Residues of persistent organic pollutants in Estonian soils (1964–2006)

Kurunthachalam Senthil Kumar[a], Mahalakshmi Priya[b], Kenneth S. Sajwan[a], Raimo Kõlli[c], and Ott Roots[d]

[a] Department of Natural Sciences and Mathematics, Savannah State University, 3219 College Street, Savannah, GA 31404, USA; kskumar@savstate.edu, kuruntha@gmail.com, sajwank@savstate.edu
[b] Department of Biotechnology, Dr N.G.P. Arts and Science College, Kalappatti Road, Coimbatore 641035, India
[c] Institute of Agricultural and Environmental Sciences, Estonian University of Life Sciences (EMU), Kreutzwaldi 1, 51014 Tartu, Estonia; Raimo.Kolli@emu.ee
[d] Estonian Environmental Research Institute, Marja 4D, 10617 Tallinn, Estonia; ott.roots@klab.ee

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Abstract. Organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs), and polybrominated diphenyl ethers (PBDEs) were analysed in selected Estonian soils. The sample collection included agricultural-rural (Ahja, Eerika), industrial-urban (Kohtla-Järve, Muuga, Kunda), and reference sites (Lahemaa and Vilsandi). The PCB concentrations were greater in Ahja-1982 and Kohtla-Järve station 1, while Eerika, other Kohtla-Järve, Muuga Port, Kunda, Lahemaa, and Vilsandi Island concentrations were low. Organochlorine pesticides were slightly higher at Kohtla-Järve stations and PBDEs at Kunda stations. Overall, the predominant contaminants were PCBs (0.43–89 ng/g dw), followed by OCPs (0.21–16 ng/g dw) and PBDEs (<0.01–3.2 ng/g dw). The occurrence of 4,4′-DDT in some samples indicated recent contamination by DDT of Estonian soils. The PBDEs in Estonian soils were reported for the first time.

Key words: soil, rural, urban, oil shale, pesticides, PCBs, PBDEs.

INTRODUCTION

Organochlorine pesticides (OCPs) have a long history of wide use in agriculture (Tanabe & Tatsukawa 1984; Loganathan & Kannan 1994), while polychlorinated biphenyls (PCBs) have been used in industries, electrical equipments, and transformer oils (Kodavanti et al. 2008). These compounds are typically very persistent in the environment and are known to accumulate in soil, sediments, plants, animals, and human beings (Kannan et al. 1992, 1995, 1997a, 1997b; Roots 1996; Senthil Kumar et al. 1999, 2001a, 2001b, 2005a, 2008; Pandelova et al. 2008). Organochlorines (OCPs and PCBs) have a wide range of both acute and chronic health effects, including cancer, neurological damage, reproductive effects, immune suppression, and birth defects (Van den Berg et al. 1998; Kodavanti et al. 2008). Many organochlorine chemicals are also suspected endocrine disruptors (Colborn & Smolen 1996). Organochlorine pesticides, such as DDTs and its metabolites (2,4′ and 4,4′-DDT, DDD and DDE), hexachlorobenzene (HCB), cyclodienes (aldrin, dieldrin, and endrin), chlordanes (heptachlor, heptachlor epoxide, *cis*-chlordane, *trans*-chlordane, *cis*-nonachlor, *trans*-nonachlor, and oxy-chlordane), HCHs (α,β,γ,δ-isomers), mirex, and industrial chemicals like PCBs, are ubiquitous environmental pollutants (Kannan et al. 1992, 1995, 1997a, 1997b; Loganathan et al. 1995; Senthil Kumar et al. 1999, 2001a, 2001b, 2005a, 2008). Several of OCPs and PCBs are included, as priority persistent organic pollutants (POPs; a dirty dozen) in the United Nations Environment Programme (UNEP) (Birnbaum & Tuomisto 2000; Feeley & Brouwer 2000; Sweeney & Mocarelli 2000). Persistent organic pollutants are also emitted unintentionally during combustion of waste and industrial materials (Weber & Kuch 2003).

Polybrominated diphenyl ethers (PBDEs) are second-generation organic compounds that were used as flame retardants (Birnbaum & Staskal 2004; BSEF 2005). These are also formed during incineration of electrical waste and electronic materials (Takasuga et al. 2005). Like other brominated flame retardants, PBDEs have been used in a wide array of products, including building materials, electronics, furnishings, motor vehicles, plastics, polyurethane foams, and textiles, as well as they have been reported in humans and wildlife (Takasuga et al. 2004, 2005, 2006b; Watanabe et al. 2004; Ishizuka et al. 2005; Senthil Kumar et al. 2005b; Inoue et al. 2006). Polybrominated diphenyl ethers are structurally akin to PCBs, consisting of two halogenated

aromatic rings linked by an ether group. The health hazards of these chemicals have attracted increasing scrutiny as they produce chronic effects and are carcinogenic to humans and wildlife (De Swart et al. 1996). Like OCPs and PCBs, PBDEs are found in lower trophic organisms to higher trophic animals (Kannan et al. 2005, 2007, 2008; Brown et al. 2006; Gerecke et al. 2006; Jaspers et al. 2006; Johansson et al. 2006; Law et al. 2006; Thuresson et al. 2006; Zhu & Hites 2006; Moon et al. 2007; Shaw et al. 2008; Roots et al. 2008a, 2008b). The Stockholm Convention suggested inclusion of PBDEs in the POPs Reviewing Committee (www.pops.int).

The Republic of Estonia in northeastern Europe is located east of the highly contaminated Baltic Sea. Estonian contribution of mass loadings of toxic contaminants to the Baltic Sea has been considered in numerous publications (Roots 1996, 2001, 2003a, 2004; Roots & Zitko 2003; Roots et al. 2004a, 2004b, 2007, 2008a, 2008b, 2008c; Schleicher et al. 2004a, 2004b; Roots & Sweetman 2007; Lukki et al. 2008; Pandelova et al. 2008). Very limited information is available on the status of PBDEs contamination in air, sediment, and biological samples from Estonia (Roots & Sweetman 2007; Roots et al. 2007, 2008a, 2008b, 2008c). To our knowledge, there has been no research reported on OCPs, PCBs, and PBDEs in Estonian soils. We anticipate that Estonia contributes certain amounts of PCBs and PBDEs to the Baltic Sea due to oil shale mining and oil shale thermal processing (Roots 2004; Schleicher et al. 2004a, 2004b; Roots & Sweetman 2007), because oil shale is one of the most important organic products found in Estonia. The relatively high chlorine content (0.22%) of oil shale compared to the other fuels could possibly lead to an increased formation of dioxins and its related compounds such as PCBs. The Estonian thermal power station is the world's largest power station burning low-grade local oil shale. Further, Estonia still has no waste incineration facilities, which would act as substantial sources at preventing PCB and PBDE pollution. In addition, Estonia has inherited a total of 1565 military sites which cover an area of 87 147 ha, or approximately 1.9% of the total land area (Raukas 1999). Therefore, contamination of Estonian soil is very likely. Recently, Roots & Sweetman (2007) reported the occurrence of several persistent organic pollutants in air samples from two Estonian monitoring stations. The occurrence of PCBs and PBDEs in Estonian food provisions and fish has also been reported (Roots et al. 2007; Roots et al. 2008b). Recent studies also revealed the presence of PCDD/DFs in various samples (Roots 1996, 2004; Roots et al. 2004a, 2004b, 2007). Considering those credits, and taking it to our advantage, in this study OCPs, PCBs, and PBDEs were analysed in soil samples collected from selected industrial (urban) and agricultural (rural) sites, and oil shale mining and cement production regions of Estonia for the first time since the former Soviet Republic contributed to the Baltic Sea pollution load.

