boDEREC-CE
WORKPACKAGE T2

O.T2.1 PILOT ACTION JADRO AND ŽRNOVNICA SPRINGS CATCHMENT

VERSION 1

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1. Introduction

The basic condition for the elimination of any kind of pollution is sufficient knowledge of its properties, origin, behavior in the natural environment, and its reaction to various types of technological interventions. Knowledge and findings gained within the boDEREC-CE project are supported by new data, obtained mainly through project monitoring actions, focused on detailed documentation of time-space changes of PPCPs concentrations throughout the designated 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 (groundwater or surface water) which serve as a source for its production. Monitoring was performed at 8 pilot sites in different regions and hydrological conditions in Central Europe.

This report summarizes pilot action activities at Jadro and Žrnovnica springs catchment in Croatia. The monitoring system was designed to gain insights into the occurrence of pharmaceuticals and personal care products in Jadro and Žrnovnica springs used for water supply, and to help understand the hydrogeologically complex karst catchment.

A substantial part of monitoring was sampling and laboratory analyses, 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 the assessment of attenuation in the natural environment and the effectiveness of different water technologies. Further processing of the data was performed within the T3 and T4 workpackages, which include construction of modeling tools, synthesis of results, and dissemination activities.

2. Pilot site characteristics

Jadro and Žrnovnica springs catchment is a typical Dinaric karst catchment located in the central part of Southern Croatia (Fig. 1). The majority of the catchment area is covered with littoral, thermophilic forests and shrublands of downy oak, followed by sub-Mediterranean and epi-Mediterranean dry meadows. Agricultural land is located primarily within karst poljes, practically only catchment areas with soil cover (Jukić & Denić-Jukić, 2009). The most common types of soil are calcocambisol on limestone and calcomelanosol. Both springs are located upstream of the most populated area (Split and surrounding coastal areas) and are outside their direct pollution impact (Fig. 1).

Figure 1. Location of the Croatian pilot action area – Jadro and Žrnovnica springs catchment

2.1. Geographical and hydrological conditions

The whole catchment area is characterized by a dynamic and complex morphology made out of intertwining mountains and hills that stretch to the coast. According to Croatia's geomorphological regionalization (Bognar, 1999), the catchment area of Jadro and Žrnovnica springs belongs to the widespread megageomorphological region of the mountainous Dinaric system, mezzogeomorphological region of Central Dalmatia and its archipelago, and several minor sub-geomorphological regions. The outer edges of the wider catchment area are composed of Svilaja Mountain in the north, Sinjsko polje in the northeast-east, Mosor Mountain in the southeast-south, Kozajk Mountain in the south, Moseć Mountain and hills of Lećevica in the west. In-between mountainous terrain several poljes spread: Muć-Postinj polje (~400 ha), Dicmo polje (~300 ha), Dugopolje (~190 ha), and Konjsko polje (~150 ha). The majority of morphological structures have typical Dinaric orientation i.e. NW-SE which alters into E-W (Hvar orientation) towards the east.

Jadro (4.3 km in length) and Žrnovnica (4.8 km in length) are karstic rivers that receive water through the karstified aquifer (Kapelj et al., 2012), and end their flow into the Adriatic Sea. Jadro River spring discharges at an altitude of around 35 m a.s.l. south of Klis settlement and southwest of the Mosor Mountain (1339 m a.s.l.) (Fig. 2). Jadro spring had a maximal discharge of 52.47 m^3/s in 2015, minimal discharge of 2.3 m3/s in 2018, while its mean discharge is 9.24 m3/s (data period 2011-2019). The springing zone of Žrnovnica River occurs northeast of the Split city and near Žrnovnica settlement, at the foot of the Mosor Mountain, and altitudes ranging from 77 to 90 m a.s.l. The maximal Žrnovnica spring discharge was 17 m^3/s in 2015, minimal was 0.31 m^3/s in 2015, while mean discharge is 1.94 m^3/s (data period 2009-2019). The estimated hydrological-hydrogeological catchment area of Jadro and Žrnovnica together ranges from 250 to 500 km^2 (Bonacci, 1978; Fritz et al., 1988; Kapelj et al., 2012) as catchment boundaries have not yet been determined with a higher level of certainty. Cetina River flows along the assumed eastern catchment boundary, at an aerial distance of approx. 15 km from the springs and altitudes around 300 m a.s.l. (Fig. 2). The catchment is predominantly made out of highly permeable carbonate rocks of the Mesozoic and Paleogene ages. Flysch deposits and clastites represent hydrogeological barriers and at their contact with permeable rocks, springs of Jadro and Žrnovnica emerge.

