



Linking toxicity profiles to pollutants in sludge and sediments



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HIGHLIGHTS

- Constrained correspondence analysis linked contaminant concentrations to toxicity.
- In sludge samples Hg, As, HCH, PBDEs and HBCD influenced the toxicity profiles.
- In sediments Hg, As, HCH, PBDEs, DDT HCH and HBCD influenced the toxicity profiles.

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ABSTRACT

Obtaining a complex picture of how pollutants synergistically influence toxicity of a system requires statistical correlation of chemical and ecotoxicological data. In this study, we determined concentrations of eight potentially toxic metals (PTMs) and four groups of organic pollutants in 15 sewage sludge and 12 river sediment samples, then linked measured contaminant concentrations to the toxicity of each matrix through constrained correspondence analysis (CCA).

In sludge samples, Hg, As, hexachlorohexane (HCH), polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecane (HBCD) influenced the toxicity profiles, with the first four having significant effects and HBCD being marginally significant. In sediment samples, Hg, As, PBDEs, hexachlorobenzene (HCB), dichlorodiphenyltrichloroethane (DDT), HBCD, HCH and polycyclic aromatic hydrocarbons (PAHs) were found to explain toxicity profiles with Hg, As, PBDEs, HCB, DDT, HBCD, and HCH having significant effects and PAHs being marginally significant. Interestingly, HCH was present in small amounts yet proved to have a significant impact on toxicity. To the contrary, PAHs were often present in high amounts, yet proved to be only marginally significant for sediment toxicity. These results indicate that statistical correlation of chemical and ecotoxicological data can provide more detailed understanding of the role played by specific pollutants in shaping toxicity of sludge and sediments.

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1. Introduction

Excessive use of natural resources and a large scale synthesis of xenobiotic compounds have generated a number of environmental problems. Waste water treatment plants (WWTPs) have been reported as potential major sources of environmental pollutants. Many xenobiotic compounds and pathogenic organisms remain intact despite wastewater treatment processes and can

enter the environment through discharge of wastewater effluents and subsequent usage of sewage sludge [1–3]. In the European Union, production of sewage sludge is approximately 11.5 Mt dry weight (dw) y^{-1} [4,5], up to 70% of which is re-used in agriculture or is disposed of through composting, landfilling or incineration. Sewage Sludge Directive 86/278/EEC sets limits for seven heavy metals, however no general limits currently exist for the presence of persistent organic pollutants (POPs) and the amount of these compounds in land-applied sludge is not regulated. One example of such POP deposition is the release of 24,000–36,000 $kg\ year^{-1}$ of polybrominated diphenyl ethers (PBDEs) through sewage sludge land applications in the US [2] and similar quantities across Europe and Asia [6]. This is despite the fact that lower brominated PBDEs were banned in Europe and the USA in 2004 and

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2006, respectively [7]. Thus due to the outdatedness of Sewage Sludge Directive 86/278/EEC, several EU countries have implemented stricter values for selected contaminants. The European Commission aims to review this Directive and therefore has dedicated projects to sewage sludge monitoring. In addition to the traditionally monitored inorganic and organic contaminants, such as PTMs, polychlorinated biphenyls (PCBs), polychlorinated dibenzodioxins (PCDDs) and dibenzofurans (PCDFs) as well as PAHs, emerging pollutants are investigated, including brominated flame retardants (BFRs), ingredients of personal care products, pharmaceuticals, some industrial chemicals, etc. The presence of these contaminants in sewage sludge has been documented in several studies [8–11].

POPs and PTMs tend to bind to organic matter, thus their primary removal from influent during waste water treatment processes occurs via sedimentation and sorption to sludge particles, which then leads to concentration of these contaminants in sewage sludge [12–15]. However, POPs and PTMs have also been documented in WWTP effluents [12,15,16]. Consequently, sedimentation accounts for the primary route of environmental deposition of these POPs, dominating over biotic or abiotic degradation and uptake by aquatic organisms [14,17,18].

Multivariate statistical tools have been demonstrated to help in understanding how biological systems respond to toxic stress [19–22]. In this study, we used multivariate statistics to unfold the relationship between environmental concentrations of organic pollutants and PTMs with their ecotoxicological impacts. We hypothesized that not all pollutants will equally influence the resultant toxicity profiles, with some being significant and others marginally significant or insignificant. In order to examine this hypothesis, we sampled and analyzed two matrices: stabilized sewage sludge, which is often re-used for agricultural purposes, and sediments sampled below WWTPs effluent drains. The analyses included: (i) determining the content of four groups of organic pollutants [BFRs, organochlorinated pesticides (OCPs), PAHs and PCBs] and PTMs (Hg, As, Cd, Cr, Cu, Ni, Pb, Zn); (ii) characterizing the ecotoxicological status of the samples and their water extracts; and (iii) evaluating which chemicals can be used to explain toxicity profiles.

2. Materials and methods

2.1. Sample collection

Stabilized sewage sludge was collected from 15 WWTPs located on several Czech rivers (Table 1), surface sediments (0–10 cm) were collected with stainless steel samplers ~300–500 m below the effluent drain of 12 of the WWTPs (Table 1). Collected samples were transported at 4 °C to the laboratory and stored for a maximum of 3 days at 4 °C prior to the analysis.

