Interreg
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boDEREC-CE

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BOARD FOR DETECTION AND ASSESSMENT OF PHARMACEUTICAL DRUG RESIDUES IN DRINKING WATER - CAPACITY BUILDING FOR WATER MANAGEMENT IN CE

Interreg Central Europe project co-financed by the European Regional Development Fund

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TAKING **COOPERATION** FORWARD

FOREWORD

Water is one of the most valuable resource for today's civilization and vital factor that determines the quality of our lives. The technological advancement of laboratory instruments and analytical methods brought to light an array of questions regarding the occurrence and fate of anthropogenic substances referred to as emerging contaminants (ECs) that occur globally in the water environment. ECs encompass newly synthesised compounds as well as those that are present in the environment for some time but were not perceived as detrimental to the environment and human health. In both surface and groundwater, ECs are generally found in low concentrations of ng/L to µg/L, however, their persistency, transport, and (eco)toxicity are still insufficiently explored. The majority of these substances are not part of a routine water monitoring programmes. Interreg Central Europe project boDEREC-CE "Board for Detection and Assessment of Pharmaceutical Drug Residues in Drinking Water – Capacity Building for Water Management in Central Europe" recognized this as an issue that should be tackled by strong transnational cooperation of renowned experts and relevant stakeholders through common course of action and policy on EU level. Thus, the project offers an opportunity for integrated management of waterworks, recommendations for the enhancement of current legislation on drinking water standards for vast EC group of pharmaceuticals and personal care products (PPCPs). boDEREC-CE sets an innovative approach by implementing eight pilot areas across Central Europe, grouped in three clusters (groundwater, surface water, and karstic extraction sites), where behaviour of PPCPs, their natural attenuation and removal efficacy of different treatment techniques was thoroughly studied via jointly developed monitoring methodology and common project's PPCPs database.

As a Lead Partner of boDEREC-CE project, Croatian Geological Survey wants to express gratitude to all Project Partners and to the whole project consortium for fostering a fruitful transnational cooperation and focusing efforts for accomplishing all project goals.

Ph.D. **Josip Terzić**, Head of the Department of Hydrogeology and Engineering Geology

boDEREC-CE Project Leader

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boDEREC-CE Project Facts & Figures

The boDEREC-CE (Board for Detection and Assessment of Pharmaceutical Drug Residues in Drinking Water - Capacity Building for Water Management in CE, CE1412) project was approved for co-financing within the third Call of Interreg Central Europe, under the Programme's priority "3 Cooperating on natural and cultural resources for sustainable growth in CENTRAL EUROPE". With a total budget of 2,328,140.81 €, co-funded by the European Regional Development Fund, the project aimed to achieve the specific Programme's objective "3.1 To improve integrated environmental management capacities for the protection and sustainable use of natural heritage and resources" throughout its 3-year implementation period.

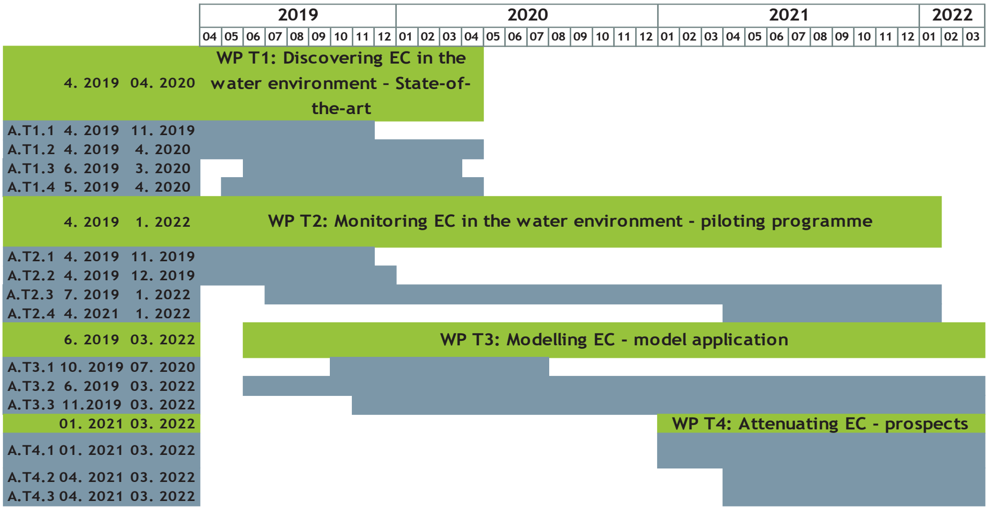
boDEREC-CE started on April 1, 2019, and lasted until March 31, 2022. The joint cooperation of 12 partners from 7 EU countries (Austria, Croatia, Czech Republic, Germany, Italy, Poland, and Slovenia) was supervised by the Lead Partner - Department of Hydrogeology and Engineering Geology of the Croatian Geological Survey.

Table 1.1 Project partners list

PROJECT PARTNER	PARTNER ABBREVIATION	COUNTRY
Croatian Geological Survey	HGI-CGS	Croatia
Split Water and Sewerage Company Ltd.	VIK-Split	Croatia
Czech University of Life Sciences Prague	CULS	Czech Republic
Public Water Utility JP VODOVOD-KANALIZACIJA SNAGA Ljubljana	JP VO-KA SNAGA	Slovenia
University of Silesia	US	Poland
University of Ljubljana	UL	Slovenia
Silesian Waterworks PLC	GPW	Poland
Technical University of Munich	TUM	Germany
Regional Agency for Prevention, Environment and Energy in Emilia-Romagna	ARPAE	Italy
District Basin authorities of Po river	ADBPO	Italy
Centre for Applied Research and Technology at Dresden University of Applied Sciences	ZAFT	Germany
University of Natural Resources and Life Sciences, Vienna	BOKU	Austria

The project is structured into three thematic work packages (Table 1.2) aimed at achieving specific project objectives through the implementation of planned activities and related deliverables and outputs.

Table 1.2 Overview of the project work packages and timeline



	4. 2019	04. 2020	WP T1: Discovering EC in the water environment - State-of-the-art
A.T1.1	4. 2019	11. 2019	
A.T1.2	4. 2019	4. 2020	
A.T1.3	6. 2019	3. 2020	
A.T1.4	5. 2019	4. 2020	
	4. 2019	1. 2022	WP T2: Monitoring EC in the water environment - piloting programme
A.T2.1	4. 2019	11. 2019	
A.T2.2	4. 2019	12. 2019	
A.T2.3	7. 2019	1. 2022	
A.T2.4	4. 2021	1. 2022	
	6. 2019	03. 2022	WP T3: Modelling EC - model application
A.T3.1	10. 2019	07. 2020	
A.T3.2	6. 2019	03. 2022	
A.T3.3	11.2019	03. 2022	
	01. 2021	03. 2022	WP T4: Attenuating EC - prospects
A.T4.1	01. 2021	03. 2022	
A.T4.2	04. 2021	03. 2022	
A.T4.3	04. 2021	03. 2022	

The University of Ljubljana was the leader of the first thematic work package related to state-of-the-art of emerging contaminants in the water environment. The second thematic work package, focused on monitoring the emerging contaminants in different water resources, was led by the Czech University of Life Sciences in Prague. The main objective of the third thematic work package, supervised by the Technical University of Munich, was modelling the transport of emerging contaminants in water. The last thematic work package, focused on the prospects and new approaches for the attenuation of emerging contaminants in water, was managed by Split Water and Sewerage Company Ltd.

CONTENTS

1. INTRODUCTION

Emerging substances have recently gained increasing attention because of the concerns about their potential impacts on human health and the ecosystem as a whole (Dulio et al., 2018). They reach natural water resources by a wide range of routes and sources, the majority of which are anthropogenic. There are still a lot of open questions concerning them, including which compounds belong to this group, their classification, properties, effects on human health and the environment, possibilities of natural attenuation and technical removal, and their proper monitoring, regulation and control (Lapworth et al., 2012). Given their widespread use and frequent detection throughout the water environment (Stefanakis and Becker, 2016), pharmaceuticals and personal care products (PPCPs) are in the focus of the boDEREC-CE project. The scarcity of studies on this topic consequently leads to the unawareness of crucial actors such as water managers. Therefore, the main boDEREC-CE goal was to highlight the importance of these issues which have to be tackled, to enable more efficient management of water resource and their control within Central Europe and beyond. The main objective of the project was to develop and test appropriate monitoring and modelling activities, in different hydrological systems under environmental pressures of emerging contaminants, based on an innovative approach applied in pilot areas across CE countries (Fig. 1.1).

This provides the basis for an integrated waterworks' management of emerging substances, which facilitates preserving and/or increasing

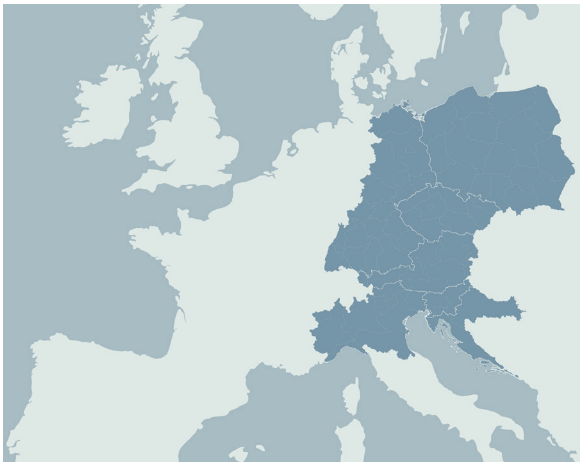


Figure 1.1 Countries participating in the boDEREC-CE project

drinking water quality, in line with the objectives of the Water Framework Directive (2000/60/EC) and Drinking Water Directive (2020/2184), aimed at securing drinking water quality.

The project activities were separated into four thematic work packages that were interrelated and overlapped over time. The project activities started with a broad overview of emerging contaminants (ECs), including definitions, classifications, regulations, and current knowledge at national levels. Other activities focused on a single type of ECs, such as pharmaceuticals and personal care products (PPCPs). The residues of PPCPs are known to be pseudo-persistent due to their continuous use and discharge into the environment (Ellis, 2006). Moreover, because of the numerous potential sources (Dalma & Haydee, 2018; Hirsch, Ternes, Haberer, & Kratz, 1999; Kolpin & Meyer, 2002), this group of pollutants is ubiquitous in the environment (i.e. rivers, lakes, and groundwater). Hence, monitoring was established in 8 pilot sites, where the water was systematically sampled over the period of two years, in order to assess the frequency and concentrations of PPCPs in different water resources (surface water, groundwater, and karst aquifers). The analyses' results were used to develop PPCPs transport models and to determine their behaviour in different environments, as well as to develop a PPCPs decision-making tool (modePROCON) which would assist water managers in planning measures to control and protect drinking water resources. In the final step, the natural attenuation potential and technical removal solutions for PPCPs have been assessed in accordance with the collected results. The developed decision - making support tool for selecting treatment option/method for mitigating PPCP concentrations and the Transnational Strategy for PPCP Mitigation in Drinking Water - provides a concrete step towards the new and improved legislation by offering specific solutions even after the project's lifetime. Even though the boDEREC-CE project was carried out in Central European countries, the variety of pilot sites and drinking water treatment technologies make it possible to extrapolate the gained knowledge across the territory of all EU countries.

This monograph provides a brief overview of the activities carried out within the boDEREC-CE project, as well as their results which are presented in the following chapters. The project's outcomes will introduce the issue of emerging substances and corresponding solution methods to many stakeholders who have not encountered this problem so far, and will also broaden the knowledge and offer support in the decision-making process of those who are already tackling this global challenge.

2. EMERGING CONTAMINANTS/ PHARMACEUTICALS IN DRINKING WATER RESOURCES

2.1. Introduction to the Problem

The emerging contaminants or contaminants of emerging concern (ECs) have been recognized as significant pollutants in the recent years. They are widespread in the aquatic environment and can have adverse impacts on human and wildlife health. All 12 project partners were involved in collecting the existing information on emerging contaminants using the available national and transnational references.

The problems associated with ECs belong to a very broad field. In academia and various other applied fields, researchers and managers are currently dealing with a wealth of information about ECs that has not yet been synthesized at a level where it can be understood and directly translated into practice and daily life. Such synthesis is urgently needed, and the endeavours and goals of the boDEREC-CE project contribute to these efforts, among others.

One of the objectives of the boDEREC-CE project was to define ECs and fully develop the procedures to collect the available data and information. The boDEREC-CE procedure for data collection and the creation of the state-of-the-art (SOA) tool can be applied as a step-by-step learning process. The information for the SOA was collected based on the block diagram shown in Figure 2.1. According to the process described in Figure 2.1, the ECs need to be defined. Once they are defined, the next step is to identify the problems associated with them. Certain compounds give rise to specific problems, and for this reason, monitoring strategies have to be tailored to them. An important aspect of monitoring ECs refers to the utilized analytical techniques. These issues relate primarily to ECs that occur at very low concentrations. Based on the monitoring results, mitigation strategies have to follow.

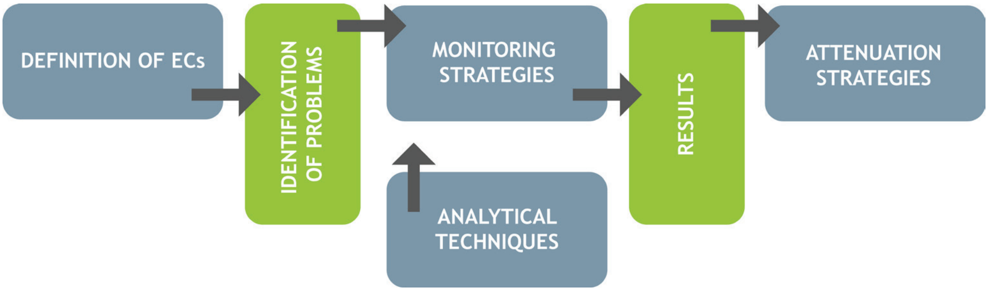


Figure 2.1 Procedures for collecting state-of-the-art information about emerging contaminants in the water environment.

As a part of the boDEREC-CE project SOA, a learning tool has been developed for those working on a similar project or interested in the topic of ECs. It includes the collection and analysis of available data from the literature and other available public sources of information on the topic of ECs, focusing on the project partner countries. The data was collected both at the national level and from international sources, ranging from web sources to scientific papers. Currently, issues related to the aquatic environment are high on the agenda of environmental studies and policies, but paradoxically there are many open questions about what ECs are and how they should be defined.

The term “emerging contaminants” is well-accepted from the terminological perspective. However, discussion among partners and review of the literature has shown that we are still far from the agreement on what is meant by it and what substances are involved. Against this background, it was decided that emerging contaminants need to be identified more precisely in the first step of the SOA.

2.2. Definition of Emerging Contaminants

In accordance with the data included in national reports and reviewed literature, there is no globally accepted definition of ECs. Definitions of ECs appear in certain scientific papers, project reports, and websites. Some of the sources provide a variety of definitions and some debate the commonly used terms and definitions used in the field. This review proves that the scientific and non-scientific community have a strong interest in the issue of ECs. It is a field of strong interest, and it is still in the early research phases.

The existing definitions mainly describe the most common general characteristics of ECs. In the existing definitions, it has been recognised that ECs do not refer only to one type but encapsulate a myriad of different groups (as the plural term itself indicates) which are most commonly referred to as chemicals or chemical compounds, substances, or simply, pollutants. Some of the definitions also include microorganisms.

For a unique and firm definition, we can quite simply start with the fact that ECs represent a certain subclass of contaminants. Contaminants are defined as substances present above the natural background which have the potential to become pollutants, whereas pollutants, in turn, are defined as substances that have adverse biological effects (Chapman, 2007). The term pollutant is, consequently, not synonymous with the contaminant and should not be equated with it, but it does represent a subclass of contaminants. Not defining contaminants as pollutants themselves is, therefore, important because they can be introduced into the environment where they are more or less bioavailable depending on many chemical and environmental factors as will be explained in the following chapters.

Defining ECs as a subclass of potential pollutants provides a group term for substances, compounds, mixtures, and microorganisms and, thus, eliminates the problem encountered earlier.

Some existing definitions of ECs also consider this distinction, such as the one provided by the NORMAN network, a network of reference laboratories, research centres, and related organisations for monitoring of emerging environmental substances which was established in 2005 within the framework of a European project. The NORMAN project defines emerging substances and emerging pollutants separately with the following description (NORMAN Network Website, 2020):

"Emerging substances can be defined as substances that have been detected in the environment, but which are currently not included in routine monitoring programmes at EU level and whose fate, behaviour and (eco)toxicological effects are not well understood."

"Emerging pollutants can be defined as pollutants that are currently not included in routine monitoring programmes at the European level and which may be candidates for future regulation, depending on research on their (eco)toxicity, potential health effects, and public perception and on monitoring data regarding their occurrence in the various environmental compartments."

The defining characteristics of this subclass of potential pollutants need to be narrowed down and detailed further. ECs' descriptions most often include their characteristic sources, levels, occurrence, and behaviour, interaction with the environment, our knowledge, and consideration of them. In the following paragraphs, these characteristics are described in more detail, covering the chemical, environmental and legislative frames of their occurrence.

2.2.1. Sources

EC sources are most often anthropogenic although they can also be natural. An example of anthropogenic ECs are pharmaceuticals, while an example of natural ones are biogenic hormones or microorganisms. The ECs sources are also described as being varied and continuously used in everyday life and other activities (e.g. industry, agriculture). The sources of ECs can, thus, be described as various, widespread, regularly or even constantly present, and in many cases, they are not simple but complex, composed or consisting of many different individual ECs.

2.2.2. Levels

The concentrations of ECs that are most often studied are usually low, but they can range from ng/l to mg/l (Salimi, 2017). Even though their concentrations can be as low as trace elements, they are still relatively high considering that they were, not so long ago, expected to be non-existent in the natural environment. On the contrary, it would seem that some ECs are ubiquitous, as they are constantly being found globally in different parts of the environment, especially in different aquatic environments. This is particularly true of those ECs that have high mobility and high persistency.

As most ECs are artificially created, they can prove to be good tracers despite their low quantity as they indicate the presence of anthropogenic activity. The examples of the newly studied potential tracers of urban wastewater in groundwater include carbamazepine, artificial sweeteners, and certain pesticides (McCance et al., 2018).

2.2.3. Behaviour and Interaction

A defining characteristic of ECs is their potential to induce direct or indirect adverse effects in biota. Many of them are bioactive and affect different processes in organisms. They could be bioaccumulative and, therefore, biomagnify and/or they could be persistent in the environment, meaning that they have potential for a long-term transport from their entry points to the natural environment. For example, ECs can circle the aquatic environment, entering the surface or groundwater by wastewater and reappearing in drinking water originating from those sources. Not all ECs are persistent, some are susceptible to (bio)degradation, creating by-products in the form of metabolites and/or transformation products that may be persistent and even more toxic than the parent compound (López-Serna et al., 2013).

2.2.4. Knowledge and Occurrence

ECs are generally considered to be new compounds, although the word encompasses not just newly produced compounds, but also compounds that are new in terms of their detection or identification. It can be noticed that different researchers talk about different types of ECs, and our knowledge on some of them varies. The umbrella term ECs, thus, takes on a different meaning (of a subgroup of ECs) in each case. Therefore, it is not recommended to use the umbrella term ECs only to represent pharmaceuticals, for example, but to recognize that it can mean many different subgroups of natural or anthropogenic potential pollutants, which have different characteristics, histories, and documented information.

A review by Sauvé and Desrosiers (2014) highlights the relativity of the term "emerging" and states that the distinction, in this case, needs to be three-fold:

- contaminants that were not known in the past, meaning they were not yet produced (did not exist) or were not yet detected or identified,
- contaminants that existed, were detected and identified but for which concerns about their adverse effects have only just been raised, and
- contaminants with already identified adverse effects the knowledge on which is currently being updated with the newly conducted studies.

Only the first category of contaminants is truly "emerging", while for the rest, the term CECs (contaminants of emerging concern) is more appropriate, even though both terms are nowadays being used interchangeably.

The list of chemicals classified as ECs isn't fixed. It is continually evolving, with new compounds being added, and some being removed from the list after having been regulated or proven to be harmless.

2.2.5. Regulation

Most of the currently recognized ECs are not included in the routine environmental monitoring programmes and are not regularly monitored. This is, however, not true for all types of ECs; for example, certain pesticides may have already been included in the routine national monitoring (i.e. atrazine).

This means that most ECs are currently unregulated but they do represent potential candidates for future legislative measures, which could include regulatory monitoring and determination of the criteria, limiting their occurrence in the environment. We could say that this is intrinsic to the nature of ECs – constant emergence of new types of ECs or emergence of new interest in existing ECs cannot result in immediate regulatory changes. On the contrary, they will always be lagging behind due to the ongoing research as it can take some time to confirm the urgency of regulation, and also due to the complexities of the processes of preparation and adoption of the new regulatory measures. As such, a constant stream of new knowledge and information on the potential pollutants and their ecotoxicology forces regulatory agencies to frequently re-evaluate their norms and guidelines. An example of this are the Priority and Watch Lists including ECs that were put forward by the EU legislators.

One of the problems with recognizing a compound as an EC is that it is also dependent on the location to which it relates, and EC lists differ from place to place. ECs are regionally defined in some areas of the world (e.g., the United States or the European Union), but in many nations, there are still no official lists of these compounds or they are currently being formed.

2.2.6. Proposed Definition

ECs include a variety of substances and mixtures that originate from either natural or anthropogenic sources, occurring in trace or higher concentration levels in various environmental compartments. They have already been regulated or they are candidates for future legislative measures. They are either newly created, detected or our knowledge or interest in them has increased only recently. They are suspected or confirmed to have the potential to cause adverse effects in the environment if they are present in certain quantities and, as such, present a risk to the natural environment, including humans.

Pursuant to the review of national reports and additional literature, we propose the following definition of ECs within the framework of the boDEREC-CE project and future research:

Emerging contaminants represent a group of potential pollutants that are either newly created, newly identified, newly detected, or newly researched.

2.3. Groups of ECs

There are several ways of classifying ECs. These classifications are used to ensure a systematic overview and categorization of what is otherwise a long and diverse list of potential pollutants. There are some well-established acronyms, which are being used in the field of ECs.

In the classification of ECs groups they are most often grouped according to the intended use or their source. This highlights the required consideration of sources of these contaminants in the environment. Furthermore, they are grouped according to their chemical properties, their effect, and the levels at which they occur in the environment (quantitative classification). Figure 2.2 shows the basis for several classification schemes presented in the following chapters.

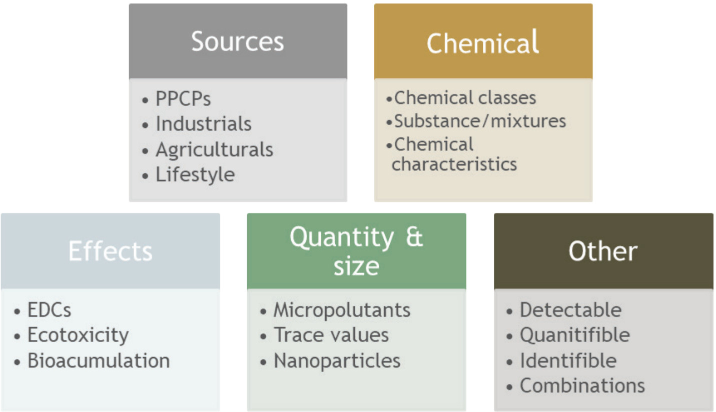


Figure 2.2 Different types of EC classifications.

2.3.1. Classification Based on Sources

A human component is central to EC studies since the sources of ECs are most often anthropogenic, meaning they originate from human activity. ECs are also associated with anthropogenic matter and materials, also termed artificial or man-made. However, some ECs are naturally produced with no human contribution at all. Certain ECs can be either anthropogenic or naturally occurring.

ECs and their sources are further classified according to their purpose of use in different human activities. The main classification includes:

- industrial chemicals,
- pharmaceuticals,
- personal care products (PCPs),
- agricultural chemicals (pesticides),
- and lifestyle compounds.

The main groups of ECs, which are classified based on their source, have their subgroups, which are classified according to their chemical class or, again, by their use.

2.3.2. Chemical Classification

Chemical classifications of ECs follow the basic chemical classifications of substances, starting with the separation into elements or compounds and pure substances or mixtures. An additional chemical classification distinguishes organic from inorganic matter, the former referring to carbon compounds and the latter to compounds without carbon. Chemical classifications also group substances with similar properties, such as polarity, solubility, mobility, reactivity, stability, persistence, degradability, etc.

Some groups that belong to a specific class of chemical compounds are also chemically classified, such as polybrominated diphenyl ethers (PBDEs) or per- and polyfluoroalkyl substances (PFASs).

Many metabolites – products of biochemical reactions during metabolism and some degradation products are considered as ECs as well.

2.3.3. *Classification Based on Effects*

Endocrine-disrupting compounds (EDCs) are a group of ECs that are defined by the effect they have on the environment, specifically on living organisms. They interfere with the organism’s endocrine system responsible for the production, storage, and secretion of hormones.

In the same way, ECs could be classified into those that have a pronounced impact on a certain group of organisms, for example aquatic, human, etc.

There are a couple of terms that are used concerning the effect of ECs on the environment, such as xenobiotics, bioaccumulation, biomagnification, and ecotoxicity. Xenobiotics are all chemicals that do not naturally occur in an organism. Bioaccumulation has different possible definitions and may refer to a total uptake from the environment, the accumulation over a period of time, or the total retention, which might be difficult to determine based on many unknowns, like poor or scarce data (Díaz-Cruz & Barcélo, 2015). Biomagnification refers to a process of an increase in the concentration along the food chain, which is associated with bioaccumulation and other factors, such as longevity and organism size (Díaz-Cruz & Barcélo, 2015).

The acronym PBT is used for contaminants that have the effect of being persistent, bioaccumulative, and toxic.

The substance of very high concern (SVHC) is a term used in the REACH Regulation (2020) for chemical substances that have the following negative effects: they are carcinogenic, mutagenic, toxic for reproduction, persistent, bioaccumulative, and toxic (PBT), very persistent and very bioaccumulative (vPvB), or if there is a “scientific evidence of probable serious effects to human health or the environment which give rise to an equivalent level of concern”.

2.3.4. Quantitative Classification and Classification Based on Size

ECs are sometimes referred to as micropollutants. Escher & Leusch (2012) describe micropollutants as man-made organic chemicals (pesticides, industrial chemicals, consumer products, pharmaceuticals) and natural compounds (hormones). As the name itself implies, micropollutants occur in the range below µg/l, while macropollutants can be found in the mg/l to µg/l range. Macropollutants include toxicants, for example, salts and metals (Escher & Leusch, 2012). A similar quantitative classification divides matter into trace and non-trace, the first occurring in concentrations below and the second above µg/l or ppm. With the improvements in the analytic technics and methods, substances can now be detected even at the sub ng/l levels or parts per quadrillion levels (Brooks & Huggett, 2012). Nanomaterials or nanoparticles are terms referring to size, specifically to dimensions of up to 500 nm.

2.4. Sources of ECs

As mentioned earlier, there is a wide range of possible sources of ECs and their diverse nature (Fig. 2.3). They are widespread and constantly used in modern human daily life.

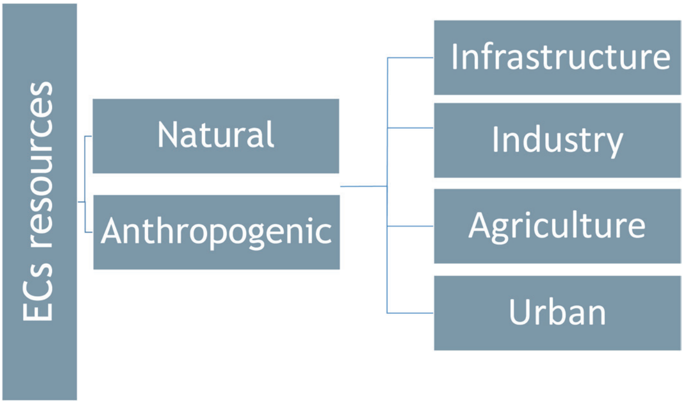


Figure 2.3 Sources of emerging contaminants.

Following the common contaminant characterization of sources that consequently determines how we study and analyse them, sources fall into “point” or “non-point” categories, the latter also known as diffuse. They are anthropogenic in most cases, originating from one or more of the main human spheres: infrastructure, agriculture, industry, or urban life.

Major EC sources include:

- pharmaceutical industries, industrial additives and agents, abandoned industrial sites, personal care products, factories, plants, mining activities,
- sewage, septic tanks, wastewater treatment plants (effluent and sludge), landfills (leachate),
- households, hospitals, urban structures, storm water runoff, roads and transport, cemeteries,
- agricultural land, farms, parks, gardens, and horticulture.

One of the principal sources of ECs discharge is wastewater, containing non-point and point sources of industries, urban runoff, wastewater from households, and water treatment facilities (Gogoi et al., 2018). Depending on the land use and industry type, wastewater has varying compositions. In the vicinity of hospitals, for example, there can be an increase of ECs in WWTPs originating from the medicinal activity and use (pharmaceuticals, diagnostic agents). The increased criminal activity contributes to a higher level of narcotics in WWTPs. ECs enter the environment mostly through wastewater treatment plants (WWTPs) having different levels of treatment (primary, secondary or tertiary) and different technologies for contaminant removal.

2.5. Priority Lists of ECs on EU Level

Growing concerns about the potential negative effects of an increasing number of new compounds, as well as compounds that have begun to be detected more frequently as a result of the development of new analytical technologies, have necessitated the identification of the compounds that pose the greatest risk to human health and the environment. Historically, several priority lists were specified that included contaminants with the potential risks to the aquatic environment. For example, in the Communication from the Commission to the Council on dangerous substances, which might be included in List I of the Council Directive 76/464/EEC, a priority list of 129 substances and groups was put forward with varying stages of research progress. Nowadays, the EU has put in place two main mechanisms – Priority Substances List (Table 2.1 and 2.2) and Watch List (Table 2.3 and 2.4) - that are described in the following chapters.

2.5.1. Priority Substances List

Under the Water Framework Directive – WFD (2000/60/EC), the European strategy against chemical pollution of surface waters was delineated, requiring the establishment of a list of priority substances (PS) and a subset list of priority hazardous substances (PHS) along with some management proposals. These priority lists include some emerging contaminants.

Decision 2455/2001/EC established the first priority list, which included 33 substances or groups of major concern and 11 within this list were determined as a priority hazard which require special inputs management. Further 14 substances were identified as being subject to a later review. Where the groups of substances have been selected, typical individual representatives are listed as indicative parameters or the indicative parameter has to be defined using analytical method. These groups of substances normally include a considerable number of individual compounds. For some groups, appropriate indicative parameters cannot be given at present.

The first list was replaced by the second priority list of the Directive on Environmental Quality Standards - EQSD (Directive 2008/105/EC), also known as the Priority Substances Directive. The second list reviewed the 14 substances proposed in the first list and added 8 other pollutants to the 33 priority pollutants.

The Directive 2009/90/EC provided technical specifications for chemical analysis and water status monitoring.

With the Proposal for the Directive amending the WFD and EQSD (COM(2011)876), 15 additional priority substances were added to the priority list (48 substances in total), 6 of which are considered as priority hazardous substances. This proposal also established a watch-list mechanism designed to allow targeted EU-wide monitoring of substances of possible concern to support the prioritisation process in future reviews of the priority substances list. The Proposal COM(2011)876 led to the adoption of the Directive 2013/39/EU. According to the Proposal COM(2011)876, there are currently 48 priority substances (Table 2.2). Diclofenac (CAS 15307-79-6), 17-beta-estradiol (CAS 50-28-2), and 17-alpha-ethinylestradiol (CAS 57-63-6) which were proposed to be included in the Priority list with COM(2011)876, shall, according to the Directive 2013/39/EU, be included in the first Watch List, in order to collect the monitoring data which will facilitate the determination of appropriate measures and to address the risk posed by those substances.

The list of priority substances has to be reviewed every six years. The priority substances and other pollutants complying with the limits present the basis for reaching the good chemical status of water bodies. On national level, river basin-specific pollutants are also identified and regulated.

Table 2.1 European Union Priority lists

1ST PRIORITY LIST **Decision 2455/2001/EC**	2ND PRIORITY LIST **Directive 2008/105/EC**	Proposed Revision of 2ND PRIORITY LIST **Proposal COM(2011)876**	AMENDED 2ND PRIORITY LIST **Directive 2013/39/EU**
33 priority substances/groups	33 priority substances/groups	48 priority substances/groups	45 priority substances/groups
11 priority hazardous	20 priority hazardous	21 priority hazardous	21 priority hazardous
14 pollutants for later review			

Table 2.2 Current list of priority substances according to Directive 2013/39/EU

Number	CAS number	EU number	Name of priority substance	Identified as priority hazardous substance
1	15972-60-8	240-110-8	Alachlor	
2	120-12-7	204-371-1	Anthracene	X
3	1912-24-9	217-617-8	Atrazine	
4	71-43-2	200-753-7	Benzene	
5	not applicable	not applicable	Brominated diphenylethers	X
6	7440-43-9	231-152-8	Cadmium and its compounds	X
7	85535-84-8	287-476-5	Chloroalkanes, C10-13	X
8	470-90-6	207-432-0	Chlorfenvinphos	
9	2921-88-2	220-864-4	Chlorpyrifos (Chlorpyrifos-ethyl)	
10	107-06-2	203-458-1	1,2-dichloroethane	
11	75-09-2	200-838-9	Dichloromethane	
12	117-81-7	204-211-0	Di(2-ethylhexyl)phthalate (DEHP)	
13	330-54-1	206-354-4	Diuron	
14	115-29-7	204-079-4	Endosulfan	X
15	206-44-0	205-912-4	Fluoranthene	
16	118-74-1	204-273-9	Hexachlorobenzene	X
17	87-68-3	201-765-5	Hexachlorobutadiene	X

Number	CAS number	EU number	Name of priority substance	Identified as priority hazardous substance
18	608-73-1	210-158-9	Hexachlorocyclohexane	X
19	34123-59-6	251-835-4	Isoproturon	
20	7439-92-1	231-100-4	Lead and its compounds	
21	7439-97-6	231-106-7	Mercury and its compounds	X
22	91-20-3	202-049-5	Naphthalene	
23	7440-02-0	231-111-14	Nickel and its compounds	
24	25154-52-3	246-672-0	Nonylphenols	X
25	1806-26-4	217-302-5	Octylphenols	
26	608-93-5	210-172-5	Pentachlorobenzene	X
27	87-86-5	231-152-8	Pentachlorophenol	
28	not applicable	not applicable	Polyaromatic hydrocarbons (PAH)	X
29	122-34-9	204-535-2	Simazine	
30	not applicable	not applicable	Tributyltin compounds	X
31	12002-48-1	234-413-4	Trichlorobenzenes	
32	67-66-3	200-663-8	Trichloromethane (chloroform)	
33	1582-09-8	216-428-8	Trifluralin	X
34	115-32-2	204-082-0	Dicofol	X
35	1763-23-1	217-179-8	Perfluorooctane sulfonic acid and its derivatives (PFOS)	X
36	124495-18-7	not applicable	Quinoxyfen	X
37	not applicable	not applicable	Dioxins and dioxin-like compounds	X
38	74070-46-5	277-704-1	Aclonifen	
39	42576-02-3	255-894-7	Bifenox	
40	28159-98-0	248-872-3	Cybutryne	
41	52315-07-8	257-842-9	Cypermethrin	
42	62-73-7	200-547-7	Dichlorvos	
43	not applicable	not applicable	Hexabromocyclododecanes (HBCDD)	X
44	76-44-8 / 1024-57-3	200-962-3 / 213-831-0	Heptachlor and heptachlor epoxide	X
45	886-50-0	212-950-5	Terbutryn	

2.5.2. Watch List

The Directive 2013/39/EU introduced a Watch List as a mechanism of collecting monitoring data and improving the information available to identify the substances of the greatest concern.

The Watch List (WL) mechanism of WFD determines that:

- WL substances and groups are to be monitored across the EU for up to 4 years,
- a maximum number of 10 substances or groups of substances shall be included in the first Watch List,
- WL increases by one at each update,
- WL increases up to a maximum of 14 substances or groups,
- WL should not contain more than 25 substances or groups at any given time and
- WL should be updated every 2 years.

The 1st Watch List was published in the Commission Implementing Decision (EU) 2015/495 and it included 10 substances. After the review, a 2nd Watch List was proposed within a JRC technical report in April 2018 (Table 2.3). In the report, it is proposed that five substances are removed and three new substances are added. The new list was put forward with the Commission Implementing Decision (EU) 2018/840 of 5 June 2018 establishing a Watch List of substances for the Union-wide monitoring in the field of water policy pursuant to the Directive 2008/105/EC of the European Parliament and of the Council and repealing Commission Implementing Decision (EU) 2015/495. The 3rd Watch list was established by the Commission Implementing Decision (EU) 2020/1161 of 4 August 2020 (Table 2.4) and it includes 9 substances/groups in total.

Table 2.3 European Union Watch Lists

1ST WATCH LIST Decision 2015/495	**2ND WATCH LIST** Decision 2018/840	**3RD WATCH LIST** Decision 2020/1161
10 substances/groups	8 substances/groups	9 substances/groups

Table 2.4 Current European Union Watch List according to the Decision 2020/1161

Name of substance / group	CAS #	EU number	Indicative analytical method	Maximum acceptable method detection limit (ng/l)
Metaflumizone	139968-49-3	604-167-6	LLE-LC-MS-MS or SPE-LC-MS-MS	65
Amoxicillin	26787-78-0	248-003-8	SPE - LC-MS-MS	78
Ciprofloxacin	85721-33-1	617-751-0	SPE - LC-MS-MS	89
Sulfamethoxazole	723-46-6		SPE-LC-MS-MS	100
Trimethoprim	738-70-5		SPE-LC-MS-MS	100
Venlafaxine and O-desmethylvenlafaxine			SPE-LC-MS-MS	6
Azole compounds			SPE-LC-MS-MS	
Clotrimazole	23593-75-1	245-764-8		20
Fluconazole	23593-75-1	627-806-0		250
Imazalil	35554-44-0	252-615-0		800
Ipconazole	125225-28-7	603-038-1		44
Metconazole	125116-23-6	603-031-3		29
Miconazole	22916-47-8	245-324-5		200
Penconazole	66246-88-6	266-275-6		1700
Prochloraz	67747-09-5	266-994-5		161
Tebuconazole	107534-96-3	403-640-2		240
Tetraconazole	112281-77-3	407-760-6		1900
Dimoxystrobin	149961-52-4	604-712-8	SPE-LC-MS-MS	32
Famoxadone	131807-57-3	603-520-1	SPE-LC-MS-MS	8,5

As stated in the Commission Directive 2014/80/EU of 20 June 2014 amending Annex II to the Directive 2006/118/EC of the European Parliament and of the Council on the protection of groundwater against pollution and deterioration, a watch list for pollutants of groundwater should be established under the Common Implementation Strategy for the Directive 2000/60/EC in order to increase the availability of monitoring data on substances posing risk or potential risk to bodies of groundwater, and thereby facilitate the identification of substances, including emerging pollutants, for which groundwater quality standards or threshold values should be set. Groundwater Watch List (GWWL) will include new or emerging substances that the Member States should include in the monitoring programmes. The Commission Implementing Strategy (CIS) Working Group on Groundwater (WG

GW) was organized to elaborate the concept for drafting this list. The methodology for GWWL is based on the occurrence of substances in the groundwater (based on the monitoring data) and the theoretical leaching potential of substances (based on the substance properties). The combined outcome of these two assessments, called "Combined Groundwater Leaching Potential Score", is linked to the substances hazard potential of forming a ranked list of "Integrated groundwater score". This list serves as a basis for the determination of substances either to be selected for the GWWL or to be listed to facilitate the Annexes I and II review process of the GWD.

In June 2019, CIS WG GW delivered a Voluntary Groundwater Watch List, which includes 11 proposed substances (Table 2.5).

Table 2.5 List of substances proposed for first Voluntary Groundwater Watch List

No.	Name of substance	Group	Acronym	Sub-group
1	Perfluorododecanoic Acid (L)	PFAS	PFDoA	PFCAs
2	Perfluoroundecanoic Acid (L)	PFAS	PFUnA	PFCAs
3	Clopidol	Pharmaceutical		
4	Crotamiton	Pharmaceutical		
5	Amidozoic Acid	Pharmaceutical		
6	Sulfadiazine	Pharmaceutical		
7	Primidone	Pharmaceutical		
8	Sotalol	Pharmaceutical		
9	Ibuprofen	Pharmaceutical		
10	Erythromycin	Pharmaceutical		
11	Clarithromycin	Pharmaceutical		

As further potential candidates, 4 substances were proposed, namely 4:2 Fluortelomerphosphatemonoester, Perfluorodecyl Phosphonic Acid, Perfluorooctyl Phosphonic Acid, and 6:2 Fluortelomerphosphatemonoester.

2.6. Data Sources

The rapid growth of technology, expansion of urban areas and lifestyle changes, agriculture, industry, and medicine have resulted in the consumption of large amounts of water in recent years and consequently, in a lot of wastewater which significantly impacts health and environment. Water sources are, thus, increasingly exposed to pollution from various sources, such as sewerage networks, discharges from wastewater treatment plants, use of fertilizers in agriculture, landfills, etc. In the aquatic environment, we are already seeing and will continue to see an increase in the number of ECs. This is due to both ever-improving analytical techniques as well as the increasing diversity of ECs resources and their increasing use. As there is still relatively little information on the occurrence of ECs in general, further research and monitoring are needed.

Within the scope of the boDEREC-CE project, a “Data Collection Tool for Emerging Contaminants” was developed within the 1st thematic work package. It represents the synthesized collection of the data on ECs in the aquatic environment, gathered by project partners on a national level, in the form of questionnaires. The data collection tool was divided into five sections, as follows:

- Section A: Identification of emerging contaminants (ECs) in the environment
- Section B: Legislation and policy related to emerging contaminants in the water environment
- Section C: Emerging contaminants appearing in the water environment
- Section D: State-of-the-art-monitoring
- Section E: Attenuation strategies

The tool provides an overview of the available data and data collection methodology. Thus, the results may be used for any further development in water management and research on emerging contaminants and strategies for their removal from the aquatic environment. Stakeholders from other sectors may use the results as a comparative tool for gathering knowledge about emerging pollutants elsewhere and methods countries involved in producing these results use to address emerging contaminants’ problems. In addition, stakeholders from the industry producing or using compounds that may enter the aquatic environment can benefit from the information collected.

2.6.1. Austria

In Austria, the information collected on ECs relates mainly to the monitoring and analysis of groundwater, wastewater, flowing water, and drinking water. It is obtained mainly from governmental and official reports, which are available to the public and refer to a longer period of time. The substances most frequently monitored were pesticides and selected pharmaceuticals. In groundwater, monitoring programs focused on pesticides in addition to standard parameters. Micro-pollutants, such as industrial chemicals, hormones, and hydrocarbons were analysed as well, together with certain selected pharmaceuticals and pesticides. In drinking water, pharmaceuticals and partly pesticides were analysed. According to the data collected, it was found that there is no standardized list of emerging contaminants to be monitored or to be considered as a reference point for the analysis. Pesticides were mainly analysed in groundwater, and the pharmaceuticals were analysed in wastewater and drinking water. The pharmaceutical substance erythromycin was detected in different media studied. The pharmaceutical substance sulfamethoxazole was selected in many programs to be monitored and analysed, but generally never detected in the final results.

2.6.2. Croatia

From the late 1990s/early 2000s until today, a number of studies related to the occurrence of specific ECs in Croatia have been conducted at a scientific and professional level. However, most studies focused only on a narrow range of compounds and were mainly of local character. The research activities were and still are focused mainly on wastewater and recipient surface water resources and a small range of compounds (e.g. antibiotics). A nationwide study on pharmaceuticals in surface waters was performed in 2013/2014, when 15 sulfonamides and 2 macrolides (azithromycin and erythromycin) were monitored along 20 rivers in Croatia, in Danube and Adriatic catchment area (Ivešić et al., 2017). Experts from Ruđer Bošković Institute researched the occurrence of pharmaceutical substances in waste, soil, and groundwater under the municipal landfill in Zagreb (Ahel et al., 1998; Ahel & Jeličić, 2001), in the Croatian wastewater treatment plants and effluents (Senta et al., 2008), as well as (pharmaceutical) industrial effluents and recipient rivers (Bielen et al., 2017; Senta et al., 2017).

The monitoring of the ECs substances from the List of Priority Substances is prescribed by the Regulation on Water Quality Standard (OG 96/2019) and has to be conducted once a month. Operational monitoring of priority substances started in 2014. In 2021, monitoring of priority substances in surface water was conducted at 119 locations within the supervisory monitoring activities.

Furthermore, monitoring of substances included on the Watch List is obligatory within 6 months of adding the substance to the list. The first monitoring of substances included in the Watch List was conducted in 2016 following the Monitoring Compliance Program (Program usklađenja monitoringa, Croatian Waters, 2016). Five measuring stations from the supervisory and operational monitoring were selected to determine the concentrations of the substances from the Watch List. These measuring stations are located on four surface water bodies (rivers Sava, Orljava, Jošava, and Česma). Monitoring of the substances from the Watch List is carried out at selected representative monitoring stations for a period of at least 12 months in accordance with the applicable Commission (EU) Regulation establishing a Watch list.

Although the reports on the official state monitoring of the ECs included in the state monitoring are available on-demand only, various project results indicated that the discharges from the pharmaceutical industries and wastewater treatment plants near larger cities may pose an ecological and public health concern.

2.6.3. Czech Republic

In the Czech Republic, most research on the occurrence of ECs in water has been carried out concerning drinking water sources. Ibuprofen, carbamazepine, naproxen, and diclofenac were detected in the samples of drinking water in low concentrations. In wastewater, which is the main source of pollutants, ECs are not monitored systematically. The efficiency of pharmaceuticals removal in wastewater treatment plants differs depending on a substance. Some of them, for example carbamazepine, seem to be persistent and pass through the facilities without any significant changes. ECs - pharmaceuticals - have also been detected in flowing streams. Small streams in large settlements are the most problematic because a large portion of the stream refers to treated wastewaters, which contain a relatively high concentration of ECs. In contrast, in the case of a large water reservoir (lake), the pharmaceuticals are diluted with a large amount of water. In groundwater, pharmaceuticals have been detected at locations where the aquifer intensively interacts with surface waters.

2.6.4. Germany

Germany's state monitoring focuses mainly on pharmaceutically active compounds, as they are bioactive and pose a major risk to the environment and human health. High consumption of personal care products and their ability to negatively impact the environment also indicate that strategic/long-term monitoring of these substances is necessary, as there are currently no data on the occurrence of these compounds in German aquatic environment. According to the database, there are monitoring data on pharmaceuticals in all parts of Germany, but their quantity varies among the federal states. While the pattern of contamination only varies very insignificantly, the extent to which a water body is contaminated varies greatly. The higher the proportion of treated wastewater in the water body, the greater the concentrations measured in the environment, meaning that there is a positive correlation between population and contamination with ECs. As wastewater treatment plant effluents are the main source for these contaminants entering the environment, measurements taken close to the outlets were greater than those taken downstream. Groundwater aquifers are not ubiquitously contaminated. Those not influenced by surface water are free from any residues of ECs. For shallow groundwater aquifers located in regions with extensive land use, it was possible to detect veterinary medicines (especially veterinary antibiotics) in the aquifers. Drinking water extracted after riverbank filtration, as the surface water is contaminated, also shows residues of pharmaceuticals in it. Hence, some compounds cannot be entirely removed during the filtration processes (LfU, 2019).

