FOREVER CHEMICALS ROUND AND ROUND

Contamination of water bodies with perfluorinated substances and brominated flame retardants in the Prague area

Václav Mach
Jitka Straková

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Contamination of water bodies with perfluorinated substances and brominated flame retardants in the Prague area

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Obsah

Summary

Per- and polyfluoroalkyl substances and brominated flame retardants are among man-made pollutants of the global environment. As surfactants, per- and polyfluoroalkyl substances have been used in many industrial applications. The most common use is in stain and water resistant textiles and in grease resistant food packaging materials. They are also used as additives in firefighting foams. Brominated flame have an inhibitory effect on combustion and thus reduce the flammability of products containing them. They are commonly used in plastics, textiles and electrical/electronic equipment. Both groups of pollutants have warranted international attention because of their resistance to decomposition under natural conditions, and therefore long-term persistence and accumulation in the environment and toxic effect for living organisms. The most toxic representatives of these groups have been designated for global elimination by the Stockholm Convention. Some representatives are restricted in the EU. Many others require further study and/or exhibit characteristic of persistent organic pollutants.

The aim of the study is to identify levels of per- and polyfluoroalkyl substances and brominated flame retardants in Prague waters, to potentially identify the main sources of pollution by the monitored substances in the Prague waters and generally contribute to a greater knowledge of pollution by the monitored substances in the Czech Republic. A total of seven river water samples, three sediment samples, and four fish samples from Prague streams, a pond, and the Vltava River were analysed for content of per- and polyfluoroalkyl substances and brominated flame retardants in the laboratory of the Department of Food Analysis and Nutrition of the University of Chemistry and Technology in Prague. According to the data collected, pollution of surface waters in Prague by per- and polyfluoroalkyl substances and brominated flame retardants is ubiquitous.

Per- and polyfluoroalkyl substances were detected in all water and fish samples, although this was not reflected in sediment samples. The highest measured concentration of per- and polyfluoroalkyl substances among analysed water samples were found in the Kopaninský stream. The concentration likely reflects the long-term use of firefighting foams at the Václav Havel Prague Airport. The total concentration of perfluoroalkyl carboxylic acids in the sample reached 164.34 ng/L. This finding adds to concerns related to the persistence of the per- and polyfluoroalkyl substances, which are nick-named Forever Chemical for their highly persistent fluorine-carbon bond.

Water sample and fish samples from the confluence of the Vltava River and the Rokytka stream in Libeň show higher concentrations of PFOS than other samples of water and fish collected in this survey. European perch caught at the site has perfluorooctanesulfonic acid concentration at the level of 17.4 µg/kg wet weight. The sample exceeds the environmental quality standard of perfluorooctanesulfonic acid established by Directive 2008/105/EC of the European Parliament and of Council. The Rokytka stream (sampled in Libeň) passes through the historical industrial area of Vysočany where contamination by legacy chemicals as well as new contaminants can be expected.

Brominated flame retardants with the properties of persistent organic pollutants (polybrominated diphenyl ethers, hexabromocyclododecane) were detected in all sediment and fish samples. However, the level of sediment contamination by polybrominated diphenyl ethers does not significantly exceed formerly measured values. Nevertheless, the presence of polybrominated diphenyl ethers in fish indicates environmental water pollution.

The continuous monitoring of per- and polyfluoroalkyl substances and brominated flame retardants into the (not only Prague) waters needs to be undertaken to safeguard surface-water as well as drinking-water quality. Reporting of per- and polyfluoroalkyl substances emissions in the Czech Pollutant Release and Transfer Register (abbreviated PRTR or IRZ in Czech) will increase the knowledge on the release sources, enabling an identification of potential contaminated sites.

Acknowledgements

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1. Introduction

Per- and polyfluoroalkyl substances and brominated flame retardants are among man-made pollutants of the global environment. Many representatives of per- and polyfluoroalkyl substances (PFAS) and brominated flame retardants (BFRs) exhibit characteristics of persistent organic pollutants (POPs) to which significant international attention is given.[1] The main reason is their resistance to decomposition under natural conditions, and therefore their long-term persistence, their accumulation in the environment and human bodies and their toxic effect for living organisms.[2 3] Per- and polyfluoroalkyl substances (PFAS) are a broad group of 4,700 organic substances, which are characterized by the fact that all carbon-attached hydrogen atoms are replaced by fluorine atoms. PFAS include a variety of subgroups such as perfluoroalkyl carboxylic acids (PFCAs), perfluoroalkyl sulfonates (PFSAs), perfluorooctanesulfonamide (PFOSA), perfluorooctane sulfamido ethanol (FOSE), perfluoroalkyl phosphonic acids (PFAPAs), and fluorinated telomeric alcohols (FTOHs).[4] As surfactants, PFAS have found use in many industrial applications. The most common use is in stain and water-resistant textiles, and in grease-resistant food packaging materials. They are also used as additives in firefighting foams and hydraulic fluids, in the production of metallised objects, semiconductors, electronic and photographic equipment, lubricants, and cosmetics.[5] In commercial products, the length of the alkylated perfluorinated chain usually varies from 4 to 20 carbon atoms. Public pressure and regulation tendencies led the industry to limit the production and use of long-chain PFAS. The industry-introduced approach of substituting long-chain PFAS with their short-chain substitutes and perfluoroalkyl ether acids was shown to be misleading. It resulted in the introduction of hexafluoropropylene oxide-dimer acid (HFPO-DA or GenX) and perfluorobutane sulfonic acid (PFBS), currently recognized as Substance of Very High Concern (SVHC), on the market.

Brominated flame retardants (BFRs) are a functional group of brominated organic substances that have an inhibitory effect on combustion and thus reduce the flammability of products containing them.[6] These include a variety of different groups of substances, such as polybrominated biphenyls (PBBs), polybrominated diphenyl ethers (PBDEs), brominated cyclic hydrocarbons (e.g. HBCD) and other compounds (e.g. tetrabromobisphenol A). They are commonly used in plastics, textiles and electrical/electronic equipment. The recycling of plastic casing of waste electronic equipment has contaminated a range of consumer products including children toys.[7] These can also be added to carpets, pillows, paints, upholstered furniture, floor coverings and many other consumer products.[8]

The most harmful PFAS and BFRs have been regulated in the EU and internationally. This is applies to perfluorooctanoic acid (PFOA), perfluorooctanesulfonic acid (PFOS) and some long chain PFAS that can degrade into them. PFOA and its salts, and PFOS and it salts have been listed by the Stockholm Convention on POPs for global elimination and restriction. The global ban was implemented into the EU POPs Regulation. Similarly, some substances belonging to BFRs – commercial mixtures of penta-, octa- and decabromodiphenyl ethers (PBDEs), hexabromocyclododecane (HBCD) – were added to the Stockholm Convention list in 2009, 2013 and 2017. Some other PFAS and BFRs were identified as a Substance of Very High Concern (SVHC).[9] Restriction of the following PFAS chemicals is currently being considered based on the Swedish, German or Norwegian proposals: (1) perfluorinated carboxylic acids (C9-14 PFCAs) including their salts and precursors (proposed by Germany and Sweden): perfluorononan-1-oic acid (PFNA); nonadecafluorodecanoic acid (PFDA); henicosafluoroundecanoic acid (PFUnDA); tricosafluorododecanoic acid (PFDoDA); pentacosafluorotridecanoic acid (PFTrDA); and heptacosafluorotetradecanoic acid (PFTDA); (2) perfluorohexane-1-sulphonic acid (PFHxS), its salts and related substances (proposed by Norway); and (3) undecafluorohexanoic acid (PFHxA), its salts and related substances (proposed by Germany). Moreover, PFHxS is also being considered for inclusion to the Stockholm Convention at the next Conference of the Parties in 2021.

PFAS and BFR representatives have some common properties, such as the ability to bioaccumulate in living organisms.[10 11] Bioaccumulation occurs when a living organism absorbs a potential contaminant into its body faster than it is removed by decomposition and excretion. The ability to accumulate in living tissues is different for different substances depending on their chemical properties. The bioaccumulation of BFRs is due to their solubility in lipids. PFAS are not only hydrophobic but also lipophobic, and their ability to bioaccumulate is due to their binding to proteins. Another property of PFAS and BFRs is their ability to be transported remotely. As a result, these substances, which are produced exclusively by human activity, occur in areas where the industrial processes in which they are produced have never been used, and some of them are practically ubiquitous throughout the world.[12 13 14] The pollution of food chains and the uncontrollable global spread of PFAS and BFRs are also associated

1 European Environmental Agency (2019): Emerging chemical risks in Europe - "PFAS". ISBN 978-92-9480-196-8, ISSN 2467-3196, doi: 10.2800/486213

2 Goldenman G., Fernandes M., Holland M., Tugran T., Nordin A., Schoumacher C., McNeill A. (2019): The cost of inaction - A socioeconomic analysis of environmental and health impacts linked to exposure to PFAS. Nordic Council of Ministers, pp. 194, ISBN 978-92-893-6065-4.

3 Jakšić K., Matek Sarić M., Čulin, J. (2020): Knowledge and attitudes regarding exposure to brominated flame retardants: a survey of Croatian health care providers. Environmental Science Pollution Research 27: 7683–7692. https://doi.org/10.1007/s11356-019-07496-7

4 Kwiatkowski C.F., Andrews D.Q., Birnbaum L.S., Bruton T.A., DeWitt J.C., Knappe D.R.U., Maffini M.V., Miller M.F., Pelch K.E., Reade A., Soehl A.,Trier X., Venier M., Wagner C.C., Wang Z., Blum A. (2020): Scientific Basis for Managing PFAS as a Chemical Class. Environmental Science and Technology Letters 7 - 8: 532–543.

5 European Environmental Agency (2019): Emerging chemical risks in Europe - "PFAS". ISBN 978-92-9480-196-8, ISSN 2467-3196, doi: 10.2800/486213

6 US EPA (2012): Brominated flame retardants. Science Inventory by US EPA. https://cfpub.epa.gov/si/si_public_record_report.cfm?Lab=NHEERL&dirEntryId=226582. Accessed 11 Nov 2020.

7 Strakova J., DiGangi J.,Jensen, G., Petrlik J., Bell L. (2018). Toxic Loophole: Recycling Hazardous Waste into New Products: https://english.arnika.org/publications/toxic-loophole-recycling-hazardous-waste-into-new-products

8 Janssen S. (2005): Brominated Flame Retardants: Rising Levels of Concern. Health Care Without Harm, pp 39.

9 European Commission (2020): Poly- and perfluoroalkyl substances (PFAS). Commission staff working document SWD(2020) 249 final, Brussels, 14.10.2020.

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

11 Gustafsson K., Björk M., Burreau S., Gilek M. (1999): Bioaccumulation kinetics of brominated flame retardants (polybrominated diphenyl ethers) in blue mussels (Mytilus edulis). Environmental Toxicology 18, 6.

