

**TENTATIVE LEVELS OF POPS IN LITHUANIAN  
ENVIRONMENT**  
*EKSPERIMENTĀLI NOTEIKTIE POP LĪMEŅI LIETUVAS APKĀRTĒJĀ  
VIDĒ*

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**Abstract.** *Persistent Organic Pollutants (POPs) are chemical substances that persist in the environment, bioaccumulate through the food web, and pose a risk of causing adverse effects to human health and the environment. The Stockholm Convention is a global treaty to protect human health and the environment from POPs. In implementing the Convention, Governments will take measures to eliminate or reduce the release of POPs into the environment. This study was done in order to evaluate tentative POPs levels in Lithuania.*

*Limited amount of PAHs and PCBs were analyzed in Šiauliai air, in two biggest Lithuanian rivers – Nemunas and Neris, and in one of the biggest waste landfill in Lapes. Sampling was done using semi permeable membrane devices (SPMDs). The same procedure of sampling and analyses was used to ensure data comparability. In general, POPs pollution levels were compared with results from other studies.*

**Keywords:** *POPs, PAHs, PCBs, SPMDs, environment, Stockholm Convention, air, water, landfill.*

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### Introduction

Persistent organic pollutants (POPs) is a common name of pollutants group that are semi-volatile, persistent and toxic to humans and wildlife [1, 2]. POPs remain in the environment for long periods, become widely distributed geographically, and accumulate in the fatty tissue of living organisms. This group of pollutants includes some of the most harmful chemicals such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCB), pesticides, dioxins, etc.

The Stockholm Convention is a global treaty to protect human health and the environment from POPs. POPs circulate globally and can cause damage wherever they travel. In implementing the Convention, Governments will take measures to eliminate or reduce the release of POPs into the environment [3, 4]. One of the first steps is estimation of current pollution. The aim of this study was to evaluate the tentative levels of POPs in Lithuanian environment.

PAHs are of special interest due to their toxicity, carcinogenicity, mutagenicity and wide distribution in the environment [5]. Airborne PAH include substances which, when inhaled, are believed can cause human health effects ranging from nausea and difficulty in breathing to lung cancer [6]. Traffic, domestic heating, refuse burning, petroleum refining, coal coking, tar paper production, aluminum smelting, thermal power, and wood preservation operation using creosote are all examples of major human and industrial PAH sources [5, 7].

PCBs are the class of non-polar, non-flammable, industrial fluids with good thermal and chemical stability, and electrical insulating properties that allowed their application as dielectric fluids in transformers and capacitors, as heat-transfer and hydraulic fluids, as plasticizers in paints, and in the formulation of lubricating and cutting oils, sealants and pressure-sensitive copy paper [8, 9, 10].

Semipermeable membrane device (SPMD) is a passive sampling method commonly used as a time-integrated measure of vapour or aqueous concentrations of persistent hydrophobic chemicals, including PAHs, PCBs and pesticides [11, 12]. The SPMDs technique is based on a

simple device which accumulates the compounds in a lipid phase after passage through a diffusion membrane layer [13].

### Materials and methods

SPMDs were deployed during 21 days in air and water. At each site, one sampler that included two or one standard SPMDs which were deployed on separate steel spiders inside a metal umbrella, were hung up at about 2-3 meters height or put in stainless steel canisters and left in water.

The umbrella was designed to protect the SPMDs from sunlight, rain, wind and direct particles deposition. Stainless steel canisters were used to protect SPMDs from damages during the sampling. Air was still able to pass freely under and around to the SPMDs.

#### Sampling sites.

**Air.** Four SPMDs were deployed in the Šiauliai city. Samples were taken in residential area, private houses area, and city centre, near heavy traffic, during autumn (10/09/2002 – 31/09/2002) and winter seasons (8/12/2002 – 30/12/2002). The average temperature was 7.7°C, average air pressure was 749 mm Hg, average amount of rain was 1.64 mm during the sampling period (21 day).

**Rivers.** Two Lithuanian rivers – Neris and Nemunas were investigated. The above-mentioned sites in Neris and Nemunas rivers were chosen near various industrial factories in order to estimate their possible influence on rivers pollution with organic pollutants. Sampling time in Neris river was performed from 6/10/2000 – 17/1/2001 and from 6/10/2000 till 27/10/2003 in Nemunas river.

**Landfills.** *Leachate sampling.* One standard SPMDs were deployed in Lapiu landfill leachate storage reservoir and three membranes were deployed into landfills surrounding streams. The mean water temperature in reservoir and surface waters during the exposure time was about 10°C.

The selected sites descriptions are presented in the Table 1.

