

Policy briefs on micropollutants in wastewater and sewage sludge

BSR WATER – Platform on Integrated Water Cooperation, 2021

Imprint

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Project note

The EU co-funded project **BSR WATER – Platform on Integrated Water Cooperation** (2018–2021; www.bsrwater.eu) aims to enhance cross-sectoral cooperation in smart water management by providing a possibility for transnational experience exchange, sharing of good practices and solutions, as well as delivering comprehensive overview of the current and future regional policy. The platform brings together experts representing diverse projects that have generated through transnational cooperation many replicable and unique solutions, covering broad variety of water-related issues.

The platform cooperation is based on practical achievements and results of seven projects addressing a wide range of water management challenges. The outcomes and practical findings of the contributing projects (IWAMA, BEST, iWater, Manure Standards, Village Waters, Reviving Baltic Resilience, CliPLivE) support the long-term development of regional environmental policy and recommendations, which will further strengthen the policy-practice link in implementation of advanced water protection measures, including smart nutrient management and sludge handling, storm water management and the energy efficiency cycle at the national and municipal levels.

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1. Policy brief on heavy metals

1.1. What are heavy metals?

Heavy metals are a group of metals and metalloids that have relatively high density and are sometimes toxic even at low concentration levels. Heavy metals naturally present in the environment and their concentrations vary broadly depending on chemistry of geological rocks which comprise certain areas, forming so called geochemical background. Since heavy metals are actively used in industrial products and processes, they are released in the environment from anthropogenic sources. Heavy metals are released to water with industrial and municipal wastewater; emitted to air from industries, car traffic and energy sector; spread with mineral fertilizers; flashed with stormwaters; leak from landfills and paints and use other sources and pathways ending up in the marine environment.

Heavy metals do not degrade in the environment being accumulated in biota and sediments. Many of their toxic effects are well known due to grievous historical experience and proved by scientific studies. Gastrointestinal and kidney dysfunction, nervous system disorders, skin lesions, vascular damage, immune system dysfunction, birth defects, and cancer are just examples of the complications of heavy metals toxic effects. Toxicity of heavy metals varies greatly between different elements. For example, mercury and cadmium are toxic in very low concentrations, while other, like cupper or nickel, are common in our daily used products.

The Baltic Sea Acton Plan 2021-2030 recognizes heavy metals as legacy pollutants. In general, the input of some of them, included in the priority list of HELCOM Recommendation 31E/1, is constantly decreasing. However, for example, assessment of the level of contamination by mercury does not demonstrate good environmental status of the marine environment. The Baltic Sea Action Plan includes a number of concrete actions aimed to prevent contamination of the marine environment by heavy metals, e.g. mercury (HL16-20), lead (HL14).

1.2. Observed facts

Data on concentrations of ten heavy metals in about two hundred and forty WWTP, mainly observed in period 2011-2016 with a few datapoints from 2005, were reported by Denmark, Estonia, Germany, Latvia, Poland and Sweden. Most data on heavy metals in WWTP, more than four thousand data points, were reported for effluents. Measurements of heavy metals in sludge and influents were reported for about a thousand and two thousand samples respectively.

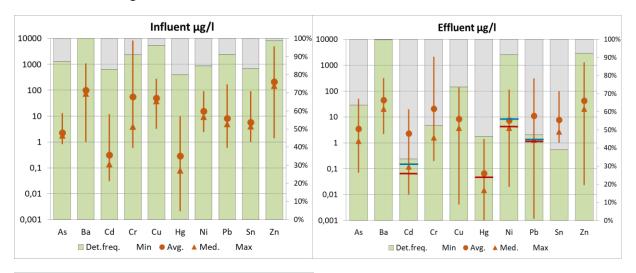
The highest detection frequency was in sludge – almost 100% cases. In influents heavy metals were detected in 89% and in effluents in 64% of samples. Barium, nickel and zinc demonstrate the highest frequency of detection, being detected in more than 80% of cases. Arsenic, chromium and copper were detected in more than 80% influent and 50% of effluent samples. Mercury, cadmium and lead were also detected in more than 80% influent but less than 50% of effluent samples.

