Organic Pollutants in Areas Impacted by Flooding in 2002: A 4-Year Survey

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Abstract This paper summarizes a 4-year survey focused on polycyclic aromatic hydrocarbons (PAHs) and halogenated persistent organic pollutants (POPs) in river sediments, soil and crops collected in the locality impacted by catastrophic floods that occurred in the western part of Bohemia in August 2002. In spite of relatively high levels of polychlorinated biphenyls (PCBs) in river sediments, the increase of these POPs in flooded arable soil was not significant. On the other hand, remarkably higher levels of PAHs and dichlorodiphenyl trichloroethane (DDTs) were found as compared to those in reference soil samples. Regardless of this increased soil pollution, no measurable elevated concentrations of POPs occurred in the wheat grown in this area.

In August 2002, heavy and continuous precipitation in the Czech Republic and surrounding regions caused extreme floods in the Vltava and Elbe basins which are major rivers in Central Europe. These disastrous floods led not only to the damage of cities and towns, but also to loss of human life and property. As documented in several earlier studies (Elhottová et al. 2006; Götz et al. 2007; Stachel et al. 2006), flood events can result in the significant contamination of arable soils, pasture and meadows by heavy metals, PAHs and other POPs.

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This problem occurs mainly due to the transportation of re-suspended highly contaminated sediments from upstream localities and depositing them on surrounding areas (Harrad et al. 1994; Cousins and Jones 1998; Meijer et al. 2003; de Wit 2002). The problem can be further exacerbated during extreme flooding where accidental leakage into the flood water of chemicals from urban areas and industrial and wastewater treatment plants may take also place.

In general terms, both qualitative and quantitative characteristics of soil and vegetation contamination play an important role in the global cycling of POPs including their transfer into the food chain. Plants (agricultural/food crops included) could accumulate these substances through their roots and/or aerial parts (Chiou et al. 2001). In the latter case, there will not only be the absorption of POPs vapours from the ambient air but also through deposition of contaminated soil, dust and various atmospheric particles which may cause elevated levels of contamination in plants (McLachlan et al. 1995; Nakajima et al. 1995; Tolls et al. 1994). The uptake of POPs by vegetation depends particularly on: (i) physical and chemical properties of the respective compound(s); i.e. their relative solubility in water and organic solvents, volatility, chemical reactivity, and biotic and abiotic degradability and (ii) plant surface morphology such as size, content of surface waxes, surface smoothness/fuzziness etc. of the leaves (Thomas et al. 1998; Jánská et al. 2006).

The current paper presented here describes a 4-year survey initiated in 2003 (i.e. 1 year after the disaster) aimed to document the impact of the floods on the contamination of arable soil and as a consequence, the potential risk of transfer of these contaminants into crops grown on this soil. For this purpose the levels of PAHs, PCBs, organochlorine pesticides (OCP) and brominated

flame retardants (BFRs), e.g. polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecane (HBCD) in sediment, soil and crops (wheat, barely) sampled in the flooded area were determined. To obtain reference values, samples were also collected and analysed from nonaffected regions adjacent to the flooded areas.

Materials and Methods

Soil (4 kg), both flooded and non-flooded, river sediment (10 kg) and crops (2 kg of whole wheat or barley spikes) were collected during summer seasons (June–August) in the locality shown in Fig. 1. An average sample was obtained by homogenizing 8 sub-samples taken within each sampling area.

The mixture of indicator PCBs (congeners No. 28, 52, 101, 118, 138, 153 and 180) dissolved in isooctane and neat standards of OCPs [hexachlorobenzene (HCB), α-, β-, γ-isomers of hexachlorocyclohexane (HCH), DDT and its degradation products DDD and DDE)] and PCB 112 were obtained from Dr. Ehrenstorfer GmbH (Germany). Individual standard solutions of PBDE congeners and α-HBCD dissolved in nonane and toluene, respectively, were obtained from Cambridge Isotope Laboratories (CIL, USA). The standard mixture 1647d of 16 priority PAHs [naphthalene (Naph), acenaphthene (Ace), fluorene (Fln), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flt), pyrene (Pyr), benz[a]anthracene (B[a]A), chrysene (Chr), benzo[b]fluoranthene (B[b]F), benzo[k]fluoranthene (B[k]F), benzo[a]pyrene (B[a]P), dibenz[a,h]anthracene (DB[ah]A), benzo[-g,h,i]perylene (B[ghi]P) and indeno[1,2,3-cd]pyrene (I[cd]P) dissolved in acetonitrile was supplied by National Institute of Standards and Technology (NIST, USA)].

