

boDEREC-CE WORKPACKAGE T2

O.T2.2 PILOT ACTION KÁRANÝ - JIZERA RIVER

VERSION 1

01 2022







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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 by the boDerec-CE project are supported by new data, obtained mainly through project monitoring actions, focused on detailed documentation of time-space changes of PPCP concentrations throughout the pilot areas. The main objective of the T2 work package was to run regular monitoring of the PPCP contents in drinking water and in raw waters (groundwaters or surface waters) which serve as a source for its production. Monitoring was performed on 8 pilot sites in different regions and hydrological conditions in Central Europe.

This report summarizes pilot action activities on locality Káraný, by the Jizera River in the Czech republic. The monitoring system was designed to characterize the conditions from the source of surface water used for the production of potable water up to the process of its technological modification to the final form.

A substantial part of monitoring was sampling and laboratory analysis, which were uniformed within the boDerec-CE project, for better comparability of the results from different project pilot sites. The data gained by monitoring served as an input for assessment of attenuation in the natural environment and the effectiveness of different water technologies. Further processing of the data was performed within T3 and T4 workpackage, which include construction of modelling tools, synthesis of results and dissemination activities.

2. Pilot site characteristics

Karany pilot site is located in the central part of Bohemia, about 30 km northeast of Prague (Figure 1).







Figure 1 Situation of Káraný pilot site with delineation of Jizera watershed

2.1. Geographical and hydrological conditions

Karany Waterworks uses water from the lower reaches of Jizera River. The length of the river is 164.6 km and the catchment area is 2193 km². Average flow rate in Mladá Boleslav is of around 20 m3/s. The river basin has a mixed nature with a balanced representation of forests and farmland. The only major industrial site is Mladá Boleslav, which has approximately 44,000 inhabitants. The city is mainly concentrated in the car industry represented by the famous Škoda brand.

In terms of potential sources of pollution by PPCPs, the greatest risk is municipal wastewater effluent. The Mladá Boleslav town is also a seat of the psychiatric hospital with a 150-year tradition. Only four more towns in the Jizera basin have more than 5,000 inhabitants (Turnov 14 000, Mnichovo Hradiště 8 700, Benátky nad Jizerou 7 000, Bakov nad Jizerou 5000). All towns are equipped with wastewater treatment plants.





Hydrogeologically the pilot site is characterized as a shallow unconfined aquifer situated in terraces of Quaternary fluvial sediments. The aquifer is naturally recharged by infiltration of precipitation and inflow from the bedrock. Quaternary sediment bedrock is formed by marl of large Czech Cretaceous basin. Marls are due to their low permeability considered as aquitard, but fractured zones allow inflows from deeper aquifers. In natural conditions groundwater from the Quaternary aquifer drains to the Jizera River. Intensive extraction of groundwater induces recharge of the aquifer from the river and in addition the aquifer is artificially recharged.

2.2. Water treatment techology

The waterwork at Káraný operates on the principle of combining two independent drinking water treatment technologies (see Figure 2). The first one is now historic, but still perfectly functioning project of bank infiltration built between 1906 and 1913. It consists of 685 wells of a depth ranging from 8 to 12 meters, spaced 20 to 40 meters apart, situated in the sand-gravel fluvial terraces ca. 250 meters from the bank of the Jizera River. The total capacity of this system is up to 1,000 l/s.



Figure 2 Scheme of Káraný waterworks (modified from Skalický 2015)

Another technology of the waterworks origins in 1968 and relies on artificial recharge. The first step of this process is a simple mechanical treatment of the surface water from the river. The treated water is then pumped into infiltration ponds (see Figure 3) from where it percolates into about 20 meters thick sandy fluvial sediments and recharges the extracted aquifer.

The water table is at an average level of 10 to 14 meters below ground so that there is in the unsaturated zone a sufficient storage space for seepage water. At a distance of approximately 200 meters from the infiltration ponds, there is a system of large-diameter wells with a total capacity of up to 900 l/s. The tapped water is a mixture of infiltrated water and original groundwater in sandy-gravel terrace inflowing from the east towards the Jizera River. Water balance model studies assume that 20 to 30% of groundwater participate in the resulting mixture, while the remaining 70 to 80% consist of water from artificial recharge. However, these proportions may vary depending on the operating conditions of the waterworks.







Figure 3 Artificial infiltration pond in Káraný

2.3. Socio - economic conditions and main end users

Kárany Waterworks represents a key source of drinking water for the capital city of Prague with more than 1 million inhabitants. For this reason, the quality of drinking water produced is a very sensitive issue which, among other things, has a considerable political and socio-economic dimension. Water technology and distribution has as a majority owner Prague Municipality, who actively supports applied research and has a strong interest in improving the quality of the technologies used.

