Potential of multi-dimensional stable isotope fingerprinting for sources identification of organophosphorus pesticides

ANKE REESE[1,2], LANGPING WU[1],HANS H. RICHNOW[1]

[1]Department for Isotope Biogeochemistry, Hemlholtz Centre for Environmental Research- UFZ, Permoserstr.15, 04318 Leipzig, Germany
[2]Eberhard-Karls University Tübingen, Geschwister-Scholl-Platz, 72074 Tübingen, Germany anke.reese@ufz.de

Organophosphorus pesticides (OPs) are a diverse family of pesticides and particularly aracicides used since the 1940s. In contrast to organochlorine pesticides, OPs have a shorter persistent time which favors their worldwide application.

However, OPs and their derivate are highly toxic. They inhibit the Acetylcholinesterase (AChE), an enzyme which is essential for neurotransmission in insects, animals and humans. The inhibition process is irreversible and it results in impairments in attention, memory, and other domains of cognition. The high toxicity and persistence of OPs in the environment is of great concern, as they have repeatedly been detected in soils, sediments waterbodies as well as food and drinking water. Thus tools are needed to understand their sources, reactive transport pathways and sinks in the environment.

Stable isotope analysis has been proved as a valuable method for the detection of origin of chemicals, as the isotopic profile reflects the isotopic composition of raw materials, synthetic pathways and purification processes. The aim of this study is to provide a database for identification of sources of OPs. To evaluate this approach, samples of active commercial OPs from more than 40 manufactures from India, China, Brazil and Germany were collected, comprising formulations of the most common OPs (e.g. dimethoate, omethoate, dichlorvos, phoxim and chlorpyrifos).

Element Analyser- Isotope Ratio Mass Spectrometry (EA- IRMS) was used to analyze the hydrogen, carbon, nitrogen and oxygen isotope composition (expressed in $\delta^{13}C$, $\delta^{2}H$, $\delta^{15}N$ and $\delta^{18}O$) of collected OP formulations. To obtain the required purity of ≥ 95 %, the separation and purification of the OP formulations were accomplished using a chromatographic column of 1 cm x 15 cm. The column was packed, from bottom to top, with glass wool, sea sand, Florisil® and sodium sulphate. Three fractions were collected using different eluents and were analyzed via GC- MS for purification check before evaporation.

The isotope compositions of 7 standard OPs obtained from Sigma-Aldrich vary from -42.63 ± 0.06‰ to -11.29 ± 0.01% for $\delta^{13}C$, from -278.82 ± 2.22% to -94.08 ± 2.29‰ for $\delta^{2}H$ and from -6.58 ± 0.40% to 1.50 ± 0.05‰ for $\delta^{15}N$, which gives the potential for characterizing sources of OPs in the environment. The preliminary results will be compared with the isotope values of commercial products to reveal more information about isotopic variability of OPs.

Our study highlights that multi isotope fingerprinting has potential for identification of sources, and provides a database of isotope composition of OPs which can also serve as a baseline for future studies on the environmental fate of OPs.