



## Measurements of persistent organic pollutants in Estonian ambient air (1990–2013)

Ott Roots<sup>a\*</sup>, Tiit Lukki<sup>b</sup>, Petra Přibylková<sup>c</sup>, Jana Borůvková<sup>c</sup>, Petr Kukučka<sup>c</sup>, Ondřej Audy<sup>c</sup>, Jiří Kalina<sup>c</sup>, Jana Klánová<sup>c</sup>, Ivan Holoubek<sup>c</sup>, Andrew Sweetman<sup>d</sup>, and Ole Schleicher<sup>e</sup>

<sup>a</sup> Estonian Environmental Research Institute, Estonian Environmental Research Centre, Marja 4D, 10617 Tallinn, Estonia

<sup>b</sup> Tallinn University, Narva mnt 25, 10120 Tallinn, Estonia

<sup>c</sup> Research Centre for Toxic Compounds in the Environment (RECETOX), Masaryk University, 753/5 Kamenice Str., 625 00 Brno, Czech Republic

<sup>d</sup> Lancaster Environment Centre, Lancaster University, LA1 4YQ Lancaster, United Kingdom

<sup>e</sup> FORCE Technology, Park Allé 345, 2605 Brøndby, Denmark

Received 15 December 2014, revised 23 February 2015, accepted 25 February 2015, available online 22 May 2015

**Abstract.** Central and Eastern Europe is a region that is expected to need more data on the concentrations of persistent organic pollutants (POPs) in the ambient air in the future. Passive air sampling is a cheap screening method for comparison of contamination on various sites or for verification of information obtained by active samplers. Passive air samplers are sensitive enough to mirror even small-scale differences, which makes them capable of monitoring spatial, seasonal, and temporal variations. Different passive air samplers were employed between 1990 and 2013 from time to time in six Estonian air monitoring stations. The concentrations of PCB and its congeners, HCB, PeCB, HCH, and DDT (the same for PBDE, PCN, PCDD/F) in Estonian ambient air were very low, but they allow tracking transboundary air pollution. The main aim of this article is analysis of changes in the ambient air pollution in Estonia during a long period of time (1990–2013). Also, selection of Lahemaa background station for monitoring POPs in the European area is addressed.

**Key words:** persistent organic pollutants, passive air sampling, Estonia, air quality.

### 1. INTRODUCTION

Persistent organic pollutants (POPs) harm human health and the environment. The atmosphere is an important contributor of persistent organic pollutants to the land and marine ecosystems (UNEP, 2002a, 2002b). POPs are included in the UNECE Convention on Long-range Transboundary Air Pollution Protocol on Persistent Organic Pollutants ([http://www.unece.org/env/lrtap/pops\\_h1.html](http://www.unece.org/env/lrtap/pops_h1.html)). The Executive Body adopted the Protocol on Persistent Organic Pollutants on 24 June 1998 in Aarhus (Denmark).

Passive air samplers (PAS) can be used for the evaluation of point sources at the scale of some square

kilometres or even less – from the local plants to diffusive emissions from transportation or household incinerators – as well as for evaluating diffusive emissions from secondary sources. Although not sensitive to short-time accidental releases PAS are suitable for measurements of long-term average concentrations at various levels. These samplers are sensitive enough to mirror even small-scale differences, which makes them capable of monitoring spatial, seasonal, and temporal variations (Agrell et al., 2001; Jaward et al., 2003, 2004a, 2004b; Klánová et al., 2006; Gioia et al., 2007; Halse et al., 2011).

Different PAS were employed between 1990 and 2013 from time to time in six Estonian air monitoring stations (Lahemaa, Kunda, Kohtla-Järve, Tallinn, Muuga, and Vilsandi). Considering results of these POPs measurements in ambient air, the Estonian Lahe-

\* Corresponding author, [ott.roots@klab.ee](mailto:ott.roots@klab.ee)

maa air monitoring station was selected as a background station for monitoring POPs in European air. Although concentrations of different POPs in Estonian ambient air were very low, they allowed tracking transboundary air pollution carried to Estonia from outside the country (Roots, 1992; Agrell et al., 2001). As the availability of data on the environmental levels of POPs in the ambient air is generally limited in Estonia (Nordic, 1999; Agrell et al., 2001; Schleicher et al., 2004a, 2004b, 2005; Roots and Sweetman, 2007; Roots et al., 2008, 2010, 2011) as well as in the whole of Central and Eastern Europe (CEE) (Nordic, 1999; Agrell et al., 2001; Lassen et al., 2003; Klánová et al., 2006, 2009; Škarek et al., 2007; Miluskaite et al., 2008; Bartoš et al., 2009; Dvorská et al., 2009; Pribylova et al., 2012), the aim of this article is to provide information on ambient air pollution with persistent organic pollutants and changes in their emission levels in Estonia from 1990 to 2013. Another aim is to analyse the potential of the Lahemaa station as a background station for monitoring POPs in the European area.

## 2. MATERIAL AND METHODS

### 2.1. Sampling sites

Five sampling sites were situated in northern Estonia along the shoreline of the Gulf of Finland and one ambient air monitoring station on Vilsandi Island in

western Estonia. Vilsandi is small: 6 km long and barely 3 km wide. A background EMEP (Co-operative programme for monitoring and evaluation of the long-range transmissions of air pollutants in Europe) site Lahemaa has been included in most European projects as a potential candidate for a background monitoring station in Europe (Table 1).

### 2.2. Sampling

The passive air samplers (PAS) consisting of polyurethane foam disks (diameter 15 cm, thickness 1.5 cm, density 0.030 g cm<sup>-3</sup>; type N 3038; Gumotex Breclav, Czech Republic) housed in protective chambers (Fig. 1) were employed in this study. A theory of passive air sampling using similar devices was described elsewhere (Shoeib and Harner, 2002; Harner et al., 2004). The sampling chambers were prewashed and solvent-rinsed with acetone prior to installation. All PolyUrethane Filter (PUF) disks were prewashed, cleaned (8 h extraction in acetone and 8 h in dichloromethane), wrapped in two layers of aluminium foil (before and after the sampling), placed in zip-lock polyethylene bags, and kept in the freezer prior to their deployment. The PUF disks were exposed for 4 weeks and the field blanks were obtained by installing and removing the PUF disks at all sampling sites. The average sampling rate of such device was estimated to be 3.5–7 m<sup>3</sup> per day (Kohoutek et al., 2006; Klánová et al., 2009; Pribylova, et al.,

**Table 1.** Characteristics of monitoring sites in Estonia (Roots and Sweetman, 2007; Roots et al., 2010)

Site	Location	Target	Site specifics
Lahemaa	59°29'40"N 25°55'50"E	A European Monitoring and Evaluation Programme (EMEP) background station. Long-range impacts	Lahemaa National Park. 80 km east of Tallinn. Long-range pollution transport is supposed to be major pollution source
Tallinn	59°27'22"N 24°41'23"E	Capital city of Estonia. Urban impacts	Near a car park
Muuga	59°29'40"N 24°55'51"E	Muuga suburban site. Industrial impacts	17 km east of Tallinn, near the main cargo harbour of the port of Tallinn. Nearly 75% of cargo loaded consisted of crude oil and oil products in mid-2010s
Kunda	59°29'40"N 26°35'30"E	Suburban area of an industrial town. Industrial impacts	120 km east of Tallinn. Major pollution sources are cement and pulp industries and transportation
Kohtla-Järve	59°24'35"N 27°16'43"E	Suburban area of an industrial town. Industrial impacts	160 km east of Tallinn. Major pollution sources are oil shale processing, chemical industry, and power engineering
Vilsandi	58°22'34"N 21°50'42"E	Background station. Long-range impacts	Vilsandi National Park for protecting the nature and cultural heritage of the coastal landscapes on western Estonian islands. Park includes ca 100 islands, surface area 180 km <sup>2</sup> . Vilsandi itself is 6 km long and 3 km wide



Fig. 1. Passive air samplers at the Lahemaa station.

2012) based on the co-employment of the active and passive samplers (giving 100–200 m<sup>3</sup> of air in 4 weeks of deployment). The exposed PUF disks were wrapped in two layers of aluminium foil, labelled, placed in zip-lock polyethylene bags and transported in a cooler at 5°C to the laboratory where they were kept in a freezer at –18°C until analysis.

### 2.3. Sample analysis

The surrogate recovery standards (PCB 30 and PCB 185 for analysis of polychlorinated biphenyls (PCB) and organochlorine pesticides (OCP); *d*8-naphthalene, *d*10-phenanthrene, *d*12-perylene for analysis of polyaromatic hydrocarbons (PAHs)) were spiked on each sample prior to extraction. One laboratory blank and one reference material were analysed with each set of ten samples. All samples were extracted with dichloromethane in a Büchi System B-811 automatic extractor. After extraction, the sample volume was reduced under a gentle stream of nitrogen at ambient temperature. Fractionation was achieved on a silica gel column; a sulphuric acid modified silica gel column was used for PCB and OCP samples. As the internal standards for PCB and OCP and PAH analyses PCB 121 and terphenyl were used, respectively. Samples were analysed using a GC-MS instrument (GC 7890/MS-MS Triple Quadrupole 7000B; Agilent) with a J&W Scientific fused silica column DB-5MS (5% Ph) in electron impact ionization mode for 16 US EPA PAHs as described earlier (Klánová et al., 2009) and SGE Analytical Science fused silica column HT-8 (8% Ph) in electron impact ionization and MS/MS mode for PCBs: PCB 28, PCB 52, PCB 101, PCB 118, PCB 153, PCB 138, PCB 180 and OCPs: hexachlorocyclohexanes (HCH) ( $\alpha$ -HCH,  $\beta$ -HCH,  $\gamma$ -HCH,  $\delta$ -HCH); 1,1'-(2,2,2-trichloroethylidene)-bis[4-chlorobenzene] (DDT); 1,1'-(2,2-dichloroethylidene)-bis[4-chlorobenzene] (DDE);

1,1'-(2,2-dichloroethylidene)-bis[4-chlorobenzene] (DDD); hexachlorobenzene (HCB); and pentachlorobenzene (PeCB).

