

Specific types of wastewater pollution in Ostrava and possibilities of decontamination through wastewater treatment plants

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Abstract. This paper provides an introduction to the problem of the occurrence of some groups of micropollutants in wastewater, namely pharmaceutically active compounds (PhAC) and drugs in the context of wastewater treatment in Ostrava (290,000 inhabitants). Wastewater treatment is an essential service that ensures the reduction of pollutants in wastewater, while also protecting human health and the environment. In Europe, most wastewater enters the sewerage system and is discharged to a wastewater treatment plant, from where it is further discharged into rivers, lakes or coastal areas. Recently, people have been focusing more on pollutants in wastewater that are not targeted by WWTP, i.e., so-called micropollutants, which are, for example, pharmaceutically active compounds, drugs, or their metabolites. The risk of these groups of micropollutants in water is, for example, the possibility of exposure to aquatic organisms or bioaccumulation in food chains. The discharge of treated wastewater from the WWTP is the central route for PhAC to enter surface waters, as current technologies for decontamination are not yet designed. On the other hand, WWTPs act as primary barriers against the spread of micropollutants. One of the basic steps in designing a decontamination technology is to know the composition of the local wastewater.

1 Introduction to the issue of wastewater

Water is an essential substance for human life as well as for the functioning of ecosystems and so there is a global effort to protect it. One of the tools for this is Agenda 2030. This is a long-term programme with the objective of sustainable environmental development from the United Nations, which was adopted in September 2015 by agreement of the global community. The 17 Sustainable Development Goals are an important part of this programme. Water is the focus of goal 6, Indicator 6.3.1 monitors the proportion of total industrial and domestic wastewater flows safely treated in accordance with national or local standards [1-3].

Wastewater treatment can and should also contribute to the overall objectives of the Green Deal for Europe, with a key role in supporting the ambition to achieve zero pollution [1].

Wastewater treatment originally focused on the prevention of disease through contamination of drinking water sources, but the understanding of the potentially harmful role of nutrients (nitrogen, phosphorus) in terms of the environment led to the Urban Waste Water Treatment Directive (UWWTD) in 1991 [4].

We now know that there are many more pollutants in wastewater than were detected in 1991. We have limited knowledge of the risks to the aquatic environment. We also know that risks are likely to occur in the future that

we may not be aware of now. In addition, the coronavirus pandemic reminded us of the importance of wastewater as a way of monitoring/tracking disease in society [5].

Although we can think of urban wastewater treatment plants (WWTP) as "pollution sources", it is important to bear in mind that pollution does not come from the WWTP themselves, but from many sources in the sewerage network - from households, industry, schools, health and other organisations, hospitals for the long-term sick, etc. - that all meet at the WWTP.

When pollution source control fails, urban wastewater treatment is the last stage to protect the environment from the release of pollutants into the environment, the so-called "end-of-pipe" control. Treatment for water purification purposes may transfer pollutants to the atmosphere, to sewage sludge and other treatment products, which may result in the need for specific solid waste management [1].

Enormous efforts to reduce wastewater pollution, based on the UWWTD and supported by other EU and national legislation and EU funding, have led to significant improvements in the quality of Europe's surface waters in recent decades [6].

2 Water protection legislation

International treaties and European Community Directives have an influence on the creation of laws,

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Government Regulations and Decrees in the creation of legislative regulations of the Czech Republic. Their importance has increased significantly after the Czech Republic's accession to the European Union, which included the obligation to implement the EC Directives into the Czech legal system and the standard-setting environment for individual areas [7].

Within the Czech legislation, several laws deal with water issues. The central law is the Water Act [8], the Water Supply and Sewerage for Public Use Act [9] and the Public Health Protection Act [10].

3 Water resources for water management

3.1 Surface water quality

Surface water represents the main area of water resources in the Czech Republic. Together with groundwater, these resources are indispensable for the functioning of the entire infrastructure of the country. Both groundwater and surface water sources are used for drinking water production. Surface water is used for water supply purposes, mainly from reservoirs. We assess raw surface and groundwater in the area of five classes: I. and II. unpolluted and slightly polluted water, III. polluted water, IV. heavily polluted water, V. very heavily polluted water. In the case of groundwater, the quality assessment, in view of the requirements of the Framework Directive (Council Directive 98/83/EC on the quality of water intended for human consumption), primarily focused on monitoring hazardous substances in water [7].

