

## 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  $^{13}\text{C}$  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<sup>plus</sup> 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  $^{13}\text{C}_{\text{DOC}}$  values in old leachate from the older landfill (M32) ( $4770 \text{ mg l}^{-1}$  and  $-21.6 \text{ ‰}$ ) in comparison with that of the younger leachate (LPS) ( $197 \text{ mg l}^{-1}$  and  $-25.7 \text{ ‰}$ ) shows a fundamentally different biodegradation pathway and more advanced microbial processes in the degradation of dissolved organic matter (DOM) in the older part of the landfill. This resulted in the accumulation of simple fatty acids (acetate and propionate concentration of  $1008 \text{ mg l}^{-1}$  and  $608 \text{ mg l}^{-1}$ , respectively) at the older part of the landfill with more enriched  $^{13}\text{C}$  values of acetic acid ( $-12.0 \text{ ‰}$ ) in comparison to that of young leachate at LPS ( $-16.9 \text{ ‰}$ ).
2. Deuterium excess provides a robust indicator of overall methane production, showing greater  $\text{CH}_4$  production in the younger parts of landfill than the older parts. The  $\text{CO}_2$  reduction pathway ( $\alpha^{13}\text{C}_{\text{CO}_2\text{-CH}_4}=1.06$ ) dominates at the younger landfill, however, acetate fermentation is the more favored  $\text{CH}_4$  production pathway at the older landfill. This can be confirmed with the less enriched  $^{13}\text{C}_{\text{DIC}}$  ( $8.5 \text{ ‰}$ ) and a lower value for  $^2\text{H}$  excess ( $9.8 \text{ ‰}$ ) 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 ( $4482 \text{ mg l}^{-1}$ , 73% of the total DOC) and low concentrations of HA ( $21 \text{ mg l}^{-1}$ , 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  $^{13}\text{C}$ -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,  $\text{CH}_4$ ,  $\text{CH}_3\text{COOH}$ , humic substances (HS), particulate organic carbon (POC), particulate inorganic carbon (PIC)) and  $\delta^{13}\text{C}$  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  $\delta^{13}\text{C}_{\text{DIC}}$ . In all proximal groundwaters, methane concentrations remain above detection and as high as  $10 \text{ mg l}^{-1}$ , close to the saturated equilibrium value for a 50% methane atmosphere in the unsaturated zone. The  $\delta^{13}\text{C}$  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  $^{13}\text{C}_{\text{DIC}}$  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.

2. Continued reaction of DOC in groundwaters is confirmed by deviation of groundwater samples from the mixing lines on diagrams of DIC vs.  $\delta^{13}\text{C}_{\text{DIC}}$  and DOC vs.  $\delta^{13}\text{C}_{\text{DOC}}$ , and by the absence of acetate. The calculated net reacted (lost) DOC (988  $\text{mg l}^{-1}$ , 368  $\text{mg l}^{-1}$ , and 272  $\text{mg l}^{-1}$  for the shallow, upper deep and lower deep aquifers, respectively) correlates with net gains in DIC (185  $\text{mg l}^{-1}$ , 117  $\text{mg l}^{-1}$  and 85  $\text{mg l}^{-1}$  for these aquifers, respectively) and is further evidence for continued reaction beyond the landfill. Acetate fermentation reactions resulted in enriched  $^{13}\text{C}_{\text{DIC}}$  for the gained DIC. However, oxidation of DOC and/or methane oxidation resulted in negative shift in  $\delta^{13}\text{C}_{\text{DIC}}$  for the gained DIC. The low amount of DIC associated with the low amount of  $\text{Ca}^{2+}$  suggests a mineralogical control through calcite precipitation.
3. Production of  $^{13}\text{C}$ -depleted organic carbon, possibly through methanotrophic bacterial activity, seems to occur in the fringes of the advancing leachate plume. Evidence includes remarkably depleted  $^{13}\text{C}_{\text{DOC}}$  at the lower part of the deep aquifer where values lower than  $-40\text{‰}$  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,  $\text{CH}_4$ ), chromatographically separated DOC components (acetate, propionate, humic substances (HS)), environmental stable isotopes ( $\delta^{13}\text{C}$ ,  $\delta^2\text{H}$ , and  $\delta^{18}\text{O}$ ), compound specific isotopic analysis (CSIA), methane production, Trail Road Landfill (TRL).