

boderec-ce Workpackage T1

O.T1.2 DATA COLLECTION TOOL FOR EMERGING CONTAMINANTS

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1. Introduction

Emerging contaminants (ECs) have become the topic of numerous investigations and projects, especially in recent years. Their occurrence, toxicity and consequently their impact on plant, animal and human life are identified and monitored.

The main goal of WP T1 is to define state-of-the-art of emerging contaminants appearing in the water environment. In detail, the aim of the work package is to give an overview of the identified contaminants, review of monitoring and analytical techniques and approaches and review of attenuation strategies. The before mentioned topics are in detail described in O.T.1.1 - *State-of-the-art of current practices in relation to emerging contaminants in the water environment*.

In this output O.T.1.2 - *Data collection tool for emerging contaminants* the data collection tool and the review of the appearance of emerging contaminants in water environment is described and reviewed in detail.

The findings of emerging contaminates appearing in the water environment are gathered from national reports and synthesised. The data reported in all of the national reports concerning the presence of emerging contaminants (pharmaceuticals, pesticides, personal care products, priority substances...) in the water environment (groundwater, spring water, river bank filtration, flowing streams, standing water bodies, wetlands, waste water and drinking/tap water) is gathered from different literature sources and scientific findings presented in governmental reports, scientific papers, published reports of monitoring programs, projects and research documents, monographs as well as conference proceedings and materials available online, published by institutions and other entities dealing with environmental issues.

From O.T.1.1 results and review of the ECs appearing in water environment, gaps in the procedures for data collections are identified and recommendations for implementation/improvement of data collection on emerging contaminants are given.





2. Data collection tool

The previous document entitled O.T.1.1 - *State-of-the-art of current practices in relation to emerging contaminants in the water environment* presents approach to conceptualization of information related to emerging contaminants. The approach was divided into four blocks which are related to four working packages inside of the project boDEREC-CE. These blocks are: Definition of emerging contaminants, Monitoring strategies, Analytical techniques, and Attenuation strategies. Based on these "Data collection tool for emerging contaminants" was created.

The data collection tool was tested in the group of project partners. The test was carried out during the preparation of the national reports (a separate report for each country, together six reports for each of the blocks). A separate questionnaire was prepared for each national report, and after completion of the national reports, they were analysed and summarised into transnational reports. After the synthesis of the transnational reports, all questionnaires were selectively merged into one data collection tool.

The data collection tool focuses on national sources of information on emerging contaminants. On the one hand, it collects data at the national level, and on the other hand, it investigates the country's relationship with the European and international levels in terms of understanding and answering open questions related to emerging contaminants. Tool not only examines research information (e.g. results of chemical analyses), but is also interested in further socio-economic implications of emerging contaminants. The questions are related to policy, administration, management and legislation. However, the main focus has been on the investigation of emerging contaminants occurrence in the aquatic environment.

Data collection tool is divided into five sections:

- 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

Data collection is represented in the form of questionnaire which is given in the appendix of the present report.





3. Review of emerging contaminants appearing in water environment

In the subchapters below the appearance of emerging contaminants is divided and described between groundwater, spring water, river bank filtration, flowing streams, standing water bodies, wetlands, waste water and drinking water.

3.1. Information available about the presence of ECs in groundwater

Data on the presence of ECs in groundwater are available from all project partner countries except **Croatia**. In countries, monitoring of ECs in groundwater is carried out as part of national monitoring and/or various studies and research. In some countries, monitoring is more developed and systematic, in some less so.



Figure 1: Pie chart of countries that have information on ECs in groundwater

In Austria, information on the occurrence of ECs (pharmaceuticals and pesticides) is collected in reports of studies and monitoring projects, which were performed within national projects under the guide of the Federal Environment Agency of Austria and the Ministry of Sustainability and Tourism. As part of the first project "Antibiotics in groundwater" ("Antibiotika im Grundwasser", Umweltbundesamt, 2010), 18 antibiotics from 50 measuring sites were analysed. 12 of 18 substances were detected with less than 1% positive results. However, no detection of those antibiotics was found in the karstic and fractal points. Due to the low number of positive results and the low concentration of analytes (the maximum was 58 ng/L for erythromycin), no further monitoring was performed. Groups of substances taken into consideration for this study were: ß-lactam-antibiotics, quinolone / gyrase inhibitors, folic acid antagonists, glycopeptides, tetracycline, lincosamide, macrolide. The second project "Monitoring program of pharmaceuticals and wastewater indicators of pharmaceuticals in ground and drinking water" ("Monitoringprogramm von Pharmazeutika und Abwasserindikatoren in Grund- und Trinkwasser", Bundesministerium für Gesundheit, BMG, AGES, 2015) tried to more closely observe possible changes in the substance discovered in the first project. In addition to the substances from the first project, some additional substances and wastewater indicators were included in the monitoring list in this project. 54 sampling sites were sampled and analyzed, only 5 and 6 of these points showed positive results in the second and fourth quarters of 2014. These positive results were related only to the following substances: erythromycin, lincomycin, sulfadimidine, sulfamethoxazole, and sulfathiazole. Groundwater is also analyzed as part of the monitoring program for the chemical and ecological status of water bodies in Austria. In particular a special monitoring program





("Water quality in Austria: 2014 - 2016", "Wassergüte in Österreich 2014 - 2016") is performed to analyse the presence of pesticides in groundwater. In the case of bentazone, the number and percentage of measuring points at which the concentration analysed was higher than the limit of quantificattation (LOQ) and the legislation limit was by far the highest compared to other substances.

In the **Czech Republic**, ECs monitoring focuses mainly on surface waters. Groundwater data are obtained indirectly by drinking water quality screening or from artificial infiltration and bank infiltration monitoring data (Kozisek et al., 2013; Hrkal et al., 2018). They also studied the occurrence and fate of pharmaceuticals in groundwater where treated wastewater infiltrates through recharge ponds (Rozman et al., 2015; Rozman et al., 2017). The result show that a range of substances occur in the infiltrating surface water, but most of it is effectively attenuated during passage through unsaturated zone. Few substances were detected in the groundwater (sulfamethoxazole, hydrochlorothiazide, gabapentin, tramadol, and sulfanilamide), however carbamazepine was confirmed to be persistent and was detected at a concentration of 890 ng/L even after longer residence time.

Also in **Italy**, research on the occurrence of ECs is mainly focused on surface waters, as they are more vulnerable to the presence of ECs. Pesticides and industrials (up to 4.78×05 and 15×106 ng/L) occur in the highest concentrations in groundwater. In a study conducted by Loos et al. (2007) detected herbicides (terbuthylazine: 7 ng/L, atrazine: 5 ng/L, simazinen: 16 ng/L and atrazine-desethyl: 11 ng/L) in tap water obtained from groundwater near Lake Maggiore. Of the pharmaceuticals, only the antimicrobial agent josamycin (concentration higher than 100 ng/L) was detected. Estrogen concentrations were below the limit of quantification, and illicit drug concentrations in groundwater have not yet been investigated (Meffe & de Bustamante, 2014). In Italy, following a study, carbamazepine, galaxolide and sulfamethoxazole sulfamethozale were proposed as "environmental trackers" to identify sources and routes of contamination / pollution (Lamastra, 2018).

Germany has a higher number of monitoring data (1141 database entries), especially on pharmaceutical residues in groundwater, because groundwater aquifer research was included in the initial monitoring programs of ECs in the aquatic environment. The results show that groundwater is not ubiquitously contaminated with pharmaceuticals (Bergmann, Fohrmann and Weber, 2011; Uba, 2019). Only if influenced by surface water, pharmaceuticals, most commonly clofibric acid, bezafibrate, diclofenac, phenazone, ibuprofen, and carbamazepine were detected. According to the results, clofibric acid may become a key parameter for monitoring pharmaceuticals in groundwater (Lfu, 2002).

