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Stable carbon isotope ratios of POPs — A tracer that can lead to the origins of pollution

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Abstract

An elemental analyzer in combination with stable isotope ratio mass spectrometry (EA–IRMS) was used to demonstrate that two samples of the chloropesticide Melipax discovered in two countries varied only by 0.1‰ in their δ^{13}C values. Gas chromatography interfaced to a stable isotope mass spectrometer (GC–IRMS) was used to study the δ^{13}C values of individual congeners in two technical polybrominated diphenyl ether products, i. e. DE-71 and DE-79, at three different concentration levels. Injections of 4 μg and 5.2 μg of DE-71 and DE-79 were most suited for the determinations. In both products, the δ^{13}C values were usually the more negative the higher the degree of bromination was. The δ^{13}C values of three hexabromo isomers BDE 138, BDE 153, and BDE 154 could be determined in both products. In all cases the δ^{13}C values of the three hexaBDEs were more depleted in δ^{13}C in the higher brominated technical octabromo diphenyl ether DE-79.

Keywords: Carbon isotopes; Compound specific isotope analysis; Organohalogen pollutants

1. Introduction

The term “organohalogen compounds” is generally used to describe a wide range of medium-sized (~250–1000 Da), semi-volatile chemicals which have been used on a multiple 1000-ton scale all over the world. Several of the compounds under this definition were classified as persistent organic pollutants (POPs) and/or persistent, bioaccumulative and toxic chemicals (PBTs). Owing to environmental concerns, quantifying of residues as well as monitoring the fate and (eco)toxicological effects of PBTs spilled in the environment is of primary importance, in which many scientists, residue control authorities, and (eco)toxicologists have been involved for decades. Meanwhile, the *occurrence* of PBTs in the environment is well-documented but their *origin* if somewhat away from a specific production source can only be estimated when the PBT was produced in different countries (Vetter et al., 2006b). Yet, the origin of the pollutant is of primary interest. For instance, such information could lead to a more detailed understanding of the global distribution and environmental fate of PBTs; it would be possible to make the producer of the pollutant responsible for a given toxic or otherwise adverse effect recognized in the environment; and this knowledge could be useful for distinguishing naturally-occurring organohalogens from anthropogenic products (Reddy et al., 2002a,b). Because the polluter-pays principle is more and more applied to environmental issues, this field of research is sometimes defined as environmental forensics.

While none of the classic methods applied to research on PBTs can provide such information, techniques that allow for the exact determination of ratios of stable isotopes are pre-destinated for the elaboration of such problems. Stable isotope ratio mass spectrometry (IRMS) is able to determine minute mass-dependent effects in structurally identical compounds owing to lower mobility and higher binding energies of the heavier isotopes (Mook, 2000). Isotopically distinct molecules will participate in reactions at slightly dissimilar rates (Ahad et al., 2000). Consequently, chemically identical compounds produced in different ways often have significantly different ratios of ^{13}C/^{12}C, ^{37}Cl/^{35}Cl, and ^{2}H/^{1}H. IRMS has been applied in different disciplines of natural sciences for the differentiation of structurally identical compounds that may stem from different sources. Initial studies in the field of PBTs focused on the determination of ^{13}C/^{12}C (Jarman et al., 1998; Reddy et al., 2000; Drenzek et al., 2002; Teuten et al., 2005; Vetter et al., 2005, 2006a,

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b; Horii et al., 2005; Armbruster et al., 2006), $^{37}Cl/^{35}Cl$ ratios (Drenzek et al., 2002; Reddy et al., 2002a,b; Holmstrand et al., 2006), and $^{2}H/^{1}H$ ratios (Armbruster et al., 2006; Vetter et al., 2006a). For evening out variations from instrument to instrument and/or analysis to analysis on the same instrument, it has become standard to determine stable isotope ratios relative to international reference standards distributed by the International Atomic Energy Agency (IAEA, Vienna, Austria). Thus, instead of isotope ratios, the enrichment or depletion of the heavier isotope relative to the reference standard is expressed as shown for carbon isotopes (Eq. (1)):

$$\delta^{13}\mathrm{C}(\text{per mil}) = 1000\,\frac{(^{13}\mathrm{C}/^{12}\mathrm{C})_{\text{sample}} - (^{13}\mathrm{C}/^{12}\mathrm{C})_{\text{standard}}}{(^{13}\mathrm{C}/^{12}\mathrm{C})_{\text{standard}}} \qquad (1)$$

Samples with positive δ-values (in per mil) are enriched in ^{13}C relative to the reference standard whereas negative δ-values (in per mil) are the result of depletion in the heavier isotope in the sample compared to the standard results. All PBTs determined so far were depleted in ^{13}C relative to the reference standard and thus have negative $\delta^{13}C$ values.