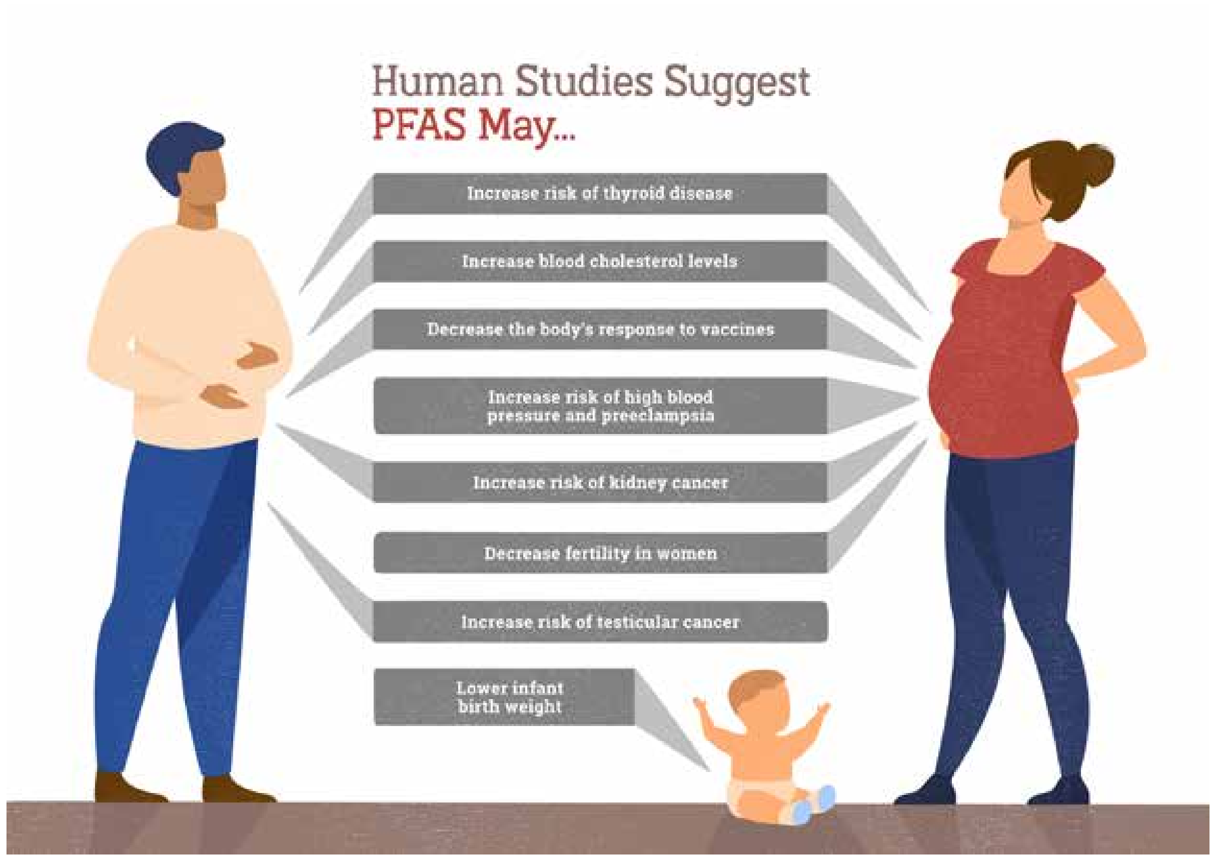
12 Gawor A., Shunthirasingham C., Hayward S.J., Lei Y.D., Gouin T., Mmereki B.T., Masamba W., Ruepert Castillo L.E., Shoeib M., Lee S.C., Harner T., Wania F. (2014): Neutral polyfluoro-alkyl substances in the global Atmosphere. Environmental Science: Processes Impacts 16: 404.

13 Cai M., Yang H., Xie U., Zhao Z., Wang F., Lu Z., Sturm R., Ebinghaus R. (2012): Per- and polyfluoroalkyl substances in snow, lake, surface runoff water and coastal seawater in Fildes Peninsula, King George Island, Antarctica. Journal of Hazardous Materials 209–210: 335–342.

14 Miller S., Cobbing M., Jackobson T., Santen M. (2015): Footprints in the snow – Hazardous PFCs in remote locations around the globe. Greenpeace, pp 48.

with the rising contamination of food products and drinking water.[15 16 17] The interrelated health problems associated with PFAS are drawn in Figure 1. Considering the large number of cases of contamination in the EU and globally, the number of people affected with a full spectrum of illnesses and the related societal and economic costs, PFAS are expected to be restricted as a class in the EU in the foreseeable future.[18]

Figure 1: Health problems associated with PFAS



15 Schecter A., Harris T.R., Shan N., Musuba A., Päpke O. (2008): Brominated flame retardants in US food. Molecular Nutrition & Food Research 52: 266-272.

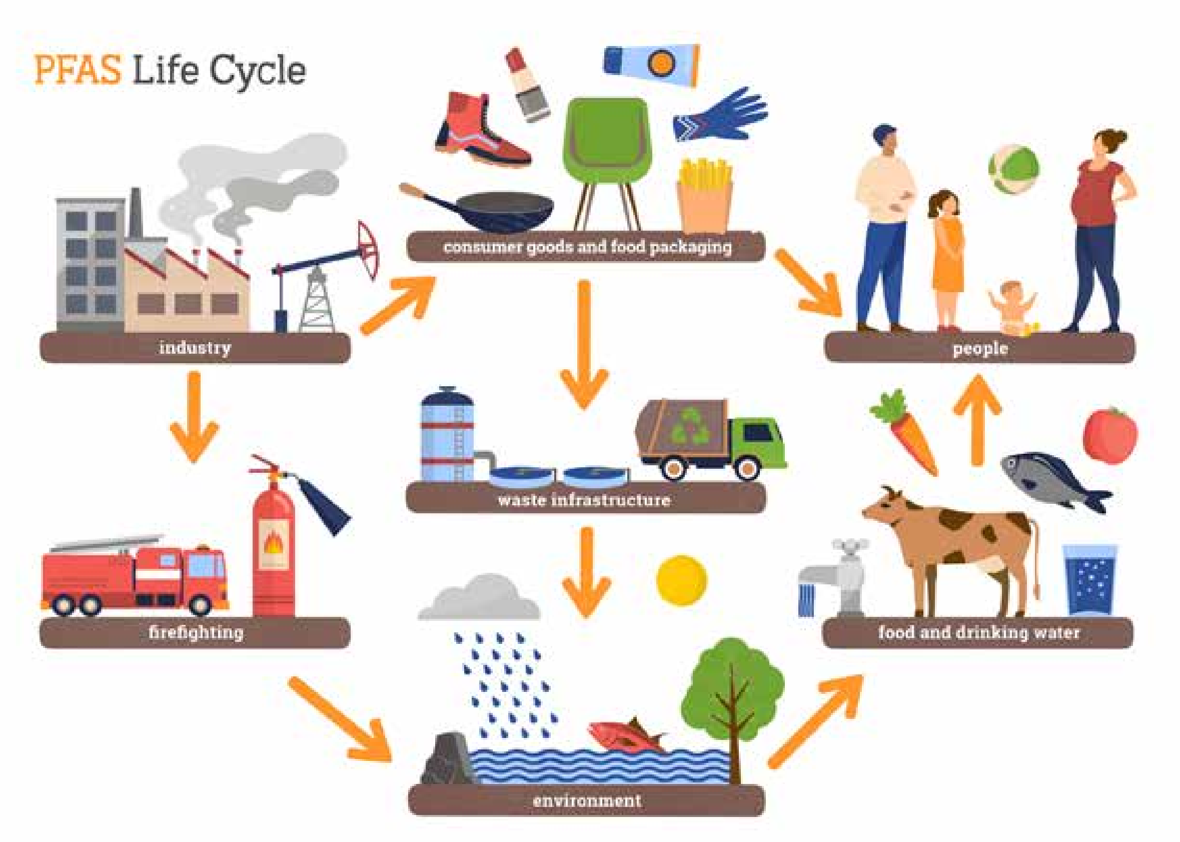
16 Weihe P., Kato K., Calafat A.M., Nielsen F., Wanigatunga A.A., Needham L.L., Grandjean P. (2008): Serum Concentrations of Polyfluoroalkyl Compounds in Faroese Whale Meat Consumers. Environmental Science and Technology 42 (16): 6291-6295.

17 Hoppin J., Kotlarz N; de Kort T., Ng-A-Tham J., Starling A., Adgate J., Jakobsson K. (2019): An overview of emerging PFAS in drinking water worldwide. Environmental Epidemiology: 3: 162-163.

18 COMMUNICATION FROM THE COMMISSION TO THE EUROPEAN PARLIAMENT, THE COUNCIL, THE EUROPEAN ECONOMIC AND SOCIAL COMMITTEE AND THE COMMITTEE OF THE REGIONS: Chemicals Strategy for Sustainability Towards a Toxic-Free Environment: https://ec.europa.eu/environment/pdf/chemicals/2020/10/Strategy.pdf

Another common characteristic of PFAS and BFRs is their deposition in sediments and bioaccumulation in organisms of aquatic ecosystems.[19 20] Sediments of watercourses and ponds may pose a risk when applied to agricultural land that may be degraded by contaminated sediment. Higher risk for human health is the entrance of these substances to the human food chain through fishery products, or through drinking water and consumer goods. The life cycle of PFAS in the environment is shown in Figure 2. In aquatic ecosystems, which are characterized by food chains that are longer than terrestrial ones, there may be a significant accumulation of PFAS and BFRs in aquatic organisms and fish.[21 22]

Figure 2: PFAS life cycle



19 Murtomaa-Hautala M., Viluksela M., Ruokojärvi P., Rautio A. (2015): Temporal trends in the levels of polychlorinated dioxins, -furans, -biphenyls and polybrominated diethyl ethers in bank voles in Northern Finland. Science of the Total Environment 526: 70-76.

20 Hou L., Jiang J., Gan Z. (2019): Spatial Distribution of Organophosphorus and Brominated Flame Retardants in Surface Water, Sediment, Groundwater, and Wild Fish in Chengdu, China. Archives of Environmental Contamination and Toxicology 77: 279–290. https://doi.org/10.1007/s00244-019-00624-x

21 Tao L., Zhang Y., Wu J.P., Wu S.K., Liu Y., Zeng Y.H., Luo X.J., Mai B.X. (2019): Biomagnification of PBDEs and alternative brominated flame retardants in a predatory fish: Using fatty acid signature as a primer. Environment International 127: 226-232.

22 Christensen K.Y., Raymond M., Blackowicz M., Liu Y., Thompson A.B., Anderson H.A., Turyk M. (2017): Perfluoroalkyl substances and fish consumption. Environmental Research 154: 145-151. https://doi.org/10.1016/j.envres.2016.12.032

The aim of the study is to identify levels of PFAS and BFRs in Prague's waters, to potentially identify main sources of pollution by the monitored substances in these waters and generally contribute to a greater knowledge of pollution by the monitored substances in the Czech Republic. Although the objective of this monitoring is to identify pollution hot-spots in the river environment in the greater Prague area, the limited number of samples in this survey cannot replace broader and continued monitoring. In order to achieve the aims, we have analysed and evaluated samples of water, sediments and fish taken at several sampling points in watercourses and a pond in the area of interest. The study was carried out by the Arnika Association which has long been dedicated to monitoring pollution with persistent organic pollutants (POPs) in the environment. The survey was funded by the City of Prague and Global Greengrants Fund.

