boDEREC-CE
WORKPACKAGE T2

O.T2.6 PILOT ACTION UPPER SILESIA INDUSTRIAL REGION.

KOZŁOWA GÓRA PA

VERSION 1

03 2022

Authors:

CONTRIBUTORS, NAME AND SURNAME	INSTITUTION
Joanna Czekaj	Silesian Waterworks PLC
Sabina Jakóbczyk-Karpierz	University of Silesia in Katowice
Kinga Ślósarczyk	University of Silesia in Katowice
Filip Wolny	Silesian Waterworks PLC

Table of contents

1. Introduction

The basic condition for the elimination of any kind of pollution is sufficient knowledge of its properties, origin, behaviour in natural environment and its reaction to various types of technological interventions. Knowledge and findings gained during the boDEREC-CE project are supported by new data, obtained mainly through project monitoring actions, focused on detailed documentation of spatial and temporal changes of PPCP concentrations throughout the pilot areas. The main objective of the T2 work package was to run regular monitoring of PPCP occurrence in drinking water and in raw water (groundwaters or surface water) which serves as a source for its production. Monitoring was performed in 8 pilot sites located in different regions of Central Europe and characterized by different hydrological conditions.

In October 2019 GPW conducted screening monitoring to investigate the potential problem of PPCP occurrence in water within the operation area – the central part of Silesian voivodeship. 5 Water Treatment Plants were selected, and 8 water samples were collected. Based on the results of laboratory analyses and taking into consideration additional factors such as:

- a wide range of water treatment technologies used at the WTPs,
- the degree of catchment area reconnoitre,
- data availability, including spatial and archival data,
- size of the catchment and dominating forms of land use

the Kozłowa Góra reservoir's catchment, together with the Kozłowa Góra WTP were selected for further Pilot Action Activities.

The description of the Upper Silesia Industrial Region Pilot Action was included in *D.T2.1.1 Description of pilot actions. Upper Silesia Industrial Region.* The monitoring methodology applied within the Kozłowa Góra Pilot Action area was described in detail under *D.T2.2.1 Methodology of monitoring – pilot predefinition Kozłowa Góra (Upper Silesia Industrial Region) PA*. The results of the two-year monitoring programme are described in *DT.2.4.1 Analysis of pilot action-specific behaviour of PPCP in the aquatic environment - Kozłowa Góra Pilot Area.*

2. Pilot site characteristics

The Kozłowa Góra Pilot Action Area is located in the central part of the Silesia region, ca. 17 km north from Katowice, outside the territory of the Upper Silesia Conurbation (Figure 1). The Kozłowa Góra WTP is located on the left bank of the Brynica river, directly below the weir from the front barrier of the Kozłowa Góra reservoir.

The Kozłowa Góra reservoir is situated in the Brynica River catchment – a left-bank tributary of the Vistula River. The water intake is located at the outlet of the Kozłowa Góra reservoir which crossed the Brynica at 28+000 km of the watercourse. The reservoir catchment covers an area of 193 km^2. Within the catchment area groundwater is observed in three multi-layered aquifers: Quaternary, Triassic, and Carboniferous. In this area, three Triassic carbonate major groundwater basins (MGBs) are located: Gliwice, Lubliniec – Myszków and Olkusz – Zawiercie. The water intake is located on the dam (the outflow weir). The reservoir was built in 1935 - 1939 for strategic purposes. In the years 1948 - 1951 the water reservoir was adapted for water supply purposes.

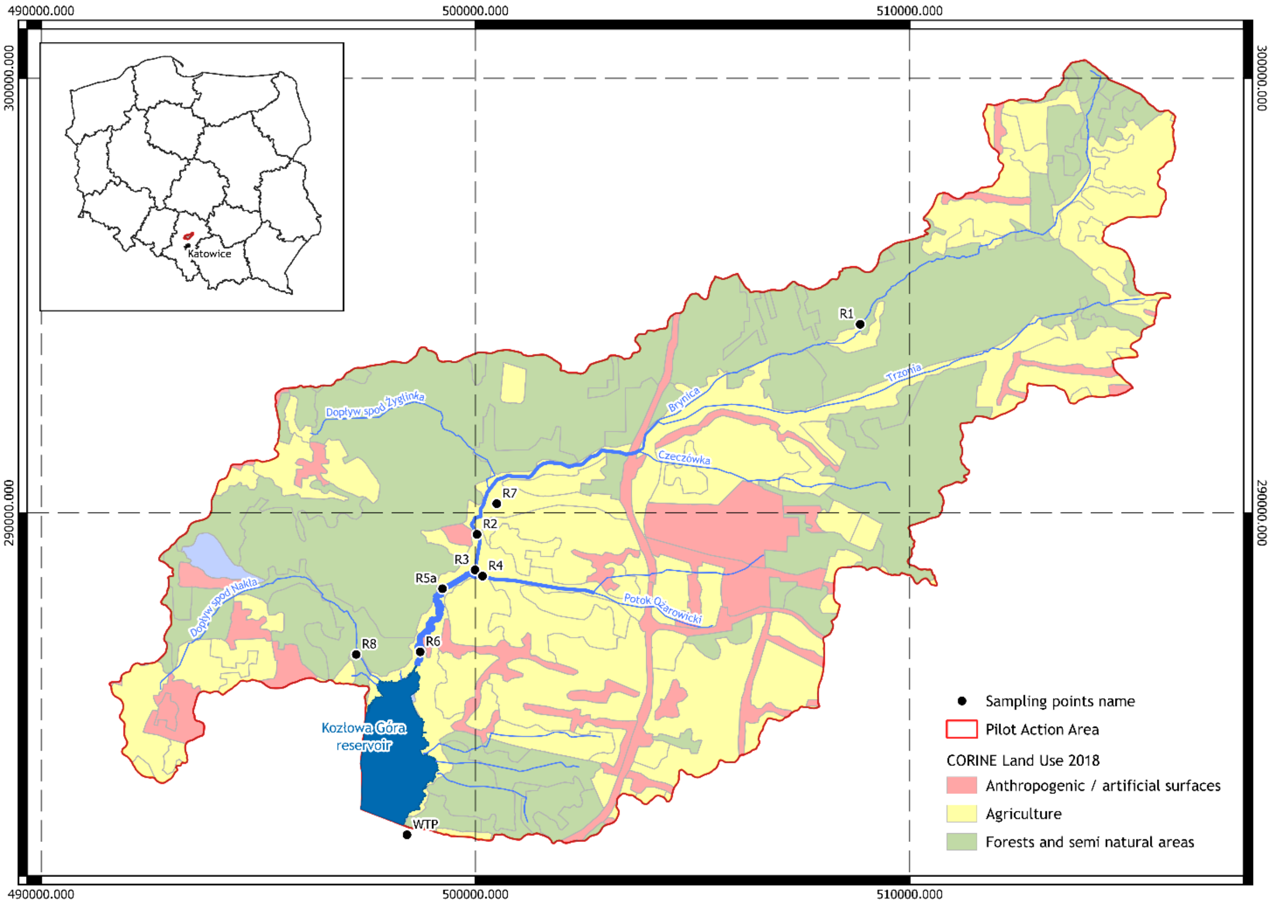

Figure 1. Location of the Kozłowa Góra Pilot Action Area.