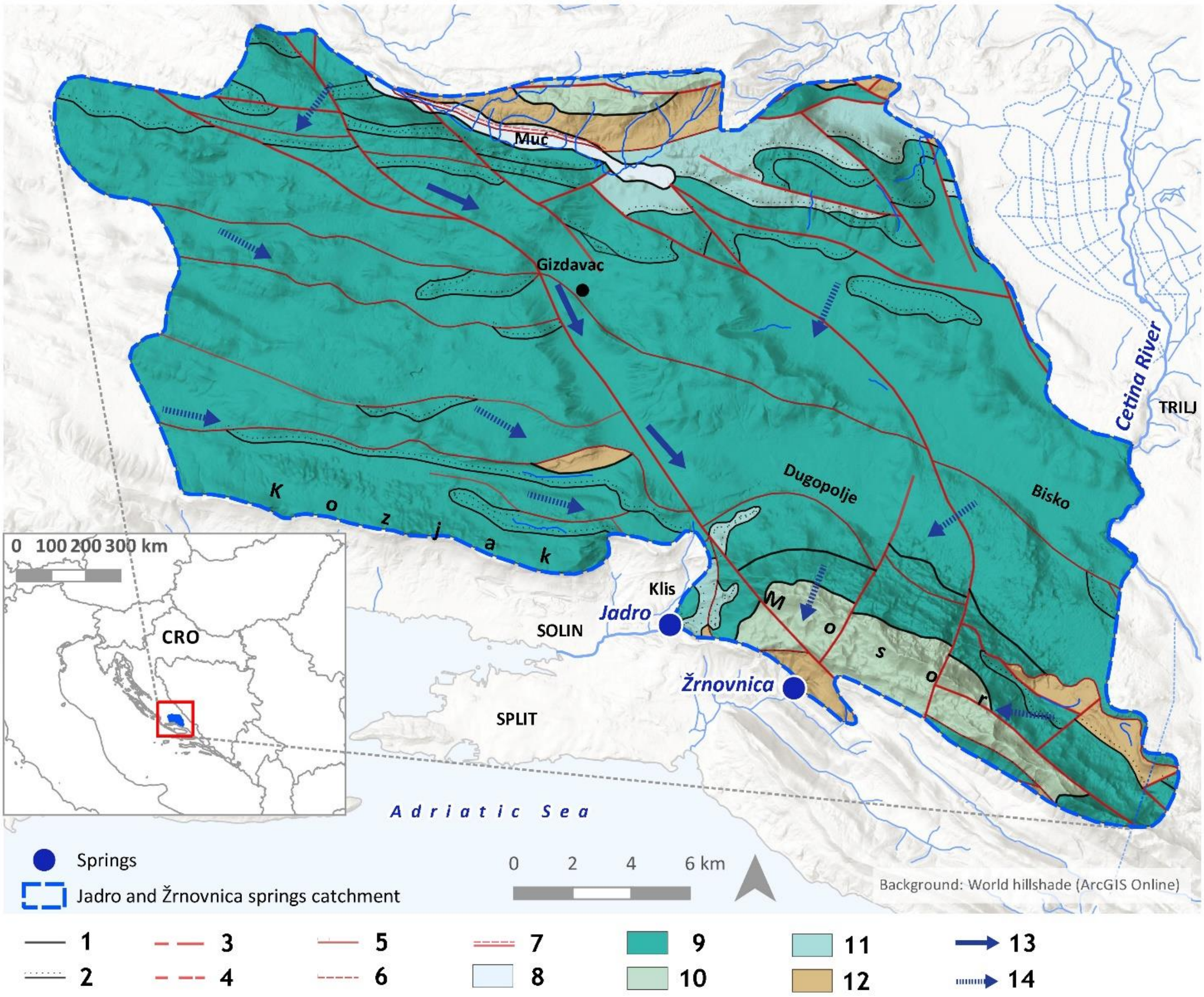


Figure 2. Hydrogeological map of Jadro and Žrnovnica springs catchment (modified from Biondić et al., 2003), 1 – normal lithostratigraphic boundary, 2 – erosional boundary, 3 – identified fault, 4 – covered fault, 5 – reverse fault, 6 – overthrust contact, 7 – covered overthrust contact, 8 – Quaternary deposits with aquifers of intergranular porosity and low permeability, 9 – carbonate rocks with aquifers of fracture-cavernous porosity and high permeability, 10 – carbonate rocks with aquifers of fracture-cavernous porosity and medium permeability, 11 – remaining clastic deposits mostly very low permeability, 12 – impermeable rocks (clay-silt deposits and low-grade metamorphic rocks), 13 – general groundwater flow direction, 14 – auxiliary groundwater flow direction.