2. Sampling sites

The capital city of Prague has a population of about 1.25 million and approximately 98% of the capital's population is connected to a sewerage system that drains wastewater to a central wastewater treatment plant. The plant has been located on Císařský Island located on the Vltava River in the northern part of Prague since 1966. During heavy rains, excess water is discharged into the Vltava River and its tributaries through a central sewer system. The Vltava River, with a length of 430.2 km, is the longest river in the Czech Republic. The river's source is in the Šumava Mountains; it flows through several cities and towns, among others Český Krumlov, České Budějovice and Prague, and empties into the Elbe River.

In its Prague section, the Vltava River receives its only major tributary – the Berounka River, and a number of smaller water streams. The most important ones include the Šárecký, Dalejský, Radotínský, Botič, Rokytka and Kunratický streams. In addition to several locations on the Vltava River, sampling was performed on the Kopaninský stream with a length of only 4.4 km. Its source is by the Václav Havel Airport Prague; it flows through the village of Přední Kopanina and its cottage settlement and empties into the Unětický stream, which is also a tributary of the Vltava River.

Water bodies in the Prague area, which have a variety of functions such as landscaping, recreational, retention or fish farming, also include a number of ponds (e.g. the Počernický pond, the Kyjský pond, the system of ponds Lítožnické, Šeberovské and Milíčovské) and other types of water reservoirs with various functions (the most important are the Hostivařská dam, and the Džbán and Jiviny dams). Motolské ponds, which were among the sampling sites, is a system of three ponds situated in the Prague 5 district on the Motolský stream. This system of ponds was built in the 1960s. As part of the construction of ponds, the Motolský stream was also technically modified at this part. The upper and lower ponds are used for extensive fish farming.

3. Methodology

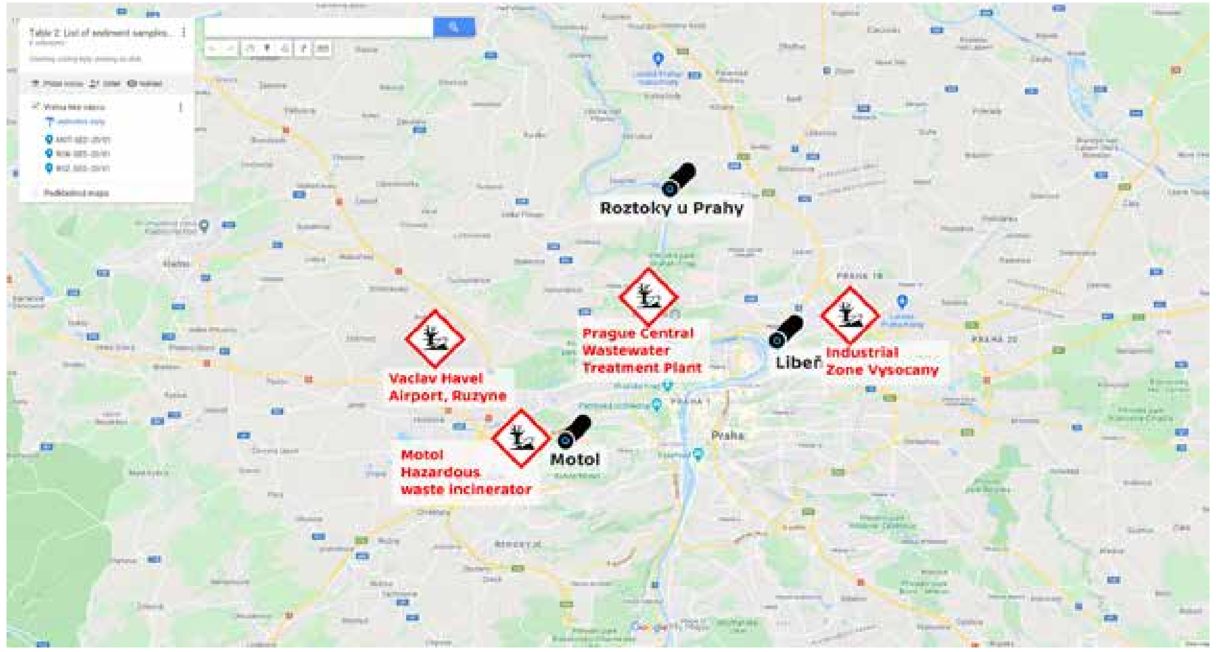
3.1 Sampling procedures

The sampling was conducted according to a sampling plan covering various sampling sites on water bodies in the area of Prague. In addition to several sampling sites on the Vltava River, samples were taken from the Motolský pond R3 and from the Kopaninský stream. Sampling sites were selected randomly on the basis of accessibility for sampling; their proximity to potential sources of pollution was taken into account. A water sample from the Kopaninský stream was selected for its proximity to Václav Havel Airport Prague. The airports are known for PFAS contamination due to their presence in firefighting foams used for industrial fires. Water and sediment samples were taken from Motolský Pond due to its proximity to medical waste incinerator, another potential pollution source. Fish, water, and sediment samples were also taken from the Rokytka stream which joins the Vltava River at Libeň. Rokytka goes through the historical industrial area of Vysočany where contamination with legacy chemicals as well as new contaminants was anticipated. The last set of water, sediment, and fish samples was taken in Podbaba and at Roztoky where some contamination from the waste water treatment plant Podbaba could be expected. A reference site with no obvious industrial sources of pollution by PFAS was selected at the upper stream of the Vltava River just below the Berounka and Vltava conflux. Exact location of the sampling sites is shown in the map below (Figure 3).

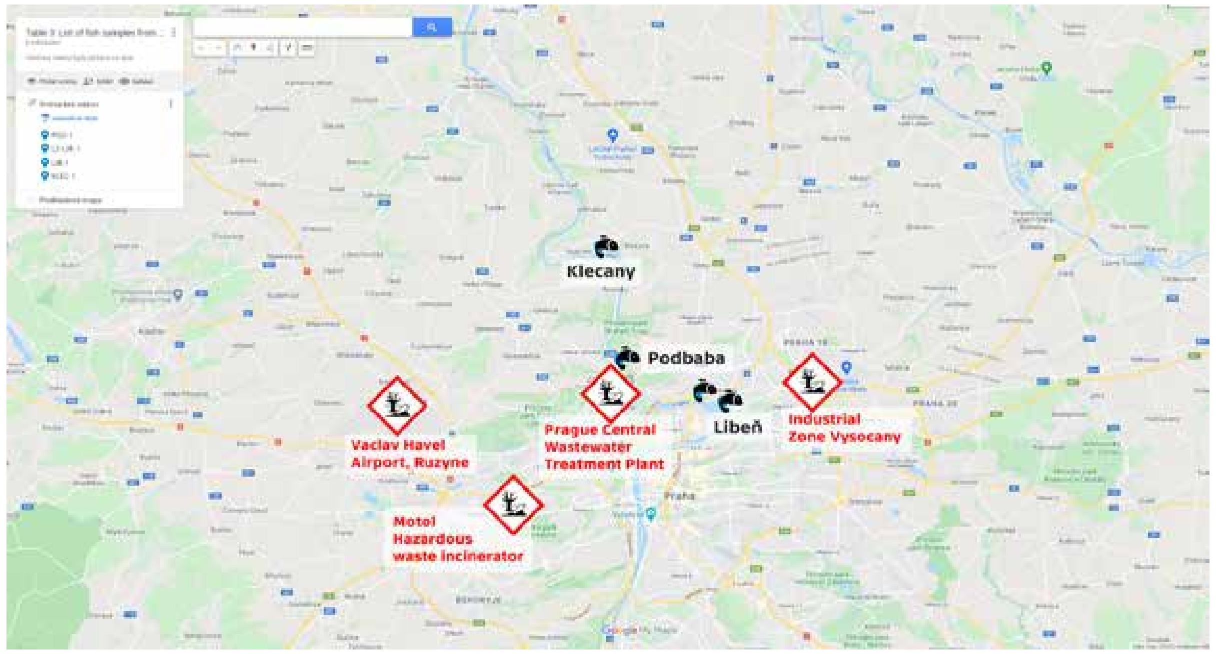
Figure 3: Maps of sampling sites

Map of the water sampling sites

Map of the sediment sampling sites



Map of the fish sampling sites



The samples of water and sediments were collected on sampling sites in July 2020. Illustrative photos from the sampling campaigns are given in Figure 4. Samples of water were taken from river or pond water in glass containers with metal screw lids; the containers were several times washed by alcohol, distilled water and subsequently by river or pond water. Samples of sediments were taken by a steel trowel or, alternatively, by a core sampler from the sediment bottom of the water body. Sediment samples were usually taken as mixed samples formed by several sub-samples taken in various points of each sampling site. The sediment samples were homogenized in a steel bowl and transferred into glass containers with metal screwed-on lids. After each sampling, all the sampling equipment was washed with alcohol, distilled water and, subsequently, by river or pond water of the respective sample. The total number of seven water samples and three sediment samples were taken during sampling at sampling sites. During transport to the laboratory, the samples were placed in cooling box and then again in a refrigerator in cold and dark conditions where they were kept until the analysis. Lists of water and sediment samples are displayed in Annex 1 followed by photographs from sampling in Annex 3.

Figure 4: Illustrative photos from sampling

Wild fish from water bodies on the area of Prague were caught in the period from August to October 2019. A total of eight individual fish were caught and processed into four fish samples. The samples included three different species of fish (common roach, common bream, and European perch). Mixed samples were always formed by fish of the same species from the same body of water. The fish were caught on four sites on the Vltava River, which are in vicinity of the sampling sites where water and sediment samples have been taken. Fish samples were stored in cold and dark conditions until the analysis. The list of fish samples displays details about the individual samples, including the designation of the sample, the fish species, the number of individuals in the sample, the date and place of capture, the length, weight and age of the fish (Annex 1).

3.2 Analytical methods

After the transport to the laboratory, samples were analysed for content of various PFAS and BFRs at the Department of Food Analysis and Nutrition of the University of Chemistry and Technology. Samples were analysed by ultra-performance liquid chromatography equipped with tandem mass spectrometer (UPLC-MS/MS) in the case of PFAS, and by gas chromatography equipped with tandem mass spectrometer (GC-MS/MS) in the case of BFRs.[23] Water samples were analysed only for content of 23 PFAS covering 9 PFCAs (PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUdA, PFDoA, PFTrDA, and PFTeDA), PFSAs (PFPrS, PFBS, PFPeS, PFHxS, PFHpS, Br-PFOS, L-PFOS, PFNS, PFDS, and PFDoS) and another four PFAS (HFPO-DA, NaDONA, 9Cl-PF3ONS, and 11Cl-PF3OUdS). PFOS was analysed specifically for contents of branched (Br-PFOS) and linear (L-PFOS) isomers. Sediment and fish samples were both analysed for content of 17 PFAS and 25 BFRs. Among the PFAS analysed in the sediment and fish samples were 11 PFCAs (PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUdA, PFDoA, PFTrDA, and PFTeDA), 5 PFSAs (PFBS, PFHxS, Br-PFOS, L-PFOS, and PFDS) and PFOSA. Among the BFRs analysed in the sediment and fish samples were 16 PBDEs (PBDE 28, PBDE 47, PBDE 49, PBDE 66, PBDE 85, PBDE 99, PBDE 100, PBDE 153, PBDE 154, PBDE 183, PBDE 196, PBDE 197, PBDE 203, PBDE 206, PBDE 207, and PBDE 209), three isomers of HBCD (α-HBCD, β-HBCD, and γ-HBCD) and several other brominated compounds (BTBPE, DBDPE, HBBz, PBEB, PBT, and OBIND). Lists of specific PFAS and BFRs that were analysed are shown in Annex 2.

