The impact of point sources of pollution on the transport of micropollutants along the river continuum

Magdalena Urbaniak, Edyta Kiedrzyńska, Marcin Kiedrzyński, Michał Mendra and Adam Grochowalski

ABSTRACT

The main objectives of the presented study were to quantify the transfer of polychlorinated dibenzo-*p*-dioxins (PCDDs)/polychlorinated dibenzofurans (PCDFs) (polychlorinated dibenzo-*p*-dioxins/polychlorinated dibenzofurans) and dioxin-like polychlorinated biphenyls (dl-PCBs) along the river continuum and to evaluate the impact of wastewater treatment plants (WTPs) located in the catchment on the river quality. The samples were collected during the spring (high water flow) and summer season (serene water flow) of 2010. The river samples were collected from five stations located along the lowland Pilica River, including two stations situated above and below the Sulejow Reservoir. At the same time, samples from the outlets of 17 WTPs were collected. As evidenced by the results, the largest WTPs discharged up to 59.09 μg toxic equivalent (TEQ) of PCDDs/PCDFs and dl-PCBs per day during high flow events and up to 26.03 μg TEQ during serene water flows. During the same time, the smallest WTPs released on average 0.81 and 0.70 μg TEQ day^{-1}, respectively. The obtained results have also demonstrated an increase in the TEQ concentration along the Pilica River continuum (from 4.75 to 6.25 pg TEQ L^{-1}). The exception were samples collected below the dam where 63% TEQ reduction was observed compared to samples collected above the reservoir.

Key words | PCDDs/PCDFs and dl-PCBs, point sources of pollution, river continuum, wastewater treatment plants

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INTRODUCTION

Human activities in the catchment have direct effects on the contamination rates in river ecosystems. One of the major threats to surface water quality are point sources of contamination derived directly or indirectly from human activities and/or industrial practices, and these are responsible for up to 50% of the current high trophic level in water bodies (Magnuszewski *et al.* 2005).

Among various substances delivered through point pollution sources, the persistent organic pollutants (POPs), including polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and dioxin-like polychlorinated biphenyls (dl-PCBs), pose a serious threat to aquatic ecosystems. Chemically, these compounds belong to a group of halogenated aromatic hydrocarbons and are characterised by high toxicity. Moreover, their long life in the environment and their ability to accumulate in soils and sediments, and in aquatic and terrestrial food chains make them a long-term threat to the environment and humans. They have been recorded around the world in many components of the aquatic environment (Fox *et al.* 1983; Crunkilton & DeVita 1997; Huntley *et al.* 1997; Camusso *et al.* 2000; Kannan *et al.* 2001, 2003; Hilscherova *et al.* 2003; Koh *et al.* 2004; Sapozhnikova *et al.* 2005; Urbaniak *et al.* 2010b). They have also been recorded in Polish rivers, reservoirs and lakes (Witt 1995; Protasowicki *et al.* 1999; Witt & Trost 1999; Wolska *et al.* 1999, 2003; Kannan *et al.* 2003; Kowalewska *et al.* 2003; Rodziewicz *et al.* 2004; Konieczka *et al.* 2005; Urbaniak *et al.* 2008, 2009a, b, 2010a, b, 2012a, b).

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The global studies have also shown that it is possible to limit the amount of PCDDs/PCDFs and dl-PCBs in the environment and thus diminish their transfer along the river continuum by reducing their emission from point pollution sources (e.g. municipal sewage and industrial wastewater, combined sewer overflows) (Fiedler 1996; Dyke *et al.* 1997; Huntley *et al.* 1997) and by allocating them in unavailable pools (Zalewski 2011). This indicates the need for further analysis in order to determine the amount and the range of pollution, and to identify the most important point sources of pollution ('red points') throughout the catchment. Therefore, as the first step towards the reduction of micropollutants concentrations and their transport along the river, we undertook research in order to analyse the current pollution state of the Pilica River and to identify the possible point sources of pollution in its catchment.

The two main objectives of this study were as follows: (1) to quantify the transfer of PCDDs/PCDFs and dl-PCBs along the Pilica River continuum; and (2) to evaluate the impact of the wastewater treatment plants (WTPs) located in its catchment on the river quality. In particular, the concentrations, toxicity (measured as toxic equivalent – TEQ) and pattern of individual congeners of PCDDs, PCDFs and dl-PCBs were analysed in the river and at the outlets from WTPs in the periods of high and serene water stages. The obtained results were further used to calculate the loads of analysed pollutants discharged through the WTP outlets and transported by the Pilica River.

THE STUDY AREA

The Pilica River (Figure 1) is one of the most significant tributaries and the longest left-hand tributary of the Vistula River, which flows into the Vistula at 457 km of the river course. The source of the Pilica River is located in the town of Pilica at an altitude of about 350 m above sea level. The overall length of the Pilica River is 342 km with a total catchment area of 9,258 km^2.

The Pilica River catchment has a diverse morphological structure and the land cover is diverse. This results in varied runoff from the catchment, which ranges from 3 to 6 $L^{-1}\,s^{-1}\,km^2$. The river bottom is mostly sandy, but in some parts of the river with a greater decline and an increased water velocity, the bottom is firm, built of pebbles and gravel. In places with a slow water flow, the bottom is muddy. The river bed is not regulated. The banks are natural with a diversified line.

The river is fed by 10 left tributaries (Dyga, Krztynia, Bialka, Luciaza, Wolborka, Gac, Rokitna, Lubjanka, Mogielanka, Dylowka) and nine right tributaries (Udorka, Uniejowka, Zwlecza, Czarna Wloszczowska, Czarna Konecka, Slomianka, Cetenka, Drzewiczka, Pierzchnia).

Eleven towns are located along the river length (Szczekociny, Koniecpol, Przedborz, Sulejow, Tomaszow Mazowiecki, Piotrkow Trybunalski, Spala, Inowlodz, Nowe Miasto, Wysmierzyce, Bialobrzegi and Warka), including the biggest ones: Tomaszow Mazowiecki (Tomaszow Maz.) – with 65,375 inhabitants and strong textile, ceramics, machinery, metal and leather industry, Nowe Miasto – with 3885 inhabitants, Bialobrzegi – with 7328 inhabitants and Warka with 11,035 inhabitants and strong brewery and fruit and vegetable industry.

Agriculture is present in over 60% of the Pilica catchment area (Ambrożewski 1996) and together with point sources of pollution results in an increased supply of nutrients, micropollutants and other contaminants into the river and the Sulejow Reservoir (Urbaniak *et al.* 2012a).

The Sulejow Reservoir is the largest hydrotechnical facility on the Pilica River, formed by damming up the Pilica River in Smardzewice in the middle reaches of the Pilica River (on 137 km of the river length). The maximum length of the Sulejow Reservoir is 15.5 km and the maximum width is 2.1 km. At the maximum capacity ($75 \times 10^6\,m^3$), the reservoir covers 22 km^2, with average and maximum depths of 3.3 and 11 m, respectively. The reservoir was constructed in 1973 as an emergency source of drinking water for the city of Lodz (800,000 inhabitants). The reservoir has also been used as a recreational area for sport activities, such as swimming, sailing and canoeing (Ambrożewski 1996).

MATERIAL AND METHODS

Hydrology of the Pilica River

Hydrological observations were conducted at six gauge stations located along the Pilica River continuum