In Poland, ECs in groundwater have been monitored in various studies. In a study conducted by Kuczyńska in 2017, 93 points were selected and 63% of the samples taken from these points were detected by pharmaceuticals. 21 of 31 compounds (estrone, estriol, 17 alpha-ethinyl estradiol, 17 beta-estradiol, testosterone, metoprolol, propanolol, diclofenac, ibuprofen, ketoprofen, naproxene, paracetamol, flurbiprofen, sulfadethine, sulfamerazine, sulfamethazine, sulfamethoxazole, sulfapyridine, enrofloxacin) were found in groundwater. The concentrations of ECs were relatively low, up to 869 ng/L. In the next study conducted by Kuczyńska & Janica (2017), the presence of 31 drugs in groundwater samples was tested. The presence of 9 substances was detected in 6 of 9 samples: carbamazepine, sulfadimethoxine, sulfamethazine, sulfamethoxazole, sulfadiazine, flurbiprofen, naproxen, doxepin and imipramine. Analytes concentrations ranged from <MQL to 252 ng/L (carbamazepine). Pharmaceuticals in groundwater were also found in the case of "Czarny Dwór" and "Zaspa" intakes in Gdańsk. Among 17 studied ECs, only non-steroidal antiinflammatory drugs (NSAIDs) and paracetamol were detected (Caban et al., 2015). ECs of the group parabens, sunscreen agents and insect repellents, phenols and pharmaceuticals and hormones are also analyzed in groundwater samples in the area of municipal landfills. 13 compounds were found in the collected water samples. All samples contained bisphenol A (up to $6.88 \ \mu g/L$) and benzophenone (up to 3.45μg/L). However, N, N-diethyltoluamide (DEET) occurred at the highest concentrations (up to 17.28 μg/L) (Kapelewska et al., 2016). The Polish Geological Institute determined concentrations of ECs, including pesticides like chloro-organic and phosphorous-organic pesticides in samples of 708 points (Cabalska et al., 2015). The concentration of pesticides exceeded the method limit of quantification (MQL) in 64 sample





points. Ignatowicz (2007) and Wołkowicz (2010) also studied the presence of pesticides and found peak concentrations of 30.0 µg/L for MCPA, 21.7 µg/L for □□HCH and 13.6 µg/L for □□HCH. Higher concentrations of pesticides were also found in groundwater in the vicinity of the chemical waste landfill (Lewkiewicz-Małysa & Konopka, 2008). The highest concentrations were found for methoxychlor (180.0 µg/L) and dichlorvos (138.8 µg/L).

In Slovenia, ECs are monitored by state monitoring, and several scientific and research projects have been carried out. Pharmaceutical substances are monitored as part of groundwater monitoring. Over a period of five years, 495 water samples were analysed at 125 measuring points, selected on the basis of data on wastewater treatment plants, settlement and agriculture (Mihorko et al., 2019). At least one pharmaceutical substance was determined in 160 samples at 58 different sites. The most commonly identified substance was carbamazepine and caffeine. Less commonly identified were sulfamethoxazole and even rarely theophylline, ketoprofen, diclofenac and gemfibrozil (Mihorko et al., 2019). The sampling results also showed that some measurement sites are more and constantly polluted as a result of urbanization and unregulated sewage network. According to currently known Austrian proposed limits for drinking water for certain pharmaceutical substances, no groundwater monitoring location in Slovenia exceeds the proposed limit values (Mihorko et al., 2019). As part of the research, the occurrence of ECs in the aquifer of Ljubljansko polje and Ljubljansko barje and Dravsko polje was determined. The aquifers of Ljubljansko polje and Ljubljansko barje are not heavily contaminated with caffeine, carbamazepine and propyphenazone, however, pollution is present (Jamnik et al., 2009). In the groundwater of Drava field results shows substances mainly from agriculture - pesticides and their degradation products - atrazine, desethyl atrazine and metachlor, from industrial environment - tetrachloroethylene, acetamide and trichloroethylene from urban areas (Koroša et al., 2017).

3.2. Information available about the presence of ECs in spring water

In three project partner countries - **Austria**, **Croatia** and the **Czech Republic**, there is no information on the presence of ECs in spring water. Other countries are exploring spring water, but to a lesser extent.



Figure 2: Pie chart of countries that have information on ECs in spring water

Germany has data on ECs in untreated water from wells, but much less compared to groundwater. The Environmental Monitoring Database for Pharmaceutical Concentrations, created in 2011 by the German Environmental Agency, contains 1,141 entries for groundwater and only 131 for water from wells. Spring





water was mainly investigated in Berlin, North-Rhine -Westphalia, and Bavaria (Bergmann, Fohrmann and Weber, 2011; Uba, 2019). As part of a project by the Bavarian Federal Environmental Agency, 29 different pharmaceuticals were investigated in well water as well as the main metabolite of cocaine and benzoylecgonine. Carbamazepine and its two main metabolites (concentrations $0.005 - 0.040 \mu g/L$), diatrizoic acid ($0.110 - 0.130 \mu g/L$), diclofenac, ibuprofen, primidone ($0.011 - 0.012 \mu g/L$), ritalinic acid, 2-Ethyl-2-phenylmalonamide ($0.007 - 0.008 \mu g/L$) and sulfamethoxazole ($0.010 - 0.019 \mu g/L$) were positively detected. Nevertheless, it can be generally said that spring water is rarely contaminated and if so with low concentrations (LfU, 2019).

Concentrations of the herbicide terbuthylazine and desethylterbuthylazine in the lowland springs of the Po River have also been detected in spring water in **Italy** (Laini et al., 2012). Estrogen was detected in groundwater emerging from mountain springs between Piedmont and Lombardy (Loos et al., 2007). Also, Perret et al. (2006) reported on pharmaceuticals in spring water.

In **Poland**, ECs in springs were explored only in springs in the region of the Cieszyn Tufa Springs (southern Poland). During the study (Ślósarczyk et al., 2019), polycyclic aromatic hydrocarbons (PAHs) were detected in water. The concentrations of 16 PAHs were determined using the GC-MS method. The total concentration of examined PAHs ranged between 0.079 and 1.3938 μ g/L. In a few samples, the sum of the concentrations of 4 PAHs (benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(ghi)perylene and indeno (1,2,3-cd) pyrene) exceeded the drinking water limit in Poland (0.1 μ g/L).

In **Slovenia**, the monitoring of ECs in spring water, especially drug residues, has been carried out by the Environment Agency since 2014 as part of national monitoring. During this time, 41 samples were analysed for 20 pharmaceutical compounds, of which 11 were determined at 5 locations in Slovenia (Mihorko et al., 2019). The presence of residues of pharmaceuticals in groundwater may imply contamination with municipal wastewater, the connection with sewage treatment plants in the hinterlands of springs, and veterinary medicinal products. Pharmaceuticals above LOQ were caffeine (0.022 - 0.120 μ g/L), carbamazepine (0.012 μ g/L), ketoprofen (0.010 μ g/L), sulfamethoxazole (0.006 μ g/L) and theophylline (0.017 μ g/L) (Mihorko et al., 2019).

3.3. Information available about the presence of ECs in the river bank filtration



5 project partners have data on the presence of ECs in river bank filtration; **Slovenia** and **Croatia** do not have this information.

Figure 3: Pie chart of countries that have information on ECs in the river bank filtration





Austria has carried out some research projects on this topic, in which the method of non-targeted analysis was used to identify ECs.

In the **Czech Republic**, the quality of drinking water in the Jizera river catchment was monitored at monthly intervals. It was found that no substances occur regularly and systematically. Acesulfame occurred most frequently, and paraxanthine only once (Hrkal et al., 2018).

In Germany, ECs, especially pharmaceuticals (commonly used or proven environmentally harmful pharmaceuticals), were monitored in drinking water obtained by river bank filtration. Among the most investigated rivers bank filtration waters in Germany is the Rhine-River. Among the positively detected substances in Bavarian riverbank filtration samples were carbamazepine and its two main metabolites (0.005 - 0.047 μ g/L), bisoprolol, bezafibrate, clofibric acid (0.005 μ g/L), diatrizoic acid (0.011 - 0.205 μ g/L), diclofenac, iopromide, and sulfamethoxazole (0.011 - 0.033 μ g/L) (LfU, 2019). The maximum measured concentration is 8.842 μ g/L of the analgesic dimethylaminophenazone which was measured within a nationwide monitoring program (Bergmann, Fohrmann and Weber, 2011).

In **Italy**, Rossetto et al. (2018) reported evaluations about the vulnerability to emerging pollutants at the Sant'Alessio induced river bank Filtration managed Aquifer recharge facility in Lucca (Serchio River).

In **Poland**, a study conducted by Dragon et al. (2018) showed the presence of pharmaceutical compounds and other micro-pollutants in both source water and bank filtrates. In total, 30 micropollutants were analyzed in 8 sampling points (1 river and 7 wells), including pharmaceuticals and pesticides. Some pharmaceuticals were detected in the Warta River, most notably theophylline (40 ng/L). During sampling in summer and autumn, pesticides were detected at a total concentration of 0.112 µg/L and 0.171 µg/L, respectively, and in winter these concentrations decreased significantly (0.031 (g/L). A study conducted by Kruć et al. (2019) involved 6 sampling points: the Warta River, 2 wells, 2 observation wells and 1 horizontal well. In this study, 75 parameters were analysed (antibiotics, anti-inflammatory, psychotropic drugs, β-blockers, X-ray contrastagents). The pharmaceuticals have been detected in both the Warta River (25 substances) and wells (13 substances). Concentrations of detected pharmaceuticals in river water were between 10.8 ng/L (sulfapyridine) and 1.470 ng/L (paraxantine). The highest concentration was found for oxypurinol: 1,050 ng/L in the Warta River, 1,359 ng/L in the horizontal well and 345 ng/L in the 1AL well.