2.2. Water treatment technology

The water at both Jadro and Žrnovnica springs undergoes only the chlorination process before it is distributed to end-users and no specific water treatment technology is needed.

2.3. Socio-economic conditions and main end-users

The water supply system of Split City and its wider surroundings (around 300,000 inhabitants) depends on the water intake at Jadro. Water and sewerage company VIK Split (project partner 02) is supplying with water taken from Jadro, Split, Solin, Kaštela and Trogir cities, as well as municipalities Podstrana, Okrug, Seget and partly Klis. Apart from considerable socio-economic dimension, spring Jadro is of historical importance, as it is used from Roman times when aqueduct, pipe network, and tunnel were built to supply

Diocletian palace with water. Žrnovnica spring supplies the nearby Žrnovnica and Donje Sitno settlements and enables irrigation of surrounding agricultural land.

Several potential pressures may result from socio-economic conditions, which are related to:

- Smaller, spatially scattered villages without proper sewerage systems and potentially leaking septic tanks, and bigger settlements without water treatment plants.
- few unsanitary landfills, which are currently in the remediation process, and there are cases of waste illegally being disposed of in karst swallow holes and caves.
- industrial sites located upstream of Jadro and Žrnovnica springs, mainly in Dugopolje area are potential sources of contaminants and risk for the drinking water quality;
- uncontrolled and inadequate use of pesticides and fertilizers in karst poljes (Dugopolje, Bisko, Muć), farms, and pastures could also be one of the organic contaminants' sources.

Within this pilot action area, the water supplier VIK Split complies with all thresholds set by the national legislation related to drinking water. Providing a high-water quality is the utmost priority of the waterworks.

3. Monitoring methodology and available data

Prior to the boDEREC-CE project, there were no studies on the occurrence of PPCPs in the karst aquifer of Jadro and Žrnovnica springs. Sampling on karst springs and Gizdavac borehole was aimed at obtaining information on PPCPs occurrence in groundwater. The intercatchment groundwater flows coming from the Cetina River were proved in previously published studies, therefore Cetina River near Trilj city was also sampled.

Within the pilot area, experts from the Department of Hydrogeology and Engineering geology of the Croatian Geological Survey also conducted hydrogeological field investigation which included collecting of water samples for analyses of major anions and cations, total organic carbon (TOC), and stable isotopes ($\delta^{18}O/\delta^{16}O$, $\delta^{2}H$), as well as *in situ* field measurements of physico-chemical parameters (temperature, pH, electrical conductivity, dissolved oxygen and bicarbonates concentration).

To improve insights into karst aquifer functioning, data loggers (electrolytic conductivity and water temperature) were installed at Jadro spring, Žrnovnica spring, and Cetina River. The loggers were first launched in March 2021. Two rain gauge data loggers were installed in February 2021 at Dugopolje and Mosor Mountain. It is envisaged to continue with data logging for at least two years, to collect enough data for making assumptions on the system's functioning.

3.1. Sampling and laboratory analysis

All samples were taken according to the internal project sampling instructions and delivered to the Povodí Vltavy laboratory in a frozen state. The analyses of the collected samples of surface water and groundwater were carried out according to valid procedures and EPA method 1694.

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 combined 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 µL 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 µm 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 (**Error! Reference source not found.**).

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 solutions with certified concentrations. 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).

