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Hydrological and environmental conditions as key drivers for spatial and seasonal changes in PCDD/PCDF concentrations, transport and deposition along urban cascade reservoirs

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HIGHLIGHTS

- ▶ We investigated the drivers for PCDDs/PCDFs transport and deposition along an urban river.
- ▶ The influence of environmental conditions on PCDDs/PCDFs, WHO-TEQ was demonstrated.
- ▶ The violent weather conditions additionally affected the final PCDDs/PCDFs concentration.

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ABSTRACT

To investigate the drivers for transport and deposition of 17 2,3,7,8-substituted PCDDs/PCDFs along an urban river, water samples from five reservoirs located along the river course were collected in January and July 2008. The concentrations of 17 congeners of PCDD/PCDF were determined and compared to environmental – physical, chemical and biological – conditions.

The obtained data revealed that the concentration of the sum of toxic PCDDs/PCDFs in water samples differ between reservoirs as well as between seasons, ranging from 12.04 pg L^{-1} in UP (first in the cascade) to 1327.94 pg L^{-1} in PR (last in the cascade) during winter of 2008; and from 34.94 pg L^{-1} in UP to 1352.50 pg L^{-1} in TR (next to last) in summer 2008. In comparison, water samples collected from the river had a concentration several times lower at the first two sites (sites no. 1 and 4) and no detectable values at the last three stations (sites no. 7, 8, 10).

The obtained data demonstrated strong or moderate correlations between the sum of 17 PCDDs/PCDFs and TEQ in reservoir water samples and physical, chemical and biological conditions, such as: Mg^{2+} (R = 0.82; R = 0.80, respectively), SO_4^{2-} (R = 0.80; R = 0.80, respectively), K^+ (R = 0.80; R = 0.80, respectively), Ca^{2+} (R = 0.67, R = 0.70, respectively), OSM (R = 0.63, R = 0.70, respectively). In addition, the positive strong correlation between TEQ concentrations and the water temperature (R = 0.63) and chlorophyll *a* content (R = 0.90) was noted. The violent weather conditions occurred during the research season with periods of intensive storm events (up to 32 mm in mid July), and thus the increased river flow velocity (up to 0.45 $m^3 s^{-1}$) could have a direct and indirect influence on PCDDs/PCDFs concentration through changes in the sedimentation/resuspension ratio and consequently in transport, deposition and degradation processes along the river/reservoirs.

1. Introduction

Rapid development of urban areas leads to changes in stream hydrology and geomorphology, which result in accelerated fluxes of matter, nutrient and organic pollutants from atmospheric deposition, urban runoff, industry, sewage treatment plants and combined sanitary overflows (Walker et al., 1999; Foster et al., 2000; Im et al., 2002; Moore et al., 2002; Jartun et al., 2008). It is estimated that each year more than 30 000 chemicals in quantities of more than 1 tone each are produced and handled in Europe alone (Brink et al., 2003). In this situation, the urban water ecosystems are commonly considered and used as receivers of pollutants and organic matter. The example is the Sokolowka River situated in

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the city of Lodz (800 thousands inhabitants) – the second biggest city in Poland. The city's water resources management is driven by its location on the watershed divide between the two major rivers in Poland: Vistula and Oder, determining the convey of water by 18 small rivers towards its outskirts. The water outflow is accelerated by channelization and conversion of most of the rivers into a combined sewerage and storm-water system in the early years of the 20th century. The dense development of the city also led to the reduced ability of the landscape to retain water. In consequence the above processes led to the washing out of organic and mineral matter and associated pollutants from the urban catchment during intensive rains. The subsequent increased flow and high hydraulic stress in aquatic ecosystems determine the further transport of matter and pollutants along urban water system.

The urban negative impacts on the river may be diminished by anthropogenic retention through construction of reservoirs, which create an efficient trap for sediments, nutrients and pollutants especially when interlinked in a cascade (Wagner and Zalewski, 2009, 2011). The decrease in the flow velocity and the increase of flocculent settling in such small reservoirs create perfect conditions for sedimentation and deposition of pollutants, such as PCDDs/PCDFs, which are strongly associated with organic particulates and in this form may be transported and deposited along the river–reservoir system (Krishnappan and Marsalek, 2002).

This paper provides data demonstrating (1) the concentration of 17 2,3,7,8-substituted PCDD/PCDF congeners in the urban river and its cascade reservoirs, (2) identification of sources affecting the obtained levels and (3) spatial and seasonal distribution of the analyzed contaminants with respect to hydrological dynamics (rain intensity, flow velocity) and environmental – physical, chemical and biological – conditions.

