about 7.5. The calcite saturation index ($logSI_{cal}$) of groundwater in M57 and M120 is equal to 0.1 indicating marginal saturation.

As tabulated in Table 1, the concentration of Cl^-, which is a conservative ion, for the upstream M79 monitoring well (737 mg l^{-1}) is much higher than that of M57 and M120 monitoring wells (73 and 42 mg l^{-1}, respectively). This is attributed to road salt from Cedarview Road and Highway number 416. The historical data at this monitoring well (M79) show evidence of road salt impact from the adjacent roadways.

DIC and DOC concentrations in upstream M57 (53 mg l^{-1} and 0.9 mg l^{-1}) and downstream M120 (50 mg l^{-1} and 0.5 mg l^{-1}) are almost the same. However, the concentrations of these parameters in M79 are much higher (104 mg l^{-1} and 8.7 mg l^{-1}). This shows evidence for leachate contamination or contamination by anthropogenic activities related to the adjacent highway (e.g. road salting; dust control, de-icing, etc.). Therefore, the groungwater quality data of M79 was excluded for required calculations as a reference groundwater.

4.2. Characteristics of the TRL leachate

As mentioned in the previous chapter, TRL contains two main parts; 1) the currently closed and capped unlined Stages 1 and 2, which are up to 30 years old and have no leachate collection system; and 2) currently active Stages 3 and 4, opened in 1991, that are lined and equipped with a leachate pumping station (LPS). The leachate from unlined parts of the

landfill (Stages 1 and 2) and also from the adjacent unlined Nepean landfill, is recognized as the main source of contamination that has been observed in the downgradient groundwaters.

In order to examine the geochemical environment and characteristics of the leachate loading from the unlined parts of the TRL site, samples were collected from M32, located on the southern portion of Stage 1, in 2003 through 2005. M32 is an important on-site monitoring well that captures pure undiluted leachate at the base of the unlined landfill. In M32 samples were pumped from the saturated zone, which is representative of leachate conditions as the main source of contamination for the underlying aquifers.

The main characteristics of the M32 leachate are summarized in Table 3. The concentration of all ions and of carbon pools (DIC, DOC and CH_4) were significantly elevated relative to reference groundwater values at this location. Leachate indicator parameters, including chloride, DIC, bromide (Br), and DOC, were observed to be significantly elevated relative to reference groundwater values (Table 1 and Table 2) at this location. Presence of methane, Fe (II), ammonium (NH_4^+), plus high concentrations of DOC (4770 mgl^{-1}) indicate strongly reducing conditions at this sampling point. These ions compete with DOC for electron-acceptors at the plume fringe.

Column separations (DAX-resin and HPLC) and CSIA of DOC fractions indicated that the M32 leachate is characterized by 1) acetic acid (1755 mgl^{-1} with $\delta^{13}C$ value of -12 ‰) and propionic acid (1313 mgl^{-1} with $\delta^{13}C$ value of -19.3‰) (Table 3); 2) acetogenic fermentation

competes with methane production in the unlined Stages 1 and 2 (previous chapter), and 3) FA is the main fraction of the HS (69% to 74% of total DOC content of leachate) (Table 4).

Landfill gas (LFG) monitoring at the TRL site has detected both CH_4 and CO_2 (with average concentrations of approximately 39% and 30% by volume, respectively, in 2005) south of the unlined Stages 1 and 2. In addition, the large amount of gas collected from unlined Stages 1 and 2 at the gas flare station (1.1E+10 L with 42% by volume CH_4, in 2005) indicates methanogenesis within the unlined parts of the landfill. This process has imparted enriched ^{13}C in DIC (+8.8 ‰) and enriched ^{2}H in leachate water (with average deuterium excess of 10‰ VSMOW over global precipitation) for the leachate from M32 (Table 3). Even more enriched $\delta^{13}C_{DIC}$ (+10.7 ‰) and $\delta^{2}H$ (average deuterium excess of 21‰) values were observed in young leachate from LPS.

4.3. Leachate-impacted groundwaters – inorganic parameters

As described in section 2, shallow and deep overburden aquifers overlie the carbonate bedrock aquifer. The water quality of the bedrock aquifer is potable and this water tapped by local water supply wells (City of Ottawa 2002). Water quality in both shallow and deep aquifers is variable, however, with evidence for impact from leachate originating from unlined parts of the landfill.

Elevated concentrations of traditional leachate indicator parameters (Cl, Br and NH_4) indicate that both shallow and deep aquifers have been contaminated along the north border of the unlined parts of the TRL site. A review of the data shows that among the monitoring

wells located in the shallow aquifer, groundwaters from M33 (located at the north part of Stage 1) and from both M37-3 and M4-2 (located at the north of Stage 1 and 2) have levels of Cl, Br, NH_4 and DOC that exceed background concentrations. In 2005, the concentrations of these indicators at M37-3 were 377, 5.1, 17.5 and 31 mg l^{-1}, respectively.

Impact on the deep aquifer beneath and beyond the southern portion of Stage 1, where there is no clay layer, is less obvious due to greater attenuation by dilution. In 2005, high concentrations of some leachate indicator parameters such as Cl (234 mg l^{-1}) and NH_4 (3.5 mg l^{-1}) were detected in M28. M4-1, located at the north border of Stage 1, is also affected by leachate indicated by high Cl concentration (132 mg l^{-1}).

Leachate impact is also suggested by reduced species, including total iron, which in these neutral pH groundwaters is taken to be Fe(II). Variable, but low NO_3^- in most wells is further evidence for reducing conditions from leachate. The p*e* – pH conditions for groundwater samples plot below the denitrification boundary (Figure 6). Nonetheless, generally reducing conditions throughout the deeper aquifer (City of Ottawa 2002) compromises this parameter as a tool to identify leachate impact.

Carbon species, including DIC, DOC and CH_4, as intrinsic components of leachate, can aid in the identification of leachate mixing in low-impacted groundwaters. Moreover, the distribution of DOC compounds as well as the ^{13}C contents for these different species represent an additional tool that can provide unambiguous evidence for the impact of leachate on marginally-impacted groundwaters. This is explored in the following sections.

4.4. Leachate-impacted groundwaters – DIC, DOC and ^{13}C

DOC is a fundamental leachate indicator parameter, with broad compositional variation. While a bulk parameter, it provides a first indication of leachate contamination in adjacent groundwaters. This parameter can also be used to show temporal trends that reflect leachate inputs prior to and after covering the unlined landfills. The effect of capping is shown by the response in M33, completed in the shallow aquifer within the boundaries of Stage 1, where DOC dropped rapidly immediately after capping of this Stage in 1988 (Figure 7a). The shallow groundwaters in M4-2 and to a lesser extent at M37-3 follow similar attenuation trends (Figure 7b) following capping of Stages 1 and 2.

Unlike the shallow aquifer, the DOC concentration in M32, completed in the zone of recharge to the deep groundwater within the boundaries of Stage 1, was highly elevated in the past and has decreased from a peak in 1995, several years after Stage 1 was covered in 1988 (Figure 8a). Figure 8b shows DOC variations in the deep aquifer beyond the landfill at M4-1, M37-2, and M39-7 (located north of Stage 1, Stage 2 and Stage 3, respectively). These are influenced by leachate and exhibit temporal trends similar to M32 (Figure 8a). Noteworthy is a spike in concentration of DOC for most sites in 1994, which followed excavation of the dewatering ponds in the late 1980s. This action reversed the upward flow from the deep aquifer, inducing migration of the leachate plume downward into the deep aquifer. Subsequent capping of stages 1 and 2 reduced the leachate component infiltrating the deep aquifer, providing the attenuation observed in Figure 7b.

Figure 9 and Figure 10 show the composition of DIC vs. $\delta^{13}C_{DIC}$ and DOC vs. $\delta^{13}C_{DOC}$ for the leachate and groundwater from different aquifers. Mixing lines were drawn based on $\delta^{13}C$ mass balance between two end members including the pristine groundwater–PG (at M57) and leachate (M32), using equations (1) and (2).

$$\delta^{13}C_{Mixture} = \frac{f\left(\delta^{13}C_{DC-Leachate} \times DC_{Leachate}\right) + (1-f)\left(\delta^{13}C_{DC-PG} \times DC_{PG}\right)}{f \times DC_{Leachate} + (1-f) \times DC_{PG}} \quad (1)$$

$$DC_{Mixture} = f \times DC_{Leachate} + (1-f) \times DC_{PG} \quad (2)$$

in which, DC represents either DOC or DIC, and f is the leachate fraction.

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 in Figure 9a and Figure 10a, 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. In addition, plots for the individual monitoring sites (Figure 9b and Figure 10b), indicate most samples are enriched in ^{13}C in both DIC and DOC over background waters.

The evolution of DIC for individual wells is plotted in Figure 11. For some, the DIC vs. $\delta^{13}C$ plot suggests simple dilution. Others deviate from the mixing zone, providing evidence for reactive attenuation. For instance, fermentation reactions (e.g. acetate fermentation) result in enriched $^{13}C_{DIC}$ for the gained DIC (e.g. M4-1, M23-1 and M23-2 on Figure 11). Combined with calcite precipitation, such groundwaters plot above this mixing line. On the other hand,

the oxidation of DOC using any of O_2, NO_3^-, ferric iron or SO_4^{2-} will impart a negative shift in $^{13}C_{DIC}$ for the gained DIC (e.g. M4-2, M37-3, M16-3 and M16-1 on Figure 11) and study groundwater would plot below the mixing line.

The high concentrations of acetate measured in M32 are not present in groundwaters and so has been lost by reaction. The acetate fermentation (^{13}C enrichment) is modeled in Figure 12. The acetate concentration in M32 leachate is 1008 mgl^{-1}. As illustrated in Figure 12a, the initial input of acetate from M32 depends on the dilution factor (df). Fermentation of this acetate results in increased DIC and enrichment of $^{13}C_{DIC}$. However, maximum $\delta^{13}C$ values from this reaction do not reach the highly enriched values observed in the groundwaters, which exceed 15 to 20‰. Further, the measured DIC concentrations are much lower than would be predicted by simple acetate fermentation. This suggests that DIC may have a secondary control, likely by calcite precipitation. Table 1 shows that calcite is close to equilibrium or slightly oversaturated in all groundwaters, and this accounts for the low Ca^{2+} concentrations as compared to M32.

By contrast, the oxidation of DOC results in depletion of $^{13}C_{DIC}$ (Figure 12b), and an increase in the DIC. Here, model results show that simple oxidation reaction would produce higher DIC concentrations than measured, again suggesting a mineralogical control through calcite precipitation. This is further supported by the decrease in Ca^{2+} from over 2 g/L in M32 to close to background levels (< 100 mg/L) in groundwaters, which is greater than can be accounted for by simple dilution.

Calculated dilution of DOC in groundwaters using leachate dilution factors, confirms reactive loss. The leachate dilution factor (df-leachate) in the groundwater has been calculated using the Cl concentrations as a conservative ion from both pristine groundwater - PG (at M57) and the leachate (at M32) end members.

$$df_{leachate-i} = \frac{Cl_i - Cl_{(Background)}}{Cl_{(Leachate)} - Cl_{(Background)}} \Rightarrow df_{PG-i} = 1 - df_{leachate-i} \quad (3)$$

Using the calculated leachate dilution factor, the initial concentrations and the net loss of DOC, and also the net gain in DIC and CH_4 have been calculated for each individual monitoring well using the following equations. The average of these values is summarized in Table 5.

$$\begin{aligned} DOC_{(Unreacted)_{initial}} &= \left(df_{leachate-initial} \times DOC_{Leachate}\right) - DOC_{Background} \\ DIC_{(Initial)_{initial}} &= \left(df_{leachate-initial} \times DIC_{Leachate}\right) - DIC_{Background} \\ CH_{4(Initial)_{initial}} &= \left(df_{leachate-initial} \times CH_{4\,Leachate}\right) - CH_{4\,Background} \end{aligned} \quad (4)$$

The average amounts of net reacted (lost) DOC for the shallow, upper deep and lower deep aquifers are about 988 mgl^{-1}, 368 mgl^{-1}, and 272 mgl^{-1}, respectively, which are correlated with significantly lower net gains in DIC for these aquifers (185 mgl^{-1}, 117 mgl^{-1} and 85 mgl^{-1}, respectively). This means DOC is oxidized at the fringe of the plume or is consumed via microbial redox reactions, and DIC is sequestered by calcite precipitation, as discussed above. The positive correlation between lost DOC and measured DIC and CH_4 in different aquifers (Figure 13) also confirms the production of methane and DIC via reactions.

Samples from the deeper zones of the lower aquifer are more depleted in $\delta^{13}C_{DOC}$ (-30 ‰ and lighter) than the other parts of the aquifer (Figure 10a). This is a very unusual feature of DOC evolution, and was initially suspected as being due to contamination by CH_4 during measurement of DOC. However, before measurement of $\delta^{13}C_{DOC}$, the DIC and CH_4 were removed from samples by extensive purging with He (Mohammadzadh et al., 2005a), and so these depleted values of $\delta^{13}C_{DOC}$ are considered to be valid. As reported in the literature, ^{13}C values of organic material range from -20‰ to -30‰ (Kerfoot et al., 2003) and that of DOC originating from landfill leachate ranges from -24‰ to -30‰) (Van Breukelen 2003).

Oxidation of dissolved organic carbon (decarboxilation or, in general, disproportionation reactions) could be responsible for both the more negative $\delta^{13}C_{DOC}$ and the decreased DOC at the lower part of the deep aquifer (3.0 mgl^{-1}, -32.3 ‰) (Figure 10a). In decarboxilation and disproportionation reactions, the ^{13}C would go preferentially to the oxidized molecules (CO_2) while ^{12}C become preferentially accumulate in the remaining reduced organic molecules like fatty acids (Roberto Gonfiantini, personal communication). However, this fractionation process is not observed during the generation of light fatty acids in the M32 leachate, as discussed in the previous chapter, where the residual DOC becomes enriched in ^{13}C.

Alternatively, we can consider the generation of DOC through consumption of a ^{13}C-depleted substrate. Here, methane is a likely candidate. In the fringes of the advancing leachate plume, where electron acceptors such as O_2 and ferric iron may reside in the aquifer, bacterial growth using a methane substrate may potentially produce a secondary organic carbon source. The much depleted ^{13}C signature of this carbon substrate would be translated

to the bacterial cells and degradation products, and may be the source of light DOC now measured at low concentrations in these deep groundwaters. However, these remarkable depletions have only been recorded in the 2003 and the 2004 sampling periods. DOC from the 2005 samples had $\delta^{13}C$ that is in the usual range (~ –26‰) for primary organic matter, suggesting that this is a transient effect that may be related to bacterial activity at the fringe of the plume.

4.5. Methane in groundwaters

Methane is formed in the landfill settings by the bacterial disproportionation of light fatty acids and by CO_2 reduction with H_2, the two predominant metabolic pathways. The methane concentration in pristine groundwater is below the detection limit (0.2 mgl^{-1}). Near the landfill, CH_4 concentrations in both the shallow and deep aquifers average about 2 mgl^{-1}, although with considerable variability. Review of the data (Table 2) for the shallow aquifer indicate that M33, M4-2 and M43 (located on top, north and south of the Stage 1, respectively) have CH_4 concentrations (3.0, 7.3 and 6.3 mgl^{-1}) which are significantly below methane saturation. CH_4 saturation is calculated to be 22 mgl^{-1} at 1 atmosphere pressure but can be greater under the higher pressures at depth below the water table. If methane in these groundwaters was derived by equilibration with influxing groundwaters that equilibrated with the phreatic zone atmosphere of up to 50% methane, then dissolved methane concentrations on the order of 5 to 10 mg l^{-1} could be anticipated. The upper deep aquifer beneath Stage 1 (at M32 and M28) and parallel to the north border of the landfill (at M4-1, M37-2, M23-2, M39-4&7, M16-2 and M77-2) is also undersaturated with methane, with maximum values of 9.9 mgl^{-1} at M4-1. The lower part of the deep aquifer (at M23-1, M39-1

and M77-1) also has minor dissolved methane (Figure 14). Nonetheless, these concentrations are greater than would be present in these groundwaters by simple dilution of M32 leachate, and suggests in-plume methane production.

Groundwater samples taken from shallow and deep aquifers have $\delta^{13}C_{CH4}$ values (averages of -56.0 and -51.5‰, respectively, Table 6) that are about 10‰ higher than the average of –60‰ for primary methane from the landfill. Based on Whiticar and Faber (1986) diagram, this methane falls into the high end of the range for biogenic methane which is consistent with production via fermentation of ^{13}C enriched acetate such as observed in M32 (-12‰). Less likely is methanogenesis via CO_2 reduction as the DIC in most groundwaters is not enriched in ^{13}C, and also as this requires a source of H_2 which is produced in the waste pile via primary anaerobic fermentation reactions. The cross plots of the $\delta^{13}C$ data of coexisting CH_4 and CO_2 (Figure 15a) has been suggested by Whiticar and Faber (1986) to provide insights to distinguish aceticlastic methanogenesis from CO_2 reduction. While confounding processes such as contributions of ^{13}C depleted DIC from oxidation of organic carbon and oxidation of methane which enriches the residual CH_4 in ^{13}C can affect such interpretations, this diagram nonetheless suggests that the acetate fermentation in the leachate plume is the main source of methane in these groundwaters.