The map of surface water quality of selected watercourses in the Czech Republic was first prepared for the period of 1991-1992, according to ČSN 75 7221 Water Quality - Classification of Surface Water Quality. From this biennium onwards, the same maps were produced each year so that they could always be compared with the current water quality status. Due to the scale of the indicators monitored in the 1990s, only comparisons according to the basic classification are made. From 1.12.2017, the amended standard ČSN 75 7221 Water Quality - Classification of Surface Water Quality, which replaces the previous 19-year-old standard, came into force [11-12].

4 Wastewater treatment plants

4.1. Classification of wastewater treatment plants

Size classification of WWTP

The basic classification of wastewater treatment plants is according to their size (capacity) - according to the population equivalent "PE" number for which the WWTP is designed. The decisive factor is the so-called population equivalent (an average individual generating 150 litres of wastewater of a certain pollution level) [13].

Types of treatment plants

Wastewater treatment plants are generally divided into several types according to their design and the processes they use to treat water. The following text presents the basic types of wastewater treatment plants divided according to the stages of treatment. In practice, many wastewater treatment plants are designed as a combination of these different types of treatment in order to achieve the optimum result depending on the composition and pollution of the specific wastewater in question.

Mechanical pretreatment, physical separation: this type of treatment plant uses mechanical processes to capture and remove solid impurities from wastewater. These processes include coarse and fine sieving, sedimentation and filtration. Mechanical scrubbers are the first stage of treatment and are used to remove larger debris such as wood, sand, rocks or floating trash.

Biological purification stage: here, microorganisms are used to break down organic matter in the water. These microorganisms, such as bacteria or algae, consume organic matter as food and convert it into harmless by-products. This is the so-called second stage of purification.

Chemical cleaning stage: chemicals must be used to remove impurities from wastewater. Chemicals can be used to neutralize the acidity or alkalinity of the water, to precipitate or flocculate impurities, or to remove specific contaminants. Chemical treatment plants are often used as a complementary process to mechanical and biological treatment plants. This is the third stage of purification, also called advanced in the literature.

Physico-chemical treatment plants: these plants combine mechanical, biological and chemical treatment processes to achieve high efficiency in removing impurities from wastewater. By combining different processes, a wider range of cleaning and removal of different types of contaminants can be achieved.

Water treatment also includes sludge management processes. However, due to the limited scope of our study, they are not the focus of this paper [14, 15]

4.2 Water management obligations in the Czech Republic

The most important legal regulations that water infrastructure operators must comply with are the Water Act and Government Regulation No. 401/2015 Coll. Among other things, these main regulations set out the conditions under which water from wastewater treatment plants can be discharged into watercourses, set emission limits and address fees for wastewater discharge.

The limits set by the water authorities in the water permit determine the maximum pollution that wastewater treatment plants can discharge into watercourses.

Compliance with the limits and obligations arising from the water permit is monitored using the IROCS portal (Integrated Reporting Obligations Compliance System). Environmental legislation requires economic entities to report information on the environmental impact of their economic activities to state institutions.

IROCS ensures the receipt and processing of selected environmental reports in electronic form and their further distribution to the relevant state institutions [16]. Wastewater treatment plant operators therefore enter the results of their discharges into the IROCS once a year. This portal can be accessed by all concerned entities (water authority, river basin authority, Czech Environmental Inspectorate).

Furthermore, WWTP operators are also obliged to monitor selected indicators in the discharged wastewater, determined by the fee report (beyond the scope of the permit). According to the Water Act, anyone who discharges wastewater into surface waters is obliged to pay a fee for pollution discharged in wastewater and a fee for the volume of wastewater discharged. The limits and rates are set out in Annex 2 to the above-mentioned Act. Limits for the same parameter may vary, e.g., the limit in the water permit for the discharge of COD is 75 mg/l and if we discharge less than this value, we are fulfilling our obligations and will not be fined. However, for the fees, the pollution discharge limit is set at 40 mg/l and if we exceed it, we will pay a fee for excessive pollution of wastewater.

Fees paid under various environmental protection laws are mandatory payments that penalise the use of natural resources, pollution of the environment and threats to the health and lives of humans, animals and flora as a result of human activities. Charges are by the "polluter pays" principle, as they contribute to reflecting (at least partially) the negative externalities in the costs of generators. In this way, they contribute to reducing the amount of pollutants released into the environment and limiting the use of natural resources [17]. The "polluter pays" principle is at the heart of EU environmental legislation [18]. By applying the polluter pays principle, polluters are incentivised to prevent environmental damage and are held responsible for the pollution they cause [19]. Pollution fees are only payable if both the balance and mass limits are exceeded. The volume fee is set at CZK 0.1 per m³ of wastewater discharged.

