PERSISTENT ORGANOCHLORINES AND BROMINATED DIPHENYL ETHERS IN SOILS COLLECTED FROM RURAL AND URBAN ESTONIA

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Abstract

Organochlorine pesticides (OCPs), PCBs, and PBDEs were analyzed in selected soil samples obtained from soil archives in Estonia. The soil samples source include agricultural (AHJA), urban area (EERIKA) and near oil terminals etc. The results revealed that PCBs were predominant contaminant (0.43-89 ng/g dry wt) followed by OCPs (0.21-16 ng/g dry wt.) and PBDEs (<0.01-1.7 ng/g dry wt.). Due to limited number of samples, a clear temporal trend could not be discerned from the data. Occurrence of 4,4'-DDT in some samples indicate recent contamination by DDT. To our knowledge, PBDEs were reported for the first time in soil samples from Estonia.

Introduction

Persistent organochlorine pesticides (POPs)-HCHs, HCB, cyclodienes, chlordanes, DDTs, mirex and industrial chemicals-polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) are ubiquitous environmental pollutants[1-2]. They are well known to produce chronic toxicity, dioxin-like toxicity to humans and wildlife. The Republic of Estonia is situated in Northeastern Europe, bounded by Latvia in the South, the Baltic Sea to the West, the Gulf of Finland to the North and Russia to the East. Estonia covers an area of 45,100 square kilometers and has an estimated population of 1,524,000 inhabitants, i.e. a population density of 33.8 persons per square kilometer. Although the use of persistent organic compounds is dropped by 78% in Estonia, very limited information is available on the status of organochlorine and polybrominated biphenyl ethers contamination in soils of Estonia.

According to Kölli et al[3]. Estonian society has a limited knowledge about local soil cover and the soil quality is important not only for food production, but also on the environmental status of the area. Declared on a state level, sustainable land use is oriented towards resolving the environmental problems of the area, as well as self-providing needs for food and technological materials[3]. Estonia still has no waste incineration facilities, which would act as substantial sources of PCBs and PBDE pollution. The Estonian thermal power station is the world's largest power station burning low-grade local Oil Shale. Both North-East Estonia and North-West Russia are extremely rich in Oil Shale. The majority of the population lives in urban areas. Estonia inherited a total of 1,565 military sites which cover an area of 81,000 hectares, or approximately 1.8% of the total land area of Estonia. Therefore, contamination of Estonian soil is very likely. Recently, Roots and Sweetman reported occurrence of several persistent organic pollutants in air samples from two Estonican monitoring stations[4]. Studies also reported occurrence of PCBs and PBDEs in Estonian food-stuffs and fish[5]. Besides one recent study shows presence of PCDD/DFs[6]. In this study we analyzed OCPs, PCBs and PBDEs in soil samples collected from industrial (urban) and agricultural (rural) and oil shale regions of Estonia.

Materials and Methods

Estonia is situated in the North-East of Europe located from 57°30′34″ to 59°49′12″N and from 21°45′49″ to 28°12′44″E. The map of Estonia and soil samples were collected are shown in Figure 1. From LAHEMAA

(59°39'55"N & 25°55'41"E), MUUGA (59°29'40"N & 24°55'51"E), KUNDA (59°30'10"N & 26°33'28"E), VILSANDI (58°22'34"N & 21°50'42"E), KOHTLA-JÄRVE (59°24'35"N & 27°16'43"E) samples collected from 0-10 cm layer in 2005 and 2006. Soil Chemistry plot was divided into 10 x 10 m subplots. The humus layer was sampled separately with a steel cylinder of known diameter. The green and litter material were excluded. The coordinates of the sample points were determined by GPS. The selected 10 x 10m sampling area was surrounded with a barrier, and from that area samples were taken at intervals of 2 m. Sixteen samples were taken from the area in total, which were later mixed together in order to have one average sample. The soil samples were kept in carefully labeled glass jars in the dark until they can be pretreated. From EERIKA and AHJA, soil samples taken (from 1964 to 2004) from arable soil plough layer. Humus content samples were taken from the topsoil layer. Soil samples were dried homogenized and sieved (1-mm sieve). Samples are stored at ambient temperature in paper bags or paper/plastic boxes. Plains of Ugandi plateau on reddish-brown non-calcareous moraine (2-8 m) with small variations in elevation. Mostly cultivated massifs of ancient fields are separated by primeval valleys and lowland forest areas. Dominated soils are Albeluvisols, which topsoil texture is mostly loamy sand or sandy loam, but the subsoil consists mainly from loamy till. The soil cover of the area is formed in udic-frigid pedo-ecological conditions.

