



Assessment of Dissolved Organic Carbon Degradation in Landfill Leachate Using Hydrogen and Carbon Isotopes

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Abstract

The composition of carbon pools is subject to seasonal variations and is 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, CH₄, CH₃COOH, and humic substances (HS)), environmental stable isotopes (d¹³C, d¹⁸O, and d²H) 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).

In this research the isotope analysis on leachate, landfill gases and various leachate DOC components indicate that: 1) microbial processes are more advanced in the degradation of dissolved organic carbon (DOC) in the leachate collected from the older parts of the landfill site (M32); 2) simple fatty acids (e.g. acetic = 1008 mg l⁻¹ and propionic = 608 mg l⁻¹, etc.) accumulate in the leachate from older part of the landfill; 3) the acetate fermentation CH₄ production pathway dominants in older parts of the landfill. While, in the younger part of the landfill (LPS), CO₂ reduction pathway ($\alpha^{13}\text{C}_{\text{CO}_2\text{-CH}_4}=1.06$ and D-excess = 20.6‰) is the more favoured CH₄ production pathway; 4) fulvic acid (FA) is the main fraction of leachate DOC and the enriched ¹³C 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.

Keywords

Landfill leachate; Dissolved organic/inorganic carbon; Environmental stable isotopes ($\delta^{13}\text{C}$, $\delta^2\text{H}$, and $\delta^{18}\text{O}$); Acetate and propionate; Humic substances



1. Introduction

Leachate quality is highly variable and its composition varies significantly among landfills. As inferred from other studies [1, 2, 12], 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) co-disposal with sewage sludge and municipal solid waste (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 [2]. 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 [2]. To date, a wide range of different types of organic compounds have been identified in landfill leachates [1, 2, 12]. Most studies conducted on DOC fractions of landfill leachate use isolation methods to investigate temporal and spatial variations [1, 6]. A few studies have been conducted on the chemical structure of leachate DOC fractions [e.g. Ref. 3] and on the characterization of the acid-precipitated and acid-soluble fractions of landfill leachate DOC [11]. Less is known regarding the isotopic composition of these fractions and the evolution of ^{13}C isotope over degradation process [e.g. Ref. 4]. The objective of this research is to measure deuterium enrichments in leachate, to isolate and characterize the concentrations and the $\delta^{13}\text{C}$ values of the principal DOC fractions of leachate, and to observe the isotopic evolution of these fractions during the degradation of organic carbon.

2. Sampling and analytical techniques

Leachate samples were collected from the Trail Road Landfill (TRL) site, owned and operated by the City of Ottawa and is located approximately 25 km west of the city (Figure 1). The leachate sampling program was restricted to LPS, LP and a monitoring well (M32) on top of the landfill. A detailed description of sampling procedures, field measurements and analytical techniques is given by Mohammadzadeh and Clark [9] and Mohammadzadeh et al. [10]. 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). All measurements were performed in the geochemistry and G.G. stable isotope laboratories at the University of Ottawa.

3. Results and discussion

3.1. Hydrogen and oxygen isotopes in leachate

The stable isotope composition of leachate water ($\delta^2\text{H}$ and $\delta^{18}\text{O}$) 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).

Figure 2 shows the $\delta^2\text{H} - \delta^{18}\text{O}$ diagram of different samples of leachate. The $\delta^{18}\text{O}$ 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 $\delta^{18}\text{O}$ of precipitation, reflecting a rapid movement of water through the pile with minimal storage in the waste.

Despite shifts in leachate $\delta^{18}\text{O}$ 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) (Figure 2). 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 [5, 8].