On the other hand, it is necessary to mention the future potential conflict between the Káraný waterworks operator and the operator of the wastewater treatment plant in Mladá Boleslav, which is the dominant source of pollution by PPCP. Although its technology perfectly complies with today's Czech legislation, it is still inactive for the vast majority of PPCP substances. However, an unwritten rule says "who pollutes, pays". Probably the most significant source of contamination is the psychiatric hospital in Kosmonosy.

It is therefore evident, that there are many subjects, which are potentially interested in results from the Czech pilot site.

3. Monitoring methodology and available data

From previous projects, monitoring results of about 100 PPCP substances are available. Monitoring took place in a monthly step during period 2017 an 2018. In addition, data on the flow of the Jizera River in daily step (1960 - 2018), climatic data (1960 - 2018), and operational data from the waterworks are available. A subsequent boDEREC-CE project monitoring completed these data.

3.1. Sampling and laboratory analysis

The boDerec-CE monitoring on all project pilot sites was conducted according to common methodology. The analyses of the collected samples of surface and groundwater were carried out according to valid procedures and EPA method 1694 in the Vltava River Basin Authority laboratory.





Samples were collected in 60 mL amber glass vials (filled only halfway). The samples were stored in a freezer (in an inclined position). They were defrosted at a maximum temperature of 30 °C on the day of analysis. It was necessary to conduct the analysis immediately after defrosting.

One method was developed for the analysis of PPCPs (LC-MS/MS with combinated ESI+ and ESI- mode). The samples of water were centrifuged in headspace vials for 10 min at about 3500 rpm. Subsequently 1.50 g of each sample were weighed in a 2 mL vial on an analytical balance. Then 1.5 μ L of acetic acid was added to each sample. An isotope dilution was performed in the next step. Deuterated internal standards of d10-carbamazepine, d6-sulfamethoxazole, d3-iopromide, d3-iopamidol, 13C2-erythromycin, d3-ibuprofen, d4-diclofenac, d3-naproxen, d5-chloramphenicol and others were used.

PPCPs were separated and detected by 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.

Method; the separation was carried out on a Waters Xbridge C18 analytical column (100 mm x 4.6 mm, 3.5 μ m particle size). The mobile phase consisted of methanol and water with 0.02 % acetic acid and 0.5 mM ammonium fluoride as the mobile phase additives. The flow rate was 0.5 mL/min. The injection volume was 0.050 mL.

The range of analysis and detection limit for each analyte is shown in the table below (Table 1).

Each series of samples were verified by calibration control and by maintaining a clean environment, equipment, and agents. The performance of the analytical system was ensured by blank and spiked samples. The chemicals used for the preparation of calibration solutions had a certified purity of 99%. Calibration solutions were prepared from neat analytes or from solutions with certified concentration. Each fifth sample in a series was processed by the method of standard addition, which was used to control the effect of the matrix of the sample and to reset the actual recovery ratio of a specific analyte. The measuring instruments were under regular control, and measuring vessels were metrologically tested.

The chemicals used were supplied from renowned manufacturers in the EU and USA: Dr. Ehrenstorfer GmbH (Augsburg, Germany), LGC Ltd. (Teddington, Middlesex, UK), Honeywell International Inc. (Morris Plains, NJ, USA), HPC Standards GmbH (Cunnersdorf, Germany), Absolute Standards Inc. (Hamden, CT, USA), CIL Inc. (Tewksbury, MA, USA), Analytika spol s.r.o. (Prague, Czech Republic).

	Pharmaceuticals	unit	Detection limit
1.	1-H-benzotriazole	ng/l	20
2.	4(5)-methyl-1-H-benzotriazole	ng/l	20
3.	4-formylaminoantipyrine	ng/l	10
4.	acebutulol	ng/l	10
5.	acesulfame	ng/l	50
6.	alfuzosin	ng/l	10
7.	atenolol	ng/l	10
8.	atorvastatin	ng/l	10
9.	azithromycin	ng/l	10
10.	bezafibrate	ng/l	10
11.	bisfenol A	ng/l	50
12.	bisfenol B	ng/l	50
13.	bisfenol S	ng/l	50
14.	bisoprolol	ng/l	10
15.	butylparaben	ng/l	10
16.	caffeine	ng/l	100
17.	carbamazepine	ng/l	10
18.	carbamazepine 10,11-dihydro-10-hydroxy	ng/l	10
19.	carbamazepine 10,11-dihydroxy	ng/l	10
20.	carbamazepine 10,11-epoxide	ng/l	10
21.	carbamazepine 2-hydroxy	ng/l	10