Monitoring of pharmaceuticals in Germany started in 2000, so that the long-term changes in concentrations may be assessed. By analysing the existing data, there is barely any change in concentrations except for some substances whose use/consumption increased/decreased leading to an increase/decrease in the concentrations measured. Due to these few changes, monitoring was stopped in 2017 which means that recent data on ECs in the aquatic environment does not exist (LfU, 2002; LfU, 2015).

2.6.5. Italy

Italy deals with many different pharmaceutically active compounds, personal care products, industrial compounds, pesticides, and other phytosanitary contaminants. Monitoring of ECs is always a selective process. The most monitored substances in surface and groundwater are currently the following: PFAS and many plant prootection products. For drugs, hormones, and PPCPs, in Italy the research activity, mainly focused on tthe integrated water cycle of urbanized and industrialized areas (Delli Compagni et. al., 2020; Riva et. al., 2019; Castiglioni et. al. 2018; Palmiotto et al., 2018), is still very limited by the quantities found in surface water, especially surface water intended for human consumption.

2.6.6. Poland

In Poland, ECs are found in different water bodies and conditions, including groundwater, spring water, riverbank filtration, flowing streams, lakes, wastewater as well as drinking water. Little data is available on the occurrence of ECs in spring water, riverbank filtration, drinking water (tap water), and groundwater. Polycyclic aromatic hydrocarbons were treated in spring water; riverbank filtration and groundwater studies focused on the emergence of pharmaceuticals and pesticides. Among the studied microcontaminants in drinking water, there were pharmaceuticals and perfluorinated compounds with the highest concentration. The most studied environments in terms of the occurrence of ECs are surface and wastewater. In flowing streams, pharmaceuticals and polycyclic aromatic hydrocarbons were studied, and the highest concentrations were measured in the case of pesticides, especially herbicides. Pharmaceuticals and polycyclic aromatic hydrocarbons were also treated in standing water bodies, where microcontaminants were also detected in small amounts; among the ECs, antibiotics were the most abundant. Higher concentrations of ECs and a higher number of micropollutants were detected in untreated wastewater. Concentrations of some pharmaceuticals (naproxen, ketoprofen, and paracetamol) were also much higher in untreated wastewater than in treated wastewater. However, most ECs detected in sewage from Polish Wastewater Treatment Plants were still present in wastewater after sewage treatment processes and it relates to all the studied groups (pharmaceuticals, hormones, PAHs).

2.6.7. Slovenia

In the last two decades, a lot of scientific research has been carried out in Slovenia in order to understand the occurrence of ECs in the Slovenian aquatic environment. This research was then followed by national monitoring, which complies with the requirements of the EU law and national legislation. In Slovenia, ECs have been detected in both wastewater and natural water bodies. In some cases, we can discuss the impact of wastewater on different components of the water cycle, but at the same time, the introduction of ECs may also be the result of other more direct routes and pollutant sources (e.g. uncontrolled waste dumps, urban drainage, etc.).

2.7. Monitoring

In the project partner countries, surface and groundwater quality is monitored more or less systematically at national level. It varies from country to country, depending on different aquatic environments and the range of ECs controlled parameters. The monitoring program complies with the requirements from the EU Water Directive.

The monitoring of emerging contaminants is not very developed in project partner countries. Surface and groundwater monitoring is carried out regularly, but only a few pollutants belonging to emerging contaminants are taken into account. Some ECs from the priority list are monitored according to the EU legislative requirements. Some ECs from the Watch List and some from different projects and studies are monitored as well. The results of these projects indicate the importance of the problem with ECs, as it has been found that waters are ubiquitously contaminated with ECs (pesticides, drugs, hormones…).

As the problem of the ECs occurrence in the aquatic environment is relatively new, no specific guidelines or regulations for sampling and analysis have been established. All the characteristics and procedures refer to general standard sampling.

Most countries are interested to know more about the properties of these hazardous substances in water. They need to record sources, routes, and behaviour of the detected substances, have control over pollution levels and take action in the event of pollution, improve methods of drinking and wastewater treatment, and identify seasonal and long-term changes in ECs concentrations.

The European projects such as boDEREC-CE provide a useful platform to synthesize and share the current state-of-the-art (SOA) knowledge with the final goal to aid the management of ECs on the transnational level. Current state-of-the-art reviews are essential for providing new information on any topic, especially for a field such as ECs because it is increasingly popular and leads to new research being conducted and new results constantly being provided. New advances in analytical extraction and measurement technologies and methods provide us with tools to detect, identify and quantify ever smaller and more reliable analysis of ECs levels in the environment. Additionally, investigating the topic of ECs is important for society in general, as it deals with the possible pollution of natural environment, which may negatively impact the ecosystems and consequently, human life.

Within the scope of the SOA survey, a learning tool and data collection tool were developed. The learning tool helps to understand the broad topic of ECs in the aquatic environment. It not only contains information from scientific sources but is also the result of the involvement of stakeholders from different organizations (e.g. water companies, wastewater treatment plants, monitoring bodies at a national and local level). With the implementation of this information source, cross-improvements are expected; between stakeholders, who put the knowledge into practice, and the academic world (research institutions, universities), which develops the knowledge at the base level. The developed data collection tool provides an overview of the available data and the methodology of data collection. Thus, the results can be used for any further development in water management and research on ECs and strategies for their removal from the aquatic environment. Stakeholders from other sectors can use the results as a comparative tool for gathering knowledge about emerging pollutants elsewhere and methods countries involved in producing these results are using to address ECs problems. In addition, stakeholders from industry producing or using compounds that may enter the aquatic environment may also benefit from the collected information.

3. PILOT SITES DESCRIPTION

The assessment of EC behaviour in the boDEREC-CE framework is based on the data and results from eight project pilot sites situated in the Central European region (Fig. 3.1). Pilot sites are located in all partner countries and are characterized by different natural characteristics and engineering solutions for water production.

From the geological point of view, the environment of quaternary, mostly fluvial sediments and karsts prevails. Other lithologies, such as magmatic and metamorphic rocks, are not represented in any of the pilot sites, since these environments usually do not provide significant water resources and therefore, large water companies are usually not bound to it. Selected pilot sites also present a variety of water production technologies. The most widespread technology is pumping from boreholes, eventually withdrawing surface water from watercourses. Two pilot sites use specific technologies of riverbank filtration and managed aquifer recharge.

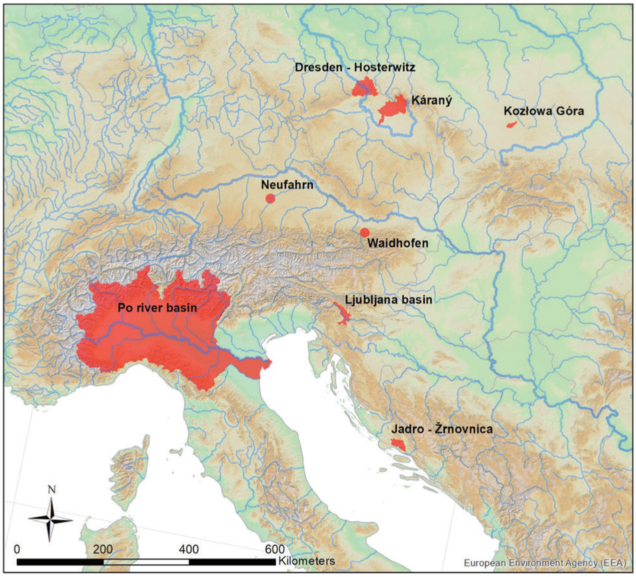


Figure 3.1 Situation of all boDEREC-CE project pilot sites.

The sources of PPCPs on different sites are similar - the mixture of agriculture, settlements, leaking sewer, and wastewater treatment plants with low PPCP removal efficiency and, consequently, surface and groundwater interaction.

3.1. Káraný-Jizera River, Czech Republic

Káraný pilot site is located in the central part of Bohemia, about 30 km northeast of Prague. Local waterworks are one of the suppliers of drinking water for the city of Prague, with more than 1 million inhabitants. The facility uses groundwater from the shallow aquifer and surface water from the lower reaches of the Jizera River.

The length of the river is 164.6 km and the catchment area is 2 193 km^2. The average flow rate in the nearest gauging station is 24 m^3/s (ČHMÚ). The river basin has mixed character with a balanced representation of forests and farmland. The largest settlement in the basin is Mladá Boleslav, with 44 000 inhabitants and an important industrial area, including the factory and headquarters of the famous Škoda brand. Hydrogeologically, the pilot site is characterized as a shallow unconfined aquifer situated in terraces of Quaternary fluvial sediments. Under natural conditions, the aquifer is recharged by infiltration of precipitation and inflow from the fractured bedrock and drains to the Jizera River. However, an intensive extraction of groundwater induces recharge of the aquifer from the river. In addition, the aquifer is artificially recharged by water from the river.

The waterwork at Káraný operates according to the principle of combining two independent drinking water treatment technologies (Fig. 3.2). The first one is now a historic, but still a 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 about 250 meters from the bank of the Jizera River. The total capacity of this system is up to 1,000 l/s (Skalický, 2015).

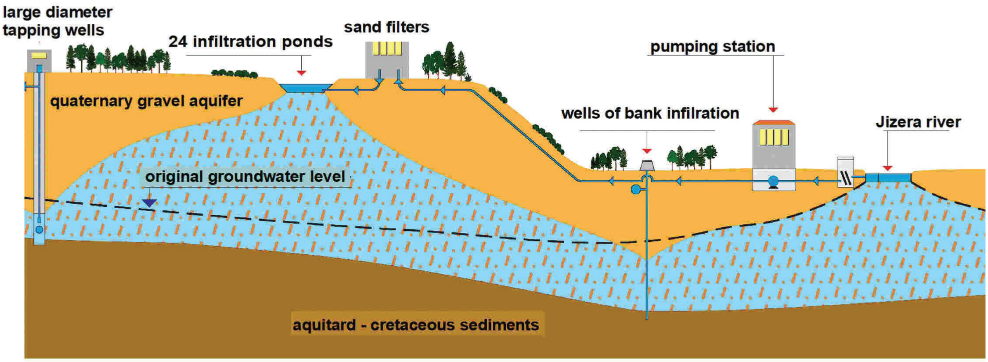


Figure 3.2 Scheme of Káraný waterworks (modified from Skalický, 2015).

Another technology of the waterworks originates in 1968 and relies on the artificial recharge (Jedlička and Knězek, 1968). 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 (Fig. 3.3) from where it percolates into about 20 meters thick sandy fluvial sediments and recharges the extracted aquifer. At a distance of approximately 200 meters from the infiltration ponds, there is a system of large-diameter wells with the total capacity of up to 900 l/s. The extracted water is a mixture of infiltrated water and original groundwater in the sandy-gravel terrace inflowing from the east towards the Jizera River (Skalický, 2015). In terms of potential sources of pollution by PPCPs, municipal wastewater effluent poses the greatest risk. The Mladá Boleslav town is also a seat of the psychiatric hospital with a 150-year-old 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.

Figure 3.3 Infiltration pond in Káraný waterworks.

3.2. Dresden/Hosterwitz, Germany

The riverbank filtration (RBF) and managed aquifer recharge (MAR) site Dresden-Hosterwitz is operated by DREWAG NETZ GmbH and located on the floodplain of the

Elbe River. The Elbe River is a transboundary perennial river and federal waterway. With a length of 1,097 km, the Elbe River originates in the Czech Republic and flows northwest into the North Sea (Bartak and Grischek, 2018). Dresden is located in a rift valley along the Elbe River, which is mainly filled with glacial deposits such as gravel and sand (Fig. 3.4). The whole catchment of the pilot site is very large. The Elbe River in Hosterwitz discharges 53,882 km², which covers most of Bohemia. The overview in Figure 3.4 represents only a minor sub-catchment, which includes a catchment area between Hosterwitz and Děčín in the Czech Republic.

The aquifer is overlain by a layer of 2 to 4 m meadow loam with a thickness of up to 15 m under normal conditions. Turonian marl forms the base of the aquifer. The marl with a thickness of 250 m is underlain by partially artesian Cretaceous sandstones, which crop out at the southwestern border of the city. The northern border is formed by an impermeable Lusatian overthrust – a contact with a granitic massif (Grischek et al. 1996). The quaternary aquifer is in hydraulic connection with the Elbe River and groundwater flows from both sides of the valley towards the river.

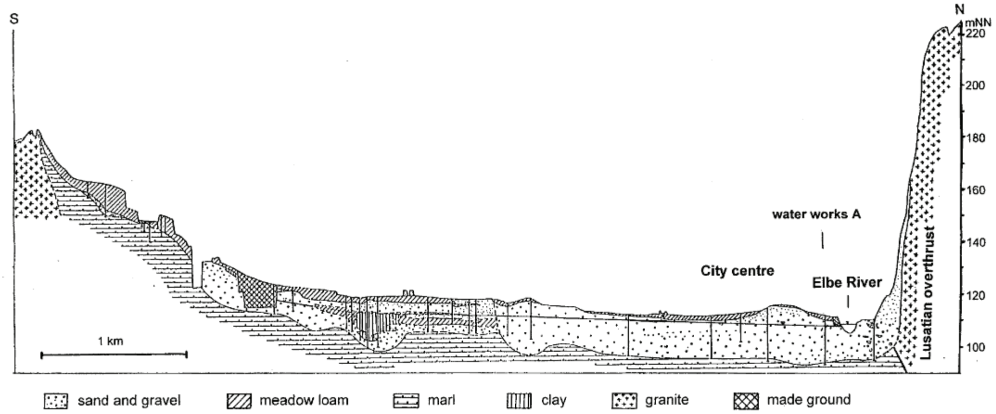


Figure 3.4 Geological cross-section (Grischek et al., 1996).

The discharge of the Elbe River varies considerably depending on precipitation, snowmelt, and discharge control in the Czech Republic. The mean discharge in Dresden (55.6 km downstream of the Czech Border) is 332 m³/s (at 184 cm river stage) and varies between 110 (75 cm) and 1,700 m³/s (547 cm) during mean low and high flow periods. The local aquifer at the pilot site comprises two stratigraphic units: the quaternary sand and gravel aquifer with a thickness of 9 to 14 m and 1 to 3 m thick overlying Holocene clay.

The Dresden-Hosterwitz waterworks, along with the waterworks Dresden-Coschütz and Dresden-Tolkewitz, supplies around 600 000 citizens and operates two separate treatment trains (Fig. 3.5): the RBF treatment train and the MAR treatment train. If the daily production is less than 20,000 m^3, RBF will be the main treatment before cascade aeration, granular activated carbon (GAC) filtration, pH adjustment, and disinfection with chlorine. The production capacity may be increased to 72,000 m^3/d through five open recharge basins supplied with pre-treated water from the Elbe River (coagulation and open multimedia sand filtration). Water is recovered with 111 siphon wells and 2 separate well groups consisting of 8 and 28 wells equipped with submersible pumps.

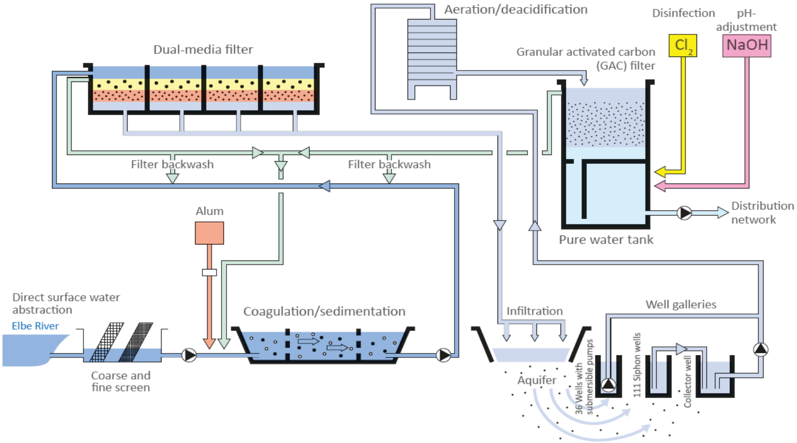


Figure 3.5 Schematic water treatment, waterworks Dresden-Hosterwitz (©DREWAG Netz GmbH).

Figure 3.6 Aerial view of water works Dresden Hosterwitz (©DREWAG Netz GmbH).

The Elbe River water is polluted by PPCPs mainly from the inputs of treated wastewater from the wastewater treatment plants (WWTPs) located upstream of Dresden and in the Czech Republic. The Dresden-Kaditz WWTP receives wastewater from pharmaceutical industries located in Dresden (e.g. GlaxoSmithKline Biologicals), agriculture (mostly horticulture), and various hospitals (e.g. Universitätsklinikum Carl Gustav Carus and Dresden-Friedrichstadt), but does not affect the pilot site located upstream.

3.3. Jadro and Žrnovnica Springs Catchment, Croatia

Jadro and Žrnovnica springs catchment is a typical Dinaric karst catchment located in the central part of Southern Croatia. 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. The Jadro River spring discharges at an altitude of around 35 m a.s.l. south of Klis settlement and southwest of Mosor Mountain (1339 m a.s.l.) (Fig. 3.7 and 3.8). Jadro spring had a maximal discharge of 52.47 m^3/s in 2015, minimal discharge of 2.3 m^3/s in 2018, while its mean discharge is 9.24 m^3/s (data period from 2011 to 2019). The springing zone of the Žrnovnica River occurs northeast of the City of Split and near Žrnovnica settlement, at the foot of Mosor Mountain, and altitudes ranging from 77 to 90 m a.s.l (Fig. 3.7 and 3.8). 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 from 2009 to 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 greater level of certainty. The 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. 3.7 and 3.8). The catchment is predominantly made out of highly permeable carbonate rocks of the Mesozoic and Paleogene age. Flysch deposits and clastites represent hydrogeological barriers and at their contact with permeable rocks, the springs of Jadro and Žrnovnica emerge.

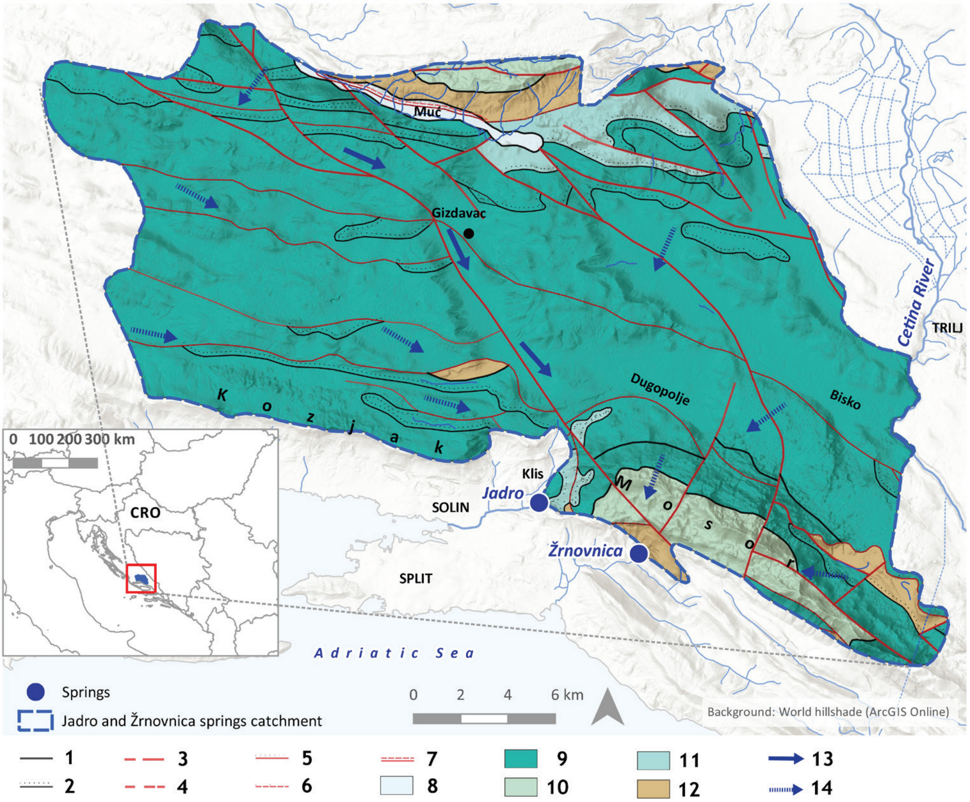


Figure 3.7 Hydrogeological map of Jadro and Žrnovnica springs catchment (modified from Biondić et al., 2003), 1 - normal lithostratigraphic boundary, 2 - erosional boundary, 3 - identified fault, 4 - covered fault, 5 - reverse fault, 6 - overthrust contact, 7 - covered overthrust contact, 8 - Quaternary 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 of 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.

The water supply system of the City of Split and its wider surroundings (around 300,000 inhabitants) depends on the water intake at Jadro, while Žrnovnica supplies the nearby Žrnovnica and Donje Sitno settlements and enables irrigation of surrounding agricultural land.

Figure 3.8 Jadro spring (1), Žrnovnica spring (2), view from Mosor Mountain on Split and wider surroundings (3), Cetina River (4).

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 the 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. Thus, the most likely sources of PPCPs are numerous smaller villages without proper sewerage systems and potentially leaking septic tanks, and larger settlements without water treatment plants. Moreover, there are 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. Potential uncontrolled and inadequate use of pesticides and fertilizers in karst poljes (Dugopolje, Bisko, Muć, Fig. 3.7) could also be one of the organic contaminants' sources.

3.4. Waidhofen a/d Ybbs, Austria

The Waidhofen a/d Ybbs pilot plant action area is located ~150 km west of Vienna in Austria. This is the municipality located in the Federal State of Lower Austria (Niederösterreich), 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) (Fig. 3.9 a). The pilot plant action is located ~10 km south of the above-mentioned town, along the River Waidhofenbach, and it covers about 10 km² (Bittner et al., 2018, Sheikhy Narany et al., 2019). However, the present research focused on the recharge area of the most important karstic spring (Kerschbaum) in the area, covering ~2.5 km² (Fig. 3.9 b) (Hacker, 2003; Bittner et al., 2018). The 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 summer (June and July) and winter months (December and January), with snowfall dominating precipitation in the winter (Bittner et al., 2018, Sheikhy Narany et al., 2019). The studied area (recharge area of Kerschbaum spring) is characterized by two surface water bodies, Waidhofenbach flowing from south to north and tributary of the Ybbs River, and Glashüttenbach, a small tributary of the Waidhofenbach, flowing west to east.

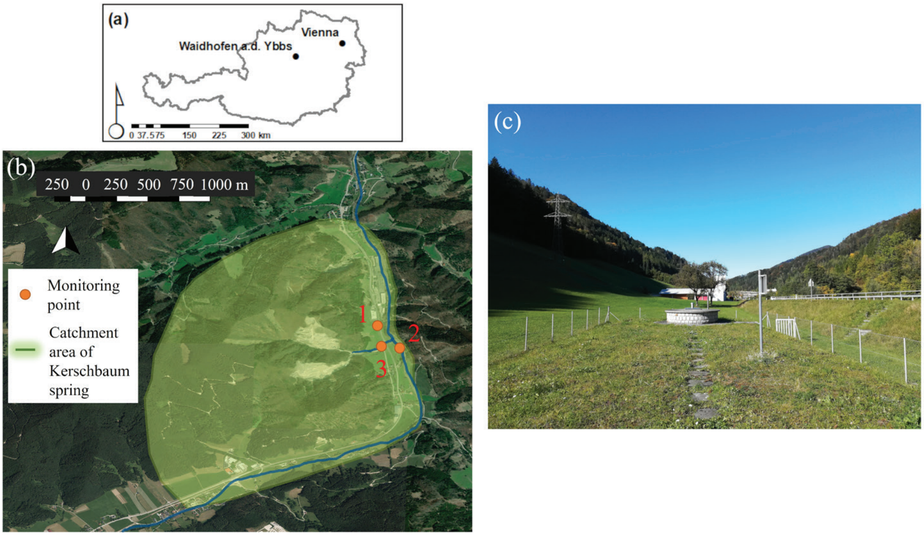
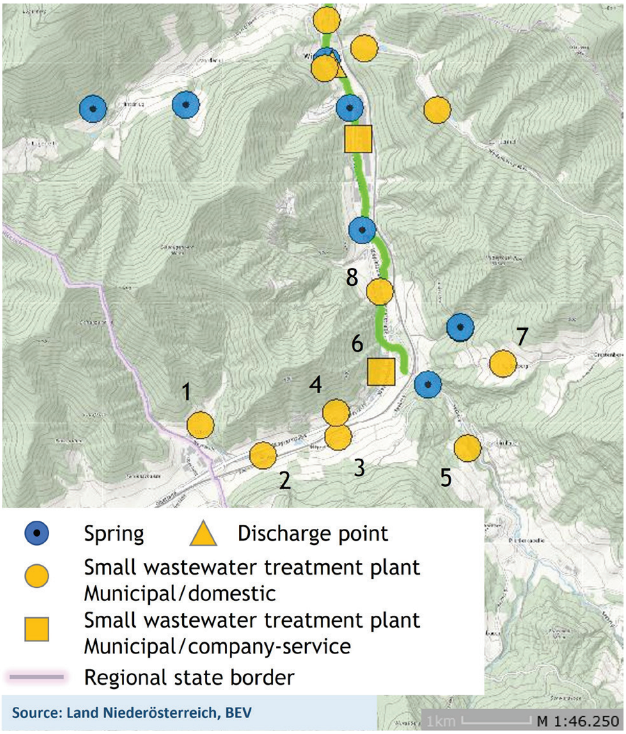


Figure 3.9 (a) Geographical location of the pilot action study area, Waidhofen a/d Ybbs; (b) recharge area of Kerschbaum spring - boundaries of the pilot area for the project, location of Kerschbaum spring (1), surface water bodies of Waidhofenbach (2) and Glashüttenbach (3); (c) view of Kerschbaum spring.

From a geological point of view, the studied area is situated within the Northern Calcareous Alps. Therefore, the dominant bedrock type present is the Main Dolomite. The investigation of the area revealed the existence of a deep karstified groundwater system, also below the Waidhofenbach Valley (Hacker, 2003; Bittner et al., 2018, Sheikhy Narany et al., 2019). Pedologically, the pilot action site is mainly characterized by the simultaneous presence of the soil types “Rendzina” (mainly limestone and dolomites) and “Loam-Rendzina” (Rendzina-like soil type evolved above colluvial material or carbonate). This influences the inhomogeneity of the vegetation growing above.

The geology of the pilot area induced the formation of several karstic springs at different altitudes. The main ones are exploited from the Municipality of Waidhofen a/d Ybbs as the 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; Sheikhy Narany et al., 2019). Those karst springs provide water supply for the total of approximately 25,000 inhabitants (including neighbouring towns), of which 11,571 live in the Municipality of Waidhofen a/d Ybbs. Kerschbaum spring (the focus of the research) 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 does not play an important role in the recharge of the mentioned spring (Bittner et al., 2018; Sheikhy Narany et al., 2019). The presence of a well-connected network of fractures and conduits is assumed. This creates the interconnected sub-terrain drainage, similar to a porous body (Bittner et al., 2018; Koeck et al., 2017). The above mentioned improves the infiltration behaviour and allows deep sub-terrain drainage (Koeck et al., 2017).



Source: Land Niederösterreich, BEV

Figure 3.10 Wastewater treatment plants present in the study area, Kerschbaum recharge area, and south to Waidhofen a/d Ybbs (Land Niederösterreich ATLAS).

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 (Bittner et al., 2018; eHYD https://ehyd.gv.at/#). 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. However, along with the Waidhofenbach, multiple settlements of private households, industrial infrastructures and small domestic wastewater treatment plants (upstream of the study area) are present, as shown in Figure 3.10. These could be considered then as the main source of potential contamination of the Waidhofenbach surface water. According to Hacker (2003), the quality of the waters of Waidhofenbach and 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.

3.5. Kozłowa Góra, Poland

The Kozłowa Góra pilot action area is located in the central part of the Silesia Region, around 17 km north from Katowice, outside the territory of the Upper Silesia Conurbation (Fig. 3.11). The pilot action area is situated in the northern part (headwaters) of the Brynica River catchment, upstream of the head dam of the Kozłowa Góra reservoir, which covers 193.93 km² and encompasses communes, which are primarily of rural or urban-rural nature.

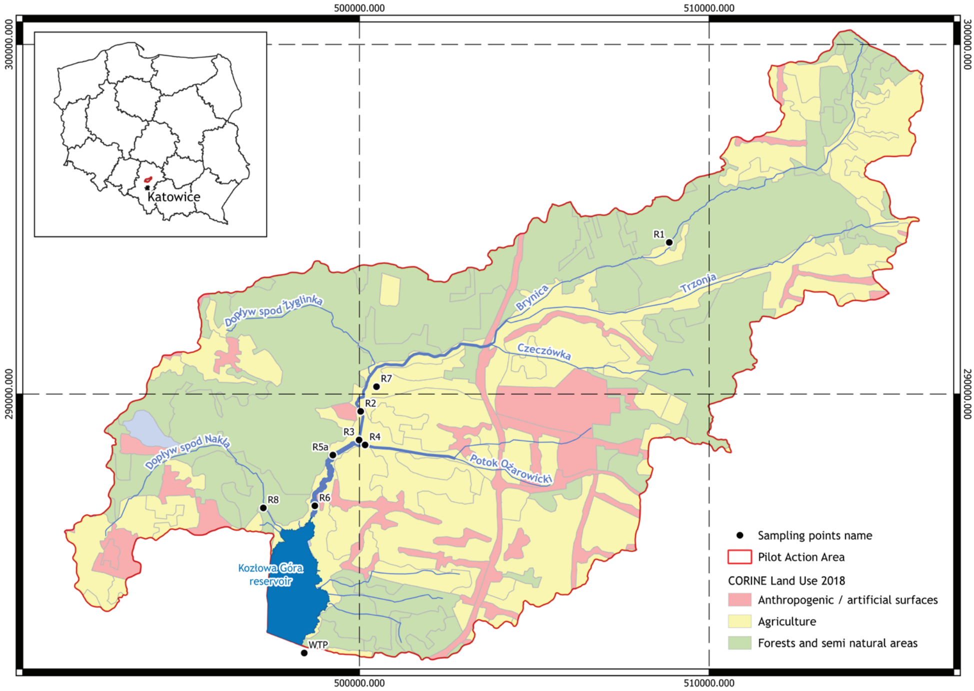


Figure 3.11 Location of the Kozłowa Góra pilot action area.

The pilot action area is located in the left-side catchment area of the Vistula River (the longest river in Poland, mouthed to 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, 1 right-bank) are characterised by short length and flow rates ranging from a few to several tens of l/s (Budzyńska et al., 1999). The Brynica River inflows directly into the Kozłowa Góra reservoir, and the discharge varies from 0.011 m^3/s to 32,446 m^3/s (Czekaj 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 it differs depending on water level (Bojarski A. et al., 2004). Besides Brynica, there are other direct inlets to the Kozłowa Góra reservoir: Dopływ z Siemoni (left bank), Potok spod Nakła (right bank) and several small streams observed periodically at the left bank of the reservoir. Within the catchment area, groundwater is observed in three multi-aquifers: Quaternary, Triassic, and Carboniferous. Three Triassic carbonate MGB are located in this area: Gliwice, Lubliniec – Myszków and Olkusz – Zawiercie.

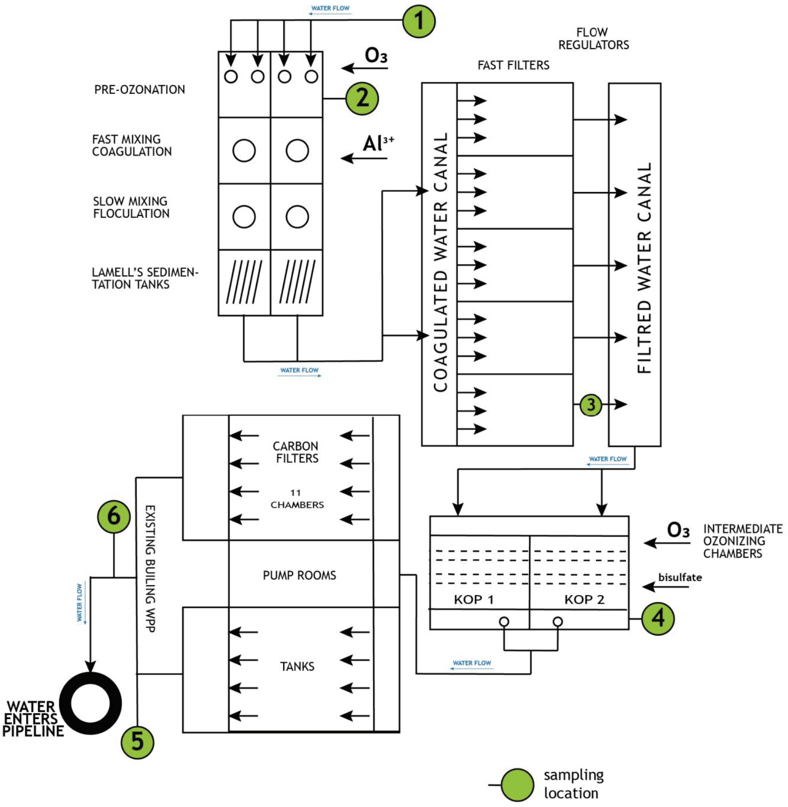


Figure 3.12 Scheme of the Kozłowa Góra water treatment plant.

The Kozłowa Góra reservoir is used as a drinking water source for WTP Kozłowa Góra, which has been operated by Silesian Waterworks PLC from the early 50s and which supplies 6 communes with nearly 403 000 inhabitants in total. The water intake is situated below the head dam at the left bank of the outflow. The raw water is transported by pipes to the WTP and then treated with several techniques such as pre-ozonation, 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 3.12).

Within the area, potential sources of PPCP pollution are related mainly to the urban fabric, as well as agriculture, and accompanying wastewater and stormwater discharges. Due to possible repellent usage against insects, forests and greenlands could be potential sources of PPCPs. Another potential source of PPCPs within the pilot action area is transport – especially Katowice airport and its additional infrastructure.

3.6. Po River basin, Italy

Po River Basin pilot site is located in the northern Italy; it is divided into 7 regions including approximately 3,200 municipalities and around 17 million inhabitants.

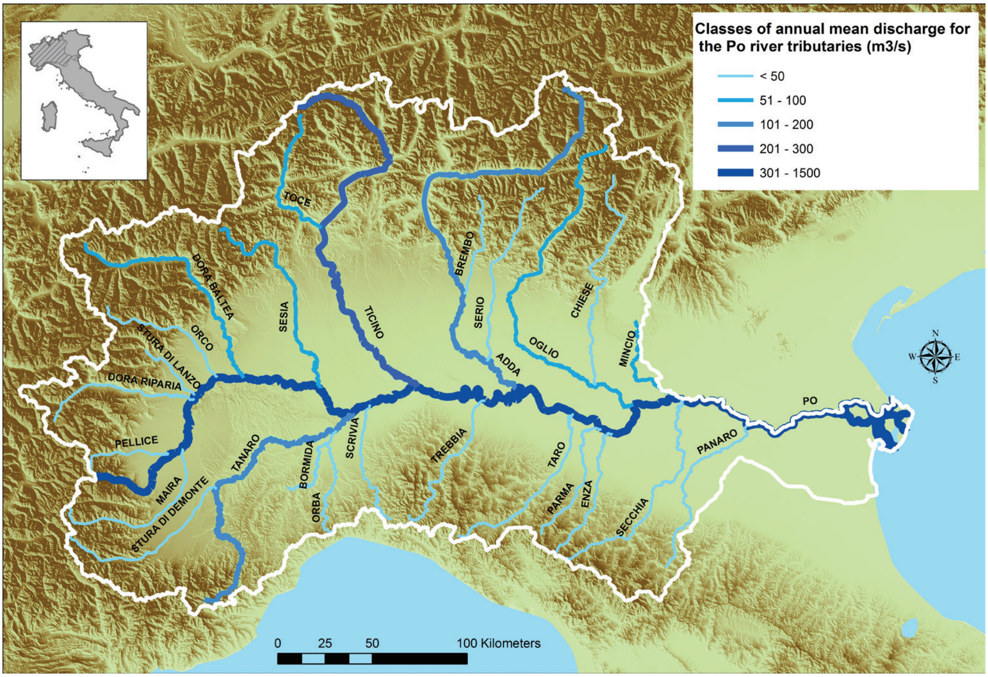


Figure 3.13 Annual mean discharge of the Po River and main tributaries.

The geography of the Po River Basin includes four main areas: mountains (Alps and Apennines), hills, plains, and coast. The Plain (Pianura Padana) comprises large urban areas like Milano and Torino, and other different landscapes including terraces, cultivated areas, artificial channel networks, and sub-Apennine landscapes. The length of the Po River is 652 km and the catchment area is 74,000 km² (Fig. 3.13). The yearly average flow rate in the Pontelagoscuro gauging station is 1,490 m^3/s (Hydrological Yearbook 2019).

The land use in the Po River basin is quite varied with 46 % of agricultural areas, 45 % of forest and grasslands, 7 % of urban areas, and 2 % of water bodies. In terms of potential sources of pollution by PPCPs, the greatest risk is represented by municipal and industrial wastewater effluent; emerging contaminants can also derive from other point pollution sources (such as illegal discharges, landfill leachate, etc.) and diffuse pollution sources (like runoff from agriculture, livestock, etc.).

The yearly mean total rainfall on the Po River Basin is 78 billion m^3; 46 billion of them are transformed in river discharge and the other 29 billion give a contribution to infiltration and evapotranspiration. The mean of the total yearly water use in the basin is 20.5 billion m^3: 16.5 for agriculture, 1.5 for industry, and 2.5 for drinking water. 6,837 wastewater treatment plants serving the population of approximately 21,500,000 are located in the Po River Basin. The area selected for the surface water hydrological and transport modelling is located in the lower part of the Po River, between the confluence of the Secchia River and the Po River delta.

Figure 3.14 view of the Pontelagoscuro Drinking Water Treatment Plant.

The boDEREC-CE monitoring activities are carried out at the Pontelagoscuro drinking water treatment plant (Fig. 3.14), which supplies the City of Ferrara and other smaller municipalities, with more than 200,000 inhabitants. The plant is situated at the closure of the whole Po Basin and, thus, water monitored at the entry point can be considered as representative for the whole basin, with its quality being influenced by the relevant hydro-meteorological situation, physico-chemical and biological processes, and by socio-economical activities.

The facility uses surface water from the lower reach of the Po River (80 %) and groundwater from the wells close to the Po river bank (20 %). The average annual withdrawal is 1,040 l/s.

The Pontelagoscuro Drinking Water Treatment Plant workflow is shown in the following figure.

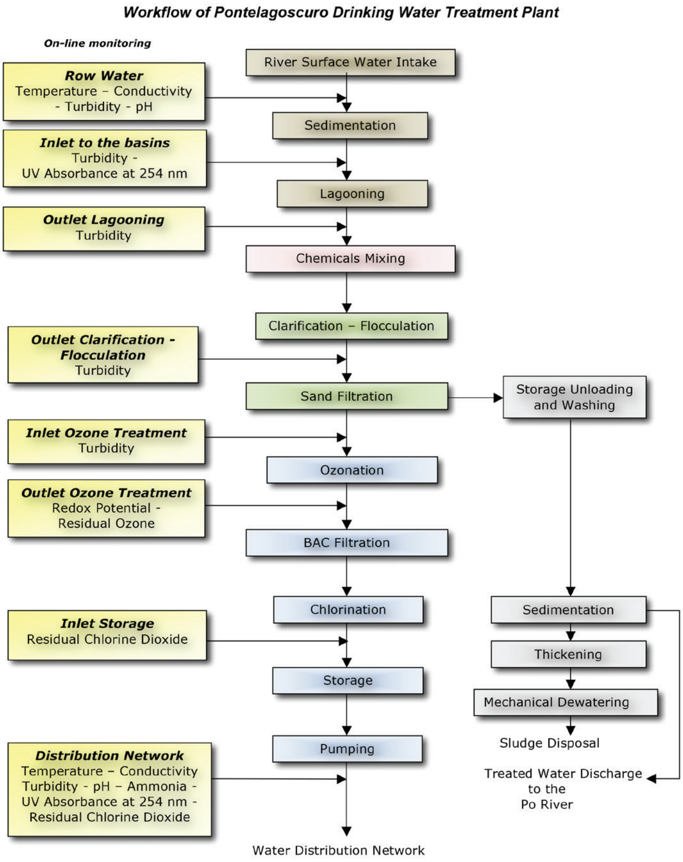


Figure 3.15 Workflow of the Pontelagoscuro Drinking Water Treatment Plant.

The abstracted water undergoes the following treatment process:

- Waters abstracted from the Po River, characterized by higher rates of suspended solids, first undergo the sedimentation and are then sent to the lagooning basins, which have multiple functions including accumulation of water (acting as a "buffer deposit" during situations where Po River water cannot be abstracted – e.g. during important floods), self-purification and self-decantation.
- Then a pre-oxidation phase with potassium permanganate ($KMnO_4$) takes place, followed by clariflocculation (CFS) in an accelerator basin and sand filtration. Finally, it's the turn of the ozonation section (O3) where the oxidation and disinfection of the water takes place.
- Waters abstracted from the floodplain wells benefit from the effects of bank filtration, which clears waters from suspended solids, but makes it richer in reduced metals. An aeration phase with oxygen is, therefore, necessary for the oxidation of the reduced metals and subsequent sedimentation followed by filtration on pyrolusite for the removal of precipitates and any suspended solids.
- Waters treated as described undergo the final phase of adsorption on Granular Activated Carbons (GAC), which operate as biologically activated carbons (BAC, Biological Activated Carbon). Groundwaters are mainly treated in GAC lines 1 and 2, while the Po River waters are mainly treated in GAC lines 3 and 4. The treatment chain ends with disinfection with chlorine dioxide (ClO2) and storage, before the introduction of potable water into the distribution network.

3.7. Neufahrn bei Freising, Germany

Neufahrn bei Freising is a municipality located in the southern part of the district of Freising (Landkreis Freising) which belongs to the administrative district of Upper Bavaria. The community is situated on the west side of the Isar River, on the border between the Munich gravel plain and the tertiary Danube-Isar hilly country, approximately 10 km south from Freising. The Isar River is the most important surface water body in the pilot area. The community of Neufahrn bei Freising covers an area of 45.51 km² and has a population of approximately 21,662 inhabitants (Gemeinde Neufahrn bei Freising, 1 July 2020).

Approximately 15 % of the municipality's land area is covered by settlements and roads, whereas the remaining part is almost entirely agricultural land. Forest areas are almost absent in the district. In terms of hydrogeology, the important lithostratigraphic units are related to the Quaternary and the Tertiary ages, as they host aquifers which are important for the regional water supply. The Quaternary sediments, glaciofluvial (terrace) deposits from the Pleistocene Age, are mostly composed of gravel and sands. On the other hand, the Tertiary sediments host the lower aquifer of the pilot area, which mostly consists of silt, sand, and gravel from fresh depositional conditions during the Neogene. Those sediments are mostly cemented but still are very permeable and primarily considered to behave like a porous aquifer. Figure 3.16 shows the Neufahrn bei Freising pilot site.

Figure 3.16 Neufahrn bei Freising pilot area. The location of the wastewater treatments plants (Garching, Gut Marienhof, and Grüneck), sampling points, and well field are indicated in the map. Adapted from Google Earth https://www.google.com/intl/it/earth/.

The only anthropogenic infrastructures which are located close to the Isar River are the wastewater treatment plants Garching, Gut Marienhof and Grüneck (Fig. 3.16). Gut Marienhof is the largest wastewater treatment plant in the area, and it handles a substantial part of Munich's wastewater (inflow: 4 - 6 m^3/s). These treatment plants discharge the treated water into the Isar River. By ground- and surface water interaction, substances that have not been removed in the treatment process may enter the shallow groundwater.

The well field in Neufahrn comprises 3 shallow wells and 6 deep wells (Fig. 3.16), whereof only the deep wells are used for the local drinking water supply to ensure high-quality water. The deep wells are screened at about 30 m to 80 m of depth (lower aquifer). On the contrary, the shallow wells are used to provide process water to the Garching research centre (e.g., for cooling purposes).

In the study area of Neufahrn bei Freising, the most likely sources of PPCPs result from agricultural practices, leaking sewer systems in the settlements, discharge of the previously mentioned wastewater treatment plants, and surface water – groundwater interaction.

3.8. Ljubljana Basin, Slovenia

The Ljubljana Basin (Fig. 3.17), with an area of 815 km^2, is located in the upper Sava Basin and is the largest Quaternary basin in Slovenia. The altitude of the basin is between 250 m and 730 m. With its central location, the basin represents the most important settlement, economic, and traffic area in Slovenia, where the main roads and railway connections converge. The Ljubljana Basin includes 31 municipalities and a total of 40 % of the Slovenian population lives there. The largest cities in the basin are Ljubljana (the capital and the largest city in the Republic of Slovenia), Kranj, Kamnik, Domžale, Škofja Loka, Bled and Vrhnika.

Figure 3.17 Ljubljansko barje – the southern part of the Ljubljana Basin.

According to the Water Framework Directive requirements, the pilot area is located in the same area as the groundwater body Savska kotlina – Ljubljansko barje (SIVTPODV1001 – Sava Basin and Ljubljana Marsh). Several aquifers, predominantly intergranualr, are defined within the groundwater body.

The groundwater body is located within the tectonic depression with predominantly fluvial-glacial sediments of the Sava River. These deposits consist of Quaternary gravelly-sandy sediments, a significant percentage of which are represented as conglomerates. Groundwater bodies and surface waters are interconnected at several locations. In the northern and central parts, the Quaternary intergranular aquifer predominates, consisting of sandy gravel deposits from the Sava River and its surface tributaries. The aquifer is extensive with medium to high yield. The second main aquifer is located in Mesozoic carbonate rocks as a karst-fissured aquifer. It is mainly located at the margins of the aquifer and in some parts extends below the Quaternary aquifer. It is extensive but locally confined by faults and other hydrogeological barriers. As a result, its yield varies from low to high.

The Ljubljansko polje is the most important unconfined intergranular aquifer in the basin and a source of drinking water for about 330.000 inhabitants of Ljubljana - the capital of Slovenia and its surroundings. The phreatic groundwater recharges from precipitation, from infiltration of the Sava River, and via groundwater inflow from the multi-aquifer system Ljubljansko barje from the south. The Sava River with its characteristics of an alpine river flows on the northern edge of Ljubljansko polje.