The δ^2H - $\delta^{18}O$ diagram (Figure 5) shows that the leachate-impacted groundwaters from both the shallow and upper deep aquifers plot on or below the OMWL. The absence of a deuterium excess in these waters reflects both dilution and lack of significant methane production. Shifts in δ^2H 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.

Evidence for the loss of methane by oxidation within the plume fringe in some groundwaters comes from the enriched $^{13}C_{CH4}$ values that exist for those groundwater, with values as high as -20‰. Methane oxidation imparts an enrichment of ^{13}C on the residual methane (Bonger et al., 1996) where microbial oxidation preferentially consumes the isotopically lighter CH_4 (Coleman and Risatti, 1981; Whiticar et al., 1986; Hackley et al., 1999). The high amount of DIC and the more negative $\delta^{13}C_{DIC}$ values in some monitoring wells support the involvement of the methane oxidation process (Figure 15b).

4.6. Leachate-impacted groundwaters – ^{13}C in DOC compounds

The dilution and evolution of the high and low molecular weight organic carbon fractions in the leachate-impacted groundwaters were investigated though separation and ^{13}C analysis of humic substances (HS), particulate organic carbon (POC) and the low molecular weight organic carbon fraction (LMW). This work focused on monitoring wells located along the north border (M4-1, M37-2 &3, M39-7) and along the south border (M34) of the landfill as well as the upgradient reference groundwater (M57).

HS were isolated from leachate-impacted groundwater according to the procedure using DAX-8 resin described in the previous chapter. The carbon concentrations and isotopic analysis for the collected HS and HPLC fractions of LMW DOC are tabulated in Table 4.

The percentages of the DOC present as FA and LMW DOC were estimated using the measured data (Table 4).

4.6.1. Evolution of dissolved organic carbon compounds

Figure 16 shows the distribution of HA, FA and the LMW DOC fractions of leachate-impacted groundwater DOC. In general, the HMW DOC (HA and FA) dominate the DOC of the leachate-impacted groundwater (76 % to 87 % of total DOC content). In the reference groundwater, HA is the major fraction of the HS (62% of the total DOC). However, in the leachate-impacted groundwater, FA is the major fraction (ranging from 55 % to 85 % of total DOC content) which is consistent with the leachate FA at M32 (previous chapter).

The LMW DOC fraction makes up 12 to 18% of the total DOC with the lowest percentages at M37-3 in the shallow aquifer. This differs from M32, for which LMW fatty acids (acetic and propionic) dominate, suggesting that this labile component of the DOC has been consumed through continued reaction in the leachate plume beyond the landfill. The predominance of HS in the groundwaters is supported by other studies done by Artiola-Fortuny and Fuller (1982), Artinger et al. (2000), and Wassenaar et al. (1990) who mentioned that the HMW DOC (hydrophobic fraction) could be the dominant fraction in the DOC pool. The calculated humic/fulvic acids (HA/FA) ratios for the leachate-impacted groundwater are below unity which is consistent with that of M32 leachate (Table 4).

With the exception of M34 ($\delta^{13}C_{DOC}$ = –38.9‰; discussed below), the $\delta^{13}C$ of bulk DOC in leachate-impacted groundwaters is close to -26.5 ‰, a value typical of C3 type vegetation, and hence shows no indication of secondary fractionation. This is in sharp contrast with the DOC measured in M32 which shows significant enrichment in ^{13}C. The distribution of ^{13}C between components of the bulk DOC, tabulated in Table 4 and graphed in Figure 16, adds some insight. On average, the $\delta^{13}C$ value of the LMW DOC fractions is close to the bulk value. For most sites, the $\delta^{13}C$ value of FA, the major fraction of HS, is about –21‰, ^{13}C-enriched compared to that of total DOC and intermediary between that measured in M32 (–20.3‰) and background FA (–22.1‰). This suggests that the FA in these groundwaters is simply derived from dilution of the leachate source in background groundwater with little subsequent modification.

DOC at M34, situated on the southern boundary of Stage 1, follows a dramatically different evolution, as discussed above. The $\delta^{13}C$ values of all DOC components, and in particular the HA and LMW fractions, are considerably depleted in ^{13}C compare to other sites. Remarkable at this site is the apparent production of HA with a very depleted $\delta^{13}C$ value. This is unrelated to degradation of organic substrates from the landfill, which produces HA with values close to –26‰ (i.e. M32 and other groundwaters). Clearly, production of high molecular weight compounds from a ^{13}C-depleted source is occurring. Cell synthesis using methane as both an energy and carbon source is suggested.

4.6.2. Total carbon, POC and PIC in suspended solids

Total carbon (TC) and the percentages of particulate organic carbon (POC) in suspended solids (SS) for the contaminated samples provide useful information on the degree of leachate influences. The $\delta^{13}C$ variation of TC in SS depends on contribution of leachate derived POC and PIC from geological materials. The results of TC and POC measurements, calculated PIC using isotope mass balance, and elemental composition of SS with their corresponding $\delta^{13}C$ values have been tabulated in Table 7.

As illustrated in Figure 17, more than 70% of the carbon content in leachate SS from LPS and LPs, more than 95% at M32, is organic, as particulate organic carbon (POC). POC contributes 10 % to 30 % of TC in collected precipitated material in leachate-impacted groundwater from monitoring wells (except for the M34 which contains more then 95% POC). Noteworthy is a large mineral component in solid material filtered from some of these leachate-impacted groundwaters.

At M34, located on south border of Stage 1, higher leachate-derived POC together with its depleted $\delta^{13}C$ value is evidence for production of ^{13}C-depleted organic carbon as suggested earlier. This is likely related to methanotrophic bacterial growth in the plume fringe.

4.7. Identification of leachate in marginally-impacted groundwaters – ^{13}C

Identification of leachate mixing and impact on surrounding shallow and deep aquifers is usually carried out with conservative indicator species such as Cl^-. While Cl^- is elevated in Stage 1 and 2 leachate (~1000 mg/L in M32), this region has high heterogeneous background

geochemistry due to significant road salt contributions as identified in M79 (>700 mg/L). Examination of the monitoring wells that are most proximal to the unlined landfill and therefore having the greatest likelihood for impact (e.g. M37 and M4) shows that the shallow groundwaters (M37-3 and M4-2) are clearly impacted. However, in the upper and lower deep aquifer groundwaters, Cl^- remains within the range of background levels, and none of the other inorganic species offers an indication of leachate impact. Other inorganic parameters, as discussed above, also fail to discriminate leachate in marginally impacted groundwaters.

Here, the chemical and ^{13}C of carbon compounds are used to identify the leachate impact on groundwaters. This application focuses on two cross sections running along the general axis of leachate migration, and transverse along the northern boundary of the landfill. To illustrate the flow system and the relative depths and length of the well screens in the nested piezometers, Figure 4 details the well logs and the geochemistry data from the area of the TRL site parallel to the landfill border (AA') and along the deep aquifer groundwater flow direction (BB'). The concentrations and $\delta^{13}C$ values of carbon pools for 2004 sampling (and 2005 sampling between parentheses) are shown in different levels (screens) on the well logs. In the following, the interaction between landfill leachate and groundwater is discussed in AA' and BB' cross sections using $\delta^{13}C$ of the carbon pools for the 2004 data.

4.7.1. Parallel to landfill border (section AA')

Monitoring wells M4 and M37 which are located on the AA' cross section parallel to the north border of the TRL site (Figure 4), are close to the oldest and unlined parts of the site (Figure 1). In contrast, M23 and M16 are close to the active and lined landfill stages. The

presence alone of methane at some of these 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 general, the carbon system demonstrates considerable heterogeneity of reaction ranging from methane oxidation to continued methanogenesis.

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 (Table 2). Mineralogical control through calcite precipitation, is confirmed by the decreased concentration of Ca^{2+} at M4-2 as compared with M37-2. This can be supported by SI-indexes which show saturation conditions for the calcite (Table 1).

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 oxidiation. 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.

Due to adjacent windows in the clay and the distance from the old part of the landfill site, the upper part of the deep aquifer and the shallow aquifer in M23 and M16 are less or un-affected by landfill leachate. M16-3 is located in a perched water table aquifer (see both cross sections AA' and BB' on Figure 4) and draws non-contaminated water which has the same $\delta^{13}C_{DIC}$ value (-17.5‰) as that of up-gradient non-contaminated groundwater (M57). Similarly, the $\delta^{13}C_{DIC}$ value at M23-3 is close to that of up-gradient pristine groundwater at M57.

4.7.2. Parallel to groundwater flow (section BB')

Figure 4 (section BB') illustrates the well logs and the concentrations and isotope data of carbon pools along the groundwater flow direction in the deep aquifer. 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 Stages 1 and 2, 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. The enriched $\delta^{13}C_{CH4}$ value at M16-1, M77-2 and M64 compared with that of M32 confirms methane oxidation in the upper part of the deep aquifer. The low amount of DIC associated with the low amount of Ca^{2+} suggests a

mineralogical control through calcite precipitation which can be supported by SI-indexes data (Table 1).

The effect of the Nepean landfill site on M77 and the rest of the monitoring wells in the flow direction resulted in an increase in the amount of DIC and enriched $^{13}C_{DIC}$. As illustrated in Figure 14, DIC decreases in the downstream direction in the upper part of the deep aquifer (Figure 14a) and correlates with a decrease of $\delta^{13}C_{DIC}$ values. In the lower part of the deep aquifer (Figure 14b), the variation of DIC and $\delta^{13}C_{DIC}$ is the same as in the upper part, except in monitoring well M77-1, which is also affected by the adjacent Nepean landfill site (Figure 14c) (Mohammadzadeh et al., 2005b).

5. Summary and conclusions

The Trail Road Landfill (TRL) is situated on a northwest-southeast ridge of glacio-fluvial sand which is locally confined by clay. This deep aquifer and discontinuous clay aquitard is overlain by sands representing a shallow aquifer in this area. Both the shallow and deep aquifers have been impacted by leachate infiltrating from the unlined portions of the landfill, which is situated above a window in the clay aquitard. However, indicators of leachate in the shallow and deep groundwaters have remained ambiguous for marginally-impacted groundwaters due to variable concentrations of both inorganic parameters like Cl^- and bulk parameters like DOC in the background groundwaters. Here, new approaches provide insights to observe minor leachate contributions to groundwaters and to help in the evaluation of potential pathways for pathogens from the landfill site into groundwater supplies.

Methane concentrations in groundwaters vary between the detection limit and 10 mg l^{-1}, and provide evidence for landfill leachate impact. Moreover, these concentrations are higher than can be attributed to contributions from the leachate plume, and indicated in-plume production beyond the landfill margins. The $\delta^{13}C$ of dissolved methane varies between that of biogenic methane from the landfill, and values as high as –20‰. The enriched values are consistent with methane production from fermentation of enriched acetate such as observed in M32 (-12‰), which is consistent with the loss of acetate in the leachate plume. In addition, methane oxidation causes more enriched ^{13}C values of dissolved methane, with a Rayleigh enrichment of ^{13}C imparted on the residual CH_4.

The concentration and $\delta^{13}C$ of dissolved inorganic carbon, DIC, remains one of the most diagnostic tools for identification of landfill leachate. Through methanogenesis, $\delta^{13}C$ value becomes highly enriched, with values as high as 20‰. This contrasts sharply with the DIC of un-impacted groundwaters, which is typically about –17‰. While dilution and calcite precipitation reduce DIC from the very high concentrations in leachate to values closer to that of natural groundwaters, its $\delta^{13}C$ value remains high. Subsequent oxidation of organic carbon and/or methane oxidation can impart a depletion of ^{13}C, although the concentration of DOC available for such reaction typically remains too low to lower the $\delta^{13}C$ of DIC by more than a few permil. The carbon isotopic composition of groundwater from different aquifers which were examined in both parallel to northern border of TRL site and deep aquifer groundwater flow direction, also shows the affect of leachate with highly enriched $^{13}C_{DIC}$ (+8.8 and +10.7 ‰ for M32 and LPS, respectively) in surrounding aquifers. The $\delta^{13}C_{DIC}$

values of leachate-impacted groundwater (-6.4 ‰, -1.0 ‰ and -0.6 ‰ for the shallow, upper deep and lower deep aquifers, respectively) remain higher compared to the $\delta^{13}C_{DIC}$ value for the up-gradient pristine groundwater (-15.2 ‰) at TRL site.

Bulk DOC concentrations and $\delta^{13}C_{DOC}$ in groundwaters peripheral to the unlined landfill 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) the loss of acetate and propionate in groundwaters; and 3) correlation between net reacted (lost) DOC (988 mgl^{-1}, 368 mgl^{-1}, and 272 mgl^{-1} for the shallow, upper deep and lower deep aquifers, respectively) and the net gains in DIC (185 mgl^{-1}, 117 mgl^{-1} and 85 mgl^{-1}) for these aquifers.

The $\delta^{13}C$ of DOC in the impacted groundwaters from the first two sampling years in 2003 and 2004 show a most unusual depletion of ^{13}C with values lower than –40‰. This is attributed to a transient effect related to a methanotrophic microbial substrate during plume advancement in the deep aquifer.

Humic acid, considered to be produced by aerobic degradation of biomass, dominates the DOC of background groundwaters. Fulvic acid, also found in natural groundwaters, is produced during degradation of landfill organics and dominates the DOC of leachate-impacted groundwaters. Thus, HA/FA ratios below unity can be diagnostic of leachate impacts. However, variable values for $\delta^{13}C$ of FA preclude its use as supporting evidence for

leachate-derived organics. Low molecular weight DOC fractions are minor components in both background and leachate-impacted groundwaters.

In summary, the unambiguous identification of landfill leachate impact on natural groundwaters can be greatly improved through a multi-proxy approach that emphasizes the analysis of ^{13}C in the different organic and inorganic carbon species in conjunction with measurements of the concentrations of other inorganic and organic compounds.

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Table 1: Field parameters, cation and anion concentrations, and calculated parameters (pe, ionic strength and calcite saturation index (SI_{cal})) for groundwater samples. All concentrations and isotopic values in mgl^{-1} and ‰ VPDB, if not stated.

	Sample ID	Date	Field Parameters				Cations										Anions							pe	DIC	HCO3	Ionic Strength	SI_{cal}
			T (°C)	pH*	Eh (mV)	DO	B	Ba	Ca	Fe	K	Mg	Mn	Na	NH_4^+	S**	Sr	F	Cl	NO2	Br	NO3	PO4	SO4					
Reference	M57	July 22, 2005	10.4	7.4	501	6.9	0.01	0.2	77	bl	1.4	16		45	0.002	7	0.1	0.2	78	bl	bl	1.8	0.1	24	8.9	48	221	0.01	0.16
	M57	July.9/2004	8.8	7.6	302	6.1		0.1	44	bl	1.7	19		55	0.309	7	0.1	0.1	69	bl	bl	1.8	0.3	16	5.4	58	277	0.01	0.20
	Average		**9.6**	**7.5**	**402**	**6.5**	**0.01**	**0.1**	**61**		**1.6**	**17**		**50**	**0.156**	**7**	**0.1**	**0.1**	**73**			**1.8**	**0.2**	**20**	**7.2**	**53**	**249**	**0.01**	**0.18**
	M120	July 21, 2005	16.0	7.4	328	3.8	0.01	0.2	88	bl	2.0	27		13	0.002	9	0.2	0.1	39	0.2b	I	2.8	bl	29	5.7	59	268	0.01	0.22
	M120	July.9/2004	12.1	7.6	297	4.4		0.1	41		1.9	22		12	0.309	11	0.1	0.1	46	0.2	0.2	1.6	0.3	30	5.2	45	217	0.01	0.13
	M120	Nov.14/2003	9.0	7.4	408	5.7			64		1.6	21		11		10			43						7.3	47	216	0.01	0.12
	Average		**12.4**	**7.5**	**344**	**4.6**	**0.01**	**0.1**	**64**		**1.8**	**23**		**12**	**0.155**	**10**	**0.2**	**0.1**	**42**	**0.2**	**0.2**	**2.2**	**0.3**	**30**	**6.1**	**50**	**234**	**0.01**	**0.16**
	M79	Nov.14/2003	9.0	6.6	189	2.5		<1	247	3.1	3.5	57	4.9	409		47			737						3.4	104	309	0.04	-0.31
Pond	DWP-SE	July 21, 2005	25.7	7.3	154	6.0	0.03	0.4	105	bl	2.6	39	0.1	21	0.008	15	0.3	bl	56	0.1	0.2	1.2	0.1	47	2.6	72	326	0.01	0.31
	DWP-SE	July.9/2004	18.5	7.6	298	6.4	0.03	0.1	50		2.6	34	bl	18	0.472	14	0.2	0.1	62	0.1	0.3	0.5	0.2	48	5.1	85	403	0.01	0.34
	DWP-SE	Nov.14/2003	4.5	7.6	216	11.0		<1	104		2.5	35	0.1	20		14			52						3.9	102	487	0.01	0.74
	DWP-NW	Nov.14/2003	5.8	7.7	253	9.2		<1	99		2.7	34		18		14			49						4.6	89	428	0.01	0.75
	Average		**13.6**	**7.5**	**230**	**8.1**	**0.03**	**0.2**	**89**		**2.6**	**36**	**0.1**	**19**	**0.240**	**14**	**0.2**	**0.1**	**55**	**0.1**	**0.2**	**0.9**	**0.1**	**48**	**4.1**	**87**	**411**	**0.01**	**0.54**
Shallow Aquifer	M16-3	July.8/2004	15.2	6.4	299	1.7		0.1	49		2.3	11		7	0.796	8	0.2	0.1	8	bl	bl	0.8	bl	23	5.2	68	165	0.01	-1.14
	M37-3	July 20, 2005	14.6	6.6	271	7.6	0.51	0.6	283	bl	18.2	64	0.7	192	17.549	14	1.2	0.2	377		5.1	69.8	21.7	46	4.7	247	748	0.04	0.17
	M37-3	July.8/2004	12.8	6.7	379	2.5	0.56	0.3	194	1.2	16.4	68	0.3	206	16.794	23	1.0	0.3	214	0.3	2.6	0.8	0.4	36	6.7	417	1334	0.03	0.33
	M37-3	Nov.6/2003	10.7	6.6	252	6.4	<1	<1	189		13.0	46	0.7	154	15.500	53			196						4.5	178	520	0.02	-0.10
	M23-3	July.8/2004	15.0	7.0	na			0.0	42	bl	0.5	14	bl	10	0.236	11	0.2	0.1	13	0.1	0.2	0.2	0.3	26		49	200	0.01	-0.49
	M43	July.8/2004	10.1	6.6	265	2.7	0.62	0.2	132	4.3	25.9	76	0.4	98	53.693	17	1.1	bl	87	0.2	0.5	0.2	0.4	41	4.7	332	996	0.03	0.04
	M4-2	July 22, 2005	9.9	6.7	165	2.7	0.06	0.3	180	7.3	23.9	38	0.2	86	17.184	17	0.7		202		0.8	0.2	0.6	61	2.9	151	492	0.02	-0.02
	M4-2	July.7/2004	8.9	7.4	220	2.5	0.06	0.1	60	0.5	16.1	23	0.1	50	42.741	10	0.5	bl	135	bl	0.2	0.4	0.2	42	3.9	194	889	0.02	0.55
	M4-2	Nov.6/2003	10.4	6.5	173	3.4		<1	132	15.6	25.7	33	0.2	77	30.200	10			120						3.1	165	477	0.02	-0.24
	M33-1	July.7/2004	18.5	6.8	na		0.07	0.0	116	10.2	25.9	34	2.3	10	29.575	11	0.2	0.1	20	0.2	0.1	0.2	0.6	25		339	1240	0.02	0.38
	M116-3	Nov.7/2003	10.0	7.0	301	8.1	<1	<1	81		1.7	17		9		23			25						5.4	47	188	0.01	-0.27
	M86	Nov.7/2003	8.4	7.5	255	9.8	<1		50		0.9	11		39		10			12						4.6	53	248	0.01	0.10
	Average		**12.0**	**6.7**	**258**	**4.7**	**0.31**	**0.2**	**126**	**6.5**	**14.2**	**36**	**0.6**	**78**	**22.427**	**17**	**0.6**	**0.2**	**117**	**0.2**	**1.4**	**9.1**	**3.4**	**38**	**4.6**	**187**	**625**	**0.02**	**-0.06**