Table 1 List of pharmaceuticals and personal care products (PPCP) analyzed within boDEREC-CE project

No.	Name	CAS#	Description	Unit	LOQ	LOD
Pharmaceuticals and personal care products						
1	1-H-benzotriazole	95-14-7	*corrosion inhibitor*	ng/l	20	7
2	1-methyl-1-H-benzotriazole	13351-73-0	*corrosion inhibitor*	ng/l	50	15
3	4(5)-methyl-1-H-benzotriazole	29385-43-1	*corrosion inhibitor*	ng/l	20	7
4	4-formylaminoantipyrine	1672-58-8	*metabolite of dipyrone (analgetic)*	ng/l	10	3
5	acebutulol	37517-30-9	*beta blocker*	ng/l	10	3
6	acesulfame	33665-90-6	*sugar substitute*	ng/l	50	15
7	alfuzosin	81403-80-7	*alpha-1 blocker*	ng/l	10	3
8	amitriptiline	50-48-6	*antidepressant*	ng/l	10	3
9	atenolol	29122-68-7	*beta blocker*	ng/l	10	3
10	atorvastatin	134523-00-5	*lipid-modifying agent*	ng/l	10	3
11	azithromycin	83905-01-5	*antibiotic*	ng/l	10	3
12	bezafibrate	41859-67-0	*fibrate*	ng/l	10	3
13	bisoprolol	66722-44-9	*beta blocker*	ng/l	10	3
14	bisphenol A	80-05-7	*alkylphenol*	ng/l	50	15
15	bisphenol B	77-40-7	*alkylphenol*	ng/l	50	15
16	bisphenol S	80-09-1	*alkylphenol*	ng/l	50	15
17	butylparaben	94-26-8	*cosmetic and pharmaceutical preservatives*	ng/l	10	3
18	caffeine	58-08-2	*stimulant*	ng/l	100	30
19	carbamazepine	298-46-4	*antiepileptic*	ng/l	10	3
20	carbamazepine 10,11-dihydro-10-hydroxy	29331-92-8	*metabolite*	ng/l	10	3
21	carbamazepine 10,11-dihydroxy	3564-73-6	*metabolite*	ng/l	10	3
22	carbamazepine 10,11-epoxide	36507-30-9	*metabolite*	ng/l	10	3
23	carbamazepine 2-hydroxy	68011-66-5	*metabolite*	ng/l	10	3
24	celiprolol	56980-93-9	*beta blocker*	ng/l	10	3
25	citalopram	59729-33-8	*antidepressant*	ng/l	20	7
26	clarithromycin	81103-11-9	*antibiotic*	ng/l	10	3
27	climbazole	38083-17-9	*antifungal*	ng/l	10	3
28	clindamycin	18323-44-9	*antibiotic*	ng/l	10	3
29	clofibric acid	882-09-7	*fibrate*	ng/l	10	3
30	cotinine	486-56-6	*metabolite of nicotine*	ng/l	20	7
31	cyclamate	139-05-9	*sugar substitute*	ng/l	100	30
32	cyclophosphamide	50-18-0	*chemotherapeutic agent*	ng/l	10	3
33	DEET	134-62-3	*repelent*	ng/l	10	3
34	diatrizoate	737-31-5	*contrast agens*	ng/l	50	15