The length of all watercourses in the Ljubljana Basin is 5 106 km and the density is 6.27 km/km^2. The highest density is found in the southern part of the basin (4.58 km/km^2), while the density is lower in the central and northern parts. The central and longest watercourse in the pilot action area is represented by the Sava River, which has its headwaters in the Ljubljana Basin and measures 80 km. The discharge characteristics of the Sava River in the upper part (north of Radovljica) of the pilot area indicate an alpine nival-pluvial regime. Therefore, the highest discharges occur in spring due to snowmelt and rain, and in autumn due to heavy precipitation. In the Ljubljana Basin, the flow regime of the Sava River and its tributaries changes to an alpine pluvial-nival regime and remains the same for the rest of the flow in Slovenia. Mean discharge is 40 m^3/s in the upstream part of the pilot area (Radovljica gauging station), and 85 m^3/s in the downstream part. Long-term trends in mean discharge from the Sava River show a slight decrease. The Sava River is a very important hydrodynamic element of the surrounding aquifers, as it substantially recharges some of them, such as in the case of Ljubljansko polje.

Intense development is underway in the Ljubljana Basin; from agriculture, industry and the introduction of new technologies to intensive tourist activities that are growing steadily year by year. At the same time, this area is becoming increasingly urbanized. All of these activities are increasing pressure on the environment, including greater pressures on water resources. The intensive development has led to an increasing number of emerging contaminants that affect the environment as a whole and the water resources.

The largest share of more than a half (55 %) of the total area of Ljubljana Basin is occupied by agricultural land. They are followed by forest and semi-natural land and artificial surfaces, with each class occupying one-fifth of the pilot area. In the central and northern parts of the Ljubljana Basin, agricultural land is intertwined with forest and semi-natural land, as well as artificial surfaces. The predominant land use in Ljubljansko polje is of agricultural and artificial character. In the southern part of Ljubljana Basin, on Ljubljansko barje, agricultural land is predominant, with some interspersed areas of forest and semi-natural and artificial land.

Although sewage, wastewater treatment plants, and landfills are an integral part of infrastructure that reduces human impact on the environment, they improve safety and quality of life, reduce the risk to residents' health, but they can also be a source of groundwater pollution. The Sava River is the main recipient of treated wastewater in the entire Ljubljana basin. On its way through the pilot area, the river interacts with groundwater. In some parts, it recharges the aquifers, and in other parts it drains them. It is estimated that in the Ljubljansko polje area, the Sava River is the third potential source of groundwater pollution.

In the Ljubljana Basin, there are 46 wastewater treatment plants, 6 landfills, and 456 points representing emissions to water bodies from industrial facilities. The latter is a potential source of pollution due to the contributing activity sectors: healthcare, pharmacy, production of engines, ceramics, perfumes, tourism, laundries, etc. Upstream of Ljubljana, there are several smaller cities with infrastructure that may affect groundwater quality and at the same time cause the potential occurrence of PPCPs. The sewerage system is mainly distributed around the urban centres. Other potential sources of groundwater pollution with PPCPs are cesspits, slurry pits, areas with no sewer system, and areas with livestock farms. There is 2 361 km of sewerage network in the entire Ljubljana Basin with the density of 2.90 km/km^2. The central sewage system in Ljubljana, the largest in Slovenia, covers the urbanized area and ends in the Central wastewater treatment plant Ljubljana with the capacity of 360.000 PE. The central wastewater treatment plant in Ljubljana treats 85 % of all wastewater from Ljubljana and its surroundings, which significantly reduces the pollution of the Ljubljanica and Sava Rivers.

4. MONITORING OF EMERGING CONTAMINANTS (PPCPS) IN THE WATER ENVIRONMENT OF THE CE REGION

4.1. Sampling Procedure and Analytical Methods

A total of 66 sites were monitored at 8 boDEREC-CE pilot sites over the period of two years. Sampling was performed mainly in quarterly intervals. All monitoring operators respected a strict sampling procedure and logistics for sample delivery to the laboratory. To ensure the comparability of results, all samples were analysed in the same laboratory – Povodí Vltavy in Plzeň. The laboratory used the following analysis procedures:

Samples were taken in 60 ml amber glass vials (only half-filled). The samples were stored in a freezer (in an inclined position). On the day of the analysis, samples were defrosted at maximally 30°C and analysis procedure immediately followed.

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 (Eppendorf 5804, Eppendorf, Germany). Subsequently 1.50 g of each sample were weighed in a 2 mL vial using an analytical balance Denver TB-215D (Denver Instrument GmbH, Germany). Then 1.5 µL of 100 % acetic acid certified for LC-MS (Honeywell) 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 0-100 % methanol certified for LC-MS (Merck) and 0-100 % ultrapure water (Merck-Millipore) with 0.02 % acetic acid and 0.5 mM ammonium fluoride certified for LC-MS (Merck) as the mobile phase additives. The flow rate was 0.5 mL/min. The injection volume was 0.050 mL.

For the estrogen group analysis, 10 mL of sample were taken into headspace vials of 20 mL volume. Then was added deuterated internal standards, and the sample in closed vial was centrifuged in headspace vials for 10 min at about 3500 rpm (Eppendorf 5804, Eppendorf, Germany). After this step, part of the sample was transferred in a 2 mL vial.

Estrogens 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 2.1 mm, 2.5 µm particle size). The mobile phase consisted of 0-100 % methanol certified for LC-MS (Merck) and 0-100 % ultrapure water (Merck-Millipore) with 0.5 mM ammonium fluoride certified for LC-MS (Merck) as the mobile phase additives. The flow rate was 0.3 mL/min. The injection volume was 0.100 mL.

The range of analysis and detection limit for each analyte is shown in the table 4.7. 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).

The samples taken in 2019 and 2020 were analysed for the presence of 102 PPCPs in total. In 2021, the laboratory included additional 7 substances, making the final list of 109 PPCPs in total. Partners could choose if they want to analyse also 7 hormones and 6 antibiotics.

The following chapters will characterize the specific behaviour of PPCPs in individual pilot sites.

4.2. Monitoring Results

4.2.1. Káraný-Jizera River, Czech Republic

The section of the Jizera River around the Sojovice weir plays the key role in the Káraný waterworks, which uses artificial recharge for the production of drinking water. The water is treated with 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 (Fig. 4.1). A varied mixture of 40 PPCPs, whose average concentration in four cases exceeds 200 ng/l, is infiltrated at the waterworks in Kárаný.

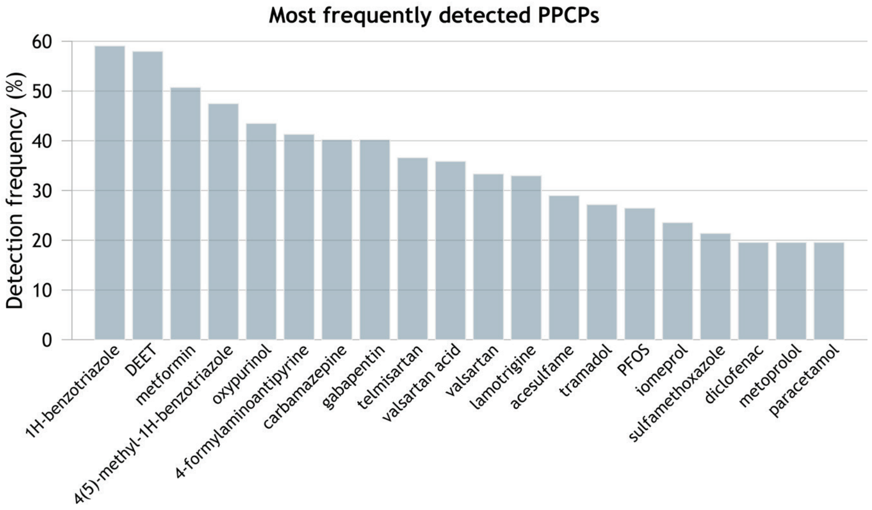


Figure 4.1 Concentrations of PPCPs in Jizera water in Sojovice weir (average taken from 37 samples from 2017 to 2021).

The results of technology simulating the natural attenuation process indicate how artificial recharge and bank infiltration clearly demonstrate the efficacy of PPCPs removal in both waterworks. A total of 35 substances were detected in the Jizera River and the majority of them fell below detection limits after the treatment. At

Káraný, 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 efficiently removed by artificial recharge and bank infiltration in Káraný, there are Sucralose, Metformin, Telmisartan, Caffeine, Saccharin, Paraxanthine, and Iomeprol.

Only eight substances occur systematically in the groundwater tapped from the system of large-diameter wells in the vicinity of the infiltration ponds in Káraný waterwork. 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 4.1). They were evidently associated with the WWTP in Mladá Boleslav.

Table 4.1 Detected PPCPs in the output from artificial recharge in Káraný (x means value under the detection limit, and empty cell means that this substance had not yet been analysed at the time of sampling).

Year		**2017**											
Month		1	2	3	4	5	6	7	8	9	10	11	12
Carbamazepine	ng/L	16	16	18	13	13	12	19	21	16	13	16	12
Sulfamethoxazole	ng/L	40	41	43	40	33	31	34	34	33	30	24	25
Acesulfame	ng/L											120	80
Oxypurinol	ng/L												
Lamotrigine	ng/L												
Primidone	ng/L												
Gabapentin	ng/L	x	x	18	27	13	11	x	x	x	x	x	x
Ibuprofen	ng/L	32	x	x	21	x	x	x	x	x	x	x	x
1H-benzotriazole	ng/L												
Paracetamol	ng/L	x	x	x	x	x	x	x	x	x	x	x	x
Methylparaben	ng/L												
Propylparaben	ng/L												
PFOS	ng/L												
Diclofenac	ng/L	x	x	x	x	x	x	x	x	x	x	x	x

Table 4.1 Detected PPCPs in the output from artificial recharge in Káraný (x means value under the detection limit, and empty cell means that this substance had not yet been analysed at the time of sampling).

Year		2018												2020		2021
Month		1	2	3	4	5	6	7	8	9	10	11	12	8	9	5
Carbamazepine	ng/L	14	x	x	x	x	11	14	19	x	25	24	22	10	17	11
Sulfamethoxazole	ng/L	24	22	24	27	52	39	14	37	x	x	41	41	25	x	5
Acesulfame	ng/L	x	96	85	110	x	x	41	127	x	x	149	126	x	79	138
Oxypurinol	ng/L	97	130	96	120	113	79	76	108	x	x	x	x	155	244	82
Lamotrigine	ng/L					x	x	19	22	x	x	34	31	24	35	21
Primidone	ng/L							X	13	x	x	14	14	11	15	
Gabapentin	ng/L	x	x	x	x	13	x	X	x	x	x	x	x	x	x	x
Ibuprofen	ng/L	x	x	x	x	x	x	X	10	x	x	20	x	x	x	x
1H-benzotriazole	ng/L													x	880	212
Paracetamol	ng/L	x	x	x	x	x	x	X	x	x	x	11	x	x	x	x
Methylparaben	ng/L													327	x	x
Propylparaben	ng/L													462	x	x
PFOS	ng/L													x	x	x
Diclofenac	ng/L	x	x	x	x	x	x	X	x	x	x	x	x	x	x	x

Bank infiltration in the case of Káraný vodárny seems to be more effective in removing PPCPs. Only one substance, Acesulfame, appears in the produced water in higher frequency and lower concentrations compared to artificial recharge (Table 4.2). 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.

Table 4.2 a) Detected PPCPs in the output from bank infiltration in Káraný (x means value under the detection limit, and empty cell means that this substance had not yet been analysed at the time of sampling).

Year		2017											
Month		1	2	3	4	5	6	7	8	9	10	11	12
Carbamazepine	ng/L	x	x	x	x	x	x	x	x	x	x	x	12
Sulfamethoxazole	ng/L	x	x	x	x	x	x	x	x	x	x	x	25
Acesulfame	ng/L										57	64	80
Oxypurinol	ng/L												
Lamotrigine	ng/L												
Primidone	ng/L												
Ibuprofen	ng/L	54	x	x	x	x	x	x	31	x	x	x	x
Gabapentin	ng/L	x	x	x	x	x	11	x	x	x	x	x	x
1H-benzotriazole	ng/L												
Paracetamol	ng/L	x	x	x	x	x	10	16	x	x	x	x	x
Methylparaben	ng/L												
Propylparaben	ng/L												
Estrone	ng/L												
Caffeine	ng/L	x	x	x	x	x	x	x	140	x	x	230	x
Paraxanthine	ng/L												
PFOS	ng/L												
Diclofenac	ng/L	x	x	x	x	x	31	x	x	x	x	x	

Carbamazepine and Sulfamethoxazole are probably some of the most problematic substances in drinking water. The same problems with their occurrence in drinking water are documented in France (Vulliet et al. 2011), the 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 in Canada (Kleywegt et al., 2011). The high levels of Carbamazepine could be explained by its high persistency.

Table 4.2 b) Detected PPCPs in the output from bank infiltration in Káraný (x means value under the detection limit, and empty cell means that this substance had not yet been analysed at the time of sampling).

Year		2018												2020		2021
Month		1	2	3	4	5	6	7	8	9	10	11	12	9	10	5
Carbamazepine	ng/L	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x
Sulfamethoxazole	ng/L	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x
Acesulfame	ng/L	x	x	x	x	x	58	x	60	58	x	x	71	57	142	x
Oxypurinol	ng/L	72	x	x	x	x	x	x	51	61	x	x	x	x	x	142
Lamotrigine	ng/L							x	x	x						
Primidone	ng/L							x	x	11						
Ibuprofen	ng/L	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x
Gabapentin	ng/L	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x
1H-benzotriazole	ng/L														x	x
Paracetamol	ng/L	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x
Methylparaben	ng/L															x
Propylparaben	ng/L															x
Estrone	ng/L							2	2	5	x	x	x	x	x	x
Caffeine	ng/L	x	x	x	x	x	x	x	x	148	x	x	x	x	x	267
Paraxanthine	ng/L															139
PFOS	ng/L															6
Diclofenac	ng/L	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x

4.2.2. Dresden-Hosterwitz, Germany

The pilot site was monitored seasonally from 2019 to 2021 at eleven sampling points in order to observe the removal efficiency of PPCPs through riverbank filtration. Since December 2020, additional points have been sampled. However, regular monitoring was not possible. Therefore, the dataset is not sufficient to analyse their behaviour and, thus, solely data of the five original sampling points is discussed in this chapter. All sampling was done from a continuously operated sampling tap. A sampling at the Elbe River was aimed at obtaining the information on the quality of surface water, which is used for the production of drinking water by RBF and MAR. The second sampling point was the Infiltrate, and the aim was to get information on pre-treated surface water quality. Mittelbrunnentrasse was sampled to get information on managed aquifer recharged (MAR) water quality. This is a mixed sample of about 36 wells. The fourth sampling point was collecting Well Niederpoyritz, which was sampled to get information on bank filtrate quality of 111 siphon wells. The fifth sampling point was drinking water after disinfection. The objective was to obtain information on drinking water quality before entering the distribution network. Final disinfection was conducted using chlorine. Furthermore, additional points along an RBF cross-section have been sampled since December 2020, but not on a regular basis. The main objective of sampling the cross-section was to study the PPCPs transport. This cross-section consists of seven monitoring well bundles between the river and the abstraction well and three monitoring wells at greater distance behind the abstraction well to monitor land-side groundwater. The available monitoring wells have short filter screens to allow depth-dependent sampling of bank filtrate or groundwater between the river and the production well. All samples were taken according to the internal project sampling instructions and delivered to the Vltava River Basin Authority laboratory in a frozen state.

From the field dataset, it remains unclear whether the attenuation of those substances is based on degradation, dilution, or metabolization. 45 substances were found in the Elbe River above the limit of quantification in comparison to 20 substances in bank filtrate samples (Fig. 4.2 and Fig. 4.3).

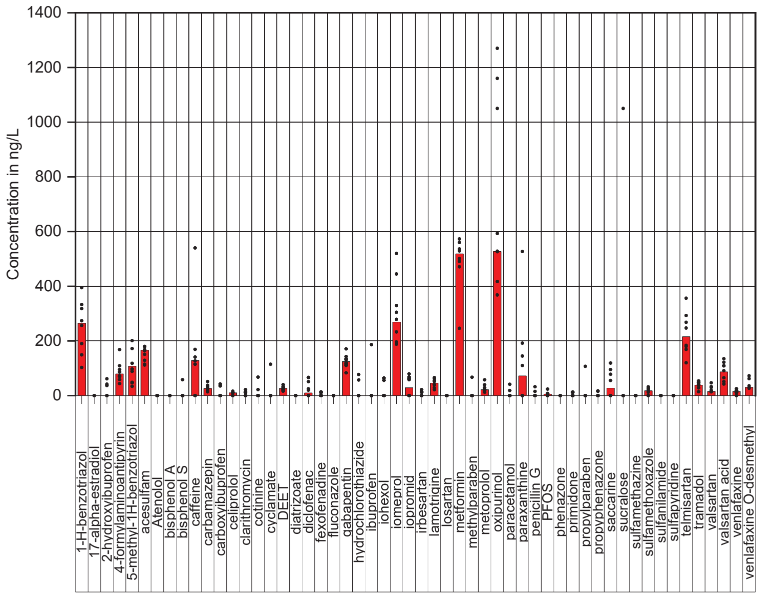


Figure 4.2 Concentrations of PPCPs in the Elbe River in the waterworks. Spheres indicating results of single samples (n=8), bars indicating the median concentration of single samples.

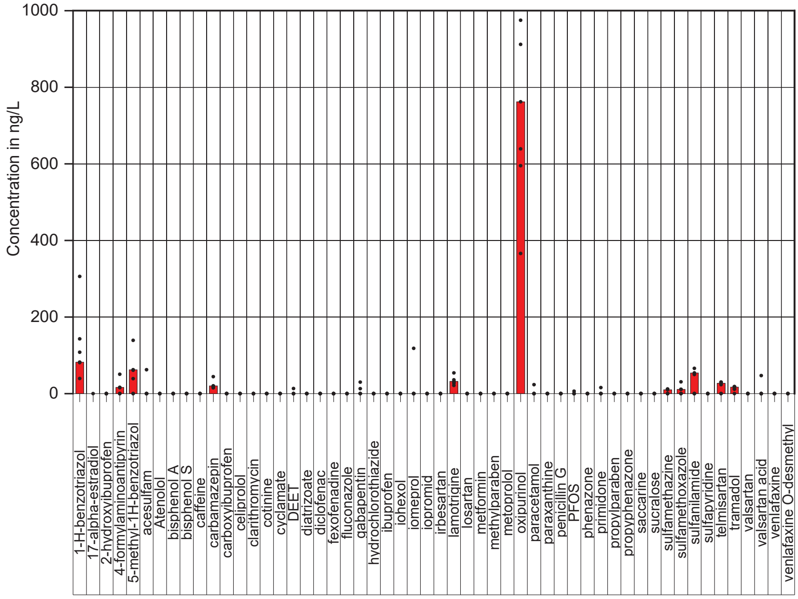


Figure 4.3 Concentrations of PPCPs in bank filtrate (Niederpoyritz). Spheres indicating results of single samples (n=7), bars indicating the median concentration of single samples.

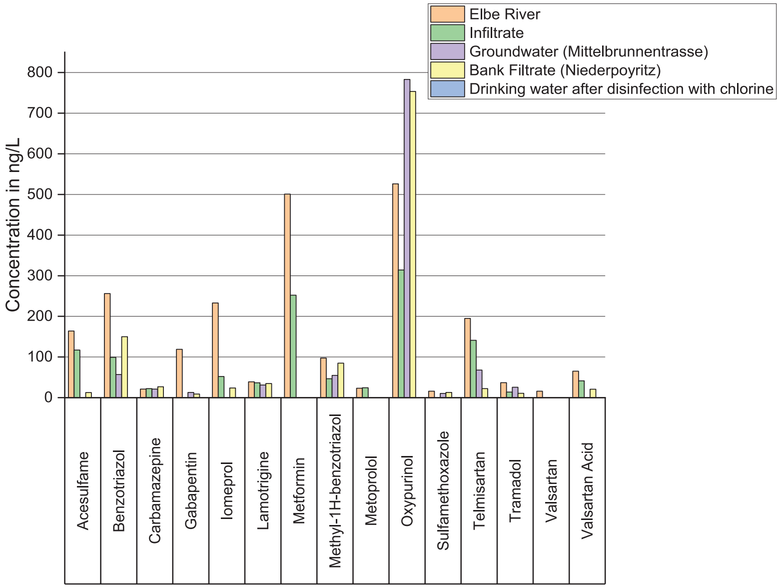


Figure 4.4 Median concentrations of most frequently found PPCPs in Dresden-Hosterwitz waterworks.

15 substances in total were found on a regular basis at lower concentrations than surface water (Fig. 4.4). In the case of oxypurinol, median concentrations in bank filtrate and MAR wells were 235 and 256 ng/L higher. In drinking water, median concentrations of these substances were 0 ng/L, indicating that GAC is efficient in removing the remaining PPCPs from raw water.

The efficiencies of removing those substances from surface water at all sampling points are shown in Figure 4.5. In the case of metoprolol, and oxypurinol, negative removal efficiencies were obtained. Metoprolol is known to be persistent in the environment. In the case of oxypurinol, which is recently reported in environmental studies, further monitoring is recommended in order to investigate its occurrence in more detail. Removal efficiencies of up to 100 % (e.g. metformin) were obtained for other substances, indicating they are attenuated or even degraded in the soil passage. Similar results were obtained at the cross-section. In groundwater samples at the cross-section however no significant PPCP contamination was found. The only two substances found in the samples were diatrizoate, a water-soluble, iodinated x-ray contrast agent and paracetamol, a common acetaminophen.

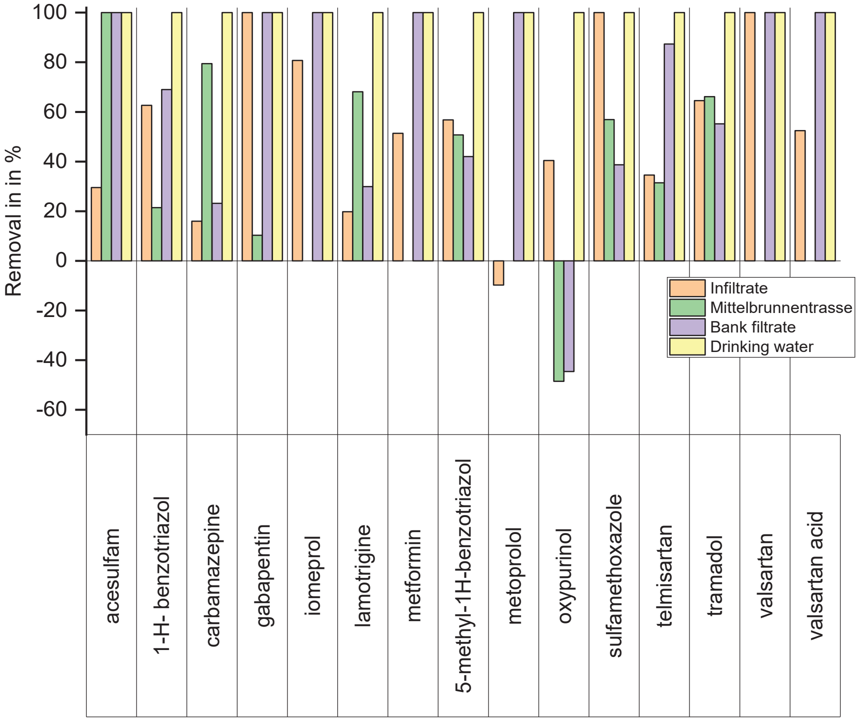


Figure 4.5 Removal efficiencies of most frequently found PPCPs in Dresden-Hosterwitz waterworks.

4.2.3. Jadro and Žrnovnica Springs Catchment, Croatia

Before the boDEREC-CE project, there were no studies on the occurrence of PPCPs in the karst aquifer of Jadro and Žrnovnica springs. All samples were taken according to the internal project sampling instructions and delivered to the Povodí Vltavy laboratory in a frozen state. 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 the Town of Trilj was also sampled.

Five sampling campaigns in total were conducted from October 2019 to November 2020. Unfortunately, monitoring was not possible on a regular basis. Thus, this dataset is insufficient to deliver some strong conclusions regarding PPCPs behaviour in the karst aquifer. For a more detailed statistical analysis and understating the PPCPs fate in such complex medium as the karst aquifer, additional monitoring campaigns are needed.

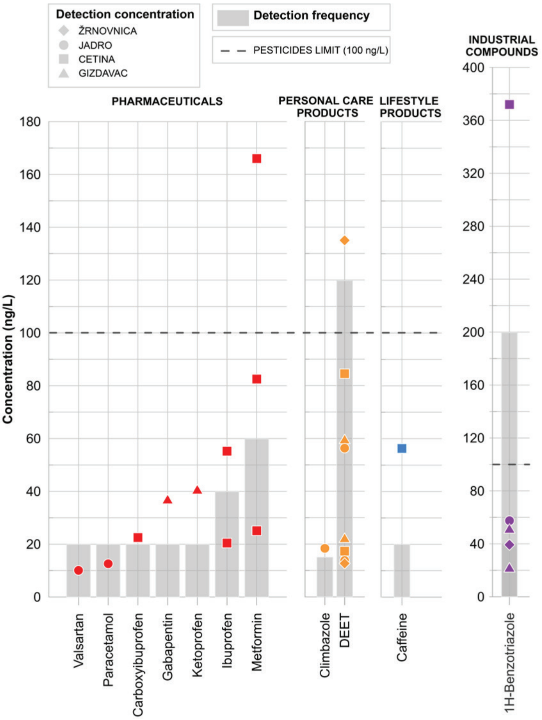


Figure 4.6 PPCPs detected in Jadro and Žrnovnica springs catchment (per main group, sampling location)

The results of five sampling campaigns indicate the presence of 11 different PPCP substances ranging from 10 ng/L for valsartan in Jadro spring to 372 ng/L for 1H-benzotriazole in the Cetina River (Fig. 4.6). 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 drug 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 the 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.

Three compounds, namely metformin, DEET, and 1H-benzotriazole were found in concentrations above the current EU pesticides limit of 100 ng/L (Fig. 4.6).

When comparing karst springs from Croatian and Austrian pilot areas, it is evident that several PPCP substances occur in both karst aquifers: DEET, valsartan, caffeine, and 1H-benzotriazole.

4.2.4. Waidhofen a/d Ybbs, Austria

The pilot action, the 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 were selected as follows: along the Glashüttenbach to observe any potential influence from the quarries situated uphill (indicated as GBD in the following graphs); along the Waidhofenbach, upstream (indicated as WBU in the following graphs) and downstream (indicated as WBD in the following graphs) of the intersection with the Glashüttenbach; and directly in the Kerschbaum spring, to observe any interaction between the Waidhofenbach and the spring through river bank infiltration (indicated as KQ in the following graphs) (see also Figure 3.9, Chapter “3.4 Waidhofen a/d Ybbs, Austria”). 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 (indicated as GBU in the following graphs). This was decided in order to understand and monitor any possible contamination source present along the mentioned creek.

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 the discussion. For this reason, and due to limited sampling campaign, only a relative guess/assumption can be made. For a more robust statistical evaluation, more monitoring campaigns and analyses should be performed.

34 in total were detected (> limit of quantification) at least once over the 8 sampling campaigns and at least at 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.

Overall, the most occurring substances in the sampling campaigns and at all sampling points are DEET (41 %), progesterone (25 %), methylparaben (22 %), simvastatin (19 %), caffeine (16 %), testosterone (16 %), and lovastatin (13 %) (Fig. 4.10). Bisphenol S, fluoxetine, paraxanthine, and PFOS were detected overall with the occurrence of 9 %. The rest of the substances were detected once or twice, overall.

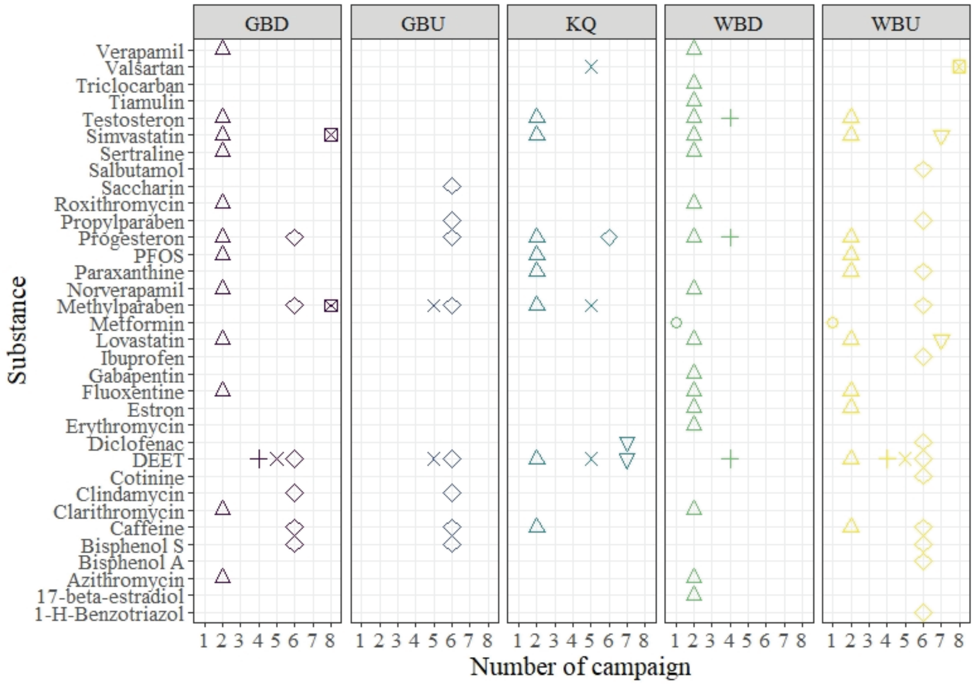


Figure 4.7 Number of detection (measured value > limit of quantification) for each substance, per sampling point (GBD, GBU, KQ, WBD, WBU) and per sampling campaign (1-8). GBU Glasshüttenbach upstream (creek), GBD Glasshüttenbach downstream (creek), KQ Kerschbaumquelle (spring), WBU Waidhofenbach upstream (creek), WBD Waidhofenbach downstream (creek).

The left side of the graph in Figure 4.8 shows 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 that the majority of the 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.

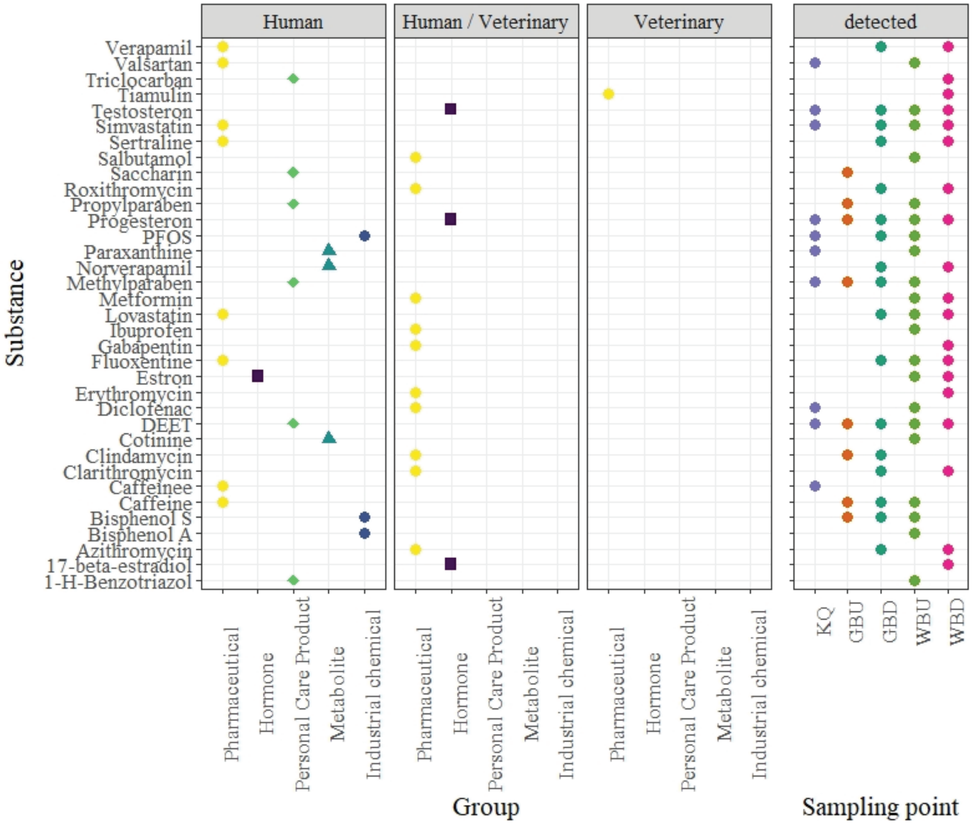


Figure 4.8 Point graph representing the detected substances (> limit of quantification) according to the use group (on the x-axis of the left side of the graph: "Pharmaceutical", "Hormone", "Personal care products", "Metabolite" and "Industrial chemical"), according to the origin group (in the faceting of the left side of the graph; "Human", "Human/ Veterinary", or "Veterinary"), and according to the sampling point ("KQ, "GBU", "GBD", "WBU", "WBD").

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 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, 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; Fig. 4.11). 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. These are represented only by the annotations in Figure 4.13, 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 points in the boxplots in the Figure 4.11. The measurement detected below the detection limit was considered in the calculation of the median and, therefore, also in the boxplot as half of the limit of quantification value. In many cases, the substance was detected above detection limit 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 of the limit of quantification. Furthermore, the concentrations values of the substances detected more than once were often 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 Chapter 5.

Overall, the low occurrences and the low measured value make us think that the contaminants are almost absent in the aquifer. Those sporadic detections might be related to point pollutions from small wastewater treatment plants (PE between 4 and 20), which may be confirmed by the fact that the majority of the detected substances are of human origin (Fig. 4.9). Furthermore, the contamination of the sample cannot be ruled out. However, a few monitoring campaigns and analysis (n=8, and n=4 for GBU and WBD) do not allow a proper and robust statistical evaluation. Therefore, more frequent monitoring might be needed to come to stronger conclusions.

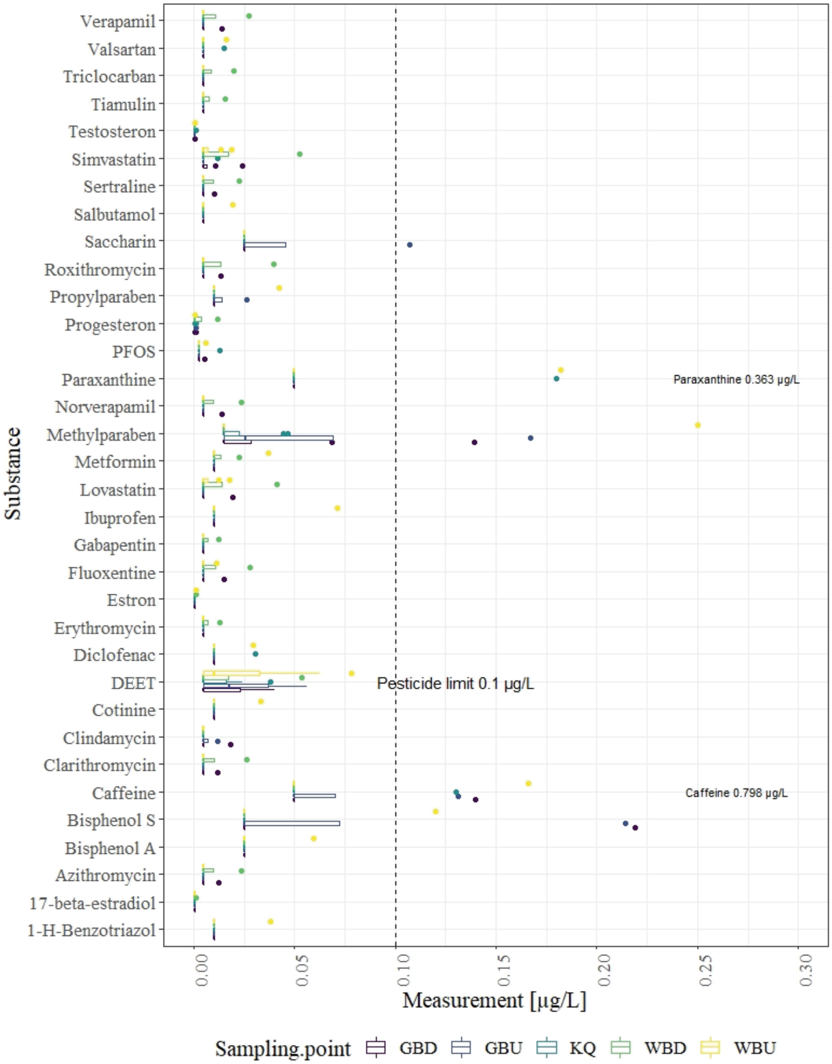


Figure 4.9 Boxplot of measured values for 34 substances over the eight (or four for GBU and WBD) sampling campaigns, for each sampling point (shown with different colour, as described in the legend). The dashed line represents the pesticide limit value for surface waters in Austria. The two annotations 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.

4.2.5. Kozłowa Góra, Poland

Before the boDEREC-CE project, there were no studies on the occurrence of PPCPs in the Brynica River catchment above the Kozłowa Góra dam. Thus, data gathered under this project is the only source of information on the presence of pharmaceutical residues and other emerging contaminants within the Polish pilot site.

Water sampling for the monitoring of PPCPs within the Kozłowa Góra pilot action area has been conducted every 3 months, starting in July 2020. Initially, both surface water and groundwater were monitored in 8 locations located within the catchment (6 samples were taken from the Brynica River, along its watercourse and its main tributary - the Ożarowicki Potok, and 2 samples were taken from wells). Furthermore, 6 other samples were taken at the Kozłowa Góra WTP after each stage of the water treatment process.

At the early stage of monitoring, the results indicated the occurrence of several PPCPs in surface water and, to a lesser extent, in groundwater (mainly DEET). The contamination of groundwater with DEET is a problem widely discussed in the literature. Kotowska et al., 2019, Lapworth et al., 2012, and Manamsa et al., 2016 indicate that this insect repellent is one of the most frequently detected emerging contaminants in groundwater. Nevertheless, other common PPCPs were detected in groundwater such as Caffeine, Saccharine, Cotinine, Paraxanthine, Ethylparaben, and Methylparaben. However, these compounds were observed only during the first sampling campaign, which indicates a temporary and local contamination source present at that time. After taking all initial findings into account and after performing preliminary modelling, the locations of some monitoring points were adjusted. Since then, only surface water has been analysed – a left-bank tributary of the Brynica was added as well as Potok spod Nakła, (in the western part of the PA) which flows directly into the reservoir.

Generally, the results for the Brynica River upstream of the Wastewater Treatment Plant (R1-R2) revealed the presence of several PPCPs (e.g., DEET, Valsartan, and Carbamazepine), but the average concentration of each substance did not exceed 100 ng/L. Both the number of substances and the concentrations were higher in the river below the WWTP (Table 4.3). Starting from R3, other contaminants occurred, e.g., Oxypurinol, Iopromide, and Diclofenac. The highest average concentration reached 865 ng/L for Sucralose in R3, i.e. just below the WWPT. At this point, the highest number of PPCPs was detected (40 compounds). However, average concentrations did not exceed 100 ng/L for most substances. The amount of PPCPs decreased along the watercourse. However, they were still present close to the Brynica's mouth (R6). At this point, 33 substances were detected, but average concentrations exceeded 100 ng/L only for four PPCPs. The highest average concentrations and median values (382 ng/L and 399 ng/L, respectively) were observed for Oxypurinol, i.e. one of the PPCPs selected for modelling studies in the Polish pilot action area. Other modelled substances (Acesulfame, Carbamazepine, DEET, and PFOS) occurred in smaller quantities (Fig. 4.10).

Table 4.3 PPCPs detected in surface water samples within the Kozłowa Góra pilot action area (July 2020 – April 2021). Substances in the table are listed from the largest to the smallest quantities.

Sampling point	No. of all detected PPCPs	No. of PPCPs with average concentrations >100 ng/L	PPCPs with average concentrations >100 ng/L
R1	11	0	-
R2	7	0	-
R3	40	11	sucralose, oxypurinol, iopromide, valsartan acid, telmisartan, diclofenac, 4-formylaminoantipyrine, gabapentin, hydrochlorothiazide, furosemide, 1H-benzotriazole
R4	16	4	metformin, benzotriazole, acesulfame, paraxanthine
R5	31	6	oxypurinol, valsartan acid, 1H-benzotriazole, telmisartan, metfomin, iohexol
R5a	36	16	oxypurinol, iopromide, telmisartan, gabapentin, valsartan acid, diclofenac, 4-formylaminoantipyrine, furosemide, acesulfame, benzotriazole, azithromycine, hydrochlorothiazide, iohexol, fexofenadine, diclofenac-4-hydroxy, benzotriazol methyl
R6	33	4	oxypurinol, valsartan acid, 1H-benzotriazole, telmisartan
R7	1	0	-
R8	9	5	metformin, caffeine, saccharin, acesulfame, cyclamate

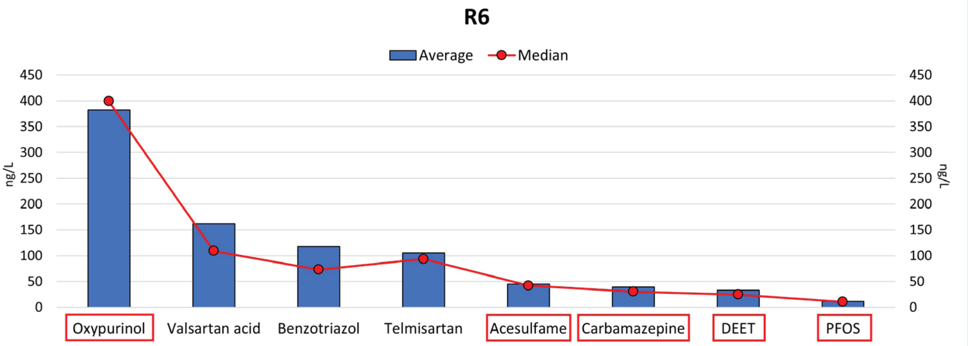


Figure 4.10 Average concentrations and median values of selected PPCPs in R6 (July 2020 – April 2021). Red frames refer to selected PPCPs for modelling tasks.

It is noteworthy that the Potok Ożarowicki (R4), the tributary of the Brynica River, provides additional quantities of some PPCPs (e.g., Metformin, Acesulfame, and PFOS) detected in the Brynica River. Nevertheless, the stream also increases the volumetric flow rate of the main river, facilitating the dilution of some other contaminants.

In April 2021, the ditch from the airport (R7) flowing into the Brynica River was sampled for the first time. As with groundwater analysed previously, except for DEET, no other contaminant was detected. This substance seems common in the water environment within the catchment, which probably results from the specific use of this substance. In the case of the Potok spod Nakła and flowing directly into the reservoir (R8), nine compounds were detected, among which Metformin was dominant. Therefore, PPCPs in raw drinking water may derive not only from the Brynica River but also from the other stream.

Some studies offer a possibility of comparing PPCP concentrations in the Kozłowa Góra pilot area with those observed in other regions of the world. It should be noted that different measurement procedures can be applied during the analyses. Also, a wide variety of data presentation methods are used in publications, with the mean, median or maximum concentrations reported. Furthermore, in some cases, only certain groups of PPCPs are investigated, e.g. pharmaceuticals or artificial sweeteners. In other cases, the data provided is ambiguous or only the number of detected substances is presented. As a result, comparison possibilities may be severely limited.

Moldovan et al. (2018) report the presence of micropollutants in the Prut River, a tributary of the Danube at the Romanian-Moldavian border. During two sampling campaigns, 57 substances were identified in the examined river. Fourteen of them were also detected in the Brynica River. The vast majority of these substances (11) are pharmaceuticals or their metabolites: four anticonvulsants also often used as medicaments for the treatment of mental illnesses (such as carbamazepine, gabapentin, or lamotrigine), three analgesics (diclofenac, phenazone, tramadol), one antibiotic (trimethoprim), one antiarrhythmic drug (sotalol), one medication for the treatment of diabetes (metformin), and one antifungal medicament (fluconazole). Furthermore, two common artificial sweeteners (acesulfame and cyclamate) are found in the Prut and the Brynica rivers. Also, an insect repellent – DEET – was detected in both rivers. The median concentration for most of these substances does not exceed 100 ng/L.

Datel and Hrabankova (2020) investigated pharmaceuticals in the Svihov drinking water reservoir in the Czech Republic between 2017 and 2018. Twenty substances were detected in raw water, 12 of them were also present in the Brynica – one artificial sweetener (acesulfame) and 11 pharmaceuticals: four anticonvulsants (carbamazepine, carbamazepine 2-hydroxy, gabapentin, lamotrigine), two analgesics (diclofenac and tramadol), two antihypertension drugs (telmisartan and hydrochlorothiazide), two antibiotics (trimethoprim, azithromycin) and oxypurinol – a metabolite of allopurinol (a medicament used in the treatment of hyperuricemia). Moreover, in both research areas, the highest maximum concentration was reported for oxypurinol – 2140 and 868 ng/L - for the Brynica River and Svihov reservoir, respectively.

4.2.6. Po River, Italy

The monitoring campaigns for the boDEREC-CE project were performed at the Hera drinking water treatment plant situated directly on the Po River at Pontelagoscuro, at the hydrographic closure of the Po Basin. They firstly allowed the evaluation of the pollution levels of raw water at the inlet of the treatment plant, providing an overview of PPCPs contamination over the entire Po basin, and then we focused on the treatment efficiency in PPCPs removal at the Pontelagoscuro drinking water treatment plant. Overall, 6 monitoring campaigns were held between September 2020 and July 2021.

During the monitoring campaigns, samples were collected at 8 different points of the plant (systematically in 6) where the analysis of the PPCPs had to be performed. In addition, during the campaigns, other water parameters were evaluated, using field probes and collecting samples to be analysed at the Arpae (PP 9) laboratory. Table 4.4 shows the parameters measured during the different sampling campaigns and the position of the sampling points along the treatment process, selected in the various campaigns.

Table 4.4 Measured parameters during the 6 campaigns, tool/methodology used, and position of monitoring points.

Measured parameters							
CAMPAIGNS	I	II	III	IV	V	VI	TOOL/METHODOLOGY
Turbidity	X	X				X	Field probe
Total dissolved solids (TDS)	X	X					Field probe
TOC	X	X	X	X	X	X	PP 9 Laboratory
UVA_{254}	X	X	X	X	X	X	PP 9 Laboratory
pH	X	X	X	X	X	X	PP 9 Laboratory
Redox	X	X					Field probe
Conductivity (20°C)	X	X	X	X	X	X	PP 9 Laboratory
Temperature	X	X	X	X	X	X	Field probe
Dissolved Oxygen	X	X					Field probe
104 PPCPs	X	X	X	X	X	X	boDEREC-CE project laboratory

7 hormones	X		X				boDEREC-CE project laboratory
5 antibiotics	X		X				boDEREC-CE project laboratory
POSITION OF MONITORING POINTS							
CAMPAIGNS	I	II	III	IV	V	VI	
Raw groundwater	X	X	X	X	X	X	
Raw Po surface water	X	X	X	X	X	X	
Post-lagooning	X	X	X	X	X	X	
Entry Ozonization		X	X	X	X	X	
Exit Ozonization						X	
Entry GAC (lines 3-4)	X	X	X	X	X	X	
Exit GAC (lines 3-4)	X	X	X	X	X	X	
Exit GAC (lines 1-2)	X						

Table 4.5 summarizes the average characteristics of the waters analysed in the 6 monitoring campaigns. In the Po River raw waters, a maximum number of 22 PPCPs were detected (concentration higher than the respective LOQ) compared to the 116 analysed (19 %), while in groundwater only 7 were detected (6 %). For this reason, the sampling points are mainly concentrated on the treatment chain of surface waters abstracted from the Po River.