MATERIALS AND METHODS

Location and pedo-ecological characterization of sampling areas

Estonia is situated in the Northeast of Europe, located 57°30′34″ to 59°49′12″N and 21°45′49″ to 28°12′44″E. The archived soil samples were collected at Ahja, Eerika, Kohtla-Järve, Muuga Port, Kunda, Lahemaa, and Vilsandi Island. The map of Estonia and location of sampling regions are shown in Fig. 1. Lahemaa (59°30′55″N, 25°55′41″E) and Vilsandi (58°22′34″N, 21°50′42″E) represent natural background (reference) areas, which are also EMEP (co-operate programme for monitoring and evaluation of the long-range transmissions of air pollution in Europe) stations. Muuga (59°29′40″N, 24°55′51″E), Kunda (59°30′10″N, 26°33′28″E), and Kohtla-Järve (59°24′35″N, 27°16′43″E) areas are influenced by industrial and urban activities. The oil terminal of the Muuga Port is the largest seaport in Estonia, allowing the loading and discharging of tankers of up to 125 000 dwt. Kunda is well known for its cement producing industries and Kohtla-Järve for its oil-shale chemistry enterprises. Eerika (58°21′43″N, 26°40′12″E) and Ahja (58°08′42″N, 27°05′36″E) are situated on agricultural or rural areas, where industrial influence is modest (Eerika, not far from Tartu) or absent (Ahja).

The soils of Lahemaa and Vilsandi Island nature preserves may be classified respectively as *Calcaric Cambisols*, whose topsoil textures are composed of calcareous sandy loam, and *Hyperskeletic-Endolithic Regosols*, where the topsoil consists of coarse carbonate sediments. The samples characterizing the Muuga Port area were taken from coastal, poor, gravelly, sandy *Salic-Epigleyic Fluvisols*, those of Kunda from fine sandy *Endogleyic-Epidystric Luvisol*, and of Kohtla-Järve from loamy *Calcaric-Endoruptic Anthrosol*. Soils of the Eerika and Ahja sampling areas are *Stagnic Albeluvisols*, with loamy sand topsoil and loamy subsoil (FAO, ISRIC & ISSS 1998; Kõlli 2002).

The Lahemaa and Kohtla-Järve sampling areas are situated on till plains with calcareous cover, Vilsandi and Kunda on limestone plains, whereas in Vilsandi the Quaternary cover is very thin and skeletal, but in Kunda – relatively thick and sandy. The Muuga area lies on a low sandy ridge of the North Estonian coastal plain. The

Fig. 1. The Estonian map with soil sampling sites.

Ahja and Eerika areas are situated on reddish-brown non-calcareous moraine (2–8 m) plain with small variations in elevation. The cultivated massifs of fields are separated by primeval valleys and lowland forest areas.

Sampling

The soil samples from Vilsandi, Muuga, Lahemaa, Kunda, and Kohtla-Järve were taken from the 0–10 cm topsoil layer or humus horizon with a steel cylinder (diameter 5.0 cm). The sampling was performed on 10 m × 10 m subplots (ICPIM 1998), which were surrounded with a barrier. A total of 16 samples were taken at intervals of 2 m from each area. The samples were later mixed together in order to have one average aggregated sample. The living parts of plants and coarse litter were removed from all samples. The Kohtla-Järve (two sites – oil-shale processing plant and city), Kunda, Muuga, and Lahemaa areas were sampled in 2005 and 2006, but the Vilsandi sample was taken only in 2006. The coordinates of the sample points were determined by the GPS. The samples were kept in carefully labelled glass jars in the dark until they were pretreated.

At Ahja and Eerika the soil samples were collected from the control plots of long-term field experiments of 1964–2004. The aggregated soil samples for each year considered were obtained from 4–5 control plot average samples, consisting of 16–20 individual samples which were taken in regular order from the ploughed layer of the plot. All plant residues were removed from the aggregated soil samples, and the homogenized samples were treated and sieved (through a 1-mm sieve). Samples were stored at ambient temperature in paper bags or

paper/plastic boxes (EC 2005). The samples for the Ahja area were composed in 1964 and 1982, those for Eerika in 1964, 1982, 1992, and 2004.

Extraction and cleanup

Polychlorinated biphenyl congeners, chlorinated pesticides, and PBDEs were analysed in soil using approved procedures. Approximately 10 g of dry soil was Soxhlet extracted using 3 : 1 methylenechloride and hexane mixture v/v for 17 h. The extract was then concentrated to 10 mL using the Rapid Vap Labconco Evaporation System (Model 79100; The Pump Works Inc. Sanford FL, USA) and exchanged to hexane. The extract was concentrated to 5 mL using a stream of nitrogen gas to evaporate the solvent and then further subjected to silica gel column chromatography to remove interfering organic and polar species and to separate the PCBs from the pesticides. In the first fraction (F1), PCBs, 4,4′-DDE, HCB, and *trans*-nonachlor were eluted using 120 mL of ultra pure hexane. The second fraction (F2), containing most of the chlorinated pesticides and PBDEs, was eluted with 100 mL of 20% methylene chloride in hexane. The F1 was concentrated using a Rapid Vap apparatus to 10 mL, followed by evaporation to 1 mL, and then micro-concentrated to 100 µL using a gentle stream of nitrogen gas. The extract was transferred to auto sampler vial and 1 µL was injected onto a gas chromatograph equipped with an electron capture detector (GC-ECD).

Instrumental analysis

Twenty-six PCB congeners (PCB-8, 18, 29, 50, 28, 52, 104, 44, 66, 101, 87, 154, 118, 188, 153, 105, 138, 187, 128, 201, 180, 170, 195, 194, 206, and 209), eleven PBDEs (PBDE-30, 28, 47, 66, 100, 99, 85, 154, 153, 138, and 183) and chlorinated pesticides (HCB, γ-HCH, aldrin, dieldrin, mirex, heptachlor, heptachlor epoxide, *trans*-nonachlor, *cis*-chlordane, 2,4′-DDE, 4,4′-DDE, 2,4′-DDD, 4,4′-DDD, 2,4′-DDT, and 4,4′-DDT) were analysed using a Varian model CP-3380 gas chromatograph (GC) with the Varian model CP-8410-auto injector (Varian, Inc. Palo Alto, CA, USA). Therefore, non-ortho PCBs (e.g. PCBs 77, 81, 126, and 169) were not considered in this study; we plan to analyse non-ortho PCBs and dioxins in the future. The GC was equipped with a DB-5 (60 m × 0.25 mm; 0.25 µm film thickness) capillary column (J&W Scientific, USA) and a ^{63}Ni electron capture detector. The initial temperature of the column was 90 °C, with a 1 min hold time and increase at the rate of 5 °C to 150 °C, and was ramped at the rate of 2 °C to 280 °C and held for 20 min. The injector and detector temperatures were 270 °C and 330 °C, respectively. Helium (1.5 mL/min) and nitrogen (28.5 mL/min) were used as a carrier and make-up gases, respectively. The standard reference material SRM 2262, obtained from the National Institute of Standards and Technology (NIST, USA), was used for the quantification of PCB congeners, and SRM 2261 from the same source was used to quantify chlorinated pesticides. The PCB and PBDE congeners and organochlorine pesticides were identified in the sample extract by comparing the retention time from the standard mixture and quantified using the response factors. Appropriate quality assurance quality control (QA/QC) analysis was performed, including reagent blank (analyte concentrations were <MDL 'method of detection limit'), calibration curve with the r^2 value of 0.99, surrogate recovery (4,4′-dibromooctafluorobiphenyl), and matrix spike recovery 100 ± 30%.