No.	Name	CAS#	Description	Unit	LOQ	LOD
35	diclofenac	15307-79-6	*NSAID*	ng/l	20	7
36	diclofenac-4-hydroxy	64118-84-9	*metabolite*	ng/l	20	7
37	diltiazem	42399-41-7	*antiarrhythmic*	ng/l	10	3
38	disopyramide	5.9.3737	*antiarrhythmic*	ng/l	10	3
39	eprosartan	133040-01-4	*antihypertensive*	ng/l	10	3
40	erythromycin	114-07-8	*antibiotic*	ng/l	10	3
41	ethylparaben	120-47-8	*cosmetic and pharmaceutical preservatives*	ng/l	10	3
42	fexofenadine	83799-24-0	*antihistamine*	ng/l	10	3
43	fluconazole	86386-73-4	*antifungal*	ng/l	10	3
44	fluoxetine	54910-89-3	*antidepressant*	ng/l	10	3
45	furosemide	54-31-9	*diuretic*	ng/l	50	15
46	gabapentin	60142-96-3	*antiepileptic*	ng/l	10	3
47	gemfibrozil	25812-30-0	*fibrate*	ng/l	10	3
48	hydrochlorothiazide	58-93-5	*diuretic*	ng/l	50	15
49	chloramphenicol	56-75-7	*antibiotic*	ng/l	20	7
50	ibuprofen	15687-27-1	*NSAID*	ng/l	20	7
51	ibuprofen-2-hydroxy	51146-55-5	*metabolite*	ng/l	30	10
52	ibuprofen-carboxy	15935-54-3	*metabolite*	ng/l	20	7
53	iohexol	66108-95-0	*contrast agent*	ng/l	50	15
54	iomeprol	78649-41-9	*contrast agent*	ng/l	50	15
55	iopamidol	60166-93-0	*contrast agent*	ng/l	50	15
56	iopromide	73334-07-3	*contrast agent*	ng/l	50	15
57	irbesartan	138402-11-6	*antihypertensive*	ng/l	10	3
58	ivermectin	70288-86-7	*antiparazitic*	ng/l	50	15
59	ketoprofen	22071-15-4	*NSAID*	ng/l	10	3
60	lamotrigine	84057-84-1	*antiepileptic*	ng/l	10	3
61	lincomycin	154-21-2	*antibiotic*	ng/l	10	3
62	losartan	114798-26-4	*antihypertensive*	ng/l	10	3
63	lovastatin	75330-75-5	*lipid-modifying agent*	ng/l	10	3
64	memantine	19982-08-2	*psychoanaleptic (anti-dementia agent)*	ng/l	20	7
65	metformin	657-24-9	*anti-diabetic drug*	ng/l	20	7
66	methylparaben	99-76-3	*cosmetic and pharmaceutical preservatives*	ng/l	30	10
67	metoprolol	51384-51-1	*beta blocker*	ng/l	10	3
68	mirtazapine	61337-67-5	*antidepressant*	ng/l	10	3
69	naproxene	22204-53-1	*NSAID*	ng/l	50	15
70	naproxene-o-desmethyl	52079-10-4	*metabolite*	ng/l	20	7
71	norverapamil	67018-85-3	*metabolite of verapamil (antiarytmic)*	ng/l	10	3
72	octyl methoxycinnamate (OMC)	5466-77-3	*UV filter*	ng/l	1000	300
73	oxcarbazepine	28721-07-5	*metabolite*	ng/l	10	3
74	oxypurinol	2465-59-0	*purine receptor modulator*	ng/l	50	15
75	paracetamol	103-90-2	*pain killer*	ng/l	10	3
76	paraxanthine	611-59-6	*metabolite of caffeine*	ng/l	100	30

No.	Name	CAS#	Description	Unit	LOQ	LOD
77	peniciline G	61-33-6	*antibiotic*	ng/l	10	3
78	PFOA (perfluorooctanoic acid)	335-67-1	*fluorosurfactant*	ng/l	10	3
79	PFOS (perfluorooctane sulfonic acid)	1763-23-1	*fluorosurfactant*	ng/l	5	1,5
80	phenazone	60-80-0	*NSAID*	ng/l	10	3
81	primidone	125-33-7	*antiepileptic*	ng/l	10	3
82	propranolol	525-66-6	*beta blocker*	ng/l	10	3
83	propylparaben	94-13-3	*cosmetic and pharmaceutical preservatives*	ng/l	20	7
84	propyphenazone	479-92-5	*NSAID*	ng/l	10	3
85	ranitidine	66357-35-5	*histamine receptor modulator*	ng/l	10	3
86	roxithromycin	80214-83-1	*antibiotic*	ng/l	10	3
87	saccharin	81-07-2	*sugar substitute*	ng/l	50	15
88	salbutamol	18559-94-9	*antiasthmatic drug*	ng/l	10	3
89	sertraline	79617-96-2	*antidepressant*	ng/l	10	3
90	simvastatin	79902-63-9	*lipid-modifying agent*	ng/l	10	3
91	sotalol	3930-20-9	*beta blocker*	ng/l	10	3
92	sucralose	56038-13-2	*sugar substitute*	ng/l	1000	300
93	sulfamerazine	127-79-7	*antibiotic*	ng/l	10	3
94	sulfamethazine	57-68-1	*antibiotic*	ng/l	10	3
95	sulfamethoxazole	723-46-6	*antibiotic*	ng/l	10	3
96	sulfanilamide	63-74-1	*antibiotic*	ng/l	50	15
97	sulfapyridine	144-83-2	*antibiotic*	ng/l	10	3
98	telmisartan	144701-48-4	*antihypertensive*	ng/l	20	7
99	tiamulin	55297-95-5	*veterinary antibiotic*	ng/l	10	3
100	tramadol	27203-92-5	*pain killer*	ng/l	10	3
101	triclocarban	101-20-2	*antibacterial agent*	ng/l	10	3
102	triclosan	3380-34-5	*antibacterial agent*	ng/l	20	7
103	trimethoprim	738-70-5	*antibiotic*	ng/l	10	3
104	valsartan	137862-53-4	*antihypertensive*	ng/l	10	3
105	valsartan acid	164265-78-5	*metabolite of valsartan (antihypertens)*	ng/l	10	3
106	venlafaxine	93413-69-5	*antidepressant*	ng/l	10	3
107	venlafaxine O-desmethyl	93413-62-8	*antidepressant*	ng/l	10	3
108	verapamil	52-53-9	*antiarythmic*	ng/l	10	3
109	warfarin	81-81-2	*antithrombotic*	ng/l	10	3