* In order to take the averrage of pH log values, first pH convert to H^+ (H^+=10^-pH), then pH recalculated from the average values of H^+ (pH=-log(H^+))

** Total S in samples

bl = blow detection limit

Table 1: Continued.

	Sample ID	Date	Field Parameters				Cations											Anions							pe	DIC	HCO3	Ionic Strength	SI_{cal}
			T (°C)	pH*	Eh (mV)	DO	B	Ba	Ca	Fe	K	Mg	Mn	Na	NH_4^+	S**	Sr	F	Cl	NO2	Br	NO3	PO4	SO4					
Upper Deep Aquifer	M114-2	July 21, 2005	14.7	7.7	260	2.3	0.01	0.3	80	bl	2.0	20	0.2	5	0.012	27	0.2	0.1	18		bl	0.1	bl	80	4.5	38	184	0.01	0.42
	M114-2	July.9/2004	12.5	7.5	299	1.1			58	bl	2.1	20	0.2	6	0.398	29	0.2	0.1	17	bl	bl	0.1	0.2	75	5.3	49	232	0.01	0.18
	M107-2	July 22, 2005	15.6	6.9	270	2.7	0.47	0.1	117	bl	3.0	42	0.2	33	0.004	49	0.2	0.2	13	0.1b	I	5.3	bl	150	4.7	83	321	0.02	-0.06
	M34	July 22, 2005	13.2	6.5	165	5.6	0.02	0.4	268	2.7	4.7	37	3.4	29	5.961	26	0.5	bl	93	bl	0.1	0.1	0.6	82	2.9	214	576	0.02	0.00
	M64	July 21, 2005	11.2	6.9	218	1.9	0.04	0.5	58	bl	2.3	46	0.1	33	0.007	7	0.4	0.3	69		0.2	bl		22	3.9	111	432	0.01	-0.20
	M64	July.9/2004	10.1	7.0	273	2.8	0.04	0.2	61		3.1	54		42	0.591	7	0.3	0.1	73	0.1	0.5	0.1	0.3	18	4.9	143	568	0.01	-0.03
	M64	Nov.14/2003	10.0	6.9	200	2.1		<1	114	0.3	2.6	43	0.5	35		5			64						3.6	151	586	0.02	0.19
	M77-2	July 21, 2005	12.5	6.8	279	1.0	0.07	0.3	163	bl	3.2	52	0.2	22	0.005	22	0.4	bl	55	bl	0.4	bl	0.1	69	4.9	129	446	0.02	0.01
	M77-2	July.9/2004	11.7	6.8	292	1.2	0.09	0.1	101		3.7	60		22	1.054	27	0.4	bl	55	0.2	0.3	0.1	0.1	69	5.2	166	598	0.02	0.00
	M77-2	Nov.7/2003	9.8	6.8	293	2.5		<1	165		3.3	42		19		22			46						5.2	164	604	0.02	0.25
	M40-4	July 20, 2005	17.2	6.0	246	1.6	0.12	0.2	163	0.2	3.3	42	2.4	20	0.006	19	4.3	0.1	21	bl	0.5		bl	62	4.3	157	220	0.02	-1.01
	M23-2	July.8/2004	12.4	7.3	154	0.3	0.03	0.6	47	2.4	1.9	47	bl	35	0.236	8	0.2	0.1	82	0.1	0.3	bl	0.2	21	2.7	79	357	0.01	0.03
	M16 -2	July 21, 2005	13.9	7.5	286	5.8	0.03	0.2	38	bl	6.7	11	0.1	9	0.443	6	0.3	0.2	51	bl	0.1	1.0	bl	22	5.0	17	80	0.00	-0.43
	M16 -2	July.8/2004	15.0	7.8	na	3.0?	0.04	0.1	26	bl	7.4	12	bl	10	1.574	7	0.3	0.2	36	0.1	0.2	0.3	0.1	15		22	108	0.00	-0.15
	M39-4	July 20, 2005	14.2	7.0	256	2.0	0.06	2.6	125	0.1	2.4	48	0.1	37	0.012	3	0.4	bl	51	bl	0.2		bl	10	4.5	124	487	0.02	0.17
	M39-4	Nov.7/2003	11.0	7.0	154	2.3		2.8	108		2.8	51		40	0.536	<2			64						2.7	143	580	0.02	0.24
	M39-7	July 20, 2005	13.5	6.9	164	1.6	0.05	0.2	150	bl	3.2	61	0.2	45	0.034	26	0.4	bl	128	0.2	0.3	bl		78	2.9	110	419	0.02	0.09
	M37-2	July 20, 2005	11.9	7.0	179	3.7	0.02	0.4	127	bl	4.2	42	0.1	32	0.078	7	0.7	bl	67	0.1	0.5	0.1	bl	22	3.2	107	430	0.02	0.16
	M37-2	July.8/2004	10.0	7.3	306	2.5	0.03		42		4.6	27		47	0.770	6	0.6	0.1	22	0.1	0.2	bl	0.2	28	5.4	94	422	0.01	0.07
	M37-2	Nov.6/2003	9.2	6.9	193	6.7		<1	91		4.4	33		51		7			55						3.4	99	382	0.01	-0.07
	M4-1	July 20, 2005	18.5	7.1	179	1.8	0.03	0.3	167	bl	8.2	73	0.1	22	0.625	1	1.0	0.1	132	0.2	0.8	0.1	0.2	3	3.1	132	560	0.02	0.47
	M4-1	July.7/2004	10.1	7.3	222	2.4	0.03	0.1	46		7.8	59	bl	19	1.209	<0.487	0.5	0.1	82	0.0	0.2	0.2	0.3	0.1	3.9	129	572	0.01	0.14
	M4-1	Nov.6/2003	9.2	7.2	155	1.9		<1	118		6.4	48	0.1	19					96						2.8	127	561	0.02	0.48
	M28	July 22, 2005	22.0	6.7	172	9.7	0.50	0.3	174	4.9	6.6	90	0.1	114	3.371	2	0.9	0.1	234	0.2	0.5	0.5	0.3	5	2.9	198	640	0.03	0.03
	M28	Nov.6/2003	10.8	6.7	163	4.2	<1	<1	192	26.3	4.5	141		160		<2			255						2.9	264	852	0.04	0.14
	M90	Nov.14/2003	9.0	7.3	155	2.2		1.6	78		2.4	27		13		3			37						2.8	86	386	0.01	0.28
	M83-2	Nov.14/2003	11.7	7.2	278	3.3		<1	152		1.5	43	0.4	20		11			91						4.9	136	582	0.02	0.51
	Average		**12.6**	**6.9**	**223**	**2.9**	**0.09**	**0.6**	**112**	**5.3**	**4.0**	**47**	**0.5**	**35**	**0.846**	**14**	**0.7**	**0.1**	**74**	**0.10.3**		**0.7**	**0.2**	**44**	**3.9**	**121**	**451**	**0.02**	**0.07**

Table 1: Continued.

	Sample ID	Date	Field Parameters				Cations										Anions							pe	DIC	HCO3	Ionic Strength	SI_{cal}
			T (°C)	pH*	Eh (mV)	DO	B	Ba	Ca	Fe	K	Mg	Mn	Na	NH_4^+	S**	Sr	F	Cl	NO2	Br	NO3	PO4	SO4					
Lower Deep Aquifer	M93	July 21, 2005	11.5	7.4	159	2.2	0.06	0.4	79	bl	3.3	30	0.1	16	0.012	8	0.7	0.2	38	bl	0.3	bl	bl	22	2.8	60	272	0.01	0.19
	M93	July.9/2004	9.6	7.5	291	1.1	0.08	0.2	47		3.7	32		16	0.536	9	0.6	0.2	35	0.1	0.3	0.2	bl	23	5.2	71	331	0.01	0.19
	M77-1	July 21, 2005	12.1	7.1	197	0.6	0.08	1.8	106	bl	3.4	41	0.1	37	0.031	6	0.6	0.2	85	bl	bl	0.2	bl	21	3.5	87	359	0.01	0.09
	M77-1	July.9/2004	10.2	7.1	230	1.2	0.10	0.6	54		4.1	44		39	0.488	6	0.6	0.1	73	bl	0.7	0.2	0.1	15	4.1	105	446	0.01	-0.02
	M77-1	Nov.7/2003	9.3	7.1	177	1.8		1.8	95	0.2	3.2	38		35		5			74						3.2	117	484	0.01	0.19
	M114-1	July 21, 2005	14.2	7.1	238	1.8	0.11	0.2	96	bl	5.7	40	0.1	15	0.050	11	1.1	0.4	32		0.3	0.1		40	4.2	80	329	0.01	0.02
	M114-1	July.9/2004	12.3	7.3	315	1.5	0.12	0.1	43		5.0	28		14	0.595	8	0.8	0.3	23	0.1	0.0	0.1	0.7	24	5.6	71	321	0.01	-0.02
	M16 -1	July 21, 2005	11.4	6.9	451	1.5	0.02	0.5	167	bl	3.8	52	0.5	38	0.010	12	0.3	bl	72	0.3	0.8	0.1	1.7	35	8.0	149	554	0.02	0.21
	M16 -1	July.8/2004	10.5	6.8	273	0.8	0.02	0.1	69		3.4	52	0.1	29	0.533	10	0.2	bl	76	0.0	0.3	0.1	0.1	31	4.9	181	661	0.02	-0.07
	M40-1	July 20, 2005	16.7	6.5	249	1.0	0.14	0.1	152	0.8	5.3	47	0.1	32	0.053	19	8.2	0.1	45	0.1	1.6		bl	55	4.3	139	391	0.02	-0.30
	M39-1	July 20, 2005	13.6	6.8	184	3.7	0.06	4.8	127	bl	5.8	42	0.1	33	0.089	4	0.5	bl	56	bl	bl	bl	bl	13	3.2	118	420	0.02	-0.04
	M39-1	Nov.7/2003	11.6	6.9	148	2.0		5.4	119	0.1	5.1	41		36		2			53						2.6	155	604	0.02	0.22
	M23-1	July 20, 2005	11.1	7.7	217	1.0	0.02	2.1	99	bl	2.9	35	0.1	25	0.005	8	0.4	0.2	89		0.1		0.1	24	3.9	68	330	0.01	0.71
	M23-1	July.8/2004	10.4	7.3	232	0.8	0.03	0.4	45		3.2	40		25	0.391	7	0.3	0.1	75	0.1	0.1	0.1	0.2	19	4.1	86	388	0.01	0.06
	M107-1	July 22, 2005	15.6	7.2	227	5.9	0.01	0.2	50	bl	1.4	14	0.1	9	0.001	12	0.1	0.1	29		bl	bl	bl	36	4.0	26	113	0.01	-0.52
	M37-1	July 20, 2005	11.1	7.6	252	7.2	0.01	0.2	51	bl	1.4	14		6	0.001	10	0.1	0.3	29	bl	bl	bl	bl	31	4.5	28	136	0.01	0.00
	M37-1	July.8/2004	10.2	7.9	276	1.1		0.1	32	bl	1.8	17	bl	6	0.216	13	0.1	0.2	21	bl	0.1	0.1	0.2	27	4.9	30	149	0.01	0.14
	M37-1	Nov.14/2003	9.0	7.4	175	4.1	<1	<1	47		1.3	14		5		9			21						3.1	34	156	0.01	-0.18
	M83-1	Nov.6/2003	12.1	7.1	131	2.1	<1	1.5	131	2.7	2.0	59	0.4	55		4			112						2.3	170	701	0.02	0.41
	M116-1	Nov.7/2003	9.0	7.2	150	1.7		1.1	68		2.3	22		23		10			39						2.7	59	258	0.01	-0.03
	Average		**11.6**	**7.1**	**229**	**2.1**	**0.06**	**1.1**	**84**	**1.0**	**3.4**	**35**	**0.2**	**25**	**0.201**	**9**	**1.0**	**0.2**	**54**	**0.1**	**0.4**	**0.1**	**0.5**	**28**	**4.0**	**92**	**370**	**0.01**	**0.06**

Table 2: Geochemical and isotopic data for the groundwater samples collected at TRL site. All concentrations in mgl^{-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 2: 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**

Table 3: Geochemical and isotopic data for source of contamination (leachate from M32 located in the northern part of unlined Stages 1). All isotopic data in ‰ VPDB (for ^{13}C) and in ‰ VSMOW (for ^{18}O and ^{2}H).

Well #	Date	Field Parameters				Cations (mg l^{-1})										Anions (mg l^{-1})							pe	DIC (mgl^{-1})	HCO3	Ionic Strength	SI_{cal}
		T (°C)	pH*	Eh (mV)	DO	B	Ba	Ca	Fe	K	Mg	Mn	Na	NH_4^+	S**	Sr	F	Cl	NO2	Br	NO3	PO4	SO4					
M32	July 22, 2005	22.0	7.2	244		1.2	18.4	2108	34.5	123	498	2.6	1068	89	9	4.4	0.0	935	26.9	0.0	0.9	54.6	10	4.2	331	1442	0.197	1.20
M32	July.6/2004	na	7.2	na		0.9	11.0	858	2.5	85	249	0.9	604337		8	2.8	0.5	748	22.8	2.8	2.2	7.2	2		339	1458	0.100	1.15
M32	Nov.7/2003	8.0	6.3	195	3.2	2.0	32.6	3378	32.5	167	706	7.8	1565	511	16			1581						3.5	200	461	0.290	-0.25
Average		15.0	6.8	219	3.2	1.4	20.7	2115	23.2	125	485	3.8	1079	312	11	3.6	0.3	1088	24.9	1.4	1.6	30.9	6	3.8	290	1040	0.195	1

* In order to take the averrage of pH log values, first pH convert to H^+ (H^+=10^-pH), then pH recalculated from the average values of H^+ (pH=-log(H^+))

** Total S in samples

	DIC		DOC		CH_4		CO_2	Acetic Acid (Propionic Acid)		H2O			
	mg l^{-1}	$\delta^{13}C_{DIC}$	mg l^{-1}	$\delta^{13}C_{DOC}$	mg l^{-1}	$\delta^{13}C_{CH4}$	$\delta^{13}C_{CO2}$	mg l^{-1}	$\delta^{13}C$	$\delta^{2}H_{H2O}$	$\delta^{18}O_{H2O}$	^{2}H Shift*	^{2}H Excess**
Minimum	200	7.0	4310	-28.8	1.6	-68.4	0.1	218 (29)	-13.7 (-20.6)	-73.0	-10.4	5.3	9.3
Maximum	339	10.7	5130	-17.4	6.8	-50.8	6.6	1755 (1313)	-10.7 (-18.5)	-68.4	-9.8	6.4	10.3
Average	290	8.5	4770	-21.6	4.8	-59.6	2.7	1008 (608)	-12.0 (-19.3)	-70.6	-10.1	5.8	9.8
Sdv.	78	1.9	419	6	1.4	12.4	3.4	815 (629)	1.5 (0.9)	2.3	0.3	0.6	0.5
n	3	3	3	3	3	3	3	4	4 (4)	3	3	3	3

*Over local meteoric water line (LMWL) **Over global meteoric water line (GMWL)

Table 4: Distribution of the total dissolved organic carbon (DOC) into humic acids (HA), fulvic acids (FA), LMW DOC fraction, and the HPLC fractions of LMW DOC and the corresponding $\delta^{13}C$ values for the leachate-impacted groundwater samples. The ratio of humic/fulvic acids (HA/FA) have been calculated using HA and FA concentrations. (Some data reported in the literature for leachate-impacted groundwater and unimpacted groundwater are given for comparison).