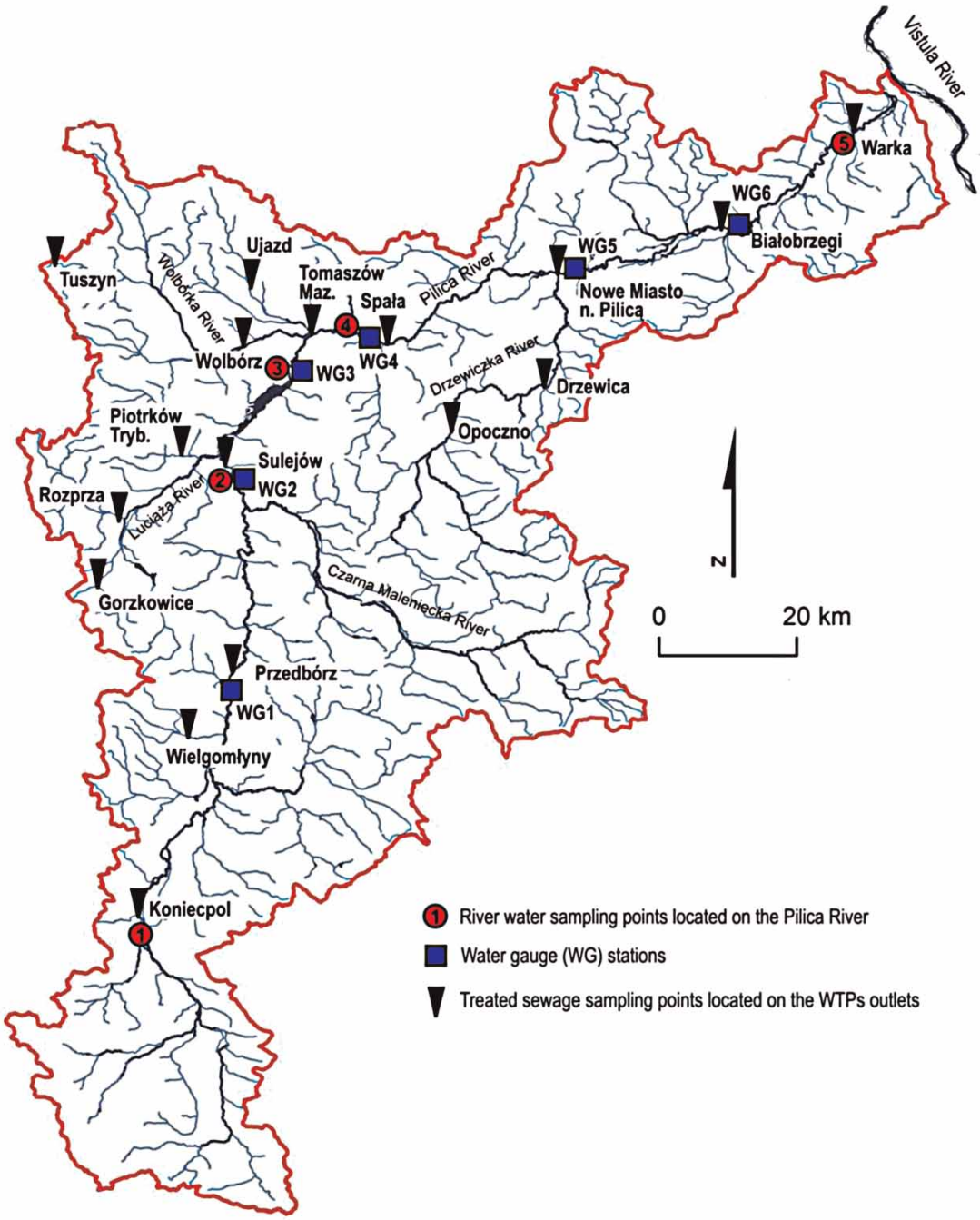

Figure 1 | Location of river water and treated sewage sampling points in the Pilica River catchment.

from the sources, at station 1 (WG 1), to the outlet into the Vistula River, at WG 6 (Table 1). Hydrological analyses at all stations were based on daily measurements of water levels in the river and converted to flow rates.

Pilica River – river water sampling

River samples were collected twice, in spring on 19–20 May 2010 (high water flow) and in summer on 26–27 September 2010 (serene water flow). The samples were collected from

Table 1 | Discharges and outflows of the Pilica River at different WG stations located along the river continuum

WG station	WG station name	River km-from the estuary	Drainage area [km^2]	Discharge [m^3 s^{-1}]			Outflow [mln m^3 day^{-1}]			Total outflow[a] [mln m^3 year^{-1}]
				Average[a]	High flow	Serene flow	Average[a]	High flow	Serene flow	
WG 1	Przedborz	201.2	2,545.2	29.4	154	24.1	2.5	13.3	2.1	929.5
WG 2	Sulejow[b]	161.3	3,935.7	53.2	145	38.3	4.6	12.5	3.3	1,683.0
WG 3	Smardzewice[c]	136.3	4,933.2	48.6	136	41.4	4.2	11.8	3.6	1,536.8
WG 4	Spala	119.4	5,967.2	51.1	155	50.7	4.4	13.4	4.4	1,615.8
WG 5	Nowe Miasto	78.8	6,712.3	61.4	140	50.8	5.3	12.1	4.5	1,941.5
WG 6	Bialobrzegi	45.3	8,656	70.1	120	54.8	6.1	10.4	4.7	2,216.0

[a]Average value for the period of 19 May 2010–19 May 2011.
[b]Inflow into the Sulejow Reservoir.
[c]Outflow from the Sulejow Reservoir.

five stations located along the lowland Pilica River (1-Koniecpol; 2-Sulejow; 3-Tomaszow Maz., 4-Spala, 5-Warka), including two stations situated above (no. 2 – Sulejow) and below (no. 3 – Tomaszow Maz.) the Sulejow Reservoir (Figure 1). River samples were collected 100–150 m above the WTP outlets into the Pilica River in order to obtain representative, well-mixed samples, which reflect the river pollution above WTP outlets.

The samples were collected in 5 L amber containers and transported to the laboratory in a car fridge at a temperature of 4 °C.

WTPs – treated wastewater sampling

On the same days (19–20 May 2010 and 26–27 September 2010), treated sewage samples of 5 L were collected from the outlets of 17 WTPs (divided into three size categories: class I: 0–1999; class II: 2000–9999, class IV: 15,000–99,999 of the population equivalent; Figure 1).

Samples were put into amber containers and transported to the laboratory in a car fridge at a temperature of 4 °C.

Samples analysis

All analytical work was performed in the accredited Laboratory for Trace Organic Analyses at the Cracow University of Technology, Cracow, Poland. The laboratory is involved in the Circuit Interlaboratories for Dioxins organised by the Interuniversity Consortium 'Chemistry for the Environment' in collaboration with LabService Analytica S.r.l.

The applied analytical methods were properly validated and the laboratory successfully passed the accreditation procedure. The accreditation granted by the Polish Centre for Accreditation No. AB 749 is valid until August 2014.

Water samples of 2 L were spiked with 60 pg of 17 ^{13}C-labelled PCDDs/PCDFs and 100 pg of 12 ^{13}C-labelled dl-PCBs (NK-LCS-G and WP-LCS respectively, obtained from Wellington Laboratories), and liquid/liquid extracted with toluene. Toluene extract after rotary evaporation to ca. 20 mL was cleaned-up as follows: concentrated extract was placed in the bottom sealed polyethylene semipermeable membrane tube of 80 μm wall thickness and cleaned up overnight with 100 mL hexane (the outer solvent). The hexane dialysate was cleaned up on a silica gel column coated with 44% sulphuric acid and alumina according to Environmental Protection Agency (EPA) 1613 standard (US EPA Method 1613 1994). The final extract was spiked with 20 μL of precision and recovery solution (EPA1613 ISS mix of 200 ng/mL of $^{13}C_{12}$-1,2,3,4-TCDD and $^{13}C_{12}$-1,2,3,7,8,9-HxCDD) prepared in nonane and evaporated to ca. 20 μL in a gentle stream of nitrogen.

Determination of 17 PCDDs/PCDFs and 12 dl-PCBs was performed by isotope dilution gas chromatography-tandem mass spectrometry (ID-GC/MS-MS) on a Thermo Scientific GCQ-1100/Trace2000 system equipped with Xcalibur data acquisition and analysis software. Separation was performed on a 30 m × 0.25 mm i.d. DB5MS J&W capillary column of 25 μm film and DB17 30 m × 0.25 mm i.d. DB5MS J&W

capillary column of 25 μm film. A sample of 2.5 μL volume was injected into a split/splitless injector at 260 °C. The GC oven was programmed as follows: an initial temperature of 130 °C held for 3 min, then a temperature ramp of 50 °C/min to 180 °C, then another temperature ramp of 2 °C/min to 270 °C. Finally, the temperature ramp was 20 °C/min to 300 °C and held for 5 min.

The resulting uncertainty was expressed as extended measurement uncertainty for $k = 2$ at the confidence level of 95%.

TEQ calculation

In order to evaluate the PCDD/PCDF and dl-PCB related toxicity of water and treated wastewater samples, the TEQ was used. The TEQ is an acronym for 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD) equivalents expressing the net toxicity of a complex mixture of different PCDDs/PCDFs and dl-PCBs. Each of the individual seven congeners of PCDDs, 10 congeners of PCDFs and 12 congeners of dl-PCBs has been assigned a toxic equivalency factor (TEF) based on its toxicity relative to that of 2,3,7,8-TCDD, which is universally assigned a TEF of 1. Multiplication of the concentration of PCDDs/PCDFs and dl-PCBs by its assigned TEF gives its concentration in terms of World Health Organization TEQ (WHO-TEQ) calculated for all PCDD/PCDF and dl-PCB congeners (Van den Berg *et al.* 2006).

Analysis of PCDD/PCDF and dl-PCB loads

In order to calculate the daily loads of PCDDs/PCDFs and dl-PCBs from WTP outlets, the daily average outflows of treated wastewater ($m^3\ day^{-1}$) were multiplied by total and TEQ concentrations ($pg\ L^{-1}$). The annual loads from WTPs were calculated using the annual WTP outflow and average total and TEQ values measured at the WTP outlets.

The annual loads for total PCDDs/PCDFs and dl-PCBs, and TEQ were calculated by multiplying the average total and TEQ concentrations by the annual Pilica River outflow measured at water gauge (WG) stations.

Statistical analysis

All data were statistically analysed (Statistica 8.0, StatSoft, Inc. 1984–2008). A Mann–Whitney *U* test was used to compare the obtained results. In order to test the correlation between the average pattern of PCDDs, PCDFs and dl-PCBs in treated wastewater and Pilica River samples, the Spearman's rank correlation coefficient was used. In both cases, the statements of significance were based on the probability level of $p \leq 0.05$.

RESULTS

Hydrological conditions along the Pilica River continuum

Hydrological analysis showed that the average discharge in the Pilica River continuum increased from 29.4 $m^3\ s^{-1}$ at WG 1 to 70 $m^3\ s^{-1}$ at WG 6 for the period of 19 May 2010–19 May 2011. An exception was WG 3 (outflow from the Sulejow Reservoir at the dam), where average discharge was lower compared to WG 2, due to retention by the Sulejow Reservoir (Table 2).