4.3 Wastewater and PhAC

Wastewater generally includes excreta, urine, "grey" water discharged from kitchens and bathrooms. Urban wastewater may also contain industrial pollution. They generally contain a variety of organic and inorganic substances and dissolved and suspended solids, microorganisms, nutrients (nitrogenous and phosphoric substances), metals, and micropollutants. Micropollutants include a range of substances, e.g., food additives, phthalates, biocides, flame retardants, pharmaceutically active substances, pesticides, plastics. A large amount of urban wastewater is generated every day [20]

Sometimes specific groups of micropollutants are gathered into separate categories, e.g., under the name Pharmaceutically Active Compounds (PhAC). Pharmaceutically Active Compounds may include various types of pollutants, for example:

1. Medication. These are pharmaceutical substances that are used in medicines. Drugs can be excreted from the human or animal body into wastewater or leaked from pharmaceutical production. Examples include analgesics, antidepressants, antibiotics, hormones and contraceptives.

2. Drug metabolites are the products of drug transformation in the body or in the environment. They can arise from the biotransformation of drugs in the human or animal body, or from the degradation of drugs in the environment. These metabolites may also be present in wastewater.

3. Contrast agents are often used in medical imaging procedures such as X-ray, CT or MRI. These substances can be discharged into wastewater and can cause pollution of the aquatic environment.

4. Veterinary medicines used in animal treatment can also be a source of pharmaceutically active substances in wastewater. Examples include veterinary antibiotics and antiparasitics.

4.4 Ostrava sewerage network

The 933-km-long sewerage network carries wastewater from both the population and commercial/industrial entities.

Wastewater treatment, mainly from Ostrava and several adjacent municipalities, is provided 98.7% of the time at the Central Wastewater Treatment Plant in Ostrava-Privoz (CWWTP). This complicated work of engineering with the highest mark of water management quality is unique in the history of Ostrava and, from the environmental point of view, with its projected capacity of 638,850 population equivalent, it allows for the city's development in the years to come.

The treatment concept is based on mechanical-biological treatment of sewage and industrial water on the principle of low-load activation with nitrification and pre-supervised denitrification with an automated control system for all technological processes [21].

Finally, the water is returned to the natural world, free of all impurities. It is discharged into streams and rivers without adversely affecting their water quality. [22] The anaerobically stabilised sludge is dewatered on centrifuges and is sanitised with lime [21].

4.5 Composition of wastewater in Ostrava

Ostrava is the third largest city in the Czech Republic with 290,000 inhabitants. It is an industrial, educational and cultural centre, which hosts, among other things, many sporting events of global importance.

Wastewater having the character of sludge or wastewater with a very high concentration of pollution is anaerobically stabilised in digestion tanks, and is the following types of wastewater: (1) wastewater from meat processing plants, (2) wastewater from malt, starch, yeast and alcohol production, (3) wastewater from milk treatment and processing, and many others [21].

Within the project and the analysis carried out, 150 substances were detected. Namely the following:

Alfuzosin, Atenolol, Atorvastatin, Azithromycin, Bezafibrate, Biperiden, Bisoprolol, carboxylate, Theophylline, Cetirizine, Cilazapril, Clarithromycin, Clemastine, Clindamycin_sulfoxide, Clindamycine, Diclofenac, Dicycloverine, Diltiazem, Disopyramide, Erythromycin, Fenofibrate, Fexofenadine, Glibenclamide, Glimepiride, Iopromide, Irbesartan, Loperamide, Meclozine, Memantine, Metoprolol, Metoprolol acid, Miconazole, N1_Acetylsufametha, N4_Acetylsufametha, Oseltamivir, Pizotifn, Propranolol, Ropinirole, Rosuvastatin, Roxythromycin, Sotalol, Sulfadiazine, Sulfamerazine, Sulfamethazine, Sulfamethizole, Sulfamethoxazole, Sulfapyridine, Tamoxifen, Triamterene, Trimethoprim, Valsartan, Verapamil, Telmisartan xazole, Terbinafine.