3.4. Information about the presence of ECs in flowing streams

All project partner countries confirm that they have information about the presence of ECs in flowing streams.

Under the Water Framework Directive and the Austrian Water Quality Monitoring Program, priority substances listed in the Directive and in the Watch list. According to the monitoring program "Water quality in Austria", those substances were monitored once a year in sediments at 5 measuring points on the Danube, Drau, Inn and Mur rivers. They also performed chemical analysis of fish samples on the Wulka, Schwechat, Schmida, Donau, Krems, Mur and Dornbirnerach rivers. Some substances could not be detected because certain thresholds of environmental quality standards were lower than the LOQ values of the methods. In 2001, a joint survey on the Danube was also carried out in Austria. Sampling points for sediments were located both within the Danube River and at the estuary of the Schwechat River and for suspended solids in the upper Danube region. Various micro-pollutants (hormones, pharmaceuticals and poly brominated flame retardants) were analysed. Two hormones were mainly detected in the sediments: estrone and 17ßestradiol, found mainly in the sediment sample of the Schwechat River. The pharmaceuticals which could be detected above the limit of quantification were erythromycin, verapamil and caffeine. The representative for flame retardants was selected as poly brominated diphenyl ethers, and it was found mainly in the sediments of the Schwechat River. ("Untersuchung von Donausedimenten und Schwebstoffen auf ausgewählte organische Stoffe", UBA, 2004). In the suspended solids sample caffeine was detected in concentration of 6.6 and 6.0 µg/kg DM. In the samples collected from the sediments, erythromycin was





detected in concentration of 6.3 μ g/kg DM, and Verapamil and Sulfadiazine in concentration 7.9 μ g/L and 5.2 μ g/kg DM respectively.

In Croatia, the first reports date back to 2009, which showed elevated concentrations of macrolide antibiotics (100-1000 ng/L) in the Sava River (Senta, 2009). In 2013, surface waters and sediments were analysed at 4 locations on the Sava River, where a wide range of chemical structures and physicochemical properties, ranging from nonpolar and hydrophobic compounds, such as petroleum hydrocarbons and PAHs, to the polar and amphiphilic compounds, including pharmaceuticals and surfactants were analysed (Smital et al, 2013). In further studies, the most widely used antibacterials including sulfonamides and macrolides along 20 rivers in Croatia were analysed and monitored (Ivešić et al., 2017). A total of 20 target compounds were analysed in 148 samples. Erythromycin, azithromycin, sulfamethoxazole, sulfapyridine, sulfadiazine, and sulfamethazine were detected. Residues of sulfonamides and macrolides were detected in 31 samples or in 20.1% of samples, at concentrations ranging from 0.1 to 5.3 µg/L. The most frequent and the highest results (0.3 to 5.3 µg/L) were detected for erythromycin in the Sava River. Elevated concentrations of macrolides were detected near Zagreb, which is probably related to the pharmaceutical industry. In a recent study (Česen et al., 2019), 19 ECs were detected in surface water at a concentration higher than LOQ. Among them, the most common was caffeine (37-1390 ng/L). Bisphenols AP (0.540-0.903 ng/L), CL2 (0.365-2.09 ng/L), P (6.45-6.49 ng/L) and Z (0.250-9.11 ng/L) were detected > LOQ for the first time in the European surface water. Active pharmaceutical ingredients naproxen, ketoprofen, carbamazepine and diclofenac; the preservative methyl paraben; CAF and UV-filter HM-BP were the most abundant ECs in the surface water (Česen et al., 2019).

In the **Czech Republic**, the presence of drugs in rivers is monitored by river basin administrators, who publish the results in annual reports (Report on the state of water management in the Czech Republic in 2017. Ministry of the Environment and Ministry of Agriculture). Concentrations of the most commonly used non-steroidal anti-inflammatory drugs (NSAIDs - ibuprofen, diclofenac, naproxen, ketoprofen and indomethacin) were investigated in watercourses in the Elbe River Basin (29 sample sites in urban and rural areas). NSAID concentrations varied considerably at certain sample sites, but the total amount of particular compounds was relatively stable during all monitored periods with only non-significant increases in the spring and autumnal months. Ibuprofen was found to be the most abundant drug with a maximum concentration of 3210 ng/L, followed by naproxen, diclofenac and ketoprofen (1423.8 ng/L, 1080 ng/L and 929.8 ng/L). Indomethacin was found only at several sampling sites (maximum concentration of 69.3 ng/L) (Maršík et al., 2016).

In **Germany**, flowing streams are the most researched type of water bodies because they are exposed to wastewater runoff from wastewater treatment plants. These contain high amounts of ECs and therefore flowing streams are particularly vulnerable to possible reverse effects, ECs may have on them. The German database contains more than 9300 monitoring results of various pharmaceuticals in rivers from all parts of Germany (Bergmann, Fohrmann and Weber, 2011; Uba, 2019). The ECs monitoring network includes 13 rivers (Bergmann, Fohrmann and Weber, 2011; Uba, 2019), including Isar, which was part of the strategic monitoring of pharmaceuticals in Bavaria. Among the positively detected substances, 4-acetaminoantipyrine has the highest concentration $(1.000 \ \mu g/L)$ and clindamycin has the lowest concentration $(0.002 \ \mu g/L)$.

In Italy, the presence of ECs in surface waters in Lombardy was investigated by Marchesi et al. (2018), trends of pollutant concentrations (PBDE, DDx- sum of DDT, DDD and DDE), PCBs and PEDs in rivers in Lombardy were demonstrated by Guzzella (2018). Viganò (2009) reported information about endocrine disruptors in the Po River. In Umbria on the river Tevere, ECs (estrogens: 17-beta-estradiol (0.19 - 0.26 ng/L) and estrone (0.40 - 1.20 ng/L); anti-inflammatory: diclofenac (11-16 ng/L); neonicotinoid: imidacloprid (10 - 25 ng/L)) have also been sampled since 2016.

In **Poland**, the occurrence of ECs in flowing streams has been studied on a number of streams, including the longest rivers in Poland (Wisła, Odra and Warta). The most explored is the Warta River. Among the ECs, compounds belonging to pharmaceuticals, hormones, pesticides, AOX and polycyclic aromatic hydrocarbons





were detected (Jancewicz et al., 2011; Dudziak & Luks-Betlej, 2004; Baranowska & Kowalski, 2012; Migowska et al., 2012; Jagoda et al., 2011; Rosińska, 2010; Kruć et al., 2019; Kasprzyk-Hordern et al., 2007; Zgoła-Grześkowiak, 2010; Dragon et al., 2018; Kasprzyk-Hordern et al., 2008; Ignatowicz, 2007; Dębska et al., 2005; Kudłak, 2010; Pistelok et al., 2017). ECs with the highest concentrations were, respectively: paraxanthine (1470 ng/L), estrone and estradiol (1.3 ng/L), 2-methyl-4-chlorophenoxyacetic acid (MCPA; 23,000 ng/L) and adsorbable organohalogens (AOX) (8500 ng/L). In the case of PPCPs, most of the research was focused on residues of non-steroidal anti-inflammatory drugs.

In **Slovenia**, the national monitoring program for the status of river water bodies has been carried out in accordance with the requirements of the Water Directive since 2007. Between years 2009 and 2018 on 813 locations water samples were analysed and 40 of them was given poor chemical status. Among all 40 samples representing poor chemical status of surface water bodies on 7 sites ECs were detected, representing 17.5%. This illustrates that for poor chemical status of surface water are responsible toxic metals. In 2018, a survey was conducted that analysed wastewater, tap water and surface water. The compound which were detected in wastewaters in high concentrations, were also detected in surface waters and groundwaters, but in in lower concentrations. In surface waters compounds, valsartan and gabapentin were determined in the range of 40-50 ng/L, as well as irbesartan but in five time's lower concentrations. Caffeine was also determined in the range of 2 ng/L. Among other compounds which were under the level of quantification sulfamethoxazole was also common (Trontelj et al., 2018).