Table 2 | Differences in the total PCDDs/PCDFs and dl-PCBs and TEQ concentrations in water samples along the Pilica River continuum at high and serene water stages

	Total concentration [pg L^{-1}]		TEQ concentration [pg TEQ L^{-1}]			
Sampling point located at the Pilica River	High flow	Serene flow	High flow	Serene flow	Decrease in total concentration between high and serene water flow [%]	Decrease in TEQ concentration between high and serene water flow [%]
1 (Koniecpol)	90.56	76.49	4.75	5.77	16	*– 21*
2 (Sulejow)	110.64	51.08	6.59	3.56	54	46
3 (Tomaszow Maz.)[a]	87.48	38.70	2.14	2.37	56	*– 11*
4 (Spala)	150.95	111.60	3.50	4.06	26	*– 16*
5 (Warka)	74.25	100.10	6.26	3.85	*– 35*	38

[a]Measured 5 km above Tomaszow Maz.

Furthermore, the analysis showed that during the first water sampling on 19–20 May 2010 (flood), discharges at different stations were more than five times (WG 1) to almost two times (WG 6) higher compared to the average annual flow (Table 1). Discharges on 26–27 September 2010 were significantly lower than the annual average. The volume of river discharges was reflected in the outflows. The total annual outflow in the Pilica River in the first transect of the river (WG 1) was 929.5 mln $m^3\,yr^{-1}$, and in the last transect – 2,216 mln $m^3\,yr^{-1}$ at station WG6 (Table 1).

Changes in the total PCDDs/PCDFs and dl-PCBs and TEQ concentrations along the Pilica River continuum

The total concentrations of 2,3,7,8-substituted PCDDs/PCDFs and dl-PCBs are presented in Table 2 and show that the river water samples were heterogeneous with values ranging from 74.25 pg L^{-1} at the last sampling point (no. 5) to 150.95 pg L^{-1} at the one before last (no. 4) during a high water flow observed for the period of spring flooding. Moreover, an increasing concentration of the sum of 17 toxic PCDDs/PCDFs and 12 dl-PCBs was observed between the first two sampling points (1 and 2) and a rapid decrease at the sampling point no. 3 located below the Sulejow Reservoir (Table 2).

The samples collected at the serene water flow during the summer season were characterised by much lower concentrations ranging from 38.70 pg L^{-1} in the middle sampling point (no. 3) up to 111.60 pg L^{-1} at position no. 4 (Table 2; Figure 1). The exception was the last sampling point where higher total concentration was observed during the serene water period (100.10 pg L^{-1}) compared to the high water period (74.25 pg L^{-1}). For both samples collected during the high water level and at the serene flow, the lowest total concentration of PCDDs/PCDFs and dl-PCBs was observed at sampling point no. 3 located below the Sulejow Reservoir (87.48 and 38.70 pg L^{-1}, respectively). The next site – no. 4 – was characterised by the highest total concentration of the analysed compounds along the Pilica River continuum (150.95 and 111.60 pg L^{-1} at high and serene water flow, respectively). The average difference of 37% was observed in the total concentration of toxic PCDDs/PCDFs and dl-PCBs between samples collected at a high and serene water level. The highest decrease (56%) in the total amount of the analysed compounds between the high and low water periods was noted for samples from site no. 3, a high decrease (54%) was also noted for samples collected at site no. 2; 26 and 15% reduction was found for samples from sites no. 4 and 1, respectively. The exception was site no. 5 where 35% increase in the total PCDDs/PCDFs and dl-PCBs was observed.

The obtained results from the high water flow also demonstrate the increase in the TEQ concentration of PCDDs/PCDFs and dl-PCBs between the first two collection sites (4.75 and 6.26 pg TEQ L^{-1}, respectively). The samples collected below the dam reservoir (no. 3) were characterised by 63% reduction of TEQ concentration compared to samples collected above the reservoir (no. 2). In the case of samples collected at the serene water flow, 33% reduction was observed between the 2nd and 3rd sampling point (Table 2). Further increase in the TEQ concentration at the last two sampling points (3.50 and 6.26 pg TEQ L^{-1} at site no. 4 and 5, respectively) recorded during the high water level may be related to the high input of TEQ discharged from WTPs in Tomaszow Maz. (59.09 μg day^{-1}), Nowe Miasto (4.00 μg day^{-1}) and Bialobrzegi (not determined), as well as to the surface runoff from the catchment. The opposite results were obtained in the case of samples collected at the serene water flow when 5% decrease in the TEQ concentration was observed between the fourth and fifth sampling points (Table 2).

Total PCDDs/PCDFs and dl-PCBs and TEQ concentrations in treated sewage

The results of the total 2,3,7,8-substituted PCDD/PCDF and dl-PCB concentration in treated sewage are presented in Table 3 and Figure 2. The highest total concentration of 732.79 pg L^{-1} was recorded for class I WTP in Wolborz during the low water period. The lowest concentration of 32.30 pg L^{-1} was also recorded during the serene water stage and was obtained for class II WTP in Tuszyn (Table 3 and Figure 2).

The average total concentration for WTPs of Class I was 81.96 and 216.92 pg L^{-1} during the high and serene water stage, respectively. The average total concentrations for WTPs of Class II and IV were 80.47 and 74.30 pg L^{-1}; and

Table 3 | Differences in total PCDDs/PCDFs and dl-PCBs and TEQ concentrations in samples collected at the outlets from WTPs at high and serene water flows

				Total concentration [pg L^{-1}]		Total concentration load [μg day^{-1}]		TEQ concentration [pg TEQ L^{-1}]		TEQ concentration load [μg day^{-1}]	
WTP	WTP class	Population equivalent of WTP	Daily average treated wastewater outflow [m^3 day^{-1}]	High flow	Serene flow	High flow	Serene flow	High flow	Serene flow	High flow	Serene flow
Spala	I	350	130	129.94	59.90	16.89	7.79	5.32	2.93	0.69	0.38
Rozprza	I	500	107	57.82	62.79	6.19	6.72	4.39	1.80	0.47	0.19
Koniecpol	I	600	100	73.93	107.48	7.39	10.75	3.59	5.49	0.36	0.55
Gorzkowice	I	700	224	53.52	326.70	11.99	73.18	3.60	4.67	0.81	1.05
Wolborz	I	800	241	100.94	732.79	24.33	176.60	5.08	5.36	1.22	1.29
Wielgomłyny	I	1,000	200	71.05	79.10	14.21	15.82	4.49	5.05	0.9	1.01
Ujazd	I	1,500	300	86.56	149.67	25.97	44.90	4.18	1.38	1.25	0.41
Average		778.6	186	81.97	216.92	15.28	47.97	4.38	3.81	0.81	0.7
Przedborz	II	2,000	373	n.c.	114.1	n.c.	42.56	n.c.	6.59	n.c.	2.46
Tuszyn	II	4,000	640	70.54	32.30	45.15	20.67	4.92	2.21	3.15	1.41
Drzewica	II	6,000	839	n.c.	92.30	n.c.	77.44	n.c.	4.41	n.c.	3.7
Sulejow	II	7,500	870	103.26	81.72	89.84	71.10	5.23	3.55	4.55	3.09
Nowe Miasto	II	2,583	1,000	67.63	51.10	67.63	51.10	4.00	3.09	4.00	3.09
Average		4,416.6	744.4	80.48	74.30	67.54	52.57	4.72	3.97	3.9	2.75
Białobrzegi	IV	58,400	1,500	n.c.	100.5	n.c.	150.75	n.c.	5.96	n.c.	8.94
Opoczno	IV	75,000	5,127	77.32	62.00	396.42	317.87	4.14	3.89	21.23	19.94
Warka	IV	99,000	9,900	66.46	65.00	657.95	643.50	2.51	2.30	24.85	22.77
Tomaszow Mazowiecki	IV	80,000	10,050	71.92	39.90	722.80	401.00	5.88	2.59	59.09	26.03
Piotrkow Trybunalski	IV	80,000	14,541	63.60	132.06	924.81	1,920.28	3.21	1.03	46.68	14.98
Average		78,480	8,223.6	69.83	79.89	675.5	686.68	3.94	3.15	37.96	18.53

n.c. – not collected due to too high water level.

69.82 and 137.06 pg L^{-1} at high and serene flow, respectively (Table 3 and Figure 2).

The daily load of total PCDDs/PCDFs and dl-PCBs into the Pilica River and its tributaries during the high water flow was in the range of 6.19 μg day^{-1} from class I WTP in Rozprza up to 924.81 μg day^{-1} for Class IV WTP in Piotrkow Trybunalski. The discharges of the analysed compounds during the period of serene flow were higher and ranged from 6.72 μg day^{-1} for class I WPT in Rozprza to 1,920.28 μg day^{-1} for class III WTP in Piotrkow Trybunalski (Table 3 and Figure 3).

The highest differences during the high and serene water flow in the total PCDD/PCDF and dl-PCB discharges were recorded for Class I WTPs where the average load was 15.28 and 47.97 μg day^{-1}, respectively. The loads from Class II and Class IV WTPs were more similar between the two sampling periods and amounted to 67.54 and 52.57 μg day^{-1} for class II WTPs; and 675.49 and 686.68 μg day^{-1} for Class IV WTPs at the high and serene water level, respectively (Table 3 and Figure 3). Despite the above described differences, the statistical analysis showed that there were no differences.

