



# Distribution of polychlorinated biphenyls, phthalic acid esters, polycyclic aromatic hydrocarbons and organochlorine substances in the Moscow River, Russia



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## ABSTRACT

The purpose of this study was to investigate the levels of polychlorinated biphenyl (PCB), phthalic acid esters (PAE), polycyclic aromatic hydrocarbons (PAH) and organochlorine substances (OCP) in the Moscow River water. Some studies have reported the occurrence of these substances in the soil of the Moscow region; however, no study has yet established an overview for these compounds in the Moscow River water. In this study the Moscow River water contamination with PAEs, PAHs and OCPs was determined. Obtained results were associated with the resident area located on the river bank, and the possible contamination sources were considered. The obtained data were compared with the data on the contamination of the different world-wide rivers. This research indicates the further study necessity of the Moscow region to cover more contaminated sites and environmental compartments.

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## 1. Introduction

Polychlorinated biphenyls (PCBs), organochlorine substances (OCP), polycyclic aromatic hydrocarbons (PAHs) and phthalic acid esters (PAEs) are of particular interest due to their endocrine disrupting properties (Teil et al., 2014; Hawliczek et al., 2011). PCBs were restricted since 1970s in the USA and the European Union and since 1993 in Russia, but these substances are still persistent in the environment. PCBs are hydrophobic substances (DellaTorre et al., 2013; Okay et al., 2009; Schmid et al., 2005; Thevenon et al., 2013) and in case of water body contamination the highly chlorinated PCBs are mainly adsorbed on sediments and suspended matter, while the low chlorinated PCBs can be found in the water column, due to their greater solubility. The process of PCBs desorption from sediments plays the key role in the fate of these substances and can be the path of water source cross contamination with further air pollution (Gong et al., 1998) or accumulation in aquatic organisms such as plankton, algae, and fish (Ondarza et al.,

2014; Renaud et al., 2004). A lot of researches show the PCBs presence in water sources world-wide (Zhou et al., 2013; Howell et al., 2011; Qumerais et al., 1994; Cailleaud et al., 2007). Many OCPs have been also included in the list of Persistent Organic Pollutants (POPs) of the Stockholm Convention. The use and manufacture of some OCPs have been banned or restricted in the 1980s in the most countries.

Many PAHs are known to have carcinogenic and mutagenic properties. Due to their world-wide occurrence in environment 16 PAHs were included in the list of priority pollutants by the US EPA and 7 of them in the European Union. The PAHs environmental contamination sources can be different, including combustion of fossil fuel, oil recycling, coke and asphalt productions, oil refining and other industrial activities (Manoli and Samara, 1999). Due to the high hydrophobicity of PAHs, the main path of surface water contamination is wet or dry atmospheric deposition (Nagy et al., 2012). Despite of their high hydrophobicity, these substances can be found in the surface water bodies world-wide and are well studied (Nagy et al., 2012; Bourgeault and Gourelay-Francé, 2013; Gateuille et al., 2014; Jin et al., 2012; Li et al., 2009; Ma et al., 2013; Patrolecco et al., 2010; Yunkera et al., 2002; Zhang et al., 2012).

PAEs are usually used as plasticizers in food packages, building, toys, medical devices such as blood storage bags, intravenous fluid

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bags and other products (Magdouli et al., 2013a). This group of substances can affect the human reproductive health even in environmental friendly level (Meng et al., 2014). Long half-lives of PAEs in the environment can be observed under anaerobic conditions, in low concentrations and cold environments (Xie et al., 2007). Most studies show that these substances are regularly found in urban environmental compartments at a significant level (Bergé et al., 2013; Dargnat et al., 2009; Dévier et al., 2013; Gao et al., 2014; Gibson et al., 2005; Magdouli et al., 2013b; Suzuki et al., 2001; Vikelsøe et al., 2002; Zuo et al., 2011).

For understanding the global fate of the chosen types of contaminants, it is important to conduct the continuous monitoring of each industrial city in the world. The Moscow River is a river of western Russia, having its source in Smolensk – the Moscow Upland, passing through the city of Moscow and then flowing into the Oka River in the city of Kolomna. The total length of the river is 503 km, while its length within the city of Moscow is about 80 km. The environmental stress on the Moscow River is high due to the fact that Moscow is the city of industrial activity. Practically all types of industrial enterprises are presented there, except mining industry. Primary industries of the city of Moscow include the chemical, petroleum, metallurgy, textile, food, energy and machinery industries. Most of the factories and enterprises are located on the Moscow River bank area and could be the contamination sources of the Moscow River. A few studies on PAH and PCB determination in the Moscow region were conducted and showed the presence of these substances in the soil (Wilcke et al., 2006, 2005; Shelepchikov et al., 2011). For example, authors (Kogut et al., 2006) investigated the PAHs contamination levels in soils of three Moscow parks and stated the high content of the total PAHs equal to 2773 µg/kg of the soil. The contaminated soil can be the indicator and the source of nearby water bodies' contamination. However no regular monitoring of these contaminants in the Moscow River water has been done over the last decades. Nevertheless, the research on the determination of the water contamination is necessary and will show the current level of environmental contamination, while the sediment and bank soil contamination reveals only the history of the river system contamination.

