Determination of the Regional Pharmaceutical Burden in 15 Selected WWTPs and Associated Water Bodies using Chemical Analysis

Status in four coastal regions of the South Baltic Sea
Germany, Lithuania, Poland and Sweden

Project MORPHEUS 2017 - 2019
Deliverable 4.1

Lead Authors:
Langas, V., Klaipėda University, Lithuania
Garnaga-Budrė, G., Environmental Protecion Agency, Lithuania
Björklund, E., Kristianstad University, Sweden

Co-authors:
Svahn, O., Kristianstad University, Sweden
Tränckner, J., Kaiser, A., University of Rostock, Germany
Luczkiewicz, A., Gdansk University of Technology, Poland

Contact information:

vlangas@hotmail.com
galina.garnaga@aaa.am.lt
erland.bjorklund@hkr.se

Cover photo

Sample loading in LC-MS, Photo: Erland Björklund

Key facts of the MORPHEUS project

MORPHEUS (Model Areas for Removal of Pharmaceutical Substances in the South Baltic) is a project financed by the European Union Interreg South Baltic Programme. The project duration is January 2017 – December 2019, with a total budget of EUR 1.6 million with a contribution from the European Regional Development Fund of EUR 1.3 million. The project has a total of 7 partners from four countries; Sweden, Germany, Poland and Lithuania: Kristianstad University (Lead Partner) – Sweden, EUCC – The Coastal Union Germany – Germany, University of Rostock – Germany, Gdansk Water Foundation – Poland, Gdansk University of Technology – Poland, Environmental Protection Agency – Lithuania and Klaipeda University – Lithuania. The project also has a total of 11 associated partners from these countries. For additional information on the project and activities please visit the MORPHEUS homepage at: www.morpheus-project.eu

The aim of this report called Deliverable 4.1 "Report on Determination of the Regional Pharmaceutical Burden in 15 Selected WWTPs and Associated Water Bodies using Chemical Analysis, Status in four coastal regions of the South Baltic Sea; Germany, Sweden, Poland and Lithuania" was to summarise information on pharmaceutical chemical burden in the coastal regions Skåne (Sweden), Mecklenburg (Germany), Klaipėda (Lithuania) and Pomerania (Poland) based on pharmaceutical occurrence at selected WWTPs and recipient waterbodies in each model area. The report is an input to Deliverable 4.2 Report on relation between pharmaceutical consumption, environmental pharmaceutical burdens and current treatment technologies (a common deliverable of WP 3 and WP4) which in turn will be the basis for Project Main Output 2 Guidance document on the need of removal of pharmaceuticals from wastewater in the coastal regions of the SBS, which is a joint Output of WP3 and WP4. Deliverable 4.1 is also fundamental to Project Main Output 3 Roadmaps for uptake of advanced treatment for at least four model site WWTPs located in the SB coastal areas.

Table of contents

Summary

Many studies have identified that the main source of surface waters pollution by pharmaceuticals is wastewater from urban wastewater treatment plants. The main task of this report is to assess the pharmaceutical load in the South Baltic four coastal regions Skåne (Sweden), Mecklenburg (Germany), Klaipeda (Lithuania) and Pomerania (Poland), i.e. the actual end-of-pipe discharges from 15 selected WWTPs and related chemical burden in wastewater receiving surface water systems. The results are highly relevant for other project tasks – prioritization the most relevant WWTPs to take action for the introduction of an advanced/fourth wastewater treatment step, and linking consumption and current treatment technologies with load estimation and environmental impact.

For the implementation of the above tasks and to assure comparability of the results between regions, a common sampling approach was outlined together with representatives from project and associated partners. Thus, these guiding principles were applied to the sampling procedures:

- To take samples at the WWTPs influent and effluent. Preference should be given to 24 hours mixing samples – proportional to time or flow;
- To take grab/spot samples upstream the WWTPs in the receiving water bodies, i.e. in surface water not impacted by wastewater spot to find out the background concentration;
- To take grab/spot samples downstream of the WWTP outlet (discharge point) at the distance of sewage and receiver water complete mixing point;
- In order to compare the data during different seasons, it was decided to take samples in the summer of 2017 and the winter of 2018

Partners from each region collected samples at WWTPs and at water bodies-wastewater receivers and sent to Kristianstad University for analysis. By applying the same validated method of analysis to all samples at Kristianstad University increased comparability of data was obtained.

For data evaluation and interpretation, the following pharmaceutical load quantification method applied: wastewater influent and effluent concentrations were multiplied with volume of wastewater per year. Water companies provided data on wastewater volume per year and other basic operational characteristics. The influent and effluent concentrations used for average calculations were the two sampling average influent and effluent concentrations for each WWTP. Average concentrations multiplied by average two-year volume of wastewater express the average pollution load per year.

The total average annual influent chemical load of 15 pharmaceuticals at 15 WWTPs reached almost 54 tons. Ibuprofen form the highest load in all WWTPs inlets, reaching almost 50 tons or 90 percent of total load. The second highest compound was paracetamol, which contributed close to 2,2 tons or 4 % of total load. Azithromycin ranked third contributing nearly 0,6 kg (1,1%) to all WWTPs. Other chemicals accounted for less than one percent of the total influent load (Table 5.1).

The total average annual effluent chemical load of 15 pharmaceuticals at 15 WWTPs reached close to 0,6 ton. Both ibuprofen and paracetamol, which occur in large amounts in inlets, were

almost completely removed during the wastewater treatment process, e.g. ibuprofen and paracetamol was detected only in 5 and 10 WWTPs respectively and in small quantities, both with less than 1% of total effluent load. The top 4 pharmaceuticals present at the highest loads in WWTPs effluents were diclofenac, azithromycin, metoprolol and carbamazepine. The highest average load of 178 kg or 30 % of the total load was calculated for the anti-inflammatory drug diclofenac. Azithromycin with 126 kg (21%) takes the second place. Metoprolol and carbamazepine contribute 100 kg (16,8%) and 92 kg (15,4%) to the total effluent load, respectively (Table 5.2).

By comparing the inlet load in kg per one million m³ of wastewater quite large differences between WWTPs were observed, ranging from 50.0 kg to 1730 kg in different WWTPs. When instead comparing outlet load in kg per one million m³ of wastewater the values were more homogenous ranging only from 2.83 kg to 10.25 kg, with an average outlet value of 5.39 kg pharmaceuticals per one million m³ of wastewater in the 155 WWTPs surrounding the South Baltic Sea. Countrywise releases were 4,00 kg in Lithuania), 6,04 kg in Germany, 6,08 kg in Poland and 5,46 kg in Sweden

Additionally, the average inlet loads per 1000 residents were calculated and varied between 8.41 kg to 110.46 kg. Outlet loads in kg per 1000 residents varied less and ranged between 0.28 kg to 0.84 kg. The average outlet loads for all 15 WWTPs was 0.46 kg per 1000 resident, countrywise it was 0.50 kg in Lithuania, 0,40 kg in Germany, 0.36 kg in Poland) and 0.62 kg in Sweden.

In the marine receiving water bodies concentrations of Oxazepam, Ciprofloxacin, Atenolol, Propanolol, Naproxen and Ibuprofen were below the Method Quantification Limit (MQL) in all samples.

Concentrations of other pharmaceuticals were higher in summer than in winter, except for Paracetamol, which was detected only in one sample in winter near the WWTP Swarzewo outlet in the Baltic Sea. Other pharmaceuticals with concentrations above the MQL in winter time were: Erythromycin, Sulfamethoxazole and Diclofenac in bottom water of Gdansk Bay, and Azithromycin in the surface water of Buck Bay.

The highest concentrations of pharmaceuticals were found in the Gdansk Bay near the outlet of Gdansk-Wschod WWTP with the highest average concentration of Carbamazepine in summer. This compound was above the MQL in all marine samples. The highest concentration of Diclofenac was also found in the surface water of Gdansk Bay in summer.

The same substances as in the Lithuanian part of the Baltic Sea but at higher concentrations were also detected in the Klaipėda Strait. Additionally, Clarithromycin, Diclofenac, Paracetamol, Ibuprofen and Metoprolol were detected in Klaipėda Strait. Concentrations of Carbamazepine, Erythromycin and Sulfamethoxazole were higher in summer, concentrations of Clarithromycin, Diclofenac, Ibuprofen, Metoprolol and Paracetamol were notably higher in winter probably due to flue season.

In the water of Curonian Lagoon near Nida only five pharmaceuticals at low concentrations were detected: Carbamazepine, Clarithromycin, Diclofenac, Estrone and Paracetamol.

In all rivers/streams/ditches waterbodies the upstream concentrations were much lower than downstream. For example for Diclofenac, upstream concentrations were 1.6 times lower in the

Czarna Wda river in winter and 920 times lower in small ditch upstream WWTP Krakow. Highest concentration of Diclofenac, Carbamazepine, Clarithromycin and Metoprolol were found in the upstream water of Czarna Wda river in summer. In the Segesholmsån river upstream of Degeberga WWTP in summer the concentrations of all pharmaceuticals were below the MQL.

Small streams/ ditches could be distinguished with high pharmaceutical concentrations downstream treated wastewater discharge points. The highest average concentrations of Diclofenac and Carbamazepine were observed in the small ditch/stream downstream Krakow WWTP, the highest average concentration of Metoprolol was found in outlet discharge point for Kristianstad WWTP in lake Hammarsjön, the highest average concentration of Clarithromycin was found in the river Tenžė downsteam Kretinga WWTP. This could be explained by low flow and dilution rate in streams. Concentration of pharmaceuticals in the river mouths were not high.

Concentration of pharmaceuticals in the waterbodies depends on different factors like consumption rate of the medicines in the area, size of the WWTP, removal efficiency of the WWTP, water flow of the receiving rivers etc. Four small-medium size WWTPs (WWTP Tollarp, WWTP Laage, WWTP Jastrzębia-Góra and WWTP Kretinga) were chosen for the comparison of concentrations of Carbamazepine, Clarithromycin, Diclofenac and Metoprolol at the inlet and outlet of WWTPs and at the downstream of receiving river. Concentrations of pharmaceuticals at the inlet and outlet of WWTPs did not correlate with the number of connected residents to the WWTP. High inlet concentrations of all 4 pharmaceuticals were at the Laage WWTP, which has only 4 516 connected residents. High concentrations of Clarithromycin, Diclofenac and Metoprolol were measured in the inlet of Kretinga WWTP, which has the highest number of residents of four WWTPs - 19150, although the inlet concentration of Carbamazepine was lowest in Kretinga WWTP. Inlet concentrations of pharmaceuticals strongly depend on the consumption rate of population in the area. The removal rates of pharmaceuticals at the above mentioned WWTPs were different for the different compounds. For example, the highest average removal efficiency of Diclofenac was at Laage WWTP with a value of 65.5 %, at Jastrzębia-Góra WWTP it was 38.8 %, at Kretinga WWTP it was 28.6 %, and at Tollarp WWTP it was negative -67.6 %. Downstream concentrations of pharmaceuticals in receiving rivers also depend on the flow of the river. For example, the average flow of Recknitz river and Vramsån river are similar – 3.1 and 3.4 m^3/s respectively, the concentrations of Diclofenac - 15.7 and 12.1 ng/L and Metoprolol - 11.4 and 14.5 ng/L in the downstream of both rivers are also similar. Concentrations of Carbamazepine - 15.7 and 5.1 ng/L and Clarithromycin – 22.7 and 3.7 ng/L also do not differ largely. The flow of the Tenžė river is only 0.58 m^3/s. The downstream concentration of pharmaceuticals in the river are much higher: Diclofenac – 367 ng/L; Metoprolol – 56.9 ng/L; Carbamazepine – 21.5 ng/L; Clarithromycin – 38.3 ng/L.

Based on these findings it is clear that there are a number of local factors to taken into account during the assessment of the concentration of pharmaceuticals in receiving waterbodies to understand the impact a specific WWTP will have on the recieving water body.

1 Introduction

The main objective of WP 4 and Deliverable 4.1 (Report on Determination of the Regional Pharmaceutical Burden in 15 Selected WWTPs and Associated Water Bodies using Chemical Analysis, Status in four coastal regions of the South Baltic Sea; Germany, Sweden, Poland and Lithuania) is to assess the pharmaceutical burden in the four coastal regions by performing chemical analysis of pharmaceuticals in wastewater and recipient water. While WP 3 and Deliverable 3.1 (Report on Pharmaceutical consumption patterns in four coastal regions of the South Baltic Sea, Germany, Sweden, Poland and Lithuania) is estimating emissions in a top-down approach based on consumption patterns, WP 4 and Deliverable 4.1 is assessing the actual end-of-the-pipe emissions and the related chemical burden in receiving water systems.

The present report provides analytical chemical data from all 4 countries and regions which enables us to perform interpretation regarding the possible relation between pharmaceutical consumption (WP 3) and actual loads of pharmaceuticals to WWTPs (WP4). This relation will be presented in Deliverable 4.2 (Report on relation between pharmaceutical consumption, environmental pharmaceutical burdens and current treatment technologies) which is a common deliverable of WP 3 and WP4). But the present report (Deliverable 4.1) also provides analytical chemical data to evaluate the actual emissions from WWTPs and the environmental chemical load, with a possible link to existing regional WWTP technologies as described in Deliverable 5.1 (Report on Inventory of existing treatment technologies in wastewater treatment plants, Case studies in four coastal regions of the South Baltic Sea; Poland, Sweden, Lithuania and Germany). The provided data is also needed for Project Main Output 3 (Guidance document on the need of removal of pharmaceuticals from wastewater in the coastal regions of the SBS) which is a joint Output of WPs 3 and 4). This Guidance document may also serve as a starting point for other regions to perform similar inventories based on the knowledge gained in the model areas. Deliverable 4.1 is also fundamental to Project Main Output 3 (Roadmaps for uptake of advanced treatment for at least four model site WWTPs located in the SB coastal areas) which will serve as concrete examples of how new technologies may be implemented at selected WWTPs that are in need of removal of pharmaceutical to reduce the local burden of micro contaminants to receiving water bodies.

2 Sampling strategy

In the MORPHEUS project, a general sampling strategy was outlined for comparability of the results between regions. However, local adaptations were required due to diverse conditions and needs in the different regions. The strategy was put in operation at 15 selected WWTPs in 15 coastal towns of the South Baltic Sea: 3 in Sweden (SE): Kristianstad, Tollarp and Degeberga; 4 in Lithuania (LT): Klapeda, Palanga, Kretinga and Nida, 4 in Poland (PL): Gdansk-Wschod, Gdynia-Debogorze, Swarzewo, Jastrzebia-Gora and 4 in Germany (DE): Rostock, Krakow, Laage and Satow. The interpretation of results was led by Lead Partner (Kristianstad University) and Klaipėda University and jointly discussed among partners to bring in the different competences of all partners. The samples were collected by each project partner within their own model area in cooperation with both associated partners and WWTP operators. Two samplings campaigns were conducted, one in the summer period in August 2017, the second sampling in the winter-spring period in February-March 2018. The samples were sent to the Lead Partners at Kristianstad University for sample preparation and analysis of the selected pharmaceuticals according to Table 1. Detailed Information on WWTPs is presented in Deliverable 5.1. (can be downloaded on www.morpheus-project.eu).

3 Chemical analysis

Analysing pharmaceuticals in polluted water, which in some cases occur at very low concentrations, requires advanced analytical methods, often based on a technique called tandem mass spectrometry. In this project a flexible and robust method developed by O. Svahn and E. Björklund in the chemical analysis laboratory MoLab (www.hkr.se/molab), Kristianstad University, Sweden was applied[1,2]. The method is validated according to an earlier method completed in 2007 by the United States Environmental Protection Agency (US EPA) for analysis of pharmaceuticals and personal hygiene products in water, soil, sediment and biomaterial using HPLC/MS/MS[3]. All analyses were performed in MoLab by O. Svahn and E. Björklund. In this project a total of 15 pharmaceuticals and antibiotics were selected as shown in Table 1 together with the Method Quantification Limits (MQL).

Table 1. Compounds analysed in this project together with their Method Quantification Limits (MQL) and therapeutic classification.

Compound	MQL (ng/L)	Class
Atenolol	2.0	C - Cardiovascular system
Azithromycin	1.1	J - Antiinfectives for systemic use
Carbamazepine	0.2	N - Nervous system
Ciprofloxacin	32	J - Antiinfectives for systemic use
Clarithromycin	1.1	J - Antiinfectives for systemic use
Diclofenac	2.1	M - Muscolo-skeleton system
Erythromycin	0.5	J - Antiinfectives for systemic use
Estrone	0.2	G - Genito urinary system and sex
Ibuprofen	10	M - Muscolo-skeleton system
Metoprolol	2.0	C - Cardiovascular system
Naproxen	9.0	M - Muscolo-skeleton system
Oxazepam	0.7	N - Nervous system
Paracetamol	1.2	N - Nervous system
Propranolol	2.0	C - Cardiovascular system
Sulfamethoxazole	1.3	J - Antiinfectives for systemic use

[1] Increased electrospray ionization intensities and expanded chromatographic possibilities for emerging contaminants using mobile phases of different pH, Journal of Chromatography B, 1033 (2016) 1-10, O. Svahn and E. Bjorklund.
[2] Tillampad miljoanalytisk kemi for monitorering och atgarder av antibiotika- och lakemedelsrester i Vattenriket, Svahn 2016 [Applied environmental analytical chemistry for monitoring and measures regarding antibiotics and drug remnants in Vattenriket, Svahn 2016]
[3] Method 1694: Pharmaceuticals and Personal Care Products in Water, Soil, Sediment, and Biosolids by HPLC/MS/MS, U.S. Environmental Protection Agency, Office of Water, Office of Science and Technology Engineering and Analysis Division (4303T), 1200 Pennsylvania Avenue, NW, Washington, DC 20460, EPA-821-R-08-002, December 2007; 72 pages.

4 Country specific information

4.1 German model area

4.1.1. Sampling strategy – Germany

Since the hydrodynamics in the coastal zones of the southern Baltic Sea is highly complex, it was decided that the German sampling campaign would not be performed in the Baltic Sea directly but instead the samples were taken in water bodies with a known flow discharge into the Baltic Sea. The samples were also taken with an additional focus on linking between pharmaceutical burdens in the wastewaters and recipient and the consumption patterns (Deliverable 4.2). In the German part of the sampling project large coastal WWTPs were avoided for two reasons; firstly, they discharge directly into the Baltic Sea and are therefore difficult to sample in the discharge point in the receiving water bodies, secondly, the first sampling period is characterized by tourism alongside the Baltic coast where the larger WWTP are located. As shown in Figure 1.1, the rivers have been sampled both upstream or downstream related to WWTP discharges, were the distance to WWTP was at least about 450 m.

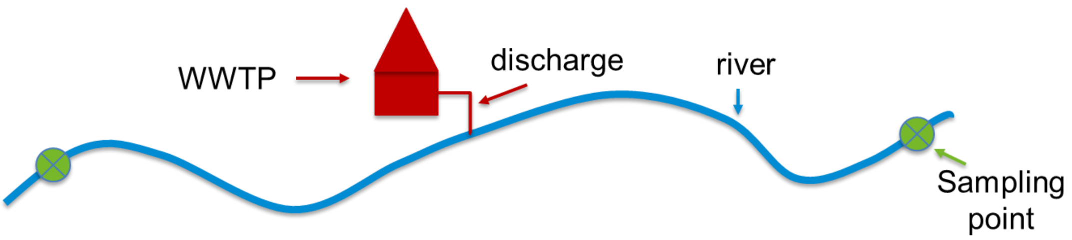


Figure 1.1 Schematic overview on chosen sampling points in water bodies in the German region. Both inlet and outlet water was sampled in the WWTP and upstream and downstream water samples in the river

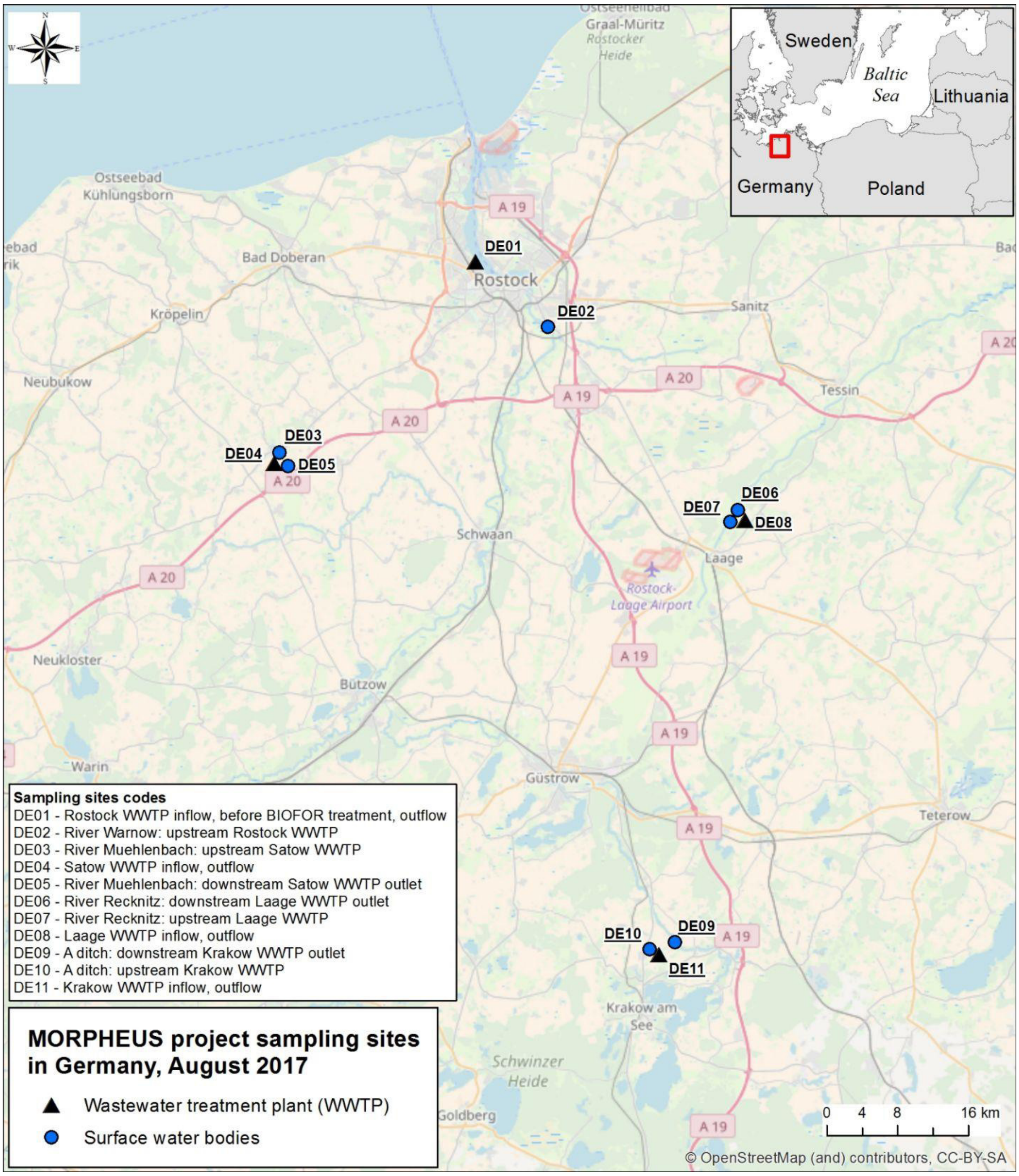
In order to represent the highly diverse landscape of WWTPs in the Mecklenburg area, different sizes of WWTPs were chosen for the sampling, see Table 1.1. The smaller ones in the rural areas were chosen if representing the single or at least main source of pharmaceutical pollution within this water body catchment. For the largest WWTP in the German model area (Rostock), only the upstream water body was sampled but instead, a special treatment step was further investigated in the WWTP called BIOFOR.