RESULTS

Polychlorinated biphenyls

Concentrations of total PCBs in rural/agricultural soils (Ahja and Eerika) of Estonia are shown in Table 1. Total PCB concentration was comparatively lower in the Ahja-1964 soil sample (23 ng/g dry weight (dw)) than in the Ahja-1982 sample (89 ng/g dw). However, total PCB concentrations in soil samples from Eerika were relatively similar during the years 1982 (29 ng/g dw) and 1992 (21 ng/g dw) but much lower in soil samples collected in 1964 (2.9 ng/g dw) and 2004 (3.4 ng/g dw). Due to the limited number of samples, the temporal trend cannot be illustrated in detail. Considering the congener composition, PCB-66 was a major congener in the Ahja sample, followed by PCB-52, 118, 101, 138, 105, and 104, however, minor variation was observed for congener profiles from soils collected in 1964 and 1982 (Fig. 2a). For example, the concentration of lower chlorinated PCBs was greater in 1982 soils, but both lower and higher concentrated chlorinated PCBs were evenly distributed in 1964 samples. Among Eerika soils, 1982 samples had high PCBs, probably due to the maximum contribution (45%) of PCB-206 (Fig. 2b). Similarly, higher PCB concentrations in Eerika-1992 samples may be due to the high contribution (39%) of PCB-194 alone. In general, the lower and higher chlorinated PCB congeners were evenly distributed in all Eerika soils except Eerika-1982 and 1992, in which only PCB-194 and 206 contributed almost 50% of total PCB concentration.

Concentrations of PCBs in samples collected from oil shale enterprises and the urban area in Kohtla-Järve and oil terminals in Muuga are shown in Table 2. The PCB concentration was approximately twelve times

Table 1. Concentrations (ng/g dw) of organohalogens in soil samples from rural and urban Estonia

	Ahja-1964	Ahja-1982	Eerika-1964	Eerika-1982	Eerika-1992	Eerika-2004
PCBs	**23**	**89**	**2.9**	**29**	**21**	**3.4**
PBDE-30	<0.03	<0.03	0.08	<0.03	0.04	<0.03
PBDE-47	<0.03	0.03	0.11	0.04	0.03	0.07
PBDE-100	0.32	<0.03	<0.03	<0.03	<0.03	0.30
PBDE-99	<0.03	<0.03	0.09	<0.03	<0.03	<0.03
PBDEs	**0.32**	**0.03**	**0.27**	**0.04**	**0.07**	**0.37**
HCB	0.05	0.22	0.05	0.50	0.05	0.01
γ-HCH	<0.01	0.01	0.03	0.31	0.26	<0.01
Aldrin	<0.01	<0.01	<0.01	0.03	0.09	<0.01
Dieldrin	<0.01	<0.01	0.02	<0.01	<0.01	<0.01
Mirex	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Heptachlor	0.58	0.93	<0.01	0.90	0.35	0.14
H. epoxide	0.01	<0.01	<0.01	0.11	0.04	<0.01
trans-Nonachlor	0.09	0.09	<0.01	0.04	0.10	0.01
cis-Chlordane	<0.01	<0.01	<0.01	<0.01	0.05	<0.01
2,4′-DDE	<0.01	<0.01	0.01	<0.01	<0.01	<0.01
4,4′-DDE	0.39	1.87	0.05	0.55	0.21	0.05
2,4′-DDD	<0.01	<0.01	0.01	<0.01	0.14	0.01
4,4′-DDD	<0.01	<0.01	0.01	<0.01	<0.01	<0.01
2,4′-DDT	<0.01	<0.01	0.08	<0.01	0.05	<0.01
4,4′-DDT	<0.01	0.01	0.15	0.28	<0.01	<0.01
OCPs	**1.1**	**3.1**	**0.42**	**2.7**	**1.3**	**0.21**

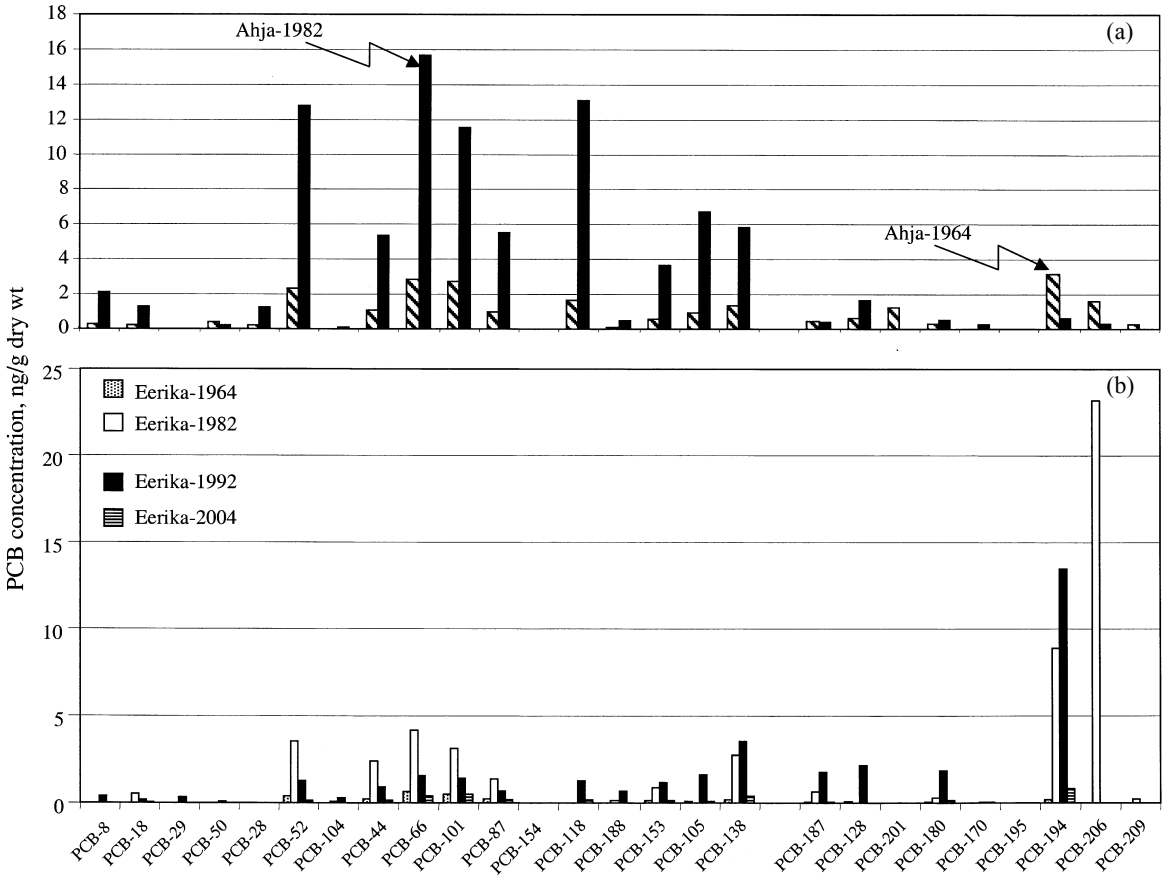

Fig. 2. Polychlorinated biphenyl (PCB) congener profiles in the soils of Ahja and Eerika stations.

