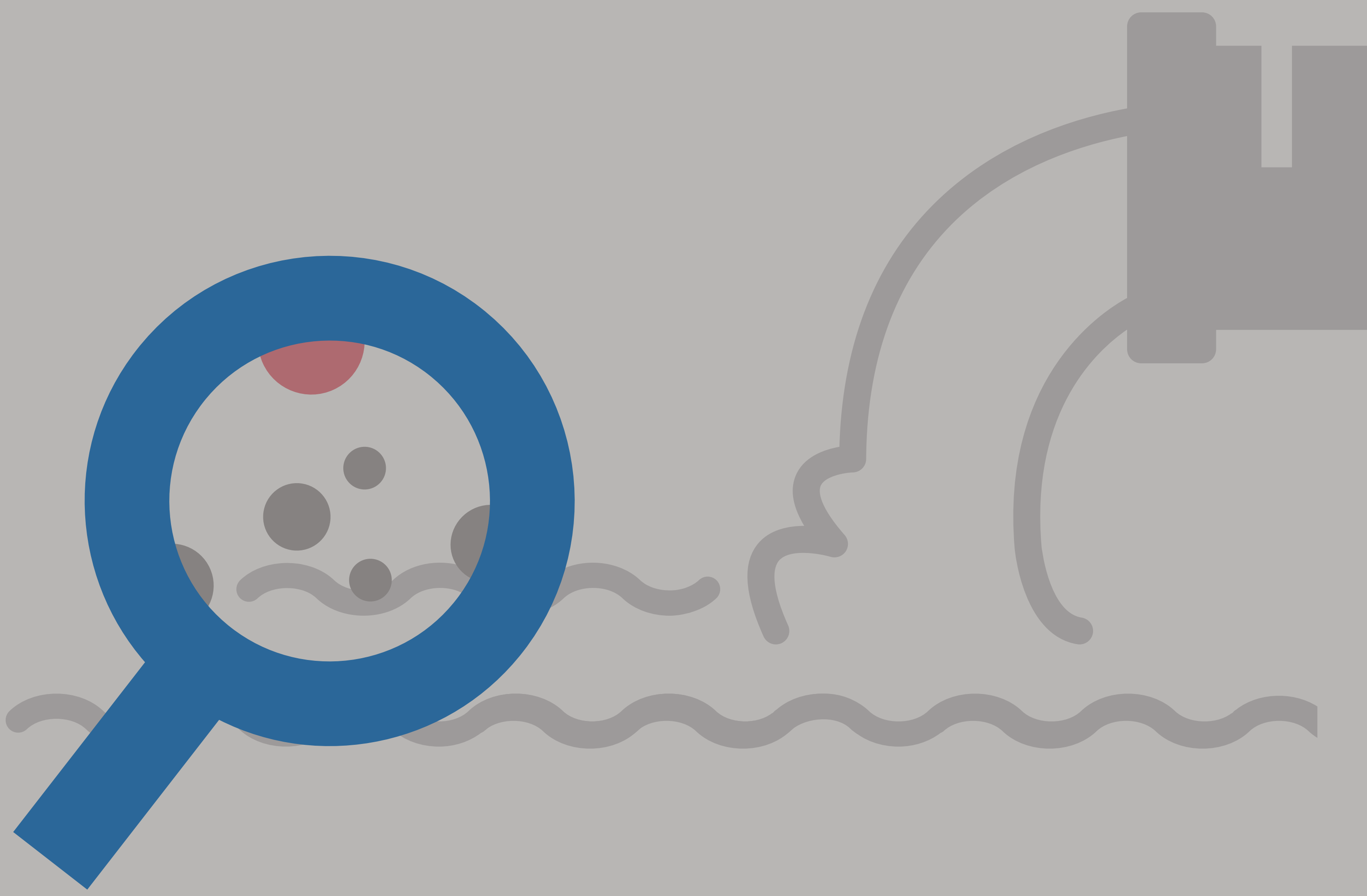
PRESSURE

Micropollutants
in wastewater and sewage sludge

Hazardous substances

BSEP n°185



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Contents

1. Introduction

The latest HELCOM assessment (HOLAS II) showed that pressure on the marine environment from contaminants was high in all parts of the Baltic Sea. The existing HELCOM framework for hazardous substances in general is mainly based on a limited number of priority contaminants and a list of about a dozen of measures to prevent their input to the marine environment. Most of the technical regulations contained in HELCOM Recommendations related to hazardous substances are currently included in legal acts of the EU and Russia. HELCOM framework for hazardous substances is currently not able to account for the full diversity of sources and pathways of contaminants to the Baltic Sea, or the risks posed to the Baltic Sea environment. The existing framework is unable to timely react on emerging challenges in the continuously transforming pattern of chemicals used in industry and emerging in consumer products, nor risks posed by co-occurring hazardous substances.

HELCOM Ministerial Declaration 2018 pointed out that among other issues levels of hazardous substances continue to be elevated and a cause for concern. Further the Ministerial Meeting re-iterated that in the agreed update of the BSAP the overall goal for hazardous substances remains unchanged - Baltic Sea with life undisturbed by hazardous substances. The Ministers agreed that HELCOM should address effectiveness of measures and recommendations for legacy pollutants and to identify the scale of problems of contaminants of emerging concern, including micropollutants in coastal and marine waters and, based on this knowledge, to consider possible cost-effective mitigation measures.

Pathways of hazardous substances released from industries are not always well known, but they are assumed to large extent end up in wastewater treatment plants (WWTP). Contaminants from households (human consumption) also usually end up in WWTPs. In areas that are not connected to centralized sewage system, contaminants form households might be released directly to the environment with limited retention in local treatment systems. Sewage sludge from these areas, depending on handling practices may also become a source of contamination.

Since WWTPs receive contaminants from various sources (households, industries, hospitals etc.), their effluents are the points where the highest concentrations of chemicals released to the aquatic environment might be observed, even when the sewage water is treated according to existing standards. Thus, effluents of WWTP can provide information on inputs of not only legacy pollutants, already accumulated in the environment in detectable concentrations, but also on the chemicals which have been recently marketed for industrial processes or consumption products and occur in the environment in extremely low, often undetectable concentrations. These micropollutants and contaminants of emerging concern are the target of the current study. In addition to data on effluents, the study includes available information on concentrations in influents to WWTPs and sludges. This paper does not consider hot spots, where sewage is intentionally or unintentionally released without treatment but data reported by WWTPs which supposedly function in normal operational mode.

The report contains comparison of observed concentrations of micropollutants in WWTPs' effluents with environment quality standards (EQSs) established for fresh and marine waters. It is fully acknowledged that these EQSs are not directly applicable for the assessment of effluents contamination, as the dilution in mixing zones in water bodies is not considered. Thus, the EQSs are used in the report only for indicative purposes to highlight potential magnitude of the problem.

Identification of the scope of the study

This report does not strive to cover all chemicals which can be found in wastewater as this is nearly impossible bearing in mind limited time and resources and the number of existing substances. This study is the implementation of the HELCOM joint action on micropollutants in the WWTP effluents. The joint action was one of 14 joint actions agreed by HOD 49-2015 (Outcome of HOD 49-2015, para 4.69). The action includes two major parts: the compilation of data on micropollutants and obtaining information on the advanced wastewater treatment techniques.

The starting point of this work was from a questionnaire, distributed among Contracting Parties, to reveal chemicals of high concern which they consider or believed to be transported to the Baltic Sea and thus cause a threat. These identified substances served to limit the number of pollutants and will thus be the focal point of this report. The top four identified substance groups of highest concern were the endocrine disruptors as nonylphenols and octylphenols, heavy metals, the group of per- and polyfluoroalkyl substances (PFAS) and pharmaceutical substances. The results of the questionnaire are discussed in more detail in the Sixth HELCOM Pollution Load Compilation (PLC-6) report "Inputs of hazardous substances to the Baltic Sea" (BSEP No 162, HELCOM 2019). The questionnaire also served to assess availability of data on measurements of those substances. As the next step, HELCOM countries were invited to report available data on observation of substances of these groups in WWTPs, rivers and coastal waters utilizing unified reporting template. As mentioned above, this report will focus on the data from WWTPs, while observations in rivers and coastal waters are considered separately in the thematic report on hazardous substances of the Seventh HELCOM Pollution Load Compilation (PLC-7) report "Inputs of hazardous substances to the Baltic Sea" (BSEP No 179, HELCOM 2021).

2. Collection of information and data coverage

The data on measurements of micropollutants were collected through regional data calls, organized by HELCOM Pressure Working Group. In the data call the data on nonylphenols, and octylphenols, heavy metals and perfluoroalkyl substances (PFAS) was requested for the period 2004-2016. The data on pharmaceuticals were supplied by Contracting Parties via two data calls: the status report on pharmaceuticals (SR) in the year 2015 and the micropollutant (MP) data-call (2017). Thus, only data which was not reported in the first call were additionally collected. Data for both data calls were collated and analysed as presented in the corresponding section of this report.

Overall, seven Contracting Parties provided data on the substances of selected groups (table 1). Lithuania provided data only for coastal water and rivers. This data is not included in this report but included in the PLC-7 thematic report on hazardous substances. Russia did not submit any data on the requested substance groups.

The requested information included substance name, CAS-number, sampled matrix (surface water, influent, effluent or sludge), date of sampling, site/WWTP name or other ID and coordinates, WWTP meta data such as treated volume of wastewater, connected PEs, nitrogen removal, type of treatment, sludge handling and min/max/mean measured concentrations, analytical method applied and detection/quantification limit. Basic "cleaning" of the data included e.g. correction of coordinates, correction of obvious typos and implausible units for reported concentrations and detection limits, harmonization of names and CAS numbers used by the different CPs for the measured parameters, linking of WWTP meta data to sampled WWTPs, separation of reported concentrations above, under or at the detection or quantification limit. Information regarding any filtering of samples before instrumental analysis is missing in the dataset, and hence comparisons between levels observed in the different countries are uncertain as particle bound chemicals may or may not be included in the reported concentrations. Note also that the limit of quantification (LOQ) and/or limit of detection (LOD) was requested for each data point, however this information was often missing. In the following the LOD and LOQ are both referred to as the detection limit (DL).

Table 1. Overview of reported data concerning WWTPs.

	Denmark	Estonia	Finland	Germany	Latvia	Poland	Sweden
phenols	x	x*		x		x	x
PFAS	x			x	x	x	x
metals	x	x		x	x	x	x
pharmaceuticals	x	x	x	x	x	x	x

*Estonian data for WWTPs are on monophenols only.

In the data call for micropollutants in WWTPs the following number of data points was reported in 241 identifiable WWTPs: 1680 data points for phenolic substances, 3730 for PFAS and 6920 for heavy metals (figures 1 a and b). The reported data include observations of these contaminants in influents, sludges and effluents of the WWTPs (table 2). Altogether, the reported data on pharmaceuticals includes 3928 and 6091 data points for the MP and SR data-calls, respectively (table 8). Data on pharmaceuticals were reported for 73 WWTPs in the MP data-call and for 79 in the ST data-call. With 50 WWTPs for which data was reported for both data calls, the total coverage is 102 WWTPs (figure 2). Detailed overviews of the data for each group of chemicals are given in the respective chapters.

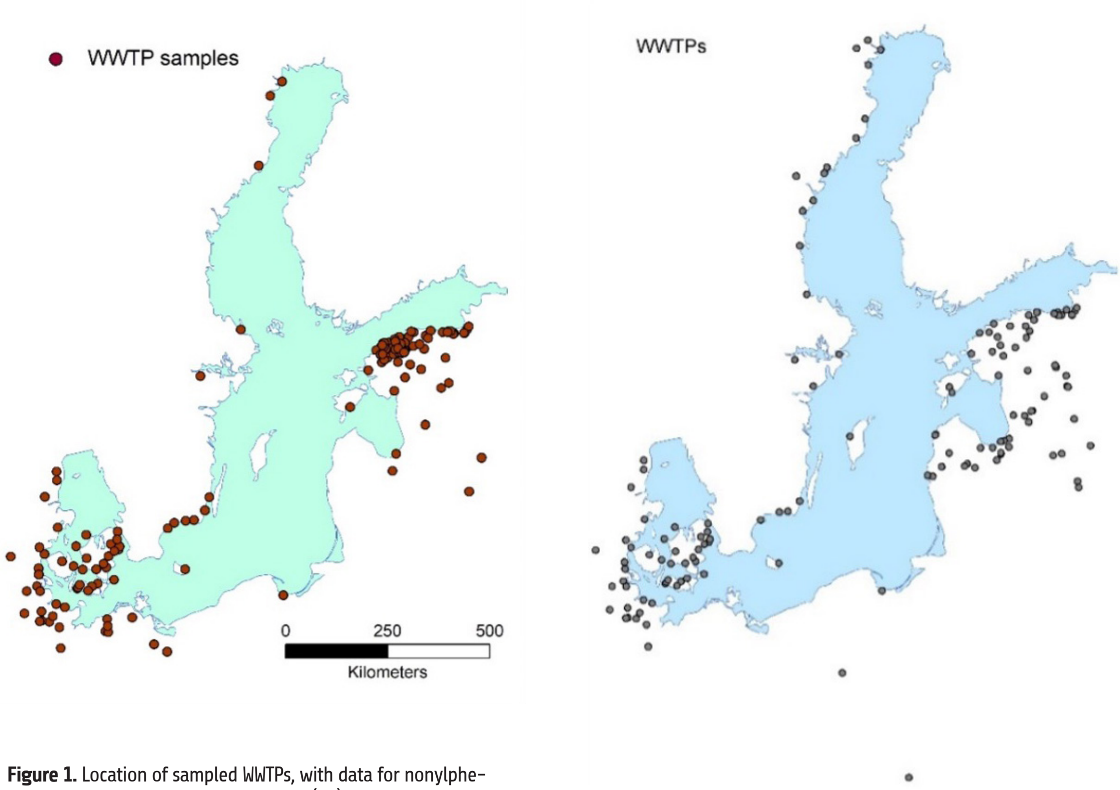

Figure 1. Location of sampled WWTPs, with data for nonylphenols, octylphenols and PFAS on the left (1a) and data for metals on the right (1b)

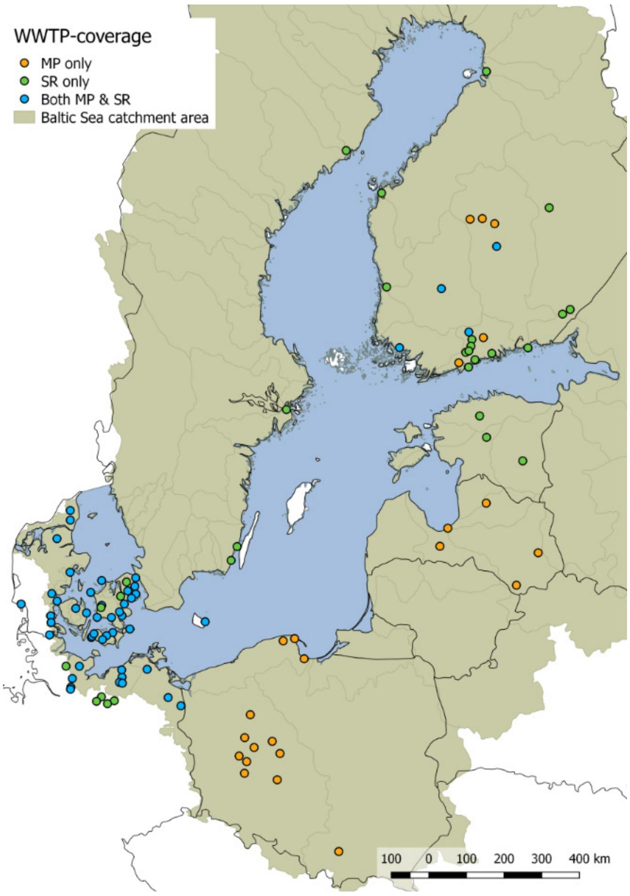

Figure 2. Combined spatial coverage of the data points reported for the two data-calls on pharmaceuticals, collected via the micropollutant (MP) and status report on pharmaceuticals (SR) data call.

Table 2. Overview of the reported data on observations of selected chemicals in influents, effluents and sludges of WWTPs.

		Denmark	Estonia	Germany	Latvia	Poland	Sweden
	WWTPs						
phenols	Effluent	x	x	x			x
	Influent	x					
	Sludge		x				x
PFAS	Effluent	x		x	x	x	x
	Influent	x				x	
	Sludge			x			x
metals	Effluent	x	x	x	x	x	x
	Influent	x	x		x	x	
	Sludge		x			x	x

3. Phenolic substances

3.1. Overview of the data on phenolic substances

Data on concentrations of a range of alkylphenols and ethoxylates were reported in respond to the HELCOM data call to its Contracting Parties. However, different combinations of names and CAS numbers were used in the reporting. This situation made the aggregation and comparison of data from the different countries difficult as it is not always clear which substances have been analysed. The confusion seems to stem partly from unclear nomenclature of these substances and unclear guidance in the EU's EQS directive regarding which molecules are included under e.g. the name "Nonylphenols" (see below). Thus, before embarking on the data analysis and description, some clarification of the nomenclature of the reported compounds is needed. Table 3 shows the chemical names and CAS number used by the CPs in the submitted data files, and the "Harmonized CAS" which indicates which name and CAS combinations that were treated as the same analysed group of chemicals in this analysis. Swedish and Finnish data on nonylphenol CAS 84852-12-3 are assumed to be equal to nonylphenol CAS 25154-52-3 as this is (in most cases) the only parameter measured. It can also be noted that different analytical instrumentation and methods are used by the Contracting Parties. Taken together, these circumstances introduce uncertainty in the data analysis for these substances. See also additional information on this matter in the Annex 1 (extra information on nonylphenols).

The detection frequency of phenolic substances in effluents, influents and sludges of WWTPs is given in table 4. The table illustrates that nonylphenol is the most frequently measured and the most frequently detected compound from this group which assumes that the data on its concentration is the most reliable. Since, monophenols, reported by Estonia, include any organic compound containing one phenolic hydroxyl group, their detection in almost all samples is natural. But this information does not concern the occurrence of nonyl- and octyl-phenols and their isomers, the substances with their hormone-like structures exhibit features characterizing them as endocrine disruptors. We should also admit that the detection frequency depends on the detection limits of analytical methods used in different countries. Broad variation of detection limits of the reported data significantly increases uncertainty of the assessment.

Table 3. Names, CAS-numbers and analytical instrument/method reported by Contracting Parties, and harmonized CAS used to aggregate data in the current data analysis.

	Reported name	Reported CAS	Analytical method	Harmonized CAS
Sweden	4-nonylphenol	104-40-5	GC-MS	104-40-5
	4-nonylphenol (branched)	84852-15-3	GC-MS	25154-52-3
Germany	Nonylphenol-p	25154-52-3	EN ISO 18857	25154-52-3
Denmark	4-nonylphenol	104-40-5	GC-MS	104-40-5
	Nonylphenol	25154-52-3	GC-MS	25154-52-3
Poland	4-nonylphenol	104-40-5	SPE-GC/MS(SIM)	104-40-5

Table 4. Detection frequency of phenolic substances.

Matrices	Country	Nonylphenol 25154-52-3	4-nonylphenol 104-40-5	Octylphenol 1806-26-4	P-tert-octylphenol 140-66-9	monophenols 108-95-2
		number of detected/number of totals				
Effluents	Sweden	16/31	0/3	0/3	23/32	
	Denmark	113/209	5/203			
	Estonia					393/395
	Germany	152/208		0/12	6/207	
	Total	281/448	5/206	0/15	29/239	393/395
	Det freq	**63%**	**2%**	**0%**	**12%**	**99%**
Sludge	Sweden	25/25	3/3	3/3	25/28	
	Estonia					8/8
	Total	25/25	3/3	3/3	25/28	8/8
	Det freq	**100%**	**100%**	**100%**	**89%**	**100%**
Influents	Denmark	144/157	11/150			
	Total	144/157	11/150			
	Det freq	**92%**	**7%**	**100%**	**100%**	

3.2. Concentrations of phenolic substances in WWTP influents, effluents and sludge

Influents

Only observations of nonylphenol and its isomer 4-nonylphenol in influents were reported (CAS 2554-52-3 and 104-40-5). Nonylphenol was detected in 92% of the reported samples, while 4-nonylphenol only in 7% samples (figure 3). Concentrations of nonylphenol vary in a range of more than two orders of magnitude from 50 to 12000 ng/l, with average concentration 1276 and median 805 ng/l (table 5). Detection limit (LOD) is reported for 93% of measurements as 50 ng/l. In general, nonylphenol demonstrate much higher concentrations in influents than its isomer 4-nonylphenol. The latter was observed in concentrations varying from 10 to 100 ng/l. Average and median values for concentrations of 4-nonylphenol are almost equal constituting 52 and 50 ng/l respectively.

