**Two-dimensional stable isotope fingerprinting for source investigation of Hexachlorocyclohexanes**

Natalija Ivdra1,2, Sara Herrero-Martín2, Julian Renpenning2, Steffen Kümmel2, Matthias Gehre2, Hans-Hermann Richnow2, Anko Fischer1

1 Isodetect – Company for Isotope Monitoring, Deutscher Platz 5b, 04103, Leipzig, [natalija.ivdra@ufz.de](mailto:natalija.ivdra@ufz.de)

2 Department of Isotope Biogeochemistry, Helmholtz Centre for Environmental Research - UFZ, Permoserstraße 15, 04318, Leipzig

Organochlorine pesticide Hexachlorocyclohexane (HCH) is one of the most relevant compounds from the group of persistent organic pollutants (POPs). HCH has been broadly produced and used worldwide as an agricultural insecticide, leading to a wide-spread contamination (Voldner 1995). HCH is generally produced as isomeric mixture containing only 8-15 % of -HCH, which is the only isomer with strong insecticidal properties. Since the application of technical mixture was banned in the late 1980s, a large scale production and purification of -HCH generated huge amounts of more toxic and persistent waste isomers (-HCH, -HCH and -HCH), which are still present in chemical waste dumps and areas around former production sites (Vijgen 2011). Due to the high environmental risk of HCHs, there is an essential need for investigating sources and potential sinks of these pollutants.

Variability of stable isotope signatures of different organic compounds found both in originally manufactured chemicals and environmental samples from contaminated sites are explained by isotope fractionation, occurring during production, purification, handling, storage, application and, finally, degradation of these substances. Thus, stable isotope analysis is an efficient tool to track sources and sinks of various pollutants in the environment, as well as assess their biotransformation processes (Meckenstock 2004, Elsner 2010 and Thullner 2012).

Carbon isotope composition of HCHs in various contaminated sites has been studied in respect to the degradation related stable isotope fractionation of these compounds (Badea 2009 and Bashir 2015). However, no comprehensive studies providing carbon and hydrogen isotope compositions of HCHs from the production sources were available up to date.

In this study we provide to date the largest database of carbon and hydrogen isotope ratios of HCH produced worldwide since 1960s till now. The data bank consists on more than 80 samples, comprising purified isomers, technical mixtures with different proportions of isomers, agricultural and pharmaceutical products. The carbon and hydrogen stable isotope ratios (expressed in 13C- and 2H-values) of pure compounds (chromatographic purity ≥95%) were determined by Elemental Analyser - Isotope Ratio Mass Spectrometry (EA-IRMS). The 13C and 2H of HCHs in technical mixtures and products were analysed by Gas Chromatography - Isotope Ratio Mass Spectrometry (GC-IRMS). For all 2H analyses a novel chromium-based reactor system was applied, combining high-temperature conversion and chromium reduction (Cr/HTC) of heteroatom-containing compounds to H2 (Gehre 2015).

Overall, 13C-values of -HCH ranged from -31.0 to -25.3 ‰ for pure compounds and from -33.0 to -24.9 ‰ for mixtures. Similar narrow ranges were observed also for the other HCH isomers (both pure and in mixtures): -33.8 to -25.8 ‰ for -HCH, -34.1 to -22.7 ‰ for -HCH and -35.9 to -23.4 ‰ for -HCH. Measured 2H values of pure isomers of HCH were in the range between -130.7 and +1.2 ‰.

Combination of C and H isotope signatures of HCH has a potential to help identifying sources of HCHs in the environment. We present a unique databank, demonstrating a spatial and temporal variability of isotopic signatures, which can be used both for source tracking of HCH and as a baseline for future studies on the environmental fate of this contaminant.