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Working together for a green Europe

Contents

Preface

Together with the EEA Grants, the Norway Grants are one of the now well-established instruments for reducing economic and social disparities in the European Economic Area (EEA) and for strengthening cooperation among European countries. Czechia has been a recipient of these funds since 2004, when it joined the European Union and thus the EEA. The EEA and Norway Grants place great emphasis on sharing and exchanging experiences between donor and recipient countries. This distinguishes them from EU funds.

In the period 2014-2021, more than EUR 34 million (roughly CZK 800 mil.) has been allocated for projects under the "Environment, Ecosystems and Climate Change" Programme (CZ-ENVIRONMENT for short). The programme was financed exclusively by Norway. This is the highest allocation from the EEA and Norway Grants programmes in Czechia in this period. Meaning that the environment is the number one priority not only in the Czech and Norwegian context, but also at the European level. Programme allocation has therefore been divided into four areas of support - biodiversity and ecosystem protection, air pollution reduction, water pollution reduction and climate change adaptation on a regional level.

In addition to the above-mentioned exchange of experience, the innovative aspect of the projects was emphasised in the Programme setting. The aim was both to cover white spots in grant policies that are not getting enough attention by other programmes and to achieve practical application of scientific knowledge that would otherwise be difficult to find funding for. Innovative projects were particularly targeted by calls in two programme support areas – biodiversity and ecosystem protection; water pollution reduction. Thanks to the high interest of applicants, the CZ-ENVIRONMENT programme supported dozens of innovative projects. The most interesting ones were presented at the Innovation in Environmental Protection conference in June 2024, where, in addition to experts from Czechia, experts from Norway, Estonia and Slovakia also took part. The content of this proceedings is a selection of contributions from that conference.

Place and date

Prague, Czechia – 4–5 June 2024

Editor

Jakub Šmída, State Environmental Fund of the Czech Republic

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Part One

Biodiversity and Ecosystem Protection

Application of innovative methods for the eradication of invasive crayfish in the Czech Republic

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Introduction

The spread of non-native invasive crayfish species is causing a significant risk to aquatic ecosystems. Invasive crayfish are formidable competitors to other organisms. Their high population densities can change the entire aquatic ecosystem. They pose an even more fundamental risk to our native crayfish populations in that they carry the so-called crayfish plague, a disease from which our native crayfish are dying. This disease is caused by the parasitic water mould Aphanomyces astaci (Saprolegniaceae, Oomycota). It was introduced to Europe in the mid-19th century and has been causing mass die-offs of native crayfish species ever since. American crayfish species are tolerant to this parasite due to long-term coevolution, but unfortunately European crayfish species are not.

A number of methods are used to deal with invasive crayfish, usually in combination, depending on local capabilities. For the conditions of the Czech Republic, suitable methods are described in the "Methodology for the control and eradication of invasive crayfish species (in Czech)" (Svobodová et al., 2020a). A web application [1] has been developed in parallel with the methodology, enabling the recording of invasive crayfish sightings in a database, their evaluation, and the suggestion of possible measures at specific sites.

The aim of our project was to apply different methods of invasive crayfish species control in practice, based on the recommendations of both methodological documents. T. G. M. Water Research Institute collaborated on the project with the state enterprise Povodí Vltavy and the Norwegian Institute for Nature Research (NINA).

We also cooperated with the Austrian consulting company blattfisch, e.U. and many experts from the field of state nature conservation and universities.

Project sites and methods

We worked at six sites with different types of standing and flowing water, four of which fall within the Natura 2000 network of SACs. The flowing waters where we applied measures against invasive crayfish were the SAC Zákolanský potok, SAC Stroupínský potok, SAC Horní Malše and on a tributary of the Svratka called Besének. Project sites of standing water included Prostřední rybník in Prague – Dolní Chabry, and Kačležský rybník in the SAC Krvavý a Kačležský rybník.

All species of invasive crayfish currently known from the wild in the Czech Republic were present at the sites: the spiny-cheek crayfish (Faxonius limosus), the signal crayfish (Pacifastacus leniusculus) and the marbled crayfish (Procambarus fallax f. virginalis).

Of the methods of crayfish control recommended by the methodology and the web app [1,2], manual harvesting and trapping, enhancement of the predatory fish stock, the creation of migration barriers, the manipulation of the water level, and overall pond restoration were tested. We complemented the control methods with the monitoring of crayfish abundance and the crayfish plague pathogen by means of environmental DNA (eDNA) detection. We also intensively addressed the most important and effective measure in combating the spread of invasive crayfish – information sharing among the general public and experts.

Measures taken and results

We created two permanent barriers at the lower edge of the **SAC Zákolanský potok** to prevent the potential migration of invasive spiny-cheek crayfish from the Vltava River (for photographs, see https://crayfish2022.vuv.cz). Similarly, these barriers will prevent the upstream migration of the stone crayfish (*Austropotamobius torrentium*), which could encounter invasive crayfish in the lower reaches of the stream in the future. The migration barrier was created by modifying existing instream steps. This involved adding an overhanging spillway edge and migration barriers on the banks. The presence of spiny-cheek crayfish at the mouth of the brook Zákolanský potok in the Vltava River was confirmed by eDNA analysis. It does not appear to be present upstream. Samples taken from the brook downstream from the installed barriers confirm that both the stone crayfish and the noble crayfish (*Astacus astacus*) are present in the catchment.

At the **SAC Horní Malše**, we caught more than 600 signal crayfish from the river using traps. This was the only possible active intervention against the spread of signal crayfish in the area that would protect the population of the critically endangered freshwater pearl mussel (*Margaritifera margaritifera*). This trapping exercise provided lessons for future action at the site: most signal crayfish (about 4.6 ind/trap) were trapped during the peak summer in July and August, when discharge was lowest (0.2–0.3 m3/s at the Leopoldschlag gauging station) and water temperature was at its highest (18 °C). In the late summer periods in June and September, trapping success was significantly lower (around 1.3 ind/trap); in addition to the crayfish life cycle, this factor is also related to the lower water temperature and higher flows in both months.

In the autumn of 2022, we stocked 1,120 (580 kg) of pikeperch (*Sander lucioperca*) in the **Kačležský rybník fishpond**. Pikeperch are known to be good predators of crayfish, in this case the local strong population of signal crayfish. After the pond was harvested in 2023, the food web and feeding preferences of signal crayfish and potentially predatory fish were analysed using stable isotope analyses of carbon and nitrogen. For both juvenile and adult signal crayfish, benthic invertebrates and cereals were the main dietary components (cereals were primarily intended as food for the common carp stock). Cannibalism was relatively low at both age stages. Other food components such as zooplankton, emergent insects, and detritus were relatively marginal food sources. The species with the best predation potential appeared to be Wels catfish (*Silurus glanis*), Northern pike (*Esox lucius*), and pikeperch (*Sander lucioperca*). Ruffe (*Gymnocephalus cernua*) and European perch (*Perca fluviatilis*) showed less of a preference for signal crayfish. The pumpkinseed (*Lepomis gibbosus*) had a significant feeding preference for juvenile signal crayfish; however, it is another invasive species itself. Common carp proved to be an insignificant species for signal crayfish eradication in the Kačležský rybník fishpond.

The study confirms that the pikeperch introduced into the pond in 2022 was an appropriate predator of invasive crayfish. The high proportion of feed grain in the diet of signal crayfish is consistent with experience in the field that the best trapping catches can be achieved with a break in feeding for several days.

We have also conducted intensive trapping for signal crayfish in the summer season at the fishpond. In 2022, we set a total of 170 traps and caught 945 signal crayfish. In the following year, we set a total of 80 traps and caught 314 crayfish. In November 2023, signal crayfish were harvested during the fishpond harvest, attended by the staff of the Nature Conservation Agency (AOPK ČR), the Hamerský Potok Association and the T.G. Masaryk Water Research Institute (VÚV TGM). Over a 14-day period, approximately 12,350 signal crayfish were harvested. Despite considerable efforts, probably only a fraction of the local population of signal crayfish was harvested. Its original size can be estimated at tens of thousands of individuals.

At the **Prostřední rybník** fishpond in Prague, we continued our efforts to eradicate the invasive marbled crayfish. A large population of this crayfish was discovered here in 2020, and most of the eradication measures were implemented in cooperation with the owner (the City of Prague) before the project started. The project activities confirmed the success of the measures implemented, although the outcome was not 100% eradication (Buřič et al., 2024). We confirmed the survival of a weak population of marbled crayfish by repeatedly recording individuals about 3 cm in size. However, the population remains weak. Despite extensive efforts, no marbled crayfish have been captured by traps. Neither eDNA sampling in the fishpond or surrounding water bodies, nor at the brook Drahanský potok, revealed the presence of marbled crayfish. Its population was therefore likely isolated at Prostřední rybník fishpond and is now being limited due to predation by stocked fish.

At the SAC **Stroupínský potok**, we used traditional methods and eDNA to search for the source of the crayfish plague recorded here in 2018–19. We were also interested in whether part of the once abundant population of the stone crayfish survived this disease. In all the sampled profiles of Stroupínský potok and its tributaries, we detected the pathogen of crayfish plague, *Aphanomyces astaci*, by eDNA, but at or beyond the limit of confident detection. The stone crayfish was not confidently detected in any profile, although in one case tentative trace amounts of its DNA were detected. Samples from Stroupínský potok showed relatively consistent weak detection of noble crayfish eDNA.

The results suggest that the crayfish plague persists in the catchment after five years, but that there is probably a remnant population of noble crayfish. The presence of stone crayfish has not been confirmed, although trace amounts of its DNA give hope for further searches for a remnant population.

We ran practical tests on the construction of temporary migration barriers on the **Besének** stream. In the upper part of the catchment, the noble crayfish is present, while in the lower

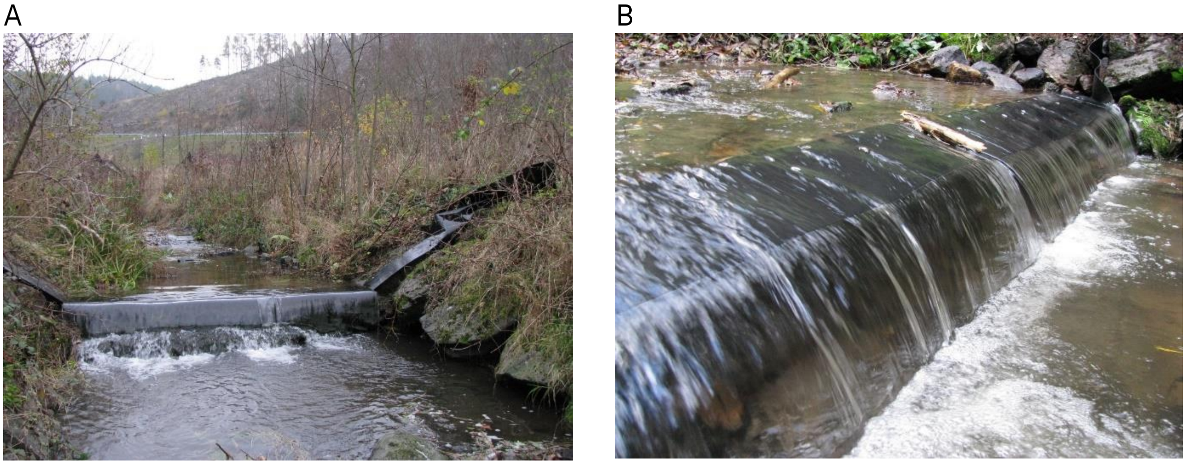

Fig. 1. Temporary migration barriers at Besének stream: A) modified masonry/concrete step, B) detail of a modified overflow edge on a log step.

part the signal crayfish population is spreading. The aim of the measure was to separate these populations and slow the upstream movement of the invasive crayfish.

The barriers were constructed by attaching plastic panels to existing channel steps (Fig. 1). This created an overhanging edge with a free-falling water beam (Fig. 2). The downstream bank was also fitted with a plastic barrier to restrict crayfish migration over land (Fig. 2). Therefore, three different steps were modified on the Besének stream between the tributary Chrastová and the settlement Dolní Žleby.

We conducted an experimental evaluation of the effectiveness of the barriers on the two downstream steps in 2022–23. We repeatedly harvested crayfish from the reach and, after tagging them with a coloured elastomer, released them back into the stream downstream from the lower barrier. In subsequent captures, we monitored whether tagged crayfish overcame the barrier. We repeated this procedure after the barriers were modified. We captured 4,589 signal crayfish from the reach during the experiment. Of these, we tagged 2,076 with a coloured elastomer. We recaptured 535 tagged individuals.

Fig. 2. Design and dimensions of the modified step on the Besének stream. Experimental verification of the passability for the signal crayfish was carried out on these steps (Image by B. Šrytrová).

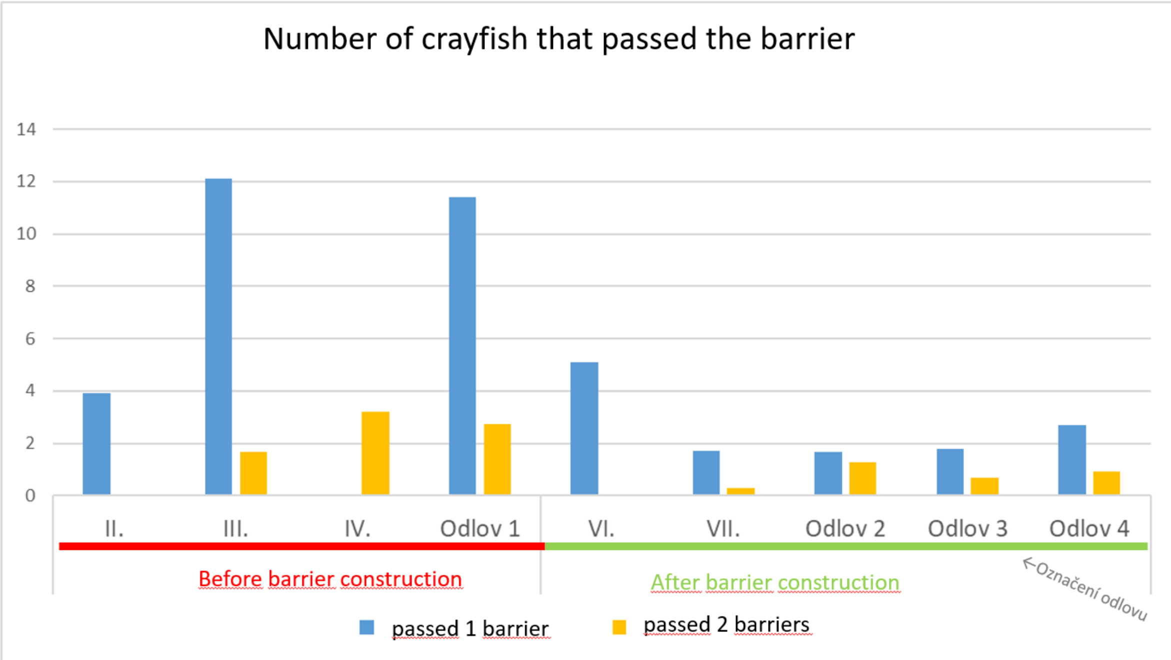

Fig. 3. Results of experimental verification of the passability of modified steps for signal crayfish. ("Odlov" = "Culling")

The evaluation showed that the construction of the barriers significantly slowed the upstream migration of signal crayfish (by almost 60%). At the same time, it is clear that the barriers installed on the steps were not 100% impassable for the crayfish (Fig. 3). Some crayfish were still able to overcome the barriers. However, the tested barriers were constructed on simple, small steps made of logs with no structural binding to the banks and bottom. Using barriers on steps made of masonry would probably yield better results. Thus, the barriers tested proved to be a relatively inexpensive and quick tool that could be used in locations where the migration of invasive crayfish might threaten the native crayfish population, either by introducing crayfish plague or by posing direct competition.

The eDNA analysis and manual survey were able to prove the occurrence of noble crayfish in the area of Dolní Žleby. Unfortunately, we also detected the DNA of the signal crayfish in this area (above the highest barrier) and its occurrence was confirmed by the discovery of two individuals. Fortunately, at the time of the experimental work (2022–23), the local population of signal crayfish was not infected with crayfish plague. However, in the Svratka River basin and directly in the Svratka River, in autumn 2023, we detected the presence of Aphanomyces astaci, which originated from the Bystřice stream, where the crayfish plague had recently been confirmed. We expected that noble crayfish populations in the Svratka River catchment would soon be affected by crayfish plague. At the time this paper was being prepared, the presence of crayfish plague was confirmed in the tributaries Nedvědička and Chlébský potok, making the migration barriers constructed on the Besének stream even more justified.

Conclusion

Our project was one of the first attempts to regulate invasive crayfish to be carried out in the Czech Republic. As far as we know, our project to modify migration barriers against the spread of invasive crayfish was the first to deploy this approach in the Czech Republic.

Complete eradication of invasive crayfish can only be attempted at small isolated sites. The example of Prostřední rybník shows that not even large-scale efforts can lead to the complete eradication of the marbled crayfish. Nevertheless, the population has been significantly reduced and the invasive crayfish is unlikely to spread further.

Hand-harvesting and trapping reveal population densities rather than substantially reduce the invasive crayfish population. In some habitat types, however, there is no other method, and trapping at least reduces the current population density and limits their reasons to migrate.

Particularly in fishponds with managed fish stocking, the abundance of invasive crayfish can be reduced by stocking suitable predatory fish.

Isolation methods, such as the modification of migration barriers described above, are of great importance in protecting spatially restricted habitats containing protected species.