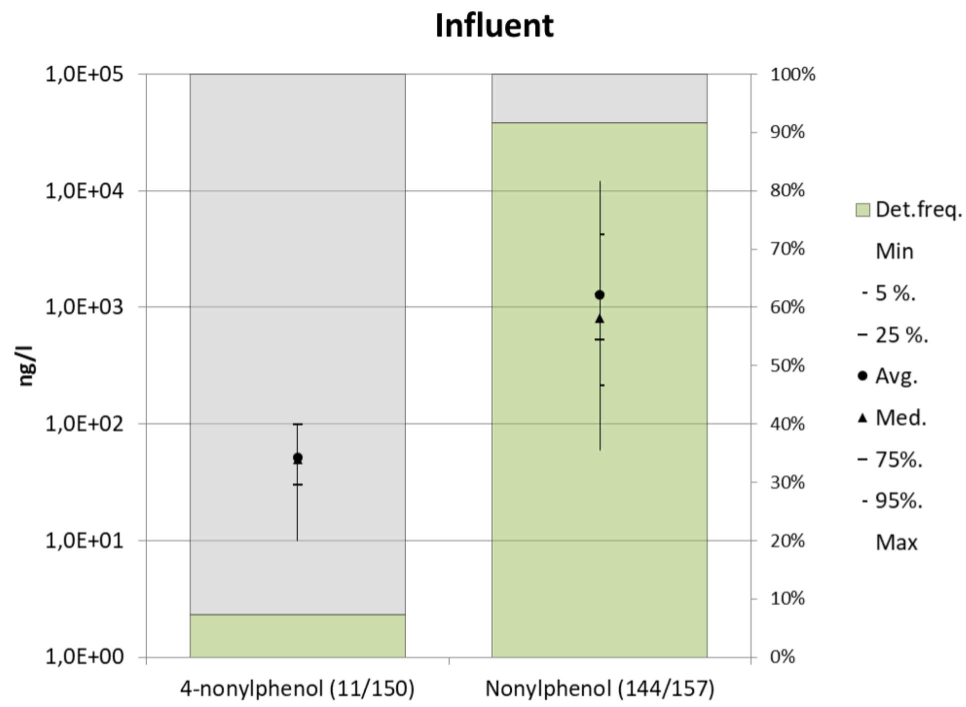

Figure 3. Detected concentrations, detection frequencies and the number of data points of nonylphenol and 4-nonylphenol in WWTP influents. The line with markings presents concentrations and the green bars show the detection frequencies. The number of samples is presented on the horizontal axis.

Table 5. Minimum, maximum, average and median concentrations of nonylphenol and 4-nonylphenol in WWTPs influents.

conc. ng/l	4-nonylphenol	nonylphenol
Min	10	60
Avg.	52	1276
Med.	50	805
Max	100	12000

Sludge

A few data on concentrations of phenolic substances in sewage sludge were reported in the data call for micropollutants in the WWTPs. However, nonylphenols and octylphenols as well as their isomers were detected in almost all reported samples (figure 4 and table 4). Nonylphenol (CAS 25154-52-3) was detected in all 25 samples. Observed concentrations vary in more than four orders of magnitude in some samples exceeding 10000 ng/g dw (table 6). Its isomer 4-nonylphenol, reported in only three observation points, was also identified in all samples exhibiting concentrations of similar magnitude. Only three octylphenol (CAS 1806-26-4) data points were reported. But all three reported concentrations are equal to 1 ng/g dw, which indicates low reliability of reported data. Much better data was reported for its isomer – p-tert-octylphenol (CAS 140-66-9). Measured concentrations vary in the same order of magnitude as concentrations of nonylphenol. However, the average level - 450 ng/g dw - is ten times lower than for nonylphenol. There was no information on detection limits for phenolic compounds in sewage sludge reported. The only exception is three p-tert-octylphenol measurements indicating concentrations below 60, 70 and 330 ng/g dw.

There is no common view on PNEC and other limit values for phenolic substances in solid matters such as sewage sludge and soils due to scarcity of effect data. European Union Risk Assessment Report (2002) provides a compilation of limit values for nonylphenol and its isomer in sludges and soils accepted in different countries by that time. The report contains information that limit value for these compounds in sludge applied for farmland set in Denmark as 10 mg/kg dw (10000 ng/g dw) since 2000 and in Sweden as 50 mg/kg dw (50000 ng/g dw) since 1997.

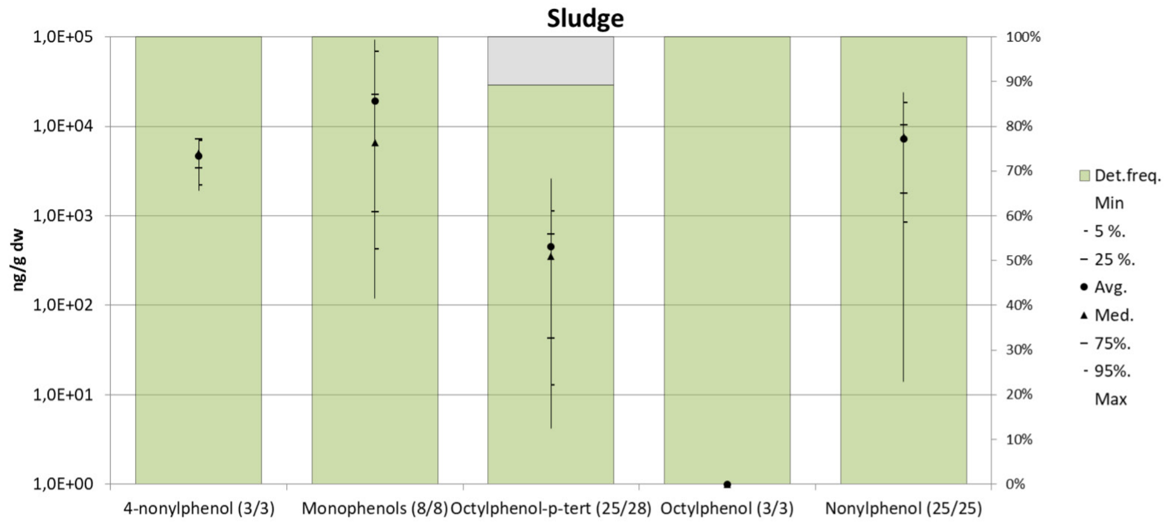

Figure 4. Detected concentrations, detection frequencies and the number of data points of phenolic substances in WWTP sludge. The line with markings presents concentrations and the green bars show the detection frequencies. The number of samples is presented on the horizontal axis.

Table 6. Minimum, maximum, average and median concentrations of phenolic substances in WWTP sludge (ng/g dw).

	4-nonylphenol	Monophenols	P-tert-octylphenol	Octylphenol	Nonylphenol
Min	1900	120	4	1	14
Avg.	4700	19027	448	1	7202
Med.	5000	6525	350	1	7600
Max	7200	93400	2600	1	24000

Effluents

The range of measured concentrations of phenolic substances above detection limits in effluents of individual WWTPs is broad, covering more than two orders of magnitude for some of them (figure 5 and table 7). Detection frequency is relatively high only for nonylphenol, which was detected in 63% of cases. There were no concentrations of octylphenol above detection limit measured and p-tert-octylphenol detected only in 12% and 4-nonylphenol in 2% of reported samples.

Concentrations of nonylphenol in effluents vary from 28 to 3700 ng/l. Average concentration of nonylphenol for the whole reported dataset is 269 ng/l while median is much lower 110 ng/l. It indicates that almost a half of measured concentrations are below 100 ng/l and elevated average value is caused by 25% of measurements with 5% of samples displaying concentrations higher than 1000 ng/l. A few datapoints where 4-nonylphenol isomer occurs, display range of concentrations within 10 and 50 ng/l, which is on the level of lowest reported concentrations of nonylphenol. Since 4-nonylphenol was detected above detection limit only in 5 samples, description of statistical distribution of the reported concentrations does not bring added value to this study.

Octylphenol was not detected in any of 15 reported samples. Thus, it can be assumed that its concentrations are extremely low in efflu-

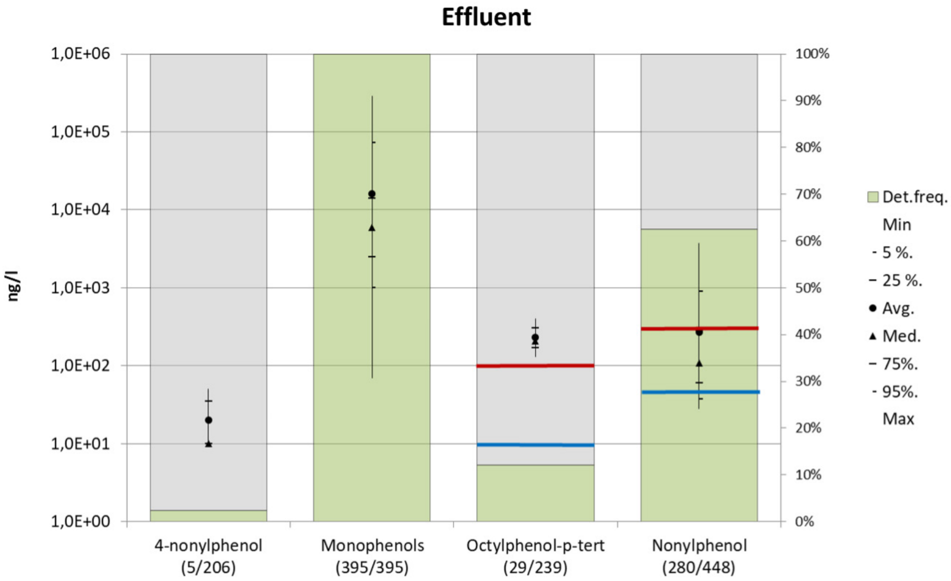

Figure 5. Detected concentrations, detection frequencies and the number of data points of phenolic substances in WWTP effluents. The line with markings presents concentrations and the green bars show the detection frequencies. The number of samples is presented on the horizontal axis. Blue lines display AA-EQS for inland waters. Red lines display chronic EQS for nonylphenol and EQS for octylphenol in marine waters. EQS values are used here for indicative comparison but not for the assessment of contamination level.

Table 7. Minimum, maximum, average and median concentrations of phenolic substances in WWTP effluents.

conc. ng/l	4-nonylphenol	Monophenols	P-tert-octylphenol	Nonylphenol
Min	10	70	130	28
Avg.	20	16107	232	268
Med.	10	6000	210	109
Max	50	290600	400	3700

ents. Concentrations of its isomer p-tert-octylphenol vary from 130 to 400 ng/l. Average value 232 ng/l and median 210 ng/l indicate relatively even distribution of observed concentrations within the interval.

Detection limits of analytical methods to measure concentrations of phenolic substances in effluents were reported for 97% of cases. Reported detection limits for nonylphenol vary in interval from 10 to 200 ng/l. However, 95% of reported detection limits are equal or below 50 ng/l. Detection limits for its 4-nonylphenol isomer are even lower varying from 1.9 to 50 ng/l. But 97% of reported measurements were performed with accuracy of 10 ng/l. Since, detected concentrations of this substance rarely exceed 10 ng/l, its detection frequency is extremely low. Detection limits for p-tert-octylphenol (primarily reported as LOQ) vary from 2 to 80 ng/l. But detection limits below 10 ng/l were reported for a few measurements. Since, most data points demonstrate concentrations of p-tert-octylphenol below detection limits, given assessment of its occurrence in WWTP effluents might be overestimated.

A threshold of 300 ng/l is currently set as limit for the annual average concentration of nonylphenols (CAS 2554-52-3) in surface water (AA-EQS specified in Directive 2013/39/E). Both median and average values for nonylphenol concentrations in effluents are below this threshold and only some cases (less than 25%) are close to or above this threshold (figure 5). It means that in some cases the EQS level for water in receiving body with a low dilution factor may be exceeded. The Swiss Ecotox Centre Eawag-EPFL has suggested a new and lower chronic EQS of 43 ng/l. This limit is exceeded in more than 75% of WWTP effluent samples.

Data for p-tert-octylphenol in effluents reveals exceedance of EQS-levels for both inland and marine waters (figure 5) in all samples, where the substance occurs in concentrations above detection limit. However, bearing in mind that detection frequency for p-tert-octylphenol is only 12%, its low concentrations might be omitted in this assessment. Since, AA-EQS value for p-tert-octylphenol in marine water is as low as 10 ng/l, reported detection limits are not sufficient for reliable assessment of its occurrence in the aquatic environment.

3.3. Brief summary

Despite of the scarcity of data on observations of phenolic compounds in WWTPs, some general conclusions can be made. In general, compiled data on concentrations of phenolic substances in influents, effluents and sludges of WWTPs in the Baltic Sea region, demonstrate presence of these compounds in wastewater and proves that some of them are currently being released to the aquatic environment through the sewerage systems. The most reliable data obtained for nonylphenol demonstrate high concentrations of this phenolic substance in wastewaters entering the WWTP. But in average, concentrations in effluents are moderate, rarely exceeding current EQS levels. Average concentration of nonylphenol in effluents is 5 times lower than in influents and median is more than 7 times lower. Elevated concentrations of nonylphenol in sewage sludges prove its removal from wastewater during the treatment process and accumulation in sludges. At the same time, comparison of the data on nonylphenol concentrations in sludge with available information on criteria for sewage sludges quality demonstrate moderate level of contamination of sewage sludges by this compound. Reported data on observations of octylphenol in sewage sludge does not allow to evaluate the level of contamination but its isomer p-tert-octylphenol was observed in sludge in concentrations more than 10 times lower than nonylphenol. Average concentrations of p-tert-octylphenol in effluents are comparable with concentration of nonylphenol and median even twice exceeds respective value for nonylphenol. However, as it was explained above, level of contamination of effluents by p-tert-octylphenol might be overestimated due to scarcity of reported data.

4. Perfluoroalkyl substances

4.1. Data overview for PFAS

In respond to HELCOM data call data on 17 perfluoroalkyl substances (PFAS) was reported. Number of samples and detection frequencies of these compounds in influents, effluents and sludges of WWTPs is given in table 8. For the whole group the most data points were reported for effluents, more than 2000 measurements. A bit less data points, 1274, were reported for influents, and fewer measurements were reported for sludges, less than 500. Most of the data on observations in effluents and influents originate from Denmark. Most frequently (72% of data points above detection limit), contaminants of the PFAS group were observed in sludges. Concentrations of compounds from this group above detection limit were observed only in 37% of influents and in about 53% of effluents.

Limits of detection (LOD) or limits of quantification (LOQ) were reported for about 80% of measurements in influents and effluents. So, LOD was mainly reported, and LOQs were reported only in a few cases. LODs deviate in broad range of values from 0.04 to 10 ng/l. For measurements in sewage sludge LODs were reported to all samples as 5 ng/g dw.

4.2. Concentrations in WWTP influents, effluents and sludge

Influents

Data on observations of PFAS in influents in the period 2011-2016 were reported only by Denmark and Poland, with the most data supplied by Denmark. Only eight PFASs were detected in influents to WWTPs according to the data reported in response to HELCOM data call on micropollutants in WWTPs (table 8). The most frequently detected compounds in influents are perfluorooctane sulfonate (PFOS), perfluorooctanoic acid (PFOA) and perfluorohexane sulfonate (PFHxS). In more than 180 measurements reported for PFOS and PFOA these two compounds were detected in 68 and 78 percent of cases, respectively. Concentrations of PFOS and PFOA in influents deviate in a broad range covering almost 3 orders of magnitude (figure 6). PFOS concentrations above detection limit vary from 0.49 to 410 ng/l. Concentrations of PFOA vary from 0.23 to 88 ng/l. Concentrations of PFHxS above detection limit was observed in all reported samples, but only three samples were reported. Concentrations observed in all three samples are deviating in a narrow interval from 2.67 to 2.83 ng/l with reported detection limit 0.08 ng/l.

Average concentrations of PFOS and PFOA observed in influents are relatively close - 12.7 and 7.8 ng/l respectively (table 9). Median values for reported concentrations of these substances are also very close and both lower than the average concentrations, which indicates that the most part of samples were below the average. Less than 25% of the measured PFOS concentrations were above average value, while for PFOA the distribution is more symmetrical. Most of the reported LODs for PFOS and PFOA are 10 ng/l but several measurements had higher sensitivity with LOD 0.08 ng/l.

Table 8. Number of data points reported for PFAS in WWTPs and detection frequencies.

Matrix	Country	Perfluorohexane sulfonate (PFHxS)	Perfluoroheptanoic acid (PFHpA)	Perfluorohexanoic acid (PFHxA)	Perfluorooctanoic acid (PFOA)	Perfluorobutane sulfonate (PFBS)	Perfluorooctane sulfonate (PFOS)	Perfluorononanoic acid (PFNA)	Perfluoropentanoic acid (PFPeA)	Perfluorobutanoic acid (PFBA)	Perfluorohexane sulfonamide (PFHxSA)	Perfluorododecanoic acid (PFDoDA)	Perfluorodecanoic acid (PFDA)	Perfluoroundecanoic acid (PFUnA)	Perfluorooctane sulfonamide (PFOSA)	Perfluorodecane sulfonate (PFDS)	Perfluorotetradecanoic acid (PF-TeDA)	Perfluoropentadecanoic acid (PF-PDA)	Perfluorotridecanoic acid (PFTDA)
		Number of detected/Total number																	
Effluent	Sweden	21/21	21/21	21/22	22/22	16/18	22/22	20/21	10/20	10/21		9/21		30/42	20/22	3/21			
	Denmark				226/241		199/241	170/241			106/241		100/241	16/241	16/241				
	Latvia				5/5		5/5												
	Germany				2/12		0/12												
	Poland	2/2	0/1	1/2	2/2	0/1	2/2			0/1						0/1			
	Total	23/23	21/22	22/24	257/282	16/19	228/282	190/262	10/20	10/22	106/241	9/21	100/241	46/283	36/263	3/22			
	Det freq	**100%**	**95%**	**92%**	**91%**	**84%**	**81%**	**73%**	**50%**	**45%**	**44%**	**43%**	**41%**	**16%**	**14%**	**14%**			
Influent	Denmark				141/180		121/180	69/180			47/180		41/180	27/180	19/180				
	Poland	3/3	0/1	0/1	2/3	0/1	3/3			0/1						0/1			
	Total	3/3	0/1	0/1	143/183	0/1	124/183	69/180		0/1	47/180		41/180	27/180	19/180	0/1			
	Det freq	**100%**			**78%**		**68%**	**38%**			**26%**		**23%**	**15%**	**11%**				
Sludge	Sweden	18/29	6/26	22/31	31/31	5/24	31/31	25/31	1/3	1/1		28/29		58/60	28/30	28/30	20/29	8/20	19/29
	Germany				4/6		3/6												
	All	18/29	6/26	22/31	34/37	5/24	34/37	25/31	1/3	1/1		28/29		58/60	28/30	28/30	20/29	8/20	19/29
	Det freq	**62%**	**23%**	**71%**	**92%**	**21%**	**92%**	**81%**	**33%**	**100%**		**97%**		**97%**	**93%**	**93%**	**69%**	**40%**	**66%**

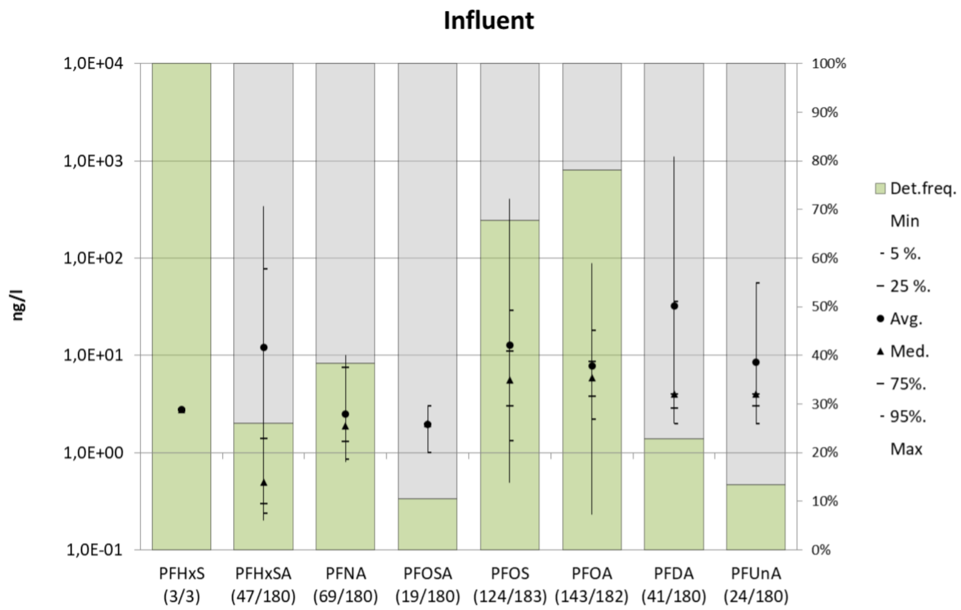

Figure 6. Detected concentrations, detection frequencies and the number of data points of PFAS in WWTP influents. The line with markings presents concentrations and the green bars show the detection frequencies. The number of samples is presented on the horizontal axis.

Table 9. Minimum, maximum, average and median concentrations of PFAS in WWTP influents (ng/l).

conc. ng/l	PFHxS	PFHxSA	PFNA	PFOSA	PFOS	PFOA	PFDA	PFUnA
Min	2.67	0.2	0.8	1	0.49	0.23	2	2
Avg	2.8	12	2.5	2	12.7	7.8	32	8.5
Med	2.8	0.5	1.9	2	5.6	5.9	4	4
Max	2.83	340	10	3	410	88	1100	56

Perfluorononanoic acid (PFNA) was detected in 69 out of 183 reported samples. Since reported LOD for all these samples is as low as 0.8 ng/l, the compound demonstrates systematically elevated concentrations in all 69 samples, which are distributed within the interval of one order of magnitude.

Perfluorohexane sulfonamide (PFHxSA), perfluorooctane sulfonamide (PFOSA), perfluorodecanoic acid (PFDA) and perfluoroundecanoic acid (PFUnA) were all detected in less than 30% of reported samples. Most of the detected concentrations are extremely low, just exceeding reported detection limits, which is indicated by very low median values for all these substances. A few measurements displaying exceptionally high concentrations of PFHxSA, PFDA and PFUnA, cause elevated average values for these compounds.