Validated analytical procedures for the examination of soil, sediment and crop samples were as follows.

Sediment/Soil

Dried sediment/soil (25 g; 16 h, 40°C) mixed with anhydrous sodium sulphate was extracted in a Soxhlet apparatus with 170 mL of dichloromethane for 8 h. PCB congener No. 112 was used as an internal standard for POPs analysis.

Wheat/Barley

Homogenized plant material (20 g) was extracted using a hexane:acetone solvent mixture (1:1, v/v) in an ultrasonic bath for 3 periods of 20 min. A crude extract was filtered through a layer of anhydrous sodium sulphate to remove water residues.

The clean-up procedure of all extracts was carried out by gel permeation chromatography employing Bio-Beads S-X3 (500 × 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 the residue was dissolved in acetonitrile for PAHs analysis and isooctane in case of halogenated POPs analysis.

Gas chromatography using two parallel electron capture detectors (GC/2ECD), was employed for the analysis of PCBs and OCPs. The GC conditions were as follows: DB-5 and DB-17 capillary columns; column temperature program: 60°C (held for 2 min) to 220°C at 30°C/min, to 240°C at 0.5°C/min and to 280°C at 2.5°C/min (held for 10 min); carrier gas helium with constant flow 1.7 mL/min, 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
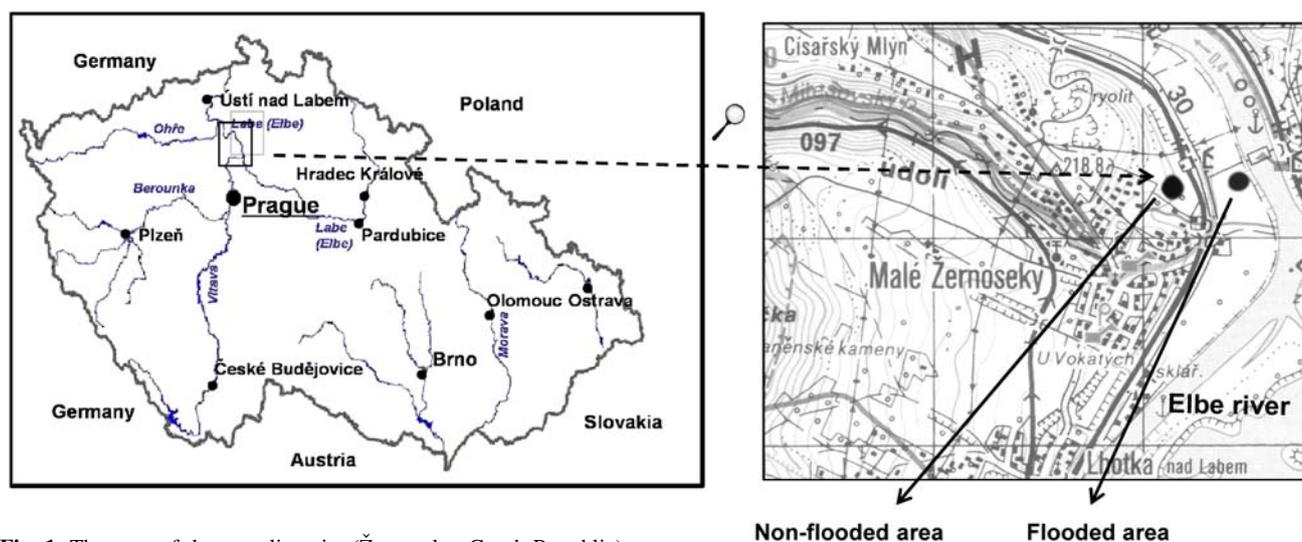

Fig. 1 The map of the sampling site (Žernoseky, Czech Republic)

quantification for PCBs and OCPs ranged from 0.3 to 0.8 µg/kg dry weight.

