**Carbon and hydrogen compound-specific stable isotope analysis of organophosphorus pesticides for characterization of the degradation pathways in contaminated aquifers**

Langping Wu1, Shujuan Lian1, Steffen Kümmel1, Anko Fischer2, Morten Bondgaard3, Anja Melvej3, Hans H. Richnow1

1 Department of Isotope Biogeochemistry, Helmholtz Centre for Environmental Research-UFZ, Permoserstraße 15, D-04318 Leipzig, Germany.

2 Isodetect GmbH - Company for isotope monitoring, Deutscher Platz 5b, D-04103 Leipzig, Germany.

3 Department of Environment ▪ Central Denmark Region, Lægårdvej 12R, 7500 Holstebro, Denmark.

Organophosphorus pesticides (OPs) have been used throughout the world since the decline in the use of organochlorine pesticides in the 1960s and 1970s. However, in recent years several governmental agencies have started to reconsider the wide use of OPs due to concern about their effects on the central nervous systems of humans. The persistence of OPs in the environment is of great concern, as they have repeatedly been found in drinking water supply wells and may pose a risk to water resources. Thus, more information of the fate of OPs in the environment with respect to potential degradation processes is essential.

At present, compound-specific stable isotope analysis (CSIA) is among the most promising tools for assessment of the *in situ* contaminant degradation within aquifers. It is applicable for proving *in situ* degradation and characterizing degradation conditions, and moreover, for characterizing degradation pathways and underlying reaction mechanisms. While most applications focus on CSIA of carbon, carbon isotope fractionation may be similar among different transformation pathways, resulting in uncertainties for qualitative and quantitative assessment of contaminant transformation. The combination of isotope fractionation of several elements may characterize the bond cleavage of the degradation reaction more precisely as the isotope fractionation of a single element. Thus, multi-dimensional CSIA may allow a more precise interpretation of the underlying degradation pathways.

CSIA is widely used in studies of chlorinated ethenes, fuel related compounds like benzene and fuel oxygenates (MTBE). However, only our previous study to date is available on the isotope fractionation associated with the hydrolysis processes of OPs. Acid-catalyzed hydrolysis of OPs may be too slow for an important reduction of OPs under typically newel or slightly acidic environmental conditions. However, alkaline hydrolysis at higher pH could be fast enough to be a very important degradation pathway for remediation approaches.

The main goal of this work is to evaluate *in situ* remediation of OPs by alkaline hydrolysis at a former dumpsite (Groyne 42) using carbon and hydrogen stable isotope analysis (2D-CSIA). The “Groyne 42” field site located Denmark is heavily contaminated witt OPs. The area is heavily contaminated by mainly OP pesticides (e.g. parathion, malathion, sulfotep) and degradation products (e.g. p-nitrophenole, di- and triesters); chlorinated herbicides (e.g. MCPA) and degradation products (e.g. cresols); and heavy metals (i.e. mercury and arsenic). In order to evaluate the stimulated *in situ* degradation of OPs due to hydrolysis supported by NaOH addition, groundwater samples were taken in both treated and untreated areas.

Analytical methods were established and verified for determining carbon and hydrogen isotope ratios of parathion using GC-IRMS. Since the pH has a strong effect on the hydrolysis mechanisms of OPs, laboratory experiments were firstly conducted to determine the enrichment factors associated with hydrolysis of parathion and methyl-parathion at different pH ranging from acidic to alkaline conditions. For example, the hydrolysis of parathion yield carbon enrichment factors (εC) of -6.8 ± 1.3 ‰ at pH 2, -6.4 ± 0.8 ‰ at pH 5, -5.8 ± 0.5 ‰ at pH 7, -3.5 ± 0.6 ‰ at pH 9, and -0.06 ± 0.1 ‰ at pH 12. The hydrolysis of methyl-parathion revealed carbon enrichment factors of -10.0 ± 1.1 ‰ at pH 2, -10.2 ± 2.3 ‰ at pH 5, -9.9 ± 0.9 ‰ at pH 7, -6.4 ± 0.6 ‰ at pH 9, and -0.3 ± 0.5 ‰ at pH 12. In addition, we investigated the potential of the dual isotope fractionation to characterize hydrolysis mechanisms at different pH levels.

CSIA of field samples revealed differences in carbon and hydrogen isotope ratios for parathion of +4.0 ‰ and +60.9 ‰ between the free phase of contaminants and the treated area as well as +4.9 ‰ and +27.2 ‰ between the free phase of contaminants and the untreated area, respectively, indicating degradation of parathion in both zones. For evaluating the predominant degradation mechanisms of parathion within the treated and untreated area, multi-dimensional CSIA concept based on the obtained carbon and hydrogen isotope enrichment factors was applied.

This study highlights the ability of multi-dimensional CSIA to distinguish the hydrolysis mechanisms of OPs, and to support the evaluation of *in situ* degradation at contaminated sites.