### 2.4. Quality assurance and quality control

Recoveries were determined for all samples by spiking with the surrogate standards prior to extraction. Recoveries were for all samples 76–100% and for PCBs/OCPs and for PAHs 71–98%. Recovery factors were not applied to any data. Recovery of native analytes measured for the reference material varied from 88% to 103% for PCBs, from 75% to 98% for OCPs, and from 72% to 102% for PAHs. The laboratory blanks were under the detection limits for all compounds. The field blanks consisted of the pre-extracted PUF disks and were taken at each sampling site. They were extracted and analysed in the same way as the samples, and the levels in field blanks never exceeded 3% of the quantities detected in the samples for PCBs, 1% for OCPs, and 3% for PAHs, indicating a minimal contamination during the transport, storage, and analysis.

More detailed specification of sampling and sample analysis methods, limits of quantifications (for PCBs and OCPs 0.1 ng/PUF per disk), quality assurance/quality control methods, and the use of field blanks are presented in (Jaward et al., 2004a, 2004b; Schleicher et al., 2004a, 2004b, 2005; Gioia et al., 2007; Roots and Sweetman, 2007; Miluskaite et al., 2008; Klánová et al., 2009; Roots et al., 2010; Halse et al., 2011; Pribylova et al., 2012). The analytical procedures were monitored using NS/EN ISO/IEC 17025 accredited routines (Klánová et al., 2009; Halse et al., 2011).

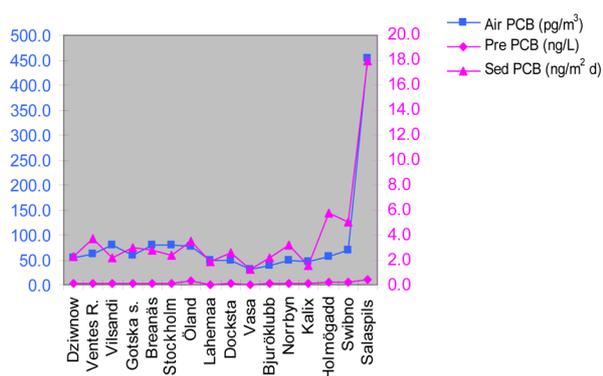
## 3. RESULTS AND DISCUSSION

The relationship between the amount of POPs captured on a PUF filter and their concentrations in the sampled air has not been mathematically fully established yet. Thus only empirically estimated information (for example based on parallel active and passive measurements) is available to interpret the results (Jaward et al., 2004a, 2004b; Kohoutek et al., 2006). Results depend on whether they were obtained by passive or active measurements. Passive air sampling is a cheap screening method for comparison of contamination on various sites or for verification of information obtained by active samplers. Different PAS were employed between 1990 and 2013 from time to time in six Estonian air monitoring stations: Lahemaa, Kunda, Kohtla-Järve, Tallinn, Muuga, and Vilsandi. Distribution of ground-boundary wind directions at regional level at Lahemaa corresponds to that measured at the Väike-Maarja meteorological station, at Kunda to the Kunda station, at

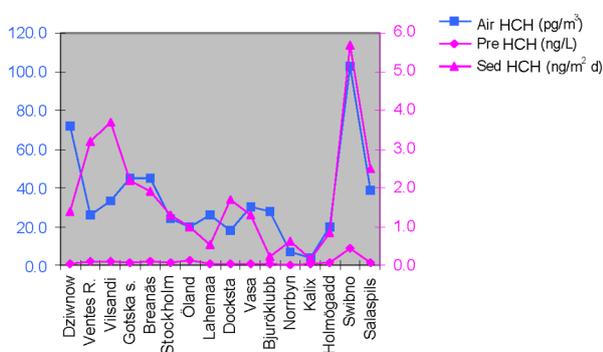
Kohtla-Järve to the Jõhvi station, and at Tallinn and Muuga to the Tallinn-Harku station (Roots et al., 2010).

### 3.1. Comparison of the previously reported results

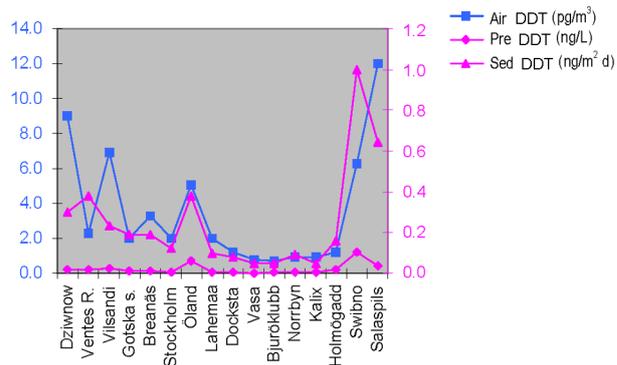
The first field study was organized in October 1990 by Lund University in order to determine POPs in the air and precipitation from six Baltic Sea countries (Estonia, Finland, Latvia, Lithuania, Poland, and Sweden). All together 16 air monitoring stations participated. Among them were two Estonian air monitoring stations – Lahemaa and Vilsandi (Figs 2–4). The median concentrations in the air samples for all stations were 57 pg/m<sup>3</sup> for PCBs, 1.6 pg/m<sup>3</sup> for DDTs, and 25 pg/m<sup>3</sup> for HCHs. The station in Latvia (Salaspils) showed the highest values of PCBs and DDTs in the air, with a median concentration of 454 pg/m<sup>3</sup> of PCBs and 12 pg/m<sup>3</sup> of DDTs. The median concentrations of HCHs were the highest in two Polish stations (Swibno 103 pg/m<sup>3</sup> and Dziwnow 72 pg/m<sup>3</sup>). At these stations DDT concentra-



**Fig. 2.** Summary PCB concentrations in the air and calculated depositions (based on Agrell et al., 2001). Pre – precipitation, Sed – deposition sedimentation.



**Fig. 3.** Summary HCH concentrations in the air and calculated depositions (based on Agrell et al., 2001). Pre – precipitation, Sed – deposition sedimentation.



**Fig. 4.** Summary of DDT concentrations in the air and calculated depositions (based on Agrell et al., 2001). Pre – precipitation, Sed – deposition sedimentation.

tions were high too, 6 and 9 pg/m<sup>3</sup>, respectively (Appendix 1, Tables 1A–3A). According to the data by Agrell et al. (2001), the rivers and the atmosphere contributed about equally to the PCB load, while for POPs atmospheric deposition to the Baltic Sea was about five to seven times more important.

The second field study was organized in 1993–1994. The analyses on PCB, made by Lund University, on the samples taken near the Gulf of Riga in the five Baltic air research stations in Estonia and Latvia showed that the air and rain water samples taken in Estonian stations (Vilsandi near Saaremaa 0.05 ng/m<sup>3</sup> and Tahkuse in western Estonia 0.15 ng/m<sup>3</sup>) were relatively cleaner compared with the samples taken in Latvia (Salaspils 0.62 ng/m<sup>3</sup>, Salacgriva 0.22 ng/m<sup>3</sup>, and Slitere 0.10 ng/m<sup>3</sup>). The movement of some POPs, for example PCB, from southern sources outside Estonia was highly significant. Estonian sampling sites were relatively clean, but allow tracking transboundary air pollution carried to Estonia by southern and south-western winds (Roots, 1992; Nordic, 1999).

Scientists of Lancaster University Environmental Chemistry and Ecotoxicology Group completed a large European-scale air sampling campaign in 2002 within the project ‘POPs Fate Modelling’. Seventy-one samplers were successfully deployed across 22 countries. Among the stations were two Estonian stations: Lahemaa, a background EMEP station, and Kohtla-Järve, an industrial (oil shale chemistry) region station. In Estonia the so-called ‘new pollutants’, which were in Estonian air for the first time analysed, attracted attention. These were polychlorinated naphthalenes (PCNs) and polybrominated diphenyl ethers (PBDEs). The PAS were changed after a six-week period (15 June–30 July 2002), and analysed by the methods presented by Jaward et al. (2003, 2004a, 2004b). For Estonia positive information was that the concentrations of PCN-12 isomers in the samples from the two Estonian air

monitoring stations were under detection limit (Foday et al., 2004) and that PBDE values in Estonian air were generally low (Gioia et al., 2007; Roots and Sweetman, 2007).

In 2004 PAS were deployed at 23 background locations along a broadly west–east transect in eight northern European countries (Ireland, the United Kingdom, Denmark, Norway, Sweden, Finland, Estonia, and Russia) and analysed for PCBs, PBDEs, PAHs, HCBs, and DDTs (Gioia et al., 2007) (Fig. 5). Among them was the Estonian Lahemaa station, a background EMEP station (sampling period 10.08.–28.10.2004) (Table 2). The cleanest air samples were collected from Norway and Estonia. By the data in (Gioia et al., 2007), advection from southern and western Europe appeared to contribute to ambient POPs levels for countries in the central and north-eastern part of the transect (among these Estonia).

