

Use of stable isotope analysis in a monitored natural attenuation program in the unsaturated zone

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Abstract

Over the past decade, natural attenuation was shown to be a cost effective strategy to manage petroleum hydrocarbon contaminated sites and the occurrence of *in situ* biodegradation is often the key process to be demonstrated for a successful monitored natural attenuation program (MNA). In order to achieve such a task, it was shown that compound-specific isotope analysis (CSIA) can be a reliable tool to assess biodegradation of organic contaminants in the saturated zone.

Carbon isotope fractionation occurs during biodegradation as a consequence of the slightly faster cleavage of chemical bonds between light isotopes (¹²C) of an element compared to heavy isotopes (¹³C). The difference in degradation rates leads to an enrichment of ¹³C-containing compounds in the residual contaminant pool compared to the initial value. Mostly used in the saturated zone via water samples, the isotope method was recently shown to be applicable as well in the unsaturated zone via gas samples. Hence, the latest results fill a gap and allow now a complete assessment of the fate of petroleum hydrocarbons in both contaminated zones.

In the saturated zone, as the migration of the organic compound is mainly due to advection, the isotope fractionation is only controlled by biodegradation. However, since diffusion is the main transport of volatile organic compounds (VOCs) in the unsaturated zone through soil air, and because ¹²C-compounds diffuse faster than ¹³C-containing compounds, isotope fractionation due to diffusion is inversely controlling the isotope fractionation compared to biodegradation. As a consequence, on one hand, the observed enrichment of ¹³C-containing compounds in the residual contaminant pool is more limited, but on the other hand, reveals useful information on source weathering. Indeed, this isotope fractionation controlled by diffusion causes the source to get enriched in ¹³C-containing compounds as the source mass is decreasing over time, and thus be used to monitor the extent of source depletion over time.

This presentation resumes the knowledge recently gained for assessing natural attenuation of petroleum hydrocarbons in the unsaturated zone with isotope analysis, from the spill moment to source exhaustion. A modeling approach focusing on $\delta^{13}\text{C}$ distribution of VOCs in a surrounding area of a NAPL source floating on the water table

with contaminants migrating upward is presented. The investigation is based on analytical solutions which predict spatio-temporal $\delta^{13}\text{C}$ profiles affected by diffusion and biodegradation of VOCs, and by source depletion. The modeling approach was previously shown to reproduce isotopes trends observed in the unsaturated zone of a field and a column experiment. We have shown that diffusion exerts a control on isotope ratios in the unsaturated zone that counteracts the fractionation created by biodegradation.

References:

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