Table 1 Analysed PPCPs





22.	celiprolol	ng/l	10
<u>23.</u> 24.	citalopram clarithromycin	ng/l ng/l	20 10
<u>24.</u> 25.	climbazole	ng/l	10
26.	clindamycin	ng/l	10
27.	clofibric acid	ng/l	10
28.	cotinine	ng/l	20
29.	cyclamate	ng/l	500
30.	cyclophosphamide	ng/l	10
31.	DEET	ng/l	10
32.	diatrizoate	ng/l	10
33.	diclofenac	ng/l	20
34.	diclofenac-4'-hydroxy	ng/l	20
35.	diltiazem	ng/l	10
36.	erythromycin	ng/l	10
37.	ethylparaben	ng/l	10
38.	fexofenadine	ng/l	10
39.	fluconazole	ng/l	10
40.	fluoxetine	ng/l	10
41. 42.	furosemide gabapentin	ng/l ng/l	50 10
42. 43.	gemfibrozil	ng/l	10
43.	hydrochlorothiazide	ng/l	50
45.	chloramphenicol	ng/l	20
46.	ibuprofen	ng/l	20
47.	ibuprofen-2-hydroxy	ng/l	30
48.	ibuprofen-carboxy	ng/l	20
49.	iohexol	ng/l	50
4 5. 50.	iomeprol	ng/l	50
51.	iopamidol	ng/l	50
52.	iopromide	ng/l	50
53.	irbesartan	ng/l	10
54.	ivermectin	ng/l	50
55.	ketoprofen	ng/l	10
56.	lamotrigine	ng/l	10
57.	lovastatin	ng/l	10
58.	memantine	ng/l	20
59.	metformin	ng/l	20
60.	methylparaben	ng/l	10
61.	metoprolol	ng/l	10
62.	mirtazapine	ng/l	10
63.	naproxene	ng/l	50
64.	naproxene-o-desmethyl	ng/l	20
65. 66.	norverapamil octyl methoxycinnamate (OMC)	ng/l	10 1000
		ng/l	
67. 68.	oxcarbazepine oxypurinol	ng/l ng/l	10 50
<u>69</u> .	paracetamol	ng/l	10
70.	paraxanthine	ng/l	100
71.	peniciline G	ng/l	10
72.	PFOA (perfluorooctanoic acid)	ng/l	10
73.	PFOS (perfluorooctane sulfonic acid)	ng/l	5
74.	phenazone	ng/l	10
75.	primidone	ng/l	10
76.	propranolol	ng/l	10
77.	propylparaben	ng/l	10
78.	propyphenazone	ng/l	10
79.	ranitidine	ng/l	10
80.	roxithromycin	ng/l	10
81.	saccharin	ng/l	50
82.	salbutamol	ng/l	10
83.	sertraline	ng/l	10
84.	simvastatin	ng/l	10
85.	sotalol	ng/l	10
86. 87.	sucralose sulfamerazine	ng/l ng/l	500 10
88.	sulfamethazine	ng/l	10
89.	sulfamethoxazole	ng/l	10
<u>89.</u> 90.	sulfanilamide	ng/l	50
GII			





92.	telmisartan	ng/l	20	
93.	tiamulin	ng/l	10	
94.	tramadol	ng/l	10	
95.	triclocarban	ng/l	10	
96.	triclosan	ng/l	20	
97.	trimetoprim	ng/l	10	
98.	valsartan	ng/l	10	
99.	valsartan acid	ng/l	10	
100.	venlafaxine	ng/l	10	
101.	verapamil	ng/l	10	
102.	warfarin	ng/l	10	

3.2. Objective of monitoring

Karany pilot site uses two independent technologies for drinking water production: bank infiltration and artificial recharge. Both technologies use surface water from the Jizera River as a source. This water is contaminated with a wide range of PPCP substances coming from the wastewater treatment plant of the city of Mladá Boleslav and the psychiatric clinic Kosmonosy.

The objective of the monitoring is to verify occurrence of PPCPs in different steps of the water extraction process on the pilot site and to characterize the efficiency of removal of PPCPs from river water by means of bank infiltration and artificial recharge. The obtained results will serve, inter alia, to compare the efficiency of PPCP removal at a German pilot site in Dresden - Hosterwitz, using similar drinking water production technology.