For successful regulation, several appropriate measures need to be combined at the site and applied over the long term.

We see considerable potential for the conservation of native crayfish species in the routine implementation of monitoring of crayfish plague and its crayfish carriers using eDNA methods. Combined with the temporary modification of migration barriers, this could limit the current spread of crayfish plague into the habitats of threatened populations of native crayfish.

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Overview of 'Prevention and Control of Non-indigenous Crayfish Species in Estonian Freshwaters' (11.10.2021 – 30.04.2024): project goals, activities and results

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Project background

The establishment and increase in the abundance, distribution, and persistence of aquatic invasive species (AIS) is a concern in Estonia. The spread of AIS may have significant ecological impacts on native communities and habitats. The project "Eradication of Aquatic Invasive Species in Estonian Freshwaters" was funded through European Economic Area (EEA) "Climate Change Mitigation and Adaptation" grants under call I – "Ecosystem resilience increased". The main objective of this project was to help protect and restore native communities' resilience to climate change by eradicating and controlling the spread of AIS.

To assess the risk of the introduction, survival and spread of 40 AIS that are of concern in the European Union, a report was prepared in 2017 (Kraut 2017). This report considered the classification of species introduction pathways developed by the Convention on Biological Diversity, the survival of species in the Estonian climate, and the probability of their introduction through the observed routes. However, an analysis of ten more species was needed.

The noble crayfish (*Astacus astacus*) is the only indigenous decapod crayfish species in Estonia. The most noble crayfish sites now have low densities, except for some populations in south-eastern Estonia and on the island of Saaremaa, which until 2006 was unique in Europe in that it had abundant noble crayfish populations and no alien crayfish species or crayfish plague. Until 2008, Estonia was one of the last countries in Europe where alien crayfish species had not been recorded in the wild. The first alien crayfish species, signal crayfish (*Pacifastacus leniusculus*), was found in Estonia in Mustjõgi River, Harju County, in 2008. As of 2020, signal crayfish have been found in numerous waterbodies across Estonia. In addition to signal crayfish, in 2017 a spiny-cheek crayfish (*Faxonius limosus*) was detected in the Pärnu River, and its distribution area continues to expand upstream, reaching the Reiu River estuary in 2020. A third alien crayfish species, the marbled crayfish (*Procambarus virginalis*), was first found in 2017 in an outflow channel of the cooling system of the Baltic Power Plant, flowing into the water reservoir of the Narva River. There are several local distribution areas of marbled crayfish, and the risk of further spread in Narva Water Reservoir and the main river is high.

The ongoing spread of alien crayfish of North American origin is the biggest threat to the native noble crayfish in Estonia. This is mainly because they act as a reservoir host for the causative agent of crayfish plague (*Aphanomyces astaci*), which is a lethal disease for noble crayfish. In addition, alien crayfish are more aggressive, fertile and resilient to changes in environmental conditions. The spread of these species has led to the extinction of a large proportion of Europe's indigenous crayfish populations. To stop the spread of alien crayfish species in Estonia, more effective methods must be developed and applied to protect local noble crayfish populations.

Furthermore, in addition to alien crayfish, the distribution of the perennial aquatic plant Nuttall's waterweed (*Elodea nuttallii*, also native to North America) needed to be mapped. The rapid growth of this species causes numerous ecological and economic problems, such as loss of invertebrate and fish diversity and recreational potential, causing unpredictable changes to the waterbody and limiting the use of water as a resource for economic purposes. In Estonia, Nuttall's waterweed was believed to be widely distributed, however, reliable information on its distribution, abundance and potential ecological impact was lacking.

These aforementioned species are included on the list of invasive alien species of Union concern under Regulation (EU) No 1143/2014 of the European Parliament and of the Council. They cannot legally be imported, kept, bred, transported, sold, used or exchanged, allowed to reproduce, grown or cultivated, or released into the environment. EU member states are obligated to manage established invasive alien crayfish species on this list.

On this basis, the project objectives were to:

1. assess the risk of the introduction, survival and spread of ten invasive non-indigenous crayfish species (NICS) in Estonia that are of concern in the EU;
2. assess and control the spread of NICS and Nuttall‘s waterweed in Estonia and implement more effective measures for the detection (including the application of eDNA-based methodology) and eradication of alien species;
3. raise public awareness and the competence of officials in terms of the threats posed by alien species, and measures to control them.

Project outcomes

Based on the objectives, the project yielded the following results:

Analysis of the introduction pathways for ten alien invasive species

The risk of the introduction, survival and spread of ten alien invasive species that are of concern in the European Union was assessed in the analysis. These species were: Andean pampas grass (*Cortaderia jubata*), Finlayson's squirrel (*Callosciurus finlaysonii*), pumpkinseed (*Lepomis gibbosus*), Himalayan knotweed (*Koenigia polystachya*), Japanese hop (*Humulus japonicus*), Japanese climbing fern (*Lygodium japonicum*), tree of heaven (*Ailanthus altissima*), box tree moth (*Cydalima perspectalis*), rusty crayfish (*Faxonius rusticus*), and New Zealand flatworm (*Arthurdendyus triangulates*). Of the species analysed, the Estonian climate is suitable for only two species – rusty crayfish and pumpkinseed.

Research into the usefulness of different eradication methods that take into account factors specific to alien species and their habitats, and evaluation of the effectiveness of eradication

At the beginning of the project, the spread and abundance of alien crayfish were mapped at each location with test fishing. In the research into different eradication methods, intensive trapping was deemed to be the only feasible option that could be used in the waterbodies studied. Reviewing the literature, we saw that biocide use is the only 100% effective eradication method. However, it was not used during the project for reasons of environmental protection and great reluctance on the part of landowners. To supplement the intensive trapping of signal crayfish in Reo Quarry and the Ropka Reservoir, hundreds of predatory fish, European eels (*Anguilla Anguilla*), were stocked in these waterbodies. Before this stocking, a mesocosm study was carried out at the Chair of Aquaculture laboratory to see if eels raised in the fish farm would start to feed on differently sized crayfish.

Intensive trapping with baited traps was carried out in all waterbodies with known or suspected alien invasive crayfish presence. The same methodology normally used for annual noble crayfish monitoring was employed. Trapping was more intensive in waterbodies where the effect was expected to be the greatest. The efficiency of trapping was calculated by multiplying the number of traps by the number of catching nights (i.e. trapping nights). By the end of the project, there had been 27,429 trapping nights at 28 waterbodies, which resulted in the catching and eradication of 24,431 alien invasive crayfish. Most of these (n = 23,835) were signal crayfish. About 20,000 were caught from the Riksu Stream, and more than 3,000 were caught from the Vääna River. At the Reo Quarry and the Ropka Reservoir, 452 and 116 signal crayfish were caught, respectively, and less than 100 crayfish came from other waterbodies. The total catches of other alien invasive crayfish species were relatively small – 335 spiny-cheek crayfish, 244 marbled crayfish, and 17 narrow-clawed crayfish. In the end, different alien invasive crayfish species were caught and eradicated from 20 waterbodies. Eradication efficiency was greatest at Reo Quarry, the Ropka Reservoir, and the Riksu Stream (mainly in parts of the stream where trapping was more intensive).

In addition, another mesocosm feeding experiment with European eel (both narrow and broadhead) was conducted to investigate their potential for alien invasive crayfish eradication. The experiment showed that stocking broadhead eels to control alien crayfish species may be more effective.

The eradication of Nuttall's waterweed was not possible because its presence was not confirmed in any of the waterbodies surveyed in 2022. Altogether, samples were collected from 27 lakes across Estonia where *Elodea* species or Nuttall's waterweed were suspected. However, as Nuttall's waterweed is morphologically very difficult to distinguish from Canadian waterweed (*Elodea canadensis*, also present in Estonia), molecular genetic analyses were carried out; these analyses did not confirm the presence of the species either.

The eDNA-based detection of noble crayfish, alien invasive crayfish and crayfish plague was carried out at 16 waterbodies across Estonia. The eDNA method successfully detected noble crayfish, signal crayfish, and spiny-cheek crayfish in lotic waterbodies with low and moderate crayfish population densities. However, in lentic environments, the detection of the invasive crayfish species was a challenge, especially at low abundance. The method was fairly efficient as most of crayfish eDNA results were confirmed by the trapping data. Although marbled crayfish was not detected with eDNA, even the negative results (detections below the limit of detection) provided valuable insight. Further improvement and analysis of additional samples are suggested for the marbled crayfish eDNA assay. While it is possible to quantify and roughly estimate the concentration of crayfish eDNA in the water, the estimation of crayfish abundance through this method still requires substantial work, as most studies (field or laboratory-based), including ours, have not established a convincing quantitative correlation. The detection of the crayfish plague pathogen and non-detection at locations with the sympatric presence of native and invasive NICS and the provision of reliable presence/absence data by the eDNA approach are important for the effective surveillance of crayfish. Therefore, when integrated into the routine monitoring of crayfish and crayfish plague, the eDNA method will be a valuable supplement to the traditional traps commonly employed to monitor, control and/or eradicate invasive crayfish in Europe.

Outreach activities

More outreach activities were carried out during the project than originally planned.

At the start of the project, a website (ais.emu.ee) was set up and was then constantly updated with all project-related activities, results, and other information. An Instagram account was also created (Aquatic_Invasive_Species).

The project started with an opening seminar, where all of the planned activities were presented to stakeholders and government agencies involved in environmental protection in Estonia. Various outreach activities were aimed at people interested in nature, as well as private landowners, through various media calls (in cooperation with the Estonian Environment Agency). Via this action, people were encouraged to report alien crayfish sightings to the Estonian Environment Agency. Similarly, all aquatic invasive species sightings could be reported using the “Report a Sighting” tab on the project website.

More active media engagement was carried out before the start of the crayfish catching season, i.e. spring–summer in 2022 and 2023. To inform the public of long-term eradication activities, information stands were set up and installed near those waterbodies. In addition, leaflets on the various crayfish species in Estonia were printed in three languages – Estonian, English and Russian, and handed out at seminars and workshops.

As young people receive most of their information from the web via video, an educational and “Report a Sighting” video was made and distributed through various media channels. Throughout the project, members of the alien crayfish control team participated in various seminars and workshops for school and university students, and alien invasive crayfish were presented at festivals. A couple of popular science articles were written in Estonian journals and a research paper entitled “Distribution of Non-Indigenous Crayfish Species in Estonia and Their Impacts on Noble Crayfish (*Astacus astacus* L.) Populations” was published.

Problems related to the alien invasive crayfish species were discussed on TV shows, and radio interviews were also given. Members of the alien crayfish control team participated in many international conferences and workshops. On 20 March 2024, at the end of the project, a conference was held together with researchers from the University of Tartu to present the project results and main conclusions.

Training of stakeholders on issues caused by aquatic invasive species and on practical eradication methods

During the project, two theoretical and two practical training courses were held for all relevant individuals whose work is related to environmental protection (e.g. the Ministry of the Environment, the Environmental Board, and municipal officials). At the theoretical training, participants were given the necessary information on how to prevent problems caused by the spread of aquatic invasive species and an overview of different eradication methods. At the end of the course, participants learnt how to identify different crayfish species and recognise Nuttall's waterweed in the wild. An overview of environmental DNA methodology was also provided. Altogether, 65 officials participated.

At the practical training, participants learnt how to use baited traps to identify different crayfish species and how to weigh and measure them. Altogether, 30 officials participated.

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Katrin Kaldre

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Regional seed mixtures as an effective tool for protecting the diversity of grassland habitats

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Project summary

The meadows in many places in the Czech Republic are not in a good shape – in the last century, they were ploughed and then re-grassed with species-poor seed mixtures. In some cases, species-rich mixtures have been used, but they often also contain alien species, species not suitable for the given site, or species produced far away from the receptor site, further eroding the genetic diversity of Czech meadow species. In ecological meadow restoration, regional seed mixtures that have been sourced locally are used to maintain or naturally enhance the biodiversity of plants and, subsequently, insects.

"Regional seed mixtures as an effective tool for protecting the diversity of grassland habitats" is a project focusing on methods that can be used for meadow restoration. Regional seed mixtures can be created by growing locally collected seeds in seed beds and then mixing individual species together, or they can be directly collected from species-rich grasslands by using specialised brush harvesters. The project researched the effectiveness of smaller brush harvesters, of which there has been only minimal experience in the Czech Republic. We used a pushed harvester and hand-held harvester. These were also compared with a big tractor harvester that had previously been used for seed collection in the White Carpathians. Meadow restoration via regional seed mixture has also been compared with the method of using green hay – the direct transfer of fresh biomass from the donor to the receptor site – and threshed material.

To achieve this, we collected seed by means of all the aforementioned methods at eight different donor sites three times per season – the end of June/beginning of July, July/August, and the end of August/beginning of September. From each collection, we took a sample for lab analysis. The harvesters were typically able to collect 50–65% of all the species present on the site, usually collecting 0.5–2(–3) grams of seeds per square metre in a single harvest. This depended, of course, on the date of collection and the ripeness of the individual species. Therefore, we developed a model to predict harvested species based on this data.

At four sites, we also established receptor fields, where we sowed seeds from the donor sites in experimental squares. These fields will be monitored long-term, so that the different methods of seed collection can also be compared in terms of actual establishing of a new meadow. It has been one year since the sowing and the project has ended, so it is too soon to have conclusive results.

Another objective of the project was to find sites suitable for seed collection across the Czech Republic. Therefore, extensive botanical monitoring was conducted. We then created a database of species-rich grasslands, containing over 30 sites of suitable meadows. The database can be found on the project website at louky.cz and can be used in future projects that would like to restore grasslands across the Czech Republic.

We also focused on educating the public about regional seed mixtures. We organised several workshops and seminars, created a website and wrote articles about correct approaches to grassland restoration, and produced three popularisation videos on the topic – these can be found on the website as well.

The project has great future potential. We would like to further extend the database of species-rich grasslands and enhance the brush harvesters to deliver greater efficiency. We also plan to cooperate with various state agencies to develop a national plan of ecological meadow restoration and secure a viable process for the certification of regional seed mixtures by law.

Many organisations worked on the project: the Czech Union for Nature Conservation, Masaryk University, the University of South Bohemia, Agrostis Trávníky, s.r.o., Local chapter ČSOP Vlašim, Local chapter ČSOP Bílé Karpaty, the Western Norway University of Applied Sciences, and the BROZ conservation association.

Tereza Štochlová

Tereza Štochlová graduated with a BSc. (bachelor's degree) in Biology and then, in 2021, an MSc. (master's degree) in Terrestrial Ecology at the Faculty of Science of Charles University.

Since then, she worked as a project manager for the Czech Union for Nature Conservation (ČSOP). She specialises in regional seed mixtures and, since 2024, she has served as an expert guarantor of the ČSOP's Restoration of Flowering Meadows programme.

Floating artificial islands create new suitable nesting sites for waterbirds

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Project summary

Intensively managed fishponds are considered the most important breeding habitat for waterbirds as nesting sites and for rearing their young. In recent decades, environmental change (including climate change) has deeply impacted waterbirds' population dynamics across their breeding distribution. Most key drivers of population change, such as reproduction success, are strongly affected by the breeding site environmental conditions. Importantly, the lack of suitable nesting sites leads to both inter- and intra-species competition for this critical resource. In this context, the Norway Grants project (2022–2024) **"Implementation of floating artificial islands to improve breeding conditions for waterbirds and increase biodiversity in fishpond ecosystems"** aimed to increase the ecological value of man-made wetlands (especially fishponds) by creating suitable new nesting sites and enhancing the ecological conditions of fish ponds to meet breeding requirements for a group of selected waterbird species (ducks, gulls and terns) of interest. This project involves the introduction of floating

Fig. 1. Gabion-based construction of floating artificial islands (photo: Tomáš Jůnek)

Fig. 2. Plants secured with coconut material, Krvavý fishpond (photo: Tomáš Jůnek)

artificial islands at intensively managed fishponds through nature-based solutions. These breeding islands directly provide alternative breeding opportunities for waterbird species of interest (the mallard, red-crested pochard, common pochard, tufted duck, black-headed gull and common tern).

Fig. 3. Breeding of common terns, Vyšatov fishpond (photo: Monika Homolková)

In relation to the technical part of this project, the main partner, VRV (Water Management Development and Construction), developed artificial-island technology during a previous project on water conditions in reservoirs in Czechia (TH02030633 – utility model 34438). The island structure consists of 16 gabion sections, each measuring 2 m^2, forming a total surface area of 32 m^2. It features a durable yet lightweight and flexible steel sandwich structure, anchored with steel spirals. Buoyancy is provided by durable plastic tubes, while coconut material secures the plants in place (see Fig. 1 for details).

In total, we installed 20 functional samples of floating artificial islands in south and north Bohemia. The successful project provided a breeding site for dozens of nests for the target species of waterbirds. The islands significantly decrease the lack of breeding possibilities for the target species by creating alternatives. We recorded nests of the following target species: the mallard (*Anas platyrhynchos*), red-crested pochard (*Netta rufina*), common pochard (*Aythya farina*), tufted duck (*Aythya fuligula*), black-headed gull (*Chroicocephalus ridibundus*), and common tern (*Sterna hirundo*). The project highlighted the importance of breeding ducks in colonies of the protective species – gulls and terns, as these provide anti-predation protection for their own nests and for the nests of duck species. The effectiveness of the islands increased in the vicinity of breeding colonies of gulls and terns (the fishponds Domin and Vyšatov in the České Budějovice district), supporting the breeding of the common pochard and tufted duck. The re-establishment of common pochard breeding thanks to a floating island was recorded in the Obecní fishpond (in the Tábor district). The project focused on protected areas (e.g. Natura 2000 sites). We noted the following issue: the degradation of vegetation caused by herbivorous species (swans and geese).