Table 1.

### Sampling sites descriptions

Air		River	
Place name, number of samples	Exposure site	Place name, number of samples	Exposure site
Šiauliai, Baltupėnų str. (S1a), (1 SPMD)	Residential area, district heating	Neris, (2 SPMDs)	Industrial area, Kaunas city centre
Šiauliai, crossroad of two main streets (S2a), (1 SPMD)	City centre, heavy traffic, < 20 m to the street.	Nemunas, (2 SPMDs)	Downstream industrial area (Kaunas city)
Šiauliai, crossroad of two main streets (S3a), (1 SPMD)	City centre, heavy traffic, < 2 m to active street.	<b>Landfills</b>	
Šiauliai, Pabalių str. 34 (S4a), (1 SPMD)	Private house area, no district heating	I M, (1 SPMD)	Leachate reservoir
Šiauliai, Medelyno secondary school (S5w) (1 SPMD)	Residential area, central heating, >300 m to a street;	I S, (1 sediments sample)	Stream, about 100 m from leachate treatment plant
Šiauliai, Medelyno kinder garden (S6w), (1 SPMD)	Residential area, central heating, >10 m to a street;	II M, II S, (1 SPMD and 1 sediments sample)	Stream, about 250 m from leachate treatment plant
Šiauliai, Pabaliu str. 34 (S4w), (1 SPMD)	Private house area, no central heating, >20 m to a street;	III M, III S, (1 SPMD and 1 sediments sample)	Marilė stream, about 300 m from landfill
Šiauliai, Zvyro 34 (S7w), (1 SPMD)	Private house area, no central heating, >50 m to a street ;	IV M, IV S, (1 SPMD and 1 sediments sample)	Marilė stream, approximately 2 km from landfill

Explanations: M – membrane, S – sediments;

*Sediment sampling.* The sediments samples were collected into dark glass bottles with aluminium folia under the lid to avoid contamination during transportation. After sampling the sediment samples were stored in a freezer.

**Field blank.** Four SPMDs as a field blanks were used at sampling sites: two for air, one for rivers and one for landfills. Standard SPMD was kept in air during deployment of membrane. Such field blank account for the contamination of the SPMDs by transportation (e.g. airborne chemicals). During analysis it was treated in the same way as deployed devices, with the exception that it wasn't exposed to water.

Before and after sampling, the SPMDs were stored at -18 °C in sealed solvent cleaned tin cans, to avoid accumulation of contaminants from the outer surface into the membrane after the sampling period was finished.

**SPMDs extraction, cleanup and analyses.**

All solvents used in the study were of glass-distilled quality (Burdick & Jackson, Neuulm, Germany).

In order to clean membrane surface from particles and lipids, SPMDs were washed in clean water, n-hexane and 1 M HCl. The membranes were carefully dried before dialysis. The compounds were dialyzed with cyclopentane: dichlormethane (95:5) mixture for three times. After extraction, three <sup>2</sup>H-labeled PAH standards and eight <sup>13</sup>C-labeled PCBs were added as internal standard for a cleanup. The spiked extracts were fractionated by gel permeation chromatography (GPC) technique as detailed in "ExposMeter" recommendations or Bergqvist et al. manuscript [13, 14]. Different columns were used in this investigation from those in the cited study, namely a 300 × 22.5 mm Envirosep-ABC HR-GPC column and a 75 × 22.5 mm Envirosep-ABC guard column. The GPC-fractions were followed by a silica column (10 mm i.d.). Further, samples were eluted with hexane: dichloromethane (1:1) and were evaporated by using rotary evaporator, for further evaporation - a stream of nitrogen. The known amount of <sup>2</sup>H-labeled dibenzofurane (Promochem, Kungsbacka, Sweden) was added just before instrumental analyses and used as recovery standard (RS). PAHs and PCBs were identified by GC/MS as described in "ExposMeter" recommendations or Bergqvist et al. manuscript [13, 14].

All results were corrected by using recovery values from the most structurally similar internal standard. Recoveries of PAHs and PCBs standards are reported in Table 2.

Table 2.