Table 2. Concentrations (ng/g dw) of organohalogens in soil samples from industrial Estonia

	Kohtla-Järve oil shale station 1	Kohtla-Järve oil shale station 2	Kohtla-Järve city station 1	Kohtla-Järve city station 2	Muuga Port 1, oil terminals	Muuga Port 2, oil terminals
PCBs	**81**	**7.0**	**0.43**	**24**	**1.0**	**4.0**
PBDE-30	0.10	0.04	0.49	<0.03	<0.03	<0.03
PBDE-47	0.06	<0.03	0.20	<0.03	0.03	0.03
PBDE-100	<0.03	<0.03	<0.03	<0.03	<0.03	0.41
PBDE-85	<0.03	<0.03	0.34	<0.03	<0.03	1.3
PBDEs	**0.16**	**0.04**	**1.03**	**ND**	**0.03**	**1.70**
HCB	0.18	0.50	0.19	0.21	<0.01	<0.01
γ-HCH	0.05	<0.01	<0.01	<0.01	<0.01	<0.01
Aldrin	<0.01	0.03	0.06	<0.01	0.02	0.05
Dieldrin	<0.01	0.05	<0.01	0.46	0.12	<0.01
Mirex	<0.01	<0.01	<0.01	<0.01	0.11	<0.01
Heptachlor	0.36	0.50	0.39	0.15	0.35	0.17
H. epoxide	<0.01	0.03	0.28	<0.01	<0.01	0.42
trans-Nonachlor	0.33	0.02	<0.01	0.02	0.09	0.03
cis-Chlordane	<0.01	<0.01	<0.01	<0.01	0.13	<0.01
2,4′-DDE	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
4,4′-DDE	0.86	<0.01	0.08	0.12	0.37	0.11
2,4′-DDD	0.60	<0.01	2.0	0.55	0.61	<0.01
4,4′-DDD	1.5	6.7	2.7	1.8	<0.01	0.23
2,4′-DDT	0.56	0.05	<0.01	1.0	<0.01	<0.01
4,4′-DDT	3.6	<0.01	11	5.0	0.32	1.9
OCPs	**8.1**	**7.9**	**16**	**9.4**	**2.1**	**2.9**

ND, not detected.

higher (81 ng/g dw) in Kohtla-Järve oil shale station 1 than in station 2 (7 ng/g dw). Similarly, Kohtla-Järve city station 2 (24 ng/g dw) had >55 times greater concentrations of PCBs than city station 1 (0.43 ng/g dw). No such variation was observed in Muuga soil samples (1.0 and 4.0 ng/g dw). The congener profile showed an entirely different pattern between Kohtla-Järve oil shale processing, city, and Muuga Port oil terminal samples (Fig. 3a–c). This may be due to higher and lower concentrations of PCBs in two different samples collected from the same area. In general, PCB-138, 180, and 128 were major congeners in Kohtla-Järve oil shale station 1, while PCB-66 and 194 were major congeners in oil shale station 2 (Fig. 3a). In samples from the Kohtla-Järve city area PCB-138 and 194 were major congeners, while city 1 station samples revealed only PCB-118, 153, 187, and 180 (Fig. 3b). Many PCB congeners were detected in Muuga Port 2, whereas only PCB-50, 52, and 188 were found in Port 1 station (Fig. 3c). Interestingly, the abundance of higher chlorinated PCBs was very low in the soil of Muuga Port oil terminals.

The contamination levels of PCBs in soil collected from Kunda, Lahemaa, and Vilsandi Island are shown in Table 3. Total PCBs (0.61–14 ng/g dw) and OCPs (0.30–1.6 ng/g dw) at these sites were comparatively lower than at Ahja, Eerika, Kohtla-Järve, and Muuga sites (Tables 1, 2). Compared to Muuga oil terminals, Kunda stations showed no higher chlorinated PCBs (Fig. 4a). PCB-66, 52, 50, and 188 were abundant at both sites. Greater contamination variation of Lahemaa EMEP stations 1 and 2 was probably due to high relative abundance of PCB-194 but also due to PCB-50, 52, and 188 detected in station 1 (Fig. 4b). Greater abundance of PCB-194 in Vilsandi (Fig. 4c) was the sole reason for a higher PCB concentration in this remote island where industrial activity is very uncommon.

Polybrominated diphenyl ethers

Concentrations of PBDEs in Ahja agricultural soil were 0.03–0.32 ng/g dw, and similar (0.04–0.27 ng/g dw) or slightly higher (0.37 ng/g dw) in Eerika soils. Of 11 PBDE congeners analysed, only 4 were detected (Table 1). The congener PBDE-47 was abundant in all samples except Ahja-1964 in which only PBDE-100 was detected.

Again, PBDEs were much lower than PCBs in oil shale and urban areas of Kohtla-Järve and oil terminal areas in Muuga (ND–1.7 ng/g dw) (Table 2). The concentration of PBDEs was 1.03 ng/g dw at Kohtla-Järve city