Sludge

Data on observations of PFAS in sludge in the period from 2004 to 2015 were reported by Sweden and Germany, with the most data provided by Sweden. 435 reported data points reflect concentrations of 15 PFASs including long and short-chain sulfonates, sulfonamides and carboxylic acids (figure 7). Six compounds were most frequently detected in sludge - perfluorooctanoic acid (PFOA), perfluorooctane sulfonate (PFOS), perfluorododecanoic acid (PFDoDA), perfluoroundecanoic acid (PFUnA), perfluorooctane sulfonamide (PFOSA), perfluorodecane sulfonate (PFDS) (table 8). Also, perfluorobutanoic acid (PFBA) was detected in a single reported sample. Among the most frequently detected compounds PFOS demonstrates the highest concentrations. Both average and median values exceed 10 ng/g dw (table 10) and observed concentrations deviate in relatively narrow interval within one order of magnitude. Concentrations of all other frequently observed compounds vary in much broader interval covering in some cases three orders of magnitude. For these five compounds, average concentration values do not exceed 10 ng/g and median is much lower than the average value which indicates domination of low concentrations in the population. For example,

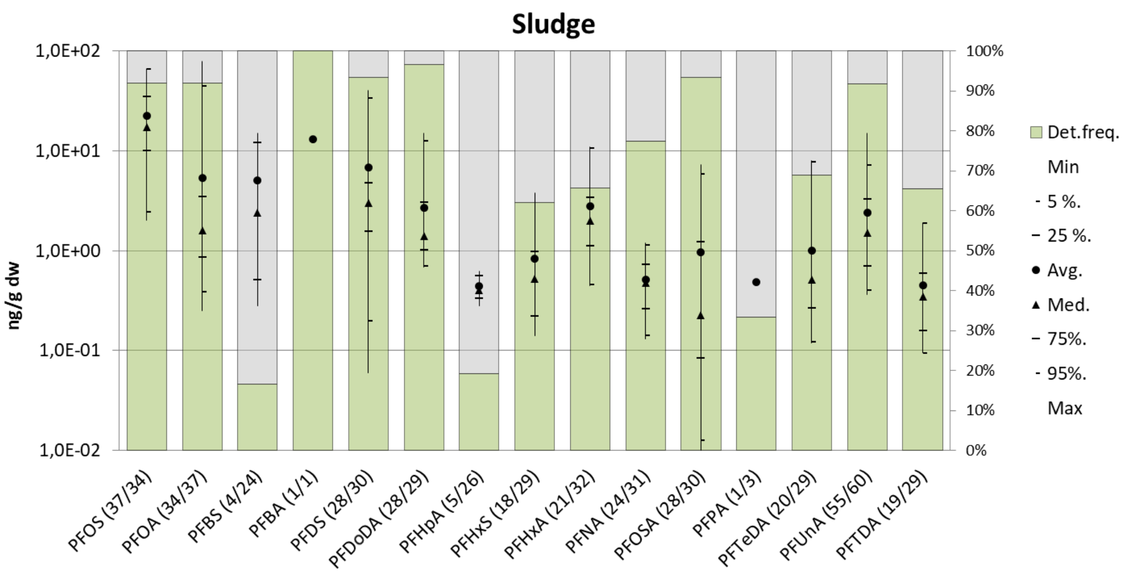

Figure 7. Detected concentrations, detection frequencies and the number of data points of PFAS in WWTP sludge. The line with markings presents concentrations and the green bars show the detection frequencies. The number of samples is presented on the horizontal axis.

Table 10. Minimum, maximum, average and median concentrations of PFAS in WWTP sludge (ng/g dw).

conc. ng/l	PFOS	PFOA	PFBS	PFBA	PFDS	PFDoDA	PFHpA	PFHxS	PFHxA	PFNA	PFOSA	PFPA	PFTeDA	PFUnA	PFTDA
Min	2.03	0.25	0.28		0.06	0.69	0.28	0.14	0.45	0.13	0.01		0.12	0.37	0.1
Avg.	22	5.4	5	13	6.8	2.7	0.4	0.8	2.8	0.5	0.9	0.5	1	2.4	0.5
Med.	17	1.6	2.4		3.0	1.4	0.4	0.5	2	0.5	0.2		0.5	1.5	0.4
Max	67	79.2	15		40	15	0.62	3.8	11	1.2	7.3		8	15	1.9

less than 25% of the samples demonstrate concentrations of PFOA higher than average value. Although the highest observed concentration of PFOA reaches 79 ng/g. PFDS demonstrates similar pattern as PFOA but with even broader distribution of observed concentrations. Reported LODs for PFASs in sludge vary in the interval from 0.01 to 5 ng/g, the majority (about 70%) being below 1 ng/g.

Among compounds with lower detection frequency relatively elevated concentrations with average value higher than 1 ng/g dw were displayed by perfluorobutane sulfonate (PFBS) and perfluorohexanoic acid (PFHxA). Relatively high concentration of PFBA in sludge was reported for a single sample which does not allow any evaluation. Other compounds (PFHpA, PFHxS, PFNA, PFPA, PFTeDA, PFTDA) included in the reported data, though some of them were detected in more than 60% cases, demonstrate concentration below 1 ng/g dw with unique samples exceeding this level.

Reported data do not allow to make evident conclusions regarding occurrence of PFAS belonging to different groups in sludge. In general, long-chain PFAS (with at least 6 perfluorinated carbon atoms) display the highest concentrations. On the other hand, only 4 out of 15 reported PFAS in sludge can be considered as short-chain, assuming that short-chain PFAS are those with fewer than 6 fluorinated carbons[1]. Also, concentration of PFOS in sludge is significantly higher than PFOA, though average concentrations of these substances in influents were almost equal. This can be explained by higher water solubility of PFOA.

Effluents

Most of the data on occurrence of PFAS in WWTP were reported for effluents. Altogether Denmark, Germany, Latvia, Poland and Sweden supplied 2027 datapoints with PFAS detected in 59% of measurements. Data on observation of 15 PFAS were reported, including long and short-chain sulfonates, sulfonamides, carboxylic acids (figure 8, table 8). Seven compounds were detected in more than 70% of reported measurements - perfluorooctanoic acid (PFOA), perfluorooctane sulfonate (PFOS), perfluorobutane sulfonate (PFBS), perfluoroheptanoic acid (PFHpA), perfluorohexane sulfonate (PFHxS), perfluorohexanoic acid (PFHxA) and perfluorononanoic acid (PFNA) (table 8). Detection frequency of five PFAS was in range between 40 and 50 percent - perfluorobutanoic acid (PFBA), perfluorodo-

1 The EC communication on PFAS: https://ec.europa.eu/environment/pdf/chemicals/2020/10/SWD_PFAS.pdf

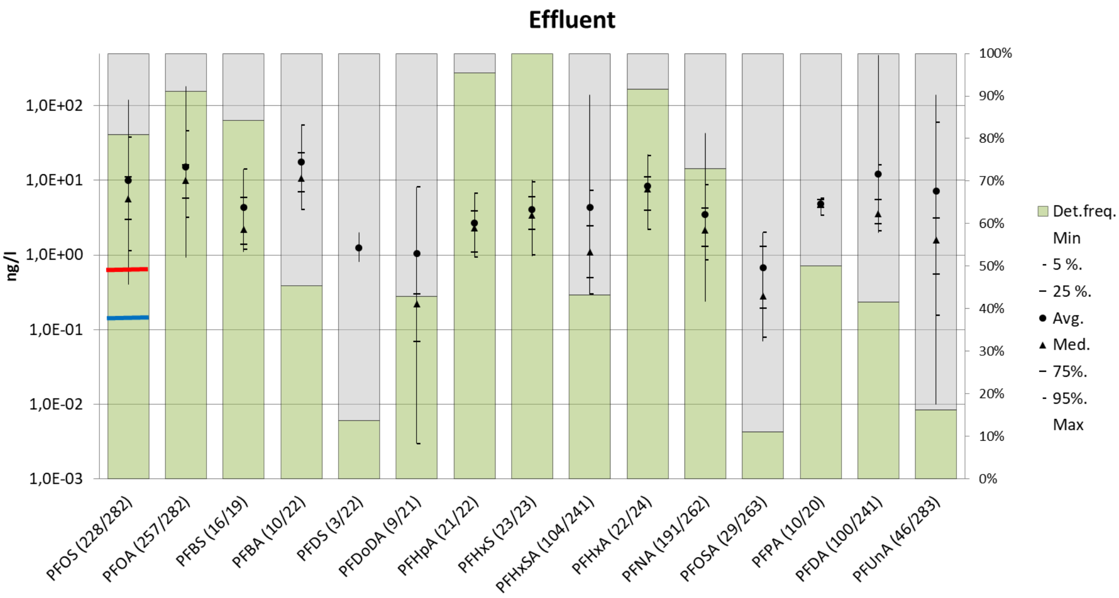

Figure 8. Detected concentrations, detection frequencies and the number of data points of PFAS in WWTP effluents. The line with markings presents concentrations and the green bars show the detection frequencies. The number of samples is presented on the horizontal axis. Red line displays AA-EQS for PFOS in inland waters, blue line in marine waters (DIRECTIVE 2013/39/EU). EQS values are used here for indicative comparison but not for the assessment of contamination level.

decanoic acid (PFDoDA), perfluorohexanesulfonic acid (PFHxS), perfluoropentanoic acid (PFPeA) and perfluorodecanoic acid (PFDA). Three other compounds - perfluorodecane sulfonate (PFDS), perfluorooctane sulfonamide (PFOSA) and perfluoroundecanoic acid (PFUnA) were detected in less than 20% of cases. Average and median values for almost all reported PFAS vary in the interval from 1 to 10 ng/l (table 11), excluding PFOA and PFBA for which both values are equal or slightly exceed 10 ng/l. The lowest concentrations are displayed by PFDoDA and PFOSA with average values close to 1 ng/l, and even lower medians. In general, observed concentrations for most of the reported PFAS in effluents vary in the interval of one or two orders of magnitude. PFDoDA and PFUnA are characterized by the highest variation of concentrations, covering interval of 4 orders of magnitude.

Detection limits were reported for 86% of samples and they vary in range from 0.04 to 10 ng/l. Most of the reported LODs (56%) are equal or below 1 ng/l. The rest is in the interval from 1 to 5 ng/l, and only 31 reported LODs are higher than 5 ng/l. Thus, since most of the average and median concentrations of PFAS are in the range from 1 to 10 ng/l these values might be slightly overestimated.

Three perfluorinated carboxylic acids - PFOA, PFBA and PFDA demonstrate the highest average concentrations exceeding 10 ng/l. However, the latter is characterized by much lower median value, indicating that high average concentration is provided by about 5% of measurements. Concentrations of PFOA in effluents are higher than PFOS. In general, concentrations of PFAS, observed in both influents and effluents to WWTPs are at similar levels. However, detection frequency in effluents is higher, which might be explained by lower LODs reported for effluents.

Environmental quality standard has been established only for PFOS (DIRECTIVE 2013/39/EU). Observed concentrations significantly exceed both standards for inland and marine waters (figure 8). Both average and median values exceed the AA-EQS for inland waters by an order of magnitude, while individual concentrations exceed this standard 200 times. This fact indicates a high probability of exceeding the AA EQS in inland surface waters.

Table 11. Minimum, maximum, average and median concentrations of PFASs in WWTP effluents (ng/l).

conc. ng/l	PFOS	PFOA	PFBS	PFBA	PFDS	PFDoDA	PFHpA	PFHxS	PFHxSA	PFHxA	PFNA	PFOSA	PFPA	PFDA	PFUnA
Min	0.4	0.93	1.1	4.1	0.82	0.003	0.92	0.98	0.3	2.2	0.24	0.07	3.4	2	0.01
Avg	10	15	4.3	17	1.2	1	2.7	4	4.3	8.4	3.5	0.7	4.8	12.2	7.2
Med	5.6	10	2.2	11		0.2	2.3	3.4	1.1	7.7	2.2	0.3	4.9	3.6	1.6
Max	120	180	14	55	2	8.1	6.8	10	140	22	43	2.0	5.8	470	140

4.3. Brief summary

Data on 15 substances belonging to PFAS group were reported in response to HELCOM call for data on micropollutants in WWTPs. Almost all reported PFAS were relatively frequently detected in the influents, effluents and sludges of WWTPs. Reported data includes long and short-chain sulfonates, sulfonamides, carboxylic acids. However, assuming that long-chain PFAS are those which contain 6 or more fluorinated carbons, eleven out of fifteen reported compounds are long chain PFAS and only four substances - PFBA, PFBS, PFPA and PFHxA - represent short chain PFAS. PFOA and PFOS are the most frequently measured compounds of this group. They were reported for all three matrixes and demonstrate one of the highest concentrations in influents and effluents. On the other hand concentration on PFOS is higher in influents and PFOA in effluents. In sludge, PFOS demonstrates the highest concentration among all PFAS, which is almost ten times higher than concentration of PFOA. Three other long-chain PFAS - PFHxS, PFHpA and PFNA - were frequently detected, at least in effluents. But their concentrations are lower than for PFAS and PFOA. Among short-chain PFAS, PFBA and PFHxA were relatively frequently detected in effluents.

Available data illustrate that PFAS in general are not removed from wastewater in WWTPs. They are observed in similar concentrations both in influents and in effluents. Some carboxylic acids, such as PFOA and PFNA, occur in higher concentrations in effluents than in influents. Especially it concerns PFOA which concentrations in effluents are almost twice higher than in influents. PFOS demonstrates slight reduction of concentrations in effluents compared to influents and accumulates in sewage sludge, where this substance occurs in the highest concentration among the whole group.

Despite the slight reduction of PFOS concentrations in water during treatment process, concentrations observed in effluents are ten and sometimes hundred times higher than any published annual average environmental quality standards. Unfortunately, PFOS is the only substance from this group with established EQSs. Since many other PFAS are detected in effluents demonstrating similar concentrations, there is a need to identify safe level of their presence in the environment.

Overall, observed concentrations of PFAS in effluents and sludge illustrate continuous release of these compounds to the aquatic environment despite restricted use or ban of some of them in the region. The data indicate that PFAS are not efficiently removed from wastewater and still pose the risk of accumulation in the marine environment.

5. Metals

5.1. Data overview for Metals

In respond to HELCOM data call on micropollutants in WWTPs data on 10 heavy metals was reported by Denmark, Estonia, Germany, Latvia, Poland and Sweden. Most data on heavy metals in WWTP were reported for effluents – 4010 data points. Measurements of heavy metals in sludge and influents were reported for 979 and 1934 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 (table 12). Detection frequency for individual metals vary depending on matrixes. In general, barium, nickel and zinc demonstrate the highest frequency of detection, being detected in more than 80% of cases for all matrixes. Though, observations of barium were not reported for sludge. Arsenic, chromium and copper were detected in more than 50% of effluent samples, in more than 80% influents and in all sludge samples. Mercury, cadmium and lead were detected in less than 50% effluents samples but in more than 80% influents and almost 100% samples of sludge. Also, tin had relatively low detection frequency in effluents (39%) but more than 80% in influents. There were no tin measurements in sludge reported.

Limits of detection and limits of quantification were reported for 82% of samples from liquids (influents and effluents) and for 75% of solids (sludge). For liquid samples almost all (except for a few percent) measurements had limits of detection (LOD), while the accuracy of analytical methods for detection of heavy metals in solids was mainly (93%) reported as limit of quantification (LOQ). Detection limits of analytical methods vary in range of several orders of magnitude for different metals and matrixes, so they will be considered individually for each metal and matrix later in this report.

5.2. Concentrations of heavy metals in WWTP influents, effluents and sludge

Influents

Data on concentrations of ten heavy metals in influents of WWTP, mainly observed in period 2011-2016 with a few datapoints from 2005, were reported by Denmark, Estonia, Latvia and Poland. But most of the data were supplied by Denmark (table 12). Although, high detection frequency is typical for all heavy metals in influents five of them lead, chromium, copper, barium and zinc were detected in more than 90% of cases (figure 9). Four out of these five metals – Cr, Cu, Ba and Zn - also demonstrate the highest concentrations in influents. Zinc is leading in the whole group with average concentrations of 212 µg/l, median 150 µg/l and variation of observed concentrations in about three folders of magnitude. The highest observed concentrations reach 5000 µg/l (table 13). Two metals – barium and chromium – were observed in concentrations exceeding a 1000 µg/l. But while for barium high concentrations were observed in more than 25% of the cases, chromium displayed such extremely high values just in few percent of cases. That is illustrated by rather low median value for concentrations of chromium, which is only 3.9 µg/l. Also, chromium demonstrates the highest variation of observed concentrations ranging in four orders of magnitude. Nickel, lead and tin also display highest concentration close and even exceeding a hundred µg/l - though, the concentration of lead 170 µg/l was observed only in one sample. Average values for concentrations of these metals are 15.41, 8.07 and 5.82 µg/l respectively and medians are also within the range from 1 to 10 µg/l. It illustrates that observed concentrations of these three metals fall primarily in the same interval. Reported concentrations of arsenic vary in the smallest interval of values compared to other heavy metals.

They just go slightly beyond interval from 1 to 10 µg/l, and average and median values for As concentrations in influents are a few microgrammes per litre. Average concentrations for cadmium and mercury in influents, derived from 189 and 177 individual measurements respectively are almost equal (Cd - 0.31 µg/l and Hg – 0.29 µg/l). Median value for mercury concentrations is lower than for cadmium illustrating that most samples display lower concentrations of Hg than Cd. However, the highest observed concentrations of these two toxic metals are almost the same.

Reported detection limits for measurements of heavy metals in influents can be split in two groups. The first group is detection limits for metals with median concentration higher than 1 µg/l. All metals except for mercury and cadmium belong to this group. For this group 82% of reported detection limits are below 1 µg/l. However, 17% of reported detection limits are higher than 5 µg/l. Detection limits for analysis of mercury vary from 0.002 to 0.1 µg/l. But 95% of reported data obtained with accuracy below 0.05 µg/l. The same concerns detection limits for Cd analysis. Despite deviation of reported detection limits within range of 3 orders of magnitude from 0.02 to 20 µg/l, 93% of reported data were obtained with accuracy below 0.05 µg/l.

Table 12. Number of data points reported for heavy metals in WWTPs and detection frequencies (number of detected/total number).

	Country	Hg	Cd	Pb	As	Ba	Cr	Cu	Ni	Sn	Zn
					Number of detected/ total number						
Effluents	Denmark	128/268	51/245	91/245	132/239	238/239	96/245	156/245		91/235	234/245
	Estonia	0/88	67/115	86/157	91/94	19/19	117/192	154/204	138/152	4/8	124/149
	Germany	3/12	1/12	4/12	5/12		12/12	12/12	12/12		11/11
	Latvia	24/30	25/33	44/45	3/3		37/40	45/46	28/29		51/52
	Poland		2/9	4/9			4/7	4/4	4/8		4/4
	Sweden	20/43	2/22	2/21	4/21	20/20	5/21	22/22	21/21		21/21
	Total	205/441	148/436	231/489	235/369	277/278	271/517	393/533	203/222	95/243	445/482
	Det.freq.	**46%**	**34%**	**47%**	**64%**	**100%**	**52%**	**74%**	**91%**	**39%**	**92%**
Influents	Denmark	165 /201	184/159	184/173	177/159	177/176	184/169	184/182		174/145	184/182
	Estonia	4 /6	21/14	21/14	8/2		21/16	21/15	21/16		23/22
	Latvia	8/14	13/19	18/19	2/2		19/19	18/19	9/9		21/21
	Poland		3/4	2/3			1/1	5/5	3/3		5/5
	Total	177/221	189/228	207/227	163/187	176/177	205/225	220/229	28/33	145/174	230/233
	Det.freq.	**80%**	**83%**	**91%**	**87%**	**99%**	**91%**	**96%**	**85%**	**83%**	**99%**
Sludge	Estonia	111/111	95/104	118/118	1/1		119/119	115/115	115/115		
	Poland	7/7	7/7	7/7			7/7	7/7	7/7		7/7
	Sweden	30/30	31/31	31/31	31/31		31/31	31/31	31/31		31/31
	Total	148/148	133/142	156/156	32/32		157/157	153/153	153/153		38/38
	Det.freq.	**100%**	**94%**	**100%**	**100%**		**100%**	**100%**	**100%**		**100%**

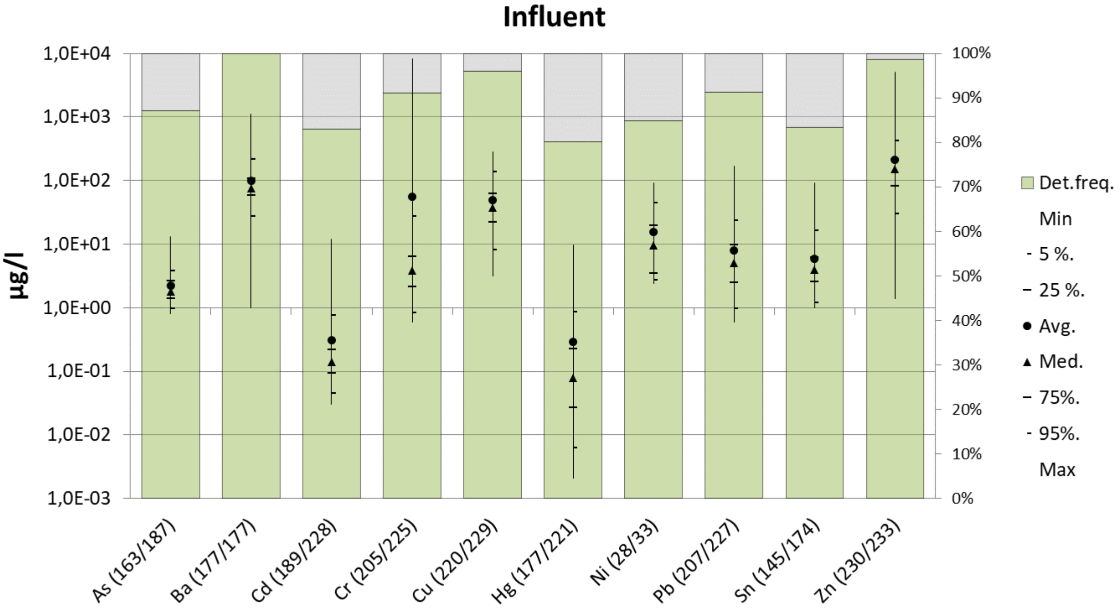

Figure 9. Detected concentrations, detection frequencies and the number of data points of heavy metals in WWTP influents. The line with markings presents concentrations and the green bars show the detection frequencies. The number of samples is presented on the horizontal axis.