The project indicated the high potential of this nature-based solution to improve the breeding possibilities of the target species, many of which have non-secure conservation status. For details, please follow us at ragoostrovy.fzp.czu.cz/en.

The MOSPREMA project has helped to develop an integrated management system that is more efficient at addressing the risk of mosquito outbreaks in Litovelské Pomoraví

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Project summary

Litovelské Pomoraví is an area that experiences high mosquito activity every spring and during summer floods. This protected landscape, situated along the Morava River, provides ideal conditions for mosquito breeding due to its numerous water and wetland ecosystems. When conditions are favourable for the development of mosquito larvae, the residents of towns and villages around the floodplain forest often suffer from prolonged mosquito outbreaks. Experts warn that climate change has further exacerbated the risk of mosquito overpopulation in recent years. The most affected municipalities include Střeň, Náklo, Horka nad Moravou, Litovel, Mladeč, and Bílá Lhota, where the outbreaks can impact up to 15,000 people.

The two-year international project MOSPREMA: Prediction and Management of Mosquito Outbreaks for Biodiversity Conservation in Floodplain Forests, launched in 2022, involved Palacký University Olomouc, the town of Litovel, nearby municipalities, the Olomouc Region, and international partners, including the Norwegian University of Science and Technology. The project identified more than a thousand high-risk pools that provide ideal breeding grounds for mosquitoes. Using a digital terrain model derived from aerial laser scanning, combined with orthophotos and ground measurement data, a unique database of high-risk pools was created. From these pools, reference sites were selected for the installation of autonomous sensors, which remotely monitor current conditions. The data collected, such as water, air, and soil temperatures, moisture levels, and water surface height, allows for timely predictions of mosquito overpopulation and enables local authorities to apply Vectobac larvicide in order to target mosquito larvae.

The autonomous sensor sets can operate for several years without human intervention. The sensors are connected to a warning system accessible by local governments, providing critical information about the water conditions. Based on this data, municipalities can better plan targeted interventions and reduce excessive larvicide use. This system replaces previously random and widespread spraying, and in doing so significantly reduces the amount of larvicide required.

The data collected, combined with additional information on mosquito larval development, will help experts to create a reliable model for predicting future mosquito population trends. This will reduce the need for periodic field inspections and make decision-making on mosquito control measures more efficient. In some parts of Litovelské Pomoraví, a special drone will be used to apply larvicide to pools located in open areas, such as meadows, avoiding the problem of the spray being blocked by forest canopy.

The project also involved testing the effectiveness of different batches of larvicides in combination with various water parameters in a biochemical laboratory. Biologists studied the impact of larvicides on non-target organisms and invertebrates and conducted egg counting in the soil to predict future outbreaks during floods.

All project activities were focused on optimising and minimising the necessary interventions to manage mosquito outbreaks in the Litovelské Pomoraví Protected Landscape Area and its surroundings. The project aimed to ensure that larvicides are introduced into the ecosystem in minimal amounts, with precise timing and maximum effectiveness. Thanks to these combined efforts, the mosquito population in Litovelské Pomoraví has been kept at a manageable level this year.

Jan Brus

He is an assistant professor specialising in environmental geoinformatics at the Department of Geoinformatics, Palacký University, Olomouc. He focuses on the use of geoinformation technologies in landscape research, environmental protection, and environmental applications. His research interests include spatial data analysis and the prediction of environmental phenomena, such as mosquito outbreaks and bee colony health. Dr Brus is the author of numerous scientific publications and actively participates in international projects that link scientific research with practical applications in the environmental field. Another area of his research involves 3D printing and the visualisation of spatial data using modern technologies.

Part Two

Water Pollution Reduction

Pharmaceuticals in surface water of Vltava River basin

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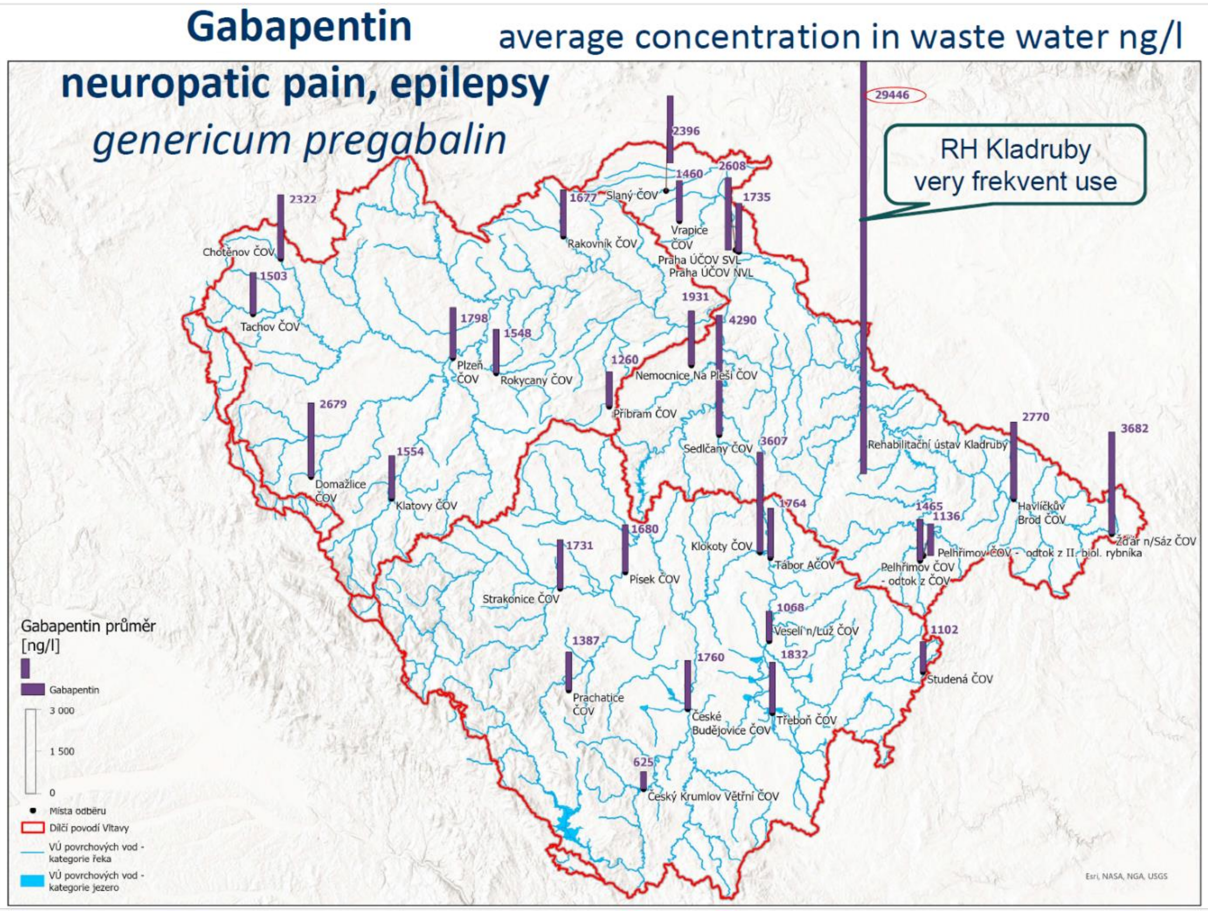
Project summary

Today's surface water pollution is no longer just about the presence of nutrients, heavy metals, polyaromatic hydrocarbons and other organic substances familiar from the "last century". In the last 20 years, there has been increasing talk about the presence of "microcontaminants" and the need to remove them both from drinking water and, more recently, from the wastewater that flows into surface waters. These micropollutants primarily include residues of pesticide substances, human and veterinary pharmaceuticals, and numerous other substances, such as radiodiagnostic agents (iomeprol, iopromide, iohexol), benzotriazole substances (used as anticorrosives), bisphenols (plastic softeners), complexones, e.g. ethylenediaminetetraacetic acid (used to reduce surface tension), phthalates, flame retardants, etc. A great deal of attention is currently also being paid to "perfluorinated substances" (PFAS), which are used in particular in various anti-wetting treatments for textiles, in fire-fighting foams, in de-icing fluids used at airports, etc. The water management laboratories of Povodí Vltavy are continuously expanding the analytical portfolio of monitored substances with new "environmentally indicated" active ingredients. In recent years, some pharmaceuticals have been added to the set of analysed substances, in particular the active ingredients of blood-pressure-lowering products, i.e. sartans, active ingredients and metabolites of cholesterol-lowering products, i.e. statins, some hormonal substances, other antibiotics, more than 20 addictive substances, and the PFAS group. The analytical portfolio also includes artificial sweeteners, such as acesulfame, saccharin and sucralose. The Organic Analysis Department at the Water Management Laboratory in Plzeň currently analyses more than 150 pesticide substances and their metabolites, more than 120 substances from the pharmaceutical group, and a large number of specific analytes from these groups. All of the above substances are analysed in surface water and a large proportion of them are also analysed in wastewater.

The scope of operational monitoring conducted by Povodí Vltavy is determined both by applicable legislation and by impact analysis. This includes, for example, monitoring pharmaceuticals downstream of human settlements and wastewater discharges from healthcare facilities, as well as tracking PFAS compounds in surface waters draining areas such as airports or factories associated with the aviation industry. In recent years, efforts have also been made to collect mixed surface water samples using automatic samplers so that representative results are obtained and different fluctuations are affected, both in terms of wastewater discharge and anomalous flows. The analysis of the aforementioned substances is carried out using gas and liquid chromatography methods with mass spectrometric detection. Povodí Vltavy water management laboratories have several GC/MS-MS and LC/MS-MS analytical systems.

The aim of our monitoring is to gather information on significant contaminants from the group of pharmaceuticals and other organic substances found in surface waters, as well as substances that originate in wastewater, including both municipal and industrial sources. Residues of pharmaceuticals and other substances can be partially classified into those that originate in significantly higher concentrations from healthcare facilities or exclusively from municipal wastewater treatment plants. However, in most cases, they result from a combination of both sources. "Medical wastewater" generally contains higher concentrations of most pharmaceuticals, but the following substance groups show particularly elevated levels: analgesics (e.g. dipyrone metabolites), anticonvulsants (carbamazepine, pregabalin), psychotropics (citalopram, lamotrigine), antiphlogistic drugs (diclofenac, phenazone), antibiotics (erythromycin, clarithromycin, trimethoprim), antiallergics (fexofenadine), diuretics (furosemide), neuropathic pain medications (e.g. gabapentin), radiodiagnostic agents (iohexol and iomeprol), and lipid-lowering drugs (rosuvastatin). For example, in the treated wastewater of the rehabilitation institute in Kladruby u Vlašimi, concentrations of some drugs in tens of micrograms per litre of wastewater were analysed, e.g. for gabapentin, the average concentration is around 29.4 ug/l. One significant group is radiodiagnostic agents (iomeprol and iopromide), found in

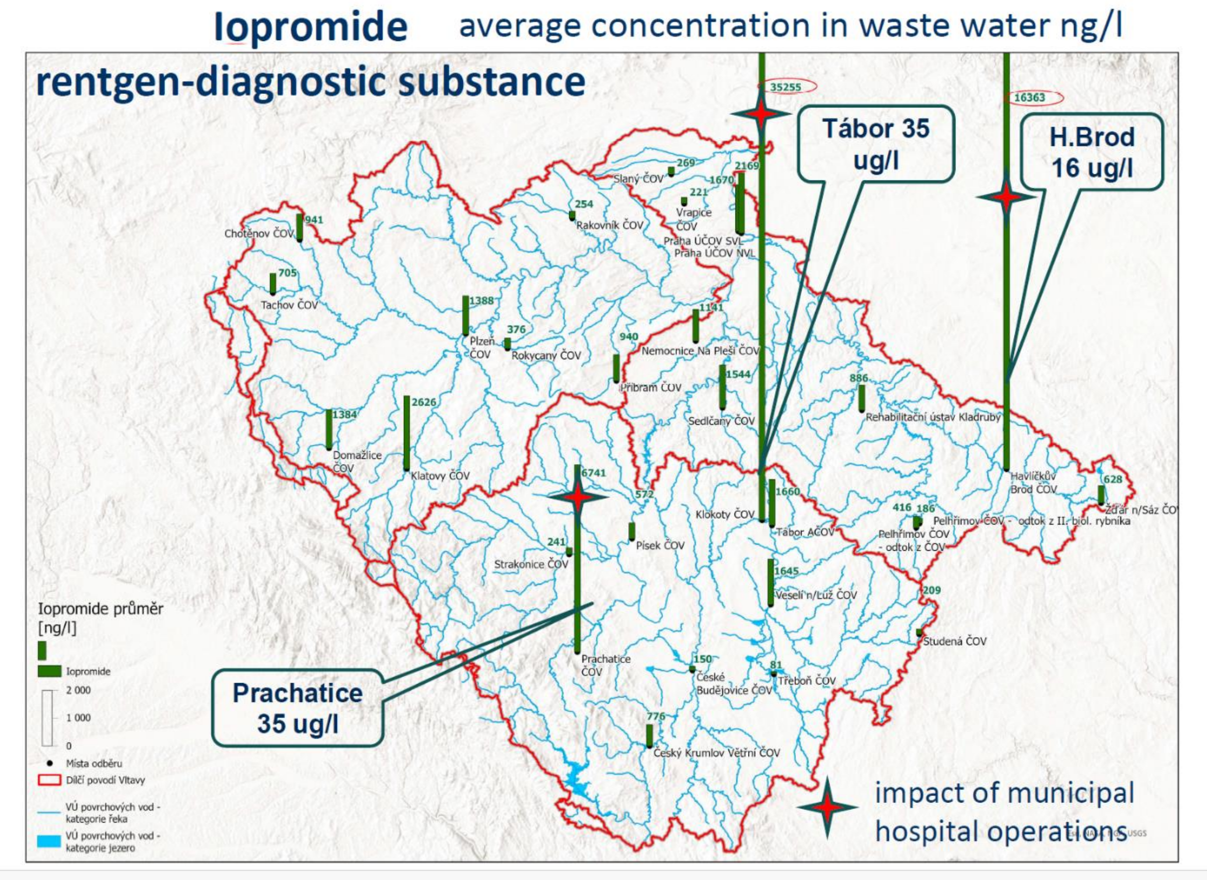


Map 1. Average concentration of gabapentin in wastewater treatment plant effluents in the Vltava River basin

Gabapentin průměr = Gabapentin average	Místa odběru = Sampling points	Dílčí povodí Vltavy = Sub-basin of the Vltava	VÚ povrchových vod – kategorie řeka = surface waterbody – river category	VÚ povrchových vod – kategorie jezero = surface waterbody – lake category	ČOV = WWTP

wastewater at high average concentrations. For example, in the wastewater flowing from Na pleši Hospital (near Mníšek pod Brdy), an iomeprol concentration of 76.3 ug/l was measured. For iopromide, the highest average concentrations were measured in the wastewater of the wastewater treatment plants in Tábor, Havíčkův Brod and Prachatice, all of which have hospitals with X-ray diagnostic methods.

In contrast, for many other pharmaceuticals, there is not such a big difference between municipal and medical wastewater, especially in terms of pharmaceuticals that are widely used in high doses across the human population. These are drugs used to treat diabetes (metformin), gout and kidney and urinary tract infections (e.g. allopurinol, analysed through its metabolite oxypurinol), drugs for high blood pressure (e.g. hydrochlorothiazide and a broad range of drugs belonging to the sartan group, in particular telmisartan and valsartan). The maximum average concentrations of metformin in wastewater (around 7 ug/l) were measured at the outflow from the Domažlice WWTP. The typical concentrations of metformin at several municipal wastewater treatment plants (e.g., Prague, Plzeň, Klatovy, Tábor, Písek, Pelhřimov) range in the lower microgram levels. Residues of blood pressure medications, particularly telmisartan and hydrochlorothiazide, are also found in high



Map 2. Average concentration of iopromide in WWTP effluents in the Vltava River basin

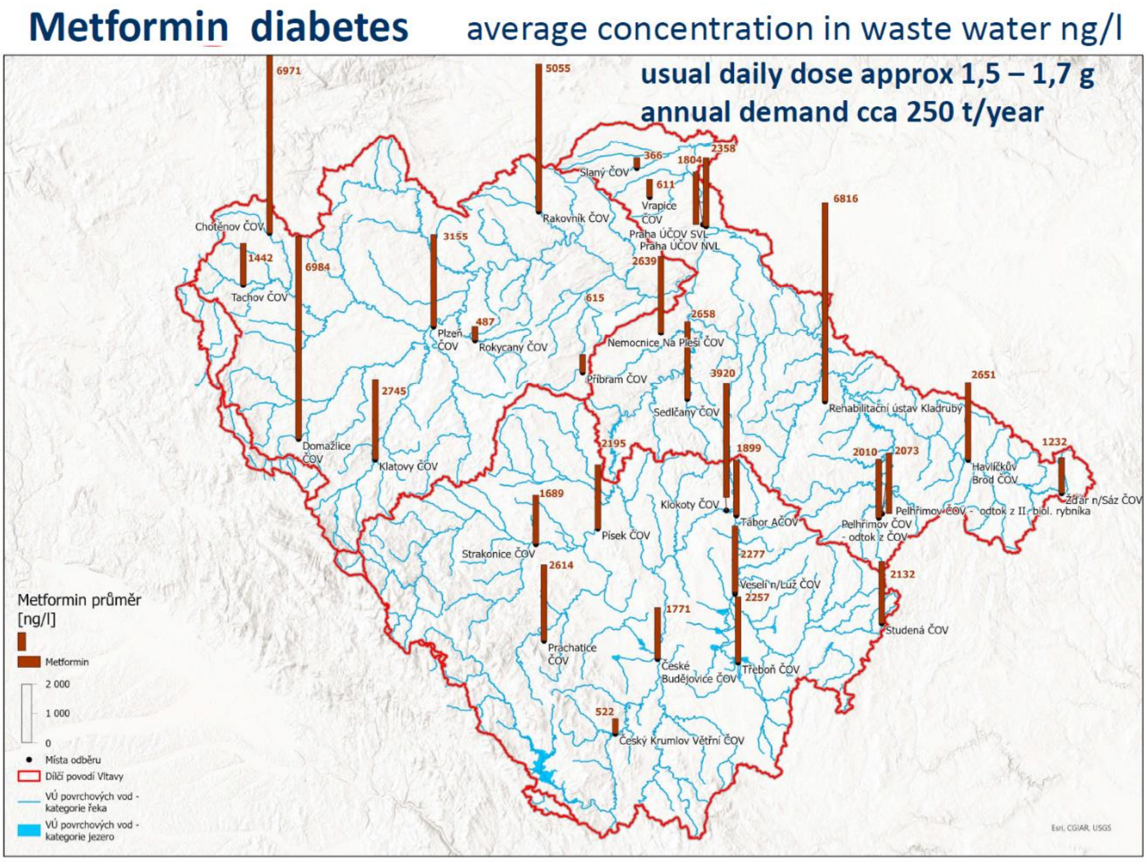
Iopromide průměr = Iopromide average	Místa odběru = Sampling points	Dílčí povodí Vltavy = Sub-basin of the Vltava	VÚ povrchových vod – kategorie řeka = surface waterbody – river category	VÚ povrchových vod – kategorie jezero = surface waterbody – lake category	ČOV = WWTP

concentrations in wastewater, both in municipal wastewater from residential areas and in wastewater from healthcare facilities. Common concentrations in both types of water are

in units of ug/l for both substances.

