boDEREC-CE
WORKPACKAGE T2

O.T2.4 PILOT ACTION WAIDHOFEN A/D YBBS – AUSTRIA

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, 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 in 8 pilot sites in different regions and hydrological conditions in Central Europe.

This report summarizes the pilot action activities carried out in the Austrian pilot area, Waidhofen a/d Ybbs, in the state of Lower Austria. The monitoring system was designed to observe any possible influence, such as infiltration, to the main spring source of water supply, from the surface bodies wetting its catchment.

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 work packages, which include construction of modelling tools, synthesis of results and dissemination activities.

2. Pilot site characteristics

Waidhofen a/d Ybbs is a municipality in Austria, situated more precisely in the federal state of Lower Austria (**Błąd! Nie można odnaleźć źródła odwołania.**, (a)), and is part of the eastern foothills of the Northern Calcareous Alps. The pilot plant action is located ~10 km south to the above-mentioned town, along the river Waidhofenbach. The selected study area of the pilot action is composed of the recharge area of one of the main springs exploited for the drinking water supply, the Kerschbaum spring (**Błąd! Nie można odnaleźć źródła odwołania.**, b, (4)).

2.1. Geographical and hydrological conditions

2.1.1. Geography

The pilot action area is part of the eastern foothills of the Northern Calcareous Alps and a well-connected network of fractures and conduits can be assumed to be present in the underground (Bittner et al., 2018; Hacker, 2003). The municipality counts 11222 inhabitants (January 2020) in an area of 131.56 km^2; however, the drinking water system supplies indirectly a total amount of ~25000 inhabitants, therefore including also neighbouring towns. However, it has been decided that the selected pilot action area for the present project should be confined to the recharge area of the main spring Kerschbaum. Here, the land cover is mostly composed of forests and meadows, and a very small percentage of quarries, and the area is crossed by two small creeks, Waidhofenbach and Glashüttenbach (runoff creek coming from the uphill quarries, which enters the first mentioned water body). Four sampling points were selected in order to observe any interaction between surface and groundwater, and to observe as well as any potential PPCPs transport behaviour. A more detailed description is given in chapter 3.3 Monitoring.

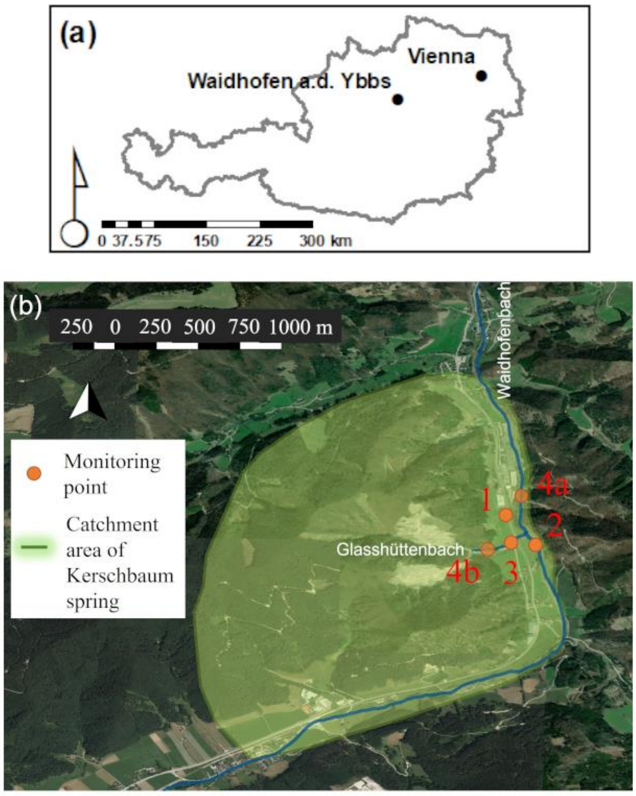

Figure 1. Geographical location of study area of the pilot action, Waidhofen a/d Ybbs (a); recharge area of Kerschbaum spring - boundaries of study area for the project (green line) (b), sampling points: (1) Kerschbaum spring, (2) Waidhofenbach upstream, (3) Glashüttenbach downstream, (4a) Waidhofenbach downstream, (4b) Glashüttenbach upstream (b).

2.1.2. Climate

The study area of Waidhofen a/d Ybbs is characterized by a warm-moderate regional climate. The annual distribution of precipitation is bimodal with maxima during both the summer (June and July) and winter months (December and January), with snowfall dominating precipitation in the winter.

The mean value of the annual cumulative sum of precipitation of the whole interval 2001 - 2016 is of 1406 mm. The annual mean of the annual cumulative sum is 115.15 mm. The calculated annual mean value of air temperature is 8.1 °C, from interval 2001-2016, measured at the Waidhofenbach gauge station. More recent precipitation (98mm cumulative annual mean) and air temperature (9.1°C annual mean) data (interval years of 2018-2020) were obtained from the open-source database “Wasserstandsnachrichten und Hochwasserprognose” from the state Lower Austria (Niederösterreich) (Amt der NÖ Landesregierung, 2021).