Table 13. Minimum, maximum, average and median concentrations of heavy metals in WWTP influents (µg/l).

	As	Ba	Cd	Cr	Cu	Hg	Ni	Pb	Sn	Zn
Min	0.81	1.00	0.03	0.6	3.2	0.002	2.4	0.6	1	1.4
Avg.	2.2	99	0.3	55	49	0.3	15.4	8	5.8	212
Med.	1.8	75	0.1	3.9	38	0.1	9.5	5	4	150
Max	13	1100	12	8300	280	9.6	91	170	92	5000

Sludge

Data on only eight heavy metals in sewage sludge were reported by HELCOM Contracting Parties in response to the data call on micropollutants. There were no measurements of barium and tin reported. The data, obtained in the period 2004-2018, was reported by Estonia, Poland and Sweden. Concentration of reported heavy metals above detection limit were observed in almost 100% samples, except for cadmium which concentration was below the detection limit in 9 out of 142 samples (figure 10, table 14).

Copper and zinc demonstrate the highest concentrations in sludge, exceeding a hundred µg/g dw. Zinc concentrations variate in a relatively narrow interval less than one order of magnitude but reach the highest value of 1851 µg/g. But both average and median values for Zn concentrations are within the range from one hundred to one thousand µg/g, indicating that individual measurements primarily show concentrations ranging from 350 to 700 µg/g with less than 25% exceeding 1000 µg/g. Individual concentrations of copper are distributed within much broader interval covering almost 3 orders of magnitude. Nonetheless, most measurements display concentrations of copper above 100 µg/g with about 25% below this value and less than 5% lower than 10 µg/g.

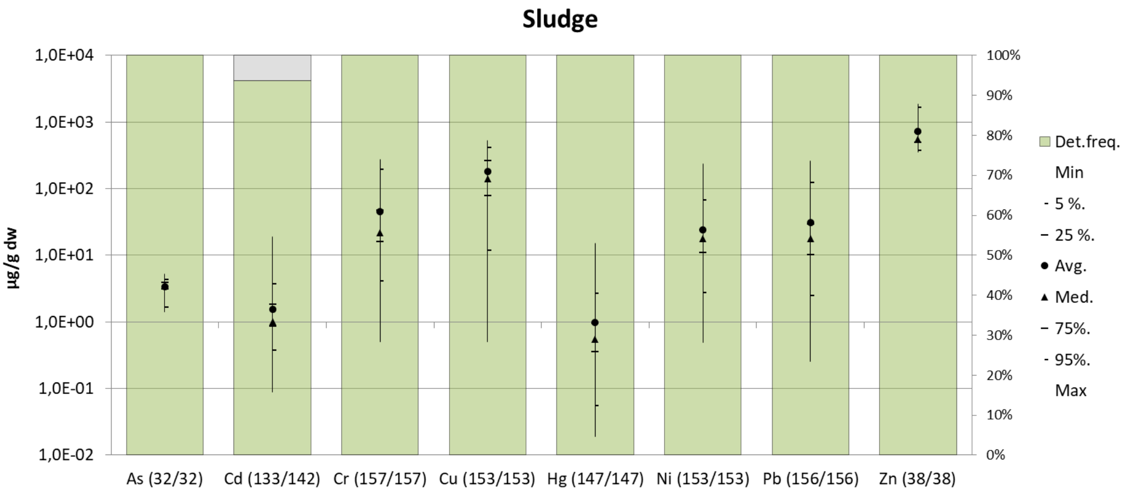

Figure 10. Detected concentrations, detection frequencies and the number of data points of heavy metals in WWTP sludge. The line with markings presents concentrations and the green bars show the detection frequencies. The number of samples is presented on the horizontal axis.

Table 14. Minimum, maximum, average and median concentrations of heavy metals in WWTP sludge (µg/g dw).

	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
Min	1.4	0.09	0.5	0.5	0.02	0.49	0.25	350
Avg.	3.4	1.6	45	180	1	24	31	718
Med.	3.5	1	22	140	0.6	18	18	549
Max	5.2	19	272	530	15	234	261	1851

Chromium, nickel and lead demonstrate average and median concentrations in interval of 10-100 µg/g. Observed concentrations of these three metals vary in range of almost 3 orders of magnitude. However, most samples demonstrate concentrations within the above-mentioned interval with just few percent above or below its borders. Only 32 observation points for arsenic were reported and concentrations vary in a narrow interval from 1.4 to 5.2 µg/g. The lowest concentrations in sewage sludge are demonstrated by cadmium and mercury. For both metals average value is close to 1 µg/g. Median for cadmium is equal to 1 µg/g but median for mercury concentrations is remarkably lower, only 0.55 µg/g. Both toxic metals in unique cases demonstrate concentrations even exceeding 10 µg/g.

Limits of quantification for analytical methods are reported for 72 percent of measurements in sewage sludge. For metals with average and median concentrations above 10 µg/g (Cr, Cu, Ni, Pb, Zc) reported LOQs vary in range from 0.005 to 0.8 µg/g, but 93% of reported measurements were done with accuracy equal or lower than 0.05 µg/g. 95% of LOQs for arsenic, cadmium and mercury measurements are below 0.005 µg/g.

There is no unified setting of limit values for concentrations of heavy metals in sewage sludge. Different limit values have been established in HELCOM countries and by the EU Directive 86/278/EEC on the protection of the environment, and in particular of the soil, when sewage sludge is used in agriculture. These limit values depend on the purpose of sewage sludge application as well as on chemistry and composition of the soil. A regional overview of limits values for sewage sludge was made in the final report of Project on Urban Reduction of Eutrophication (PURE) - Good practices in sludge management. The report was published in 2012. An extraction of that overview is given in table 15.

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.

Table 15. Limit values for concentrations in sewage sludge µg/g of dry matter.
*For soils classified as light soils, a clay content of <5%, and with a pH 5–6.
**For gardening

	Cd	Cr	Cu	Hg	Ni	Pb	Zn	As
Denmark	0.8	100	1000	0.8	30	120	4000	25**
Estonia	20	1000	1000	16	300	750	2500	-
Finland	3	300	600	2	100	150	1500	-
Germany	10(5)*	900	800	8	200	900	2500(2000)*	-
Latvia	10	600	800	10	200	500	2500	-
Lithuania category 1	1.5	140	75	1	50	140	300	-
Lithuania category 2	20	400	1000	8	300	750	2500	-
Russia group 1	15	500	750	7.5	200	250	1750	-
Russia group 2	30	1000	15000	15	400	500	3500	-
Poland	20	1000	500	16	300	750	2500	-
Sweden	2	100	600	2.5	50	100	800	-
EU directive 86/278	20–40	–	1000-1750	16–25	300–400	750–1200	2500–4000	-

Effluents

Data on analysis of 10 heavy metals in WWTP effluents in period from 2005 to 2018 were reported by Denmark, Estonia, Germany, Latvia, Poland and Sweden. Ba, Ni and Zn were detected in more than 90% of cases; As, Cr and Cu in more than 50% and Cd, Hg and Sn in less than 50% (figure 11). However, all metals except for tin were detected in more than a hundred samples which enables to assess contamination level of effluents.

Barium and zinc, the most frequently detected metals, occur in effluents in highest concentrations. Both average and median values exceed 10 µg/l (table 16). Observed zinc concentrations vary in much broader interval than barium, covering more than 4 orders of magnitude. However, most concentrations of both metals fall in the interval from 10 to 100 µg/l.

Average values for Cr and Pb concentrations also exceed 10 µg/l, but medians for both are a tenfold lower – close to 1 µg/l. It indicates that elevated average concentrations for these metals are provided by relatively small number of measurements, less than 25%. Variation of individual Pb concentrations is the highest, embracing interval of about five orders of magnitude. Average and median values for concentrations of As, Cu, Ni and Sn fall in the interval from 1 to 10 µg/l, and most of individual concentrations vary in the same range. However, the highest observed concentrations of Cu, Ni and Sn are as high as 100 µg/l. Cadmium and mercury occur in effluents in lowest concentrations. Average Cd concentration is just slightly above 1 µg/l. This value is provided by less than 25% of analysis with 5% of measured concentra-

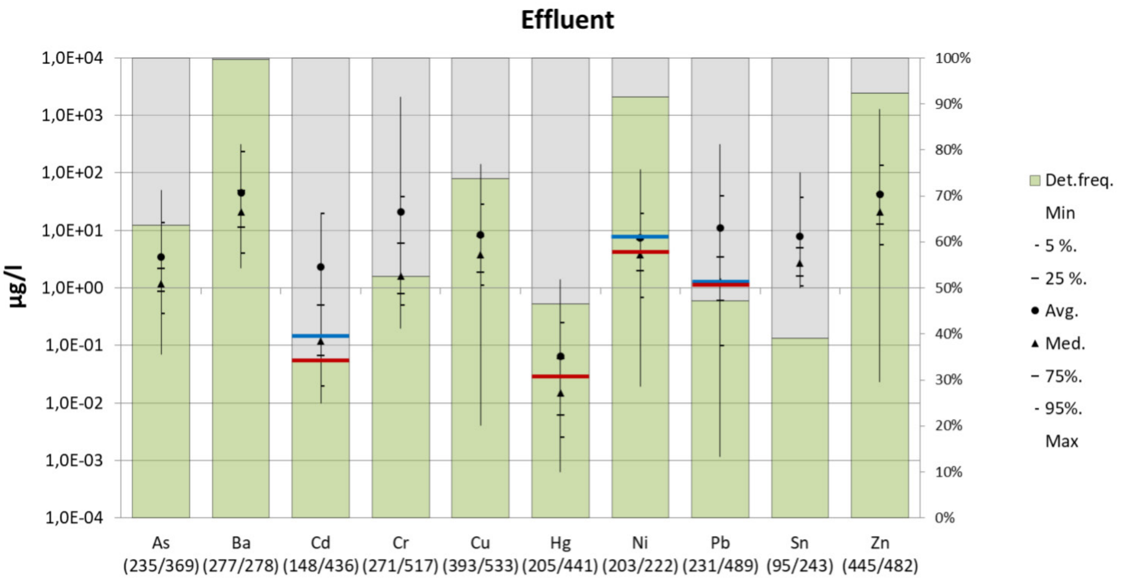

Figure 11. Detected concentrations, detection frequencies and the number of data points of heavy metals in WWTP effluents. The line with markings presents concentrations and the green bars show the detection frequencies. The number of samples is presented on the horizontal axis. Red line display AA-EQS in inland waters, blue line in other waters (the EU WFD). EQS values are used here for indicative comparison but not for the assessment of contamination level.

Table 16. Minimum, maximum, average and median concentrations of heavy metals in WWTP effluents (µg/l).

	As	Ba	Cd	Cr	Cu	Hg	Ni	Pb	Sn	Zn
Min	0.07	2.2	0.01	0.20	0.004	0.001	0.02	0.001	1	0.02
Avg.	3.5	45	2.3	21	8.5	0.07	7.3	11	7.8	42
Med.	1.2	21	0.1	1.6	3.8	0.02	3.8	1.3	2.7	21
Max	50	319	20	210	140	1.4	115	310	100	1300

tions exceeding 10 µg/l, when median is at the level of 0.1 µg/l. Both average and median values for Hg concentrations are below 1 µg/l.

Detection limits of analytical methods are reported for 77% of measurements, most of them reported as LOD and about 5% as LOQ. For metals with median concentration above 1 µg/l, 84% of detection limits are equal or below 1 µg/l. 16% of detection limits varying from 1.2 to 50 µg/l, were primarily reported for zinc. 95% of detection limits for Cd are equal or lower than 0.06 µg/l, but only 81% of reported detection limits for Hg are equal or below median value for measured concentrations – 0.02 µg/l. Thus, average contamination of effluents by mercury might be overestimated.

The EU water Framework Directive sets EQS values for cadmium, mercury, nickel and lead. These annual average environmental quality standards (AA-EQS) are identified for inland and marine water. However, for lead and nickel in inland waters EQS is set for their bioavailable forms. Bioavailability of metals depends on multiple factors including binding metals to solid particles. Since there was no detailed information on analytical methods reported including filtering or non-filtering of samples, comparison with EQS for bioavailable forms of these metals is a subject of uncertainty. Average concentrations of Cd, Hg and Pb exceed all EQSs, while medians for all of them are below. Both average and median concentrations of nickel are approximately at EQS level. However, more than 25% of samples demonstrate concentrations of Cd, Hg and Pb, which several times exceed respective EQSs, and about 5% of reported concentrations of these metals are even two orders higher than EQS.

5.3. Brief summary

Large amount of data on occurrence of heavy metals in influents, effluents and sludges of WWTP's were collected. Reported data displays high detection frequency of heavy metals and sufficient accuracy of analytical methods to detect them. However, the detection frequency in influents is higher than in effluents. In general, concentrations of heavy metals in effluents are lower than in influents. At least, it concerns median values. However, average values for such priority contaminants as As, Cd and Pb in treated waters are even higher than in sewage waters coming into WWTPs. High average values for these three heavy metals in effluents are provided by limited number of extremely high concentrations, but it also demonstrates that effectiveness of treatment is not always sufficient or that extremely contaminated wastewater is in some cases discharged to WWTPs.

On average, analysis of collected data and their comparison with limit values set in the EU and HELCOM countries demonstrates moderate level of wastewater and sludge contamination by heavy metals. Almost all data on sewage sludge display fulfilment of the EU criteria for its quality. Majority of measurements in effluents even demonstrate not exceedance of chronic EQSs. Nevertheless, more than 25% Cd, Hg and Pb analysis in effluents display exceedance of respective limit values, sometimes reaching hundredfold exceedance. It indicates that wastewater remains a significant source of heavy metals to the aquatic environment.

6. Pharmaceuticals

6.1. Data overview for pharmaceuticals

The pharmaceutical data of MP and SR data calls were processed by SYKE within the CWPharma project, funded by EU's Interreg Baltic Sea Region programme. The datasets were merged, while retaining an indicator on which data call each datapoint originated from. Processing the merged dataset included identification of duplicate entries, and entries where vital information (e.g. unit) was reported inconsistently or omitted. Altogether 4370 datapoints were excluded from the analysis. For instance, Polish data on sewage sludge were reported as contaminant mass per volume of sludge (ng/l). Since no background information (e.g. solids content, etc.) was reported, these values could not be converted into a unit comparable with the values from other countries. Therefore, the Polish sludge data (63 data points) was excluded from further analysis. On the other hand, the Danish and German datasets contained 3856 and 442 datapoints identified as duplicates, respectively.

The data set included into the analysis covered 3928 and 6091 data points for the MP and SR data-calls, respectively. The number of data points from individual Baltic Sea region (BSR) countries was unevenly distributed. Data reported from Denmark accounted for 61% of the total number of data points. Similarly, Germany accounted for 16% and Finland for 14% of the total data set. The remaining 10 % of the data points originated from Sweden, Estonia, Latvia and Poland. Denmark, Germany and Finland reported data for both data-calls, while Estonia and Sweden reported only for the SR and Latvia and Poland for the MP data-calls. No information was received from Lithuania and Russia. The distribution between countries is presented in table 17.

Data on pharmaceuticals was reported for overall 102 wastewater treatment plants. Location of the WWTPs (figure 1, in chapter 2) were either reported coordinates or collected form the Urban WasteWater Directive (UWWTD) database v6 (EEA 2017).

The reported data include measurements of pharmaceuticals in influent wastewater, effluent wastewater and sewage sludge. 59 % of the data points were reported for effluent wastewater, 33 % for influent wastewater and the remaining 8 % for sewage sludge.

The reported data covered altogether 117 individual substances, which were divided into the following 11 substance groups. The number of APIs and datapoints in each group is presented in brackets.

1. Anti-inflammatory and analgesic substances (n_{API}=17, $n_{datapoints}$=2269)
2. Antimicrobial and antiparasitic (n_{API}=29, $n_{datapoints}$=2769)
3. Cardiovascular agents (n_{API}=21, $n_{datapoints}$=1188)
4. Central nervous system (n_{API}=9, $n_{datapoints}$=535)
5. Contrast agents (n_{API}=5, $n_{datapoints}$=544)
6. Chemotherapeutic agents (n_{API}=4, $n_{datapoints}$=61)
7. Metabolic and gastrointestinal agents (n_{API}=4, $n_{datapoints}$=481)
8. Respiratory agents (n_{API}=3, $n_{datapoints}$=51)
9. Hormones and hormone antagonists (n_{API}=15, $n_{datapoints}$=1594)
10. Recreational drugs (n_{API}=6, $n_{datapoints}$=48)
11. Metabolites (n_{API}=4, $n_{datapoints}$=479)

The most common substance groups were antimicrobial and antiparasitic substances, anti-inflammatory and analgesic substances as well as hormones and hormone antagonists. Data points for these groups represented about 66 % of all the data points. Chemotherapeutic agents, possibly one of the most toxic substance groups, accounted for only 0,6 % of the data points. Interestingly Poland was the only country to report data for recreational drugs. This data accounted for 0,5 % of the total data set.

Table 17. The number of data points and WWTPs reported in both MP and SR data-calls.

Country	Data points		Number of WWTPs	
	MP	SR	MP	SR
Denmark (DK)	2533	3553	34	37
Estonia (EE)	0	270	0	3
Finland (FI)	515	895	10	19
Germany (DE)	603	977	11	16
Latvia (LV)	25	0	5	0
Poland (PL)	252	0	13	0
Sweden (SE)	0	396	0	4

6.2. Concentrations in WWTP influents, effluents and sludge

Anti-inflammatory and analgesic substances

Out of the 17 APIs categorized as anti-inflammatory and analgesic substances 13 were found in at least one sample. Data points reported for effluent wastewater accounted for 59 % of the data points, while influent wastewater and sewage sludge accounted for 37 % and 4 % respectively.

Out of the list of reported substances in this group, several are quite widely used, like e.g. Ibuprofen, Paracetamol, Diclofenac etc.

For example, circa 65 tonnes of diclofenac was estimated to be used in Baltic Sea countries annually (Äystö et al. 2020) . It is currently also used as a HELCOM pre-core test indicator. Data on this pre-core test indicator show that several samples in sea water are above suggested threshold levels. For the reported data, diclofenac was detected in 99 % of the reported analyses. For diclofenac, 76 % of the data points were reported for effluent wastewater. The concentrations in this matrix reached up to 17 200 ng/l, with an average of 2 480 ng/l. The effluent concentration for diclofenac exceeded the proposed EQS-value - 50 ng/l - in 93 % of the samples with concentrations over the LOQ.

The range of reported concentrations as well as the number of data points and detection frequencies per substance and matrix are presented in figure 12 and the total number of data points reported from each country is presented in table 18. The distribution of data points and detections between the MP and SR data-calls is presented in Annex 2.

Table 18. Number of data points reported from each country for Anti-inflammatory and analgesic substances. The substances are ordered according to the number of samples.

Substance	n det./n tot.	n det. / n tot. per country						
		DK	EE	FI	DE	LV	PL	SE
Ibuprofen	515/610	386/440	-	93/111	9/21	-	21/26	5/12
Paracetamol	302/476	270/422	4/6	13/22	-	-	15/26	-
Salicylic acid	263/423	261/421	-	-	-	-	2/2	-
Diclofenac	324/328	73/73	6/6	49/50	160/160	-	27/27	9/12
Naproxen	139/165	12/17	5/6	74/83	20/21	-	18/26	10/12
Ketoprofen	93/124	9/17	5/6	65/82	5/5	-	0/2	9/12
Flurbiprofen	5/26	-	-	-	-	-	5/26	-
Tramadol	23/23	17/17	6/6	-	-	-	-	-
Codeine	18/18	12/12	6/6	-	-	-	-	-
Fentanyl	0/18	0/12	0/6	-	-	-	-	-
Gabapentin	17/17	-	-	-	17/17	-	-	-
Propofol	11/13	11/13	-	-	-	-	-	-
Beclomethasone	0/10	-	-	0/10	-	-	-	-
Buprenorphine	0/6	-	0/6	-	-	-	-	-
Indometacin	5/5	-	-	-	5/5	-	-	-
Phenazon	5/5	-	-	-	5/5	-	-	-
Diflunisal	0/2	-	-	-	-	-	0/2	-
Tot.	**1720/2269**	**1051/1444**	**32/48**	**294/358**	**221/234**	**0/0**	**88/137**	**34/48**

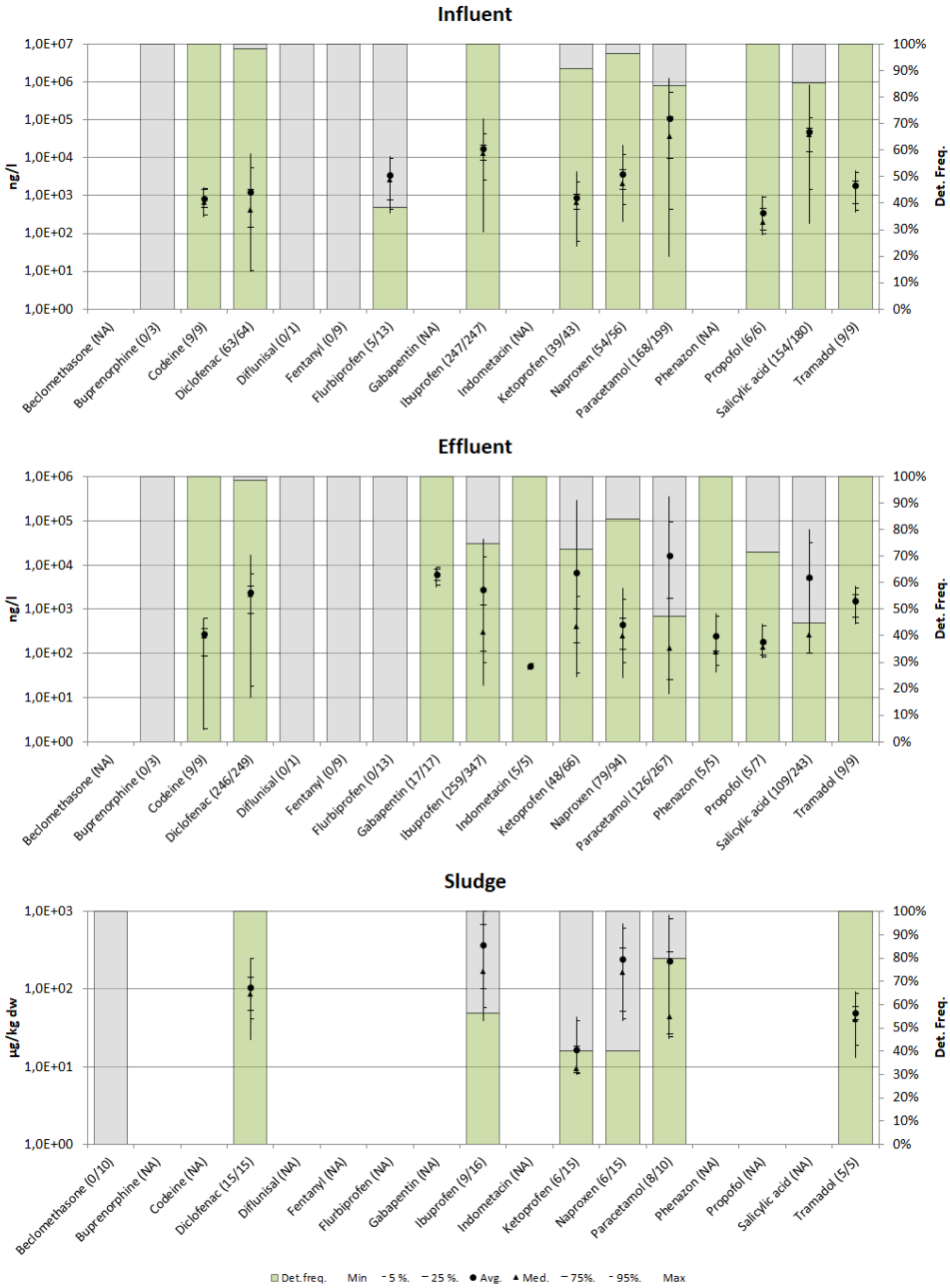

Figure 12. Detected concentrations, detection frequencies and the number of data points of analgesic and anti-inflammatory substances presented for each substance and matrix. The line with markings presents concentrations and the green bars show the detection frequencies. The number of samples is presented on the horizontal axis. (NA = not analysed)

Antimicrobial and antiparasitic

Out of the 29 APIs classified as antimicrobial and antiparasitic, 24 substances were detected in at least one sample. Data points reported for effluent wastewater accounted for 53 % of the data points, while influent wastewater and sewage sludge accounted for 35 % and 12 % respectively.