3.2. Objective of monitoring

The objective of the monitoring was to quantify the PPCPs occurrence in the karst water resources - springs of Jadro and Žrnovnica, surface water of Cetina River, and groundwater at Gizdavac borehole. Moreover, the analysis of the different water samples aimed to investigate a potential interaction between the water resources.

The obtained PPCP concentrations can also be used, in the next step, for the prioritization of contaminants, identification of potential site-specific sources, setting up of adequate water protection measures, the inclusion of specific substances in national priority substances list or watch list, as well as development of transport models.

3.3. Sampling

In total five sampling campaigns were conducted from October 2019 to November 2020 at four different sampling points (Fig. 3), selected to determine the water quality related to the PPCP concentrations in the pilot action area of Jadro and Žrnovnica springs. Unfortunately, monitoring was not possible regularly due to Covid-19 pandemic restrictions. 19 samples of water were taken in total, out of which 5 at Jadro, Žrnovnica, and Cetina River, and 4 at Gizdavac borehole.

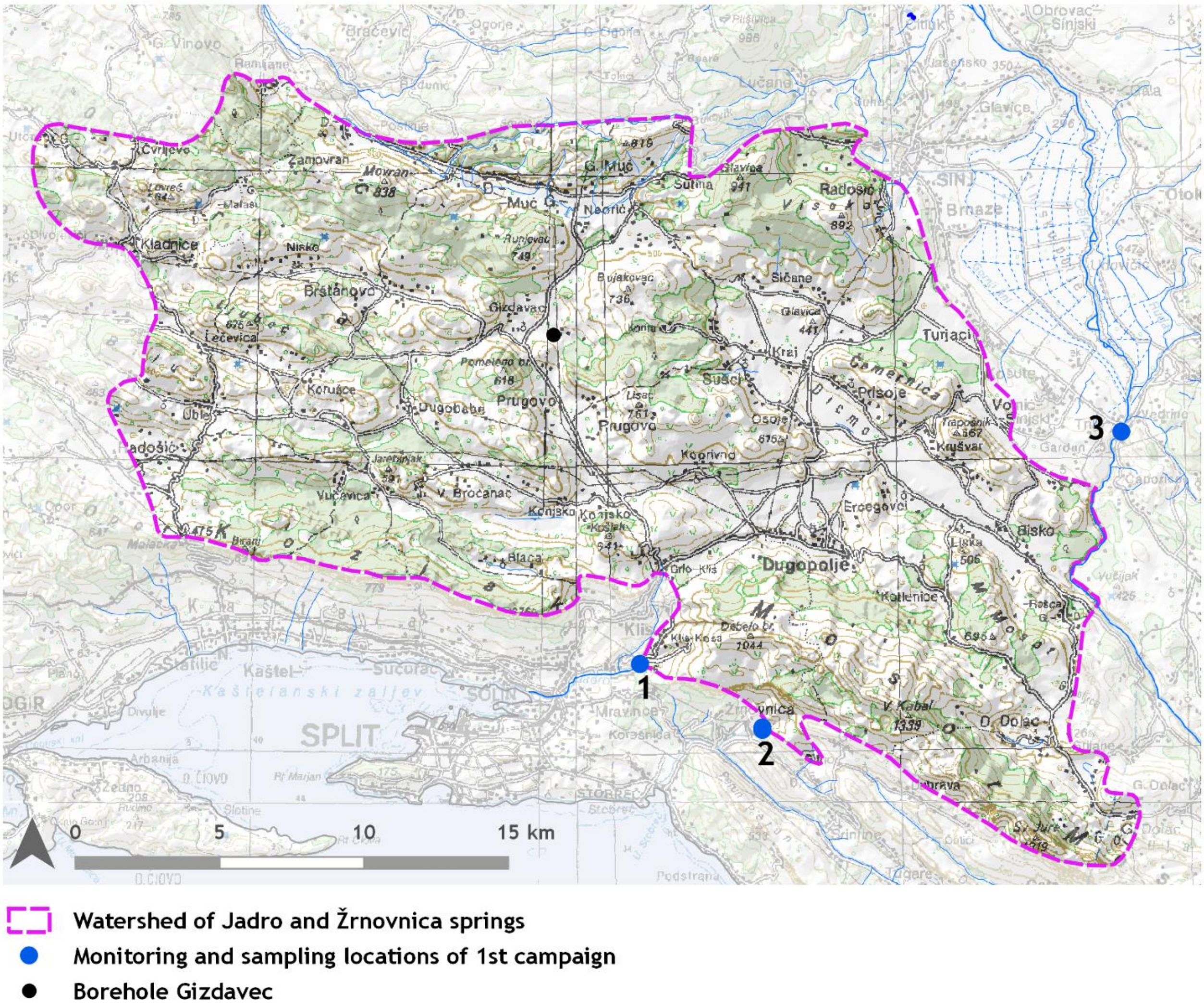
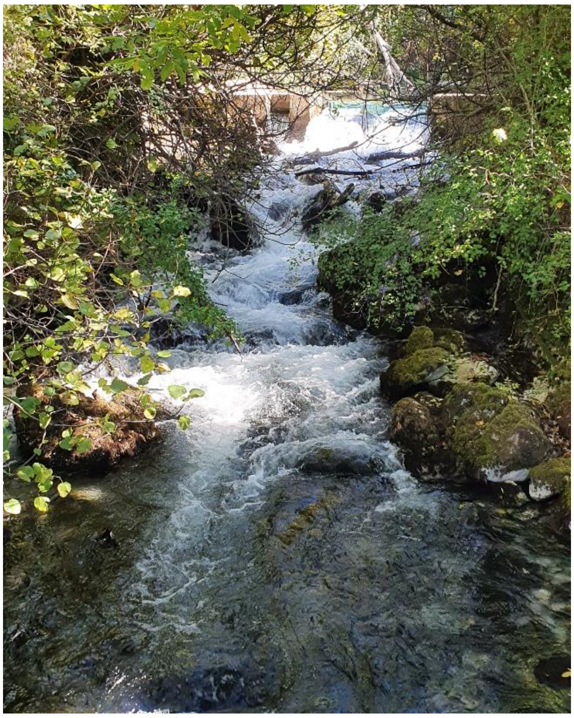