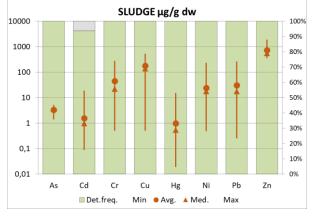
Average concentrations of chromium, copper, barium and zinc in influents are close or even exceed (for Zn) a thousand μ g/I. Average concentrations of arsenic, nickel, lead and tin are approximately ten times lower. Averages for cadmium and mercury are 0.31 and 0.29 μ g/I respectively.

In general, average concentrations of all heavy metals in effluents are ten times lower than in influents. Average concentrations of Cd, Hg and Pb exceed the annual average environmental quality standard (AA-EQS) for inland waters set by the EU WFD, while medians are below these thresholds. It displays that most

of measured concentrations are below the AA-EQS. Elevated average concentrations are provided by relatively small number of measurements. Both average and median concentrations of nickel are below the AA-EQS for inland waters.

There is no common approach to limit values for concentrations of heavy metals in sewage sludge. Reported data on concentration of heavy metals in sewage sludge demonstrate that none of the samples exceed limit values set by the EU directive 86/278 for application of sewage sludge in agriculture. Only a few threshold values set by national legislation in Denmark, Finland, Lithuania, Russia and Sweden are exceeded in a limited number of samples. As for average concentrations, the only exceedance is limit values for Cd and Hg set in Denmark.





Concentrations of heavy metals. Only concentrations above LOQ are reflected. Red lines indicate AA-EQSs for in inland surface waters and blue for other surface waters (DIRECTIVE 2013/39/EU). EQS values are used here for indicative comparison but not for the assessment of contamination level.

1.3. Key messages

Large amount of data on occurrence of heavy metals in influents, effluents and sludges of WWTP were collected. Reported data displays high detection frequency of heavy metals and sufficient accuracy of analytical methods to detect them even at low concentrations.

In general, concentrations of heavy metals in effluents are ten times lower than in influents which is mainly due to their affinity to solid particles and accumulation in sludge. However, individual samples demonstrate high concentrations of heavy metals in effluents which exceed environmental quality standards by an order of magnitude. It alarmingly signals that under certain conditions these

contaminants are still released to the aquatic environment. Thus, continuous monitoring of heavy metals in effluents should be obligatory maintained in WWTPs, where appropriate.

Since heavy metals often originate from industrial pollution, the observed high concentrations of these contaminants in effluents of municipal WWTP might be caused by releases of highly contaminated industrial wastewaters to municipal sewerages. This calls for measures to strengthen control over industrial releases and surveillance of the implementation of the legislation aiming to prevent contamination of municipal wastewater by industrial releases.

Heavy metals removed from sewage water concentrate in sludge, where moderately elevated concentrations of these contaminants were observed. The level of contamination in most cases complies with existing safety criteria. However, these criteria vary largely between countries withing the Baltic Sea region which does not allow regional assessment of the level of sewage sludge contamination.

Only three heavy metals – Cd, Hg and Pb are included in the HELCOM regional assessment of the Baltic Sea environmental health as core indicators. The Report on micropollutants indicates that some other heavy metals (e.g. copper or arsenic) might be of relevance for the assessment, which require the development of HELCOM indicators and establishing of the regional environmental quality standards.

Recycling of nutrients from sewage requires the development of respective safety standards for the sewage-based products. These standards are intended to assure safe recycling of nutrients and set equal conditions for recycled nutrients and mineral fertilizers, which often demonstrate elevated concentrations of heavy metals. These safety standards could be based on harmonized regional criteria for assessment of sewage sludge quality which might be a part of the HELCOM Recommendation on sewage sludge handling.

Since heavy metals are being continuously released from WWTPs, treatment technologies should be advanced to minimize release of these contaminants to the environment. Regional effort to minimize the release of heavy metals to the aquatic environment should not be limited by advancement of wastewater treatment technologies, the sources of heavy metals to sewage, including industrial wastewater and storm waters are to be addressed.

1.4. References

Monisha Jaishankar, Tenzin Tseten, Naresh Anbalagan, Blessy B. Mathew, Krishnamurthy N. Beeregowda. Toxicity, mechanism and health effects of some heavy metals. Interdiscip Toxicol. 2014 Nov 15.