Five antibiotics are listed in the updated Water framework directive (WFD) Watch list (2018/840/EC): erythromycin, clarithromycin, azithromycin, amoxicillin and ciprofloxacin. Data points for all of these substances were reported for each of the three matrices. The proposed EQS-values for erythromycin (20 ng/l, UBA 2014), clarithromycin (120 ng/l, Oekotoxzentrum 2016), azithromycin (19 ng/l, Loos et al. 2018), and ciprofloxacin (100 ng/l, Sahlin et al. 2018) were exceeded in 41%, 15%, 91%, and 11% of effluent

Table 19. Number of data points reported from each country for antimicrobial and antiparasitic substances. The substances are ordered according to the number of samples.

Substance	n det./n tot.	n det. / n tot. per country						
		DK	EE	FI	DE	LV	PL	SE
Sulfamethoxazole	405/561	298/422	4/6	3/16	93/99	-	-	7/18
Trimethoprim	369/486	317/423	6/6	17/22	17/17	-	-	12/18
Triclosan	433/433	421/421	-	-	12/12	-	-	-
Sulfamethizole	402/423	402/423	-	-	-	-	-	-
Erythromycin	95/117	70/73	-	-	20/21	5/5	-	0/18
Ciprofloxacin	86/103	9/12	5/6	25/31	-	-	-	47/54
Ofloxacin	54/91	-	2/6	25/31	-	-	-	27/54
Norfloxacin	52/85	-	3/6	17/25	-	-	-	32/54
Clarithromycin	76/84	65/73	6/6	-	-	5/5	-	-
Doxycycline	24/38	-	-	11/20	-	-	-	13/18
Metronidazole	6/38	-	-	1/20	-	-	-	5/18
Amoxicillin	0/30	0/12	-	-	-	-	-	0/18
Tetracycline	19/29	-	0/6	19/23	-	-	-	-
Roxithromycin	18/23	15/17	3/6	-	-	-	-	-
Azithromycin	18/22	13/17	-	-	-	5/5	-	-
Ketoconazole	14/22	-	0/6	14/16	-	-	-	-
Fluconazole	18/18	12/12	6/6	-	-	-	-	-
Miconazole	1/18	1/12	0/6	-	-	-	-	-
Ampicillin	2/18	-	-	-	-	-	-	2/18
Cefadroxil	5/18	-	-	-	-	-	-	5/18
Cefuroxime	2/18	-	-	-	-	-	-	2/18
Penicillin V	0/18	-	-	-	-	-	-	0/18
Oxytetracycline	10/16	-	0/6	10/10	-	-	-	-
Tylosin	0/14	-	-	0/14	-	-	-	-
Fendendazole	10/10	-	-	10/10	-	-	-	-
Flubendazole	9/10	-	-	9/10	-	-	-	-
Ivermectin	0/10	-	-	0/10	-	-	-	-
Penicillin G benzathine	0/10	-	-	0/10	-	-	-	-
Clindamycin	4/6	-	4/6	-	-	-	-	-
Tot.	**2132/2769**	**1623/1917**	**39/78**	**161/268**	**142/149**	**15/15**	**0/0**	**152/342**

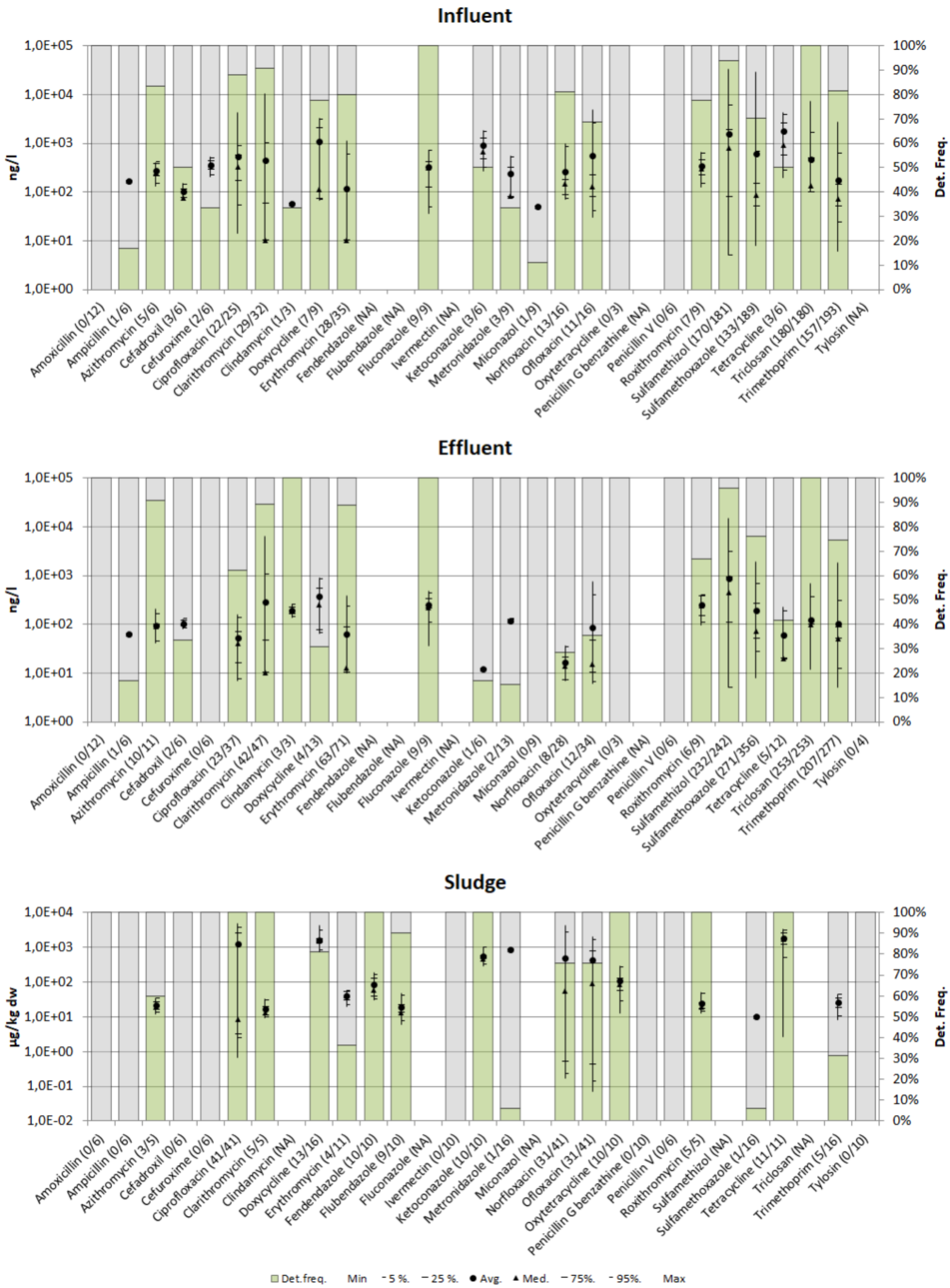

Figure 13. Detected concentrations, detection frequencies and the number of data points of antimicrobial and antiparasitic substances presented for each substance and matrix. The line with markings presents concentrations and the green bars show the detection frequencies. The number of samples is presented on the horizontal axis. (NA = not analysed)

samples, respectively. Ciprofloxacin was detected in 100 % of the reported sludge samples, and it reached maximum concentration of 4,76 mg/kg dw. Amoxicillin was not detected in any of the reported samples (n= 30). The reported limits of quantification for amoxicillin in water samples varied from 50 ng/l to 100 ng/l.

The described five antibiotics are not included as HELCOM indicators but HELCOM Expert Group on Hazardous Substances (EG HAZ) is exploring options for screening for these emerging pollutants and discuss if they could be included for e.g. non-targeted screening and are suitable for any tentative indicator development.

The range of reported concentrations as well as the number of data points and detection frequencies per substance and matrix are presented in figure 20 and the total number of data points reported from each country is presented in table 10. The distribution of data points and detections between the MP and SR data-calls is presented in Annex 2.

Cardiovascular agents

Out of the 21 APIs classified as cardiovascular agents, 17 were detected at least in one sample. Data points reported for effluent wastewater accounted for 64 % of the data points, while influent wastewater and sewage sludge accounted for 26 % and 10 % respectively. For nine out of the 21 substances data was only reported from one reporting country.

Previously bisoprolol was the most commonly detected cardiovascular agent in Baltic Sea water samples (UNESCO & HELCOM 2017), reaching

Table 20. Number of data points reported from each country for cardiovascular agents. The substances are ordered according to the number of samples.

Substance	n det./n tot.	n det. / n tot. per country			
		DK	EE	FI	DE
Furosemide	435/441	420/423	-	15/18	-
Metoprolol	332/332	17/17	6/6	37/37	272/272
Atenolol	57/75	10/12	6/6	22/36	19/21
Bisoprolol	35/60	0/17	0/6	15/16	20/21
Sotalol	43/57	-	6/6	17/30	20/21
Propranolol	46/53	15/16	-	11/16	20/21
Hydrochlorothiazide	19/22	-	-	19/22	-
Enalapril	7/20	-	-	7/20	-
Warfarin	5/20	-	-	5/20	-
Acebutolol	14/14	-	-	14/14	-
Felodipine	1/14	-	-	1/14	-
Simvastatin	1/14	-	-	1/14	-
Amiloride	7/12	7/12	-	-	-
Losartan	12/12	12/12	-	-	-
Alfuzosin	0/6	-	0/6	-	-
Cilazapril	0/6	-	0/6	-	-
Diltiazem	0/6	-	0/6	-	-
Eprosartan	4/6	-	4/6	-	-
Irbesartan	0/6	-	0/6	-	-
Telmisartan	6/6	-	6/6	-	-
Verapamil	4/6	-	4/6	-	-
Tot.	**1028/1188**	**481/509**	**32/66**	**164/257**	**351/356**

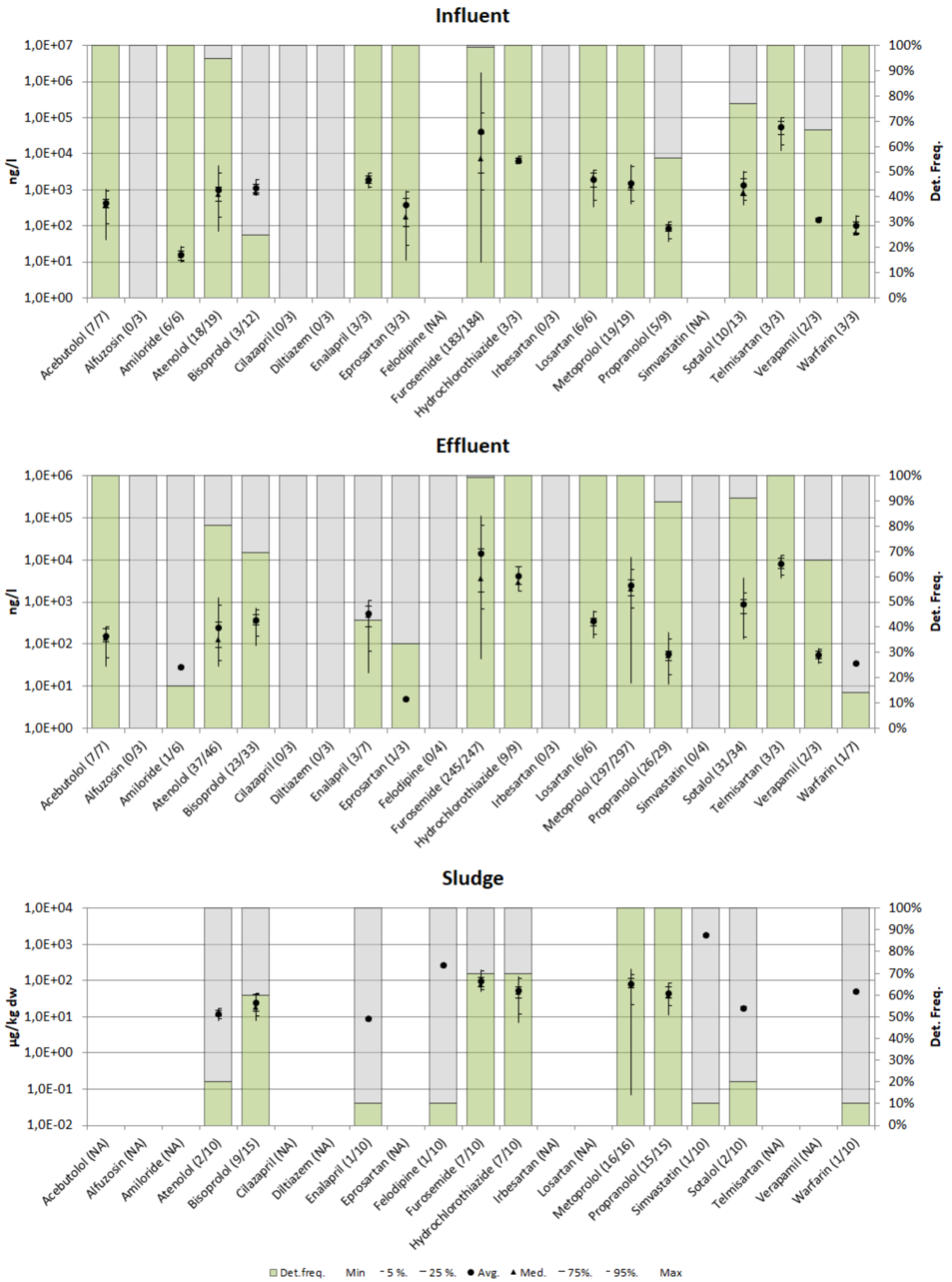

Figure 14. Detected concentrations, detection frequencies and the number of data points of cardiovascular agents presented for each substance and matrix. The line with markings presents concentrations and the green bars show the detection frequencies. The number of samples is presented on the horizontal axis. (NA = not analysed)

a maximum concentration of 128 ng/l. In the current WWTP dataset, furosemide and metoprolol were the cardiovascular agents detected most often with respective detection frequencies of 99 % and 100 %. Bisoprolol was detected in each of the three matrices with a total detection frequency of 58 %. In the effluent wastewater it was detected in 70 % of the samples, reaching a maximum concentration of 710 ng/l and an average concentration of 381 ng/l.

The range of reported concentrations as well as the number of data points and detection frequencies per substance and matrix are presented in figure 21 and the total number of data points reported from each country is presented in table 11. The distribution of data points and detections between the MP and SR data-calls is presented in Annex 2.

Central nervous system

Out of the nine APIs classified as central nervous system agents, seven were detected at least in one sample. Data points reported for effluent wastewater accounted for 74 % of the data points, while influent wastewater and sewage sludge accounted for 15 % and 12 % respectively.
By far the most commonly analyzed substance in the group was carbamazepine. It was detected in 99 % of the total number of samples. The average concentration reported for effluent wastewater (2 510 ng/l) was several times higher than the one reported for influent wastewater (312 ng/l).

Previously UNESCO & HELCOM (2017) reported primidone was detected in each of the 51 Baltic Sea water samples, reaching a maximum concentration of 58 ng/l. In the current WWTP dataset, only 17 effluent data points from Germany were reported for primidone. The substance was detected in each of the 17 effluent samples but was neither analyzed in influent wastewater nor in sewage sludge. The maximum concentration reached 1000 ng/l, while the average concentration was 529 ng/l.

The range of reported concentrations as well as the number of data points and detection frequencies per substance and matrix are presented in figure 15 and the total number of data points reported from each country is presented in table 21. The distribution of data points and detections between the MP and SR data-calls is presented in Annex 2.

Table 21. Number of data points reported from each country for central nervous system agents. The substances are ordered according to the number of samples.

Substance	n det./n tot.	n det. / n tot. per country						
		DK	EE	FI	DE	LV	PL	SE
Carbamazepine	407/413	15/17	6/6	114/117	272/273	-	-	-
Citalopram	30/33	17/17	-	13/16	-	-	-	-
Fluoxetine	15/23	-	0/6	9/10	6/7	-	-	-
Paroxetine	10/22	-	-	10/22	-	-	-	-
Primidone	17/17	-	-	-	17/17	-	-	-
Entacapone	8/10	-	-	8/10	-	-	-	-
Clonazepam	0/6	-	0/6	-	-	-	-	-
Sertraline	0/6	-	0/6	-	-	-	-	-
Diazepam	1/5	-	-	-	1/5	-	-	-
Tot.	**488/535**	**32/34**	**6/24**	**154/175**	**296/302**	**0/0**	**0/0**	**0/0**

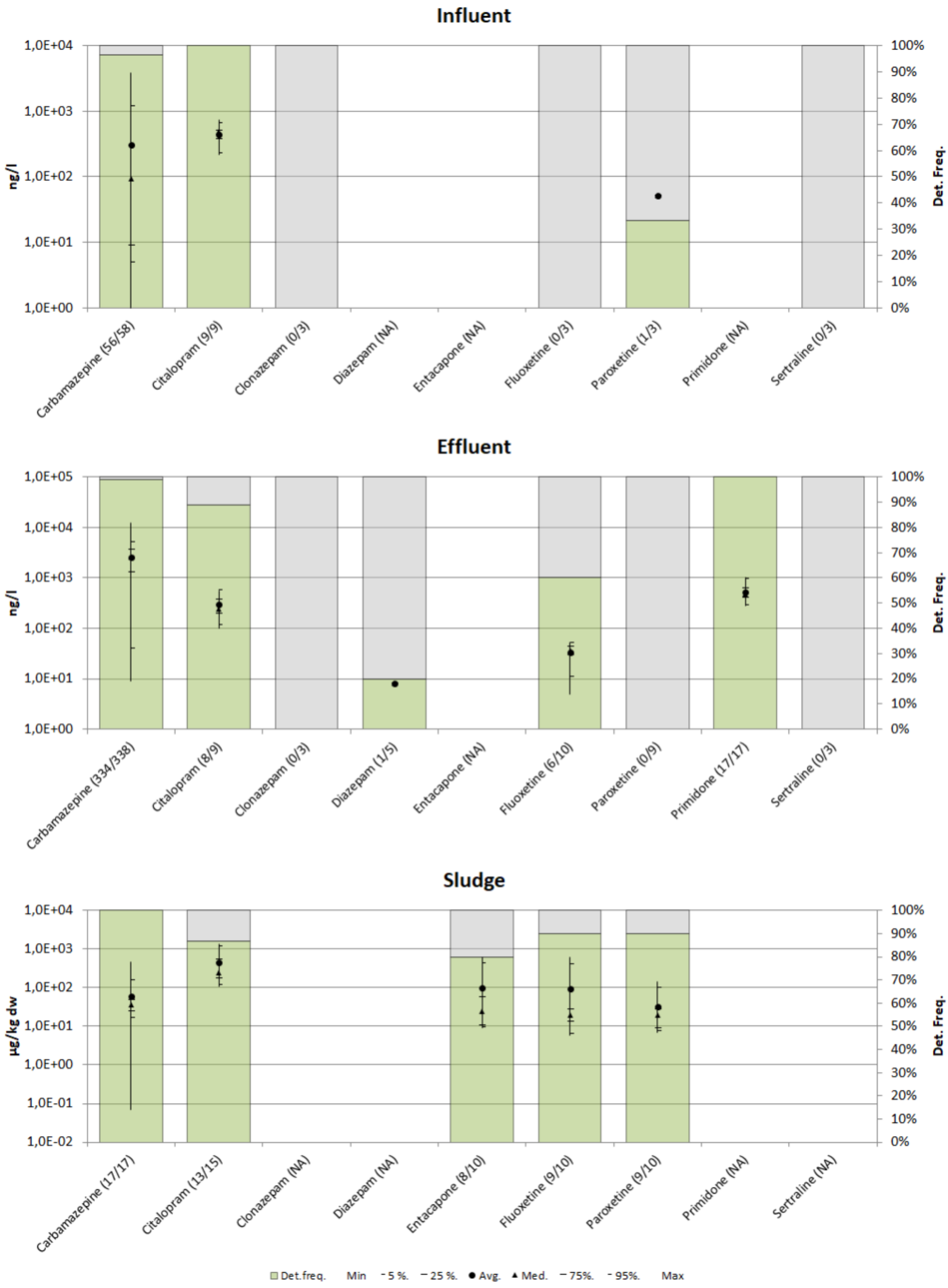

Figure 15. Detected concentrations, detection frequencies and the number of data points of central nervous system agents presented for each substance and matrix. The line with markings presents concentrations and the green bars show the detection frequencies. The number of samples is presented on the horizontal axis. (NA = not analysed)

Contrast agents

All five contrast agents were detected at least in one effluent sample. Data points reported for effluent wastewater accounted for 96 % of the data points, while sewage sludge accounted for 3 %. Measurement in sludger were reported only two contrast agents (iopamidol and iopromide). However, neither of them was detected in those samples. No results were reported concerning influent wastewater. Data points were reported only from Germany and Finland, with German data points accounting for 96 % of the total number.Two APIs (iopamidol and amidotrizoate) dominated the total number of reported datapoints on contrast agents.