3.5. Information available about the presences of ECs in standing water bodies

Data on the presence of ECs in standing water bodies are not available in **Croatia** and **Austria**. In Austria, natural standing water bodies (lakes) were included in the sampling and analysis in the report "Water quality in Austria: 2014 - 2016" ("Wassergüte in Österreich 2014 - 2016"). However, the only results showed in the report concerned water temperature, pH, electrical conductivity, dissolved oxygen, oxygen saturation [%], and alkalinity ammonium [mg/L], nitrite [mg/L], nitrate-N [mg/l], orthophosphate-P [mg/L], total phosphorus-P (unfiltered) [mg/L], chlorophyll a [µg/L] and visibility depth [m]. Other project partner countries have data, but their number is small.



Figure 4: Pie chart of countries that have information on ECs in standing water bodies





In the **Czech Republic**, monitoring of PPCP substances was carried out at the Švihov reservoir and at the Vrchlice dam. With rare exceptions, the water in the Švihov reservoir was completely clean, however a systematic and increasing trend in pesticide growth has been demonstrated in the Vrchlice reservoir as a result of the increasing cultivation of biofuels crops (Datel et al., 2018; Ferenčík, 2018).

Germany has a small amount of data on ECs in standing water bodies (the database includes only 97 entries). They sampled many different pharmaceuticals in lakes and aquacultures. Concentrations of veterinary medicines in aquacultures are, as expected, high (aquaculture in Lower Saxony, concentration of sulfadimethoxine was $0.880 \mu g/l$). Persistent or high-volume pharmaceuticals like carbamazepine, clofibric acid, diclofenac, antibiotics like clarithromycin or erythromycin were positively detected in standing surface water bodies (Bergmann, Fohrmann and Weber, 2011).

In Poland, too, little is known about the occurrence of ECs in standing water bodies, however, some information is available in the literature and monitoring reports. Analysis of 6 drug residues in two lakes in northern Poland (in Gdansk and its suburbs) showed significant residues of fenoprofen, diflunisal, diclofenac and ibuprofen (up to 0.528 µg/L) (Dębska et al., 2005). In three selected lakes (Lanskie, Maroz and Rybnik power station reservoir) the occurrence of various commonly used veterinary antibacterial compounds was observed. The antibiotics were determined with optimized and validated analytical methods by liquid chromatography-tandem mass spectrometry. The results showed that no antibiotics at concentrations above the LOQs established for used methods were detected in the examined samples (Gbylik-Sikorska et al., 2014). Drożdżyński et al. (2009) collected surface water samples from the area of intensive farming in Wielkopolska (west-central part of Poland). A total of 55 samples were taken, 25 of which were obtained from lakes, 18 from rivers and 12 from ponds. The study covered 42 herbicides (and their metabolites), insecticides and fungicides commonly used in plant protection. 43 water samples contained residues of plant protection products used in intensive agricultural production. The most frequently found in the analysed samples were residues of atrazine (60.0%), desethyl atrazine (56.4%), carbendazim (45.4%), simazine (36.4%), desisopropylatrazine (34.5%), isoproturon (29.1%) and ethofumesate (21.8%). In total, residues of 29 out of 42 analysed pesticides were found, however their concentrations were usually very low. An interesting conclusion is that all pond water samples were contaminated with pesticides and the concentration were higher compared to lake water samples. Pistelok et al. (2015) in their work presented the results of analyses of selected PAHs in 5 reservoirs in Silesian region (southern Poland) based on monitoring research carried out by the Voivodship Inspectorate for Environmental Protection in Katowice. The average concentration of sum of benzo(k)fluoranthene and benzo(b)fluoranthene for the 5 reservoirs ranged between 0.0007 to 0.0058 µg/L, whereas average sum of benzo(g, h, i)perylene and indeno(1,2,3cd)pyrene ranged from 0.0009 to 0.0079 μ g/L.

In Italy, the most common herbicides in Lake Maggiore are terbuthylazine (max. concentration 7 ng/L), atrazine (5 ng/L), simazine (16 ng/L), diuron (11 ng/L) and atrazine-desethyl (11 ng/L) (Loos et al., 2007). Trends in pollutant concentrations (PBDE, DDx -sum of DDT, DDD and DDE-), PCBs and PEDs in Lombardy lakes were presented by Guzzella (2018).

In **Slovenia**, the chemical status of standing water bodies is assessed in accordance with national decrees and regulations. Priority substances are monitored in 11 lakes and 3 retention basins. The only available information regarding ECs is the chemical status of standing water bodies, which is assessed as good (ARSO, 2019a).

3.6. Information available about the presences of ECs in wetlands

Most project partner countries do not have data on the presence of ECs in wetlands, with the exception of the Czech Republic and Germany.







Figure 5: Pie chart of countries that have information on ECs in wetlands

Two studies have been conducted in the **Czech Republic** in which the concentrations of pharmaceutical products were studied by experiments in the laboratory and on a built-up wetland used as a treatment plant. Experiments in laboratory in vitro conditions show that the concentration of model NSAID ibuprofen was significantly decreased by cell suspension cultures of two tested species, Melilotus albus and Rheum palmatum. The following findings obtained on intact plants of common reed (Phragmites australis), which is the dominant specie of many wetland ecosystems around the world, growing in sterile conditions confirmed the absorption as well as metabolic degradation of added ibuprofen. Results achieved in laboratory conditions both during in vitro and hydroponic experiments were verified in real conditions in constructed wetland for ibuprofen and also for other widely spread acidic NSAIDs naproxen, ketoprofen, and diclofenac (Marsika et al., 2015). The second study examined the capabilities of four constructed wetlands. The concentrations of 31 pharmaceuticals were followed; a detailed evaluation of removal was done for 14 substances detected in at least 75% of the inflow wastewater samples. They found large differences in disposal efficiency between both systems and between pharmaceutical products (Vymazal et al., 2017).

Germany, which has a very limited amount of data, has also considered the removal of trace substances, inter alia, pharmaceuticals like diclofenac and carbamazepine, as well as its main metabolites in wetlands, in research projects. It has been found that altogether, biodegradation processes in wetlands are able to decrease most anti-inflammatories, analgesics, steroids and some endocrine disruptors. However, compounds recalcitrant to biodegradation are insufficiently removed. Among these compounds are carbamazepine, diclofenac, iopromide, metropolol, and sotalol (Rühmland, 2015).

3.7. Information available about the presences of ECs in waste water

All project partner countries analyse municipal wastewater and effluents from treatment plants to determine the occurrence of pharmaceutical compounds, micropollutants, pesticides... Some countries obtain data through research / projects and some through monitoring programs.

Austria carried out the first analyses of pharmaceuticals in wastewater treatment plants in 1998 and detected erythromycin and trimethoprim at a concentration of 3 μ g/L ("Antibiotika im Grundwasser-Sondermessprogramm im Rahmen der Gewässerzustandsüberwachungsverordnung", UBA, 2010). In a project in which selected antibiotics were analyzed in groundwater, high concentrations of these were found. Trimethoprim (330 ng/L) appeared in the highest concentrations in the second quarter of 2008 and Clarithromycin (1800 ng/L) in the fourth quarter ("Antibiotika im Grundwasser-Sondermessprogramm im Rahmen der Gewässerzustandsüberwachungsverordnung", UBA, 2010). As part of the project "Emissions of





organic and inorganic pollutants from municipal wastewater treatment plants" ("Emissionen organischer und anorganischer Stoffe aus kommunalen Kläranlagen", UBA, 2009), they wanted to create a database for determining priority substances to be monitored in effluents from wastewater treatment plants. From a larger number of substances, after a longer monitoring, four substances were obtained that need to be monitored in emissions. Diuron which is included in the WFD priority list was also included. The key among them is diuron. They also wanted to create a database for the project "Emission of micro-pollutants from settlement and traffic areas" ("Spurenstoffemissionen aus Siedlungsgebieten und von Verkehrsflächen", BMLFUW, 2014). Different micro-pollutants in different emission pathways (treated wastewater, combined and separated systems discharges, road runoff, deposition and groundwater) were analysed (e.g. metals, industrial chemicals like bisphenol A, nonylphenols, perfluorinates and organotin compounds, polybrominated diphenyl ethers). The results showed that in wastewater effluents hydrophilic substances were detected, for instance PFOS, PFOA, hormones, plant protection active substances. In accordance with the Water Framework Directive, the project "Emissions of selected priority and other substances from municipal waste water treatment plants" ("Emissionen ausgewählter prioritärer und sonstiger Stoffe aus kommunalen Kläranlagen", UBA, 2017) monitored emissions at eight selected wastewater treatment plants. The two pharmaceutical active compounds were among the substances with the highest concentration values detected.

