Emerging Organic Micropollutants (perfluorinated alkyl substances, pharmaceuticals, pesticides and their metabolites) in surface waters of the Czech Part of the Elbe River Basin

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1. Introduction

Organic micropollutants, namely polar organic micropollutants (e.g. Polar pesticides and their degradation products, human and veterinary pharmaceuticals, polyfluorinated alkyl compounds - PFCs and others) are among the important synthetic organic pollutants (xenobiotics) that often exhibit undesirable toxicological and ecotoxicological properties (persistence, bioaccumulation, toxicity, carcinogenicity, mutagenicity, reproductive effects, estrogenic effects). Substances with these properties are on the list of priority substances in European legislation (Directive 2000/60/EC of the European Parliament and of the Council of 20 October 2000 establishing a framework for Community action in the field of water policy; Directive 2008/105/EC of the European Parliament and of the Council of 16 December 2008 on environmental quality standards in the field of water policy). Due to insufficient information from real surface water monitoring, Watch Lists have been established for selected potential priority substances since 2015 by means of Commission (EU) Implementing Decisions.

The individual Watch Lists included for example hormones, antibiotics, neonicotinoid insecticides, azole pesticides and pharmaceuticals, UV filters. A combination of liquid chromatography and tandem mass spectrometry is often used for their determination. High-resolution mass spectrometry is used to confirm and identify new xenobiotics. Most of these substances have already been implemented by the laboratory, but have not been able to reach all the required limits [1, 2]. In order to achieve the required very low limits of determination (sometimes tens to thousands of ng/l), the most sensitive analytical instrumentation is needed. Grant funding will be used for its acquisition: Ålesund Call-3A from the Norway Grants 2014-2021 programme "Environment, Ecosystems and Climate Change", mediated and co-financed by the State Environmental Fund of the Czech Republic.

2. Methods

For the sensitive determination of organic micropollutants are preferentially used standardised analytical methods where available, for example [3], but these methods must be adopted for laboratory condition and instrumentation. Up-to date modern instrumentation, for example ultrahigh-performance liquid chromatograph connected to tandem mass spectrometry (UHPLC-MS/MS) or gas chromatograph connected to single quadrupole or better triple quadrupole (GC-MS or GC-MS/MS) are standards for today's analytics of trace and ultra-trace organic micropollutants. For ultra-trace determination (sub ng/l) of substances with highest effects (hormones, pyrethroid insecticides, tributyltin, etc.) are still necessary very laborious extraction and cleaning steps prior to chromatographic determination.

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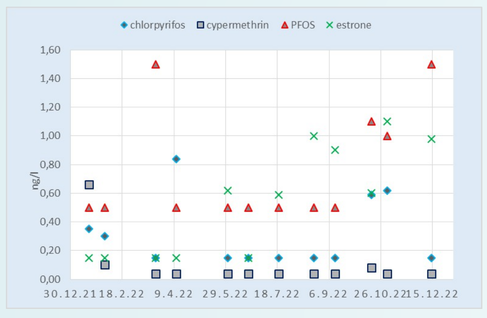
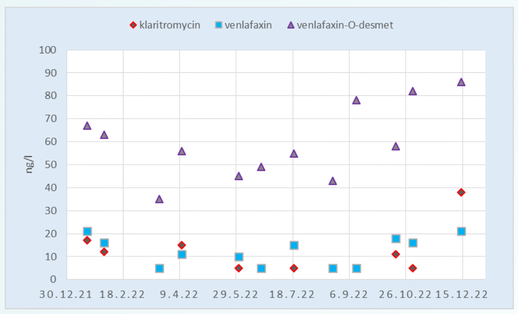
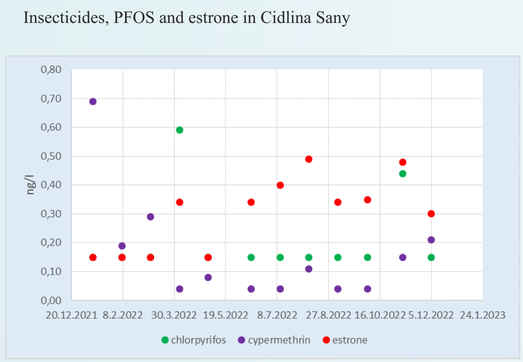


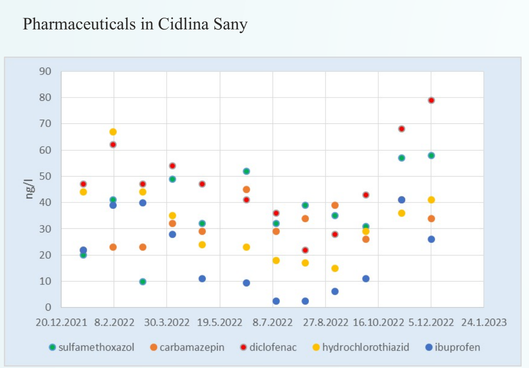
Insecticides, PFOS and estrone in Cidlina Sany