Well #		Total DOC		Humic Acid (HA)			Fulvic Acid (FA)			LMW DOC			HPLC Fractions of LMW DOC			HA/FA
		($mg\ L^{-1}$)*	$\delta^{13}C$ ‰	($mg\ L^{-1}$)	% of DOC	$\delta^{13}C$ ‰	($mg\ L^{-1}$)	% of DOC	$\delta^{13}C$ ‰	($mg\ L^{-1}$)	% of DOC	$\delta^{13}C$ ‰	($mg\ L^{-1}$)	% of LMW DOC	$\delta^{13}C$ ‰	
Reference	M57	5.0	-26.3	3.1	62.2	-22.0	1.6	31.4	-22.2	0.3	6.1	-22.0	0.2	65.5	-32.9	1.98
Leachate-Polluted Groundwater	M39-7	6.7	-26.7	1.2	18.5	-21.5	4.4	66.1	-21.2	1.1	15.9	-24.4	0.2	16.9	-33.2	0.28
	M37-2	3.7	-27.4	0.3	6.9	-29.6	2.7	72.5	-21.1	0.7	18.1	-25.1	0.4	53.8	-33.4	0.10
	M4-1	7.2	-26.8	0.5	7.2	-23.0	5.5	75.7	-21.3	1.3	17.5	-25.3	0.6	49.3	-31.7	0.10
	M34	20.0	-38.9	6.0	29.9	-54.9	11.1	55.3	-26.7	2.9	14.7	-35.9	0.4	14.6	-34.4	0.54
	M37-3	57.5	-26.5	2.1	3.6	-24.7	48.8	84.8	-25.4	6.6	11.5	-26.8	3.7	55.4	-31.5	0.04
	Average	**19.0**	**-29.2**	**2.0**	**13.2**	**-30.7**	**14.5**	**70.9**	**-23.1**	**2.5**	**15.5**	**-27.5**	**1.0**	**38.0**	**-32.8**	**0.2**
Literature Values	Leachate-LPS[a]	219.1	-25.7	28.2	12.9	-22.9	160.4	73.2	-26.2	30.5	13.9	-27.1	11.4	37.3	-34.8	0.18
	Leachate-M32[a]	6125.8	-18.4	21.3	0.3	-28.1	4482.5	73.2	-20.3	1622.0	26.5	-8.0	226.4	14.0	-13.0	0.05
	Leachate[b]				4 to 44			7 to 72			-					
	Unpollted groundwater[c]				3 to 97			1 to 67			1 to 32					
	Leachate-polluted groundwater[d]				8 to 15			44 to 62			-					

* Sum of HA, FA and LMW DOC

[a]Mohammdzadeh et al, 2007 (the previouse chapter); [b]Nanny and Ratasuk, 2002; [c]Gorn et al., 1996; [d]Christensen et al., 1998

Table 5: The average amount of net reacted (lost) DOC and net gained in DIC for the shallow, upper deep and lower deep aquifers at TRL site. All isotope data in ‰ VPDB.

		Measured Components (mgl^{-1})							Initial Components (mgl^{-1})			Reacted or Gained Components (mgl^{-1})		
		Cl (mgl^{-1})	DOC	$\delta^{13}C_{DOC}$	DIC	$\delta^{13}C_{DIC}$	CH4	$\delta^{13}C_{CH4}$	DOC (Unreacted)	DIC	CH4	ΔDOC(Reacted)	ΔDIC (Gained)	ΔCH4 (Gained)
Shallow Aquifer	Minimum	8	2	-32	49	-21	0.0	-75	34	19	0.0	31	49	0.0
	Maximum	377	77	-19	417	19	7.3	-44	2332	89	2.3	2302	391	6.0
	Average	150	21	-27	200	-6	2.4	-59	1011	45	0.9	988	185	3.5
	Sdv.	114	25	4	118	13	3	43	731	43	0.7	718	111	3
	n	9	9	9	9	9	9	9	9	9	9	9	9	9
Upper D. Aquifer	Minimum	13	1	-40	17	-21	0.0	-71	32	0	0.0	28	17	0.1
	Maximum	234	13	-18	214	22	6.0	-38	1431	0	1.4	1418	214	5.1
	Average	67	4	-29	117	-1	1.9	-54	372		0.4	368	117	2.4
	Sdv.	47	3	5	50	12	2	50	296		0.3	294	50	2
	n	25	25	25	25	25	25	25	25	25	25	25	25	25
Lower D. Aquifer	Minimum	21	1	-54	26	-17	0.0	-64	82	0	0.1	81	26	0.0
	Maximum	89	5	-24	181	14	6.2	-37	515	0	0.5	513	181	5.7
	Average	51	3	-33	85	-1	1.8	-54	274		0.3	272	85	1.7
	Sdv.	24	1	8	45	9	2	46	151		0.2	150	45	2
	n	18	18	18	18	18	18	18	18	18	18	18	18	18

Table 6: Gas phase methane concentration (in % by volume) at TRL site for 2004 (revised from Dillon Consulting Ltd., 2005).

	M57	M56	GM2	M34	GM13	GM12	GM1	GM14	M107-3	M58
January		0.0	0.05	.7	60.3	43.0	63.0	51.7	30.0	
February	0.1	0.1	0.2	47.4	36.3	52.6	59.9	62.2		8.0
March		0.2	0.2	35.9	58.5	53.8	62.7	62.1	50.2	
April		0.0	0.0	36.7	48.7	51.1	59.4	62.4		
May		0.2	0.1	55.8	57.8	50.6	58.2	61.3	47.8	
June	0.1	0.0	0.1	54.9	57.9	53.4	58.8	61.6	42.2	2.4
July		0.0	0.0	55.2	57.9	53.7	57.7	60.4	41.9	
August		0.0	0.0	57.6	24.7	55.6	59.8	58.1	0.0	
September	0.2	0.0	0.0	57.4		55.0	59.3	56.6	47.0	0.9
October								37.7	37.3	
November		0.0	0.0	54.8	57.3	46.0	61.0	60.7	47.1	
December	0.0	0.0	0.0	53.4	55.6	56.2	60.3	57.8	36.4	2.8
Average	**0.1**	**0.1**	**0.1**	**47.9**	**46.8**	**51.9**	**60.0**	**58.4**	**38.0**	**3.1**

Table 7: Total carbon contents (TC), particulate organic carbon (POC), particulate inorganic carbon (PIC) and elemental composition of suspended solids with their corresponding $\delta^{13}C$ values of suspended solids. All samples were collected in July 2005.

Location	Well #	TC[1]								POC[2]								PIC[3]	
		$\delta^{13}C$ ‰	C (mg/Kg)[4]	%C	% N	% H	% S	H/C	N/C	$\delta^{13}C$ ‰	C (mg/Kg)[4]	%C	% N	% H	% S	H/C	N/C	$\delta^{13}C$ ‰	C (mg/Kg)
Reference	M57	-7.1	25	1.79	0.06	1.73	0.16	11.49	0.03	-27.4	3	0.27	0.05	2.09	0.10	91.48	0.17	-4.5	22
Leachate-Polluted Groundwater	M39-7	-18.0	61	5.68	0.24	1.19	1.25	2.50	0.04	-30.0	20	2.15	0.23	2.46	1.11	13.68	0.09	-12.0	40
	M37-2	-5.3	21	2.04	0.08	1.51	0.26	8.85	0.03	-28.5	2	0.25	0.06	2.05	0.23	98.48	0.21	-3.0	19
	M37-3	-6.9	7	0.59	0.08	1.25	0.24	25.15	0.12	-27.1	1	0.16	0.07	1.79	0.18	136.05	0.37	-2.7	6
	M4-1	-0.1	27	2.22	0.11	1.61	0.17	8.63	0.04	-34.5	3	0.34	0.06	1.92	0.22	67.60	0.15	4.6	24
	M34	-51.4	285	19.09	3.19	4.07	9.99	2.54	0.14	-52.3	277	23.69	4.04	3.87	6.11	1.95	0.15	-21.9	8
Leachate	LP1	-29.9	120	11.23	1.14	2.34	0.73	2.48	0.09	-31.0	86	8.20	0.91	2.51	0.50	3.65	0.09	-27.1	34
	LP6	-21.1	162	14.94	2.87	2.81	14.73	2.24	0.16	-21.0	109	11.59	2.35	2.44	6.99	2.51	0.17	-21.2	52
	LPS	-11.9	180	16.55	2.34	2.32	3.29	1.67	0.12	-16.0	113	10.74	1.93	2.96	2.41	3.28	0.15	-4.9	67
Inside Landfill Site	M32	-20.3	333	32.77	0.74	5.09	0.45	1.85	0.02	-30.5	327	5.70	0.92	3.53	0.42	7.38	0.14		6

[1]TC = Total carbon (in suspended solids)

[2]POC = particle organic carbon (acidified suspended solidsusing 10 % HCl)

[3]PIC = particle inorganic carbon, calculated based on isotope mass balance

[4]Calculated based on standard calibration curve

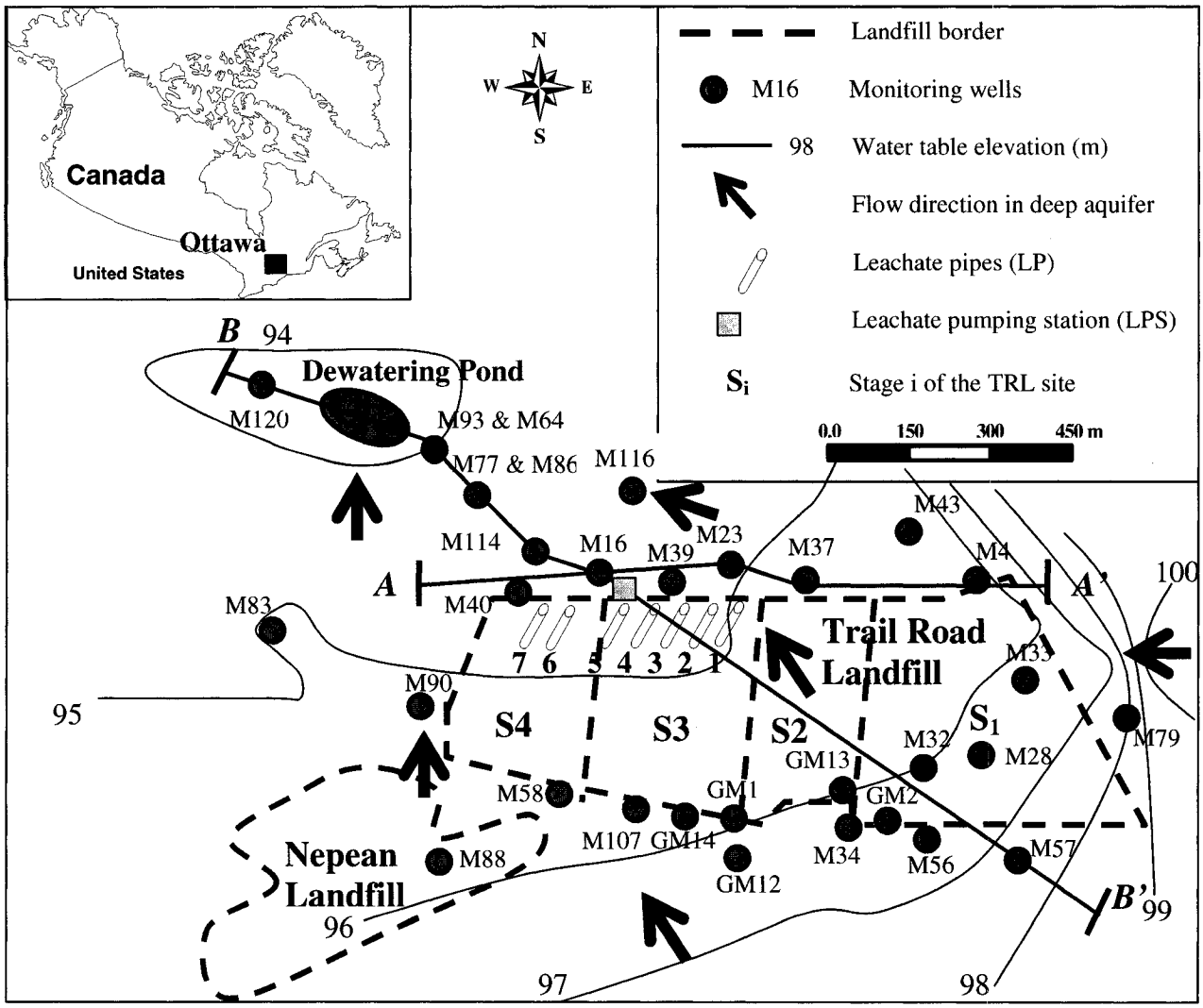

Figure 1: Plan view of study area and flow direction in deep aquifer.

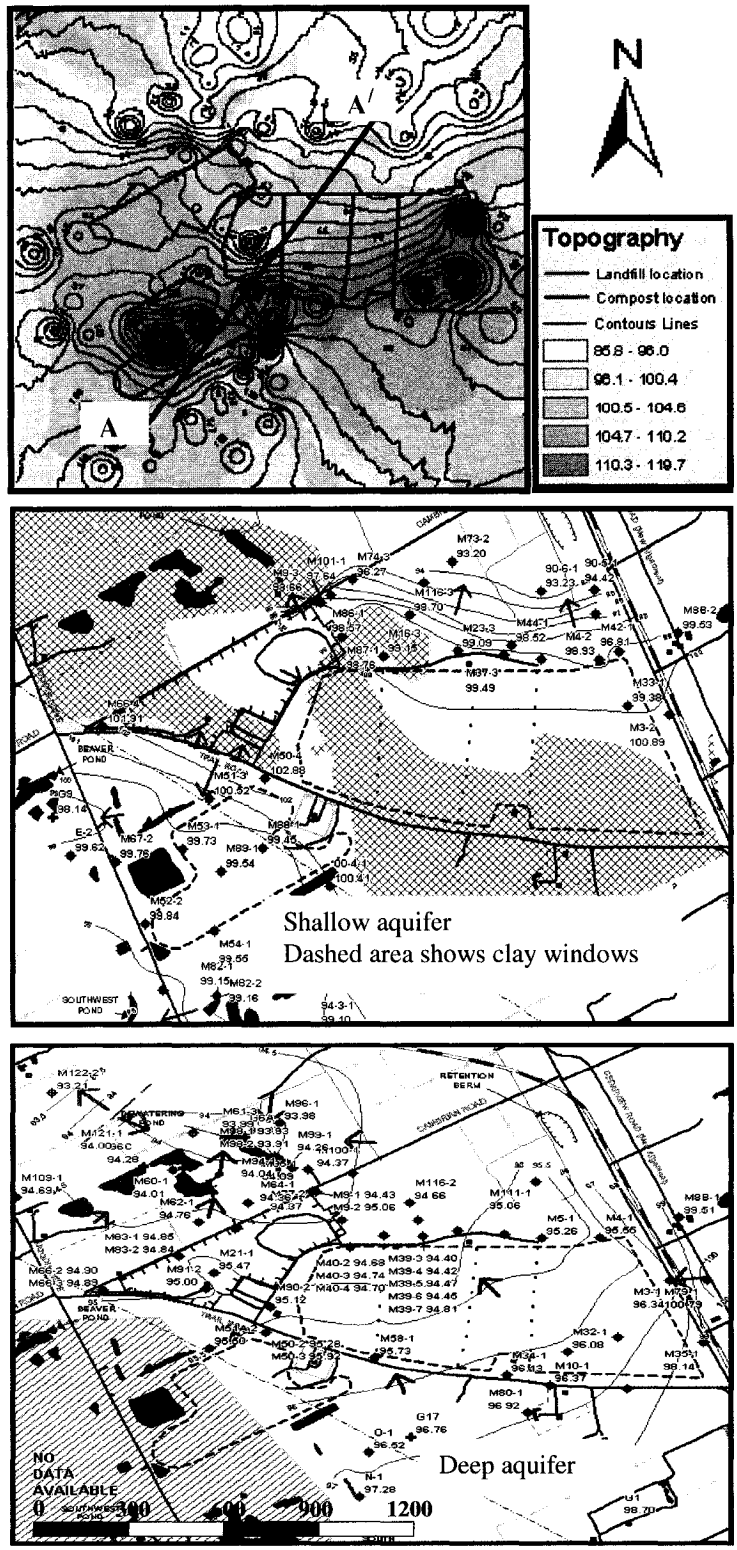

Figure 2: Surface contour (topography) map and the flow directions in both the shallow and the deep aquifers (after Golder Associates Ltd. 2002 and City of Ottawa, 2002).