Table 4.5 reports for every monitoring point on the percentage of detected PPCPs with respect to the total analysed substances and the average ± standard deviation of the measured parameters. The list of substances still detected at the outlet of the GAC filtration process in each monitoring campaign is reported in the last row - Iopamidol (IPM), metformin (MTF), caffeine (CAF), acesulfame (ACS).

Monitoring point	Detected PPCPs	UVA$_{254}$	TOC	pH	Conductivity (25°C)
	%	1/cm	mg/L	-	µs/cm
Raw Po river	10-19	0.04±0.017	2.0 ± 0.2	8.0 ± 0.83	405 ± 79.2
Raw floodplain wells	4-6	0.02±0.002	1.0 ± 0.04	7.7 ± 0.19	552 ± 80.0
Post-lagooning	10-16	0.05±0.019	2.1 ± 0.31	8.2 ± 0.40	381 ± 79.1
Entry Ozonation	10-14	0.03±0.021	1.2 ± 0.54	7.7 ± 0.50	399 ± 88.1
Entry GAC (lines 3-4)	2-4	0.02±0.008	1.2 ± 0.28	7.9 ± 0.30	436 ± 68.9
Exit GAC (lines 3-4)	2-3	0.01±0.007	0.9 ± 0.23	7.5 ± 0.50	415 ± 59.1
PPCPs after GAC	IPM (I, II, III, IV, V, VI); MTF (I, II, III, IV, V, VI); CAF (II); ACS (III, V, VI), DEET (V)				

Observing the percentage of PPCPs in the sampling points, it is noted that, proceeding along the process chain, there is a decrease in the number of compounds detected; the same happens for the average values of the parameters UVA254 and TOC, while the pH and conductivity values remain practically constant.

Figure 4.11 shows the PPCPs detected during the 6 campaigns, and the relative concentrations, in the two raw waters. The raw water of the Po River is characterized by a wide variety of PPCPs. The substances at higher concentrations (> 100 ng/L) are iopamidol, metformin, oxypurinol, iomeprol, acesulfame, 1H-benzotriazole, iopromide, but also caffeine and paraxanthine which are identified only in one campaign, due to the high LOQ value adopted. The substance with the highest concentration both in the Po surface water and in groundwater is IPM, which is a radiological contrast agent. In the Po River, but not in groundwater, three other PPCPs of the same type (iomeprol, iopromide, and iohexol) were also found. Other PPCPs found in the Po River are:

- five antihypertensives (irbesartan, sotalol, telmisartan, valsartan, and valsartan acid),
- four antiepileptics (carbamazepine, hydroxycarbamazepine, gabapentin, lamotrigine,
- two stimulants (caffeine and paraxanthine),
- two UV filters (1H-benzotriazole and methyl-benzotriazole),
- two artificial sweeteners (acesulfame and saccharin),
- diabetes drug (metformin),
- an enzyme inhibitor (oxypurinol),
- a pain reliever (paracetamol),
- an anti-inflammatory (ibuprofen),
- a bronchodilator (salbutamol),
- an antibiotic (lincomycin),
- an antidepressant (venlafaxine),
- an antihistamine (fexofenadine),
- and an insect repellent (DEET).

The concentrations of various PPCPs in the water of the Po River vary from approximately from 10 to 1,800 ng/L: this contamination is greater, in terms of the number of PPCPs and concentration, than that of the water extracted from floodplain wells. For example, iopamidol is the substance with the highest concentration even in groundwater, but with values of around 33 % of those measured in Po River, followed by ossipurinol and acesulfame, showing concentration values respectively approximating to half and two-thirds approximately of those found in surface waters.

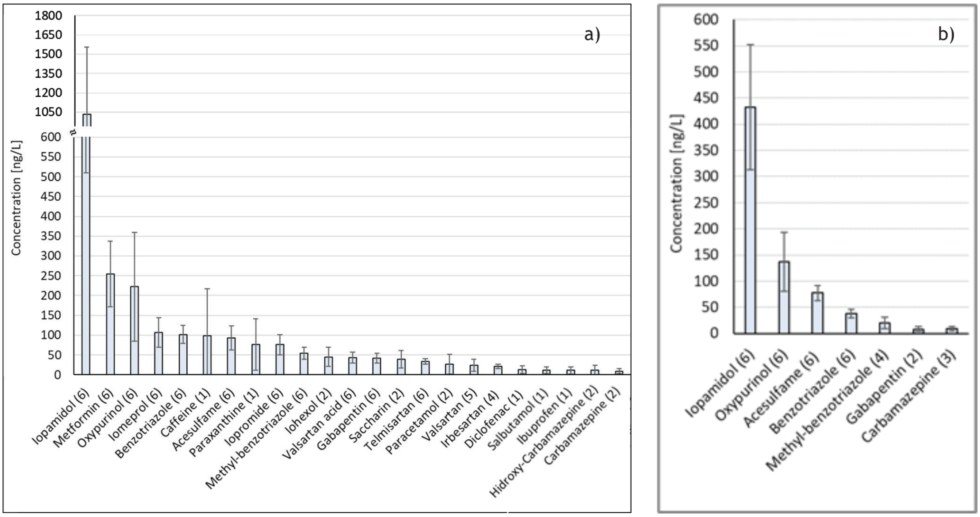


Figure 4.11 Concentration of PPCPs (mean ± standard deviation) in the raw waters abstracted from the Po River (a) and groundwater (b). The number of times each compound was detected during the 6 campaigns is reported in brackets and the respective abbreviations are also reported.

Figure 4.12 shows the sum of the PPCPs concentrations detected at various sampling points during the 6 campaigns. Marked variability of the concentration of PPCPs is observed in different campaigns, which may be due to the seasonal use of the drugs analysed, to the different hydrological conditions of the Po River, to the uncertainty of the analytical method, and to the restrictions due to the SARS-CoV-2 pandemic in the periods preceding the sampling dates. Furthermore, as already seen, there is a marked difference in concentration between the raw waters of the Po River and those of the floodplain wells, probably due to the phenomenon of bank filtration and the partial protection offered by clay layers confining the extraction aquifers. As regards to the treatment chain followed by the raw water of the Po River, wide variability in concentration may be observed at the post-lagooning and entry-ozonation monitoring points. There is no significant reduction in PPCPs concentrations in the clariflocculation and sand filtration sections. Finally, there is a very marked decrease in the concentration of PPCPs operated by ozonation and adsorption on activated carbon, with also a marked reduction in variability.

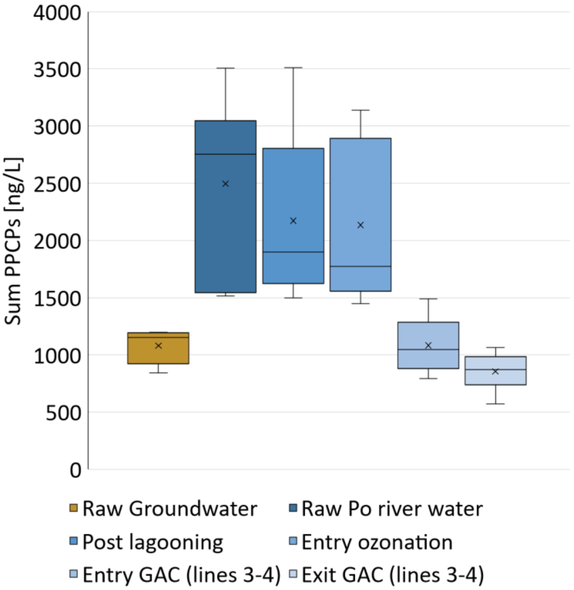


Figure 4.12 Boxplot of the sum of PPCPs concentrations in each sampling point, considering all 6 monitoring campaigns.

The concentrations of PPCPs detected along the surface waters treatment chain are shown in Figure 4.13. Almost all PPCPs are removed progressively through the treatment chain, with some fluctuations in concentrations, especially for OSS, ACS, and SAC. In line with the literature, the two processes that have shown an impact in the reduction of a wide variety of PPCPs are ozonation (on average 12 are detected at the inlet and 5 are lower than the respective LOQ at the outlet) and adsorption on GAC (on average 6 are detected at the inlet and 4 are lower than the respective LOQ at the outlet). Only two PPCPs (IPM and MTF) leaving the adsorption section were systematically detected: IPM and MTF are the PPCPs with the highest concentration in the Po River and are characterized by low reactivity with ozone (low logK_{O3}) and low affinity with activated carbon, being hydrophilic compounds (low log K_{OW} value). Finally, the ACS artificial sweetener was detected at the outlet of the adsorption section (87 ng/L), but not at the inlet (concentration below LOQ = 50 ng/L). It was detected at the inlet only once during the third campaign, probably due to ACS breakthrough in GAC filters, favoured by its hydrophilicity (low log K_{OW} value).

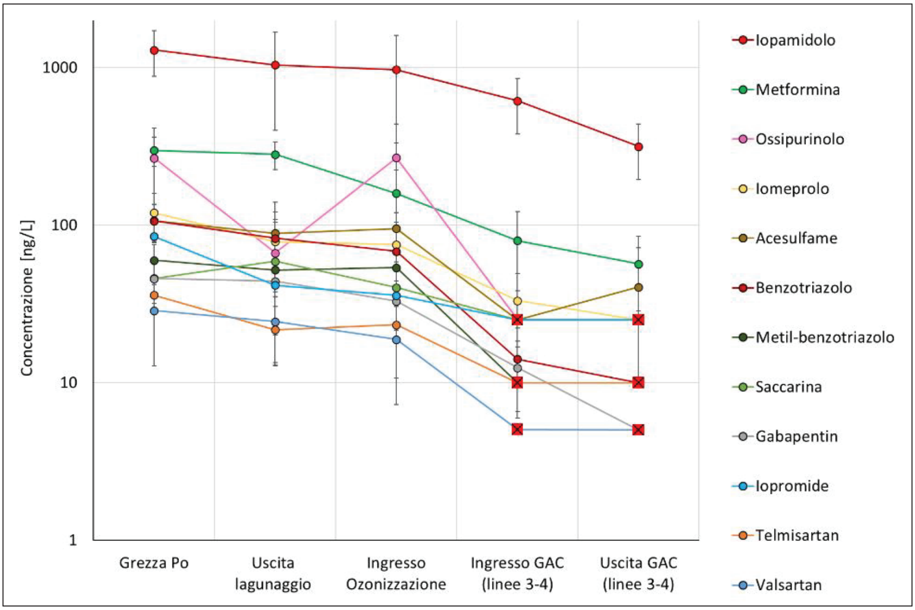
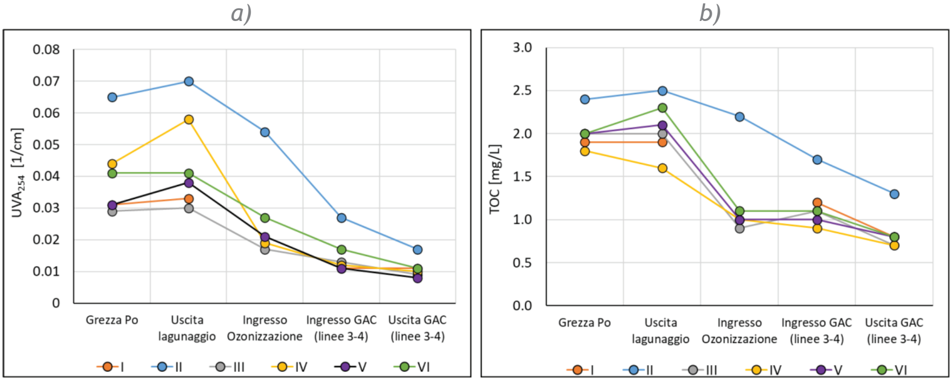


Figure 4.13 Concentration of PPCPs (mean ± standard deviation) detected along the surface waters treatment line. The censored values (lower than LOQ for all 6 campaigns) are marked with a red square containing an x. The logarithmic scale was used to represent all values in a single graph.

The same as PPCPs decreasing trend along the treatment line occurs for the descriptive parameters of the organic substance, UVA254, and TOC, as can be better observed in Figure 4.14.


a)

b)

Figure 4.14 Values of (a) UVA254 and (b) TOC in each sampling point of the Po River waters inside the treatment plant.

Considering the analogous trends of the PPCPs and the water parameters along the treatment chain, with the reference to the 6 campaigns, the average of the sum of the concentrations of all the PPCPs detected at each sampling point (6) was correlated to the average value of the parameters, UVA254 and TOC, as shown in Figure 4.15. A good linear correlation may be observed (R2 respectively equal to 0.82 and 0.87 for UVA254 and TOC), which can be used for an estimate of the PPCPs removal in the plant given UVA254 and TOC, which are parameters of easier and immediate measurement, and which can therefore be used as proxy variables of the total PPCPs contamination in the water along the plant treatment chain.

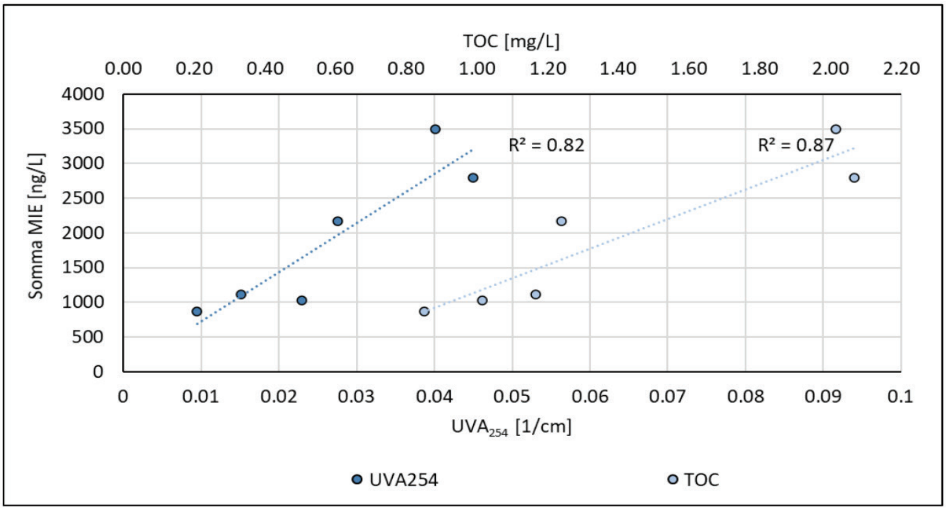


Figure 4.15 Correlation between the sum of PPCPs concentrations and the water parameters UVA254 and TOC. Linear regressions and related R2 are reported.

4.2.7. Neufahrn bei Freising, Germany

The well field of Neufahrn bei Freising is located west of the Isar River and supplies process water from the shallow wells and drinking water from the deeper wells. In the pilot area, a substantial part of Munich's wastewater is treated at the Gut Marienhof WWTP and discharged into the river.

As it can be seen in Table 4.6, the deeper aquifer is almost free of any measured PPCPs. Only the insect repellent DEET can be found in some samples at very low concentrations below 30 ng/L, which is six orders of magnitude lower than a reported provisional guideline value for drinking purposes (Schriks et al. 2010). In the shallow aquifer, low concentrations of some PPCPs were observed. Whereas oxypurinol was analysed in each sample, DEET and diatrizoate were present in

50 % of the samples. Additionally, bisphenol A, 1H-benzotriazole, caffeine, PFOS, and salbutamol were detected once. In contrast to the very low concentrations in the extraction wells, the PPCP concentrations in the Isar River were higher. In Garching, in the upper part of the river, more PPCPs were detected and the observed concentrations were below 100 ng/L. Thus, they are in the same order of magnitude as the concentrations detected in the shallow aquifer. At 4 km downstream (sampling point Isarbrücke), the PPCP concentrations were increased up to one order of magnitude. Additional PPCPs can be found; for example, the pharmaceuticals, diclofenac, iomeprol, and telmisartan. This observed difference may be explained by the PPCP containing effluent of the wastewater treatment plant. The effluent exhibited the highest measured PPCP concentrations for all sampling campaigns. Compared to the downstream PPCP concentrations, these are one order of magnitude higher. The maximum PPCP concentration was observed for iomeprol (16 µg/L) and oxypurinol (15 µg/L).

The results indicated that the river water and the extracted water by the wells differ in their composition of PPCPs. Therefore, the two water sources are very unlikely to impact each other. For further interpretations, a PPCP transport model is required.

Compared to other drinking water sources, PPCP concentration in the extracted well may be disregarded. However, the concentrations in the river downstream of the wastewater treatment plant are comparable to detected concentrations in other surface water sources in this project.

Table 4.6 Observed concentrations in ng/L of selected PPCP in the river water, the effluent of the wastewater treatment plant, and the shallow and deep wells for the 7 conducted sampling campaigns. Empty cells indicate when the measured concentrations are lower than the limit of detection.

LOCATION	Isar - Garching							Isar - Isarbrücke						
MONTH	1	2	3	4	5	6	7	1	2	3	4	5	6	7
Benzotriazole	63.4	57.9	36.5	51.5	81.9	79.7	54.4	600	490	69.9	367	348	302	347
DEET				61.7	42.7					18.6	26.3	49.5	62.3	53.7
Diatrizoate	66.8	65.8	60.4	65.7	168	56.8	66.5	361	243	55.4	161	335	139	125
Diclofenac								133	78.8	21.3	113	57.4	78.4	51.8
Gabapentin	14	21.7	14.4	31.2	25.7	19.9	12.6	77.8	81.9	31.9	77	151	163	110
Iohexol	109	63.5	74.8	74.5	90	76.1	51.8	241	148	206	323	301	163	87.6
Iomeprol								435	169	52.1	583	353	182	132
Lamotrigine		10.9			16.3	12.4		64.6	58.1	13.6	56.5	60.7	65.7	55.8
Metformin	69.2	37.6	24.1	56.8	45.8	42.2	34	102	85.8	38.8	91.4	170	117	93.5
Oxypurinol	140	67.2	111	51.9			56.8	1270	579	231	725			370
Telmisartan								76	47	21.5	52.7	54	66.8	40.9
Valsartan	13.9	12	17	28.5	38.9	20.5	13.3	59.8	25.7	37.2	134	319	151	97.5
Valsartan acid	24.2	16	20.2		31.6	25.9	14.8	139	129	32	25	36.6	41.1	38

LOCATION	WWTP effluent				
MONTH	3	4	5	6	7
Benzotriazole	7390	8420	5030	1840	3830
DEET	14.7	61	77.1	52.8	404
Diatrizoate	457	263	1010	520	548
Diclofenac	1960	1790	1120	761	643
Gabapentin	1030	602	1300	1470	632
Iohexol	1180	5970	3920	546	516
Iomeprol	5380	16000	7320	1800	2030
Lamotrigine	810	961	924	688	620
Metformin	840	1000	2660	959	646
Oxypurinol	12900	15100	11700	8880	7340
Telmisartan	850	668	711	685	393
Valsartan	1630	2030	3720	1140	355
Valsartan acid	1240	295	127	148	297

LOCATION	Shallow well						Deep well					
MONTH	2	3	4	5	6	7	2	3	4	5	6	7
Benzotriazole			20.7									
DEET			42.2	20.1		13.7			19.1	30.1	13.1	
Diatrizoate	94.5				56.3	68						
Diclofenac												
Gabapentin												
Iohexol												
Iomeprol												
Lamotrigine												
Metformin												
Oxypurinol	73.6	75.4	53.6	51.8	88.5	85.5						
Telmisartan												
Valsartan												
Valsartan acid												

4.2.8. Ljubljanska kotlina, Slovenia

With its central location, the Ljubljanska kotlina (Ljubljana Basin) represents the most important settlement, economic, and transport area in Slovenia. About 40 % of the Slovenian population lives in this area. Intensive development takes place in the Ljubljana Basin, ranging from agriculture, industry, and the introduction of new technologies to intensive tourist activities, which are increasing year by year. At the same time, this area is becoming increasingly urbanized. All these activities increase the pressure on the environment and also on water resources.

In the pilot area of Ljubljanska kotlina, surface water samples were collected together at three locations on the Ljubljanica and Sava rivers: Ljubljanica, Sava Medno, and Sava Dolsko. All three sites are located in the central part of the pilot area, near Ljubljana, the largest city in Ljubljanska kotlina. The Ljubljanica sampling site is located on the southern outskirts of Ljubljana and is an indicator of pollution in the southern part of the pilot action area, which is part of the Ljubljansko barje (Ljubljana marsh). The Sava Medno sampling point is located north of Ljubljana and is an indicator of pollution in the northern part of the pilot action area. The Sava Dolsko sampling point is located east of Ljubljana, at the exit of the pilot area. It is an indicator of the presence of pollutants in the City of Ljubljana and, consequently, in the whole Ljubljanska kotlina.

According to the sampling results, 32 different compounds were detected in the entire area of the pilot action in the Ljubljanska kotlina. The largest number of different compounds (29) was detected at the Sava Dolsko sampling point, followed by Sava Medno (21) and Ljubljanica (19).

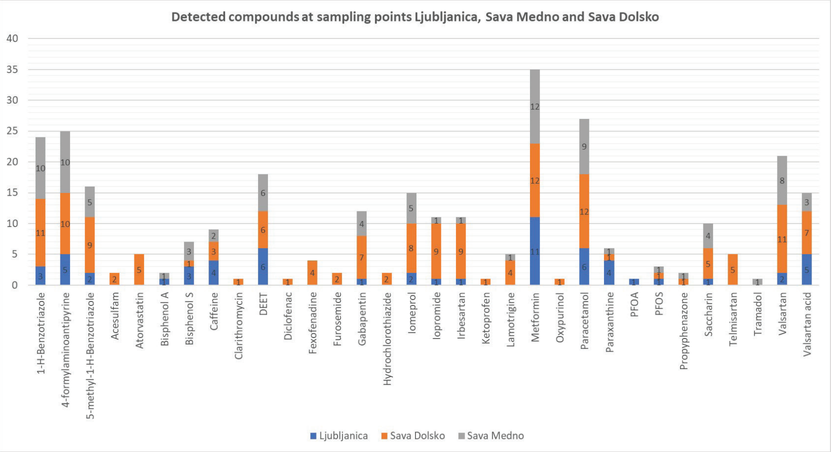


Figure 4.16 Detected compounds at the sampling points Ljubljanica, Sava Medno, and Sava Dolsko.

Figure 4.16 shows all the compounds detected at all three analysed sampling points. It illustrates at which sampling site a single compound occurred and, in addition to the total number of detections, how often it occurred at each sampling site. The most frequently detected was metformin (35 times), which is a drug used to treat type 2 diabetes. It is followed by paracetamol, which was detected 27 times and is used to relieve pain and reduce fever. 4-formylaminoantipyrine, 1H-benzotriazole, and valsartan were also detected more than 20 times.

If we also look at how often a single compound was detected at a single sampling site, we find that compounds are repeated the least frequently at the Ljubljanica sampling site and the most frequently at the Sava Dolsko sampling site. This indicates that the southern part is less polluted than the rest of the pilot area. 10 compounds were detected only at the Sava Dolsko sampling site. These compounds are acesulfame, atorvastatin, clarithromycin, diclofenac, fexofenadine, furosemide, hydrochlorothiazide, ketoprofen, oxypurinol, and telmisartan. Atorvastatin, fexofenadine, and telmisartan were the most common. All ten of these compounds are active ingredients in various pharmaceuticals, thus showing the urban impact or the impact of pollutants on the waters of the City of Ljubljana.

Figure 4.17 shows the average concentration of each compound at the Ljubljanica sampling site. Paraxanthin and caffeine occur in the highest concentrations. The mean concentration for paraxanthine is 659.25 ng/L and for caffeine 356.75 ng/L. Caffeine is a very common substance in the environment due to its widespread use. It is present in the environment at concentrations below 1 µg/L due to its good degradability. It can be used to assess the proximity of a pollution source. The presence of caffeine in the surface or groundwater is a direct evidence of anthropogenic pollution of the environment; its presence may indicate recent pollution from municipal sewage. Paraxanthin is the major metabolite of caffeine (Jamnik et al., 2009). PFOS (6.8 ng/L) has the lowest concentrations at the Ljubljanica sampling site.

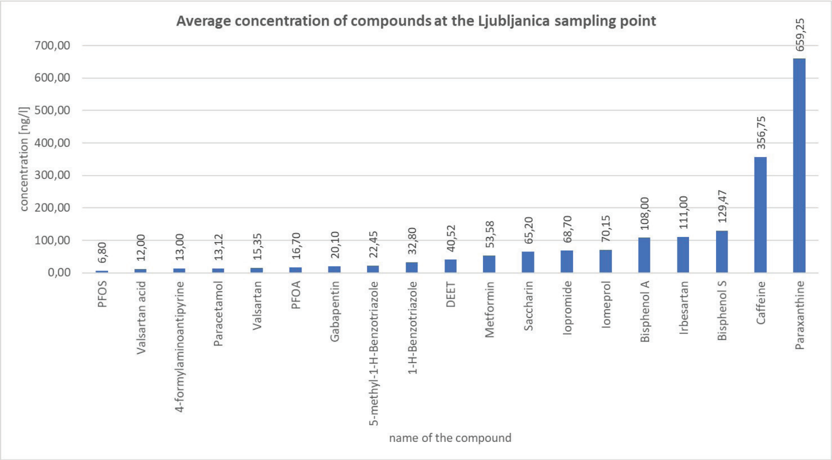


Figure 4.17 Average concentration of compounds at the Ljubljanica sampling point.

As at the Ljubljanica sampling site, paraxanthine and caffeine occur in the highest concentrations at the Sava Medno sampling site (Fig. 4.18). Paraxanthin was detected only once with a concentration of 1000 ng/L and caffeine twice with an average concentration of 429 ng/L. PFOS (9 ng/L) also appears here with the lowest concentrations.

At the Sava Dolsko sampling site, the highest concentrations were found for propyphenazone and iopromide (Fig. 4.19). Propyphenazone was detected only once at a concentration of 829 ng/L, and for iopromide, the average concentration was 241.11 ng/L. At the lowest concentrations (7 ng/L), PFOS occurs, as it did at the other two sampling sites. Propyphenazone is an active ingredient that is a component of drugs that affect the nervous system and is classified as an analgesic.

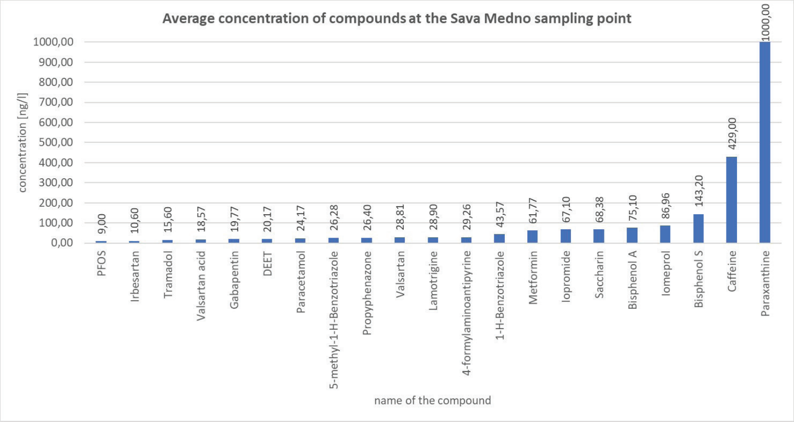


Figure 4.18Average concentration of compounds at Sava Medno sampling point.

It is used in conjunction with acetaminophen and caffeine to treat fever and pain. It is much more sustained than caffeine (Jamnik et al., 2009). Iopromide is an X-ray contrast agent used in various types of imaging studies, such as CT (Internet 1).

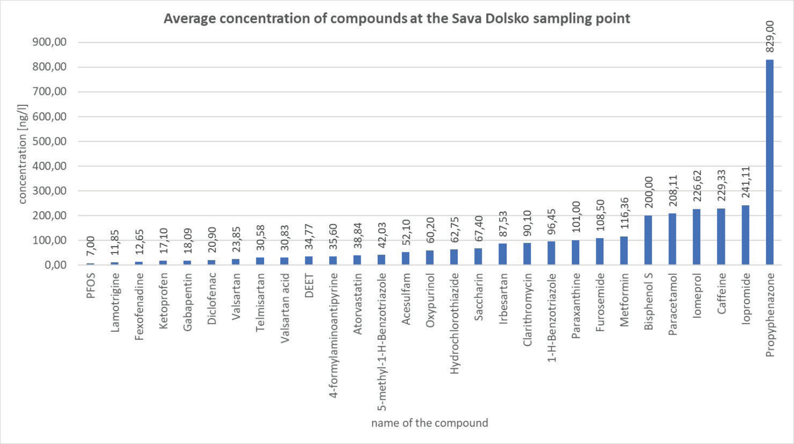


Figure 4.19 Average concentration of compounds at the Sava Dolsko sampling point

Trontelj, Klančar, and Roškar (2018) analysed the pollution of some Slovenian rivers with different substances. Valsartan and gabapentin were detected in the highest concentrations (in the range of 40-50 ng/L). Irbesartan, valsartan, and caffeine were present in all samples analysed. As can be seen from the Fig. 4.17, all the substances mentioned were also detected quite frequently in the Ljubljana Basin.

4.3. Comparison of “Twins” Pilot Areas

This chapter aims to compare project sites that have either similar natural conditions or use identical technologies for wastewater treatment or drinking water production. These comparisons will serve to generalize the project results to the European dimension.

4.3.1. Comparison of Dresden and Káraný Pilot Areas

For the drinking water production, Dresden and Kárány waterworks use more or less identical river water. In addition, they use the same production technology, bank infiltration, which commonly shows high removal efficiencies for PPCPs based on natural attenuation processes.

Table 4.7 summarizes the comparison of the efficiency of PPCPs removal from raw river water by the technology used in Káraný and Dresden. The results show the ability to remove substances that were detected in the river water, but after the infiltration process falls under the detection limits in both waterworks (green field in Table 4.7). The exact opposites are PPCPs substances, for which artificial recharge or bank infiltration are almost ineffective in their removal. These are the five substances in Table 4.7 marked in red.

The results of monitoring showed that the oxypurinol is the only “problematic” substance in Dresden. It is detected in the Elbe water in concentrations of hundreds of ng/L, and bank infiltration is ineffective in its removal. The situation is similar to primidone, but this substance occurs in extremely low concentrations in the Elbe water. The Dresden waterworks has a very low ability to remove the following PPCP substances: carbamazepine, lamotrigine, and sulfamethoxazole.

In terms of PPCP removal efficiency, there is a problem with sulfamethoxazole in the artificial recharge in Káraný waterwork. However, bank infiltration systematically reduces this substance below the limit of detection. There are indications of very low efficiency in removing two other substances using artificial recharge, namely 1H-benzotriazole and methylparaben. However, these results have not been supported by sufficient data yet. Oxypurinol and paraxanthin are the greatest problems in the Káraný waterworks from the point of view of low removal efficiency and high contents in hundreds of ng/L at the inlet, i.e. in river water.

Table 4.7 Comparison of PPCPs removal efficiency in Dresden and Káraný waterworks

PPCP compound	DRESDEN			KÁRANÝ				
	ELBE River	bank filtrate	removal efficiency %	JIZERA River	bank filtrate	removal efficiency %	artificial recharge	removal efficiency %
1H-benzotriazole	265		100	210	25	88.1*	25	0*
sulfamethoxazole	18	11	38.8	18		100	3.3	0*
methylparaben				15		100	30	0*
oxypurinol	561	753	0	380	142	62.6	97	74.6
primidone				17		100	11	36.2
lamotrigine	46	31	32.6	38		100	22	42.5
paraxanthine			100	160		24.8*		100
caffeine	121		100	120		16.7*		100
carbamazepine	24	20	16.7	23		100	14	39.1
PFOS	3		100	12		70.5*		100
sucralose				500		66		100
metformin	515		100	479		67		100
acesulfame	158		100	279		68	80	71.3
telmisartan	216	23	89.4	223		69		100
iomeprol	292		100	123		70		100
gabapentin	125		100	110		71	5	95.5
saccharin	28		100	74		72		100
4-formylaminoantipyrine	80	15	81.2	53		73		100
iboprofen-2-hydroxy	18.3		100	46		74		100
valsartan acid	101		100	45		75		100
DEET	23.7		100	44		76		100
tramadol	41	12	70.7	41		77		100
propylparaben				32		78	10	68.9
ibuprofen				29		79	10	65.5
iopromid	29		100	25		80		100
hydrochlorothiazode				25		81		100
iohexol				25		82		100
diclofenac	23		100	25		83		100
paracetamol				20		84	5	75
valsartan acid	101		100	20		85		100
metoprolol	22		100	17		86		100
celiprolol	10		100	11		87		100
irbesartan	6		100	10		88		100
Cotininechloramphenicol				10		89		100
ibuprofen-carboxy				10		90		100
vaenlaflaxine	15		100	10		91		100
penicillin G				5		92		100
chlarithromycin	6		100	5		93		100
erythromycin				5		94		100
sulfapyridin				5		95		100
trimetoprim				5		96		100
triclocarban				5		97		100
sotalol				5		98		100
estriol				5		99		100
estron				2		100		100
5-methyl-1H-benzotriazol	93	61	34.4					
cyclamate								
venlaflaxine-O-desmethyl								
bisphenol A								
bisphenol S								
1-methyl-1H-benzotriazol								

PPCP compound	DRESDEN			KÁRANÝ				
	ELBE River	bank filtrate	removal efficiency %	JIZERA River	bank filtrate	removal efficiency %	artificial recharge	removal efficiency %
prophyphenazone								
carbamazepin-2-hydroxy								
clofibric acid								
fexofenadine								
*Remark: low reliability of information								

4.3.2. Comparison of Po River Basin and Kozłowa Góra Pilot Areas

The Po River basin and the Kozłowa Góra pilot action areas share much in common in terms of PPCP analyses. In both areas, sampling campaigns focused largely on water purified at water treatment plants. Therefore, these two pilot areas should be treated as “twin sites”. At the first site, water was sampled at a treatment plant in Pontelagoscuro, Italy, at the Po basin hydrographic closure, during six campaigns. At the second twin site, the Kozłowa Góra pilot area in Poland, water was sampled during five campaigns (two additional campaigns will be conducted in the upcoming months). In this area, the investigated water treatment plant is located on the left bank of the Brynica River, directly below the front dam of the Kozłowa Góra reservoir. In both cases, raw water and water after several successive stages of treatment was analysed to study the removal efficiency after these stages.

It should, nevertheless, be noted that the Po and the Brynica river basins are quite different in terms of dimensions, number of inhabitants, and industry types present in the compared areas. The Po River basin covers an area of roughly 74,000 km^2, while the Brynica basin covers nearly 193 km^2. The local population follows the same pattern, with roughly 17 million people living in the Po basin, and slightly less than 30,000 in the Brynica basin.

On the other hand, the land use distribution in the compared areas is not that different according to the Corine Land Cover 2018 (Fig. 4.20). Both basins are covered mostly by agricultural and forested areas, with a slightly larger share of forested areas in the Brynica basin. In the Po basin, due to its dimensions and the presence of the Alpine and Apennine chains bordering the basin, these two types of land use are not homogeneously distributed, with forested areas concentrated in the mountain parts of the basin and agricultural areas covering the plains. In the Brynica basin, the distribution of cultivated areas is mostly linked to urban settlements.

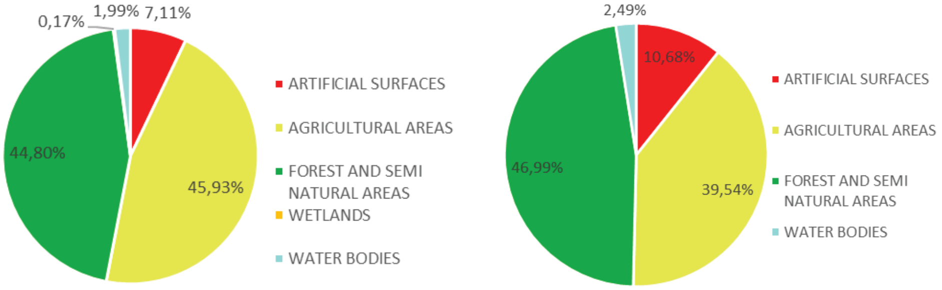


Figure 4.20 Land use according to Corine Land Cover 2018 in the Po River basin (left) and the Brynica basin (right).

For the Po River basin, only gross information is available on the main sources of contaminants. Industrial and urban wastewater discharges represent the most important point source of contaminants, while agriculture and livestock breeding are the sources of diffuse pollution. By deriving data from the inventory of emissions and losses (updated in 2019 and published in the updated Po River Management Plan[1]), a total of 44 urban wastewater treatment plant discharges, 119 industrial wastewater discharges (treated and untreated), 2 urban and industrial wastewater treatment plant discharges, and 4 waste disposal sites have been identified in the basin, but this database is not complete and definitive.

In terms of possible sources of contamination with PPCPs, the Brynica basin is characterised in great detail. Due to its small area compared to the Po basin, many significant point sources have been identified. The significant sources of contamination are linked to urban and industrial wastewater discharges, livestock farms, and fuel facilities. Linear contamination sources are related to larger roads crossing the area, and to rivers with low-quality waters.

The above-mentioned differences between the twin sites, including those related to their areas, population, types of land use as well as the differences in hydrologic conditions and medication preferences in Italy and Poland may affect the types and concentrations of PPCPs that reach the compared water treatment plants.

Of the 102 PPCPs monitored, 19 were found above the limit of detection in raw water at the inlets of both treatment plants (Fig. 4.21). Additionally, 10 substances were only found at the Pontelagoscuro WTP, whereas 5 other substances are specific to the Kozłowa Góra WTP. The number of substances detected during each sampling campaign was 11 and 9, for Pontelagoscuro and Kozłowa Góra respectively. Merely four substances – gabapentin, oxypurinol, benzotriazole methyl, and valsartan acid – were detected at both sites during every campaign.

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[1] Document 2 "Summary of Significant Pressures and Impacts Analysis, Attachment 2.6 Report on the 2° Inventory of Emissions and Losses in the Po District Pursuant to Art. 78ter of D.lgs. 152/06" - https://www.adbpo.it/PianoAcque2021/ELABORATI_PIANO/Elaborato_02_PressioniImpatti/PPdGPo2021_Elab_2_PressioniImpatti_22dic20_sito.pdf

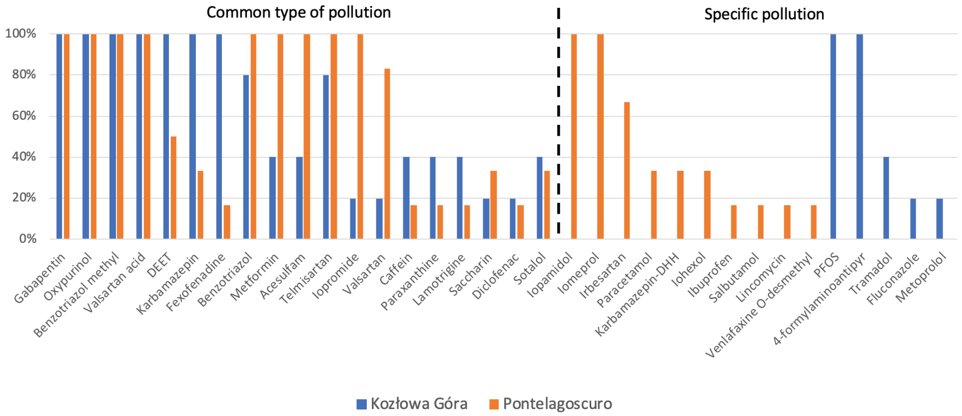


Figure 4.21 Detection frequencies of PPCPs at the inlets of the Pontelagoscuro and Kozłowa Góra WTPs (note the different number of sampling campaigns – 6 at Pontelagoscuro; 5 at Kozłowa Góra).

Concentrations of PPCPs in raw water usually did not exceed 100 ng/L. At Pontelagoscuro, the highest concentration in raw water was reported for iopamidol (an X-ray contrast agent). At Kozłowa Góra, paraxanthine was the substance with the highest concentration. In both investigated areas, a vast majority of contaminants was completely removed from drinking water. However, treatment processes were not fully effective for a particular group of substances. Acesulfame and metformin appeared at the output of both compared treatment plants. Additionally, three other PPCPs remained detectable at the output of the Kozłowa Góra WPT (DEET, valsartan acid, and PFOS) and two PPCPs were found at the output of the Pontelagoscuro WTP (caffeine and iopamidol). Nevertheless, most of the above-mentioned substances were detected sporadically, i.e. during one or two sampling campaigns, and their removal efficiencies were relatively high (ca. 62-89 %).

Removal efficiencies below 100 % for some substances are common and have been reported in many research papers that discuss the occurrence of PPCPs in raw water at WTPs and during treatment processes. The most recent research findings indicate that the conventional treatment of water can be enhanced with novel treatment processes such as advanced oxidation (Monteiro and Boxall, 2010) or membrane technologies such as microfiltration and reverse osmosis (Hu et al., 2015). Due to a high treatment cost per unit volume, these processes may, however, not be economically feasible.

Figure 4.22 presents boxplots with the sums of concentrations of all detected PPCPs (>LOQ) in all sampling campaigns at each monitoring point, i.e. after certain

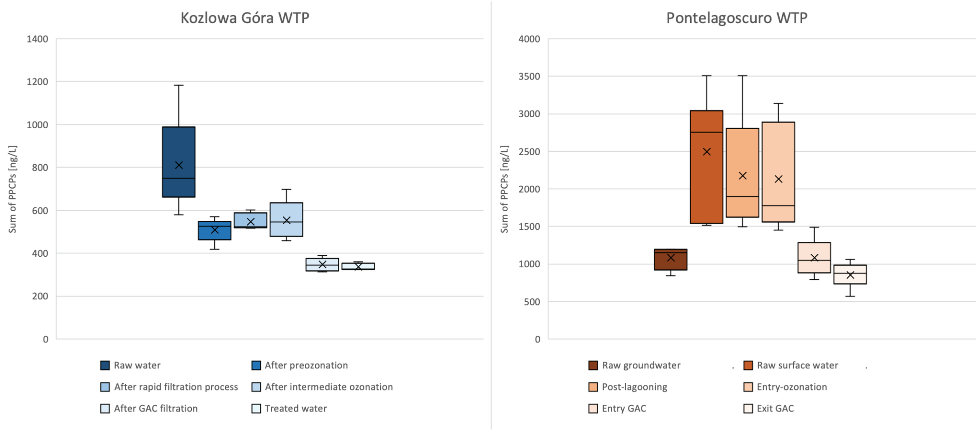


Figure 4.22 Boxplots with sums of concentrations for all detected PPCPs (>LOQ) in all sampling campaigns at each monitoring point at the Kozłowa Góra and Pontelagoscuro WTPs. The horizontal line represents the median concentration sum, the x mark represents the average (note the different scales used for the two WTPs).

stages of the treatment process. Please note that the compared WTPs differ in terms of treatment stages. Moreover, for the Pontelagoscuro WTP, treated water is sampled before the final chlorination, and therefore is not the same water that will be distributed to users.

The data presented above should not be used to rank the two compared water treatment plants or any other plants. Numerous parameters and factors impact the removal of emerging contaminants. Differences in the treatment stages and the initial contaminant concentrations, as well as analytical limitations related to the detection of PPCPs, severely limit the possibility of conducting direct comparisons.

4.3.3. Comparison of Jadro and Žrnovnica Springs Catchment and Waidhofen a/d Ybbs Pilot Areas

The pilot actions of the catchment area of the Jadro/Žrnovnica springs and the pilot action of Waidhofen a/d Ybbs can be considered “twin” areas because of the similar geological characteristics: both areas are characterised by solid carbonate rocks (limestone and dolomite) forming karstic aquifers.

However, the comparison between the two pilot areas, in terms of substance detection, could be carried out only marginally. The catchment area of the two springs in Croatia covers a territory of approximately 250 – 500 km^2 (according to different authors), much larger than that of the approximately 3 km^2 catchment area of the studied spring in the Waidhofen/Ybbs pilot area (Kerschbaumquelle).

Similarly, the Jadro and Žrnovnica pilot area is characterised by a higher population density than that of Waidhofen/Ybbs, leading probably to different land use and land cover patterns and different pollution sources. In the Waidhofen/Ybbs pilot area, the main land cover is forest/vegetation, with a small percentage of land use designated as quarries. Although forest/vegetation is the main land cover in the Jadro and Žrnovnica pilot area as well, some more human-related land cover/use patterns are present, such as cultivation patterns, pastures, and industrial sites. Despite these differences, a similar PPCP source can potentially be found: the presence of domestic/municipal wastewater treatment plants located upstream from the Waidhofenbach creek and therefore upstream from the spring in Waidhofen/Ybbs, and the presence of septic tanks in the settlements of the Jadro and Žrnovnica catchment.

The sampling campaigns were performed at different points: the sampling activity in Jadro/Žrnovnica included two springs, one borehole, and one river sampling point, while the sampling activity in Waidhofen/Ybbs included only one karstic spring and three creek sampling points. Furthermore, the sampling campaigns were performed at different times; for Jadro and Žrnovnica the sampling was more focused in autumn and spring seasons, and for Waidhofen/Ybbs more in spring and summer seasons. This might induce different precipitation and river flow values, and therefore potentially different dilution of contaminants. Nevertheless, some general comparisons can be performed.

The total number of analysed substances differs per year and sampling campaign, as in the year 2021 the laboratory extended the list of available substances from 114 (102 pharmaceuticals, 7 hormones, 5 antibiotics) to 122 (109 pharmaceuticals, 7 hormones, and 6 antibiotics). In the samples from the Jadro and Žrnovnica catchment, 114 substances were analysed in all sampling campaigns, except for the last one where the analysis of hormones and antibiotics was omitted. The samples from Waidhofen/Ybbs collected in the first four campaigns were analysed for the occurrence of 114 substances in total, while in the four samples of May, July, and August 2021, 122 substances were analysed in total. A total of 11 substances were detected above the limits of quantification in the Croatian pilot area, while in the Austrian pilot area there were 34 in total.

In both karstic catchments, the majority of the detected contaminants belong to the group of pharmaceuticals. However, it must be highlighted that such a total number of detected contaminants in both pilot sites could be reduced if the occurrence through the entire monitoring period is observed. If only detections occurring more than twice are considered, and discarding the sporadic detections of once or twice, the number of detected substances decreases to only 11 out of 34 in Austria and to only 3 out of 11 in Croatia.

Figure 4.23 shows that 7 substances were detected in both karstic pilot actions.