Figure 3. Sampling locations chosen within Jadro and Žrnovnica springs catchment, 1- Jadro spring; 2-Žrnovnica spring; 3- Cetina River.

Individual sampling points are characterized as follows:

Jadro spring	
Objective: to obtain information on the quality of spring water used for water supply	
Method of sampling: sampling directly from the spring.	

Žrnovnica spring	
Objective: to obtain information on the quality of spring water used for water supply	
Method of sampling: sampling directly from the spring	

Gizdavac borehole	
Objective: to obtain information on the quality of groundwater	
Method of sampling: sampling from the borehole; borehole was purged with three well volumes of water	

Cetina River	
Objective: to obtain information on the quality of surface water of Cetina River, which is presumably influencing the outflow of Jadro and Žrnovnica springs	
Method of sampling: sampling directly from the river, in the middle of the watercourse	

4. Monitoring results

This analysis is based on 5 monitoring campaigns conducted in the pilot area Jadro and Žrnovnica springs catchment, located in Croatia. All project raw monitoring data are gathered in the deliverable D.T2.3.1. Analysis of the behavior of PPCP is further assessed in terms of the T3 work package, by application of modeling tools.

4.1. Water resources

The results of five sampling campaigns indicate the presence of 11 different PPCP substances in the range from 10 ng/L for valsartan in Jadro spring to 372 ng/L for 1H-benzotriazole in Cetina River (Table 2). Three compounds, namely metformin, DEET, and 1H-benzotriazole were found in concentrations above the current EU pesticides limit of 100 ng/L. Out of eleven detected substances, seven are pharmaceuticals, two substances belong to personal care products, one is a lifestyle product, and one is an industrial compound. Seven compounds were detected only once. Metformin, a medicine used to treat diabetes and hyperglycemia, was detected in three campaigns, while analgesics/anti-inflammatory drugs ibuprofen and insect repellent DEET were found in two campaigns. Industrial compound 1H-benzotriazole is found in water samples at all sampling sites, suggesting an anthropogenic influence. The highest number of compounds (seven in total) was detected in Cetina River, while Žrnovnica had the smallest number of detected PPCPs (two in total). Jadro spring and groundwater from the Gizdavac borehole had four different PPCP substances each.