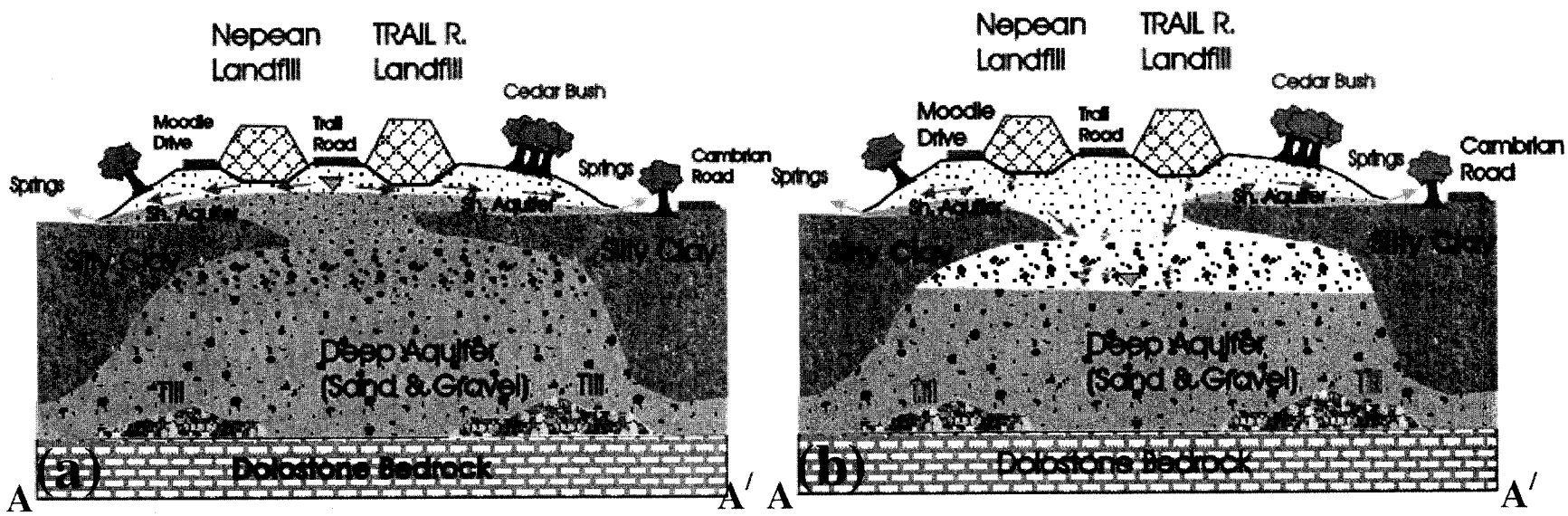

Figure 3: Schematic cross sections of hydrogeological unit in study area, for the trend of cross section see Figure 2. (a) before generating dewatering pond and (b) after dewatering pond was generated.

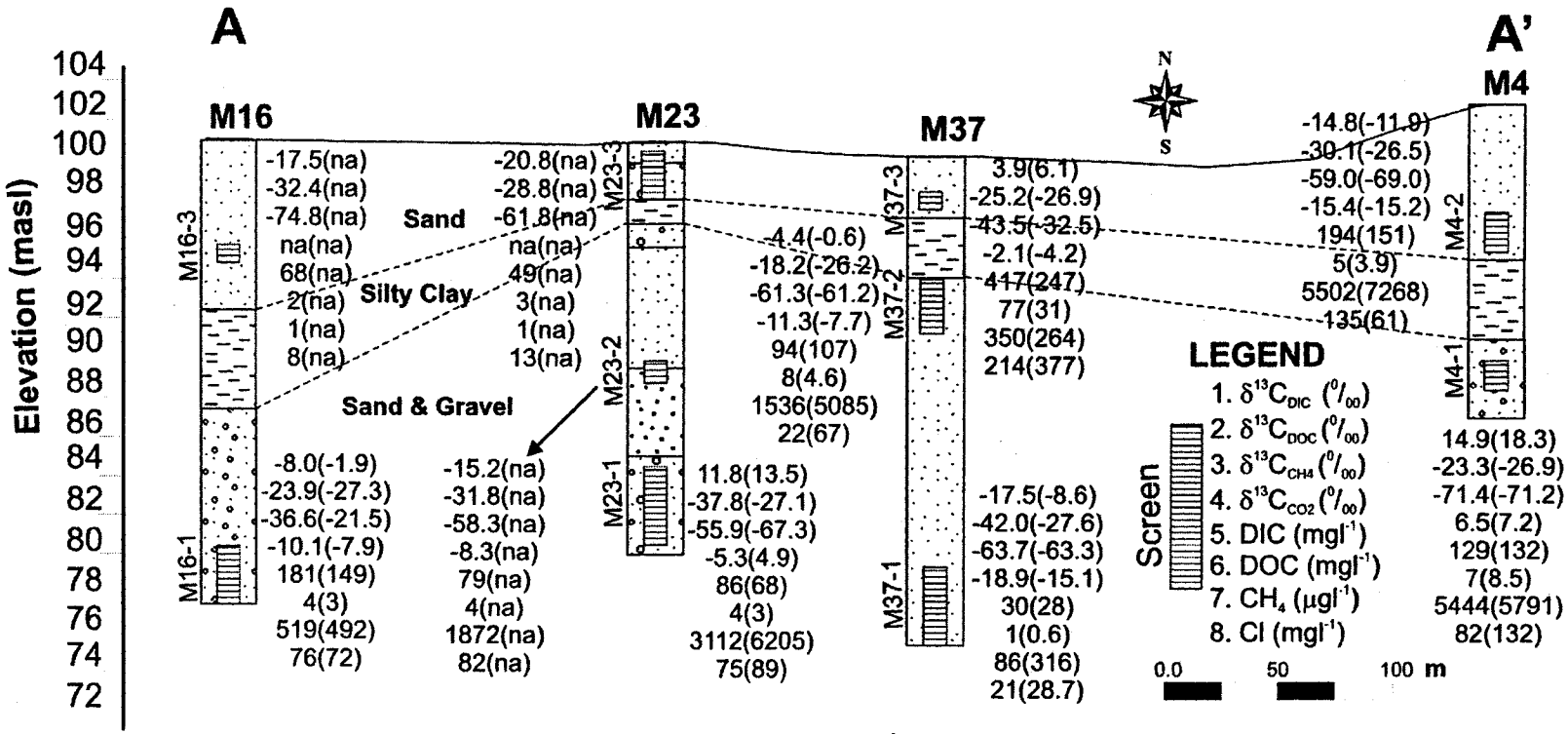

Figure 4: Geological cross section in parallel to landfill border (AA') and at groundwater flow directions in the deep aquifer (BB') which shows both shallow and deep aquifers, separated by a discontinuous clay aquitard (for the trend of selected monitoring wells, see Figure 1). The concentrations and $\delta^{13}C$ values of carbon pools for 2004 sampling (and 2005 sampling between parentheses) are shown in different levels (screens) on the well logs.

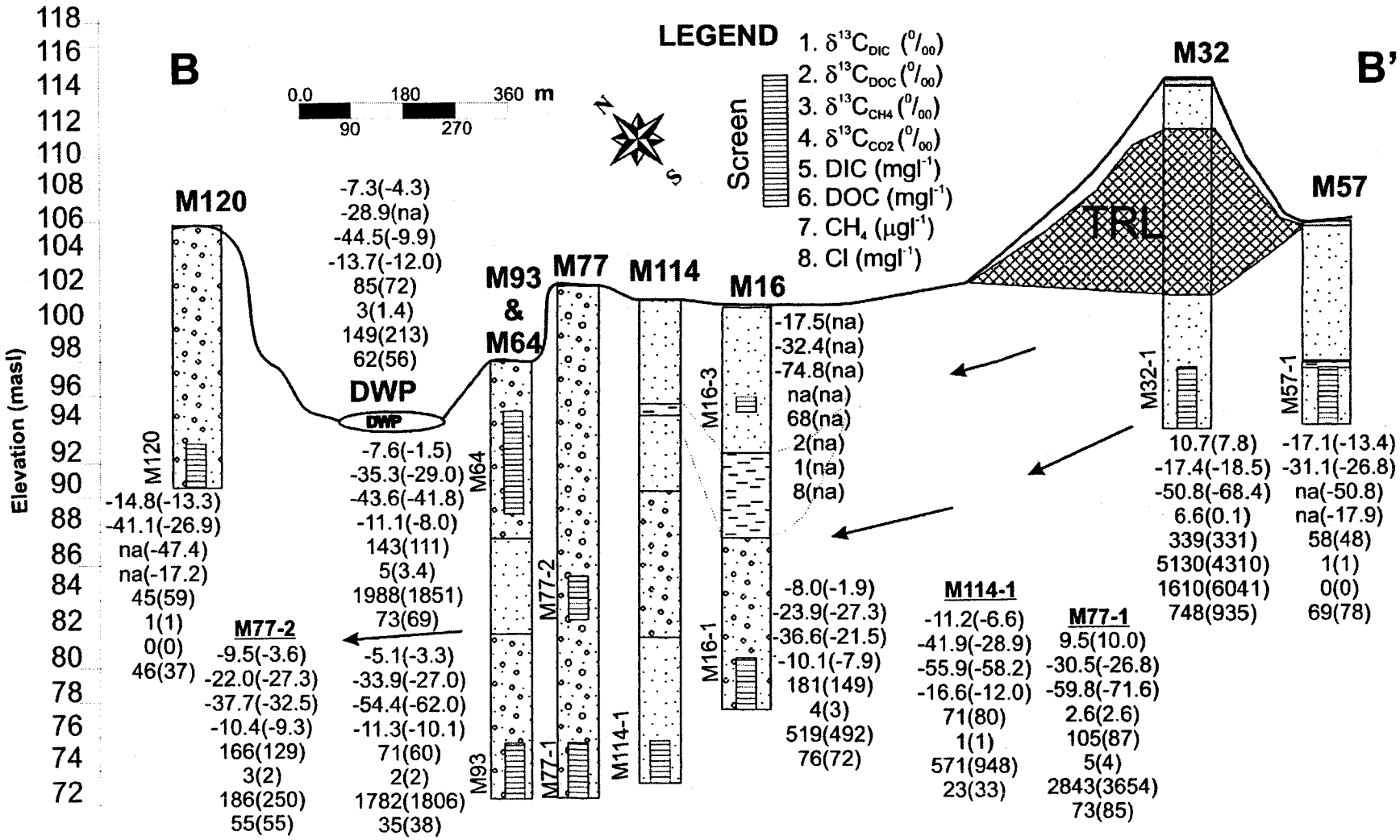

Figure 4: Continue.

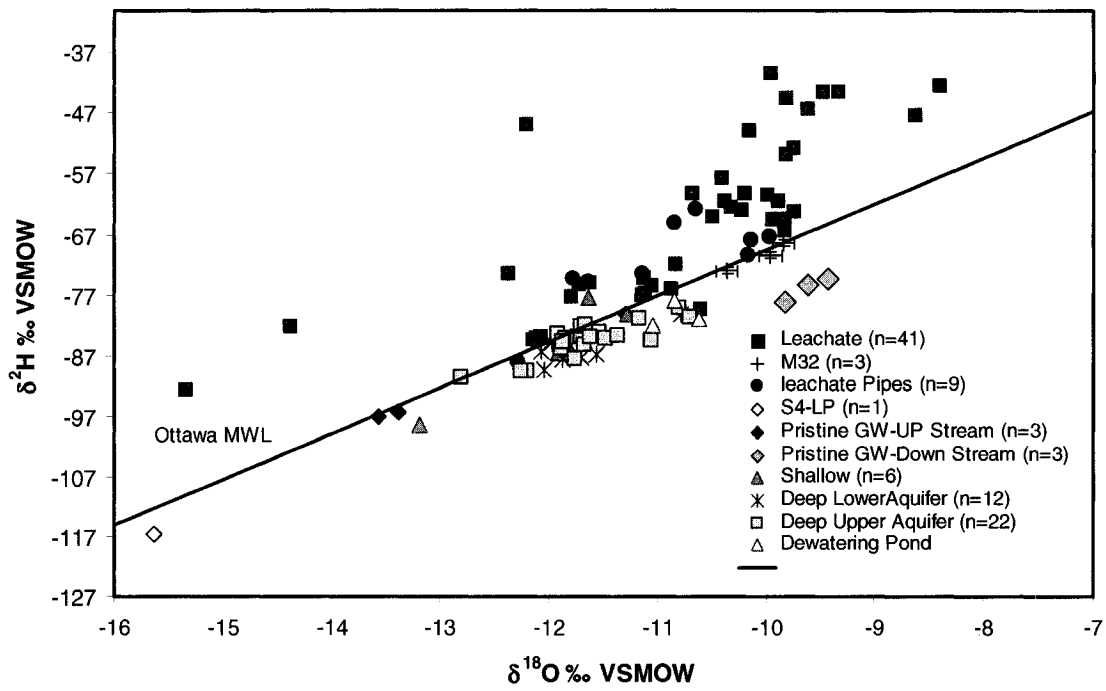

Figure 5: δ^2H and $\delta^{18}O$ values for samples from municipal TRL site. Included in this plot are: the isotopic composition of leachate, the groundwater samples from different aquifers and the surface ponds. The Ottawa meteoric water line (OMWL) is based on IAEA/WMO GNIP, 2004.

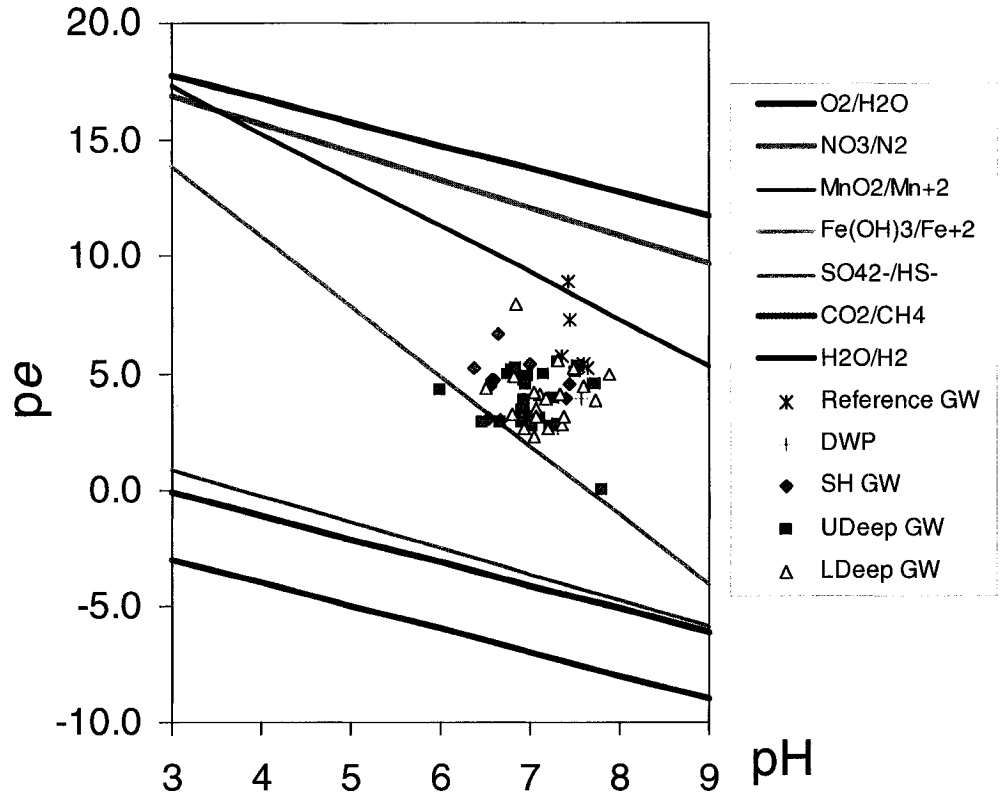

Figure 6: p*e* – pH diagram and the stability line for principal redox buffering pairs in natural water with plotted groundwater samples from different aquifers at TRL site. The stability lines were drawn based on equations in previous chapter. All gas pressures were assumed 1 atmosphere and activity of NO_3^-, Mn^{2+}, Fe^{2+}, and activity ratio of SO_4^{2-}/HS^- were assumed $10^{-3.15}$ mol/L, 10^{-6} mol/L, 10^{-6} mol/L, and 1, respectively.