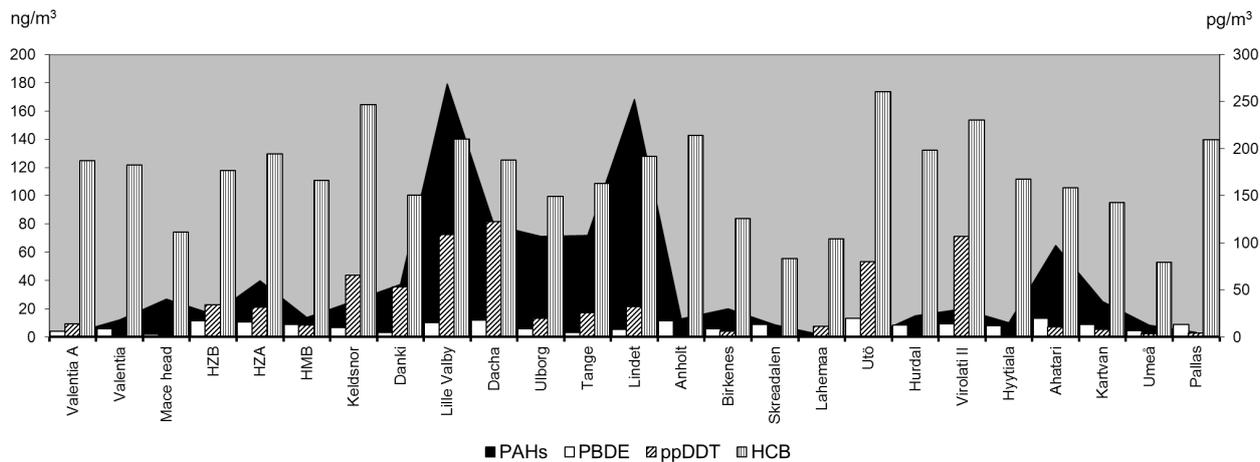
In the coordinated campaign in various European countries (34 countries and 86 sites) during late summer 2006 samplers were exposed for about 3 months (Halse et al., 2011). Among the sites was the Estonian Lahe-

maa station (sampling period 06.07.–10.10.2006) (Table 3). As at the beginning of August 2006 the wind was flowing from the north-east at a relatively high speed (4–7 m/s), it brought in air from the north-western part of Russia (Leningrad Oblast and Karelia) suffering several big forest fires at the time (Roots et al., 2008, 2010). Therefore for example naphthalene concentrations in the Lahemaa and Kunda stations increased 9 and 6 times and for benzo(*a*)pyrene 6.5 and 2.5 times, respectively (Klánová et al., 2006).

**Table 2.** Concentrations of POPs (pg/m<sup>3</sup>) in ambient air at the Lahemaa station and concentration ranges for all other sites (A. Sweetman, personal information)

Site	PCB*	PBDE	pp DDT	HCB
Lahemaa	63.65	1.66	11.57	104.52
Other sites	34.95–	1.66–	3.55–	79.44–
	508.37	20.00	122.6	260.99

\* – sum of 7 compounds.



**Fig. 5.** Concentrations of POPs (pg/m<sup>3</sup>) and PAHs (ng/m<sup>3</sup>) in the air at the Lahemaa station and concentration ranges for other sites (Gioia et al., 2007; A. Sweetman, personal information). HZA, HZB, HMB – replicate samplers at the Hazelrigg and High Muffles sites.

**Table 3.** Concentrations of POPs (pg/m<sup>3</sup>) and PAHs (ng/m<sup>3</sup>) in the air of the Lahemaa station and concentration ranges of all 86 sites (Halse et al., 2011)

	Σ7 PCB*	Σ3 HCH*	Σ4 DDT*	Σ8 PAH*	HCB	Σ4* chlordanes
Lahemaa**	20.77	43.51	12.83	3.73	46.43	2.20
All 86 sites	2.17–121.40	8.63–310.76	1.06–323.63	0.19–34.93	22.78–115.49	0.16–19.38

\* – sum of 7, 3, 4, 8, and 4 compounds, respectively.

\*\* In August–September 2006 the great forest fires near the Estonian and Finnish borders with Russia (Leningrad Oblast and Karelia) caused elevated concentrations of fine particles and some POPs in the Lahemaa station air. Wind direction was from Russia towards Estonia and Finland.

### 3.2. Emissions of persistent organic pollutants

At present, the Estonian Environmental Agency uses the CollectER tool for the calculation of emissions from diffuse sources. Data on point sources (emissions and burnt fuel) are transferred from OSIS (Välisõhu saasteallikate infosüsteem – Estonian ambient air pollutants infosystem) to CollectER (EEA, 2013). The national emission inventory data that are stored in the CollectER annual inventory databases are used for reporting (Kohv et al., 2012, 2013). In 2010 the emissions of pollutants had increased due to increasing biomass consumption in the energy and residential sectors (Fig. 6) (Kohv et al., 2012). These estimates are subject to large uncertainty as emission factors (EFs) used in this inventory were derived from only one general study and need not be representative for Estonia; moreover, the used EFs do not depend on the type of combustion appliance. For example, HCB EFs are two times higher in the cooking stove compared to the other combustion facilities, and PCDD/Fs EFs in the fireplace are ca 46 times higher compared to the masonry heater and the cooking stove. These three facilities are typically used in Estonian households (Mõts et al., 2013).

At the beginning of the 2000s the project ‘Dioxin in Candidate Countries’ was carried out on behalf and with financial support of the European Commission, DG Environment (Quass et al., 2004). The very low dioxin emissions from two Estonian power plants, oil plant, and cement factory are due to the very efficient combustion in the furnaces thanks to very high temperatures, turbulence, and long retention times (Quass et al., 2004; Roots, 2004; Schleicher et al., 2004a, 2004b, 2005; Roots and Sweetman, 2007).

As measurements of real dioxin emissions in Estonia were highly needed, in March 2003 PCDD/Fs emissions were measured from two power plants (Estonian and Baltic Power Plants) and the shale oil producing plant located near the town of Narva in NE Estonia. The Danish environmental assistance to Eastern Europe (DANCEE) sponsored the project, and dk-TEKNIK ENERGY & ENVIRONMENT (now FORCE Technol-

ogy) was responsible for measurements, which were conducted in cooperation with the Estonian Environmental Research Centre in Tallinn (Schleicher et al., 2004b, 2005).

The two power plants produce more than 90% of the electricity consumed in Estonia by combusting more than 10 million tonnes of oil shale per year, which is around 85% of the total consumption of oil shale in the country. These power plants are the world’s largest thermal power stations burning low-grade oil shale. All the measured concentrations of dioxins emitted from the Estonian and Baltic Power Plants are very low. The total annual dioxin emission from the two oil shale fired power plants (Fig. 7) into the air is estimated at 160 to 300 mg International Toxicity Equivalents (I-TEQ) (Schleicher et al., 2004b, 2005), which is more than ten times lower than previous estimations (Lassen et al., 2003).

All the measured concentrations of dioxin emissions from the shale oil plant were very low, and much lower than the EU emission limit value for municipal solid waste incineration (MSWI): 0.1 ng I-TEQ/m<sup>3</sup> (n,d). The total emission of dioxins is estimated at 0.2 mg I-TEQ/year into air and 700 mg/year with ash (Schleicher et al., 2004a). The naphthalene and PAH concentrations were much lower than the Danish emission limit values (Guidances for Air Emission Regulation, 2002).

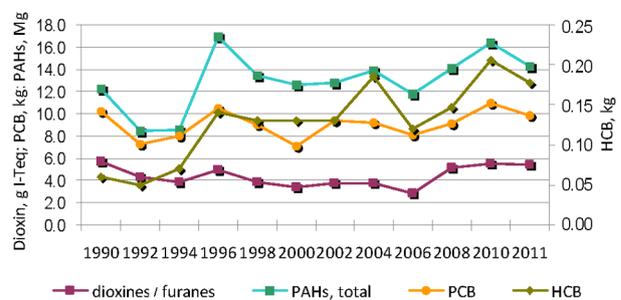


Fig. 6. Emissions of POPs and PAH in the period 1990–2011 (Kohv et al., 2013).

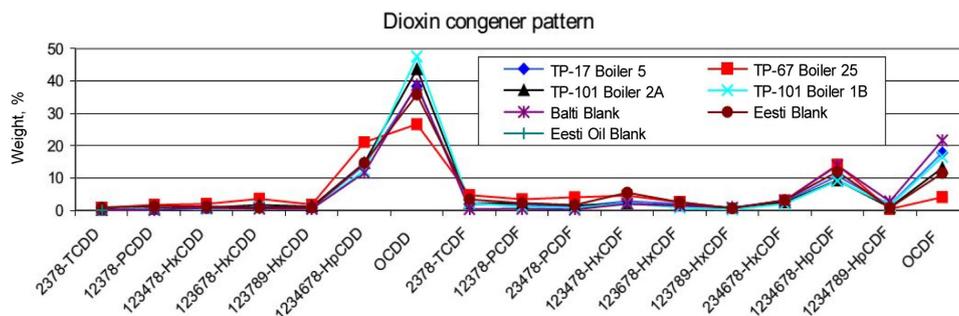
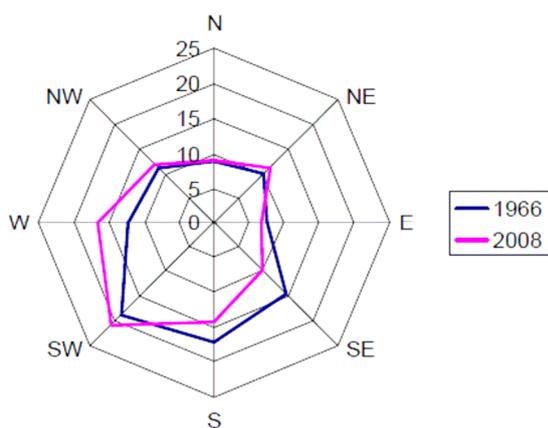


Fig. 7. Dioxin congener pattern for all emission samples and blanks (Schleicher et al., 2004b).