2.1.3. Geology

The municipality of Waidhofen a/d Ybbs and the pilot action situated 10 km to the south, are located in the Lower – Upper Austria Limestone Pre-Alps area, morphologically characterized by the absence of high mountain forms (maximum altitude is 969 m.s.l) (Hacker, 2003). The study area on which the sampling / monitoring activities and transport model focus is the Kerschbaum recharge area (2.5 km^2, see **Błąd! Nie można odnaleźć źródła odwołania.**). From a geological point of view, the studied area is situated within the geological area of the Northern Calcareous Alps. The dominant bedrock type present in the studied area is the Main dolomite, as seen from Figure 2. The main bed-rock which forms the massifs of the study area is the Main dolomite (“Hauptdolomite”, grey area in Figure 2**Błąd! Nie można odnaleźć źródła odwołania.**), as seen in Figure 2 (Koeck et al., 2017; Narany et al., 2019), and it can reach up to 1000 m in thickness (Koeck et al., 2017; Narany et al., 2019). Despite dolomitic bedrocks are characteristic for karst aquifers, their typical features (such as sinkholes, caves, dolines) are only marginally present (Hacker, 2003; Narany et al., 2019). Nevertheless, Hacker (2003) was able to proof the presence of a deep karstified aquifer system within the Glashütten massif (Narany et al., 2019).

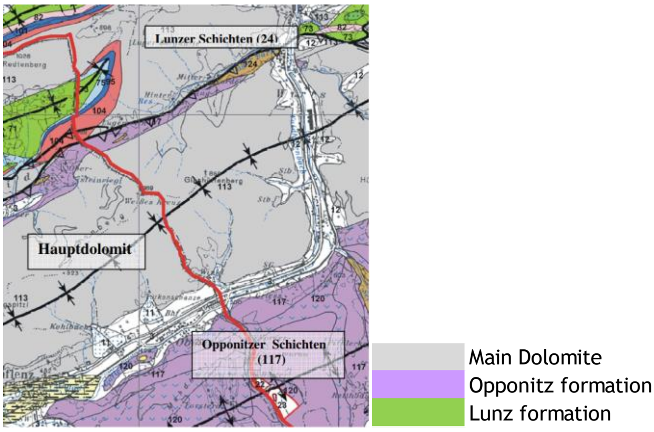

Figure 2. Geological and tectonic map of the pilot action area (Hacker, 2003)

2.1.4. Hydrology

2.1.4.1. Surface water

Within the study area (the recharge area of the Kerschbaum spring) the two surface water bodies present are the Waidhofenbach, tributary of the Ybbs river, and the Glashüttenbach, small tributary of the Waidhofenbach, as seen in Figure 1, b. The highest value of the monthly mean of water levels is reached during the winter and summer months (Figure 3, a, time series October 2018 – July 2020). No time series data concerning the discharge of Waidhofenbach nor of Glashüttenbach are available.

2.1.4.2. Groundwater - Drinking water sources

The geology of the study area (karstifiable bedrocks) induced the formation of several karstic springs at different altitudes. The main ones are exploited from the municipality of Waidhofen a/d Ybbs as main drinking water source: Kerschbaum (annual mean discharge ~34 L/s), Hinterlug (~11 L/s), Mitterlug (~4 L/s), Glashütten (~8 L/s) and Hieslwirt (~6 L/s) springs (Bittner et al., 2018; Hacker, 2003; Narany et al., 2019). Those karst springs provide water supply for a total of ~25000 inhabitants (including neighbouring towns), of which 11571 live in the municipality of Waidhofen a/d Ybbs (Koeck et al., 2017; Narany et al., 2019). No further drinking water treatment is needed (Koeck et al., 2017).

The present study focuses on the most important spring for the drinking supply system, which is Kerschbaum spring (recharge area of 2.5 km^2, as in Figure 1, b) (Hacker, 2003; Narany et al., 2019). The spring is fed by karst aquifers of the Main Dolomite, and the absence of significant sinkholes in the study area leads to the assumption that point-infiltration has not an important role for the recharge of the named spring (Bittner et al., 2018; Narany et al., 2019). Figure 3, b shows the monthly mean, minimum and maximum values of the discharge (m^3/d) of the Kerschbaum spring for each year of the time interval 2001 – 2016. The annual mean discharge for the period 2001 – 2016 is 2933 m^3/d (~34 l/s).