The range of reported concentrations as well as the number of data points and detection frequencies per substance and matrix are presented in figure 23 and the total number of data points reported from each country is presented in table 13. The distribution of data points and detections between the MP and SR data-calls is presented in Annex 2.

Table 22. Number of data points reported from each country for contrast agents. The substances are ordered according to the number of samples.

Substance	n det./n tot.	n det. / n tot. per country						
		DK	EE	FI	DE	LV	PL	SE
Iopamidol	170/267	-	-	0/10	170/257	-	-	-
Amidotrizoate	246/252	-	-	-	246/252	-	-	-
Iopromide	5/15	-	-	0/10	5/5	-	-	-
Iohexol	5/5	-	-	-	5/5	-	-	-
Iomeprol	5/5	-	-	-	5/5	-	-	-
Tot.	**431/544**	**0/0**	**0/0**	**0/20**	**431/524**	**0/0**	**0/0**	**0/0**

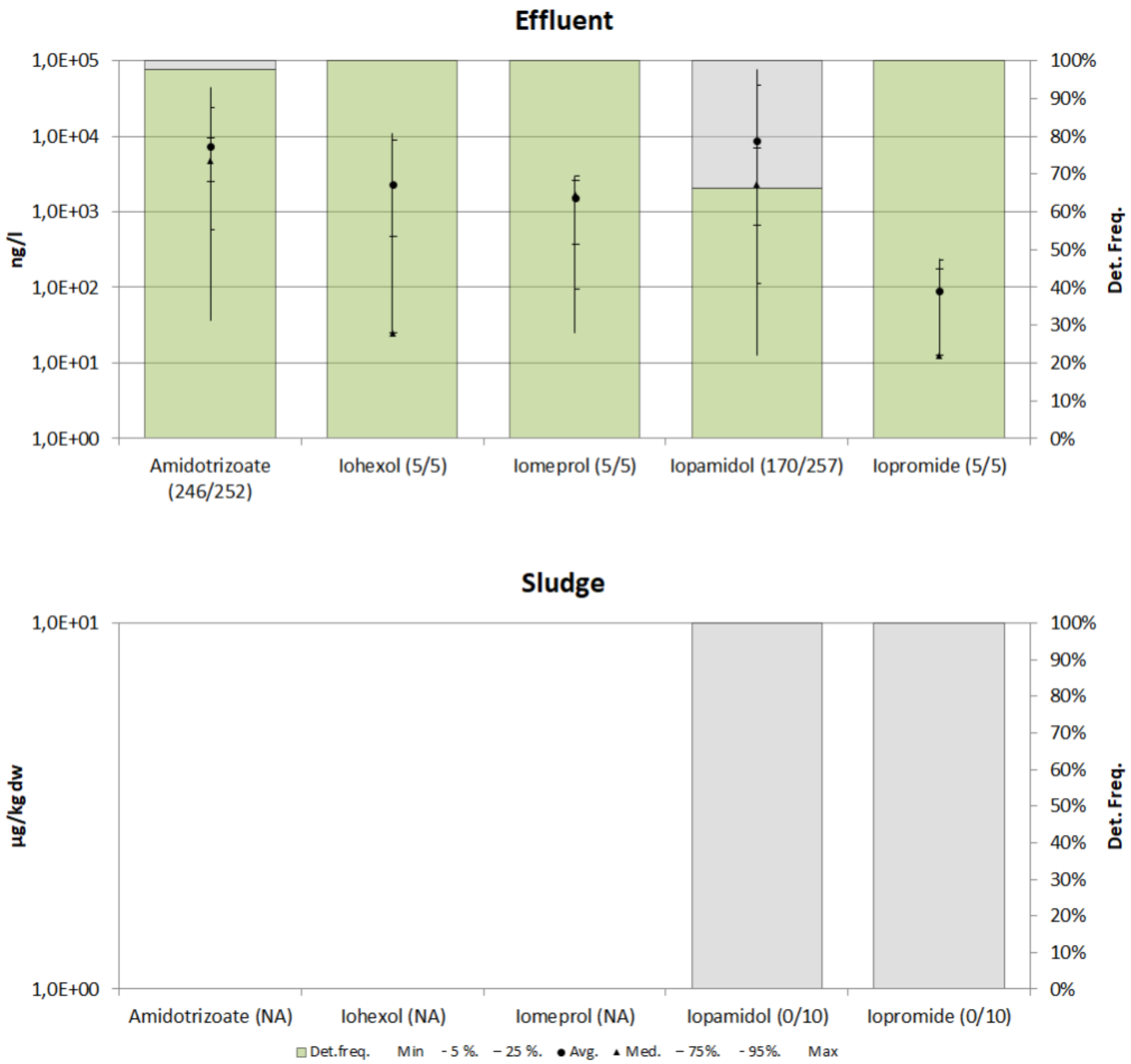

Figure 16. Detected concentrations, detection frequencies and the number of data points of contrast agents presented for each substance and matrix. The line with markings presents concentrations and the green bars show the detection frequencies. The number of samples is presented on the horizontal axis. (NA = not analyzed)

Chemotherapeutic agents

Out of the four APIs classified as chemotherapeutic agents, two were detected at least in one sample. Data points reported for effluent wastewater accounted for 28 % of the data points, while influent wastewater and sewage sludge accounted for 15 % and 57 % respectively. None of the APIs were detected in effluent samples.

Results concerning chemotherapeutic agents were reported only by Denmark and Finland. Results for capecitabin were reported only by Denmark, while results for cyclofosfamide, ifosfamide and methotrexate were only reported by Finland.

The range of reported concentrations as well as the number of data points and detection frequencies per substance and matrix are presented in figure 24 and the total number of data points reported from each country is presented in table 14. The distribution of data points and detections between the MP and SR data-calls is presented in Annex 2.

Table 23. Number of data points reported from each country for chemotherapeutic substances. The substances are ordered according to the number of samples.

Substance	n det./n tot.	n det. / n tot. per country						
		DK	EE	FI	DE	LV	PL	SE
Capecitabine	4/17	4/17	-	-	-	-	-	-
Methotrexate	1/16	-	-	1/16	-	-	-	-
Cyclofosfamide	0/14	-	-	0/14	-	-	-	-
Ifosfamide	0/14	-	-	0/14	-	-	-	-
Tot.	**5/61**	**4/17**	**0/0**	**1/44**	**0/0**	**0/0**	**0/0**	**0/0**

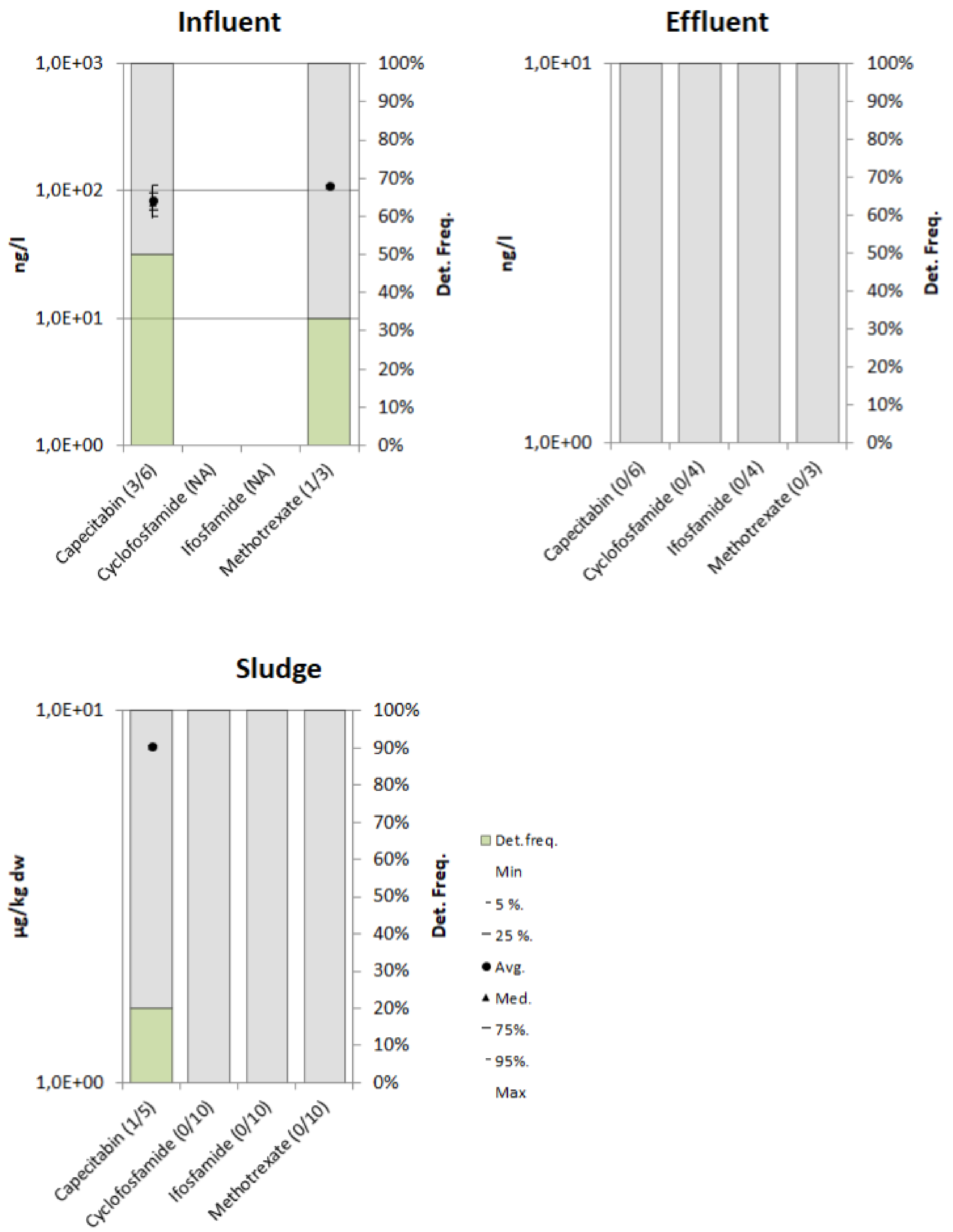

Figure 17. Detected concentrations, detection frequencies and the number of data points of chemotherapeutic agents presented for each substance and matrix. The line with markings presents concentrations and the green bars show the detection frequencies. The number of samples is presented on the horizontal axis. (NA = not analyzed)

Metabolic and gastrointestinal agents

Out of the four APIs classified as metabolic and gastrointestinal agents, three were detected at least in one sample. Data points reported for effluent wastewater accounted for 55 % of the data points, while influent wastewater and sewage sludge accounted for 39 % and 6 % respectively.

The most commonly analysed substance in the group was cimetidine, with data points on it accounting for 88 % of the total number of data points on the group. All data points on cimetidine were reported by Denmark (table 15).

Previously clofibric acid was reported to have been detected in 65 % of Baltic Sea marine water samples (UNESCO & HELCOM 2017). In the current WWTP dataset the substance was analyzed in only 10 sewage sludge samples and in neither of the water matrices. All data on clofibric acid in sewage sludge samples was reported from Finland.

The range of reported concentrations as well as the number of data points and detection frequencies per substance and matrix are presented in figure 25 and the total number of data points reported from each country is presented in table 15. The distribution of data points and detections between the MP and SR data-calls is presented in Annex 2.

Table 24. Number of data points reported from each country for metabolic and gastrointestinal agents. The substances are ordered according to the number of samples.

Substance	n det./n tot.	n det. / n tot. per country						
		DK	EE	FI	DE	LV	PL	SE
Cimetidine	244/422	244/422	-	-	-	-	-	-
Bezafibrate	21/34	-	-	16/29	5/5	-	-	-
Gemfibrozil	6/15	-	-	1/10	5/5	-	-	-
Clofibric acid	0/10	-	-	0/10	-	-	-	-
Tot.	**271/481**	**244/422**	**0/0**	**17/49**	**10/10**	**0/0**	**0/0**	**0/0**

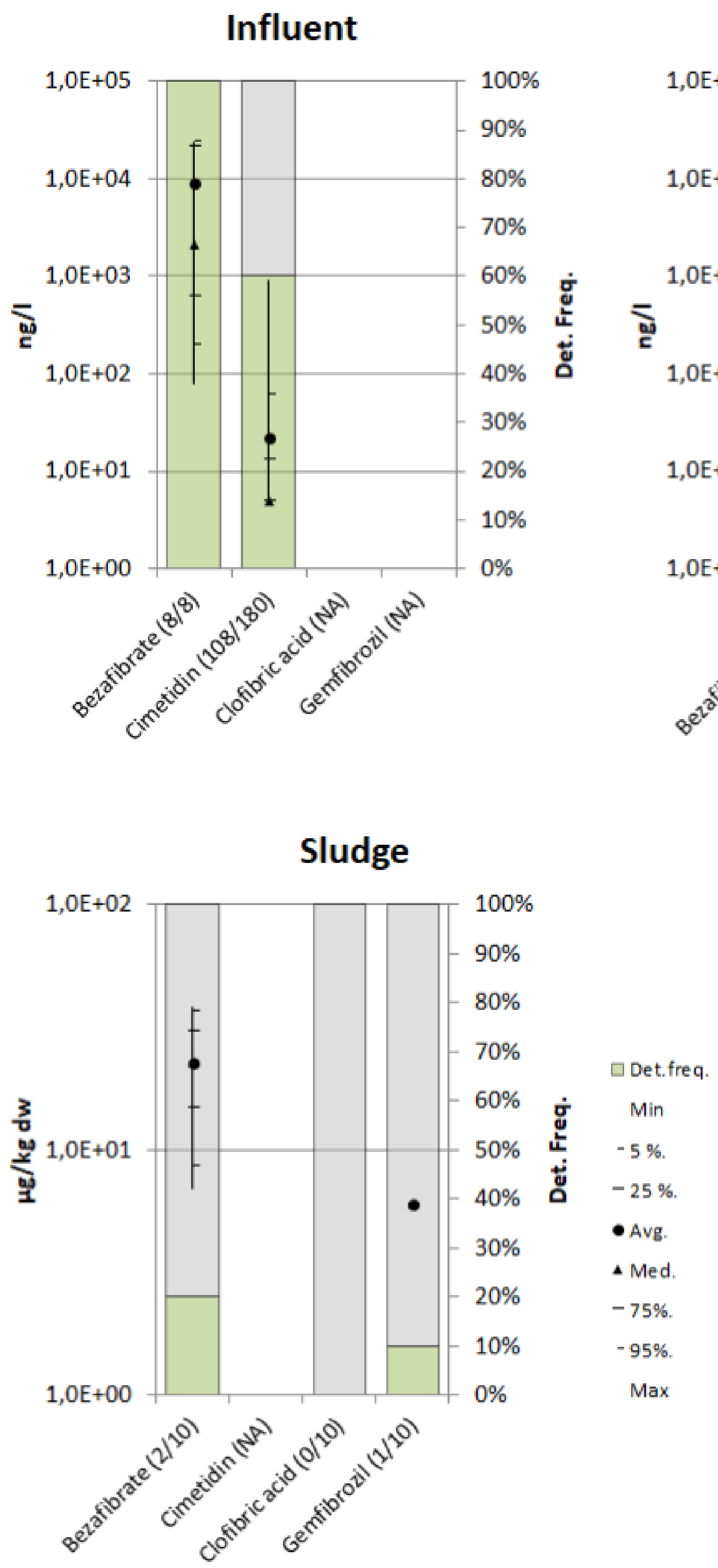

Figure 18. Detected concentrations, detection frequencies and the number of data points of metabolic and gastrointestinal agents presented for each substance and matrix. The line with markings presents concentrations and the green bars show the detection frequencies. The number of samples is presented on the horizontal axis. (NA = not analysed)

Respiratory agents

Out of the three APIs classified as respiratory agents, only salbutamol was detected in the samples. Data points reported for effluent wastewater accounted for 35 % of the data points, while influent waste water and sewage sludge accounted for 6 % and 59 % respectively. Data points were reported only from Finland and Germany (table 16).

The range of reported concentrations as well as the number of data points and detection frequencies per substance and matrix are presented in figure 26 and the total number of data points reported from each country is presented in table 16. The distribution of data points and detections between the MP and SR data-calls is presented in Annex 2.

Table 25. Number of data points reported from each country for respiratory agents. The substances are ordered according to the number of samples.

Substance	n det./n tot.	n det. / n tot. per country						
		DK	EE	FI	DE	LV	PL	SE
Salbutamol	6/27	-	-	2/22	4/5	-	-	-
Terbutaline	0/14	-	-	0/14	-	-	-	-
Clenbuterol	0/10	-	-	0/10	-	-	-	-
Tot.	**6/51**	**0/0**	**0/0**	**2/46**	**4/5**	**0/0**	**0/0**	**0/0**

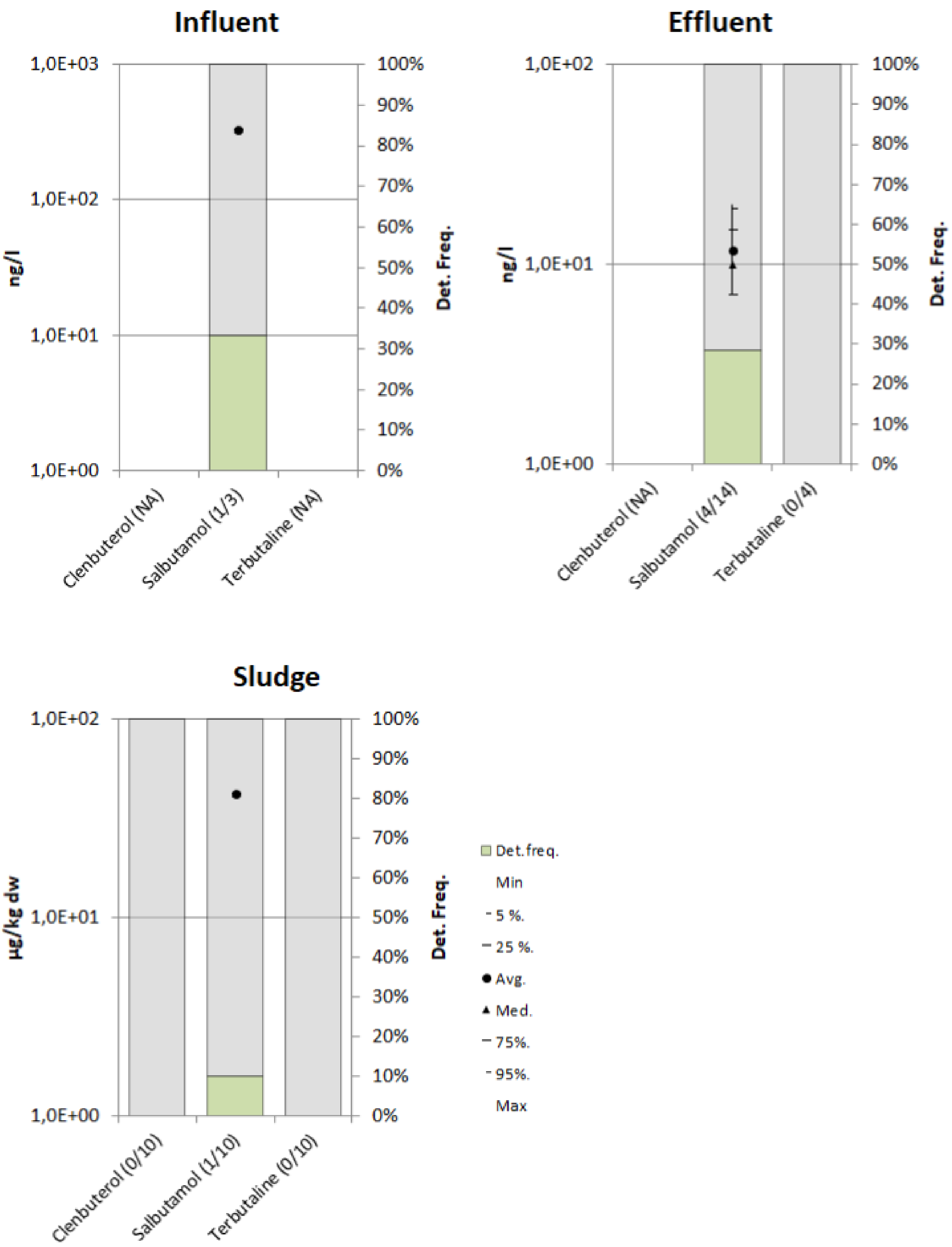

Figure 19. Detected concentrations, detection frequencies and the number of data points of respiratory agents presented for each substance and matrix. The line with markings presents concentrations and the green bars show the detection frequencies. The number of samples is presented on the horizontal axis (NA = not analysed)

Hormones and hormone antagonists

Out of the 15 APIs classified as hormones and hormone antagonists, 11 were detected at least in one sample. Data points reported for effluent wastewater accounted for 55 % of the data points, while influent waste water and sewage sludge accounted for 40 % and 5 % respectively.