Figure 1. The map showing Estonia and stars represent sampling locations.

PCB congeners, chlorinated pesticides and PBDEs were analyzed in soil using approved procedures. Approximately 10 g dry soil was Soxhlet extracted using 3:1 methylenechloride and hexane mixture v/v for 17 hrs. The extract was then concentrated to 10-mL using Rapid Vap Labconco Evaporation System (Model 79100) 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 subjected to silica gel column chromatography to remove interfering organic and polar species and to separate the PCBs from the pesticides. In 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 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 on to gas chromatograph equipped with electron capture detector (GC-ECD).

PCB congeners, PBDEs and chlorinated pesticides were analyzed using a Varian model CP-3380 gas chromatograph (GC) with Varian model CP-8410-auto injector. The GC was equipped with a DB-5 (60m; 0.25mm.; 0.25µm film thickness) capillary column (J&W Scientific, USA) and a ^{63}Ni electron capture detector. The column initial temperature is 90°C with a 1 min hold time and increase at the rate of 5°C to 150°C and ramped at the rate of 2°C to 280°C and held for 20 min. The injector and detector temperature were 270°C and 330°C respectively. Helium (1.5 mL/min) and nitrogen (28.5mL/min) were used as a carrier and make up gasses respectively. The standard reference material SRM 2262 obtained from National Institute of Standards and Technology was used for the quantification of PCB congeners, and SRM 2261 from the same source was used to quantify chlorinated pesticides. Twenty eight PCBs congeners, eleven PBDE congeners and 15 different chlorinated pesticides were analyzed. PCB, PBDE congeners and 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 analysis was performed including: reagent blank (analyte concentrations were <MDL "method of detection limit"), calibration curve with r^2 value of 0.99, surrogate recovery (4,4'-dibromooctafluorobiphenyl) and matrix spike recovery were 100±30%.

Results and Discussion

Table 1 shows total PCBs (total of 28 major congeners), total PBDEs (total of 11 major congeners) and 15 pesticides collected in agricultural area (AHJA, 1964 and AHJA 1982) and industrial area (EERIKA 1964, 1982, 1992, 2004). Total PCB concentration was comparatively lower in 1964 AHJA soil samples than 1982 AHJA soil. Due to limited number of samples, temporal trend cannot be explained. However, soil samples from EERIKA indicated relatively higher total PCB concentrations during the years 1982 and 1992 than the soil sample collected during 2004 (3.4 ng/g dry wt.). Considering the congener composition, PCB 66 was major congener in AHJA sample followed by PCB 52, 118 however minor variation has been noticed for several congeners. In general, the lower chlorinated PCB congeners contain relatively higher percent contribution than higher chlorinated congeners. Congener profile of PBDE cannot be discussed due to their trace levels. Among OCPs, HCB, γ-HCH, heptachlor, trans-nonachlor and p,p'-DDE was most frequently detected.

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**
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	ND	0.01	0.03	0.31	0.26	ND
Aldrin	ND	ND	ND	0.03	0.09	ND
Dieldrin	ND	ND	0.02	ND	ND	ND
Mirex	ND	ND	ND	ND	ND	ND
Heptachlor	0.58	0.93	ND	0.90	0.35	0.14
H. Epoxide	0.01	ND	ND	0.11	0.04	ND
Trans-Nonachlor	0.09	0.09	ND	0.04	0.10	0.01
Cis-Chlordane	ND	ND	ND	ND	0.05	ND
2,4'-DDE	ND	ND	0.01	ND	ND	ND
4,4'-DDE	0.39	1.87	0.05	0.55	0.21	0.05
2,4'-DDD	ND	ND	0.01	ND	0.14	0.01
4,4'-DDD	ND	ND	0.01	ND	ND	ND
2,4'-DDT	ND	ND	0.08	ND	0.05	ND
4,4'-DDT	ND	0.01	0.15	0.28	ND	ND
OCPs	**1.1**	**3.1**	**0.42**	**2.7**	**1.3**	**0.21**