3.2. Carbone isotope of the bulk DOC and DIC in leachate

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. For the young leachates, the average concentration of DOC is relatively low reflecting dilution in the uncapped setting, and with $\delta^{13}\text{C}$ values close to typical biomass precursors (-26 ‰):

$$\text{LPS} - \text{DOC} = 197 \text{ mg } \Gamma^{-1}, \delta^{13}\text{C} = -25.7\text{‰}$$

$$\text{LP} - \text{DOC} = 117 \text{ mg } \Gamma^{-1}, \delta^{13}\text{C} = -26.0 \text{‰}$$

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

$$\text{M32} - \text{DOC} = 4770 \text{ mg } \Gamma^{-1}, \delta^{13}\text{C} = -21.6 \text{‰}$$

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 DIC (Figure 3c). Variation from dilution is demonstrated by the strong shift in $\delta^{18}\text{O}$ of the leachate (Figure 2, and Figure 3b). This effect of significant seasonal dilution of the leachate and strong seasonal shift in $\delta^{18}\text{O}$ underlines the rapid movement of infiltration water through the waste.

The much greater concentration together with the enriched $^{13}\text{C}_{\text{DOC}}$ 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 = $349 \text{ mg } \Gamma^{-1}$, LP = $494 \text{ mg } \Gamma^{-1}$, and M32 = $290 \text{ mg } \Gamma^{-1}$, but also affected by seasonal dilution (Figure 3c). For all, however, the $^{13}\text{C}_{\text{DIC}}$ is highly enriched ($+10.7 \text{‰} \pm 4.2$, $n=41$ for the LPS, and $+4.7 \pm 3.8$, $n=8$ for the LP and $+8.5 \text{‰} \pm 1.0$, $n=3$ 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. Between ^2H excess and $\delta^{13}\text{C}_{\text{DIC}}$ in LPS a positive trend was found.

3.3. Major components of leachate DOC

The leachate DOC fractions investigated include acetic acid (AA) and propionic acid (PA) as well as refractory HS such as FA and 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 CH₄ during acetoclastic methanogenesis.

The concentration of AA (between 218 and 1755 mg l⁻¹) and PA (between 29 and 1313 mg l⁻¹), two simple short-chain fatty acids with low molecular weight, are the dominant components of DOC in M32. Methanogenesis in the older leachate samples is characterized by the production of these compounds through fermentation reactions (Figure 4). By contrast, the concentration of AA in young leachate at LPS is only about 24 mg l⁻¹ ($\sigma = 1.0$, $n=3$) and there was no measurable PA. The high amount of AA and PA in older leachate from M32 (1008 mg l⁻¹ and 608 mg l⁻¹, respectively) in comparison with that of younger leachate from LPS (24 mg l⁻¹ and lower than detection limit (1.0 mg l⁻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 mg l⁻¹) and more enriched values of ¹³C_{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 ‰).

The percentages of the DOC present as FA and LMW DOC were estimated using the measured data and the distribution of HA, FA and the LMW DOC fractions of landfill leachate DOC is shown in Figure 5. 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 86.1 % of total DOC content of both older and young leachates (Figure 5).

At the TRL site, the calculated HA/FA ratios for all leachate samples are below unity which for some researchers reflects aging of the landfill leachate. The ratio in younger leachate from LPS (0.18) is approximately 3.6 times greater than that 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 mg l⁻¹), whereas there is not much difference in concentration of HA between LPS (28 mg l⁻¹) and M32 (21 mg l⁻¹). HA forms just about 0.3% of the total DOC at M32 (Figure 5).

3.4. Compound specific isotope analysis of DOC components

The average $\delta^{13}\text{C}$ 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 ¹³C values due to greater selectivity by bacteria for metabolizing material with the weaker ¹²C bonds. A more enriched ¹³C 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 to the equations in Figure 4.

Isotope fractionation associated with CO₂ reduction ($\alpha^{13}\text{C}_{\text{CH}_4\text{-CO}_2}$) is about 0.935, thus imparting a depletion greater than about 65‰ on the $\delta^{13}\text{C}$ of methane, whereas methane from acetate fermentation is less than about 50‰ depleted from $\delta^{13}\text{C}$ of CO₂. In order to better understand methane production in the young and old leachates, the evolution of ¹³C in these components during transformation is a useful tracer.

The $\delta^{13}\text{C}$ 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 $\delta^{13}\text{C}$ value of the minor acetate in young leachate at LPS is considerably less enriched in ¹³C than in M32, with $\delta^{13}\text{C} = -16.9$ ‰ ($\sigma = 0.1$, n=3) and there was no propionic acid measured in LPS.