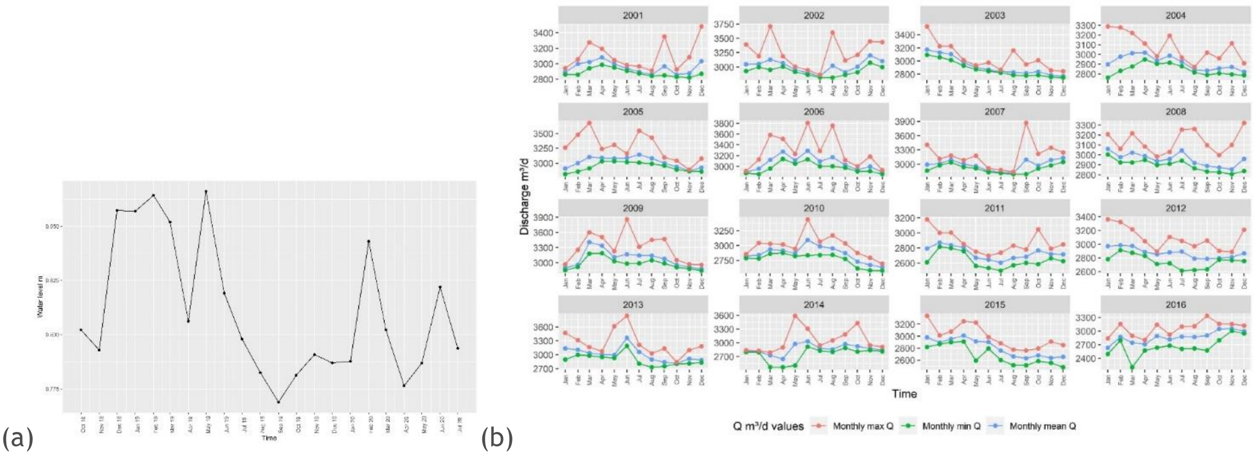

Figure 3. (a) Water level (m) values of the Waidhofenbach for the time period October 2018 – July 2020. (b) Mean, minimum and maximum monthly values of Kerschbaum spring discharge (m³/d) for each year of the time interval 2001 – 2016.

2.1.5. Sources of PPCPs

A detailed land-use campaign was performed by Köck et al. (Koeck et al., 2017). In Figure 4, it is possible to notice that the majority of the land within the Kerschbaum spring recharge area is covered by different types of forests and a very small percentage by quarries. In detail, the main land-uses are: bluegrass – beech forest (light green, code 1 Figure 4), white sedge – beech forest (green, code 2 Figure 4), Christmas rose – beech forest (dark green, code 3 Figure 4), quarries (grey, code 11 Figure 4), very little presence of wood barley – breech forest (petroleum, code 4 Figure 4) and of maple – ash forest (purple, code 6 Figure 4), special areas (white, code 12 Figure 4). This leads to the assumption that no specific source of PPCPs could come from the forest land use, therefore no infiltration to the recharge area occurs.

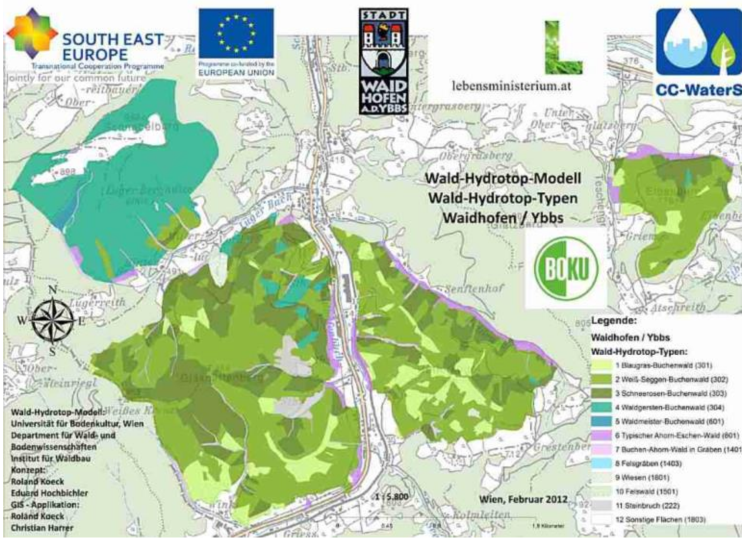

Figure 4. Land-use map of the study area, created by Köck et al. during the Interreg PROLINE-CE project (Koeck et al., 2017).

Moreover, along the Waidhofenbach multiple settlements of private households, industrial infrastructures and small domestic wastewater treatment plants (upstream to the study area, PE between 4 and 20) are present. These could be considered as the main source of potential contamination of the surface water Waidhofenbach. According to Hacker (2003), the quality of the waters of the Waidhofenbach and the Kerschbaum spring show similar characteristic fluctuations, leading to the assumption of a hypothetical interaction between the two: ~10% of young water, <1 year, composes the spring water in Kerschbaum (Hacker, 2003) . Following this assumption, any contamination present in Waidhofenbach would possibly reach the Kerschbaum spring water in diluted concentrations.

Figure 5 shows the presence of small wastewater treatment plants, as municipal/domestic (orange dots in the map) and as municipal/company-service (orange squares in the map), which are located along the Waidhofenbach and which discharge into the same or one of the tributaries, before the Kerschbaum spring (Land Niederösterreich ATLAS). The identified WWTPs can be considered small plants because of the low range of PE, between minimum 4 and maximum 20 PE, and low range of discharge between 0.75 and 3.75 m^3/s. The main characteristics (amount of discharge, water body of the discharge, PE, type of plant, treatment) are listed in Table 1 in the deliverable D.T.3.3.1.

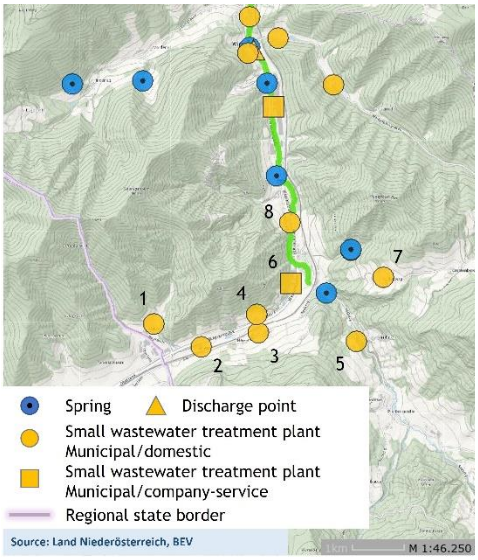

Figure 5. Wastewater treatment plants present in the study area, Kerschbaum recharge area, south to Waidhofen a/d Ybbs (Land Niederösterreich ATLAS).