### 3.3. Comparison of results from Lahemaa and some Central and Eastern European stations during 2006–2012 (2013)

Estonia, Northeast Europe, is located in a transitional zone between a maritime climate in the west and a continental climate in the east. Changes in the percentages of eight main surface wind directions at 14 meteorological stations in Estonia were studied during 1966–2008. At the Lahemaa station the percentages of western (W) and south-western (SW) winds have clear positive trends (increase 5–8%) (Fig. 8) while south-eastern (SE), eastern (E), and north-eastern (NE) winds showed negative tendencies in winter. It appeared that there had been much less changes for certain directions (N, S) and months (April, July, October, November, December) and much more changes for other directions (W, SE) and months (January, February, March, May, June) (Jaagus and Kull, 2011).

Advection from the south and west of Europe appeared to contribute to ambient POPs levels for countries in the central and north-eastern part of the transect (Gioia et al., 2007). Major emissions of  $\alpha$ -HCH in Poland,  $\gamma$ -HCH in France, PCBs in Germany, Poland, and the Czech Republic, and DDT in the Czech Republic and Germany measured in 1997–1999 had significantly decreased by 2004–2006 (Dvorská et al., 2009). It was estimated that air from the south, south-east, and south-west accounted for approximately 80% of the wet deposition and 50% of the gaseous deposition of dioxins (PCDD/F) to the Baltic Sea (Sellström et al., 2009).



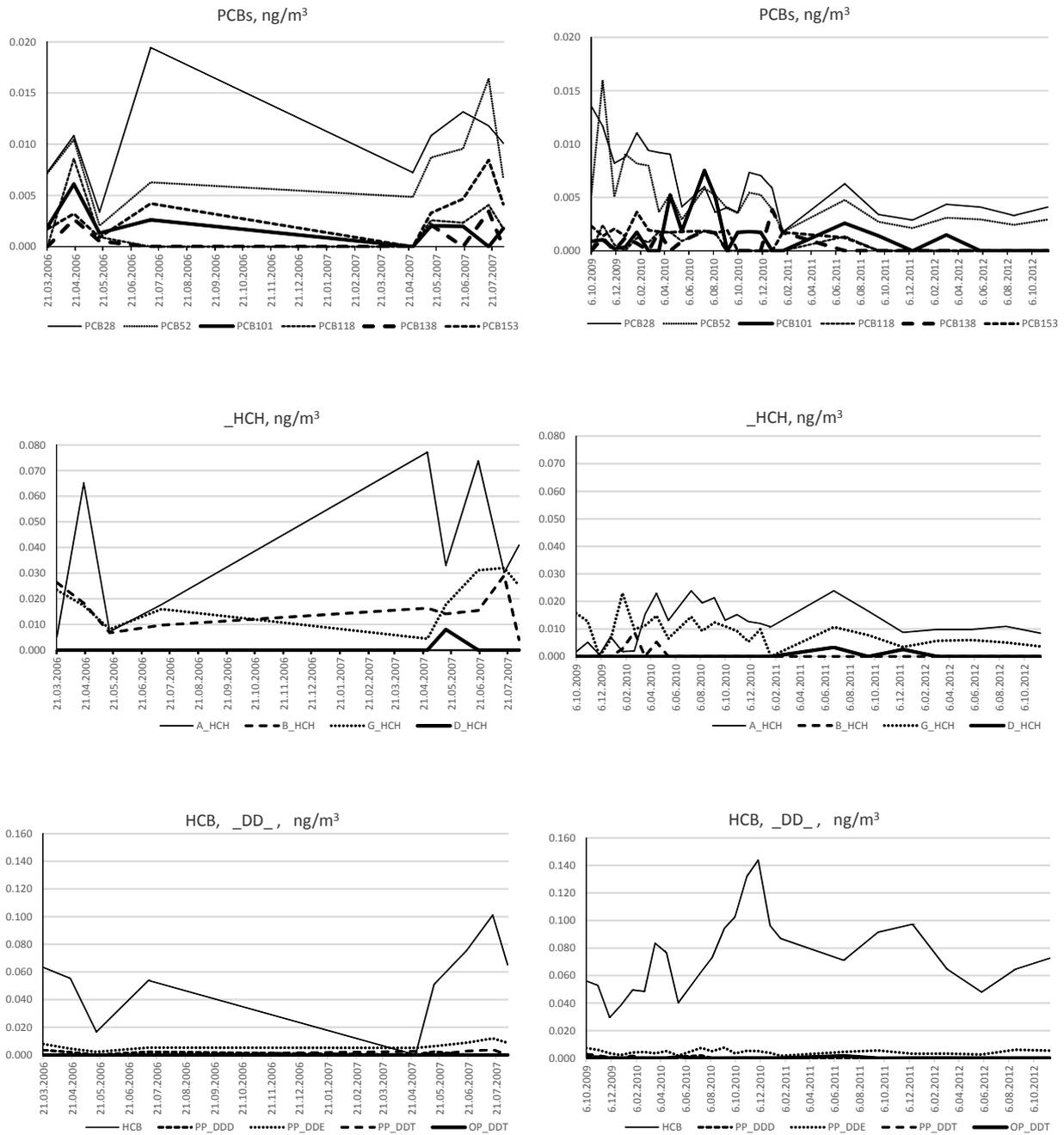
**Fig. 8.** Distribution of ground-boundary wind direction at regional level according to the Väike-Maarja meteorological station located close to the Lahemaa monitoring site (Jaagus and Kull, 2011).

The model monitoring network in the Czech Republic has been functioning since 2005, and passive air sampling surveys of Central and Eastern Europe (CEE) were initiated in 2006 (Klánová et al., 2006; Kohoutek et al., 2006). Samples were exposed in eight CEE countries (Bosnia and Herzegovina, Czech Republic, Estonia, Latvia, Lithuania, Romania, Serbia, and Slovakia) (Fig. 9) over 4-weeks periods. The Estonian data are presented in (Klánová et al., 2006; Roots et al., 2008, 2010). During all four sampling periods of the study the wind speeds followed the main course of long-term seasonal wind speed at ground level (Kull and Laas, 2003) and at 850- or 500-hPa level (Keevallik and Soomere, 2008). The concentrations of PCB and its congeners, HCB, PeCB, HCH, and DDT were very low in Estonian ambient air (Klánová et al., 2006; Roots et al., 2008, 2010) and soil (Klánová et al., 2006; Sajwan et al., 2008; Kumar et al., 2009; Roots et al., 2011).

Compared to 2006–2007, the concentrations of HCHs, PCBs, and DDTs in the ambient air at Lahemaa had significantly decreased by 2009–2012 (Fig. 10 and Appendix 1, Tables 4A–6A). Two easily volatile PCB compounds (PCB 28 and 52) accounted for about 50% of the sum of the concentrations of 7 PCBs (PCB 28, 52, 101, 118, 138, 153, and 180) in the ambient air at Lahemaa. Long-range pollution transport is supposed to be a major pollution source. In an earlier study (Roots et al., 2010) we found that the relatively consistent ratio of HCB and PeCB fluctuated between 2.5 and 5.6 in 2006, but in 2009–2012 it increased to 11.9 (July–September 2011). This indicates that the HCB and PeCB do not stem from incineration processes but are



**Fig. 9.** MONET Project sampling sites in Central, Eastern, and Southern Europe, 2006 (<http://monet-ceec.eu>).



**Fig. 10.** Seasonal pattern of analysed POPs in the air at the Lahemaa station in 2006–2007 and 2009–2012 (RECETOX, GENASIS database system [www.genasis.cz](http://www.genasis.cz)).

mainly evaporates of industrial HCB with a minor impact of PeCB. The evaporate theory is consistent with the finding of higher HCB and PeCB values in the warm months (July, August, September) of our studies. In July and August 2010 very high concentrations of particulate matter (PM) PM10 and PM2.5 were analysed in the Lahemaa ambient air, respectively 13.20 and 7.60  $\mu\text{g}/\text{m}^3$  in July and 11.03 and 6.94  $\mu\text{g}/\text{m}^3$  in August (Kabral

et al., 2012). To detect the PBDEs source the correlation between PCBs and PBDEs in Estonian soil was analysed. If there was a significant correlation, then the source of PBDEs would be the same as for the accumulation of PCBs in soil. However, the results showed a very weak correlation ( $r^2 = 0.165$ ), and therefore the PBDE source in North Estonia is entirely different than that of PCBs (Kumar et al., 2009).

The import of OCPs was prohibited in Estonia at the end of 1967, and none of these pesticides have ever been produced in Estonia (Müür, 1996). All the old OCP stocks in Estonia have been destroyed (Roots et al., 2010). Based on the data on PCBs, OCPs, and PBDEs in a limited number of soil samples from Estonia, the contamination level with these POPs seems to be relatively low (Sajwan et al., 2008; Kumar et al., 2009; Roots et al., 2011).

#### 4. CONCLUSIONS

The level of contamination with persistent organic pollutants seems to be relatively low in Estonia as the limited number of ambient air and soil samples suggest. The concentrations of HCHs, PCBs, and DDTs measured in the ambient air at Lahemaa in 2006–2007 had significantly decreased by 2009–2012. The very low POPs emissions from the Estonian two power plants, the shale oil plant, and the cement plant are due to the very efficient combustion in the furnaces achieved by very high temperatures, turbulence, and long retention times. The concentrations of PCB and its congeners, HCB, PeCB, HCH, DDT, PBDE, and PCN in the Estonian ambient air were very low, but they allow tracking transboundary air pollution carried into the country.