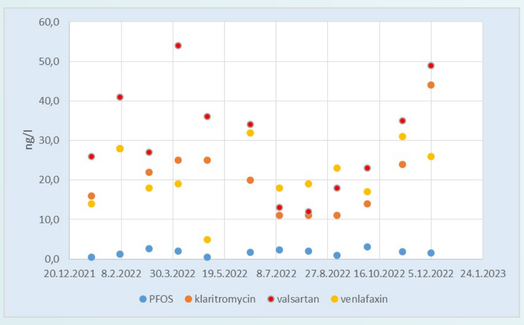
Pharmaceuticals in Cidlina Sany



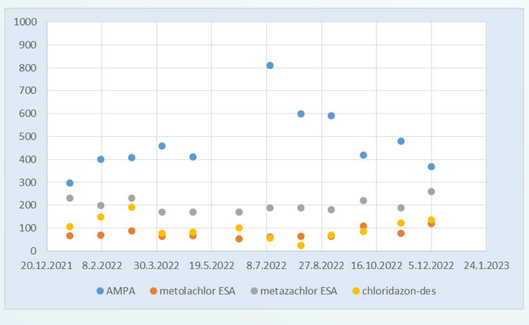
Insecticides and estrone in Labe Schmilka right bank



Pharmaceuticals in Labe Schmilka right bank



PFOS and pharmaceuticals in Labe Schmilka right bank



Pesticide metabolites in Labe Schmilka right bank

Fig. 1: The New Chromatographic Mass Spectrometric System consisting of Triple Quad Waters XEVO TQ Absolute coupled with gas chromatographs Agilent 8890A via APGC interface and UHPLC Waters Acquity acquired with financial support of The State Environmental Fund of the Czech Republic, as the Programme Operator of the Programme „Environment, Ecosystems and Climate Change", supported by the Norway Grants 2014–2021. System will be used for ultrasensitive analyses of selected water pollutants: Polyfluorinated Alkyl Compounds (PFAC's), pharmaceuticals, hormones, pesticides, etc.

Fig. 2: High resolution Waters Xevo G3 QTof coupled with gas chromatograph Agilent 8890A via APGC interface and UHPLC Waters Acquity acquired with financial support of The State Environmental Fund of the Czech Republic, as the Programme Operator of the Programme „Environment, Ecosystems and Climate Change", supported by the Norway Grants 2014–2021. System will be used for pesticide and pharmaceutical screening, confirmation of potential interferences and untarget screening of new emerging contaminants.

Fig. 3: Waters Triple Quad XEVO TQ-XS coupled with UHPLC Acquity used for multiresidue analyses of pesticides, their metabolites and pharmaceuticals in surface waters measured in positive ionization mode.

3. Results and discussion

Following Graphs in pictures 1 and 2 represent real concentrations of selected micropollutants in small river Cidlina, which has very intensive agricultural character with small towns and villages in its basin. Figure 1 illustrates need for very low limits of quantitation (LOQ), because of low Environment Quality Standards (EQS). Chlorpyrifos (LOQ= 0,3 ng/l), cypermethrin (LOQ= EQS= 0,08 ng/l), PFOS (LOQ=1 ng/l, EQS=0,6 ng/l), estrone (LOQ=0,3 ng/l, EQS= 0,4 ng/l), venlafaxine and venlafaxine-O-desmethyl (LOQ= 10 ng/l, EQS= 6 ng/l). For clarity reasons values below LOQ are set to the half of LOQ.

Fig. 4: Agilent Technologies Triple Quad 6495A coupled with UHPLC 1290 used for multiresidue analyses of pesticides, their metabolites, pharmaceuticals and perfluorinated alkyl substances in surface waters measured in negative ionization mode.

Fig. 5: Agilent Technologies Triple Quad GC-MS/MS 7000C coupled with gas chromatograph 7890B used for measurement of nonpolar chlorinated pesticides, PCB's, PBDE's in solid matrices and waters.

Fig. 6: Agilent Technologies Single Quad GC-MS 5975C EI/CI (negative chemical ionization) coupled with gas chromatograph 7890A used for measurement of chlorinated paraffins, pyrethroids (cypermethrin), PBDE's in solid matrices and waters.

4. Coclusions

Current hydroanalytical techniques allow us to determine a wide range of organic micropollutants at very low concentrations. Nevertheless, some of the substances with the highest negative effects are still a challenge for analysts. In addition, we should also be concerned with the analysis of related substances (analogues, substitutes, new groups of substances), which often have even greater adverse effects on ecosystems and, consequently, on humans. For this purpose, high-resolution mass spectrometry using libraries, databases and internet resources is a powerful tool.

Literature:
[1] Ferencik, M.; Blahova, J.; Schovankova, J.; Siroka, Z.; Svobodova, Z.; Kodes, V.; Stepankova, K.; Lakdawala, P.: Residues of selected anticonvulsive drugs in surface waters of the Elbe River basin (Czech Republic). Water 2022, 14, 4122. https://doi.org/10.3390/w14244122.
[2] Skocovska M, Ferencik M, Svoboda M, Svobodova Z (2021), Residues of selected sulfonamides, non-steroidal anti-inflammatory drugs and analgesics-antipyretics in surface water of the Elbe river basin (Czech Republic). Vet Med-Czech 66, 208–218. https://doi.org/10.17221/180/2020-VETMED.
[3] ČSN EN ISO 21676:2018 Water quality — Determination of the dissolved fraction of selected active pharmaceutical ingredients, transformation products and other organic substances in water and treated waste water — Method using high performance liquid chromatography and mass spectrometric detection (HPLC-MS/MS or -HRMS) after direct injection.

Norway grants
STÁTNÍ FOND ŽIVOTNÍHO PROSTŘEDÍ ČESKÉ REPUBLIKY
Společně pro zelenou Evropu
Podpořeno Norskem prostřednictvím Norských fondů

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