DETERMINATION OF CHIRAL ORGANIC COMPOUNDS IN ENVIRONMENTAL MATRICES WITH TWO DIMENSIONAL GAS CHROMATOGRAPHY COUPLED TO TRIPLE QUADRUPOLE MASS SPECTROMETRY

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Introduction

Polychlorinated biphenyls (PCBs) belong to the 12 most harmful classes of persistent organic pollutants as specified in the Stockholm convention.[1] They have been widely used since the 1930s mainly as insulators in transformers and capacitors, as heat exchange fluids, as paint additives, and in plastics. PCBs are nowadays ubiquitously present in the environment and accumulate throughout the food chain. Due to high enough rotational energy barriers of the central C-C bond, two stable conformational isomers can be distinguished under environmental conditions for some tri- and tetra-*ortho*-chlorine substituted PCBs such as PCB 95, 132, 149 and 174.[2]

Organochlorinated pesticides (OCPs) such as hexachlorocyclohexanes (HCH), chlordanes, and DDT have been used heavily in the past century in agriculture, forestry, and public health worldwide to control insect populations. Several OCPs as α-HCH, trans-chlordane, cis-chlordane, and o,p'-DDT are the chiral compounds, and their technical mixtures are composed of two stereoisomers.[3] Once applied, the pesticides are a subject to the microbial degradation processes leading often to the enantioselective depletion.[4]

Two-dimensional gas chromatography (GC-GC) also known as "heart-cutting" or "multidimensional" GC is a relatively old coupling technique developing extensively throughout its history.[5] While ion trap mass spectrometry has been combined with two-dimensional GC, triple quadrupole mass spectrometers (MS–MS) have not yet been used with GC–GC to quantify the atropisomeric PCBs.[6,7,8]

Here, we apply this new coupling technique to chiral compounds, such as PCBs and OCPs, which were extracted from soil and air samples of Czech Republic, former Yugoslavia and Oman.

Materials and Methods

Soil samples were collected from several sampling sites in Czech Republic, countries of former Yugoslavia, and sultanate Oman. Air samples were collected at the same sites using the polyurethane foam based passive air samplers. Samples (filters from the air sampler or 5 grams of the dry soil) were extracted with dichloromethane (DCM) in a Büchi System B-811 automatic extractor. A glass column (30 cm length, 1 cm I.D.) filled with 5 g of silica gel (activated overnight at 150^{o} C, and modified by sulfuric acid) was used for a clean-up. Elution was performed by DCM: *n*-hexane (1:1) mixture (30 mL), and the sample was concentrated under a gentle stream of nitrogen to the final volume of 1 mL.

The GC-GC system is described in Bucheli & Brändli[2]. Briefly, it consisted of two Varian CP3800 gas chromatographs (Varian, Walnut Creek, CA, USA) connected by a Deans switching systems and a heated transfer capillary. The achiral separation of PCBs was carried out in the first GC on a HT-8 capillary column. The atropisomeric PCBs were heart-cut by Deans switching at their respective retention times (time windows of 0.75-1.00 min), transferred via a 1m fused silica capillary column (Agilent, 0.25mm I.D.) and condensed at the begin of the chiral column (Chirasil Dex, 25 m, 0.25mm I.D., 0.25μm film thickness, Varian) in the second GC. Once the transfer of all atropisomeric PCBs and their respective internal standards was completed, the oven

program of the second GC was run. The chiral PCBs were detected with a triple quadrupole mass spectrometer (Varian 1200, Varian) in the electron impact mode.[2]

The method was modified for determination of α-HCH, trans- and cis-chlordane, o,p'-DDD and o,p'-DDT by adapting the cutting windows and monitored ions.

Enantiomeric fraction (EF) values were used to describe enantiomeric signatures:

$$EF = \frac{E_1}{E_1 + E_2} \quad \text{or} \quad EF = \frac{E_+}{E_+ + E_-}$$

where E_1 and E_2 are the first and the last eluting enantiomer whenever the identity of the (+) and (–) forms is unknown. The EF = 0.5 represents a racemic mixture. For PCBs 132, 149 and 174 the elution order of individual enantiomers was specified using the enantiopur standards. In case of PCB 95, α-HCH, cis- and trans-chlordane, o,p'-DDT and o,p'-DDD, E_1 and E_2 values were used for the calculation of EF.

Results and Discussion

In the soil samples from the Czech Republic, former Yugoslavia and Oman, EF values of investigated compounds were significantly shifted from 0.5 in many sampling sites (Table 1).

Table 1. Range of EF values in the soil samples

Compound	PCB 95	PCB 132	PCB 149	PCB 174	α-HCH	o,p'-DDD	o,p'-DDT
Country							
Czech Rep.	0.41-0.50	0.46-0.54	0.49-0.53	0.48-0.52	0.49-0.52	0.37-0.50	0.40-0.51
former Yugoslavia	0.46-0.52	0.48-0.51	0.49-0.51	0.48-0.51	NM	NM	NM
Oman	0.47-0.52	0.49-0.56	0.49-0.54	0.48-0.50	NM	NM	NM

NM=not measured

EF values vary within the countries in almost the same ranges as in between the countries.

The most apparent EF shifts were observed for PCB 95, o,p'-DDD and o,p'-DDT. EF values of other compounds were close to racemic. Our results correspond to the results published by Wiberg et al.[4] They investigated several Alabama soils and found a great variability in EF values of o,p'-DDT while EF values of α-HCH were close to racemic.

For PCB 95, o,p'-DDD and o,p'-DDT the EF values, in majority of samples, were lower than 0.5 which indicates an enrichment of the second eluting enantiomer in all cases. Microbial degradation of the chiral compounds in the soil is enantioselective, and it leads to the enrichment/reduction of the individual enantiomer amounts. Extent of degradation can be influenced by pH, temperature, microbial characteristics of the soil and many other circumstances, which can cause a variability of EF values at the different sites. An exposure time since the initial application is another factor that has to be considered.

The fact that chlordane was not detected in any of the soil samples is not surprising since this pesticide was never used in the investigated region.

Variability of EF values in the soil profile was also studied (Table 2) since different conditions (temperature, microorganism species, etc.) can lead to the differences in a compound degradation. Soil samples were taken in three different depths, the total concentration of POPs was generally decreasing with depth. In several cases, POP level in the deepest layer was so low that estimation of EF value was not possible. Noticeable EF value differences in the soil profile were observed for several POPs, however, this issue deserves a further investigation.

Table 2. EF values in the soil layers

Compound	PCB 95	PCB 132	PCB 149	PCB 174	α-HCH	o,p'-DDD	o,p'-DDT
Depth [cm]							
0-5	0.45	0.51	0.50	0.50	0.51	0.46	0.47
25-35	0.39	0.52	0.53	0.49	0.50	0.46	0.45
75-85	0.51	NM	0.50	NM	0.53	0.50	NM

Air samples were collected at the soil sampling stations in the Czech Republic, former Yugoslavia and Oman using the passive air samplers, and analyzed for PCBs. Irrespective of the samples origin, their EF values did not differ significantly from the value of a racemic mixture, and they ranged from 0.49 to 0.51. Since the POP volatilization from the soils is an important source of these compounds in the atmosphere, it can be expected that EF values of PCBs in the atmosphere should correspond to those in the soil. However, the influence of the long-range transport of volatile compounds from other locations as well as continuous mixing of the ambient air layers has to be considered and seems to outweigh local soil sources.

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