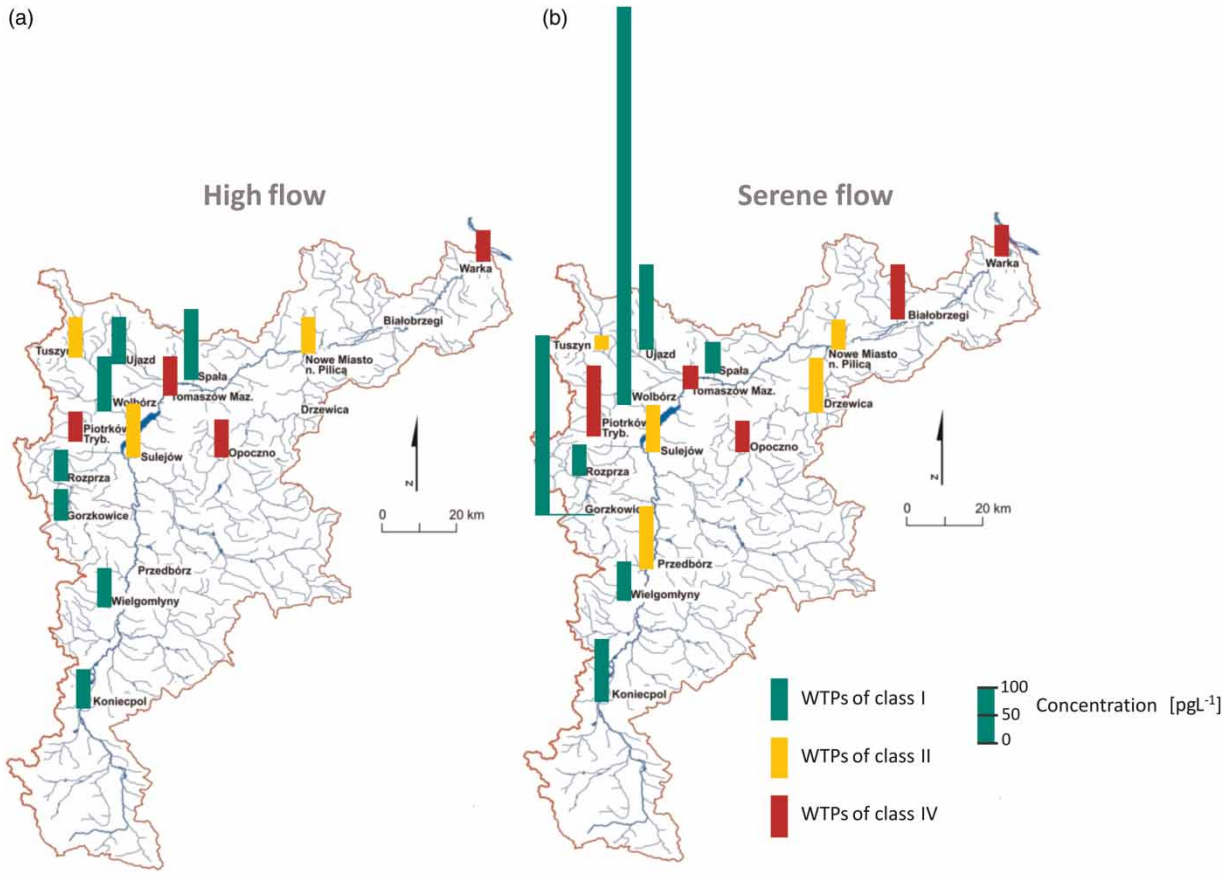

Figure 2 | Total concentration of toxic PCDDs/PCDFs and dl-PCBs collected from WTP outlets during high and serene water flows.

In the case of TEQ concentrations, the lowest value was recorded for WTP in Piotrkow Trybunalski (1.03 pg TEQ L^{-1}) and the highest TEQ concentration was recorded for WTP in Przedborz (6.59 pg TEQ L^{-1}). Both results were obtained at the low water flow (Table 3 and Figure 4).

The results of TEQ concentration showed also that the average values were higher for samples collected at the high water flow (4.38; 4.72 and 3.94 pg TEQ L^{-1} in WTPs of Class I, II and IV) compared to samples collected at the serene water stage (3.81 pg TEQ L^{-1}; 3.97 pg TEQ L^{-1}; 3.15 pg TEQ L^{-1} in WTPs of Class I, II and IV, respectively). Nevertheless, the statistical analysis showed no relevant differences between the two sampling periods.

The results from WTPs show the higher impact of the largest WTPs (Class IV), which have discharged up to 59.09 μg TEQ of total PCDDs/PCDFs and dl-PCBs per day during high flow events and up to 26.03 μg TEQ during serene water flows (Table 3 and Figure 5). During the same time, the smallest WTPs (Class I) released on average 0.81 and 0.70 μg TEQ of PCDDs/PCDFs and dl-PCBs per day, respectively (Table 3 and Figure 5). The average load of TEQ from WTPs of Class II was 3.90 and 2.75 μg TEQ day^{-1} during the high and serene water flow, respectively (Table 3 and Figure 5). The average load of TEQ from the largest WTPs of Class IV was 37.96 μg TEQ day^{-1} at the high water stage and 18.53 μg TEQ day^{-1} at the serene one (Table 3 and Figure 5). Similarly, the average higher TEQ concentrations for all 17 WTPs were recorded during the high water flow (average 4.34 pg TEQ L^{-1}) compared to samples collected during the relatively stable hydrological conditions (average 3.54 pg TEQ L^{-1}) (Table 3).

Comparison of PCDD, PCDF and dl-PCB congeners' pattern in treated wastewater and Pilica River samples

The results of differences in the pattern of PCDDs (the contribution in the total of 2,3,7,8-substituted PCDDs), PCDFs

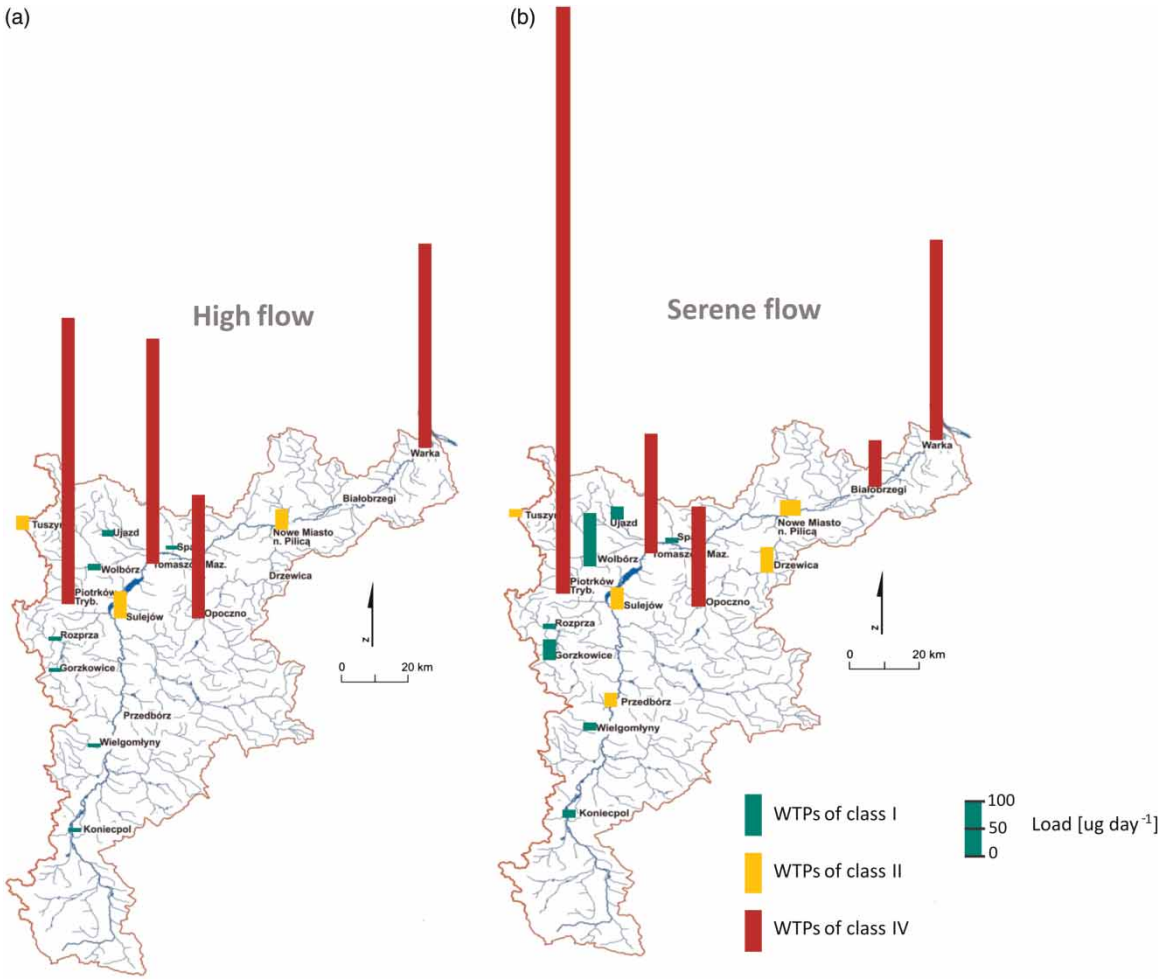

Figure 3 | Loads of the total PCDDs/PCDFs and dl-PCBs delivered to the Pilica River and its tributaries by WTP outlets during high and serene water flows.

(the contribution in the total of 2,3,7,8-substituted PCDFs) and dl-PCB congeners (the contribution in the total of dl-PCBs) along the Pilica River continuum and at the WTP outlets located in the Pilica River subcatchments are presented in Table 4. The correlation between the pattern of analysed compounds in river and treated wastewater samples are presented in Table 5.