All of the above and other substances enter surface waters with wastewater. Surface waters are generally significantly polluted with pharmacological residues, especially if they are streams that are not very voluminous and at the same time serve as recipients of wastewater for larger residential agglomerations, or if wastewater from a larger healthcare facility flows into them. In general, it can be said that residues of substances that hardly degrade or metabolise in the aquatic environment are also present in surface waters in high concentrations. These include the above-mentioned substances metformin, gabapentin, tramadol, carbamazepine, and several others.

The highest concentrations of pharmaceuticals are typically measured in small watercourses downstream of WWTP outfall. The concentration of pharmaceuticals in large streams is typically significantly lower than in small ones, even when they receive wastewater from large agglomerations, as is the case with the Vltava River downstream of Prague. The figure below shows the evolution of concentrations of selected drugs on the



Map 3. Average concentration of metformin in wastewater treatment plant effluents in the Vltava River basin

Metformin průměr = Metformin average	Místa odběru = Sampling points	Dílčí povodí Vltavy = Sub-basin of the Vltava	VÚ povrchových vod – kategorie řeka = surface waterbody – river category	VÚ povrchových vod – kategorie jezero = surface waterbody – lake category	ČOV = WWTP

Vltava-Zelčín profile (before the confluence of the Vltava and Elbe Rivers). Although the concentrations of pharmacological residues here are lower than in small watercourses, from a "balancing" perspective these are not negligible outflows. Almost all the graphs below show a significant decrease in certain pharmaceuticals in the water of the Vltava River (Vltava-Zelčín profile), which is very likely related to the intensification and modernisation of the central wastewater treatment plant in Prague Troja.

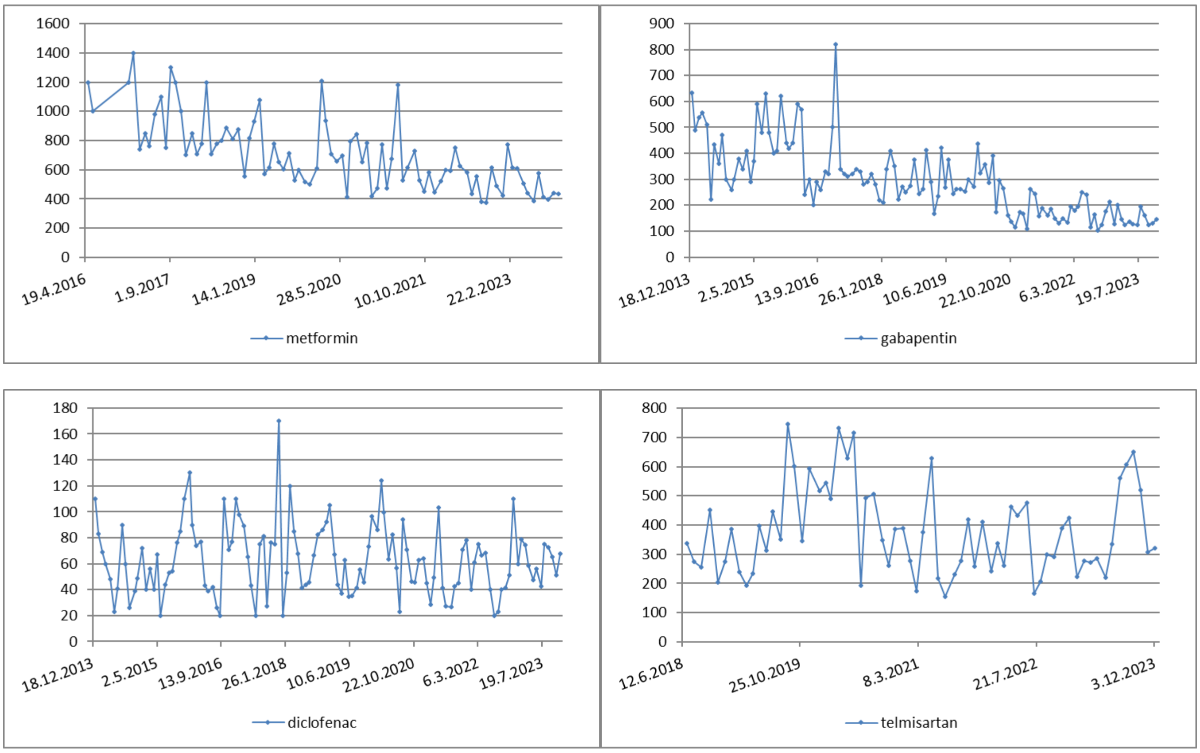


Fig. 1. Concentration trends of metformin, gabapentin, diclofenac and telmisartan in the surface water of the Vltava-Zelčín profile (ng/l)

Conclusion

The Povodí Vltavy water management laboratories have been monitoring drug residues and other specific substances in surface waters for many years. This paper provides examples of the occurrence of these substances in "treated" wastewater from human settlements and healthcare facilities. The discharge of wastewater into surface water has a direct impact on its quality, both in small and large streams, as well as in reservoirs and tanks that serve as sources of drinking water.

In view of the high concentrations of certain pharmaceuticals in surface waters and their likely "cocktail" effect (not only on aquatic ecosystems), it is necessary to start implementing measures that will lead to a lower load of these substances in surface waters, e.g. by introducing technological treatment steps to remove these substances from wastewater.

Marek Liška

Head of the Povodí Vltavy Water Management Laboratories Division. He graduated in hydrobiology from the Department of Parasitology and Hydrobiology, Faculty of Science, Charles University in Prague. Here, he continued his doctoral studies focused on the bioaccumulation of trace elements in the biomass of aquatic organisms. Upon completing his studies, he worked at the laboratory of the Želivka water treatment plant and, since 1996, he has been working for the Povodí Vltavy Water Management Laboratories Division. His expertise lies in the monitoring of streams and reservoirs, and assessment of the ecological and chemical status of water (especially nutrients). In recent years, he has also focused on the study and evaluation of pesticides, pharmaceuticals, and other specific substances in our surface waters.

Monitoring of pesticides in the environment and methods for their elimination

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Introduction

The consumption of pesticides in agriculture is constantly increasing. The main reason for their application is the increase in crop production, which would have fallen by a third without them. There are also certain disadvantages associated with the use of pesticides. As a result of the high consumption of pesticides, there is increasing concern about their negative impact on the environment. Due to their persistence in water, resistance to degradation, accumulation potential, and toxicity, non-target organisms can be affected, including, for example, microorganisms and invertebrates, as well as plants, fish, and humans, without exception. They reach water sources not only through diffusion, but also through leaching and surface runoff. Since these substances often fail to degrade completely, the pesticides contained in wastewater can pass through WWTPs unchanged and thus reach surface waters directly. Therefore, an important step is their monitoring (not only in surface water), which allows us to identify sources of pollution and quantify their amount [1-3].

Another ecological problem is invasive plants originally imported into the Czech Republic as ornamental plants, partly because of the rapid growth of fruits and seeds. However, many types of invasive plants in nature negatively affect the species composition because they are able to change the properties of the soil and the processes taking place in it. Invasive plants often alter the ion and water content of the soil, thereby altering the hydrological conditions and salinity of the habitats and preventing the growth of naturally occurring plants. In addition, there is the risk, with certain species, of hybridisation with closely related wild species and the creation of new invasive organisms. Disposal processes are often time-consuming and financially demanding or focus on eliminating the use of pesticides that are already problematic in the environment [4, 5]. For that reason, invasive plants appear to be a suitable material for the preparation of activated carbon.

Experiment

Monitoring of pesticides

Pesticide monitoring was carried out at seven sampling sites over a period of 12 months to capture one full agricultural season. Sampling sites included rivers, small watercourses and ponds in the city of Ostrava and the town of Potštát, Czech Republic. Pesticides were monitored in surface water, sediments, and riparian plants. All collection points are located near a field and, since they are small streams or small ponds, are strongly influenced by field management.

Pesticides in surface waters were monitored once a month. Sampling was carried out in glass sample boxes. The samples were kept in a refrigerator at 4 °C until analysis. They were then filtered through 47 mm microfilters and processed using solid phase extraction, which included the use of EnvirElut pesticide SPE columns. The samples were then measured using LC-MS/MS.

Pesticides in sediments were monitored four times a year. Sampling was carried out in glass sample boxes. The samples were subsequently fully dried and processed using the modified QuEChERS method; the aqueous phase was processed by SPE. The samples were then measured using LC-MS/MS.

Pesticides in plants were monitored four times a year. Collection was carried out in resealable bags. The plants were subsequently mixed, with the addition of water, and dried at 70 °C. Subsequently, the samples were processed as sediment samples and measured.

An HPLC gradient liquid chromatograph (Shimadzu, Japan) with a QTRAP 6500+ mass detector (Sciex, Canada) was used for the analysis of pesticides. An electrospray was used as an ion source. A Synergy Fusion RP 80Å (50 x 2 mm, 4 µm) column (Phenomenex, USA) was used for the analysis, which allows for the analysis of a mixture of polar and non-polar substances. 5 mM ammonium formate in MeOH (MF A) and 5 mM ammonium formate in H_2O (MF B) were used as mobile phases. Gradient MF B: 0 → 0.5: 90% B; 0.5 → 1: 60% B; 1→8: 10% B; 8.2 → 9: 90% B. The analysis was based on the identification of MRM transitions.

Preparation of activated carbon

The invasive plants *Reynoutria japonica* (RJ) and *Impatiens glandulifera* (IG) were used for the preparation of activated carbon. Both plants were dried and ground into sawdust. Subsequently, the sawdust was activated with H_3PO_4 and NaOH at an activation biomass-to-activator ratio of 1:2. Prior to pyrolysis, convection carbon was added to the flask as a combustion initiator. Microwave pyrolysis was carried out in a microwave reactor for 20 min at 400 and 600 W. After pyrolysis, the samples were washed to neutral pH, then dried and ground to a size below 0.09 mm. The prepared materials were subsequently characterised and used for the adsorption of pesticides from water.

Sorption experiments

Four sorbents were prepared, which were subsequently tested for pesticide adsorption. Kinetic experiments were conducted in batch mode, where 5 mg of AC was added to 50 mL of pesticide solution. Samples were taken at regular intervals. After the end of the experiment, the samples were filtered and measured on a liquid chromatograph with mass detection.

Adsorption experiments were conducted in batch mode, where 5 mg of AC was added to a pesticide solution of increasing concentration (0.01-1 mg L^{-1}). After the end of the experiment, the samples were filtered and measured on a liquid chromatograph with mass detection.

Results

Monitoring of pesticides

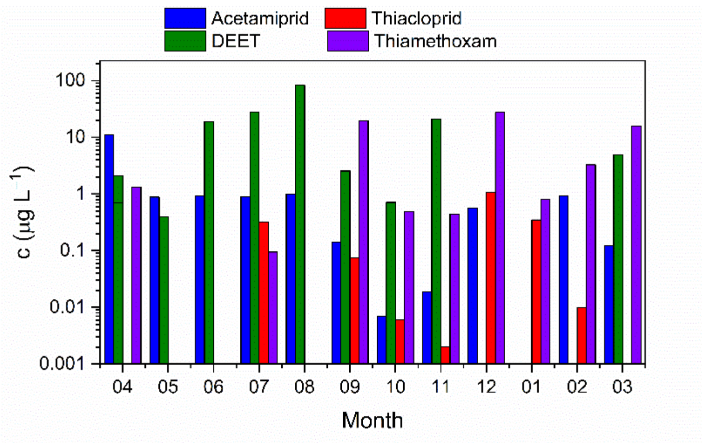

Fig. 1. Concentration of selected pesticides at the Opava – Kateřinský potok (stream) sampling point.

Based on the monitoring of pesticides in surface waters, four pesticides were selected that occurred in higher concentrations at the majority of sampling points.

Fig. 1 shows an example of the measured concentration of selected pesticides in the Opava – Kateřinský potok (stream) sampling point (N49.949389, E17.931167). The graph shows that the concentration of DEET is many times higher than that of other pesticides, especially in the summer months, when the consumption of repellents is higher. It can also be seen that the concentration of pesticides increases in the months in which they are applied to fields.

About 40 other pesticides were also detected in the samples. These pesticides were only qualitatively identified. Pesticides detected in surface and plant samples were the same. Smaller amounts of pesticides were detected in sediment samples.

Sorption experiment

The measured adsorption data was evaluated using the Langmuir isotherm (Fig. 2). It can be seen from the figure that all substances are better sorbed on sorbents prepared by

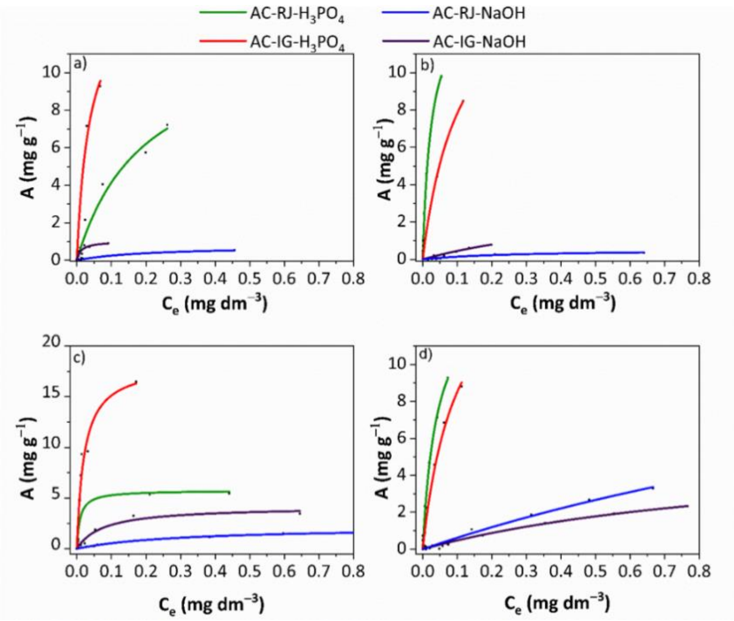

Fig. 2. Adsorption isotherms (Langmuir model) of (a) Acetamiprid (b) DEET (c) Thiacloprid (d) Thiamethoxam adsorbed on activated carbons prepared from Reynoutria japonica (RJ) and Impatiens glandulifera (IG) activated by H_3PO_4 or NaOH.

activation with H_3PO_4, which is related to higher porosity and the higher representation of oxygen-containing surface groups.

Conclusion

Based on the monitoring of pesticides in surface waters, four pesticides were selected that occurred in higher concentrations at all sampling points. There was found to be a significant increase in the concentration detected during the summer months, which could pose a potential risk to non-target organisms. Based on the consistency of pesticides detected in water, sediments, and plants, it can be concluded that the pesticides everywhere are from the fields. Some of the detected substances have long been banned, but it is still possible to find them in the environment.

Four sorbents were prepared from invasive plants. The highest sorption capacity was shown by the sorbent from *Reynoutria japonica* and then from *Impatiens glandulifera*, which was prepared by activation with H_3PO_4. With acetamiprid and thiacloprid, the best sorbent was prepared from *Impatiens glandulifera*, followed by *Reynoutria japonica*. The opposite was true for DEET and thiamethoxam. Conversely, sorbents prepared by activation with NaOH show a lower sorption capacity. This work shows that invasive plants appear to be suitable material for the preparation of activated carbon.

