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PCDDs, PCDFs, PCBs and OCPs in sediments from selected areas in the Slovak Republic

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HIGHLIGHTS

- PCDDs/PCDFs, PCBs and OCPs in bottom sediments of polluted and background areas of Slovakia.
- Considerably higher sediment levels in industrial areas.
- Environmental risk associated with metallurgical plants in Slovakia.

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ABSTRACT

Within our research project, 34 river bottom sediments were collected in 2006–2007 at five areas across Slovakia with industrial sources of persistent organic pollutants (Košice, Krompachy, Nemecká, Šala, Nováky) and one background area (Starina). Sediments were analyzed for seven 2,3,7,8-substituted polychlorinated dibenzo-*p*-dioxins (PCDDs) and 10 dibenzofurans (PCDFs), 12 dioxin-like and 6 indicator polychlorinated biphenyls (PCBs), hexachlorobenzene (HCB) and 1,1,1,-trichloro-2,2-bis(*p*-chlorophenyl)ethane (p,p′-DDT) with 1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethylene (p,p′-DDE).

Analytical procedure based on accelerated solvent extraction followed by a semi-automated clean-up and fractionation was used. Determination of target compounds was performed by HRGC–HRMS analysis.

Total WHO toxic equivalent WHO_{1998}-PCDD/F/dl-PCB-TEQ concentrations ranged from 0.26 to 559 pg TEQ g^{-1} dry matter (dm), with a median 2.2 pg TEQ g^{-1} dm. The sums of six indicator PCBs were in the range 0.56–1014 ng g^{-1} dm, with a median 11.8 ng g^{-1} dm. The concentrations of organochlorine pesticides HCB and p,p′-DDE/DDT varied from 0.15 to 34.8 ng g^{-1} dm, with a median 0.91 ng g^{-1} dm and 0.46–34.1 ng g^{-1} dm, with a median 6.7 ng g^{-1} dm, respectively.

The most abundant congeners in all sediment samples among dioxins, furans and PCBs were OCDD, 1,2,3,4,6,7,8-HpCDF, PCB-118 and PCB-153.

1. Introduction

Sediment is an essential, integral and dynamic part of river originating from weathering and erosion of inorganic and organic material. Transported sediment settles along the river banks, reservoirs and lakes by sedimentation (Apitz et al., 2006). Some contribution to creation of bottom sediment represents the deposition of solid particles from the air. These are also the penetration pathways of persistent organic pollutants (POPs) in river basins and sediment. A decisive factor for the sorption of POPs in sediment is the organic carbon. Its quantification is a significant stage of the analytical process by assessment of sediment contaminated with POPs.

Due to the process of accumulation and desorption of toxic pollutants in the sediment – water system, the sediment represents the bioavailable fraction of toxic compounds for benthic organisms and aquatic animals. Therefore, the fluvial sediment is an important environmental indicator of water pollution with POPs.

Our target group of POP compounds includes: polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), polychlorinated biphenyls (PCBs) and some organochlorine pesticides (OCPs). Chemical and physical properties of these compounds are dependent on their molecular structure. These properties together with the character of the environment determine the behavior and toxic effects of pollutants in living organisms (Safe, 2000; El-Shahawi et al., 2010). In general, POPs are

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well known as persistent, toxic and lipophilic compounds. Their lipophilicity and environmental and biological resistance leads to bioaccumulation in the food chain. The various biochemical and toxic responses to POPs were studied and described previously: endocrine disruption, immune dysfunction, thyroid disorders and dysglycemia, breast cancer, reproduction defects, dental defects in children, etc. (Safe, 1994, 2000; Pavuk et al., 2003; Langer et al., 2007).

PCDDs and PCDFs are unintentionally formed by anthropogenic activities. The main sources of these two types of toxic pollutants in Slovakia are hazardous, hospital, industrial and municipal waste incineration and high temperature metallurgical processes. Some other relevant sources involves cement kilns, fossil fuel burning, uncontrolled combustion of household/garden waste, pulp and paper mills, chemical manufacturing, forest fires, etc. (Thomas and Spiro, 1994; Kulkarni et al., 2008; El-Shahawi et al., 2010). The main source of environmental pollution with PCBs and OCPs in the past was the production and use of these compounds in industry and agriculture. Today, they enter the environment because of improper handling of hazardous waste. These processes followed by irrigation and floods lead to environmental pollution of agricultural fields, meadows and river basins and subsequently to contamination of sediment.