The first analyses of pharmaceutical compounds in **Croatian** wastewater showed that phenazone compound propyphenazone with concentrations up to 1.0 μ g/L occurs most frequently (Jeličić and Ahel, 2003). As part of the EMCO project, the first results showed that the most abundant antimicrobial sulphonamide was sulfamethoxazole (0.3 to 2.0 μ g/L); norfloxacin (0.01 to 3.0 μ g/L) and ciprofloxacin (0.01 to 2.6 μ g/L) were the most abundant fluoroquinolones, while azithromycin (0.02 to 1 μ g/L) and erythromycin were the most prominent macrolide antibiotics (Terzić et al., 2005). A nation-wide screening (Senta et al., 2013) showed ubiquitous occurrence of human-use antimicrobials in the raw wastewater samples with total concentrations ranging from 2 to 20 μ g/L), while veterinary antimicrobials were typically present in much lower concentrations (<100 ng/L).

In the **Czech Republic** only sporadic data are available from wastewater treatment plants in Prague, Horní Beřkovice and Mladá Boleslav. All the information obtained shows a very low removal efficiency of most pharmaceuticals. Similarly low efficiency has been demonstrated for constructed wetlands (Rozman et al., 2015; Hrkal et al., 2018; Vymazal et al., 2017).

In **Germany**, data exists on waste water treatment plant influents as well as effluents for a number of waste water treatment plants, for which there are more than 2000 entries in the database (Bergmann, Fohrmann and Weber, 2011). In Bavaria, the Federal Environmental Agency has included the effluents of four WWTPs in its strategic monitoring program of pharmaceuticals. One of these WWTPs is located in Dietersheim. Its outlet is let into the Isar upstream of the action plan (LfU, 2002; LfU, 2015). Among the measured values, the highest is 2,300 μ g/L for 4-acetaminoantipyrine and the lowest is 0.074 μ g/L for roxithromycin.

In **Poland** the presence of emerging contaminants in wastewater was determined in both untreated and treated sewage. In many cases ECs concentrations in sewage before treatment processes exceeded 1µg/L (Wontorska & Wąsowski, 2018). However, this value was not exceeded in any case of PAHs (Pistelok et al., 2015). Since wastewater treatment plants often do not remove most ECs, these compounds are also present in already treated wastewater. In the case of pharmaceuticals, the highest concentrations were found for naproxen (up to 10380 ng/L) and ketoprofen (up to 9200 ng/L) in untreated wastewater from treatment plant in Poznań (Kasprzyk-Hordern el al., 2008) and at the Koziegłowy treatment plant, paracetamol (51400 ng/L) (Zając, 2017). In addition to the mentioned drugs, diclofenac (up to 2890 ng/L) was present in the treated wastewater in high concentrations due to its low removal efficiency (Kasprzyk-Hordern el al., 2008). There are also studies on only presence of pharmaceuticals and polycyclic aromatic hydrocarbons (PAHs) in untreated and treated wastewater from three WWTPs: Białystok, Łomża and Suwałki (Kotowska & Jasińska, 2011). According to this research, the number of detected compounds in sewage before and after treatment





was, respectively: 4 and 0 for PAHs, 2 and 0 for pharmaceuticals (Białystok), 2 and 0 for PAHs, 3 and 1 for pharmaceuticals (Łomża), 8 and 2 for PAHs, 4 and 1 for pharmaceuticals (Suwałki).

In **Slovenia**, the presence of cyclophosphamide and ifosfamide can be detected in hospital wastewater. Both compounds with UV / O3 biological treatment with H2O2 have been shown to have a removal efficiency of 99% (Česen et al., 2015). Analysis of samples from 9 wastewater treatment plants (from wastewater and river water) showed the presence of 48 compounds of emerging concern (Česen et al., 2018). Also, 48 compounds were found in the research of wastewater from three Slovenian and three Croatian wastewater treatment plants and the Sava River (Česen et al., 2019). In 2018, samples were taken from wastewater treatment plants, surface water and tap water and the highest concentrations were measured for: paracetamol, tramadol, salicylic acid, atorvastatin, rosuvastatin, metformin, hydrochlorothiazide and diclofenac (Trontelj et al., 2018). As part of the research on the inflow and outflow of wastewater at one of the largest wastewater treatment plants in Slovenia, the results showed that the effect of water treatment is substantial for most substances. Exception is carbamazepine which practically non-degradable. Overall, it is observed that the number of substances determined is growing over the years. Active substances used to relieve pain, with anti-inflammatory effects and substances for lowering body temperature are predominant (Sovič et al., 2019).

In Italy, Verlicchi et al. (2010, 2013) and Verlicchi & Girardini (2019) reported on micropollutants in hospital effluents as a source of ECs and on the evaluation of their removal efficiency in treatment trains. As part of the FRAME project, they the National Institute of Health (ISS) and the Water Research Institute (CNR-IRSA) coordinated risk assessment and implementation of legislation. They analysed ECs such as drugs, pesticides and metabolites, PFAS, antibiotics, water disinfection byproducts in different stages of purification treatments and aimed to identify the best treatment technologies suitable to break down these contaminants.

3.8. Information available about the presences of ECs in drinking/tap water

Information on the presence of ECs in drinking water is available in all project partner countries except Croatia. **Croatia** monitors drinking water in accordance with the Drinking Water Directive, and also sets additional parameters at the national level, which do not include ECs.



Figure 6: Pie chart of countries that have information on ECs in drinking/tap water





In Austria, drinking water, as well as groundwater (see 2.1), was investigated in the framework of the project "Monitoring program of pharmaceuticals and wastewater indicators of pharmaceuticals in groundand drinking water", ("Monitoringprogramm von Pharmazeutika und Abwasserindikatoren in Grund- und Trinkwasser", Bundesministerium für Gesundheit, BMG, AGES, 2015) a follow up of the project "Antibiotics in groundwater". In Austria, 50 measuring points were selected for sampling and analysis of drinking water. Of all measuring points, 2 points during the second quarter of the year 2014 and 5 points during the fourth quarter were observed. The only substance measured was sulfamethoxazole. Organic pollutants were investigated as part of the report on "Drinking water in Austria" ("Österreichischer Trinkwasserbericht 2017", Bundesministerium für Arbeit, Soziales, Gesundheit und Konsumenschutz, 2017). Among the whole Austria around 260 samples were analyzed. The results showed detected concentration values higher than the limit of quantification of three pesticides (boscalid, bentazone, and terbuthylazine), eight relevant metabolites (atrazine-desethyl-desisopropyl) and eight non relevant metabolites.

The first comprehensive assessment of pharmaceuticals in drinking water in the **Czech Republic** examined samples from public water supply systems that supply 50.5% of the Czech population. In the initial survey of tap water from 92 major supply zones using mostly surface water, no pharmaceutical exceeded the limit of quantification (LOQ = 0.5 ng/L). In a second survey, samples were collected from the outlet of 23 water treatment plants (WTPs) considered of high risk because they use surface waters influenced by wastewater. Ibuprofen was the most frequently found pharmaceutical (19 samples), followed by carbamazepine (12), naproxen (8), and diclofenac (3); concentrations ranged from 0.5 to 20.7 ng/L. A follow-up survey included tap and outlet samples from eight of the 23 WTPs with the highest concentrations. Pharmaceuticals were detected in only three tap water samples. Regarding risks to consumers, these results suggest that a relatively small population (<10%) is exposed to quantifiable concentrations of pharmaceuticals in tap water and that an extremely high margin of safety is associated with these exposures (Kozisek et al., 2013).

In **Germany**, due to the legal framework, very few tests are carried out in tap water. In 1998, only one sampling on pharmaceuticals in tap water was carried out at eight sites in Cologne (Bergmann, Fohrmann and Weber, 2011). However, more information is available on ECs (pharmaceuticals) in drinking water that was addressed in the Bavarian Environment Agency project. The results showed that 69% of the probes did not contain residues from pharmaceuticals, and only carbamazepine was detected in 25% of the probes (concentrations between 0.006 μ g/L and 0.077 μ g/L). Few additionally showed positive results for sulfamethoxazole and primidone (concentrations for positive detections ranged between 0.02-0.05 μ g/L). In monitoring centers close to the Main, Danube, and Regnitz, X-ray contrast media (amidotrizoic acid and iopamidol) were detected (LfU, 2019).

In **Italy** encountered concentration of herbicides (terbuthylazine: 7 ng/L, atrazine: 5 ng/L, simazine: 16 ng/L, diuron: 11 ng/L and atrazine-desethyl: 11 ng/L) in the surface tap water produced from the Maggiore Lake (Loos et al., 2007). This indicates incomplete removal by sand filtration and chlorination used in the waterworks of the Maggiore Lake for production of tap water (Meffe & de Bustamante, 2014). From 2010 onwards, on drinking water purification plant in Pontelagoscuro, the following contaminants are monitored at the inlet and outlet: estrogens (17- α -ethinyl estradiol (ee2), 17- β -estradiol (e2), estriol (e3), estrone (e1)), polyalkyphenols (bisphenol a (bpa), 4-n-nonylphenol (np), 4-octylphenol (op), 4-t-octylphenol (t-op)) and fluorinated acids (perfluorootanoic acid (pfoa), perfluorooctanesulfonic acid (PFOS)).