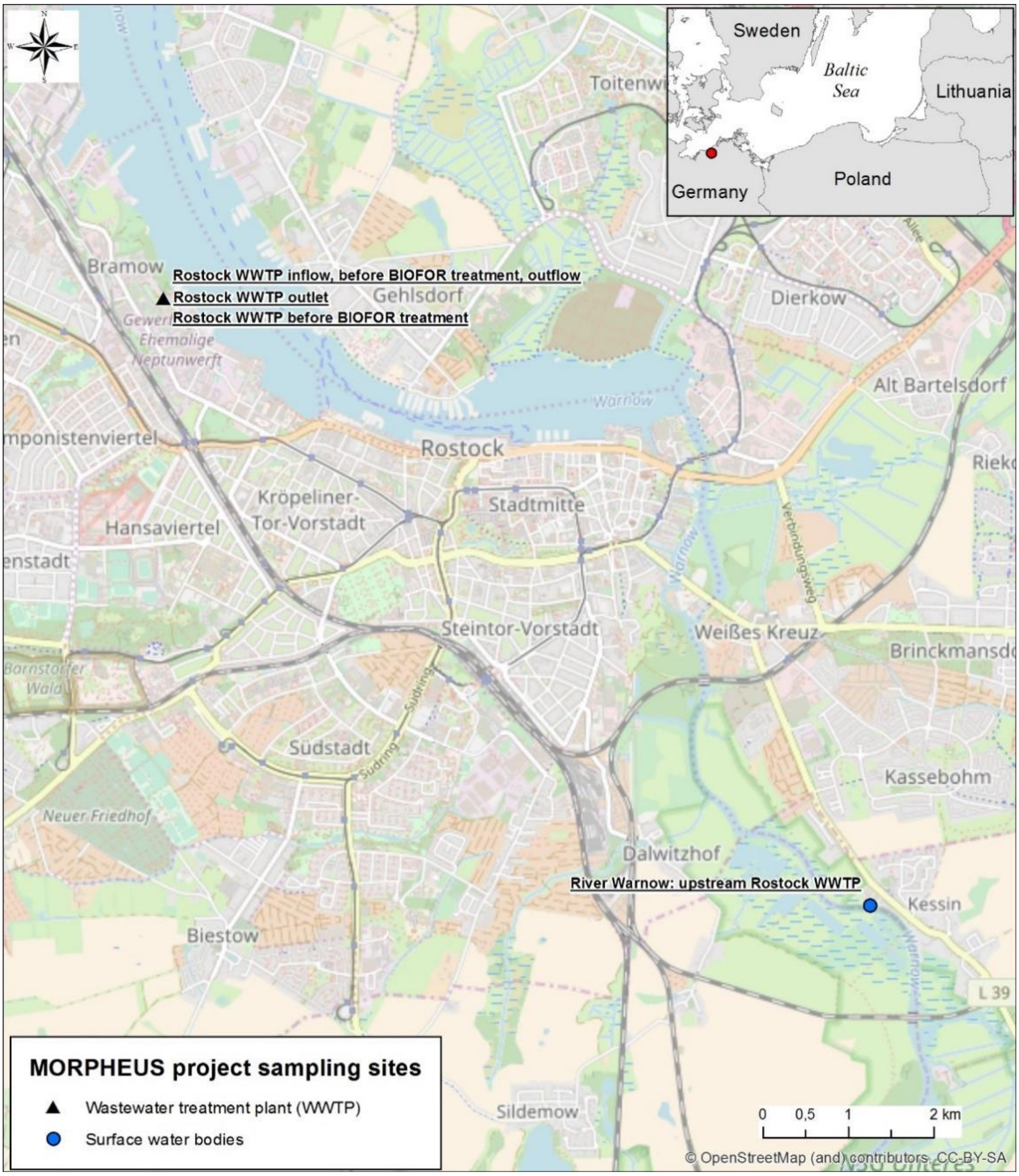
Table 1.1 Chosen German WWTPs for sampling in MORPHEUS and their sizes

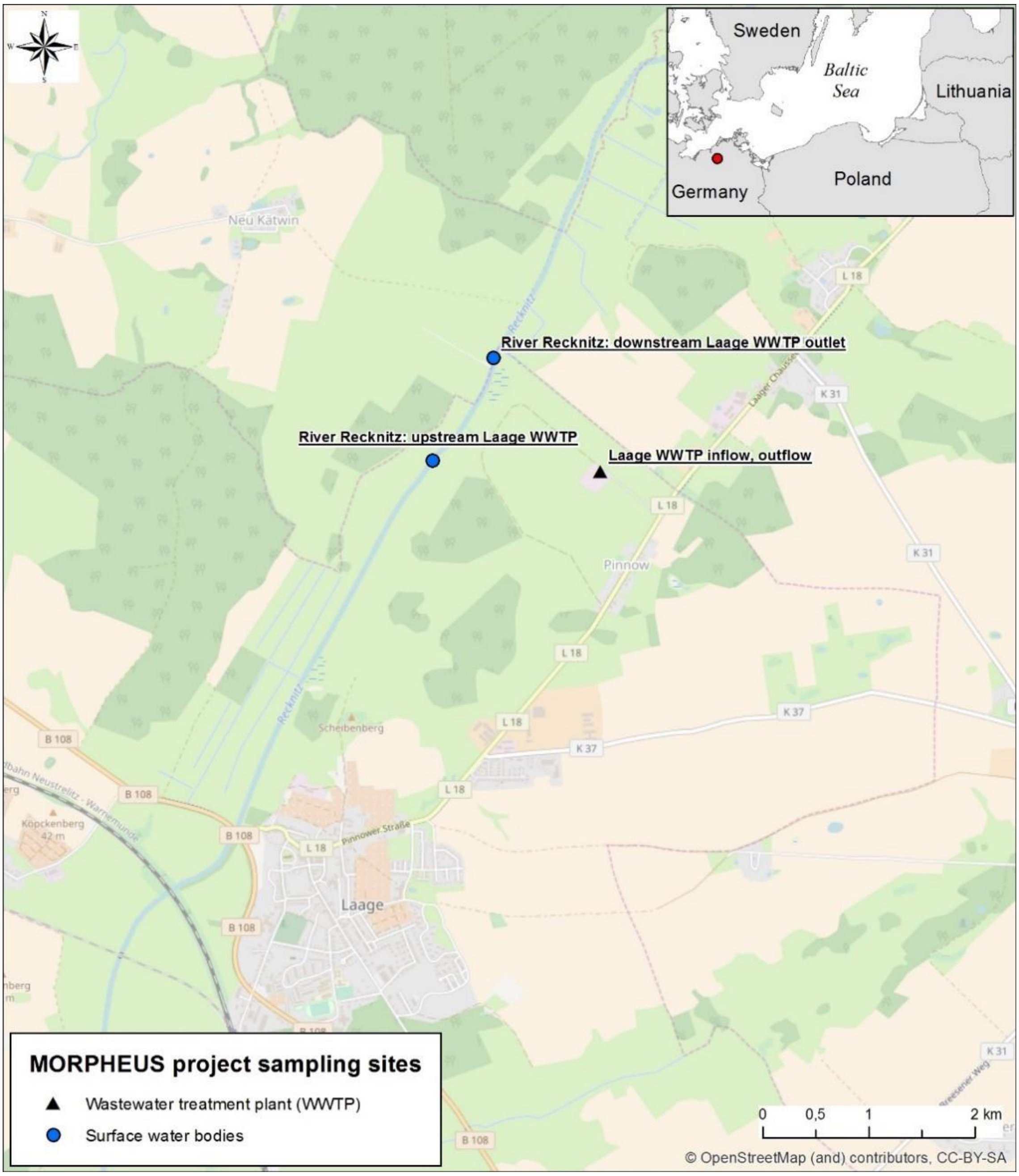
Size class (PE)	Name WWTP	Total capacity (PE)	Actual (PE)
5(>100000)	Rostock	400000	342483
4(10001-100000)	Laage	20000	12658
3(5001-10000)	Krakow	7500	6209
2(1000-5000)	Satow	2500	2300

4.1.2. Sampling locations – Germany

An overview of the locations of the sampled WWTPs and the upstream and the downstream sampling points are shown in Figure 1.2. In total 32 samples were taken. A summary is shown in table 1.2




Sweden
Baltic Sea
Lithuania
Germany
Poland
Rostock WWTP inflow, before BIOFOR treatment, outflow
Rostock WWTP outlet
Rostock WWTP before BIOFOR treatment
River Warnow: upstream Rostock WWTP
Bramow
Gehlsdorf
Dierkow
Alt Bartelsdorf
Rostock
Warnow
Kröpeliner-Tor-Vorstadt
Hansaviertel
Stadtmitte
Steintor-Vorstadt
Weißes Kreuz
Brinckmansdo
Südstadt
Kassebohm
Neuer Friedhof
Dalwitzhof
Kessin
Biestow
Sildemow
L 39
MORPHEUS project sampling sites
Wastewater treatment plant (WWTP)
Surface water bodies
0 0,5 1 2 km
© OpenStreetMap (and) contributors, CC-BY-SA


Sweden
Baltic Sea
Lithuania
Poland
Germany
Neu Katwin
River Recknitz: downstream Laage WWTP outlet
River Recknitz: upstream Laage WWTP
Laage WWTP inflow, outflow
Pinnow
Scheibenberg
Laage
MORPHEUS project sampling sites
Wastewater treatment plant (WWTP)
Surface water bodies
0 0,5 1 2 km
© OpenStreetMap (and) contributors, CC-BY-SA


Sweden
Baltic
Sea
Lithuania
Germany
Poland
NSG Nebel
L 37
Lüdershagen
Kolln
Strigg
Nebel
K 25
Klein Grabow
Koppelow
Groß Grabow
A ditch: downstream Krakow WWTP outlet
A ditch: upstream Krakow WWTP
Krakow WWTP inflow, outflow
Charlottenthal
Ahrenshagen
L 11
Groß Tessin
NSG Cossensee
MORPHEUS project sampling sites
Wastewater treatment plant (WWTP)
Surface water bodies
0 0,5 1 2 km
© OpenStreetMap (and) contributors, CC-BY-SA

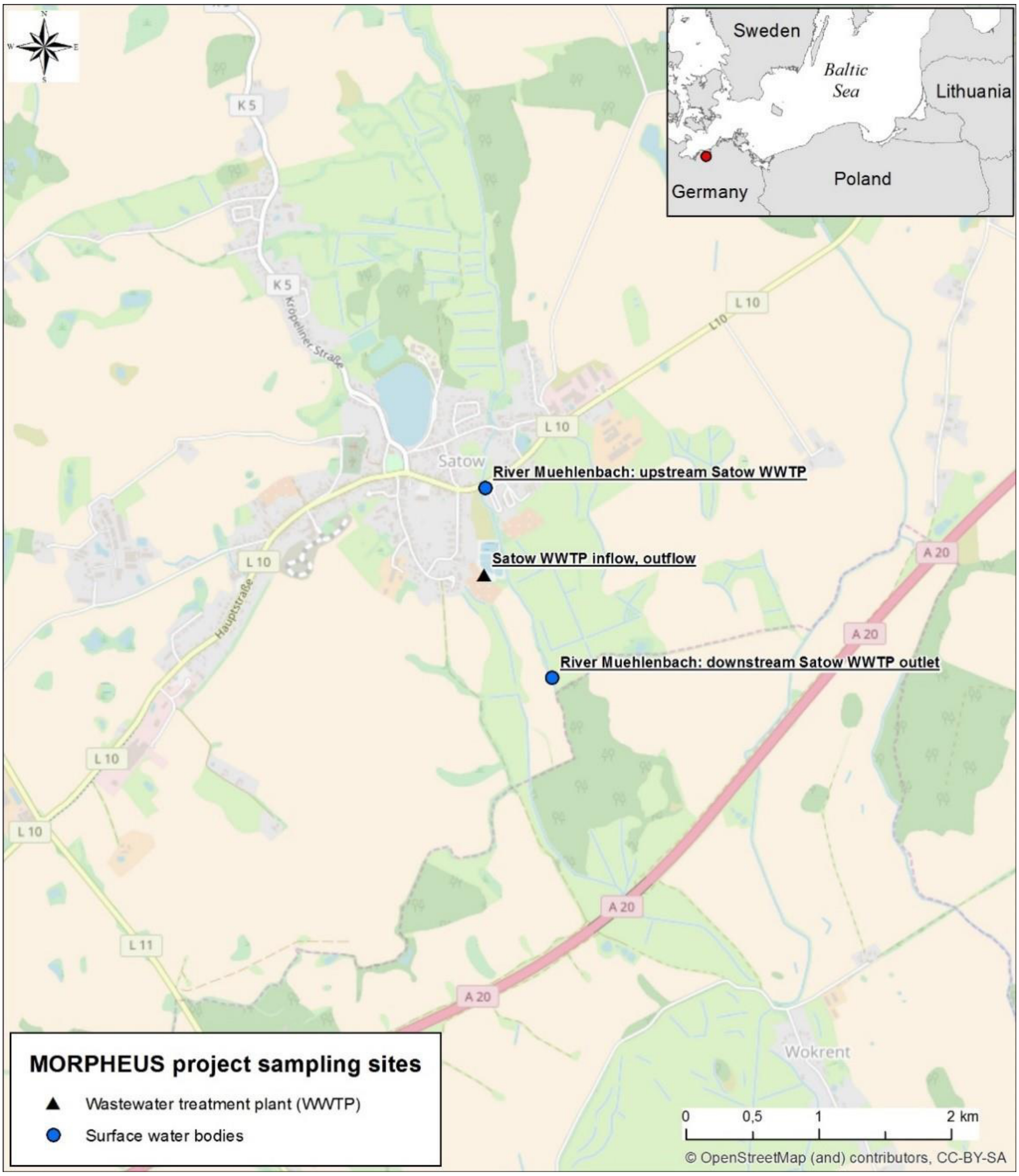


Figure 1.2 Location of sampled WWTPs and their discharge points in the model area of Germany. In the map the river sampling points are also indicated.

Table 1.2 Summary of the types and number of samples in Mecklenburg area during the summer sampling campaign August 2017 and winter sampling campaign February-March 2018

Receiving water bodies + WWTP	Season	Upstream/ background concentration	WWTP Inlet	WWTP Outlet	At WWTP (before BIOFOR-treatment)	Downstream
River Warnow + WWTP Rostock	Summer	1	1	1	1	-
	Winter	1	1	1	1	-
River Recknitz + WWTP Laage	Summer	1	1	1	-	1
	Winter	1	1	1	-	1
Small ditch + WWTP Krakow	Summer	1	1	1	-	1
	Winter	1	1	1	-	1
River Mühlenbach +	Summer	1	1	1	-	1
	Winter	1	1	1	-	1
∑ Samples of different types	Summer + Winter	8	8	8	2	6
∑ Samples	**32** (16 summer, 16 winter)					

4.1.3. Site-specific information on the WWTPs and receiving water bodies – Germany

The WWTP Rostock (DE01) is located directly in Rostock, close to the river Warnow currently serving both inhabitants of Rostock Municipality and other small nearby villages. The inlet of the WWTP was sampled after mechanical treatment, the outlet after the final clarifier and directly before the additional treatment step called BIOFOR ®. The receiving water body Warnow was sampled appr. 7 km upstream of the WWTP outlet.

The WWTP Laage (DE08) is located south of Rostock in a rural area and discharges into the river Recknitz. At the WWTP, the wastewater inlet after the grit chamber (mechanical treatment) as well as the outlet after the final clarifier were sampled. In this water body samples were collected upstream and downstream of the outlet.

The WWTP Krakow (DE11) is located in the south of Rostock County and has the largest distance to the Baltic Sea. At the WWTP, the inlet wastewater sample was taken after the grit chamber in summer, and in the mechanical treatment pool/grill in winter. The outlet wastewater sample was taken after the final clarifier. The receiving water body is a small ditch flowing about 2 km into the river Nebel. The ditch was sampled both upstream and downstream of the WWTP outlet.

The WWTP Satow (DE04) is located south-west of Rostock city and discharges into the river Mühlenbach within the Warnow catchment. At the WWTP, samples were taken before the mechanical treatment pool/grill in the summer and behind the grill in winter due to accessibility of the inlet water. The discharge was sampled behind an after-cleaning pond with high residence time. The river was sampled upstream and downstream of the WWTP outlet.

4.1.4. Short information on the WWTPs – Germany

The four selected model-WWTPs vary according to the designed capacity from 2500 (Satow) up to 400000 PE (Rostock). Similarly, the connected number of inhabitants is the highest for WWTP Rostock with 235645 in 2017; only 1303 inhabitants connected to WWTP Satow (Table 1.3a).

Table 1.3a Basic information about the 4 WWTPs operating parameters in 2016 according to water companies provided information

	Maximum dimension (capacity) PE	**[1)]Actual number PE**	**Connected number of residents**	**Industry %**	**Annual volume, thousands m^3**	**[2)]Daily flow average m^3/day**	**N-tot Out mg/L**	**P-tot Out mg/L**	**Recipient**
WWTP Rostock	~ 400000	342483	235645	No data	16894	42314	15,1	0,18	Warnow delta, coastal waters
WWTP Laage	~ 20000	12658	4516	63	321	880	115	29,4	River Recknitz
WWTP Krakow	~7500	6209	3964	36	253	630	112	17,2	Small ditch (discharging into Warnow catchment)
WWTP Satow	2500	1303	1303	No data	80	-	-	-	Mühlenbach (discharging into Warnow catchment)

WWTP Laage shows a higher share of industrial wastewater than WWTP Laage, for the other WWTPs, no data was obtained. For the outflow, the total nitrogen and total phosphorus concentrations have been recorded whereby all WWTP fulfil the legal requirements related to their size classes (see Deliverable 5.1). The treatment techniques of the four WWTPs differs mainly in the design of the biological step. Whereas WWTP Krakow and Laage apply a conventional nitrification/denitrification system, the system at WWTP Satow is based on SBR with both denitrification and nitrification phases. Furthermore, the wastewater at WWTP Rostock is treated in two biological steps; firstly in an aerated activated sludge basin; secondly in a N/DN-BIOFOR®-reactor where post-nitrification and post-denitrification take place. For more information, see Table 1.3b and Deliverable 5.1.

Table 1.3b Basic information about the 4 WWTPs treatment processes in 2016 according to water companies provided information

Treatment plant	Coarse debris screen	Chamber for sand and grit removal	Primary sedimen-tation	Biological step	Chemical treatment	Sludge treatment
WWTP Rostock	No, 3 x fine screen	Yes Aerated.	Yes 2 settling tanks (round basins)	Yes activated sludge method UCT as pre-denitrification plus an additional second biological treatment in the N/DN-BIOFOR tanks (post-nitrification and post denification)	Yes Desulphurisation into the digester (iron)	Digestion + incineration
WWTP Laage	Yes	Yes Aerated.	No	Yes conventional nitrification and	No	Agriculture
WWTP Krakow	Yes	Yes Aerated.	No	Yes conventional nitrification and	No	Agriculture
WWTP Satow	Yes	No	No	Yes SBR as activated sludge method	No	Agriculture

4.1.5. Sampling procedures – Germany

For the realization of the planned sampling, equipment was required for grab sampling; 24-h-mixing-samples, on-site measurements, and laboratory quick tests as well as for storage/shipment. The applied materials are shown in Table 1.4.

The sampling at the WWTPs were coordinated with the local operators. At WWTP Laage, Krakow and Satow; A. Melzer (technician) and A. Kaiser (researcher) took the samples and on-site measurements. Only at WWTP Rostock, the samples were extracted from in-house 24-h-mixing samplers by the staff themselves and stored until shipment. The summer samples at the WWTP Satow was a 2-h-mixing sample by usage of the grab sampling tools. The remaining WWTP-samples were all taken by applying portable 24-h-mixing samplers. All water bodies were sampled as grab samples by A. Melzer and A. Kaiser.

Table 1.4. Sampling equipment applied in German Model Area

Grab samples	24-h-mixing samples	On-site/ own laboratory measurements	Storage/Shipment
Beakers	MAXX TP II (with vacuum pump), time-dependent	WTW-340i (probes for pH, conductivity, Temperature)	Cooling box
Glass bottle	Tubes	WTW-325 (capacitive O_2 probe)	Ice packs
Telescopic rod	Portable batteries	Quick-tests HACH: LCK514, LCK314, LCK304, LCK303	External insulation for parcel
Rope	[frost-protection]		Sampling bottles provided by LP
Distilled water for cleaning equipment			

Before taking the sample, the bottles and materials were firstly cleaned and secondly flushed with the sampled water itself to avoid dilution effects. Figure 1.3 and 1.4 shows the automatic sampler during summer and winter sampling.

Figure 1.3. Sampler in winter

Figure 1.4. And in summer

The summer samples were collected from 21.08. until 28.08.2017. The winter samples were collected from 26.02. until 05.03.2018. The summer grab samples (2-h-mixing) of inflow and outflow at WWTP Satow were taken from 8 to 10am, when the highest concentrations of pharmaceuticals in the municipal wastewater was expected.

At smaller WWTPs, with hydraulic retention times lower than 1 day, the sampling in the outflow was performed simultaneously to the inflow (Krakow and Laage). At WWTP Satow, the pond attached behind the SBR-technique does not allow any estimations of flow times. Solely at WWTP Rostock, the hydraulic retention time is app. 1 day which results in a sampling delay of 24 hours.

The grab samples in the receiving water bodies were timed according to 24-h-mixing samples and expected flow times from sampling point to WWTP outlets. Hence, only the river Warnow was sampled one day before the 24-h-sampling started at WWTP Rostock, the other water body samples were taken at the same day as the WWTP samples.

Problems occurred during sampling. The sampling in summer 2017 was done without any major problems, only the bottle sizes had been mixed up so that the large ones (volume 500 mL) contained wastewaters and the small ones (volume 100 mL) contained recipient samples when arriving in Sweden for analysis. At WWTP Satow, the 2-h-mixing sample was collected with some difficulties in timing since the wastewater inflow was highly fluctuating while the outflow was stable. It was therefore decided to take a 24-h-mixing sample instead during the winter campaign.

The sampling in winter 2018 demanded some changes in sampling procedure. During the week, permanent frost and temperatures down to -18°C occurred at the Krakow site (night from Wednesday to Thursday). In order to protect the 24-h-mixing-samplers from cold, a frost protection coverage was installed which was able to hold the temperature at 5°C (see Figure 1.3). The amount of snow varied strongly, e.g. 20 cm new snow on Tuesday. All sampled water bodies were at least partly free of ice during sampling. However, some of the samples taken at night got frozen within the tubes leading to the sampler. A complete 24-h-sample is therefore not guaranteed for WWTP Laage (inlet and outlet). The sampling location at WWTP Krakow (inlet) could not be ensured, therefore sample was taken in the grill/screen chamber alternatively. Unluckily, the tubes got stacked by waste material so that fewer wastewater samples were collected (24-h-mixing not ensured). It was estimated that the WWTP Krakow (inlet) mixing sample only contained about 17-20 sampling points according to the total volume in the sampler.

4.1.6. Results of on-site measurements and pharmaceutical analysis – Germany

On-site measurements in water bodies.

In Tables 1.5 and 1.6, the on-site measurements are presented for water bodies/ receiving waters of WWTP outlets. In the summer period the temperature is varying from 12.9 to 18.6°C. In smaller water bodies, a rise is observed. The pH is nearly constant from 7.48 up to 8.05. I contrast, the oxygen saturation is always lower downstream than upstream (largest drop in ditch near WWTP Krakow with Δ = 4.3 mg/L). The conductivity varies between the different receiving water bodies from 1100 (ditch) to 667 µS/cm (Warnow).

The on-site measurements of the winter samples in water bodies only contain values for the ditch near WWTP Krakow and the upstream river of WWTP Rostock. The temperature was always measured as slightly above freezing-point. The pH-values varied from 7.3 up to 8.1. Compared to summer sampling, the oxygen saturation reversed: upstream of the WWTP Krakow outlet, 5.1 mg/L were measured, and downstream a value of 11.9 mg/L was observed.

Table 1.5 On-site measurements in water bodies during summer sampling in Germany

WWTP–receiving river/ditch name	Sample ID (up/down)	T [°C]	pH [-]	O_2 [mg/L]	Conductivity [µS/cm]
Rostock - Warnow	DE-R5 (upstream)	18.6	7.65	4.85	667
	-	-	-	-	-
Krakow - Saegegraben	DE-K5 (upstream)	14.7	7.64	7.65	1100
	DE-K8 (downstream)	16.3	7.48	4.16	1048
Laage - Recknitz	DE-L5 (upstream)	14.5	7.82	8.46	810
	DE-L8 (downstream)	14.5	7.85	8.00	812
Satow - Mühlenbach	DE-S5 (upstream)	12.9	8.03	9.02	681
	DE-S8 (downstream)	15.5	8.05	8.94	720

Table 1.6. On-site measurements in water bodies during winter sampling in Germany

WWTP–receiving river/ditch name	Sample ID (up/down)	T [°C]	pH [-]	O_2 [mg/L]	Conductivity [µS/cm]
Rostock - Warnow	DE-R5 (upstream)	1.2	8.13	13.1	720
	-	-	-	-	-
Krakow - Saegegraben	DE-K5 (upstream)	2.8	7.27	5.13	1264
	DE-K8 (downstream)	0.7	7.68	11.92	1140
Laage - Recknitz	DE-L5 (upstream)	n.a.	n.a.	n.a.	n.a.
	DE-L8 (downstream)	n.a.	n.a.	n.a.	n.a.
Satow - Mühlenbach	DE-S5 (upstream)	n.a.	n.a.	n.a.	n.a.
	DE-S8 (downstream)	n.a.	n.a.	n.a.	n.a.

Quick tests of WWTP samples in summer and winter. The results of the quick tests in laboratory shown in Table 1.7 helped to characterize the general pollution loads of the inflowing wastewater at each WWTP. Seasonal variations can be observed at the three smaller WWTPs. Values from Satow show the highest variation (Δ = 761 mg/L). The COD of the inflow at WWTP is extraordinarily high which might be the result of additional input collected from further septic tanks pumped from a silo during low-load-periods (e.g. night). Here, no dilution has occurred so that highly concentrated domestic wastewater is potentially brought in.

Table 1.7. Results of quick tests in laboratory (Univ. Rostock) for COD and ammonia of WWTP samples in summer 2017 and winter 2018

		Summer 2017	Winter 2018	
WWTP name	Sample IDs (in/out)	COD [mg/L]	COD [mg/L]	NH4-N [mg/L]
Rostock	DE-R2/R6 (inflow)	974	1001	60.2
	DE-R4/R8 (outflow)	32	39.9	0.029
Krakow	DE-K2/K6 (inflow)	1008	1282	90.8
	DE-K3/K7 (outflow)	28.90	36.4	8.15
Laage	DE-L2/L6 (inflow)	2637	2458	49.2
	DE-L3/L7 (outflow)	25.2	38	0.217
Satow	DE-S2/S6 (inflow)	1015	1776	53.6
	DE-S3/S7 (outflow)	51.7	64.6	34.3

Results of chemical analysis of pharmaceuticals in WWTPs – Germany.

Except for WWTP Satow, the WWTP were sampled as 24-h-mixed samples; either time-dependent (Laage, Krakow) or flow-proportional (Rostock) based on the applied technique. Concentration measurements are also dependent on the incoming wastewater flow. Hence, industrial wastewater and surface run-off water from combined sewer systems may dilute the domestic wastewater wherein the main pharmaceutical loads are expected.