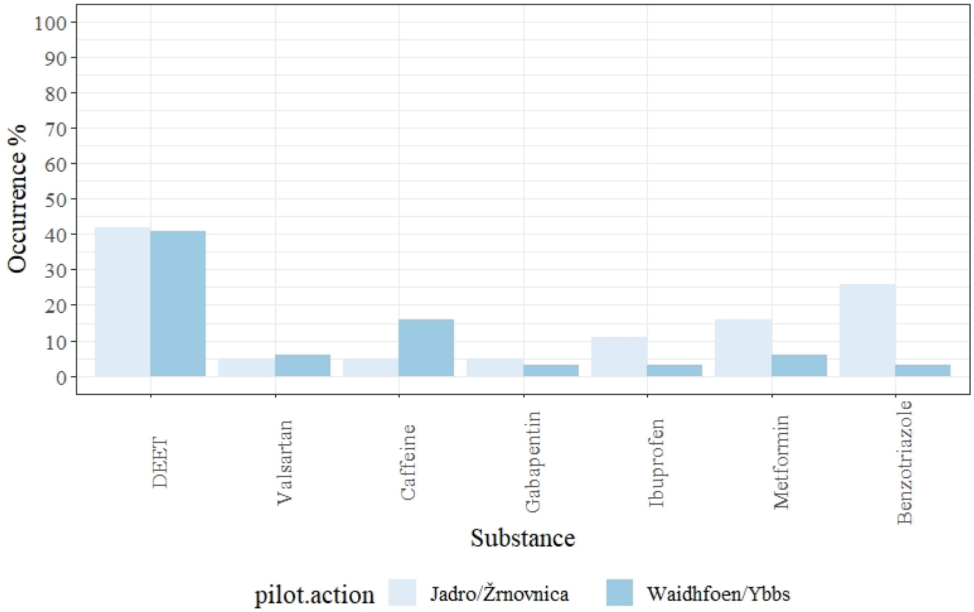


Figure 4.23 Comparison of occurrence values (%) of the substances detected in both pilot actions (light blue refers to the Jadro/Žrnovnica pilot action and the darker blue to the Waidhofen/Ybbs pilot action). The total number of samples in Jadro/Žrnovnica was 19, and in Waidhofen/Ybbs there were 32.

However, most of the substances were detected with a different occurrence rate between the two sites (1H-benzotriazole, caffeine, gabapentin, ibuprofen, metformin). The only two substances comparable in terms of occurrence are DEET (occurring at 42 % and 41 % in Jadro/Žrnovnica and Waidhofen/Ybbs respectively) and Valsartan (occurring at 5 % and 6 % in Jadro/Žrnovnica and Waidhofen/Ybbs respectively). In both cases, no substance was detected in each sampling campaign, resulting in a 100 % occurrence rate. DEET was the most frequently detected substance in both cases. As a matter of fact, DEET was one of the most frequently detected compounds in the pan-European survey on persistent organic compounds in groundwater, with a frequency of 53 % (Loos et al., 2010).

Figure 4.24 shows the ranges of the measured values of the 7 commonly detected substances in both pilot actions. The median values of the substances are comparable between the two pilot actions, except for caffeine, 1H-benzotriazole, and metformin. The outlier values of caffeine show higher concentration detections in Waidhofen/Ybbs. In contrast, 1H-benzotriazole and metformin were found at higher concentrations in Jadro/Žrnovnica.

Overall, the low occurrences and the low measured values indicate that PPCPs are almost absent in the aquifer. The sporadic detections in both pilot actions 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 are of human origin. The contamination of the samples cannot be ruled out. However, the few monitoring campaigns and analyses do not allow for a proper and robust statistical evaluation. Therefore, more frequent monitoring might be needed to come to stronger conclusions.

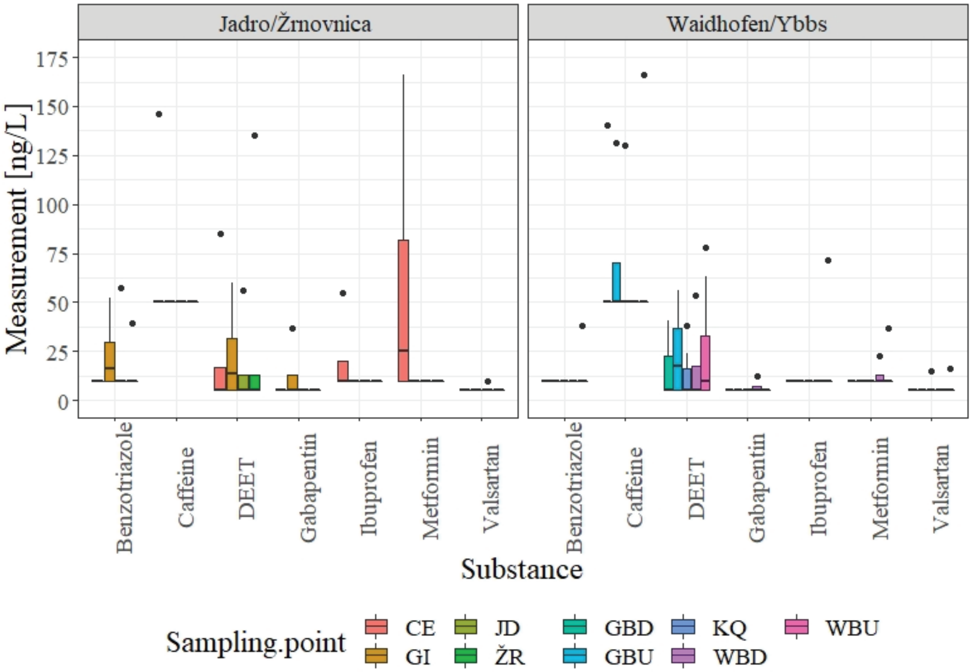


Figure 4.24 Boxplots of the measured values of the substances detected in both pilot actions. The left part of the figure shows the results of the Jadro/Žrnovnica pilot action, and the right part of the figure shows the results of the Waidhofen/Ybbs pilot action. The measured values of each substance are also shown for each sampling point: CE, JD, GI, and ŽR for Jadro/Žrnovnica, and GBD, GBU, KQ, WBD, and WBU for Waidhofen/Ybbs (see legend and see pilot action chapters). Two outliers fall out of the figure range: 1H-benzotriazole with 372 ng/L in Jadro/Žrnovnica, and caffeine with 798 ng/L in Waidhofen. They are, however, included in the calculation of the boxplots.

4.4. PPCP Pollution in Central European Water Resources

Disclaimer: *It is to be noted how partners had different number of samples, sampling locations as well as sampling campaigns per pilot action area (described in respective subchapters of chapter 3 and 4). Also, in some pilot areas partners analysed samples taken during different stages of water treatment or in wastewater treatment plant.*

All PPCP compounds, hormones, and antibiotics that were detected in the designated pilot areas of the CE region (groundwater, surface water, and treated water resources) are shown in table 4.7. The table also encompasses the limits of quantification and the limits of detection of the Povodí Vltavy laboratory, as well as the total detection number per compound.

Table 4.8 Results of boDEREC-CE monitoring at 8 pilot actions within the CE region

No.	Name	CAS#	Description	Unit	LOQ	LOD	Detection number
	Pharmaceuticals and personal care products						
1	1H-benzotriazole	95-14-7	corrosion inhibitor	ng/l	20	7	163
2	1-methyl-1H-benzotriazole	13351-73-0	corrosion inhibitor	ng/l	50	15	1
3	4(5)-methyl-1H-benzotriazole	29385-43-1	corrosion inhibitor	ng/l	20	7	131
4	4-formylaminoantipyrine	1672-58-8	metabolite of dipyrone (analgetic)	ng/l	10	3	114
5	acebutulol	37517-30-9	beta blocker	ng/l	10	3	4
6	acesulfame	33665-90-6	sugar substitute	ng/l	50	15	80
7	alfuzosin	81403-80-7	alpha-1 blocker	ng/l	10	3	-
8	amitriptiline	50-48-6	antidepressant	ng/l	10	3	4
9	atenolol	29122-68-7	beta blocker	ng/l	10	3	10
10	atorvastatin	134523-00-5	lipid-modifying agent	ng/l	10	3	11
11	azithromycin	83905-01-5	antibiotic	ng/l	10	3	24
12	bezafibrate	41859-67-0	fibrate	ng/l	10	3	7
13	bisoprolol	66722-44-9	beta blocker	ng/l	10	3	27
14	bisphenol A	80-05-7	alkylphenol	ng/l	50	15	19
15	bisphenol B	77-40-7	alkylphenol	ng/l	50	15	-
16	bisphenol S	80-09-1	alkylphenol	ng/l	50	15	19
17	butylparaben	94-26-8	cosmetic and pharmaceutical preservatives	ng/l	10	3	-
18	caffeine	58-08-2	stimulant	ng/l	100	30	48
19	carbamazepine	298-46-4	antiepileptic	ng/l	10	3	111
20	carbamazepine 10,11-dihydro-10-hydroxy	29331-92-8	metabolite	ng/l	10	3	22
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	10
23	carbamazepine 2-hydroxy	68011-66-5	metabolite	ng/l	10	3	7
24	celiprolol	56980-93-9	beta blocker	ng/l	10	3	12
25	citalopram	59729-33-8	antidepressant	ng/l	20	7	9
26	clarithromycin	81103-11-9	antibiotic	ng/l	10	3	28
27	climbazole	38083-17-9	antifungal	ng/l	10	3	10

No.	Name	CAS#	Description	Unit	LOQ	LOD	Detection number
28	clindamycin	18323-44-9	antibiotic	ng/l	10	3	16
29	clofibric acid	882-09-7	fibrate	ng/l	10	3	1
30	cotinine	486-56-6	metabolite of nicotine	ng/l	20	7	23
31	cyclamate	139-05-9	sugar substitute	ng/l	100	30	7
32	cyclophosphamide	50-18-0	chemotherapeutic agent	ng/l	10	3	1
33	DEET	134-62-3	repelent	ng/l	10	3	160
34	diatrizoate	737-31-5	contrast agens	ng/l	50	15	29
35	diclofenac	15307-79-6	NSAID	ng/l	20	7	54
36	diclofenac-4-hydroxy	64118-84-9	metabolite	ng/l	20	7	21
37	diltiazem	42399-41-7	antiarrhythmic	ng/l	10	3	6
38	disopyramide	5.9.3737	antiarrhythmic	ng/l	10	3	-
39	eprosartan	133040-01-4	antihypertensive	ng/l	10	3	2
40	erythromycin	114-07-8	antibiotic	ng/l	10	3	8
41	ethylparaben	120-47-8	cosmetic and pharmaceutical preservatives	ng/l	10	3	3
42	fexofenadine	83799-24-0	antihistamine	ng/l	10	3	51
43	fluconazole	86386-73-4	antifungal	ng/l	10	3	25
44	fluoxetine	54910-89-3	antidepressant	ng/l	10	3	4
45	furosemide	54-31-9	diuretic	ng/l	50	15	19
46	gabapentin	60142-96-3	antiepileptic	ng/l	10	3	111
47	gemfibrozil	25812-30-0	fibrate	ng/l	10	3	-
48	hydrochlorothiazide	58-93-5	diuretic	ng/l	50	15	35
49	chloramphenicol	56-75-7	antibiotic	ng/l	20	7	-
50	ibuprofen	15687-27-1	NSAID	ng/l	20	7	16
51	ibuprofen-2-hydroxy	51146-55-5	metabolite	ng/l	30	10	19
52	ibuprofen-carboxy	15935-54-3	metabolite	ng/l	20	7	9
53	iohexol	66108-95-0	contrast agent	ng/l	50	15	40
54	iomeprol	78649-41-9	contrast agent	ng/l	50	15	65
55	iopamidol	60166-93-0	contrast agent	ng/l	50	15	26
56	iopromide	73334-07-3	contrast agent	ng/l	50	15	44
57	irbesartan	138402-11-6	antihypertensive	ng/l	10	3	40
58	ivermectin	70288-86-7	antiparazitic	ng/l	50	15	-
59	ketoprofen	22071-15-4	NSAID	ng/l	10	3	9
60	lamotrigine	84057-84-1	antiepileptic	ng/l	10	3	91
61	lincomycin	154-21-2	antibiotic	ng/l	10	3	4
62	losartan	114798-26-4	antihypertensive	ng/l	10	3	12
63	lovastatin	75330-75-5	lipid-modifying agent	ng/l	10	3	4
64	memantine	19982-08-2	psychoanaleptic (anti-dementia agent)	ng/l	20	7	5
65	metformin	657-24-9	anti-diabetic drug	ng/l	20	7	140
66	methylparaben	99-76-3	cosmetic and pharmaceutical preservatives	ng/l	30	10	32
67	metoprolol	51384-51-1	beta blocker	ng/l	10	3	54
68	mirtazapine	61337-67-5	antidepressant	ng/l	10	3	8
69	naproxene	22204-53-1	NSAID	ng/l	50	15	6
70	naproxene-o-desmethyl	52079-10-4	metabolite	ng/l	20	7	9
71	norverapamil	67018-85-3	metabolite of verapamil (antiarytmic)	ng/l	10	3	3
72	octyl methoxycinnamate (OMC)	5466-77-3	UV filter	ng/l	1000	300	-
73	oxcarbazepine	28721-07-5	metabolite	ng/l	10	3	14

No.	Name	CAS#	Description	Unit	LOQ	LOD	Detection number
74	oxypurinol	2465-59-0	purine receptor modulator	ng/l	50	15	120
75	paracetamol	103-90-2	pain killer	ng/l	10	3	54
76	paraxanthine	611-59-6	metabolite of caffeine	ng/l	100	30	42
77	peniciline G	61-33-6	antibiotic	ng/l	10	3	3
78	PFOA (perfluorooctanoic acid)	335-67-1	fluorosurfactant	ng/l	10	3	3
79	PFOS (perfluorooctane sulfonic acid)	1763-23-1	fluorosurfactant	ng/l	5	1,5	73
80	phenazone	60-80-0	NSAID	ng/l	10	3	16
81	primidone	125-33-7	antiepileptic	ng/l	10	3	29
82	propranolol	525-66-6	beta blocker	ng/l	10	3	9
83	propylparaben	94-13-3	cosmetic and pharmaceutical preservatives	ng/l	20	7	15
84	propyphenazone	479-92-5	NSAID	ng/l	10	3	8
85	ranitidine	66357-35-5	histamine receptor modulator	ng/l	10	3	5
86	roxithromycin	80214-83-1	antibiotic	ng/l	10	3	3
87	saccharin	81-07-2	sugar substitute	ng/l	50	15	48
88	salbutamol	18559-94-9	antiasthmatic drug	ng/l	10	3	9
89	sertraline	79617-96-2	antidepressant	ng/l	10	3	10
90	simvastatin	79902-63-9	lipid-modifying agent	ng/l	10	3	8
91	sotalol	3930-20-9	beta blocker	ng/l	10	3	29
92	sucralose	56038-13-2	sugar substitute	ng/l	1000	300	14
93	sulfamerazine	127-79-7	antibiotic	ng/l	10	3	-
94	sulfamethazine	57-68-1	antibiotic	ng/l	10	3	6
95	sulfamethoxazole	723-46-6	antibiotic	ng/l	10	3	59
96	sulfanilamide	63-74-1	antibiotic	ng/l	50	15	8
97	sulfapyridine	144-83-2	antibiotic	ng/l	10	3	24
98	telmisartan	144701-48-4	antihypertensive	ng/l	20	7	101
99	tiamulin	55297-95-5	veterinary antibiotic	ng/l	10	3	2
100	tramadol	27203-92-5	pain killer	ng/l	10	3	75
101	triclocarban	101-20-2	antibacterial agent	ng/l	10	3	1
102	triclosan	3380-34-5	antibacterial agent	ng/l	20	7	-
103	trimetoprim	738-70-5	antibiotic	ng/l	10	3	16
104	valsartan	137862-53-4	antihypertensive	ng/l	10	3	92
105	valsartan acid	164265-78-5	metabolite of valsartan (antihypertens)	ng/l	10	3	99
106	venlafaxine	93413-69-5	antidepressant	ng/l	10	3	38
107	venlafaxine O-desmethyl	93413-62-8	antidepressant	ng/l	10	3	35
108	verapamil	52-53-9	antiarythmic	ng/l	10	3	6
109	warfarin	81-81-2	antithrombotic	ng/l	10	3	-

No.	Name	CAS#	Description	Unit	LOQ	LOD	Detection number
			Hormones				
1	17a-ethinylestradiol	57-63-3	estrogen steroid hormone	ng/l	2	0.7	1
2	17-alpha-estradiol	57-91-0	estrogen steroid hormone	ng/l	1	0.3	1
3	17-beta-estradiol	50-28-2	estrogen steroid hormone	ng/l	1	0.3	1
4	estriol	50-27-1	estrogen steroid hormone	ng/l	10	3	-
5	estrone	53-16-7	estrogen steroid hormone	ng/l	1	0.3	2
6	progesterone	57-83-0	female sex hormone	ng/l	0.5	0.15	18
7	testosterone	58-22-0	male sex hormone	ng/l	0.5	0.15	5

No.	Name	CAS#	Description	Unit	LOQ	LOD	Detection number
			Antibiotics				
1	enoxacin	74011-58-8	fluoroquinolone antibiotic	ng/l	2	0.7	-
2	enrofloxacin	93106-60-6	fluoroquinolone antibiotic	ng/l	1	0.3	-
3	norfloxacin	70458-96-7	fluoroquinolone antibiotic	ng/l	1	0.3	-
4	ciprofloxacin	93107-08-5	fluoroquinolone antibiotic	ng/l	10	3	1
5	ofloxacin	82419-36-1	fluoroquinolone antibiotic	ng/l	1	0.3	1
6	doxycycline	564-25-0	tetracycline antibiotic	ng/l	0.5	0.15	-

Several compounds that are included in the current Watch List (Table 2.4) were detected within boDEREC-CE monitoring campaigns (Table 4.7): sulfamethoxazole (59 times), venlafaxine (38 times), venlafaxine O-desmethyl (35 times), fluconazole (25 times), and trimethoprim (16 times). Moreover, some of the compounds that are included in the Voluntary Groundwater Watch List (Table 2.5) were also detected (Table 4.7): sotalol (29 times), clarithromycin (28 times), ibuprofen (16 times), and erythromycin (8 times).

According to the results of boDEREC-CE PPCP monitoring campaigns, 1H-benzotriazole (detection frequency of 59 %) is the most frequently detected compound in water resources of the CE region. With a detection frequency of 53 %, 1H-benzotriazole was also one of the most frequently detected compounds in the survey on persistent organic compounds in European groundwater bodies (Loos et al., 2010). In the EU-wide survey of polar organic persistent pollutants in European river waters, Loos et al. (2009) also pointed out 1H-benzotriazole as one of the most frequently and at the highest concentration levels detected compounds. According to Arp & Hale (2019), 1H-benzotriazole is recognized as a very persistent, very mobile, and toxic substance (vPvM & PMT) under the REACH (Regulation (EC) No 1907/2006). Except for PFOS, none of the 20 most frequently detected PPCPs in the CE region are included in the Priority Substances List, while sulfamethoxazole is the only one included in the Watch List.

Figure 4.26 shows the three most frequently detected PPCPs per each pilot area. The insect repellent DEET was the most frequently detected compound in four out of eight pilot areas. Purine receptor modulator oxypurinol was the most frequently detected compound in two out of eight pilot areas. The anti-diabetic drug metformin was the most frequently detected compound in Ljubljanska kotlina, while diatrizoate, a contrast agent used during X-ray imaging, was the most frequently detected PPCP in Neufahrn bei Freising. Interestingly, diatrizoate was detected solely in the Neufahrn bei Freising pilot area, suggesting a presence of a specific source of pollution. Along with oxypurinol, radiopaque contrast agent iopamidol and artificial sweetener acesulfame were the most frequently detected PPCPs in Po River basin.

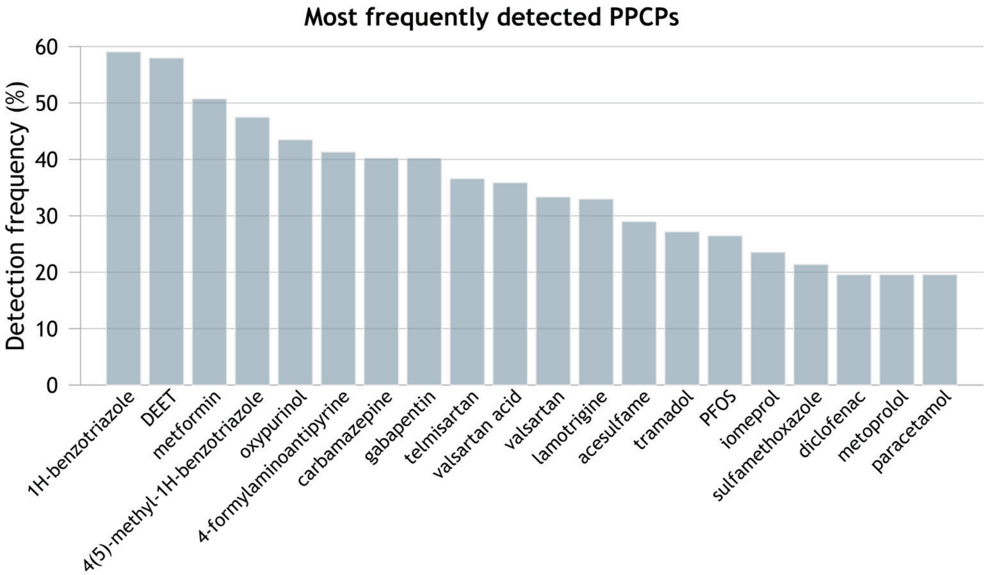


Figure 4.25 Detection frequency of 20 most frequently detected PPCPs in designated pilot areas of the CE region.

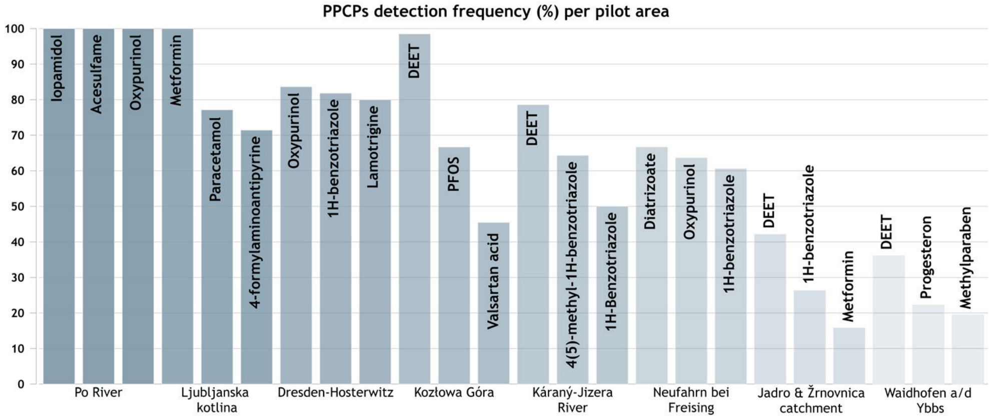


Figure 4.26 The three most frequently detected PPCPs per pilot area.

Comparison of the occurrence of selected PPCP substances in seven watercourses in Central Europe can be seen in Table 4.9. The relatively significant homogeneity of the detected PPCP substances in boDEREC-CE watercourses is an interesting finding.

Table 4.9 PPCPs occurrence in seven watercourses in CE region (occurring at every site (8x and 7x) marked in red; occurring at most sites (6x) marked in orange; occurring at most sites (5x) marked in yellow; occurring at some sites (4x) marked in light green; occurring at some sites (3x) marked in dark green).

	Elbe	Isar	Jizera	Po	Sava	Brynica	Cetina	Waidhofen
DEET	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥
Metformin	🟥	🟥	🟥	🟥	🟥	🟥	🟥	
Caffeine	🟥	🟥	🟥	🟥	🟥		🟥	🟥
Valsartan	🟧	🟧	🟧	🟧	🟧	🟧		
Valsartan acid	🟧	🟧	🟧	🟧	🟧	🟧		
Gabapentin	🟧	🟧	🟧	🟧	🟧			🟧
1H-benzotriazole	🟧	🟧	🟧	🟧	🟧		🟧	
Benzotriazoel methyl	🟧	🟧	🟧	🟧	🟧	🟧		
Diclofenac	🟧	🟧	🟧	🟧	🟧	🟧		
Iopromide	🟧	🟧	🟧	🟧	🟧	🟧		
Irbesartan	🟧	🟧	🟧	🟧	🟧	🟧		
Paracetamol	🟧	🟧	🟧	🟧	🟧	🟧	🟧	
Iohexol	🟨	🟨	🟨	🟨		🟨		
Ibuprofen	🟨	🟨	🟨	🟨			🟨	
Oxypurinol	🟨	🟨	🟨	🟨	🟨			
Acesulfame	🟨	🟨	🟨	🟨	🟨			
Lamotrigine	🟨	🟨	🟨	🟨	🟨			
Saccharin	🟨	🟨	🟨	🟨	🟨			
Paraxanthine	🟨	🟨	🟨	🟨	🟨			
Iomeprol	🟨	🟨	🟨	🟨	🟨			
Clarithromycin	🟨	🟨	🟨		🟨			🟨
Erythromycin	🟩	🟩	🟩			🟩		🟩
4-formylaminoantipyrine	🟩	🟩	🟩		🟩			
Peniciline G	🟩	🟩	🟩			🟩		
Tramadol	🟩	🟩	🟩			🟩		
Carbamazepine	🟩	🟩	🟩	🟩				
Metoprolol	🟩	🟩	🟩			🟩		
PFOS	🟩	🟩	🟩		🟩			
Fexofenadine	🟩	🟩		🟩	🟩			
Hydrochlorothiazide	🟩	🟩	🟩		🟩			
Methylparaben	🟩	🟩	🟩					🟩
Bisphenol S	🟢	🟢			🟢			
Carbamazepine 10,11-dihydro-10-hydroxy		🟢		🟢		🟢		
Celiprolol	🟢		🟢			🟢		
Cotinine	🟢	🟢	🟢					
Iopamidol		🟢		🟢		🟢		
Primidone	🟢	🟢	🟢					
Venlafaxine	🟢	🟢	🟢					
Venlafaxine O-desmethyl	🟢	🟢		🟢				
Sulfamethoxazole	🟢	🟢	🟢					

The Table 4.9 shows how rivers Elbe, Jizera, Po, and Isar have a more or less identical composition in terms of PPCPs concentrations. Identical substances occur in the waters of these rivers and their absolute average concentrations are usually very close. The second group of rivers is the Sava and Brynice. The amount of detected PPCP substances is lower compared to the previous group, but still significant. Both groups are connected by an identical type of pollution characteristic of all Central European watercourses. However, they differ in the greater heterogeneity of specific substances - some drugs are missing in their waters.

The karst watercourse in Waidhofen and Cetina River, where PPCPs represent only a rare contamination, have very clean water. This fact is probably due to the extreme dilution capacity of the karst environment.

5. MODELLING OF EMERGING CONTAMINANTS

Hydrological and solute transport models are of great importance in the field of water resources investigation. In the last decades, a large number of scientists and practitioners have developed models of increasing complexity to investigate both the quantity and quality of water resources (Kuwayama, Young, & Brozovi, 2017; Singh, 2018). Conceptual and numerical models are simplifications of real-world systems aimed at improving the understanding of water resources (Solomatine & Wagener, 2011), predicting future scenarios (Solomatine & Wagener, 2011), and improving water management strategies (Montanari, 2011).

Modelling this group of pollutants may be extremely challenging and a standardised approach has not been well established yet (Geissen et al., 2015). PPCPs are not commonly studied or monitored even though they may potentially enter the aquatic environment through several pathways (Geissen et al., 2015; Mandaric et al., 2017). Furthermore, they are usually detected in freshwater at low concentrations (Giger et al., 2003; Spongberg et al., 2011) leading to higher uncertainty in the measured data (Datta, Kang, Chen, & Ye, 2018) and requiring a very accurate model to correctly predict their transport and fate. Nowadays, even if practitioners are still unlikely to develop models for PPCPs, modelling these compounds is becoming one of the most important topics of research in the field of water resources management.

The behaviour of these contaminants in the water matrix depends on the physicochemical properties of the pollutant and on the characteristics of the receiving aquatic compartment (Ebele, Abdallah, & Harrad, 2017; Geissen et al., 2015) such as volatility, solubility, sorbability, degradability and persistence (Ebele et al., 2017; Geissen et al., 2015). The physicochemical properties of a substance regulate the mobility of the target compound, and the redox potential controls the degradability (Barbieri et al., 2012; Ying, Kookana, & Dillon, 2004). Adsorption is regulated by the octanol-water partition K_{OW}, expressed as $\log(K_{OW})$, the soil-water partition coefficient K_d and the solubility in water SW (Sanchez-Vila et al., 2015).

Most pharmaceutical drugs are hydrophilic molecules (i.e. $\log(K_{OW}) < 4$), and are therefore often detected in water (Müller, Scheytt, & Asbrand, 2012). Finally, the redox state of a substance is also fundamental, as it controls chemical reactions and strongly affects the rate of biodegradation of the compounds (Christensen, Bjerg, & Banwart, 2000).

Transport of contaminants in the water environment can be mathematically described by the Advection-Dispersion-Reaction Equation (ADRE). This equation takes into consideration all the governing mechanisms which describe the fate of contaminants in surface water and groundwater: advection, hydrodynamic dispersion, biodegradation, and sorption (Sanchez-Vila et al., 2015). To solve the ADRE, several parameters are required, such as dispersion, sorption, and decay coefficients, as well as the flow velocity. In particular, the distribution of the flow velocity in the system, which is generally derived from the solution of the flow problem, is a fundamental prerequisite for solving the transport problem. In conclusion, to investigate the fate and transport of PPCPs in water matrices, two models are needed: the hydrological flow model and the transport model.

5.1. Modelling of PPCPs in Surface Water

A wide range of ECs is found in lakes and rivers and monitoring studies have recently been performed worldwide (Hrkal et al., 2018; Ngo et al., 2020; Tang et al., 2017). Fairbairn et al. (2016) documented that concentrations and loading of ECs in rivers are strongly related to land use, season, and transport pathways. Hosseini et al. (2013) stated that a precise estimation of streamflow and velocity is essential to properly predict PPCP concentrations in rivers. Furthermore, to estimate the concentration of PPCPs in rivers, the GREAT-ER (Geo-referenced Regional Exposure Assessment Tool for European Rivers) (Aldekoa et al., 2013) and PhATE (Pharmaceutical Assessment and Transport Evaluation) (Hosseini et al., 2016) models were developed. The first one is a deterministic model with a stochastic approach (Aldekoa et al., 2013), while the second model is based on the solution of mass balance equations (Hosseini et al., 2016). River plug-flow modelling was applied by Osorio et al. (2012) to estimate the decay constant k for a list of selected pharmacologically active compounds (PhACs) in Mediterranean rivers. By using this model, it was found that the variation load of the investigated compounds is connected to the average load discharged upstream, and the obtained results identify it as a useful method for management purposes at the basin or water-body scale. In a more recent study, Diamantini & Bellin (2018) proposed an analytical model, based on solving the ADRE, to investigate the transport of five pharmaceutical compounds discharged in surface water by Wastewater Treatment Plants (WWTPs). This modelling approach, which takes into consideration fluctuations of touristic presence and seasonality of streamflow in alpine catchments, was able to show temporal and spatial patterns of PPCPs in surface water. Overall, countries that derive drinking water from surface water tend to observe higher concentrations of PPCPs in drinking water in comparison to groundwater sources (Aus der Beek et al., 2016), highlighting the importance of appropriately investigating the behaviour and transport of these compounds in water bodies. Despite the strong advancement of knowledge on ECs in recent years and the development of new analytical solutions and models, the understanding of the fate and transport of many ECs in the aquatic environment remains inadequate (Fairbairn et al., 2016). Therefore, modelling the transport of ECs in surface water remains challenging, highlighting the importance of the boDEREC-CE findings.

5.2. Modelling of PPCPs in Aquifers

The presence of PPCPs in aquifers was observed later than in surface water, because most of the time they are detected at extremely low concentrations, and mainly at the discharge of WWTPs (Sanchez-Vila, Jurado, Folch, Carrera, & Fern, 2015). However, a larger number of pollutants are detected in groundwater (Tang et al., 2017), although, in general, the concentration values are lower than in surface water (Sanchez-Vila et al., 2015). To detect and establish the quantification strategies for ECs in aquifers, several analytical methods have been developed (Agüera et al., 2013; Rasheed, Bilal, Nabeel, Adeel, & Iqbal, 2019). Nham et al. (2015) applied a one-dimensional flow and reactive transport model relying upon data collected during field-scale experiments to simulate the transport of sixteen organic contaminants during soil aquifer treatment. Moreover, EC release scenarios may be assessed by using parametrised models and catchment-scale transport. Henzler et al. (2014) applied 2D numerical flow and transport models (i.e., MODFLOW and MT3DMS) to investigate the fate and transport of organic compounds during riverbank filtration. It was observed that three out of twelve compounds show a conservative behaviour, while the remaining nine, including for example carbamazepine, diclofenac, and sulfamethoxazole, also show degradation and sorption. Even though certain analytical solutions and models have been set up to investigate the fate and transport of PPCPs in groundwater, a knowledge gap still exists and the boDEREC-CE project is aimed at filling this gap.

5.3. Modelling of Emerging Contaminants – Model Application

This section summarises the main activities and results of the modelling of emerging contaminants within the scope of the boDEREC-CE project.

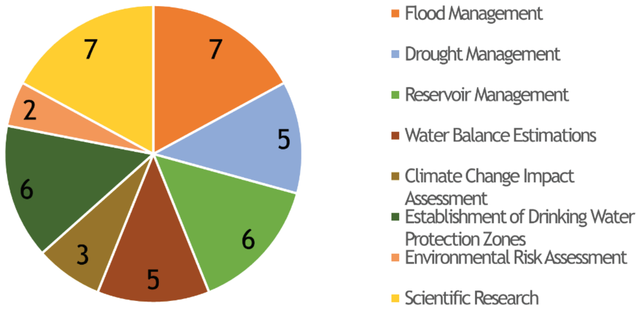
The first objective was to review existing country-specific frameworks for model applications of water management systems at a transnational scale. Another objective was to engage stakeholders, to collect their experiences and needs related to modelling tools, and to develop modePROCON, a model-based decision-making tool for emerging contaminants. The standardised training procedure for modePROCON was implemented through a Massive Open Online Course, as well as through modePROCON showcasing for groundwater, surface water and karst water pilot sites. The final goal was to set up hydrological and transport models for each pilot area.

5.3.1. Peer Review of Modelling Activities in Water Management Systems

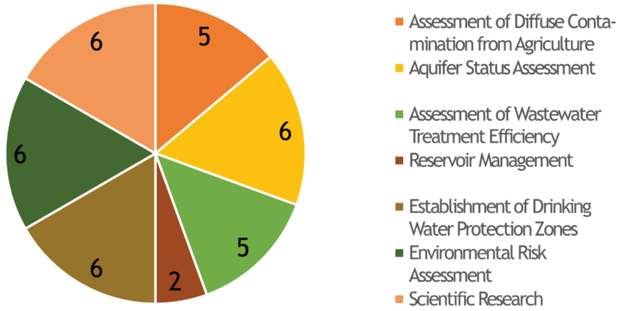
To gain a transnational overview of existing country-specific frameworks for model applications in water management systems, an analysis was performed to understand how and where hydrological models are applied in the countries involved in the boDEREC-CE project. In recent years, the use of models to analyse and predict the quantity and quality of water resources has become more applicable (Loucks & van Beek, 2017). However, the development differs between Central European countries, not only concerning the general application of models but also in terms of which models are applied. Moreover, while some European countries already see the application of models as a good practice in attempting to address and answer a variety of questions related to environmental assessments, their implementation within legal frameworks can still be considered a grey area. The main findings of a country-specific legislation analysis point to a rather sparse legislative framework for the application of hydrological models. Most of the existing national regulations linked to EU laws, in particular the Water Framework Directive, indirectly require the application of hydrological models. Such legislation requires the use of hydrological models in the management of river basins, such as for assessing environmental risks, aquifer status, and for managing and controlling floods. However, the use of hydrologic models is rarely compulsory.

Figures 5.1 a-b show an overview of the purposes for which hydrologic models are commonly applied in the countries contributing to the boDEREC-CE in terms of water quantity and quality. Finally, Figure 5.1 c gives an overview of the institutions, both private and public, which apply hydrological models in the boDEREC-CE countries.

(a) **For which purposes, in terms of water quantity, are hydrological models used in the countries involved in boDEREC-CE?**



(b) **For which purposes, in terms of water quality, are hydrological models used in the countries involved in boDEREC-CE?**



(c) **Who applies hydrological models for the mentioned purposes?**

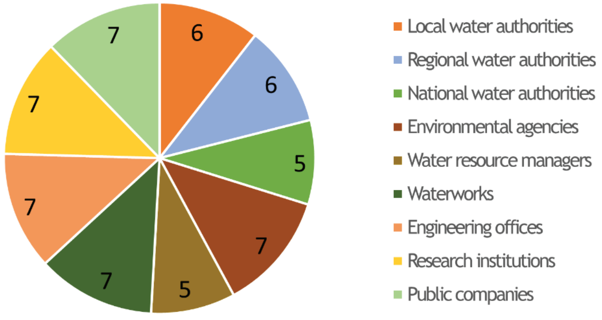


Figure 5.1 (a-b) Overview of the purposes for which hydrological models are commonly applied in the boDEREC-CE countries in terms of water quantity and quality. (c) Institutions of both private and public nature using hydrological models in the boDEREC-CE countries. The numbers in the pie chart correspond to the number of partner countries which a particular issue relates to.

5.3.2. Identification of Needs, Elaboration of Solutions and Capacity Building

National stakeholder workshops were performed to establish a strong stakeholder engagement, to communicate the advantages and disadvantages of different modelling tools, and to exchange experiences and needs for the application of water resources management models. Furthermore, in order to ensure high-quality results, a continuous feedback procedure was established, and capacity-building training courses were conducted. In the first series of national stakeholder workshops, three main topics were addressed by all countries to ensure comparable results at the transnational level:

1. Challenges and concerns in relation to emerging contaminants in the daily operations of stakeholders.
2. Experiences gained and solutions found when dealing with emerging contaminants.
3. Helpful tools to improve stakeholders' work.

82 entities were represented in the national start-up stakeholder workshops. Scientific or research institutions were mainly represented by universities' faculty members and staff members of private research institutes and laboratories. Public entities comprised governmental organisations (GOs), national and regional authorities, and public/governmental service providers. Finally, private stakeholder groups in water management were mainly private water suppliers, waterworks, and environmental NGOs. Although the total number of participants varied between the national start-up stakeholder workshops, the distribution between the sectors was rather equal. In all workshops, intersectional, interdisciplinary groups of stakeholders from various backgrounds shared their experiences and knowledge, which allows the boDEREC-CE partners to draw valuable conclusions in the light of developing the modePROCON decision-support tool. Table 5.1 shows an overview of the discussion results concerning the three topics covered during national workshops.

Table 5.1 Transnational summary of challenges and concerns when dealing with ECs (Topic 1), of experiences gained and solutions found when dealing with ECs (Topic 2) and summary of helpful tools that could improve stakeholders' daily work (Topic 3). ☑ indicates that at least one of the stakeholders participating in the workshop indicated that the statement is true or has experience in the specific field.

	Topic 1	Topic 2				
Country	ECs perceived as problematic	Lack of knowledge of ECs	Public aware of ECs	Encounter ECs in daily work	Experience in ECs detection	Experience in ECs treatment
AT	☑	-	☑	☑	☑	-
HR	☑	☑	-	little	-	-
CZ		☑	☑	☑	☑	-
DE	☑	-	☑	☑	☑	☑
IT	N/A	N/A	N/A			
PL	☑	☑	N/A	little	little	-
SI	☑	-	N/A	☑	☑	-

	Topic 3					
	Monitoring Data	Ecotoxicological Data	Modelling	Regulations	Informational Campaigns	Decision-support tool
AT	☑	☑	☑	☑	-	☑
HR	☑	N/A	N/A	☑	☑	N/A
CZ	☑	☑	☑	N/A	☑	☑
DE	☑	☑	☑	☑	-	☑
IT	☑	☑	☑	N/A	-	☑
PL	☑	☑	☑	☑	☑	N/A
SI	☑	☑	☑	☑	☑	☑

The development of modePROCON as a model-based decision-making tool for emerging contaminants and the establishment of an online training course for modePROCON are the fundamental results of modelling activities conducted in the scope of the boDEREC-CE project. modePROCON is described in more detail in section 5.4. A Massive Open Online Course was developed to train the users for modePROCON. The course consists of nine tutorials that are available online.

5.3.3. Proof-f-Concept: Model Applications for Selected Pilot Actions

To investigate the fate of PPCPs, hydrological flow and transport models were developed at all boDEREC-CE pilot sites. Pilot sites were divided into three clusters based on the type of water resources: 1) surface water, 2) groundwater, and 3) karst aquifers. For modelling, available existing data, as well as data collected and analysed within the boDEREC-CE project were used. In the first step, a flow model was developed for each pilot site. In the second step, transport models were developed by considering the PPCPs of most concern in the area. Table 5.2 gives an overview of the modelling tools applied by the project partners.

Table 5.2 Modelling tools applied by the boDEREC-CE countries for setting up the hydrological and transport model

Pilot actions in boDEREC-CE	Hydrological models	Transport model
DRESDEN-HOSTERWITZ, DE[1]	Flow model set-up with MODFLOW- OWHM	Transport model set-up with MT3DMS
PO RIVER BASIN, IT[1]	Flood numerical modelling system used includes hydrological-hydraulic chain HEC-HMS-RAS	HEC-RAS 5.07 - Water quality module
KOZŁOWA GÓRA, PL[1]	Hydrological model set-up with SWAT (Soil and Water Assessment Tool; for ArcGIS) integrated with AEM3D (the reservoir model)	A conceptual transport model* was set-up
NEUFAHRN MUNCHEN, DE[2]	Hydrological model set-up with MODFLOW-2005	1D and 2D analytical models according to Batu (2006)
LJUBLJANSKO KOTLINA, SL[2]	Groundwater model set-up with Visual ModFlow Professional, version 4.2.0.153, which used ModFlow 2000 (USGS)	HYDRUS-1D program solves the advection-dispersion equation for solute transport
KÁRANÝ-JIZERA, CZ[2]	DRUtES used as modelling tool for solving the water flow governing equations	DRUtES used as modelling tool for solving the solute transport governing equations
WAIDHOFEN/YBBS, AUS[3]	Hydrological model set-up with semi-distributed model LuKARS (Land use change modelling in KARSt systems)	A conceptual transport model* was set-up
JADRO CATCHMENT, CRO[3]	The adaptable modelling platform applied for the hydrological model is KarstMod	A conceptual transport model* was set-up

[1] SURFACE WATER PILOT SITES; [2] GROUNDWATER PILOT SITES; [3] KARST AQUIFER PILOT SITES

***A conceptual model represents hydrological systems by using physical concepts and simplified mathematical conceptualisation of the systems.**

Since each pilot area has different natural characteristics, available and measured data, and frameworks for water extraction, the tools used for modelling differ widely. The results obtained in all pilot sites within the boDEREC-CE project, concerning both the hydrological and transports models, are described in detail in section 5.5.

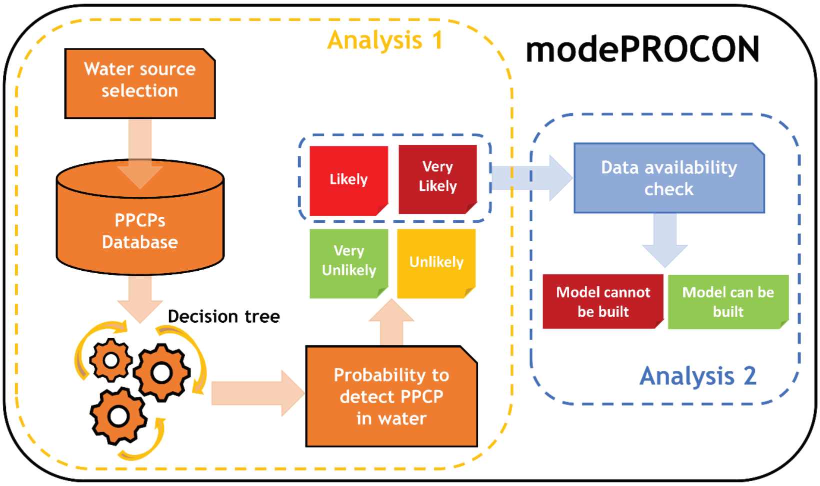


Figure 5.2 modePROCON design. The yellow dashed box includes the steps of the first analysis, while the blue dashed box indicates the second evaluation stage.

5.4. modePROCON - Model-Based Decision-Making Tool for ECs

Decision support system (DSS) tools are of great importance in the field of water resources management (Rianna and Rizzo, 2019; Rumbaur et al., 2013). Specifically, in terms of emerging contaminants, there is a knowledge gap regarding the potential risks they may carry in drinking water and wastewater systems (Becker and Stefanakis, 2016; Richmond et al., 2017). For this reason, decision-making tools are fundamental in helping water managers and stakeholder groups to face this issue. One of the main objectives of boDEREC-CE is to involve stakeholders in working on strategies, action plans, and tools developed during the project to increase the quality of drinking water. Therefore, the active participation of stakeholders within the project underlines the importance of developing modePROCON as a tool to support decision-making processes in water management systems regarding PPCPs. In many cases, water managers, public authorities, and stakeholder groups do not have sufficient data to properly investigate the fate and transport of PPCPs in the environment. Consequently, they also encounter problems in evaluating potential risks to people's health and the environment.

modePROCON is a model-based decision-making tool for emerging contaminants developed to support the potential users in decision-making processes by evaluating a series of data required to perform a transport model for PPCPs detected in water sources. modePROCON has a Graphical User Interface (GUI) developed in Python and is a standalone application, easily accessible to users.

The tool uses information gathered both from monitoring activities (sampling and analysing of water samples) at all pilot sites, integrated into a catalogue of 115 PPCPs, hormones, and antibiotics analysed within the project; and from workshops organised within the boDEREC-CE project through communication with different stakeholders. modePROCON consists of two main analyses that allow the user to identify whether a transport modelling study is suggested and feasible based on data availability. The two analyses are listed below and the tool design is shown in Figure 2:

1. **Qualitative probability to detect a PPCP in water sources (Analysis 1):** this preliminary phase is built to define the likelihood of a compound being in surface water, groundwater, and karst aquifer. At the end of this stage, the tool classifies the selected PPCPs into four main categories, depending upon the PPCP having a low or very low probability of being found in water, versus high or very high probability.
2. **Data availability check for model set up (Analysis 2):** this phase consists of an evaluation of a series of input data required to set up a surface water, groundwater, or karst aquifer model. The data availability check is specific for each area where a PPCP is detected. If all input data necessary to implement both a conceptual and/or a numerical model are available, the tool will suggest that a modelling study is feasible. On the contrary, if only one input is unknown, the reason why modelling is not possible shall be explained, together with possible solutions to obtain the missing input.

5.5. Hydrological and Transport Models of Pilot Sites

The following paragraphs give an overview of the hydrological and transport models developed by the project partners.