DIRECTIVE 2013/39/EU OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 12 August 2013

Directive 86/278/EEC on the protection of the environment, and in particular of the soil, when sewage sludge is used in agriculture

Good practices in sludge management. 2012. Project on Urban Reduction of Eutrophication (PURE), Turku, Finland.

HELCOM Recommendation 38/1 on sewage sludge handling.

2. Policy brief on phenolic substances: nonyl- and octylphenols

2.1. What are Nonyl- and octylphenols?

Nonyl- and octylphenols are families of organic compounds belonging to a large group of alkylphenols. These families also include large number of isomers. It causes certain difficulty in aggregation and comparison of data supplied from different countries, since the nomenclature of these substances is sometimes unclear.

Nonyl- and octylphenols are mainly manufactured compounds, though unique cases when nonylphenol is produced in nature are also known. These substances are used in industry as antioxidants, lubricating oil additives, laundry and dish detergents, emulsifiers, and solubilizers as well as intermediate products to produce phenolic resins, paints, pesticides and some other commercial products. These phenolic substances are not volatile, assuming that waterborne input is their main pathway to the environment. They are also moderately soluble demonstrating tendency to absorb in soils and sediments.

The toxicity of nonyl- and octylphenols is caused by their ability to mimic hormones and cause reaction of respective receptors. That's why the compounds were classified as endocrine disrupters and included in the HELCOM priority list of contaminants. These substances are capable of interfering with the hormonal system of numerous organisms. The impact includes feminization of aquatic organisms, decrease in male fertility and the survival of juveniles.

Octyl- and nonylophenols are included in the HELCOM List of Priority Hazardous Substances, established by Recommendation 31E/1. The Baltic Sea Action Plan 2021-2030 addressed calling HELCOM Contracting Parties to introduce by 2027 measures based on the best available scientific knowledge and technologies to restrict the use and prevent releases of phenolic compounds (HL21).

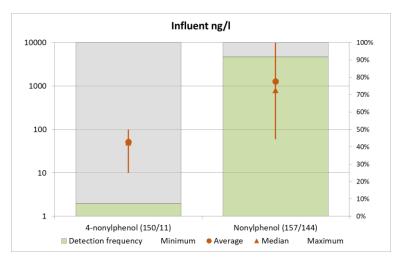
2.2. Observed facts

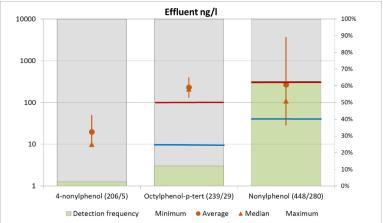
More than thousand and a half measurements of phenolic substances in influents, sludges and effluents from about two hundred WWTPs were reported in response to HELCOM call for micropollutants. Despite nonyl- and octylphenols and their isomers were of specific interest of this call, about four hundred analyses of total monophenols were also reported. Certain inconsistency between reported names of substances and their CAS numbers also slightly complicated the data analysis.

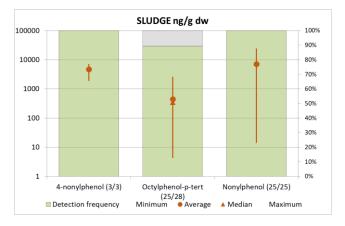
Despite detection limits for phenolic substances vary in an order of magnitude, reported data in general allows adequate evaluation of occurrence of these substances in effluents, especially, nonylphenol. However, most of the data for 4-nonylphenol and p-tert-octylphenol isomers were reported below the detection limits.

Generally, the collated data shows that nonylphenol is the most frequently observed compound in both influents and effluents. Its concentrations vary in the range of three orders of magnitudes. In influents both average and median concentrations are around a thousand ng/l while in effluents average value is seven times lower and median is even ten times lower. Octylphenol and its isomer was not reported for influents and a few samples where 4-nonylephenol was observed in influents demonstrate concentrations much lower than nonylphenol. The same concerns observations of octylphenols and 4-nonylphenol in effluents.

Elevated concentrations of all phenolic substance except for octylphenol were observed in sludge. However, nonylphenol demonstrates the highest average and median values, which are around seven and a half thousands ng/g dry weight. These values for p-tert-octylphenol are ten times lower. There was no data on other phenolic compounds sufficient for statistical analysis reported.