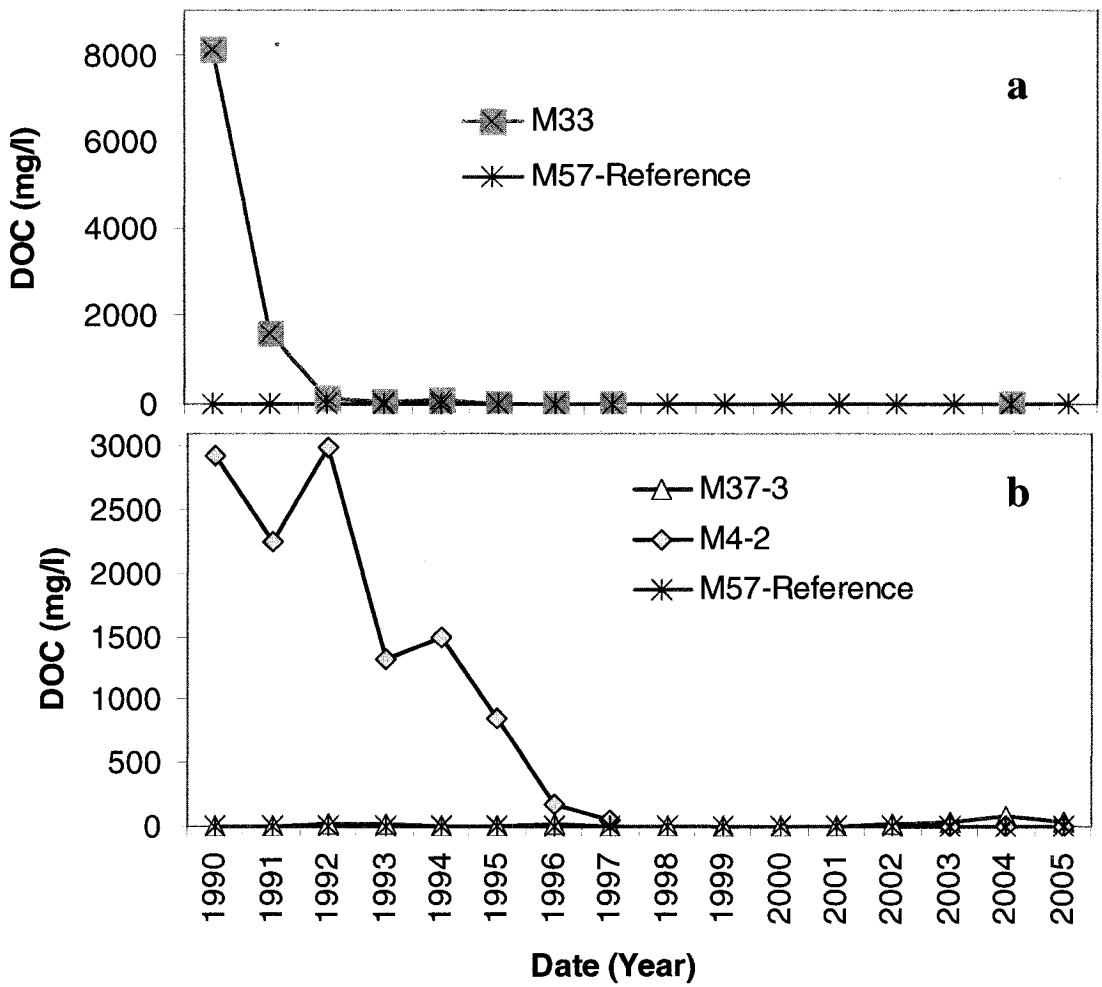

Figure 7: DOC variation in shallow aquifer at M33 (top of Stage 1), M4-2 and M37-3 (at north border of Stages 1 and 2, respectively) and M57 (upgradient reference groundwater) (Data for the period of 1990 to 2002 from Golder Associate Ltd.).

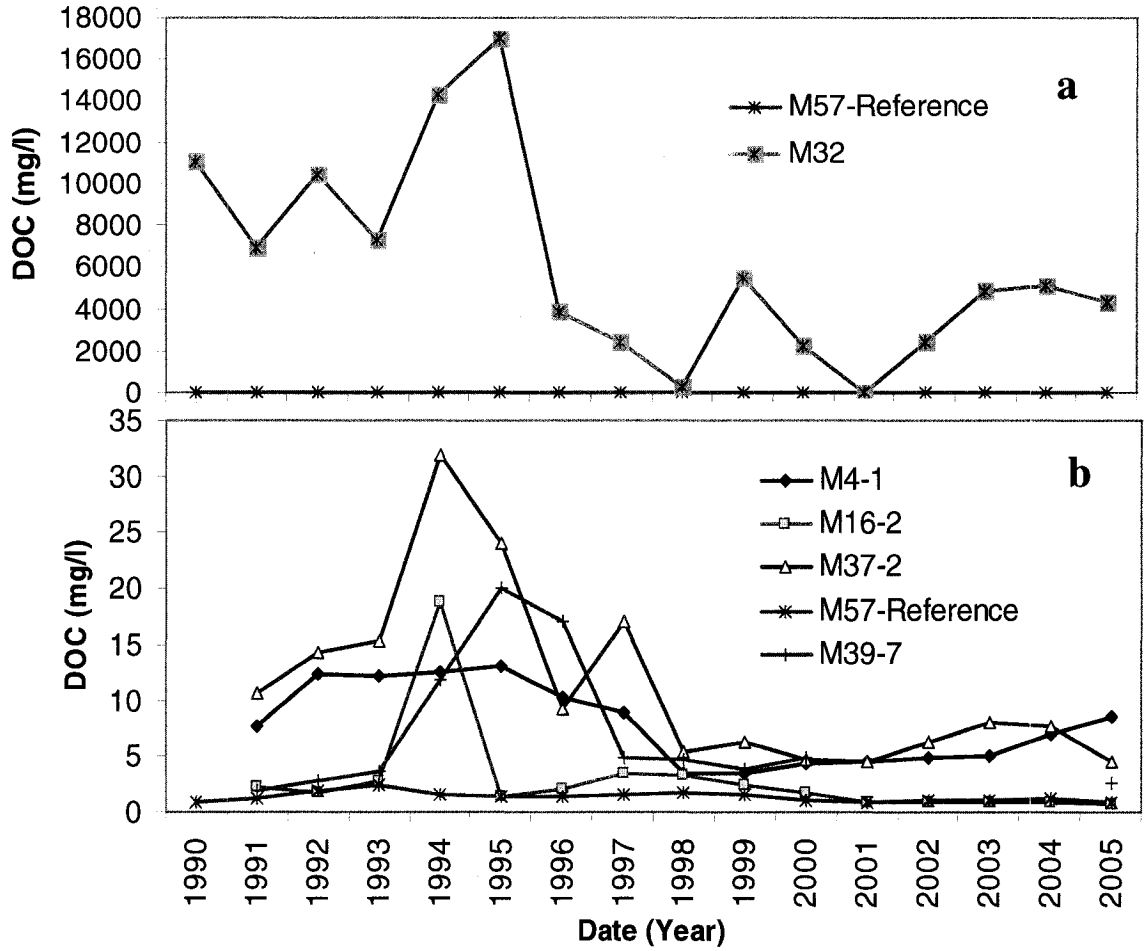

Figure 8: DOC variation in deep aquifer at M4-1, M37-2, M39-7, M16-2 (located north of Stage 1, Stage 2, Stage 3 and Stage 4, respectively) and M57 (upgradient reference groundwater) (Data for the period of 1990 to 2002 from Golder Associate Ltd.).

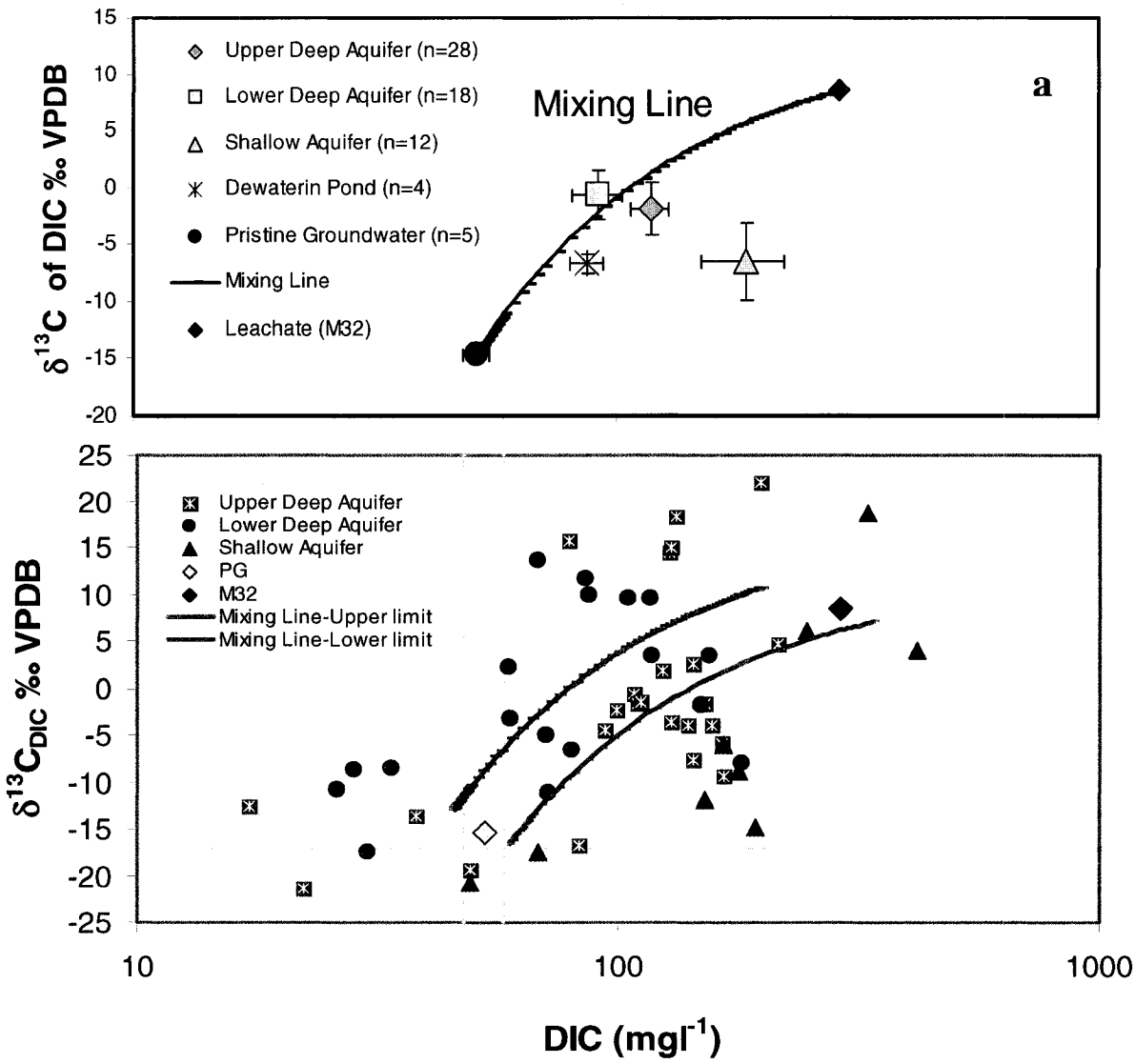

Figure 9: Cluster analysis of relationship between $\delta^{13}C_{DIC}$ and DIC concentration in different aquifers (a) at individual monitoring wells (b) at TRL site. Included in this plot are: the characteristics of leachate (from M32); contaminated groundwater; surface ponds; and pristine (background) groundwater (PG). Error bars show the uncertainty of the DIC concentration and isotopic ($\delta^{13}C$) measurements. The dashed lines in (b) show the range of background groundwater and the solid lines show the upper and lower limits of mixing zone between the two end members drawn based on mass balance and the range of DIC and $\delta^{13}C$.

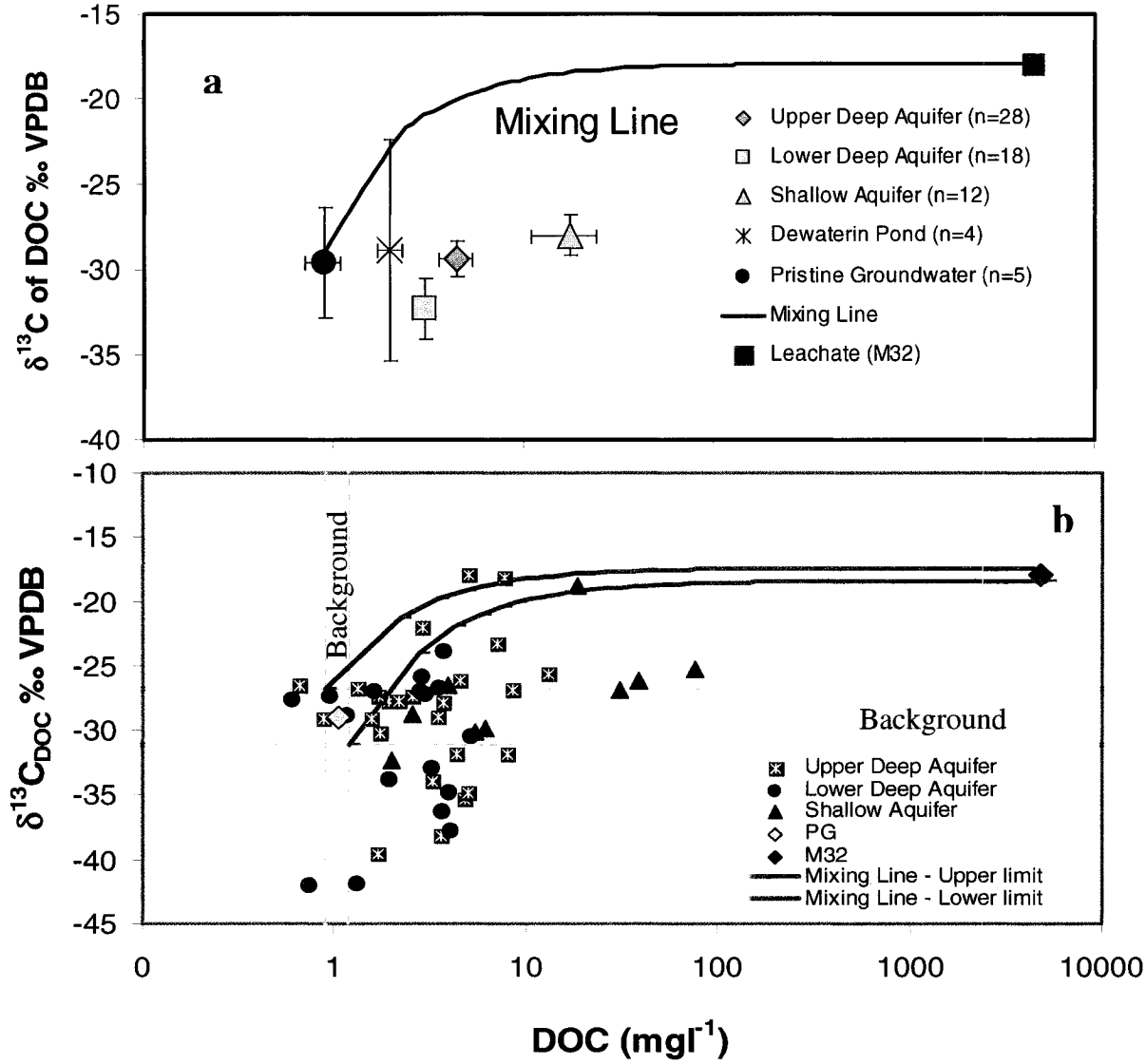

Figure 10: Cluster analysis of relationship between $\delta^{13}C_{DOC}$ and DOC concentration in different aquifers (a) at individual monitoring wells (b) at TRL site. Included in this plot are: the characteristics of leachate (from M32); contaminated groundwater; surface ponds; and pristine (background) groundwater (PG). Error bars show the uncertainty of the DOC concentration and isotopic ($\delta^{13}C$) measurements. The dashed lines in (b) show the range of background groundwater and the solid lines show the upper and lower limits of mixing zone between the two end members drawn based on mass balance and the range of DOC and $\delta^{13}C$.