The obtained results showed a similar PCDD pattern in river and treated wastewater samples with the elevated value for octachlorinated dibenzo-*p*-dioxin (OCDD) (up to 63%) and 1,2,3,4,7,8-HxCDD (up to 23%).

A similar situation was observed in the case of PCDFs with an almost homogeneous pattern for river and WTP samples with the contribution of individual congeners ranging from 2.38% for 1,2,3,7,8-PeCDF to 25.72% for 1,2,3,4,6,7,8-HpCDF. Lower contents (up to 10%) were recorded for TCDD, 1,2,3,7,8-PeCDF and 1,2,3,6,7,8-HxCDF. Higher percentages (up to 26%) were observed for higher chlorinated congeners (hepta- and octachlorinated dibenzofurans – HpCDFs and OCDF).

In the case of dl-PCBs, PCB-118 had the highest contribution – up to 35.38% – whereas other dl-PCB congeners ranged from 1.64 to 24.37%.

The obtained results demonstrated strong correlation between Pilica River samples and samples collected at the WTP outlets (up to 0.98; $p \leq 0.05$). The highest correlation was observed during the high water flow when only one correlation coefficient was not statistically significant. In the case of serene flow, there were higher differences between Spearman's rank correlation coefficients, which ranged

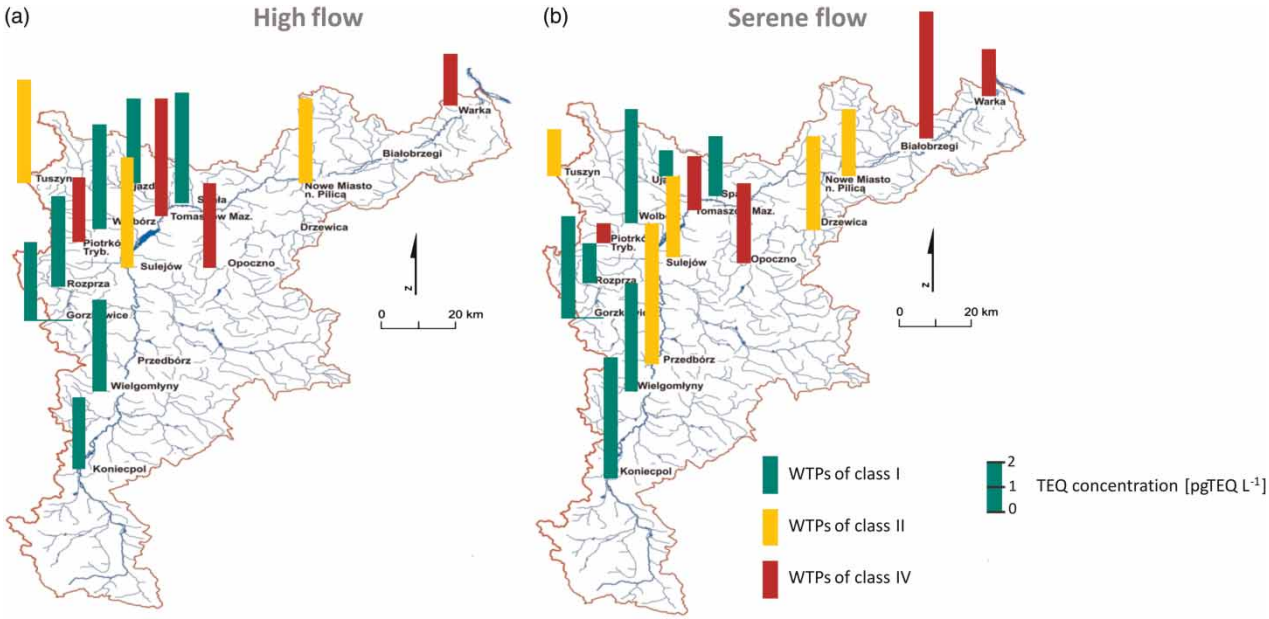

Figure 4 | TEQ concentrations of PCDDs/PCDFs and dl-PCBs in samples collected from WTP outlets during high and serene water flows.

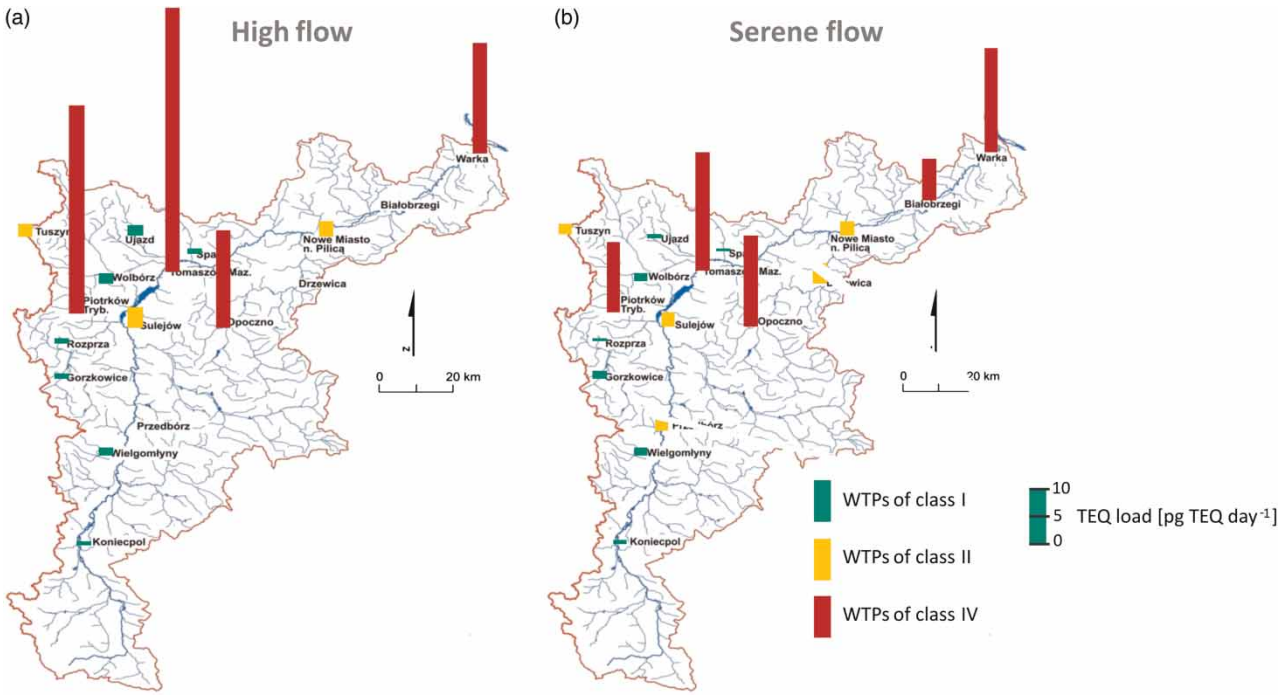

Figure 5 | Loads of TEQ concentrations delivered to the Pilica River and its tributaries by WTP outlets during high and serene water flows.

Table 4 | Variation in the average pattern of PCDDs (the contribution in the total 2,3,7,8-substituted PCDDs), PCDFs (the contribution in the total 2,3,7,8-substituted PCDFs) and dl-PCB congeners (the contribution in the total dl-PCBs) in the treated wastewater (average for all the studied WTPs from the given subcatchment located between studied river profiles) and in the Pilica River water samples

	High flow									Serene flow								
Congener	Monitoring profile in Koniecpol [%]	Treated wastewater from Koniecpol-Sulejow subcatchment [%]	Monitoring profile in Sulejow [%]	Treated wastewater from Sulejow-Tomaszów Maz. Subcatchment [%]	Monitoring profile in Tomaszow Maz. [%]	Treated wastewater from Tomaszow Maz –Spala subcatchment [%]	Monitoring profile in Spala [%]	Treated wastewater from Spala-Warka subcatchment [%]	Monitoring profile in Warka [%]	Monitoring profile in Koniecpol [%]	Treated wastewater from Koniecpol-Sulejow subcatchment [%]	Monitoring profile in Sulejow [%]	Treated wastewater from Sulejow-Tomaszów Maz. Subcatchment [%]	Monitoring profile in Tomaszow Maz. [%]	Treated wastewater from Tomaszow Maz–Spala subcatchment [%]	Monitoring profile in Spala [%]	Treated wastewater from Spala-Warka subcatchment [%]	Monitoring profile in Warka [%]
2378-TCDD	9.41	10.04	9.05	10.78	3.20	9.89	12.92	8.12	8.99	12.86	9.65	9.76	4.14	12.20	7.68	9.09	7.67	7.95
12378-PeCDD	13.99	13.21	12.79	12.93	3.40	13.84	13.70	10.62	12.45	13.79	11.32	11.63	4.75	14.63	9.59	9.09	10.78	9.09
123478-HxCDD	21.95	20.55	22.67	19.06	4.80	21.17	20.74	17.77	20.45	19.44	17.11	18.39	8.51	17.07	15.22	19.32	15.38	15.91
123678-HxCDD	9.89	10.07	11.96	9.66	3.10	10.52	9.20	8.26	12.37	11.01	11.98	9.57	4.39	9.76	7.77	19.32	12.34	7.95
123789-HxCDD	16.53	16.19	17.36	15.01	6.59	15.43	14.68	13.18	18.14	16.36	17.03	14.82	6.29	14.63	11.02	11.36	11.54	11.36
1234678-HpCDD	17.01	15.56	15.12	17.27	49.95	15.77	15.66	12.42	16.49	12.86	11.90	11.44	9.06	17.07	13.74	10.23	14.82	12.50
OCDD	11.22	14.37	11.05	15.30	28.97	13.38	13.11	11.65	11.13	13.68	21.00	24.39	62.85	14.63	34.98	21.59	27.48	35.23
2378-TCDF	5.53	4.80	6.06	7.35	4.59	4.96	5.29	5.31	4.70	6.24	5.39	11.34	6.20	3.51	5.28	18.84	10.56	5.12
12378-PeCDF	2.38	5.43	5.91	6.52	4.84	5.98	6.20	6.15	5.66	6.96	6.11	6.03	5.36	6.14	4.77	4.83	8.01	5.58
23478-PeCDF	10.30	8.52	9.89	10.01	13.93	10.82	10.34	10.78	8.48	10.52	9.57	14.92	9.01	8.77	11.38	7.73	12.44	9.30
123478-HxCDF	10.73	9.87	10.47	10.35	8.58	10.89	11.01	11.73	11.34	12.34	11.62	7.85	10.15	10.53	9.78	10.14	14.24	11.16
123678-HxCDF	9.92	8.45	8.31	9.36	7.82	8.79	8.39	8.72	8.65	8.60	10.03	9.07	8.38	7.89	7.81	6.28	10.39	7.91
234678-HxCDF	13.03	10.59	12.33	11.60	7.90	10.55	10.71	10.95	13.94	10.66	9.82	6.71	10.32	13.16	8.65	10.14	13.82	10.70
123789-HxCDF	10.09	8.88	9.19	9.79	7.48	10.32	10.16	10.40	9.97	9.74	8.72	6.80	8.36	9.65	8.54	8.21	18.24	9.30