Inlet concentrations (Table 1.8):

For some compounds, a clear difference of winter and summer can be observed in inlet concentrations, more precisely for Ciprofloxacin, Clarithromycin, partly Ibuprofen, and Sulfamethoxazole. Extraordinary high inlet concentrations have been measured for Ibuprofen, whereby all inlets reveal values above 280 µg/L up to 3.1 mg/L. However, the removal rate of Ibuprofen is above 93% at each of the investigated WWTPs. Furthermore, high inlet concentrations were found for Azithromycin, Carbamazepine, Diclofenac, Metoprolol and Paracetamol. On the contrary, the lowest concentrations were measured for Oxazepam and Propranolol as well as for Estrone. When comparing the sampled WWTP inlets with each other, the concentrations of Azithromycin, Clarithromycin, Ibuprofen, Naproxen and Sulfamethoxazole vary by factors from 15 up to 1,050. Besides, the seasonal difference was the highest at WWTP Krakow. Here, a potential reason could lie in the fact that sampling was conducted in winter before the screen, in summer behind the screen so that inflow concentrations may vary. Additionally, the higher inlet concentrations found in winter could be affected by more infections, colds etc. at this time of the year so that the intake of pharmaceuticals, such as Ibuprofen, Clarithromycin and Paracetamol will be higher.

Outlet concentrations (Table 1.8):

Among the WWTP outlet concentrations measured, low values were found for Atenolol, Ciprofloxacin, Clarithromycin (only in summer), Estrone, Ibuprofen (except Satow in winter), Naproxen, Oxazepam, Paracetamol and Propranolol. 11 analyses showed concentrations even below MQL. The highest outlet concentrations up to µg/L-levels were measured for Carbamazepine, Diclofenac and Metoprolol at all WWTPs, for Clarithromycin at WWTP Laage and Krakow as well as for Ibuprofen at WWTP Satow, respectively. In the outlet of WWTP Krakow, Azithromycin was measured around 500 ng/L both in summer and winter despite the large difference in inlet concentrations about 1,523 ng/L and 14,935 ng/L, respectively. This supports the reasonable suspicion that the inlet sampling procedure and spot is important to consider. However, seasonal effects on intake amounts are likely, too.

Special samples at Rostock before BIOFOR treatment step (Table 1.9):

At WWTP Rostock, additional samples have been collected to investigate whether the second biological treatment of the BIOFOR has a significant effect on removal rates of pharmaceuticals. Hence, the intermediate samples at the BIOFOR inlet indicate the removal without BIOFOR, the total removal rates include finally both biological treatments. In general, it can be stated that the removal is improved by the second treatment step. The most obvious increases of removal rates due to BIOFOR treatment are observed for Atenolol, Azithromycin, Diclofenac, Metoprolol, and the highest one for Clarithromycin with an increase from 3 % up to 75 %. When comparing BIOFOR inlet with outlet concentrations, similar levels are measured for Estrone, Ibuprofen, Naproxen, Paracetamol and Sulfamethoxazole. This means that the second treatment step has no further influence on the removal of these pharmaceuticals. It was striking that increasing mean concentrations have been observed for Carbamazepine, Ciprofloxacin, and also slightly for Oxazepam. Since Oxazepam was measured at all sampling spots in both summer and winter samples, with similar concentrations from 20 up to 41 ng/L it can be assumed that neither the intake is highly relevant nor is the removal at this WWTP significant. The measurements for Carbamazepine is constant over all sampling spots in summer but increasing mainly during winter season from 703 ng/L (inlet BIOFOR) to 984 ng/L. This pharmaceutical is known to be persistent and probably accumulates in the basins of the BIOFOR treatment. The removal of Ciprofloxacin is at a good level both in summer and winter before reaching the BIOFOR, only in summer an increase in concentration was observed. In winter, the BIOFOR treatment even improves the total removal rate up to 100 %. Reasons for this variation are not known yet but may occur due to de-conjugation or reallocation processes of this pharmaceutical. Similarly, the removal rates for Erythromycin are at medium level in summer, but in winter, concentrations are increasing at the WWTP Rostock from the inlet to the inlet BIOFOR nearly by a factor 5. It was not yet further investigated which biological/chemical processes of Erythromycin that take place at the WWTP.

Table 1.8 Seasonal inlet, outlet concentrations in WWTPs

Compound	Inlet Concentrations in ng/L								Outlet Concentrations in ng/L							
	Summer				Winter				Summer				Winter			
	Rostock	Laage	Krakow	Satow	Rostock	Laage	Krakow	Satow	Rostock	Laage	Krakow	Satow	Rostock	Laage	Krakow	Satow
	24h	24h	24h	2h	24h	24h	24h	24h	24h	24h	24h	2h	24h	24h	24h	24h
Atenolol	751	336	329	981	584	177	161	358	60	14	16	28	195	51	52	249
Azithromycin	1 566	4 943	1 523	9 782	2 137	910	14 935	2 197	89	77	487	60	90	67	686	50
Carbamazepine	1 108	2 187	2 896	1 209	711	975	3 642	840	1 112	1 217	3 144	792	984	996	2 868	495
Ciprofloxacin	191	314	460	159	708	256	1 177	533	157	118	92	18	0	0	0	0
Clarithromycin	559	527	725	8	635	8 516	6 145	24	62	38	106	2	252	2 285	2 802	81
Diclofenac	3 200	3 815	4 446	6 073	3 394	5 158	4 880	2 063	1 643	1 160	1 782	880	2 362	1 925	3 998	1 728
Erythromycin	272	832	407	84	71	22	143	0	147	102	506	36	147	19	369	47
Estrone	77	50	73	42	82	31	88	38	0	1	2	5	1	1	2	24
Ibuprofen	303 801	280 856	782 200	1 279 143	962 699	352 919	3 105 199	1 287 413	0	0	137	277	0	69	712	3 532
Metoprolol	2 767	4 549	6 862	5 562	2 958	2 768	7 490	3 766	1 201	507	845	313	1 608	607	4 173	2 466
Naproxen	921	202	6 038	5 667	731	190	3 874	7 008	73	5	87	36	86	15	139	150
Oxazepam	37	19	41	54	23	19	31	22	34	11	36	18	27	14	36	20
Paracetamol	12 824	8 177	6 023	15 878	13 154	8 283	17 045	10 382	0	0	0	126	15	21	11	101
Propranolol	86	70	135	57	84	64	165	41	56	18	69	9	111	47	163	33
Sulfamethoxazole	1 434	430	1 121	4 149	634	391	545	188	395	31	111	482	192	84	147	440

Table 1.9 Seasonal inlet, BIOFOR inlet (intermediate) and outlet concentrations in Rostock WWTP

	Inlet Concentrations in ng/L		**BIOFOR Inlet Concentrations in ng/L**		**Outlet Concentrations in ng/L**		**Elimination rate without BIOFOR, %**	**Elimination total, %**
Compound	**Summer**	**Winter**	**Summer**	**Winter**	**Summer**	**Winter**	**Summer + Winter**	**Summer + Winter**
Atenolol	751	584	228	367	60	195	53	79
Azithromycin	1 566	2 137	328	945	89	90	67	95
Carbamazepine	1 108	711	1 171	703	1 112	984	-2	-19
Ciprofloxacin	191	708	7	133	157	0	89	59
Clarithromycin	559	635	133	1 086	62	252	3	75
Diclofenac	3 200	3 394	2 884	2 092	1 643	2 362	24	40
Erythromycin	272	71	226	414	147	147	-231	-30
Estrone	77	82	5	1	0	1	96	100
Ibuprofen	303 801	962 699	0	96	0	0	100	100
Metoprolol	2 767	2 958	2 216	1 787	1 201	1 608	30	51
Naproxen	921	731	167	65	73	86	86	90
Oxazepam	37	23	41	20	34	27	0	-6
Paracetamol	12 824	13 154	0	20	0	15	100	100
Propranolol	86	84	78	89	56	111	2	2
Sulfamethoxazole	1 434	634	440	176	395	192	71	71

Results of chemical analysis – German water bodies (Table 1.10):

In Table 1.10, the measurements are presented for upstream and downstream sampling points in the water bodies related to WWTP outlets, respectively, as well as summer and winter samples. Overall, the highest concentrations were found in winter for ibuprofen, 167.5 ng/L near WWTP Krakow and 23.8 ng/L near WWTP Laage. All other sampling spots did not show occurrences of ibuprofen above MQL. Several pharmaceuticals have not been detected in any upstream water body, namely Atenolol, Azithromycin, Ciprofloxacin and Naproxen.

Comparing the upstream measurements related to the WWTPs, it appears that most of the pharmaceuticals were detected in the river Warnow (upstream of WWTP Rostock). This result seems to be reasonable since more than 80 smaller WWTP are discharging their treated wastewater into the Warnow upstream of the sampling spot. Particular attention should be paid on the pharmaceuticals which are detected in nearly all of the upstream river samples, such as Carbamazepine, Estrone and Diclofenac. Carbamazepine showed the highest measurements with 35.5 ng/L (summer) and 15.5 ng/L (winter) in the river Warnow. At this spot, also the Diclofenac concentration was the highest with up to 13.5 ng/L, whereby all remaining upstream water bodies revealed values below 6 ng/L or even below MQL.

The downstream measurements show a different picture of occurrences than in the upstream sampling spots. For nearly all of the compounds an increase of concentration, which is expected, can be observed both in summer and winter. Concentrations differs a lot related to pharmaceutical. Only ciprofloxacin was not detected at all. Comparing the three receiving water bodies, the small ditch downstream of WWTP showed the highest concentrations overall. Here, the concentrations raised up to 2.167 µg/L (Carbamazepine in summer), for Clarithromycin, Diclofenac and Metoprolol also above 1 µg/L. This most likely lies in the fact that the ratio of wastewater to river water is comparatively high with a poor dilution rate of wastewater resulting. Depending on the pharmaceutical, both winter and summer samplings show maximum measurements in this small ditch. Even the difference of summer and winter sample results for single pharmaceuticals varies by a factor up to 68 (Clarithromycin) or from below MQL up to 354.4 ng/L.

Table 1.10 Seasonal variations of concentrations in the receiving waters in ng/L

Compound	**Warnow River**		**Recknitz River**				**Small ditch/stream**				**Mühlenbach stream**			
	Summer & Winter													
	WWTP Rostock		**WWTP Laage**				**WWTP Krakow**				**WWTP Satow**			
	Upstream	**Upstream**	**Upstream**		**Downstream**		**Upstream**		**Downstream**		**Upstream**		**Downstream**	
Atenolol	-	-		-		-		-		10.9		-		12.2
Azithromycin	-	-		-		-		-		354.4		-		3.4
Carbamazepine	35.4	15.5	4.0	0.8	16.6	14.7	0.7	0.2	2 167.7	527.5	0.4	0.2	54.7	29.1
Ciprofloxacin	-	-		-		-		-		-		-		-
Clarithromycin	1.8	7.1	0.4	2.7	0.6	44.8		4.9	16.1	1 096.4		-	1.0	5.8
Diclofenac	8.2	13.5	4.0	2.5	16.0	38.8	4.0	1.1	874.5	1 013.1	5.2	-	56.2	95.6
Erythromycin	1.5	0.9		-	1.0	0.6		-	486.7	277.6		-	1.8	2.8
Estrone	0.3	0.6	0.6	0.6	0.7	0.7	0.8	0.8	1.3	1.3	0.5	0.3	1.0	1.5
Ibuprofen	-	-		23.8		63.5		167.5		197.9		-		230.2
Metoprolol	6.5	9.8	1.0	2.3	6.6	16.2		-	376.5	1 017.0		-	25.7	143.4
Naproxen	-	-		-		9.6		-	27.7	20.0		-	4.8	*6.5*
Oxazepam	0.4	*0.3*		-		-		-	24.4	10.0		-	1.4	1.1
Paracetamol	-	1.3		1.4		1.8		7.8		1.7		*0.8*	4.4	6.1
Propranolol	0.2	*0.3*		-	0.3	*0.6*	0.2	-	30.8	38.2		-	0.4	*1.4*
Sulfamethoxazole	3.5	*1.2*		-		4.1		-	56.5	51.0		-	17.9	17.0

4.1.7. Calculated chemical load in German WWTPs and removal rates

Chemical load from the WWTPs (Tables 1.11 and 1.12):

For the estimation of pharmaceutical load to and from 4 WWTPs, wastewater influent and effluent, concentrations were multiplied with volume of wastewater per year. The influent and effluent concentrations used for calculations were the average concentrations for each WWTP.

Removal rates (based on data from Table 1.12):

In general, it can be observed that the removal rates vary over a large span from -0.91 up to 1.00 between different pharmaceuticals and investigate WWTPs. The main trend of removal efficiency at these convential WWTPs can be summarized in the following groups:

a) Very good removal rates for Azithromycin, Ibuprofen, Naproxen, Paracetamol and mostly Estrone (>0.90)

b) Medium removal rates for Atenolol, Ciprofloxacin, Clarithromycin (except at WWTP Satow), Diclofenac, Metoprolol and Sulfamethoxazole (except at WWTP Satow)

c) Low removal rates for Carbamazepine, Erythromycin, Oxazepam and Propranolol

It can be concluded that depending on the selected pharmaceutical, conventional WWTPs are partly able to remove the residues in low concentrations sufficiently so that outlet concentrations are not representing a pharmaceutical burden to the receiving water bodies (group a). For other pharmaceuticals, more detailed investigations are required since they also vary among the sampled WWTPs. However, even though the removal rate is low, Oxazepam and Propranolol do not seem to be a burden due to very low absolute concentrations (max. 163 ng/L).

Combined with the concentrations measured directly, it could be concluded that compounds with either high inflow concentrations and medium elimination rates or medium inflow concentrations and low elimination rates have to be considered as relevant when investigating the pharmaceutical burden to the environment. Therefore, at least Carbamazepine, Diclofenac and Metoprolol should be considered for further investigations, in some cases also Clarithromycin.

Table 1.11. Seasonal inlet and outlet loads in WWTPs

Compound	Inlet Load in kg/a								Outlet Load in kg/a							
	Summer				Winter				Summer				Winter			
	Rostock	Laage	Krakow	Satow	Rostock	Laage	Krakow	Satow	Rostock	Laage	Krakow	Satow	Rostock	Laage	Krakow	Satow
	24h	24h	24h	2h	24h	24h	24h	24h	24h	24h	24h	2h	24h	24h	24h	24h
Q [m³/a]	**15 292 154**	**264 956**	**220 103**	**64 662**	**15 292 154**	**264 956**	**220 103**	**64 662**	**15 292 154**	**264 956**	**220 103**	**64 662**	**15 292 154**	**264 956**	**220 103**	**64 662**
Atenolol	11.48	0.09	0.07	0.06	8.93	0.05	0.04	0.02	0.91	0.00	0.00	0.00	2.99	0.01	0.01	0.02
Azithromycin	23.95	1.31	0.34	0.63	32.68	0.24	3.29	0.14	1.36	0.02	0.11	0.00	1.37	0.02	0.15	0.00
Carbamazepine	16.94	0.58	0.64	0.08	10.88	0.26	0.80	0.05	17.01	0.32	0.69	0.05	15.05	0.26	0.63	0.03
Ciprofloxacin	2.91	0.08	0.10	0.01	10.82	0.07	0.26	0.03	2.41	0.03	0.02	0.00	0.00	0.00	0.00	0.00
Clarithromycin	8.54	0.14	0.16	0.00	9.71	2.26	1.35	0.00	0.95	0.01	0.02	0.00	3.85	0.61	0.62	0.01
Diclofenac	48.93	1.01	0.98	0.39	51.91	1.37	1.07	0.13	25.12	0.31	0.39	0.06	36.13	0.51	0.88	0.11
Erythromycin	4.15	0.22	0.09	0.01	1.09	0.01	0.03	0.00	2.24	0.03	0.11	0.00	2.24	0.01	0.08	0.00
Estrone	1.18	0.01	0.02	0.00	1.26	0.01	0.02	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00
Ibuprofen	4645.77	74.41	172.16	82.71	14721.74	93.51	683.46	83.25	0.00	0.00	0.03	0.02	0.00	0.02	0.16	0.23
Metoprolol	42.31	1.21	1.51	0.36	45.23	0.73	1.65	0.24	18.37	0.13	0.19	0.02	24.60	0.16	0.92	0.16
Naproxen	14.08	0.05	1.33	0.37	11.18	0.05	0.85	0.45	1.12	0.00	0.02	0.00	1.31	0.00	0.03	0.01
Oxazepam	0.57	0.00	0.01	0.00	0.35	0.01	0.01	0.00	0.52	0.00	0.01	0.00	0.42	0.00	0.01	0.00
Paracetamol	196.10	2.17	1.33	1.03	201.15	2.19	3.75	0.67	0.00	0.00	0.00	0.01	0.23	0.01	0.00	0.01
Propranolol	1.31	0.02	0.03	0.00	1.29	0.02	0.04	0.00	0.86	0.00	0.02	0.00	1.69	0.01	0.04	0.00
Sulfamethoxazole	21.93	0.11	0.25	0.27	9.69	0.10	0.12	0.01	6.05	0.01	0.02	0.03	2.93	0.02	0.03	0.03

Table 1.12. Average (summer + winter) inlet and outlet loads in WWTPs and removal rates at the WWTPs

	Mean Inlet Load in kg/a				Mean Outlet Load in kg/a				Mean Elimination Rates of WWTP			
	Rostock	Laage	Krakow	Satow	Rostock	Laage	Krakow	Satow	Rostock	Laage	Krakow	Satow
Q [m³/a]	15 292 154	264 956	220 103	64 662	15 292 154	264 956	220 103	64 662				
Atenolol	10.21	0.07	0.05	0.04	1.95	0.01	0.01	0.01	0.79	0.84	0.82	0.64
Azithromycin	28.32	0.78	1.81	0.39	1.37	0.02	0.13	0.00	0.95	0.96	0.82	0.99
Carbamazepine	13.91	0.42	0.72	0.07	16.03	0.29	0.66	0.04	-0.19	0.21	0.06	0.38
Ciprofloxacin	6.87	0.08	0.18	0.02	1.20	0.02	0.01	0.00	0.59	0.81	0.90	0.94
Clarithromycin	9.13	1.20	0.76	0.00	2.40	0.31	0.32	0.00	0.75	0.83	0.70	-0.78
Diclofenac	50.42	1.19	1.03	0.26	30.62	0.41	0.64	0.08	0.40	0.66	0.39	0.51
Erythromycin	2.62	0.11	0.06	0.00	2.24	0.02	0.10	0.00	-0.30	0.50	-0.91	0.05
Estrone	1.22	0.01	0.02	0.00	0.00	0.00	0.00	0.00	1.00	0.98	0.98	0.61
Ibuprofen	9683.76	83.96	427.81	82.98	0.00	0.01	0.09	0.12	1.00	1.00	1.00	1.00
Metoprolol	43.77	0.97	1.58	0.30	21.48	0.15	0.55	0.09	0.51	0.83	0.66	0.64
Naproxen	12.63	0.05	1.09	0.41	1.21	0.00	0.02	0.01	0.90	0.95	0.97	0.99
Oxazepam	0.46	0.00	0.01	0.00	0.47	0.00	0.01	0.00	-0.06	0.34	-0.01	0.38
Paracetamol	198.63	2.18	2.54	0.85	0.12	0.00	0.00	0.01	1.00	1.00	1.00	0.99
Propranolol	1.30	0.02	0.03	0.00	1.27	0.01	0.03	0.00	0.02	0.50	0.25	0.52
Sulfamethoxazole	15.81	0.11	0.18	0.14	4.49	0.02	0.03	0.03	0.71	0.86	0.82	-0.23

4.2 Lithuanian model area

4.2.1. Sampling strategy – Lithuania

National law governs the sampling procedures. The ***Law on Environmental Monitoring*** (20 November 1997, No. VIII-529) (Žin. 112-2824) specify the content, structure and implementation of environmental monitoring, the rights and duties as well as responsibility of the entities participating in the process of environmental monitoring.

The Law requires: a programme for environmental monitoring of economic entities must be co-ordinated and approved in accordance with the procedure laid down by the Regulations of Environmental Monitoring of Economic Entities. The number of monitored parameters of regulated pollutants in wastewater and frequency of their laboratory control differs depending on the size of the town, settlement or agglomeration and the volume and type of wastewater discharged therefrom.

The ***Regulations of Environmental Monitoring of Economic Entities*** (Order No. D1-546 of the Minister of Environment of 16 September 2009) (Žin. 113-4831;148-0) establishes the following main requirements for municipal wastewater monitoring:

- the wastewater volume must be measured by automatic flow measurement devices when PE > 2000;

- for the assessment of pollutants treatment efficiency, the measurements should be carried out in the WWTP influent and effluent;

- discharged effluent samples must be taken with automatic sampling devices (> 2000 PE) in the same exact location in accordance with ISO 5667 standards within 24 hours;

- pollutants to be measured in wastewater are determined by the Wastewater Management Regulations and specified in environmental permits, in surface water bodies - in accordance with the Regulations of Environmental Monitoring of Economic Entities prepared and approved programme for environmental monitoring of economic entities (general indicators, specific for economic activity, etc);

- in flowing surface water bodies (rivers, streams, canals) shall be sampled upstream of the effluent outlet in an unaffected location and after complete mixing of the effluent approximately 0.5 km downstream the outlet;

- in the flow-through the water reservoir (lakes, ponds) with rapid water exchange, one sample shall be taken at an unpolluted site, i.e. upstream the outlet, the other 0.5 km downstream the outlet;

- samples from surface water bodies are taken at the same frequency and at the same time as wastewater samples.

There are four agglomerations/urban areas situated in the Lithuanian coastal area with a direct impact on the Curonian Lagoon and the Baltic Sea: the municipalities of Klaipėda city (the third largest city in Lithuania), Palanga, Kretinga and Nida towns. Therefore, the WWTP of the mentioned agglomerations were selected as the most relevant WWTPs and receiving water bodies for the assessment of pollution load and impact on ambient waters with pharmaceutical substances in the Lithuanian coastal region. All seaside towns are characterized by an influx of tourists in summer time, especially in the Palanga and Nida resort towns.

Pharmaceuticals have not previously been analysed in the selected WWTPs.

4.2.2. Sampling locations – Lithuania

A general overview of the 4 sampling areas is shown in Figure 2.1. In addition, three wastewater samples were taken from potential pollution sources in Klaipėda city - Klaipėda Republican Hospital (LT07, summer 2017 and winter 2018) and existing regional landfill leachate (LT14) in summer 2017.

A total of 22 sites were sampled during August 2017. The number of sampling sites were reduced to 16 in February-March 2018. The landfill leachate and surface water monitoring stations in the Klaipėda Strait, the Baltic Sea and Akmena-Danė river were excluded from sampling in winter-spring 2018 period. In total 38 samples were analysed for their content of pharmaceuticals. A summary of the types and number of samples in the Klaipėda Region are shown in Table 2.1.

Table 2.1. Summary of the types and number of samples in Klaipėda Region during the summer sampling campaign August 2017 and winter-spring sampling campaign February-March 2018.