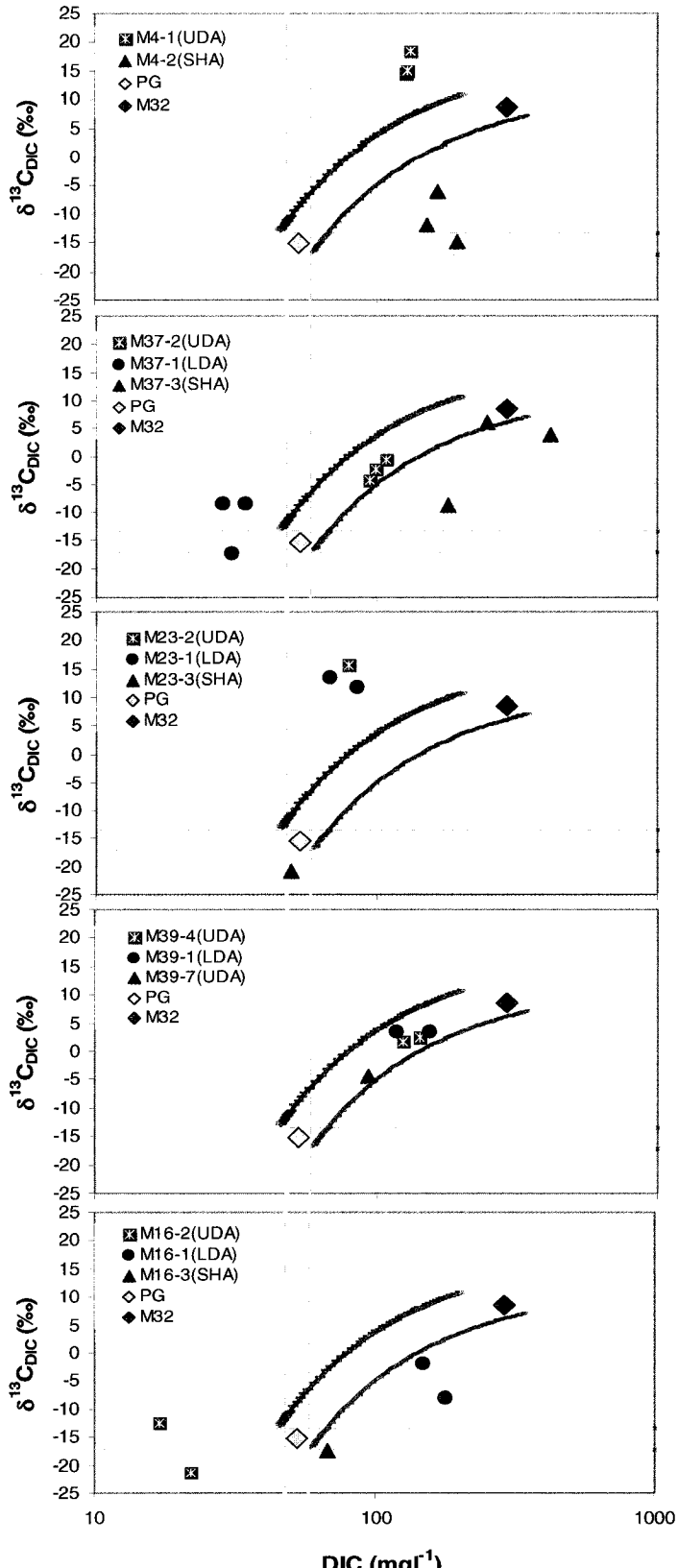

Figure 11: The $\delta^{13}C_{DIC}$ vs. DIC at some selected monitoring wells, located at north border of TRL site. The dashed lines show the range of background groundwater and the solid lines show the upper and lower limits of mixing zone between the two end members, the pristine (background) groundwater and the leachate at M32.

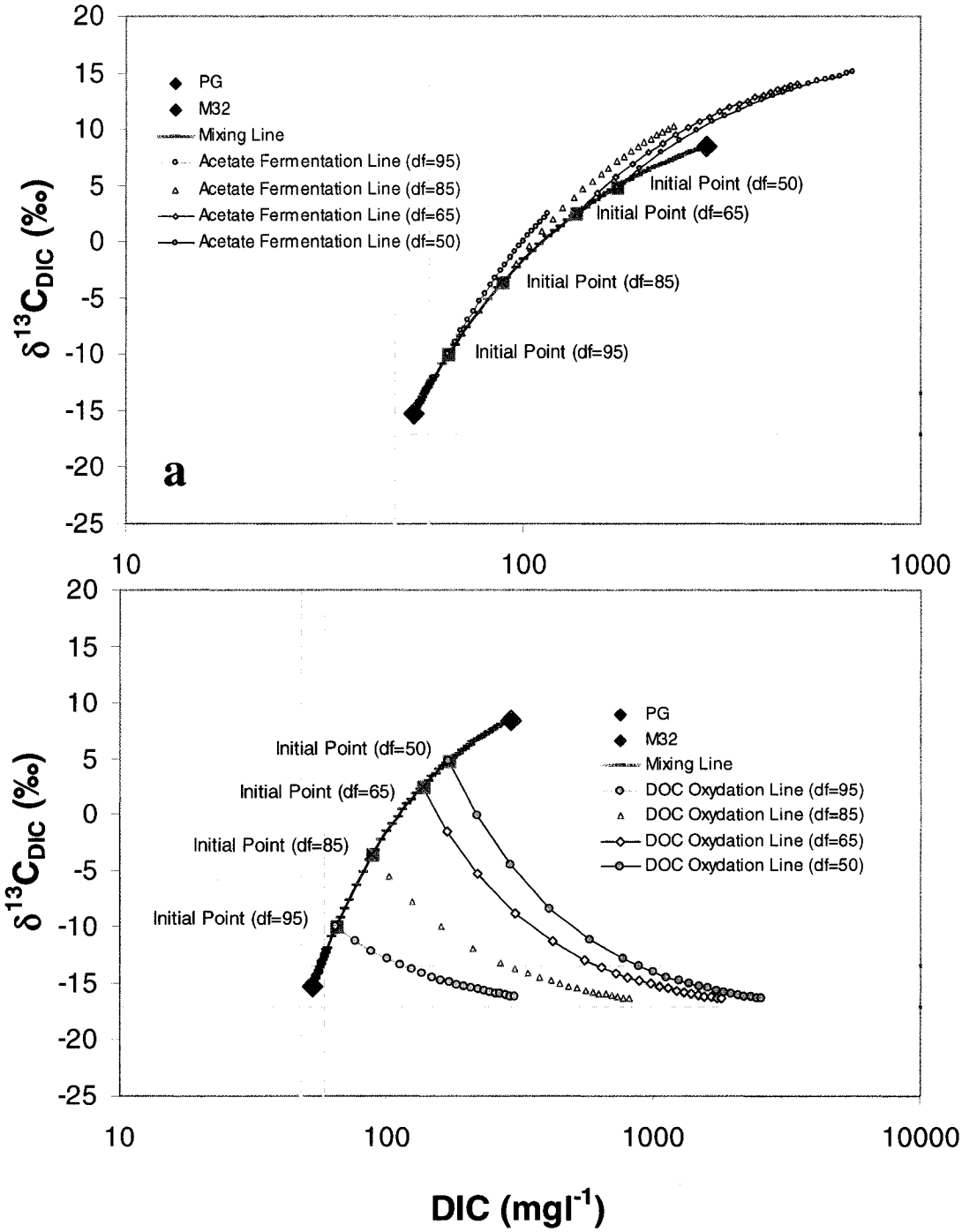

Figure 12: Modelling of the acetate fermentation (a) and the DOC oxidation (b) affects on total DIC and $\delta^{13}C_{DIC}$.

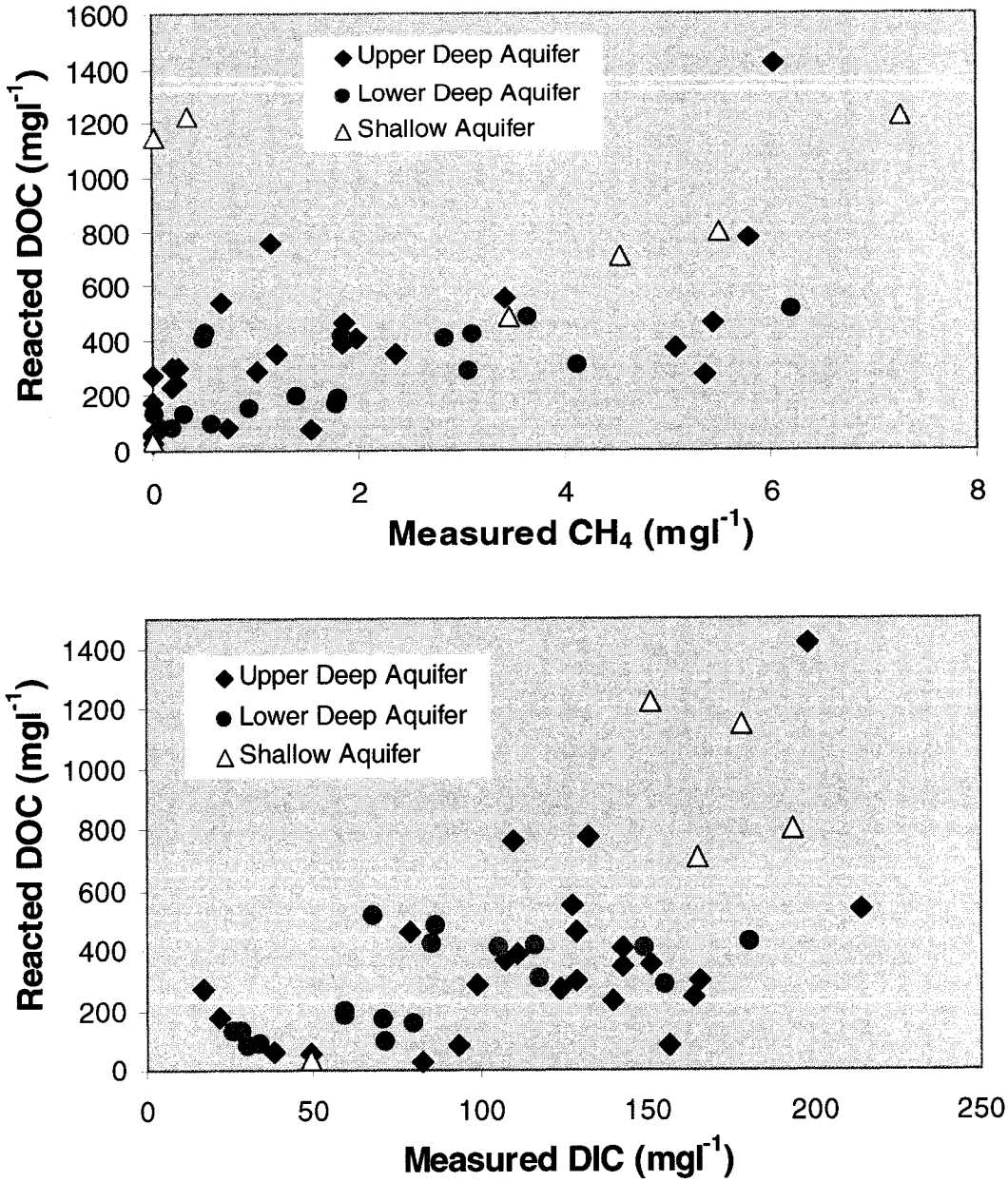

Figure 13: Reacted (lost) DOC vs. measured CH_4 and DIC for shallow and deep aquifers.

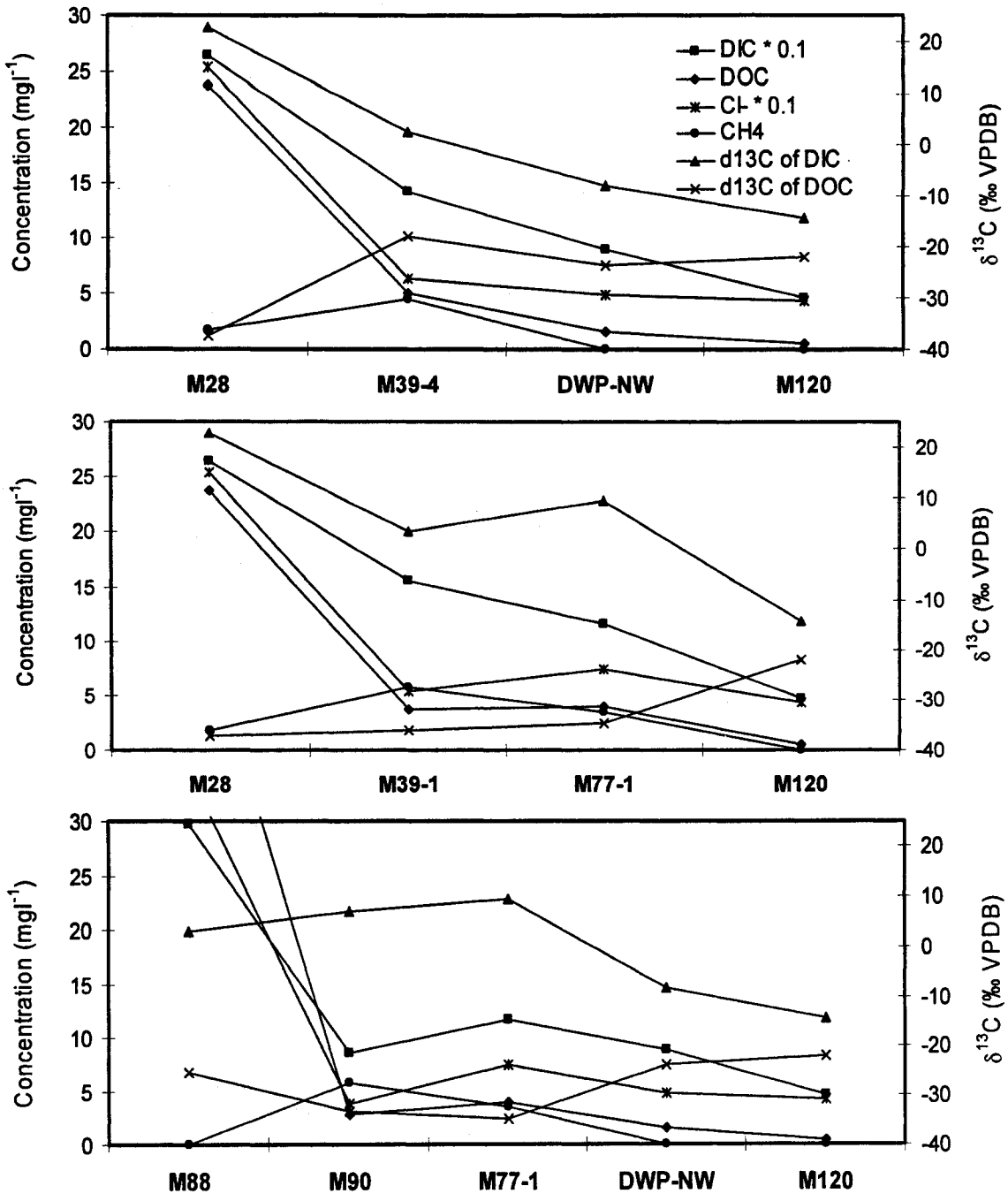

Figure 14: Concentration of various parameters (DIC, DOC, CH_4 and Cl^-) and isotopic composition of $\delta^{13}C$ along the flow path in leachate plume in the upper (a) and lower parts of the deep aquifers (b and c) at Trail Road landfill site. For the location of selected monitoring wells, see Figure 1.

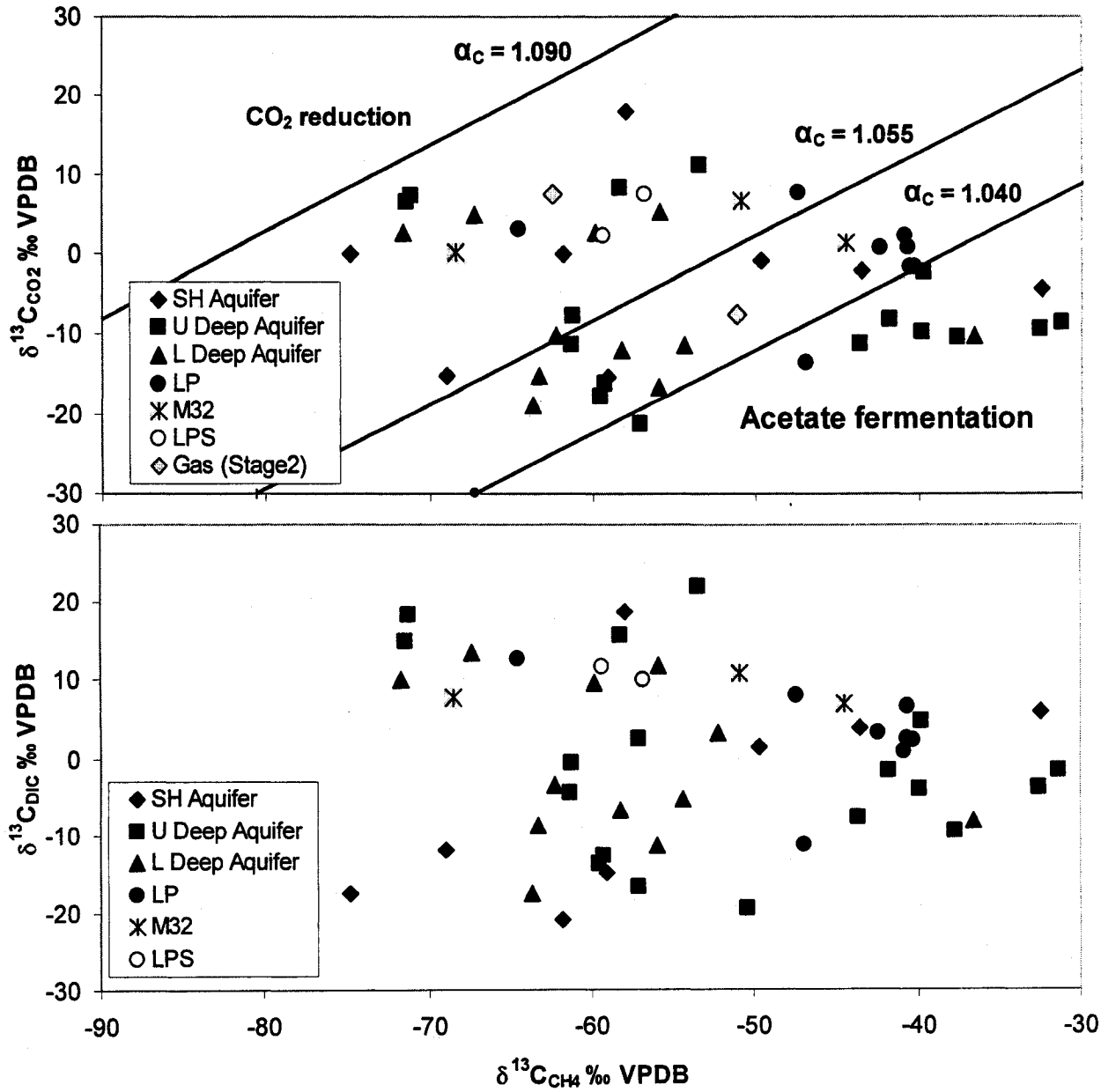

Figure 15: Cross-plot of $\delta^{13}C_{CH4}$ vs. $\delta^{13}C_{CO2}$ and $\delta^{13}C_{DIC}$ for the TRL site. Included in this plot are: the ^{13}C characteristics of leachate and leachate-polluted groundwater. Lines of equal carbon fractionation are drawn to represent CH_4 production by acetate fermentation or CO_2 reduction after Whiticar et al., 1986. For the description of leachate data see previous chapter.