As illustrated in Figure 5, 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 ¹³C value of LMW DOC of the older M32 leachate (-8.0‰ and -13.0‰), as compared to the $\delta^{13}\text{C}$ value of bulk DOC (-18.4‰). This is consistent with the enrichment trend for $\delta^{13}\text{C}$ for acetate.

The $\delta^{13}\text{C}$ 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 $\delta^{13}\text{C}$ value of FA (the major fraction of HS) is -26.2‰. This is slightly higher than the $\delta^{13}\text{C}$ value of corresponding LMW DOC (-27.1‰), but is lower by about 3.3‰ compared to the equivalent $\delta^{13}\text{C}$ value of HA (-22.9‰). In the older leachate (M32), by contrast, the $\delta^{13}\text{C}$ value of FA (-20.3‰) is significantly enriched compared to the HA (-28.1‰). Like the LPS leachate, the $\delta^{13}\text{C}_{\text{FA}}$ is close to that of the bulk DOC (-18.4‰).

4. Summary and conclusions

In general, the following conclusions can be made from the geochemical parameters, the carbon geochemistry of different carbon pools (DIC, DOC, CH₄, CH₃COOH, and HS), the environmental stable isotopes ($\delta^{13}\text{C}$, $\delta^{18}\text{O}$, and $\delta^2\text{H}$) 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 CH₄ production than in the older landfill. Methanogenesis must be dominated by CO₂ reduction ($\alpha^{13}\text{C}_{\text{CO}_2\text{-CH}_4}=1.06$). This was confirmed by more enriched ¹³C of DIC at LPS (10.7 ‰). However, the very minor accumulation of LMW fatty acids (propionate is below detection limit and acetate <30 mg l⁻¹) indicates that acetoclastic methanogenesis must also take place. Low concentrations of all DOC components with lower $\delta^{13}\text{C}$ values, indicate rapid conversion of DOC to methane at LPS, which allows little accumulation of intermediate products.

2. The high amount of DOC (4770 mg l^{-1}) and that of low fatty acids (acetate and propionate are 1008 mg l^{-1} and 608 mg l^{-1} , respectively) shows a fundamentally different biodegradation pathway in the older part of the landfill site (M32). Enriched values of $^{13}\text{C}_{\text{DOC}}$ 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 $< 10\text{‰}$) and is in an acetate fermentation phase with accumulation of LMW fatty acids.

3. Due to high concentrations of FA (4482 mg l^{-1} , 73% of the total DOC) and low concentration of HA (21 mg l^{-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.

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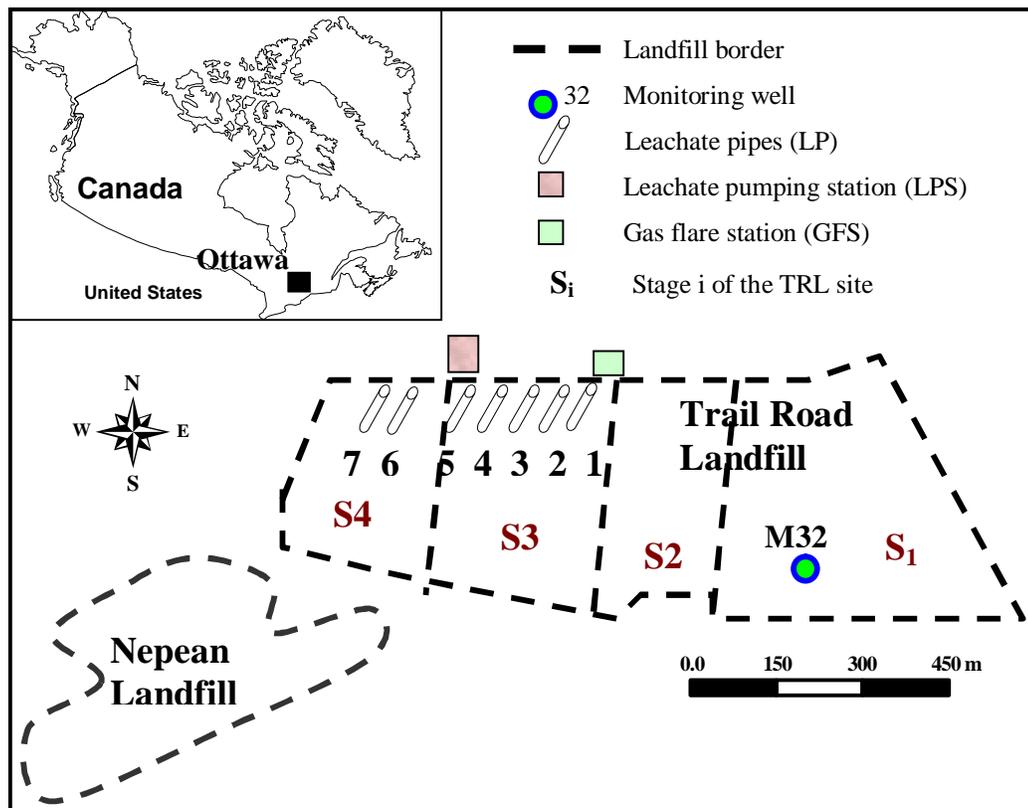