2.2. Socio – economic conditions and main end users

As mentioned above, the 5 springs and the pumping well represent the main source of freshwater for the municipality of Waidhofen a.d. Ybbs. Along the Waidhofenbach, several small settlements and industrial infrastructures exist, exhibiting pressure on the creek and potentially on the springs located close to it, e.g. the Kerschbaum spring.

3. Monitoring methodology and available data

3.1. Sampling and laboratory analysis

The boDEREC-CE monitoring on all project pilot sites was conducted according to a 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 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 (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).

Table 1 Analysed PPCPs

	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

22.	celiprolol	ng/l	10
23.	citalopram	ng/l	20
24.	clarithromycin	ng/l	10
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.	furosemide	ng/l	50
42.	gabapentin	ng/l	10
43.	gemfibrozil	ng/l	10
44.	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
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.	norverapamil	ng/l	10
66.	octyl methoxycinnamate (OMC)	ng/l	1000
67.	oxcarbazepine	ng/l	10
68.	oxypurinol	ng/l	50
69.	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.	sucralose	ng/l	500
87.	sulfamerazine	ng/l	10
88.	sulfamethazine	ng/l	10
89.	sulfamethoxazole	ng/l	10
90.	sulfanilamide	ng/l	50
91.	sulfapyridine	ng/l	10

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

As described in the previous chapter 2.1.5, the selected pilot area is characterized by the presence of quarries. It is not known yet, if these might have an impact on the quality of the raw source of water. Furthermore, the interaction between the creek Waidhofenbach and the Kerschbaum spring is not certain. Finally, the Waidhofenbach drains several small settlements upstream. Therefore, the monitoring activities aimed to better understand the influence of the Waidhofenbach and/or quarries on the spring and determine the potential source of contamination.

3.3. Sampling

The pilot site was monitored in a network of four sampling points. Their location is shown in Figure 6. The sampling points to monitor the occurrence of PPCPs in the area were selected as follows: along the Glashüttenbach to observe any potential influence from the quarries situated uphill; along the Waidhofenbach, upstream (2) and downstream (4a) of the intersection with the Glashüttenbach; and directly in the Kerschbaum spring (1), in order to observe any interaction between the Waidhofenbach and the spring through riverbank infiltration. After the first four sampling campaigns, the sampling point at the Waidhofenbach downstream was substituted with a new sampling point, placed along the Glashüttenbach upstream (4b). This was decided in order to understand and monitor any possible contamination source present along the mentioned creek.

The monitoring activities were carried out during the two years period 2019 – 2021. In total 8 sampling campaigns were performed, with a total of 32 samples.

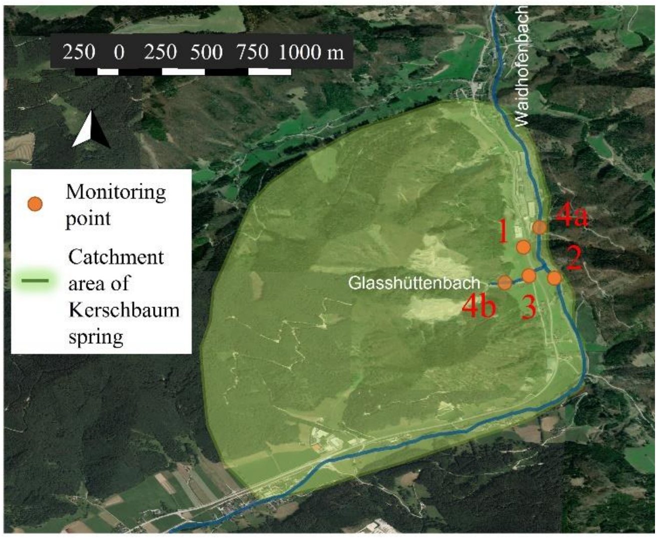

Figure 6 Sampling point locations in the Waidhofen pilot area.

The individual sampling points are characterized as follows:

Waidhofenbach upstream of Glashüttenbach	
Objective: obtain information on the quality of the Waidhofenbach before the creek from the dolomite quarries enters the Waidhofenbach, and on potential contamination coming from upstream domestic wastewater treatment plants.	
Method of sampling: sampling directly from surface water.	

Waidhofenbach downstream of Glashüttenbach	
Objective: obtain information on the quality of the Waidhofenbach after the creek from the dolomite quarries enters the Waidhofenbach.	
Method of sampling: sampling directly from surface water.	

Glashüttenbach downstream	

Objective: obtain information on water quality of the creek that drains the quarries.	
Method of sampling: sampling directly from surface water.	

Glashüttenbach upstream	
Objective: obtain information on water quality of the creek that drains the quarries, and through the comparison with Glashüttenbach downstream, obtain information and to understand and monitor any possible contamination source present along the mentioned creek. After the first four sampling campaigns, this sampling point substituted the sampling point Waidhofenbach downstream.	
Method of sampling: sampling directly from surface water.	