Concentrations of nonyl- and octylphenols. Only concentrations above LOQ are reflected. Red lines indicate AA-EQSs for nonyl- and octylphenols in inland surface waters (DIRECTIVE 2013/39/EU). Blue line indicate AA-EQS for oclylphenol in other surface waters (DIRECTIVE 2013/39/EU) and new chronic EQS for nonylphenol (the Ecotox Centre Eawag-EPF). EQS values are used here for indicative comparison but not for the assessment of contamination level.

There is rather limited information on predicted non-effect concentrations (PNEC) of phenolic substances in sludges and soils. According to data given in the European Union Risk Assessment Report (2002), concentrations of nonylphenols measured in sludge are significantly lower than respective PNECs.

Both average and median concentrations of nonylphenol in effluents are lower than AA-EQS for inland waters but higher than the threshold for new chronic EQS for nonylphenol (the Ecotox Centre Eawag-EPF). However, concentrations in individual samples ten times exceed AA-EQS for inland waters. Average and median for p-tert-octylphenol concentrations exceed both AA-EQSs for this substance. But these values might be overestimated, since the substance was detected only in 12% of measurements.

2.3. Key messages

Data on concentrations of phenolic substances in influents, sludges and effluents from WWTPs compiled through the HELCOM call for micropollutants does not allow comprehensive estimation of the magnitude of input of these substances to the aquatic environment from sewage systems in the Baltic Sea region.

The data demonstrate that both phenolic substances are being currently released to municipal wastewater systems. Especially, it concerns nonylphenol and p-tert-octylphenol isomer. Nonetheless, concentrations in effluents are moderate and only in some cases might lead to deterioration of environmental health of water bodies.

Conventional municipal wastewater treatment plants almost ten times reduce concentrations of phenolic substances in wastewater. However, additional treatment still needs to be applied to minimize releases of these compounds to the aquatic environment.

During wastewater treatment process, phenolic substances tend to be accumulated in sludge. Concentrations of some substances in sludge are significantly elevated but remain below identified PNECs. However, available information is not sufficient for the assessment of risks for soil and ground contamination through application of recycled products based on sewage sludge.

Systematic monitoring of octyl- and nonylphenols as well as their isomers, based on harmonised monitoring methodology, has to be organized across the Baltic Sea region (for the EU member states as implementation of WFD). Analytical methods, providing sufficient quality of measurements, should be elsewhere applied for the monitoring.

Safety requirements for recycling products based on sludges from WWTPs potentially containing phenolic substances need to be developed.

Targeted measures to prevent releases of octyl- and nonylphenols as well as their isomers, need to be developed based on the best available scientific knowledge, to prevent contamination of the aquatic environment.

2.4. References

European Union Risk Assessment Report 4-NONYLPHENOL (BRANCHED) AND NONYLPHENOL. 2002.

DIRECTIVE 2013/39/EU OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 12 August 2013.

Swiss Ecotox Centre: Proposals for Acute and Chronic Quality Standards. 2016.

3. Policy brief on PFAS

3.1. What is PFAS?

Per- and polyfluoroalkyl substances (PFAS) are a large family of synthetic organic chemicals with diverse properties and uses. Since, carbon-fluorine is one of the strongest chemical bonds, all PFAS or their degradation products are highly persistent in the environment, demonstrating tendency of accumulation. Due to their properties PFAS are actively used in industries such as metal plating, textile, manufacturing of fluoropolymers. These substances are also contained in products such as fire-fighting foam, hydraulic oil, ski waxes and some others.

Environmental contamination by PFAS arises from various sources including facilities where these substances are manufactured or used for industrial production as well as releases from products containing them. Significant PFAS contamination has for example been found in groundwater near fire-fighting training sites and airports, where the fire-fighting foams are continuously used. The relative importance of each source is temporally variable, specific to each substance and not well quantified. Some PFAS tend to be transported over long distances in air. Two 8-carbon PFAS (PFOS and PFOA) are included in Stockholm Convention list of persistent organic pollutants.