Receiving water bodies + WWTP	**Season**	**Upstream/** background concentration	**WWTP Inlet**	**WWTP Outlet**	**Near WWTP outlet**	**Downstream**	**Waste water**
Klaipėda Strait + Klaipėda WWTP	Summer	1	1	1	1	2	
	Winter	-	1	1	1	1	
Klaipėda Strait + Klaipėda WWTP + Klaipėda Republican Hospital (wastewater)	Summer						**1**
	Winter						**1**
Klaipėda Strait + Klaipėda WWTP + Klaipėda Regional Landfill (leachate)	Summer						**1**
	Winter						**-**
Baltic Sea + Palanga WWTP	Summer	1	1	1	1	-	
	Winter	-	1	1	1	-	
Akmena-Danė River +River Tenžė +Kretinga WWTP	Summer	-	1	1	1	2	
	Winter	-	1	1	1	1	
Curonian Lagoon + Nida WWTP	Summer	1	1	1	1	1	
	Winter		**1**	**1**	**1**	**1**	
∑ **Samples of different types**	Summer + Winter	3	8	8	8	8	3
∑ **All Samples**		**38** (22 summer, 16 winter)					

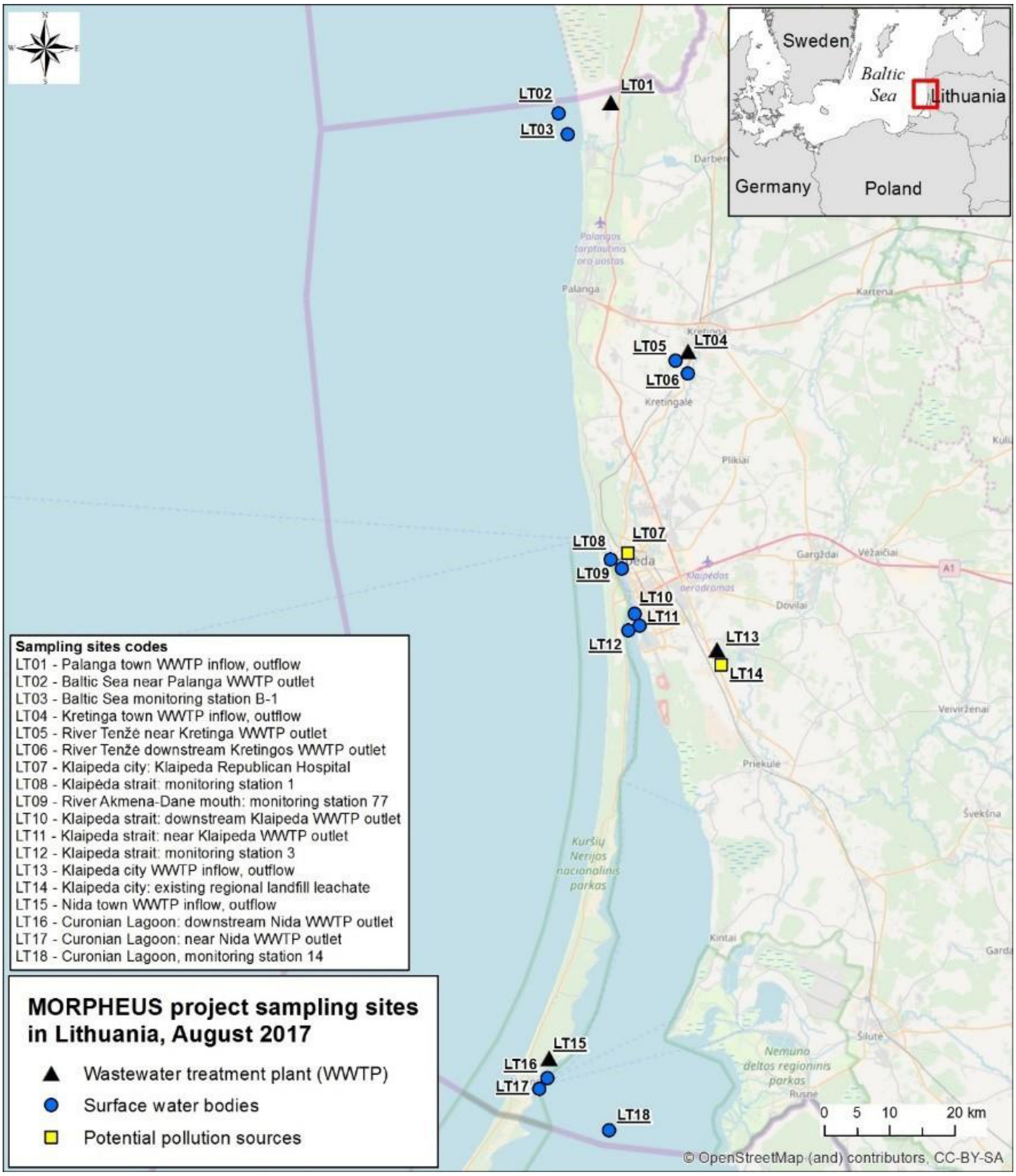


Figure 2.1 General overview of the 4 sampling areas in Klaipėda Region Lithuania in the summer sampling campaign in August 2017. Samples were taken at the same locations in February-March 2018 winter-spring sampling campaign, except for the background monitoring stations in the Baltic Sea (LT03), Curonian Lagoon (LT18), Klaipėda Strait (LT08, LT12), monitoring station in Akmena-Danė river mouth (LT09)

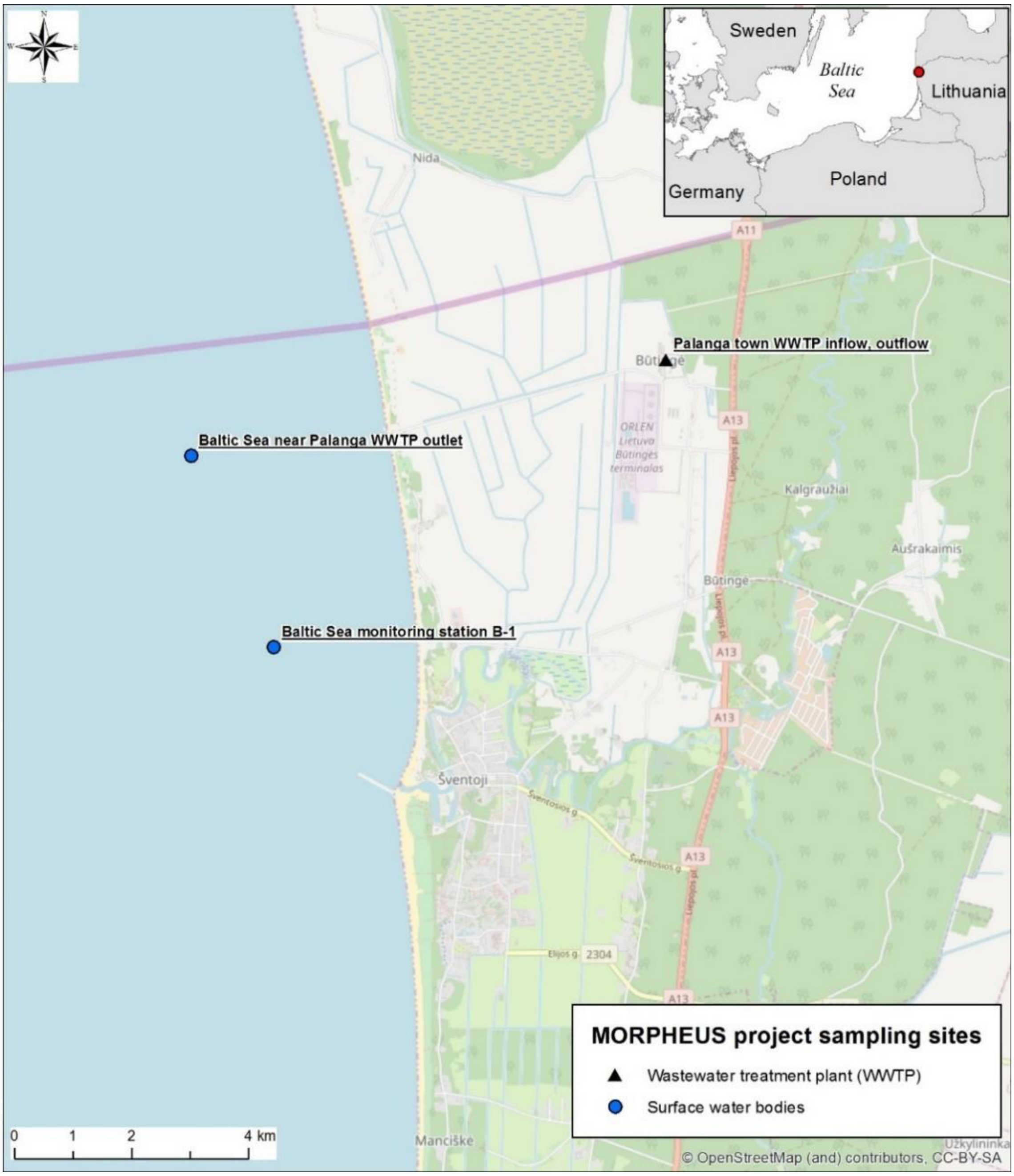
4.2.3. Site-specific information on the WWTPs and receiving water bodies – Lithuania

Palanga WWTP (LT01) discharges wastewater by ~2 km offshore subsea pipeline into the Baltic Sea coastal waters. Population from Šventoji, a resort settlement on the Baltic coast are also served by sewerage system connected to Palanga town wastewater treatment facility. The following bottom sampling stations were selected in the receiving coastal waters: close to subsea outlet (LT02) and monitoring station B-1, 2000 m to the south of outlet (LT03) for the assessment of background concentrations in the coastal areas of the Baltic Sea – see Figure 2.2 below.

Kretinga WWTP (LT04) treated wastewater discharges into river Tenžė - a straightened drainage ditch, which flows into the Akmena-Danė river that runs through the Klaipėda city and enters the Klaipėda Strait. Three sampling points were selected in receiving water bodies: near the Kretinga WWTP outlet in the river Tenžė (LT05), 1.6 km downstream Tenžė (LT06), which is also a national monitoring point and Akmena-Danė mouths (LT09) for the preliminary assessment of the input to the Klaipėda Strait.

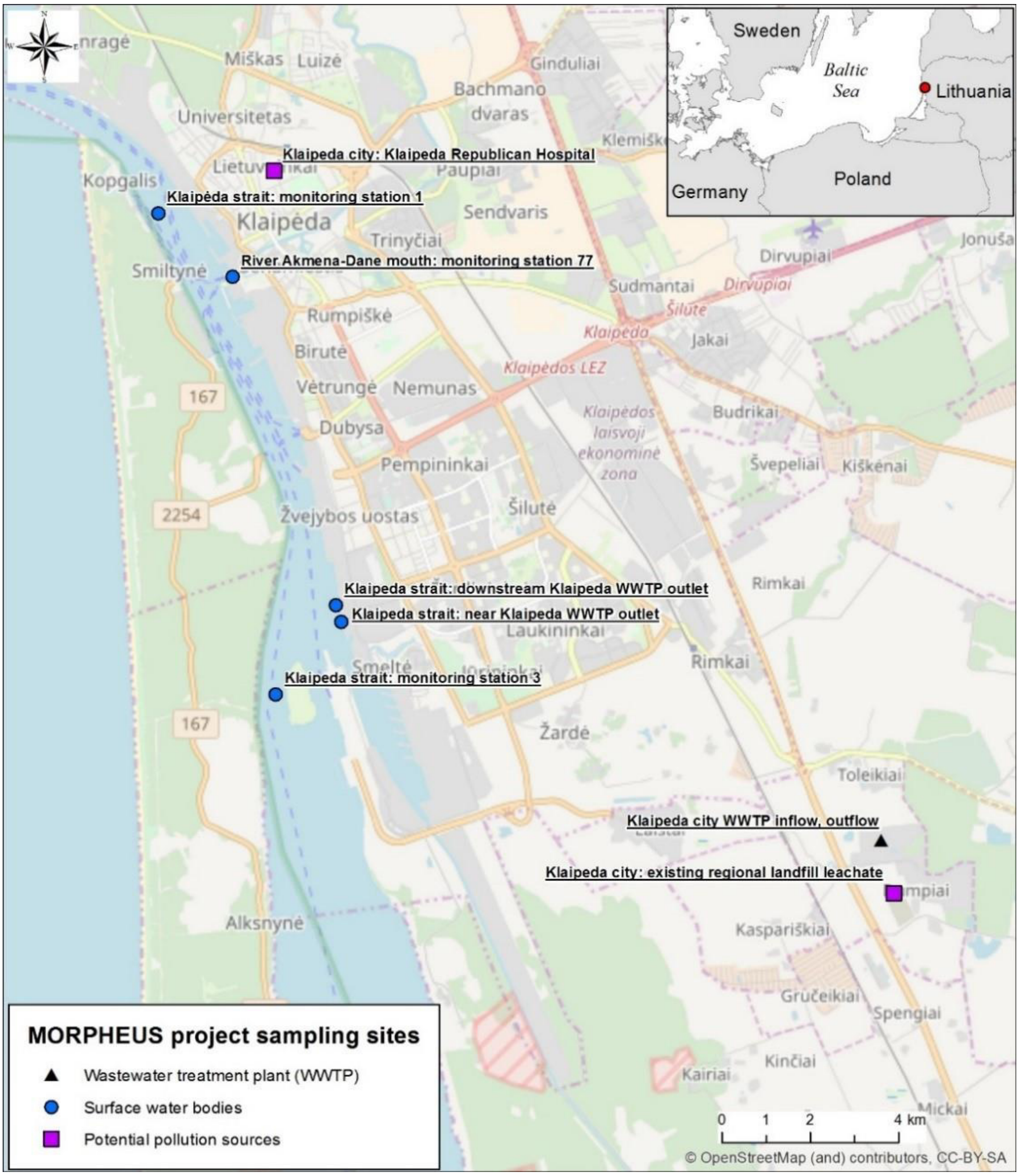
Klaipėda WWTP (LT13) Effluents from the Klaipėda WWTP is discharged into the Klaipėda Strait (part of the Curonian Lagoon) with prevailing currents from Curonian Lagoon into the Baltic Sea. Besides, Gargždai and Priekulė towns sewerage systems with populations of about 15000 and 1270, respectively are connected to Klaipėda WWTP. Samples were taken close to WWTP outlet (LT11), 500 m downstream outlet (LT10), state monitoring station 3 for the assessment of background concentrations in the Curonian Lagoon before entering the Strait (LT12), and monitoring station 1 for the preliminary assessment of input to the Baltic Sea via Klaipėda Strait (LT08).

Nida WWTP (LT15) Neringa municipality is situated in Curonian Spit comprising of several villages with separate wastewater collection and treatment systems. Nida resort town is an administrative centre of Neringa municipality with the largest number of inhabitants. Wastewater from Nida WWTP discharged into the Curonian Lagoon by about 450 meters long underwater pipeline at a 2.5 m depth. Bottom samples were taken at these sites: close to outlet (LT17) and 500 m to the north of the outlet (LT16), plus monitoring station 14 for the assessment of background concentrations (LT18) – see Figure 2.2 below.



Sweden
Baltic Sea
Lithuania
Germany
Poland
Nida
Palanga town WWTP inflow, outflow
Baltic Sea near Palanga WWTP outlet
Baltic Sea monitoring station B-1
Būtingė
Kalgraužiai
Aušrakaimis
Šventoji
MORPHEUS project sampling sites
Wastewater treatment plant (WWTP)
Surface water bodies
0 1 2 4 km
Manciškė
© OpenStreetMap (and) contributors, CC-BY-SA


Sweden
Baltic Sea
Lithuania
Germany
Poland
Kretinga town WWTP inflow, outflow
River Tenžė near Kretinga WWTP outlet
River Tenžė downstream Kretingos WWTP outlet
Kretinga
Kretingalė
MORPHEUS project sampling sites
Wastewater treatment plant (WWTP)
Surface water bodies
0 1 2 4 km
© OpenStreetMap (and) contributors, CC-BY-SA


Sweden
Baltic Sea
Lithuania
Germany
Poland
Klaipeda city: Klaipeda Republican Hospital
Klaipėda strait: monitoring station 1
River Akmena-Dane mouth: monitoring station 77
Klaipeda strait: downstream Klaipeda WWTP outlet
Klaipeda strait: near Klaipeda WWTP outlet
Klaipeda strait: monitoring station 3
Klaipeda city WWTP inflow, outflow
Klaipeda city: existing regional landfill leachate
MORPHEUS project sampling sites
Wastewater treatment plant (WWTP)
Surface water bodies
Potential pollution sources
0 1 2 4 km
© OpenStreetMap (and) contributors, CC-BY-SA

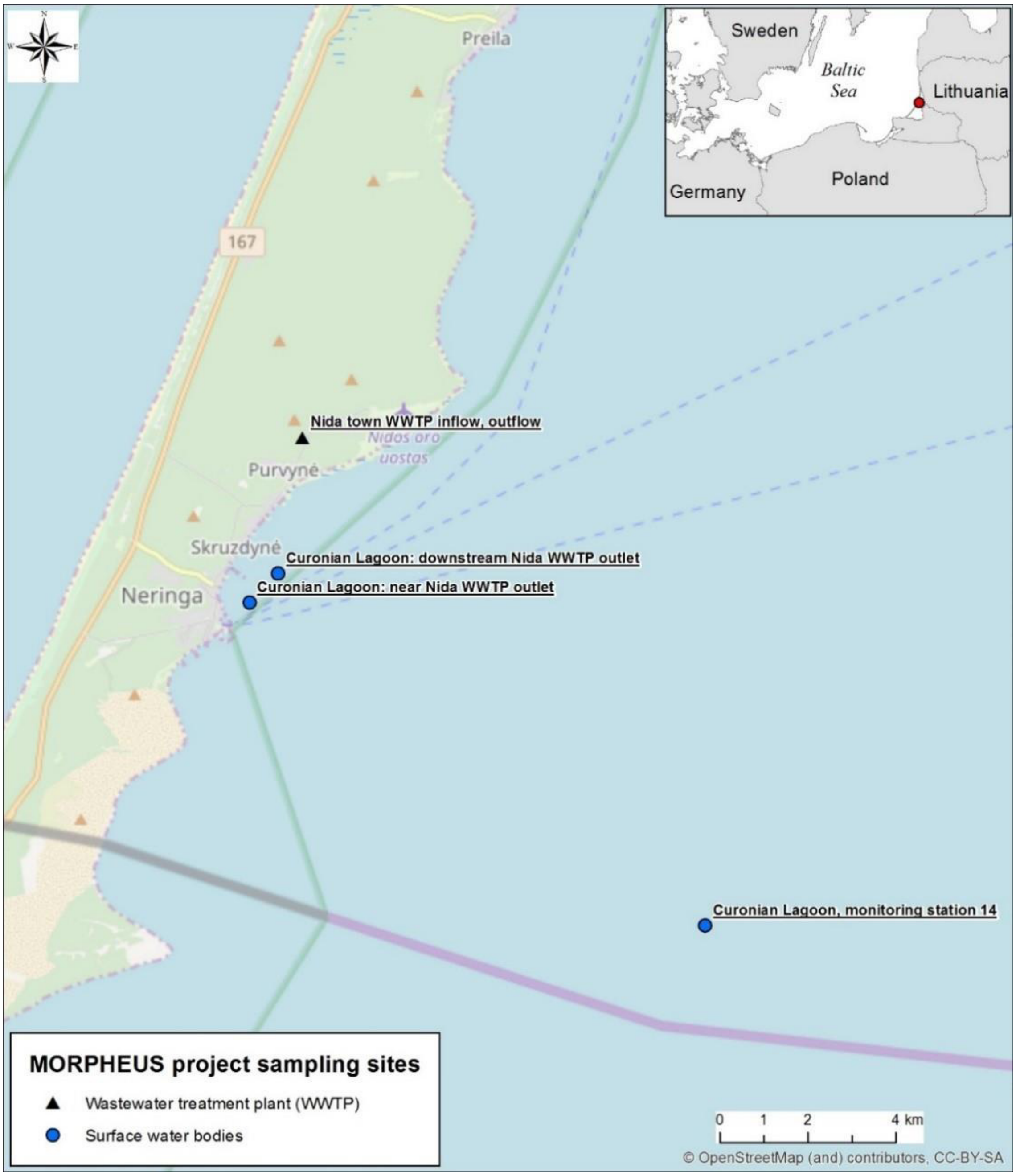


Figure 2.2 A more detailed scheme of sampling locations of the Lithuanian WWTPs, potential pollution sources and in the effluents receiving water bodies

Curonian Lagoon with Klaipėda Strait. The Curonian Lagoon with Klaipėda Strait belongs to one of the four river basin districts of Lithuania - the largest Nemunas river basin district (RBD). The Nemunas RBD comprises the Lithuanian parts of the Nemunas and Prieglius River basins and of the Curonian Lagoon (*Kuršių marios*), as well as the Lithuanian Coastal Rivers Basin and coastal waters of the Baltic Sea.

According to the Nemunas River Basin District Management Plan (2015, EPA), the total length of the Nemunas river is 937 km, and the basin area constitutes 97 928 km^2. The Lithuanian part of the basin covers the area of 46 626 km^2. The Nemunas Basin drains the territories of Belarus, Lithuania, Russian Federation (Kaliningrad Region), Latvia (only about 100 km^2), and Poland. The resulting total area of the Nemunas RBD in Lithuania (excluding the coastal and Curonian Lagoon with Klaipėda Strait as transitional waters assigned thereto) is 47 814 km^2 or 73 % of the Lithuanian territory.

The Curonian Lagoon is a lagoon in the southwest of the Baltic Sea, with an area of 1 584 km^2. The lagoon is separated from the Baltic Sea by the Curonian Spit (*Kuršių nerija*). Only the northern part of the Curonian Lagoon (402.03 km^2 or ~25 %) belongs to Lithuania, while the southern part lies in the Kaliningrad Region of the Russian Federation. The Curonian Lagoon is a shallow body of water, with a largest natural depth of only 5.8 m and an average depth – 3.8 m. However, the prevailing depth of the Lithuanian part of the lagoon is 1.8 – 2.6 m. The water volume of the lagoon is 6 km^3. At its northern end, the Curonian Lagoon is connected to the Baltic Sea by Klaipėda Strait (the narrowest place between piers is 390 m).
25 rivers and streams enter the Curonian Lagoon. The catchment area of the Lagoon totals to 100 500 km^2, 98 % of which belongs to the Nemunas River (Nemunas RBD Management Plan, 2015, EPA).

According to long-term (1960–2007) water balance calculations, the inflow of brackish water from the Baltic Sea to the Curonian Lagoon is 6.1 km^3/year and the freshwater outflow from the Curonian Lagoon to the sea by a narrow navigable strait is 27.6 km^3 /year (Jakimavičius & Kovalenkovienė 2010) or 878 m^3/s. Under the influence of prevailing western winds, the currents in the Klaipėda Strait can also change in the opposite direction. During the year the currents of salt water can be noticed about 53 times and last for 74 days. Mostly it lasts for 1 day, and very rarely for 6 days. In the remaining days of the year water flows from the Curonian Lagoon into the Baltic Sea (Klaipėda Port entrance rehabilitation project C, M. Steenberg & J, Kriauciuniene, 2002).

The analysis of pollution sources and assessment of their impact revealed that the following key factors affect the ecological status of water bodies in the Nemunas RBD, and at the same time the status of the Nemunas River and its inflow predominantly determines the water quality in the Curonian Lagoon:

- diffuse pollution, the main driver of which is agricultural pollution loads;
- point pollution, which consists of loads from dischargers of WWTP, stormwater runoff, and industrial wastewater in towns and settlements;
- transboundary pollution, which consists of pollution loads coming from the neighbouring countries. Calculations show that pollution coming to the Curonian Lagoon from Belarus, and Russia - Sovetsk and Neman towns it Kaliningrad region may be accounting for about 30-40 % of the nitrogen and phosphorus compounds (Nemunas RBD Management Plan, EPA, 2017).

It is estimated that the main source of pollution of the Curonian Lagoon is pollution loads transported by the Nemunas. The loads directly entering the Curonian Lagoon from point pollution sources amount to 0.5-7 % of the total pollution meanwhile the remaining share is carried by rivers, mainly by the Nemunas. Klaipėda city is the main Curonian Lagoon and the Baltic Sea direct point pollution source in Lithuania.
Discharges from Nida town WWTP make only a small part of the total pollution load to the Curonian lagoon.

Akmena-Danė River Basin. All 4 MORPHEUS project WWTPs are situated in the Lithuanian Coastal Rivers Basin which was assigned to the Nemunas River Basin District (RBD) according WFD and occupies the area of 1 077 km^2, which makes up 2.3 % of the total area of the Nemunas RBD.

The whole of the Lithuanian Coastal Rivers Basin is situated in the Coastal Lowland (*Pajūrio žemuma*). The largest river in this basin is the Akmena-Danė, which flows out of the Coastal Lowland and enters the Baltic Sea via Klaipėda Strait in Klaipėda city. From the springs to the town of Kretinga, the river is called Akmena, and further – Danė. The average annual runoff rate is 13.1 l/s/km^2, the average discharge at the mouth of the river is about 7.6 m^3/s. The wood density in the Lithuanian Coastal Rivers Basin is 27 %, agricultural lands occupy 30-40 %, bogs, marshes and swamps - 2.3 % of the area of the basin. The river network consists of 161 rivers longer than 3 km and 650 rivers shorter than 3 km, with the aggregate length totalling to 2 774 km. The density of the river network is 1.6 km/km^2 (Nemunas RBD Management Plan, EPA, 2015).

The main identified sources of impacts in the Lithuanian Coastal Rivers Basin are municipal and industrial wastewater, and stormwater-surface runoff. Kretinga WWTP discharges effluents into the Tenžė river, tributary of the Akmena-Danė River. The impact of the Tenžė is felt up to the very mouth of the Akmena-Danė, where more than 20 dischargers of Klaipėda town rainwater are situated, thus contributing to the pollution of this river. The Akmena-Danė river has been identified as a water body at risk due to pollution with nutrients and hazardous substances.

4.2.4. Short information on the WWTPs – Lithuania

The annual volume treated water in 4 WWTPs varied from 230 000 m^3 in Nida to 1 471 000 m^3 in Kretinga, 2 879 000 m^3 in Palanga and 15 100 000 m^3 in Klaipėda in 2016 (Table 2.2a). The relative size of the WWTPs based on 2016 annual volumes of treated wastewater, assigning Nida WWTP a value of 1, thereby varies with a factor of 6.4 in Kretinga, 12.5 in Palanga and 66 in Klaipėda.

The actual number of PE is also different, from 3 130 PE (BOD) in Nida to 28 727 in Kretinga, 19 945 PE in Palanga and 210 070 PE in Klaipėda WWTP; a factor 9 in Kretinga, 6.4 in Palanga and 67 in Klaipėda. According to two-years (2015 and 2016) monitoring data, average concentrations of the organic substances BOD and COD in Klaipėda WWTP influents represent typical domestic wastewater characteristics with averages of 354 and 732 mgO_2/l respectively. The influent in Kretinga and Nida WWTPs are characterized by higher concentrations of organic substances COD and BOD. The main quality parameters in Palanga WWTP influent are lower compared to the rest of the WWTPs, probably because of high infiltration of up to 60 percent and without any significant industrial activity. For more information, see Deliverable 5.1.

In general, the treatment steps in the 4 WWTPs are similar, and they all have mechanical and biological treatment. Additional chemical treatment is applied occasionally only in Klaipėda and Palanga WWTPs (Table 2.2b).