Kerschbaum spring	
Objective: obtain information on groundwater quality in the Kerschbaum spring and observe any interaction between the Waidhofenbach and the spring through river bank infiltration.	
Method of sampling: the sample is taken from a groundwater / directly from the spring.	

4. Monitoring results

This analysis is based on a 2-year monitoring of PPCP in pilot area located by Waidhofen a/d Ybbs, in Lower Austria, Austria. The detailed description of the results of the monitoring analysis are included already in the deliverable D.T.2.4.1.

4.1. Water resource

The pilot action, recharge area of the Kerschbaum spring, is the most important part of the drinking water supply in Waidhofen a/d Ybbs. The sampling points to monitor the occurrence of PPCPs in the area are indicated in the graphs as follows: Glashüttenbach downstream as GBD; Waidhofenbach upstream as WBU and Waidhofenbach downstream as WBD; the Kerschbaum spring as KQ; Glashüttenbach upstream, indicated as GBU.

To the authors knowledge, no prior monitoring concerning PPCPs in Waidhofen a/d Ybbs was performed, therefore only the values measured during the project lifetime are available for discussion. For this reason, due to the limited sampling campaign only a relative guess/assumption can be made. For a more robust statistical evaluation, more monitoring campaigns and analysis should be performed.

Out of 122 analysed substances, 34 were detected (> LOQ) at least once over the 8 sampling campaigns and at least in one sampling point. Sampling 1 to 8 represent the eight sampling campaigns made in December 2019 (1), June 2020 (2), July 2020 (3), September 2020 (4), May 2021 (x2) (5, 6), July 2021 (7), August 2021 (8), respectively. The total number of samples analysed was 8 for each sampling point, except for WBD and GBU, in which only four samples were analysed: for WBD samples were collected during the first 4 sampling campaigns, and for GBU samples were collected during the last four sampling campaigns.

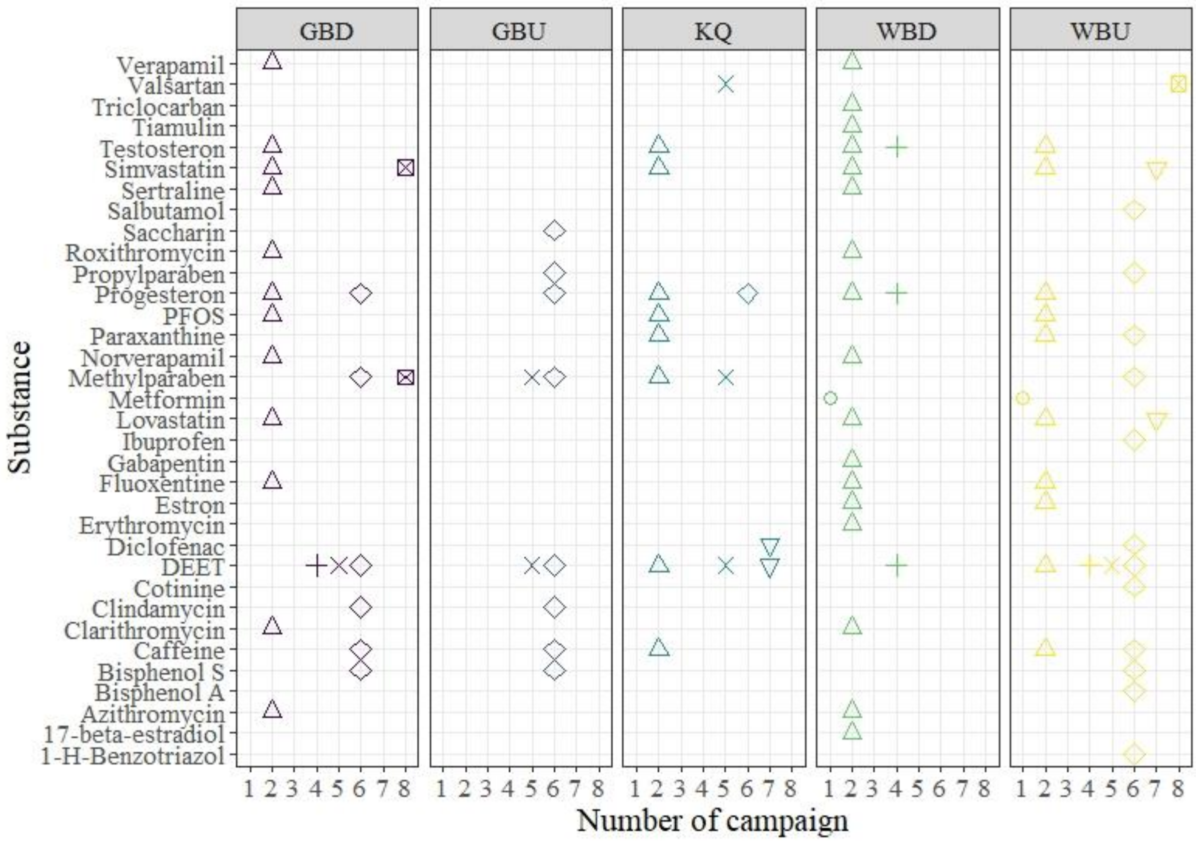

Figure 7. Number of detection (measured value > LOQ) for each substance, per sampling point (GBD, GBU, KQ, WBD, WBU) and per sampling campaign (1-8).