Figure 1: Plan view of study area, sampling location and site operation.

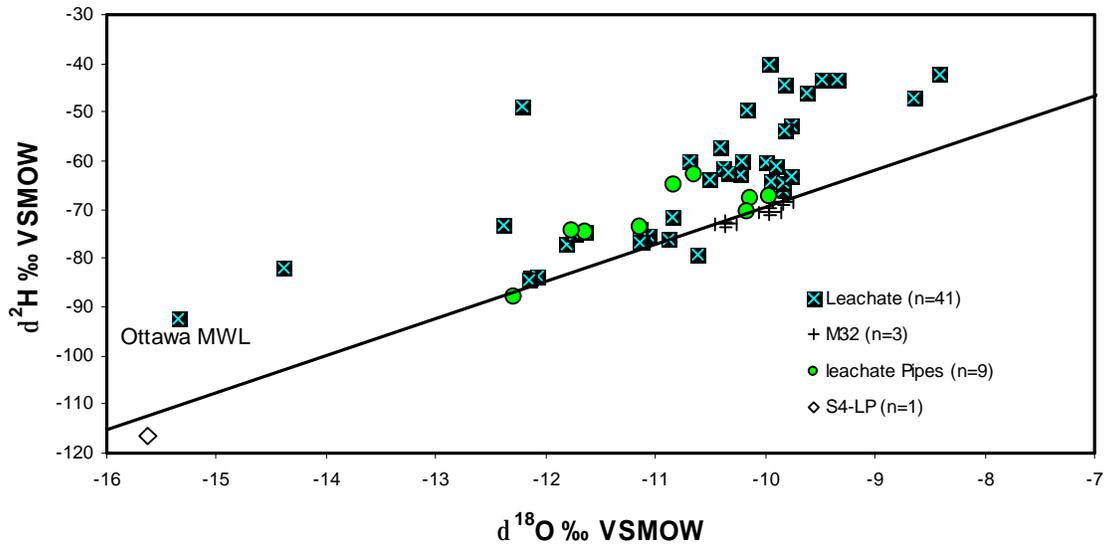


Figure 2: $\delta^2\text{H}$ and $\delta^{18}\text{O}$ of leachate water from the TRL site.