2.1. Geographical and hydrological conditions

The Kozłowa Góra pilot action area is situated in the northern part (headwaters) of the Brynica River catchment, upstream to head dam of the Kozłowa Góra reservoir, which covers an area of 193,93 km^2 and encompasses communes which are primarily rural or urban in character. Local population in the pilot action area does not exceed 30,000 residents. Almost 47% of the area is covered by forests and semi-natural areas according to Corine Land Cover 2018. Agricultural areas constitute slightly less than 40%. Anthropogenic/artificial surfaces cover ca. 10.5% of the pilot action area (Figure 1).

The pilot action area is located in the left-side catchment area of the Vistula River (the longest river in Poland, which empties into the Baltic Sea) and is supplied with water from the Brynica River (a tributary of the Przemsza River) along with its tributaries. The Brynica River tributaries (3 left-bank and 1 right-bank streams) are characterised by a short length and flow rates ranging from a few to several dozen dm^3/s (Budzyńska A. et al., 1999). The Brynica River flows directly into the Kozłowa Góra reservoir, the discharge varies from 0.011 m^3/s to 32.446 m^3/s (Czekaj J. et al., 2017). Kozłowa Góra is a dam reservoir located at km 28+000 of the Brynica River watercourse. The reservoir surface area at normal water damming level (278.08 m a.s.l.) is 5.268 km^2 and differs depending on the water level (Bojarski A. et al., 2004). Besides Brynica, there are other that empty into the Kozłowa Góra Reservoir: Dopływ z Siemoni (left bank stream), Potok spod Nakła (right bank stream) and several other small streams observed periodically at the left bank of the reservoir.

Potential sources of PPCP pollution in the investigated area are related mainly to urban fabric, as well as agriculture, and accompanying wastewater and stormwater discharges. Forests and greenlands can also be considered as potential sources of PPCPs due to possible large-scale use of insect repellents. Another potential source of PPCPs within the Pilot Action area is transport – especially associated with the Katowice airport and its additional infrasturucture.

2.2. Water quality

The quality of surface water and groundwater in the Kozłowa Góra Pilot Action area was investigated in 4 time periods: June 2020, January, June and September 2021. Water samples were collected from the Brynica river and its 5 tributaries, from the Potok spod Nakła, the Kozłowa Góra reservoir, and 4 wells extracting groundwater from the Quaternary aquifer. 18 water samples were collected in each sampling campaign. In period 4, six additional sampling points (R12 – R17) located on streams were included (Figure).

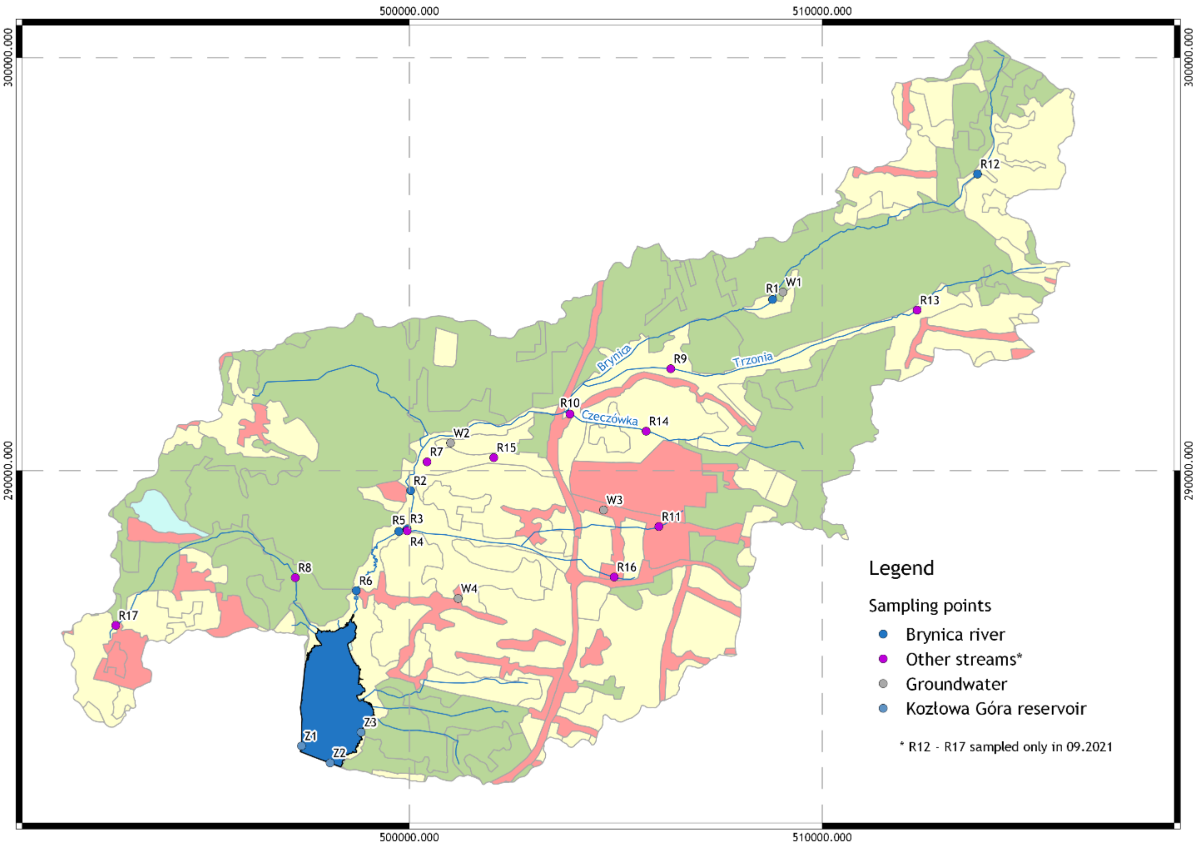

Figure 2. Sampling points for chemical analyses of water within the study area.

Water quality investigation comprised the determination of the in-situ measured parameters (temperature, pH, electrical conductivity, Eh, dissolved oxygen) and concentrations of the following constituents: HCO_3^-, SO_4^{2-}, Cl^-, Ca^{2+}, Mg^{2+}, Na^+, K^+, PO_4^{3-}, total organic carbon (TOC), NH_4^+, NO_2^-, and NO_3^-. Details on the methods applied in the study and the results of the performed investigation were described in the *D.T2.4.1 report*. In this report, the summary of the chemical composition of surface water and groundwater is provided, with a highlight of contaminated areas.

The ratios of major ions in all sampled surface water and groundwater is provided in the Piper diagram (Figure 3).