[23] Kalachova K., Pulkrabova J., Cajka T., Hajslova J. (2013): Determination of Brominated Flame Retardants (BFRs) in Fish Tissue using an Optimized Extraction/Cleanup Procedure and the Agilent 7000 Triple Quadrupole GC/MS System. Application Note, Agilent Technologies, Inc.

4. Results

A complete listing of PFAS concentrations detected in water and fish samples is shown in Tables 6, and 7, respectively. PFAS were not detected in sediment samples (LOD 0.3 µg/kg DW). A comparison of total concentrations of perfluoroalkyl sulfonates (PFSAs), perfluoro alkyl carboxylic acids (PFCAs), and HFPO-DA (known as GenX) in water samples is given in Figure 5. A detailed look at most concentrated PFAS representatives detected in water samples is given in Figure 6.

Table 6: Perfluorinated compound concentrations in water samples [ng/L]. PFTrDA, PFTeDA, PFPrS, PFPeS, PFNS, PFHpS, PFDS, PFDoS, NaDONNA, 9Cl-PF3ONS, and 11Cl-PF3OUdS were not detected in water samples (LOD 0.02 ng/L).

Perfluorinated compound	MOT-V -20/01	ROK-V -20/01	POVLT-V -20/01	RAD-V -20/01	LAH-V -20/01	KOP-V -20/01	ROZ-V -20/01
PFHxA	5.41	5.64	3.33	3.02	2.57	102	2.47
PFHpA	2.40	3.51	1.68	1.39	1.08	56.9	1.10
PFOA	3.43	3.45	1.65	1.20	1.11	4.41	1.22
PFNA	1.02	0.912	0.610	0.517	0.432	0.807	0.450
PFDA	1.39	0.924	0.464	0.223	0.246	0.285	0.234
PFUdA	0.140	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
PFDoA	0.159	0.128	0.034	<0.02	<0.02	<0.02	0.03
PFBS	<0.02	<0.02	<0.02	<0.02	<0.02	2.56	<0.02
PFHxS	0.798	1.56	1.00	0.718	0.776	1.53	0.807
Br-PFOS	0.879	5.06	1.24	0.397	0.309	10.7	0.758
L-PFOS	1.83	11.0	2.73	0.593	0.535	8.17	0.995
HFPO-DA	<0.02	<0.02	3.39	1.70	1.34	1.14	1.29
Sum of 9 PFCAs	13.95	14.57	7.77	6.35	5.44	164.35	5.52
Sum of 10 PFSAs	3.51	17.63	4.97	1.71	1.62	22.92	2.56
Total	17.46	32.20	16.13	9.76	8.40	188.42	9.37

Figure 5: Comparison of total concentrations of pefluoralkyl sulfonates (PFSAs), perfluoroalkyl carboxylic acids (PFCAs), and HFPO-DA (GenX) in water samples

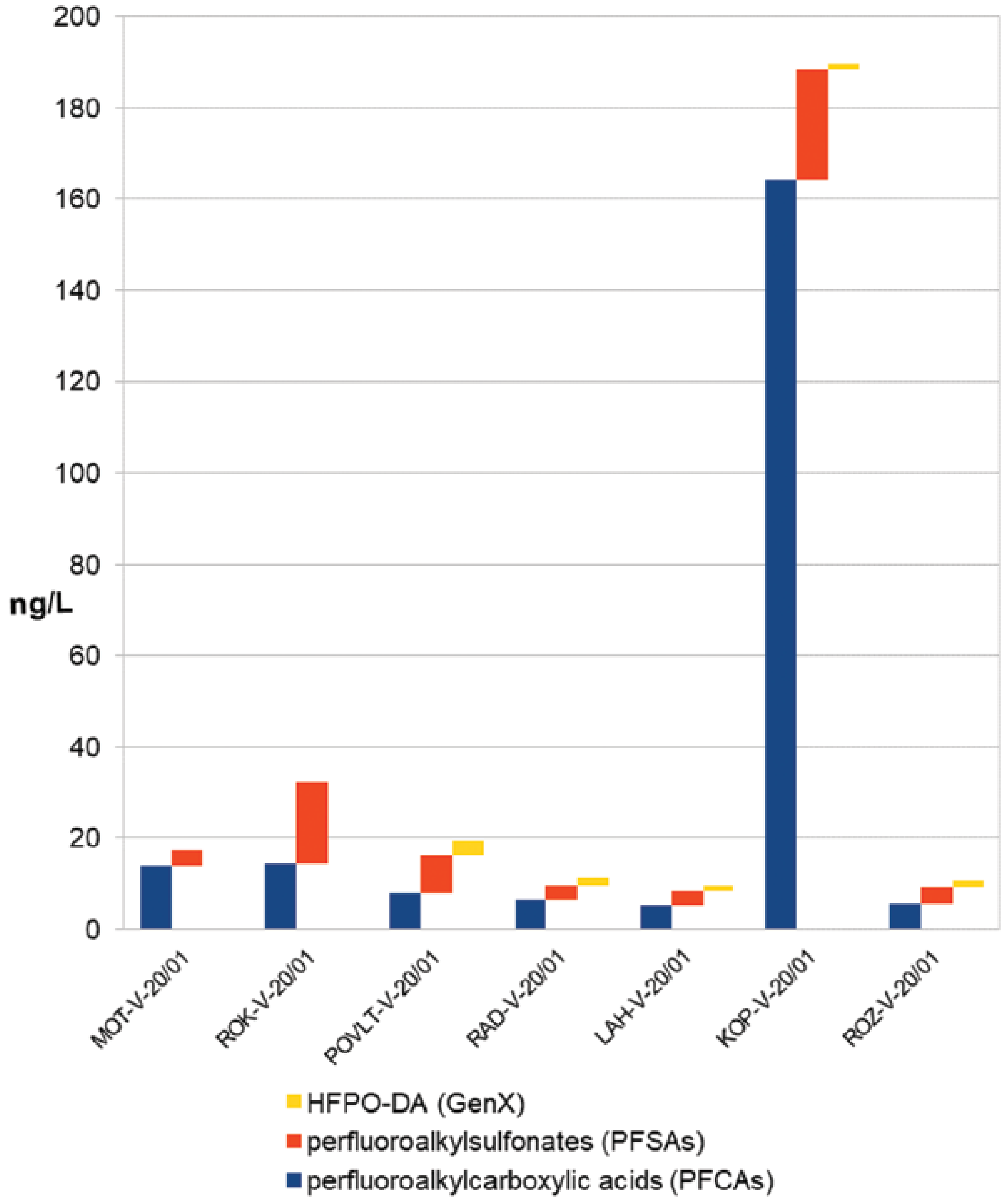


Figure 6: The most concentrated PFAS representatives detected in water samples

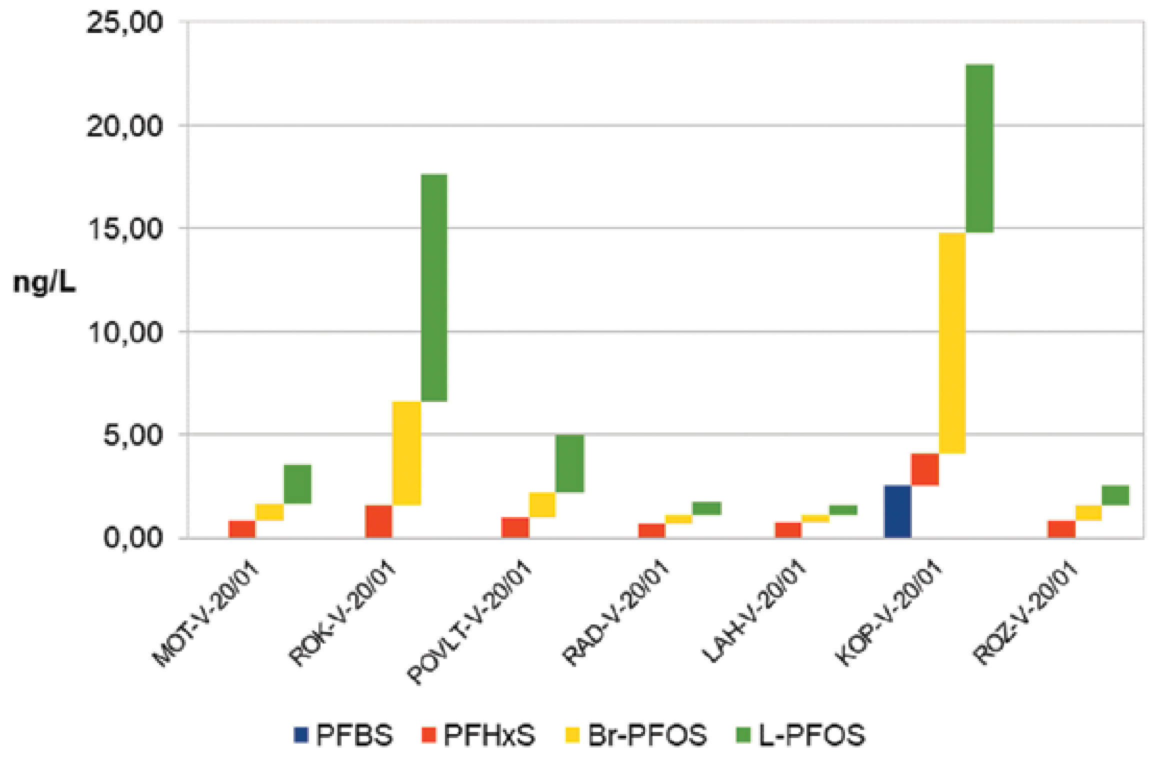


Table 7: Perfluorinated compound concentrations in fish samples [µg/kg WW]. PFHpA and PFBS were not detected in fish (LOD 0.006 µg/kg WW).