As can be seen in Figure 7 **Błąd! Nie można odnaleźć źródła odwołania.**overall the sampling campaigns and all the sampling points, the most occurring substances are DEET (41%), progesterone (25%), methylparaben (22%), simvastatin (19%), caffeine (16%), testosterone (16%), lovastatin (13%). Bisphenol S, Fluoxetine, Paraxanthine and PFOS were detected overall with an occurrence of 9%. The rest of the substances were detected once or twice, overall.

Figure 8 shows on the left side of the graph the origin (human or animal) and the use groups of the detected substances (“Pharmaceutical”, “Hormone”, “Personal care product”, “Metabolite”, “Industrial chemical”), in relation to the place of detection on the right side of the graph. It is possible to observe how the majority of detected PPCPs (19 out of 34) are categorized as “Pharmaceuticals”, mainly of human and human / veterinary use. The second most detected group is “Personal care product” (6 out of 34), from human origin. These are followed by “Hormone” (4) from human and human/veterinary origin, and “Metabolite” and “Industrial chemicals” (3), from human origin.

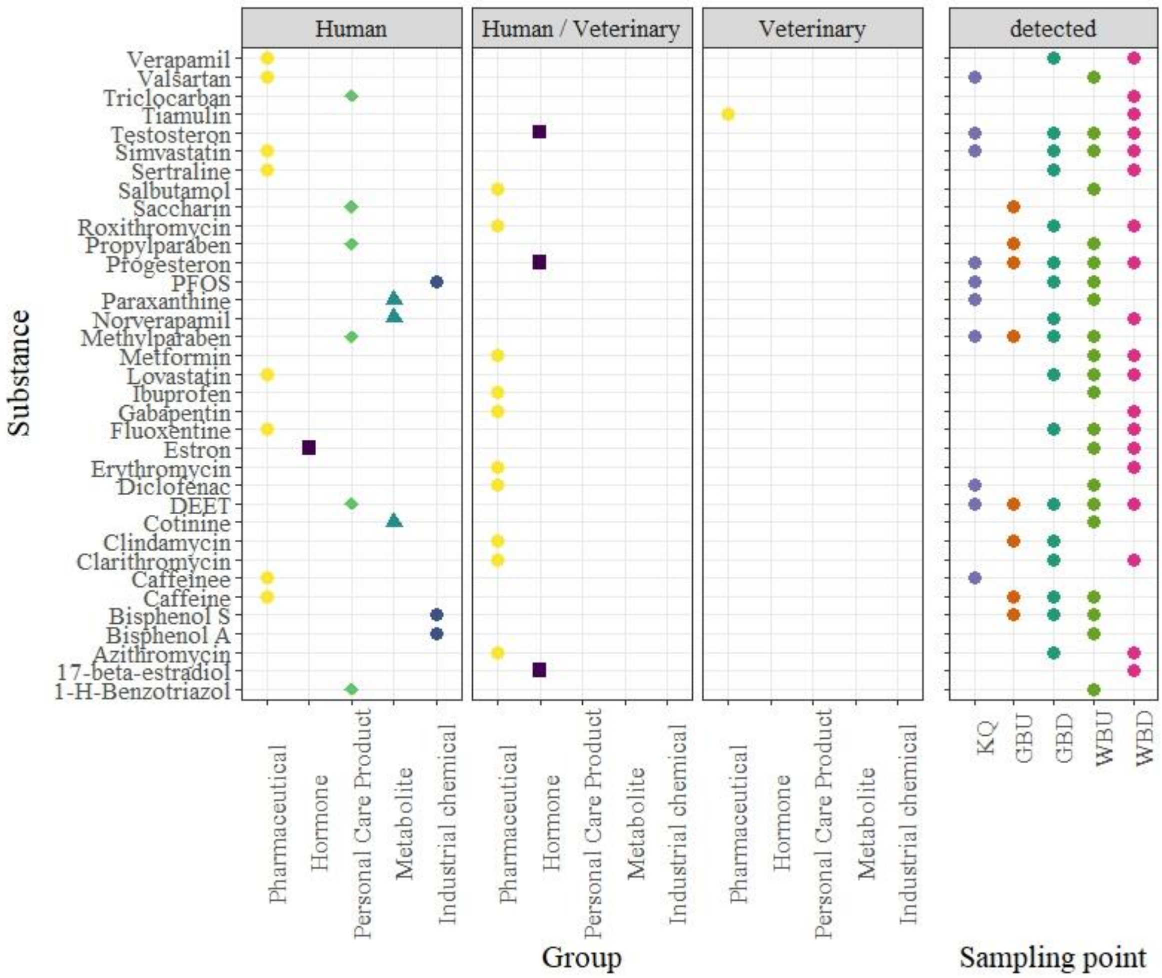

Figure 8. Point graph representing the detected substances (>LOQ) according to the use group (on the x axis of the left side of the graph: “Pharmaceutical”, “Hormone”, “Personal care products”, “Metabolite” and “Industrial chemical”), according to the origin group (in the faceting of the left side of the graph; “Human”, “Human/Veterinary”, or “Veterinary”), and according to the sampling point (“KQ, “GBU”, “GBD”, “WBU”, “WBD”).