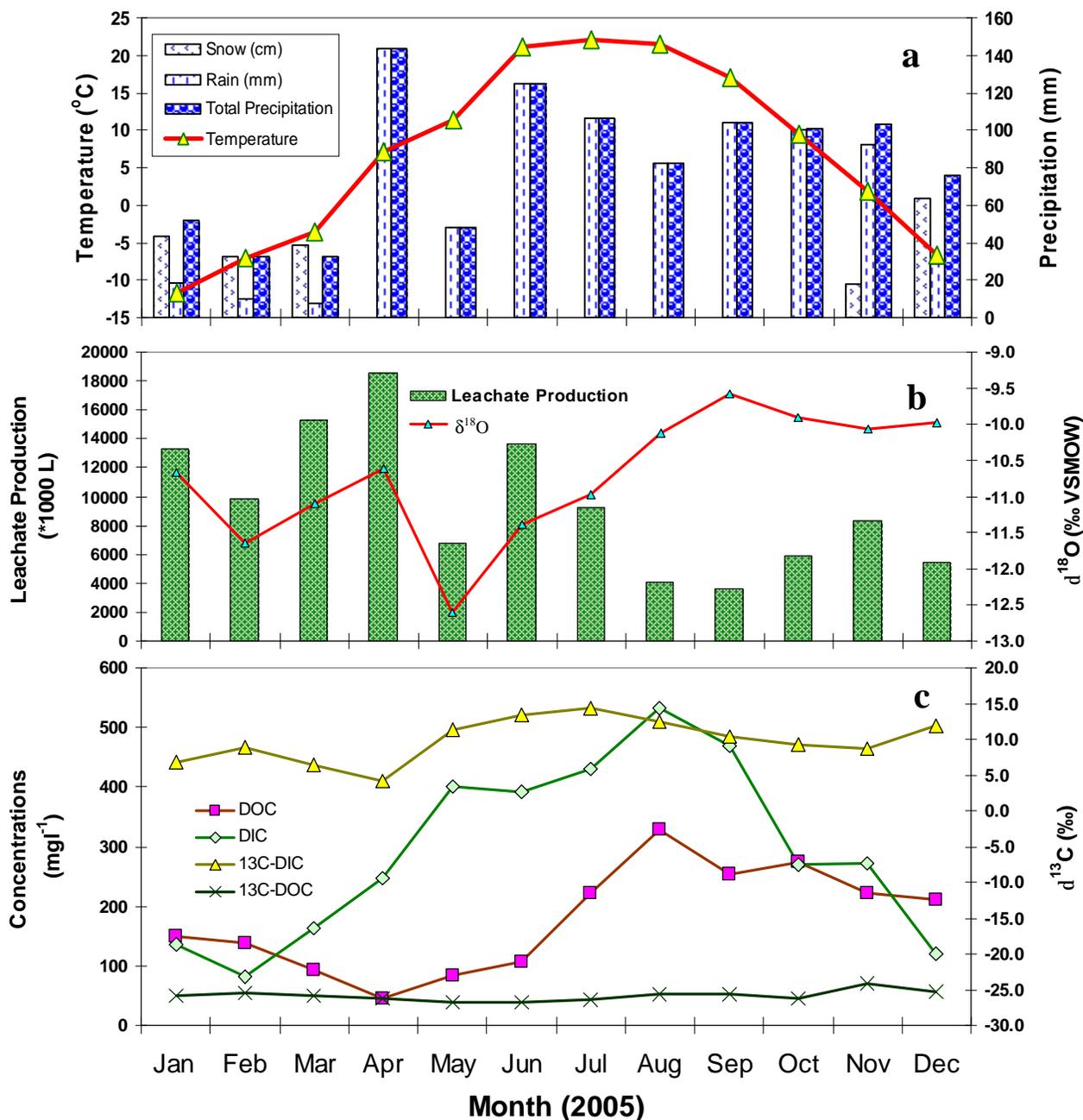


Figure 3: Variations of DIC, DOC and isotopic ($\delta^{13}\text{C}$) composition in leachate from LPS with time. The top histograms show the meteorological parameters (temperature and precipitation), the monthly production of the leachate at TRL site which was calibrated by inventories of truck loads (hauling leachate from LPS) and seasonal variation of $\delta^{18}\text{O}$.