**IS recoveries (numbers are given in percents)**

Compound	S1a	S2a	S3a	S4a	S5w	S6w	S4w	S7w	IM	IIM	IIIM	IIVM	IS	IIS	IIIS	IIVS	Neris1	Neris2	Nemunas
<b>PAH, %</b>																			
IS-ACE	182	170	126	82	62	86	69	124	77	72	44	74	73	31	33	55	26	29	71
IS-FL	157	153	136	139	62	86	69	124	108	104	55	104	103	42	78	206	68	79	73
IS-BP	139	140	135	132	99	85	113	98	105	81	29	53	133	17	6	194	91	66	79
<b>PCB, %</b>																			
IS #28	97	85	9	6	54	62	57	15	107	147	50	101	93	35	86	92	87	89	85
IS #52	112	86	52	61	62	64	66	22	94	135	48	92	35	32	71	82	43	70	74
IS #101	52	49	66	41	52	60	58	61	84	154	50	101	93	36	90	94	65	41	35
IS #118	128	102	112	80	79	92	81	88	122	158	54	105	99	40	99	105	69	71	72
IS #105	91	78	74	61	73	85	78	81	117	153	53	107	125	39	99	102	69	77	79
IS #153	99	97	102	77	76	82	73	71	90	153	47	94	91	36	89	92	79	76	78
IS #138	124	101	109	82	67	82	75	74	115	135	45	87	30	34	85	87	75	73	75
IS #180	105	95	103	77	72	83	73	79	113	116	50	98	23	37	94	93	70	63	64

**Sediments samples preparation.** Sediments were dried in the oven for couple of days at 40°C temperature until constant weight. Then 10-20% (about 1g) of each sample was dried in the oven at 110°C until constant weight and dry weight of the samples was calculated, further, samples were placed in the oven at 500°C over the night, to determinate total amount of the organic carbon (TOC) in the samples. The portion of the solution of labelled  $^{13}\text{C}$  compounds used for the SPMD analyses as Internal Standard was added, and the sediment samples were extracted using the Soxhlet extractor with 170ml of toluene for each sample over the night. The extract was further cleaned with GPC-system and the silica gel column as described above.

**Analysis.** SPMD samples from landfills were prepared the same way as described above, but different instrument was used. High resolution gas chromatography (HRGC)/low resolution mass spectrometry (LRMS) - instrument system used in the analysis for landfill samples, included a non-polar capillary column (J&W DB-5, 60 m\* 0.32 mm i.d., 0.25-mm film thickness Folsom, CA, USA) and a Fisons MD 800/GC 8000 operating in selected ion recording (SIR) mode. In the mass spectrometry, an auto sampler injects 1 $\mu\text{l}$  samples into a split less injector. In the SIR mode two most abundant ions of the native compounds and the standards are monitored. The instrument detection limit (IDL) refers to the smallest signal above background noise that an instrument can reliably detect (approximately 1 pg/injection). The analyzed compounds from the sample's chromatograms were identified by retention time. Recoveries of PAH and PCB standards are reported in Table 2.

The amounts of investigated pollutants were calculated by using "ExposMeter" recommendations and reported in  $\text{ng}/\text{m}^3$  for air,  $\text{ng}/\text{l}$  for water and  $\text{ng}/\text{g}$  dry weight for sediments [13].

### Results

$\Sigma\text{PAH}_{16}$  (US EPA) and  $\Sigma\text{PAH}_{24}$  concentrations in landfill sediment samples varied, respectively, between 53 – 293  $\text{ng}/\text{g}$  d.w. and 63 - 408  $\text{ng}/\text{g}$  d.w.; in atmospheric gas phase ranged between 48 - 275  $\text{ng}/\text{m}^3$  and 54 – 336  $\text{ng}/\text{m}^3$ ; in rivers –were found between 16 - 23  $\text{ng}/\text{l}$  and 20- 24  $\text{ng}/\text{l}$ ; and, as was mentioned above, lowest PAHs concentrations were found in landfill streams water samples, and varied between 4-12  $\text{ng}/\text{l}$  ( $\Sigma\text{PAH}_{15}$ ) and 5-15  $\text{ng}/\text{l}$  ( $\Sigma\text{PAH}_{24}$ ) (Fig. 1).