Figure 8 also shows how the most occurring substance mainly come from a human origin (10 substances out of 12), and only two of them (Testosterone and Progesterone) are of human and/or animal origin. This let assume how the main potential source might come from human contamination, untreated or treated wastewater. Furthermore, the very little detected industrial chemicals can be related as well to human origin, since the three substances (Bisphenol A, Bisphenol S and PFOS) are widely used in plastic, waterproof coatings etc.

The most critical sampling point is the karstic spring since it is the main source of drinking water. In this case the highest relative occurrence was of the insecticide DEET(37.5%, 3 out of 8 samples in KQ), followed by methylparaben and progesterone, detected in 2 out of 8 samples in KQ (25%). Caffeine, diclofenac, paraxanthine, PFOS, simvastatin, testosterone and valsartan were detected once in KQ. Hence, this might be related to a sporadic presence or a potential contamination of the samples.

The insecticide DEET was detected with high occurrences also along the Glashüttenbach, 50% and 37.5% at GBU and GBD respectively, and detected as well in the upstream Waidhofenbach at 50%. Likewise, methylparaben and progesterone were detected as well along the Glashüttenbach (50% GBU, and 25% GBD; 25% at GBU and GBD, respectively) and the Waidhofenbach (12.5% for both). Despite the high occurrences compared to the rest of the substance, the detected concentrations of DEET were all below the pesticide guideline value of 0.1 µg/L for surface water (max detected value was 0.078 µg/L, in WBU, and the lowest detection was in KQ 0.038 µg/L, Figure 9). The detection values of methylparaben and progesterone were very low and sporadic in the spring, hence not considered problematic.

The highest concentrations were detected for caffeine (0.798 µg/L) and its metabolite paraxanthine (0.363 µg/L), in Waidhofenbach upstream, and for Methylparaben (0.250 µg/L) in Waidhofenbach upstream and for Bisphenol S (0.219 µg/L) in Glashüttenbach downstream. These are represented only by the annotations in the **Błąd! Nie można odnaleźć źródła odwołania.**, due to the reduced x-axis limits for the better visualization of the graph.

The ranges of the measured values of the 34 detected substances over the 8 campaigns are shown for each of the sampling point in the boxplots in Figure 9. The pesticide guideline value of 0.1 µg/L was included in Figure 9, as reference for the insecticides and/or pesticides detected. The measurement results below the LOQ were considered in the calculation of the median and therefore also in the boxplot as half of the LOQ value. In many cases, the substance was detected > LOQ only once or twice over the sampling campaigns and the sampling points, therefore the range of the boxplot is very narrow, and often mainly corresponding to the half LOQ. Furthermore, often the concentrations values of the substances detected more than once were higher in the sampling points along the creeks (Glashüttenbach and Waidhofenbach), and they decreased in the spring (Kerschbaumquelle). This might be related to the possible infiltration relation from the Waidhofenbach to the spring, as described in the Chapter 5.

Overall, the low occurrences, and the low measured value let think that the contaminants are almost absent in the aquifer. Those sporadic detections might be related to point pollutions from small wastewater treatment plants, which can be confirmed by the fact that the majority of the detected substances have a human origin (Figure 8). Furthermore, the contamination of the sample cannot be ruled out. However, the few monitoring campaigns and analysis (n=8, and n=4 for GBU and WBD) do not allow a proper and robust statistical evaluation. Therefore, a more frequent monitoring might be needed to come to stronger conclusions.