5.5.1. Káraný-Jizera, Czech Republic

5.5.1.1. Hydrological Model

The hydrological model selected for the pilot area Káraný-Jizera in the Czech Republic is DRUtES (Kuraz & Mayer, 2008). The tool is an open-source code that has been comprehensively developed since the late 2000s (Kuraz et al, 2013; Kuraz et al, 2014; Kuraz et al, 2015; Kuraz et al, 2019). The water flow in variably saturated media is described by coupling hydrodynamic and thermodynamic equations. Dirichlet boundary conditions are used since the study area is bounded to the south by the Elbe River, to the west by the Jizera River, and to the east by the Mlynařice River. The flow domain was considered here as a two-dimensional cross-section between the Jizera River and the system of pumping wells. The flow domain will cover a saturated and an unsaturated zone and will be described by the Richards (1931) equation with groundwater modification by Neuman (1973). The groundwater table for two distinct conditions (period of drought and period of intense rainfall) is depicted in Figure 5.3.

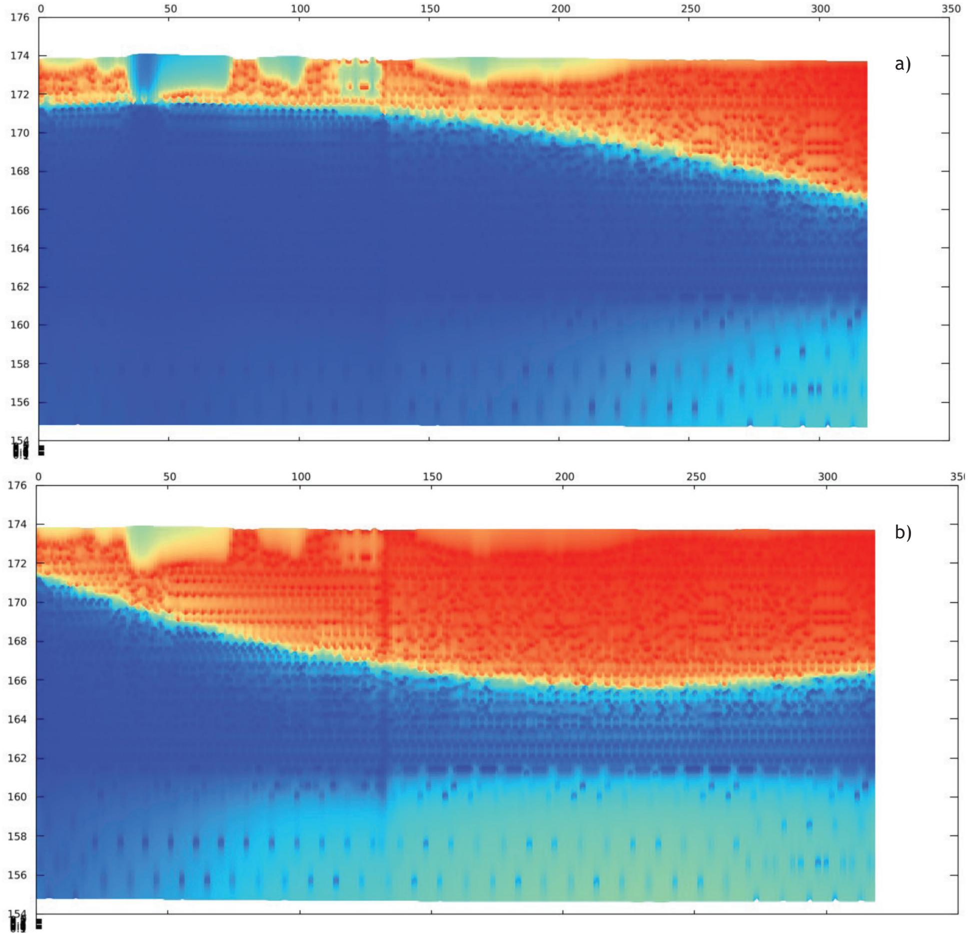


Figure 5.3 (a) Groundwater table during wet periods. (b) Groundwater table during periods of drought.

5.5.1.2. Transport Model

In the pilot area of Káraný-Jizera in the Czech Republic, one hundred fifty pharmaceuticals were periodically analysed. However, significant concentrations both in surface and groundwater were detected just for two compounds:

- Oxypurinol: an active metabolite of allopurinol that is cleared renally (Stocker et al., 2012).
- Acesulfame-K: a synthetic calorie-free sugar substitute (artificial sweetener).

The DRUtES code (Kuraz & Mayer, 2008) was used for solving the solute transport equation. Monitoring data from surface water were used as a boundary condition for the groundwater model. Transport modelling for the surface water system was not required. Figure 5.4 shows the results of Acesulfame-K simulated concentration in the pumping well compared to the measured concentrations.

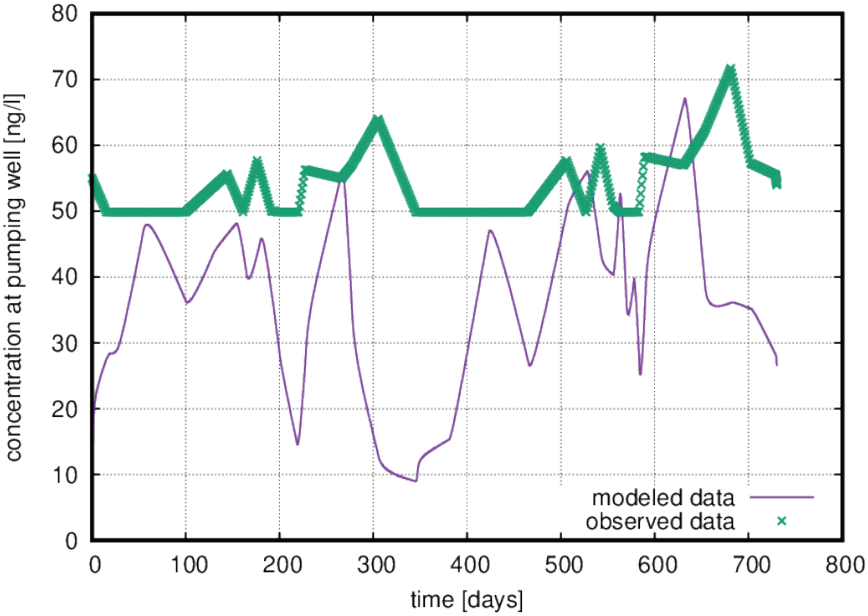


Figure 5.4 Simulated concentration of Acesulfame - K in pumping well over time and observed data.

The model was able to describe contaminant transport in the aquifer under unsteady conditions governed by meteorological conditions and by the changing concentrations in the Jizera River. However, due to the limited monitoring data, the simulated concentration reaches a similar magnitude to the measured data, but the trend is not always maintained.

5.5.2. Dresden-Hosterwitz, Germany

5.5.2.1. Hydrological Model

The hydrological numerical model for the riverbank filtration and managed aquifer recharge site Dresden-Hosterwitz in Germany is set up using MODFLOW-OWHM (Harbaugh, 2005). MODFLOW-OWHM is a modular three-dimensional finite-difference groundwater model published by the U.S. Geological Survey (Chiang and Kinzelbach, 2003). The Elbe River flows in the northeast of the study area, while the groundwater follows the topography of the valley recharging the river. In the numerical model, groundwater levels are used as boundary conditions to the west and east of the study area. The Elbe River is simulated with the RIV-Package, which is a specific package of MODFLOW for investigating the interaction between surface water and groundwater (Chiang, 2005).

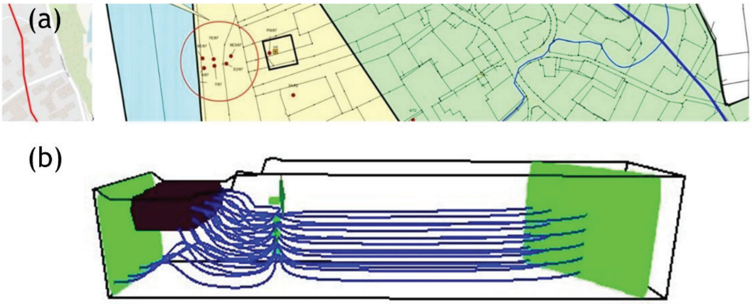


Figure 5.5 (a) Top-view of the model area. The red dots indicate the observation wells. The production well is depicted inside the black rectangle. The red line illustrates the piezometric contour line 107 m NHN and the blue line is the piezometric contour line 108 m NHN. (b) Flow-path lines marked in blue from the River Elbe (shown in brown) towards the well 145, and groundwater from the landside and the opposite side of the river (fixed heads, shown in green).

The model for the homogenous, isotropic aquifer and average leakage factor for the riverbed is calibrated using a piezometer level measured at an observation well located between the river and the well 145 (Fig. 5.5 a). The discrepancy between the simulated and observed water levels is below the maximum calibration target (i.e. 0.5 m), indicating a satisfactory accuracy of the model. Figure 5.5 b shows the resultant flow-path lines.

Figure 5.5 illustrates the water sources recharge the production well 145. These are riverbank filtrate from the Elbe River, land-side groundwater from the eastern boundary, and a small quantity of groundwater flowing below the riverbed from the opposite side of the river. These findings are in accordance with those made by Paufler et al. (2018) for a riverbank filtration site located downstream on the opposite side of the Elbe River.

5.5.2.2. Transport Model

In the riverbank filtration and managed aquifer recharge site Dresden-Hosterwitz, two PPCPs were selected to be modelled in order to investigate how the advection and dispersion processes represent the evolution of the compounds at the sampling point "Well Niederpoyritz":

- Acesulfame-K: is an artificial sweetener often marketed under the trade names Sunett and Sweet One and also known as E950 (UK Food Standard Agency, 2013).
- 4-formylaminoantipyrine: is an excreted metabolite of aminophenazone, a medication with analgesic, anti-inflammatory, and antipyretic effects (medchemexpress.com, 2020).

A backward particle tracking using MODPATH 6 code by USGS (Pollock, 2012) was used for computing the flow paths and the travel time. In addition, a 2D model, representing a cross-section of the groundwater flow system at Niederpoyritz, was used to simulate solute transport based on the solution of the advection-dispersion equation. Figures 5.6 a-b show the model results.

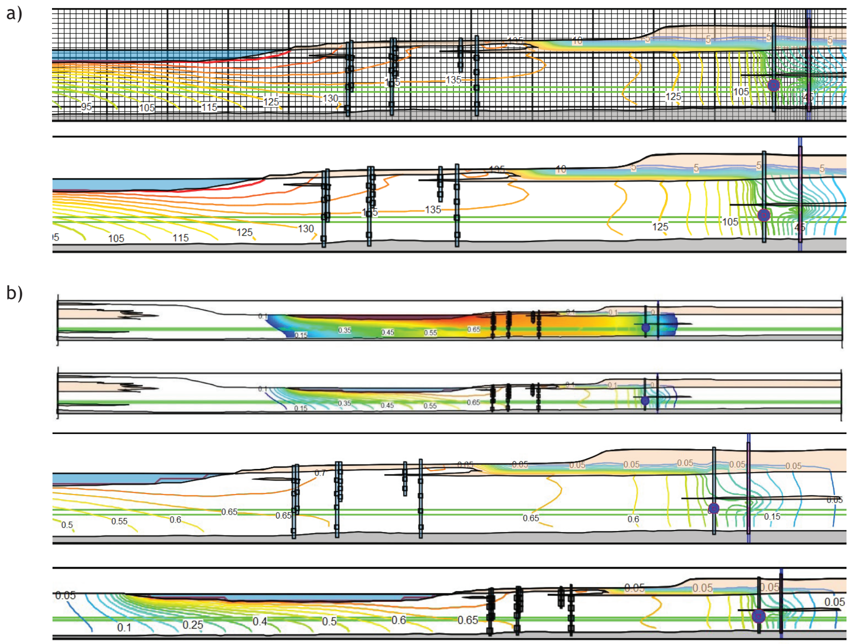


Figure 5.6 (a) Simulation results of Acesulfame transport from the Elbe River to the production well. The data is presented in ng/L. (b) Simulation results of 4-formylaminoantipyrine transport from the Elbe River to the production well. The data is presented in µg/L.

The results for acesulfame show an overestimation of the concentration in the production well. This can be due to 1) the fact that biodegradation processes have not been considered, 2) higher concentration in the Elbe River when the bank filtrate is directed to the production well, or 3) the assumption of concentration equal to zero in land-side groundwater. Moreover, the variation in concentration values is due to the observed and simulated changes in the water river level (Fig. 5.6 a). In the case of 4-formylaminoantipyrine, the simulated concentration is very close to the measured one (Fig. 5.6 b).

5.5.3. Jadro and Žrnovnica Springs Catchment, Croatia

5.5.3.1. Hydrological Model

For the Jadro and Žrnovnica springs catchment pilot area in Croatia, the adaptable modelling platform KarstMod (Mazzilli et al., 2019) is applied to set up the hydrological model. As literature shows, KarstMod can reproduce the structure of most conceptual lumped models of karst systems. This tool is aimed at simulating the rainfall-discharge relationship of karst springs at a daily or hourly scale.

The Jadro and Žrnovnica aquifer model consists of three interconnected compartments: one representing the epikarst, one representing the conduit flow, and the last one characterising the matrix. Figure 5.7 shows the simulated (Q_s) and observed (Q_{obs}) discharge time series for the warm-up, calibration, and validation periods.

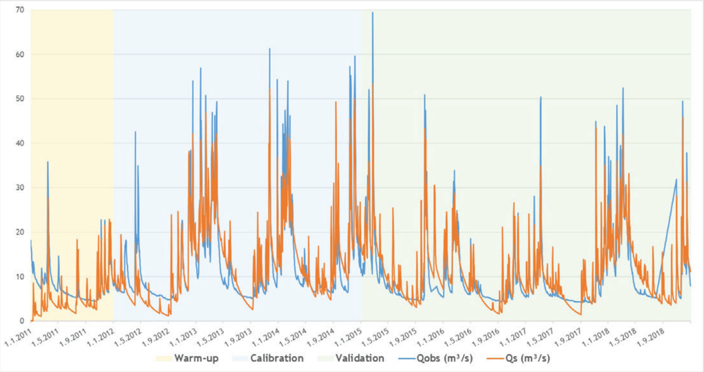


Figure 5.7 Model results: Observed and simulated discharge for the warm-up, calibration, and validation periods.

The dynamic of the discharge time series is better simulated during the calibration and validation periods, even though the high-flow peaks during winter and spring months are not accurately replicated. Conversely, simulated values for the warm-up period are significantly lower than the observed ones.

A common challenge in karst modelling is the identification of the model parameters (Hartmann, Barberá, & Andreo, 2017). For the Jadro and Žrnovnica spring catchment case study, seven parameters representing the main hydrogeological processes have been chosen for the calibration procedure in KarstMod. The model is applied to investigate the groundwater flow in the dynamic Dinaric karst aquifer, relying on precipitation and spring discharge time series. Finally, the model highlights the matrix-conduits flow exchanges, and the reservoir storage capacity.

5.5.3.2. Transport Model

For the Jadro and Žrnovnica springs catchment pilot area, four PPCPs – measured in more than one sampling campaign were selected to be modelled:

- **1H-benzotriazole:** 1H-benzotriazole is a xenobiotic contaminant of emerging concern due to polarity, recalcitrance, and widespread use (industrial application as anticorrosive in metalworking, tar remover, and protective coating in the construction industry, water-cooling systems and dry-cleaning equipment, cleaning, and washing agents). Benzotriazoles are bicyclic heterocyclic compounds containing three nitrogen atoms and a fused benzene ring. 1H-Benzotriazole is the reference compound for the group.
- **DEET:** is an active ingredient in many repellent products (EPA).
- **Ibuprofen:** is the third most popular, highly prescribed, and most sold over-the-counter medicine in the world according to Marchlewicz et al. (2015), with therapeutic doses ranging from 600 to 1200 mg/day (Chopra and Kumar, 2020).
- **Metformin:** is an antidiabetic and antihyperglycemic medication, used for the treatment of type II diabetes.

The model explaining the transport and fate of PPCPs in the karst aquifer in the Jadro and Žrnovnica springs catchment was made on a conceptual basis, due to the hydrogeological complexity and heterogeneous properties of this insufficiently explored aquifer and data scarcity. The small number of identified ECs and their limited temporal resolution (a singular event for the majority of compounds) represents a hindrance for modelling their transport and behaviour in complex environments such as karst aquifers. The Cetina River stood out with the highest average concentrations of the detected compounds, while the Jadro spring had the lowest ones, as shown in Figure 5.8.

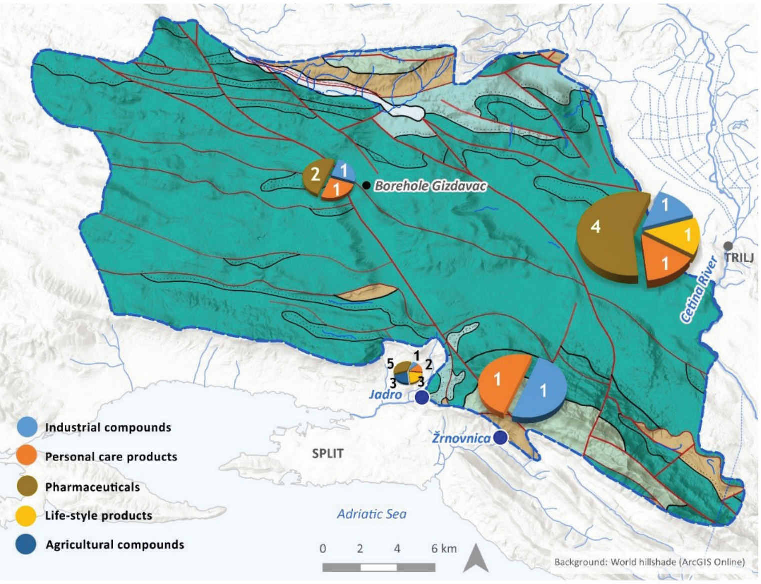


Figure 5.8 Spatial distribution of the main ECs in the Jadro and Žrnovnica catchment. The diagrams' size represents the average concentration of the detected ECs with the number of detected compounds per group.

5.5.4. Waidhofen a/d Ybbs, Austria

5.5.4.1. Hydrological Model

The hydrological model for the pilot area of Waidhofen a/d Ybbs in Austria is set up using the semi-distributed LuKARS (Land Use Change Modelling in KARSt Systems) introduced by Bittner et al., 2018. The model is implemented in the QGIS plugin FREEWAT (Bittner et al., 2020) and applied to the catchment area of the Kerschbaum spring. By using this tool, it is possible to investigate the land-use change impact in karst systems (Bittner et al., 2018).

The catchment is divided into four hydrotopes, which are distinctive landscape units that show homogenous hydrological properties. Specifically, one hydrotope is defined for the quarry land use area, while the remaining three describe different forest types. The daily precipitation, discharge, air temperature, and snow depth are used as input data for setting up the hydrological model, together with spatial data such as land use, orthophoto, soil texture, and soil thickness. The snow and hydrograph models are calibrated and validated by considering two different periods. Figure 5.9 shows the results of the calibrated and validated model.

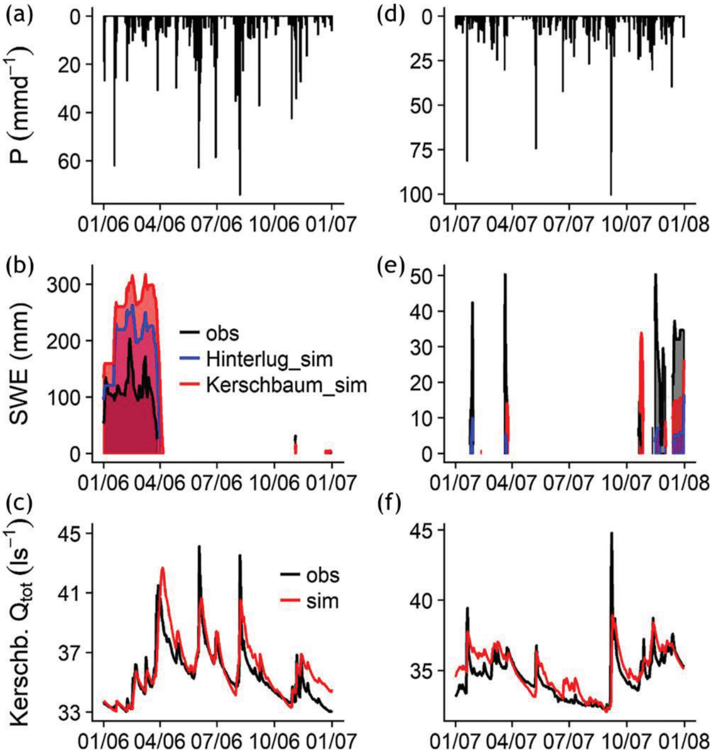


Figure 5.9 (a-b-c) Calibration results: precipitation (P), transformed snow water equivalent (SWE) time series, and comparison between the observed (obs) and simulated (sim) discharge time series (Q_{tot}) for the Kerschbaum spring (Bittner et al., 2018). (d-e-f) Validation results: precipitation (P), transformed snow water equivalent (SWE) time series, and comparison between the observed (obs) and simulated (sim) discharge time series (Q_{tot}) for the Kerschbaum spring (Bittner et al., 2018).

The comparison between the experimental observations and the simulated spring discharge (Q_{tot}) shows an accurate model for the most part. The model can adequately reproduce the total discharge of the catchment, even if some peaks are either over- or underestimated. This finding is also confirmed by the assessment of the model performance obtained by computing the Nash-Sutcliff Efficiency and the Mean Absolute Error [l/s] for both calibration and validation periods. The snow model highlights an overestimation of the snow water equivalent during the calibration period and an underestimation of the snow water equivalent during the validation period. However, it well replicates the timing of snow retentions and snowmelt during both periods (Fig. 5.9 b-e) (Bittner et al. 2018).

5.5.4.2. Transport Model

Due to the limited information on the Waidhofen a/d Ybbs monitoring site, a conceptual model was developed to describe the transport of the targeted substances. The PPCPs considered in the modelling study are:

- DEET: is used as the active component for various insect repellent products (Aronson et al., 2012; Weeks et al., 2012).
- Progesterone and Testosterone: are usually part of a bigger group of substances, steroid hormones. They are usually also included in the list of endocrine disruptor substances.
- Caffeine: is a neuro, cardiac and respiratory stimulant and used as well as a diuretic for humans (Korekar et al., 2020; Moore et al., 2008). It is found in certain medicines and in certain food and beverages (Korekar et al., 2020; Moore et al., 2008; Rodríguez-Gil et al., 2018).
- Paraxanthine: is considered the main metabolite of caffeine.
- PFOS: Perfluoro octane sulfonate is part of the group known as perfluorinated compounds (PFCs), used as industrial chemicals for the industrial production of consumer goods, and known to be persistent, and bioaccumulative (Cordner et al., 2019; Houde et al., 2011).
- Simvastatin: is a cholesterol and lipid-lowering drug (Tete et al., 2020).

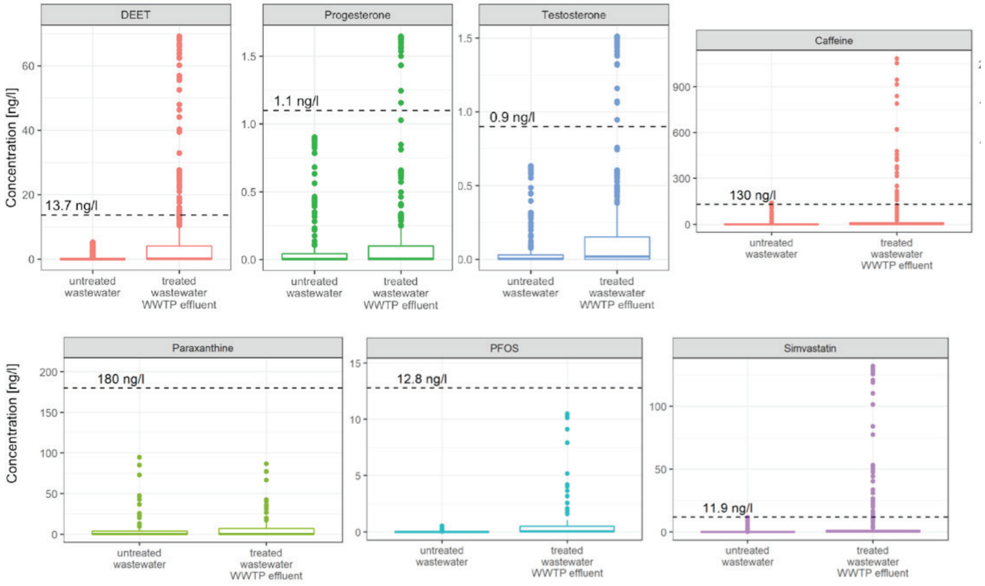


Figure 5.10 Estimated concentrations in the spring from scenario analysis. The black dashed horizontal lines represent the observed concentrations in the spring.

The transport model considers the attenuation of the concentration of contaminants during the transport from the source to the Kerschbaum spring, through dilution, mixing with not contaminated water, and natural degradation. The conceptual model is designed to compare two possible sources of contamination: 1) untreated wastewater and/or 2) wastewater treatment plant (WWTP) effluents. For each contamination pathway a big number of scenarios that consider different hydrological conditions and also the range of substance properties are simulated. Figure 5.10 shows the results for the scenario analysis of the two possible contamination pathways in the Kerschbaum spring.

For the majority of the investigated scenarios for all PPCPs, the measured concentrations in the spring are not reached. Therefore, only extreme values, represented by the dots of the boxplots, reach or exceed these values. For DEET, Progesterone and Testosterone only values from the scenario of contamination from WWTP-effluents reach or exceed the observed concentrations in the Kerschbaum spring. In the case of the substances Paraxanthine and PFOS, none of the considered cases in both contamination sources can explain the observed concentrations in the spring. Finally, for Caffeine and Simvastatin, in both contamination scenarios, the conceptual model can explain the observed concentrations in the spring.

5.5.5. Kozłowa Góra, Poland

5.5.5.1. Hydrological Model

The hydrological model for the Kozłowa Góra pilot area in Poland is developed using **SWAT** (Soil and Water Assessment Tool for ArcGIS) (Neitsch et al., 2005) integrated with **AEM3D** for the reservoir model (Hodges and Dallimore, 2019). SWAT is applied to predict the influence of land management practices and climate change on water, sediment, and the nutrients cycle in large complex watersheds. On the other hand, AEM3D is suitable to simulate velocity, temperature, salinity, nutrients, and biogeochemistry in surface waters, and for performing transport simulations under different flow conditions.

For the case study of Kozłowa Góra, SWAT is used to perform the hydrological investigation, while AEM3D is applied to simulate water flow velocity in the reservoir, retention time, water temperature, nutrients concentration, virtual tracer, and biological compounds (IOŚ-PIB-JARS, 2018, Czekaj J. et. al., 2018). The model for Kozłowa Góra consists of seventeen sub-basins, based on hydrographic division, where the creeks' network is simplified to one stream for each sub-basin. Figure 5.11 shows the results of the SWAT and AEM3D models. Overall, both mathematical models can reproduce the experimental observations.

The model results show that the percentage of particular water balance components, such as evapotranspiration, surface runoff, and percolation, differ in time. Moreover, SWAT results highlight high spatial variability among the eleven sub-basins considered in the area concerning outflow rate, evapotranspiration rate, percolation rate, and runoff values (Figure 5.11 a). Finally, it was found that the parameters which influence the model outputs more are the hydraulic conductivity, the depth of water in the shallow aquifer, the effective hydraulic conductivity of the river channels, and the Manning coefficient for overland flow. By applying AEM3D, it was observed that one of the most important outputs for the reservoir model is the retention time (Figure 5.11 b). In the investigated area, the highest retention time (average 315 days) is highlighted considering the lowest inflow into the reservoir. Thus, the lowest retention time (average 34 days) is obtained during the highest inflow rate.

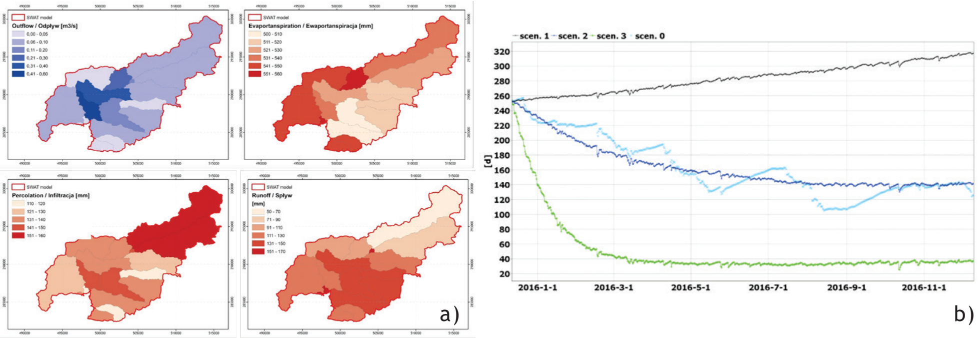


Figure 5.11 (a) SWAT model results: Spatial distribution of the average values of the water balance components in the period from 2012 to 2017. (b) AEM3D model results: Retention time of water outflowing from the reservoir by considering four scenarios. Scenario 0: inflows rate calculated with SWAT model, scenario 1: low flow rate in inflows, scenario 2: average flow rate in inflows, scenario 3: high flow rate in inflows.

5.5.5.2. Transport Model

For the Kozłowa Góra pilot area, five compounds were selected for the development of the transport model. The choice was based on the monitoring results and the modelling approach:

- PFOS: belongs to the group of perfluoroalkyl acids (PFAAs) which are anthropogenic substances that do not occur naturally in the environment (EPA, 2017).
- DEET: is a chemical commonly used as the active ingredient in many insect repellent products.
- Carbamazepine: is often used as an anticonvulsant drug for the treatment of epilepsy (Beltran A. et al., 2009, Asgari S. et al., 2017, Rezaei Kahkha, M.R, 2018).

- Oxypurinol: is an active metabolite of the commonly prescribed anti-gout agent - allopurinol (Burke, V. et al., 2018).
- Acesulfame-K: is widely used as an artificial sweetener in food, personal care products, and pharmaceutical preparations (Castronovo S. et al., 2016).

Due to limited information on PPCP occurrences in the Kozłowa Góra pilot area, it was decided to conceptualise the transport of these compounds in water. The conceptual model was set up as a graphic representation of the processes observed within the catchment, relying on spatial data and referring to the results of the SWAT model. The transport of each substance was described by considering different processes determining concentrations, different sources of selected PPCPs, land use, and the outcomes of the isotope analysis. Figure 5.12 shows the results of the conceptual model for DEET, carbamazepine, acesulfame-k, oxypurinol, and PFOS.

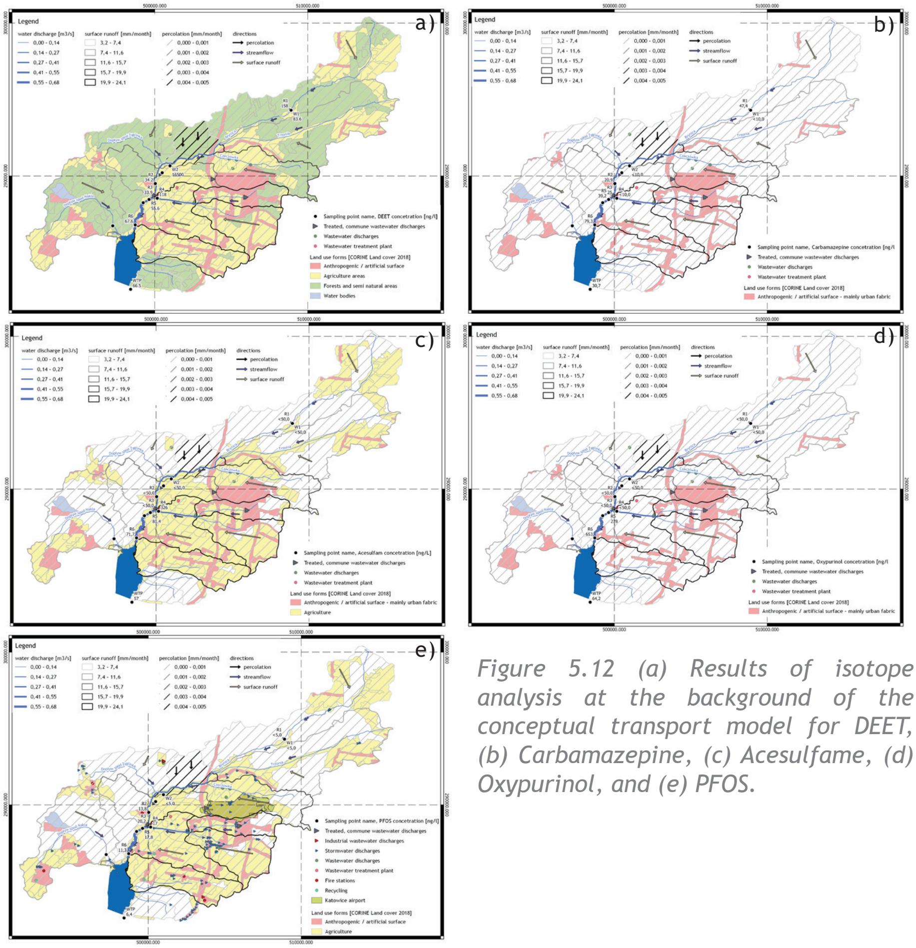


Figure 5.12 (a) Results of isotope analysis at the background of the conceptual transport model for DEET, (b) Carbamazepine, (c) Acesulfame, (d) Oxypurinol, and (e) PFOS.

Based on the analysis performed, it was possible to determine the most likely potential sources for the five PPCPs of interest. In the case of DEET, carbamazepine, acesulfame, and PFOS, runoff water from agricultural fields, urban areas, and anthropogenic fields are identified as possible sources. Moreover, in the case of DEET, forest areas may also contribute to the contamination, while carbamazepine and acesulfame wastewater discharge can be an additional possible source. For PFOS, also stormwater and industrial wastewater discharge may be considered a cause of pollution. In contrast, no certain source was identified for oxypurinol, even though it was measured at a concentration higher than the detection limit in a location impacted by pollutants of mixed origin.

5.5.6. Po River Basin, Italy

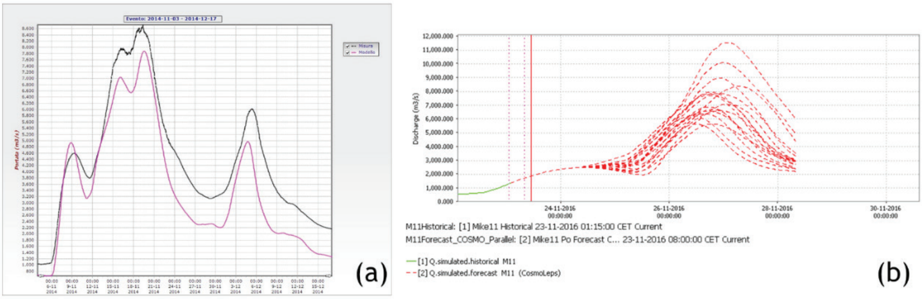
5.5.6.1. Hydrological Model

The hydrological model for the Po River Basin area in Italy is set up using FEWS (Flood Early Warning System) and DEWS (Drought Early Warning System). These systems are developed within international OGC/WMO standards and are aimed at providing capabilities and tools for hydrological modelling. FEWS/DEWS are based on pre-defined user-configurable modelling chains in which several what-if scenarios may be implemented, to simulate different possible conditions and operations, especially at water control structures (Casicci et al, 2006). The FEWS/DEWS system can be used to support water management by performing hydrological-hydraulic and water balance simulations, short-, medium- and long-range hydrological predictions, seasonal hydrological forecasts, climate change scenarios, and statistical analyses.

The used flood numerical modelling system consists of three hydrological-hydraulic chains (i.e. HEC-HMS-RAS; Mike NAM-HD; Topkapi-Sobek). Real-time and predicted data of precipitation and temperature, obtained from meteorological suites with lead times from 18 h to 120 h, are used as input data for the modelling chains. The water balance and low flow numerical modelling system consists of one hydrological-water balance chain (Topkapi-RIBASIM). Real-time and predicted data of daily precipitation and temperature, obtained from meteorological and climate suites with lead times from 15 days to 90 days, are used as input data for the modelling chain.

Figure 5.13 illustrates examples of results of the flood and water balance models obtained with the above-mentioned tools.

Figure 5.13 a shows the comparison, in the calibration phase, between the simulated discharge using the hydrological-hydraulic Topkapi-Sobek flood modelling chain and the observed discharge at Pontelagoscuro section considering a simulation time of approximately 45 days including the flood peak observed on November 19, Flood models



Water balance/low flow models

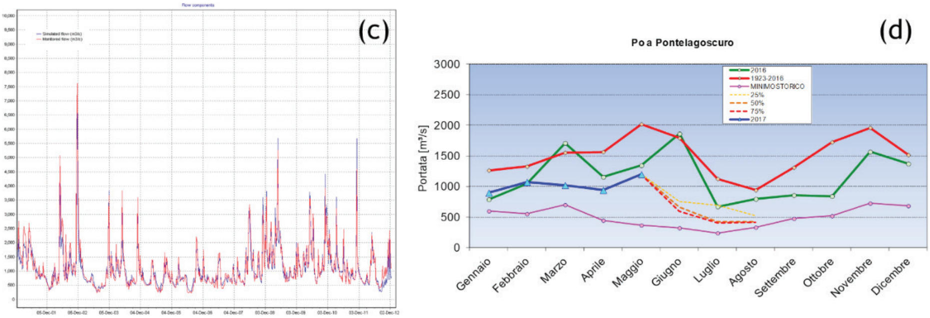


Figure 5.13 (a-b) Results of the flood model at Pontelagoscuro and Piacenza, Italy. (c-d) Results of the water balance/low flow model at Boretto and Pontelagoscuro, Italy.

2014. In this example, the dynamic of the observed discharge is well replicated by the model, even though the simulated discharge decreases more rapidly than the observed one. Figure 5.13 b illustrates an example of flood prediction at an hourly scale resulting from the COSMO-LEPS[1] -Mike NAM-HD chain considering 120 hours lead time at the Po River section of Piacenza, Italy. Figure 5.13 c shows the comparison, in the calibration phase, between the daily simulated discharge using the Topkapi-RIBASIM chain and the observed discharge at the hydrological station of Boretto located upstream of Pontelagoscuro, during the period from 2001 to 2012. The model results show a good match with the observations. Finally, Figure 5.13 d displays an example of the seasonal low flow prediction obtained with the hydrological water balance low flow Topkapi-RIBASIM chain. The predicted monthly discharges percentiles are represented by dashed red, orange, and yellow lines. The input for the chain is the ECMWF[2] seasonal forecast downscaled with a weather generator at the Po River section of Pontelagoscuro; the observed monthly discharge is depicted in blue, the historical mean and minimum monthly discharge in red and purple, and the monthly discharge measured during 2016 (previous year) in green.

[1]European Centre for Medium-Range Weather Forecasts; [2]COSMO Consortium Limited Area Ensemble Prediction System

5.5.6.2. Transport Model

In the Po River Basin area, modeling activities were mainly aimed at highlighting the role of hydrology in contaminant transport processes; three compounds were selected to be modelled:

- Iopamidol: is an X-ray contrast agent (pubchem.ncbi.nlm.nih.gov, 2020).
- Diclofenac: is a non-steroidal anti-inflammatory drug (pubchem.ncbi.nlm.nih.gov, 2020).
- Sufamethoxazole: is broad spectrum antibiotic (pubchem.ncbi.nlm.nih.gov, 2020).

HEC-RAS 5.07 free software was chosen for setting up the surface water transport model for the Po River Basin pilot area. In order to approximate the behaviour of these compounds in the river, certain assumptions were made. First of all, the release of the contaminant was assumed to be continuous. Secondly, the initial concentration was assumed constant in the whole river, and finally, the river branches were modelled as one-dimensional channels assuming that the downstream boundary conditions do not influence the mass flow in the channel.

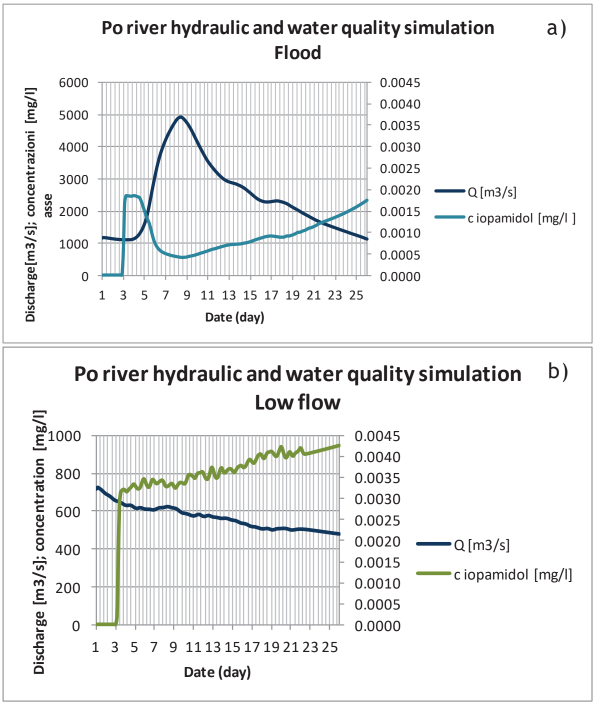


Figure 5.14 Simulated Iopamidol concentration during a flood event and low flow conditions.

In this section, the results for the transport of iopamidol are presented for a flood event and during low flow conditions and shown in Figure 5.14 a-b.

Iopamidol concentration mainly derives from 1) initial concentration and 2) mass flux propagation from the upstream boundary. Considering flood conditions (Fig. 5.14 a), the travel time of iopamidol from the upper boundary to the considered section of the Po River is about 15-18 hours. In contrast, in low flow conditions (Fig. 5.14 b), the travel time is higher, from 18-21 hours.

5.5.7. Neufahrn bei Freising, Germany

5.5.7.1. Hydrological Model

The hydrological model for the Neufahrn bei Freising pilot area in Germany is set up with MODFLOW-2005 (Harbaugh, 2005). The eastern boundary of the model is limited by the Isar River (Fig. 5.15) to consider and simulate the exchange processes that occur at the surface water – groundwater interface. The implementation of the southern and northern boundaries is based on measurements of groundwater levels in several piezometers.

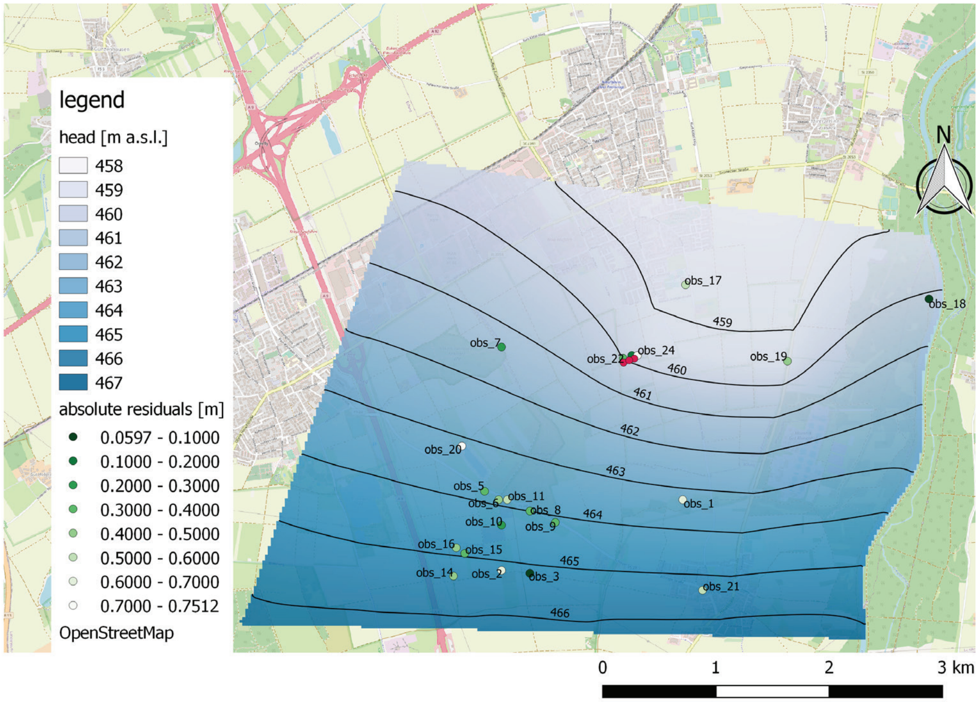


Figure 5.15 Model domain, piezometers used for model calibration, and contour lines of the groundwater table under steady flow conditions.

The western boundary represents a no-flow boundary, which means that the model assumes no transboundary fluxes. Finally, the processes occurring in the unsaturated zone, such as infiltration and evapotranspiration, are considered in the whole model domain. The model structure incorporates the three shallow wells of the water supply association Freising-Süd (Schuler et al., 1992). Figure 5.15 shows the model results under steady flow conditions.

The numerical model is calibrated with the help of twenty-four observation wells located in the study area (Fig. 5.15). Finally, to assess the model performance, the Mean Error [m], the Mean Absolute Error [m] and Root Mean Square Error [m] are used as evaluation criteria. The results highlight a positive agreement between the measured and simulated groundwater levels, leading to the conclusion that the model represents a good estimation of the hydrological conditions of the site.

5.5.7.2. Transport Model

In Neufahrn bei Freising the transport model included compounds that were detected at least two times in the groundwater during the sampling campaigns performed within the boDEREC-CE project. Thus, the PPCPs of interest were:

- Diatrizoate: an iodinated contrast agent used during X-ray (Radjenovic et al., 2013).
- Oxypurinol: an active metabolite of allopurinol that is cleared renally (Stocker et al., 2012). Moreover, the anti-gout agent allopurinol, which is widely metabolized into oxypurinol, is one of the most prescribed pharmaceuticals in Germany (Funke et al., 2015).
- DEET: an active ingredient in many repellent products (EPA).

Instead of a numerical solution of the differential transport equation, one-dimensional (1D) and two-dimensional (2D) analytical solutions were applied according to Batu (2006) to study the fate and transport of the above-listed PPCPs in the Neufahrn bei Freising pilot area. As for the 1D model, the conservative and adsorptive behaviour of diatrizoate, oxypurinol and DEET, as well as biodegradation coupled with sorption processes, were analysed. In the 2D model, sorption and biodegradation were included. The initial concentration of the compounds was assumed to be in the range of reported value in the literature of untreated wastewater. Figure 5.16 shows the 1D and 2D transport model results.

The sorption coefficients of Diatrizoate and Oxypurinol are very small, and therefore the trend concerning conservative behaviour and linear sorption is very similar, meaning that sorption does not play a major role in the transport processes. In contrast, the sorption coefficient of DEET is two orders of magnitude higher, and the arrival time to steady-state for this compound is retarded (Figures 5.16 a-b-c).