Table 2.2a Basic information about the 4 WWTPs operating parameters in 2016 according to water companies provided information

	Maximum dimension (capacity) PE	[1] Actual number PE	Connected number of residents	Industry PE	Annual volume, thousands m^3	[2] Daily flow average m^3/day	COD-Cr In kg/year	COD-Cr Out kg/year	BOD_7 In kg/year	BOD_7 Out kg/year	N-tot In kg/year	N-tot Out kg/year	P-tot In kg/year	P-tot Out kg/year	Recipient
Klaipėda WWTP	~ 259 429	210 070	~170 000	No data	15 100	41 370	11493214	687 396	5 367 295	83 841	1 317 777	149 913	132 125	5 450	Klaipėda Strait
Palanga WWTP	~ 21 500	19 945	~13 000	No industries	2 879	7 888	1 093 790	108 108	509 583	8 617	117 751	13 251	22 312	1 688	The Baltic Sea (coastal waters)
Kretinga WWTP	~31 697	28 727	~19 150	230	1 471	4 031	1 320 281	44 299	733 985	6 130	100 175	8 013	16 152	606	River Tenžė (tributary of the Akmena-Danė
Nida WWTP	6 700	3 130	1 714	No industries	230	630	173 859	12 637	79 969	1 174	20 132	4 364	2 171	824	Curonian Lagoon

1. Calculated number based on total incoming BOD_7 to the WWTP
2. Calculated as annual volume divided by 365 days

Table 2.2b. Basic information about the 4 WWTPs treatment processes in 2016 according to water companies provided information

Treatment plant	Coarse debris screen	Chamber for sand and grit removal	Primary sedimentation	Biological step	Intermediate sedimentation	Chemical step	Final sedimentation	Polishing step
Klaipėda WWTP	Yes	Yes Aerated.	Yes Sludge removed for treatment.	Yes 4 parallel aerotanks with conventional nitrogen and phosphorous removal;	Yes Part of the sludge pumped back to the biological step. Excess sludge removed for treatment.	Yes Organic carbon occasionally used to support denitrification (poliflock MT 12 ECO).	Yes Sedimentation and removal of sludge for treatment: digested in mesophilic regime, dewatered (SM approx. 25%) and, dried in dryer (SM approx. 95%).	No
Palanga WWTP	Yes	Yes	Yes	Yes 2 parallel aerotanks for conventional N and P removal with denitrification basin followed by, anaerobic, anoxic and oxic phases; the wastewater stream entering the biological part is divided to support denitrification and dephosphatation	Yes Part of the sludge pumped back to the biological step. Excess sludge removed for treatment.	Yes, occasional application of chemical treatment using flocculants Al_2O_3 and Brentapilus VP1.	Yes Sedimentation and removal of sludge for treatment	No
Kretinga WWTP	Yes	Yes	Yes	Yes 2 parallel aerotanks for biological treatment; activated sludge technology used for conventional nitrogen removal	Yes Part of the sludge pumped back to the biological step. Excess sludge removed for treatment.	No	Yes Sedimentation and removal of sludge for treatment	No
Nida WWTP	Yes	Yes	Yes	Yes biological treatment system, activated sludge technology used for conventional nitrogen removal	Yes	No	Yes Sedimentation and removal of sludge for treatment	No

4.2.5. Sampling procedure – Lithuania

Sampling at the WWTPs. The sampling at WWTPs was performed by the personnel of the Environmental Protection Agency Environment Research Department and has been coordinated with the operators of WWTPs. Samples were taken during 16-22 August 2017 and 13 February - 28 March 2018. Spot/grab samples were sampled at Nida WWTP, while in Klaipėda, Palanga and Kretinga WWTPs 24-h-composite-time-dependent automatic samplers were used (Figures 2.3 and 2.4). Wastewater temperature and pH were measured during sampling. Wastewater samples were sampled according to LST ISO 5667-10:2011 method (Table 2.3).

Figure 2.3 Sampling at Nida WWTP (winter 2018)

Figure 2.4 24-h-composite-time-dependent automatic sampler at Kretingos WWTP (summer 2017)

Spot samples of wastewater of Klaipėda Republican hospital were taken in summer 2017 and winter 2018. Sample of filtrate (leachate) from the regional Dumpiai landfill (JSC Klaipėda Region waste management center) was taken only in summer 2017 (Figures 2.5 and 2.6). Samples were sampled according to LST ISO 5667-10:2011 method.

Figure 2.5 Sampling of landfill filtrate (summer 2017)

Figure 2.6 Sampling of hospital wastewater (winter 2018)

Sampling in surface water bodies. The personnel of Environmental Protection Agency Environment Research Department performed the sampling in surface waters bodies-wastewater effluent receivers. Samples were taken in 16-22 August 2017 and 13 February - 28 March 2018. In the Curonian Lagoon in August 2017 and in the Baltic Sea in August 2017 and March 2018 samples were taken from the research vessel (R/V) "Vėjūnas". Rosette of 5 L plastic watersamplers Hydro-Bios and CTD90 for the measurements of environmental parameters were used. In February-March 2018, due to the ice cover, samples were taken from the coast (near the Klaipėdos WWTP outlet) and from the ice (near the Nida WWTP outlet – Figure 2.7). Samples were taken according to the method LST ISO 5667-9:2009.

Figure 2.7 Sampling in Curonian Lagoon in August 2017 and February-March 2018

Samples were also taken from the rivers Tenžė in August 2017 and February 2018 and Akmena-Danė in August 2017. Spot samples were taken from the river banks according to the method ISO 5667-6:2014 (Figure 2.8).

Figure 2.8 Sampling in Tenžė river in February 2018

Table 2.3 Sampling methods and equipment used in Lithuanian Model Area

Object	Inflow/outflow sampling	Sampling at the effluent receiver
WWTP Klaipėda	LST ISO 5667-10:2011; 24-h-composite-time-dependent, pH-meter PH3110	Klaipėda Strait Summer - LST ISO 5667-9:2009, R/V "Vėjūnas", rosette of 5 L plastic watersamplers Hydro-Bios; CTD90; Winter – LST ISO 5667-9:2009, surface water taken from the coast, 5 L plastic water sampler Hydro-Bios; pH-meter, conductometer
WWTP Nida	grab sample, pH-meter PH3110	Curonian Lagoon Summer - LST ISO 5667-9:2009, R/V "Vėjūnas", rosette of 5 L plastic watersamplers Hydro-Bios; CTD90; Winter – LST ISO 5667-9:2009, surface water taken from ice, 5 L plastic water sampler Hydro-Bios; pH-meter, conductometer
WWTP Palanga	LST ISO 5667-10:2011; 24-h-composite-time-dependent, pH-meter PH3110	Baltic Sea LST ISO 5667-9:2009, R/V "Vėjūnas", rosette of 5 L plastic watersamplers Hydro-Bios; CTD90
WWTP Kretinga	LST ISO 5667-10:2011; 24-h-composite-time-dependent, pH-meter PH3110	River Tenžė ISO 5667-6:2014, from the bank, Oximeter Oxi 320; pH-meter PH3110; conductometer WTW Cond 3110
Republic Klaipėda Hospital, Vilties str.	Spot sampling, LST ISO 5667-10:2011, plastic beaker, pH-meter PH3110	-
JSC "Klaipėda region waste management center" (KRATC), Regional Dumpiai landfill	Spot sampling, LST ISO 5667-10:2011, plastic beaker, pH-meter PH3110	-

4.2.6. Results of on-site measurements and pharmaceutical analysis – Lithuania

On-site measurements in water bodies. In Tables 2.4 and 2.5 the on-site measurements are presented for surface waterbodies - WWTP effluents receivers. In the summer period the temperature is varying from 16 °C in the river Tenžė to 21 °C in the Curonian Lagoon. The pH varies from 7.5 in the river Tenžė to 8.8 in the Curonian Lagoon. The average dissolved oxygen concentration varies from 8.4 mg/L in Curonian Lagoon, to 5.59 mg/L in Klaipėda Strait, 6.6 mg/L in the Baltic Sea, 4.34 mg/L in river Tenžė and 5.32 mg/L in Akmena-Danė river. The conductivity varies between the different receiving waterbodies: from 380 µS/cm in the Curonian Lagoon to 10980 µS/cm in the Klaipėda Strait at the monitoring station 1 (outflow to the sea).

Table 2.4 On-site measurements in water bodies during 2017 summer sampling in Lithuania

WWTP – receiving waterbody	Sampling location	Depth [m]	T [°C]	pH	O_2 [mg/L]	Salinity [PSU]	Conductivity, [µS/cm]
Nida WWTP - Curonian Lagoon	downstream outlet 500 m	1.2	21.02	8.79	8.60	0.2	380
	near the outlet	0.8	21.34	8.82	9.34	0.2	380
	monitoring station 14 (background)	0.5	20.07	8.63	7.33	0.2	380
Klaipėda WWTP - Klaipėda Strait	near the outlet	4.5	20.37	8.19	5.34	2.54	4060
	downstream outlet 500 m	4.4	20.17	8.07	4.93	3.38	5610
	monitoring station 3 (background)	9.1	19.75	7.97	5.87	5.94	2830
	monitoring station 1 (outflow to the sea)	13.1	19.34	7.99	6.22	7.09	10980
Palanga WWTP - Baltic Sea	monitoring station B-1 (background)	9	19.12	8.13	6.40	6.61	10250
	near the outlet	13	19.09	8.15	6.80	6.72	10370
Kretingos WWTP - river Tenžė	near the outlet	0	19	7.5	5.05	-	1416
	downstream outlet about 1500 m	0	16	7.7	3.63	-	707
Akmena-Danė river mouth	monitoring station LTR77	0	21	8.1	5.32	-	1945

During the winter sampling the temperature is varying from slightly above the freezing point 0.1 °C in the Curonian Lagoon to 6.2 °C in the river Tenžė. The pH varies from 7.47 in the Baltic Sea to 8.80 in the river Tenžė. The average dissolved oxygen concentration varies from 7.20 mg/L in river Tenžė to 9.20 mg/L in Klaipėda Strait and almost 13 mg/L in the Baltic Sea. In the Curonian Lagoon due to low temperature, dissolved oxygen concentration wasn't measured. The conductivity varies between the different receiving waterbodies from 342 µS/cm in the Curonian Lagoon to 1357 µS/cm in the river Tenžė near the outlet.

Table 2.5 On-site measurements in water bodies during winter sampling in Lithuania

WWTP – receiving waterbody	Sampling location	Depth [m]	T [°C]	pH	O_2 [mg/L]	Salinity [PSU]	Conductivity, [µS/cm]
Nida WWTP - Curonian Lagoon	downstream outlet about 2000 m	2.0	0.1	8.24	-	0.193	342
	near the outlet	2.5	0.1	8.27	-	0.198	379
Klaipėda WWTP - Klaipėda Strait	near the outlet	10	1.6	7.60	8.99	0.250	477
	downstream outlet 1000 m	6	0.4	7.98	9.40	0.200	389
Palanga WWTP -Baltic Sea	near the outlet	24	1.5	7.47	12.99	7.190	-
Kretingos WWTP - river Tenžė	near the outlet	-	6.2	8.80	7.50	-	1357
	downstream outlet about 1500 m	-	2.3	8.70	6.90	-	514

Results of chemical analysis of pharmaceuticals in WWTPs – Lithuania

Inlet concentrations (Table 2.6):

All of the 15 selected pharmaceutical substances were detected in the four WWTPs influents with the exception of Nida. Table 2.6 below shows that Ibuprofen had the highest concentrations of in all WWTPs influents. The maximum concentration reaching 290416 and 287283 ng/L was detected for Ibuprofen in Klaipėda and Kretinga, respectively in winter and 219839 ng/L in Kretinga in summer. High concentrations ranging from 31316-81960 ng/L were also found in the remaining treatment plants in both seasons, except Nida with 8275 ng/L in winter.

High concentrations between 2196 ng/L in Nida and 20011 ng/L in Kretinga were measured for the anti-inflammatory drug Paracetamol.

Diclofenac ranked third with evenly distributed concentrations, the lowest 535 and highest 4551 ng/L respectively in winter and summer in Nida.
Clarithromycin concentration of 2871 in Klaipėda and 4114 ng/L in Kretinga was measured in winter. Summer concentrations were lower, in the range 127-475 ng/L except in Klaipėda reaching 1327 ng/L.
A concentration of 1 µg/L was exceeded by Metoprolol and ranged from 523 ng/L (Nida) to 1874 ng/L (Kretinga) as well as by Naproxen with 55 ng/L in Nida and 1753 ng/L in Kretinga.
The rest of the compounds did not exceed 1 µg/L, the lowest concentrations were observed for Propranolol (from 0.1 ng/L in Nida to 24.9 ng/L in Klaipėda). Low inlet concentrations are also typical for Oxazepam (10.5-73 ng/L), Estrone (17.8-124.5 ng/L) and in summer: for Ciprofloxacin (16.6-45.2 ng/L) and Azithromycin (11.9-182.3).
Four substances were not detected in Nida influent: Atenolol, Ciprofloxacin, Erythromycin, Sulfamethoxazole in winter.

Outlet concentrations (Table 2.6):
The highest concentration was detected for anti-inflammatory drug Diclofenac in all WWTPs with a maximum value of 3499 ng/L in Kretinga and the lowest of 1548 ng/L in Klaipėda summer samples (the measurements in Nida are not taken into account). Average (summer + winter) concentration of 2657 ng/L was highest in Kretinga.
One order of magnitude lower concentration was measured for Metoprolol and ranged from 409 ng/L in Kretinga summer sample to 1425 ng/L in Klaipėda winter sample. It should be noted that Metoprolol winter concentrations were higher compared to summer in all three WWTPs. Average concentration of 1106 ng/L was highest in Klaipėda.
Clarithromycin ranks third in terms of average concentrations, with the highest concentration of 1298 ng/L in Klaipėda and the lowest of 74 ng/L in Kretinga. Winter concentrations were several times higher compared to summer.
Carbamazepine concentrations ranged from 101 ng/L (Kretinga) to 528 ng/L (Klaipėda). Summer concentrations slightly exceed winter values.
Ibuprofen was not detected in any of the WWTP outlet water, Paracetamol was not detected in any of the summer samples and in Klaipėda and Palanga winter samples measurements. Ciprofloxacin was not detected in any winter measurements, while in summer concentrations varied from 5.2 ng/L to 13.7 ng/L.
High Sulfamethoxazole values up to 468 ng/L and 115 ng/L were found in Klaipėda and Palanga WWTPs.
Concentrations of almost all remaining compounds were less than 100 ng/L, and the lowest concentrations were measured for Propranolol and Estrone.

Results of Nida winter 2018 effluent analysis could not be fully taken into account due to contradictory pharmaceutical removal values compared to the other WWTPs. This may have been due to low wastewater/influent temperature.

Table 2.6 Seasonal inlet, outlet concentrations in WWTPs.

	Inlet Concentrations in ng/L								Outlet Concentrations in ng/L							
Compound	Summer 2017				Winter 2018				Summer 2017				Winter 2018			
	Klaipėda	Palanga	Kretinga	Nida	Klaipėda	Palanga	Kretinga	Nida	Klaipėda	Palanga	Kretinga	Nida	Klaipėda	Palanga	Kretinga	Nida
	24h	24h	24h	grab	24h	24h	24h	grab	24h	24h	24h	grab	24h	24h	24h	grab
Atenolol	108.1	175.2	229.7	67.7	111.3	59.9	140.7	nd	15.4	13.2	9.7	10.9	35.8	19.1	23	nd
Azithromycin	37.0	76.4	182.4	11.9	582.6	205.4	593.8	14.3	13.4	19.9	12.1	11.0	127.6	52.5	12.7	36.3
Carbamazepine	522.4	285.9	168.9	429.8	312.8	178.8	120.4	21.8	527.7	414.3	186.9	190.0	361.7	211.7	101.4	65.6
Ciprofloxacin	16.6	20.4	45.2	31.0	628.8	179	454.8	nd	5.2	5.4	13.7	10.6	nd	nd	nd	nd
Clarithromycin	126.5	474.8	1326.7	243.6	2871.2	662.3	4113.9	46.7	229.3	150.2	73.7	62.0	1297.7	532.8	507.8	197.4
Diclofenac	2703.8	1833.5	4240.2	4551.1	2720.8	1624.5	3506.3	535	1547.6	1776.2	3499.2	1164.6	2788.9	1651.5	1815.3	1146.3
Erythromycin	95.5	49.9	359.2	2.5	76.1	10.1	147.5	nd	75.2	29.3	33.0	3.9	85.2	20.2	57.4	0.6
Estrone	89.2	72.5	124.5	65.0	74.9	38.1	60.6	17.8	0.5	2.0	5.6	0.6	1.6	4.6	3.2	0.9
Ibuprofen	31315.8	81959.7	219838.8	43391.8	290416	36374.8	287283.2	8275.2	nd	nd	nd	nd	nd	nd	nd	nd
Metoprolol	1128.7	1068.7	1874.0	480.7	1676.2	1023.3	1755.6	522.6	786.2	712.0	409.4	356.8	1424.7	971.5	757.8	695.9
Naproxen	784.8	902.6	1471.6	122.8	1311.5	957.1	1752.8	54.8	nd	nd	50.7	63.5	98.1	67.5	110.4	10.8
Oxazepam	42.2	30.9	68.3	35.3	73.2	36.3	67.9	10.5	61.7	47.8	69.0	51.8	73.1	38.9	39.3	16.1
Paracetamol	4136.6	11125.9	20010.9	11164.8	14392.8	3977.1	15918.4	2195.5	nd	nd	nd	nd	nd	nd	11.6	46
Propranolol	0.7	0.5	1.0	0.1	24.9	6.9	10.9	*1.1*	0.7	0.3	0.3	nd	22.6	3.1	3.4	3
Sulfamethoxazole	965.5	426.0	351.3	8.8	731.6	364.8	251.4	nd	467.8	114.5	61.7	7.1	446.4	96.3	36.6	12.1

Results of chemical analysis – Lithuanian water bodies (Table 2.7).

In Table 2.7 the concentrations of pharmaceuticals in the water bodies-wastewater receivers: Baltic Sea, Curonian Lagoon, Klaipėda Strait, river Tenžė and river Akmena-Danė are presented. The table contains both summer and winter samples.

a) Despite the dilution rate, several pharmaceuticals were still noted in marine water samples: Carbamazepine up to 4.4 ng/L, Erythromycin up to 0.7 ng/L, Estrone up to 0.4 ng/L and Sulfamethoxazole up to 2.1 ng/L were detected at low concentrations (above tMQL).
b) The same substances as in the Baltic Sea but at a bit higher concentrations were also detected in the Klaipėda Strait: Carbamazepine up to 6.3 ng/L, Erythromycin up to 0.8 ng/L, Estrone up to 0.4 ng/L and Sulfamethoxazole up to 2.9 ng/L. Additionally, Clarithromycin up to 6.5 ng/L, Diclofenac up to 15.2 ng/L, Paracetamol up to 14 ng/L, Ibuprofen up to 23.1 ng/L and Metoprolol up to 8.8 ng/L.
c) In the water of Curonian Lagoon near Nida only five pharmaceuticals at low concentrations were detected: Carbamazepine up to 5.7 ng/L, Clarithromycin up to 1.1 ng/L, Diclofenac up to 2.9 ng/L, Estrone up to 0.3 ng/L and Paracetamol up to 1.4 ng/L.
d) All 15 pharmaceuticals were found in the water of river Tenžė. Highest concentrations were detected near the outlet of the Kretinga WWTP. Although 1.5 km downstream after dilution concentrations of pharmaceuticals had notably decreased.
e) Ibuprofen was found in Klaipėda Strait and Tenžė river only in winter samples. The highest concentration was 148.6 ng/L near the outlet of the Kretinga WWTP.
f) Highest concentration of Paracetamol was also detected in winter – 14 ng/L in the Klaipėda Strait near the outlet of the Klaipėda WWTP. At lower concentrations Paracetamol has also been found in summer up to 6.8 ng/L in the Klaipėda Strait and 7 ng/L in Akmena-Danė river.
g) High concentrations of Diclofenac were found in Tenžė river up to 2460 ng/L during both seasons, however in Curonian Lagoon and Klaipėda Strait it was detected only during winter season. Notable higher winter concentrations in Tenžė river near the WWTP outlet can also be seen for Azithromycin, Clarithromycin, Erythromycin, Metoprolol and Naproxen.

Table 2.7 Seasonal variation of concentrations in receiving surface waters

Compound	Summer 2017 & Winter 2018, ng/l																		
	Detected in 101 of 180 analysis, 56%; Detected in 57 of 105 analysis, 54%																		
	Curonian Lagoon (Nida WWTP)					Klaipėda Strait (Klaipėda WWTP)						Baltic Sea (Palanga WWTP)			River Tenžė (drainage ditch) (Kretinga WWTP)				Akmena-Danė River mouth
	Monitoring st. 14 (background conc.)	Near outlet	Near outlet	Downstream outlet	Downstream outlet	Monitoring. st. 3 (background	Near outlet	Near outlet	0.5 km downstream outlet	0.5 km downstream outlet	Monit.st.1 (outflow to	Monit.st. B-1 (background conc.)	Near outlet	Near outlet	Near outlet downstream	Near outlet downstream	1,5 km downstream	1,5 km downstream	
Atenolol															9.1	35.1	1.2	*1.2*	
Azithromycin															12.6	195.5	1.5		
Carbamazepine	5.4	5.1	4.9	5.7	4.9	5.8	6.3	3	5.7	3.9	6	4.4	4.2	2.4	173.3	159.6	36.4	6.5	9.9
Ciprofloxacin															130.6	84.6			
Clarithromycin	1.1	1		1.1		0.9	1.4	4.4	0.9	6.5	0.7	0.1	0.1		85.4	2609.7	15.6	60.9	3.4
Diclofenac			2.5		2.9	1.9	5.6	15.2	2.8	14.9			0.5		2047.5	2460.1	621.5	112.6	8.5
Erythromycin	0.4	0.4	*0.2*	0.4	*0.2*	0.6	0.8	*0.4*	0.6	0.7	0.6	0.7	0.6	*0.3*	46.2	192.5	7.73	4.3	1
Estrone	0.2	0.3		0.3		0.2	0.2	0.3	0.4	0.2	0.2	0.4	0.3		4.1	3.9	2.9	0.7	1.2
Ibuprofen								23.1		10.2						148.6		56.1	
Metoprolol	0.1	0.1		0.1		0.7	2.6	7.1	1.3	8.8	0.3	0.2	0.1	*0.4*	410.3	992.9	70.8	42.9	4.2
Naproxen															16.5	82.4	7.9		
Oxazepam	0.2			0.3		0.2	0.4	*0.4*	0.3	*0.5*	0.3	0.3			53.8	60.8	11.5	2.4	1.4
Paracetamol			*0.8*		1.4		5.5	14	6.8	3.7				*0.7*				3.2	7
Propranolol															2.2	8.6	0.4		
Sulfamethoxazole	0.9	0.7		0.6		1.7	2.9		2.3	*1.1*	1.8	2.1	1.8	*1.1*	44.5	55.3	7.6	2.4	1.9

4.2.7. Calculated chemical load in Lithuanian WWTPs and removal

Chemical load from the WWTPs (Table 2.8). For the estimation of pharmaceutical load to and from 4 WWTPs, wastewater influent and effluent concentrations were multiplied with volume of wastewater per year. Data on wastewater volume in 2017 and 2018, e.g. during the sampling years, was provided by water companies. The influent and effluent load used for calculations were the average load for each WWTP.

The average calculation data in grams, kilograms and percentage distribution per 2017 and 2018 year is provided in tables 2.9 and 2.10.

The total wastewater influents load by all 15 pharmaceuticals at 4 WWTPs varied from 2459.8 kg or 78 % of the total amount in Klaipeda, which is the largest wastewater treatment plants by volume of treated sewage, to 11.5 kg or 0.4 % in Nida which is the smallest treatment plant. In Kretinga and Palanga WWTPs the received load was 433.22 kg (13,8%) and 235.08 kg (7,5%), respectively. The total influent load at all 4 WWTPs was 3139.59 kg.

Ibuprofen form the highest load in inlets, reaching 2786.4 kg or almost 90 % of the total load. The second highest compound was **Paracetamol** which contributed 186.47 kg or 5,9 % of the total load. **Diclofenac** ranked third contributing 53.47 kg (1,7%) to all WWTPs. Other chemicals accounted for less than one percent of the total influent load.

The situation has changed significantly, i.e. composition of pharmaceuticals and loads, in effluent/treated wastewater, see Table 2.10. Both **Ibuprofen** and **Paracetamol**, which occur in large amounts in inlets, were removed during wastewater treatment process, e.g. **Ibuprofen** were not detected in any of the 4 WWTPs effluents, while **Paracetamol** was detected only in Kretinga and Nida WWTPs outlets in small quantities, reaching 14.5 g, or 0,02 % of the total load. The top 5 pharmaceuticals present at the highest loads in WWTP effluents were: **Diclofenac Metoprolol**, **Clarithromycin**, **Carbamazepine** and **Sulfamethoxazole**. The highest average load of 41.88 kg or 44 % of total load was calculated for the anti-inflammatory drug **Diclofenac**. **Metoprolol** with 19.8 kg (21%) takes the second place. **Clarithromycin**, **Carbamazepine** and **Sulfamethoxazole** contribute 12.04 kg (12.7%), 8.17 kg (8,6%) and 7.35 kg (7,8%) to the total effluent load respectively. Similar as in inlet sewage, Klaipeda contribute almost 77 kg or 81 % of the pharmaceutical load of the 4 WWTPs effluents. By comparing the calculated average influent and effluent loads, the overall pharmaceutics load during the treatment process decreased from 3139.59 kg in influents to 94.54 kg in effluents, or by 94 %. This could be explained by large quantities of **Ibuprofen** in influent with subsequent removal during wastewater treatment.

Removal rates (based on data from Table 2.11) The removal rates in WWTPs were calculated for all pharmaceuticals and expressed as percentage of pharmaceuticals removed in the WWTP calculated as follows: removal efficiency = (average two-year inlet load — average two-year outlet load) / average two-year inlet load) * 100 %. Loads for the 2017 and 2018 years were used to calculate average inlet/outlet loads. It should be noted, that the removal rates consider only the removal of pharmaceuticals from the aqueous phase.

Results of Nida WWTP removal efficiency could not be fully taken into account due to contradictory removal values compared to the remaining WWTPs. According to explanations by the treatment plant technicians, this may have been due to low influent temperatures. Some deviations from the overall elimination trend may also be related to grab sampling, instead of 24h composite samples in the other WWTPs.

Removal rates for pharmaceuticals that were not detected in effluent waters indicates that removal is 100 %. Only **Ibuprofen** was efficiently 100% removed during the wastewater treatment process. **Paracetamol** showed almost the same removal efficiency of nearly 100 %.
High (> 90%) average removal rates were shown for **Ciprofloxacin**, **Estrone** and **Naproxen**, except Nida WWTP.
Good removal rates of **Atenolol** and **Azithromycin**, reching more than 70 % in Klaipeda, Palanga and Kretinga WWTPs.
A few drugs, such as **Diclofenac, Erythromycin** and **Metoprolol,** except Kretinga WWTP, were eliminated with < 50%.