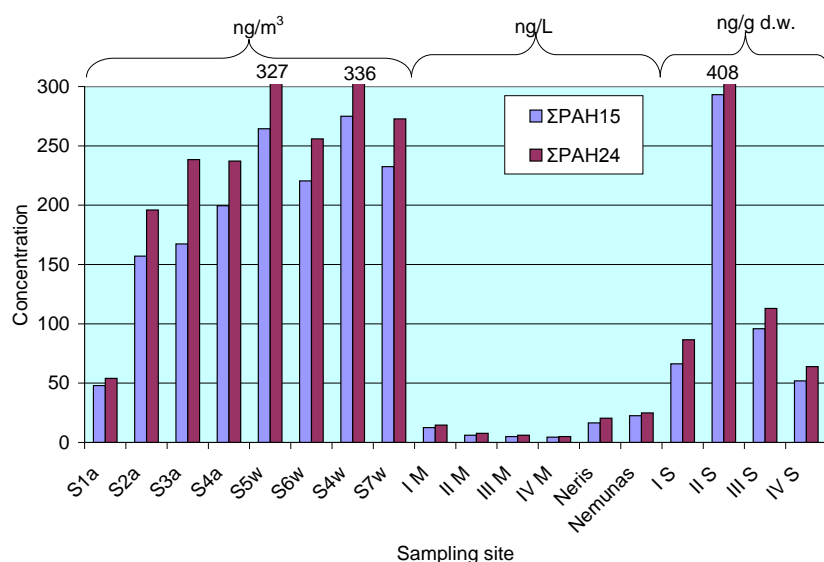


Fig. 1. PAH concentrations in air

PCB levels estimated are presented in Fig. 2.  $\Sigma\text{PCB}_{11}$  concentrations in landfill sediment samples varied between 0.81 – 117.15  $\text{ng}/\text{g}$  d.w.; in rivers and landfill streams water samples, respectively, concentrations varied 1.02 – 1.3216 and 0.06 – 4.43  $\text{ng}/\text{l}$ ;  $\Sigma\text{PCB}_{11}$  concentrations in atmospheric gas phase ranged between 0.19 – 0.27  $\text{ng}/\text{m}^3$ .

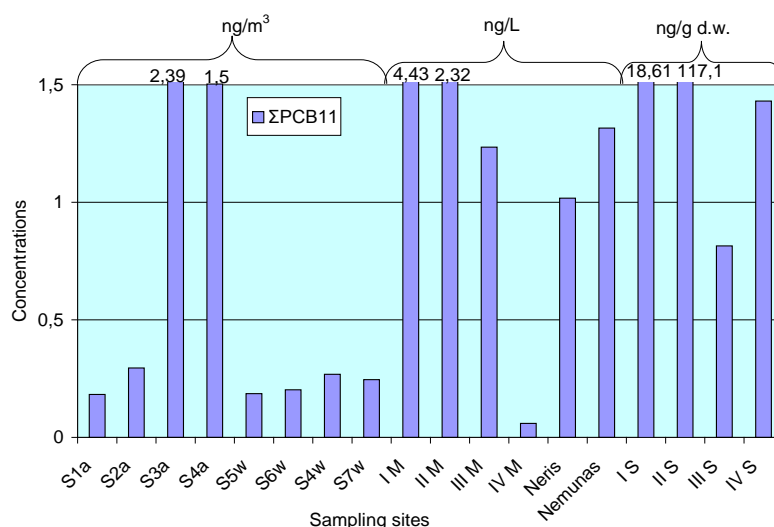
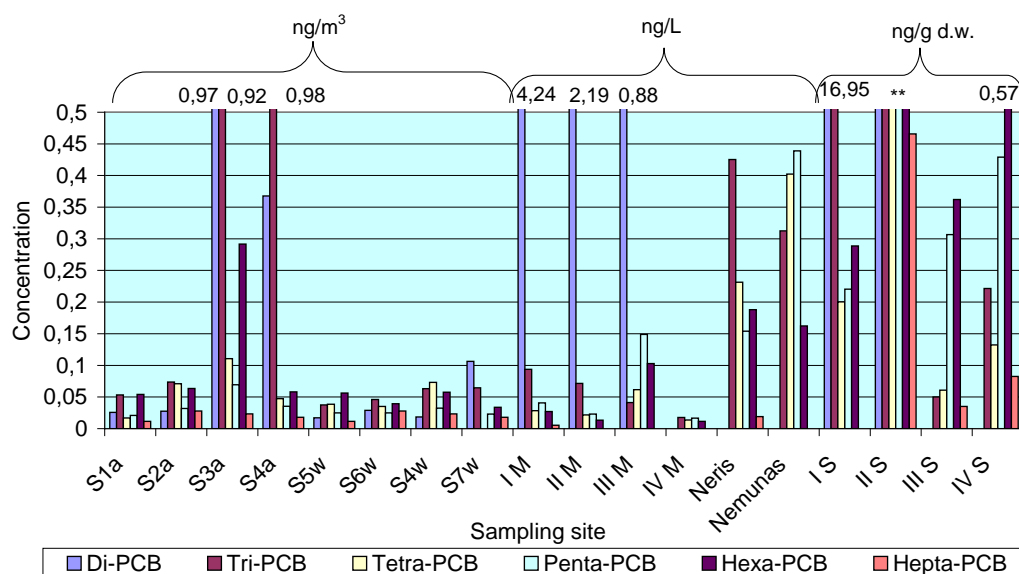


Fig. 2. ΣPCB<sub>11</sub> concentrations at sampling places



\*\* Di-PCB 101,77; Tri-PCB 3,75; Tetra-PCB 2,07; Penta-PCB 4,59; Hexa-PCB 4,50;

Fig. 3. Concentrations of PCBs congener groups at sampling places

### Discussion

**PAHs.** It is surprising that relatively low PAHs concentrations in landfill surrounding comparing with PAHs levels in Lithuanian rivers were detected. This presumably indicates that emissions of PAHs to rivers from industry are quite high.

