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## MONITORED NATURAL ATTENUATION OF A COMPLEX MIXTURE OF ORGANOCHLORINES USING COMPOUND-SPECIFIC ISOTOPE ANALYSIS

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### ABSTRACT (Calibri, 12pt bold)

In France, chlorinated hydrocarbons represent the third most commonly detected groundwater contaminant class (19%, directly after heavy metals, 22%, and mineral-oil hydrocarbons, 33%; Medde, 2012). The fate and behaviour of organic contaminants in aquifer systems depend on a number of physicochemical and biological processes, which may lead to natural attenuation. To apply *in situ* attenuation by naturally occurring or enhanced biodegradation as a cost-effective remediation option at these sites, it becomes primordial to accurately identify and quantify ongoing biotransformation processes. Determination and quantification of these processes are crucial for contaminated site risk assessment and sustainable groundwater management strategies.

Compound-specific isotope analysis (CSIA) by online-coupling of gas chromatography and isotope ratio mass spectrometry (GC-IRMS) offers a versatile tool to study the origin of a pollution and/or to decipher multiple contamination sources, to verify if biodegradation of organic pollutants is occurring, to identify degradation mechanisms, and to determine the rate and extent of in-situ biodegradation. In the last decade, compound-specific isotope analysis (CSIA) has evolved as a diagnostic tool for contaminated site investigation and for monitoring the efficiency of intrinsic natural or enhanced remediation processes, and is now available for studying an increasing number of environmental pollutants (Elsner et al. 2012). Chemical compounds contain heavy and light stable isotopes in a certain ratio, i.e.  $^{13}\text{C}/^{12}\text{C}$ , D/H, and  $^{15}\text{N}/^{14}\text{N}$ . In general, molecules containing the lighter isotope react faster than those containing the heavier isotope. Bond-breaking processes induced by microbial metabolism, can cause a large isotope fractionation leading to an enrichment of heavy isotopes in the residual fraction of the contaminant. CSIA allows interpreting these changes in the isotopic composition of individual organic compounds, thus providing a direct proxy for chemical transformations. CSIA permits qualitative and quantitative information on *in situ* (bio)degradation, can distinguish different reaction mechanisms, and provides additional means for source allocation and differentiation (Schmidt et al. 2004, Blessing et al. 2009, Braeckevelt et al. 2012, Negrel et al. 2012).

We applied compound-specific carbon isotope analysis (CSIA) in a remediation study to evaluate the potential of monitored natural attenuation (MNA) at an industrial site. The study site is an organochlorine production site with a long operational history and leaking facilities or accidental spills released high amounts of contaminants to soil and groundwater. A control and monitoring program of DNAPL at the study site is installed since the 80s. A hydraulic confinement separated the DNAPL source from the contamination plume that consists of lighter, more soluble chlorinated compounds, mainly PCE, TCE, DCE, TeCA, DCA, TCP and DCP. Biostimulation using acetate and H<sub>2</sub> amendment was performed in a limited area within the plume.

The aim of the present work is to demonstrate the potential of the CSIA approach for monitoring in-situ biodegradation and for characterizing and quantifying transformation processes of chlorinated pollutants in groundwater towards the ultimate goal of an implementation of natural and/or enhanced bioremediation at the contaminated site. To this end, a total of four monitoring wells in the source zones and nine groundwater wells within the downgradient contaminant plume over several kilometres length were sampled and stable carbon isotope ratios of the aforementioned chlorinated compounds were

analyzed. The use of headspace solid-phase micro extraction as sample pre-concentration and extraction technique allowed for compound-specific carbon isotope analysis for most of the compounds even at concentrations in the low ppb-range ( $\geq 3\mu\text{g/L}$ ). Significant  $^{13}\text{C}$  isotope enrichments with shifts of up to 10‰ were observed along the anoxic flow path of the plume. Observed fractionation is compound- as well as pathway-specific (aerobic and anaerobic biodegradation). Field data evaluated using the Rayleigh equation demonstrate that dispersion plays a major role, esp. within the oxic zones of the plume. For a reliable quantification of the extent of in-situ biodegradation within the aquifer, the selection of appropriate isotope enrichment factors representative of the specific biogeochemical conditions at the site is crucial (Pooley et al. 2009). Isotope enrichment factors for the aforementioned organochlorine compounds that have been determined in laboratory microcosm studies under aerobic and anaerobic conditions, respectively, will be presented and compared to the extent of isotope fractionation observed at our field site. In our contribution we will demonstrate the usefulness of the CSIA approach to determine both the nature and the extent of natural attenuation of chlorinated contaminants in the field. In addition, we will present new developments with respect to analytical techniques and demonstrate, based on experience from field studies, how isotope signatures can help revealing different pollution sources and/or spill events.

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