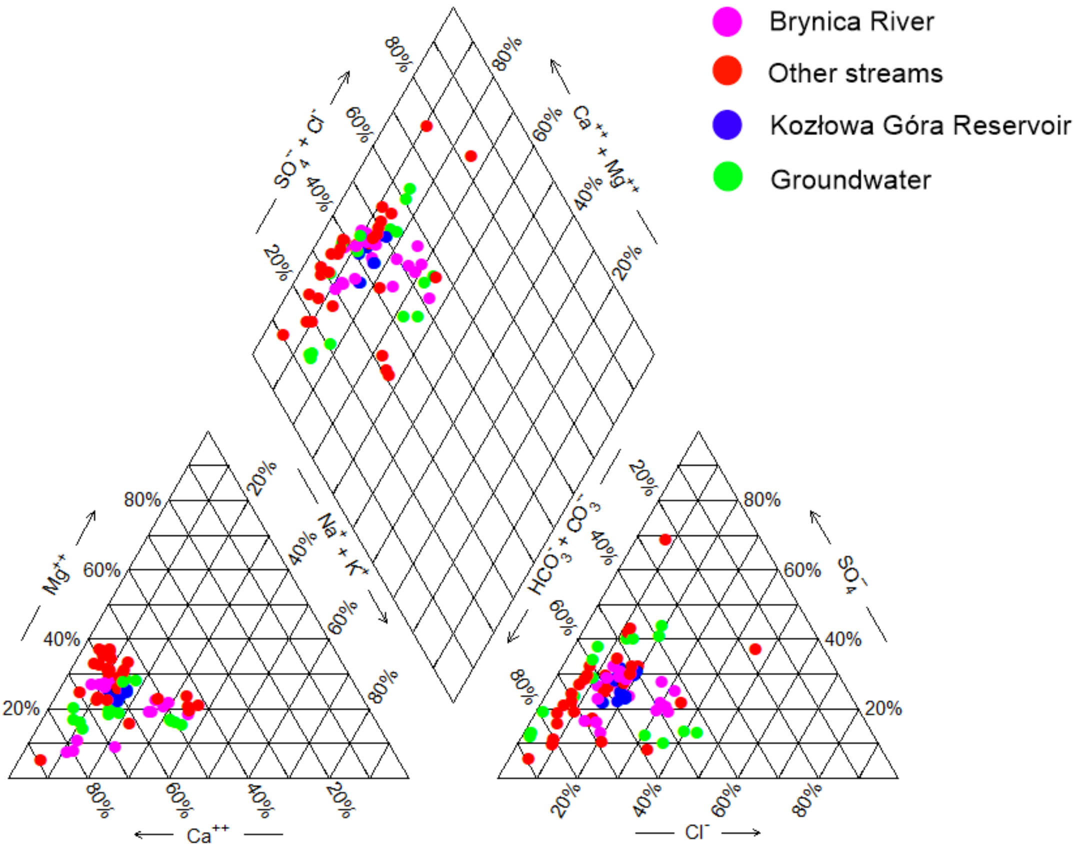

Figure 3. Piper diagram for water sampled within the Kozłowa Góra Pilot Action area.

2.2.1. The Brynica river and other streams

Water from the Brynica river, its tributaries, and the Potok spod Nakła is characterised by seasonal changes in temperature, from 1.0°C in winter to 18.8 °C in summer. The pH of water varies throughout the hydrological year from slightly acidic to slightly alkaline (6.55 - 7.94). Sampled water is freshwater (EC from 210 to 1010 µS/cm) with varying concentration of dissolved oxygen (O_2 from 2.6 to 10.5 mg/L). Eh values range from -93 to 206 mV. Concentrations of major ions reveal variability within the catchment area. The following ranges were observed in the sampled water: Ca^{2+} from 27 to 120 mg/L, Mg^{2+} from 4.5 to 38 mg/L, Na^+ from 4.2 to 65 mg/L, K^+ from 1.1 to 22 mg/L (occasionally 90 mg/L), HCO_3^- from 48.2 to 466 mg/L, SO_4^{2-} from < 10 to 110 mg/L, Cl^- from 6.7 to 114 mg/L. Concentrations of nutrients in sampled streams are generally low, mostly: NO_3^- from 0.4 to 22.6 mg/L, NO_2^- from <0.002 to 0.1 mg/L, NH_4^+ from <0.01 to 0.25 mg/L, and PO_4^{3-} from <0.05 to 0.14 mg/L. However, some streams are permanently or periodically polluted with nutrients. Elevated concentrations of NH_4^+ were noticed in R3 (up to 0.85 mg/L), R5 (up to 0.52 mg/L), R8 (up to 0.82 mg/L) and R11 (up to 24.47 mg/L). Elevated concentrations of NO_2^- were found in R3 (up to 0.394 mg/L), R5 (up to 0.253 mg/L) and in R11 (up to 0.148 mg/L). TOC concentrations were generally in the range from 3.9 to 24 mg/L, but elevated concentrations were found in R13 (up to 53 mg/l), R10 (up to 63 mg/L) and in R11 (up to 120 mg/L). Moreover, studies conducted for the additional sampling point in the Potok spod Nakła (R17) in September 2021 revealed a strong degradation of water by nutrients (NH_4^+ = 51.52 mg/L, PO_4^{3-} = 12.5 mg/L, and TOC = 50 mg/L).

2.2.2. The Kozłowa Góra reservoir

Water from the Kozłowa Góra reservoir is also characterised by seasonal changes in temperature, from 0.5°C in winter to 24.6°C in summer. Water pH ranges from 6.58 to 8.5. It is freshwater (EC ranges from 335 to 460 μS/cm), saturated with dissolved oxygen (O2 ranges from 6.27 to 10.1 mg/L). Eh values are in the range from +90 to +189 mV. Concentrations of major ions are lower and more stable compared to water from the Brynica river and other streams. The following ranges were observed in the water sampled from the reservoir: Ca^{2+} from 45 to 78 mg/L, Mg^{2+} from 11 to 20 mg/L, Na^{+} from 10 to 16 mg/L, K^{+} from 3.8 to 5.3 mg/L, HCO_3^{-} from 119 to 177 mg/L, SO_4^{2-} from 40 to 66 mg/L, and Cl^{-} from 19 to 32 mg/L. Concentrations of nutrients in the reservoir water are very low: NO_3^{-} from 0.9 to 3.5 mg/L, NO_2^{-} from 0.01 to 0.033 mg/L, NH_4^{+} from <0.01 to 0.21 mg/L, and PO_4^{3-} from <0.05 to 0.027 mg/L.