2.2. Chemicals

The mixture of indicator PCBs (congeners no. 28, 52, 101, 118, 138, 153 and 180) dissolved in isooctane and neat standards of OCPs, including hexachlorobenzene (HCB), α -, β -, γ -isomers of hexachlorocyclohexane (HCH), all isomers of dichlorodiphenyltrichloroethane (DDT) and their degradation products (DDD and DDE), and PCB 112 were obtained from Dr. Ehrenstorfer GmbH (Germany). Standard solutions of PBDE congeners (concentration 50 $\mu\text{g ml}^{-1}$ in nonane): 2,4,4'-triBDE (BDE 28); 3,4,4'-triBDE (BDE 37); 2,2',4,4'-tetraBDE (BDE 47); 2,2',4,5'-tetraBDE (BDE 49); 2,3',4,4'-tetraBDE (BDE 66); 2,2',3,4,4'-pentaBDE (BDE 85); 2,2',4,4',5'-pentaBDE (BDE 99); 2,2',4,4',6'-pentaBDE (BDE 100); 2,2',4,4',5,5'-hexaBDE (BDE 153); 2,2',4',4,5',6'-hexaBDE (BDE 154);

2,2',4,4',5',6'-hepta-BDE (BDE 183) and deca-BDE (BDE 209) and α -HBCD (50 $\mu\text{g ml}^{-1}$ in toluene), all with declared purity $\geq 98\%$, were obtained from Cambridge Isotope Laboratories (CIL, Andover, USA). The standard mixture 1647d of 16 priority PAHs (naphthalene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, dibenz[a,h]anthracene, benzo[g,h,i]perylene and indeno[1,2,3-cd]pyrene) dissolved in acetonitrile was supplied by the National Institute of Standards and Technology (NIST, USA).

Organic solvents (cyclohexane, dichloromethane, ethylacetate and isooctane) of "organic trace analyses" grade were all supplied by Merck (Darmstadt, Germany). Anhydrous sodium sulfate supplied by Penta Chrudim (Chrudim, Czech Republic) was heated at 600 °C for 5 h and then stored in desiccator before use. Styrene-divinylbenzene gel (Bio Beads S-X3, 200–400 mesh) was purchased from Biorad Laboratories (Hercules, CA, USA). Sulfuric acid (98%) was obtained from Merck (Darmstadt, Germany).

2.3. Analytical procedures

Validated analytical procedures for the examination of sewage sludge/sediment were as follows:

Dried sediment or sewage sludge (20 g; 16 h, 40 °C) was mixed with anhydrous sodium sulfate to form a flowing powder and transferred into Soxhlet extraction thimbles. Extraction was performed by dichloromethane in a Soxhlet apparatus with 170 ml of dichloromethane for 8 h. PCB congener no. 112 was used as an internal standard for POP analysis.

The clean-up procedure of all extracts was carried out by gel permeation chromatography employing Bio-Beads S-X3 (500 \times 8 mm i.d.) in a stainless steel column and a mobile phase of cyclohexane:ethylacetate solvent mixture (1:1, v/v). Collected fractions were concentrated and residue was dissolved in acetonitrile for PAH analysis and isooctane for halogenated POP analysis.

An HP 5890 gas chromatograph equipped with 2 electron capture detectors from Agilent Technologies (USA) was used for the analysis of PCBs and OCPs. The GC conditions were as follows: DB-5 (5% phenyl-methylpolysiloxane) and DB-17 (50% phenyl-methylpolysiloxane) capillary columns (60 m \times 0.25 mm i.d. \times 0.25 μm film thickness); column temperature program: 60 °C (held for 2 min) to 220 °C at 30 °C min^{-1} , to 240 °C at 0.5 °C min^{-1} and to 280 °C at 2.5 °C min^{-1} (held for 10 min); carrier gas helium with constant flow 1.7 ml min^{-1} , injector temperature: 280 °C; injection volume: 1 μl using the splitless injection mode (splitless time: 2 min) and ECD detectors temperatures were 300 °C. Limits of quantification for PCBs and OCPs ranged from 0.3 to 0.8 $\mu\text{g kg}^{-1}$ dry weight.

An Agilent 6890 gas chromatograph coupled to a mass spectrometer 5975 XLD Inert (Agilent Technologies, USA) operating in a negative chemical ionization (NCI) was used for the GC/MS analysis of PBDEs and HBCD. A concentrated extract (1 μl) was injected onto a DB-XLB (30 m \times 250 μm i.d. \times 0.1 μm film thickness) capillary column. DecaBDE was determined using the same GC instrument equipped with a shorter DB-XLB column (15 m \times 0.25 mm i.d. \times 0.1 μm film thickness). The GC conditions were as follows: DB-XLB capillary column, temperature program: 105 °C (held for 2 min) to 300 °C at 20 °C min^{-1} (held for 5 min); carrier gas: helium with constant flow 1.5 ml min^{-1} ; injection temperature: 275 °C; injection volume: 1 μl using the pulsed splitless injection mode (splitless time: 2 min). Monitored ions (m/z) were 79, 81, 159 and 161 (PBDEs), 79, 81, 158 and 159 (HBCD), 485 and 487 (BDE 209) and 326, 328 (PCB 112, internal standard). Reagent gas methane (purity 99.995%) was set at a pressure 2×10^{-4} mBar. An ion source temperature was 150 °C and a quadrupole temperature 105 °C. Lim-

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