A gas chromatograph coupled to a mass spectrometric detector with a quadrupole analyzer operated in the negative chemical ionization mode (GC/MS-NCI) was used for the analysis of PBDEs and HBCD in purified extracts. 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 (held for 5 min); carrier gas: helium with constant flow 1.5 mL/min; 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 160 (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. Limits of quantification for BFRs ranged from 0.01 to 0.5 µg/kg dry weight.

A high performance liquid chromatographic system with a fluorescence detector (Hewlett-Packard 1100 Series) was used for PAHs analysis. The separation of PAHs was carried out on a SUPELCOSIL^{TM} LC-PAH (250 mm × 4.6 mm i.d.) column with the guard column SUPELCOSIL^{TM} LC-18 (20 mm × 4.0 mm i.d.), (SUPELCO, USA), under the following chromatographic conditions: gradient elution (A – acetonitrile, B – water; 0 min – 55% A, 20 min – 100% A,

29 min – 100% A), a mobile phase flow rate of 1 mL/min, an injection volume of 20 µL, a column temperature of 35°C. Limits of quantification for PAHs ranged from 0.05 to 0.8 µg/kg for soil/sediment and from 0.05 to 0.08 µg/kg for cereal samples.

Soil and sediment moisture was determined gravimetrically after drying at 105°C for 24 h.

To demonstrate the accuracy of the data generated by analysis of abiotic matrices, CRMs BCR 536 – chlorobiphenyls in freshwater harbour sediment and BCR 535 – PAHs in freshwater harbour sediment obtained from the Community Bureau of Reference, Belgium were employed. The recoveries of the methods used were for all matrices in satisfactory ranges of 84–98%, 86–99%, 86–96%, and 89–103% for PAHs, PCBs, OCPs and BFRs, respectively. The repeatability expressed as the relative standard deviation (n = 6), ranged from 2–14%, 4–12%, 5–11% and 3–13% for PAHs, PCBs, OCPs and BFRs, respectively.

Results and Discussion

As shown in several recent studies, contamination of the terrestrial environment may occur as a result of floods causing a mobilization of pollution sinks. The risk of increased POP levels in food crops grown in areas impacted by floods is therefore an issue of high concern. To investigate

Table 1 Concentration of monitored analytes in sediment, flooded soil and non-flooded soil (µg/kg dry weight)

	Non-flooded soil				Flooded soil				Sediment			
	2003	2004	2005	2006	2003	2004	2005	2006	2003	2004	2005	2006
Dry mass (%)	89	90	84	79	83	85	84	90	60	71	73	52
Σ 3-ring PAHs	23.2	16.2	20.7	21.8	102	96.2	79.8	52.9	825	3114	2221	1561
Σ 4-ring PAHs	84.9	118	93.3	82.6	602	643	405	275	3722	6818	3941	5004
Σ 5- and 6-ring PAHs	72.7	102	73.1	74.7	421	497	318	211	2218	3099	2504	2767
Σ 12 PAHs	181	237	187	179	1125	1235	803	538	6766	13032	8666	9332
Σ PCBs	2.2	3.0	3.4	3.1	7.2	6.6	4.0	5.3	79.9	68.5	85.2	60.2
Σ DDTs	8.9	6.9	10.1	12.0	140	135	115	73.8	48.2	73.5	41.4	52.1
HCB	0.9	0.9	0.5	0.7	1.0	1.2	2.1	1.7	3.1	10.8	3.3	4.4
Σ HCHs	0.8	0.5	0.6	1.9	0.9	0.6	0.9	2.1	1.9	1.6	0.9	5.1
Σ PBDEs	0.2	0.2	0.2	0.2	0.3	0.3	0.4	0.3	4.5	2.6	3.7	3.4
HBCD	n.a.	n.a.	n.d.	n.d.	n.a.	n.a.	n.d.	n.d.	n.a.	n.a.	1.8	1.6
BDE 209	n.a.	n.a.	n.d.	n.d.	n.a.	n.a.	n.d.	n.d.	n.a.	n.a.	4.5	4.1

Σ 3-ring PAHs = sum of Phe and Ant

Σ 4-ring PAHs = sum of Flt, Pyr, B[*a*]A and Chr

Σ 5- and 6-ring PAHs = sum of B[*b*]F, B[*k*]F, B[*a*]P, DB[*ah*]A, B[*g,h,i*]P and I[1,2,3-*cd*]P