In previous studies we showed that several PBTs from different producers differed in their $\delta^{13}C$ and $\delta^{2}H$ values (Vetter et al., 2005, 2006a,b; Armbruster et al., 2006; Vetter and Gleixner, 2006) and that long-range transport appears not to significantly change the isotopic content of PBTs (Vetter et al., 2006b). However, some questions remained open. In this paper we discuss the progress of our attempts to use isotopic data to distinguish PBTs with the same structure that differ only in their way or place of production. For this reason we performed new EA–IRMS and GC–IRMS experiments in order to provide new insights into the relevance of isotopic data in research on PBTs.

2. Materials and methods

2.1. Chemicals and standards

Standards of DE-71 (technical pentabromo diphenyl ether mixture, CAS-No. [32534-81-9]), and DE-79 (technical octabromo diphenyl ether mixture CAS-No. [32536-52-0]) were from Great Lakes Chemical Cooperation (Indianapolis, IN, USA). DE-numbers refer to the average weight-% of bromine. Polybrominated diphenyl ether (BDE) congener identification was according to Gaul et al. (2006). DE-71 was analyzed at concentrations of 0.4, 4, and 40 µg/µL and DE-79 at concentrations of 0.52, 5.2, and 52 µg/µL (1 µL injected). 1-kg packages of Melipax® (Fahlberg-List, former GDR), produced in 1979 (charge nr. 0008.10.79), were found in 1997 in Jena (Germany) (Armbruster et al., 2006) whereas a 50-kg sample (labelled "Melipax Popras", produced by Fahlberg-List) was discovered in 2006 in Slowakia and analyzed here for the first time. The charge number printed on the 50-kg sacks was 1263-11/79. Despite the different code system (hyphen and sledge instead of dots), we assume that both products were produced in the same plant in October and November 1979, respectively. Both products contained 10% of camphechlor with 67–69% chlorine according to label. Q1 was synthesized according to Wu et al. (2002) and re-crystallized from *n*-hexane. Origin and quality of solvents was described by Armbruster et al. (2006).

2.2. Elemental analyzer in combination with stable isotope ratio mass spectrometry (EA–IRMS)

A Euro EA 3000 elemental analyzer (Hekatech, Wegberg, Germany) was connected to a Delta plus XP mass spectrometer via a Conflo III Interface (Thermo Finnigan MAT, Bremen, Germany) using the parameters described by Armbruster et al. (2006) and Vetter et al. (2006a). About 5 mg of Melipax was weighed into tin capsules (3.5 × 5 mm, Hekatech, Wegberg, Germany). Acetanilide (Hekatech) was used as working standard (Armbruster et al., 2006).

2.3. Gas-chromatography–combustion–isotope-ratio-mass spectrometry (GC–C–IRMS)

Compound specific carbon isotope analyses were performed with a 6890 gas chromatograph (Agilent, Waldbronn, Germany) coupled to a Delta plus XP mass spectrometer (Thermo-Finnigan, Bremen, Germany) via a GCC III interface. Samples were injected at 270 °C via a split/splitless injector used in the splitless mode (split opened after 1 min). The carrier gas helium was used at a constant flow of 1.5 mL/min. A 60 m × 0.25 mm i.d. column coated with 0.25 d_f VF-5 ms (Varian, Darmstadt, Germany) was installed in the GC oven. BDEs were analyzed using the following oven program: 70 °C (hold time 1.5 min), at 30 °C/min to 230 °C, at 4 °C/min to 270 °C (hold time 16.17 min), and at 5 °C/min to 300 °C (hold time 30 min for DE-71 or 50 min for DE-79). For Q1, we started at 80 °C for 2 min; then the temperature was ramped at 20 °C/min to 130 °C and finally at 5 °C/min to 250 °C (2 min). The GCC oxidation reactor temperature was set at 940 °C. Carbon stable isotope ratios are expressed in $\delta^{13}C$ notation (Eq. (1)), which is the per mil [‰] deviation of the sample relative to a reference gas calibrated with NBS 22. To date, suitable reference standards for halogenated compounds are not available. Thus, the $\delta^{13}C$ values [‰] reported in

Fig. 1. Photos of authentic Melipax products discovered in (a) Germany (1997) and (b) Slovakia (2006).