Perfluorinated compound	POD-1	L2-LIB-1	LIB-1	KLEC-1
PFBA	4.46	2.93	26.5	0.917
PFPeA	0.021	<0.013	<0.013	0.064
PFHxA	<0.006	<0.006	0.015	<0.006
PFOA	0.007	0.012	0.008	<0.006
PFNA	<0.006	0.051	0.101	<0.006
PFDA	0.122	0.212	1.39	0.082
PFUdA	0.143	0.180	1.27	0.090
PFDoA	0.231	0.320	1.19	0.182
PFTrDA	0.057	0.123	0.240	0.044
PFTeDA	0.027	0.062	0.124	0.038
PFHxS	0.019	0.006	<0.006	0.012
Br-PFOS	0.431	0.262	0.911	0.352
L-PFOS	3.51	1.62	16.5	4.83
PFDS	<0.006	<0.006	0.064	<0.006
PFOSA	0.051	0.046	0.073	0.037
Sum of 11 PFCAs	5.07	3.89	30.80	1.42
Sum of 5 PFSAs	3.96	1.89	17.43	5.19
Total	9.09	5.83	48.30	6.64

Content of BFRs detected in samples of sediments and fish are listed in Tables 8 and 9, respectively.

Table 8: Brominated flame retardant concentrations in sediment samples [µg/kg DM].PBDE congeners 28, 49, 66, 85, 100, 153, 154, 196, 197, 203 (LOD 0.01 µg/kg DM), PBDE congeners 206, 207 (LOD 0.5 µg/kg DM), α- and β-HBCD isomers (LOD 0.75 µg/kg DM) and several new BFRs (BTBPE, PBEB, PBT, and OBIND; LOD 0.01 µg/kg DM) were not detected in sediment samples.

Brominated flame retardant	MOT-SED-20/01	ROK-SED-20/01	ROZ-SED-20/01
PBDE 47	0.033	<0.01	<0.01
PBDE 99	<0.01	0.143	0.329
PBDE 183	<0.01	0.069	0.064
PBDE 209 (decaBDE)	<5.0	8.01	5.63
γ-HBCD	<0.75	1.13	<0.75
DBDPE	<10	60.0	19.9
HBBz	<0.01	0.075	0.029
Commercial PentaBDE mixture	**0.033**	**0.143**	**0.329**
Comemrcial OctaBDE mixture	**< LOD**	**0.069**	**0.064**
Sum of 16 PBDEs	**0.033**	**8.22**	**6.22**
Total	**0.033**	**69.44**	**26.16**

Table 9: Brominated flame retardant concentrations in fish samples [µg/kg WW]. PBDE congeners 85, 196, 197, 203 (LOD 0.005 µg/kg WW) and 206, 207, 209 (LOD 0.05 µg/kg WW), and new BFRs (DBDPE, LOD 0.1 µg/kg WW); HBBz, PBEB, PBT (LOD 0.005 µg/kg WW); and OBIND (LOD 0.05 µg/kg WW) were not detected in fish samples.

Brominated flame retardant	POD-1	L2-LIB-1	LIB-1	KLEC-1
PBDE 28	**0.012**	**0.047**	**0.006**	**0.027**
PBDE 47	**0.315**	**2.40**	**0.205**	**0.680**
PBDE 49	**0.014**	**0.108**	**0.018**	**0.036**
PBDE 66	<0.005	**0.007**	**0.006**	<0.005
PBDE 99	<0.003	**0.018**	**0.088**	**0.007**
PBDE 100	**0.047**	**0.416**	**0.040**	**0.090**
PBDE 153	<0.003	**0.160**	**0.012**	**0.007**
PBDE 154	**0.038**	**0.442**	**0.021**	**0.072**
PBDE 183	<0.003	**0.009**	<0.003	<0.003
α-HBCD	**0.830**	**8.50**	**1.31**	**0.531**
β-HBCD	<0.01	**0.184**	<0.01	<0.01
γ-HBCD	**0.049**	**0.295**	<0.01	**0.077**
BTBPE	<0.01	**0.036**	<0.01	**0.010**
Commercial PentaBDE mixture	**0.34**	**2.58**	**0.32**	**0.75**
Commercial OctaBDE mixture	**0.09**	**1.03**	**0.07**	**0.17**
Sum of 16 PBDEs	**0.426**	**3.61**	**0.395**	**0.920**
Sum of 6 PBDEs[I)]	**0.412**	3.48	0.372	0.883
Sum of HBCD isomers	**0.88**	**8.80**	**1.31**	**0.61**
Total	**1.30**	**12.62**	**1.71**	**1.54**

[I)] Sum of 6 PBDEs refers to sum of PBDE 28, PBDE 47, PBDE 99, PBDE 100, PBDE 153, and PBDE 154.

5. Discussion

5.1 Václav Havel Airport Prague – main PFAS-pollution hot-spot in Prague

In comparison with other studies, one of our water samples has shown significantly higher concentrations of PFCAs. This water sample marked KOP-V-20/01 was taken in the Kopaninský stream which flows from the Václav Havel Airport Prague. The water taken from the stream at a publicly accessible location (outside the airport area itself) shows a total concentration of 9 PFCAs 164.34 ng/L. This value is comparable with PFCAs concentrations that have been found in waters of big industrial agglomerations in China.

The total concentrations of different nine PFAS in surface water from East Lake (Wuhan, China) ranged from 30.12 to 125.35 ng/L.[24] Another study from China found the median concentration of PFOA in surface water of principal watersheds of Shanghai as high as 50.67 ng/L.[25] A study from to the mouths of 14 major rivers (including the Rhine, Danube, Elbe, Oder, Seine, Loire, and Po)[26] can serve as a comparison in a European context. However, the character of major European rivers at the mouth is different than the character of Vltava and other sampled waters inside of Prague. The highest concentration measured was 200 ng/L for PFOA in the Po River. The total concentration of four PFCAs (PFHxA, PFHpA, PFOA, and PFNA) at the mouths of the Elbe River and the Oder River was determined as high as 25.97 ng/L and 7.46 ng/L, respectively. The total concentration of measured PFCAs in the Kopaninský stream is significantly higher compared to common values in surface waters in Europe.

To evaluate the potential source of PFCAs in the Kopaninský stream, it is necessary to evaluate the possibility of common sources of these substances. Sources of PFCAs contamination could include: food packaging materials, Teflon for the production of non-stick kitchen utensils, Gore-Tex used as waterproof layer of outdoor clothing and footwear, ski waxes, waxes and floor cleaners, additives in paints, active ingredients of biocides, hydraulic fluids in aviation extinguishing foams, electrical engineering, and the photographic industry. The source of the Kopaninský stream is in the area of the Václav Havel Prague Airport. The Airport is a likely source of PFCAs in the environment as PFCA-containing firefighting foams have been used at the airports.

In France, a study of PFAS used as surfactants in fluorosurfactant based foams (FSBFs) examined concentrations of those emerging chemicals in the vicinity of four sites where FSBFs are or were intensively used[27]. PFAS profiles were heavily influenced by parameters such as the route of PFAS transport after use (runoff, seepage, direct discharge), time elapsed since the cessation of firefighting activities, and firefighting foam composition. The PFAS concentrations found near the examined sites are the highest recorded in France and resulted in the closure of certain drinking water resources. For a precise interpretation of the measured PFAS concentrations and to set protective measures eliminating PFAS spreading, the above-mentioned parameters need to be studied.

[24] Zhou Y., Tao Y., Li H. et al. (2016): Occurrence investigation of perfluorinated compounds in surface water from East Lake (Wuhan, China) upon rapid and selective magnetic solid-phase extraction. Scientific Reports 6: 38633. https://doi.org/10.1038/srep38633

[25] Sun R., Wu M., Tang L., Li J., Qian Z., Han T., Xu G. (2018): Perfluorinated compounds in surface waters of Shanghai, China: Source analysis and risk assessment. Ecotoxicology and Environmental Safety 149: 88-95. https://doi.org/10.1016/j.ecoenv.2017.11.012

[26] McLachlan S., Holmstrom K., Reth M., Berger U. (2007): Riverine Discharge of Perfluorinated Carboxylates from the European Continent. Environmental Science and Technology 41: 7260-7265.

[27] Dauchy X., Boiteux V., Bach C., Rosin C., Munoz J.F. (2017): Per- and polyfluoroalkyl substances in firefighting foam concentrates and water samples c ollected near sites impacted by the use of these foams. Chemosphere 183: 53e61.

5.2 Firefighting foams, industrial activities, and consumer goods - sources of PFAS in Prague waters?

The water sample from Kopaninský stream accompanied by the sample ROK-V-20/01 from the confluence of the Vltava River and the Rokytka stream in Libeň has also shown higher concentrations of PFOS than other samples of water collected in this survey. Based on information from the airport, the use of firefighting foams with high contain of PFOS/PFOA for firefighters exercises was stopped in 2011[28] in accordance with the European legislation (Directive 2006/122/EC). A potential explanation is that higher concentrations of PFOS in the Kopaninský stream may be due to the historical burden of the area. This finding adds to concerns related to the persistence of the per- and polyfluoroalkyl substances, which are nick-named Forever Chemical for their highly persistent fluorine-carbon bond.

In Norway, a firefighting training facility (FTF) was examined 15 years after the use of PFOS-based firefighting foams (AFFF) were ceased. Detailed mapping of the soil and groundwater revealed high concentrations of per- and polyfluoroalkyl substances (PFAS). [29] PFOS accounted for 96% of the total PFAS concentration in the soil with concentrations ranging from < 0.3 µg/kg to 6500 µg/kg. The average concentration of PFOS in the groundwater down-gradient of the site was 22 µg/l (6.5–44.4 µg/l), accounting for 71% of the total PFAS concentration.

The findings of higher PFOS concentrations in the Rokytka stream (Libeň) is supported by findings of the highest measured PFOS in the fish sample taken in the area in comparison with the other collected fish. The Rokytka stream (sampled in Libeň) passes through the historical industrial area of Vysočany where contamination by legacy chemicals as well as new contaminants can be expected. Nevertheless, the comparison of our PFOS measurements with the average PFOS concentration in more than 100 European rivers (39 ng/L)[30] assumes that the Prague waters do not collect any serious industrial pollution. Our findings on the contribution of these two tributaries (Koapninský and Rokytka streams) to the overall PFOS pollution of Vltava River as well as industrial contribution to the PFAS pollution of waters need to be further assessed.

Taking the other uses of PFAS into account, we may assume that the consumer goods contributes to the PFAS burden of Prague waters. According to existing research, the waste water

[28] https://www.prg.aero/monitoring-vlivu-provozu [cited 28 November 2020]

[29] Høisæter Å., Pfaff A., Breedveld G.D. (2019): Leaching and transport of PFAS from aqueous film-forming foam (AFFF) in the unsaturated soil at a firefighting training facility under cold climatic conditions. Journal of Contaminant Hydrology 222: 112–122.

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

treatment plant effluent is a major source of perfluoroalkyl acids (PFAAs) in surface water.[31] [32] However, this fact is not supported by the data collected. The samples of water, sediment and fish taken in Podbaba and Klecánky – areas potentially affected by the waste water treatment plant, do not exhibit significantly higher concentrations of PFOS or other PFAAs than the other samples collected in this survey.

5.3 Pollution of water sediments

From the broad group of examined BFRs, some congeners of PBDEs, HBCD, DBDPE and HBBz are found in the collected samples of sediments. Other analysed BFRs are below the quantification limit in the samples. In sediment samples from three sampling sites, PBDEs are detected in all of them, HBCD in one, and both HBBz and DBDPE in two. The sample of sediment taken in the Motolský pond (MOT-SED-20/01) contained a smaller number of monitored BFRs and, at the same time, also a significantly lower concentration of 11 PBDEs than other samples taken in the Vltava River (ROK-SED-20/01 and ROZ-SED-20/01).