Source: EuChemS newsletter

Certain PFAS are known to cause toxic effects for reproduction and can harm the development of fetuses, others demonstrate to cause cancer. Some PFAS are also suspected of interfering with the human endocrine (hormonal) system. Due to persistence PFAS tend to be accumulated in the environment. Though, long chained (6 or more fluorinated carbons) PFAS demonstrate bioaccumulation and sorption to sediments and soil, whereas short chain PFAS are more mobile in the aquatic environment. Some PFAS, so-called precursors, can also be transformed to other compounds of this group in the environment. Currently more than 4700 different PFAS are known, and as specific components are banned new substances from the same group are often used as a substitution.

Perfluorooctane sulfonate (PFOS) Perfluorooctanoic acid (PFOA) are included in the HELCOM List of Priority Hazardous Substances, established by Recommendation 31E/1. The Baltic Sea Action Plan 2021-2030 considers per- and polyfluoroalkyl substances as contaminants of emerging concern. It addresses the problem calling to introduce by 2027 measures based on the best available scientific knowledge and technologies to restrict the use and prevent releases of perfluorinated alkyl substances (HL21) and, particularly, to limit the use of firefighting foam containing per- and polyfluoroalkyl substances (PFAS) at sea and in the catchment area and promote sustainable alternatives (HL29).

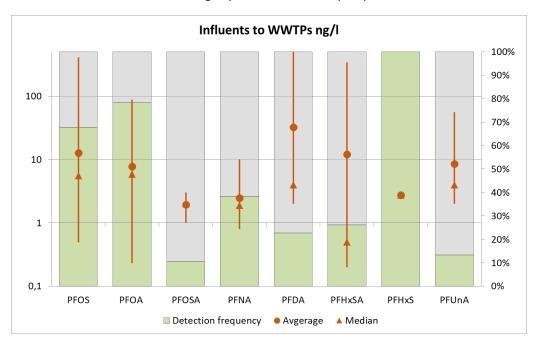
3.2. Facts on PFAS in WWTPs in the Baltic Sea Region

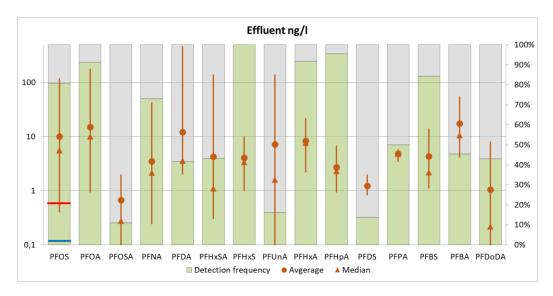
Data on concentrations of fifteen compounds belonging to PFAS group, observed in the period from 2004 to 2018, was reported in response to HELCOM call for data on micropollutants in WWTP. The data massif contains more than three and a half thousands individual measurements of PFAS in influents, sludge and effluents from more than two hundred wastewater treatment plants.

Detection frequency for reported PFAS greatly varies between the compounds, which is to large extent due to variation of analytical detection limits in the range of three orders of magnitude. In some cases, reported detection limits for individual measurements are higher than the annual average Environmental Quality Standards (AA-EQS) established by the EU legislation which subsequently affects the quality of assessment results.

Perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) are the most frequently measured compounds of this group. They were reported for all three matrixes, being detected in more than 70% of samples and demonstrate one of the highest among all reported compounds average concentrations. Though, individual concentrations of some other compounds were observed at the same level, but scarcity of data does not allow reliable assessment.

In general, almost no reduction of concentrations in effluents compared to influents to WWTPs was observed. Even more, PFOA demonstrate remarkable increase of concentration in effluents, which might be the result of degradation of PFOA precursors during wastewater treatment process. The highest average concentrations of PFOS in sludges and slight reduction of its content in effluents compared to influents indicate that PFOS is slightly removed from liquid phase.





Concentrations of PFAS. Only concentrations above LOQ are reflected. Red lines indicate AA-EQSs for in inland surface waters and blue for other surface waters (DIRECTIVE 2013/39/EU). EQS values are used here for indicative comparison but not for the assessment of contamination level

The EU legislation sets Environmental Quality Standards (EQS) only for PFOS in inland and marine waters. The average concentration of PFOS in effluents exceeds more than ten times the AA EQS for inland waters and almost hundred times AA EQS for marine environment. Exceedance of the EQSs reached three orders of magnitude in individual samples.