These are largely drugs used for e.g., high blood pressure, to treat symptoms of Parkinson's disease, antihistamines used to treat allergies, and antibiotics. For example, Memantine is a drug that is primarily used to treat Alzheimer's disease, which is a neurodegenerative disease of the brain. Triamterene is a drug that is used as a diuretic, which means that it helps to remove excess water and salts from the body. Metoprolol is a beta-blocker that is used to treat high blood pressure, heart failure, coronary artery disease, and as heart attack prevention. Metoprolol acid is the active metabolite of the drug metoprolol. It is the form into which metoprolol is converted in the body.

Another group of substances detected in wastewater are drugs and their derivatives. For example: 6-acetylmorphine, Alprazolam, Amitriptyline, Amphetamine, Benzoylcegonine, Caffeine, Cannabinol, Carbamazepine, Catinone, Citalopram, Clomipramine, Clonazepam, Cocaine, Codeine, COOH, Dihydro CBZ, Donepezil, Epoxy CBZ, Haloperidol, Ketamine, Lamotrigine, Maprotiline, MDA, MDEA, MDMA, Mephedrone, Metamphetamine, Methadone, Mianserin, Mirtazapine, Morphine, N-Desmethylocitalopram, Norketamine, Norsertraline, O-Desmethylenlafaxine, Oxazepam, Oxcarbazepine, Oxycodone, Sertraline, THC, Tramadol, trans-dihydro dihydroxy CBZ, Trazodone, Venlafaxine, Vortioxetine.

Several partial conclusions can be drawn from the above:

1. Ostrava, as a densely populated city, often hosting events of global significance, faces the problem of pharmaceuticals and drugs in its wastewater.

2. The study shows that the amount of pharmaceuticals and drugs in Ostrava's wastewater is high.

3. Pollution of wastewater by detected substances is a problem in Ostrava that requires attention and solutions.

4. The occurrence of these substances in Ostrava's wastewater may have a negative impact on the environment, especially on aquatic ecosystems.

4.6 Sustainability

Many urban wastewater treatment plants have invested in technologies to better control processes and use less

electricity, with non-CO₂ greenhouse gas emissions falling by 20% between 2005 and 2017 [23].

The overarching perspective of the European Green Deal and the 8th Environment Action Programme [24] also take better account of the wider role that wastewater treatment can provide in mitigating climate change. Rather than "waste", we should consider treated water and sewage sludge as resources for reuse and recycling in a circular economy concept. Cleaner water provides more natural habitats than polluted water, which benefits biodiversity. Investing in pollution prevention is key to ensuring sustainability [24].

Capturing biogas from the processes and performing anaerobic digestion can be used to support the energy self-sufficiency of the treatment plant. Energy efficiency measures include heat recovery from wastewater processes and the use of space to accommodate wind turbines and solar panels that provide renewable energy [15].

The sludge obtained from the wastewater is stabilised in digestion tanks in Ostrava, then thickened, dewatered and finally transported for further processing. The stabilisation of the sludge produces sludge gas, which is used for heating or power generation [22].

5 Wastewater treatment plant reserves

5.1 Categories of substances which are difficult to remove from the aquatic environment at the WWTP

Wastewater treatment plants are capable of removing a wide range of substances from wastewater, but there are certain categories of substances that may be difficult to remove completely or require specific procedures for removal; micropollutants are listed in Figure 1 [1]. Some of these categories include, for example:

1. Heavy metals such as lead, mercury, cadmium and chromium. These metals are often found in industrial wastewater and may require special procedures for their effective removal, such as chemical precipitation or adsorption.

2. Some organic substances such as pesticides, pharmaceuticals, hormones or hard-to-degrade substances may be resistant to conventional treatment processes. Biological treatment plants may be limited in their ability to remove these substances completely, and therefore advanced processes such as adsorption onto activated carbon or oxidation by chemicals or ultrasound are sometimes necessary for effective removal.

3. Some microorganisms and viruses: While biological treatment plants are capable of removing many types of microorganisms and viruses, there are certain species that can be resistant to conventional cleaning processes. This includes, for example, certain types of resistant bacteria or viruses such as hepatitis A or norovirus. Special procedures may be required to remove these pathogens from wastewater, such as disinfection with chemicals, UV radiation or ozone.