To assess long-term trends in the atmospheric levels of POPs, required for the effectiveness evaluation of the Stockholm Convention, selected background sites in the CEE region continue to be monitoring within the framework of the MONET passive sampling network. The Lahemaa background station seems to be an appropriate candidate for continuous background monitoring of POPs in Europe.

In order to improve the quality of the environment in Europe, the technologies used in power engineering and industry need to be optimized.

#### ACKNOWLEDGEMENTS

This work was carried out with the support of the Estonian State Monitoring Programme (ESMP); core facilities of the Research Centre for Toxic Compounds in the Environment (RECETOX) – National Infrastructure for Research of Toxic Compounds in the Environment, project No. LM2011028, funded by the Ministry of Education, Youth and Sports of the Czech Republic under the activity ‘Projects of major infrastructures for research, development and innovations’; and large European-scale air sampling campaigns. The United States Department of Energy (DOE) and the United States Environmental Protection Agency (Contract No. DE-FG09-96SR18558) supported analyses of the Estonian soil samples.

#### APPENDIX 1

#### SUPPORTING MATERIAL

**Table 1A.** Summary PCB concentrations in the air and precipitation and calculated depositions (Agrell et al., 2001)

Latitude	Station	Air, pg/m <sup>3</sup>	Precipitation, ng/L	Deposition, ng/m <sup>2</sup> -d
54°00'	Dziwnow	55 ( <i>n</i> = 5)	1.4 ( <i>n</i> = 2)	2.3 ( <i>n</i> = 2)
54°15'	Swibno	69 ( <i>n</i> = 6)	4.4 ( <i>n</i> = 4)	5.0 ( <i>n</i> = 4)
55°25'	Ventes R.	61 ( <i>n</i> = 10)	2.0 ( <i>n</i> = 15)	3.7 ( <i>n</i> = 15)
56°14'	Öland	76 ( <i>n</i> = 21)	8.3 ( <i>n</i> = 15)	3.5 ( <i>n</i> = 15)
56°17'	Breanäs	79 ( <i>n</i> = 21)	2.8 ( <i>n</i> = 12)	2.8 ( <i>n</i> = 12)
56°50'	Salaspils	454 ( <i>n</i> = 20)	10.7 ( <i>n</i> = 15)	17.9 ( <i>n</i> = 15)
58°20'	Vilsandi	79 ( <i>n</i> = 9)	1.5 ( <i>n</i> = 9)	2.2 ( <i>n</i> = 9)
58°21'	Gotska s.	60 ( <i>n</i> = 24)	2.0 ( <i>n</i> = 15)	3.0 ( <i>n</i> = 15)
59°17'	Stockholms s.	80 ( <i>n</i> = 21)	1.3 ( <i>n</i> = 10)	2.4 ( <i>n</i> = 10)
59°30'	Lahemaa	49 ( <i>n</i> = 16)	0.8 ( <i>n</i> = 12)	1.8 ( <i>n</i> = 12)
63°02'	Vasa	32 ( <i>n</i> = 27)	0.9 ( <i>n</i> = 12)	1.2 ( <i>n</i> = 12)
63°03'	Docksta	50 ( <i>n</i> = 24)	1.8 ( <i>n</i> = 15)	2.6 ( <i>n</i> = 15)
63°32'	Norrbyn	48 ( <i>n</i> = 24)	1.8 ( <i>n</i> = 17)	3.2 ( <i>n</i> = 14)
63°36'	Holmögadd	57 ( <i>n</i> = 23)	4.9 ( <i>n</i> = 12)	5.7 ( <i>n</i> = 12)
64°31'	Bjuröklubb	38 ( <i>n</i> = 24)	2.9 ( <i>n</i> = 13)	2.2 ( <i>n</i> = 13)
65°44'	Kalix	47 ( <i>n</i> = 24)	2.4 ( <i>n</i> = 14)	1.5 ( <i>n</i> = 14)
	All stations	57 ( <i>n</i> = 299)	2.3 ( <i>n</i> = 192)	2.7 ( <i>n</i> = 192)

**Table 2A.** Summary DDT concentrations in the air and precipitation and calculated depositions (Agrell et al., 2001)

Latitude	Station	Air, pg/m <sup>3</sup>	Precipitation, ng/L	Deposition, ng/m <sup>2</sup> ·d
54°00'	Dziwnow	9.0 ( <i>n</i> = 5)	0.21 ( <i>n</i> = 2)	0.30 ( <i>n</i> = 2)
54°15'	Swibno	6.3 ( <i>n</i> = 6)	1.24 ( <i>n</i> = 3)	1.0 ( <i>n</i> = 3)
55°25'	Ventes R.	2.3 ( <i>n</i> = 10)	0.18 ( <i>n</i> = 15)	0.38 ( <i>n</i> = 15)
56°14'	Öland	5.1 ( <i>n</i> = 21)	0.71 ( <i>n</i> = 13)	0.38 ( <i>n</i> = 13)
56°17'	Breanäs	3.3 ( <i>n</i> = 20)	0.17 ( <i>n</i> = 12)	0.19 ( <i>n</i> = 12)
56°50'	Salaspils	12.4 ( <i>n</i> = 20)	0.40 ( <i>n</i> = 15)	0.64 ( <i>n</i> = 15)
58°20'	Vilsandi	6.9 ( <i>n</i> = 8)	0.28 ( <i>n</i> = 5)	0.23 ( <i>n</i> = 5)
58°21'	Gotska s.	2.0 ( <i>n</i> = 24)	0.15 ( <i>n</i> = 15)	0.19 ( <i>n</i> = 15)
59°17'	Stockholms s.	2.0 ( <i>n</i> = 21)	0.09 ( <i>n</i> = 10)	0.12 ( <i>n</i> = 10)
59°30'	Lahemaa	2.0 ( <i>n</i> = 16)	0.06 ( <i>n</i> = 12)	0.1 ( <i>n</i> = 12)
63°02'	Vasa	0.8 ( <i>n</i> = 26)	0.03 ( <i>n</i> = 12)	0.05 ( <i>n</i> = 12)
63°03'	Docksta	1.2 ( <i>n</i> = 24)	0.08 ( <i>n</i> = 15)	0.08 ( <i>n</i> = 15)
63°32'	Norrbyn	0.9 ( <i>n</i> = 24)	0.07 ( <i>n</i> = 16)	0.09 ( <i>n</i> = 16)
63°36'	Holmögadd	1.2 ( <i>n</i> = 22)	0.18 ( <i>n</i> = 8)	0.16 ( <i>n</i> = 8)
64°31'	Bjuröklubb	0.7 ( <i>n</i> = 22)	0.04 ( <i>n</i> = 11)	0.05 ( <i>n</i> = 11)
65°44'	Kalix	0.9 ( <i>n</i> = 24)	0.07 ( <i>n</i> = 14)	0.05 ( <i>n</i> = 14)
	All stations	1.6 ( <i>n</i> = 281)	0.13 ( <i>n</i> = 178)	0.15 ( <i>n</i> = 178)

**Table 3A.** Summary HCH concentrations in the air and precipitation and calculated depositions (Agrell et al., 2001)

Latitude	Station	Air, pg/m <sup>3</sup>	Precipitation, ng/L	Deposition, ng/m <sup>2</sup> ·d
54°00'	Dziwnow	72 ( <i>n</i> = 5)	0.63 ( <i>n</i> = 2)	1.4 ( <i>n</i> = 2)
54°15'	Swibno	103 ( <i>n</i> = 6)	8.65 ( <i>n</i> = 3)	5.7 ( <i>n</i> = 3)
55°25'	Ventes R.	26 ( <i>n</i> = 10)	1.63 ( <i>n</i> = 15)	3.2 ( <i>n</i> = 15)
56°14'	Öland	20 ( <i>n</i> = 21)	2.5 ( <i>n</i> = 13)	0.98 ( <i>n</i> = 13)
56°17'	Breanäs	45 ( <i>n</i> = 21)	1.8 ( <i>n</i> = 12)	1.9 ( <i>n</i> = 12)
56°50'	Salaspils	39 ( <i>n</i> = 20)	1.3 ( <i>n</i> = 15)	2.5 ( <i>n</i> = 15)
58°20'	Vilsandi	33 ( <i>n</i> = 28)	2.1 ( <i>n</i> = 5)	3.7 ( <i>n</i> = 5)
58°21'	Gotska s.	45 ( <i>n</i> = 24)	1.4 ( <i>n</i> = 15)	2.2 ( <i>n</i> = 15)
59°17'	Stockholms s.	24 ( <i>n</i> = 21)	1.0 ( <i>n</i> = 10)	1.3 ( <i>n</i> = 10)
59°30'	Lahemaa	26 ( <i>n</i> = 16)	0.31 ( <i>n</i> = 12)	0.53 ( <i>n</i> = 12)
63°02'	Vasa	30 ( <i>n</i> = 16)	0.38 ( <i>n</i> = 12)	1.3 ( <i>n</i> = 12)
63°03'	Docksta	18 ( <i>n</i> = 24)	0.92 ( <i>n</i> = 15)	1.7 ( <i>n</i> = 15)
63°32'	Norrbyn	7 ( <i>n</i> = 24)	0.16 ( <i>n</i> = 17)	0.61 ( <i>n</i> = 17)
63°36'	Holmögadd	20 ( <i>n</i> = 23)	1.3 ( <i>n</i> = 8)	0.82 ( <i>n</i> = 8)
64°31'	Bjuröklubb	28 ( <i>n</i> = 15)	0.46 ( <i>n</i> = 10)	0.22 ( <i>n</i> = 10)
65°44'	Kalix	4 ( <i>n</i> = 21)	0.33 ( <i>n</i> = 14)	0.16 ( <i>n</i> = 14)
	All stations	25 ( <i>n</i> = 275)	1.0 ( <i>n</i> = 178)	1.3 ( <i>n</i> = 178)