2.2.3. Groundwater

The shallow groundwater, sampled in 4 wells, is characterized by a temperature ranging from 6.8°C in winter to 14.6°C in summer, and pH values in the range of 6.37 - 7.61. Sampled groundwater is classified as freshwater and low mineralised water (EC ranges from 182 to 1650 μS/cm), with dissolved oxygen concentrations from 4.09 to 7.79 mg/L. Eh values range from -13 to 238 mV. Concentrations of major ions are within the wide ranges: Ca^{2+} from 37 to 184 mg/L, Mg^{2+} from 4.2 to 34 mg/L, Na^{+} from 3.0 to 135 mg/L, K^{+} from 2.6 to 38 mg/L, HCO_3^{-} from 63.4 to 592 mg/L, SO_4^{2-} from 21 to 104 mg/L, and Cl^{-} from 4.0 to 256 mg/L. Chemical analyses of the groundwater collected from the wells W1 and W3 revealed natural water types: HCO_3-SO_4-Ca in W1 and HCO_3-Ca-Mg (occasionally HCO_3-SO_4-Cl-Na) in W3. In W2 and W4, more altered water types were observed: HCO_3-SO_4-NO_3-Ca-Mg, SO_4-HCO_3-Cl-Ca-Mg, and NO_3-SO_4-HCO_3-Ca-Mg for W2, and HCO_3-Cl-Ca-Na, HCO_3-Cl-Ca-Mg-Na, and HCO_3-SO_4-Ca-Mg for W4. The concentrations of nutrients in groundwater are generally low. The following ranges were observed: NO_3^{-} from 7.5 to 25 mg/L, NO_2^{-} from 0.01 to 0.1 mg/L, NH_4^{+} from <0.01 to 0.3 mg/L, and PO_4^{3-} from <0.05 to 0.1 mg/L. However, high concentrations of PO_4^{3-} (up to 3. 2 mg/L) and elevated NO_2^{-} concentrations (up to 0.24 mg/L) were observed in groundwater collected from the W3 well. In W2, high concentrations of NO_3^{-} were found (up to 79.7 mg/L), exceeding the drinking water limit (50 mg/L).

2.3. Water treatment techology

The Kozłowa Góra reservoir is used as a drinking water source since the 1950s. The Water intake is located at the reservoir frontal dam which is equipped with six channels located at the bottom - the two left channels supply the WTP Kozłowa Góra with water, while four other channels allow the passage of waters.

The following water treatment processes are used to purify water at WTP Kozłowa Góra: pre-ozonation of raw water, contact coagulation in the fast and slow mixing chambers, rapid filtration on the anthracite-sand filers, indirect ozonation, filtration through activated carbon deposits, and disinfection with sodium hypochlorite (Figure 4).

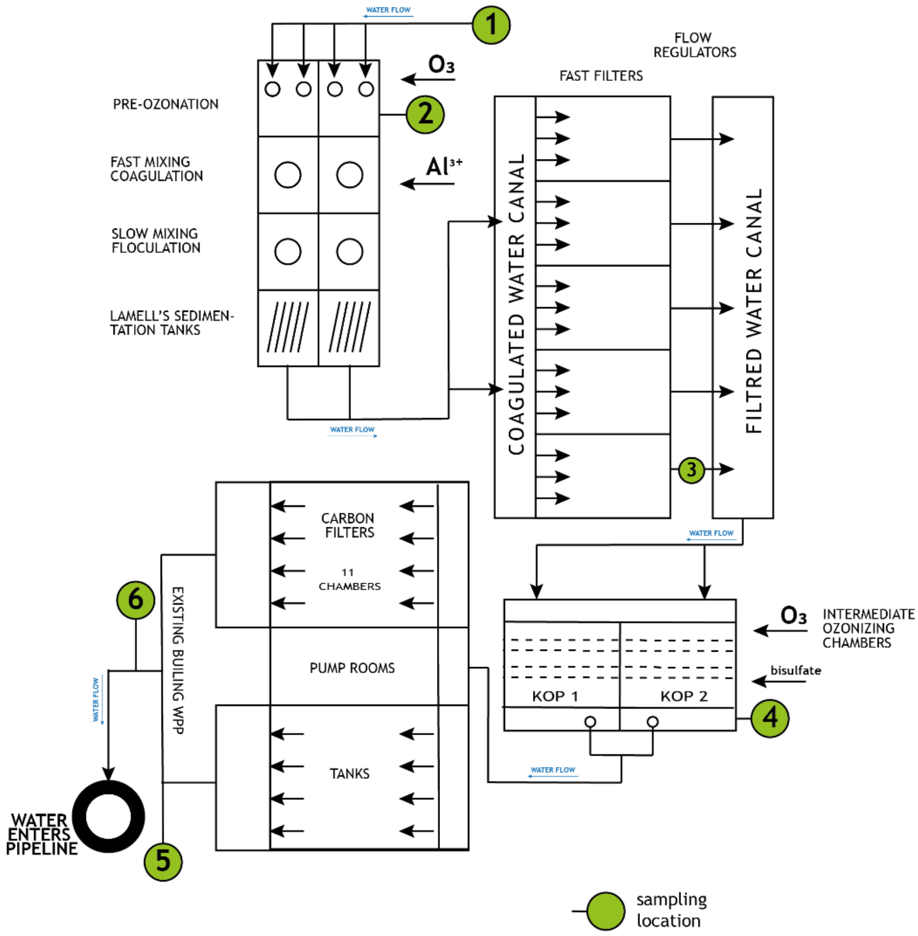

Figure 4. Scheme of the water treatment process at WTP Kozłowa Góra and location of the sampling points.

2.4. Socio - economic conditions and main end users

Silesian Waterworks PLC (GPW) is a producer and a wholesaler of drinking water in Upper Silesia Industrial Region. GPW is one of the biggest waterworks in Poland. Drinking water is treated in eleven Water Treatment Plants. Next, it is transported through a network of main pipelines with a total length of 871 km to network surge tanks. GPW supplies drinking water to 66 communes of the Silesian Voivodship and three communes of the Lesser Poland Voivodship covering an area of approx. 4 300 km^2. Nearly 3 million residents are supplied with drinking water from surface water sources (ca. 86% in 2021) and groundwater sources (ca. 14% in 2021).

One of the water treatment plants of the GPW operation system is the Kozłowa Góra WTP, which supplies drinking water to the following communes: Piekary Śląskie, Bobrowniki, Radzionków, Bytom, Chorzów and Świętochłowice. The daily production of drinking water at this WTP is ca. 12,000 m^3.

3. Monitoring methodology and available data

3.1. Objective of monitoring

The overall objective of the PPCP monitoring in the Kozłowa Góra catchment area was to investigate the occurrence of pharmaceuticals and personal care products in the Brynica river and its tributaries. The PPCP monitoring in the catchment area allowed to determine changes in PPCP concentrations along the Brynica watercourse, seasonal variability in the number and concentrations of PPCPs, the influence of the main sources of PPCPs on water quality. Monitoring also allowed indicating other possible contamination sources. The results of the monitoring are used to validate conceptual transport model of selected PPCP in Kozłowa Góra Pilot Action area (*see DT3.3.5*).

The PPCP monitoring at the Kozłowa Góra WTP was crucial to verify the occurrence of PPCPs in different steps of the water treatment process and characterise the efficiency of PPCP removal. Moreover, the obtained results were used to compare the efficiency of PPCP removal at the Italian pilot site in the Po River basin, which uses a similar drinking water production technology (*see D.T4.3.1*).