Σ PCBs = sum PCB 28, 52, 101, 118, 138, 153 and 180

Σ DDTs = sum *o,p'*-DDE , *p,p'*-DDE, *o,p'*-DDD, *p,p'*-DDD, *o,p'*-DDT and *p,p'*-DDT

Σ HCHs = sum α-HCH, β-HCH and γ-HCH

Σ PBDEs = sum BDE 28, 47, 49, 66, 85, 99, 100, 153, 154 and 183

n.a. = not analysed; n.d. = not detected

Fig. 2 (**a**) Relative abundance of PAH groups and PAHs content in cereals, (**b**) relative abundance of PAH groups in soil and sediment. NF = non-flooded area, F = flooded area, Sum of 3-ring PAHs = sum of Phe and Ant, Sum of 4-ring PAHs = sum of Flt, Pyr, B[a]A and Chr, Sum of 5- and 6-ring PAHs = sum of B[b]F, B[k]F, B[a]P, DB[ah]A, B[g,h,i]P and I[1,2,3-cd]P
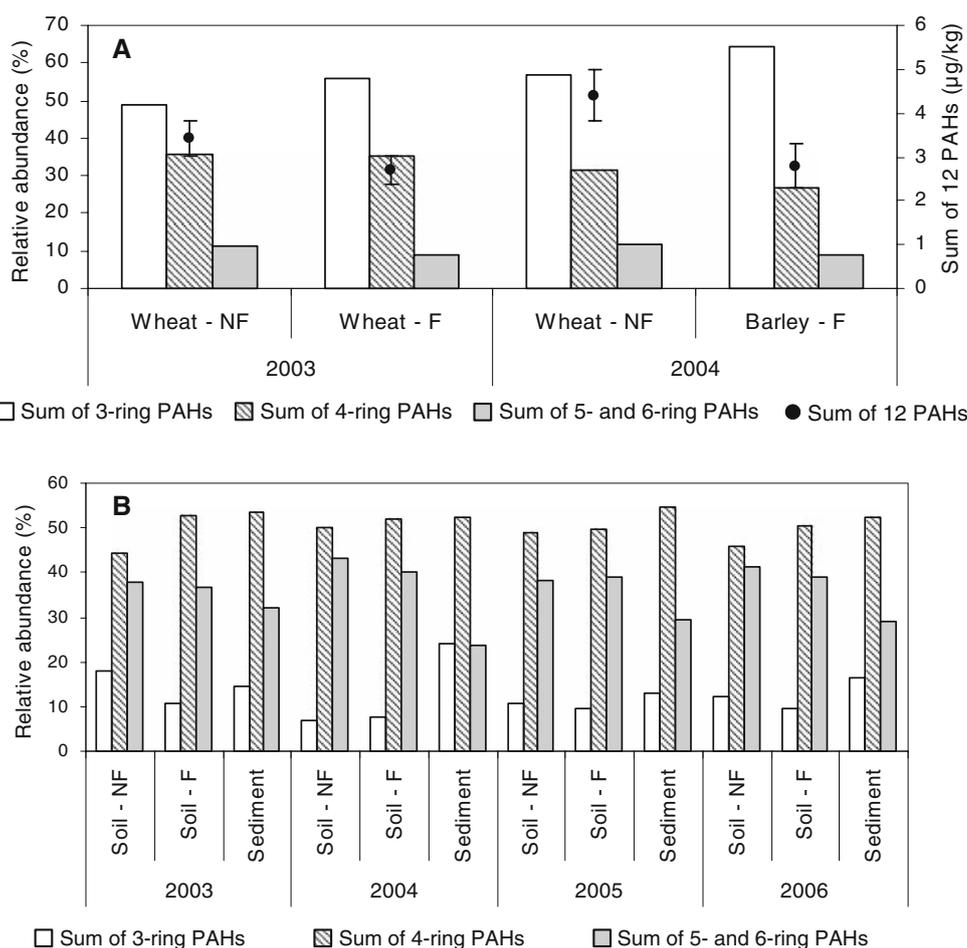
the extent of terrestrial contamination due to floods in 2002, the locality at the Elbe River was selected. The choice of our sampling site was based on the historical data documenting contamination events (both industrial and municipal effluents) upstream from this locality. The overview of POP levels (represented by 12 PAHs; 7 indicator PCB congeners; DDT isomers and their major break-down products DDE and DDD; HCH isomers; 11 PBDE major congeners; and HBCD) that were determined in sediment and flooded soil collected in the monitored locality together with "reference"(non-flooded soil) are shown in Table 1.