(*continued*)

Table 4 | continued

Congener	High flow									Serene flow								
	Monitoring profile in Koniecpol [%]	Treated wastewater from Koniecpol-Sulejow subcatchment [%]	Monitoring profile in Sulejow [%]	Treated wastewater from Sulejow-Tomaszów Maz. Subcatchment [%]	Monitoring profile in Tomaszow Maz. [%]	Treated wastewater from Tomaszow Maz –Spala subcatchment [%]	Monitoring profile in Spala [%]	Treated wastewater from Spala-Warka subcatchment [%]	Monitoring profile in Warka [%]	Monitoring profile in Koniecpol [%]	Treated wastewater from Koniecpol-Sulejow subcatchment [%]	Monitoring profile in Sulejow [%]	Treated wastewater from Sulejow-Tomaszów Maz. Subcatchment [%]	Monitoring profile in Tomaszow Maz. [%]	Treated wastewater from Tomaszow Maz–Spala subcatchment [%]	Monitoring profile in Spala [%]	Treated wastewater from Spala-Warka subcatchment [%]	Monitoring profile in Warka [%]
1234678-HpCDF	12.52	10.67	11.20	11.37	19.97	11.74	11.98	11.60	12.01	11.35	12.02	13.15	13.60	13.16	18.76	10.14	25.72	12.56
1234789-HpCDF	13.45	11.76	15.16	13.24	8.41	12.70	13.44	13.24	13.77	11.83	11.07	7.80	12.53	14.04	8.76	12.08	17.49	13.95
OCDF	12.05	21.03	11.48	10.43	16.48	13.25	12.47	11.11	11.48	11.76	15.66	16.33	16.08	13.16	16.28	11.59	16.82	14.42
PCB-77	4.88	3.98	5.60	5.28	8.68	6.72	4.40	7.32	5.68	7.98	8.82	7.17	10.72	5.60	24.38	5.36	9.26	4.87
PCB-126	4.85	4.88	6.56	5.06	3.96	7.96	3.63	7.65	6.44	4.79	4.84	5.91	1.64	5.60	2.83	3.05	4.96	4.01
PCB-169	8.01	7.71	11.82	5.79	2.59	7.20	2.47	3.39	6.44	7.71	5.55	6.33	3.11	14.22	11.15	3.78	8.64	4.73
PCB-81	7.15	11.15	10.30	9.41	8.68	14.88	12.21	15.14	9.09	12.23	12.71	13.08	3.39	9.48	4.27	5.97	9.59	7.45
PCB-105	6.48	7.28	6.01	8.78	8.22	7.12	13.29	7.43	8.71	7.71	7.89	7.59	14.48	7.33	9.39	6.70	11.45	10.74
PCB-114	9.94	10.47	9.66	10.70	8.37	10.20	5.26	10.61	13.26	10.64	10.22	10.13	4.80	9.91	4.51	9.62	8.26	9.74
PCB-118	20.06	14.90	14.75	14.37	29.68	9.51	27.05	12.66	7.20	10.90	12.49	13.08	35.38	11.21	23.83	15.96	16.91	9.17
PCB-123	8.17	9.95	8.37	10.68	8.68	11.35	6.49	10.86	12.88	9.84	9.82	10.13	6.95	10.34	4.43	9.26	7.92	12.46
PCB-156	5.99	5.97	5.31	6.01	4.57	4.83	12.13	4.86	6.82	6.38	6.28	5.91	7.94	6.03	5.71	9.38	5.81	7.88
PCB-157	8.95	8.80	7.67	8.96	6.09	7.90	5.02	7.85	9.09	7.45	7.33	7.17	3.85	6.90	3.31	10.11	5.79	10.46
PCB-167	7.71	8.01	7.32	8.46	6.70	7.53	4.79	7.44	8.33	8.78	8.28	8.44	4.75	8.19	4.05	11.21	6.75	11.46
PCB-189	7.83	6.90	6.66	6.49	3.81	4.78	3.25	4.79	6.06	5.59	5.77	5.06	2.99	5.17	2.14	9.62	4.66	7.02

Table 5 | Spearman's rank correlation coefficient between the average pattern of PCDDs (the contribution in the total 2,3,7,8-substituted PCDDs), PCDFs (the contribution in the total 2,3,7,8-substituted PCDFs) and dl-PCB congeners (the contribution in the total dl-PCBs) in the treated wastewater (average for all the studied WTPs from the given subcatchment located between studied river profiles) and the Pilica River water samples ($p = 0.05$)

	High flow				Serene flow			
Congener	Treated wastewater from Koniecpol-Sulejow subcatchment vs river water from Sulejow profile	Treated wastewater from Sulejow-Tomaszów Maz. subcatchment vs river water from Tomaszow Maz. profile	Treated wastewater Tomaszow Maz – Spala subcatchment vs river water from and Spala profile	Treated wastewater Spala -Warka subcatchment vs river water from and Warka profile	Treated wastewater from Koniecpol-Sulejow subcatchment vs river water from Sulejow profile	Treated wastewater from Sulejow-Tomaszów Maz. subcatchment vs river water from Tomaszow Maz. profile	Treated wastewater Tomaszow Maz – Spala subcatchment vs river water from and Spala profile	Treated wastewater Spala -Warka subcatchment vs river water from and Warka profile
PCDDs	0.89	0.79	0.96	0.87	*0.75*	*0.73*	*0.65*	0.85
PCDFs	0.92	0.67	0.98	0.81	*0.45*	0.89	*0.28*	0.74
dl-PCBs	0.85	0.65	*0.39*	0.70	0.92	*0.24*	*−0.12*	*0.14*
PCDDs/PCDFs and dl-PCBs	0.87	0.43	0.67	0.75	0.80	*0.34*	*0.30*	0.61

0.39 – not statistically relevant.

from 0.92 to −0.12, and 10 values were not statistically relevant.

Assessment of total PCDDs/PCDFs and dl-PCBs and TEQ loads transported by Pilica River and discharged by WTPs

The average total and TEQ concentrations measured in the Pilica River water and treated wastewater from WTPs located in its subcatchments were multiplied by the annual Pilica River outflow and WTP outflows (Table 6). Unfortunately, the outflow of the Pilica River in the mouth section was not available as there is no WG station located there. Consequently, the available data help to calculate the loads for three stations only: Sulejow, Tomaszow Maz. and Spala.

The obtained results showed that from 19 May 2010 to 19 May 2011, the total average PCDD/PCDF and dl-PCB load transported by the Pilica River was 136.09 g in Sulejow, 96.95 g in Tomaszow Maz. and 212.00 g in Spala. At the same time, the average TEQ load was 8.54; 3.46 and 6.10 g in Sulejow, Tomaszow Maz. and Spala, respectively (Table 6).

In the case of WTPs, the annual average loads of the total PCDDs/PCDFs and dl-PCBs from a given Pilica River subcatchment ranged from 0.017 g (subcatchment from Koniecpol to Sulejow) up to 0.566 g (subcatchment from Sulejow to Tomaszow Maz.). The loads of TEQ ranged from 0.00096 g in Sulejow to 0.017 g in Spala (Table 6).

DISCUSSION

Poland as a European Union member state is obliged to implement the objectives of the Water Framework Directive 2000/60/EC of the European Parliament and Council of the European Union of 23 October 2000 establishing a framework for the Community Action in the field of water policy and to achieve a good ecological status of aquatic ecosystems by 2015.

At the same time, the Stockholm Convention, ratified by Poland in 2004, commits the EU members to actions aiming at: (1) reducing the risks posed by POPs through their production, use and emission control; and (2) assessing the environmental contamination and exposure of human populations to their adverse effects.