3.2. Sampling and laboratory analysis

The PPCPs monitoring programme started in July 2020 with a sampling campaign conducted once per 10 weeks, as follows:

1. in July 2020 – between 20 – 23.07.2020.
2. in October 2021 – between 19 – 21.10.2020.
3. in January 2021 – between 22 – 21.01.2021.
4. in April 2021 – between 25 – 26.04.2021.
5. in July 2021 – on 26.07.2021.
6. in October 2021 – between 24 – 25.10.2021.
7. in January 2022 – on 24.01.2022.

The PPCP monitoring in the catchment area was performed at 8 sampling points (Figure 1). Initially, the monitoring network consisted of 2 domestic wells (W1 and W2), 5 points located downstream of the Brynica river (R1-R3 and R5-R6), and 1 sampling point on the Potok Ożarowicki – a tributary of the Brynica (R4).

Starting from April 2021 the monitoring network was modified in accordance with the findings of *D.T3.3.3* report. The wells were replaced by additional sampling points to examine surface waters: a ditch from the airport (R7) and the Potok spod Nakła stream (R8). Moreover, the R5 sampling point, located on the Brynica river, was moved approx. 200 m downstream (R5a).

Additionally, starting from July 2021, discharge from the Wastewater Treatment Plant (WWTP) "Ożarowice" was sampled - treated wastewater is discharged directly to the Brynica river, between sampling points R2 and R3 which might significantly influence water quality.

The PPCP monitoring at the Kozłowa Góra Water Treatment Plant is conducted after main stages of the technological process. Thus, six samples are collected (Figure 4):

- WTP1 - raw water, pumped to preozonation chambers.
- WTP2 - water after preozonation.
- WTP3 - filtrated water, after rapid filtration process (together with coagulation and sedimentation).
- WTP4 - water, after intermediate ozonation.
- WTP5 - filtrated water, after activated carbon (GAC) filtration.
- WTP6 - treated water, injected to water supplying system.

Water samples were collected in two 60 ml amber glass vials with a screw cap according to Sampling Guidelines prepared by the WPT2 Leader and Povodi Vltavy laboratory. The containers were half full and frozen at a 45° angle position after fieldwork to stabilize the sample. After freezing, samples were stored in a thermobox filled in with dry ice and transported to the laboratory.

PPCPs were separated and detected with LC–MS/MS methods based on direct injection of the sample into a chromatograph. A 1290 ultra-high-performance liquid chromatograph (UHPLC) coupled with an Agilent 6495B Triple Quad Mass Spectrometer (MS/MS) of Agilent Technologies, Inc. (Santa Clara, CA, USA) were used.

4. Monitoring results

Detailed results of the PPCP monitoring were described in the *DT.2.4.1 Analysis of pilot action-specific behaviour of PPCP in the aquatic environment - Kozłowa Góra Pilot Area*.

4.1. Water resources

The PPCP monitoring within the Kozłowa Góra catchment area was conducted every 10 weeks, from July 2020 to January 2022. The number of detected substances in each sample is presented in Table 1. The monitoring covered PPCP analyses in three types of water samples:

- SURFACE WATER (samples R1, R2, R3, R4, R5/R5a, R6, R7, and R8)
  In total, 64 out of 109 analysed PPCP were detected in surface water samples (the Brynica river and other streams). The highest number of detected compounds was reported in the R3 sample in January 2022.
- GROUNDWATER (samples W1 and W2)
  In total, 7 out of 109 analysed PPCP were detected in groundwater (domestic wells). The highest number of detected compounds was reported in the W1 sample in July 2020. Groundwater was sampled only at the beginning of the PPCP monitoring, i.e. July 2020 and October 2020.
- WASTEWATER EFFLUENT (sample WWTP)
  In total, 72 out of 109 analysed PPCP were detected in the wastewater effluent (WWTP "Ożarowice"). The highest number of detected compounds was reported in January 2022. Wastewater effluent was sampled only at the end of the PPCP monitoring, i.e. July 2021, October 2021, and January 2022.

Table 1. Number of detected PPCPs in the monitoring points (at concentrations >LoQ).

Date / Sample	July 2020	October 2020	January 2021	April 2021	July 2021	October 2021	January 2022
SURFACE WATER							
Brynica in Zendek village (R1)	2	3	11	4	2	7	7
Ditch from the airport (R7)	no data	no data	no data	1	3	1	3
Water gauge Brynica - Brynica (R2)	5	4	7	3	5	5	5
Brynica, below wastewater discharge (R3)	8	27	12	38	8	5	53
Potok Ożarowicki (R4)	15	6	5	6	2	3	13
Brynica, below Potok Ożarowicki inflow (R5/R5a)	22	26	31	36	19	8	37
Brynica, inflow to Kozłowa Góra reservoir (R6)	28	16	18	29	30	29	21
Potok spod Nakła (R8)	no data	no data	no data	9	4	4	2
GROUNDWATER							
Digged well in Zendek (W1)	1	1	1	no data	no data	no data	no data
(Digged well in Ożarowice) (W2)	7	1	0	no data	no data	no data	no data
WASTEWATER EFFLUENT							
WWTP "Ożarowice" (WWTP)	no data	no data	no data	no data	63	59	65

The most important part of the monitoring within the catchment area was the determination of PPCP concentrations in rivers supplying the Kozłowa Góra reservoir, which is a source of drinking water. In general, PPCP concentrations varied depending on the season. Among the analysed substances, the highest concentrations, exceeding 1,000 ng/L, were reported for Diclofenac, DEET, Gabapentin, Hydrochlorothiazide, Oxypurinol, Sucralose, Telmisartan, and Valsartan acid. Several PPCPs, such as 1-H-Benzotriazole, 4-formyloamino-antipyrine, Azithromycin, Caffeine, Diatrizoate, Diclofenac-4'-hydroxy, Furosemide, Iopromide, Metformin, Paraxanthine, Tramadol, Valsartan, and Valsartan acid, were observed in the maximum range of 500 – 1,000 ng/L. Other substances occurred in lower quantities, mostly up to 100 ng/L (Table 2).

Table 2. Maximum concentrations (C) of PPCPs in surface water in all sampling campaigns (substances listed in the alphabetical order).