There are three hormones in the WFD Watch list (2018/840/EC): 17α-ethinylestradiol, 17β-estradiol and Estrone. These substances were analyzed in each of the three WWTP matrices, and they accounted for 90 % of the total number of data points on the group. The detection frequencies for each of the three substances was slightly lower in effluent samples than in influent samples. The reported maximum concentrations in effluent samples for 17α-ethinylestradiol, 17β-estradiol and Estrone were 300 ng/l, 91 ng/l and 610 ng/l, respectively.

The proposed EQS-values for 17α-ethinylestradiol and 17β-estradiol are 0.035 ng/l and 0.4 ng/l, respectively (Loos et al. 2018). The effluent concentrations of 17α-ethinylestradiol and 17β-estradiol exceeded these values in 100 % of the samples exceeding the LOQ. Similarly, estrone concentrations in effluent waste water exceeded the proposed EQS-value (3.6 ng/l, Loos et al. 2018) in 69 % of the samples exceeding the LOQ. The described three substances are not included as HELCOM-indicators due to lack of reliable monitoring data. However, hormones are considered for inclusion in the assessment of the state of the Baltic Sea marine environment in future.

The range of reported concentrations as well as the number of data points and detection frequencies per substance and matrix are presented in figure 27 and the total number of data points reported from each country is presented in table 17. The distribution of data points and detections between the MP and SR data-calls is presented in Annex 2.

Table 26. Number of data points reported from each country for hormones and hormone antagonists. The substances are ordered according to the number of samples.

Substance	n det./n tot.	n det. / n tot. per country						
		DK	EE	FI	DE	LV	PL	SE
17β-estradiol	269/500	257/453	-	12/45	-	-	0/2	-
17α-ethinylestradiol	172/475	165/421	0/6	0/40	-	5/5	2/3	-
Estrone	374/457	360/422	0/6	9/22	-	5/5	0/2	-
Progesterone	13/29	-	0/6	10/20	-	-	-	3/3
Estriol	2/28	-	0/6	2/20	-	-	0/2	-
Testosterone	6/20	-	-	6/20	-	-	-	-
Tamoxifen	1/18	1/12	0/6	-	-	-	-	-
Hydrocortisone	4/16	-	-	4/16	-	-	-	-
Norethisterone	1/12	1/12	-	-	-	-	-	-
Methylprednisolone	1/10	-	-	1/10	-	-	-	-
Levonorgestrel	3/9	-	0/6	-	-	-	-	3/3
Etonogestrel	0/6	-	0/6	-	-	-	-	-
Finasteride	0/6	-	0/6	-	-	-	-	-
Flutamide	0/6	-	0/6	-	-	-	-	-
Diethylstilbestrol	0/2	-	-	-	-	-	0/2	-
Tot.	**846/1594**	**784/1320**	**0/54**	**44/193**	**0/0**	**10/10**	**2/11**	**6/6**

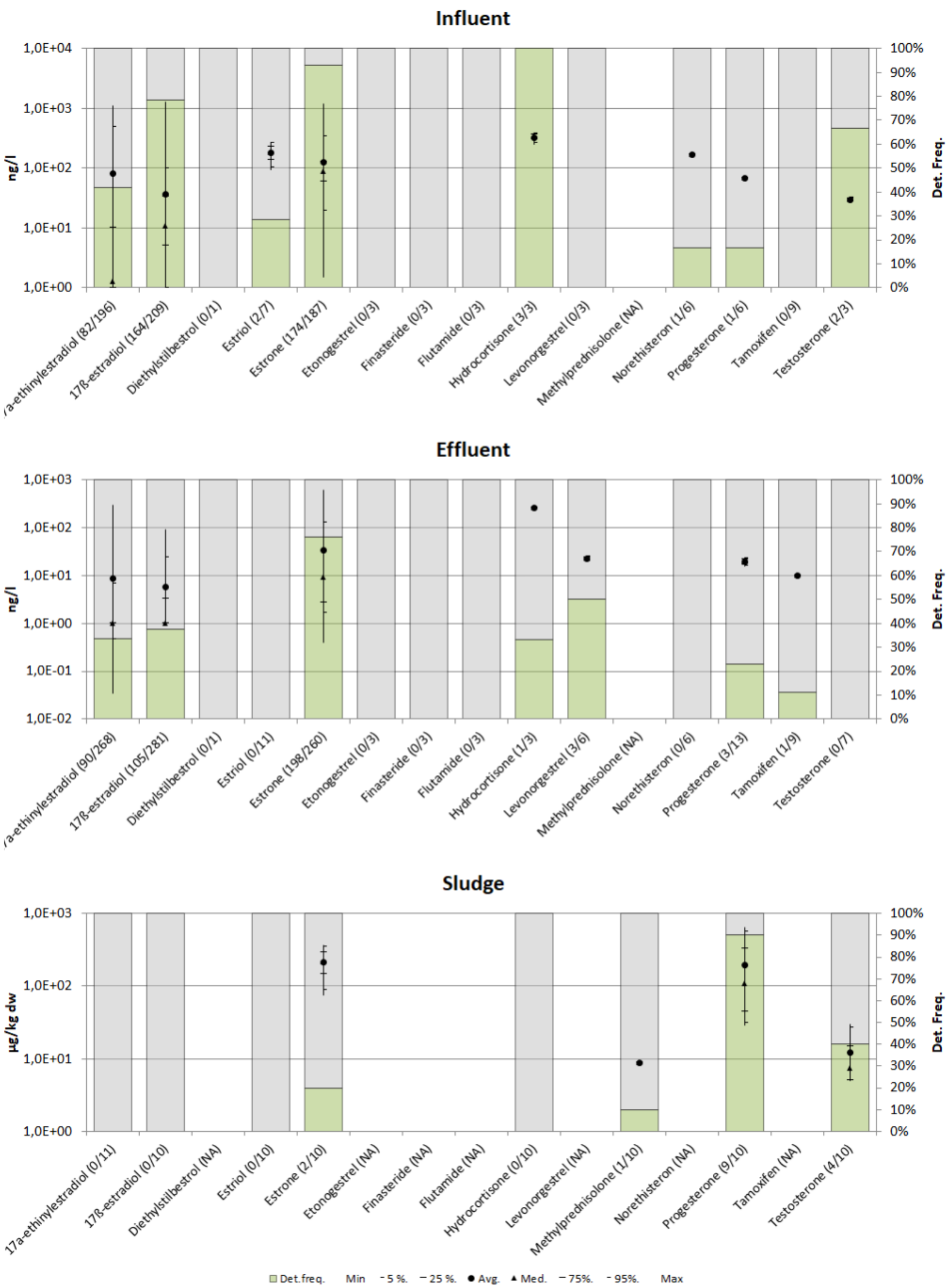

Figure 20. Detected concentrations, detection frequencies and the number of data points of hormones and hormone antagonists presented for each substance and matrix. The line with markings presents concentrations and the green bars show the detection frequencies. The number of samples is presented on the horizontal axis. (NA = not analysed)

Recreational drugs

The dataset contained information on eight substances classified here as recreational drugs. Concentrations of two of these substances (methylenedioxypyrovalerone (MDPV) and meta-chlorophenylpiperazine (mCPP)) were reported >LOD. These data points were excluded from further analysis. The six remaining substances were detected in each reported sample. All data concerning recreational drugs were reported by Poland for the MP data call, and the data points covered only influent and effluent waste waters.

The most frequently analyzed substance in the group was MDMA (ecstasy). The substance was detected in both influent and effluent waste waters.

The range of reported concentrations as well as the number of data points and detection frequencies per substance and matrix are presented in figure 21.

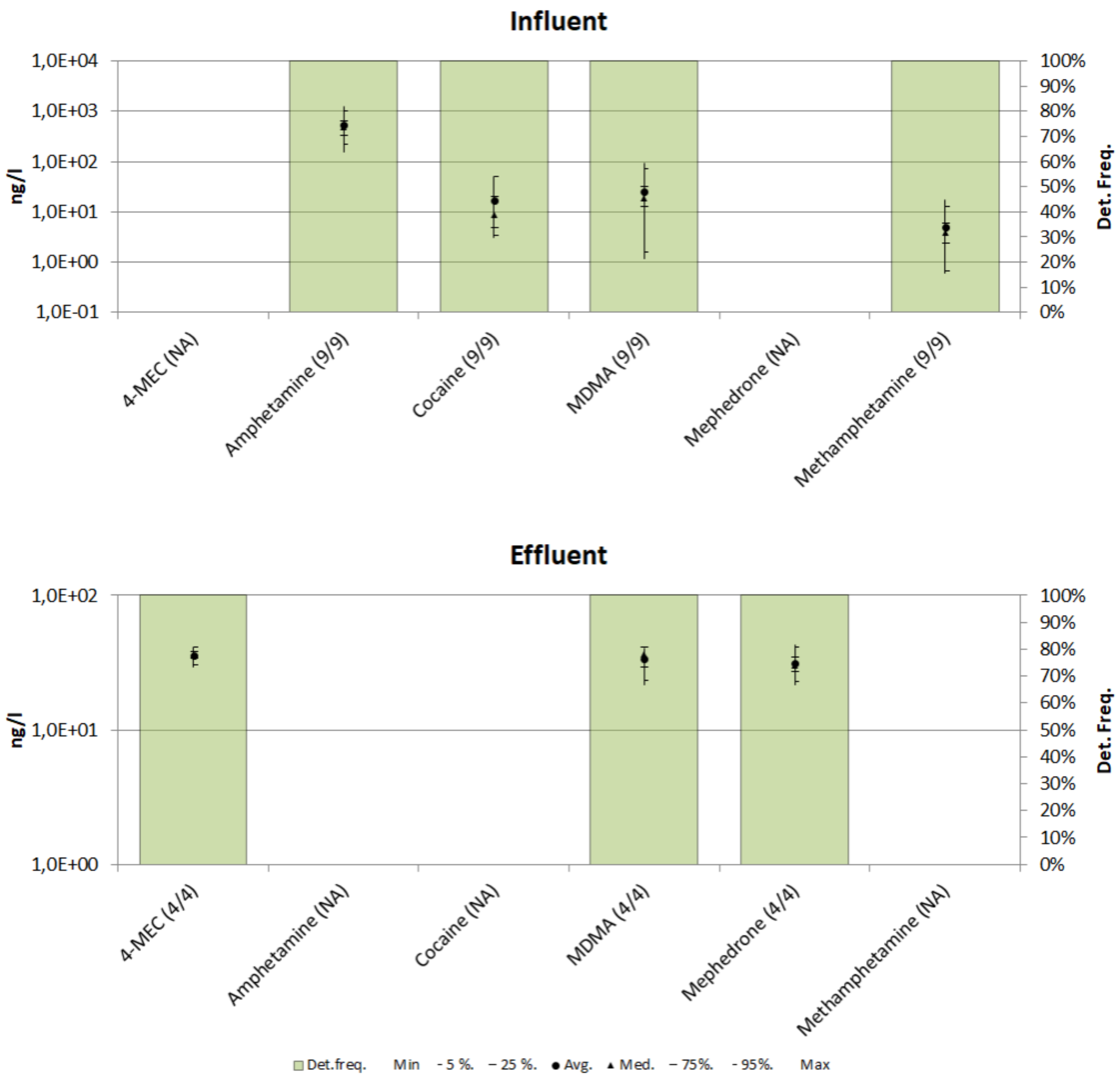

Figure 21. Detected concentrations, detection frequencies and the number of data points of metabolites presented for each substance and matrix. The line with markings presents concentrations and the green bars show the detection frequencies. The number of samples is presented on the horizontal axis. (NA = not analysed)

Metabolites

The dataset contained results for four metabolites: one for ibuprofen (2-hydroxyibuprofen), two for diclofenac (4OH- diclofenac, 5OH-diclofenac) and one for cocaine (benxoylecgonine). 2-hydroxyibuprofen was the most often analyzed metabolite. It was detected in 97 % of the samples. 59 % of the data points were reported for effluent wastewater and the remaining 41 % for influent wastewater. No data was reported for sewage sludge. All of the reported data points for 2-hydroxyibuprofen were reported by Denmark, thus, despite the high number of data points, the spatial coverage of the data was low.

Interestingly the detection frequency and median concentration in Danish effluent wastewaters were higher for 2-hydroxyibuprofen (97 %, 770 ng/l) than for the parent compound, ibuprofen (85 %, 330 ng/l). Diclofenac and cocaine metabolites were only reported by Poland.

The range of reported concentrations as well as the number of data points and detection frequencies per substance and matrix are presented in figure 29 and the total number of data points reported from each country is presented in table 18. The distribution of data points and detections between the MP and SR data-calls is presented in Annex 2.

Table 18. Number of data points reported from each country for metabolites. The substances are ordered according to the number of samples.

Substance	n det./n tot.	n det. / n tot. per country						
		DK	EE	FI	DE	LV	PL	SE
2-hydroxyibuprofen	413/423	413/423	-	-	-	-	-	-
4OH-diclofenac	20/24	-	-	-	-	-	20/24	-
5OH-diclofenac	18/24	-	-	-	-	-	18/24	-
Benzoylecgonine	8/8	-	-	-	-	-	8/8	-
Tot.	**459/479**	**413/423**	**0/0**	**0/0**	**0/0**	**0/0**	**46/56**	**0/0**

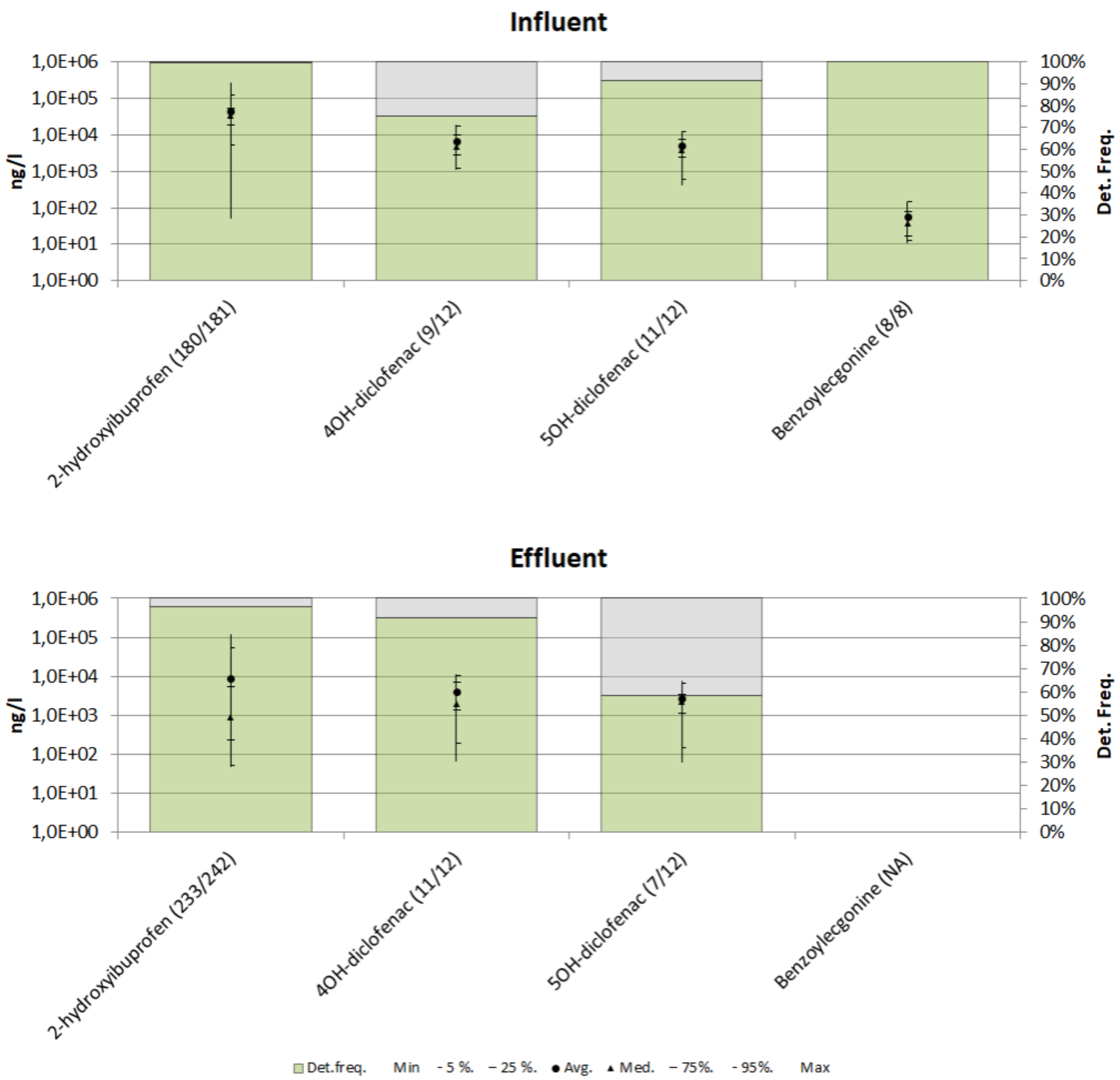

Figure 22. Detected concentrations, detection frequencies and the number of data points of metabolites presented for each substance and matrix. The line with markings presents concentrations and the green bars show the detection frequencies. The number of samples is presented on the horizontal axis. (NA = not analysed)

6.3. Brief summary

The collated and analysed data on pharmaceuticals at WWTPs – derived from influents, effluents and sludge – is the most comprehensive compilation of data on pharmaceuticals in the Baltic Sea region. Data of more than 100 different pharmaceuticals were analysed and revealed that still large knowledge gaps exist. For example, several substances 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. Moreover, to assess which of them cause risk to the environment, their concentrations in environmental samples should be compared to relevant ecotoxicological data. Furthermore, detection limits and analysis methods should be aligned among countries and preferably an equally distributed dataset should be achieved. In general, many substances from all 11 substance groups are found at high detection frequencies and are found in effluents at similar orders of magnitude as in the influents. For example, data on anti-inflammatory and analgesic substances showed that the overall detection frequency was high (about 76%). In the case of diclofenac, one of the most highly prioritized pharmaceuticals within the EU water framework directive (2000/60/EC), the detection frequency was between 98-100 % of the reported analyses (influent/effluent/sludge) and effluent samples exhibited concentrations which exceeded the proposed EQS-value for the substance in 93 % of the samples. Data on antimicrobial and antiparasitic substances contained five antibiotics, which were listed on the second WFD watch list (2018/840/EC), and showed that overall detection frequency for the group was above 75%. Furthermore, several effluent samples exceeded the proposed EQS-level. In the case of azithromycin, concentrations exceeded the EQS-value in 91 % of the samples. Although the five antibiotics in the WFD watch list (erythromycin, ciprofloxacin, clarithromycin, amoxicillin, azithromycin) are not included in the HELCOM indicators, though, the use of some APIs of this group in the assessment of contamination of the Baltic Sea marine environment is considered. Similar discussion is also ongoing for three hormones on the WFD watch list, namely 17β-estradiol, 17α-ethinylestradiol and estrone. Here, concentrations in effluent waste water exceeded the proposed EQS-value for estrone in 61 % of the quantified samples (53 % of all samples) and for 17α-ethinylestradiol and 17β-estradiol in 100 % of the quantified samples (34 % and 37 % of all reported samples, respectively).

Overall, the data on pharmaceuticals in WWTPs reveals that many of these substances are observed in effluents at almost the same concentration level as in influents. It indicates currently low removal level of these compounds and the need of more measures to minimize their release to the environment (chapter 7). This could be achieved in many ways, e.g. targeting pharmaceuticals at their source (e.g. prescription and consumption reduction) as well as by improving technologies at WWTPs to increase their removal efficiency. Different technologies will be discussed in the next chapter. However, the mitigation of pharmaceutical emissions will likely require measures outside the technical facilities of WWTPs as well. According to CWPharma project, these can include e.g. elimination of improperly managed pharmaceutical waste and increasing the sewer network coverage of centralized WWTPs as well as taking environmental aspects into consideration when selecting medication (Äystö & Stapf 2020).

7. Brief on technologies for removing micropollutants from wastewater

The HELCOM joint action on micropollutants incudes a summary report on advanced wastewater treatment techniques considering among other aspects their feasibility, costs, and good practices and management options. This section provides a brief overview of four innovative technologies used to remove micropollutants from wastewaters.

The Baltic Sea is typically loaded with 1-10 t/a of each individual organic micropollutant (e.g., pharmaceuticals, biocides, flame retardants and other compounds) via sewerage systems (i.e. 1-10.000 t/a in total). The highest concentrations of micropollutants in the Baltic Sea occur where wastewater is either directly (via pipes) or indirectly (via rivers) discharged. Although a broad range of micropollutants are partially biodegraded in conventional wastewater treatment plants (WWTP), treated urban wastewater remains an important point source of chemicals in the Baltic Sea.