Acknowledgement

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CarbonCLEAN®: Demonstration pilot project for the removal of pharmaceuticals from wastewater

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Objectives

In this project, we demonstrated the efficiency of removing selected pharmaceuticals in real wastewater and in the real technological conditions of a wastewater treatment plant (WWTP). We identified the possible need for partial technological modifications of the filtration equipment so that it could be used in normal operation. From a technical perspective, replaceable textile filters with CarbonCLEAN® sorbent were used. We tested biochar (4073) on standard solutions and real wastewater. Then, the first prototype of the textile filter was prepared and tested on standard solutions and real wastewater. Finally, we selected the most suitable type of textile filter and constructed a pilot unit.

Biochar (4073) characterisation

Biochar (Fig. 1) was prepared by pyrolysis of digestate from wood and greenery (60%) and corn separation (40%) at 470 °C for 25 minutes. The specific surface area of BET is 571.6 ± 9.2 m^2/g, grain size 0.09 mm, content of -OH groups 0.386 ± 0.02 mmol/g, and elemental composition 82.03 % C, 0,74 % H, 0.285 % N, 16.95 % O. We tested the sorption properties of the biochar, after which the biochar was applied to a textile filter. In this project, three types of textile filters were prepared (Fig. 2).

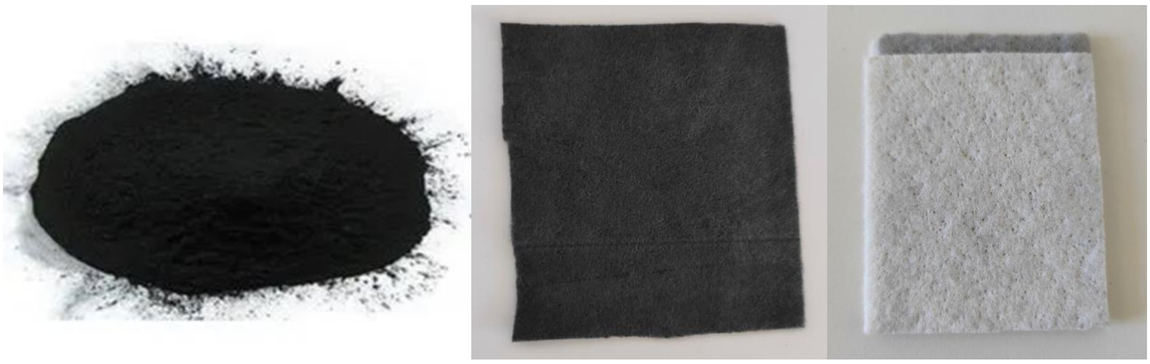

Fig. 1. Left – biochar 4073, centre – first prototype of textile filter, right – pilot textile filter.

Each filter type was tested. The liquid flow through one or more layers and the sorption capacity were tested.

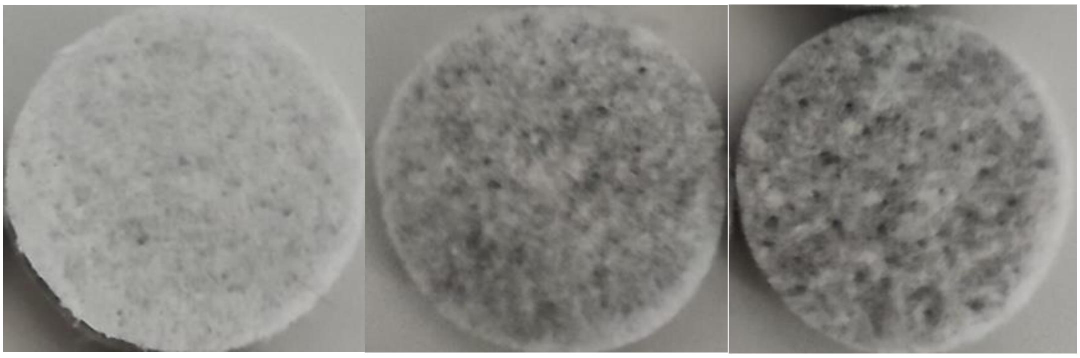

Fig. 2. Left – 2.1.0 – 200 g/m2, 100% PES calendered (core), impregnation in a bath of 300 ml water + 3 g 4073, flow rate 0.717 ml/s; centre – 2.1.1 – 200 g/m2, 100% VS (core), impregnation in a bath of 300 ml water + 3 g 4073, flow rate 0.719 ml/s; right – 2.1.2 – 200 g/m2, 100% VS (core), impregnation in a bath of 300 ml water + 3 ml PAL + 3 g 4073, flow rate 0.712 ml/s

Results of sorption tests on first prototype

We tested a drug solution with a concentration of 1 ug/L and 100 ug/L. This solution was applied to one or three layers of textile filter. The drug removal results are presented in Table 1.

Table 1. Overview of tested analytes and their removal percentages

Analytes	Conc 1 ug/L (%)/1 layer	Conc 100 ug/L (%)/1 layer	Conc 1 ug/L (%)/3 layers	Conc 100 ug/L (%)/3 layers
3-hydroxykarbamazepin	92,4 ± 9,2	48,0 ± 4,8	98,9 ± 9,9	92,2 ± 9,2
4-hydroxydiklofenac	90,8 ± 9,1	49,4 ± 4,9	96,6 ± 9,7	82,9 ± 8,3
Acebutolol	100 ± 10	74,8 ± 7,5	100 ± 10	98,0 ± 9,8
Acetylsulfadiazin	77,9 ± 7,8	24,7 ± 2,5	97,2 ± 9,7	39,7 ± 4,0
Carbamazepin	94,0 ± 9,4	45,1 ± 4,5	98,4 ± 9,8	89,3 ± 8,9
Clarithromycin	97,4 ± 9,7	87,8 ± 8,8	97,4 ± 9,7	95,2 ± 9,5
Diclofenac	91,4 ± 9,1	56,2 ± 5,6	100 ± 10	95,7 ± 9,6
Ketoprofen	95,7 ± 9,6	33,2 ± 3,3	100 ± 10	76,6 ± 7,7
N-acetylsulfamethoxazol	94,2 ± 9,4	50,4 ± 5,0	98,6 ± 9,9	90,2 ± 9,0
N-acetylsulfapyridin	90,1 ± 9,0	38,6 ± 3,9	98,8 ± 9,9	85,0 ± 8,5
Propranolol	98,4 ± 9,8	86,6 ± 8,7	98,5 ± 9,9	100 ± 10
Roxithromycin	97,2 ± 9,7	82,7 ± 8,3	97,3 ± 9,7	92,3 ± 9,2
Sotalol	86,3 ± 8,6	29,0 ± 2,9	97,4 ± 9,7	78,8 ± 7,9
Sulfamethoxazol	35,4 ± 3,5	5,60 ± 0,56	73,7 ± 7,4	9,80 ± 1,0
Sulfapyridin	75,2 ± 7,5	24,1 ± 2,4	96,0 ± 9,6	58,5 ± 5,9
Tramadol	95,2 ± 9,5	30,6 ± 3,1	98,4 ± 9,8	88,1 ± 8,8
Venlafaxin	96,1 ± 9,6	39,0 ± 3,9	97,9 ± 9,8	90,9 ± 9,1

Results of sorption tests on three types of filters

Standards (%)	core /1	2.1.0/1	2.1.1/1	2.1.2/1	core /3	2.1.0/3	2.1.1/3	2.1.2/3
Acebutolol	98.6	100	100	98.8	95.3	97.4	96.3	96.0
Atenolol	89.1	92.0	97.0	100	94.7	94.2	94.5	100
Azithromycin	100	100	100	100	100	100	100	100
Clarithromycin	100	100	100	100	100	100	100	100
Clofibric acid	0	44.2	2.5	1.1	0	0	3.8	0
Erythromycin	93.6	9.1	93.7	94.0	89.4	84.5	90.7	90.7
Gabapentin	37.5	82.0	53.7	100	18.6	37.5	16.7	54.1
Hydrochlorothiazide	21.4	39.6	0	29.8	3.8	25.6	7.3	15.7
Ketoprofen	55.8	95.7	67.4	82.8	29.7	84.4	25.8	59.8
Metoprolol	100	100	100	100	95.3	100	96.0	95.9
Pentoxifyllin	58.3	100	71.3	88.4	18.2	82.9	14.0	66.0
Phenazone	26.4	100	44.9	81.1	24.8	89.6	25.2	46.6
Propranolol	94.5	94.5	94.5	94.5	92.7	92.9	92.8	92.9
Propyphenazone	16.8	96.1	43.4	66.7	38.8	74.4	40.0	50.3
Sotalol	70.3	83.4	86.3	96.6	89.8	88.6	89.3	93.2
Tramadol	100	100	100	100	94.0	100	95.0	94.6
Trimethoprim	100	100	100	100	94.0	95.4	95.4	96.2
Venlafaxine	100	100	100	100	100	100	100	100

Some drugs were not sufficiently removed, but this can be resolved by using multiple layers of textile filter. The 2. 1. 0 filter was selected as the best filter.

Pilot technology

Based on the testing of filters in the laboratory, a pilot unit was prepared (Fig. 3), where three layers of the 2.1.0 filter were tested. The unit was tested at two sites in the Czech Republic, in Zlín and Ostrava. For the removal of drugs, real water from a municipal wastewater treatment plant and hospital wastewater was used. The removal results are presented in Table 3.

Fig. 3. Pilot technology with textile filter (2.1.0)

Table 3. Real wastewater

	Ostrava (%)	Zlín (%)
Acebutolol	94.5	89.4
Acetaminophen	96.1	88.1
Atenolol	95.3	90.9
Caffeine	89.1	79.3
Carbamazepine	90.2	93.5
Clofibric acid	99.3	95.5
Diclofenac	72.6	87.8
Hydrochlorothiazide	83.0	88.0
Ketoprofen	94.6	91.1
Metoprolol	90.9	89.4
Pentoxifyllin	98.1	92.4
Primidon	95.1	92.1
Propranolol	99.4	93.7
Propyphenazone	99.3	96.3
Sulfamethoxazole	90.0	86.3
Tramadol	78.2	97.3
Trimethoprim	91.8	91.9
Venlafaxine	91.2	90.8
Efficiency average	**91.6**	**90.8**

Conclusion

The project developed a pilot unit for the removal of pharmaceuticals using textile filters containing biochar. The average efficiency of pharmaceutical removal on real wastewater was more than 90%.

Acknowledgement

I would like to thank the management and employees of the WWTP in Ostrava.

Sylvie Kříženecká

In 2007 she completed her PhD studies at the Faculty of Chemical Technology in Pardubice in the field of Inorganic Chemistry, although she has been working in analytical chemistry since 1994.

Since 2004 she has been a researcher at the Faculty of Environment in Ústí nad Labem, where she has been working in analytical chemistry, mainly focusing on the development and validation of chromatographic methods. She is also involved in testing of new non-traditional sorbents, determination of micropollutants in all types of water and analysis of persistent environmental pollutants.

Validation testing of advanced oxidation processes for the removal of pharmaceuticals from WWTP effluent

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Introduction

The project "Validation testing of advanced oxidation processes for the removal of pharmaceuticals from WWTP effluent" was aimed at the long-term assessment of ozonation used as a quaternary treatment process coupled with nature-based solutions (NBS) for pharmaceutical (PHA) removal from wastewater treatment plant (WWTP) effluents. In total, 141 PHAs were monitored, with the main focus on pharmaceuticals listed in the State Environmental Fund of the Czech Republic Indicative List (IND).

The objective of the project was to implement the long-term assessment of tested technologies with a view to reaching at least 80% of the average reduction of IND substances from wastewater along the entire technological line of the WWTP. As part of the project, an innovative approach to the effective operation of ozonation was implemented, based on a surrogate parameter that refers to the actual removal rate of PHAs. The effect of NBS (artificial wetland, biofilter) as a post-ozonation treatment for additional PHA removal and ecotoxicity management was also assessed.

In the project, ozonation was the main technology responsible for PHA reduction from WWTP effluents. Ozone, as a strong oxidising agent, reacts in an aquatic environment with organic compounds in two ways: (i) direct oxidation of organic compounds using ozone, which is relatively slow and selective; (ii) fast, non-selective hydroxyl radical oxidation, which exhibits reaction rates with pollutants that are an order of magnitude higher.

After ozonation, NBS were added to the technological line to ensure the quality of the final effluent. NBS include various mechanisms that mimic or use natural processes, such as biological degradation or physical and chemical sorption. In the project, three NBS were investigated as post-ozonation treatment: (i) gravel biofilter (GF); (ii) gravel-biochar biofilter (GBF); and (iii) constructed wetland with gravel-biochar filter (CW). These were compared with the granulated activated carbon filter as a reference.

A current operational issue with technologies for PHA removal is that we are unable to quantify the concentrations of pharmaceuticals with an acceptable time delay, and therefore we are unable to evaluate directly the operational efficiency. To bypass the time limitation, a surrogate parameter for the actual removal rate is a promising way to reliably manage these technologies. In the project, the parameter of the relative decrease in UV absorbance at a wavelength of 254 nm (ΔUV254) was investigated as a parameter indicating the current removal rate of monitored substances or set of monitored substances (IND). The absorbance of UV at 254 nm is regularly used in spectrophotometry for the determination of the organic pollution sum. Unfortunately, it is not possible to use this method to determine concentrations of individuals or sums of PHAs due to the negligible concentration levels in comparison with total organic pollution. However, based on numerous previous studies, a very good correlation was observed between the ΔUV254 parameter in the treatment process and the removal of the monitored PHAs. The successful implementation of this approach could enhance the efficiency of the technologies used for PHA reduction and ensure the fulfilment of the required limits.

Pharmaceutical removal in current activated sludge at WWTPs

During the long-term assessment at Blansko WWTP, it was possible to determine the average level of IND reduction in current processes at the WWTP. The results show that conventional mechanical-biological WWTPs are not designed to remove this type of pollution. The reduction in these substances depends considerably on their chemical structure and their biodegradability, or transformation into metabolites. For these reasons, the observed removal of individual PHAs covers the entire spectrum from 0% to 99% (Fig.). The variation in the average removal of IND was considerable within the evaluated pairs of samples (WWTP inflow-outflow) and ranged from 41% to 60% within the IND.

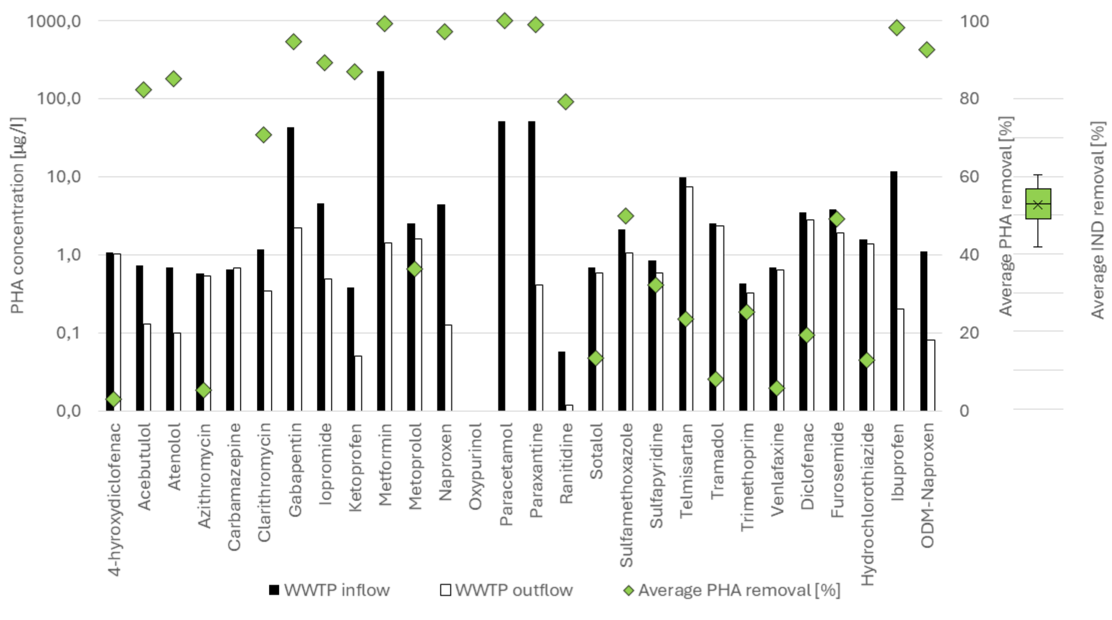

Fig. 1. Concentrations and removal of individual PHAs at Blansko WWTP (left), average removal of IND at Blansko WWTP (box plot, right)

Effect of ozonation on pharmaceutical reduction

Depending on the ozone dose applied, ozonation was very efficient at reducing PHAs from WWTP effluent, and all the investigated PHAs were significantly reduced. The pharmaceuticals carbamazepine, diclofenac, trimethoprim, sotatol, and furosemide were easily removed at a level of more than 80% even at low ozone doses (0.3 mg O_3 / mg TOC); on the other hand, iomeprol and metformin were not removed above 80% even at ozone doses of 1.5 mg O_3 / mg TOC. Also, PHAs monitored under the upcoming European Union Urban Wastewater Treatment Directive were reduced by 80% at an ozone dose of 0.8 mg O_3 / mg TOC (Fig.).