**Table 4A.** Concentrations of POPs (ng/PAS) in the air at five Estonian air monitoring stations from March to August 2006 (Klánová et al., 2006) with starting and ending dates of exposure

	Start	21.03.06	19.04.06	17.05.06	12.07.06	21.03.06	19.04.06	17.05.06	12.07.06	21.03.06	19.04.06	17.05.06	12.07.06	21.03.06	19.04.06	17.05.06	12.07.06	21.03.06	19.04.06	17.05.06	12.07.06
	End	19.04.06	17.05.06	12.07.06	08.08.06	19.04.06	17.05.06	12.07.06	08.08.06	19.04.06	17.05.06	12.07.06	08.08.06	19.04.06	17.05.06	12.07.06	08.08.06	19.04.06	17.05.06	12.07.06	08.08.06
Sampling days	29	28	56	27	29	28	56	27	29	28	56	27	29	28	56	27	29	28	56	27	
POP	Tln_01-1	Tln_01-2	Tln_01-3	Tln_01-4	Muuga_02-1	Muuga_02-2	Muuga_02-3	Muuga_02-4	Lahemaa_03-1	Lahemaa_03-2	Lahemaa_03-3	Lahemaa_03-4	Kunda_04-1	Kunda_04-2	Kunda_04-3	Kunda_04-4	Kohtla-J_05-1	Kohtla-J_05-2	Kohtla-J_05-3	Kohtla-J_05-4	
PCB28	11.4	36.3	17.3	48.1	1.2	5.4	1.9	2.4	0.8	1.2	0.7	1.9	3	1.2	0.6	1.4	2.5	3.5	2.5	4.2	
PCB52	4.2	11.3	6.3	13.1	0.7	3.1	1.4	2.7	0.8	1.1	0.4	0.6	0.7	1.2	0.4	1	2.1	5.8	2	1.8	
PCB101	1	3.2	2.3	3	0.3	1	0.9	0.8	0.2	0.7	0.3	0.3	0.2	0.3	0.2	<LOQ	0.9	5.7	1.3	1.1	
PCB118	1.2	3.2	2.5	3.2	0.3	1.6	0.8	0.8	<LOQ	1	0.2	<LOQ	0.4	0.6	0.1	0.5	1.3	8.7	1.2	1.2	
PCB153	0.5	1.6	0.7	1.4	0.3	0.6	0.4	0.6	0.2	0.4	0.2	0.5	0.2	0.5	0.1	0.4	0.6	2.1	0.6	0.9	
PCB138	0.4	1.2	0.6	0.9	<LOQ	0.4	0.2	0.2	<LOQ	0.3	0.1	<LOQ	0.2	0.2	>LOQ	<LOQ	0.4	1.6	0.4	0.3	
PCB180	<LOQ	0.6	0.2	0.3	<LOQ	0.2	<LOQ	0.5	<LOQ	<LOQ	<LOQ	<LOQ	0.2	<LOQ	<LOQ	0.3	<LOQ	0.3	<LOQ	<LOQ	
$\alpha$ -HCH	6.2	19.9	5.2	2.3	0.9	13.6	0.5	56.6	0.6	6.6	1.2	1.6	7.6	11.6	0.5	2.4	13.6	4.3	0.4	2	
$\beta$ -HCH	6.8	8	2.7	2.5	4	5.5	1.5	3.1	3	2	1.5	1	3.3	2.7	0.3	0.9	8.2	4.2	1.7	3.6	
$\gamma$ -HCH	6.4	6.7	4	4.2	2.4	5.5	2.6	3.8	2.6	1.8	1.5	1.6	2.5	2.4	0.7	1.5	4.6	2.7	2.5	3.9	
<i>o,p'</i> -DDE	0.3	<LOQ	0.2		<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.2	0.2	0.1	<LOQ	
<i>p,p'</i> -DDE	1.7	1.8	1.3	1.7	0.9	1.5	0.7	0.9	0.9	0.5	0.5	0.6	0.9	0.6	0.4	0.7	1.6	1.2	1.1	1	
<i>o,p'</i> -DDD	0.3	0.3	0.3		<LOQ	<LOQ	0.1	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.4	0.2	0.1	<LOQ	
<i>p,p'</i> -DDD	0.6	0.8	0.5	0.3	<LOQ	0.5	0.3	0.5	0.4	0.2	<LOQ	0.2	0.3	<LOQ	0.2		0.6	0.3	0.3	<LOQ	
<i>o,p'</i> -DDT	0.2	<LOQ	0.1		<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.1	<LOQ
<i>p,p'</i> -DDT	0.5	0.8	0.2	0.6	0.2	0.6	0.4	0.4	<LOQ	<LOQ	<LOQ	<LOQ	0.6	<LOQ	0.2	<LOQ	0.9	0.4	0.2	0.4	
PeCB	3.2	3.2	0.8	1.6	2.3	2.5	0.7	1.2	2.2	1.6	0.6	1	2.3	1.7	0.6	1.3	2.8	2.2	0.5	2	
HCB	8	8.3	2.9	5.5	<LOQ	7.3	2.9	<LOQ	6.6	5.3	2.5	4.6	5.9	5.6	2.2	4.6	8.7	6.7	2.8	<LOQ	

**Table 5A.** Concentrations of POPs (ng/m<sup>3</sup>) in the air at the Lahemaa air monitoring station with starting and ending dates of exposure in 2006–2012 (RECETOX, GENASIS database system, www.genasis.cz)

POP	21.03.2006	19.04.2006	17.05.2006	12.07.2006	25.04.2007	15.05.2007	19.06.2007	17.07.2007	2.08.2007
PCBs (indicator)									
PCB28	0.007	0.011	0.003	0.019	0.007	0.011	0.013	0.012	0.010
PCB52	0.007	0.010	0.002	0.006	0.005	0.009	0.010	0.016	0.007
PCB101	0.002	0.006	0.001	0.003	<LOQ	0.002	0.002	<LOQ	0.002
PCB118	<LOQ	0.009	0.001	<LOQ	<LOQ	0.003	0.002	0.004	0.002
PCB138	<LOQ	0.003	0.001	<LOQ	<LOQ	0.002	<LOQ	0.003	<LOQ
PCB153	0.002	0.003	0.001	0.004	<LOQ	0.003	0.005	0.008	0.004
PCB180	<LOQ	<LOQ							
OCPs (basic)									
A_HCH	0.005	0.065	0.007	0.018	0.077	0.033	0.074	0.030	0.041
B_HCH	0.026	0.018	0.007	0.010	0.016	0.014	0.015	0.029	0.004
G_HCH	0.023	0.017	0.008	0.016	0.004	0.018	0.031	0.032	0.025
D_HCH	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.008	<LOQ	<LOQ	<LOQ
HCB	0.063	0.055	0.017	0.054	<LOQ	0.051	0.076	0.101	0.065
PP_DDD	0.003	0.002	<LOQ	0.002	<LOQ	0.002	<LOQ	<LOQ	<LOQ
PP_DDE	0.008	0.004	0.002	0.005	0.005	0.006	0.009	0.012	0.009
PP_DDT	<LOQ	<LOQ	<LOQ	<LOQ	0.003	<LOQ	0.003	0.004	<LOQ
OP_DDT	<LOQ	<LOQ							

POP	6.10.2009	3.11.2009	2.12.2009	29.12.2009	27.01.2010	25.02.2010	23.03.2010	20.04.2010	19.05.2010	14.07.2010	10.08.2010	9.09.2010
PCBs (indicator)												
PCB28	0.014	0.012	0.008	0.009	0.011	0.009	0.009	0.009	0.004	0.006	0.004	0.004
PCB52	0.005	0.016	0.005	0.009	0.008	0.008	0.004	0.005	0.003	0.006	0.005	0.004
PCB101	0.001	0.001	0.000	0.000	0.002	<LOQ	<LOQ	0.005	0.002	0.008	0.005	<LOQ
PCB118	<LOQ	0.002	0.001	<LOQ	0.001	0.001	0.002	0.002	0.001	0.002	0.002	<LOQ
PCB138	<LOQ	0.001	<LOQ	0.001	0.001	<LOQ	0.002	<LOQ	0.001	0.002	0.002	<LOQ
PCB153	0.002	0.001	0.002	0.001	0.004	0.002	0.002	0.002	0.002	0.002	0.002	0.002
PCB180	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
OCPs (basic)												
A_HCH	0.002	0.005	0.001	0.007	0.002	0.002	0.015	0.023	0.013	0.024	0.019	0.021
B_HCH	<LOQ	<LOQ	<LOQ	<LOQ	0.003	0.009	<LOQ	0.005	<LOQ	<LOQ	<LOQ	<LOQ
G_HCH	0.016	0.013	<LOQ	0.006	0.023	0.010	0.011	0.015	0.007	0.014	0.009	0.012
D_HCH	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
HCB	0.056	0.053	0.030	0.038	0.050	0.049	0.084	0.077	0.040	0.063	0.073	0.094
PP_DDD	0.001	0.001	0.000	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.001	0.002	<LOQ	<LOQ
PP_DDE	0.007	0.006	0.004	0.002	0.004	0.004	0.004	0.005	0.002	0.007	0.005	0.008
PP_DDT	0.003	0.002	0.001	<LOQ	0.002	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
OP_DDT	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.001	<LOQ	<LOQ	<LOQ