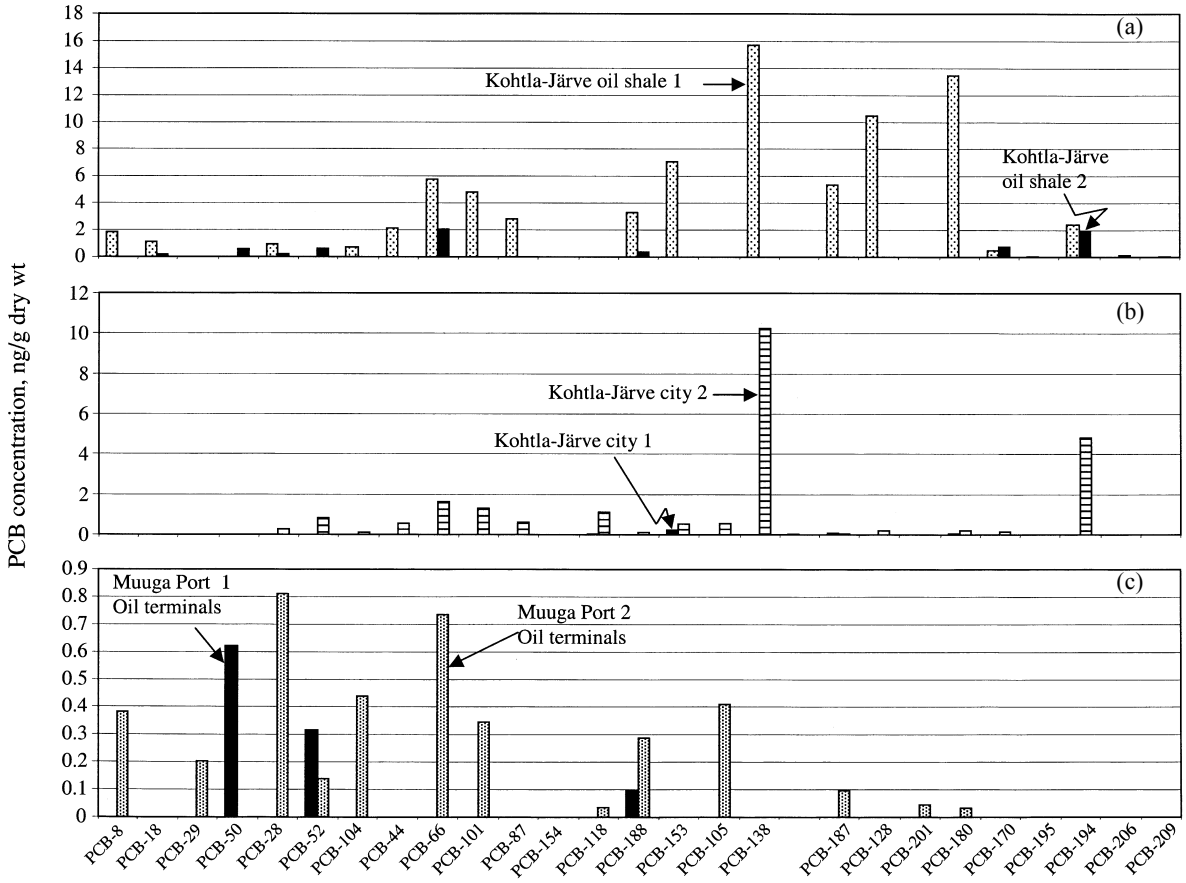

Fig. 3. Polychlorinated biphenyl (PCB) congener profiles in Kohtla-Järve oil shale and city, and Muuga Port stations.

Table 3. Concentrations (ng/g dw) of organohalogens in soil samples from Estonia

	Kunda station 1	Kunda station 2	Lahemaa EMEP 1	Lahemaa EMEP 2	Vilsandi Island EMEP
PCBs	**1.0**	**2.8**	**0.61**	**14**	**12**
PBDE-30	0.48	<0.03	0.10	<0.03	<0.03
PBDE-47	0.08	1.35	0.06	0.08	<0.03
PBDE-66	0.14	<0.03	<0.03	<0.03	<0.03
PBDE-100	<0.03	<0.03	<0.03	<0.03	0.21
PBDE-99	0.87	<0.03	0.07	<0.03	<0.03
PBDE-85	<0.03	<0.03	0.48	<0.03	<0.03
PBDEs	**1.6**	**1.1**	**0.70**	**0.08**	**0.21**
HCB	0.38	0.03	0.03	0.06	0.33
γ-HCH	<0.01	<0.01	<0.01	<0.01	<0.01
Aldrin	0.19	0.04	0.04	0.08	<0.01
Dieldrin	<0.01	<0.01	<0.01	<0.01	<0.01
Mirex	0.09	0.03	<0.01	<0.01	<0.01
Heptachlor	0.78	0.20	0.13	0.29	0.13
H. epoxide	<0.01	<0.01	0.01	<0.01	<0.01
trans-Nonachlor	0.06	0.02	0.02	0.12	0.05
cis-Chlordane	0.01	<0.01	<0.01	<0.01	<0.01
2,4′-DDE	<0.01	<0.01	<0.01	<0.01	<0.01
4,4′-DDE	0.07	<0.01	0.06	0.21	<0.01
2,4′-DDD	<0.01	0.77	<0.01	<0.01	<0.01
4,4′-DDD	<0.01	<0.01	<0.01	<0.01	<0.01
2,4′-DDT	<0.01	<0.01	<0.01	<0.01	<0.01
4,4′-DDT	<0.01	<0.01	<0.01	<0.01	<0.01
OCPs	**1.6**	**1.1**	**0.30**	**0.76**	**0.52**

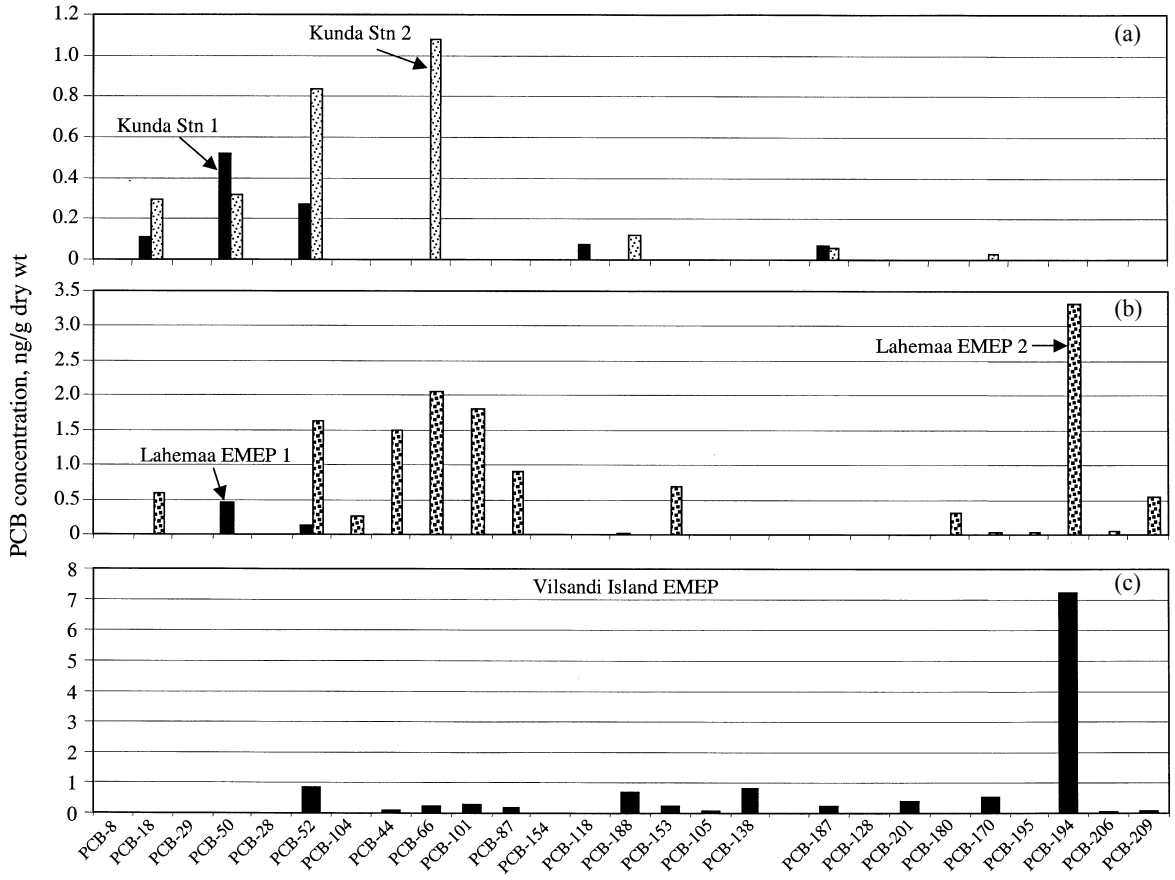

Fig. 4. Polychlorinated biphenyl (PCB) congener profiles in Kunda, Lahemaa, and Vilsandi Island soils.

station 1 but no PBDEs were detected at station 2. At station 1 PBDE-47 was abundant, followed by PBDE-30, 85, and 100. Three PBDE congeners were detected at Muuga Port 2, while at port 1 only PBDE-47 was found.