Negative values indicate a higher average load of a pharmaceutical substance in effluent than in influent, which might be interpreted as an increase in the pharmaceuticals quantity during the wastewater treatment due to deconjugation. This is typical for the nervous system group medicines **Carbamazepine and Oxazepam.**
The removal rates in WWTPs were also calculated for all pharmaceuticals by comparing the reported influent and effluent concentrations in summer and winter seasons (Table 2.12). This reflects a similar pattern of pharmaceutical transformation during wastewater treatment processes as in load calculations in the Table 2.11.
There is no significant difference in the average removal efficiency of all compounds between summer and winter seasons reaching about 55 %. Average removal in winter of all compounds is more effective in Klaipeda and Kretinga, while in Palanga in summer time.
It could be said that the average concentration reduction of all compounds in both seasons are similar in Klaipeda and Palanga, with removal of 45 and 48 %, respectively. The best average treatment rates are in Kretinga WWTP, reaching almost 75 %. The same tendencies but with minor difference are observed when comparing percentage of load removal.

Table 2.8 Annual inlet and outlet load in WWTPs, grams per year

Compound	Inlet load, g/a								Outlet load, g/a							
	Summer 2017				Winter 2018				Summer 2017				Winter 2018			
	Klaipeda 24h	Palanga 24h	Kretinga 24h	Nida grab	Klaipeda 24h	Palanga 24h	Kretinga 24h	Nida grab	Klaipeda 24h	Palanga 24h	Kretinga 24h	Nida grab	Klaipeda 24h	Palanga 24h	Kretinga 24h	Nida grab
Q [m³/2017/2018]	**16 924 719**	**3 419 509**	**1 858 060**	**319 584**	**13314730**	**2 917 600**	**1 269 465**	**309619**	**16 924 719**	**3 419 509**	**1 858 060**	**319 584**	**13314730**	**2 917 600**	**1 269 465**	**309619**
Atenolol	1829.6	599.0	426.7	21.6	1481.9	174.8	178.6	0	260.6	45.0	18.0	3.5	476.7	55.7	29.2	0
Azithromycin	625.9	261.2	338.8	3.8	7757.2	599.3	753.8	4.4	226.3	68.1	22.5	3.5	1699.0	153.2	16.1	11.2
Carbamazepine	8841.0	977.6	313.9	137.4	4164.8	521.7	152.8	6.7	8930.5	1416.8	347.3	60.7	4815.9	617.7	128.7	20.3
Ciprofloxacin	280.1	69.8	84.0	9.9	8372.3	522.3	577.4	0.0	88.7	18.5	25.4	3.4	0.0	0.0	0.0	0.0
Clarithromycin	2141.3	1623.5	2465.2	77.9	38229.3	1932.3	5222.5	14.5	3880.0	513.5	136.9	19.8	17278.5	1554.5	644.6	61.1
Diclofenac	45760.4	6269.6	7878.5	1454.5	36226.7	4739.6	4451.1	165.6	26192.4	6073.8	6501.7	372.2	37133.5	4818.4	2304.5	354.9
Erythromycin	1617.0	170.7	667.3	0.8	1013.3	29.5	187.2	0.0	1273.2	100.2	61.4	1.2	1134.4	58.9	72.9	0.2
Estrone	1509.0	247.9	231.3	20.8	997.3	111.2	76.9	5.5	8.6	6.9	10.4	0.2	21.3	13.4	4.1	0.3
Ibuprofen	530010.6	280261.9	408473.7	13867.3	3866810.6	106127.1	364696.0	2562.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Metoprolol	19102.4	3654.3	3481.9	153.6	22318.2	2985.6	2228.7	161.8	13306.7	2434.6	760.7	114.0	18969.5	2834.4	962.0	215.5
Naproxen	13281.7	3086.3	2734.4	39.2	17462.3	2792.4	2225.1	17.0	0.0	0.0	94.2	20.3	1306.2	196.9	140.1	3.3
Oxazepam	713.7	105.7	126.8	11.3	974.6	105.9	86.2	3.3	1044.1	163.5	128.3	16.6	973.3	113.5	49.9	5.0
Paracetamol	70010.5	38045.2	37181.4	3568.1	191636.2	11603.6	20207.9	679.8	0.0	0.0	0.0	0.0	0.0	0.0	14.7	14.2
Propranolol	11.8	1.8	1.8	0.0	331.5	20.1	13.8	0.3	11.3	1.2	0.5	0.0	300.9	9.0	4.3	0.9
Sulfamethoxazole	16340.0	1456.6	652.8	2.8	9741.1	1064.3	319.1	0.0	7916.7	391.6	114.5	2.3	5943.7	281.0	46.5	3.7
∑	**712075**	**336831**	**465059**	**19369**	**4207517**	**133330**	**401377**	**3621**	**63139**	**11234**	**8222**	**618**	**90053**	**10707**	**4418**	**691**
% of total annual WWTPs load	**46.4**	**22**	**30.3**	**1.3**	**88.6**	**2.8**	**8.5**	**0.1**	**75.9**	**13.5**	**9.9**	**0.7**	**85.0**	**10.1**	**4.2**	**0.7**

Table 2.9. Average inlet load

Compounds	Average inlet load, g/a (2017+2018)/2				∑, compounds, g/a	∑, kg/a	%	Average inlet load, %			
	Klaipeda	Palanga	Kretinga	Nida				Klaipeda	Palanga	Kretinga	Nida
Atenolol	1655.7	386.9	302.7	10.8	2356.1	2.36	0.08	70.27	16.42	12.85	0.46
Azithromycin	4191.5	430.2	546.3	4.1	5172.2	5.17	0.16	81.04	8.32	10.56	0.08
Carbamazepine	6502.9	749.6	233.4	72.1	7558.0	7.56	0.24	86.04	9.92	3.09	0.95
Ciprofloxacin	4326.2	296.0	330.7	4.9	4957.9	4.96	0.16	87.26	5.97	6.67	0.10
Clarithromycin	20185.3	1777.9	3843.8	46.2	25853.2	25.85	0.82	78.08	6.88	14.87	0.18
Diclofenac	40993.5	5504.6	6164.8	810.1	53473.0	53.47	1.70	76.66	10.29	11.53	1.51
Erythromycin	1315.1	100.1	427.3	0.4	1842.9	1.84	0.06	71.36	5.43	23.19	0.02
Estrone	1253.1	179.5	154.1	13.1	1599.9	1.60	0.05	78.32	11.22	9.63	0.82
Ibuprofen	2198410.6	193194.5	386584.8	8214.7	2786404.7	2786.40	88.75	78.90	6.93	13.87	0.29
Metoprolol	20710.3	3319.9	2855.3	157.7	27043.2	27.04	0.86	76.58	12.28	10.56	0.58
Naproxen	15372.0	2939.4	2479.8	28.1	20819.2	20.82	0.66	73.84	14.12	11.91	0.13
Oxazepam	844.2	105.8	106.5	7.3	1063.7	1.06	0.03	79.36	9.95	10.01	0.69
Paracetamol	130823.4	24824.4	28694.6	2123.9	186466.3	186.47	5.94	70.16	13.31	15.39	1.14
Propranolol	171.7	11.0	7.8	0.2	190.7	0.19	0.01	90.04	5.77	4.09	0.10
Sulfamethoxazole	13040.5	1260.5	485.9	1.4	14788.4	14.79	0.47	88.18	8.52	3.29	0.01
∑, g	2459796.1	235080.3	433217.8	11495.0							
∑ kg	2459.80	235.08	433.22	11.50							
% ot total WWTPs load	78.3	7.5	13.8	0.4							
∑ ∑ kg	**3139.59**										

Table 2.10 Average outlet load

Compounds	Average outlet load, g/a (2017+2018)/2				∑, compound, g/a	∑, kg/a	%	Average outlet load, %			
	Klaipeda	Palanga	Kretinga	Nida				Klaipeda	Palanga	Kretinga	Nida
Atenolol	368.7	50.4	23.6	1.7	444.4	0.44	0.47	82.97	11.34	5.31	0.38
Azithromycin	962.6	110.6	19.3	7.4	1099.9	1.10	1.16	87.52	10.06	1.75	0.67
Carbamazepine	6873.2	1017.2	238.0	40.5	8169.0	8.17	8.64	84.14	12.45	2.91	0.50
Ciprofloxacin	44.3	9.2	12.7	1.7	68.0	0.07	0.07	65.15	13.53	18.68	2.50
Clarithromycin	10579.3	1034.0	390.8	40.5	12044.5	12.04	12.74	87.84	8.58	3.24	0.34
Diclofenac	31662.9	5446.1	4403.1	363.5	41875.6	41.88	44.29	75.61	13.01	10.51	0.87
Erythromycin	1203.8	79.6	67.1	0.7	1351.2	1.35	1.43	89.09	5.89	4.97	0.05
Estrone	15.0	10.2	7.2	0.2	32.6	0.03	0.03	46.01	31.29	22.09	0.61
Ibuprofen	0.0	0.0	0.0	0.0	0.0	0.00	0.00	0.00	0.00	0.00	0.00
Metoprolol	16138.1	2634.5	861.4	164.8	19798.7	19.80	20.94	81.51	13.31	4.35	0.83
Naproxen	653.1	98.5	117.2	11.8	880.6	0.88	0.93	74.17	11.19	13.31	1.34
Oxazepam	1008.7	138.5	89.1	10.8	1247.1	1.25	1.32	80.88	11.11	7.14	0.87
Paracetamol	0.0	0.0	7.4	7.1	14.5	0.01	0.02	0.00	0.00	51.03	48.97
Propranolol	156.1	5.1	2.4	0.5	164.1	0.16	0.17	95.12	3.11	1.46	0.30
Sulfamethoxazole	6930.2	336.3	80.5	3.0	7350.0	7.35	7.77	94.29	4.58	1.10	0.04
∑, g/a	76596.0	10970.2	6319.7	654.2							
∑ **kg/a**	76.60	10.97	6.32	0.65							
% ot total WWTPs load	81.0	11.6	6.7	0.7							
∑ ∑ **kg/a**	**94.54**										

Table 2.11 Percentage of pharmaceuticals removal in WWTPs. Calculated according to wastewater influent and effluent loads

	Average inlet load, kg/a				Average outlet load, kg/a				Average removal rate, %			
	Klaipeda	Palanga	Kretinga	Nida	Klaipeda	Palanga	Kretinga	Nida	Klaipeda	Palanga	Kretinga	Nida
Atenolol	1.66	0.39	0.30	0.01	0.37	0.05	0.02	0,00	77.7	87.0	92.2	83.8
Azithromycin	4.19	0.43	0.55	0.00	0.96	0.11	0.02	0,01	77.0	74.3	96.5	-79.9
Carbamazepine	6.50	0.75	0.23	0.07	6.87	1.02	0.24	0,04	-5.7	-35.7	-2.0	43.8
Ciprofloxacin	4.33	0.30	0.33	0.00	0.04	0.01	0.01	0,00	99.0	96.9	96.2	65.3
Clarithromycin	20.19	1.78	3.84	0.05	10.58	1.03	0.39	0,04	47.6	41.8	89.8	12.3
Diclofenac	40.99	5.50	6.16	0.81	31.66	5.45	4.40	0,36	22.8	1.1	28.6	55.1
Erythromycin	1.32	0.10	0.43	0.00	1.20	0.08	0.07	0,00	8.5	20.5	84.3	-75.0
Estrone	1.25	0.18	0.15	0.01	0.02	0.01	0.01	0,00	98.8	94.3	95.3	98.5
Ibuprofen	2198.41	193.19	386.58	8.21	0.00	0.00	0.00	0,00	100.0	100.0	100.0	100.0
Metoprolol	20.71	3.32	2.86	0.16	16.14	2.63	0.86	0,16	22.1	20.6	69.8	-4.5
Naproxen	15.37	2.94	2.48	0.03	0.65	0.10	0.12	0,01	95.8	96.6	95.3	58.0
Oxazepam	0.84	0.11	0.11	0.01	1.01	0.14	0.09	0,01	-19.5	-30.9	16.3	-47.9
Paracetamol	130.82	24.82	28.69	2.12	0.00	0.00	0.01	0,01	100.0	100.0	100.0	99.7
Propranolol	0.17	0.01	0.01	0.00	0.16	0.01	0.00	0,00	9.1	53.6	69.2	-150.0
Sulfamethoxazole	13.04	1.26	0.49	0.00	6.93	0.34	0.08	0,00	46.9	73.3	83.4	-114.3
∑	**2459.80**	**235.08**	**433.22**	**11.50**	**76.60**	**10.97**	**6.32**	**0,65**				
Total removal of all drugs in WWTP									**96.9**	**95.3**	**98.5**	**94.3**

Table 2.12 Percentage of pharmaceuticals removal in WWTPs in summer and winter seasons. Calculated according to concentrations in wastewater influent and effluent

	Efficiency of removal in %								**Average efficiency of removal, % (summer + winter)**			
Compound	**Klaipeda**		**Palanga**		**Kretinga**		**Nida**					
	Summer 2017	Winter 2018	Summer 2017	Winter 2018	Summer 2017	Winter 2018	Summer 2017	Winter 2018	Klaipeda	Palanga	Kretinga	Nida
Atenolol	85,8	67,8	92,5	68,1	95,8	83,7	83,9		76,7	86,2	91,1	84,0
Azithromycin	63,8	78,1	74,0	74,4	93,4	97,9	8,0	-153,8	77,2	74,3	96,8	-80,2
Carbamazepine	-1,0	-15,6	-44,9	-18,4	-10,7	15,8	55,8	-200,9	-6,5	-34,7	0,3	43,4
Ciprofloxacin	68,3	100,0	73,6	100,0	69,7	100,0	65,8		99,2	97,3	97,3	65,8
Clarithromycin	-81,2	54,8	68,4	19,6	94,4	87,7	74,5	-322,7	49,1	39,9	89,3	10,7
Diclofenac	42,8	-2,5	3,1	-1,7	17,5	48,2	74,4	-114,3	20,1	0,9	31,4	54,6
Erythromycin	21,3	-12,0	41,3	-100,0	90,8	61,1	-58,3		6,5	17,3	82,2	-83,3
Estrone	99,4	97,9	97,2	87,9	95,5	94,7	99,0	94,9	98,7	94,0	95,2	98,1
Ibuprofen	100,0	100,0	100,0	100,0	100,0	100,0	100,0	100	100,0	100,0	100,0	100,0
Metoprolol	30,3	15,0	33,4	5,1	78,2	56,8	25,8	-33,2	21,2	19,5	67,8	-4,9
Naproxen	100,0	92,5	100,0	93,0	96,6	93,7	48,2	80,3	95,3	96,4	95,0	58,1
Oxazepam	-46,3	0,1	-54,7	-7,2	-1,0	42,1	-46,7	-53,3	-16,8	-29,2	20,4	-48,0
Paracetamol	100,0	100,0	100,0	100,0	100,0	99,9	100,0	97,9	100,0	100,0	100,0	99,7
Propranolol	4,3	9,2	37,0	55,1	74,5	68,8	100,0	-172,7	9,4	54,1	69,5	-150,0
Sulfamethoxazole	51,6	39,0	73,1	73,6	82,4	85,4	19,8		46,1	73,3	83,7	-118,2
Average	42,6	48,3	52,9	43,3	71,9	75,7	50,0	-45,2	51,7	52,6	74,7	8,6

4.3 Polish model area

4.3.1. Sampling strategy – Poland

Legal and technical situation in Poland. Polish accession to EU has caused a dynamic growth in the wastewater sector, especially in large municipalities. Currently in the Pomeranian Voivodeship 83.2% of the population is connected to WWTPs, but a notable disproportion is observed between urban and rural zones. In some areas, where construction of centralized wastewater system is regarded as too expensive, the septic tanks are predominant and used for wastewater accumulation. Polish regulation also allows the use of small/individual WWTPs (< 5 m^3/d), which can discharge effluent to soil or water within the limits of the owner's ground (for details see Del. 5.1).

In Poland the discharge limits for nutrients depend on the WWTP size. Importantly, since 2016, the WWTPs in the range 10 000 – 15 000 PE should limit also nutrients, thus in the near future (the next 10 to 20 years) small WWTPs are intended to undergo modernization in terms of extensive nutrients removal or are intended to liquidation.

The Polish part of the MORPHEUS project focused on the metropolitan area (called: the Tri-City) as well as the Czarna Wda catchment in the Pomeranian Voivodeship. There four WWTPs were chosen as model objects (Figure 3.1). Three of them: Gdansk-Wschod WWTP, Gdynia-Debogorze WWTP and Swarzewo WWTP (all with more than 100 000 PE) are the largest WWTPs in the region (share of treated load in the metropolitan area of Tri-City > 90% and > 50% in Pomeranian Voivodeship) and discharge directly to the coastal area of the Baltic Sea. Their influents and effluents were sampled together with their marine outfalls, which are located about 2 km from the coastline. Thus, during the sampling campaigns the samples at the discharge point were taken directly above submarine collectors mounted with diffusers at a depth of about 8m (surface and bottom water were collected. In case of the Jastrzebia-Gora WWTP (with a capacity for 62 000 PE), which discharges to the Czarna Wda river, this WWTP is suspected to represents the single or at least main source of pharmaceutical pollution in Czarna Wda river body catchment, as the treated wastewater constitutes a significant share of the river flow.

It should also be noted that all WWTPs are located in the coastal region and are highly influenced by an increased wastewater load during the summer season. The temporal growth of the population due to tourism causes the seasonal inflow to increase 1.5- to 7- fold in the summer, which is particularly noticeable in WWTPs with smaller sewer network, such as Swarzewo WWTP and Jastrzebia-Gora WWTP. Besides the hydraulic overload and other technological problems caused by tourisms, another important issue is the management of wastewater originating from manholes/septic tanks. This type of wastewater is delivered to WWTPs by slurry/vacuum tanks and is usually higher contaminated than municipal wastewater reaching WWTPs via sewerage system. In case the share of manholes/septic tank wastewater is significant in the total WWTP inflow (as in case of Swarzewo WWTP and Jastrzebia-Gora WWTP), serious operational and technological problems may arise.

Besides four WWTPs and their receivers also the Vistula river mouth was sampled. Vistula river carries waters from its catchment (area over 100 000 km^2) to Gdansk Bay. The Vistula catchment is essentially agricultural (63% of land use) with an important proportion of forested area. These riverine waters are suspected to be rich in nitrogen and phosphorus compounds, and may effect on the coastal waters of receiver.

4.3.2. Sampling locations – Poland

In Figure 3.1. the geographical position of the WWTPs is given, while in Figure 3.2 a more detailed overview of the sampling locations (WWTPs) is shown. All together two sampling campaigns were carried out: in the summer-2017 (August) and winter-2018 (February) period. Summary of the types and number of samples are given in Table 3.1. A total of 33 samples were taken.

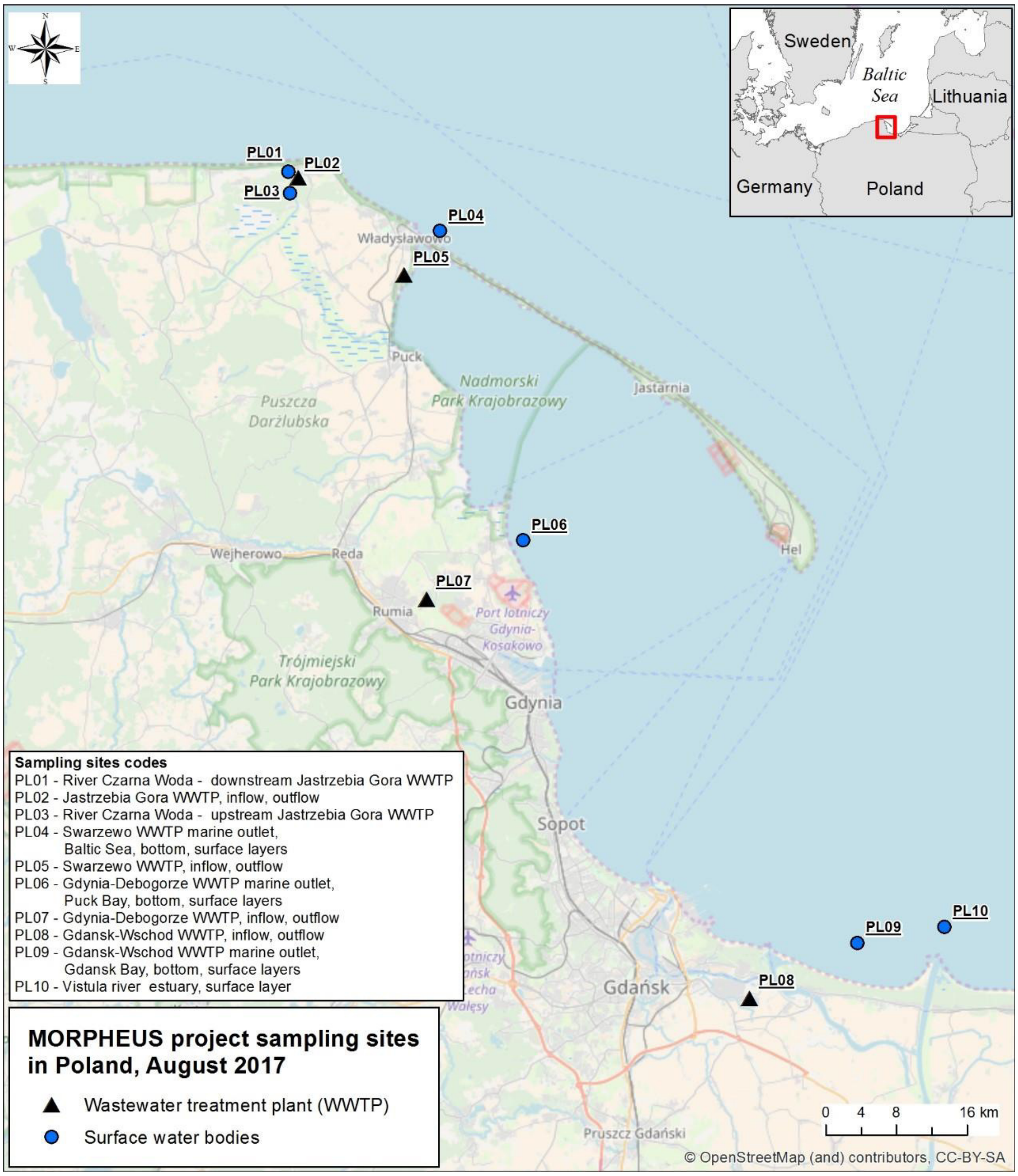
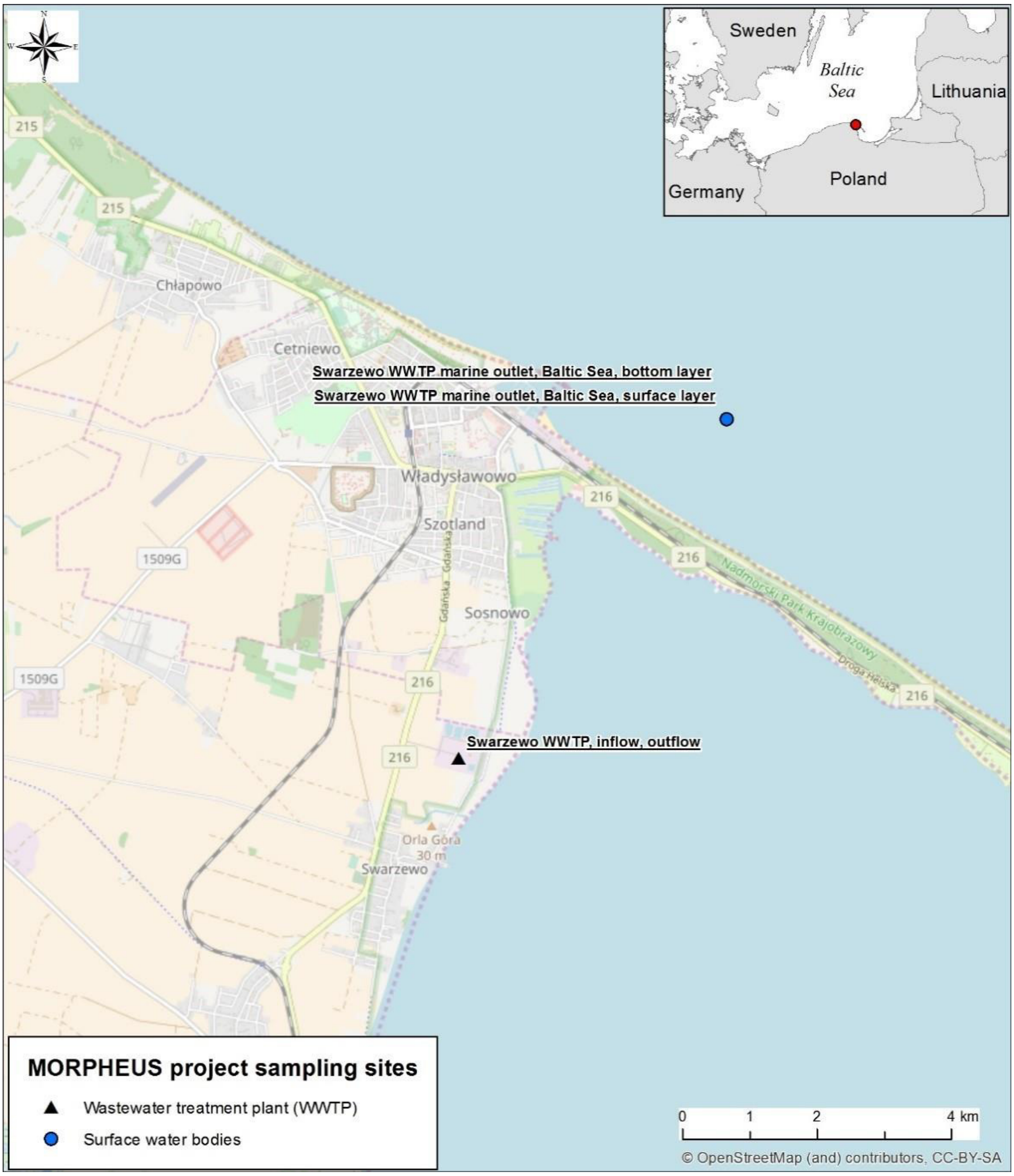


Figure 3.1 The geographical position of the WWTPs.