Of all the tested matrices, the highest PCB concentrations ranging from 28.5 to 85.2 μg/kg dry weight, were found in river sediments. Concentrations of these POPs in flooded soils were significantly lower (4.0–7.2 μg/kg dry weight) and only slightly exceeded the levels in the non-flooded soil (2.2–3.4 μg/kg dry weight). Among the monitored PCBs, congeners 138, 153 and 180 were the most abundant in all the tested porous media samples. This may indicate historical contamination by higher chlorinated technical mixtures (Delors were produced and widely used

in the former Czechoslovakia) coming from industrial areas located upstream from the selected locality.

The major OCPs detected both in soil and sediment samples were p,p'-DDE, p,p'-DDT and HCB. In contrast to the levels of PCBs detected, the relative amounts of DDT compounds were significantly higher (by one order of magnitude) in the flooded compared to the non-flooded soil. This can be explained by lower log K_{ow} of DDT isomers as compared to values tabulated for higher chlorinated PCBs. Due to PCBs being more lipophilic than DDT they are more likely to be associated with sediments. While no distinct time trend was observed for PCBs within the survey period; DDT isomers slowly declined. The major transformation products of p,p'-DDT, i.e. p,p'-DDE accounted for 20–50% of the total amount of DDT isomers detected. Overall, the flood event significantly contributed to the contamination of soil by DDT, but the levels of other halogenated POPs in the river sediments were relatively low.

In the examined samples, the BFRs detected were mainly represented by PBDE congeners. The predominate congener was BDE 47 but some others such as BDE 85, 99

and 100, were also present at levels exceeding the detection limits of the analytical method.

Regarding PAHs, they showed a similar pattern to DDT compounds in that their increase in soil due to flooding was clearly shown. The concentrations of PAHs were higher by approximately one and a half times compared to their "reference" levels and like DDT isomers, successively decreased with time during this study. Comparing the profiles of PAHs, no significant differences were found in the flooded and non-flooded matrices. In both cases, the dominating PAHs contained 4 aromatic rings and were followed by those with 5 and 6 aromatics rings. The "light", more volatile and more water-soluble PAHs (3-aromatic rings) represented only a minor fraction of the PAHs found in the examined soil samples.

As with the soil and sediment matrices discussed above, crops grown in the same locality were monitored, both in flooded and non-flooded areas. These were examined for POPs in 2003 and 2004. Since PBDEs were not detected in any sample and levels of PCBs and OCPs were close to LOQs in cereals sampled from flooded and non-flooded areas, only the results for PAHs are reported. The PAH concentrations together with the relative abundance of individual PAH groups (classified according to the number of aromatic rings) are shown in Fig. 2a. Considering a relatively high uncertainty associated with the measurement of very low PAH levels occurring in cereals, any significant impact of higher pollution of flooded soil on the PAH levels in cereals could be observed. In plant material "light" PAHs, which are present in the atmosphere in vapour phase, were found but in soil, heavier species were more abundant (Fig. 2b). Such data indicates that cereal contamination by PAHs was mainly caused by atmospheric emissions.

The results obtained for POP levels in flooded and non-flooded samples were also assessed in terms of the maximum tolerable values given by the Ministry of Environment of the Czech Republic (Czech Decree No. 13/1994 Coll.) for arable soil. The levels of DDT group exceeded in the years 2003–2005 the limit of 100 μg/kg dry weight assigned for the sum of persistent OCPs. The levels of PAHs approached the limit of 1,000 μg/kg dry weight in years 2003 and 2004. For OCPs, flooded arable soil slightly exceeded the tolerable values. In general terms, the results of the current study documenting the adverse effects of floods on contamination of the terrestrial ecosystem, are in a good agreement with the study by Elhottová et al. (2006) carried out immediately after the flooding in 2002. Although the sampling sites in the current study were geographically close to those of Elhottová et al. (2006), lower OCP and PCB levels both in non-flooded and flooded samples and higher PAH levels were found in this survey.