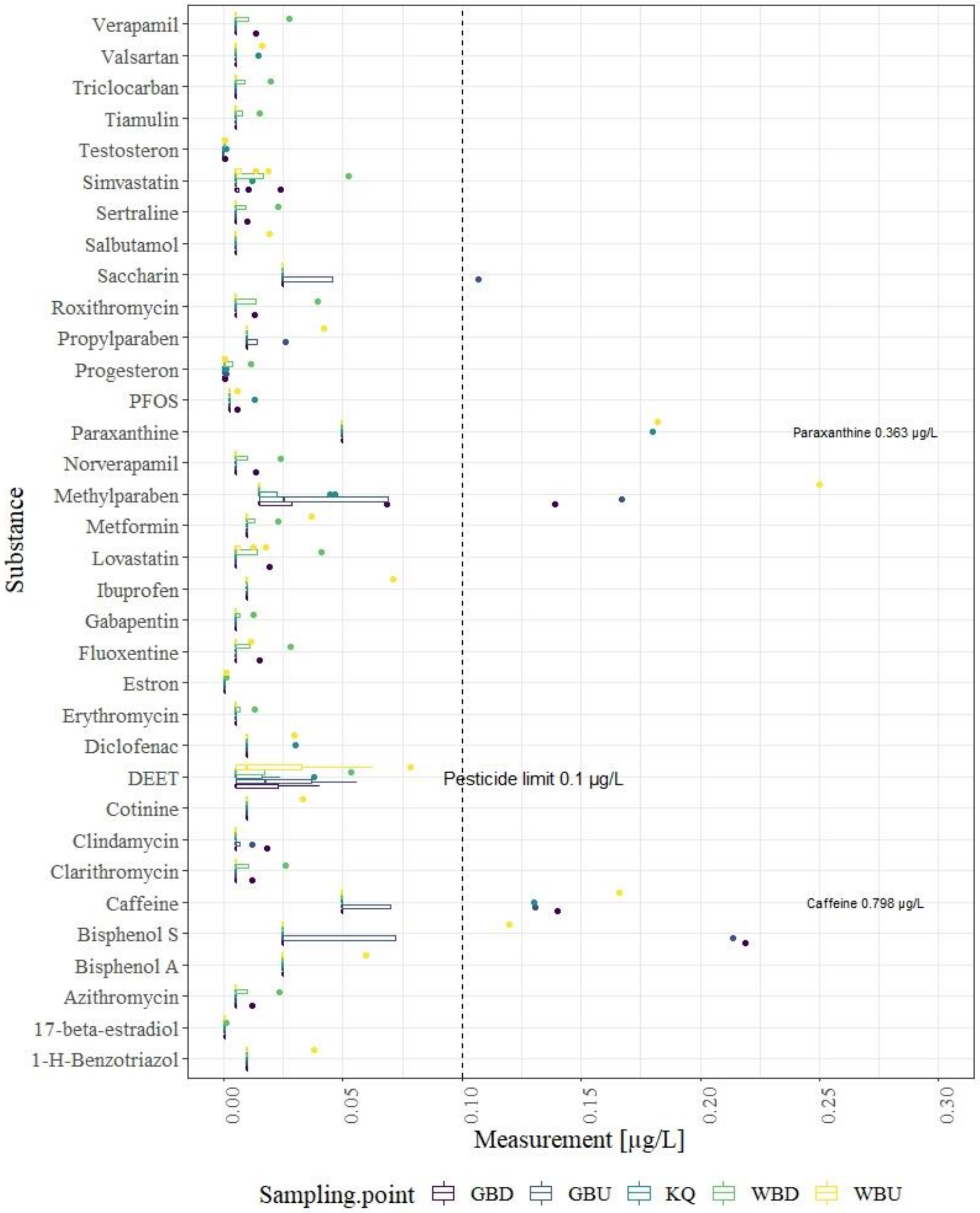

Figure 9. Boxplot of measured values of 34 substances over the eight (or four for GBU and WBD) sampling campaign, for each sampling point (shown with different colour, as described in the legend). The dashed line represents the pesticide limit value for surface waters in Austria. The two annotations indicate two measured values of caffeine (0.798 µg/L) and paraxanthine (0.363 µg/L), respectively, which are included in the boxplot calculation, but had to be excluded from the limits of the graph.

5. Conclusion

The monitoring results document the occurrence of PPCPs in the catchment area of the Kerschbaum spring, nearby Waidhofen a/d Ybbs, used as water resource for the same waterworks. The most detected substances were identified to be of human origin, such as the insecticide DEET, the hormones Progesterone and Testosterone, the PCP Methylparaben and the pharmaceuticals Simvastatin, Caffeine and Lovastatin. Despite the medium occurrence of few substances, all the concentrations were very low, at the ng/L range. This together with the sporadic occurrence of the other detected substances and with the absence of all the rest of the substances, let assume that the PPCPs are not a problem for the studied catchment. Furthermore, according to the different concentrations of PPCPs detected in the two sampling points Waidhofenbach (upstream and downstream) and the Kerschbaum spring, it cannot be clearly stated if a natural attenuation, as riverbank filtration could effectively occur.

6. References

Amt der NÖ Landesregierung, 2021. Wasserstandsnachrichten und Hochwasserprognose (accessed 19.01.2021). https://www.noe.gv.at/wasserstand/#/en/Messstellen.

Bittner, D., Sheikhy Narany, T., Kohl, B., Disse, M., Chiogna, G., 2018. Modeling the hydrological impact of land use change in a dolomite-dominated karst system. Journal of Hydrology 567, 267–279.

Hacker, P., 2003. Hydrologisch-hydrogeologische Untersuchungen im Bereich des Glashüttenberges zur Frage des engeren Schutzgebietes für die Kerschbaumer-Quelle. ARC Seibersdorf research GmbH.

Koeck, R., SIegel, H., Hochleitner, M., Gerhardt, E., 2017. D.T.2.1.4 Descriptive documentation of pilot actions and related issues: PROLINE-CE, work package T.2, activity T.2, Pilot action 1.2: Waidhofen/Ybbs. http://proline-ce.fgg.uni-lj.si/externalapp/content/deliverables/T2/PROLINE-CE_T2_DT214_PA12_AT_Waidhofen.pdf.

Land Niederösterreich ATLAS. Web GIS ATLAS. Land Niederösterreich BEV.

Narany, S.T., Bittner, D., Chiogna, G., Disse, M., 2019. Spatial and temporal variability in hydrochemistry of a small-scale dolomite karst environment. Environmental Earth Sciences 78 (9), 273.

Nestroy, O., Aust, G., Blum, W.E.H., Englisch, M., Hager, H., Herzberger, E., Kilian, W., Nelhiebel, P., Ortner, G., Pecina, E., Pehamberger, A., Schneider, W., Wagner, J., 2011. Systematische Gliederung der Böden Österreichs: Österreichische Bodensystematik 2000 in der revidierten Fassung von 2011. Österreichische Bodenkundliche Gesellschaft (accessed 21.01.2021). https://www.bodensystematik.de/OEBG-Systematik.pdf.