2. Materials and methods

2.1. Sediment samples and sampling sites

Five areas (Fig. 1) across Slovakia with potential sources of POPs pollution were chosen: Šala with the Duslo chemical plant (production of pesticides, fertilizers, rubber-making chemicals, etc., hazardous waste incineration); Nemecká with the Petrochema refinery (production of mineral oils, incl. transformer oils, etc., hazardous waste incineration); Krompachy with the Kovohuty metallurgical plant (copper production, scrap copper processing); Košice with the U.S. Steel metallurgical plant (iron ore sintering) and municipal waste incinerator; and Nováky with chemical plant (chlorinated paraffins production). The neighbourhood of the Starina water reservoir in the north-east of Slovakia was chosen as a background area (Fig. 1). All the sampling sites are described in Table 1.

In these areas, 34 samples of bottom sediment were collected in 2006–2007 in co-operation with the Water Research Institute (WRI), Bratislava, Slovakia. A global positioning system (GPS) was used for precise localization of the sampling points. The GPS data are presented in Table 1. The samples were collected by standardised sampling methods commonly used by the WRI within its monitoring activities. A scoop, Ekman bottom grab sampler or core sampler were used in dependence on depth (0.3–39 m) and water dynamics (river, pond, lake, weir, and reservoir). There is no information about the consistence of individual sediment samples. Visual assessment and particle size analysis were not performed by WRI.

After open air drying, the sediment samples were sieved through an 80-μm sieve. Total organic carbon (TOC) and black carbon (BC) were determined in this sediment fraction at the Soil Science and Conservation Research Institute, Bratislava, Slovakia.

2.2. Standards, analytes and chemicals

The compounds of interest were seven 2,3,7,8-chlorosubstituted dibenzo-*p*-dioxins (PCDDs) and ten dibenzofurans (PCDFs); twelve dioxin-like PCBs (dl-PCBs) involving four non-ortho and eight mono-ortho PCB congeners; six indicator PCBs (ind-PCBs); hexachlorobenzene (HCB) and 1,1,1,-trichloro-2,2-bis(*p*-chlorophenyl)ethane (p,p′-DDT) with 1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethylene (p,p′-DDE). Extraction standard solutions added to a sample prior to extraction comprised all the ^{13}C-surrogates except 1,2,3,7,8,9-hexaCDD and octaCDF. For the determination of $^{13}C_{12}$-PCDD/F and non-ortho PCB congener recoveries, a syringe standard solution of 1,2,3,4-tetraCDD and 1,2,3,7,8,9-hexaCDD added to sample residues prior to GC injection was used. A syringe standard of $^{13}C_{12}$-PCB-32 and $^{13}C_{12}$-PCB-188 was used for the determination of the ^{13}C-labeled extraction standard recoveries of mono-ortho-PCBs, ind-PCBs, HCB, p,p′-DDE, and p,p′-DDT.

Toluene and *n*-hexane for the analysis of dioxins, furans and PCBs (Sigma–Aldrich, Germany), sulphuric acid p.a. (95–97%), silica gel 60 (0.063–0.200 mm) for column chromatography, anhydrous sodium sulphate of residual analysis grade quality, copper fine powder p.a., potassium hydroxide p.a. (all Merck, Germany), nitrogen 3.0 and helium 4.6 (Messer Tatragas, Slovakia) and silver nitrate p.a. (Medika, Slovakia) were used.

2.3. Extraction and clean-up

About 10 g of dried homogenised sediment sample was accelerated solvent extracted (ASE® 300, Dionex, USA) after addition of ^{13}C-labeled extraction standard solutions (at least 24 h prior to extraction). Copper powder to eliminate sulphur was added to the sample in a 34-mL cell. The extraction was performed with toluene at 10.3 MPa and 100 °C in two 5-min cycles. After the evaporation of toluene by a TurboVap® II concentrator (Zymark, USA), residues were diluted in *n*-hexane and applied on a multi-layer silica column: 44% sulphuric acid/potassium hydroxide/silver nitrate on activated silica gel. The pre-cleaned extract was then cleaned-up and fractionated using a semiautomatic PowerPrep™ system (Fluid Management Systems, USA) equipped with three commercial disposable columns: H_2SO_4/silica + KOH/silica + $AgNO_3$/silica, basic alumina and active carbon on Celite 545 (Fluid Management Systems, USA). Two fractions were captured. The *n*-hexane–dichloromethane (1:1) fraction from the basic alumina column contained

Fig. 1. Samplig sites: Krompachy, Košice, Nemecká, Šala, Nováky and Starina.