C [ng/L]	July 2020	October 2020	January 2021	April 2021	July 2021	October 2021	January 2022
> 1,000		Oxypurinol		Oxypurinol Sucralose	DEET Oxypurinol Sucralose		Diclofenac Gabapentin Hydrochlorothiazide Oxypurinol Sucralose Telmisartan Valsartan acid
500 - 1,000	DEET Metformin Oxypurinol		Caffeine Metformin Oxypurinol Paraxanthine Valsartan	Iopromide Metformin	Valsartan acid	Oxypurinol	1-H-Benzotriazole 4-formylamino-antipyrine Azithromycin Diatrizoate Diclofenac-4'-hydroxy Furosemide Iopromide Tramadol
100 - 500	1-H-Benzotriazole 4-formylamino-antipyrine 5-methyl-1-H-Benzotriazole Acesulfame Caffeine Cyclamate Diclofenac Fexofenadine Hydrochlorothiazide Iohexol Paraxanthine Telmisartan Valsartan acid	Metformin Telmisartan Valsartan acid	1-H-Benzotriazole 4-formylamino-antipyrine Acesulfame DEET Diclofenac Gabapentin Iohexol Saccharin Telmisartan Valsartan acid	1-H-Benzotriazole 4-formylamino-antipyrine 5-methyl-1-H-Benzotriazole Acesulfame Azithromycin Caffeine Cyclamate Diclofenac Diclofenac-4'-hydroxy Fexofenadine Furosemide Gabapentin Hydrochlorothiazide Iohexol Saccharin Telmisartan Valsartan acid	1-H-Benzotriazole 4-formylamino-antipyrine 5-methyl-1-H-Benzotriazole Carbamazepine Diatrizoate Diclofenac Fexofenadine Furosemide Gabapentin Hydrochlorothiazide Methylparaben Saccharin Sotalol Telmisartan Tramadol	1-H-Benzotriazole 4-formylamino-antipyrine Carbamazepine DEET Diclofenac Fexofenadine Gabapentin Hydrochlorothiazide Iomeprol Iohexol Iopromide Methylparaben Telmisartan Valsartan acid	5-methyl-1-H-Benzotriazole Acesulfame Bisoprolol Caffeine Carbamazepine Clarithromycin Cyclamate DEET Fexofenadine Fluconazole Iohexol Metformin Metoprolol Lamotrigine Paraxanthine Phenazone Sotalol Sulfapyridin Venlafaxine Venlafaxine O-desmethyl

C [ng/L]	July 2020	October 2020	January 2021	April 2021	July 2021	October 2021	January 2022
50 - 100	Carbamazepine Ibuprofen-2-hydroxy Metoprolol Saccharin Tramadol	1-H-Benzotriazole 4-formylamino-antipyrine 5-methyl-1-H-Benzotriazole Acesulfame Carbamazepine DEET Diclofenac Fexofenadine Hydrochlorothiaz-ide Iohexol	5-methyl-1-H-Benzotriazole Carbamazepine Furosemide Fexofenadine Hydrochlorothiaz-ide Ibuprofen-2-hydroxy Ibuprofen-carboxy Iopromide Metoprolol Paracetamol Sotalol	Bisoprolol Carbamazepine DEET Iomeprol Lamotrigine Metoprolol Paracetamol Sotalol Tramadol Valsartan	Diclofenac-4'-hydroxy Metoprolol Venlafaxine O-desmethyl	Diclofenac-4'-hydroxy Furosemide Metformin PFOS Propylparaben Sotalol Tramadol Venlafaxine O-desmethyl	Bisphenol S Clindamycin Saccharin Sulfamethoxazol-e Trimethoprim Valsartan
10 - 50	Bisoprolol Cotinine Clindamycin Diclofenac-4'-hydroxy Fluconazole Gabapentin Ibuprofen-carboxy Lamotrigine PFOS Sotalol Sulfapyridin Simvastatin Valsartan Venlafaxine	Azithromycin Bisoprolol Diclofenac-4'-hydroxy Fluconazole Furosemide Gabapentin Lamotrigine Metoprolol PFOS Sotalol Sulfamethoxazo-le Sulfapyridin Tramadol Valsartan Venlafaxine	Azithromycin Bisoprolol Diclofenac-4'-hydroxy Fluconazole Lamotrigine PFOS Sulfamethoxazo-le Sulfapyridin Tramadol Trimetoprim Venlafaxine O-desmethyl	Carbamazepine 10,11-epoxid Carbamazepine-2-hydroxy Clarithromycin Clindamycin Diclofenac-4'-hydroxy Fluconazole Iomeprol Losartan PFOS Phenazone Sulfapyridin Trimetoprim Venlafaxine Venlafaxine O-desmethyl	Azithromycin Bisoprolol Carbamazepin-e 10,11-dihydro-10-hydroxy Carbamazepin-e-2-hydroxy Clindamycin Fexofenadine Fluconazole Lamotrigine Metformin PFOS Simvastatin Sulfamethoxazo-le Sulfapyridin Venlafaxine	5-methyl-1-H-Benzotriazole Azithromycin Bisoprolol Fluconazole Lamotrigine Metoprolol PFOS Sulfamethoxazo-le Sulfapyridin Telmisartan Venlafaxine	Acebutolol Atenolol Carbamazepin-e 10,11-dihydro-10-hydroxy Carbamazepine 10,11-epoxid Carbamazepin-e-2-hydroxy Citalopram Climbazole Cotinine Ibuprofen-2-hydroxy Ketoprofen Losartan Memantine Naproxen O-desmethyl Paracetamol PFOS Primidone Propranolol Propylparaben

4.2. Water treatment plant

During the six sampling campaigns 27 different PPCPs were detected at a concentration >LoQ (Limit of Quantification) at the WTP. The number of observed substances changed over time – merely 8 substances were detected in raw water (at the input of the WTP) in October 2020, while 17 were detected in April 2021 particular monitoring campaigns. Table 3 features the number of PPCPs detected after each stage of water treatment whereas Table 4 presents the names of detected substances.

Table 3. Number of detected PPCPs after each stage of the treatment process (WTP1-WTP6) at the Kozłowa Góra WTP.

Date / Sample	July 2020	October 2020	January 2021	April 2021	July 2021	October 2021	January 2022
WPT1	16	8	15	17	13	13	16

WPT2	5	4	9	6	5	6	8
WPT3	5	5	8	5	6	6	7
WPT4	6	6	7	5	5	5	6
WPT5	3	1	3	3	1	1	3
WPT6	2	2	2	3	2	4	2

Table 4. Substances detected in water at the Kozłowa Góra WTP at least in one stage of the treatment process (WTP1-WTP6).