ND= not detected

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

of	Kohtla-Järve #1 Oil-Shale	Kohtla-Järve #2 Oil-Shale	Kohtla-Järve City 1	Kohtla-Järve City 2	Muuga Port -1 Oil Terminals	Muuga Port -2 Oil Terminals
PCBs	**81**	**7.0**	**0.43**	**24**	**1.0**	**4.0**
PBDEs	**0.16**	**0.04**	**1.0**	**ND**	**0.03**	**1.7**
HCB	0.18	0.50	0.19	0.21	ND	ND
γ-HCH	0.05	ND	ND	ND	ND	ND
Aldrin	ND	0.03	0.06	ND	0.02	0.05
Dieldrin	ND	0.05	ND	0.46	0.12	ND
Mirex	ND	ND	ND	ND	0.11	ND
Heptachlor	0.36	0.50	0.39	0.15	0.35	0.17
H. Epoxide	ND	0.03	0.28	ND	ND	0.42
Trans-Nonachlor	0.33	0.02	ND	0.02	0.09	0.03
Cis-Chlordane	ND	ND	ND	ND	0.13	ND
2,4'-DDE	ND	ND	ND	ND	ND	ND
4,4'-DDE	0.86	ND	0.08	0.12	0.37	0.11
2,4'-DDD	0.60	ND	2.0	0.55	0.61	ND
4,4'-DDD	1.5	6.7	2.7	1.8	ND	0.23
2,4'-DDT	0.56	0.05	ND	1.0	ND	ND
4,4'-DDT	3.6	ND	11	5.0	0.32	1.9
OCPs	**8.1**	**7.9**	**16**	**9.4**	**2.1**	**2.9**

ND= not detected

Concentrations PCBs, PBDEs and OCPs in soil collected from Oil Shale area, urban city and oil terminal in Kohtla-Jarve and Muuga Port are shown in Table 2. Approximately, eight times higher PCB concentration was noticed in Kohtla-Järve Oil Shale station-1 than station-2. Similarly Kohtla-Järve city station-2 had several fold

greater PCBs than city station-1. There was not such variation have been noticed in Muuga port soil samples. Congener profile showed entirely different pattern in between Kohtla-Järve Oil Shale, city and oil terminal samples. This may be due to higher and lower concentrations of PCBs in two different samples collected from same area. More number of samples must be analyzed to confirm the observations. Again PBDEs were very lower levels and 1.0 ng/g was noticed in Kohtla-Järve city station-1. OCPs were significantly greater in Kohtla-Järve Oil Shale station-2 followed by Kohtla-Järve city station 1. Occurrence of 4,4'-DDT in these samples indicate recent input of DDT in these area.

Contamination levels of PCBs, PBDEs and OCPs in soil collected from Kunda, Lahemaa and Vilsandi are shown in Table 3. Total PCBs and OCPs in these sites were comparatively lower than Ahja, Eerika, Kohtla-Järve sites. However, PBDEs congeners were consistently detected and the total PBDE concentrations were slightly higher. Most commonly detected PBDE congener was: PBDE-47. Based on the data on PCBs, OCPs and PBDEs in limited number of soil samples from Estonia, the contamination level of these persistent organic pollutants seem to be relatively low. However, Further analysis with more number of samples are needed in order to confirm the contamination levels as well as temporal trends of PCBs, OCPs and PBDEs in the Estonian soils. Future monitoring of PBDEs in environmental and biological samples is necessary since, PBDE congeners are being detected in soil samples of Estonia.

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

Sample ID	Kunda Stn 1	Kunda Stn 2	Lahemaa EMEP 1	Lahemaa EMEP 2	Vilsandi Island EMEP
PCBs	**1.0**	**2.8**	**0.61**	**14**	**12**
PBDEs	**1.6**	**1.4**	**0.70**	**0.08**	**0.21**
HCB	0.38	0.03	0.03	0.06	0.33
γ-HCH	ND	ND	ND	ND	ND
Aldrin	0.19	0.04	0.04	0.08	ND
Dieldrin	ND	ND	ND	ND	ND
Mirex	0.09	0.03	ND	ND	ND
Heptachlor	0.78	0.20	0.13	0.29	0.13
H. Epoxide	ND	ND	0.01	ND	ND
Trans-Nonachlor	0.06	0.02	0.02	0.12	0.05
Cis-Chlordane	0.01	ND	ND	ND	ND
2,4'-DDE	ND	ND	ND	ND	ND
4,4'-DDE	0.07	ND	0.06	0.21	ND
2,4'-DDD	ND	0.77	ND	ND	ND
4,4'-DDD	ND	ND	ND	ND	ND
2,4'-DDT	ND	ND	ND	ND	ND
4,4'-DDT	ND	ND	ND	ND	ND
OCPs	**1.6**	**1.1**	**0.30**	**0.76**	**0.52**

ND= not detected

Acknowledgements
The United States Department of Energy (DOE) and United States Environmental Protection Agency (Contract No. DE- FG09- 96SR18558) supported the research. The authors are thankful to Subhadra Vemu and Nanditha Billa for their help in data analysis.

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