In comparison with the surveys conducted by Arnika Association on various rivers in 2011[33] and 2016[34], the sums of PBDEs of our measurement (0.033 - 8.22 µg/kg DM) represent values within the range of the concentrations found in the both referred studies. The results of the BIOBROM project[35] cover several samples of river sediments. According to the findings of the BIOBROM project, only the congener PBDE 209 exceed 50 µg/kg DM of sediment in half of all samples, which was not even the highest measured value in the samples of our study. The Central Agricultural Inspection and Testing Institute of Czech Republic analysed 23 sediment samples for the presence of 9 PBDE congeners (PBDE 28, PBDE 47, PBDE 66, PBDE 85, PBDE 99, PBDE 100, PBDE 153, PBDE 154, PBDE 183). The mean concentration of the sum of the 9 PBDE congeners in river sediments in the cited study is 0.48 µg/kg DM.[36] All three samples of sediments taken for our research have values of the mentioned 9 PBDEs below the referred level. It can be concluded that the ranges of PBDE in water sediments in Prague do not exceed common ranges of PBDE pollution outside of Prague. One sediment sample shows HBCD at a relatively low concentration of 1.13 µg/kg DM. The Arnika Association's survey of BFRs conducted in 2011[37] found HBCD concentrations in the range of 0.4 to 37.5 µg/kg DM in two dozen river sediment samples.

All three samples of sediments show PFCAs, PFSAs and PFOSA concentrations below the limit of quantification. As there are no long-term average measurements from Czech rivers, nor are there any European legislative limits for the content of PFAS in sediments, we can only compare our results with other reports from the Czech Republic and Europe. A study of Arnika Association at thirty-two localities on various Czech rivers[38] found the presence of several groups of PFAS, with PFOS being the most common. The concentration of PFOS in the referred study is in the range of 0.2–17.7 µg/kg DM of sediment. Another study carried out on sediments from six sampling sites in the Czech Republic by Arnika Association,[39] including one site on the Vltava River in Prague, found the mean PFOS concentration as much as 0.61 µg/kg DM of sediment. An average PFOS level 0.79 µg/kg DM was found during regular annual measurements in river sediments at five localities in the Morava River basin.[40] Moreover, PFOS concentrations were measured in sediments of the Orge River in France (4.3 µg/kg DM),[41] the Main River in Germany (0.58 µg/kg DM),[42] the Danube, Rhine, and Scheldt rivers (13.9 µg/kg DM),[43] the Llobregat River in Spain (11.4 µg/kg DM),[44] the Scheldt River in the Netherlands (0.08 µg/kg DM),[45] various rivers and canals in the Netherlands (0.5-8.7 µg/kg DM)[46] and the L'Albufera Natural Park in Spain (4.8 µg/kg DM).[47] When compared with the above-mentioned research in Europe, it can be concluded that our PFOS findings of sediments collected in waters in the Prague area are basically lower than common values that have been found in river sediments in Europe over the past few years.

5.4 Pollution of fish by PFAS

Perfluorinated compounds of all three groups – PFCAs, PFSAs and PFOSA – were found in the fish samples collected. The Arnika Association's research conducted on various Czech rivers[48] found the presence of the same three groups of PFAS in sediments of the Oder River and the Elbe River. The concentrations of PFCAs, PFSAs and PFOSA in fish samples of the referred study have been in the range of 1.61 - 6.52 µg/kg WW, 2.86 - 19.7 µg/kg WW, and 0.04 - 0.19 µg/kg WW, respectively. Fish samples of this study were in the same range of measured concentrations as referred ranges of the groups of PFAS, except for one sample collected at the confluence of the Vltava River with the Rokytka stream for a sum of 11 PFCAs (30.8 µg/kg WW). These

[31] Hamid H., Li L. Y. (2016): Role of wastewater treatment plant in environmental cycling of poly- and perfluoroalkyl substances. Ecocycles 2(2): 43-53. DOI: 10.19040/ecocycles.v2i2.62

[32] Zhang, C., Yan, H., Li, F. et al. (2015): Occurrence and fate of perfluorinated acids in two wastewater treatment plants in Shanghai, China. Environ Sci Pollut Res 22: 1804–1811. https://doi.org/10.1007/s11356-013-2044-8

[33] Arnika Association (2011): Occurrence of perfluorinated and brominated compounds in fish and sediment samples from selected localities of the Czech Republic. Water Live Project - final report in Czech, Arnika Association - Toxic Substances and Waste Program, pp 49.

[34] Mach V., Petrlík J. (2016): Pollution of watercourses by persistent organic pollutants in selected areas of interest. Arnika Association - Toxic Substances and Waste Program Prague, in Czech, pp 29.

[35] Pulkrabová J., Hajšlová J., Poustka J., Hrádková P.: Brominated Flame Retardants in River Sediments and Sewage Sludge Collected in the Czech Republic. Project BIOBROM.

[36] Central Agricultural Inspection and Testing Institute in Brno (2015): Inspection and monitoring of foreign substances in food chains. Report in Czech for 2014, pp 89.

[37] Arnika Association (2011): Occurrence of perfluorinated and brominated compounds in fish and sediment samples from selected localities of the Czech Republic. Water Live Project - final report in Czech, Arnika Association - Toxic Substances and Waste Program, pp 49.

[38] Arnika Association (2011): Occurrence of perfluorinated and brominated compounds in fish and sediment samples from selected localities of the Czech Republic. Water Live Project - final report in Czech, Arnika Association - Toxic Substances and Waste Program, pp 49.

[39] Mach V., Petrlík J. (2016): Pollution of watercourses by persistent organic pollutants in selected areas of interest. Arnika Association - Toxic Substances and Waste Program Prague, in Czech, pp 29.

[40] Bečanová J., Komprdová K., Vrana B., Klánová J. (2016): Annual dynamics of perfluorinated compounds in sediment: A case study in the Morava River in Zlín district, Czech Republic. Chemosphere 151: 225-233.

[41] Labadie P., Chevreuil M. (2011): Partitioning behaviour of perfluorinated alkylcontaminants between water, sediment and fish in the Orge River (nearby Paris, France). Environmental Pollution 159: 391-397.

[42] Becker A.M., Gerstmann S., Frank H. (2008): Perfluorooctanoic acid and perfluorooctane sulfonate in the sediment of the Roter Main river, Bayreuth, Germany. Environmental Pollution 156: 818-820.

[43] De Voogt P., De Coen W., Dewolf W., Heimstad E., Mclachlan M., Van Leeuwen S.,Van Roon A. (2006): Perfluorinated Compounds in the European Environment (PERFORCE). Institute for Biodiversity and Ecosystem Dynamics, Universiteit van Amsterdam.

[44] Campo J., Perez F., Masia A., Pico Y., Farre M., Barcelo D. (2015): Perfluoroalkylsubstance contamination of the Llobregat River ecosystem (Mediterranean area, NE Spain). Science of the Total Environment 503: 48-57.

[45] Esparza X., Moyano E., de Boer J., Galceran M.T., van Leeuwen S.P.J. (2011): Analysis of perfluorinated phosponic acids and perfluorooctane sulfonic acid in water,sludge and sediment by LC-MS/MS. Talanta 86: 329-336.

[46] Kwadijk C.J.A.F., Korytár P., Koelmans A.A. (2010): Distribution of perfluorinated compounds in aquatic systems in The Netherlands. Environmental Science and Technology 44: 3746-3751.

[47] Pico Y., Blasco C., Farre M., Barcelo D. (2011): Occurrence of perfluorinated compounds in water and sediment of L'Albufera Natural Park (Valencia, Spain). Environmental Science Pollution Research 19: 946-957.

[48] Mach V., Petrlík J. (2016): Pollution of watercourses by persistent organic pollutants in selected areas of interest. Arnika Association - Toxic Substances and Waste Program Prague, in Czech, pp 29.

results suppose that generally the pollution levels of PFAS in fish living in the Vltava River is comparable to that which has been found in various Czech rivers.

The highest PFOS concentrations among fish were measured in the LIB-1 sample. This is a mixed sample of three European perches caught at the confluence of the Vltava River and the Rokytka stream whose PFOS concentration is as high as 17.4 µg/kg WW. The same sample also contained significantly higher concentrations of other monitored PFAS (sum of 11 PFCAs, sum of 5 PFSAs and PFOSA) than the other three fish samples. The higher concentrations of PFOS was in the fish sample at the historical industrial area Vysočany where contamination with legacy chemicals as well as new contaminants can be expected.

In the United States, a survey of fish from the Ohio, Missouri, and Upper Mississippi rivers conducted in 2005[49] shows a mean PFOS concentration of 60 fish samples from all three rivers as high as 105 µg/kg WW, which is five times that of the highest concentration of PFOS we found in the most polluted sample. Compared to the level found at considerably polluted sites, the fish samples have not shown an enormous concentration of PFAS.

5.5 Pollution of fish by BFRs

Water pollution by PBDEs is reflected in all fish samples, however, the PBDE levels follow commonly occurring values. In 2005, a survey of PBDEs was carried out on 80 fish caught in the Vltava and Elbe river basins.[50] The mean concentrations of 10 PBDEs (PBDE 28, PBDE 47, PBDE 49, PBDE 66, PBDE 85, PBDE 99, PBDE 100, PBDE 153, PBDE 154, PBDE 183) were 9.8 µg/kg WW, 7.5 µg/kg WW and 3.8 µg/kg WW in bream, chub, and perch, respectively. The sums of the same 10 PBDEs in our results are significantly lower (three samples) or comparable (one sample) than the above mentioned means. The PBDEs in our samples of fish have not shown any significant difference from commonly measured values. In comparison to our findings with studies of PBDE content in fish from retail stores in the United States,[51] we find higher value in one sample of common bream from the Vltava River at Povltavská (3.61 µg/kg WW). It is worth mentioning that the PBDE congeners observed in this survey and set of PBDE congeners in the study from the US are not completely same. Nevertheless, the mentioned fish sample also had the highest measured value of PBDEs concentration from the fish samples collected in our study. The sample comes from Libeň, which supposedly reflects the historical burden of industrial area of Vysočany, where contamination by legacy chemicals as well as new contaminants can be expected.

[49] Ye X., Strynar M.J., Nakayama S.F., Varns J., Helfant L., Lazorchak J., Lindstrom A.B. (2008): Perfluorinated compounds in whole fish homogenates from the Ohio, Missouri, and Upper Mississippi Rivers, USA. Environmental Pollution 156: 1227-1232.

[50] Hajšlová J., Pulkrabová J., Poustka J., Čajka T., Randák T. (2007): Brominated flame retardants and related chlorinated persistent organic pollutants in fish from river Elbe and its main tributary Vltava. Chemosphere 69: 1195-1203.

[51] Schecter A., Harris A.T., Shah N., Musumba A., Päpke O. (2008): Brominated flame retardants in US food. Molecular Nutrition & Food Research 52: 266-272.