Achieving the objectives defined by the Water Framework Directive and the Stockholm Convention, as well as by the Polish legislation (OJ 2001 No. 115, item. 1229 Act

Table 6 | Loads of total and TEQ concentration of PCDDs/PCDFs and dl-PCBs transported by the Pilica River and discharged by the studied WTPs

Sampling point located at the Pilica River	Total outflow[a] [mln m^3 $year^{-1}$]	Average total concentration load[b] [g $year^{-1}$]	Average TEQ concentration load[b] [g $year^{-1}$]	Studied WTPs located in given Pilica River subcatchments	Wastewater outflow (from the studied WTPs located in the subcatchment – from the source of the Pilica River up to the given sampling point) [mln m^3 $year^{-1}$]	Wastewater outflow (from the studied WTPs located in the given subcatchment) [mln m^3 $year^{-1}$]	Average total concentration load[c] (from the studied WTPs located in the given subcatchment) [g $year^{-1}$]	Average TEQ concentration load[c] (from the studied WTPs located in the given subcatchment) [g TEQ $year^{-1}$]
1 (Koniecpol)	d.n.a.	–	–	–	–	–	–	–
2 (Sulejow)	1,683.00	136.09	8.54	Koniecpol Wielgomlyny Przedborz	0.25	0.25	0.017	0.00096
3 (Tomaszow Maz.)[a]	1,536.80	96.95	3.46	Gorzkowice Rozprza Sulejow Piotrkow Tryb.	5.99	0.55	0.566	0.013
4 (Spala)	1,615.80	212.00	6.10	Tuszyn Wolborz Ujazd Tomaszow Maz.	10.09	4.10	0.267	0.017
5 (Warka)	d.n.a.	–	–	Spala Opoczno Drzewica Nowe Miasto Bialobrzegi	16.84	6.75	0.198	0.011

[a]Average value for the period of 19 May 2010–19 May 2011.
[b]Average load calculated based on the total annual outflow and average total or TEQ concentration of PCDDs/PCDFs and dl-PCBs.
[c]Average load calculated based on the annual outflow from the studied WTPs and average total or TEQ concentration of PCDDs/PCDFs and dl-PCBs.
d.n.a. – data not available.
a – measured 5 km above Tomaszow Maz.

of 18 July 2001, the Water Law) may be difficult due to several commonly occurring threats to the quality of lotic waters and the Baltic water, including eutrophication and transport of micropollutants, including PCDDs/PCDFs and dl-PCBs along the river continuum and their accumulation in reservoirs and the Baltic Sea, as well as their bioaccumulation in aquatic organisms and biomagnification in the trophic chain.

On the one hand, this is a result of unplanned activities in the catchment area, which caused the reconstruction of the original, mosaic structure of ecosystems, disrupting the water circulation and biogeochemical processes in nature, intensifying the erosion and transport of biogenic compounds and micropollutants (Forman & Gordon 1981; Hansen & di Castri 1992; Chmielewski 2001; Krauze 2002; Mainstone & Parr 2002; Wagner-Łotkowska 2002; Kiedrzyńska *et al.* 2004, 2008a, b; Magnuszewski *et al.* 2005, 2007; Hilton *et al.* 2006; Urbaniak *et al.* 2009a, b, c, 2010a, b, 2012a, b; Wagner *et al.* 2009; Zalewski & Kiedrzyńska 2010; Kiedrzyńska & Zalewski 2012). On the other hand, this is the effect of point sources of pollution, which is responsible for about 50% of the current high level of contamination in water ecosystems by nutrients and POPs (Magnuszewski *et al.* 2005; Urbaniak *et al.* 2008, 2009a, b, c, 2012a, b; Zalewski & Kiedrzyńska 2010; Kiedrzyńska & Zalewski 2012).

Transport of PCDDs/PCDFs and dl-PCBs along the river continuum

The plethora of data on the transfer of PCDDs/PCDFs and dl-PCBs along the river continuum indicates a concomitant

permanent increase in their concentration downstream (Fox *et al.* 1983; Crunkilton & DeVita 1997; Huntley *et al.* 1997; Camusso *et al.* 2000; Kannan *et al.* 2001; Hilscherova *et al.* 2003; Kowalewska *et al.* 2003; Koh *et al.* 2004; Rodziewicz *et al.* 2004; Konieczka *et al.* 2005; Sapozhnikova *et al.* 2005; Urbaniak *et al.* 2010b, 2012a, b). The transport of PCDDs/PCDFs and dl-PCBs occurs also along the Pilica River continuum. Our previous study focused on dl-PCB transport along the Pilica River (Urbaniak *et al.* 2012a) showed that samples were heterogeneous with values ranging from 2.92 to 26.30 ng kg^{-1} of dry weight with the maximum concentration at the last site located near the mouth section of the river.

The results obtained in the present study showed two different patterns depending on the water flow. Samples collected at the high water flow reflected an increase in the total and TEQ concentration along the first two sampling points (no. 1 and no. 2). The samples were collected at the beginning of the vegetation season (in May 2010) following the fertilisation of fields. Thus the high water levels prevailing in the surrounding agricultural areas located in the Pilica River floodplain (between the towns of Przedborz and Sulejow) become a source of nutrients (Kiedrzyńska *et al.* 2008a, b), fertilisers and pesticides, which are considered to be a source of PCDDs/PCDFs and dl-PCBs. Similar results were obtained by Minomo *et al.* (2011) on the basis of seasonal analysis of PCDDs/PCDFs and dl-PCBs in the water of the Ayse River in Japan. The authors demonstrated that the highest concentrations of the analysed compounds in May results from the use of pesticides and herbicides. Similar relationships were obtained by Kakimoto *et al.* (2006); whereas the study by Elsknes *et al.* (2013) confirmed the contamination of commonly used fertilisers by PCDDs/PCDFs and dl-PCBs.

A further decrease in the total and TEQ concentrations below the Sulejow Reservoir may result from the deposition and burial of the analysed micropollutants in the sediments and biota of the reservoir. Our previous study (Urbaniak *et al.* 2012a) also demonstrated a decrease in the concentration of toxic non-ortho PCBs in the sediments of the Sulejow Reservoir from 1.89 in the middle section to 1.04 ng kg^{-1} in the dam section of the reservoir. The mono-ortho PCBs declined from 7.32 to 5.50 ng kg^{-1}, respectively. The detailed analysis showed 29% reduction in the total dl-PCB concentration, with 45% reduction in non-ortho PCBs, 25% reduction in mono-ortho PCBs and 40% reduction in WHO-TEQ concentrations along the Sulejow Reservoir. Moreover, the results of sediment samples collected from the river above and below the Sulejow Reservoir showed 79% reduction in the total dl-PCB (from 13.76 to 2.92 ng kg^{-1}) and TEQ concentration (from 0.53 to 0.11 ng TEQ kg^{-1}) below the dam (Urbaniak *et al.* 2012a). Furthermore, the results of annual loads showed that the Pilica River transported fewer PCDDs/PCDFs and dl-PCBs in its section located below the Sulejow Reservoir (Table 6).

The increase in the TEQ concentration in the last two sampling points recorded during the high water level may be related to the load of pollutants from the rainwater drainage in Tomaszow Maz. and Opoczno. The untreated rainwater is discharged directly to the Pilica River (in the case of Tomaszow Maz.) and to the Drzewiczka River – the tributary of Pilica (in the case of Opoczno). Moreover, in the case of Opoczno, the other three WTPs of Class I discharge their sewage into the rivers with the total amount of about 600 m^3 day^{-1}. Additionally, the obtained results on the pattern of congeners (Table 4) indicate that the increase in TEQ and decrease in total PCDDs/PCDFs and dl-PCBs between the last two sampling points can be related to the decrease in PCB-118 content of about 20% between the two above-mentioned points. The congener PCB-118 has low TEF and thus even its high concentration slightly contributes to total TEQ. Moreover, the higher total and TEQ concentration in samples collected from the downstream section of the Pilica River (nos. 4 and 5) can be related to a larger drainage area (Table 2) and consequently, the higher input of diffuse pollution from these parts of the river catchment. The drainage area at sampling point no. 2 (Sulejow) is 3,935.7 km^2, whereas at sampling point 4 (Tomaszow Maz.) and 5 (Warka) it is 5,967.2 and 9,200 km^2, respectively. Similar results of the increased pollution level along the river continuum were reported by Sapozhnikova *et al.* (2005) on the basis of the Dniestr River research. Also the results of Qi *et al.* (1999) and Koh *et al.* (2004) demonstrated an increase in the concentration of PCBs congeners along the river flow and the river length.

The results from the serene water flow demonstrated a decrease in the total and TEQ concentrations along the first three sampling points and an increase at the fourth

site. There might be three causes of these observations: the self-purification of the meandering river by willow communities at its upper section (Points 1 and 2), the burial of PCDDs/PCDFs and dl-PCBs in the Sulejow Reservoir (sampling Points 2 and 3) and the impact of the largest WTPs (sampling Point no. 4) located in this river subcatchment. The self-purification of the Pilica River between the towns of Przedborz (sampling Point no. 1) and Sulejow (sampling Point no. 2) was described in the study of Kiedrzyńska *et al.* (2008a) and Skłodowski *et al.* (in preparation). The authors demonstrated the effect of macrophytes and riparian willow communities on the water quality improvement in this section of the Pilica River as its riverbed has a natural, meandering character and the river banks are covered with riparian willow communities and wetlands, which are a priority for European conservation. The burial of PCDDs/PCDFs and dl-PCBs in the sediments of the Sulejow Reservoir and the improvement of the Pilica River quality below the dam was described in the previous study of Urbaniak *et al.* (2010a, 2012a) and mentioned in the earlier section of this chapter.