Stormwater (rainwater in contact with and collected by urban surfaces such as roofs, road and building surfaces) can become a dominant source of micropollutants which are present on surfaces exposed to rain, such as buildings (e.g., biocides) and roads (e.g., PAH). **Combined sewer overflow** from sewer systems which collect both wastewater and stormwater during large rainfall events can also contain high pollutant loads.

To reduce the amount of micropollutants entering the Baltic Sea, the benefits and disadvantages of different technologies capable of removing micropollutants have been compared. Most of the technologies listed below are able to remove up to 90% of compounds (with variation between <20% to >99.9%).

- **Membrane bioreactors (MBR)** increase the removal of biodegradable micropollutants in comparison to conventional WWTPs and are a reliable barrier against microplastics and microbial contamination.
- **Ozonation** can remove a large variety of compounds, as demonstrated at several full-scale wastewater treatment plants, and provides partial disinfection of wastewater. A disadvantage is the formation of potentially toxic transformation products, which requires mandatory biological post-treatment after ozonation. However, high bromide concentrations in the wastewater can lead to the formation of bromate, which is a carcinogenic compound.
- **Activated carbon (AC)** can successfully remove numerous micropollutants, as demonstrated at several full-scale wastewater treatment plants. In the case of powdered activated carbon (PAC) application, PAC is recirculated into the main biological wastewater treatment step for more efficient usage and is eventually removed along with excess sludge. However, the dried excess sludge can then no longer be subsequently used in agriculture, which presents a problem for many areas in the Baltic Sea catchment. The main environmental drawback of AC comes from the burning of fossil fuels during its production and regeneration, which results in a high carbon footprint. Unlike ozonation, AC can also remove per- and polyfluoroalkyl compounds (PFAS).
- **Dense membranes**, such as **reverse osmosis** or **nanofiltration** membranes, are an established technology in potable water reuse and can remove both micropollutants

and microplastics. However, the removed compounds must be destroyed in a separate step. Compared to ozone or AC, using dense membranes for the protection of surface water is not economical.

- **Biofilm technologies** can remove even more biologically degradable compounds than conventional WWTPs. As all biofilm systems rely on biodegradation, they have a limited effect on fully inert chemicals. Moving bed biofilm reactors **(MBBRs)** have already been tested in the Scandinavian context, but a full-scale demonstration for micropollutant removal is missing due to the poor cost-benefit of MBBRs in comparison to ozone or AC. **Biofilters**, e.g. retention soil filters, for polishing of secondary effluent can also significantly increase micropollutant removal, but require large surface areas and thus are more suitable for smaller catchments. They additionally provide partial disinfection and can remove microplastics.

BONUS CLEANWATER estimated that removing micropollutants from wastewater will cost around 0.2 €/m^3 (Total operation costs, depending on size of treatment plant, and local energy costs (Mulder et al. 2015). A more recent CWPharma project estimated that the cost for removing micropollutants from municipal wastewater ranges between 0.05-0.25 €/m^3 (total costs including investment and operation) (Stapf et al. 2020). Costs are very site specific and can be affected by the following non-exhaustive list of factors: economy of scale, use of existing infrastructure, need for additional water hydraulics, organic matter background of treated water, cost for electricity, etc.

Regarding the protection of surface water and the Baltic Sea, the two most mature technologies for medium to large WWTPs are activated carbon and ozone. Both technologies are already operational at numerous full-scale plants in Sweden, Germany and Switzerland. Dense membranes are technologically mature but not economical for the desired purpose of surface water protection. Biofilm technologies are mature in regard to implementation but lack a systematic performance comparison with other technologies. Nevertheless, they may contribute to a significant load reduction if applied at the manifold of smaller WWTPs present in the Baltic Sea catchment.

It should be noted that apart from dense membranes, no technology is capable of removing all micropollutants. Therefore, realistic and economically feasible load reduction targets are needed on a national and/or BSR level: Switzerland and Germany have proposed design criteria which enable 80 % removal of a select set of compounds. Such criteria could also be developed for the Baltic Sea region taking into account realistic and socio-economically feasible targets.

8. Conclusions and recommendations

This report provides the most comprehensive compilation of existing data on selected micropollutants at WWTPs in the Baltic Sea region. However, there are data gaps that need to be addressed in order to carry out a more comprehensive assessment of the extent of contamination by phenolic substances, PFAS, metals and pharmaceuticals. Reporting from all Contracting Parties with harmonized analytical methods – sensitive enough to detect substances at the level of the proposed environmental quality standards or the threshold values –currently remains challenging. Thus, an intensified collaboration and synergy is strongly encouraged. This compilation for data on micropollutants at WWTPs highlights that there is no sufficient removal of micropollutants, from all the assessed substance groups. Thus, the previously expressed concern by the Contracting Parties for these substance groups is justified and reveals the urgent need for improvement.

Technological solutions exist already and are capable – after application at WWTPs - to increase removal efficiency to almost 80% for most of the substances. To implement the urgently needed new measures and technology, the framework for hazardous substances needs to be updated and include issues on emerging pollutants. The acquired information should thus be considered for incorporation in the Baltic Sea regional policy framework for hazardous substances in line with HELCOM Baltic Sea Action Plan. Setting of an effective regional system to monitor priority and legacy pollutants and collect information on alarming contaminants and draw attention of regional experts and policy makers to emerging challenges with subsequent prompt respond through new measures is the key for prevention of deterioration of the aquatic environment and achieving the ambitious goal the 2021 Baltic Sea Action Plan.

Actions for reducing the input of micropollutants and also microplastic into the Baltic Sea were explored and summarised in brief by BONUS CLEANWATER project. Overall, BONUS CLEANWATER the project recommends focusing on removing organic micropollutants from effluent wastewater, while testing in which cases cost effective measures can be followed to decrease pollution in stormwater and combined sewer overflow. BONUS CLEANWATER proposed that HELCOM considers the following actions:

- **Implement a plan to remove micropollutants from wastewater**, especially where drinking water resources are affected or are getting scarce or ecosystems need protection
- **Implement a holistic plan to decrease loads of micropollutants and microplastics into the Baltic Sea**, considering that most inputs result from conventional wastewater effluents

Finally, BONUS CLEANWATER pointed out that it is crucial for the acceptance of the policy to ensure adequate financing of the measures. Considering the high investments necessary following new regulations in wastewater treatment it will be important to work with regulation, where it will be possible for wastewater treatment plants to predict emerging permanent requirements on micropollutants and micropollutants removal.

Generally, suggested measures for reducing the input of hazardous substances are from the following areas:

1. Increase regionally harmonized monitoring and assessment effort to fill in knowledge gaps on sources and pathways of contaminants, which will be crucial in identifying and avoiding pollution sources;
2. Further develop methodological and technical base for monitoring and assessment to obtain adequate and reliable information for the whole Baltic Sea area;
3. Apply innovative technical solutions at WWTPs to increase complex removal of contaminants with subsequent monitoring of their efficiency;
4. Strengthen HELCOM requirements regarding removal of contaminants from wastewater;
5. Avoid or reduce usage of substances of concern in industry and households via policies, public awareness and other regulatory and non-regulatory measures;
6. Avoid or reduce leakage of micropollutants from diffuse sources, such as pharmaceuticals from improper disposal of medicinal waste or PFAS from contaminated soils, via policies, public awareness and other regulatory and non-regulatory measures;
7. Increase collaboration and synergies between different organisations and processes addressing the problem of contamination of the environment by hazardous substances on a national and international level.

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Annex 1.

Extra information: Names and CAS for nonylphenols (clarification for all nonylphenols, i.e. from WWTPs, rivers and coastal waters)

National agencies responsible for submitting the data to HELCOM were contacted and asked to clarify which molecules that were analysed. According to the contact person at the Swedish EPA, in the Swedish dataset 4-nonylphenol (branched) 84852-15-3 in fact represents the sum of linear and branched isomers. 4-nonylphenol 104-40-5 includes only the straight isomers, and constitutes <10% of the technical product "4-nonylphenol". This parameter has been reported separately only on a few occasions. All Swedish analyses are supposedly only of phenols with the OH-group in para-position.

Lithuanian data, however, includes separate data entries for three CAS-numbers (which are all compared separately to the EQS of nonylphenol in the status evaluation) according to the Lithuanian contact person:

1. Nonylphenol (CAS 84852-15-3) or 4-nonylphenol (branched) – technical product, mixture of ring and branched chain isomers.
2. Nonylphenol (technical) (CAS 25154-52-3) – technical product, mixture of linear chain isomers.
3. 4-n-Nonylphenol (CAS_104-40-5) branched and linear – substances with a linear and/or branched alkyl chain with a carbon number of 9 covalently bound in position 4 to phenol.
4. Latvian "Nonylphenol" 25145-52-3 is, according to the Latvian contact person, the sum of 4-n-nonylphenol and 4-t-nonylphenol.

Note that the EUs EQS directive from 2008 lists Nonylphenols (4-Nonylphenol) with CAS 84852-15-3, and this has been amended in 2013 footnote 5 and 6 in Annex I: Nonylphenol (CAS 25154-52-3, EU 246-672-0) including isomers 4-nonylphenol (CAS 104-40-5, EU 203-199-4) and 4-nonylphenol (branched) (CAS 84852-15-3, EU 284-325-5). Octylphenol (CAS 1806-26-4, EU 217-302-5) including isomers 4-(1,1',3,3'-tetrametylbutyl)-phenol (CAS 140-66-9, EU 205-426-2).

Annex 2.

Total number of analyses and detections for each matrix.

Substance	Influent					Effluent					Sludge				
	MP		SR		Det. Freq. (%)	MP		SR		Det. Freq. (%)	MP		SR		Det. Freq. (%)
	n (tot.)	n (>LOQ)	n (tot.)	n (>LOQ)		n (tot.)	n (>LOQ)	n (tot.)	n (>LOQ)		n (tot.)	n (>LOQ)	n (tot.)	n (>LOQ)	
Anti-inflammatory and analgesic agents															
Beclomethasone	-	-	-	-	-	-	-	-	-	-	-	-	10	0	0.0%
Buprenorphine	-	-	3	0	0.0	-	-	3	0	0.0	-	-	-	-	-
Codeine	-	-	9	9	100.0	-	-	9	9	100.0	-	-	-	-	-
Diclofenac	36	36	28	27	98.4	47	47	202	199	98.8	-	-	15	15	100.0
Diflunisal	1	0	-	-	0.0	1	0	-	-	0.0	-	-	-	-	-
Fentanyl	-	-	9	0	0.0	-	-	9	0	0.0	-	-	-	-	-
Flurbiprofen	13	5	-	-	38.5	13	0	-	-	0.0	-	-	-	-	-
Gabapentin	-	-	-	-	-	12	12	5	5	100.0	-	-	-	-	-
Ibuprofen	120	120	127	127	100.0	144	124	203	135	74.6	-	-	16	9	56.2
Indometacin	-	-	-	-	-	-	-	5	5	100.0	-	-	-	-	-
Ketoprofen	28	25	15	14	90.7	33	24	33	24	72.7	-	-	15	6	40.0
Naproxen	41	39	15	15	96.4	61	49	33	30	84.0	-	-	15	6	40.0
Paracetamol	95	93	104	75	84.4	103	89	164	37	47.2	-	-	10	8	80.0
Phenazon	-	-	-	-	-	-	-	5	5	100.0	-	-	-	-	-
Propofol	-	-	6	6	100.0	-	-	7	5	71.4	-	-	-	-	-
Salicylic acid	80	80	100	74	85.6	84	84	159	25	44.9	-	-	-	-	-
Tramadol	-	-	9	9	100.0	-	-	9	9	100.0	-	-	5	5	100.0

Antimicrobial and antiparasitic agents															
Amoxicillin	-	-	6	2	33.3	-	-	6	0	0.0	-	-	6	0	0.0
Ampicillin	3	1	22	21	88.0	3	1	34	22	62.2	1	1	40	40	100.0
Azithromycin	23	23	9	6	90.6	38	38	9	4	89.4	-	-	5	5	100.0
Cefadroxil	-	-	3	1	33.3	-	-	3	3	100.0	-	-	-	-	-
Cefuroxime	3	1	6	6	77.8	7	0	6	4	30.8	-	-	16	13	81.2
Ciprofloxacin	23	23	12	5	80.0	54	53	17	10	88.7	-	-	11	4	36.4
Clarithromycin	-	-	-	-	-	-	-	-	-	-	-	-	10	10	100.0
Clindamycin	-	-	-	-	-	-	-	-	-	-	-	-	10	9	90.0
Doxycycline	-	-	9	9	100.0	-	-	9	9	100.0	-	-	-	-	-
Erythromycin	-	-	-	-	-	-	-	-	-	-	-	-	10	0	0.0
Fendendazole	3	3	3	0	50.0	3	1	3	0	16.7	-	-	10	10	100.0
Flubendazole	3	0	6	3	33.3	7	1	6	1	15.4	-	-	16	1	6.2
Fluconazole	-	-	9	1	11.1	-	-	9	0	0.0	-	-	-	-	-
Ivermectin	-	-	16	13	81.2	-	-	28	8	28.6	1	1	40	30	75.6
Ketoconazole	-	-	16	11	68.8	4	1	30	11	35.3	1	1	40	30	75.6
Metronidazole	-	-	3	0	0.0	-	-	3	0	0.0	-	-	10	10	100.0
Miconazol	-	-	-	-	-	-	-	-	-	-	-	-	10	0	0.0
Norfloxacin	-	-	6	0	0.0	-	-	6	0	0.0	-	-	6	0	0.0
Ofloxacin	-	-	9	7	77.8	-	-	9	6	66.7	-	-	5	5	100.0
Oxytetracycline	79	79	102	91	93.9	83	83	159	149	95.9	-	-	-	-	-
Penicillin G benzathine	79	79	110	54	70.4	104	98	252	173	76.1	-	-	16	1	6.2
Penicillin V	3	3	3	0	50.0	7	3	5	2	41.7	1	1	10	10	100.0
Roxithromycin	180	180	-	-	100.0	253	253	-	-	100.0	-	-	-	-	-
Sulfamethizol	82	82	111	75	81.3	102	102	175	105	74.7	-	-	16	5	31.2
Sulfamethoxazole	-	-	-	-	-	4	0	-	-	0.0	-	-	10	0	0.0

Tetracycline	-	-	6	2	33.3	-	-	6	0	0.0	-	-	6	0	0.0
Triclosan	3	1	22	21	88.0	3	1	34	22	62.2	1	1	40	40	100.0
Trimethoprim	23	23	9	6	90.6	38	38	9	4	89.4	-	-	5	5	100.0
Tylosin	-	-	3	1	33.3	-	-	3	3	100.0	-	-	-	-	-
Cardiovascular agents															
Acebutolol	-	-	7	7	100.0	-	-	7	7	100.0	-	-	-	-	-
Alfuzosin	-	-	3	0	0.0	-	-	3	0	0.0	-	-	-	-	-
Amiloride	-	-	6	6	100.0	-	-	6	1	16.7	-	-	-	-	-
Atenolol	3	3	16	15	94.7	23	17	23	20	80.4	-	-	10	2	20.0
Bisoprolol	3	3	9	0	25.0	19	18	14	5	69.7	-	-	15	9	60.0
Cilazapril	-	-	3	0	0.0	-	-	3	0	0.0	-	-	-	-	-
Diltiazem	-	-	3	0	0.0	-	-	3	0	0.0	-	-	-	-	-
Enalapril	3	3	-	-	100.0	7	3	-	-	42.9	-	-	10	1	10.0
Eprosartan	-	-	3	3	100.0	-	-	3	1	33.3	-	-	-	-	-
Felodipine	-	-	-	-	-	4	0	-	-	0.0	-	-	10	1	10.0
Furosemide	82	82	102	101	99.5	86	86	161	159	99.2	-	-	10	7	70.0
Hydrochlorothiazide	3	3	-	-	100.0	7	7	2	2	100.0	-	-	10	7	70.0
Irbesartan	-	-	3	0	0.0	-	-	3	0	0.0	-	-	-	-	-
Losartan	-	-	6	6	100.0	-	-	6	6	100.0	-	-	-	-	-
Metoprolol	3	3	16	16	100.0	121	121	176	176	100.0	1	1	15	15	100.0
Propranolol	3	0	6	5	55.6	19	16	10	10	89.7	-	-	15	15	100.0
Simvastatin	-	-	-	-	-	4	0	-	-	0.0	-	-	10	1	10.0
Sotalol	3	0	10	10	76.9	19	16	15	15	91.2	-	-	10	2	20.0
Telmisartan	-	-	3	3	100.0	-	-	3	3	100.0	-	-	-	-	-
Verapamil	-	-	3	2	66.7	-	-	3	2	66.7	-	-	-	-	-
Warfarin	3	3	-	-	100.0	7	1	-	-	14.3	-	-	10	1	10.0

Central nervous system agents															
Carbamazepine	28	28	30	28	96.6	146	144	192	190	98.8	1	1	16	16	100.0
Citalopram	3	3	6	6	100.0	3	2	6	6	88.9	-	-	15	13	86.7
Clonazepam	-	-	3	0	0.0	-	-	3	0	0.0	-	-	-	-	-
Diazepam	-	-	-	-	-	-	-	5	1	20.0	-	-	-	-	-
Entacapone	-	-	-	-	-	-	-	-	-	-	-	-	10	8	80.0
Fluoxetine	-	-	3	0	0.0	2	1	8	5	60.0	-	-	10	9	90.0
Paroxetine	3	1	-	-	33.3	7	0	2	0	0.0	-	-	10	9	90.0
Primidone	-	-	-	-	-	12	12	5	5	100.0	-	-	-	-	-
Sertraline	-	-	3	0	0.0	-	-	3	0	0.0	-	-	-	-	-
Contrast agents															
Amidotrizoate	-	-	-	-	-	98	98	154	148	97.6	-	-	-	-	-
Iohexol	-	-	-	-	-	-	-	5	5	100.0	-	-	-	-	-
Iomeprol	-	-	-	-	-	-	-	5	5	100.0	-	-	-	-	-
Iopamidol	-	-	-	-	-	98	64	159	106	66.1	-	-	10	0	0.0
Iopromide	-	-	-	-	-	-	-	5	5	100.0	-	-	10	0	0.0
Chemotherapeutic agent															
Capecitabin	-	-	6	3	50.0	-	-	6	0	0.0	-	-	5	1	20.0
Cyclofosfamide	-	-	-	-	-	4	0	-	-	0.0	-	-	10	0	0.0
Ifosfamide	-	-	-	-	-	4	0	-	-	0.0	-	-	10	0	0.0
Methotrexate	3	1	-	-	33.3	3	0	-	-	0.0	-	-	10	0	0.0
Metabolic and gastrointestinal agents															
Bezafibrate	3	3	5	5	100.0	7	3	9	8	68.8	-	-	10	2	20.0
Cimetidin	79	79	101	29	60.0	83	83	159	53	56.2	-	-	-	-	-
Clofibric acid	-	-	-	-	-	-	-	-	-	-	-	-	10	0	0.0
Gemfibrozil	-	-	-	-	-	-	-	5	5	100.0	-	-	10	1	10.0

Respiratory agents															
Clenbuterol	-	-	-	-	-	-	-	-	-	-	-	-	10	0	0.0
Salbutamol	3	1	-	-	33.3	7	0	7	4	28.6	-	-	10	1	10.0
Terbutaline	-	-	-	-	-	4	0	-	-	0.0	-	-	10	0	0.0
Hormones and hormone antagonists															
17α-ethinylestradiol	81	81	115	1	41.8	93	88	175	2	33.6	-	-	11	0	0.0
17β-estradiol	83	80	126	84	78.5	91	83	190	22	37.4	-	-	10	0	0.0
Diethylstilbestrol	1	0	-	-	0.0	1	0	-	-	0.0	-	-	-	-	-
Estriol	4	2	3	0	28.6	8	0	3	0	0.0	-	-	10	0	0.0
Estrone	83	81	104	93	93.0	96	91	164	107	76.2	-	-	10	2	20.0
Etonogestrel	-	-	3	0	0.0	-	-	3	0	0.0	-	-	-	-	-
Finasteride	-	-	3	0	0.0	-	-	3	0	0.0	-	-	-	-	-
Flutamide	-	-	3	0	0.0	-	-	3	0	0.0	-	-	-	-	-
Hydrocortisone	3	3	-	-	100.0	3	1	-	-	33.3	-	-	10	0	0.0
Levonorgestrel	-	-	3	0	0.0	-	-	6	3	50.0	-	-	-	-	-
Methylprednisolone	-	-	-	-	-	-	-	-	-	-	-	-	10	1	10.0
Norethisteron	-	-	6	1	16.7	-	-	6	0	0.0	-	-	-	-	-
Progesterone	3	1	3	0	16.7	7	0	6	3	23.1	-	-	10	9	90.0
Tamoxifen	-	-	9	0	0.0	-	-	9	1	11.1	-	-	-	-	-
Testosterone	3	2	-	-	66.7	7	0	-	-	0.0	-	-	10	4	40.0
Recreational drugs															
4-MEC	-	-	-	-	-	4	4	-	-	100.0	-	-	-	-	-
Amphetamine	9	9	-	-	100.0	-	-	-	-	-	-	-	-	-	-
Cocaine	9	9	-	-	100.0	-	-	-	-	-	-	-	-	-	-
MDMA	9	9	-	-	100.0	4	4	-	-	100.0	-	-	-	-	-
Mephedrone	-	-	-	-	-	4	4	-	-	100.0	-	-	-	-	-

Methamphetamine	9	9	-	-	100.0	-	-	-	-	-	-	-	-	-	-
Metabolites															
2-hydroxyibuprofen	79	79	102	101	99.4	83	83	159	150	96.3	-	-	-	-	-
4OH-diclofenac	12	9	-	-	75.0	12	11	-	-	91.7	-	-	-	-	-
5OH-diclofenac	12	11	-	-	91.7	12	7	-	-	58.3	-	-	-	-	-
Benzoylecgonine	8	8	-	-	100.0	-	-	-	-	-	-	-	-	-	-