The aims of this study were to: (i) determine the contamination levels of PCBs, OCPs, PAHs and PAEs in the water samples taken from the Moscow River in a high environmental stress area; (ii) associate the results with the residential area, and (iii) compare the contamination levels of the Moscow River with the world levels of the surface water bodies contamination.

## 2. Materials and methods

A diagram presenting all the steps of the experimental procedures performed in this study is shown in Fig. 1 in Supplementary materials.

### 2.1. Standards and reagents

The substances, used as the analytical standards, are represented in Table 1 (in supplementary materials).

All standards, hexane, methanol and dichloromethane were obtained from Merck. Milli-Q water was obtained by purification and deionization of tap water immediately prior to use with a Seralpur PRO 90 CN (Seral, Germany).

### 2.2. Sampling location and collection

The surface water samples were collected from the four sampling sites along the direction of the Moscow River flow in October

2013. The sampling sites are shown in Fig. 1. The four sampling sites were chosen due to the high environmental influence on the Moscow River. The sample 1 (55°44'46.7"N; 37°38'17.2"E) was collected in the center of the city of Moscow near the Big Ustinskiy Bridge where the traffic is high. The sample 2 (55°43'14.0"N; 37°39'24.3"E) from Krutitskaia bank and the sample 3 (55°41'12.4"N; 37°42'53.9"E) from Pechatniki park reflect the situation in the industrial zone. The sampling site 2 was chosen in proximity to the Paveletskiy railroad station. The sampling point 4 (55°38'59.1"N; 37°40'35.4"E) is located a few kilometers downstream from the discharge of the wastewater treatment plant.

All samples were collected in the afternoon to ensure similar environmental conditions (e.g. temperature and humidity). The water samples were collected using 1 L glass bottles and methanol was added to prevent the target substances adsorption on the bottles' glass walls. Only one sample was collected from each site. The samples were transported to the laboratory on the same day and were stored at 4 °C until extraction.

### 2.3. Sample extraction

The extraction procedure of all samples was conducted at the next day after sampling. Polydimethylsiloxane (PDMS) rods were used for extraction of the target substances. A method was developed and verified by the authors (Montero et al., 2004), was proved as efficient, simple, inexpensive approach and presents good precision for organic contaminants extraction from water. In terms of extraction efficiency and accuracy characteristics the use of the PDMS rods is comparable to the stir bar sorptive extraction (SBSE), which is in routine use (Popp and Paschke, 1997; Paschke et al., 2007; Van Pinxteren et al., 2010).

A silicone elastomer (O.D. 2 mm) was cut in 2-cm-long pieces. Prior the first use, the silicon rods were conditioned by placing into a flask containing 100 ml of methanol/dichloromethane mixture (1:1) and were sonicated for 10 min. This procedure was repeated with the fresh solvent mixture, followed by drying step using a lint-free tissue. The rods were then exposed to heat overnight at 250 °C in a nitrogen stream of 30 ml min<sup>-1</sup>. The silicon rods were then stored in the brown glass bottle until the extraction procedure.

The water samples were brought to normal temperature before extraction. The extraction procedure was previously described in detail (Paschke et al., 2007). In brief, extraction was conducted in the 500 ml triple-neck round-bottom glass flasks. The walls of each flask were rinsed with methanol and 500 ml of water sample was placed directly in the flask. Three silicon rods were put into each water sample as shown in Fig. 2 in Supplementary materials. Extraction flasks with water samples were then horizontally shaken (KS15A control, Edmund Bühler GmbH, Hechingen, Germany) at 100 min<sup>-1</sup> for 24 h. After extraction silicon rods were dried using a lint-free tissues, put into 1.5 ml vials and stored in the freezer until analysis.

### 2.4. Instrumental analysis

The silicon rods analysis was performed on an Agilent system (Agilent Technologies, Palo Alto, CA, USA) coupled to a Gerstel TDS A thermo desorption device and mass selective detector (5973 network MSD detector, Agilent); see Montero et al. (Montero et al., 2004) for details. The conditions for the thermo desorption system were as follows: desorption temperature 300 °C; desorption time 10 min and helium flow rate 50 ml min<sup>-1</sup> (solvent vent mode). The target compounds were determined on HP-5 (5% phenyl 95% methylsiloxane) capillary column (60 m × 250 µm i.d., 0.25 µm film thickness). The GC oven temperature program started from 60 °C (5 min) to 180 °C at 15 °C/min, to 220 °C at 2 °C/min and to 300 °C at

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