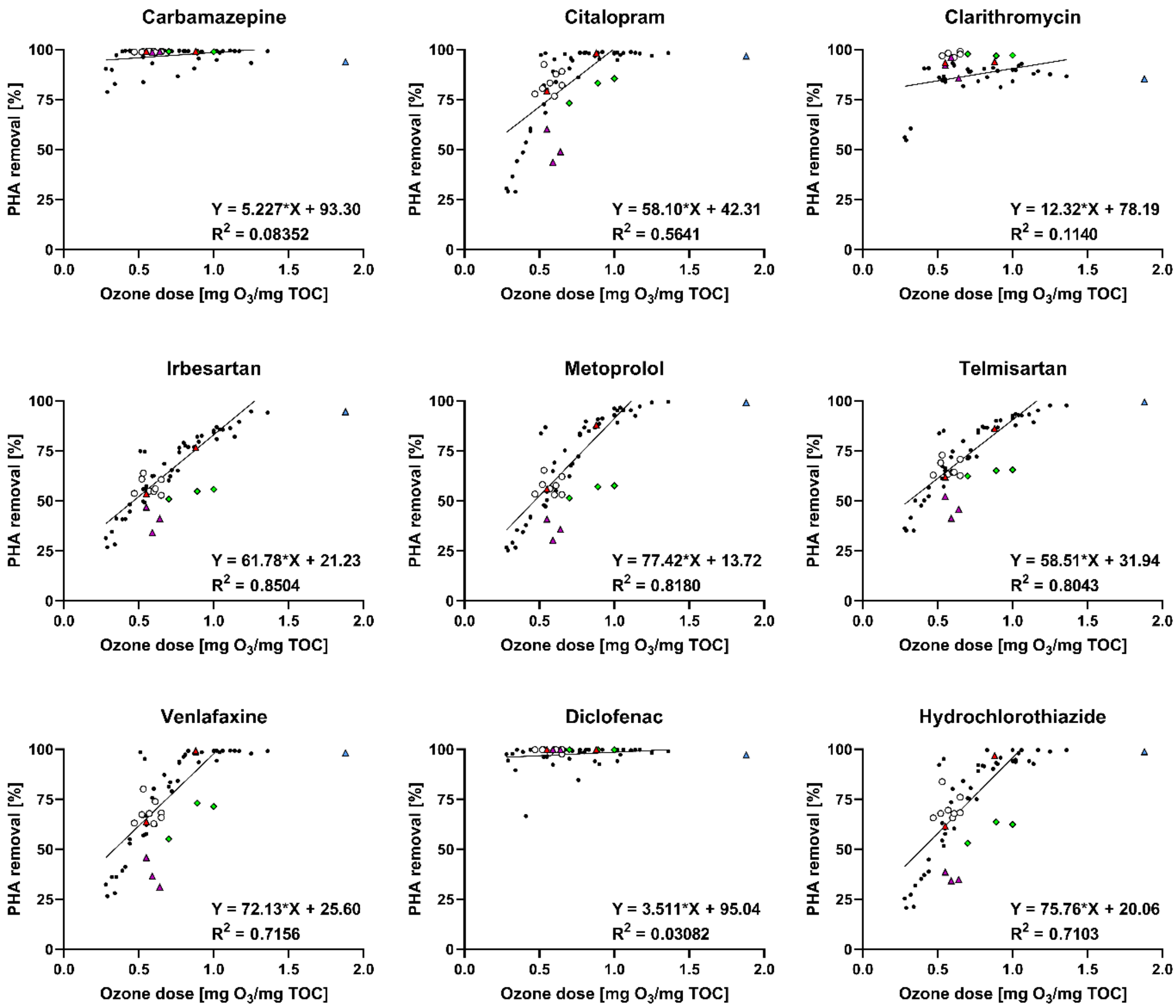

Fig. 2. Individual PHA removal based on the ozone dose

Demonstration of ΔUV254 as a surrogate parameter of actual overall pharmaceutical removal

The objective of the project was to achieve an average reduction of IND by at least 80% along the entire technological line of the WWTP. If we assume the removal of IND at the WWTP is at a level of 41% (the minimum observed value during the project), it was necessary to ensure at least a 66% additional reduction of IND in quaternary treatment.

To secure the required reduction, an automated ozone dose regulation based on ΔUV254 was applied. Based on the first-stage results, a ΔUV254 parameter in the range of 25±2% was set as a sufficient operational point to achieve the required level of reduction of IND. In the evaluation stage, the parameter ΔUV254 ranged from 23.4% to 26.1% and the average removal of the IND was above the 66% limit in each tested sample, ranging from 69% to

82%, and averaging 74% (Fig., white points). The ozone doses relative to the flow rate were in the range of 3–5 g O_3 / m^3.

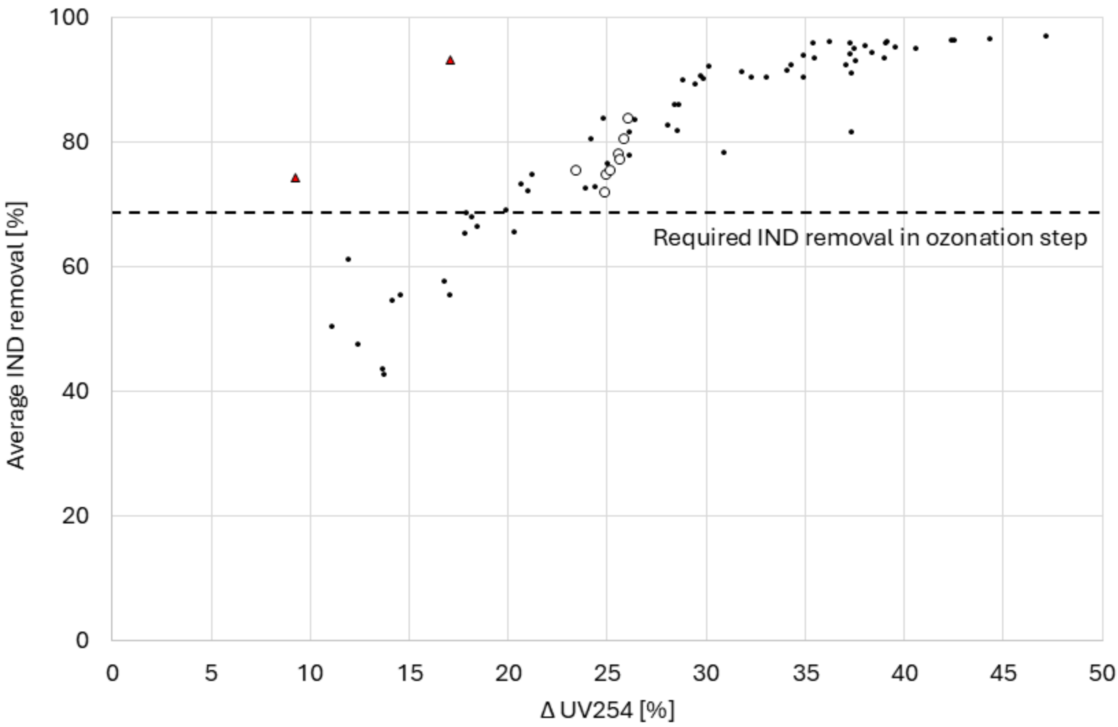

Fig. 3. Average IND removal based on ΔUV254

Nature-based solutions as a post-ozonation treatment

NBS had a positive effect on final effluent in terms of additional PHA and nitrogen pollution reduction. The CW show the best results, alongside PHA removal (82% on average) and nitrogen pollution (83%). High additional removal of PHAs was also reported in GBF (82%), but nitrogen removal decreased to 20% on average. GF reported moderate additional PHA removal at an average of 30% and negligible nitrogen removal. The main purpose of the NBS as a post-ozonation treatment was to secure the toxicity level of the final effluent. According to the ecotoxicity test measuring the inhibition of luminescence in *Vibrio Fischeri*, during the assessment period no statistically significant negative trends in terms of ecotoxicity were observed in the final effluent in comparison with current effluent at the WWTP.

Conclusion

The use of ozonation as a quaternary step of treatment is an effective way to significantly reduce emerging contaminants from WWTP effluents in order to meet upcoming national and international regulatory requirements. Coupled with an innovative approach to real-time operation and with low-cost nature-based post-ozonation treatment, it leads to efficient, reliable, safe and cost-effective operation at municipal WWTPs.

Tomáš Macsek

In 2021, he completed his doctoral studies at the Faculty of Civil Engineering, Brno University of Technology in the field of Water Management and Water Structures.

He has worked as a researcher at the AdMaS research center (Faculty of Civil Engineering, BUT) since 2015. His research field is the occurrence of micropollutants in water and methods of their removal at wastewater treatment plants.

Decentralised removal of micropollutants from infectious hospital wastewater

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Basic project information

The project "Decentralised removal of micropollutants from infectious hospital wastewater" was submitted as part of the NF Call-3B 3.3.2.1 – "Trondheim" by the project promoter, Pražské vodovody a kanalizace, a.s. (PVK), and its project partner, Thomayer University Hospital (TUN). It succeeded in the two-round call and was therefore supported by a grant from the people of Norway. The main objective of the project was to reduce environmental pollution caused by the partner's hospital wastewater treatment plant (WWTP) by implementing a quaternary wastewater treatment step. We needed to achieve the primary requirement of a minimum 90% pharmaceutical removal rate.

Hospital WWTP

TUN WWTP is a mechanical-biological facility dimensioned for an average daily inflow of 200 m^3/day (1,500 population equivalent). The technological line of the WWTP before the upgrade consisted of mechanical pre-treatment, biological treatment, and activated sludge separation (Fig. 1). This line was preserved in its entirety during upgrading, so it is presented in the present tense.

Wastewater (WW) is brought to the WWTP through a channel, which, during higher precipitation, drains excess water through an emergency overflow directly into the municipal sewer network. Automatic mechanical bar racks with an integrated screenings press are installed in the inlet trough, from which the water flows into a vertical sand trap and then into the aeration tank (AT). Aeration is provided by fine bubble aerators and two automatically alternating blowers controlled by an oxygen probe system and frequency converters. The activated sludge mixture then flows into a circular secondary settling tank (SST), where the activated sludge settles and is scraped into the central sludge area. The treated wastewater overflows over the SST weir into a Parshall flume. Before being discharged into the public sewer, the water is hygienically treated with NaClO.

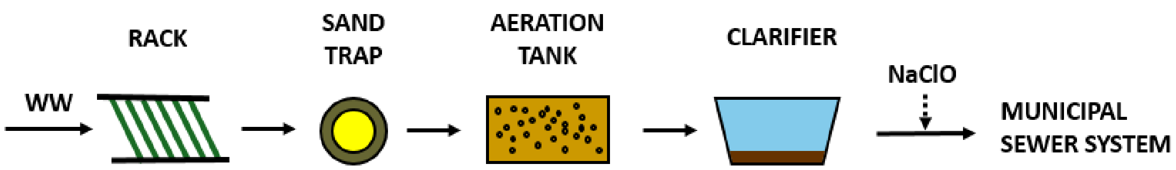

Fig. 1: Technological scheme of TUH WWTP before modernization

WWTP upgrade

As part of the TUN WWTP upgrade, three elements were added: the hygienic treatment of the WWTP bypass, a rotary drum microscreen for the mechanical pre-treatment of WW, and the introduction of quaternary wastewater treatment by microfiltration, ozonation, and granular activated carbon (GAC) filtration.

During heavy rainfall, part of the wastewater is discharged several times a year through an overflow into the public sewer network. As part of the project, the lacking hygienic treatment of the overflow was added. Now, NaClO is dosed during this discharge.

A rotary drum microscreen was added beyond the automatic mechanical racks to reduce the load of undissolved substances on the biological treatment stage (Fig. 2). Between the racks and the sand trap, the wastewater is diverted into an accumulation tank, where a submersible pump is located that pumps the water into the microscreen with an integrated screenings press. After passing through the screen, the water gravitationally flows into a pipe leading to the sand trap and further to the biological stage of the TUN WWTP. Treated WW from the quaternary stage, which is brought from the main TUN WWTP building through a pipeline to the mechanical pre-treatment building, is used for backwashing the drum screen.

The last and main part of the modernisation was the quaternary treatment designed for a flow rate of 5-10 m^3/hour (Fig. 2). It starts immediately after the secondary settling tank. The WW is drawn from the concrete outflow structure and gravitationally flows into storage tanks, from which it is transported by a submersible pump to the microfiltration. Microfiltration provides mechanical protection for the subsequent technological units. Its efficiency is monitored by a pair of turbidimeters at the inlet and outlet. The filter fabric is cleaned by an integrated backwash system that uses the produced filtrate. The filtrate is gravitationally guided into a pumping tank for ozonation in the basement of the WWTP building, from where it is pumped to the ozonation unit, which consists of an ozone generator, dosing system, contact tank, and destructor. The generator contains a cooled compressor, air dryer, oxygen generator, and ozone generator. In the ozonation unit, the WW

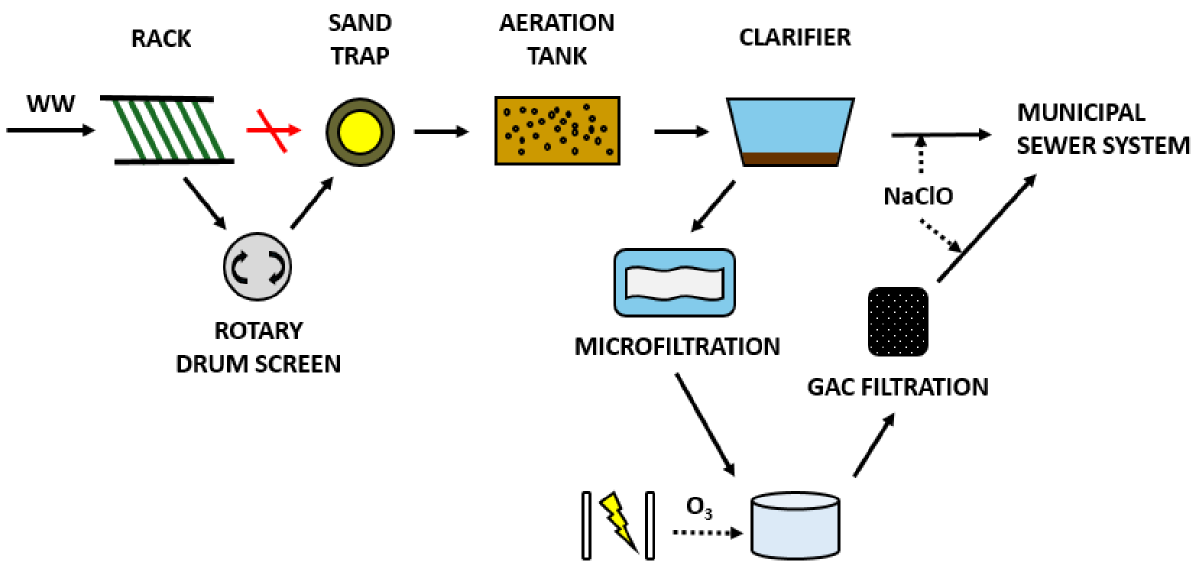

Fig. 2: Technological scheme of upgraded TUH WWTP

is first enriched with ozone before entering the contact tank. A partial stream is drawn from the main water stream, where the pressure is increased at the pump and ozone is subsequently drawn in from the injector in the pipe. This partial ozone-enriched stream is mixed with the main stream in a static mixer, ensuring optimal ozone dissolution. The ozonated WW then enters the contact tank. In the contact tank, the micropollutants oxidise and decompose. Unreacted ozone is discharged into the destructor, where it decomposes into a harmless gas. Water from the contact tank is fed to a pair of parallel GAC filters. The treated water from the GAC filtration is discharged into a tank in the basement of the main building and used as service water for the needs of the WWTP, including regular filter backwashing, rotary drum microscreen flushing, and microfiltration cleaning. Excess water from the sump flows to the hygienic treatment and measuring structure.

Results and discussion

The initial monitoring of the operation of the upgraded WWTP took place in the form of a 14-day intensive sampling campaign, in which 15 samples were taken at each of the 3 sampling points ("AT inlet", "SST outlet", "GAC filtration outlet"). The aim of the sampling campaign was to determine not only the concentrations of basic physico-chemical parameters, but also, and especially, the concentrations of micropollutants.

The efficiency of micropollutant removal was assessed by a summary indicator including 30 out of 33 substances from the indicative list of substances created by the grant provider. The individual analytes were the following pharmaceuticals and their metabolites: acebutolol, atenolol, azithromycin, carbamazepine, clarithromycin, diclofenac-4-hydroxy, diclofenac, furosemide, gabapentin, hydrochlorothiazide, ibuprofen, ibuprofen-2-hydroxy, ibuprofen-carboxyl, iopromide, ketoprofen, metformin, metoprolol, naproxen, naproxen-o-desmethyl, oxypurinol, paracetamol, paraxanthine, ranitidine, sotalol, sulfamethoxazole, sulfapyridine, telmisartan, tramadol, trimethoprim, venlafaxine.

Of the physico-chemical parameters, the indicators of total suspended solids (TSS), chemical oxygen demand by potassium dichromate (COD_{Cr}) and total organic carbon (TOC) were selected for the purposes of this paper. The results of these indicators show that the quaternary technology achieved extraordinary removal efficiency of more than 80% for all three indicators when compared to the outflow from the secondary settling tank.

Table 1: Evaluation of TSS, CODCr and TOC removal rate at the upgraded TUH WWTP

Sampling point	TSS		COD_{Cr}		TOC	
	(ng/l)	(%)	(ng/l)	(%)	(ng/l)	(%)
AT inlet	230 ± 99	-	687 ± 157	-	-	-
SST outlet	72.3 ± 35.9	-	133 ± 110	-	34.3 ± 12.0	-
GAC filtration outlet	4.0 ± 1.7	94.5	9.5 ± 5.3	92.9	5.8 ± 1.7	83.0

The efficiency of the removal of micropollutants on the indicative list was also calculated from the concentrations in the "SST outlet" and "GAC filtration outlet" profiles. Although the existing WWTP technology reduced the concentration of the sum indicator from more than 0.5 mg/l at the AT inlet to less than a tenth at the SST outlet, the concentration of pharmaceuticals in the outflow from the SST remained very high. However, the quaternary technology achieved a removal efficiency of 99.4%, which led to an average sum concentration of pharmaceuticals at the outlet of the GAC filters of 153 ng/l (Tab. 2).