July 2020	October 2020	January 2021	April 2021	July 2021	October 2021	January 2022
1-H-Benzotriazole 4-formylamino-antipyrine 5-methyl-1-H-benzotriazole Acesulfam Caffeine Carbamazepine DEET Fexofenadine Fluconazole Gabapentin Methylparaben Oxypurinol Paraxanthine PFOS Saccharin Telmisartan Valsartan acid	4-formylamino-antipyrine 5-methyl-1-H-benzotriazole Caffeine Carbamazepine DEET Fexofenadine Gabapentin Oxypurinol Paraxanthine PFOS Valsartan acid	1-H-Benzotriazole 4-formylamino-antipyrine 5-methyl-1-H-benzotriazole Carbamazepine DEET Diclofenac Fexofenadine Gabapentin Metformin Methylparaben Metoprolol Oxypurinol PFOS Sotalol Telmisartan Tramadol Valsartan acid	1-H-Benzotriazole 4-formylamino-antipyrine 5-methyl-1-H-Benzotriazole Acesulfam Carbamazepine DEET Fexofenadine Gabapentin Iopromide Lamotrigine Metformin Oxypurinol PFOS Sotalol Telmisartan Tramadol Valsartan Valsartan acid	1-H-Benzotriazole 4-formylamino-antipyrine 5-methyl-1-H-Benzotriazole Carbamazepine DEET Fexofenadine Gabapentin Lamotrigine Methylparaben Oxypurinol PFOS Telmisartan Valsartan acid	1-H-Benzotriazole 4-formylamino-antipyrine Carbamazepine Ketoprofen DEET Ethylparaben Fexofenadine Fluconazole Gabapentin Lamotrigine Methylparaben Oxypurinol PFOS Telmisartan Tramadol Valsartan acid	1-H-Benzotriazole 4-formylamino-antipyrine Carbamazepine DEET Fexofenadine Fluconazole Gabapentin Iopromide Metformin Metoprolol Oxypurinol PFOS Sotalol Telmisartan Tramadol Valsartan acid Venlafaxine O-desmethyl

The sum of PPCP concentrations observed in the treated water differs along the technological process. The total concentration of PPCP observed in raw water oscillated between 309.9 ng/L in October 2020 and 1,112.6 ng/L in July 2020 (Figure 5). Water after the preozonation process (WTP2) was characterized by a PPCP concentration between 124.2 and 336.3 ng/L observed in October 2020 and January 2021, respectively. Total PPCP concentration investigated after rapid filtration (WTP3), oscillated between 246 and 386 ng/L. Water after intermediate ozonation (WTP4) is characterized by a PPCP concentration between 235.1 and 522 ng/L. At the end of the process, the concentrations of PPCPs decreased significantly and ranged between 16.4 – 252.1 and 21.9 – 126.2 ng/L in WTP5 and WTP 6 sampling points, respectively (Figure 5).

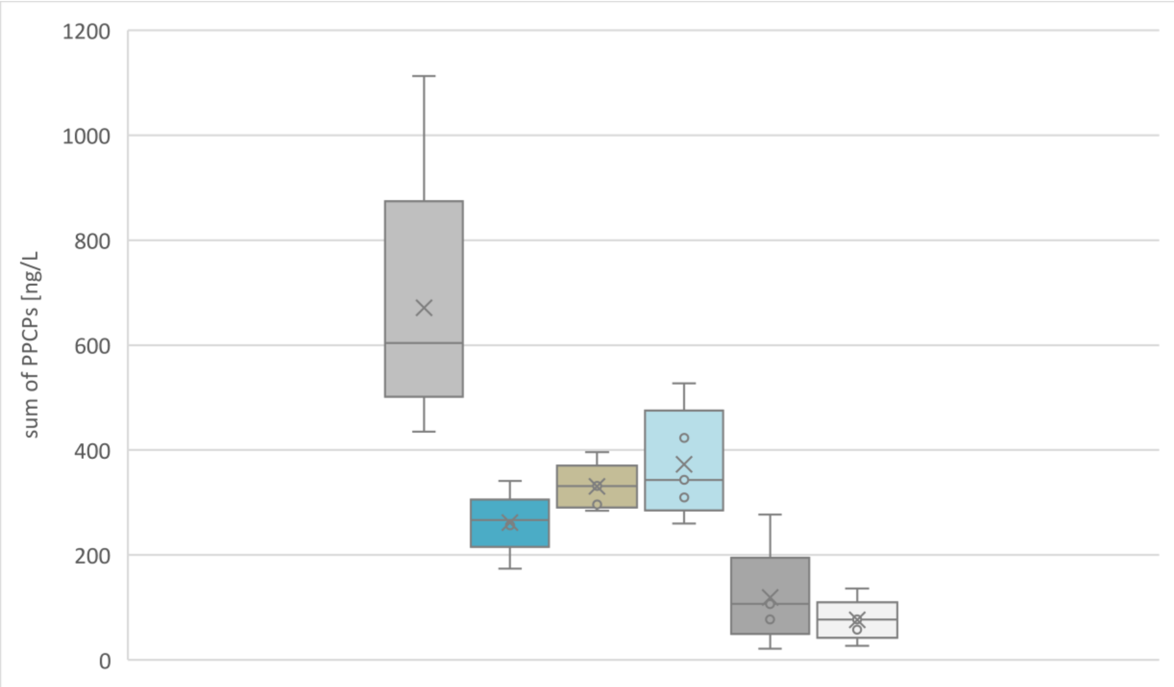

Figure 5. The sum of PPCP concentrations after different stages of the water treatment process.

4.2.1. Water treatment efficiency

In the report "*Efficiency analysis of pharmaceuticals removal from water on WTP Kozłowa Góra*", done for **5 monitoring campaigns** (October 2022 – July 2021), Weber and his team (2022) have analysed efficacy of the water treatment process, also considering the operating parameters (technological conditions of WTP operation). The authors emphasized the high efficiency of the whole water treatment process and indicated that the highest efficiency of removing PPCP compounds was achieved during preozonation. The substances that were present in detectable amounts (above LoQ) after preozonation were generally successfully eliminated in further steps, especially during activated carbon filtration (Table 5).

Table 5. Substances detected after stages of water treatment process.

WPT1: Raw water	WPT2: preozonation	WPT3: + coagulation, sedimentation, and rapid filtration	WPT4: + second stage ozonation	WPT5: + carbon filters	WPT6: + disinfection
1-H-Benzotriazole	1-H-Benzotriazole	1-H-Benzotriazole			
4-formylamino-antipyrine					
5-methyl-1-H-benzotriazole					
Acesulfame				Acesulfame	Acesulfame
Caffeine			Caffeine		
Carbamazepine					
DEET	DEET	DEET	DEET	DEET	DEET
Diclofenac					
Fexofenadine	Fexofenadine	Fexofenadine			
Fluconazole					

Gabapentin	Gabapentin	Gabapentin	Gabapentin		
Iopromide	Iopromide				
Lamotrigine					
Metformin	Metformin	Metformin	Metformin	Metformin	Metformin
Methylparaben		Methylparaben	Methylparaben		Methylparaben
Metoprolol					
Oxypurinol	Oxypurinol	Oxypurinol	Oxypurinol		
Paraxanthine			Paraxanthine		
PFOS	PFOS	PFOS	PFOS	PFOS	PFOS
Saccharin					
Sotalol					
Telmisartan	Telmisartan	Telmisartan			
Tramadol					
Valsartan					
Valsartan acid	Valsartan acid	Valsartan acid	Valsartan acid	Valsartan acid	Valsartan acid
Total no: 25	*Total no: 10*	*Total no: 10*	*Total no: 9*	*Total no: 5*	*Total no: 6*

The removal efficiency rate differs depending on substances as well as processes and parameters applied. E.g. for the preozonation process the maximum efficacy differs between 80,28 and 8,90% for 4-formylaminoantipyrine and Metformin, respectively, under 5 g/m^3 ozone dose and *ca.* 20 min. contact time. Filtration together with coagulation process is most efficient for DEET removal – 68,05%. The highest efficiency of the carbon filters was observed for valsartan acid, Gabapenin and Oxipurinol – more than 72% with an average contact time of 60 min. (Weber et al., 2022).