2. Materials and methods

2.1. Study area

The Sokolowka River (drainage area of 45.4 km^2) represents a highly urbanized and industrialized catchment contaminated with heavy metals and organic compounds due to sewage and storm-water disposal. The river length from the spring to the estuary is 13.3 km, 13.0 km – within the territory of the City of Lodz. The main river-bed was channelized by concrete slabs, to straighten the course and deepen the bed for the purpose of storm water detention (Jokiel and Maksymiuk, 2002; Biezanowski, 2003; Kujawa and Kujawa, 2003; Wagner and Zalewski, 2009).

Five reservoirs selected for the analysis located along the Sokolowka River (Fig. 1) differ from each other in their age, size, theoretical water residence time, light intensity and inflow. All of them can be regarded as small, riverine reservoirs, with short water retention time (Table 1).

2.1.1. The Upper Pond (UP)

UP – situated in the Adam Mickiewicz Park in the vicinity of a large housing development, has the surface area of 16 400 m^2 and capacity of 22 500 m^3. The average water retention time is 9 d. The age of the reservoir is estimated at more than 100 years (Jokiel and Maksymiuk, 2002; Biezanowski, 2003; Kujawa and Kujawa, 2003; Wagner and Zalewski, 2009).

2.1.2. The Lower Pond (LP)

LP – also situated in the Adam Mickiewicz Park. The pond covers the area of 11 000 m^2, its capacity is 11 100 m^3 and the average water retention time – 4 d. The age of this reservoir, similarly to the aforementioned one, is more than 100 years (Jokiel and Maksymiuk, 2002; Biezanowski, 2003; Kujawa and Kujawa, 2003; Wagner and Zalewski, 2009).

2.1.3. The Zgierska Reservoir (ZR)

Located in the estate area, ZR was build in 2003 in a trough of an old fish pond (called Chachuły Pond) as the first element of the Sokolowka River valley renaturisation (Wagner and Zalewski, 2009, 2011). The surface area of ZR is 18 600 m^2, capacity 24 000 m^3, and the mean water retention time 8 d (Jokiel and Maksymiuk, 2002; Biezanowski, 2003; Kujawa and Kujawa, 2003; Wagner and Zalewski, 2009).

The nearest catchment area, as well as the littoral zone of the reservoir, has been planted with crops and aquatic plants used for purification of inflowing storm waters and roads runoff. Moreover, the outlets of storm-water canals were equipped with separators and sedimentation ponds for the reduction of organic chemical compounds.

2.1.4. The Teresa Reservoir (TR)

TR is also newly constructed pond situated in the estate area in a trough of the old Kondracki Pond. The reservoir was built laterally on a right riverbank. The surface area is 4000 m^2 with the capacity of 4100 m^3 (Jokiel and Maksymiuk, 2002; Biezanowski, 2003; Kujawa and Kujawa, 2003; Wagner and Zalewski, 2009).

2.1.5. The Pabianka Reservoir (PR)

PR is placed on the outskirts of the city, in the middle section of the river valley which has maintained a semi natural character. Additionally, this reservoir is a recipient of waters from the Sokolowkas's tributary – the Brzoza River (Fig. 1), which is also a storm water receiver. The surface area of PR is 15 000 m^2, the capacity – 20 000 m^3, the average water retention time – 3 d (Jokiel and Maksymiuk, 2002; Biezanowski, 2003; Kujawa and Kujawa, 2003; Wagner and Zalewski, 2009).

2.1.6. The river water samples

Apart from reservoirs, water samples were also collected directly from the river. All collection sites are depicted in Fig. 1.

2.2. Sampling

Ten water samples of 5 L were collected twice in 2008: during the winter (28.01.2008 – only samples from the reservoirs) and summer season (23.07.2008 and 24.07.2008 – samples from the reservoirs and the river, respectively), using 5 L Teflon jars. The sampling sites in the river and reservoirs are depicted in Fig. 1. After collection, samples were directly transported to the laboratory where they were extracted and purified for 17 2,3,7,8-substituted PCDDs/PCDFs.

For the assessment of environmental conditions, water samples were collected twice in January and three times in July, in order to measure Total Phosphorus (TP), Total Nitrogen (TN), Total Suspended Matter (TSM), Organic Suspended Matter (OSM), Mineral Suspended Matter (MSM), ions (anions: Cl^-, Br^-, NO_3^-, PO_4^{2-}, SO_4^{2-}, F^-, and cations: K^+, Mg^{2+}, Ca^{2+} Na^+, NH_4^+) and chlorophyll *a* content. During the sampling, water temperature, pH, conductivity and oxygen content were measured.

2.3. Extraction and clean-up

Water samples of 5 L were spiked with the isotopically ^{13}C-labeled PCDD/PCDF standards (Cambridge Isotopes Laboratories, USA). Extraction was operated by shaking the samples with an addition of 300 mL of methylene chloride for 2 min with periodic venting. After that samples were allowed to separate the organic layer from the aqueous phase for minimum 10 min. The methylene