3.3. Key messages

Data on concentrations of PFAS in influents, sludges and effluents from WWTPs compiled through the HELCOM call for micropollutants provides the most comprehensive information on releases of these substances to the aquatic environment from sewage systems in the Baltic Sea region.

The data demonstrate that several toxic substances belonging to PFAS are currently being released to the aquatic environment through wastewater treatment plants across the region and pose remarkable threat to the Baltic Sea marine environment due to their persistency and ability for accumulation, even though, monitoring in the marine environment does not reveal exceedance of the Environmental Quality Standards at this moment.

Scarcity of observations together with insufficient quality of analytical procedures do not allow to assess prevalence of various types of PFAS (e.g. long-chained, short-chained etc) in the effluents.

Conventional wastewater treatment is inefficient for removal of PFAS from wastewater. In some cases, transformation of substances from precursors might even lead to increasing of their concentrations during wastewater treatment process.

Systematic monitoring of PFAS, based on harmonised monitoring programmes, has to be organized across the Baltic Sea region, for the EU member states taking into consideration established monitoring for the WFD and respective requirements. Analytical methods, providing sufficient quality of measurements, should be elsewhere applied for the monitoring.

Biological effects of PFAS should be further investigated to lay basis for the development of Environmental Quality Standards and subsequently safety requirements for potentially PFAS containing recycling products based on sludges from WWTPs.

General regulation, including restrictions, for the whole PFAS group needs to be developed, based on the best available scientific knowledge to cease continuous contamination of the aquatic environment, and prevent substitution of one toxic PFAS compound by another.

3.4. References

Poly- and perfluoroalkyl substances (PFAS). 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. Brussels, 14.10.2020

DIRECTIVE 2013/39/EU OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 12 August 2013.

Sara Valsecchi, Daniela Conti, Riccardo Crebelli, Stefano Polesello, Marianna Rusconi, Michela Mazzoni, Elisabetta Preziosi, Mario Carere, Luca Lucentini, Emanuele Ferretti, Stefania Balzamo, Maria Gabriella Simeone, Fiorella Aste. Deriving environmental quality standards for perfluorooctanoic acid (PFOA) and related short chain perfluorinated alkyl acids. Journal of Hazardous Materials. 22 April 2016.

Johansson, J. and Undeman, E. 2020. Perfluorooctane sulfonate (PFOS) and other perfluorinated alkyl substances (PFASs) in the Baltic Sea – Sources, transport routes and trends. Helcom Baltic Sea Environment Proceedings n°173.

EuChemS newsletter. August 14, 2020.

4. Policy brief on pharmaceuticals in WWTP

4.1. What are pharmaceuticals?

Pharmaceuticals are natural or synthetic substances of various chemical composition which are used in the diagnosis, treatment, or prevention of disease and for restoring, correcting, or modifying organic functions. Most pharmaceuticals are designed to act at low concentrations so that they can be tolerated by the human or animal body, and to last long enough to have their intended effect. Pharmaceuticals are classified into different therapeutic groups according to their chemical characteristics, structure and how they are used to treat specific disease. Pharmaceuticals are vital for well-being of modern society as the treatment of many diseases in humans and animals relies on effective pharmaceuticals.

Industrial releases of pharmaceuticals can be major local sources of active pharmaceutical ingredients (APIs) to the environment (e.g. Fick et al. 2009), and industrial emissions can increase the API load received at WWTPs (Scott et al. 2018). For the Baltic Sea region, comprehensive estimates on industrial emissions are currently lacking. Wastewater treatment plants are considered as a major pathway of pharmaceuticals to environment in the Baltic Sea region. Pharmaceuticals occur in sewage as they are excreted or washed off as well as thrown away into sinks and toilets. As pharmaceuticals are also widely used in veterinary medicine or even prophylactically in animal husbandry and fish farms, spreading manure or releases from aquaculture are important pathways to the environment. Potentially, pharmaceuticals can leak into the environment from landfills.