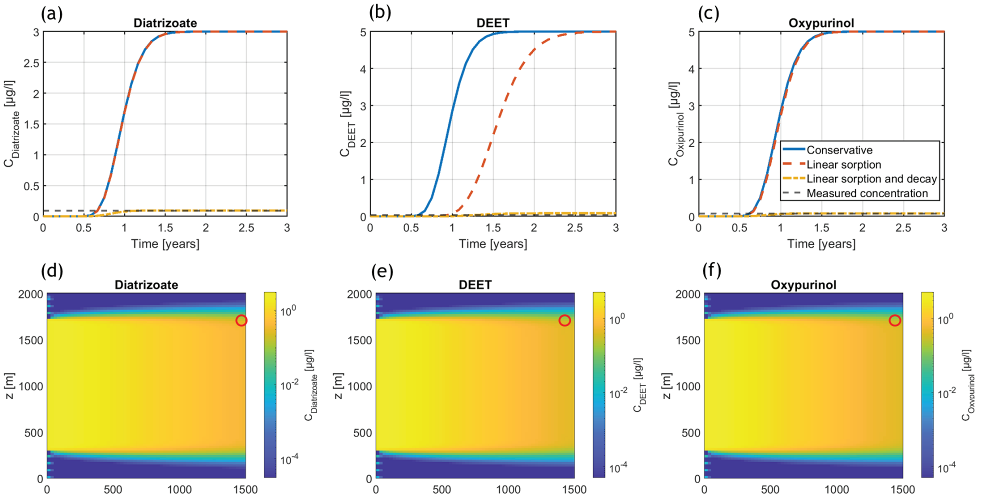


Figure 5.16 (a-b-c) 1D transport model: breakthrough curve at the wells (x = 2500 m) of diatrizoate, DEET and oxypurinol for a conservative behaviour, linear sorption and sorption and biodegradation considering an inlet concentration of 3, 5, 5 µg/l and a DT50 of 68, 90 and 56 days, respectively. (d-e-f) Simulated concentration of diatrizoate, DEET and oxypurinol on a logarithmic scale for a 2D steady-state transport model, considering sorption and biodegradation, assuming the inlet concentration and the DT50 equal to the 1D model. The red circle indicates the well.

Nevertheless, the measured concentration of the three compounds in the wells can be explained considering biodegradation. As for the 2D model, considering the same input parameters of the 1D model, the simulated concentrations slightly overestimated the measured concentrations, which could be fixed by modifying 2D parameters.

5.5.8. Ljubljanska Kotlina, Slovenia

5.5.8.1. Hydrological Model

The hydrological model for the Ljubljanska kotlina study area in Slovenia is set up using Visual MODFLOW Professional, version 4.2.0.153, which uses MODFLOW 2000 (USGS) (Hill et al., 2000) for numerical modelling of groundwater flow and groundwater-surface water interaction.

The Ljubljanska kotlina unconfined aquifer is divided into four layers that have different values of hydraulic conductivity. The Sava and Ljubljanica rivers, which flow across the study area, are implemented as river boundaries in the model, while the west and south boundary conditions are specified by groundwater levels. The model is set up by considering both high and low groundwater levels. This is done because the groundwater partially changes direction towards the drinking water wells according to different hydrological and meteorological conditions. Figure 5.17 shows the model results considering low and high groundwater levels.

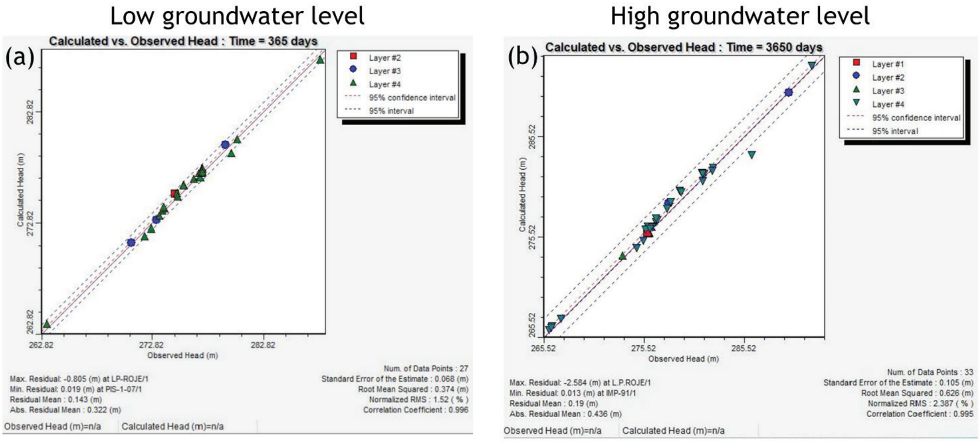


Figure 5.17 (a) Model results: Comparison of observed and calculated groundwater levels in the Ljubljansko Polje aquifer considering low groundwater level. (b) Model results: Comparison of observed and calculated groundwater level in the Ljubljansko Polje aquifer considering high groundwater level.

5.5.8.2. Transport Model

In the Ljubljanska kotlina study area, the contaminants considered in the transport model are:

- **Carbamazepine:** is often used as an anticonvulsant drug for the treatment of epilepsy (Beltran A. et al., 2009; Asgari S. et al., 2017; Rezaei Kahkha, M.R, 2018).
- **Caffeine:** is a neuro, cardiac and respiratory stimulant and used as a diuretic for humans as well (Korekar et al., 2020; Moore et al., 2008). It is found in certain medicines and in certain food and beverages (Korekar et al., 2020; Moore et al., 2008; Rodríguez-Gil et al., 2018).
- **Propyphenazone:** is a derivative of phenazone with similar analgesic and antipyretic effects.

An unsaturated zone transport model was selected for the model set-up as a direct-type problem in the HYDRUS-1D environment (Šimůnek et al., 2013). The model simulates advective and dispersive solute transport with kinetic linear sorption where diffusive transport mechanisms are excluded on the assumption of higher transport velocities decreasing the effectiveness of diffusion compared to transport by advective-dispersive mechanisms.

Figure 5.18 shows the transport model results for the three compounds listed above.

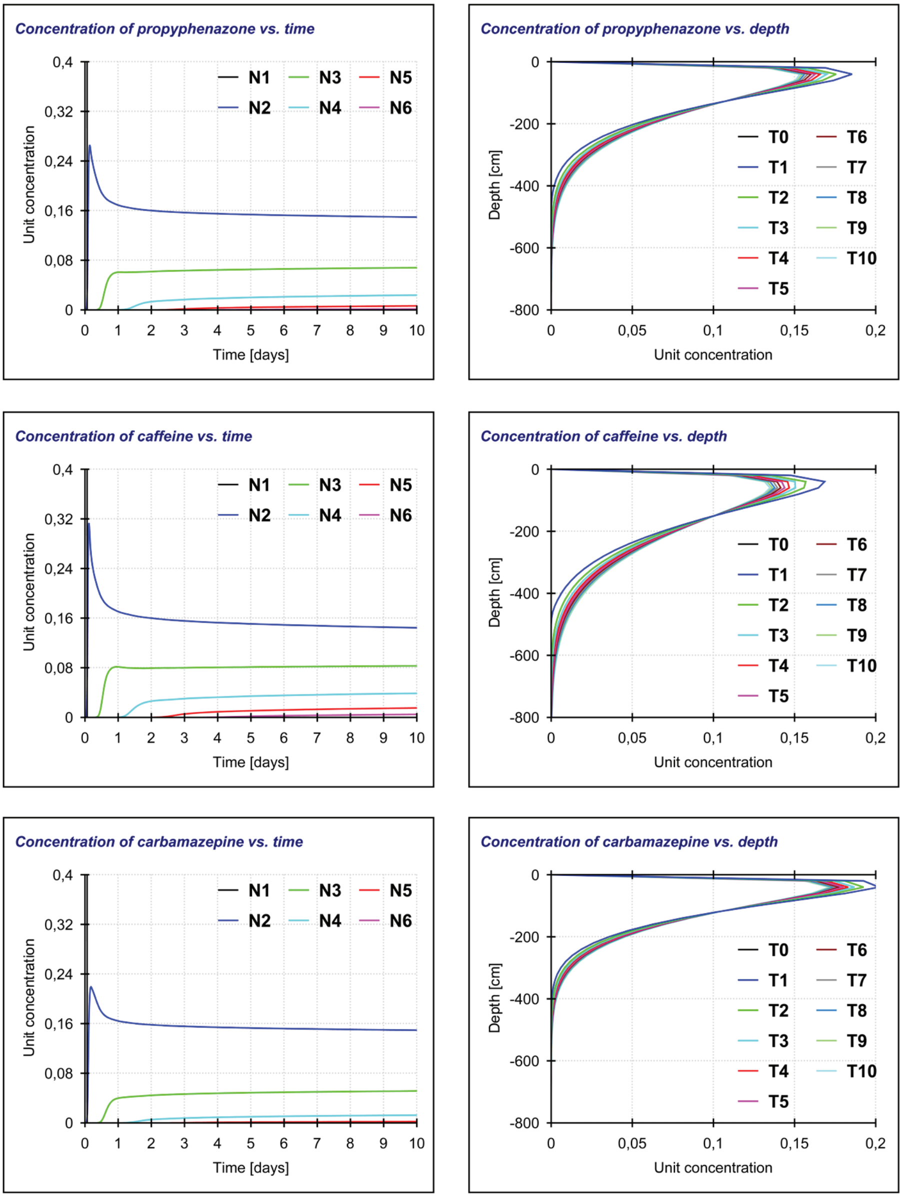


Figure 5.18 Concentrations of the three modelled ECs through time and profile of unsaturated zone.

In Figure 5.18, differences can be observed in the time of concentration of pulse arrival and peak value of the three modelled PPCPs. This behaviour can be explained by the differences in their transport characteristics.

However, a decrease in concentration can be seen in all three cases following the pulse deeper through the unsaturated zone and therefore demonstrating the impact of retention properties.

Major remarks on modelling activities:

- A transnational review of the existing country-specific framework for model application is fundamental for gaining an overview of the actors involved in modelling activities and their goals
- Decision-making tools are of great importance in the field of water management
- modePROCON will help water managers and stakeholder groups in approaching modelling of PPCPs
- The case studies are interesting for the identification of the issues encountered when modelling PPCPs in the three cluster areas (i.e. surface water, groundwater and karst aquifer)

6. ATTENUATION OF EMERGING CONTAMINANTS FOR WATER SUPPLY PURPOSES (NATURAL ATTENUATION AND TECHNICAL REMOVALS)

By the end of the project's lifetime, a decision-making support tool and transnational strategy concerning mitigation of PPCPs in drinking water resources will be delivered by the project partners. Efficient mitigation of PPCPs requires the combination of legislative and non-legislative action, so it is necessary to develop new approaches and prospects in legislative actions. As the main result of capacity-building activities conducted within boDEREC-CE, waterworks will be provided with the Decision-Making Support Tool (wwDEMAST) for selecting treatment options/ methods for mitigating PPCP concentrations. This tool will be developed for and used by public water suppliers in case of increasing PPCP trends. Furthermore, wwDEMAST will contribute to the development of new and improved guidelines and legislation related to PPCPs in drinking water. The Transnational Strategy for PPCP Mitigation in Drinking Water (TRAST-PPCP) will encompass new prospects in legislative solutions, provided by experts, for mitigation of emerging contaminants (PPCPs), defining necessary steps for optimisation of organisational structures and future-oriented drinking water management.

6.1. Properties of Emerging Contaminants

Selection of PPCPs

The collection of PPCPs resulting from the boDEREC-CE project is broad and representative, as it contains ubiquitous compounds (carbamazepine, diclofenac), popular over-the-counter (OTC) drugs (ibuprofen, paracetamol), different therapeutic classes, such as antibiotics (sulfamethoxazole), antidiabetics (metformin), antihypertensives (valsartan), or anticonvulsants (lamotrigine, gabapentin), but also PPCP metabolites (oxypurinol, 4-formylaminoantipyrine, 4(5)-methyl-1H-benzotriazole, and valsartan acid), personal care products (DEET, 1H-benzotriazole), artificial sweeteners such as acesulfame, etc.

To assess their properties, attenuation capacities and removal possibilities, compounds that were 20 most frequently detected during boDEREC-CE monitoring campaigns have been selected (Table 6.1).

Properties of selected PPCPs

Out of many physicochemical descriptors available in literature, only a few were selected (log K_{OW}, log K_{OC}, Henry's law constant, and molecular weight MW), as they characterise properties of each respective PPCP, i.e. environmental factors that affect their spreading, mobility, transport, and attenuation in the environment. They may be used for fast targeting of hazardous PPCPs and/or tracking of their environmental fate.

The selected indicators are (see Table 6.1):

- Octanol–water partition coefficient (log K_{OW}) is a standard measure of a compound's hydrophobicity and polarity, which affect pharmaceutical fate by varying sorption, partition, hydrolysis, photodegradation, and biodegradation processes. Hydrophobic compounds will adsorb more to the organic matter present and become more recalcitrant toward degradation. Hydrophilic compounds remaining in solution are generally more prone to degradation and attenuation. Pharmaceuticals with high log K_{OW} and high molecular weights are easily adsorbed to soils and sediments and removed from aqueous phases. On the other hand, those with low log K_{OW} tend to remain in aqueous phases. The log K_{OW} numbers for the selected PPCPs (Table 6.1) range from the low value of -2.79 (iomeprol) to the high value of 4.51 (diclofenac).
- Organic-carbon-based sorption coefficient (log K_{OC}) measures the mobility of a substance in the soil. A very high value means it is strongly adsorbed onto soil and organic matter and does not move throughout the soil. A very low value means it is highly mobile in soil. K_{OC} is a very important input parameter for estimating environmental distribution and the environmental exposure level of a chemical substance. In the list of the selected PPCPs, the lowest log K_{OC} value has been estimated for 1H-benzotriazole (0.16), whereas the highest values have been assigned to ibuprofen (3.53).
- Henry's law constant (also called the air-water partition coefficient) is the ratio of a compound's partial pressure in air to the concentration of the compound in water at a given temperature. It is the key parameter for determining a chemical's environmental distribution behaviour. It reflects the relative volatility of a particular substance and represents a major property

to describe fate and transport modeling in environmental risk assessment. Chemical substances with high Henry's law constant values will volatilize from water into air and be distributed over a large area. Chemical substances with low Henry's law constant values tend to persist in water and may be adsorbed onto soil or sediment.

- Molecular weight (in g/mol) is a mass of a molecule of a substance; may be relevant indiscussing (de)sorption, transport, and volatilisation properties of the respective PPCP.

All physicochemical properties in Table 6.1 have been collected from the PubChem database (https://pubchem.ncbi.nlm.nih.gov/), which is maintained by the National Centre for Biotechnology Information (NCBI) and the ChemSpider database (http://www.chemspider.com/), which is owned by the Royal Society of Chemistry.

Several selected indicators correlate well with the PBT index, a term that expresses the inherent environmentally damaging characteristics of PPCPs. The abbreviation PBT stands for:

P - persistence, or ability to resist degradation in water;

B - bioaccumulation, or accumulation in adipose tissue of aquatic organisms;

T - toxicity, or the potential to induce toxic effects in the aquatic organisms.

In addition, the PBT index is included as a measure of environmental hazard and expresses the inherent environmentally damaging characteristic of the respective PPCP. Each of the PBT parameters is assigned a numerical value (0, 1, 2, or 3), and the total value constitutes the PBT index for the PPCP. The PBT index can assume values in the interval 0 - 9. The higher the value of a substance, the greater its danger to the environment. This index is a simple descriptor, which can be used for a quick orientation and ranking of the respective PPCPs. In combination with hydrogeological and transport characteristics of pilot sites, the identification of the most alarming PPCPs may be facilitated.

The above classification model was presented by Wennmalm and Gunnarsson (2005) and the results for around 200 active drug substances can be found on the Stockholm County Council's website for pharmaceutical information (See http://www.janusinfo.se/miljo). The PBT index classification may be easily upgraded and expanded (Gramatica et al., 2015), or some popular tools such as the US EPA PBT Profiler may be applied (US EPA PBT Profiler, 2006.).

Table 6.1 The 20 most frequently detected PPCPs and their physicochemical indicators

Compound	CAS#	MW (g/mol)	log K_{ow}*	log K_{oc}*	Henrys law constant (atm-m^3/mol at 25 C)*	PBT
1H-benzotriazole	95-14-7	119.1	1.44	2.998	1.47E-07	0
DEET	134-62-3	191.3	2.18	2.73	2.08E-08	0
metformin	657-24-9	129.1	-1.4	2.149	7.64E-16	4
4(5)-methyl-1H-benzotriazole	29385-43-1	133.15	1.71	3.217	1.62E-07	-
oxypurinol	2465-59-0	152.1	-2.17	2.367	1.24E-14	6
4-formylaminoantipyrine	1672-58-8	231.25	0.5	1.804	2.01E-11	0
carbamazepine	298-46-4	236.3	2.45	3.588	1.08E-10	4
gabapentin	60142-96-3	171.2	-1.1	1.771	1.81E-10	0
telmisartan	144701-48-4	514.6	8.42	-	-	5
valsartan acid	164265-78-5	266.25	1.83	-	-	4
valsartan	137862-53-4	435.5	3.65	6.011	1.81E-18	4
lamotrigine	84057-84-1	256.1	0.99	3.131	2.22E-11	4
acesulfame	33665-90-6	201.2	-1.33	1.302	9.63E-09	0
tramadol	27203-92-5	26.37	2.51	2.905	1.54E-11	0
PFOS	1763-23-1	500.13	-1.08	3.0**	4.34E-7	-
iomeprol	78649-41-9	777.1	-2.79	0.27***	-	3
sulfamethoxazole	723-46-6	253.3	0.89	3.185	9.56E-13	6
diclofenac	15307-79-6	296.2	4.51	2.39	-	4
metoprolol	51384-51-1	267.36	1.88	0.60***	2.1E-11	4
paracetamol	103-90-2	151.2	0.46	1.79	6.42E-13	5

*(source: Estimation Programs Interface Suite™ for Microsoft Windows, v. 4.11, United States Environmental Protection Agency, Washington, DC, USA (2012))

**Zareitalabad et al. (2013)

*** Sallwey et al. (2020)

6.2. *Natural Attenuation*

According to the PBT indices in Table 6.1, the values for two PPCPs (oxypurinol and sulfamethoxazole) and two PPCPs (telmisartan and paracetamol) amount to 6 and 5 respectively, indicating that it may be of interest to study them further from the standpoint of an environmental hazard. Seven PPCPs (lamotrigine, carbamazepine, valsartan, valsartan acid, metformin, diclofenac, and metoprolol) and one PPCP (iomeprol) are assigned the value of 4 and 3 respectively. They may be considered substances with a moderate environmental risk, as defined by the

PBT index only. However, these estimates should be corrected by a) other chemo-physical parameters (log K_{OW}, log K_{OC}, Henry's law constant, and MW; Table 6.1), and b) specific hydrogeological and transport characteristics of the different types of water (karst, surface, and groundwater).

The most frequently selected compound for the transport model is DEET (4 pilot actions), followed by acesulfame-K and oxypurinol (in 3 pilot actions).

DEET was selected for modelling in four pilot areas (Dresden-Hosterwitz, Waidhofen a/d Ybbs, Kozłowa Góra, and Neufahrn bei Freising). During the boDEREC-CE monitoring it was detected at all pilot actions, along with 1H-benzotriazole.

DEET is commonly used as an insect repellent and it was one of the most frequently detected ECs in a pan-European survey of groundwater (Loos et al., 2010). DEET had a PBT index of 0. Schaefer and Siddiqui (2002) conducted an OECD Guideline 301B study with DEET that showed biodegradation of 83.8 % in 28 days, while Kumar (2003) observed rapid biodegradation reaching up to 40 % in 7 days. Based on the log K_{OW} value of 2.18, it can be assumed that DEET is hydrophilic and will not likely bioaccumulate in aquatic species. The minimal min log K_{OC} of 1.64 (Scheytt et al., 2005) suggests it is weakly adsorbed onto soil and organic matter i.e. very mobile. Furthermore, the Cramer classification (Cramer et al., 1978) based on chemical structure suggests it is a non-toxic substance.

The artificial sweetener acesulfame-K, often used in soft drinks, was selected for modelling in three pilot areas (Káraný-Jizera, Kozłowa Góra, and Dresden-Hosterwitz). Acesulfame-K is persistent during wastewater treatment and recognised as a marker of anthropogenic contamination in water resources and wastewater. In karst aquifers, no retardation of acesulfame-K has been observed (Hillebrand et al., 2015), while its estimated half-life in a wastewater plume within a porous aquifer is at least 15 years (Robertson et al., 2013). Relatively high persistence and conservative transport behaviour (Scheurer et al., 2009) make acesulfame-K a useful indicator for investigating the long-term impacts of domestic wastewater. Like DEET, it has a PBT index of 0. In the absence of experimental data, the log K_{OW} value was predicted in EPI SuiteTM (-1.33; KOWIN v1.68 model) and with Prometheus software (-0.68), indicating that acesulfame-K tends to remain in aqueous phases and sorption is unlikely. The minimal calculated log K_{OC} value of 0.25 (Sallwey et al., 2020) indicates it is very mobile in the water phase. Furthermore, a Cramer class of III (Cramer et al., 1978) suggests acesulfame-K is a substance with chemical structures that permit no strong initial presumption of safety or may even suggest significant toxicity or have reactive functional groups.

Oxypurinol was selected for modelling purposes in three pilot areas (surface water pilot area of Kozłowa Góra, and groundwater areas of Káraný-Jizera and Neufahrn bei Freising). Oxypurinol is a metabolite of allopurinol, an inhibitor of xanthine oxidoreductase, and is used to prevent gout. The major route of elimination of allopurinol is through metabolism to oxypurinol. In comparison to allopurinol, which has a short half-life (about 1 hour), oxypurinol has a much longer half-life. Therefore, no allopurinol may be detected in wastewater. Moreover, researchers have proposed oxypurinol as a new marker for contamination of the aquatic environment (Funke et al., 2015). Tracking of oxypurinol revealed its presence in rivers and streams, groundwater as well as in finished drinking water (up to 300 ng/ L). In monitoring campaigns within the boDEREC-CE project, the highest (peak) concentration of oxypurinol was measured in Kozłowa Góra (1590 ng/L). No oxypurinol was detected in karst water pilot areas (Waidhofen a/d Ybbs; Jadro and Žrnovnica springs catchment). This may reveal a hydrogeological impact on the environmental fate of the respective PPCP. Due to relatively low log K_{OW} value (-0.68), oxypurinol tends to remain in aqueous phases, and sorption is unlikely, i.e. oxypurinol is weakly adsorbed onto soil and organic matter (log Koc = 2.37). In addition, its PBT index value of 6 supports its selection as an emerging contaminant.

Another PPCP (in addition to oxypurinol, Table 6.1) which is characterised by a relatively high PBT index of 6 is sulfamethoxazole. It is included in the Watch List under the Water Framework Directive and is one of the top-selling antibiotics. Sulfamethoxazole is regularly indicated, in various formulations, in combination with trimethoprim. The latter is also listed as a target PPCP for monitoring campaigns within boDEREC-CE, but, interestingly, was in no case (except in Neufahrn bei Freising, 2019; 12.8 ng/L) detected above the limit of quantification. In water, sulfamethoxazole is not expected to adsorb to suspended solids and sediment, based upon the estimated log K_{OC} = 1.86.Also, volatilisation from water surfaces is not expected to be an important fate process based upon this compound's estimated Henry's Law constant (log H_{cp} = 7.18). If released to soil, sulfamethoxazole is expected to have high mobility. In general, sulphonamide antimicrobials are not readily biodegraded and persist in soils. The compound is non-biodegradable in sewage treatment and does not undergo hydrolysis under field conditions.

Paracetamol or acetaminophen (PBT index = 5) is one of the most widely used over-the-counter analgesics and is one of the most frequently detected anthropogenic compounds in the aqueous environment. The environmental fate of acetaminophen may be predicted using physicochemical properties characterised by indicators in Table 1. Acetaminophen is expected to have very high mobility in soil (log K_{OC} = 1.32). Volatilisation from moist soil surfaces (or water surfaces) is not expected to be an important fate process based upon an estimated Henry's Law constant of log H_{cp} = 7.18 and it is not expected to volatilise from dry soil surfaces. Hydrolysis in water is not an important environmental fate process since this compound lacks functional groups that hydrolyse under environmental conditions (pH 5 to 9). Acetaminophen is a typical example of a PPCP, which transforms during chemical treatment (chlorination of water) resulting in by-products (benzoquinone and benzoquinone-imine) that are up to 60 times more toxic than the parent compound. Therefore, in addition to selected physicochemical descriptors and measured concentrations during monitoring campaigns, the mechanism of environmental fate must be considered.

Lastly, the most frequently detecte PPCP - 1H-benzotriazole, had a PBT index of 0. Its chemical properties indicate very high mobility in water (log K_{OC} = 0.16). Volatilisation from water surfaces is not expected based upon Henry's Law constant of log H_{cp} = 1.49. It can be used as a corrosion inhibitor, but also as an antimicrobial in cosmetics. Therefore, for an efficient attenuation protocol for benzotriazole in the aquatic environment, it is of importance to determine what the main use of 1H-benzotriazole is – industrial or personal care. 1H-benzotriazole and its methylated analogue (methyl-1H-benzotriazole) may be used as a model system where the use and the source are important information in designing mitigation/attenuation actions.

6.3. Technical Options for Removal of Emerging Contaminants

Conventional water treatment processes are not specifically designed for PPCP removal. Thus, advanced materials and technologies are required to eliminate PPCPs to ensure water safety. However, the main obstacle to the increased application of efficient technologies in municipal water treatment is their high cost. A careful assessment of available technologies for each respective PPCP is, therefore, warranted. In the following section, several technologies have been selected from recent literature, and their removal efficiency was evaluated with respect to selected PPCPs.

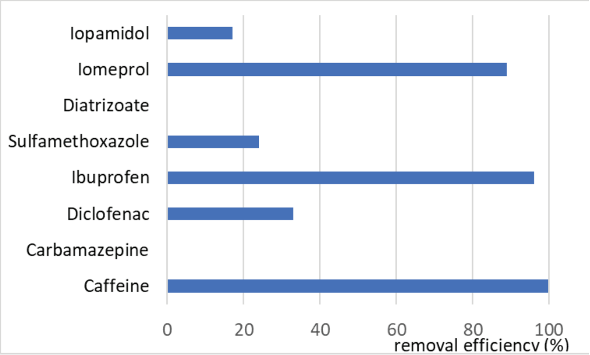


Figure 6.1 The removal efficiency of PPCPs by combining biological treatment with other processes (Grit removal/primary clarifier/denitrification/nitrification/second clarifier) (Ternes et al., 2007).

Figure 6.1 summarises the removal efficiency of several selected PPCPs by combining biological treatment (Grit removal/primary clarifier/denitrification/nitrification/second clarifier) with other processes (Ternes et al., 2007). The removal rate (0 – 99.7 %) depends greatly on the physicochemical properties of each respective PPCP. A search for more comprehensive technology, which could cover a full range of PPCPs detected in water, is still an ongoing issue.

Ozonation, which is an advanced oxidation process, may be a promising removal method. All selected PPCPs (Fig. 6.2) were eliminated by a removal efficiency of >90 % (except for sulfamethoxazole). However, the collection of PPCPs is limited, while the removal efficiency strongly depends on the type (microbubble vs. ejector) of ozone ejection (Ilho et al., 2022). The additional adverse property of ozonation is high energy consumption, which may result in high costs.

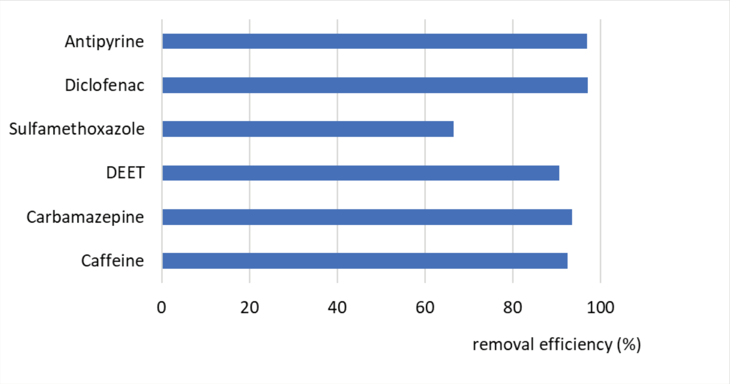


Figure 6.2. The removal efficiency of selected PPCPs by ozonation in microbubble (Ilho et al., 2022).

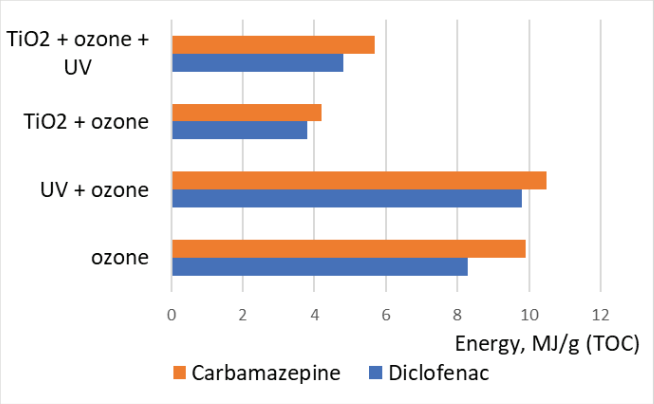


Figure 6.3 Energy consumption of different ozonation/oxidation processes used for carbamazepine and diclofenac removal (Jankūnaitė et al., 2017.).

The energy requirements to decompose 1 g of total organic carbon (TOC) by ozonation and employing the combination of UV with ozonation (Fig. 6.3) were higher than those for the other two oxidation systems, namely TiO2+O3 and TiO2+UV+O3. Depending on the target PPCPs, it varied between 5.4 and 9.8 MJ/g (TOC) and 7.5–10.6 MJ/g (TOC), respectively. Compared to the treatment of carbamazepine, the degradation of intermediate products formed during diclofenac decomposition was less energy-intensive (Jankūnaitė et al., 2017.).

In Figure 6.4, the removal efficiency of various water treatment technologies concerning individual PPCPs is compared (Yang et al., 2017).

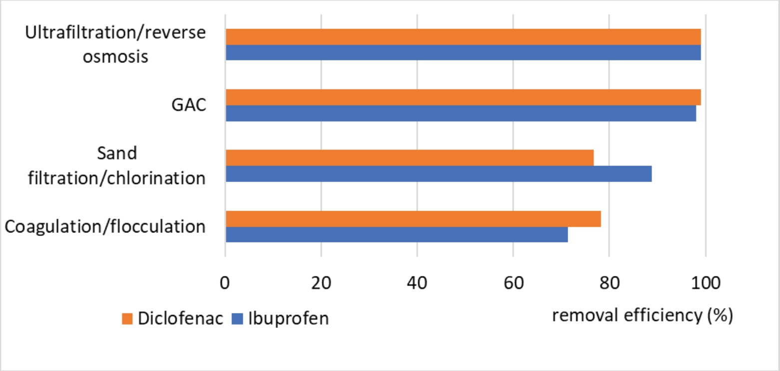


Figure 6.4 The efficiency of different technologies for removal of ibuprofen and diclofenac (Yang et al., 2017).

Finally, it is convenient to estimate the performance of selected technology for a series of PPCPs, by comparing removal efficiency and physicochemical parameters of PPCPs (Fig. 6.5). A group of six targeted PPCPs (from Table 6.1) were eliminated by a pre-ozonation/flocculation/sedimentation protocol (Padhye et al., 2014) and different removal rates were obtained, which may be correlated to a log K_{OC}, i.e. the organic-carbon based sorption coefficient (from Table 6.1). It is clear that different dependencies exist in the diagram. Similar results were obtained when the removal efficiency of integrated membrane systems (MBR-RO/NF) was correlated with log K_{OW} values of the selected PPCPs (Wang et al., 2018). All this reveals the difficulties in selecting an optimal water treatment technology for a given set of PPCPs.

Two more properties of water treatment technologies, which may hinder their performance, must be considered:

- seasonal variation of removal efficiency, and
- by-products formation during treatment processes.

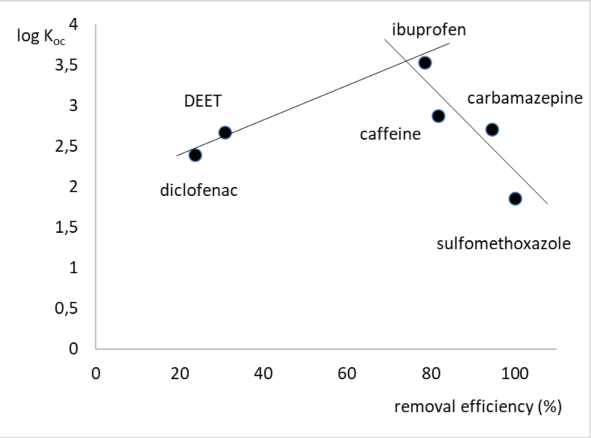


Figure 6.5 The removal efficiency of the pre-ozonation/flocculation/sedimentation protocol for a series of PPCPs, correlated with log K_{OC} values of compounds (Padhye et al., 2014).

The first issue is displayed in Figure 6.6, which includes seasonal variation in selected PPCP (ibuprofen and sulfamethoxazole) removal using primary settling and activated sludge processes. In both cases, the median value of removal efficiency is much higher during the summer period (Castiglioni et al., 2006).

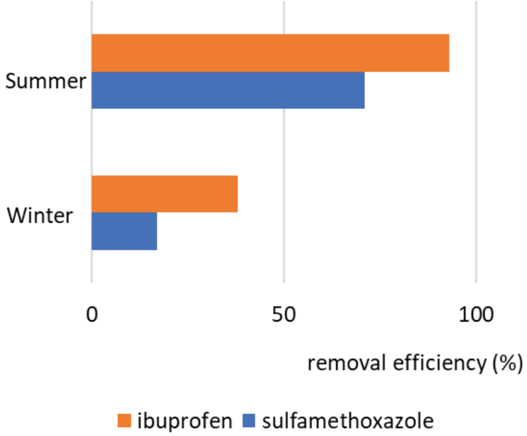


Figure 6.6 Seasonal variation (summer vs. winter) in PPCP removal using primary settling and activated sludge processes (Castiglioni et al., 2006).

Other environmental factors may also influence the removal efficiency: waterbody depth, vegetation, suspended particulate matter, dissolved organic matter, temperature, etc. This is why a comparative analysis, such as the one performed within boDEREC-CE, including different areas and categories of water (i.e. karst, surface, and groundwater) is required.

The second issue is presented in Figure 6.7, which displays by-products formed during oxidation and advanced oxidation of selected pharmaceuticals. As stated earlier, newly formed products may be more toxic than the parent PPCP or may lack the toxicological data/information.

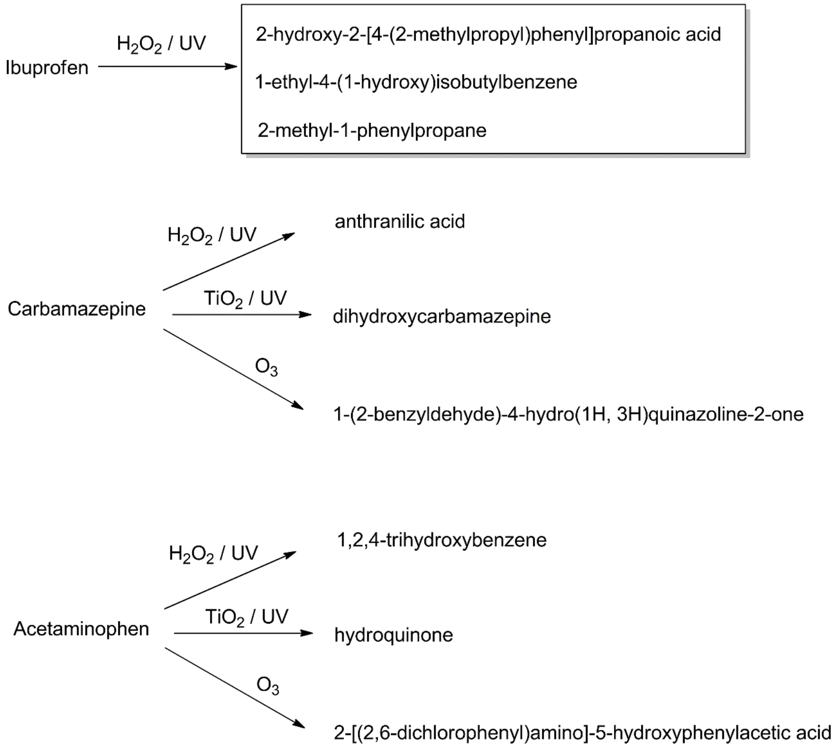


Figure 6.7 By-products formed during oxidation and advanced oxidation of selected PPCPs

7. COMMUNICATION-RELATED CHAPTER

Nowadays, water is one of the most valuable raw materials and its availability is one of the most important factors that determine the quality of our lives. Water resources are constantly endangered by different sources of pollution associated with human activity. One of the largest pollutant groups, which are currently of interest, are emerging contaminants (EC), especially pharmaceuticals and personal care products (PPCPs). Unfortunately, despite this interest, there are no policies or any common recommendations for the protection of drinking water resources, including monitoring and modelling the fate of PPCPs in water and, finally, attenuating them. This is where boDEREC-CE sets a whole package of research tasks as well as communication activities.

boDEREC-CE is not only focused on the study of PPCP behaviour in the environment – from the pollution source via watercourse up to the water intake. An additional aim of the project is to assess the effectiveness of attenuating PPCP contamination using different types of drinking water treatment technologies. The boDEREC-CE results are intended for stakeholders and main target groups of the project (water-oriented actors, public authorities, water utilities, research institutions), are of practical importance and could potentially be implemented by them in the future. Close cooperation has been established with the stakeholders and particular attention has throughout the project been paid to proper communication.

Project communication takes place on two different levels: internal – with project partners and external – with the stakeholders and target groups. External communication is implemented to help raise awareness and increase knowledge on the project itself, the performed activities, and the obtained results. Involving stakeholders, target groups, and the general public, into a project to guarantee the project’s sustainability is always a challenge. Thus, the boDEREC-CE Work Package Communication and the associated activities aimed to ensure a proper information flow between the project partners and to transmit the most important project results between these partners and, successively, to all target groups.

Within the WP Communication, various types of activities were performed, including digital activities, media relations, publications, and, most importantly, the organisation of events. The boDEREC-CE project, and its results, are easily accessible online through the project's website and social media profiles. boDEREC-CE is available on Facebook and YouTube – which can be easily accessed by the international general public, as well as on LinkedIn – in an effort to reach the worldwide community of experts, and on ResearchGate – for scientists and researchers.

Project partners also share their findings and project results via scientific and thematic papers. The partners publish in international as well as in local scientific and trade journals. They also present the results of their participation in the boDEREC-CE project at conferences and symposia, where additional information is published in the form of abstracts in conference proceedings.

The communication activities within the boDEREC-CE project include public meetings and events organised by project partners. One of the most important events are workshops for stakeholders organised in each partners' country. The workshops are held to reach the main target group representatives, present project aims, its execution, and results. Furthermore, feedback is obtained from target groups and is used in establishing project outputs - tools and strategy. Unfortunately, the boDEREC-CE project has experienced certain difficulties due to the COVID-19 pandemic. The restrictions and lockdowns forced the partnership to move most of the communication activities, especially events, to the Web (Fig. 7.1).

The main challenge was the organisation of the Midterm Conference online. It was held on 1 December 2020 to summarise the completed tasks after the first half of the project's lifetime. The main aim of the meeting was to involve stakeholders in the project, share experiences and build capacity for the implementation of future project outputs. One of the main points was announcing the concept of the first boDEREC-CE tool - modePROCON. The Midterm Conference was held via Microsoft Teams, but, in order to gain more audience, the meeting was also streamed live on YouTube. More than 100 participants from 11 countries participated in this event on MS Teams and more than 220 viewers from the general public attended the live stream on YouTube.

The conference was divided into three thematic sessions and a discussion panel. The agenda included (1) the introduction to the PPCP water pollution problem and its mitigation, (2) the boDEREC-CE project implementation progress with the leaders' presentation of work package outputs, and (3) the presentation of the modePROCON tool concept. The last part of the Midterm Conference was a transnational discussion panel. The main aim of the discussion among international experts was to share experiences concerning the presence of PPCPs in water and the implementation of modelling for water management needs in particular countries. The nine panellists mainly represented the water sector in Central Europe. However, there was also an opportunity to confront European experiences with the ones from Peru.

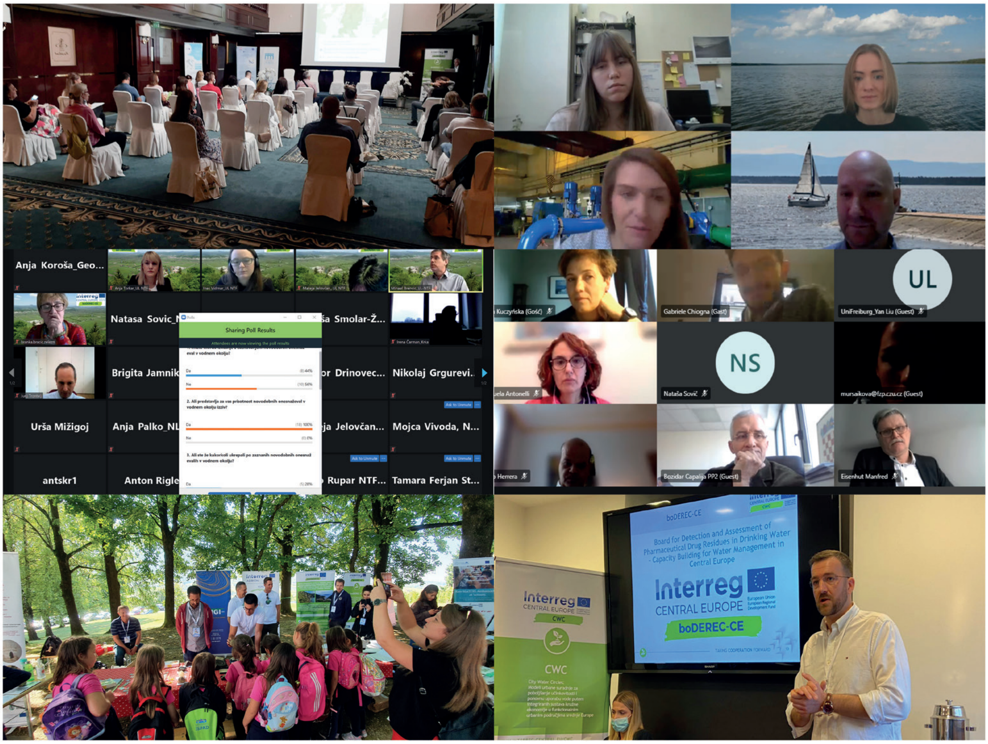


Figure 7.1 Collage of photos and screens taken during exemplary events organised within the project.

The panellists emphasised the need for filling the current knowledge gap in the detection and assessment of PPCPs in drinking water and shared their opinions on different approaches. They also underlined he need for upgrading analytical procedures which should also consider PPCP metabolites. Moreover, in their opinion, thresholds for human consumption should be set. They agreed that the implementation of policies and strategies, as well as proper communication, are the most important tools that can help in dealing with the problem of PPCP pollution. The panellists also discussed possible monitoring strategies and suggestions for policy-makers which consider the high costs of PPCP monitoring and the lack of PPCP monitoring data (single results, no long-term monitoring of the EC). The panel participants highlighted the need to combine modelling with the preparation of a PPCP monitoring network as well as the importance of implementing a water risk assessment that focuses on monitoring indicator substances. At the end of the discussion, all panellists agreed that there is no possibility of reducing the PPCP pollution risk to zero with the current knowledge and technologies. The panellists suggested minimalising the risk by using the holistic approach, considering catchments as a whole. They also emphasised the need to communicate the problem of PPCP pollution and raise awareness among consumers.

The findings of the Midterm conference and the discussion panel meet the boDEREC-CE targets and are a great input in the realisation of the project.

The boDEREC-CE project involves more than 125 stakeholders. They represent target groups such as: higher education and research institutes, public authorities, infrastructure and services providers including water utilities. Moreover, the project has reached more than 11,000 people so far (e.g. participants of public events, social media followers).

The stakeholders' feedback indicates that there is a significant lack of knowledge on the occurrence of PPCPs in the water environment and the processes of their attenuation. Initiatives such as the boDEREC-CE project are highly welcomed by the stakeholders. Water suppliers in particular are looking forward to establishing guidelines and strategies which could be implemented in their daily operation.

The final boDEREC-CE results, outputs, and project findings will be presented to stakeholders during the Final Conference to be held on 2nd March 2022.

8. CONCLUSIONS AND FUTURE OUTLOOK

The presence of emerging contaminants (ECs) and in particular Pharmaceuticals and Personal Care Products (PPCPs) in drinking water is a topic that has gained increased attention over the recent years (Barceló & Petrovic, 2007), becoming at the same time one of the most urgent environmental issues. New advances in analytical extraction and measurement technologies enabled us to discover substances like ECs occurring in the environment in such small concentration levels as ng/L. ECs originate mainly from anthropogenic activities such as industry, agriculture, or urban life. Waste disposed of in landfills and wastewater is recognised as the principal source of ECs, providing entry into the environment through various release mechanisms and in all stages of the water cycle.

There are still differing viewpoints on fundamental concepts like the definition and classification of ECs, as well as significant issues regarding monitoring and legislation. The reason for this is the large number of chemicals that fall into this group (more than 1000 different substances or mixtures), which represents a major problem in resolving the most significant concerns and unknowns. ECs are most often classified according to their intended use but can also be categorised in many different ways (quantitatively, by chemical characteristics, effects, etc.). Consequently, there is no globally uniform definition of ECs, while existing ones mainly describe their most common general characteristics. Within the framework of the boDEREC-CE project, and based on a review of national reports and literature sources, the following definition of ECs is proposed:

"Emerging contaminants represent a group of potential pollutants that are either newly created, newly identified, newly detected or newly researched."

Within the scope of the first thematic boDEREC-CE work package, a learning tool focused on state-of-the-art of current practices in relation to emerging contaminants in the water environment was developed based on knowledge and experience of project partner countries. Moreover, a data collection tool providing an overview of the occurrence of ECs in the water environment of project countries was also delivered. Both tools contribute to raising awareness and filling the knowledge gaps of a wider scientific and professional public on ECs in the water environment.

Most of the ECs are scarcely regulated and are not part of regular monitoring activities. Although there is a common European framework guiding the national legislatures of all partner countries, there are considerable differences in the research and monitoring stages of each country. The boDEREC-CE project aimed to address a wide range of issues related to PPCPs through project activities focusing on their monitoring and modelling. Eight pilot locations in seven countries were chosen for monitoring of PPCPs in order to explore their types, concentrations, and detection frequencies. Over the period of two years, 66 sampling sites were monitored, mostly at quarterly intervals. The pilot sites vary from one to another in terms of both natural characteristics and water production technologies. Alluvial sediments and karstified carbonates of various ages are predominant. Extraction wells, bank filtration, regulated aquifer recharge, and captured spring water were among the used water-production technologies. The 20 most frequently detected PPCP substances (in descending order of detection number) are: 1-H-benzotriazole, DEET, metformin, 4(5)-methyl-1-H-benzotriazole, oxypurinol, 4-formylaminoantipyrine, carbamazepine, gabapentin, telmisartan, valsartan acid, valsartan, lamotrigine, acesulfame, tramadol, PFOS, iomeprol, sulfamethoxazole, diclofenac, metoprolol, and paracetamol. DEET which had the highest detection frequency - occurred in water resources of all pilot actions. This substance is not included in the current Priority Substances List and Watch List.