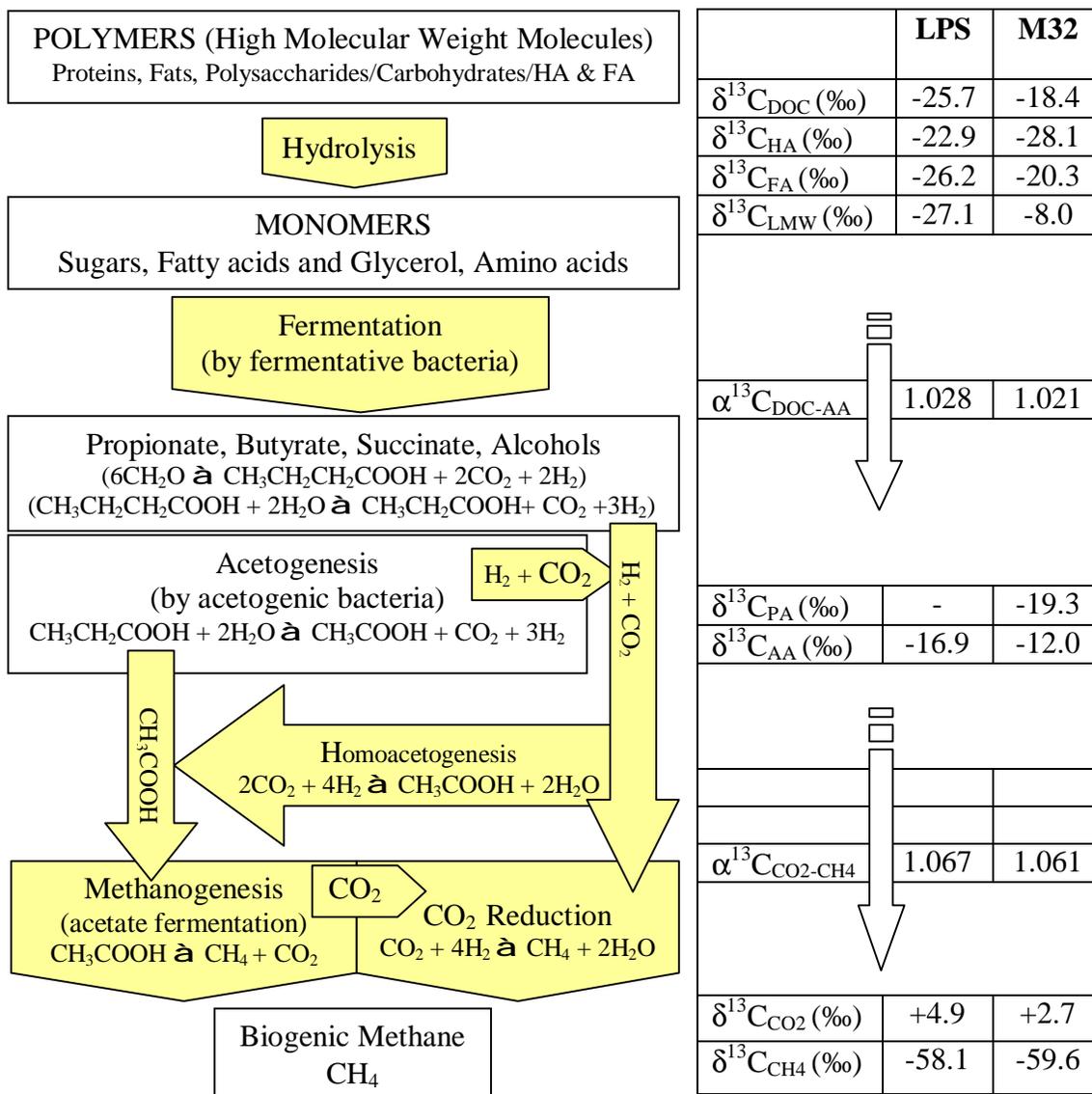


Figure 4: The general pathways of CH_4 generation and evolution of the $\delta^{13}\text{C}$ values for the DOC components during DOC degradation at anaerobic conditions in both young leachate (LPS) and older leachate (M32) at TRL site (DOC = total dissolved organic carbon, HA = humic acid, FA = fulvic acid, LMW = low molecular weight DOC, PA = propionic acid and AA = acetic acid). All isotopic data in ‰ VPDB.