Since pharmaceuticals are designed to affect biological processes at low concentrations, their occurrence in the environment directly affects the ecological balance. Some of them are also persistent in the environment, spread through water and soil and accumulate in sediments, plants and wildlife. Furthermore, the metabolites of some pharmaceuticals can transform back into the active substance in WWTP conditions and in the environment. Some pharmaceuticals have toxic effects to biota, such as endocrine disruption properties which cause problems in e.g. reproduction. Antimicrobial (antibiotic and antifungal) pharmaceuticals may play a role in accelerating the development, maintenance and spread of resistant bacteria and fungi. But in many cases environmental effects of pharmaceuticals are not well known. Also, the possible combined effects from exposure to many pharmaceuticals and other chemicals is not well known.

Pharmaceuticals are recognized as contaminant of emerging concern in the Baltic Sea Action Plan 2021-2030. It includes a number of actions aimed to improve existing knowledge on the occurrence and environmental effects of pharmaceuticals (HL22, HL24), make this knowledge available for broad expert society (HL22), identify priority substances (HL23) and undertake actions to mitigate the release of pharmaceuticals to the marine environment (HL25-27).

4.2. Observed facts

Data on pharmaceutical in wastewater treatment plants in the Baltic Sea region was compiled through HELCOM data calls and processed within the CWPharma project. The final data set contained over 10 000 data points from Denmark, Estonia, Finland, Germany, Latvia, Poland and Sweden, covering altogether over 100 WWTPs.

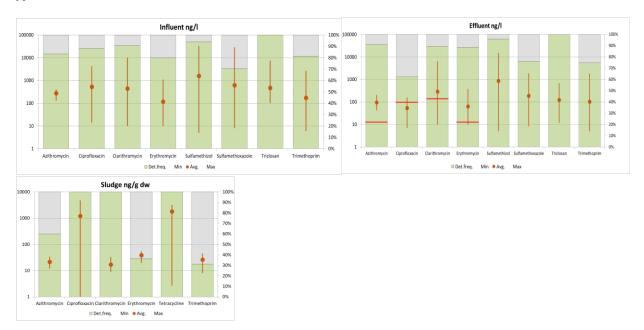
The reported data covers altogether 117 individual APIs, which were divided into 11 therapeutic groups. Two thirds of the reported data concern substances from three groups: anti-inflammatory and analgesic substances, antimicrobial and antiparasitic, and hormones and hormone antagonists.

Out of the 29 APIs classified as antimicrobial and antiparasitic, 24 were detected in at least one sample. Most of the data (more than 400 data points for each API) were reported for sulfamethoxazole, trimethoprim, triclosan and sulfamethizol, with detection frequencies ranging from 72% to 100%. The detection frequencies of erythromycin, ciprofloxacin, clarithromycin and azithromycin, included in the updated Water Framework Directive (WFD) watch list (DIRECTIVE 2013/39/EU), fall within the same range. Concentrations of the latter set of APIs in effluents is somewhat lower than in influents. However, the average concentrations of erythromycin, clarithromycin and azithromycin in effluent water exceed the proposed AA-EQSs. Concentrations in sludges vary widely between APIs but the highest are displayed by ciprofloxacin and tetracycline which were detected in sludge in a hundred percent of samples.

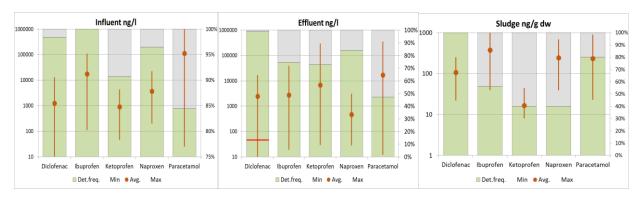
Out of the 17 APIs categorized as anti-inflammatory and analgesic substances 13 were found in at least one sample. Most of the countries reported data on ibuprofen, paracetamol, diclofenac, naproxen and ketoprofen. They were detected in about 80% of samples from influents, sludge and effluents. Average concentrations of ibuprofen, paracetamol and naproxen in effluents were ten times lower than in influents. However, diclofenac and ketoprofen demonstrate reverse tendency. For example, average concentration of ketoprofen in effluents were several times higher than in inflowing sewage water. Average concentrations of ibuprofen, paracetamol and naproxen in sludge several times exceed a hundred ng/g dw. Concentration of diclofenac proposed as EQS for HELCOM pre-core indicator is exceeded in 93 percent of quantified samples, and in average is fifty times higher than the EQS while individual measurements reveal thousand-fold exceedances.