*Continued overleaf*



Table 6A. Continued

POP	6.10.2009	3.11.2009	2.12.2009	29.12.2009	27.01.2010	25.02.2010	23.03.2010	20.04.2010	19.05.2010	14.07.2010	10.08.2010	9.09.2010
	3.11.2009	2.12.2009	29.12.2009	27.01.2010	25.02.2010	23.03.2010	20.04.2010	19.05.2010	14.07.2010	10.08.2010	9.09.2010	5.10.2010
A_HCH	0.18	0.56	0.07	0.8	0.2	0.2	1.6	2.4	2.2	2.2	2	2
B_HCH	<0.02	<0.02	<0.02	<0.02	0.32	0.92	<0.02	0.6	<0.02	<0.02	<0.02	<0.02
D_HCH	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
G_HCH	1.66	1.42	<0.02	0.7	2.6	1	1.2	1.6	1.2	1.4	1	1.2
OP_DDD	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
OP_DDE	0.12	0.12	<0.02	<0.02	0.18	0.04	0.2	<0.02	<0.02	<0.02	<0.02	<0.02
OP_DDT	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	0.2	<0.02	<0.02	<0.02
PP_DDD	0.12	0.12	0.04	<0.02	<0.02	<0.02	<0.02	<0.02	0.2	0.2	<0.02	<0.02
PP_DDE	0.82	0.7	0.39	0.26	0.48	0.46	0.4	0.6	0.4	0.8	0.6	0.8
PP_DDT	0.32	0.22	0.06	<0.02	0.18	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
PECB	1.32	1.52	0.68	1.88	0.38	1.72	2.6	1.6	0.8	1	1	1.8
HCB	5.5	5.54	2.96	4.14	5.36	4.68	8.4	7.6	6	5.4	7	8.4
PCB28	1.46	1.32	0.87	1	1.26	0.96	1	1	0.8	0.6	0.4	0.4
PCB52	0.58	1.82	0.54	1.04	0.94	0.82	0.4	0.6	0.6	0.6	0.6	0.4
PCB101	0.1	0.12	0.02	0.04	0.2	<0.02	<0.02	0.6	0.4	0.8	0.6	<0.02
PCB118	<0.02	0.28	0.06	<0.02	0.14	0.08	0.2	0.2	0.2	0.2	0.2	<0.02
PCB138	<0.02	0.14	<0.02	0.14	0.08	<0.02	0.2	<0.02	0.2	0.2	0.2	<0.02
PCB153	0.26	0.16	0.22	0.16	0.42	0.2	0.2	0.2	0.4	0.2	0.2	0.2
PCB180	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02

POP	5.10.2010	3.11.2010	1.12.2010	30.12.2010	25.01.2011	28.06.2011	20.09.2011	14.12.2011	7.03.2012	31.05.2012	22.08.2012	14.11.2012
	3.11.2010	1.12.2010	30.12.2010	25.01.2011	23.02.2011	20.09.2011	14.12.2011	7.03.2012	31.05.2012	22.08.2012	14.11.2012	5.02.2013
A_HCH	1.4	1.6	1.4	1.2	1.2	5.233	4.494	2.591	2.636	2.092	2.758	2.448
B_HCH	<0.02	<0.02	<0.02	<0.02	<0.02	<0.66	<0.66	<0.66	<0.66	<0.73	<0.73	<0.73
D_HCH	<0.02	<0.02	<0.02	<0.02	<0.02	1.047	<0.72	0.85	<0.72	1E-06	1E-06	1E-06
G_HCH	1.2	1	0.6	1	<0.02	2.666	2.277	1.065	1.654	1.456	1.401	1.117
OP_DDD	<0.02	<0.02	<0.02	<0.02	<0.02	<0.33	<0.33	<0.33	<0.33	<0.53	<0.53	<0.53
OP_DDE	<0.02	<0.02	<0.02	<0.02	<0.02	<0.2	<0.2	<0.2	<0.2	<0.31	<0.31	<0.31
OP_DDT	<0.02	<0.02	<0.02	<0.02	<0.02	0.554	<0.36	<0.36	<0.36	<0.72	<0.72	<0.72
PP_DDD	<0.02	<0.02	<0.02	<0.02	<0.02	<0.36	<0.36	<0.36	<0.36	<0.54	<0.54	<0.54
PP_DDE	0.4	0.6	0.6	0.4	0.2	1.506	1.909	1.09	1.115	0.867	2.067	1.802
PP_DDT	<0.02	<0.02	<0.02	<0.02	<0.02	0.468	<0.39	<0.39	<0.39	1E-06	1E-06	1E-06
PECB	2	3.4	5.2	2.8	3.6	1.118	3.629	5.621	1.687	0.609	1.779	4.631
HCB	10.4	13.4	15.4	9.4	9.4	13.07	22.17	26.52	15.37	8.558	14.15	19.23
PCB28	0.4	0.8	0.8	0.6	0.2	1.691	1.042	0.916	1.324	1.078	0.97	1.282
PCB52	0.4	0.6	0.6	0.4	0.2	1.393	0.87	0.69	0.984	0.841	0.75	0.936
PCB101	0.2	0.2	0.2	<0.02	<0.02	0.832	0.469	<0.32	0.496	<0.57	<0.57	<0.57
PCB118	<0.02	<0.02	<0.02	<0.02	<0.02	0.445	<0.24	<0.24	<0.24	<0.44	<0.44	<0.44
PCB138	<0.02	<0.02	<0.02	0.4	0.2	<0.34	<0.34	<0.34	<0.34	<0.5	<0.5	<0.5
PCB153	<0.02	<0.02	<0.02	<0.02	0.2	0.409	<0.27	<0.27	<0.27	<0.44	<0.44	<0.44
PCB180	<0.02	<0.02	<0.02	<0.02	<0.02	<0.32	<0.32	<0.32	<0.32	<0.39	<0.39	<0.39

## REFERENCES

- Agrell, G., Larsson, P., Okla, L., Bremle, G., Johansson, N., Klavins, M., Roots, O., and Zelechowska, A. 2001. Atmospheric and river input of PCBs, DDTs and HCHs to the Baltic Sea. In *A System Analysis of the Baltic Sea* (Wulff, F., Rahm, L., and Larsson, P., eds), pp. 149–175. Ecological Studies, **148**. Springer-Verlag, Berlin.
- Bartoš, T., Čupr, P., Klánová, J., and Holoubek, I. 2009. Which compounds contribute most to elevated airborne exposure and corresponding health risks in the western Balkans? *Environ. Int.*, **35**, 1066–1071.
- Dvorská, A., Lammel, G., and Holoubek, I. 2009. Recent trends of persistent organic pollutants in air in central Europe – air monitoring in combination with air mass trajectory statistics as a tool to study the effectivity of regional chemical policy. *Atmos. Environ.*, **43**, 1280–1287.
- EEA 2013. European Union emission inventory report 1990–2011 under the UNECE Convention on Long-range Transboundary Air Pollution (LRTAP), Technical Report No. 2013/10, European Environmental Agency, Copenhagen.
- Foday, M., Jaward, F. M., Farrar, N. J., Harner, T., Sweetman, A. J., and Jones, C. K. 2004. Passive air sampling of polycyclic aromatic hydrocarbons and polychlorinated naphthalenes across Europe. *Environ. Toxicol. Chem.*, **23**, 1355–1364.
- Gioia, R., Sweetman, A. J., and Jones, K. C. 2007. Coupling passive air sampling with emission estimates and chemical fate modelling for persistent organic pollutants (POPs): a feasibility study for Northern Europe. *Environ. Sci. Technol.*, **41**, 2165–2171 (+ supplementary material).
- Guidances for Air Emission Regulation. 2002. Limitation of air pollution from installations. *Environmental Guidelines*, No. 1. <http://www.mst.dk/udgiv/Publications/2002/87-7972-035-8/pdf/87-7972-036-6.PDF> (accessed 23.03.2015).
- Halse, A. K., Schlabach, M., Eckhardt, S., Sweetman, A., Jones, K. C., and Breivik, K. 2011. Spatial variability of POPs in European background air. *Atmos. Chem. Phys.*, **11**, 1549–1564.
- Harner, T., Shoeib, M., Diamond, M., Stern, G., and Rosenber, B. 2004. Using passive air samplers to assess urban–rural trends for persistent organic pollutants. I. Polychlorinated biphenyls and organochlorine pesticides. *Environ. Sci. Technol.*, **38**, 4474–4483.
- Jaagus, J. and Kull, A. 2011. Changes in surface wind directions in Estonia during 1966–2008 and their relationships with large-scale atmospheric circulation. *Estonian J. Earth Sci.*, **60**, 220–231.
- Jaward, F. M., Farrar, N. J., Harner, T., Prevedouros, C., Sweetman, A. J., and Jones, C. K. 2003. Atmospheric PBDEs and PCNs across Europe: results of passive sampling programme. *Organohalogen Compounds*, **62**, 1–4.
- Jaward, F. M., Farrar, N. J., Harner, T., Sweetman, A. J., and Jones, C. K. 2004a. Passive air sampling of PCBs, PBDEs, and organochlorine pesticides across Europe. *Environ. Sci. Technol.*, **38**, 34–41.
- Jaward, F. M., Farrar, N. J., Harner, T., Sweetman, A. J., and Jones, C. K. 2004b. Passive air sampling of polycyclic aromatic hydrocarbons and polychlorinated naphthalenes across Europe. *Environ. Toxicol. Chem.*, **23**, 1355–1364.
- Kabral, N., Pauklin, T., and Teinmaa, E. 2012. *Õhusaaste kauglevi seire ja uuringud*. Eesti Keskkonnauuringute Keskus, Leping 4-1/39, Tallinn.
- Keevallik, S. and Soomere, T. 2008. Shifts in early spring wind regime in North-East Europe (1955–2007). *Climate Past*, **4**, 147–152.
- Klánová, J., Čupr, P., and Holoubek, I. 2006. Application of passive sampler for monitoring of POPs in ambient air. Part II: pilot study for development of the monitoring network in the Central and Eastern Europe (MONET\_CEEC). RECETOX MU Brno. *RECETOX–TOCOEN REPORTS*, 319.
- Klánová, J., Čupr, P., Holoubek, I., Borůvková, J., Příbylová, P., Kareš, R. et al. 2009. Monitoring of persistent organic pollutants in Africa. *J. Environ. Monitor.*, **11**, 1952–1963.
- Kohoutek, J., Holoubek, I., and Klánová, J. 2006. Methodology of passive sampling. TOCOEN, s.r.o.Brno, RECETOX MU Brno. *RECETOX–TOCOEN REPORTS*, 300.
- Kohv, N., Heintalu, H., Mandel, E., and Link, A. 2012. *Estonian Informative Inventory Report 1990–2010*. Submitted under the Convention on Long-Range Transboundary Air Pollution. Estonian Environment Information Centre.
- Kohv, N., Heintalu, H., Mandel, E., and Link, A. 2013. *Estonian Informative Inventory Report 1990–2011*. Submitted under the Convention on Long-Range Transboundary Air Pollution. Estonian Environment Information Centre.
- Kull, A. and Laas, A. 2003. Sustainable management of wind resources in coastal areas in Estonia. In *Sustainable Planning and Development. The Sustainable World* (Beriatos, E., Brebbia, C. A., Coccossis, H., and Kungolos, A., eds), pp. 69–78. WIT Press, Southampton, Boston.
- Kumar, K., Priya, M., Sajwan, K., Kölli, R., and Roots, O. 2009. Residues of persistent organic pollutants in Estonian soils (1964–2006). *Estonian J. Earth Sci.*, **58**, 109–123.
- Lassen, C., Hansen, E., Jensen, A. A., Olendrzyński, K., Kolsut, W., Żurek, J. et al. 2003. Survey of dioxin sources in the Baltic Region. *Environ. Sci. Pollut. R.*, **10**, 49–56.
- Miluskaite, A., Klánová, J., Holoubek, I., Rimselyte, I., and Kvietkus, K. 2008. Persistent organic pollutants in Lithuania: assessment of air and soil contamination. *Lithuanian Journal of Physics*, **48**, 357–366.
- Möts, K., Maasikmets, M., Teinmaa, E., Vainumäe, K., Lehes, L., Atumäe, T., and Kimmel, V. 2013. European Aerosol Conference 2013, Prague. *Digital Handbook EAC 2013*. <http://eac2013.cz/> (accessed).
- Müür, J. 1996. Plant protection products use in Estonia. In *Estonian Environment 1995*, pp. 66–68. Estonian Environmental Information Centre, Tallinn.