Sweden
Baltic Sea
Lithuania
Germany
Poland
River Czarna Woda - downstream Jastrzebia Gora WWTP
Jastrzebia Gora WWTP, inflow, outflow
River Czarna Woda - upstream Jastrzebia Gora WWTP
MORPHEUS project sampling sites
Wastewater treatment plant (WWTP)
Surface water bodies
0 0,5 1 2 km
© OpenStreetMap (and) contributors, CC-BY-SA


Sweden
Baltic Sea
Lithuania
Germany
Poland
Chłapowo
Cetniewo
Swarzewo WWTP marine outlet, Baltic Sea, bottom layer
Swarzewo WWTP marine outlet, Baltic Sea, surface layer
Władysławowo
Szotland
Sosnowo
Nadmorski Park Krajobrazowy
Droga Helska
Swarzewo WWTP, inflow, outflow
Orla Góra 30 m
Swarzewo
215
216
1509G
MORPHEUS project sampling sites
Wastewater treatment plant (WWTP)
Surface water bodies
0 1 2 4 km
© OpenStreetMap (and) contributors, CC-BY-SA

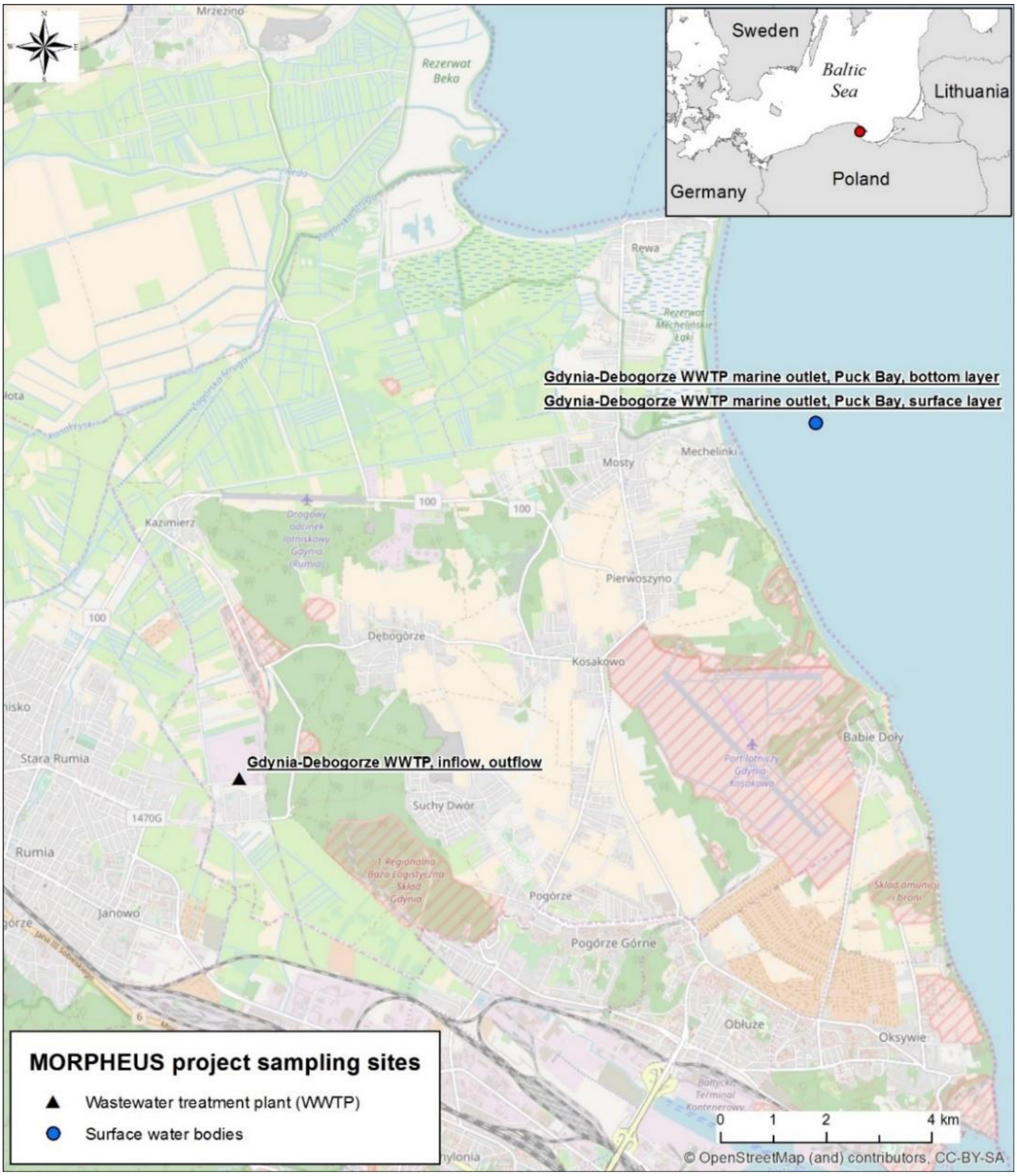

Sweden
Baltic Sea
Lithuania
Germany
Poland
Gdynia-Debogorze WWTP marine outlet, Puck Bay, bottom layer
Gdynia-Debogorze WWTP marine outlet, Puck Bay, surface layer
Gdynia-Debogorze WWTP, inflow, outflow
MORPHEUS project sampling sites
Wastewater treatment plant (WWTP)
Surface water bodies
0 1 2 4 km
© OpenStreetMap (and) contributors, CC-BY-SA

Figure 3.2 A more detailed scheme of sampling locations of the Polish WWTPs and in the effluents receiving water bodies

Table 3.1 Summary of the types and number of samples collected during the summer (August 2017) and winter (February 2018) sampling campaign

Receiving water bodies + WWTP	**Season**	**WWTP inlet**	**WWTP outlet**	**Upstream WWTP discharge**	**Downstream WWTP discharge**
Czarna Wda river + Jastrzebia-Gora WWTP	Summer	1	1	1	1
	Winter	1	1	1	1
Receiving water bodies + WWTP	**Season**	**WWTP inlet**	**WWTP outlet**	**Marine outflow surface water**	**Marine outflow bottom water**
Baltic Sea + Swarzewo WWTP	Summer	1	1	1	1
	Winter	1	1	1	-
Puck Bay (Baltic Sea) + Gdynia-Debogorze WWTP	Summer	1	1	1	1
	Winter	1	1	1	1
Gdansk Bay (Baltic Sea) + Gdansk-Wschod WWTP	Summer	1	1	1	1
	Winter	1	1	1	1
Vistula River	**Season**			Estuary surface water	
Vistula river mouth	Summer			1	
	Winter			1	
∑ Samples of different types	**Summer + Winter**	**8**	**8**	**10**	**7**
∑ Samples	33 (17 summer season & 16 winter season)				

4.3.3. Site-specific information on the WWTPs and receiving water bodies – Poland

Pomeranian Voivodeship (Polish: *Pomorskie*) is one of sixteen provinces of Poland, situated in the north, bordering the shore of the Baltic Sea. The Voivodeship area is equal to 18 293 km^2 (urban area: 106 761 ha, and rural area: 1 724 273 ha) and a total population of 2 219 635 people (1 478 802 in urban and 740 833 in rural area in 2015). Pomeranian Voivodeship is located on the Vistula River, at the bottom of its catchment. The Vistula Lagoon as well as the Bay of Gdansk, and its shallow western branch Puck Bay provid excellent natural conditions for water sports (yachting, kitesurfing, kayaking etc). The economy of the Pomeranian Voivodeship combines recreational, agricultural and industrial areas. The Port of Gdansk and the Port of Gdynia are important transport hubs, but besides shipyards and maritime industry other important branches include refinery, food, pharmaceuticals, cosmetics, and furniture.

4.3.4. Short information on the WWTPs – Poland

Detailed information about the four WWTPs, chosen as model objects in MORPHEUS project are shown Table 3.2a and Table 3.2b.

Jastrzebia Gora WWTP (PL02). At Jastrzebia Gora WWTP the designed capacity equals 7 305 m^3/d and a pollutant load corresponding to 62 000 PE. In 2015 the average daily inflow rate equalled 1 678 m^3/d, and ranged from 529 m^3/d to 5 592 m^3/d, while the average pollutant load was 12 540 PE. Treated wastewater from Jastrzebia Gora WWTP is directed to the Czarna Wda river, a direct tributary to the Baltic Sea. Czarna Wda was sampled upstream (PL01) and downstream (PL02) the treated wastewater discharge point (Figure 3.4).

Figure 3.4 From left Jastrzebia-Gora WWTP, with sampling upstream and downstream of the discharge point into Czarna Wda River

Swarzewo WWTP (PL 05). The Swarzewo WWTP serves 35 668 inhabitants from numerous towns and villages located in the coastal area. The designed capacity equals 18 000 m^3/d (pollutant load 180 000 PE), but the inflow is highly influenced by tourism, and increases even 10 times in the summer time (in 2015 from 2 856 m^3/d to 21 832 m^3/d). SBR system is used for biological treatment. Treated wastewater is discharge into the Gdansk Bay via submarine collector completed with a set of diffusers about 1.4 km from the coastline. At the Swarzewo WWTP discharge point (PL04) surface and bottom marine water were collected (Figure 3.5).

Figure 3.5 From left Swarzewo WWTP, with sampling of the discharge point – marine outfall into Baltic see (Nansen bottle was used for bottom and surface water collection)

Gdynia-Debogorze WWTP (PL07). Gdynia-Debogorze WWTP is the second largest WWTP in the MORPHEUS model area, which serves mainly the population of Gdynia and surrounding smaller towns and communities (about 360 000 inhabitants). The biological step applies the Bardenpho process with a simultaneous denitrification in the Carussel system. Treated wastewater is discharged to the Puck Bay (PL06), Natura 2000 area, 2.3 km from the coastline, where diffusers of submarine collector are located (at a depth of about 8 m). Both surface and bottom water was collected, Figure 3.6.

Figure 3.6 From left Gdynia-Debogorze WWT, with sampling of the discharge point – marine outfall into Puck Bay (Nansen bottle was used for bottom and surface water collection)

Gdansk-Wschod WWTP (PL08). Gdansk-Wschod WWTP is the largest wastewater treatment plant in northern Poland located upon the Baltic Sea. It serves about 571 350 inhabitants from Gdansk municipality and nearby towns and villages using advanced biological treatment (A2/O system). The treated wastewater is directed to the Gdansk Bay (PL09), 2.3 km from the coastline (diffusers of submarine collectors are mounted at a depth of about 10 m), in Natura 2000 area, (Figure 3.7)

Figure 3.7 From left Gdansk-Wschod WWT, with sampling of the discharge point – marine outfall into Gdansk Bay (Nansen bottle was used for bottom and surface water collection)

Vistula River mouth (PL10). Vistula River is the most important and the longest river in Poland as well as in the area of the Baltic Sea. The length of Vistula is 1047 km and the river basin covers 194,424 km^2 (87% in Poland). The river sources are located at a height of 1106 meters above the sea level in the Silesian Beskid Mountains. The Vistula flows directly into the Gulf of Gdansk through a straight, man-made outlet, with an average annual flow of 1054 m^3/s at the mouth. The Vistula plume might extend up to 9–27 km from the river mouth, depending mainly on a combination of factors such as: the wind speed and direction, the river water discharge rate, sea level etc. During the summer and winter campaigns surface water was collected in this point.

Table 3.2a Basic information about the 4 WWTPs in Polish model area (in 2015) according to water companies provided information

WWTP	Connected number of residents	Designed flow and load capacity	Average flow average load	Annual volume thousand m^3	COD In ton/year	COD Out ton/year	BOD_5 In ton/year	BOD_7 Out ton/year	N-tot In ton/year	N-tot Out ton/year	P-tot In ton/year	P-tot Out ton/year	Recipient
Jastrzebia Gora	~10 000	7 305 m^3/d 62 000 PE	1 678 m^3/d* 12 540 PE	610	641 256	551	289 698	274	55 429	54	6 615	6	Czarna Wda river
Swarzewo	~35 668	18 000 m^3/d 180 000 PE	6 164 m^3/d* 149 000 PE.	2 250	2 837 073	2 572	1 397 163	1 299	384 501	335	41 172	36	The Baltic Sea (coastal waters)
Gdynia-Debogorze	~360 000	73 000 m^3/d 440 000 PE	55 294 m^3/d 476 000 PE.	20 180	21 998 718	21 999	9 566 415	9 570	1 911 265	1 911	240 169	240	Puck Bay (coastal waters)
Gdansk-Wschod	~571 350	120 000 m^3/d 840 200 PE	92 958 m^3/d 742 521 PE.	33 930	33 454 654	32 079	1 5845 155	15 609	3 087 600	2 795	373226	351	Gdansk Bay (coastal waters)

* high second flow variability: for Jastrzebia Gora from 529 m^3/d to 5 592 m^3/d; for Swarzewo from 2 856 m^3/d to 21 832 m^3/d

Table 3.2b Basic information about the technology applied in 4 WWTPs in Polish model area (in 2015) according to water companies provided information

Treatment plant	Coarse debris screen	Chamber for sand and grit removal	Primary sedimen-tation	Biological step	Chemical treatment	Sludge treatment
WWTP Gdansk-Wschod	Yes	Yes Aerated.	Yes radial primary settling tanks	Yes biological reactors working in an anaerobic/anoxic/oxic (A2/O) system (advanced biological nutrients removal), secondary settling tanks with recirculation of excess sludge.	Yes PIX dosing system for occasional phosphorus removal	Disgestion + incineration
WWTP Gdynia-Debogorze	Yes	Yes Aerated.	Yes radial primary settling tanks	Yes biological reactors working in the Bardenpho system with simultaneous denitrification in Carussel system (advanced biological nutrients removal), secondary settling tanks with recirculation and excess sludge	Yes PIX dosing system for occasional phosphorus removal	Disgestion + incineration
WWTP Sawarzewo	Yes	Yes Aerated.	No	Yes six sequencing batch reactors (with sludge age about 63 days) are operated in a conventional nitrification-denitrification process, with methanol used as an external source of organic carbon, treated wastewater is directed to two stabilization ponds	Yes PIX dosing system for occasional phosphorus removal	Disgestion + Composting + used in agriculture.
WWTP Jastrzebia Gora	Yes	Yes	No	Yes biological treatment of wastewater takes place in a five-stage (modified) Bardenpho process, which requires the use of multiple tank zones operated in anaerobic (pre-denitrification), anoxic (dephosphatation), anaerobic (denitrification), and aerobic (nitrification) modes, followed by radial secondary settling tanks; treated wastewater undergo UV disinfection prior to discharge to the receiver.	No	Aerobic stabilization (sludge dewatering and hygienisation with lime, CaO)

4.3.5. Sampling procedure – Poland

The summer samplings were collected from 23 until 30 of August 2017, while the winter sampling from 27 until 28 February 2018. The sampling at the WWTPs has been coordinated with the local operators - inflow (after mechanical treatment) and outflow (after the final clarifier) of each WWTP was sampled by the plants' exploiters. At the WWTPs all samples were collected taking into account the hydraulic retention time (app. 1 day), which resulted in a delay of 24 hours between inflow and outflow sampling. In case of receivers, they were sampled by PP5 at the same time as WWTP's outflows. The sampling procedure, equipment and materials are given in Table 3.3

Table 3.3. Sampling procedure, equipment and materials used in Polish Model Area

Object	Inflow/outflow sampling	Receiver sampling	Physical and chemical analyses
WWTP Gdansk-Wschod	24h-continuous flow-proportional, automatic sampler, plastic bottle 100 m	Costal water of Gdansk Bay, bottom and surface water, grab sample, Nansen bottle, plastic bottle 100 m	pH and conductivity - by a portable multiparameter meter, the HL-HQ40d multi, HACH, Germany; total nitrogen (TN), N-NH_4, and N-NO_3, total phosphorus (TP) and P-PO4, chemical oxygen demand (COD), chloride (Cl^-), sulfate (SO_4^{2-}), and sulfides (S^{2-}) – by a XION 500 spectrophotometer (Dr. Lange, GmbH, Germany; 5-day biochemical oxygen demand (BOD_5) – by a manometric respirometric BOD OxiTop® method; total suspended solids (TSS) – by a gravimetric method.
WWTP Gdynia-Debogorze	24h-continuous flow-proportional, automatic sampler, plastic bottle 100 m	Costal water of Puck Bay, bottom and surface water, grab sample, Nansen bottle, plastic bottle 100 m	
WWTP Swarzewo	24h-time proportional samples	Costal water of Baltic Sea, bottom and surface water, grab sample, Nansen bottle, plastic bottle 100 m	
WWTP Jastrzebia Gora	24h-continuous flow-proportional, automatic sampler, plastic bottle 100 m	Czarne Wda river upstream and downstream about 400 m from WWTP discharge, manual grab sampling from the bridge, centre of the main flow, plastic bottle 100 mL	
Vistula River mouth	grab sample	Vistula estuary surface water, grab sample, Nansen bottle, plastic bottle 100 mL	

Problems occurred during sampling. The sampling in summer 2017 was done without any problems, while during the winter 2018 some changes in the sampling procedure were made. Due to adverse weather conditions bottom samples from the Baltic Sea (WWTP Swarzewo outflow) were not collected.

4.3.6. Results of on-site measurements and pharmaceutical analysis – Poland

On-site measurements in water bodies. The results of physical and chemical characteristics of the samples collected during summer and winter campaigns are given in Tables: 3.4 and 3.5. Raw wastewater parameters are rather typical. Redox potential below 0 mv, noted in Swarzewo WWTP (-308 mV – August 2017 and -34 mV – February 2018) and Jastrzebia Gora WWTP (- 298 mV – August 2017 and -64 mV – February 2018) confirmed high share of condensed wastewater originating from septic tanks. It is especially noticeable during the summer season, when the amount of wastewater increases even 10 times due to the tourisms (for details see Del. 5.1). In case of Gdynia Debogorze, low BOD_5/COD ratio (<0.5) support the suspicion of high share of low biodegradable industrial wastewater in the inflow.

In case of marine coastal waters, the obtained values of basic parameters (TSS, BOD_5, COD, TN, TP) in August 2017 were, in general, comparable to those, obtained in Vistula river estuary, but higher in the winter season (February 2018). Interestingly, samples taken from the surface water at the marine outfalls were also similar to those collected just above the diffusers, indicating good dilution and diffusion rate of discharging wastewater. In case of Czarna Wda river, the influence of wastewater discharge was noticeable, especially in the summer time, when, as mentioned above, the amount of wastewater significantly increases.

Table 3.4. Physical and chemical characterization of sampling points during summer campaign August 2017

SUMMER	date	pH	conductivity	redox	TP	P-PO$_4$	TN	N-NH$_4$	N-NO$_3$	N-NO$_2$	COD	BOD$_5$	SO$_4^{2-}$	Cl$^-$	TSS
Sampling place			[mS/cm]	[mV]	[mg/L]	[mg/L]	[mg/L]	[mg/L]	[mg/L]	[mg/L]	[mg/L]	[mg/L]	[mg/L]	[mg/L]	[mg/L]
WWTP Gdansk-Wschod (Qav = 95 000 m^3/d, PE=750 000) and its receiver coastal waters of Gdansk-Bay															
Inflow (24h-flow-proportional)	28/29.08	7.7	1.48	ND	7.9	4.59	70.4	59.4	0.987	0.025	765	360	ND	ND	340
Outflow (24h-flow-proportional)	28/29.08	7.9	0.975	ND	0.3	0.05	6.03	0.15	3.98	0.043	27.8	2.2	69.6	112	4.4
Marine outflow 0.1 m below water level*	30.08	8.1	10.94	44.8	0.041	0.038	0.434	0.035	0.011	0.004	22.4	2	564	4325	1.4
Marine outflow 10 m below water level*	30.08	8.2	11.42	47.7	0.056	0.036	0.424	0.037	0.029	0.003	51.1	2.2	580	3687	2.6
WWTP Gdynia-Debogorze (Qav = 60 000 m^3/d. PE = 500 000) and its receiver coastal waters of Puck-Bay															
Inflow (24h-flow-proportional)	28/29.08	7.5	1.39	ND	8.6	4.6	79.4	57.2	1.3	0.26	1200	430	ND	ND	540.0
Outflow (24h-flow-proportional)	28/29.08	8.0	0.916	ND	0.96	0.95	7.0	0.42	4.8	0.11	34.9	3	105	111	5.0
marine outflow 0.1 m below water level*	30.08	8.4	10.93	154.1	0.081	0.007	0.272	0.035	0.113	0.008	28.4	3.6	526	3758	3
marine outflow 8 m below water level*	30.08	8.4	10.32	159.4	0.079	0.011	0.683	0.032	0.087	0.009	12.4	1.2	555	4325	16
WWTP Swarzewo (Qav = 6 200 m^3/d. PE=150 000) and its receiver coastal waters of Baltic Sea															
Inflow (24h-flow-proportional)	23/24.08	7.1	2.35	-307.9	13.9	6.67	124	83.8	1.64	0.545	1375	800	239	404	390.0
Outflow (24h-flow-proportional)	24/25.08	7.6	1.376	22.9	0.394	0.370	10.400	0.285	9.95	0.152	29.9	3.4	109	284	1.3
marine outflow 0.1 m below water level*	25.08	8.0	11.04	28	0.077	0.016	0.65	0.019	0.093	0.009	34	3.6	129	4254	2.2
marine outflow 7 m below water level*	25.08	7.9	11.34	39.4	0.057	0.017	0.625	0.019	0.075	0.008	33	2.1	490	4254	3.8
WWTP Jastrzebia Gora (Qav = 1 700 m^3/d. PE = 13 000) and its receiver Czarna Wda river															
Inflow (24h-flow-proportional)	27/28.08	7.5	1.388	-298.5	10.5	6.96	72.3	63.4	0.781	0.297	1184	945	192	113.4	343.3
Outflow (24h-flow-proportional)	28/29.08	7.4	0.894	29.4	0.756	0.585	5.85	0.068	3.84	0.03	31.6	3.9	76.5	141.8	3.3
upstream 0.1 m below water level*	29.08	7.6	1.024	45.7	0.095	0.163	1.11	0.044	0.523	0.028	22.5	2.5	39.4	14.2	2.7
downstream 0.1 m below water level*	29.08	7.7	1.061	34.4	0.189	0.216	1.76	0.047	0.881	0.026	24.9	3.1	40.5	14.2	3.5
Vistula River															
Estuary 0.1 m below water level*	30.08	8.3	8.00	45.4	0.065	0.11	0.009	0.043	0.023	0.004	32.8	3.6	419	2198	2.6

ND – not detected

Table 3.5. Physical and chemical characterization of sampling points during winter campaign February 2018

WINTER	date	pH	conductivity	redox	TP	$P\text{-}PO_4$	TN	$N\text{-}NH_4$	$N\text{-}NO_3$	$N\text{-}NO_2$	COD	BOD_5	SO_4^{2-}	Cl^-	TSS
Sampling place			[mS/cm]	[mV]	[mg/L]	[mg/L]	[mg/L]	[mg/L]	[mg/L]	[mg/L]	[mg/L]	[mg/L]	[mg/L]	[mg/L]	[mg/L]
WWTP Gdansk-Wschod (Qav = 95 000 m^3/d. PE=750 000) and its receiver coastal waters of Gdansk-Bay															
inflow (24h-flow-proportional)	27.02	7.8	1.680	ND	9.2	5.4	91.2	65.2	ND	ND	1000	721	ND	ND	470
outflow (24h-flow-proportional)	28.02	7.8	1.250	ND	0.28	0.05	8.0	<0.015	5.36	0.21	36.5	4.1	94.3	161	6.7
marine outflow 0.1 m below water level*	28.02	8.1	10.00	115.9	0.104	0.07	0.479	0.027	0.093	<0.015	0.393	< DL	3878	586	2.5
marine outflow 10 m below water level*	28.02	7.1	13.21	117.8	0.108	0.08	0.349	0.036	0.056	<0.015	1.16	0.69	4428	677	2.5
WWTP Gdynia-Debogorze (Qav = 60 000 m^3/d. PE = 500 000) and its receiver coastal waters of Puck-Bay															
inflow (24h-flow-proportional)	27.02	ND	ND	ND	11.3	5.43	97.9	66.7	ND	ND	1000	470	ND	ND	470
outflow (24h-flow-proportional)	28.02	7.9	1.151	ND	0.85	0.67	6.00	**0.33**	3.80	0.0720	36.9	3.2	147	ND	<5
marine outflow 0.1 m below water level*	28.02	7.3	12.35	123.5	0.118	0.09	0.329	<0.015	0.047	<0.015	0.302	< DL	4104	622	1.7
marine outflow 8 m below water level*	28.02	8.0	12.27	95.5	0.097	0.06	0.362	0.023	0.047	<0.015	0.324	< DL	1213	317	54.9
WWTP Swarzewo (Qav = 6 200 m^3/d. PE=150 000) and its receiver coastal waters of Baltic Sea															
inflow (24h-time-proportional)	27.02	7.8	3.08	-34.4	19.4	10.86	146.2	92	2.37	0.184	920	644	545	128	624
outflow (24h-timr-proportional)	28.02	7.7	2.37	56.9	2.32	9.53	16.4	0.638	10.5	0.081	20.01	13.8	456	245	12.7
marine outflow 0.1 m below water level*	28.02	7.4	12.24	123.8	0.168	0.08	0.4275	0.296	0.198	<0.015	0.322	< DL	3886	585	6
marine outflow 7 m below water level*	28.02	Not sampled due to the weather conditions													
WWTP Jastrzebia Gora (Qav = 1 700 m^3/d. PE = 13 000) and its receiver Czarna Wda river															
inflow (24h-flow-proportional)	28.02	7.3	1.255	-64.8	9.97	7.08	72.5	58.5	0.851	0.177	982	687.4	111	137	330
outflow (24h-flow-proportional)	28.02	7.4	0.883	116.6	0.14	7.74	4.33	0.179	3.46	0.027	26.2	16.9	136	186	29.6
upstream 0.1 m below water level*	28.02	7.3	0.449	142.4	0.314	0.28	1.726	0.271	1.55	<0.015	0.074	< DL	16	93	1.7
downstream 0.1 m below water level*	28.02	7.4	0.437	136.2	0.366	0.25	1.965	0.279	1.48	<0.015	0.075	< DL	15	94	4.7
Vistula River															
Estuary 0.1 m below water level*	28.02	8.1	10.76	101.3	<0.5	<0.05	0.85	<0.015	<0.23	<0.015	0.404	< DL	3547	534	3.9

ND – not detected. <DL – below detection limit

Results of pharmaceuticals analysis in WWTPs – Poland. Besides basic physical and chemical analyses mentioned above, the Lead Partner in Sweden performed laboratory analysis of selected pharmaceuticals in the wastewater and water bodies – sewage receivers. The obtained results are given in Table 3.6 to 3.8.