Out of the 15 APIs classified as hormones and hormone antagonists, 11 were detected at least in one sample. The most frequently reported are 17β -estradiol, 17α -ethinylestradiol and estrone, detected in 54, 36 and 82 percent of samples respectively. These three hormones are in the Water Framework Directive watch list (DIRECTIVE 2013/39/EU). Average concentrations of these hormones in effluents are approximately one tenth of that in influents. However, their average concentrations in effluent samples still exceed AA-EQSs more than ten-fold, with individual samples showing over hundred-fold exceedances. The reported analytical detection limits for 17β -estradiol and 17α -ethinylestradiol are higher than their respective AA-EQSs.

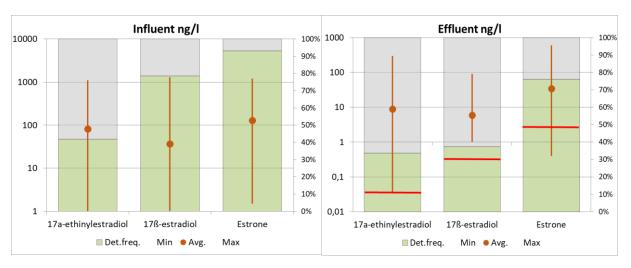
Α



В



C



Concentrations of antimicrobial and antiparasitic APIs (A), anti-inflammatory and analgesics (B) and hormones (C). Only concentrations above LOQ are reflected. Red lines in pics A and B indicate AA-EQSs for inland waters given in DIRECTIVE 2013/39/EU, red line in pic B indicates threshold for <u>HELCOM pre-Core</u> <u>indicator on diclofenac</u>. EQS values are used here for indicative comparison but not for the assessment of contamination level.

4.3. Key messages

The collated and analysed data on pharmaceuticals in WWTPs — derived from influents, effluents and sludge — is the most comprehensive compilation of this type of data in the Baltic Sea region. However, the analysis demonstrates that large knowledge gaps still exist. For example, several APIs are only analysed in one of the three matrices, but to assess the environmental impact of the micropollutants, and the need for measures to remove them, a holistic overview on their presence and concentration levels in influents, effluents and sludge alike is needed, as well as better geographical coverage.

The assessment of risk caused by pharmaceuticals to the environment requires comparison of their concentrations in environmental samples to relevant ecotoxicological data. This demands further investigation of environmental effects of various active pharmaceutical ingredients and identification of their non-effect concentrations. Since distribution of manure or the use of sewage-based recycled products might be a pathway for some pharmaceuticals to the aquatic environment, respective safety standards are to be developed.

Detection limits and analysis method should be aligned among countries. Analytical methods, sufficient to detect APIs at concentrations close to respective environmental quality standards, should be applied throughout the region.

A database containing information on the occurrence and concentrations of APIs in wastewater, inland surface waters, ground waters and in the marine environment is to be established and made available for expert community. This would help creating a scientifically sound basis for strengthening the management cycle for this group of hazardous substances. This database would also serve as the main source of information for the development of respective indicators of the state of the Baltic Sea or advancement of existing ones (e.g. diclofenac).

Concentrations of almost all most frequently reported pharmaceuticals, for which environmental quality standards (EQS) in river waters have been proposed, demonstrate high level of exceedance of these EQSs in WWTPs effluents. Even the limited data compiled in this report proves that active pharmaceutical substances, including those with scientifically proven environmental effect, are continuously released.

In general, many substances from all 11 therapeutic groups are frequently detected, demonstrating concentrations in effluents at similar level as in influents. In some cases, such as diclofenac and ketoprofen, concentrations in effluents are even higher than in influents. It demonstrates that conventional wastewater treatment is not efficient for removing pharmaceuticals from sewage water.

Low removal level of APIs from wastewater, limited capacity to restrict their use and their continuous input to the aquatic environment prominently show the need of more measures to minimize their release. These measures should not only be focused on improving technologies at WWTPs to increase their removal efficiency but also target pharmaceuticals at their source (e.g. prescription, consumption reduction, responsible handling and disposal, pretreatment for large hospitals and pharmaceutical manufactories) (e.g. Thisgaard et al. 2020).

4.4. References

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