5.6 Data comparison with environmental standards

There are no hygienic limits imposed on the market for PFAS and BFRs in Czech and European legislation for food, therefore it is not possible to assess the health safety of the collected fish in a standardized procedure. Likewise, there are no legal standards for the occurrence of PFAS and BFRs in sediments of surface waters. On the other hand, some examined compounds are listed as priority regarding water policy of the European Union in Directive 2008/105/EC of the European Parliament and of Council that established environmental quality standards for water and fish samples for those substances.[52] The recently reviewed and adopted Drinking Water Directive 98/83/EC introduced standards for PFAS in drinking water. The new Directive includes a limit value of 0.1 µg/L for a sum of 20 individual PFAS listed in Annex III (PFBA, PFPA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFDoDA, PFTrDA, PFBS, PFPS, PFHxS, PFHpS, PFOS, PFNS, PFDS, perfluoroundecane sulfonic acid, perfluorododecane sulfonic acid, perfluorotridecane sulfonic acid), as well as a limit value of 0.5 µg/L for total PFAS concentration. The limit value of 0.5 µg/L will only apply once a method for measuring "PFAS total" is available. The method should be available in 3 years time. Different environmental standards for emerging chemicals are summarized in Table 10.

Table 10: Environmental quality standards for priority substances related to PFAS and BFRs in European Union

Name of substance	Inland surface waters[VI]		Other surface waters		Biota[VII]	Drinking water
	Maximal allowable concentration [ng/L]	Annual average [ng/L]	Maximal allowable concentration [ng/L]	Annual average [ng/L]	[µg/kg WW]	[ng/L]
20 PFAS[I]	not defined	not defined	not defined	not defined	not defined	100
PFAS total[II]	not defined	not defined	not defined	not defined	not defined	500
PFOS[III]	36 000	0.65	7200	0.13	9.1	*
PBDEs[IV]	140	not defined	14	not defined	0.0085	not defined
HBCD[V]	500	1.6	50	0.8	167	not defined

[I*] 20 individual PFAS (including PFOS*) listed in Annex III of the Drinking Water Directive 98/83/EC: PFBA, PFPA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFDoDA, PFTrDA, PFBS, PFPS, PFHxS, PFHpS, PFOS, PFNS, PFDS, perfluoroundecane sulfonic acid, perfluorododecane sulfonic acid, perfluorotridecane sulfonic acid.
[II] The limit value of 500 ng/L for PFAS total will only apply once a method for measuring "PFAS total" is available (no later than 3 years after the Directive adoption)
[III] The environmental quality standards of PFOS refer to PFOS with its derivatives.

[52] Directive 2008/105/EC of the European Parliament and of Council of 16 December 2008, on environmental quality standards in the field of water policy, amending and subsequently repealing Council Directives 82/176/EEC, 83/513/EEC, 84/156/EEC, 84/491/EEC, 86/280/EEC and amending Directive 2000/60/EC of the European Parliament and of the Council (consolidated version in September 2020).

[IV] For the group of priority substances covered by brominated diphenyl ethers, the environmental quality standards refer to the sum of the concentrations of congener numbers 28, 47, 99, 100, 153 and 154.
[V] The environmental quality standards of HBCD is applied to the total concentration of all isomers of HBCD.
[VI] Inland surface waters consist of rivers and lakes and related artificial or heavily modified water bodies.
[VII] The biota environmental quality standard relates to fish. An alternative biota taxon, or another matrix, may be monitored instead, as long as the environmental quality standards applied provide an equivalent level of protection.

5.6.1 Comparison with environmental standards for PFAS

The most concentrated PFAS in the water samples is PFOS for which the environmental quality standards in the Directive 2008/105/EC of the European Parliament and of Council applies.[53] For inland surface waters, such as rivers and ponds, there are two environmental quality standards for PFOS: the maximal allowable concentration (36 000 ng/L) and the annual average (0.65 ng/L). The first one is not exceeded in any of the samples, but the annual average environmental quality standard is exceeded in all of them. If the measured PFOS concentrations were also annual averages, the surface waters in the city of Prague would exceed the legislative standards of the European Union.

Directive 2008/105/EC of the European Parliament and of Council set out the environmental quality standard for PFOS as 9.1 µg/kg WW for aquatic biota.[54] The stated environmental quality standard of PFOS is exceeded in one of four fish samples (LIB-1). It is the mixed sample of three European perches caught at confluence of the Vltava River and the Rokytka stream that has PFOS concentration as much as 17.4 µg/kg WW.

5.6.2 Comparison with environmental standards for BFRs

PBDEs are among the priority substances of the European Union's water policy. Directive 2008/105/EC of the European Parliament and of Council[55] sets out an environmental quality standard for the sum of 6 PBDE congeners (PBDE 28, PBDE 47, PBDE 99, PBDE 100, PBDE 153, and PBDE 154) for biota as 0.0085 µg/kg WW. The environmental quality standard for the sum of the 6 PBDE congeners was exceeded in all four fish samples. Based on our findings, several water bodies on the territory of Prague can be classified as polluted by PBDEs within the framework of European legal standard. In contrast, HBCD concentrations in fish samples complies with the environmental quality standard of 167 µg/kg WW set out in the directive.

[53] Directive 2008/105/EC of the European Parliament and of Council of 16 December 2008, on environmental quality standards in the field of water policy, amending and subsequently repealing Council Directives 82/176/EEC, 83/513/EEC, 84/156/EEC, 84/491/EEC, 86/280/EEC and amending Directive 2000/60/EC of the European Parliament and of the Council (consolidated version in September 2020).

[54] Directive 2008/105/EC of the European Parliament and of Council of 16 December 2008, on environmental quality standards in the field of water policy, amending and subsequently repealing Council Directives 82/176/EEC, 83/513/EEC, 84/156/EEC, 84/491/EEC, 86/280/EEC and amending Directive 2000/60/EC of the European Parliament and of the Council (consolidated version in September 2020).

[55] Directive 2008/105/EC of the European Parliament and of Council of 16 December 2008, on environmental quality standards in the field of water policy, amending and subsequently repealing Council Directives 82/176/EEC, 83/513/EEC, 84/156/EEC, 84/491/EEC, 86/280/EEC and amending Directive 2000/60/EC of the European Parliament and of the Council (consolidated version in September 2020).

6. Conclusions and Recommendations

Seven samples of water, three samples of sediments and four samples of fish from various water bodies were analysed in order to obtain data related to PFAS and BFRs pollution in the territory of Prague (Czech Republic). According to the data collected, pollution of surface waters in Prague by PFAS and BFRs is ubiquitous. PFAS were detected in all water and fish samples. Water samples from industrially non-affected (reference) sites were not exceptions. However, PFAS pollution was not found in sediment samples. Brominated flame retardants with the properties of persistent organic pollutants (polybrominated diphenyl ethers, hexabromocyclododecane) were also detected in all sediment and fish samples. Moreover, the other surveyed brominated flame retardants which are often used as alternatives to banned PBDEs were found in two of four sediment samples and in all fish samples. Nevertheless, the measured values usually do not exceed common values of PFAS and BFRs contamination of European waters.

The highest measured concentrations of PFOS and PFCAs in water samples collected in this study were measured in the Kopaninský stream (total concentration of 9 PFCAs 164.34 ng/L). This value is significantly higher compared to common values in surface waters in Europe. It is comparable with PFCAs concentrations that have been found in waters of big industrial agglomerations. The Václav Havel Prague Airport is a likely source of PFAS into the environment as PFAS-containing firefighting foams have been used at the Airport. The Airport should be immediately working on the proclaimed replacement of PFAS-containing firefighting foams, extend its monitoring of environmental compartments (water, soil, biota) in the vicinity of the Airport, and elaborate detailed risk assessment to take immediate steps towards elimination of toxic chemicals emission into the environment.

Comparably higher concentrations of PFAS and PFSAs were found in the fish and water samples, respectively, from the Rokytka stream in Libeň. Another fish sample from the same area of Libeň exhibits the highest measured concentrations of PBDEs among analysed samples. The samples coming from Libeň might reflect the historical burden of industrial area of Vysočany where contamination with legacy chemicals as well as new contaminants can be expected. The contribution of the Kopaninský (affected by the Airport) and Rokytka (affected by the industrial Vysočany) streams to the overall pollution of the Vltava River by PFAS and BFRs need to be further examined.

The continuous monitoring of PFAS and BFRs into the (not only Prague) waters needs to be undertaken to safeguard surface-water as well as drinking-water quality. Reporting PFAS emissions in the Czech Pollutant Release and Transfer Register (PRTR, IRZ in Czech) would increase the knowledge about release sources, enabling an identification of potential contaminated sites. Such a recommendation is in line with the 'Review of E-PRTR implementation and related guidance'[56] which recommends adding PFHxS, PFOS and PFOA reporting requirements to the European PRTR.

[56] https://circabc.europa.eu/ui/group/f80de80b-a5bc-4c2b-b0fc-9c597dde0e42/library/b4eacd-6d-4425-479a-a225-77306de6b060?p=1&n=10&sort=modified_DESC [cited 28 November 2020]

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8. Annexes

Annex 1 – Collected samples

Table 1: List of water samples taken on sampling sites.

Sample ID	Date of sampling	Sampling site	Coordinates	Possible source of pollution
MOT-V-20/01	July 23, 2020	Motolský pond called R3, Prague	50.0693323N 14.3400060E	Healthcare waste incinerator
ROK-V-20/01	July 23, 2020	Confluence of the Vltava River and the Rokytka stream, Prague	50.1078117N, 14.4668342E	Vysočany industrial area
POVLT-V-20/01	July 23, 2020	The Vltava River at Povltavská, Prague	50.1136015N 14.4578187E	Vysočany industrial area
RAD-V-20/01	July 23, 2020	The Vltava River after the confluence with the Berounka River, Prague	49.9979184N 14.4015046E	Pollution not expected
LAH-V-20/01	July 23, 2020	The Vltava River at ferry Lahovičky, Prague	50.0023414N 14.4012615E	Pollution not expected
KOP-V-20/01	July 23, 2020	The Kopaninský stream, Prague	50.1139017N 14.2890232E	Václav Havel Airport Prague
ROZ-V-20/01	July 23, 2020	the Vltava River at Klecánky ferry, Prague	50.1663087N 14.4025799E	Waste water treatment plant

Table 2: List of sediment samples taken on sampling sites.

Sample ID	Date of sampling	Sampling site	Coordinates	Possible source of pollution
MOT-SED-20/01	July 23, 2020	Motolský pond called R3, Prague	50.0693323N 14.3400060E	Healthcare waste incinerator
ROK-SED-20/01	July 23, 2020	Confluence of River Vltava and the Rokytka stream, Prague	50.1078117N, 14.4668342E	Vysočany industrial area
ROZ-SED-20/01	July 23, 2020	the Vltava River at Klecánky ferry, Prague	50.1663087N 14.4025799E	Waste water treatment plant

Table 3: List of fish samples from sampling sites.