- Nordic. 1999. Nordic Environmental Research Programme for 1993–1997. Final Report and Self-Evaluation. *TemaNord Environment*, 548, 136–140.
- Pribylova, P., Kares, R., Boruvkova, J., Cupr, P., Prokes, R., Kohoutek, J. et al. 2012. Levels of persistent organic pollutants and polycyclic aromatic hydrocarbons in ambient air of Central and Eastern Europe. *Atmos. Pollut. Res.*, **3**, 494–505.
- Quass, U., Pulles, T., and Kok, H. 2004. The DG Environment project “Dioxin Emissions in Candidate Countries”: scope, approach and first results. *Organohalogen Compounds*, **66**, 878–883.
- Roots, O. 1992. Interpreting observations on the transport and wet deposition of airborne pollutants over the Baltic Sea and West-Estonian islands. *AMBIO*, **21**, 321–322.
- Roots, O. 2004. Polychlorinated biphenyls (PCB), polychlorinated dibenzo-p-dioxins (PCDD) and dibenzofurans (PCDF) in oil shale and fly ash from oil shale-fired power plant in Estonia. *Oil Shale*, **21**, 333–339.
- Roots, O. and Sweetman, A. 2007. Passive air sampling of persistent organic pollutants in two Estonian monitoring stations. *Oil Shale*, **24**, 483–494.
- Roots, O., Holoubek, I., Cupr, P., Klanova, J., Kallis, A., and Kuningas, K. 2008. Air and soil pollution. Part I: Organochlorine pesticides in the north- and north-eastern part of the Estonia. *Ecological Chemistry*, **17**, 88–92 (St. Petersburg University and THESA).
- Roots, O., Roose, A., Kull, A., Holoubek, I., Čupr, P., and Klánová, J. 2010. Distribution pattern of PCBs, HCB and PeCB using passive air and soil sampling in Estonia. *Environ. Sci. Pollut. R.*, **17**, 740–749.
- Roots, O., Zitko, V., Kumar, K. S., Sajwan, K., and Loganathan, B. G. 2011. Contamination profiles and possible trends of organohalogen compounds in the Estonian environment and biota. In *Global Contamination Trends of Persistent Organic Chemicals* (Loganathan, B. G. and Lam, P. K.-S., eds), pp. 305–333. CRC Press, Taylor & Francis Group.
- Sajwan, K., Kumar, K., Roots, O., Kölli, R., Moverly, H., and Loganathan, B. 2008. Persistent organochlorines and brominated diphenyl ethers in soil collected from rural and urban Estonia. *Organohalogen Compounds*, **70**, 2474–2477.
- Schleicher, O., Jensen, A., Roots, O., Herrmann, T., and Tordik, A. 2004a. Dioxin and PAH emissions from a shale oil processing plant in Estonia. *Organohalogen Compounds*, **66**, 1665–1671.
- Schleicher, O., Jensen, A., Roots, O., Herrmann, T., and Tordik, A. 2004b. Dioxin emission from two oil shale fired power plants in Estonia. *Organohalogen Compounds*, **66**, 4089–4095.
- Schleicher, O., Roots, O., Jensen, A. A., Herrmann, T., and Tordik, A. 2005. Dioxin emission from two oil shale fired power plants in Estonia. *Oil Shale*, **22**, 563–570.
- Sellström, U., Egeback, A. L., and McLachlan, M. S. 2009. Identifying source regions for the atmospheric input of PCDD/Fs to the Baltic Sea. *Atmos. Environ.*, **43**, 1730–1736.
- Shoeib, M. and Harner, T. 2002. Characterization and comparison of three passive air samplers for persistent organic pollutants. *Environ. Sci. Technol.*, **36**, 4142–4151.
- Škarek, M., Čupr, P., Bartoš, T., Kohoutek, J., Klánová, J., and Holoubek, I. 2007. A combined approach to the evaluation of organic air pollutants – a case study of urban air in Sarajevo and Tuzla (Bosnia and Herzegovina). *Sci. Total Environ.*, **384**, 182–193.
- UNEP. 2002a. Regionally Based Assessment of Persistent Toxic Substances. Europe Regional Report. Geneva.
- UNEP. 2002b. Regionally Based Assessment of Persistent Toxic Substances. Mediterranean Regional Report. Geneva.

## Püsiivad orgaanilised saasteained Eesti välisõhus

Ott Roots, Tiit Lukki, Petra Příbylová, Jana Borůvková, Petr Kukučka, Ondřej Audy, Jiří Kalina, Jana Klánová, Ivan Holoubek, Andrew Sweetman ja Ole Schleicher

Enamik püsivatele orgaanilistele ühenditele (POS-idele, *persistent organic pollutants* (POPs)) pühendatud uurin-gutest Eesti välisõhus on tehtud koostöös teiste riikide teadlastega ja nende riikide finantseeritud. Esimesed POS-idele pühendatud koostööprojektid käivitusid Eestis juba 1990. aastate algul. POS-id on põhiliselt kloori sisaldavad ühendid, mis oma mürgisuse, püsivuse ja bioakumuleeruvuse tõttu ohustavad inimese tervist ning kahjustavad elus-organisme ja ökosüsteeme. Oma eeltoodud omaduste tõttu võivad POS-id õhu, vee, mulla, elusorganismide, jäätmete ja toidu kaudu kanduda saasteallikatest õige kaugele. Tänapäeval kasutatakse välisõhu püsivate orgaaniliste saasteainete sisalduse uurimisel nn passiivseid proovleid. Üldjuhul antakse sisaldused filtrisse pidama jäänud POS-ide kohta. Ajavahemikul 1990–2013 mõõdeti POS-ide sisaldusi välisõhus pisteliselt järgmistes õhuseirejaamades: Lahemaal, Kundas, Kohtla-Järvel, Tallinnas, Muugal, Vilsandil ja Tahkusel. POS-ide sisaldused Eesti välisõhus on suhteliselt väikesed, kuid on mõjutatud õhusaaste kaugülekandest väljaspool Eestit. Näitena olid 2006. aasta augustis ja septembris POS-ide ning PAH-ide suured sisaldused Kirde- ja Põhja-Eesti seirejaamades tingitud õhusaaste kauglevist. Põhjuseks olid suured metsatulekahjud Venemaa Karjala ja Leningradi oblastis. Lahemaa õhuseirejaam on valitud Euroopa paljudesse projektidesse kui POS-ide foonijaam. POS-ide sisalduste mõõtmised Lahemaa jaamas jätkuvad ka käesoleval aastal.