These differences document the variability of collected environmental data and indicate possible uncertainties associated with their interpretation. These differences highlight possible causes such as time after flooding, time course degradation, differential flood flows, topography and sampling plans and perhaps further work should concentrate in these areas. This would assist in further studies, evaluation and possible modelling and risk assessment in future flooding situations.

References

Chiou CT, Sheng G, Manes MA (2001) Partition-limited model for the plant uptake of organic contaminants from soil and water. Environ Sci Technol 35:1437–1444. doi:10.1021/es0017561

Cousins IT, Jones KC (1998) Air–soil exchange of semivolatile organic compounds (SOCs) in the UK. Environ Pollut 102:105–118. doi:10.1016/S0269-7491(98)00069-4

de Wit CA (2002) An overview of brominated flame retardants in the environment. Chemosphere 46:583–624. doi:10.1016/S0045-6535(01)00225-9

Elhottová D, Krištůfek V, Tříska J, Chrastný V, Uhlířová E, Kalčík J, Picek T (2006) Immediate Impact of the flood (Bohemia, august 2002) on selected soil characteristics. Water Air Soil Pollut 173:177–193. doi:10.1007/s11270-005-9054-1

Harrad SJ, Sewart AP, Alcock R, Boumphrey R, Burnett V, Duarte-Davidson R et al (1994) Polychlorinated biphenyls (PCBs) in the British environment: sinks sources and temporal trends. Environ Pollut 85:131–146. doi:10.1016/0269-7491(94)90079-5

Götz R, Bauer O-H, Friesel P, Herrmann T, Jantzen E, Kutzke M et al (2007) Vertical profile of PCDD/Fs, dioxin-like PCBs, other PCBs, PAHs, chlorobenzenes, DDX, HCHs, organotin compounds and chlorinated ethers in dated sediment/soil cores from flood-plains of the river Elbe, Germany. Chemosphere 67:592–603. doi:10.1016/j.chemosphere.2006.09.065

Jánská M, Hajšlová J, Tomaniová M, Kocourek V, Vávrová M (2006) Polycyclic aromatic hydrocarbons in fruits and vegetables grown in the Czech Republic. Bull Environ Contam Toxicol 77:492–499. doi:10.1007/s00128-006-1091-y

McLachlan MS, Welsch-Pausch K, Tolls J (1995) Field validation of a model of the uptake of gaseous SOC in *Lolium multiflorum* (Welsh Ray Grass). Environ Sci Technol 29:1998–2004. doi:10.1021/es00008a018

Meijer SN, Ockenden WA, Sweetman A, Breivik K, Grimalt JO, Jones KC (2003) Global distribution and budget of PCBs and HCB in background surface soils: implications for sources and environmental processes. Environ Sci Technol 37:667–672. doi:10.1021/es025809l

Nakajima D, Yoshida Y, Suzuki J, Suzuki S (1995) Seasonal changes in the concentration of polycyclic aromatic hydrocarbons in azalea leaves and relationship to atmospheric concentration. Chemosphere 30:409–418. doi:10.1016/0045-6535(94)00420-Y

Stachel B, Christoph EH, Götz R, Herrmann T, Krüger F, Kühn T et al (2006) Contamination of the alluvial plain, feeding-stuffs and foodstuffs with polychlorinated dibenzo-p-dioxins, polychlorinated dibenzofurans (PCDD/Fs), dioxin-like

polychlorinated biphenyls (DL-PCBs) and mercury from the River Elbe in the light of the flood event in August 2002. Sci Total Environ 364: 96–112. doi:10.1016/j.scitotenv.2005.07.004

Thomas GO, Sweetman AJ, Ockenden WA, Mackay D, Jones KC (1998) Air-pasture transfer of PCBs. Environ Sci Technol 32:936–942. doi:10.1021/es970761a

Tolls J, McLachlan MS (1994) Partitioning of semivolatile organic compounds between air and *Lolium multiflorum* (Welsh ray grass). Environ Sci Technol 28:159–166. doi:10.1021/es00050a022