Sample ID	Fish species	Number of individuals in a sample	Date of sampling	Sampling site	Length of fish with tail [cm]	Weight of fish [g]	Age of fish [year]	Possible source of pollution
POD-1	Common roach (*Rutilis rutilis*)	2	September 5, 2019	the Vltava River after the Waste water treatment plant outlet in Podbaba, Prague	30, 31	294, 359	6, 7	Waste water treatment plant
L2-LIB-1	Common bream (*Abramis brama*)	2	August 8, 2019	the Vltava River at Povltavská, Prague	53, 47	1756, 876	11, 10	Vysočany industrial area
LIB-1	European perch (*Perca fluvitatilis*)	3	September 4, 2019	Confluence of the Vltava River and the Rokytka stream, Prague	19, 16, 15.5	90, 51, 43	4, 3, 3	Vysočany industrial area
KLEC-1	European perch (*Perca fluvitatilis*)	1	September 5, 2019	the Vltava River at Klecánky, Prague	25	223	7	Waste water treatment plant

Annex 2 – Analysed substances

Table 4: List of perfluorinated substances analysed in the laboratory

Abbreviation	Chemical Name	CAS Registry Number	Group of PFC
PFBA	Perfluorobutanoic acid	375-22-4	Perfluorinated carboxylic acids
PFPeA	Perfluoropentanoic acid	2706-90-3	Perfluorinated carboxylic acids
PFHxA	Perfluorohexanoic acid	307-24-4	Perfluorinated carboxylic acids
PFHpA	Perfluoroheptanoic acid	375-85-9	Perfluorinated carboxylic acids
PFOA	Perfluorooctanoic acid	335-67-1	Perfluorinated carboxylic acids
PFNA	Perfluorononanoic acid	375-95-1	Perfluorinated carboxylic acids
PFDA	Perfluorodecanoic acid	335-76-2	Perfluorinated carboxylic acids
PFUdA	Perfluoroundecanoic acid	2058-94-8	Perfluorinated carboxylic acids
PFDoA	Perfluorododecanoic acid	307-55-1	Perfluorinated carboxylic acids
PFTrDA	Perfluorotridecanoic acid	72629-94-8	Perfluorinated carboxylic acids
PFTeDA	Perfluorotetradecanoic acid	376-06-7	Perfluorinated carboxylic acids
PFPrS	Perfluoropropane sulfonic acid	423-41-6	Perfluoroalkylsulfonates
PFBS	Perfluorobutane sulfonic acid	375-73-5	Perfluoroalkylsulfonates
PFPeS	Perfluoropentane sulfonic acid	2706-91-4	Perfluoroalkylsulfonates
PFHxS	Perfluorohexane sulfonic acid	355-46-4	Perfluoroalkylsulfonates
PFHpS	Perfluoroheptane sulfonic acid	375-92-8	Perfluoroalkylsulfonates
Br-PFOS	Branched-chain isomer of perfluorooctanesulfonic acid	1763-23-1	Perfluoroalkylsulfonates
L-PFOS	Linear-chain isomer of perfluorooctanesulfonic acid	1763-23-1	Perfluoroalkylsulfonates
PFNS	Perfluorononane sulfonic acid	68259-12-1	Perfluoroalkylsulfonates
PFDS	Perfluorodecane sulfonic acid	335-77-3	Perfluoroalkylsulfonates
PFDoS	Perfluorododecane sulfonic acid	120226-60-0	Perfluoroalkylsulfonates
PFOSA	Perfluorooctanesulfonamide	754-91-6	Perfluoroalkylsulfonic amids
HFPO-DA	Hexafluoropropylene oxide-dimer acid	13252-13-6	Perfluoroalkylethercarboxylic acids
NaDONA	Sodium dodecafluoro-3H-4,8-dioxanonanoate	958445-44-8	Other perfluorinated compounds
9Cl-PF3ONS	9-Chlorohexadecafluoro-3-oxanonane-1-sulfonate	73606-19-6	Other perfluorinated compounds
11Cl-PF3OUdS	11-Chloroeicosafluoro-3-oxaundecane-1-sulfonate	83329-89-9	Other perfluorinated compounds

Table 5: List of brominated flame retardants analysed in the laboratory

Abbreviation	Chemical Name	CAS Registry Number	Group of BFR
PBDE 28	2,4,4′-Tribromodiphenyl ether	41318-75-6	Polybrominated diphenyl ethers
PBDE 47	2,2′,4,4′-Tetrabromodiphenyl ether	5436-43-1	Polybrominated diphenyl ethers
PBDE 49	2,2′,4,5′-Tetrabromodiphenyl ether	243982-82-3	Polybrominated diphenyl ethers
PBDE 66	2,3′,4,4′-Tetrabromodiphenyl ether	189084-61-5	Polybrominated diphenyl ethers
PBDE 85	2,2′,3,4,4′-Pentabromodiphenyl ether	182346-21-0	Polybrominated diphenyl ethers
PBDE 99	2,2′,4,4′,5-Pentabromodiphenyl ether	60348-60-9	Polybrominated diphenyl ethers
PBDE 100	2,2′,4,4′,6-Pentabromodiphenyl ether	189084-64-8	Polybrominated diphenyl ethers
PBDE 153	2,2′,4,4′,5,5′-Hexabromodiphenyl ether	68631-49-2	Polybrominated diphenyl ethers
PBDE 154	2,2′,4,4′,5,6′-Hexabromodiphenyl ether	207122-15-4	Polybrominated diphenyl ethers
PBDE 183	2,2′,3,4,4′,5′,6-Heptabromodiphenyl ether	207122-16-5	Polybrominated diphenyl ethers
PBDE 196	2,2′,3,3′,4,4′,6,6′-Octabromodiphenyl ether	None	Polybrominated diphenyl ethers
PBDE 197	2,2′,3,3′,4,4′,6,6′-Octabromodiphenyl ether	None	Polybrominated diphenyl ethers
PBDE 203	2,2′,3,4,4′,5,5′,6-Octabromodiphenyl ether	None	Polybrominated diphenyl ethers
PBDE 206	2,2′,3,3′,4,4′,5,5′,6-Nonabromodiphenyl ether	None	Polybrominated diphenyl ethers
PBDE 207	2,2′,3,3′,4,4′,5,6,6′-Nonabromodiphenyl ether	None	Polybrominated diphenyl ethers
PBDE 209	Decabromodiphenyl ether	1163-19-5	Polybrominated diphenyl ethers
BTBPE	1,2-Bis(2,4,6-tribromophenoxy)ethane	37853-59-1	Bromobenzenes
DBDPE	Decabromodiphenyl ethane	84852-53-9	Bromobenzenes
HBBz	Hexabromobenzene	87-82-1	Bromobenzenes
PBEB	Pentabromoethylbenzene	85-22-3	Bromobenzenes
PBT	Pentabromotoluene	87-83-2	Bromobenzenes
α-HBCD	α Isomer of 1,2,5,6,9,10-Heaxbromocyclododecane	3194-55-6	Brominated cyclic hydrocarbons
β-HBCD	β Isomer of 1,2,5,6,9,10-Heaxbromocyclododecane	3194-55-6	Brominated cyclic hydrocarbons
γ-HBCD	γ Isomer of 1,2,5,6,9,10-Heaxbromocyclododecane	3194-55-6	Brominated cyclic hydrocarbons
OBIND	Octabromotrimethylphenylindane	None	Other brominated compounds

Annex 3 – Photos from sampling campaign


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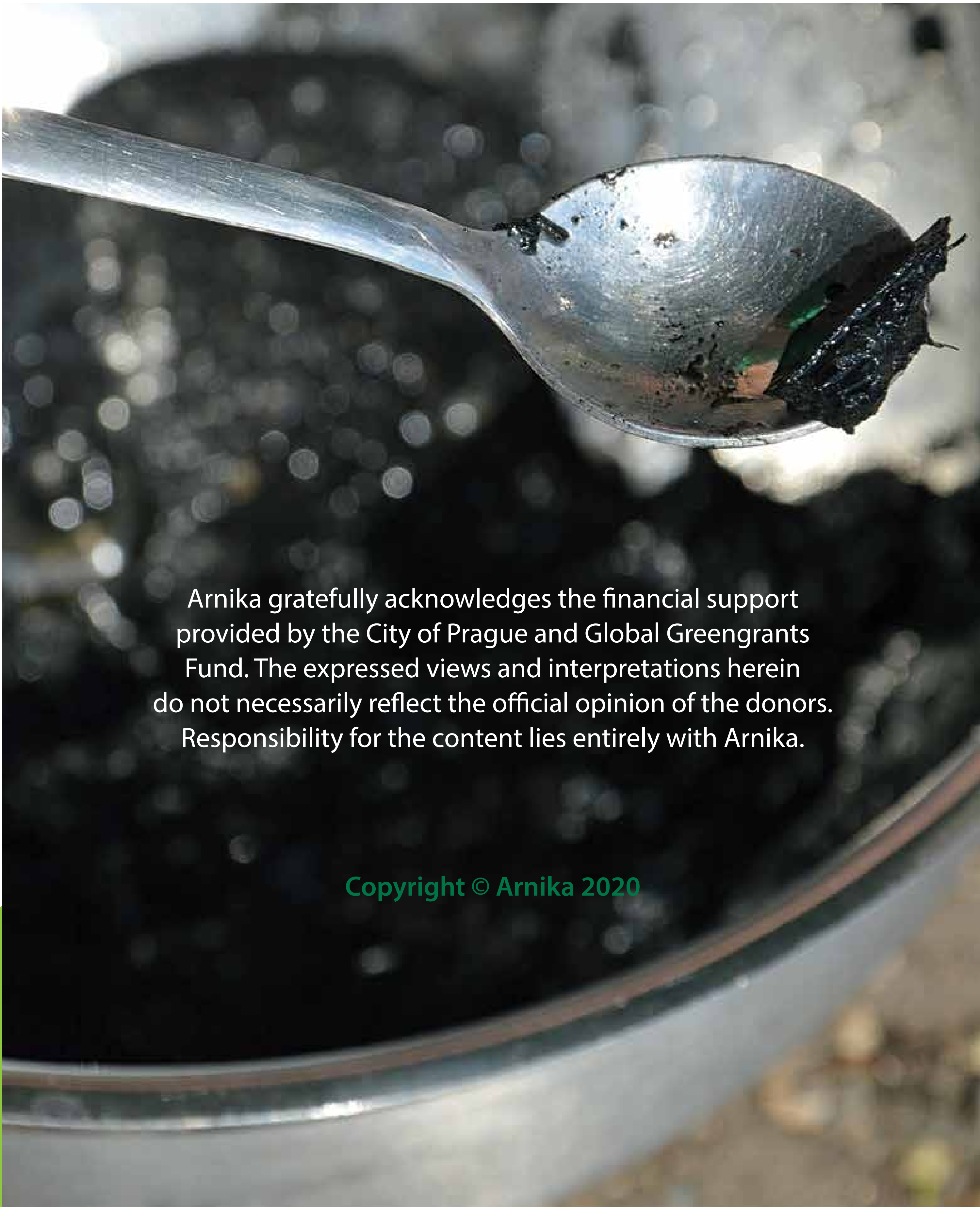

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