

# TOXAPHENE IN THE CZECH AQUATIC AND TERRESTRIAL ECOSYSTEMS

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## Introduction

Toxaphene is still residual organochlorinated pollutant in the Czech environment after more than 20 years of its application. Within the years 1963-1985, almost 1000 tons of technical toxaphene was used for the treatment of cole-seed against rape beetle (*Meligethes aeneus*) and lucerne against lucerne flower midge (*Contarinia medicaginis*) (1-4). It has never been analyzed till our pilot study (5). Results show that toxaphene is not present in abiotic matrices with low content of organic material (COM), e.g. arable soils from various agricultural regions and grass-land soils. Toxaphene application was banned almost twenty years ago (1) and then it has been undergoing to degradation by sunlight and soil microorganisms in treated areas, that's why the toxaphene levels are below detection limit or it is not detected at present. On the other hand, toxaphene was determined in the matrices with high COM such as forest soils or litter from remoted areas, e.g. mountains. It refers to the atmospheric transport of toxaphene and slower degradation in these matrices. Following detailed study of this pesticide fate in terrestrial ecosystem confirmed previously described results (5). This study also includes data about aquatic ecosystem.

## Materials and methods

Soil samples were collected in the background area of Košetice (Middle European Monitoring of PBT Compounds Observatory). Samples of arable soils were obtained from a basal monitoring program of the Central Institute of Supervising and Testing in Agriculture, Brno. Fish samples were obtained from the State Veterinary Administration of the Czech Republic. Others were sampled for research project of RECETOX.

Samples were prepared for analysis using method described previously (5). Each cleaned up sample was spiked with 4 ng <sup>13</sup>C<sub>12</sub> PCB 105 as internal standard and evaporated to 100 µl under a gentle nitrogen stream.

Analyses were performed using a Finnigan GCQ gas chromatograph coupled with an external ionization ion-trap mass spectrometer. A DB5-MS column (60 m x 0.25 mm i.d. x 0.25 µm film thickness) was used for chromatographic separations. The experimental conditions were as follows: helium, as carrier gas with a linear velocity of 30 cm/s, splitless injection of 1 µl, splitless time 1 min, temperature of injector 250 °C. The GC oven temperature program was used: isothermal at 80 °C for 1 min, 20 °C/min to 200 °C, 1.5 °C/min to 260 °C, 15 °C/min to 300 °C, and then isothermal at 300 °C for 10 min. The ion trap was operated in MS/MS mode and instrumental conditions are described previously (5).

The average recovery of 22 toxaphene congeners is 83 % at level of 4 ng of each congener spiked in sediment, soil or fish oil. Instrumental detection limit ranges from 0.5 to 2.1 pg per injection. Identification of individual congeners is carried out using retention time and ratios of daughter ions.

## Results and discussion

Toxaphene was used as insecticide for the treatment of the oil and fodder plants in our country for a long time in the past, but now it has not been detected in arable soils from agricultural areas or its levels have been below detection limit (5). For twenty years, since its application was prohibited,

toxaphene might be the subject of evaporation and atmospheric transport or degradation in soil or run-off into aquatic compartments, especially sediments.

However the toxaphene was determined in forest soils from both mountains and lowlands, that are known for high COM, particularly of 20 to 40 %. We supposed that toxaphene was transported into these areas through atmosphere. Following transformation has gone very slowly due to strong adsorption to soils rich in organic material. The toxaphene soil concentration ranged from 1.3 to 9.5 ng/g, in litter from 0.6 to 5.4 ng/g and the toxaphene profiles were very similar in these two matrices from the same site. Some needles were contaminated by the trace amount of toxaphene residues and that was why we could not compare them with toxaphene profiles determined in forest soil and litter in certain locality and evaluate whether the needles were contaminated by technical toxaphene presumably occurring in the atmosphere or by toxaphene residues evaporating from the forest soil. The toxaphene profile in terrestrial samples was different from technical toxaphene profile by higher abundance of the persistent congeners such as Parlar 26, Parlar 50 and Parlar 62 than in technical mixture. Similar changes have already been described in various animal species (6,7).

The concentrations in sediments from both the aquatic ecosystems (rivers and stagnant waters) are below detection limit (0.1 ng/g). Only Hx-sed and Hp-sed were detected in some sediments. These two toxaphene metabolites originate from toxaphene congeners with more chlorine atoms, specially from congeners with geminal dichloro group on ring position C-2 (8,9). Hp-sed was identified only informatively without analytical standard according to relative retention index obtained from correlation between our retention and the published one (10). For identification, we also used the comparison of EI mass spectra of these metabolites (9) and furthermore the similarity of daughter mass spectra of heptachlorobornanes, particularly Parlar 32 and Hp-sed. The traces of persistent congeners Parlar 26 and Parlar 50 were detected in the Vltava river sediment only. The situation in aquatic biota (various fishes) was similar. Besides toxaphene metabolites, the very low levels of persistent congeners Parlar 26 and Parlar 50 were determined in some fish. The contamination of fish in the Vltava river is higher than in stagnant waters presumably owing to higher contamination of corresponding sediment and higher bioavailability from sediments, which are effectively resuspended by watercourse.

Toxaphene is still present in the Czech environment. Toxaphene was determined in fish and sediment from very contaminated waters like the Vltava river. It also occurs in forest soils and litter from all investigated localities.

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