Table 2. An overview of PPCPs detected in Jadro and Žrnovnica springs catchment (approximate concentrations in ng/L are given)

Sample name	CE	ŽR	JD	GI	CE	JD	ŽR	GI	CE	JD	ŽR	GI	CE	JD	ŽR	GI	CE	JD	ŽR
Date	October 2019			March 2020				July 2020				September				November 2020			
Name	ng/L																		
Ibuprofen	~55	<20	<20	<20	~20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20
Ibuprofen-carboxy	~22	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20
Paracetamol	~12	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
Caffeine	<100	<100	<100	<100	~146	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100
Metformin	~166	<20	<20	<20	~82	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	~25	<20	<20
1H-Benzotriazol	<20	<20	<20	~22	<20	~57	~39	~52	~372	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20
DEET	<10	<10	<10	<10	<10	<10	<10	~22	~17	~13	~13	<10	<10	<10	<10	~60	~84	~56	~135
Climbazole	<10	<10	<10	<10	<10	<10	<10	<10	<10	~18	<10	<10	<10	<10	<10	<10	<10	<10	<10
Ketoprofen	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	~41	<10	<10	<10	<10	<10	<10	<10
Gabapentin	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	~37	<10	<10	<10	<10	<10	<10	<10
Valsartan	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	~10	<10

5. Conclusion

The monitoring results document the occurrence of PPCPs in the karst catchment of Jadro and Žrnovnica springs used for water supply. In total out of 109 analyzed compounds, only 11 were detected. Given such low detected concentrations of PPCP substances in karst water resources, the plan was to hire another laboratory with more sensitive equipment (lower detection limits). However, due to a small number of available adequate laboratories, high analysis prices, and limited operation due to Covid-19, this task was unsuccessful.

Cetina River stood out with the highest average concentrations of detected compounds, while Jadro spring had the lowest ones. The source of contamination in the Cetina River is presumably irrigated agricultural land and urban areas (only part of the Trilj city is connected to wastewater treatment plant) located upstream of the sampling point. Out of 25 detections in total, pharmaceuticals were detected 11 times. The Cetina River and Jadro spring had the most versatile groups of EC compounds. Žrnovnica spring had only two detections, which belong to industrial, and personal care product groups.

Principal Coordinates Analysis performed in R and based on measured electrolytic conductivity, water temperature, and detected PPCP compounds showed how there is no statistically significant correlation between those variables (PERMANOVA, $p<0.05$). Hence, conclusions about PPCP relations to measured parameters could not be given.

The small number of identified PPCP substances and their limited temporal resolution (a singular event for the majority of compounds), represents a hindrance for delivering some strong conclusions on their transport and behavior in complex environments such as karst aquifers. For a more detailed statistical analysis and understanding of the PPCPs fate in such complex medium as the karst aquifer, additional monitoring campaigns are needed.

The results of the hydrogeological field investigation will be published in the upcoming scientific paper, disseminating and promoting boDEREC-CE pilot activities.

6. References

Biondić, B.; Biondić, R.; Brkić, Ž. Basic Hydrogeological Map of Croatia 1:300 000. Croatian Geological Survey, Zagreb 2003.

Bognar, A. (1999). Geomorphological regionalization of Croatia. Acta Geographica Croatica, 34. (1.), 7-26.Bonacci, O. 1987. Karst Hydrogeology, Springer Verlag, Berlin, 184.

Fritz, F., Pavičić, A., Renić, A., Kapelj, J. Izvori Jadro i Žrnovnica. Dio hidrogeoloških istražnih radova potrebnih za prijedlog zona sanitarne zaštite, Zagreb 1988 (Hrvatski geološki institut, Fond stručne dokumentacije, br. 140).

Jukić, D., Denić-Jukić, V., 2009. Groundwater balance estimation in karst by using a conceptual rainfall-runoff model. J. Hydrol. 373, 302–315. http://dx.doi.org/10.1016/j.jhydrol.2009.04.035.

Kapelj, S., Kapelj, J. & Švonja, M. 2012. Hydrogeological characteristics of Jadro and Žrnovnica catchment. Tusculum, Vol. 5, 205-216.