4. Microplastics are a new phenomenon.

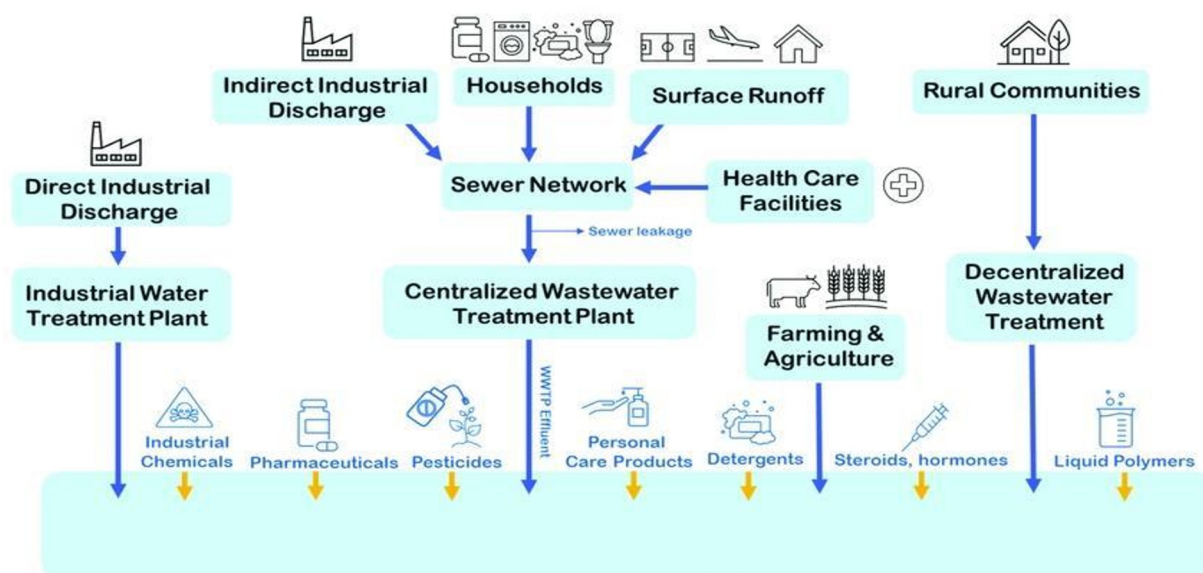


Fig. 1. Sources of micropollutants in water [40]

5.2 Micropollutants in the aquatic environment

PhAC have been of increasing concern in recent decades with regard to health and safety, as many of them may have adverse effects on non-target organisms due to their presence in the aquatic environment [25, 26].

PhAC are often present in the aquatic environment at trace concentrations ranging from ng/l to ug/l or even lower [2].

These pollutants can accumulate in the bodies of organisms (including humans) through food chains, mainly aquatic animals, even at concentrations of ng/l, causing adverse mutagenic, reproductive, genotoxic and carcinogenic effects [27-29]

The survival, reproduction and growth of *Daphnia sp.* are adversely affected by ibuprofen. Scientists [30-31] have described an increase in litter size, presumably to compensate for reproductive damage. Given the frequency of NSAID (including the aforementioned diclofenac and paracetamol) in wastewater, they pose a serious risk to aquatic organisms. They could also threaten organisms higher up the food chain, including humans [30].

Among the most toxic substances of the studied paracetamol, chlorpromazine, diclofenac sodium and propranolol, according to the study by De Oliveira et al. [32] also includes propranolol (EC_{50} relative to reproduction was 0.132 mg/l). In addition to a significantly lower reproductive capacity, crustaceans also have a reduced metabolism, slower heart rate and growth disorders.

Negative effects associated with the presence of psychoactive drugs in the aquatic environment include, for example, behavioural changes in aquatic organisms resulting from the mechanism of action of these substances. Fish lose their natural behavioural patterns, become less fearful and are easier food for predators. Changes in migratory or reproductive behaviour are related to this. Histological changes in organs were also observed. As part of a project focused on the study of the occurrence of psychoactive substances in the aquatic environment and their effects on aquatic organisms, researchers looked in detail at six selected psychoactive substances - citalopram, sertraline and venlafaxine, tramadol, the benzodiazepine oxazepam and the illegal drug methamphetamine. Researchers exposed fish, crayfish and dragonflies to these substances at concentrations found in surface waters and studied how they were affected. Some of these drugs have a greater negative effect than others. For example, it has been found that there is a reduction in the feeding rate in exposed (affected) dragonfly larvae. Behavioural patterns, such as time spent in hiding, activity, movement speed and burrow excavation, were influenced in crayfish. In fish, degenerative changes in the heart and liver, differences in food intake, changes in behavioural parameters such as courage or discovering new objects have been observed. There was a decrease in social interactions after exposure of fish to tramadol, which led to a decrease in cohesion of the schools of fish [33].