Polybrominated diphenyl ether congeners were consistently detected at Kunda and Lahemaa stations (1.0–3.2 ng/g dw) (Table 3). Their concentrations were slightly higher than at the Ahja, Eerika, Kohtla-Järve, and Muuga oil terminal sites (Tables 1, 2). The most common PBDE congener was PBDE-47.

Organochlorine pesticides

Among OCPs, HCB, γ-HCH, heptachlor, *trans*-nonachlor, and 4,4′-DDE were the most frequently detected pesticides (Table 1). Agricultural soil sampled in 1982 had maximum total OCP concentrations (3.1 ng/g dw), while the minimum concentration (0.42 ng/g dw) was observed in Eerika-1964 soils. Hexachlorobenzene and 4,4′-DDE were recorded in all agricultural and industrial soil samples. Mirex was not found in any of the six samples analysed. γ-HCH was recorded in four samples. Chlordane heptachlor and *trans*-nonachlor were abundant. The occurrence of 4,4′-DDT in the soil samples (Table 1) suggested continuing soil pollution with this compound.

The concentrations of OCPs were significantly greater at Kohtla-Järve city 1 station than at city 2, but almost identical at oil shale stations 1 and 2, and Muuga Port stations 1 and 2 (Table 2). Heptachlor was detected in all six samples, while *trans*-nonachlor, 4,4′-DDE, 4,4′-DDD, and 4,4′-DDT were present in five of the six samples analysed. The occurrence of 4,4′-DDT (except Kohtla-Järve oil shale station 2) indicates recent input of DDT in other five areas.

In Kunda, Lahemaa, and Vilsandi Island HCB, heptachlor, and *trans*-nonachlor were detected in all samples. Interestingly, γ-HCH, dieldrin, 2,4′-DDE, 4,4′-DDD, 2,4′-DDT, and 4,4′-DDT were not recorded at all (Table 3). The Kunda stations showed OCPs >1 ng/g dw but not the other EMEP stations (Lahemaa and Vilsandi).

Correlation was analysed between PCBs and PBDEs (Fig. 5) in order to understand the PBDEs source. If there is significant correlation, then the source of PBDEs

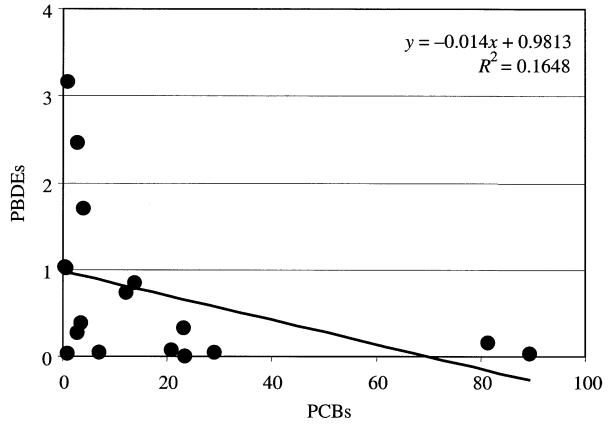

Fig. 5. The correlation matrix of polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) in Estonian soils.

is the same as for PCBs accumulation in soil. The results showed a very weak correlation (r^2 = 0.165), and therefore the PBDE source is entirely different than that of PCBs.

DISCUSSION

Polychlorinated biphenyls

Among the chemicals analysed, PCBs were predominant, followed by legacy chlorinated pesticides and PBDEs. Some studies are available on PCBs in Estonia, but most of them focus on biological, air, or sediment samples. Based on the results of this and other studies, contamination of PCBs in Estonia can be classified into four categories. The greatest source is oil shale mining in Northeast Estonia. Oil shale mining is an important economic and social issue for oil shale regions. In the short term, world oil shale processing may have increased from about 16 million tonnes in 2000 to about 23 million tonnes in 2006. Estonian thermal power plants, which are the world's largest thermal power plants, burn low-grade local oil shale. The disadvantage of oil shale is its low calorific value, which causes an extraordinarily high amount of pollution (dioxins, furans, PCBs, PBDEs, PAHs, etc.), of both air and soil. Concentrations of total PCBs in oil shale and fly ash are 8.6–9.0 and 1.1–2.4 μg/kg, respectively (Roots 2004). However, when compared to Finland, Russia, and other western European countries, Estonian PCB levels are very low (this study; Jaward et al. 2004; Gioia et al. 2007; Roots & Sweetman 2007). Passive air samplers were deployed at 23 background locations along a broadly west–east transect in eight northern European countries (Ireland, United Kingdom, Denmark, Norway, Sweden, Finland, Estonia, and Russia) for 8–11 weeks during August–October 2004. Lower PCB concentrations were determined in Estonia, as well as DDT, PBDEs, and PAHs for the Lahemaa station than in Ireland, Norway, Finland, and Sweden, while the highest levels were recorded in Russia, Denmark, and United Kingdom (Gioia et al. 2007).

Olsson et al. (2002) documented the lowest PCB concentrations along the Estonian coast, but also in the northern Bothnian Bay and in the Kattegat. The highest levels of PCBs were measured at urban sites in Russia, France, Italy, Sweden, the United Kingdom, Eastern Europe, Croatia, Hungary, and finally Estonia (at the Kohtla-Järve site the sum of 29 PCBs was 790 pg/m^3 – 99 ng/sample). For most samples, the levels for the sum of 29 PCBs ranged from 2.5 to 280 ng/sample (Jaward et al. 2004). Concentrations of PCBs in soils of the Kohtla-Järve areas were 0.43–81 ng/g dw (Table 2). These results suggest that part of the PCBs in soil has arisen from oil shale burning. Effluents from the Järve biological sewage purification station at Kohtla-Järve were analysed for PCBs in 2006 (Roose & Roots 2005; Roots & Sweetman 2007). Two of the three sewage water samples, taken from the effluents discharged to the Gulf of Finland from the Järve purification station, exceeded the Estonian PCB concentration (95 and 103 μg/l) limits for PCB in sewage waters (50 μg/l). Consequently, PCBs derived from oil shale burning contribute to contamination of the neighbourhoods.

The second major source of PCBs considered was old transformers, and condensers that contain PCBs and are still in use in Estonia. In total, roughly 20 000 transformers were in use in Estonia. With the average of 1.5 mg PCBs/kg, the transformers would contain a total of ca 15 kg PCB (PCB/PCT DE 1999). The research conducted within the Nordic Environment Research Programme (1999) concluded that the PCBs hot spot in the river water, nearest to the Estonian coast in the Gulf of Finland, was situated in the mouth of the Neva River (Russian Federation) and its tributary. Another site of elevated PCB concentrations close to the Estonian coast was in the mouth of the Daugava River in the Gulf of Riga (Agrell et al. 2001). Therefore, electrical transformers and condensers constitute additional PCB sources to Estonian soils. Figures 2–4 show congener profiles which indicate various sources of PCBs for Estonian soils.

The third group of PCBs can be identified as PCBs that entered the Estonian environment in large quantities for more than 37 years and bio-accumulated and deposited in soils and sediments (Koppe & Keys 2001). Long-range transport prevailed in Estonia and its coastal sea, although the interactions of airborne POPs with surface media are not sufficiently understood (Scheringer et al. 2004). At the present time, long-range transport of PCBs

from southern sources outside Estonia is dominating (Agrell et al. 2001; Gioia et al. 2007; Roots & Sweetman 2007), which is supported by their higher concentrations in the Ahja-1982 (89 ng/g dw) agricultural soil samples (Table 1). Therefore long-range transport of PCBs to Estonia cannot be ignored. Vilsandi Island is considered to be a pristine environment due to less industry and human activities. The concentration of PCBs on Vilsandi is 12 ng/g dw, thus higher than at Kunda stations, one Lahemaa station, both Muuga Port stations, Kohtla-Järve city station 1, the oil shale station, and two Eerika stations (Tables 1–3), which further confirms long-range transport of PCBs into Estonian soils.