WTP outlets as sources of PCDDs/PCDFs and dl-PCBs in the Pilica River

Within the Pilica River catchment, the largest WTPs (80,000 population equivalent), like Piotrkow Trybunalski, Tomaszow Maz. and Warka, exist in its lower section (below Sulejow Reservoir) and discharge from 9,900 to 14,541 m^3 day^{-1} of treated wastewater into the river. Apart from them, the upper and middle section of the Pilica River catchment is dominated by small (<100 m^3 day^{-1} of treated wastewater discharged) and medium (from 100 to 1,500 m^3 day^{-1} of treated wastewater discharged) WTPs of Class I and II.

The obtained results demonstrated that the average load of PCDDs/PCDFs and dl-PCBs and the average load of TEQ concentrations through the WTP outlets ranged from 15.28 up to 686.68 μg day^{-1}, and from 0.81 to 37.96 μg day^{-1}, respectively. The annual loads of PCDDs/PCDFs and dl-PCBs from all WTPs located in a given Pilica River subcatchment ranged from 0.017 g to 0.566 g per year. To our knowledge, there is no other data for comparison of the obtained load values. The only one publication which can be used as a reference is the study by Oleszek-Kudlak *et al.* (2005). The authors, on the basis of incoming and outgoing water from the WTP in Zabrze (Poland), showed the increase in the International TEQ (I-TEQ) concentration from 11.6 to 58.4 pg I-TEQ m^{-3} during the treatment processes. Although the authors did not evaluate the loads of the analysed compounds at the WTP outlet, they demonstrated that the total PCDDs/PCDFs did not change significantly during the water purification in the WTP and amounted to 963.0 and 935.3 pg m^{-3} for incoming and outgoing water, respectively. The authors also demonstrated an increase in the concentration of highly toxic 1,2,3,7,8-PeCDD, 1,2,3,7,8-PeCDF and 2,3,4,7,8-pentaCDF congeners in the outgoing water, and a decline in less toxic OCDD during the treatment process with the maximum of 40% of the total PCDD concentration. In the case of total PCDDs, a decrease in their concentration was noted; the opposite situation was observed for PCDFs, the total concentration of which increased in the outgoing water.

In our case, the content of OCDD in the outgoing water was lower during the first sampling period at the high water stage and ranged from 11.65 to 15.30%; whereas at serene flow, it increased to 62.85%. Moreover, comparative analyses of PCDD/PCDF and dl-PCB patterns demonstrated a strong correlation between river and treated wastewater samples (up to 0.98; Table 5). However, higher correlation coefficients were obtained in the season of high water flow, whereas during serene flow, these relationships were weaker and the majority of obtained correlation values were not statistically relevant (Table 5). This indicates that during a flooding season, the purified wastewater from WTP outlets and the river water are almost identical. Such a situation might have the following causes: (1) during the high water flow, the WTPs did not purify the incoming wastewater sufficiently due to too high water volume; (2) during high water levels, the higher impact of diffuse sources of pollution occurs as a result of runoff of pollutants deposited on the catchment surface. Consequently, at high water levels, the role of WTP discharges is limited because of the diffuse sources of pollution as the annual loads of PCDDs/PCDFs and dl-PCBs discharged through the WTPs located in a given Pilica River subcatchment were several times lower than the loads transported by the Pilica River (Table 6) and accounted for max. 0.6% of the total Pilica

River load (at Tomaszow Maz. profile). It should be emphasised that the total number of WTPs in the Pilica catchment is 143 (Kiedrzyńska *et al.* in preparation). Thus the studied 17 WTPs did not reflect the total loads of PCDDs/PCDFs and dl-PCBs into the Pilica River as they represent only 12% of the total number of WTPs in the Pilica River catchment. Therefore, more detailed, temporal and spatial analysis of all existing (municipal and industrial) WTPs is required.

The other problem is the lack of regulation on the release of toxic congeners of PCDDs/PCDFs and dl-PCBs by municipal WTPs in Poland. Article 41 of the Polish Water Law (OJ 2001 No. 115, item. 1229 Act of July 18, 2001, the Water Law) prohibits the discharges of indicator PCBs (PCB 28, 52, 101, 138, 153 and 180) into the river ecosystems through the WTP outlets, nevertheless it does not regulate the concentration of toxic congeners of PCDDs/PCDFs and dl-PCBs. The Regulation of the Minister of Environment dated 24 July 2006 on the conditions to be met when discharging sewage into waters or soil, and on the substances of particular adverse impact on the water environment (Journal of Laws 2006 no. 137, item 984), also prohibits the discharges of PCBs with treated wastewater, but this regulation applies only to industrial WTPs. Other regulations, e.g. Regulation (EC) No. 166/2006 of the European Parliament and of the Council of 18 January 2006 concerning the establishment of a European Pollutant Release and Transfer Register, and amending the Council Directives 91/689/EEC and 96/61/EC, established the threshold of 0.0001 kg per year for releases of PCDD + PCDF (as TEQ) and 0.1 kg per year for releases of PCBs from municipal WTPs into the water column. However, this regulation applies only to municipal WTPs with a population equivalent of 100,000. Thus, it does not cover the WTPs located in the Pilica River catchment as their highest population equivalent is equal to 99,000 (WTP in Warka). The Directive 2008/105/EC of the European Parliament and of the Council of 16 December 2008 on environmental quality standards in the field of water policy, amending and subsequently repealing the Council Directives 82/176/EEC, 83/513/EEC, 84/156/EEC, 84/491/EEC, 86/280/EEC and amending the Directive 2000/60/EC of the European Parliament and of the Council, lists (in Annex III) dioxins and PCBs as substances subject to review for possible identification as priority substances or priority hazardous substances. Nonetheless, to date there is no regulation on their limits in treated wastewater and/or receiving river water.

In order to assess the quality of lotic water, the Japanese environmental quality standard of 1 pg TEQ L^{-1} should be mentioned (Minomo *et al.* 2011). According to this limit, the obtained results of TEQ concentrations in the Pilica River water showed that all samples exceeded this limit from two to more than six times (Table 2).

The effect of hydrological conditions on the transport of PCDDs/PCDFs and dl-PCBs along the river continuum

The year of 2010 can be characterised by varying hydrological conditions with periods of floods (May–June) and serene river flows (July–October) (Table 1). Based on the obtained measurements, the discharges during the high flow period in May 2010 were 2 to 5 times higher than the average discharge recorded for the whole year. Whereas discharges recorded at the serene flow in September 2010 had values lower than the average (Table 1). The same situation was observed for the outflow.

Such drastic changes in the river discharges could have a great influence on the transport of particulate matter and the associated PCDDs/PCDFs and dl-PCBs along the river. The research on this issue was described in the previous publications of Kiedrzyńska *et al.* (2008b, 2010) and Urbaniak *et al.* (2012a). During high water flows, deeper layers of sediments can be resuspended and thus can mobilise the previously accumulated pollutants (Kiedrzyńska *et al.* 2008b) and consequently increase the load of micropollutants in the river water, whereas the period of serene water levels are characterised by intensive sedimentation processes (Mullis *et al.* 1996). Therefore, sediments and consequently the associated micropollutants mobilised during high flow events can be deposited during low water stages (Magnuszewski *et al.* 2005, 2007; Altinakar *et al.* 2006; Urbaniak *et al.* 2012a, b).

Transport of the suspended sediment load by the Pilica River was reported by Kiedrzyńska *et al.* (2008b) who showed that during the period of 2002 and 2004, the total outflow of the Pilica River amounted to 3,500 mln m^3. During this time the Pilica River transported 33,054 t (ton) of the total suspended sediment load, including the mineral

fraction of 49% (16,192 t) and the organic fraction of 51% (16,861 t). Additionally, the authors estimated that 42% of the suspended sediment load was transported during floods (observed during 38% of the study time) and 58% of the suspended sediment load was transported during low water discharges (occurring for 62% of the study time).

In the case of our study, the higher concentrations of total PCDDs/PCDFs and dl-PCBs were observed during the high flow. This may indicate the role of both WTP discharges and the runoff of the analysed pollutants from the catchment surface.

CONCLUSIONS

The concentrations and transfer of the analysed pollutants along the river continuum are accelerated by the widespread point and diffuse sources of pollution, which continuously deliver PCDDs/PCDFs and dl-PCBs to the river ecosystems.

In the case of the presented study, the largest WTPs discharged up to 59.09 μg TEQ of PCDDs/PCDFs and dl-PCBs to the river per day during high flow events, and up to 26.03 μg TEQ during serene water flows. During the same time, the smallest WTPs released on average 0.81 and 0.70 μg TEQ day^{-1}, respectively. Similarly, the total concentration of PCDDs/PCDFs and dl-PCBs in the Pilica River water was higher during a high water flow compared to a serene water flow. Moreover, at both water stages, the concentration of the analysed pollutants increased along the river continuum. The exception were samples collected below the dam reservoir where the reduction in the total and TEQ concentrations was observed due to deposition and burial of the analysed micropollutants in the sediments and biota of reservoirs as reported in the previous works by Urbaniak *et al*. (2008, 2010b, 2012a) on the role of the Sulejow Reservoir in the transport of micropollutants along the Pilica continuum.

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