A knowledge gap about the potential risk that ECs may pose in drinking water and wastewater systems was identified through stakeholder workshops and training courses organised in the scope of the boDEREC-CE project. Water managers, public authorities, and stakeholder groups lack sufficient data to effectively explore the fate and transport of PPCPs in the environment. This represents a barrier in assessing the potential threats of ECs to human health and ecosystems. In order to investigate the fate of PPCPs in three cluster areas: 1) surface water, 2) groundwater, and 3) karst aquifers; boDEREC-CE experts set up flow and transport models in each pilot area. The results showed different approaches when dealing with the presence and modelling of PPCPs in water. In particular, in setting up the transport model, each project partner implemented different strategies and tools, based on the natural characteristics of the area, frameworks for water extraction, available hydrological and hydrogeological data, and the available measured concentration of PPCPs.

As a result of modelling activities, a model-based decision-making tool for PPCPs called “modePROCON” was developed. The tool consists of two main analyses that allow the user (e.g. water managers) to determine whether a transport modelling study is recommended and achievable based on data availability. As stated by different stakeholders during the organised national stakeholder workshops, many parameters required for modelling are often unknown to them. The modePROCON will provide all the necessary input data along with the chemical and physical properties of a list of PPCPs, guiding the user towards the decision on whether a model can or cannot be built. Thus, the use of modePROCON might provide a step forward in the mitigation of risk to human health and the environment.

There are no attenuation measures specifically designed for the removal of ECs from water, while advanced technologies produce high installation, operation, and maintenance costs. Certain attenuation protocols for the removal of PPCPs have already been evaluated by some environmental agencies or research projects. Literature concerning these measures is available and should be reviewed before any technology is implemented. However, the treatment and/or removal technologies may be relevant only after the occurrence, toxicity, and fate of PPCPs in water are fully evaluated in a specific area (karst, surface, and groundwater). The assessment of their fate in the water environment is of special importance because treatment procedures may induce chemical transformations of PPCPs that result in the product being more toxic than the parent compound. It is important to differentiate between the term “removal” and “problem solved”. The disappearance of PPCPs is always followed by the appearance of by-products, some with an unknown or high risk to the environment and human health.

An estimation of the possibility for natural attenuation and technical removal was done based on 20 PPCPs selected from boDEREC-CE monitoring activities. The analysis of persistence, bioaccumulation, and toxicity indices (PBT) provides valuable preliminary insights into PPCP pollution and it is recommended prior to introducing a robust chemical/physical treatment on site (river, well, municipality, etc.). The assessment results indicated that oxypurinol, sulfamethoxazole, telmisartan, and paracetamol may induce the highest environmental risk. These substances should be further studied from the standpoint of an environmental hazard, by taking into account other parameters such as their physicochemical indicators (e.g. log KOW, log KOC, Henry’s law constant), hydrogeological, and transport characteristics. Sulfamethoxazole is included in the current EU Watch List according to the Decision 2020/1161. The other three compounds could be candidates for priority and watch lists. Results and monitoring campaigns within boDEREC-CE support an attenuation strategy that includes small pilot experiments, orientation testing with more frequent samplings, source tracking, and a network generated for a fast and effective information/data exchange.

A number of activities conducted in the scope of the boDEREC-CE project sparked visibility on this still insufficiently understood topic and identified a number of outstanding concerns that will have to be addressed in future initiatives. The following are the most critical topics that should be properly addressed: ECs classification, insufficient monitoring, sampling procedure, analytical methods, challenging regulations, gaps in knowledge of institutions related to the water supply and protection of the aquatic environment. Growing population and industrial activity, as well as climate change leading to a reduction in quantity and deterioration of water quality, make this topic even more important and challenging. Thus, ignoring it could result in much more serious consequences for human health and the entire ecosystem. Only sufficient knowledge can enable the implementation of correct and timely measures and help to avoid the adverse effects of emerging contaminants on our life and health.

9. REFERENCES

Agüera, A., Martínez Bueno, M. J., & Fernández-Alba, A. R. (2013). New trends in the analytical determination of emerging contaminants and their transformation products in environmental waters. Environmental Science and Pollution Research, 20(6), 3496–3515. doi:10.1007/s11356-013-1586-0

Ahel, M., & Jeličić, I. (2001). Phenazone Analgesics in Soil and Groundwater below a Municipal Solid Waste Landfill. Pharmaceuticals and Care Products in the Environment, 100–115. doi:10.1021/bk-2001-0791.ch006

Ahel, M., Mikac, N., Ćosović, B., Prohić, E., & Soukup, V. (1998). The impact of contamination from a municipal solid waste landfill (Zagreb, Croatia) on underlying soil. (R. M. Ghosh M.M., Ed.) Water science and Technology, 37, 203-210. doi:10.1016/S0273-1223(98)00260-1

Aldekoa, J., Medici, C., Osorio, V., Pérez, S., Marcé, R., Barceló, D., & Francés, F. (2013). Modelling the emerging pollutant diclofenac with the GREAT-ER model: Application to the Llobregat River Basin. Journal of Hazardous Materials, 263, 207–213. doi:10.1016/j.jhazmat.2013.08.057

Asgari, S., Bagheri, H., Es-haghi, A., & AminiTabrizi, R. (2017). An imprinted interpenetrating polymer network for microextraction in packed syringe of carbamazepine. Journal of Chromatography A, 1491, 1–8. doi:10.1016/j.chroma.2017.02.033

Aronson, D., Weeks, J., Meylan, B., Guiney, P. D., & Howard, P. H. (2011). Environmental release, environmental concentrations, and ecological risk of N,N-Diethyl-m-toluamide (DEET). Integrated Environmental Assessment and Management, 8(1), 135–166. doi:10.1002/ieam.271

Aus der Beek, T., Weber, F.-A., Bergmann, A., Hickmann, S., Ebert, I., Hein, A., & Küster, A. (2016). Pharmaceuticals in the environment-Global occurrences and perspectives. Environmental Toxicology and Chemistry, 35(4), 823–835. doi:10.1002/etc.3339

Barbieri, M., Carrera, J., Ayora, C., Sanchez-Vila, X., Licha, T., Nödler, K., … Barceló, D. (2012). Formation of diclofenac and sulfamethoxazole reversible transformation products in aquifer material under denitrifying conditions: Batch experiments. Science of The Total Environment, 426, 256–263. doi:10.1016/j.scitotenv.2012.02.058

Barceló, D., & Petrovic, M. (2007). Pharmaceuticals and personal care products (PPCPs) in the environment. Analytical and Bioanalytical Chemistry, 387(4), 1141–1142. doi:10.1007/s00216-006-1012-2

Batu, V. (2006). Applied Flow and Solute Transport Modeling in Aquifers. Fundamental Principles and Analytical and Numerical Methods. [S.l.]: CRC PRESS.

Beltran, A., Marcé, R. M., Cormack, P. A. G., & Borrull, F. (2009). Synthesis by precipitation polymerisation of molecularly imprinted polymer microspheres for the selective extraction of carbamazepine and oxcarbazepine from human urine. Journal of Chromatography A, 1216(12), 2248–2253. doi:10.1016/j.chroma.2009.01.024

Benotti, M. J., Trenholm, R. A., Vanderford, B. J., Holady, J. C., Stanford, B. D., & Snyder, S. A. (2009). Pharmaceuticals and Endocrine Disrupting Compounds in U.S. Drinking Water. Environmental Science & Technology, 43(3), 597–603. doi:10.1021/es801845a

Bielen, A., Šimatović, A., Kosić-Vukšić, J., Senta, I., Ahel, M., Babić, S., … Udiković-Kolić, N. (2017). Negative environmental impacts of antibiotic-contaminated effluents from pharmaceutical industries. Water Research, 126, 79–87. doi:10.1016/j.watres.2017.09.019

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

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. doi:10.1016/j.jhydrol.2018.10.017

Bittner, D., Rychlik, A., Klöffel, T., Leuteritz, A., Disse, M., & Chiogna, G. (2020). A GIS-based model for simulating the hydrological effects of land use changes on karst systems – The integration of the LuKARS model into FREEWAT. Environmental Modelling & Software, 104682. doi:10.1016/j.envsoft.2020.104682

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.

Bonacci, O. 1987. Karst Hydrogeology, Springer Verlag, Berlin, Pg. 184

Brooks, B. W. (ed.), Huggett, D. B. (ed.) 2012: Human Pharmaceuticals in the Environment: Current and Future Perspectives. Emerging Topics in Ecotoxicology:

Principles, Approaches and Perspectives, Volume 4. Springer Science+Business Media, LLC.

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

Burke, V., Schneider, L., Greskowiak, J., Baar, P., Sperlich, A., Dünnbier, U., & Massmann, G. (2018). Trace Organic Removal during River Bank Filtration for Two Types of Sediment. Water, 10(12), 1736. doi:10.3390/w10121736

Casicci et al. (2006). An operational system for the po flood forecasting in Italy. 7th International Conference on Hydroinformatics. Nice, France

Castiglioni, S., Bagnati, R., Fanelli, R., Pomati, F., Calamari, D., Zuccato, E. (2006). Removal of Pharmaceuticals in Sewage Treatment Plants in Italy. Environ. Sci. Technol. 40, 357−363

Castiglioni, S., Davoli, E., Riva, F., Palmiotto, M., Camporini, P., Manenti, A., Zuccato, E. (2018). Mass balance of emerging contaminants in the water cycle of a highly urbanized and industrialized area of Italy, Water Research, Volume 131, Pages 287-298, ISSN 0043-1354, https://doi.org/10.1016/j.watres.2017.12.047.

Castronovo, S., Wick, A., Scheurer, M., Nödler, K., Schulz, M., & Ternes, T. A. (2017). Biodegradation of the artificial sweetener acesulfame in biological wastewater treatment and sandfilters. Water research, 110, 342–353. https://doi.org/10.1016/j.watres.2016.11.041

Chapman, P. M. 2007: Determining when contamination is pollution — Weight of evidence determinations for sediments and effluents. Environment International 33: 492–501, doi:10.1016/j.envint.2006.09.001.

Chiang W-H. (2005). 3D-Groundwater Modeling with PMWIN: A Simulation System for Modeling Groundwater Flow and Transport Processes. Springer, Berlin. doi: https://doi.org/10.1007/3-540-27592-4

Chiang, W.-H., Kinzelbach, W. (2003). 3D-Groundwater Modeling with PMWIN: A Simulation System for Modelling Groundwater Flow and Pollution. Springer, Berlin. doi: 10.1007/978-3-662-05549-6

Chopra, S., & Kumar, D. (2020). Ibuprofen as an emerging organic contaminant in environment, distribution and remediation, Heliyon, 6(6), e04087, ISSN 2405-8440, https://doi.org/10.1016/j.heliyon.2020.e04087

Christensen, T. H., Bjerg, P. L., Banwart, S. A., Jakobsen, R., Heron, G., & Albrechtsen, H.-J. (2000). Characterization of redox conditions in groundwater contaminant plumes. Journal of Contaminant Hydrology, 45(3-4), 165–241. doi:10.1016/s0169-7722(00)00109-1

Commission Directive 2009/90/EC of 31 July 2009 laying down, pursuant to Directive 2000/60/EC of the European Parliament and of the Council, technical specifications for chemical analysis and monitoring of water status

Commission Directive 2014/80/EU of 20 June 2014 amending Annex II to Directive 2006/118/EC of the European Parliament and of the Council on the protection of groundwater against pollution and deterioration

COM(2011)876 - Amendment of Directives 2000/60/EC and 2008/105/EC as regards priority subs

Commission Implementing Decision (EU) 2015/495 of 20 March 2015 establishing a watch list of substances for Union-wide monitoring in the field of water policy pursuant to Directive 2008/105/EC of the European Parliament and of the Council (notified under document C(2015) 1756)

Commission Implementing Decision (EU) 2018/840 of 5 June 2018 establishing a watch list of substances for Union-wide monitoring in the field of water policy pursuant to Directive 2008/105/EC of the European Parliament and of the Council and repealing Commission Implementing Decision (EU) 2015/495 (notified under document C(2018) 3362)

Commission Implementing Decision (EU) 2020/1161 of 4 August 2020 establishing a watch list of substances for Union-wide monitoring in the field of water policy pursuant to Directive 2008/105/EC of the European Parliament and of the Council (notified under document number C(2020) 5205)

Common Implementation Strategy for the Water Framework Directive and the Floods Directive. Voluntary Groundwater Watch List V. 3.1 (June 2019). https://circabc.europa.eu/sd/a/e6882891-d4a2-4a64-9cf7-f04e13b0d17e/Voluntary%20Groundwater%20Watch%20List%20(Endorsed%20V3.1%20-%20June%202019).pdf

Council Directive 76/464/EEC of 4 May 1976 on pollution caused by certain dangerous substances discharged into the aquatic environment of the Community

Cordner, A., De La Rosa, V. Y., Schaider, L. A., Rudel, R. A., Richter, L., & Brown, P. (2019). Guideline levels for PFOA and PFOS in drinking water: the role of scientific uncertainty, risk assessment decisions, and social factors. Journal of exposure science & environmental epidemiology, 29(2), 157–171. https://doi.org/10.1038/s41370-018-0099-9

Cramer, G. M., Ford, R. A., & Hall, R. L. (1976). Estimation of toxic hazard—A decision tree approach. Food and Cosmetics Toxicology, 16(3), 255–276. doi:10.1016/s0015-6264(76)80522-6

Croatian Waters 2016. Monitoring compliance programme. In Croatian: Program usklađenja monitoring.

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.

Czekaj, J. et al., 2018: Report of PROLINE-CE Workpackage T2, Activity T2.1. Set up of pilot specific management practices. D.T2.2.4 Partner-specific interim pilot action progress report. Pilot Action 2.2: Kozłowa Góra. Interreg Central Europe PROLINE-CE.

ČHMÚ. Web portal of the Czech Hydrometeorological Institute. Registration sheet of the Předměřice profile. Accessed on 18.3.2021 at: https://hydro.chmi.cz/hpps/evlist.php?seq=2497648

Dalma, K. E., & Haydee, K. M. (2018). Numerical Modeling of Chemical Compounds' Fate and Kinetics in Living Organisms: An Inverse Numerical Method for Rate Estimation from Concentration. Numerical Simulations in Engineering and Science. doi:10.5772/intechopen.76611

Datta, A. R., Kang, Q., Chen, B., & Ye, X. (2018). Fate and Transport Modelling of Emerging Pollutants from Watersheds to Oceans : A Review. Advances in Marine Biology (1st ed.). Elsevier Ltd. https://doi.org/10.1016/bs.amb.2018.09.002

Decision No 2455/2001/EC of the European Parliament and of the Council of 20 November 2001 establishing the list of priority substances in the field of water policy and amending Directive 2000/60/EC

Delli Compagni, R., Gabrielli, M., Polesel, F., Turolla, A., Trapp, S., Vezzaro, L., Antonelli, M. (2020). Chapter Six - Modeling tools for risk management in reclaimed wastewater reuse systems: Focus on contaminants of emerging concern (CECs), Editor(s): Paola Verlicchi, Advances in Chemical Pollution, Environmental Management and Protection, Elsevier, Volume 6, Pages 181-220, ISSN 2468-9289, ISBN 9780323856843, https://doi.org/10.1016/bs.apmp.2020.07.010.

Diamantini, E., Mallucci, S., & Bellin, A. (2019). A parsimonious transport model of emerging contaminants at the river network scale. Hydrology and Earth System Sciences, 23(1), 573-593. doi:10.5194/hess-23-573-2019

Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for Community action in the field of water policy

Directive 2006/118/EC of the European Parliament and of the Council of 12 December 2006 on the protection of groundwater against pollution and deterioration

Directive 2008/105/EC of the European Parliament and of the Council of 16 December 2008 on environmental quality standards in the field of water policy, amending and subsequently repealing Council Directives 82/176/EEC, 83/513/EEC, 84/156/EEC, 84/491/EEC, 86/280/EEC and amending Directive 2000/60/EC of the

European Parliament and of the Council

Directive 2013/39/EU of the European Parliament and of the Council of 12 August 2013 amending Directives 2000/60/EC and 2008/105/EC as regards priority substances in the field of water policy

Directive (EU) 2020/2184 of the European Parliament and of the Council of 16 December 2020 on the quality of water intended for human consumption

Díaz-Cruz, M. S. (ed.), Barcélo, D. (ed.) 2015: Personal Care Products in the Aquatic Environment. The Handbook of Environmental Chemistry, Volume 36. Springer International Publishing Switzerland.

Dulio, V., van Bavel, B., Brorström-Lundén, E., Harmsen, J., Hollender, J., Schlabach, M., … Koschorreck, J. (2018). Emerging pollutants in the EU: 10 years of NORMAN in support of environmental policies and regulations. Environmental Sciences Europe, 30(1). doi:10.1186/s12302-018-0135-3

Ebele, A. J., Abdallah, M. A., & Harrad, S. (2017). Pharmaceuticals and personal care products (PPCPs) in the freshwater aquatic environment. Emerging Contaminants, (2016). https://doi.org/10.1016/j.emcon.2016.12.004

Ellis, J. B. (2006). Pharmaceutical and personal care products (PPCPs) in urban receiving waters. Environmental Pollution, 144(1), 184–189. doi:10.1016/j.envpol.2005.12.018

Emilia-Romagna, 2019. Hydrological Yearbook.

EPA. (2017). Technical Fact Sheet – Perfluorooctane Sulfonate (PFOS) and Perfluorooctanoic Acid (PFOA).

Escher, B., Leusch, F. 2012: Bioanalytical Tools in Water Quality Assessment. IWA Publishing, doi:10.2166/9781780400778.

Fairbairn, D. J., Karpuzcu, M. E., Arnold, W. A., Barber, B. L., Kaufenberg, E. F., Koskinen, W. C., … Swackhamer, D. L. (2016). Sources and transport of contaminants of emerging concern: A two-year study of occurrence and spatiotemporal variation in a mixed land use watershed. Science of The Total Environment, 551-552, 605-613. doi:10.1016/j.scitotenv.2016.02.056

Fritz, F., Pavičić, A., Renić, A., Kapelj, J. 1988. Jadro and Žrnovnica springs. Part of the hydrogeological investigation for water protection zones, Zagreb (Repository of the Croatian Geological Survey, No. 140).

Funke, J., Prasse, C., Lütke Eversloh, C., & Ternes, T. A. (2015). Oxypurinol – A novel marker for wastewater contamination of the aquatic environment. Water Research, 74, 257–265. doi:10.1016/j.watres.2015.02.007

Geissen, V., Mol, H., Klumpp, E., Umlauf, G., Nadal, M., Ploeg, M. Van Der, … Ritsema, C. J. (2015). Emerging pollutants in the environment : A challenge for water resource management. International Soil and Water Conservation Research, 1-9. https://doi.org/10.1016/j.iswcr.2015.03.002

Gemeinde Neufahrn bei Freising - https://www.neufahrn.de/

Giger, W., Alder, A. C., Golet, E. M., Kohler, H. E., Mcardell, C. S., Molnar, E., … Suter, M. J. (2003). Occurrence and Fate of Antibiotics as Trace Contaminants in Wastewaters, Sewage Sludges, and Surface Waters, 57(9), 485–491

Gogoi, A., Mazumder, P, Tyagi, V. K., Chaminda, G. G. T., An, A. K., Kumar, M. (2018). Occurrence and fate of emerging contaminants in water environment: A review. Groundwater for Sustainable Development 6: 169–180, doi:10.1016/j.gsd.2017.12.009.

Gramatica, P., Cassani, S., & Sangion, A. (2015). PBT assessment and prioritization by PBT Index and consensus modeling: Comparison of screening results from structural models. Environment International, 77, 25–34. doi:10.1016/j.envint.2014.12.012

Grischek, T., Nestler, W., Piechniczek, D., Fischer, T., 1996. Urban Groundwater. In: Dresden, Germany. Hydrogeology Journal 4, 48–63.

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

Harbaugh, Arlen (2005): MODFLOW-2005. The U.S. Geological Survey Modular Ground-Water-Model - The Ground-Water Flow Process: U.S. Geological Survey Techniques and Methods 6-A16, variously p.

Hartmann, A., Barberá, J. A., & Andreo, B. (2017). On the value of water quality data and informative flow states in karst modelling. Hydrology and Earth System Sciences Discussions, (May), 1–22. https://doi.org/10.5194/hess-2017-230

Henzler, A. F., Greskowiak, J. & Massmann, G. (2014). Modeling the fate of organic micropollutants during river bank filtration (Berlin, Germany). Journal of contaminant hydrology, 156, 78-92. https:// 10.1016/j.jconhyd.2013.10.005

Hill, M., Banta, E., Harbaugh, A.W., Anderman, E.R. (2000). MODFLOW-2000, the U.S. Geological Survey modular ground-water model-User guide to the observation, sensitivity, and parameter-estimation processes and three post-processing programs. U.S. Geological Survey Open-File Report 00-184

Hillebrand, O., Nödler, K., Sauter, M., & Licha, T. (2015). Multitracer experiment to evaluate the attenuation of selected organic micropollutants in a karst aquifer. Science of The Total Environment, 506-507, 338–343. doi:10.1016/j.scitotenv.2014.10.102

Hirsch, R., Ternes, T., Haberer, K., & Kratz, K.-L. (1999). Occurrence of antibiotics in the aquatic environment. Science of The Total Environment, 225(1-2), 109–118. doi:10.1016/s0048-9697(98)00337-4

Hodges B., Dallimore C., 2019. Aquatic Ecosystem Model: AEM3D v1.0 User Manual. Hydronumerics, p. 167.

Hosseini, N. A. A., Parker, W. J. J., & Matott, L. S. L. (2012). Modelling Concentrations of Pharmaceuticals and Personal Care Products in a Canadian Watershed. Canadian Water Resources Journal / Revue Canadienne Des Ressources Hydriques, 37(3), 191–208. doi:10.4296/cwrj2012-949

Houde, M., De Silva, A. O., Muir, D. C. G., & Letcher, R. J. (2011). Monitoring of Perfluorinated Compounds in Aquatic Biota: An Updated Review. Environmental Science & Technology, 45(19), 7962–7973. doi:10.1021/es104326w

Hrkal, Z., Eckhardt, P., Hrabánková, A., Novotná, E., & Rozman, D. (2018). PPCP Monitoring in Drinking Water Supply Systems: The Example of Káraný Waterworks in. https://doi.org/10.3390/w10121852

Hu A., Ma Y., Wu J., Oakes K. (2015). Removal of pharmaceuticals and personal care products from wastewater. In: L.M. Barrett (Ed.) Wastewater Treatment (pp.81-109). Hauppauge, New York: Nova Science Publishers Inc.

Huerta-Fontela, M., Galceran, M. T., & Ventura, F. (2011). Occurrence and removal of pharmaceuticals and hormones through drinking water treatment. Water Research, 45(3), 1432–1442. doi:10.1016/j.watres.2010.10.036

Ilho, K., Jaiyeop, L. (2022). Comparison of ozonation removal for PPCPs in secondary treated sewage by microbubble generator and ejector, Environmental Engineering Research; 27(2): 200163

Internet 1: https://go.drugbank.com/drugs/DB09156

IOŚ-PIB – JARS Consortium, 2018: Development of hydrological model of the Kozłowa Góra reservoir's catchment area and model of ecosystems of the reservoir. Archives of Silesian Waterworks PLC

Ivešić, M., Krivohlavek, A., Žuntar, I., Tolić, S., Šikić, S., Musić, V., … Galić, N. (2017). Monitoring of selected pharmaceuticals in surface waters of Croatia. Environmental Science and Pollution Research, 24(29), 23389-23400. doi:10.1007/s11356-017-9894-4

Jamnik, B., Auersperger, P., Urbanc, J., Lah, K., Prestor, J. 2009. Ostanki zdravil kot pokazatelj antropogenih vplivov na podzemno vodo Ljubljanskega polja in Ljubljanskega barja. Geologija, 52/2, 241-248.

Jankūnaitė, D., Tichonovas, M., Buivydiene, D., Radžiūnienė, I., Račys, V., & Krugly, E. (2017). Removal of Diclofenac, Ketoprofen, and Carbamazepine from Simulated Drinking Water by Advanced Oxidation in a Model Reactor. Water, Air, &

Soil Pollution, 228, 1-15.

Jedlička, B., Kněžek, M. 1968. Artificial recharge. Hydrogeol. 1, 131–148.

Jukić, D., Denić-Jukić, V., 2009. Groundwater balance estimation in karst by using a conceptual rainfall-runoff model. J. Hydrol. 373 (3-4), 302–315. https://doi.org/10.1016/j.jhydrol.2009.04.035.

Kapelj, S., Kapelj, J., Švonja, M. 2012. Hydrogeological characteristics of Jadro and Žrnovnica catchment. Tusculum, 5 (1), 205-216.

Kleywegt S, Pileggi V, Yang P, Hao C, Zhao X, Rocks C, et al. Pharmaceuticals, hormones and bisphenol A in untreated source and finished drinking water in Ontario, Canada—occurrence and treatment efficiency. Sci Total Environ 2011;409:1481–8. Land Niederösterreich ATLAS. Web GIS ATLAS. Land Niederösterreich BEV.

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.

Kolpin, D. W., Furlong, E. T., Meyer, M. T., Thurman, E. M., Zaugg, S. D., Barber, L. B., & Buxton, H. T. (2002). Pharmaceuticals, Hormones, and Other Organic Wastewater Contaminants in U.S. Streams, 1999−2000: A National Reconnaissance. Environmental Science & Technology, 36(6), 1202–1211. doi:10.1021/es011055j

Korekar, G., Kumar, A., & Ugale, C. (2020). Occurrence, fate, persistence and remediation of caffeine: a review. Environmental science and pollution research international, 27(28), 34715–34733. https://doi.org/10.1007/s11356-019-06998-8

Kotowska U., Kapelewska J., Kotowski A., Pietuszewska E., 2019. Rapid and Sensitive Analysis of Hormones and Other Emerging Contaminants in Groundwater Using Ultrasound-Assisted Emulsification Microextraction with Solidification of Floating Organic Droplet Followed by GC-MS Detection. Water 11(8), 1638.

Kumar, P. Ready Biodegradability of N,N-Diethyl-3-Toluamide. Navi Mumbai (IN): Jai Research Foundation. Gujarat, for Alkyl Amines Chemicals Limited. (2003) Study 4347.

Kuraz, M., Mayer., P. (2008). DRUtES – an open source library for solving coupled nonlinear convection -diffusion –reaction equations. http://www.drutes.org.

Kuraz, M., Mayer, P., Pech, P. (2014). Solving the nonlinear Richards equation model with adaptive domain decomposition. Journal of Computational and Applied Mathematics, 270:0 2 –11.

Kuraz, M., Mayer, P., Pech, P. (2015). Solving the nonlinear and nonstationary Richards equation with two-level adaptive domain decomposition (dd-adaptivity).

Applied Mathematics and Computation. 267. 10.1016/j.amc.2015.03.130.

Kuraz, M., Jacka, L., Blöche,r J. R, Leps, M. (2019). Automated calibration methodology to avoid convergence issues during inverse identification of soil unsaturated hydraulic properties.Computer & Mathematics with Applications. under review

Kuwayama, Y., Young, R., & Brozović, N. (2017). Groundwater Scarcity. Competition for Water Resources, 332–350. doi:10.1016/b978-0-12-803237-4.00019-7

Landesamt für Umwelt (LfU), ed. 2002: Arzneimittel in der Umwelt, F+E Vorhaben 2000-2002, Schlussbericht.

Landesamt für Umwelt (LfU), ed. 2015: Arzneimittelwirkstoffe, Metaboliten und polare Spurenstoffe in Abwasser, Oberflächengewässern und Uferfiltrat.

Landesamt für Umwelt (LfU), ed. 2019: https://www.lfu.bayern.de/analytik_stoffe/arzneimittel wirkstoffe/roh_trinkwasser/index.htm (10.10.2019).

Lapworth, D. J., Baran, N., Stuart, M. E., & Ward, R. S. (2012). Emerging organic contaminants in groundwater: A review of sources, fate and occurrence. Environmental Pollution, 163, 287–303. doi:10.1016/j.envpol.2011.12.034

Loos, R., Gawlik, B.M., Locoro, G., Rimaviciute, E., Contini, S., Bidoglio, G., 2009. EU-wide survey of polar organic persistent pollutants in European river waters. Environ. Pollut. 157, 561-568. https://doi.org/10.1016/j.envpol.2008.09.020.

Loucks, D. P., & van Beek, E. (2017). Water Resource Systems Planning and Management. doi:10.1007/978-3-319-44234-1

López-Serna, R., Jurado, A., Vázquez-Suñé, E., Carrera, J., Petrović, M., & Barceló, D. (2013). Occurrence of 95 pharmaceuticals and transformation products in urban groundwaters underlying the metropolis of Barcelona, Spain. Environmental Pollution, 174, 305-315. doi:10.1016/j.envpol.2012.11.022

Manamsa K., Crane E., Stuart M., Talbot J., Lapworth D., Hart A., 2016. A national-scale assessment of micro-organic contaminants in groundwater of England and Wales. Science of the Total Environment 568: 712-726.

Mandaric, L., Diamantini, E., Stella, E., Cano-paoli, K., Valle-sistac, J., Molins-delgado, D., … Petrovic, M. (2017). Contamination sources and distribution patterns of pharmaceuticals and personal care products in Alpine rivers strongly affected by tourism. Science of the Total Environment. https://doi.org/10.1016/j.scitotenv.2017.02.185

Marchlewicz, A., Guzik, U., & Wojcieszyńska, D. (2015). Over-the-Counter Monocyclic Non-Steroidal Anti-Inflammatory Drugs in Environment-Sources, Risks, Biodegradation. Water, air, and soil pollution, 226(10), 355. https://doi.org/10.1007/s11270-015-2622-0

Mazzilli, N., Guinot, V., Jourde, H., Lecoq, N., Labat, D., Arfib, B., … Bertin, D. (2019). KarstMod: A modelling platform for rainfall - discharge analysis and modelling dedicated to karst systems. Environmental Modelling & Software, 122, 103927. https://doi.org/https://doi.org/10.1016/j.envsoft.2017.03.015

McCance, W., Jones, O. A. H., Edwards, M., Surapaneni, A., Chadalavada, S., Currell, M. (2018). Contaminants of Emerging Concern as novel groundwater tracers for delineating wastewater impacts in urban and peri-urban areas. Water Research 146: 118-133, doi:10.1016/j.watres.2018.09.013.

MedChemExpress (MCE): https://www.medchemexpress.com/

Moldovan Z., Marincas O., Povar I., Lupascu T., Longree P., Simovic Rota J., Singer H., Alder A.C., 2018. Environmental exposure of anthropogenic micropollutants in the Prut River at the Romanian-Moldavian border: a snapshot in the lower Danube river basin. Environmental Science and Pollution Research 25: 31040-31050.

Montanari, A. (2011). Uncertainty of Hydrological Predictions. Treatise on Water Science, 459–478. doi:10.1016/b978-0-444-53199-5.00045-2

Monteiro S.C., Boxall A.B. (2010) Occurrence and fate of human pharmaceuticals in the environment. Rev Environ Contam Toxicol. 202:53-154. doi: 10.1007/978-1-4419-1157-5_2.

Moore, M., Greenway, S., Farris, J., Guerra, B., 2008. Assessing Caffeine as an Emerging Environmental Concern Using Conventional Approaches. Archives of environmental contamination and toxicology 54, 31–35.

Moore, M. T., Greenway, S. L., Farris, J. L., & Guerra, B. (2008). Assessing caffeine as an emerging environmental concern using conventional approaches. Archives of environmental contamination and toxicology, 54(1), 31–35. https://doi.org/10.1007/s00244-007-9059-4

Müller, B., Scheytt, T., Asbrand, M., & de Casas, A. M. (2012). Pharmaceuticals as indictors of sewage-influenced groundwater. Hydrogeology Journal, 20(6), 1117–1129. doi:10.1007/s10040-012-0852-4

Neitsch S.L., Arnold J.G., Kiniry J.R., Williams J.R., 2011. Soil And Water Assessment Tool. Theoretical Documentation Version 2009. Texas Water Resources Institute, p. 618.

Neuman, S.P. (1973). Calibration of distributed parameter groundwater flow models viewed as a multiobjective decision process under uncertainty Water Resour. Res., 9 (4), pp. 1006-1021, 10.1029/WR009i004p01006

Ngo, T. H., Van, D.-A., Tran, H. L., Nakada, N., Tanaka, H., & Huynh, T. H. (2020). Occurrence of pharmaceutical and personal care products in Cau River, Vietnam. Environmental Science and Pollution Research, 28(10), 12082–12091. doi:10.1007/s11356-020-09195-0

Nham, T., Thuy, H., Greskowiak, J., Nödler, K., Azizur, M., Spachos, T., … Licha, T. (2015). Science of the Total Environment Modeling the transport behavior of 16 emerging organic contaminants during soil aquifer treatment. Science of the Total Environment, 514, 450–458. https://doi.org/10.1016/j.scitotenv.2015.01.096

NORMAN network (2020) Definition of emerging contaminant. https://www.norman-network.com/?q=node/19

Osorio, V., Marcé, R., Pérez, S., Ginebreda, A., Luís, J., & Barceló, D. (2012). Occurrence and modeling of pharmaceuticals on a sewage-impacted Mediterranean river and their dynamics under different hydrological conditions. Science of the Total Environment, The, 440, 3–13. https://doi.org/10.1016/j.scitotenv.2012.08.040.

Padhye, L. P., Yao, H., Kung'u, F. T., & Huang, C.-H. (2014). Year-long evaluation on the occurrence and fate of pharmaceuticals, personal care products, and endocrine disrupting chemicals in an urban drinking water treatment plant. Water Research, 51, 266–276. doi:10.1016/j.watres.2013.10.070

Palmiotto, M., Castiglioni, S., Zuccato, E., Manenti, A., Riva, R., Davoli, E. (2018). Personal care products in surface, ground and wastewater of a complex aquifer system, a potential planning tool for contemporary urban settings, Journal of Environmental Management, Volume 214, Pages 76-85, ISSN 0301-4797, https://doi.org/10.1016/j.jenvman.2017.10.069.

Pollock, David (2012): User Guide for MODPATH Version 6. A Particle-Tracking Model for MODFLOW: U.S. Geological Survey Techniques and Methods 6–A41, 58

Po River Basin District Authority, 2019. Inventory of emission and losses.

PubChem: https://pubchem.ncbi.nlm.nih.gov/

Radjenovic, J., Flexer, V., Donose, B., Sedlak, D. & Keller, J. (2013). Removal of the X-ray Contrast Media Diatrizoate by Electrochemical Reduction and Oxidation. Environmental science and technology. 47. https://doi.org/10.1021/es403410pSkalický, M., 2015. Artificial recharge of the Káraný site as a tool for solving the lack of groundwater for water use (in Czech). In Proceedings of the "Groundwater in Water Treatment 2015", Pardubice, Czech Republic, 1–2 April 2015.

Rasheed, T., Bilal, M., Nabeel, F., Adeel, M., & Iqbal, H. M. N. (2018). Environmentally-related contaminants of high concern: Potential sources and analytical modalities for detection, quantification, and treatment. Environment International. doi:10.1016/j.envint.2018.11.038

REACH website https://echa.europa.eu/regulations/reach/understanding-reach (19.3.2020)

Regulation (EC) No 1907/2006 of the European Parliament and of the Council of 18 December 2006 concerning the Registration, Evaluation, Authorisation and

Restriction of Chemicals (REACH), establishing a European Chemicals Agency, amending Directive 1999/45/EC and repealing Council Regulation (EEC) No 793/93 and Commission Regulation (EC) No 1488/94 as well as Council Directive 76/769/EEC and Commission Directives 91/155/EEC, 93/67/EEC, 93/105/EC and 2000/21/EC

Regulation on water quality standard (OG 96/2019). In Croatia: Uredba o standard kakvoće voda. https://narodne-novine.nn.hr/clanci/sluzbeni/2019_10_96_1879.html

Rezaei Kahkha, M. R., Oveisi, A. R., Kaykhaii, M., & Rezaei Kahkha, B. (2018). Determination of carbamazepine in urine and water samples using amino-functionalized metal-organic framework as sorbent. Chemistry Central journal, 12(1), 77. https://doi.org/10.1186/s13065-018-0446-x Richards L. A., 1931: Capillary conduction of liquids through porous mediums. Journal of Applied Physics, 10 (5):0 318–333.

Riva, F., Zuccato, E., Davoli, E., Fattore, E., Castiglioni, S. (2019). Risk assessment of a mixture of emerging contaminants in surface water in a highly urbanized area in Italy, Journal of Hazardous Materials, Volume 361, Pages 103-110, ISSN 0304-3894, https://doi.org/10.1016/j.jhazmat.2018.07.099.

Robertson, W. D., Van Stempvoort, D. R., Solomon, D. K., Homewood, J., Brown, S. J., Spoelstra, J., & Schiff, S. L. (2013). Persistence of artificial sweeteners in a 15-year-old septic system plume. Journal of Hydrology, 477, 43–54. doi:10.1016/j.jhydrol.2012.10.048

Rodríguez-Gil, J. L., Cáceres, N., Dafouz, R., & Valcárcel, Y. (2018). Caffeine and paraxanthine in aquatic systems: Global exposure distributions and probabilistic risk assessment. The Science of the total environment, 612, 1058–1071. https://doi.org/10.1016/j.scitotenv.2017.08.066

Salimi, M., Esrafili, A., Gholami, M., Jonidi Jafari, A., Rezaei Kalantary, R., Farzadkia, M., Kermani, M., & Sobhi, H. R. (2017). Contaminants of emerging concern: a review of new approach in AOP technologies. Environmental monitoring and assessment, 189(8), 414. https://doi.org/10.1007/s10661-017-6097-x

Sallwey, J., Jurado, A., Barquero, F., & Fahl, J. (2020). Enhanced Removal of Contaminants of Emerging Concern through Hydraulic Adjustments in Soil Aquifer Treatment. Water, 12(9), 2627. doi:10.3390/w12092627

Sanchez-Vila, X., Vàzquez-Suñé, E., Rodríguez-Escales, P., Jurado, A., Folch, A., Carles-Brangarí, A., … Fernàndez-Garcia, D. (2015). Emerging Organic Contaminants in Aquifers: Sources, Transport, Fate, and Attenuation. Emerging Contaminants in River Ecosystems, 47–75. doi:10.1007/698_2015_5010

Sauvé, S., & Desrosiers, M. (2014). A review of what is an emerging contaminant.

Chemistry Central journal, 8(1), 15. https://doi.org/10.1186/1752-153X-8-15

Schaefer, E. C., Siddiqui, A. I. DEET: Ready Biodegradability by the Carbon Dioxide Evolution Test Method. Easton (MD): Wildlife International, for the DEET European Union Joint Venture/CSPA. (2002) Project 538E-102.

Scheurer, M., Brauch, H.-J., & Lange, F. T. (2009). Analysis and occurrence of seven artificial sweeteners in German waste water and surface water and in soil aquifer treatment (SAT). Analytical and Bioanalytical Chemistry, 394(6), 1585–1594. doi:10.1007/s00216-009-2881-y

Scheytt, T., Mersmann, P., Lindstädt, R., & Heberer, T. (2005). Determination of sorption coefficients of pharmaceutically active substances carbamazepine, diclofenac, and ibuprofen, in sandy sediments. Chemosphere, 60(2), 245–253. https://doi.org/10.1016/j.chemosphere.2004.12.042

Schriks, M., Heringa, M. B., van der Kooi, M. M. E., Voogt, P. de, van Wezel, A. P. (2010). Toxicological relevance of emerging contaminants for drinking water quality. In: Water research 44 (2), S. 461–476. DOI: 10.1016/j.watres.2009.08.023.

Senta, I., Krizman-Matasic, I., Terzic, S., & Ahel, M. (2017). Comprehensive determination of macrolide antibiotics, their synthesis intermediates and transformation products in wastewater effluents and ambient waters by liquid chromatography–tandem mass spectrometry. Journal of Chromatography A, 1509, 60–68. doi:10.1016/j.chroma.2017.06.005

Senta, I., Terzić, S., & Ahel, M. (2008). Simultaneous Determination of Sulfonamides, Fluoroquinolones, Macrolides and Trimethoprim in Wastewater and River Water by LC-Tandem-MS. Chromatographia, 68(9-10), 747–758. doi:10.1365/s10337-008-0780-6

Sheikhy Narany, T., Bittner, D., Disse, M., & Chiogna, G. (2019). Spatial and temporal variability in hydrochemistry of a small-scale dolomite karst environment. Environmental Earth Sciences, 78(9). doi:10.1007/s12665-019-8276-2

Singh, V. P. (2018). Hydrologic modeling: progress and future directions. Geoscience Letters, 5(1). doi:10.1186/s40562-018-0113-z

Skalický, M., 2015. Artificial recharge of the Káraný site as a tool for solving the lack of groundwater for water use (in Czech). In Proceedings of the “Groundwater in Water Treatment 2015”, Pardubice, Czech Republic, 1–2 April 2015.

Solomatine, D. P., & Wagener, T. (2011). Hydrological Modeling. Treatise on Water Science, 435–457. doi:10.1016/b978-0-444-53199-5.00044-0

Spongberg, A. L., Witter, J. D., Acuña, J., Vargas, J., Murillo, M., Umaña, G., … Perez, G. (2011). Reconnaissance of selected PPCP compounds in Costa Rican surface waters. Water Research, 45(20), 6709–6717. doi:10.1016/j.watres.2011.10.004

Stefanakis, A. I., Becker, J. A., 2016. A Review of Emerging Contaminants in Water: Classification, Sources, and Potential Risks. In A. McKeown, & G. Bugyi (Eds.), Impact of Water Pollution on Human Health and Environmental Sustainability (pp. 55-80). Hershey, PA: IGI Global. doi:10.4018/978-1-4666-9559-7.ch003

Stocker, S. L., McLachlan, A. J., Savic, R. M., Kirkpatrick, C. M., Graham, G. G., Williams, K. M. and Day, R. O. (2012). The pharmacokinetics of oxypurinol in people with gout. British Journal of Clinical Pharmacology.74(3), 477–489. DOI: 10.1111/j.1365-2125.2012.04207.

Šimůnek, J., Šejna, M., Saito, H., Sakai, M., & van Genuchten, M. (2013). The HYDRUS-1D Software Package for Simulating the Movement of Water, Heat, and Multiple Solutes in Variably Saturated Media, Version 4.17, HYDRUS Software Series 3, Department of Environmental Sciences, University of California Riverside, Riverside, California, USA, pp. 343.

Tang, Y., Peng, X., Yang, W., Zhang, Y., Yin, M., & Liang, Y. (2017). Emerging Pollutants – Part I : Occurrence , Fate and Transport, 89(10), 1810–1828. https://doi.org/10.2175/106143017X15023776270665

Ternes, T. A., Bonerz, M., Herrmann, N., Teiser, B., & Andersen, H. R. (2007). Irrigation of treated wastewater in Braunschweig, Germany: An option to remove pharmaceuticals and musk fragrances. Chemosphere, 66(5), 894–904. doi:10.1016/j.chemosphere.2006.06.035

Tete, V. S., Nyoni, H., Mamba, B. B., & Msagati, T. A. M. (2019). Occurrence and spatial distribution of statins, fibrates and their metabolites in aquatic environments. Arabian Journal of Chemistry. doi:10.1016/j.arabjc.2019.08.003

Tiktak, A., Boesten, J., Linden, T. Van Der, & Kruijne, R. (2002). Original article Modelling the leaching and drainage of pesticides in the Netherlands : the GeoPEARL model, (October 2015). https://doi.org/10.1051/agro.

Trontelj, J., Klančar, A., Roškar, R. 2018. Pojavljane zdravilnih učinkovin in njihovih metabolitov v slovenskih vodah. Farmacevtski vestnik, 69, 101-106.

UK Food Standard Agency: https://www.food.gov.uk/

US-EPA PBT Profiler, 2006. Persistent, Bioaccumulative, and Toxic Profiles Estimated for Organic Chemicals On-line. The United States Environmental Protection Agency (Available from: http://www.pbtprofiler.net/

Vulliet, E., Cren-Olivé, C., & Grenier-Loustalot, M.-F. (2009). Occurrence of pharmaceuticals and hormones in drinking water treated from surface waters. Environmental Chemistry Letters, 9(1), 103–114. doi:10.1007/s10311-009-0253-7

Wang, Y., Wang, X., Li, M., Dong, J., Sun, C., & Chen, G. (2018). Removal of Pharmaceutical and Personal Care Products (PPCPs) from Municipal Waste Water with Integrated Membrane Systems, MBR-RO/NF. International Journal of Environmental

Research and Public Health, 15(2), 269. doi:10.3390/ijerph15020269

Wang, C., Shi, H., Adams, C. D., Gamagedara, S., Stayton, I., Timmons, T., & Ma, Y. (2011). Investigation of pharmaceuticals in Missouri natural and drinking water using high performance liquid chromatography-tandem mass spectrometry. Water Research, 45(4), 1818–1828. doi:10.1016/j.watres.2010.11.043

Water supply plan of Split-Dalmatia County 2008. Accessed on 18.5.2021 at: https://www.dalmacija.hr/Portals/0/docs/Skupstina/2011/24/12a.%20vodplanst.pdf

Weeks, J. A., Guiney, P. D., & Nikiforov, A. I. (2012). Assessment of the environmental fate and ecotoxicity of N,N-diethyl-m-toluamide (DEET). Integrated environmental assessment and management, 8(1), 120–134. https://doi.org/10.1002/ieam.1246

Wennmalm, Å., Gunnarsson, B. Public Health Care Management of Water Pollution with Pharmaceuticals: Environmental Classification and Analysis of Pharmaceutical Residues in Sewage Water. Ther Innov Regul Sci 39, 291–297 (2005). https://doi.org/10.1177/009286150503900307

Yang, Y., Ok, Y. S., Kim, K.-H., Kwon, E. E., & Tsang, Y. F. (2017). Occurrences and removal of pharmaceuticals and personal care products (PPCPs) in drinking water and water/sewage treatment plants: A review. Science of the Total Environment, 596-597, 303-320

Y Ying, G.-G., Kookana, R. S., & Dillon, P. (2004). Attenuation of Two Estrogen Compounds in Aquifer Materials Supplemented with Sewage Effluent. Groundwater Monitoring & Remediation, 24(2), 102-107. doi:10.1111/j.1745-6592.2004.tb00718.x

Zareitalabad, P., Siemens, J., Hamer, M., Amelung, W. (2013). Perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) in surface waters, sediments, soils and wastewater - A review on concentrations and distribution coefficients. Chemosphere, 91(6), 725-32. https://doi.org/10.1016/j.chemosphere.2013.02.024

Zhang, Q.-Q., Ying, G.-G., Pan, C.-G., Liu, Y.-S., & Zhao, J.-L. (2015). Comprehensive Evaluation of Antibiotics Emission and Fate in the River Basins of China: Source Analysis, Multimedia Modeling, and Linkage to Bacterial Resistance. Environmental Science & Technology, 49(11), 6772–6782. doi:10.1021/acs.est.5b00729

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