The fourth source of PCBs contamination in Estonia originates from the Soviet Union era (Roots 2003b), since Estonia inherited 1565 military sites that cover a territory of 87 147 ha, or approximately 1.9% of the total land area of Estonia. In general, Estonia faces similar environmental problems resulting from former Soviet military activities as the other Baltic states: air-fields severely contaminated with air craft fuel, artillery and bombing ranges contaminated with UXO, ordnance depots with hazardous materials and abandoned chemicals (PCB barrels), and tank terminals with oil spills, often resulting in severe soil contamination with hydrocarbons and PCBs. Consequently, these are the four major reasons for the PCBs contamination in Estonia. Russian PCB formulation Sovol contained 51% chlorine by weight with medium chlorinated PCB congeners (Takasuga et al. 2006a). Congener-specific data for this study show that the Ahja, Kohtla-Järve, and Lahemaa areas contained a similar proportion of Sovol (Figs 1–3). Therefore, part of this PCB contamination was expected to arise from Russian PCB formulation for electrical instruments and former Russian electrical equipment. This may be the reason for the PCB contamination, along with long-range transportation from western Russia.

Polychlorinated biphenyls in Estonian air and fish

Air samplers were deployed at two Estonian stations, in the Lahemaa background EMEP station and Kohtla-Järve industrial (oil shale) region. The levels of PCBs in air, precipitation, and deposits in Vilsandi and Lahemaa were 79 and 49 (pg/m^3), 1.5 and 0.8 (ng/L), and 2.2 and 1.8 (ng/m^2/d), respectively (Agrell et al. 2001). Concentrations of PCBs in soils of Vilsandi Island (12 ng/g dw) and Lahemaa (0.61–14 ng/g dw) corresponded to those of air, precipitation, and deposition samples. The PCB in air samples near the town of Riga (Latvia) came from the original industrial PCB mixture. This refers either to long-range transportation or a local waste centre situated near the Gulf of Riga. Above the Baltic Sea the concentration of PCB homologues proved to be higher with southwest winds (Duinker & Bouchertall 1989; Roots 1995; Agrell et al. 2001; Roots & Sweetman 2007). This endangers the Estonian islands of Saaremaa (Vilsandi) and Hiiumaa, since these winds are prevailing on the Baltic Sea. The concentrations of PCB-118 in flounder and perch were 6.9–82 and 16–52 ng/g fat, respectively (Roots 2001).

Polybrominated diphenyl ethers

Contamination trends of PBDEs in Estonian soils were one of the lowest. Unlike legacy organochlorine pesticides and PCBs, PBDEs are considered to be second-generation toxic compounds and therefore contamination was expected to be minimal. However, PBDE levels in soil may increase in the future due to lack of incineration facilities in Estonia. Burning of plastics, waste electronic goods, and oil shale may provide an additional PBDEs load in the Estonian soil. The sum of PBDEs in the air of Kohtla-Järve was 3.02 and of Lahemaa 6.0 ng/g per sample. Concentrations of PBDEs in soils of Kohtla-Järve and Lahemaa were ND–1.03 ng/g dw and 0.84–1.0 ng/g dw, respectively (Tables 2 and 3). Altogether, PBDE values in Eastern Europe (Estonia) were generally low. The PBDEs have been produced since the 1970s. Detection of PBDE-100 in the 1964 sample was probably due to contamination during storage and handling (e.g. in the museum).

Some studies have reported that PBDE concentrations in Estonian food were all below 4 ng/g fat, whereas the majority of concentrations were below 2 ng/g fat (Roots et al. 2008b). In wild fish the concentrations varied between 0.65 and 2.3 on fresh weight basis. The highest concentrations in foodstuff, wild fish excluded, were recorded in two fish oil samples (5.1 and 4.0 ng/g fat) imported from Russia. Polychlorinated diphenyl ethers in Estonian foodstuffs such as meat, butter, milk, and fish oil were in the range of 0.05–1.5 ng/g fat weight (Roots et al. 2008b).

PBDE-47 was a prevalent congener in soils analysed in this study. Our results were similar to the data obtained from various biological samples (Takasuga et al. 2004; Watanabe et al. 2004). The congener profiles of PBDEs in aquatic fauna differed from those of the commercial PBDE formulations, particularly by a much higher proportion of the congener 47 (Roots et al. 2008b). The concentrations of PBDE-47, 100, 99, 154, and 153 in the air sample from Lahemaa were 12, 4.4, 25, 2.1, and 2.9 pg/m^3 and the sum of eight PBDE congeners was 48 pg/m^3 (Roots & Sweetman 2007). In soils of Lahemaa only PBDE-30, 47, 99, and 85 were detected (Table 3). These results proved that the physico-chemical behaviour

of PBDE congeners may vary in air and soil samples. Further detailed study is needed to delineate any final conclusions. To our knowledge this is the first study of PBDEs in soil samples from Estonia.

Organochlorine pesticides

The major OCPs detected in all analysed soil samples of Estonia were HCB and 4,4′-DDE in agricultural and industrial soils, heptachlor in Kohtla-Järve and Muuga Port soils, and HCB, heptachlor, and *trans*-nonachlor in Kunda, Lahemaa, and Vilsandi Island soils (Tables 1–3). The usage of OCPs in Estonian environment has been quite limited. Nevertheless, in 1957, 226 tonnes of pesticides were used in Estonia, mainly DDT and HCHs and to a lesser degree seed dressing products (Müür 1996). According to the Order from 21.10.1967 approved by the Government, the import of chlororganic plant protection products was prohibited in Estonia. Only DDT and toxaphene were used until 1971 and 1984, respectively, and some old stocks have still remained in Estonia. The stocks of banned pesticides in three Baltic countries in 2000 were as follows: Estonia, DDT – 6 tonnes and HCH – 3 tonnes; Latvia, DDT – 172 tonnes and HCH – 155 tonnes; Lithuania, DDT – 80 tonnes and HCH – 24 tonnes (SBSER 2000). By now all old POP residues have been destroyed in Estonia.

Today no POP pesticides are used in Estonia. It is interesting to note that aldrin, dieldrin, endrin, heptachlor, HCB, mirex, and chlordane have never been used in or imported to Estonia. In soils analysed in this study all these unused chemicals have been detected very frequently (Tables 1–3). These results probably suggest atmospheric transport of those chemicals to Estonian soils. Other studies have reported lower than permitted target levels of aldrin, dieldrin, endrin, DDT, HCHs, and HCB in the sediment samples from Estonia (Roose & Roots 2005).