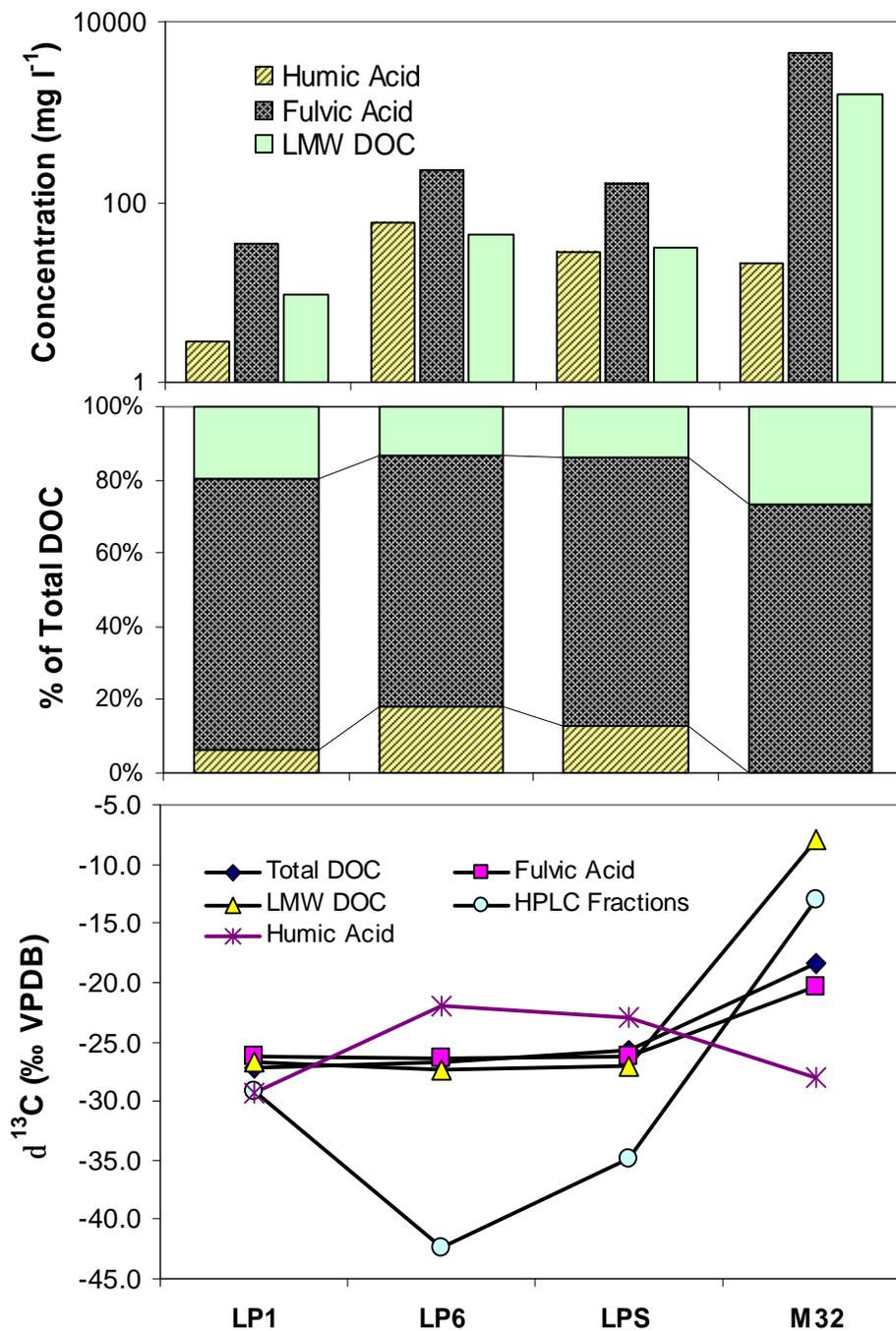


Figure 5: Concentrations and the distribution of humic substances and variations of the $\delta^{13}\text{C}$ values of DOC fractions in leachate samples.