3.3. Sampling

In 2017 - 2018, a detailed monitoring of PPCP substances took place in the area of interest. This included data from the main source of contamination in Mladá Boleslav, through its transport in the Jizera watercourse to changes taking place in various drinking water production technologies. For this reason, the monitoring of the Bo DEREC CE project focused only on the source of surface water from Jizera, which is used for drinking water production (RIV). Furthermore, the quality of drinking water produced by bank infiltration (BF) and artificial recharge (AR) was monitored. Finally, the last monitored objects were 5 wells, characterizing the "natural background" of groundwater coming from the east (HS1, HS2, HS3, HS4, HS5). Situation of sampling points is shown in Figure 4.

In total 14 samples were taken in Káraný site during years 2020 and 2021.







Figure 4 Sampling points in Káraný site

Individual sampling points are characterised as follows:





Point RIV Sojovice weir

Objective: obtain information on the quality of surface water from the Jizera River, which is used for the production of drinking water by artificial infiltration.

Method of sampling: sampling directly from surface water from the bank above the weir.



Point BF Bank infiltration

Objective: get information on groundwater quality coming from bank infiltration. This is a mixed sample of about 600 wells situated along the Jizera River

Method of sampling: sampling from the bank infiltration pumping station

Point AR Artificial recharge

Objective: get information on groundwater quality coming from artificial recharge. This is a mixed sample of about 45 wells situated along the artificial recharge basins

Method of sampling: sampling from the artificial recharge pumping station

Points HS Groundwater background	
Objective: get information on groundwater quality coming from quaternary and cretaceous aquifer from East.	
Method of sampling: the sample is taken from a well in a dynamic state, that is, after pumping out volume of water, ensuring the exchange of water in the well.	







4. Monitoring results

This analysis is based on a 2 year monitoring of PPCP in pilot area Káraný, located by the Jizera River in the Czech Republic and other available results from the same area form years 2018 and 2018. All project monitoring data are gathered in deliverable D.T2.3.1. Analysis of behaviour of PPCP during water treatment is further assessed in terms of T3 work package, by application of modelling tools.

Water resource

4.1. Water resource

The section of the Jizera River around the Sojovice weir plays a key role of the Káraný waterworks, which uses artificial recharge for the production of drinking water. This water is the source for further treatment, more or less using natural purification processes. Despite the predominant decreasing trend of most pollutants in the Jizera River downstream of Mladá Boleslav, their detected number and concentrations in absolute values remain at relatively high levels (Figure 5). Out of 113 analysed substances, 35 substances were detected in the river water. The median concentrations of five substances (Sucralose, Metformin, Oxypurinol, Acesulfam and Telmisartan) exceed 200 ng/l. For another five substances median exceeds 50 ng/l (Benzotriazol, Paraxanthine, Iomeprolol, Caffein and Gabapentin). Further 25 substances occur typically in tens of ng/l.



Figure 5 Concentrations of PPCPs in ng/L in Jízera by Sojovice weir (median from period 2017-2021)





4.2. Water treatment efficiency

The results of technologies simulating natural attenuation process, which are artificial recharge and bank filtration, clearly demonstrate the efficacy of PPCPs removal in both waterworks facilities. A total of 35 substances were detected in Jizera river water and majority of them fell below detection limits after the treatment. The mechanical pre-treatment of the river water before infiltration does not affect the monitored substances.

Among the substances that appear in relatively high concentrations in river water, but are efficienty removed by artificial recharge and bank infiltration in Káraný are Sucralose, Metformin, Telmisartan, Caffein, Saccharin, Paraxanthin and Iomeprol.

Only eight substances occur systematically in groundwater tapped from the system of large-diameter wells in the vicinity of the infiltration ponds in Káraný waterworks. The most important is a group of six substances that appear systematically in drinking water produced by artificial recharge technology. These are Carbamazepine, Sulfamethoxazole, Acesulfame, Lamotrigine, Primidone and Oxypurinol (Table 2). They were evidently associated with the WWTP in Mladá Boleslav.