Concentrations of OCPs have been recorded in air samples from Estonia. For example, DDT in air, precipitation, and deposition in Vilsandi and Lahemaa were 6.9 and 2.0 pg/m^3, 0.28 and 0.06 ng/L, and 0.23 and 0.1 ng/m^2/d, respectively. Likewise, HCHs in air, precipitation, and deposition in Vilsandi and Lahemaa were 33 and 26 pg/m^3, 2.1 and 0.31 ng/L, and 3.7 and 0.53 ng/m^2/d, respectively, by the Nordic Environment Research Programme 1999. These observed concentrations correspond to the levels found in soils in our study (Table 3). Geometrical mean concentrations of chlororganic pesticides were: α-HCH 5–17 pg/m^3, γ-HCH 0.3–4 pg/m^3, and HCB 10–38 pg/m^3 (NERP 1999; Agrell et al. 2001). In general, higher α-HCH and γ-HCH levels generally occurred in South and East Europe. Since we did not analyse α-HCH and γ-HCH concentrations in soils, they were mostly not detected except in Ahja-1982 and Eerika soils, where the concentration was 0.01–0.31 ng/g dw (Tables 1, 2).

The critical limits for hazardous substances in soil available in literature are as follows: for PCBs, 1–10; for aldrin, 0.1–5; for dieldrin, 0.05–2; for endrin, 0.1–5; for DDT, 0.1–5; for HCHs, 0.05–2; and for HCB, 2–25 on mg/kg basis. The concentrations of OCPs in soils analysed in this study were well below the critical limits (Tables 1–3). Besides, the survey in Estonia near Tallinn and in the oil shale region indicated that OCP concentrations of sewage water were below target levels (Roose & Roots 2005). The OCP concentrations analysed in the Kohtla River sediments in northeastern Estonia in 2002 were <5 to <10 ng/g (Roose & Roots 2005).

In Estonia the OCPs in fish were studied by Roots (1996). In flounder (*Platichtys flesus*) near the coastal area of Vilsandi Island the OCPs were in the following order: 4,4′-DDD 45–4129 > 4,4′-DDE 10–1521 > γ-HCH 6.1– 255 > 4,4′-DDT 14–91 on ng/g fat. In case of perch (*Perca fluviatilis*) the order varied slightly: 4,4′-DDE 22–119 > 4,4′-DDD 0.4–51 = 4,4′-DDT 1.2–50 > γ-HCH 2.1–31 on ng/g fat. The content of POPs in flounder and perch from the coastal waters of Estonia was not a danger to human health. Greater levels of DDTs may be due to extensive use of DDT in former East Germany in the mid-1980s (Heinisch et al. 1994). Similarly detections of DDT in 2006 soil samples in this study may provide information for long-range transport as demonstrated elsewhere (Agrell 1999; Agrell et al. 2001). In addition, it was possible that DDT was recently used and discharged from the Latvian or closely adjoining territory (Olsson et al. 1999).

The concentration of DDT and PCB in breast milk in Estonia was studied from 1971 to 1984 (Roots 1996). The results were comparable to results in Sweden and Finland. It was concluded that the daily intake of DDT and PCB of newborn babies did not exceed the acceptable daily intake level proposed by the World Health Organization (Holoubek et al. 2001).

CONCLUSIONS

Based on the data on PCBs, OCPs, and PBDEs in a limited number of soil samples from Estonia, the contamination level of these persistent organic pollutants seems to be relatively low. The results also confirm that Estonia is one of the cleanest eastern European countries. Oil shale burning seems to have less impact in producing PCBs and PBDEs than reported in the other studies on the formation of PCDD/DFs and PAHs. Mass loading of PCBs and PBDEs into the Baltic Sea was found to be lower than in other Baltic countries. Further analysis

with a larger number of samples is needed in order to confirm the contamination levels as well as temporal trends of PCBs, OCPs, and PBDEs in Estonian soils. Future monitoring of PBDEs in environmental and biological samples is necessary, since PBDE congeners are being detected in soil samples of Estonia.

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Püsivate orgaaniliste saasteainete jääkide sisaldus Eesti muldades (1964–2006)

Kurunthachalam Senthil Kumar, Mahalakshmi Priya, Kenneth S. Sajwan, Raimo Kõlli ja Ott Roots

Käesoleva töö tähtsus seisneb eelkõige selles, et arhiveeritud mullaproove kasutades minnakse "ajas tagasi" aastatesse enne kloororgaaniliste pestitsiidide kasutamise keelustamist Eestis. Selgitamaks paljudel eri viisidel ja põhjustel Eestimaa muldkattesse sattunud püsivate, toksiliste, loodusele võõraste ning ökosüsteemidele ohtlike ainete (kloororgaanilised pestitsiidid, polüklooritud bifenüülid ja polübroomitud difenüüleetrid) esinemist (või foonitaset) muldades, analüüsiti erineva ümbritseva keskkonna tingimustes (saastumise ning maakasutuse suhtes) kujunenud muldade huumushorisondi proovide saasteainete sisaldust. Rekognoosi alusmaterjalina kasutati nii aastakümnetetaguseid (1964, 1982, 1992) kui ka viimaste aastate (2004–2006) eri muldade huumushorisondi arhiveeritud liitmullaproove. Arhiveeritud mullaproovide positiivseks küljeks on proovivõtu alal ja ajal esinenud olukorra fikseeritus, mida saab vajaduse korral uutele andmetele lisada.

Uurimise alla võetud ainete kontsentratsiooni määrati kolmes erineva antropogeense mõjuga Eestimaa piirkonnas. Põhja-Eesti rannikulähedastest aladest esindavad Kohtla-Järve, Kunda ja Muuga tugeva tööstusliku mõjuga piirkondi. Samas piirkonnas asuvat Lahemaa uurimisala (UA) ja Lääne-Eesti saarte mullastiku seisundit kajastavat Vilsandi UA-d tuleks aga vaadelda looduslike foonialadena. Lõuna-Eesti punakaspruunil moreenil kujunenud mullastikku esindavad Eerika ja Ahja UA-delt eri aegadel võetud mullaproovid.

Foonialadest on põuakartlikema iseloomuga Vilsandi, kus peamisteks muldadeks on väga õhukesed paepealsed ja korese- (klibu-) rikkad liivased rähkmullad. Lahemaa UA muldadeks on keskmise viljakusega rähk ja leostunud liivsavimullad. Tööstuspiirkondadest on Kohtla-Järvel valdavad õhukesel moreenkattel (paas ulatub mullaprofiili) kujunenud parasniisked kuni alaliselt liigniisked (märjad ehk glei-) leostunud mullad, millest on aga osalise segamise läbi moodustunud segatud koreserikkad tehismullad. Kunda mullad on neutraalse või nõrgalt happelise reaktsiooniga peenliivakad gleistunud leetunud ja leostunud gleimullad. Muuga UA valdavaks mullaks on vähe arenenud sooldunud veeriserikas liiv-gleimuld. Eerika ja Ahja UA-d asuvad sellele piirkonnale tüüpilisel kahkjal mullal, mille huumushorisondi lõimiseks on saviliiv ning alusmullaks liivsavi.

Esialgsete tulemuste põhjal võib öelda, et uuritud püsivate orgaaniliste ühendite (POÜ) sisaldus Eesti mullaproovides on teiste Euroopa piirkondadega võrreldes suhteliselt madal. See annab alust järeldada, et Eestis on valdavalt tegemist muldadega, mis on vähe saastunud. Kuni käesoleva ajani oli peamine oht POÜ sisalduse suurenemiseks meie mullaproovides saasteainete kauglevi väljastpoolt Eestit. Eestis puudusid ohtlike jäätmete põletustehased ja kloororgaaniliste ühendite jäägid hävitati Soomes ning Saksamaal. Kuid alates 2008. aastast on olukord muutunud.