In **Poland**, ECs were discovered as part of various studies. During the development of a new procedure of the DLLME method for the determination of selected anti-inflammatory drugs were detected ibuprofen, ketoprofen, naproxen and diclofenac (Zgoła-Grześkowiak, 2010). Three water samples were analysed, including one sample of tap water in the laboratory. Three out of four pharmaceuticals were identified: naproxen (13 ng/L), ibuprofen (< 6 ng/L) and diclofenac (4 ng/L). In the case of the study on developing a new multi-residual method for the simultaneous determination of seventeen pharmaceuticals in drinking water (SPE-GC/MS(SIM)) (Caban et al., 2015), treated water from groundwater intakes in Gdańsk ("Czarny Dwór" and "Zaspa") and surface water intakes "Straszyn" were studied. Among the 17 determined pharmaceuticals the following compounds were detected in drinking water: paracetamol (72-172.7 ng/L),





ibuprofen (<MQL to 4.3 ng/L), ketoprofen (16.0 - 58.8 ng/L), naproxen (< MQL). Drinking water was also studied in terms of the presence of perfluorinated compounds (PFCs) in Gdańsk, Gdynia and Gdynia-Bojano intakes (Rostowski et al., 2008). The concentration of perfluorooctanoic acid (PFOA) in the studied water was <0.005 - 0.0969 ng/L, the content of pentafluorobenzoic acid (PFBA) was 0.0545 ng/L and in the case of PFOS it was 0.0983 - 0.689 ng/L.

In **Slovenia** investigation performed by Faculty for the pharmacy 15 samples of drinking water were taken. The analysis showed that 13 out of 50 substances were present in measurable concentrations; they were mostly in the range between 1 and 2 ng/L. Only in two samples higher values were determined, for azithromycin (25 ng/L) and for caffeine (15 ng/L) and its metabolite 1,7 dimethylxanthine (5 ng/L) (Trontelj et al., 2018).

3.9. Analysis ECs appearing in water environment

In Austria, the information collected on ECs relates mainly to the monitoring and analysis of groundwater, wastewater, flowing water and drinking water. They were obtained mainly from government and official reports, which are available to the public and relate 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, hydrocarbons, were analysed as well together with certain selected pharmaceuticals and pesticides; in drinking water, pharmaceuticals and partly pesticides were analysed. Based on the data collected, it was found that there is not a standardized list of emerging contaminants to be monitored or to be considered as a referee for analysis. Pesticides were mainly analysed in groundwater, while pharmaceuticals were analysed in wastewater and drinking water. The pharmaceutical substance erythromycin was detected in all 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.

Although the reports on the official state monitoring of the ECs included in the state monitoring area not publically available in **Croatia**, various project results showed that discharges from the pharmaceutical industries, wastewater treatment plants can pose an ecological and public health concern mainly in the Sava River in Zagreb area.

In the **Czech Republic**, most research on the occurrence of ECs in water has been carried out in relation to drinking water sources. Ibuprofen, carbamazepine, naproxen and diclofenac were detected in samples of drinking water in low concentrations. In wastewater, which is the main source of pollutants, ECs are not monitored systematically. The removal efficiency of pharmaceuticals in waste water treatment plants differs for different substances. Some of them, like 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 have been shown to be most problematic because large portion of the stream are 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, where aquifer is intensively interacting by surface waters.

Germany pointed out that according to the monitoring of ECs, there are many different chemical substances that constantly enter the aquatic environment such as pharmaceutically active compounds, personal care products, analgesics, endocrine disruptors, antibiotics, illicit drugs. Their ability to accumulate, biological persistence and ecotoxicological effects are important. State monitoring focuses mainly on pharmaceutically active compounds because they are bioactive and pose a major risk to the environment and human health. The high consumption of personal care products and their ability to have a negative impact on the environment also indicate that strategic / long-term monitoring of these substances would





be necessary, as there are currently no data on the occurrence of these compounds in the German aquatic environment.

According to the database, there is monitoring data on pharmaceuticals in all parts of Germany, but their quantity varies between 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 waste water 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 waste water treatment plant effluents are the main source for these contaminants entering the environment, measurements taken close to the outlets were greater than 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 an 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 long-term changes in concentrations can be assessed. Analysing exiting data, there is barely any change in concentrations except for some substances for which use/consumption has 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).

In Italy, too, they deal with many different pharmaceutically active compounds, personal care products, industrial compounds, pesticides and other phytosanitary contaminants. Monitoring of ECs is always a selective process. In Italy the most monitored substances in surface and ground water are currently: PFAS and many plant protection products. For drugs, hormones and PPCPs, the research areas are still very limited, by the quantities involved in surface water, especially those intended for human consumption.

In Poland, ECs are found in different water bodies and conditions, including groundwater, spring water, river bank filtration, flowing streams, lakes, wastewater as well as drinking water. Little data is available on the occurrence of ECs in spring water, river bank filtration, drinking water (tap water) and groundwater. Polycyclic aromatic hydrocarbons have been treated in spring water; river bank filtration and groundwater studies have 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 have also been treated in standing water bodies, where microcontaminants have also been 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 of ECs in sewage from Polish Wastewater Treatment Plants is still present in wastewater after sewage treatment processes and it relates to all the studied groups (pharmaceuticals, hormones, PAHs).

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 follows from the requirements of EU law and national legislation. In Slovenia, ECs have been detected in both wastewater and natural water bodies. In some cases, we can discuss about 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.).





4. Identified gaps in the procedures for data collections

The main findings resulting from the data collection at national and international level based on the data collection tool are summarized as follows. The main findings relate to the occurrence of emerging contaminants in the aquatic environment.

The countries participating in the boDEREC- CE project have only recently started to systematically monitor and collect data on the occurrence of EC in different aquatic compartments. Most of them started monitoring at the end of the 1990s, and some of them only recently. From this point of view, the data sets are relatively short and not systematic. At the same time, the data on different aquatic compartments are not directly comparable. For some countries, some compartments are more important than others and, as a result, data are not available for some parts of the water cycle in some countries. In most cases the main focus is on groundwater, surface water and waste water. Common to all countries are the ECs, which are defined in a priority lists resulting from European legislation. There are only a few monitored substances that are not included in these lists. The most frequently monitored EC are: pharmaceuticals, pesticides and personal care products. The organization of the monitoring of EC in the aquatic environment is usually linked to the regional organization of the country. In most of the countries participating in the project there is no nationally organized monitoring covering and referring to the whole area. The presence of ECs is usually assessed by different monitoring programs or research studies.

Tables 1 to 3 summarise the available data on emerging contaminants in the aquatic environment. Table 1 shows whether data are available for a given aquatic compartment in the participating countries. Tables 2 and 3 analyse the available data in more detail. The focus is on the description of data type and quality.

	IDENTIFIED GAPS in data collection							
COUNTRY	GROUND WATER	SPRING WATER	RIVER BANK FILTRATION	FLOWING STREAMS	STANDING WATER BODIES	WETLANDS	WASTE WATER	DRINKING /TAB WATER
AUSTRIA	yes	no	yes	yes	no	no	yes	yes
CROATIA	no	no	no	yes	no	no	yes	no
CZECH REPUBLIC	yes	no	yes	yes	yes	yes	yes	yes
GERMANY	yes	yes	yes	yes	yes	yes	yes	yes
ITALY	yes	yes	yes	yes	yes	no	yes	yes
POLAND	yes	yes	yes	yes	yes	no	yes	yes
SLOVENIA	yes	yes	no	yes	yes	no	yes	yes

Table 1 Identified GAPS in data collection on emerging contaminants

*yes - countries have data on ECs *no - countries do not have data on ECs





	2)			
COUNTRY	GROUNDWATER	SPRING WATER	RIVER BANK FILTRATION	FLOWING STREAMS
AUSTRIA	yes * mainly data on pharmaceuticals and pesticides are available * data are only available from various reports, studies and projects (no state monitoring)	no	yes * very little data - some research projects	yes * little data - monitoring once per year
CROATIA	no	no	no	yes * little data * data available for shorter periods of time * research is carried out only at individual locations * monitoring only some ECs
CZECH REPUBLIC	yes * groundwater data are available indirectly from drinking water data * research is not conducted on the entire national territory, it focuses only on individual areas * data are available for shorter periods of time	no	yes * short monitoring time - small amount of data * research is carried out only at individual locations	yes * only information on drugs are available
GERMANY	yes * monitoring only some ECs	yes * much less data than for groundwater * research is carried out only in individual parts of the country * data are obtained only within various projects (no state monitoring) * monitoring only some ECs	yes * monitoring of only some ECs, mainly pharmaceuticals	yes * monitoring of only some ECs, mainly pharmaceuticals
ITALY	yes * much less data than in the case of surface waters * monitoring only some ECs * data available from	yes * research is carried out only at certain locations in the country * data are obtained only in the framework	yes * status not reported	yes * research is carried out only at certain locations in the country * short monitoring time