year		2017											2018													020	2021	
month	ng/L	I	Ш	ш	IV	v	vi	VII	VIII	IX	х	XI	XII	1	Ш	=	IV	v	VI	VII	VIII	IX	x	XI	XII	VIII	IX	v
Carbamazepin	ng/L	16	16	18	13	13	12	19	21	16	13	16	12	14	х	х	х	х	11	14	19	х	25	24	22	10	17	11
Sulfamethoxazol	ng/L	40	41	43	40	33	31	34	34	33	30	24	25	24	22	24	27	52	39	41	37	х	х	41	41	25	х	5
Acesulfam	ng/L											120	80	х	96	85	110	х	х	х	127	х	х	149	126	х	79	138
Oxypurinol	ng/L													97	130	96	120	113	79	76	108	х	х	х	х	155	244	82
Lamotrigine	ng/L																	х	х	19	22	х	х	34	31	24	35	21
Primidone	ng/L																			х	13	х	х	14	14	11	15	х
Gabapentin	ng/L	х	х	18	27	13	11	х	х	х	х	х	х	х	х	х	х	13	х	х	х	х	х	х	х	х	х	х
lbuprofen	ng/L	32	х	х	21	х	х	х	х	х	х	х	х	х	х	х	х	х	х	х	10	х	х	20	х	х	х	х
Benzotriazol	ng/L																									х	880	212
Paracetamol	ng/L	х	х	х	х	х	х	х	х	х	х	х	х	х	х	х	х	х	х	х	х	х	х	11	х	х	х	х
Methylparaben	ng/L																									327	х	30
Propylparaben	ng/L																									462	х	х
PFOS	ng/L																									х	х	х
Diclofenac	ng/L	х	х	х	х	х	х	х	х	х	х	х	х	х	х	х	х	х	х	х	х	х	х	х	х	х	х	х

Table 2 Detected PPCPs in the output from artificial recharge in Káraný (x means value under the detection limit, empty cell means that at time of sampling this substance had not yet been analyzed).

Bank infiltration in the case of Káraný vodárny seems to be a more effective technology in removing PPCPs. The only substance, Acesulfame, appears in the produced water in a higher frequency and in lower concentrations than artificial recharge (Table 3). Bank infiltration at the Káraný site perfectly reduces the concentrations of Carbamazepine and Sulfamethoxazole below the detection limit. Other substances appear only at random frequency, unsystematically and in very low concentrations.





year							20	17						2018													20	2021
month	ng/L	1	Ш	Ш	IV	V	VI	VII	VIII	IX	Х	XI	XII	-	=	Ш	IV	V	VI	VII	VIII	IX	Х	XI	XII	VIII	IX	V
Carbamazepin	ng/L	х	х	х	х	х	х	х	х	х	х	х	х	х	х	х	х	х	х	х	х	х	х	х	х	х	х	х
Sulfamethoxazol	ng/L	х	х	х	х	х	х	х	х	х	х	х	х	х	х	х	х	х	х	х	х	х	х	х	х	х	х	х
Acesulfam	ng/L										57	64	х	х	х	х	х	58	х	60	58	х	х	71	57	142	х	х
Oxypurinol	ng/L												72	х	х	х	х	х	х	51	61	х	х	х	х	х	142	х
Lamotrigine	ng/L																		х	х	х	х	х	х	х	х	х	х
Primidone	ng/L																		х	х	11	х	х	х	х	х	х	х
lbuprofen	ng/L	54	х	х	х	х	х	х	31	х	х	х	х	х	х	х	х	х	х	х	х	х	х	х	х	х	х	х
Gabapentin	ng/L	х	х	х	х	х	11	х	х	х	х	х	х	х	х	х	х	х	х	х	х	х	х	х	х	х	х	х
Benzotriazol	ng/L																									х	х	25
Paracetamol	ng/L	х	х	х	х	х	10	16	х	х	х	х	х	х	х	х	х	х	х	х	х	х	х	х	х	х	х	х
Methylparaben	ng/L																									х	х	х
Propylparaben	ng/L																									х	х	х
Estron	ng/L																		2	2	5	х	х	х	х	х	х	х
Caffein	ng/L	х	х	х	х	х	х	х	140	х	х	230	х	х	х	х	х	х	х	х	148	х	х	х	х	х	267	х
Paraxantine	ng/L																									х	139	х
PFOS	ng/L																									10	6	х
Diclofenac	ng/L	х	х	х	х	х	31	х	х	х	х	х	х	х	х	х	х	х	х	х	х	х	х	х	х	х	х	х

 Table 3 Detected PPCPs in the output from bank infiltration in Káraný (x means value under the detection limit, empty cell means that at time of sampling this substance had not yet been analyzed).





5. Conclusion

The monitoring results document occurrence of PPCPs in Jizera River, which is water resource for Káraný waterworks. According to concentrations of PPCPs detected in treated water, the applied technologies of artificial recharge and bank filtration are relatively efficient in their removal. The more efficient technology is apparently bank filtration. Carbamazepine and Sulfamethoxazole are probably one of the most problematic substances in drinking water not only in Káraný waterworks but worldwide. The same problems with their occurrence in drinking water are documented in France (Vulliet et al. 2011), USA (Benotti et al. 2008), Wang et al. 2011) and Canada (Kleywegt et al. 2011). Notably, Carbamazepine was observed at a concentration exceeding 600 ng/L in the study conducted by in Canada (Kleywegt et al. (2011). The high levels of Carbamazepine could be explained by its high persistency.





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