5.3 Degradation of drugs in the aquatic environment

Water and aquatic ecosystems are the most important element for human life and the life of other fauna and flora. When the natural water cycle in nature is disturbed, sooner or later a collapse always occurs. For this reason, aquatic ecosystems must be protected and managed as the most precious and irreplaceable resource

on Earth. [7] Processes capable of the effective removal or degradation of a wide range of micropollutants are currently under intensive investigation worldwide. The most effective processes include various advanced oxidation processes (AOP) such as the Fenton reaction, ozonation and their modifications, as well as the application of ferrates, highly efficient carbon-based sorbents, and membrane technologies. To achieve the best possible parameters at the outlet of the wastewater treatment plant, these processes can be combined in different ways depending on the type of technology at the wastewater treatment plant and the composition of the water itself. In particular, the inclusion of these processes as a tertiary treatment of runoff water has good prospects. The successful elimination of pharmaceuticals from wastewater is a process that depends on several factors: the initial concentration of the substance, its physico-chemical properties and, last but not least, the chosen treatment method. The most efficient of these processes is biodegradation and photodegradation (UVA and UVB), while sorption and evaporation are only applicable to hydrophilic substances ($\log K_{ow} > 4$) with a moderately high Henry's constant ($11-12^{Pa/m^3} \cdot mol$) [34, 35].

The process by which drugs are degraded by microorganisms is called biodegradation. The presence of readily degradable carbon in excess of ammonium ions is required to activate this process; once the conditions are met, the enzymes responsible for degradation are not stopped by the subsequent presence of ammonium ions. Other substances containing carbon or nitrogen can affect the process. [36] The sorption of a drug onto activated sludge is dependent on two processes: absorption and adsorption. Absorption is the hydrophobic interaction of the aliphatic and aromatic part with the lipophilic membrane of the organism or the lipid part of the sludge. Adsorption is the electrostatic bonding of the positively charged part of the structure and the negatively charged outside of the biomass. As the drug is not degraded during sorption, it remains active, making it inappropriate to further use the sludge for agricultural purposes, for example [37]. However, it is probably a very important process in the aquatic environment [38]. One of the other options to remove pharmaceuticals from wastewater is the use of adsorption carbon, which binds xenobiotics and thus eliminates them from the aquatic environment. This method is more effective for chemical substances than flocculation and sand filtration. The ability to adsorb the substance is limited by the presence of other structures (competition occurs) [39].

6 Conclusion

Wastewater contains a variety of micropollutants such as pesticides, pharmaceutically active compounds, drugs, etc., which can have a dangerous impact on the aquatic environment and the organisms living there. The environmental impact of different groups of micropollutants, similarly to microplastics, is currently

being intensively investigated. Certain types of medicines, hormones and drugs and their metabolites are capable of affecting, for example, the behaviour of aquatic animals, their reproductive capacity, etc. in small quantities (even in tens or hundreds of ng/l). At present, a considerable part of foreign work focuses on the behaviour of these micropollutants in the environment. Scientific studies over the last five years have shown the presence of pharmaceuticals in particular, not only in wastewater, surface water and groundwater, but also in the bodies of aquatic organisms. In addition, some of these substances have the ability to accumulate in the environment (in animal bodies or plants) and thereby enter the food chain [1].

The conclusions or challenges of this study include: (1) The monitoring and reduction of PhAC in wastewater must be one of the objectives of environmental planning in Ostrava. (2) The ISBU project, see Acknowledgements, of which VŠB-TUO is the principal investigator, seeks to develop technology to help reduce the occurrence of PhAC in wastewater. (3) Collaboration between the science and technology community - the university and the water company - is key to finding solutions to the problem. (4) The project on which the article was published may help to educate and inform the public about the risks associated with the occurrence of PhAC in the environment. (5) Solving the problem of PhAC in wastewater is a long-term task that requires the coordinated efforts of various actors in Ostrava.

It is important to understand that there is a wide range of specific types of pollution that we cannot yet effectively remove from water, and therefore we need to look for advanced technologies and methods, and continue to develop and improve the ability of wastewater treatment plants to remove these substances. This is also the direction in which the ISBU project is heading. The aim of this project is to design a technology for the removal of, among other things, pharmaceutically active substances.

The paper was prepared within the framework of the grant project entitled "Innovative carbon-based sorbents as an effective method of wastewater treatment" (project no.: 3213200008, ISBU, Environment, Ecosystems and Climate Change Programme, funded by Norway Grants 2014-2021).

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