Table 2 Identified GAPS in data collection on emerging contaminants with explanations (1/2)





	various research activities (no state monitoring)	of various studies (no state monitoring) * monitoring only some ECs		
POLAND	yes * data obtained on the basis of various researches, pilot studies (no state monitoring) * mainly available data on pharmaceuticals and pesticides	yes * very little data available - only one study was conducted in southern Poland	yes * little data - short monitoring time * data obtained from studies in one region * monitoring only some ECs	yes * monitoring only some ECs * data are obtained in various studies (no state monitoring)
SLOVENIA	yes * short data collection time * monitoring only some ECs	yes * short data collection time and small number of samples * monitoring only some ECs	no	yes no shortcomings

Table 3 Identified GAPS in data collection on emerging contaminants with explanations (2/2)

COUNTRY	IDENTIFIED GAPS in data collection (2/2)				
	STANDING WATER BODIES	WETLANDS	WASTE WATER	DRINKING/TAB WATER	
AUSTRIA	no	no	yes * data available from various projects * monitoring only some ECs	yes * data available from various projects and reports * monitoring of only selected ECs	
CROATIA	no	no	yes * monitoring of only some ECs - mainly pharmaceuticals * data are available mainly from various projects and studies	no	
CZECH REPUBLIC	yes * in some locations short monitoring time	yes * data are available only from individual studies (no state monitoring)	yes * only sporadic data are available * research is conducted only at individual locations * monitoring only some ECs	yes * monitoring of only selected ECs, mainly pharmaceuticals * research is carried out only at individual locations	





	yes	yes	yes	yes
GERMANY	* little data limited to certain parts of the country * monitoring of only some ECs, mainly pharmaceuticals	* limited amount of data - some research projects	* monitoring of only some ECs, mainly pharmaceuticals	 very little data on tap water from households - only one sampling of pharmaceuticals was carried out at eight locations in Cologne in 1998 data on ECs (mainly pharmaceuticals) in drinking water are available for a shorter period of time mainly from projects
ITALY	yes	no	yes	yes
	* research is carried out only at certain locations in the country		* data are available from various studies and projects * monitoring only some ECs	 * monitoring only some ECs * research is carried out only at individual locations
POLAND	yes	no	yes	yes
			* status not reported	* little data - research is carried out only at individual locations
SLOVENIA	yes	no	yes	yes
	* little information			

The different project partner countries pointed out different difficulties and deficiencies in the collection of EC-related data. The differences are due both to the different natural conditions in the country and to the different use, management and administration of water resources. In some countries groundwater is an important source of drinking water, in some other countries there are combined drinking water sources where surface water is an important or even predominant source. The data collected show that more importance is given to aquatic compartments that are important for water supply (groundwater, surface water), but less data is available from compartments that are an important part of the water cycle but are not a source of drinking water (e.g. wetlands, natural standing bodies).

If data on EGs in the aquatic environment show a clear understanding of their presence in different compartments, the relationships with socio-economic aspects of EGs are not so clear. There is a different understanding among countries of the social impacts and influences of EGs. The answers to questions related to legislation, policy, management and governance show that from this point on there is a common-law understanding of the European framework legislation, but all other aspects are not well understood and there is a different awareness at all levels.





5. Recommendations

Based on the experiences of the project partners and their stakeholder network, it is possible to formulate recommendations for the implementation and improvement of data collection on emerging contaminants. These are based on the present review of the occurrence of emerging contaminants in the water environment and the analysis of the collected data.

In order to investigate possible long-term changes in concentrations of different substances or changes in pollution in the future, it is recommended to continue collecting data on emerging contaminants in the aquatic environment. There is common understanding that emerging contaminants occur in the aquatic environment and that newly developed analytical techniques need to be used for this purpose. It is not so clear how this information must be communicated to water policy, water management and governance.

Based on the analysis and interpretation of the collected data, the following recommendations can be made:

- existing monitoring of aquatic environment must be upgraded with new emerging contaminants,
- in relation to emerging contaminants all aquatic compartments must be monitored; more data are needed for wetlands and standing bodies,
- new up to date analytical techniques must be included into regular monitoring,
- better understanding of emerging contaminants ecotoxicological impact on aquatic environment is needed,
- European and national legislation related to emerging contaminants must be updated based on the existing experiences, there is a gap in transfer of scientific and professional knowledge to legislation,
- understanding of socio-economic implications of emerging contaminants must be improved; especially how results of monitoring are transferred to common and wider understanding.

6. Conclusion

The rapid growth of technology, the expansion of urban areas and changes in lifestyle, agriculture, industry and medicine have consumed large amounts of water and, as a result, produced wastewater. All these activities have significant impacts on health and the environment. Despite a better understanding of the water cycle, water resources are still exposed to pollution from various sources such as sewerage networks, discharges from wastewater treatment plants, the use of fertilizers in agriculture, landfills and many other potential sources of pollution. In the aquatic environment, we are seeing an increase in the number of pollutants produced. This is due both to constantly improving analytical techniques and to the increasing diversity of sources of new pollutants and their uses. On the basis of the results of data collection and their interpretation, we can conclude that emerging contaminants are likely to have effects on the environment, but not much is known about the effects on human health. As there is still relatively little information on the occurrence of emerging contaminants in general, further research and monitoring is needed. In the future it would be necessary to continue the implementation of water monitoring in all aquatic compartments, including all potentially critical points, and to extend the set of substances monitored.





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ANNEX I

DATA COLLECTION TOOL FOR EMERGING CONTAMINANTS





Section A

A. Identification of emerging contaminants (ECs) in the environment

- 1. What are emerging contaminants (write your explanation)?
- 2. How are ECs grouped in your country?
- 3. Report/Write a list of compounds considered as ECs in your country
- 4. What are the sources of ECs in your country?
- 5. What are the release mechanisms and what are possible pathways of ECs in the water environment?
- 6. Which ECs are in the priority lists at national scale?
- 7. How are relevant ECs was found in certain water bodies?

Section **B**

B. Legislation and policy related to emerging contaminats in the water enviroment

I. Policies, politics and management

- 1. Is there a discussion on EC at the political level in your country?
 - □ Yes
 - □ No
- 2. Is country communicating EC policy with political bodies at international level?
 - Communication with European Community to the commission
 - Communication with European Community parliament initiatives
 - Communication with UN agencies
 - Communication with other (professional) international organizations
- 3. Who is publicly discussing EC?
 - □ Politics at the state level political parties
 - Politics at the regional level
 - □ Local communities
 - □ Non-governmental organizations NGOs
 - □ Industry
 - Professional organizations





- □ Grass roots movements
- Other _____
- 4. Are there initiatives for governance on ECs?
- 5. Are there any political initiatives to establish new legislation on ECs?
- 6. Are political and policy questions related to ECs present in the media and how?
- 7. Can you recognize any policies about ECs at national level?
- 8. Are questions about ECs contaminants included in River Basin Management Plan(s) in relation to Water Framework Directive (WFD)?
- 9. Is the information on ECs contaminants included into the evaluation of chemical status of water bodies?
- II. Legislation
 - 1. Is there legislation about ECs in your country? If not, are there any recommendations about ECs in your country?
 - 2. How are ECs regulated on the national level?
 - 3. How national legislation is structured in relation to ECs?
 - 4. Are there any umbrella documents in relation to ECs which have a status of obligatory guidelines?
 - 5. Are there any legal criteria which define critical values of EC?
 - 6. Are there any voluntary guidelines which are accepting as a rule of conduct by national authorities?

Section C

C. Emerging contaminants appearing in the water environment

- 1. Is there any information available about the presence of ECs in groundwater?
 - □ Yes
 - □ No

If yes, please describe Click here to enter text.

- 2. Is there any information available about the presence of ECs in spring water?
 - □ Yes
 - □ No

If yes, please describe Click here to enter text.

- 3. Is there any information available about the presence of ECs in river bank filtration?
 - □ Yes
 - □ No





If yes, please describe Click here to enter text.