It should be noted that in most cases the removal of a given substance took place with its decrease below the level of quantification limit. Thus, it must be assumed that the reported efficiency of the treatment process can be even higher than determined.

At the end of the water treatment process only 6 out of 25 substances are detectable (at concentrations above LoQ) – Acesulfame, DEET, Metformin, Methylparaben, PFOS and Valsartan acid (Table 5). Despite this, the high decrease in concentration of those substances is observed what should be emphasized. Also, it should be noted that the concentrations of Acesulfam at the WTP are relatively small, and oscillate between <50 and 66,3 ng/L. Thus, the concentrations at the end of the process are within the uncertainty of the analytical method, which is 35%. The average removal efficiency of Valsartan acid, after the whole water treatment process, is 88,44% and the most efficient processes is ozonation and activated carbon filtration. In case of DEET the average removal efficiency rate is 66,11%. The maximum observed reduction of PFOS concentration is 59,68% and the most effective process here is activated carbon filtration. Metformin concentration is reduced by up to 53,38% and the most significant process is intermediate ozonation (which reduces the substance concentration by 30%). The average reduction of Methylparaben concentration only at the activated carbon filters exceeded 50%.

A sudden increase of substance concentrations along the technological process is also noteworthy (Table 5). Unfortunately, due to a limited number of monitoring campaigns, there is no possibility to exclude sampling and analytical errors or specificity of the technological processes. Nevertheless, other authors indicate the possibility of a reverse transformation of pharmaceutical metabolites or their conjugates into parent compounds (Kruglova et al., 2014, Verlicchi et al., 2021, Martinez-Alcala I. et al., 2021). Blair et al. (2015) pointed the possibility of the negative removal efficiency rate in such a situation.

5. Conclusion

PPCP concentrations and the number of detected contaminants in surface water varied depending on seasons of the year. The highest values were reported in winter, which presumably resulted, among others, from environmental conditions. Concentrations of individual contaminants in surface waters usually did not exceed 100 ng/L. However, some compound concentrations were in the range of 100 – 500 ng/L, and for several contaminants they even reached 1,000 ng/L. DEET, Oxypurinol, and Sucralose were PPCPs detected at the highest concentrations. The main source of PPCPs are wastewater discharges from the WWTP "Ożarowice". Groundwater contamination with PPCPs may occur locally, but its influence on surface water quality is negligible.

As PPCPs were detected in surface water, some substances may also be observed in raw water at the WTP Kozłowa Góra. At this WTP up to 27 substances were detected during six campaigns. The number and concentration of the observed substances changed over time and typically decreased after each treatment stage. The analysis of the PPCP monitoring results at Kozłowa Góra WTP emphases the high efficiency of the whole water treatment system and indicates that the highest removal efficiency was achieved during the preozonation process and activated carbon filtration.

6. References

Blair, B., Nikolaus, A., Hedman, C., Klaper, R., Grundl, T., 2015. Evaluating the degradation, sorption, and negative mass balances of pharmaceuticals and personal care products during wastewater treatment. Chemosphere 134, 395–401. https://doi.org/10.1016/j.chemosphere.2015.04.078.

Bojarski A., Szczęsny J., Wojtas S., 2004: Maintenance and operation manual. Kozłowa Góra water reservoir in Wymysłów. Engineering company Cermet-Bud Sp. z o.o., Kraków.

Budzyńska A, Rozlał K., Rzętała M., 1999: Park in Świerklaniec and the Kozłowa Góra reservoir as a nature and landscape complex, [in:] Rzętała M., Human-environment interaction in geographical research, SKNG WNoZ UŚ, Sosnowiec, 115-123.

Czekaj, J. et al., 2017: Report of PROLINE-CE Workpackage T2, Activity T2.1. Set up of pilot specific management practices. D.T2.1.4 descriptive documentation of Pilot Actions and related issues. Pilot Action 2.2: Kozłowa Góra. Interreg Central Europe PROLINE-CE, p. 50.

D.T2.1.1 Description of pilot actions. Upper Silesia Industrial Region. Czekaj Joanna, Ferenc Katarzyna, Bartkiewicz Ewelina.

D.T2.2.1 Methodology of monitoring – pilot predefinition Kozłowa Góra (Upper Silesia Industrial Region) PA. Czekaj Joanna, Mietelska Aleksandra, Bartkiewicz-Mzyk Ewelina.

D.T2.4.1 Analysis of pilot action-specific behaviour of PPCP in the aquatic environment. Kozłowa Góra Pilot Area, Poland. Czekaj Joanna, Ferenc Katarzyna, Jakóbczyk - Karpierz Sabina, Mlekodaj Laura, Paciej Jarosław, Różkowski Jacek, Ślósarczyk Kinga, Wolny Filip.

D.T3.3.3 First set-up for modeling transport of emerging contaminants in hydrological systems. Kozłowa Góra Pilot Area, Poland. Czekaj Joanna, Sitek Sławomir, Ślósarczyk Kinga.

D.T3.3.5 Final emerging contaminants transport model for pilot action. Kozłowa Góra Pilot Area, Poland. Wolny Filip, Czekaj Joanna, Ślósarczyk Kinga, Sitek Sławomir.

D.T4.3.1 Monograph of the boDEREC-CE project: *Board for Detection and Assessment of Pharmaceutical Drug Residues in Drinking Water - Capacity Building for Water Management in CE*. Reberski Lukač Jasmina, Selak Ana (ed.)

Kruglova, A., Ahlgren, P., Korhonen, N., Rantanen, P., Mikola, A., Vahala, R., 2014. Biodegradation of ibuprofen, diclofenac and carbamazepine in nitrifying activated sludge under 12 ◦C temperature conditions. Sci. Total Environ. 499, 394–401. https://doi.org/10.1016/j.scitotenv.2014.08.069

Martínez-Alcala I., Guillen-Navarro J.M., Lahora A., 2021: Occurrence and fate of pharmaceuticals in a wastewater treatment plant from southeast of Spain and risk assessment. Journal of Environmental Management, 279, https://doi.org/10.1016/j.jenvman.2020.111565

Verlicchi, P., Al Aukidy, M., Zambello, E., 2012. Occurrence of pharmaceutical compounds in urban wastewater: removal, mass load and environmental risk after a secondary treatment—a review. Sci. Total Environ. 429, 123–155. https://doi.org/10.1016/j.scitotenv.2012.04.028.

Weber Ł., Szambelanczyk K., Jedraszak M. and Samelak P., 2022: Efficiency analysis of pharmaceuticals removal from water on WTP Kozłowa Góra. Silesian Waterworks archives.