The total sum of 15 U.S. EPA PAHs in landfill samples, showed a net decline in concentrations going further from landfill, as it could be expected.

Naphthalene is one of the most volatile PAHs and therefore easy to loose in the analysis. It could be that naphthalene calculated concentrations are too low; this should be taken into consideration. Due to the chromatographic interferences the determination of fluorine in many landfills samples was impossible. For this reason it was excluded from US EPA 16. Phenanthrene was the most abundant individual PAHs in all samples, except sediment samples. Concentrations in air samples ranged between 23 ng/m<sup>3</sup> and 109 ng/m<sup>3</sup>, in river samples varied from 3.27 to 7.69 ng/l, in landfill's water samples concentrations were 0.64 – 5.81 ng/l, in sediments – from 2.86 to 34.83 ng/g d.w.

**PCBs.** Elevated PCBs concentrations were found in water samples close to landfill leachate treatment plant, going further from it PCBs concentrations in water samples decreases and

increases in sediments. It is known that PCBs tend to be associated with particles or with and organic carbon.

25 of 28 targeted PCB congeners were detected in Neris and Nemunas. The background site values were exceeded by most of the PCBs congener concentrations in Nemunas river and vary from 0,06 to 0,3 ng/L for each congener. In Neris concentration of PCBs#28 (0,43 ng/L) was elevated compare with the concentration of other PCB congeners such as PCB#31 (0,24 ng/L), PCB#44 (0,134 ng/L), PCB#52 (0,14 ng/L), PCB#110 (0,164 ng/L). Since the concentration of PCB #28 and #31 was found to be elevated compared to the more chlorinated congeners, it is suggested that the pollution in Neris might be recent, consist of fresh PCB and/or close to ongoing effluent. Such PCB pattern might also be influenced by the highly chlorinated PCB congeners tendency to be bound to dissolved organic matter and suspended particulate material within the water column reducing their availability for membrane uptake.

The PCBs profile of congener group concentrations in 8 sampling places (S3a, S4a, S7w, I M, II M, III M, I S, II S) are dominated by Di-PCBs, followed by Tri-PCBs, Fig. 3. Concentration of different PCB homologues decreased from PCB #15 to PCBs #180, indicating that there might be fresh pollution of PCBs source, as these PCBs (di-, tri- ) are very volatile and their concentrations tend to decrease significantly in a few years. Thereby, the strong temperature dependence of vapor pressure, and the rate of evaporation from various environmental surfaces, has been shown to affect the atmospheric concentrations of PCBs congener distribution [15, 16]. Temperature dependency is generally increasing with the degree of chlorination [17].

Consequently, results indicated high Di-PCBs concentrations in landfill surrounding streams (fresh pollution source), but others PCBs congeners concentrations were relatively low compared to PCBs concentrations found in rivers (Fig. 3). Concentrations in water close to landfill (M) and in sediments (S) showed that there was a leak of PCBs from landfill (Fig. 1, 2, 3). Elevated PCBs concentrations in sediments samples could be related to PCBs association with particles or with/and organic carbon.

Significantly lower concentrations of PCBs were found in air winter samples than in air autumn samples, this appearance could be related to lower temperatures and correspondingly less volatilization (Fig. 2).

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### **Conclusions**

In this screening study wide range of PAHs and some PCBs were analyzed from different environmental medias. The highest PAHs concentrations were found in the air, because of their evaporation. PAHs concentrations were highest close to the heavy traffic. In Šiauliai air autumn samples di-, tri- PCBs indicated fresh undiscovered PCBs pollution source. Air samples were approximately six times more polluted with analyzed PAHs and three times more polluted with analyzed PCBs in comparison with Swedish urban background sites. Results indicated that rivers are more polluted with POP's compared with stream waters close to landfills. Higher concentration of PCB#28 (0,43 ng/L), to compare with PCB#110 (0,16 ng/L), might reflect recent pollution in Neris river. In general PCB and PAH levels in Lithuanian rivers were 2-10 times higher than the corresponding values from Swedish waters. The total sum of EPA 15 PAHs showed a net decline in concentrations going further from the landfill (from 11,76 to 1,82 ng/l).

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