- 4. Is there any information about the presence of ECs in flowing streams?
 - □ Yes
 - □ No

If yes, please describe Click here to enter text.

- 5. Is there any information available about the presences of ECs in standing water bodies (lakes, retention basin, etc.)?
 - □ Yes
 - □ No

If yes, please describe Click here to enter text.

- 6. Is there any information available about the presences of ECs in wetlands?
 - □ Yes
 - □ No

If yes, please describe Click here to enter text.

- 7. Is there any information available about the presences of ECs in waste water?
 - □ Yes
 - □ No

If yes, what are the values Click here to enter text.

- 8. Is there any information available about the presences of ECs in drinking water/tap water?
 - □ Yes

No No

If yes, what are the values Click here to enter text.

Section D

D. State-of-the-art in monitoring

- I. Aims and objectives of monitoring
 - 1. Is there official state monitoring of ECs present in your country?
 - 2. Which are the objectives of the ECs monitoring?
 - □ Surveillance
 - Operational
 - □ Investigative monitoring
 - □ Other Click here to enter text.





- 3. Are you aware of any monitoring of ECs which was performed for scientific purpose (e.g. research project)?
- 4. Are ECs pollutant loads to be considered?
- 5. What are the results of research projects on ECs?
- 6. Which kind of water body has to be monitored?
- 7. Where is sampling for ECs is performed?
 - □ Springs
 - Groundwater observational boreholes
 - Groundwater water supply wells
 - □ Flowing water
 - □ Standing water bodies natural
 - □ Standing water bodies artificial
- 8. For water body where monitoring is performed, describe general natural conditions (define if applicable) repeat answers if there are more water bodies

Discharge Click here to enter text.

Recharge area <u>Click here to enter text.</u>

Type of surface water body Click here to enter text.

Land use in the recharge area Click here to enter text.

Type of the aquifer \Box porous \Box karstic \Box fissured rocks \Box combined \Box other Click here to enter text.

Depth to the groundwater level Click here to enter text.

Thickness of the aquifer Click here to enter text.

Surface area of the aquifer <u>Click here to enter text.</u>

- 9. Is monitoring of ECs performed on the recharge zones of drinking water resources and drinking water protection zones?
- 10. Which are the expectations of the monitoring program?
- 11. Which kind of ECs substances (groups) are analysed?
- 12. How information about ECs is included in the evaluation of chemical status of water bodies in relation to WFD?

Surface water bodies Click here to enter text.

Groundwater bodies Click here to enter text.

Artificial water bodies Click here to enter text.

13. Who is responsible for the interpretation of the ECs monitoring results?

Quality status Click here to enter text.

Ecotoxicological issues Click here to enter text.

Human health issues <u>Click here to enter text.</u>

At present no organization is responsible for such issues <u>Click here to enter text</u>.





II. Criteria for sampling locations

- 1. Which guidelines/regulations are used for ECs sample collection (e.g. WHO: collect natural water samples from midstream section of rivers, at depth of 20-50 cm)?
- 2. Are there any official national standards on the EC sampling?
- 3. Are there in the vicinity of the sampling location any discharges with potential EC in the water?
 - □ Yes
 - □ No

If yes, please describe Click here to enter text.

III. Sampling type and frequency

- 1. Who is performing the monitoring of ECs and how often is it carried out?
- 2. What is spatial representation for any type of monitoring sites?
- 3. According to the environmental medium monitored, which type of active sampling is applied?
 - □ In situ (water samples in field)
 - □ In laboratory (collected water samples)
 - □ Laboratory batch sediment extraction (sediment pore water samples)
- 4. What is time frequency for active sampling?
- 5. How do you sample for active sampling?
 - Grab sampling / Snapshots (manually)
 - □ Mixed samples (manually)
 - □ Automatic sampling
- 6. Is monitoring with passive samplers performed in your country?
 - □ Yes
 - □ No

If yes, please describe procedures for passive monitoring (e.g. monitoring with chemcatchers etc.)

- 7. Which established standards/official methods are applied?
 - □ EPA
 - □ ISO
 - □ CEN
 - □ Other <u>Click here to enter text.</u>
- 8. For which environmental medium is the passive sampling applied?
 - □ Water samples
 - □ Sediment pore water samples
- 9. Which category of passive sampling is applied?
 - □ Membrane-based (liquid sampling)





 \Box Semi permeable membrane device (SPMD)

 \Box Supported liquid membrane (SLM)

 \Box Others Click here to enter text.

- Diffusion-based (liquid sampling)
 - □ Solid phase micro extraction (SPME)

 \Box Others Click here to enter text.

- □ Living organisms based
- □ Others
 - □ Polar Organic Chemical Integrative Sampler (POCIS)
 - □ Polydimethylsiloxane (PDMS)

□ Others Click here to enter text.

- 10. Which is the sorbent material used for the receiving phase of the sampler?
 - □ Solvent
 - Chemical reagent
 - □ Absorbent polymer
 - Porous adsorbent material

Describe in detail: the compound group to be analysed, the uptake processes and the driving forces, the material used and the selected passive sampler.

IV. Sample containers and sampling

- 1. Which kind of sampling vessels are used?
 - □ Glass bottles (describe in detail)
 - □ Plastic vessels (describe in detail)
 - □ Aluminium bottles
- 2. Which guidelines/regulations are used for choosing the right sample containers?
- 3. Which kind of preparation of sample containers is performed?
 - □ Washed with ultra-pure/distilled/deionized water
 - Organic solvent
 - □ Rinsed with sampling water
 - □ Other <u>Click here to enter text.</u>
- 4. Which is the optimum sample volume needed for analysis?
- 5. Which are the requirements for filling the containers?
 - □ Avoiding turbulences
 - □ Avoiding air contact in container





□ Other <u>Click here to enter text</u>.

V. Sampling storage / transportation (in field)

- 1. Is an additional sample stabilization/preservation performed?
 - □ Protection from light
 - □ Adding of chemicals
 - Correction of pH (e.g. fixing and stabilization)
 - □ Other <u>Click here to enter text.</u>
- 2. What are the needed conditions of the transportation the samples into the lab?
 - □ Reduced temperature (show the needed degree centigrade value)
 - Time needed to deliver the samples (e.g. 24h/48h etc.)
 - Other <u>Click here to enter text.</u>
- 3. Are there any other steps that should be performed before transportation (filtration, centrifugation...)?
 - Yes
 - □ No

If yes, describe in detail. Click here to enter text.

VI. Sampling preservation (in the laboratory)

- 1. Is an additional sample preservation step performed in the lab?
 - □ Protection from light
 - □ Adding of chemicals
 - □ Changing of pH
 - □ Filtration
 - □ Centrifugation
 - □ Other <u>Click here to enter text.</u>
- 2. Which is the maximum allowed time between sampling / arriving of samples in the lab and analysis?

VII. Sample analysis

- 1. Which kind of sample preparation is performed before analysis?
 - □ Solid-phase extraction (SPE)
 - □ Liquid-liquid extraction (LLE)
 - □ Stir-bar extraction (SBE)
 - □ Evaporation





- □ Others Click here to enter text.
- 2. What are laboratory analytical standards and procedures? Are they ISO/IEC 17025 accredited (for sampling, for analysis of ECs)?
- 3. Which analytical approach is applied?
 - Targeted
 - Non-targeted
- 4. Which method of analysis is applied?
 - Liquid Chromatography (LC-MS): describe in detail
 - Gas Chromatography (GC-MS): describe in detail
 - □ Others Click here to enter text.
- 5. Describe the quality assurance performed for the analysis.
- 6. Describe the performance characteristics of the method(s) used for analysis (LOD, LOQ, precision, accuracy, etc.)
- 7. Are screening and fingerprinting methods applied?

Section E

E. Attenuation strategies

- I. Active attenuation measures
 - 1. Are you aware of any internationally available technology for the removal of ECs?
 - 2. Are you aware of any nationally available technology for the removal of ECs?
 - 3. Are active attenuation measures present in your country?
 - 4. Are you aware of any program for removal or treatability of ECs in waste water?

Internationally Click here to enter text.

Nationally Click here to enter text.

- 5. Are there any pilot experiments in waste water treatment performed for the removal of ECs?
- 6. Are you aware of any in situ treatment for ECs in surface water bodies?
- 7. Are you aware of any in situ treatment for ECs in bodies?
- 8. If ECs are considered with River Basin Management Plan what are prescribed strategies for the chemical status improvement?
- 9. Is natural attenuation considered in relation to ECs and is it being harnessing?
- 10. Are active attenuation measures effective and how do is the effectivnes measured?





II. Passive attenuation measures

- 1. Are passive attenuation measures present in your country?
- 2. Are passive attenuation measures being implemented?