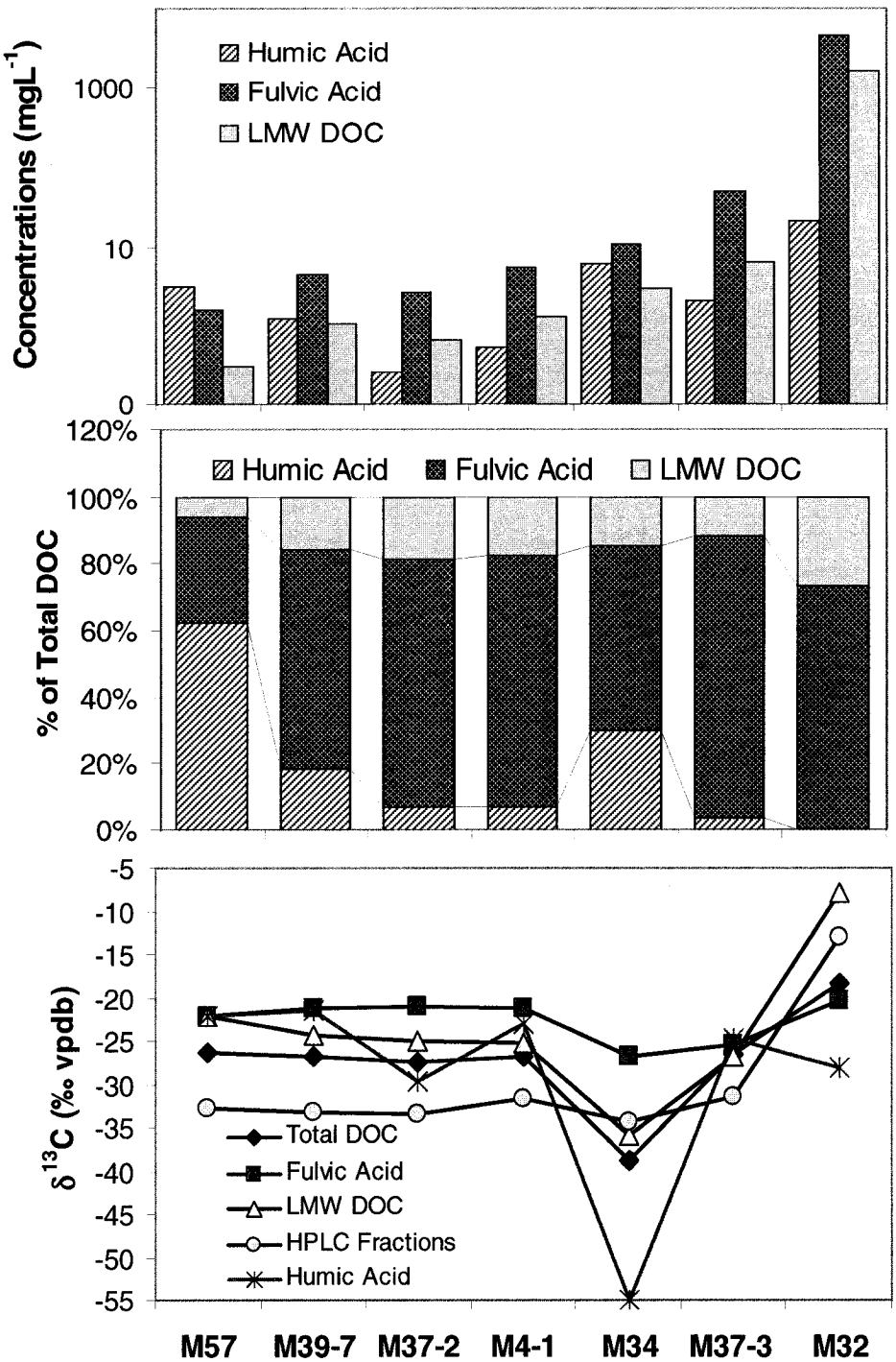

Figure 16: Distribution of humic substances as well as the variations of $\delta^{13}C$ values of DOC fractions in leachate-polluted groundwater samples.

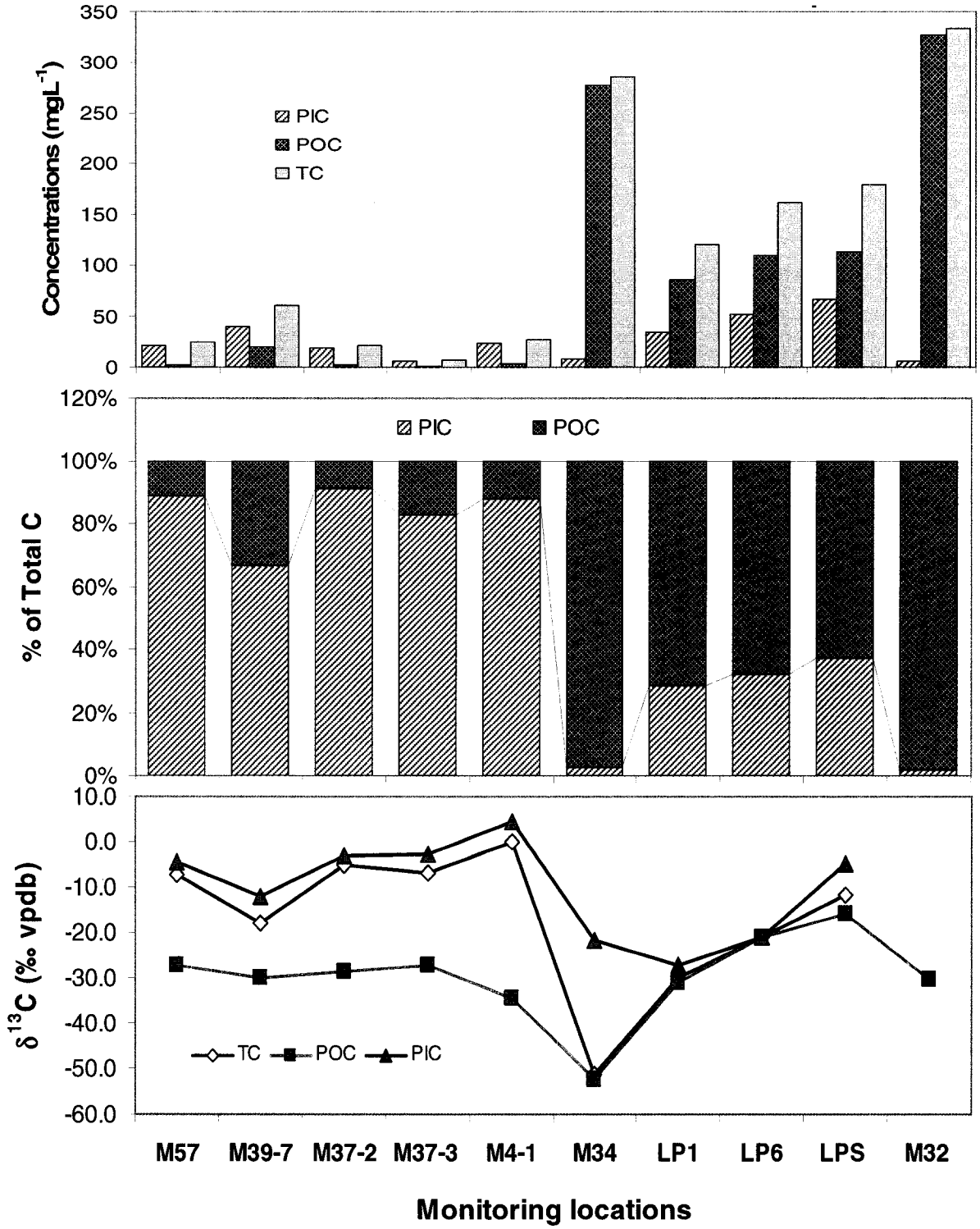

Figure 17: Distribution of particulate organic carbon (POC) and particulate inorganic carbon (PIC) and the variation of $\delta^{13}C$ values for suspended solids in leachate and leachate-polluted groundwater samples.

Conclusions and Recommendations

1. Conclusions and Recommendations

The Trail Road municipal solid waste landfill, near Ottawa, Ontario, Canada, has been in operation for over forty years. Early, unlined stages that leak leachate to the underlying aquifers are juxtaposed with later configurations engineered with basal liners and collection systems for both leachate and methane. The site is ideal for studies of leachate formation and impacts on groundwaters. This research develops the use of stable isotopes in conjunction with inorganic and organic geochemistry as a method to investigate leachate and methane production at this site, and for the unambiguous identification of leachate-impacted groundwaters.

To characterize the Trail Road MSW landfill and its potential influences on the surrounding groundwater, le achate samples were collected in 2003 through 2005 from the pumping station (LPS) for leachate generated in stages with recently emplaced waste, from a monitoring well (M32) situated at the base of the earliest stage where old leachate seeps into the subsurface, and from groundwater monitoring wells completed in the shallow and deep aquifers around the landfill. In addition, the study employed data for the leachate produced at LPS and generated gases at gas flaring station (GFS) from the City of Ottawa, Dillon Consulting Limited and Golder Associates Ltd. for assessing seasonal variation of leachate.

A new methodological approach for compound-specific isotope analysis of carbon species was developed that involves a series of methods including dissolved organic carbon separations on DAX-8 resin, liquid chromatography separations of lower molecular weight fractions (HPLC), total carbon analysis (TCA) of separates, and stable isotope ratio mass

spectrometry by continuous-flow technology (CF-IRMS). The following conclusions on sources and fate of contamination (i.e. leachate) in the surrounding aquifers were drawn from results of this research.

1.1.Landfill leachate generation

At TRL site, refuse is buried over many years. Therefore, the extent of decomposition of organic materials and the biodegradation pathways of organics is diverse at different areas of the landfill. LPS drains a mixture of young (active Stage 4) and 14 year old (Stage 3) leachate, plus leachate re-circulated through Stage 4. M32 captures leachate from older waste with an average age of 28 years at the base of the unlined Stage 1.

Deuterium excess provides a robust indicator of overall methane production, showing greater CH_4 production in leachate from the younger parts of the landfill (Stages 3 and 4) than that of the older parts (Stages 1 and 2). Younger landfill is dominated by methanogenesis by CO_2 reduction ($\alpha^{13}C_{CO2\text{-}CH4}$=1.06) with minor accumulation of LMW fatty acid (propionate is below detection limit and acetate <30 mgl^{-1}). This was confirmed with enriched $^{13}C_{DIC}$ (10.7 ‰), and much greater ^{2}H excess (20.6 ‰) for leachate from LPS. However, the older landfill favours acetogenesis with accumulation of LMW fatty acid (acetate and propionate are 1008 mgl^{-1} and 608 mgl^{-1}, respectively). In the older landfill, acetate fermentation dominates with minor methane production via CO_2 reduction, due possibly to the landfill cap which allows less water; and the earlier degradation of labile organics. Evidence for lower methane production includes the less enriched $^{13}C_{DIC}$ (8.5 ‰) and lower ^{2}H excess (10 ‰) at M32 as compared with the LPS.

The high amount of DOC (4770 mgl^{-1}) and that of low fatty acids shows a fundamentally different biodegradation pathway in the older part of the landfill site (M32). Significant enrichments of ^{13}C in low molecular weight DOC (especially acetate with $\delta^{13}C$ value of -12.0 ‰) demonstrate a reduced reaction rate that emphasizes isotope fractionation during degradation of high molecular weight compounds. This is reflected by the enriched values of $\delta^{13}C_{DOC}$ for the bulk DOC of the older leachate at M32 (–21.6 ‰) in comparison with that of the young leachate at LPS (–25.7 ‰). A significant decrease in the HA/FA ratio between LPS and M32 is observed due to the high concentrations of FA (4482 mgl^{-1}, 73% of the total DOC) and low concentration of HA (21 mgl^{-1}, 0.3% of the total DOC) in the older leachate. This is reflected by less aromatic carbon in M32 (3% and 5% for POC and HA, respectively) in comparison with that of young leachate from LPS (10% and 28% for POC and HA, respectively).

1.2.Evaluating leachate impacts on surrounding aquifers

Reviewing of traditional leachate indicator parameters (Cl, Br, NH_4, DOC) indicate that both shallow and deep aquifers have been contaminated underneath and at the north border of the unlined parts of the landfill since emplacement began in the 1960s. However, these indicator parameters are ambiguous for marginally impacted groundwaters due to their elevated background concentrations. The development of isotope methods for various organic and inorganic carbon compounds enhances the identification of leachate mixing in marginally-impacted groundwaters.

The application of these methods sheds light on the magnitude of leachate impact but also on the degree of continued reaction within the leachate plume. Mixing and reaction are two main processes which attenuate leachate impact beneath and downgradient of the TRL site. The concentrations of principal carbon compounds and inorganic species (DIC, DOC, CH_4, Cl^-) are highly elevated beneath the unlined Stage 1 (M28) and decrease along the flow path within the leachate plume due to these combined processes.

Methane concentrations are higher than can be attributed to mixing contributions from leachate, and indicated in-plume production beyond the landfill margins. The $\delta^{13}C$ of dissolved methane varies between that of biogenic methane from the landfill, and values enriched as high as –20‰ due to methane oxidation, with a Rayleigh enrichment imparted on the residual CH_4.

The concentration and $\delta^{13}C$ of dissolved inorganic carbon, DIC, remains one of the more valuable diagnostic tools for identification of landfill leachate. Through methanogenesis, this value becomes highly enriched in ^{13}C, with values as high as 20‰, and contrasts sharply with the DIC for un-impacted groundwaters of about –17‰. Further, this enriched value seems to be little impacted by subsequent dilution and calcite precipitation. The carbon isotopic composition of groundwater from different aquifers, which were examined in both parallel to the northern border of TRL site and the deep aquifer groundwater flow direction, also shows the affect of leachate with highly enriched $^{13}C_{DIC}$ (+8.8 and +10.7 ‰ for M32 and LPS, respectively) on surrounding aquifers. The $\delta^{13}C_{DIC}$ values of leachate-impacted groundwater (-6.4 ‰, -1.0 ‰ and -0.6 ‰ for the shallow, upper deep and lower deep

aquifers, respectively) remain enriched compared to the $\delta^{13}C_{DIC}$ value for the up-gradient pristine groundwater (-15.2 ‰) at the TRL site.

Bulk DOC concentrations and $\delta^{13}C_{DOC}$ in groundwaters peripheral to the unlined landfill are also affected by a combination of dilution and continued reaction. Evidence includes: 1) deviation of groundwater samples from the mixing lines between leachate and pristine groundwater on diagrams of DOC vs. $\delta^{13}C_{DOC}$; 2) lack of leachate acetate in groundwaters; and 3) strong correlations between lost DOC in excess of mixing (988 mgl^{-1}, 368 mgl^{-1}, and 272 mgl^{-1} for the shallow, upper deep and lower deep aquifers, respectively) and the net gains in DIC (185 mgl^{-1}, 117 mgl^{-1} and 85 mgl^{-1} for these aquifers, respectively).

The $\delta^{13}C$ of DOC in the impacted groundwaters from the first two sampling years in 2003 and 2004 show a most unusual depletion with values lower than –40‰. This is attributed to a transient effect related to a methanotrophic microbial substrate during plume advancement in the deep aquifer. Humic acid dominates the DOC of background groundwaters while fulvic acid, also found in natural groundwaters and is produced during degradation of landfill organics, dominates the DOC of leachate-impacted groundwaters. Thus, HA/FA ratios below unity can be diagnostic of leachate impacts.

1.3. Recommendations for further research

Methanogenesis is a key process at any landfill site, important for both energy production and as an environmental hazard. Further work on development of the isotope mass balance

method will refine this tool for establishing the methane production rate and evaluation of the efficiency of gas collection systems.

The observation of exceptional depletions in the $\delta^{13}C$ of DOC in some groundwaters on the periphery of the leachate plume is intriguing. Speculation that this is a transient effect involving methanotrophic bacteria should be evaluated with additional sampling and more advanced analysis including biochemical markers and additional compound specific isotope analysis.