Table 2: Sum concentration of 30 pharmaceuticals and their metabolites at the TUH WWTP

Sampling point	Detected analytes	Average concentration (ng/l)	Removal rate DN - GAU (%)
AT inlet	29 out of 30	518,188	-
SST outlet	28 out of 30	46,761	-
GAC filtration outlet	5 out of 30	153	99.4

In the inlet and outlet from the existing WWTP technology, almost all the monitored analytes were regularly detected. However, in the samples taken at the GAC filtration outlet, only 5 analytes were detected at least once during the 15 sampling events. Gabapentin, sulfamethoxazole, telmisartan, and paracetamol were found once or twice, with their concentrations only slightly exceeding the detection limit (10 ng/l for paracetamol and gabapentin, 20 ng/l for telmisartan, and 3 ng/l for sulfamethoxazole). The exception was metformin, which was found above the quantification limit in 13 out of 15 samples with an average concentration of 95 ± 62 ng/l.

Conclusion

The pilot project “Decentralised removal of micropollutants from infectious hospital wastewater” was successfully completed by building the first quaternary hospital wastewater treatment stage in Czechia. Its efficiency was confirmed by a sampling campaign. The physico-chemical parameters were removed by more than 80% between the outlet from the secondary settling tank and the GAC filtration outlet (TSS – 94.5%; COD_{Cr} – 92.9 %; TOC – 83.0%). In addition, micropollutants, measured as the sum concentration of 30 pharmaceuticals and their metabolites, were removed by a remarkable 99.4% to give an average effluent concentration of 153 ng/l. The positive results and the significance of the project also led to several project presentation opportunities. Two press conferences were held, professionals had the opportunity – and will have further opportunities – to hear about the project at several conferences, and the project was also selected as one of the seven projects supported by grant from the people of Norway for a mini-documentary that is available on the YouTube channel of the State Environmental Fund of the Czech Republic.

Acknowledgement

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Robert Kvaček

He works as a drinking water technologist at Pražské vodovody a kanalizace, a.s. In addition to operational matters, he is also involved in water management projects in the water and wastewater sectors. He holds a Master's degree in Water Technology from the University of Chemistry and Technology in Prague, from which he graduated in 2022. He is also pursuing his PhD studies at the same institution, focusing on nanofiltration in water treatment.

Utilisation of advanced oxidation processes for effective removal of gabapentin and ibuprofen from wastewater

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Introduction

Wastewater is the main source of substances belonging to trace organic compounds (TOrCs), or micropollutants. Unfortunately, wastewater treatment plants cannot completely remove these substances using standard technological procedures [10]. A lot of hazardous substances are therefore released by a recipient in residual concentrations (µg/l–ng/l) into other components of the environment, including streams, rivers, lakes, oceans, soil, and groundwater, and into the food chains of organisms [7, 8, 12].

The application of advanced oxidation processes (AOPs) provides a viable and effective attenuation option due to the oxidation of a wide range of TOrCs. AOPs belong to *in situ* chemical treatment based on the generation of strong oxidants (OH-radicals) for the oxidation of organic compounds [10]. Hydroxyl radicals (OH) attack organic pollutants through four basic pathways: radical addition, hydrogen abstraction, radical combination, and electron transfer. The OH generation is expressed as Eq. 1 [3].

$$3O_3 + H_2O \rightarrow 2{\cdot}OH + 4O_2 \quad (1)$$

Material and methods

Sampling at a flow rate of 4 m^3/h was conducted after (I) UV/O_3 treatment and (II) UV treatment, while wastewater recirculation was tested at degrees ranging from 0 to 4. The samples were collected in sterilised one-litre high-density polyethylene (HDPE) bottles. Residual gabapentin and ibuprofen were detected by liquid chromatography tandem-mass spectrometry (LC-MS/MS) (Agilent 1290 Infinity II + Agilent 6495 C).

Results

The results from pilot testing, showing the percentage efficiency of gabapentin and ibuprofen removal at a flow rate of 4 m^3/h and the 0th to 4th wastewater recirculation stages are presented in Fig. . These results compare AOP treatment (UV/O_3) and secondary UV treatment. The AOP + UV treatment was more effective with ibuprofen. There was a slight reduction in efficiency in the 0th wastewater recirculation, which may have been due to measurement error. However, after the 1st recirculation, the efficiency gradually increased, and by the 3rd recirculation stage >90% removal of the monitored drugs was achieved. As the stage of recirculation increased, the residual concentration of substances gradually decreased and thus the overall percentage-based efficiency of the technological process decreased.

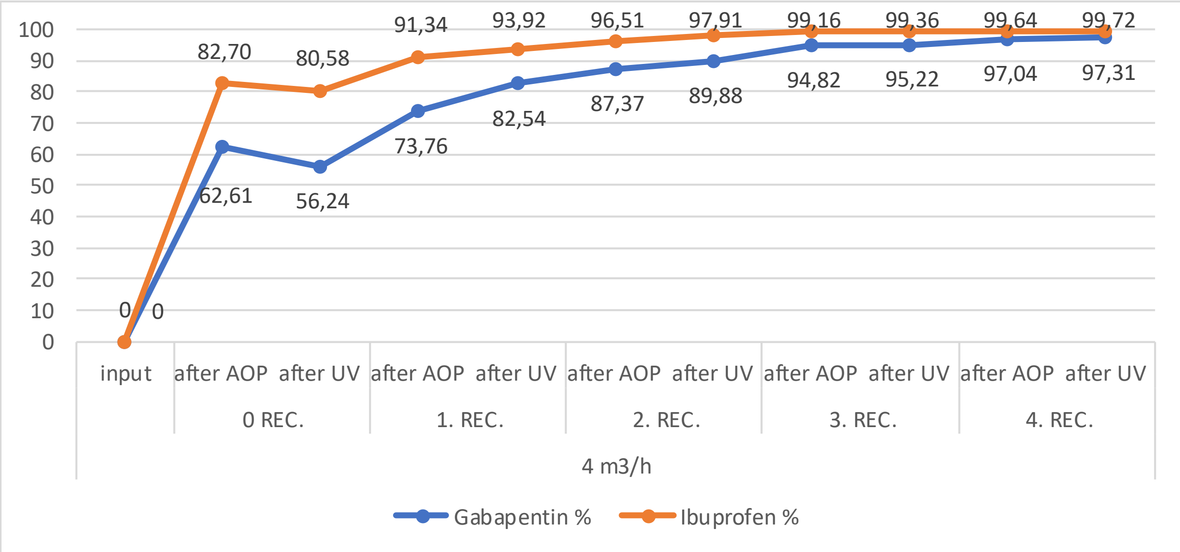

Fig. 1. Percentage of gabapentin and ibuprofen removal using UV/O3 and secondary UV light at a 4 m3/h flow rate and 0–4 recirculations of wastewater

Discussion

The search for appropriate technological procedures is a priority in reducing the residual pollution of watercourses. There is still a lack of research on the detection and toxicity of byproducts formed by AOPs or UV radiation, as well as studies conducted under operational conditions. With ibuprofen, eleven byproducts with single-bond OH or single-bond COOH groups were identified, most of which contained 2–6 carbons after UV/O_3 treatment [9]. The evaluation of their toxicity is still a matter of time. The main negative effects of ibuprofen confirmed on aquatic organisms have been adverse effects on fish reproduction, e.g. Japanese rice fish *Oryzias latipes* [4], male-biased sex differentiation of *Danio rerio* [2], perturbations in the brain of zebrafish, and kidney [5], liver and gill deformation, e.g. *Clarias gariepinus* [11]. At the same time, it must be assumed that primary substances can form certain transformation products that may be more toxic than their parent compound, e.g. Gabapentin-lactam (GBP-L), the transformation product of gabapentin in biological processes. GBP-L causes adverse impacts on aquatic organisms even at very low concentrations [5, 6]. The ozonation of gabapentin leads to the formation of a carboxylic acid group and simultaneous nitrate formation [1], but a more detailed description of gabapentin and byproducts remains missing and needs further exploration.

Conclusions

Utilisation of the AOP process (UV/O_3 method) and secondary UV radiation at a flow rate of 4 m^3/h was successful and led to the 90% removal of gabapentin and ibuprofen in a pilot experiment at the Moravský Beroun WWTP. The research was focused on detecting the concentration of selected primary drugs after the aforementioned treatments. However, the detection and determination of potential byproduct toxicity formed after AOPs and UV radiation is necessary to recommend the use of this method in WWTPs.

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Use of water treatment technologies for the final treatment of effluents from wastewater treatment plants

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Introduction

This paper presents the outputs of the PHARWAT project *(Reduction of Surface Water Pollution by Pharmaceutical Substances in Biologically Treated Wastewater*), which addressed the issue of reducing anthropogenic pollution by pharmaceutical substances (pharmaceuticals, drugs) in wastewater, which leads to the accumulation of unnaturally occurring substances in the environment. At present, wastewater treatment plants do not have technologies capable of completely eliminating these pollutants from wastewater, and they are introduced into the environment (primarily into surface waters). Due to the clear dominance of pharmaceutical input to the environment from diffuse sources (wastewater from the population) [2,3,6], the project focused on the elimination or reduction of the input of these substances from effluents of biological wastewater treatment plants. After laboratory tests, the technologies developed at both centres were pilot tested and promise to be very effective in removing these contaminants from wastewater.

It is very difficult, and currently practically unrealistic, to limit primary sources of pollution, i.e. to ban or significantly reduce the use of pharmaceuticals. The logical way forward is to produce environmentally friendly pharmaceuticals, address concentrated wastewater (hospitals, aftercare facilities), and implement general awareness campaigns leading to the proper management of pharmaceuticals. This path is certainly the right one, but it will be a long one and will necessarily undergo gradual evolution. However, the studies below describe the actual situation and practices in developed countries, which the Czech Republic should also aim to approach. Moreover, the recently adopted updated Urban Wastewater Treatment Directive obliges wastewater treatment plants serving over 150,000 (population equivalent) PE, and, over time, those over 10,000 PE in sensitive areas, to remove micropollutants. However, this concerns not only municipal wastewater and wastewater from point sources such as hospitals, but also, in the case of antibiotics, animal farms where the use of antibiotics is still a common practice.

Pharmaceuticals are clearly one of the priority groups of environmental micropollutants in general, and their subset of hormonal substances is also an element of the separately discussed endocrine disruptors. A key reference is the review on this topic [4]. Pharmaceutical compounds such as antibiotics, non-steroidal anti-inflammatory drugs (NSAIDs), anticonvulsants, β-blockers, etc., have emerged as new classes of water pollutants due to their potential or proven adverse effects on human health and the aquatic environment. The aforementioned comprehensive review systematically assessed the data currently available on the global presence and removal of 43 pharmaceutical compounds in municipal wastewater treatment plants (WWTPs) from 2010 to 2020. It assessed the global daily mass load and pharmaceutical emissions in different regions. The environmental risks of pharmaceuticals in treated wastewater from WWTPs were also assessed. Finally, guidelines and regulations related to the presence of pharmaceuticals in the aquatic environment were summarised and discussed. Various official regulations, guidelines, and rules focus on measures that can be used to mitigate the presence of pharmaceuticals in the environment. Research needs and future recommendations were also identified and proposed.

- Significant differences were observed in the concentration of pharmaceutical substances in influents and wastewater from municipal WWTPs from various geographical areas.
- Differences in drug concentrations could be attributed to several factors, such as consumption rates and patterns, sampling and analysis methods, seasonal variation, and population size and density.
- Acetaminophen and caffeine recorded the highest concentrations in WWTP influents. Meanwhile, the highest concentrations in treated wastewater were detected for naproxen, caffeine and carbamazepine.
- Although WWTPs using tertiary processes are more effective at removing pharmaceuticals, it was found that several pharmaceuticals could still be detected in such treated wastewater even after tertiary treatment.
- Average daily mass load and emissions were often reported in Asian countries. Acetaminophen (473 g/1,000 PE/day) and atenolol (592 g/1,000 PE/day) recorded the highest average mass loads. The highest observed daily emissions were reported for amoxicillin (944 g/day) and sulfamethoxazole (688.38 g/day).
- The daily quantity of pharmaceutical products can be strongly influenced by consumption rates in a given country, population size, and population density. However, emissions are affected by the removal efficiency and characteristics of WWTPs.
- Twelve of the studied drugs recorded RQ > 1 (risk quotient determined by environmental risk assessment), indicating that these drugs may have a significant potential impact on aquatic organisms.
- Various regulatory guidelines and regulations (the European Union Strategic Approach to Pharmaceuticals in the Environment and the European Action Plan against Antimicrobial Resistance, European Commission, 2019; Pharmaceutical Residues in Freshwater: Hazards and Policy Responses, OECD, 2019) can successfully mitigate the presence of pharmaceuticals in the aquatic environment.

Other studies [6] have shown that in terms of frequency, analgesics, anti-inflammatory pharmaceuticals, especially naproxen, ibuprofen and acetaminophen, and the antibiotics erythromycin, sulfamethoxazole and trimethoprim are the most commonly present. In terms of concentrations, the highest concentrations in hospital wastewater were for caffeine and acetaminophen (analgesics), lincomycin, ofloxacin, trimethoprim and ciprofloxacin (antibiotics). The most abundant substances in foul water are acetaminophen, salicylic acid and ibuprofen (analgesics), followed by oxytetracycline and lincomycin (antibiotics). Most studies focus on wastewater monitoring. Although antibiotic concentrations are higher in hospital wastewater, significant dilution is evident in urban wastewater. The mass balance input of the most commonly occurring pharmaceuticals into the environment comes from municipal wastewater from the general population, with point sources (hospitals in this study) assessed as insignificant. However, a number of specific pharmaceuticals were reported as being discharged from hospitals.

Approaches to dealing with the presence of pharmaceutical substances vary from country to country, including in Europe. While Sweden, for example, focuses on addressing sources, recent studies have demonstrated that discharge leaking from WWTPs is the primary source of pharmaceutical release into the environment [2,3]. Other measures, such as raising public awareness, using alternative medicines that are less toxic to the environment, and developing green pharmaceuticals, may certainly be effective, but immediate action should be taken to stop the release of pharmaceuticals into the environment. In contrast to Sweden, Switzerland has accelerated a different approach by focusing on upgrading its WWTPs across the country with advanced treatment processes (e.g. ozone and activated carbon). Similarly, the Netherlands has taken a similar approach by focusing on upgrading its WWTPs and increasing knowledge of the efficiency of advanced processes on a pilot scale [1,5].

Micropollutants, including pharmaceuticals, are present in concentrations ranging from ng/l to µg/l, and compared to the residual value of organic pollution after biological treatment of municipal wastewater (tens of mg/l), technologies globally recommended for micropollutant removal (advanced oxidation technologies, membrane technologies and final sorption technologies) are always limited by non-specific effectiveness, and therefore the maximum total organic pollution must be removed in the first stage. For these purposes**, it is advisable to supplement the existing WWTPs with practically water supply technology, i.e. coagulation (or a combination of coagulation and sorption on activated carbon) and separation of suspended solids (filtration) followed by filtration on activated carbon**; alternatively, it is necessary to calculate a higher consumption of oxidising or sorption factors. Only then is it cost-effective to introduce technologies requiring the high consumption of oxidising agent (ozone, peroxide or other oxidizing agents) or activating agent (UV, plasma, etc.) or the high consumption of highly efficient but expensive specific sorbents (graphene, graphene oxide, modified zeolites). For membrane technologies, nanofiltration may be considered, but this requires the removal of suspended solids and, again, is operationally expensive.

Material and methods

Laboratory tests

Coagulation tests were conducted in the laboratory to reduce residual organic contamination (COD) using iron ($FeCl_3$) and aluminium (PAX-XL19 and PAX-18). Further, pH-adjusted coagulations were performed using the same coagulants to determine the effects of pH. Biologically treated wastewater from Liberec WWTP was used for all tests after filtration on sand filters.

Fig. 1. Laboratory column tests of AOP with heterogeneous catalyst (magnetite)

The next step involved Advanced Oxidation Process (AOP) column tests with heterogeneous catalysts. For this testing, glass columns with a length of 250 mm, an inner diameter of 21.5 mm, a catalyst height of 235 mm and a column volume (without filling) of 85 ml H_2O (Fig. 1) were used. A Watson Marlow pump with Marprene tubing with an inner diameter of 0.88 mm and a wall thickness of 0.8 mm was used for pumping through the column. Two preselected catalysts were tested: a nano-iron spinel and crushed magnetite (1–4 mm). Before use, both materials were washed 10 times in distilled water until the water was completely clear. The volume of the column filled with the catalyst spinel was 63 ml H_2O, and for magnetite it was 27 ml H_2O. The columns were operated at residence times of 1.5 and 3 hours.

Municipal WWTP effluent was used for testing; hydrogen peroxide concentrations of 500, 1,000, 1,500 and 2,000 mg/l were tested. The amount of peroxide dosed was always verified using a Quantofix Relay device and test strips. For verification purposes, the above method was compared with a Hach hydrogen peroxide test kit, model HYP-1. After column AOP tests, single-point adsorption tests were conducted with granular activated carbon S835 (GAU, Brenntag) at concentrations of 1 g/l and 2 g/l and Biochar sorbent > 4 mm at a concentration of 1 g/l. The contact times for both materials were 5 minutes and 10 minutes.

During laboratory and pilot tests, it was found that high concentrations of peroxide (1-2 g/l) had to be used in heterogeneous catalysis to eliminate or significantly reduce pharmaceutical concentrations, and the subsequent lifetime of the filter with burel-treated sand to eliminate residual peroxide was unsustainably low (2–3 months).

Therefore, other applicable AOPs – ozonation and UV oxidation with hydrogen peroxide support – were also tested, focusing on the combination of oxidant concentration and residence time.

Pilot units

Based on the results of the above-mentioned tests, pilot units for the quaternary treatment stage were installed at three municipal WWTPs. Each unit is equipped with its own control system with remote monitoring and control, with the online measurement of basic variables. Samples are also taken here for residual pharmaceutical analysis.

The first stage after sand filtration of the WWTP effluent is a filter with a heterogeneous catalyst (granular magnetite), in front of which peroxide is dosed. The residual peroxide is eliminated on the burel-treated filter sand. The water is then fed to the MBBR for biosorption and biological removal of the biodegradable micropollutants and oxidised products that are present. The final stage is classic sorption filtration on activated carbon.

Fig. 2. Pilot technology for the quaternary treatment of filtered, biologically treated wastewater (composition from right to left) by combining the Fenton process with heterogeneous catalyst, the elimination of residual peroxide, biological treatment in the MBBR, and final sorption on activated carbon. Liberec WWTP

Pharmaceuticals in the tested wastewater are determined using a Sciex X500R mass spectrometer with an Exion LC AC liquid chromatograph. A YMC Triart C18 column was used with 0.1% formic acid and methanol as mobile phase components. For quantification, the MRM HR method was used in positive mode. Due to the need to determine lower concentrations of the analytes monitored, solid-phase extraction (SPE) was employed for their pre-concentration and purification. Oasis HLB columns from Waters were used. Columns of 1 ml volume with 30 mg of sorbent were chosen. A 25 ml sample was extracted. The columns were washed with 30% methanol and eluted with a solution of 50% methanol and 50% dichloromethane. The extracts were then evaporated with a stream of nitrogen and reconstituted to 0.5 ml in the mobile phase.

Results and discussion

Coagulation with ferric chloride resulted in the most efficient COD reduction at a dose of 50 mg/l iron (a reduction from 30 mg/l to 10 mg/l COD), while also efficiently clarifying the wastewater, although the pH dropped to 4. Using PAX-XL19 also resulted in a reduction within a dose range of 25–200 mg/l PAX, but the lowest values reached only 18 mg/l from the original 30 mg/l COD. The use of PAX-18 coagulant without pH adjustment had almost no effect. Test results showed that COD can be reduced efficiently (up to 65%) using with ferric salts for coagulation at lower pH. While the subsequent pH adjustment will ensure a reduction in iron while maintaining a reduced COD value, this control system results in additional operational costs, risks, and higher chemical input. In the case of wastewater from Liberec WWTP, a dose of 10 mg/l Fe can reduce COD by 50% while maintaining pH above 6.

During AOP column testing, the positive effect of the magnetite catalyst (1–4 mm fraction) was demonstrated. At a dose of 1,500 mg/l peroxide, most pharmaceuticals present at concentrations in the hundreds of ng/l were eliminated, with almost 80% efficiency for Tramadol and 60% for Metroprolol. At a dose of 2,000 mg/l peroxide, there was near-total elimination of the monitored pharmaceuticals (Fig. 3). The results showed that a dose of

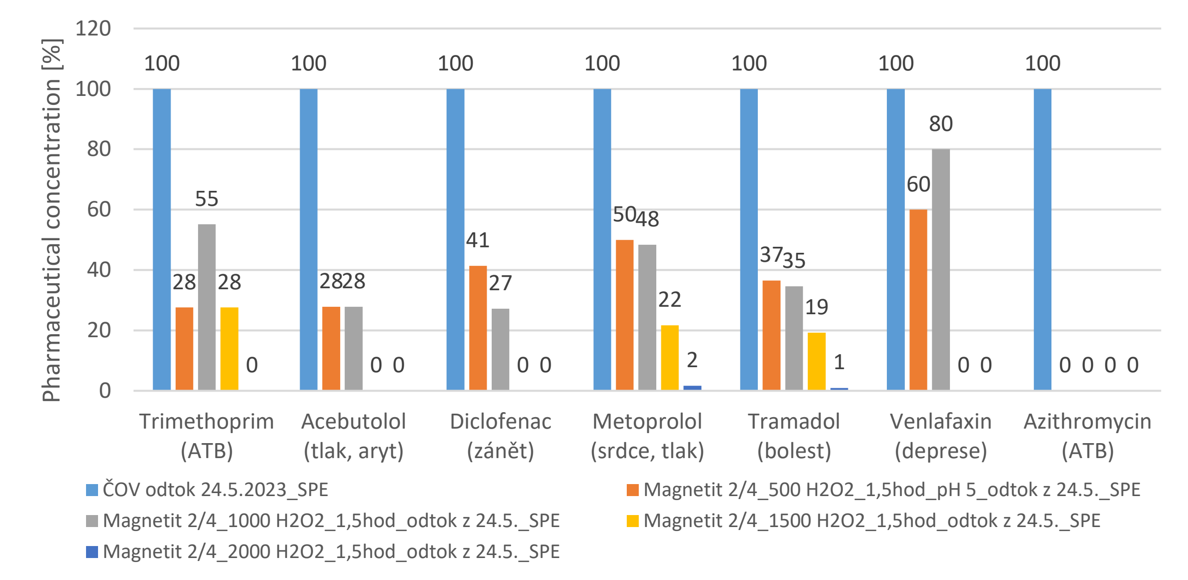

Fig. 3. Removal of selected pharmaceuticals in AOP laboratory tests – Fenton with heterogeneous catalyst

Trimethoprim	Acebutolol	Diclofenac	Metoprolol	Tramadol	Venlafaxin	Azithtomycin
ATB	pressure, arrhyt.	inflammation	heart, pressure	pain	depression	ATB

WWTP effluence 24.5.2023_SPE	Magnetite 2/4_500 H2O2_1.5 h_pH 5_effluent from 24.5_SPE
Magnetite 2/4_1000 H2O2_1.5 h_effluent from 24.5_SPE	Magnetite 2/4_1500 H2O2_1.5 h_effluent from 24.5_SPE
Magnetite 2/4_2000 H2O2_1.5 h_effluent from 24.5_SPE	

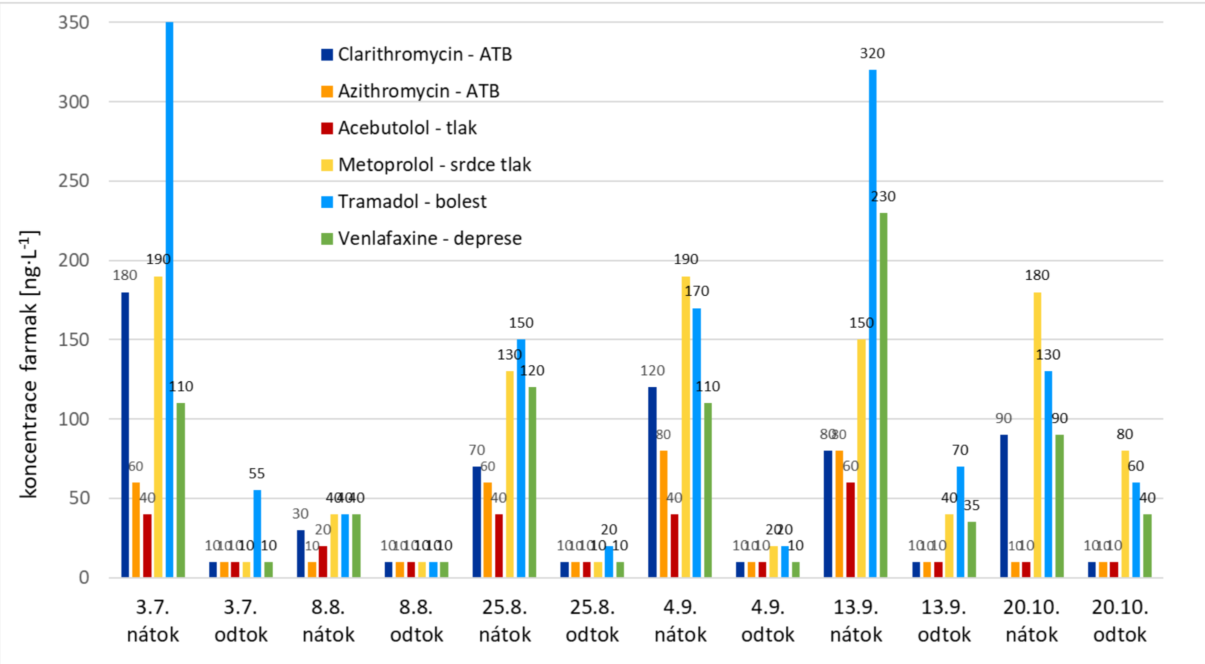

Fig. 4. Removal of selected pharmaceuticals in the AOP pilot test – Fenton with heterogeneous catalyst (without adsorption end stage)

dtPharmaceutical concentration	Tlak - pressure	Srdce, tlak - heart, pressure	Bolest - pain	Deprese - depression
		nátok: influent	odtok: effluent	

2,000 mg/l peroxide has almost 100% efficiency and a dose of 1,500 mg/l has efficiency of 70% or more. By lowering the pH value (5), the efficiency at a peroxide concentration of 500 mg/l was comparable to that at a concentration of 1,000 mg/l.

Below are the results of the pilot unit at Liberec WWTP for selected pharmaceuticals, which confirmed the laboratory results. At a peroxide concentration of 2 g/l (July to August 2023), most of the monitored pharmaceuticals were removed with high efficiency. Subsequent reduction of the peroxide dose by 20% (approx. 1.6 g/l in September) led to a decrease in removal efficiency (Tramadol and Venlafaxine); with a further reduction (October 2023) to approx. 1.2 g/l, the efficiency for a number of pharmaceuticals was even lower (Tramadol, Venlafaxine, Metoprolol, and others).

With a peroxide dose of 1.2 g/l during heterogeneous magnetite catalysis, the overall pharmaceutical removal efficiency was monitored by assessing the effluent concentrations of pharmaceuticals beyond an activated-carbon-filled filter with a contact time of 20 minutes. The results showed the elimination of the monitored pharmaceuticals from the wastewater.

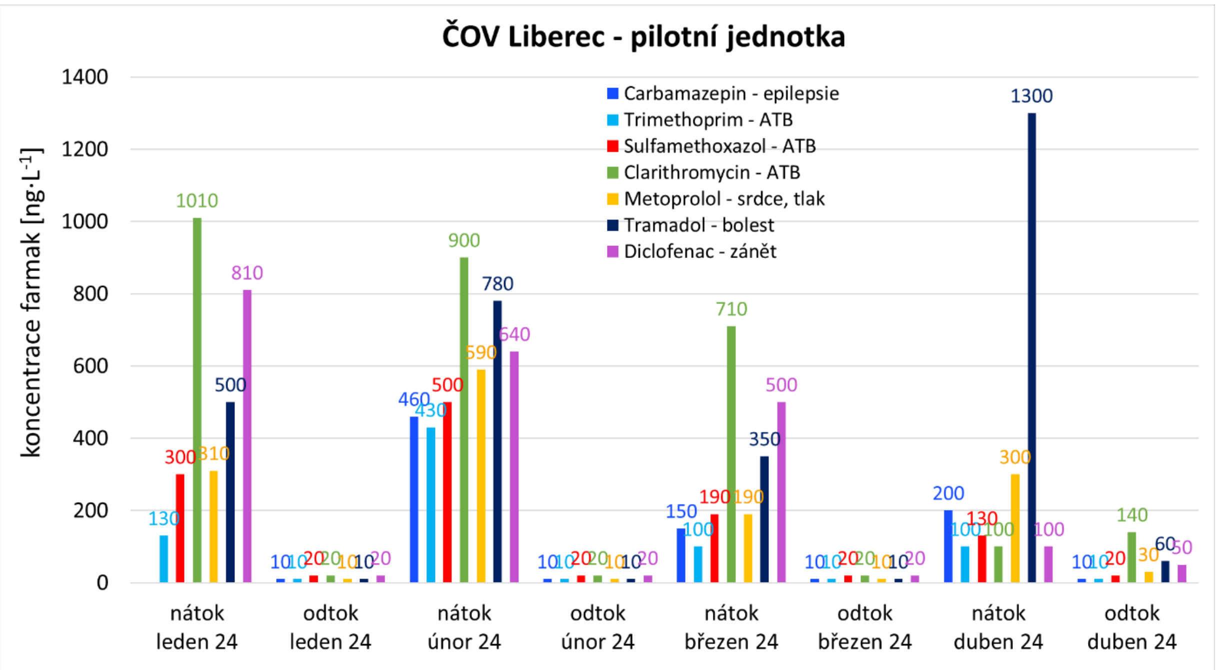

Fig. 5. Overall removal efficiency of selected pharmaceuticals in pilot technology (AOP – Fenton with heterogeneous catalyst with adsorption end stage)

Pharmaceutical concentration		Epilepsie - epilepsy		Srdce, tlak-heart, pressure		Bolest- pain	Zánět - inflammation
influent Jan 24	effluent Jan 24	influent Feb 24	effluent Feb 24	influent Mar 24	effluent Mar 24	influent Apr 24	effluent Apr 24

Given the necessarily high peroxide concentrations, the oxidation of pharmaceuticals using ultraviolet (UV) radiation and in combination with hydrogen peroxide was also tested. With regard to the economics of the process (UV tube power input versus residence time determining the technology demand in kWh/m^3), the effect of contact time in the UV tube at low peroxide concentrations (5 mg/l) was tested. The effect of peroxide concentration at a sustainable energy intensity of 1 kWh/m^3 is shown in the presentation of this paper.

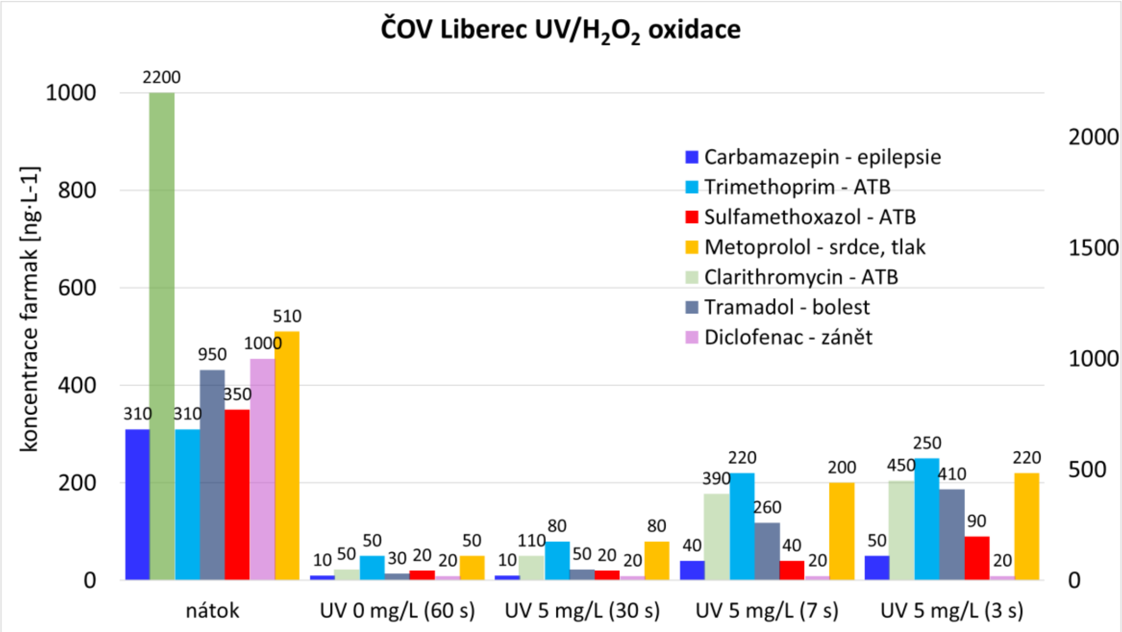

Fig. 6. Removal efficiency of selected pharmaceuticals using UV in combination with hydrogen peroxide

Pharmaceutical concentration	Epilepsie - epilepsy	Srdce, tlak - heart, pressure	Bolest - pain	Zánět - inflammation
		nátok: influent		

Conclusions

AOP using the Fenton reaction with a heterogeneous catalyst (magnetite) is an option, alongside ozone oxidation (with the risks associated with this technology), for the removal of pharmaceutical substances from biologically treated wastewater. The tests conducted indicate that the concentration of peroxide determines the efficiency of drug removal – without pH adjustment, efficient concentrations are above 1 g/l. Lowering the pH when applying iron coagulant brings the complementary advantage of reducing the input COD concentration and at the same time precipitating residual phosphorus concentrations to achieve the low limit values required by the new Urban Wastewater Treatment Directive. The combination of UV application with hydrogen peroxide is a more economically and operationally efficient approach, though at significantly lower peroxide concentrations (tens of mg/l). High-quality filtration is then a prerequisite for the necessary final sorption stage, which removes drug residues and residues from any AOP.

Addressing the influent organic pollution levels into the quaternary treatment stage is a prerequisite for economically viable final wastewater treatment, and coagulation is one of the options that does not require an increase in volumes in the secondary treatment stage.

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