Pharmaceuticals found in WWTP' inlet (see Table 3.6):

a) Among the analysed pharmaceuticals the highest concentrations were noted for Ibuprofen, from 200 µg/L up to 1.6 mg/L.
b) During the summer time high inlet concentrations, above 1 µg/L were also noted for Clarithromycin, Diclofenac, Naproxen, Azithromycin, Paracetamol, Ibuprofen and Carbamazepine, while in the winter time, additionally for Azithromycin, Ciprofloxacin and Metoprolol concentrations exceeded 1 µg/L.
c) For some pharmaceuticals, such as Azithromycin, Ciprofloxacin, Ibuprofen, Diclofenac and partly Clarithromycin, clear difference in winter and summer inlet concentration can be seen. These compounds belong to antimicrobials, anti-inflammatory drugs and pain killers, so their elevated concentrations in raw wastewater during the winter time can be explained by increasing consumption due to infections;

Pharmaceuticals found in WWTP' outlet (see Table 3.7):

a) In outflow Ibuprofen was not detected.
b) The highest concentrations were noted for Azithromycin (up to 4 µg/L), Clarithromycin (up to 2.9 µg/L), Metoprolol (up to 1.3 µg/L), Diclofenac (up to 3.7 µg/L) and Carbamazepine (up to 2.3 µg/L).

Removal rates (see Table 3.8):

a) The effectiveness of the biological processes in removing the analysed pharmaceuticals varied in a wide range, from -266% up to 100%;
b) Ciprofloxacin, Estrone, Naproxen, Paracetamol, and Ibuprofen were removed with the highest efficiency at over 90%.
c) The lowest or even negative removal was observed for Oxazepam, Erythromycin, Azithromycin, Propranolol, and Carbamazepine.

Load of tested pharmaceuticals received, removed and discharged (see Table 3.9):

For the estimation of pharmaceutical load, the wastewater mean concentrations (summer and winter season) of pharmaceuticals detected in WWTP's influent and effluent were multiplied by the volume of wastewater treated per year.

a) In the raw wastewater of each tested WWTP, Ibuprofen and Paracetamol were detected in the highest load, reaching in Jastrzebia Gora WWTP 387 kg and 23 kg per year, respectively, and in Gdansk-Wschod WWTP up to 17 127 kg and 947 kg per year, respectively.
b) among antimicrobial agents, Azithromycin load in the raw wastewater was elevated, reaching in the Jastrzebia Gora WWTP 4.1 kg per year and up to 265 kg per year in Gdansk-Wschod WWTP
c) Azithromycin load was also the highest among the tested pharmaceuticals in the treated wastewater, reaching 1.4 kg per year in the Jastrzebia Gora WWTP and up to 63.3 kg per year in Gdansk-Wschod WWTP

d) Similar load as for Azithromycin was observed for Diclofenac with 1.0 kg per year in treated wastewater at Jastrzebia Gora WWTP and 57.2 kg per year in Gdansk-Wschod WWTP
e) Metoprolol and Carbamazepine are also directed to the receivers in similar loads, reaching up to 40 kg per year in the treated wastewater of Gdansk-Wschod WWTP.

It can be concluded that some pharmaceuticals can be removed efficiently by conventional WWTPs, while for others pharmaceuticals more detailed investigations are required, especially if negative removal rates are observed. In this case, a holistic approach is needed, which besides wastewater treatment technology also consider sewage sludge treatment. However, even though the removal rate is high, compounds with elevated inflow concentrations are still detected in the treated wastewater. Their constant discharge constitute an important load of pharmaceuticals introduced into the receivers each year, which need to be considered as relevant in environmental burden investigations.

Table 3.6. WWTPs inlet concentrations of tested pharmaceuticals]

Compound	Inlet Concentrations, ng/L							
	Summer				Winter			
	Gdansk-Wschod	Gdynia-Debogorze	Swarzewo	Jastrzębia-Gora	Gdansk-Wschod	Gdynia-Debogorze	Swarzewo	Jastrzębia-Gora
Atenolol	135.2	157.4	156.3	197.5	155.9	192.6	108.5	24.3
Azithromycin	789.8	403.5	1993.5	2165.7	14849.2	24144.9	11650.4	11201.0
Carbamazepine	1999.9	1885.1	1716.3	1055.0	1990.2	1824.1	1891.4	1090.6
Ciprofloxacin	474.7	563.1	1062.2	494.9	2835.3	4302.3	5873.2	3323.2
Clarithromycin	1436.4	1367.7	2400.4	1569.1	4460.5	5008.9	7294.1	922.5
Diclofenac	2430.4	2867.4	3818.1	2063.1	3740.6	4687.7	7713.3	3331.9
Erythromycin	94.0	56.0	85.7	75.0	9.9	13.5	14.2	4.6
Estrone	58.1	67.8	82.6	49.8	83.3	95.5	90.2	83.0
Ibuprofen	118224.5	197600.6	399005.8	197922.9	891340.2	1482866.3	1603084.1	1066146.7
Metoprolol	769.7	805.2	603.5	747.9	1446.8	1373.0	897.4	752.3
Naproxen	2215.1	3011.8	1925.2	1655.8	3928.5	4748.8	3840.7	2785.9
Oxazepam	25.5	28.7	19.7	14.5	26.6	25.8	21.3	30.6
Paracetamol	27699.8	31867.5	51807.0	33767.3	28101.4	35529.8	45627.7	40272.6
Propranolol	30.7	28.2	32.5	28.5	42.2	44.3	44.7	33.3
Sulfamethoxazole	606.4	629.4	618.4	387.5	576.2	827.5	538.4	2019.8

Table 3.7. WWTPs outlet concentrations of tested pharmaceuticals

Compound	Outlet Concentrations, ng/L							
	Summer				Winter			
	Gdansk-Wschod	Gdynia-Debogorze	Swarzewo	Jastrzębia-Gora	Gdansk-Wschod	Gdynia-Debogorze	Swarzewo	Jastrzębia-Gora
Atenolol	31.8	18.8	9.4	48	59	34	21.3	10.5
Azithromycin	894.4	1 568.70	769.7	1 535.30	2837	3988.7	1114.3	3021.7
Carbamazepine	ND	ND	ND	1 454.40	2332.6	2028.6	1819.8	1207.7
Ciprofloxacin	24.6	31.1	ND	22.6	109.8	171.9	ND	72
Clarithromycin	330.8	299.7	314	155.9	2300	2866	2584.1	886
Diclofenac	2 004.80	2 640.40	1 344.40	816.8	3370.6	3701.1	3114.5	2482.5
Erythromycin	73.8	78.1	75.5	45.7	64.6	35.3	15.3	11.9
Estrone	3.5	6.9	1.7	2.3	3.1	7.5	1.2	1.5
Ibuprofen	ND	ND	ND	ND	ND	ND	ND	ND
Metoprolol	569	672.2	398.1	394.2	1314.9	1210.8	618.1	444.2
Naproxen	ND	51.7	27.6	55	169.1	36.7	55.6	46.3
Oxazepam	29.6	37.5	23.9	22.3	39.8	37.7	29.1	32.9
Paracetamol	ND	ND	ND	ND	7.4	24.2	32.4	12.7
Propranolol	26.5	27.6	22.1	9.8	54.4	46.5	37.5	25.7
Sulfamethoxazole	185.4	177.5	125.9	125.3	210.3	242.6	141.7	296.6

ND – not detected

Table 3.8. WWTPs removal efficiency of tested pharmaceuticals

Compound	**Removal efficiency, %**							
	Summer				**Winter**			
	Gdansk-Wschod	Gdynia-Debogorze	Swarzewo	Jastrzębia-Gora	Gdansk-Wschod	Gdynia-Debogorze	Swarzewo	Jastrzębia-Gora
Atenolol	76.5	88.1	94	75.7	62.2	82.3	80.3	56.9
Azithromycin	-13.2	-288.8	61.4	29.1	80.9	83.5	90.4	73
Carbamazepine	100	100	100	-37.9	-17.2	-11.2	3.8	-10.7
Ciprofloxacin	94.8	94.5	100	95.4	96.1	96	100	97.8
Clarithromycin	77	78.1	86.9	90.1	48.4	42.8	64.6	4
Diclofenac	17.5	7.9	64.8	60.4	9.9	21	59.6	25.5
Erythromycin	21.5	-39.5	11.9	39.1	-554.4	-162.4	-7.5	-161.1
Estrone	94	89.8	98	95.4	96.3	92.2	98.7	98.2
Ibuprofen	100	100	100	100	100	100	100	100
Metoprolol	26.1	16.5	34	47.3	9.1	11.8	31.1	40.9
Naproxen	100	98.3	98.6	96.7	95.7	99.2	98.6	98.3
Oxazepam	-16.1	-30.8	-21.2	-53.8	-49.7	-46.4	-36.7	-7.6
Paracetamol	100	100	100	100	100	99.9	99.9	100
Propranolol	13.7	2	32	65.5	-28.8	-4.9	15.9	22.7
Sulfamethoxazole	69.4	71.8	79.6	67.7	63.5	70.7	73.7	85.3

ND – not detected

Table 3.9 Load of tested pharmaceuticals received, removed and discharged to the receivers by tested WWTPs. Mean elimination rates recalculated

Compound	**WWTP mean inlet loads, kg/a**				**WWTP mean outlet loads, kg/a**				**Mean Elimination Rates, %**			
	Gdansk-Wschod	Gdynia-Debogorze	Swarzewo	Jastrzebia-Gora	Gdansk-Wschod	Gdynia-Debogorze	Swarzewo	Jastrzebia-Gora	Gdansk-Wschod	Gdynia-Debogorze	Swarzewo	Jastrzebia-Gora
Atenolol	4.94	3.53	0.30	0.07	1.54	0.53	0.03	0.02	68.8	85.0	90.0	71.4
Azithromycin	265.31	247.72	15.35	4.09	63.30	56.08	2.12	1.40	76.1	77.4	86.2	65.8
Carbamazepine	67.69	37.43	4.06	0.66	39.57	20.47	2.05	0.82	41.5	45.3	49.5	-24.2
Ciprofloxacin	56.15	49.10	7.80	1.17	2.28	2.05	ND	0.03	95.9	95.8	100.0	97.4
Clarithromycin	100.04	64.35	10.91	0.76	5.61	3.02	0.35	0.05	94.4	95.3	96.8	93.4
Diclofenac	104.69	76.24	12.97	1.65	57.18	37.35	3.50	1.01	45.4	51.0	73.0	38.8
Erythromycin	1.76	0.70	0.11	0.02	2.35	1.14	0.10	0.02	-33.5	-62.9	9.1	0.0
Estrone	2.40	1.65	0.19	0.02	0.11	0.14	0.003	0.001	95.4	91.5	98.4	95.0
Ibuprofen	17 127	16 957	2 252.21	387.10	0.0	0.0	0.0	0.0	100.0	100.0	100.0	100.0
Metoprolol	37.60	21.98	1.69	0.46	31.96	19.00	1.14	0.26	15.0	13.6	32.5	43.5
Naproxen	104.23	78.31	6.49	1.36	2.87	0.89	0.09	0.03	97.2	98.9	98.6	97.8
Oxazepam	0.88	0.55	0.05	0.01	1.18	0.76	0.06	0.02	-34.1	-38.2	-20.0	-100.0
Paracetamol	946.66	680.12	109.61	22.67	0.13	0.24	0.04	0.004	100.0	100.0	100.0	100.0
Propranolol	1.24	0.73	0.09	0.02	1.37	0.75	0.07	0.01	-10.5	-2.7	22.2	50.0
Sulfamethoxazole	20.06	14.70	1.30	0.74	6.71	4.24	0.30	0.13	66.6	71.2	76.9	82.4

Results of chemical analysis – Polish water bodies. The bottom and surface water at WWTPs' marine outfalls and Vistula river mouth were collected as grab samples. In the same manner Czarna Wda River was sampled upstream and downstream the treated wastewater discharge. The obtained results are given in Table 3.10 and 3.11.

Pharmaceuticals found in receivers and Vistula river mouth:

a) Despite the dilution rate several pharmaceuticals were still noted in marine water samples. In each of them Sulfamethoxazole, Carbamazepine and partly Metoprolol and Diclofenac were detected.
b) Similar pattern was observed for Czarna Wda River's upstream and downstream samples.
c) In each Vistula River mouth sample Erythromycin, Sulfamethoxazole, Diclofenac and Carbamazepine were quantified, while Estradiol, Etinylestradiol, Naproxen and Ibuprofen were not detected
d) Compared to marine water, higher concentration of pharmaceuticals were noted in Czarna Wda River's samples, even upstream the treated wastewater discharge.
e) In the wastewater receivers, among the tested compounds the highest concentrations were noted for Carbamazepine (up to 175.5 ng/L), Diclofenac (up to 125.9 ng/L), Metoprolol (up to 46.9 ng/L) and Sulfamethoxazole (up to 12.0 ng/L).
f) In the Vistula River mouth the highest concentrations were noted for Carbamazepine (up to 37.7 ng/L), Sulfamethoxazole (up to 6.5 ng/L) and Diclofenac (up to 5.1 ng/L).
g) Ibuprofen and Etinylestradiol were not detected.
h) In general higher concentrations of pharmaceuticals were noted in summer season compared to winter season.

It can be concluded that the dilution and diffusion rates are important factors influencing the pharmaceuticals concentration in wastewaters' receivers. However, despite the very negligible share of treated wastewater in the marine waters, the presence of pharmaceuticals was still noted in the Baltic Sea costal area. Therefore, the pharmaceuticals fate in the receivers (biodegradation, deposition in the sediments, accumulation in the receiver waters as inert compounds) and their environmental burden needs to be studied in details.

Table 3.10. Concentrations of tested pharmaceuticals in WWTPs' receiver - costal water of Baltic Sea [ng/L]

Compound	Gdansk Bay				Puck Bay				Baltic Sea			
	WWTP Gdansk-Wschod				WWTP Gdynia-Debogorze				WWTP Swarzewo			
	bottom water		surface water		bottom water		surface water		bottom water		surface water	
	summer	winter	summer	winter	summer	winter	summer	winter	summer	winter	summer	winter
Atenolol	ND	ND	*0.5*	ND	ND	ND	ND	ND	ND	NT	ND	ND
Azithromycin	*0.0*	ND	*7.3*	ND	*1.4*	ND	*1.8*	*1.1*	*0.0*	NT	*0.1*	ND
Carbamazepine	*4.3*	*5.1*	*37.0*	*3.0*	*9.0*	*2.8*	*6.5*	*2.9*	*3.0*	NT	*3.0*	*2.6*
Ciprofloxacin	ND	ND	ND	ND	ND	ND	ND	ND	ND	NT	ND	ND
Clarithromycin	*0.1*	ND	*6.3*	ND	*0.4*	ND	*0.4*	*nd*	*0.1*	NT	*0.1*	ND
Diclofenac	ND	*2.4*	*22.1*	*0.8*	*3.7*	*1.1*	*2.5*	*1.0*	ND	NT	ND	*0.5*
Erythromycin	*2.0*	*0.6*	*1.9*	ND	*3.0*	ND	*0.6*	ND	*1.1*	NT	*0.8*	ND
Estrone	*0.2*	ND	*0.3*	ND	*0.3*	ND	*0.3*	ND	*0.3*	NT	*0.3*	ND
Ibuprofen	ND	ND	ND	ND	ND	ND	ND	ND	ND	NT	ND	ND
Metoprolol	*0.1*	*1.0*	*8.5*	*0.4*	*0.7*	*0.4*	*0.2*	*0.5*	*0.1*	NT	*0.1*	ND
Naproxen	ND	ND	ND	ND	ND	ND	ND	ND	ND	NT	ND	ND
Oxazepam	ND	ND	*0.6*	ND	ND	ND	ND	ND	ND	NT	ND	ND
Paracetamol	ND	ND	ND	ND	ND	ND	ND	ND	ND	NT	ND	*1.2*
Propranolol	ND	ND	*0.3*	ND	ND	ND	ND	ND	ND	NT	ND	ND
Sulfamethoxazole	*1.5*	*1.9*	*5.9*	*1.2*	*3.0*	*0.9*	*2.5*	*1.0*	*1.8*	NT	*1.6*	*1.1*

ND – not detected; NT – not tested

Table 3.11. Concentrations of tested pharmaceuticals in WWTP's receiver - Czarna Wda River, and in the Vistula River mouth [ng/L]

Compound	**Czarna Wda River**				**Vistula River**	
	WWTP Jastrzębia-Góra					
	river upstream		**river downstream**		**mouth**	
	summe r	winter	summer	winter	summe r	winter
Atenolol	ND	ND	*4.2*	*0.6*	ND	*nd*
Azithromycin	ND	ND	*1.8*	ND	*0.9*	ND
Carbamazepine	*52.4*	*14.9*	*175.5*	*23.0*	*37.7*	*8.3*
Ciprofloxacin	ND	ND	ND	ND	*0.2*	ND
Clarithromycin	*3.6*	ND	*16.0*	ND	*1.1*	ND
Diclofenac	*55.2*	*27.3*	*125.9*	*42.7*	*4.1*	*5.7*
Erythromycin	*0.7*	ND	*5.2*	ND	*1.4*	*0.5*
Estrone	*0.6*	*0.6*	*0.8*	*0.7*	*0.2*	ND
Ibuprofen	ND	ND	ND	ND	ND	ND
Metoprolol	*11.1*	*4.5*	*46.9*	*7.1*	ND	*1.9*
Naproxen	ND	ND	*5.4*	ND	ND	ND
Oxazepam	*0.7*	ND	*2.3*	*0.3*	*0.6*	ND
Paracetamol	ND	*2.7*	ND	*2.3*	ND	*1.2*
Propranolol	*0.4*	*0.3*	*1.1*	*0.3*	*0.0*	*nd*
Sulfamethoxazole	*2.1*	*1.0*	*12.0*	*1.9*	*6.5*	*2.7*

ND – not detected

4.4 Swedish model area

4.4.1. Sampling strategy - Sweden

The County Administrative Board of Skåne, Sweden, in 2014 issued a supervisory guide entitled *"Läkemedelsrester i avloppsvatten"* [Drug residues in wastewater][2]

The County Board writes, "*Pharmaceutical substances are not traditionally included in the sampling packages used for checks of outlet water. Within the scope of supervision, the issue should be made current of whether there is reason to increase the environmentally hazardous activities' self-inspection regarding pharmaceuticals (e.g. industries, livestock agriculture, waste treatment plants and wastewater treatment plants).*" Further down the County Board propose that *"The County Administrative Board of Skåne also considers that sampling of pharmaceutical substances shall take place with regard to outlet wastewater from treatment plants dimensioned for more than 200 pe and upstream and downstream of the treatment plant. This applies to both municipal treatment plants and private treatment plants in industrial parks, conference facilities, treatment centres and the like."* These 3 sampling points together with a 4th sampling point, at the wastewater treatment plant's inlet water, is illustrated in Figure 4.1.

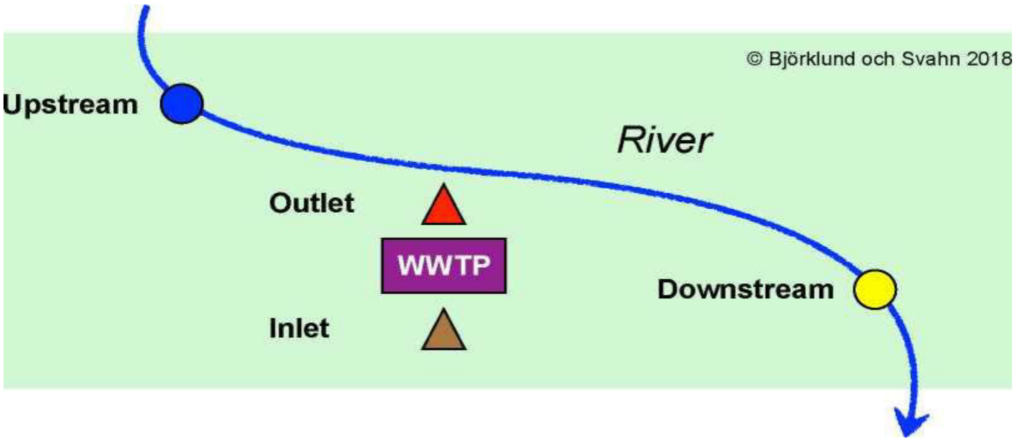


Figure 4.1 Three sampling points proposed by the County Administrative Board of Skåne and a fourth sampling point at the wastewater treatment plant's inlet water.

In Region Skåne all four types of sampling points were included. In one case surface water from a lake situated downstream one of the WWTPs were also included as described in more detail below.

4.4.2. Sampling locations - Sweden

A general overview of the 3 sampling areas is shown in Figure 4.2. In total 3 WWTPs ending in 3 different river systems were sampled.

[2] Supervisory guide from the County Administrative Board of Skåne (TVL-info 2014:12) - Läkemedelsrester i Avloppsvatten [Drug Remnants in Wastewater]; 6 pages.

Each sampling point was given a unique code starting with SE for Sweden and then a number from 01-14. These were:

* **Kristianstad WWTP** – outlet in **Helge å river** ending in the Baltic Sea (Hanöbukten Bay).
Upstream SE01, WWTP inlet and outlet SE02, downstream SE03, SE04, SE05 and SE09.
* **Tollarp WWTP** – outlet in **Vramsån river**, thereafter ending in Helge å river.
Upstream SE06, WWTP inlet and outlet SE07, downstream SE08.
* **Degeberga WWTP** – outlet in **Segesholmsån river**, ending in the Baltic Sea (Hanöbukten Bay).
Upstream SE11, WWTP inlet and outlet SE12, downstream SE13 and SE14.
A fourth surface sampling point was taken at one occasion (August 2017) as a background point in a small creek named **Forsakarsbäcken**, SE10. Forsakarsbäcken ends in Helgeå river and was assumed to contain no pharmaceuticals.

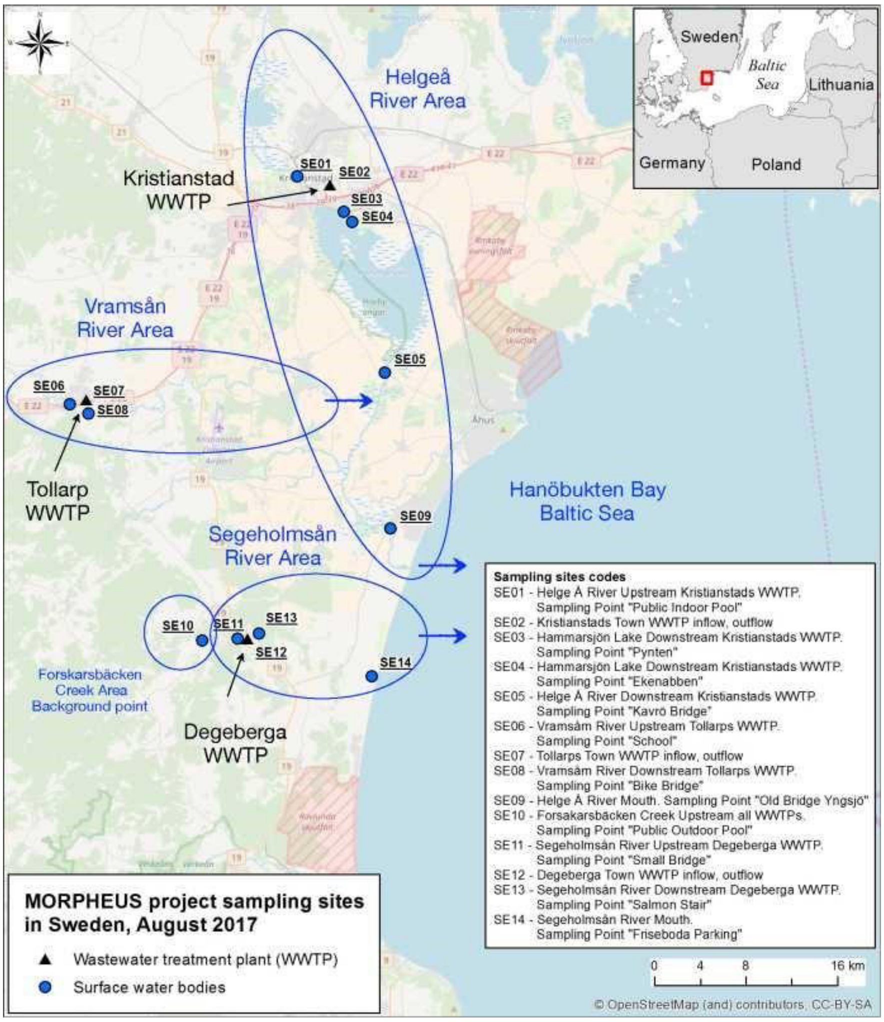
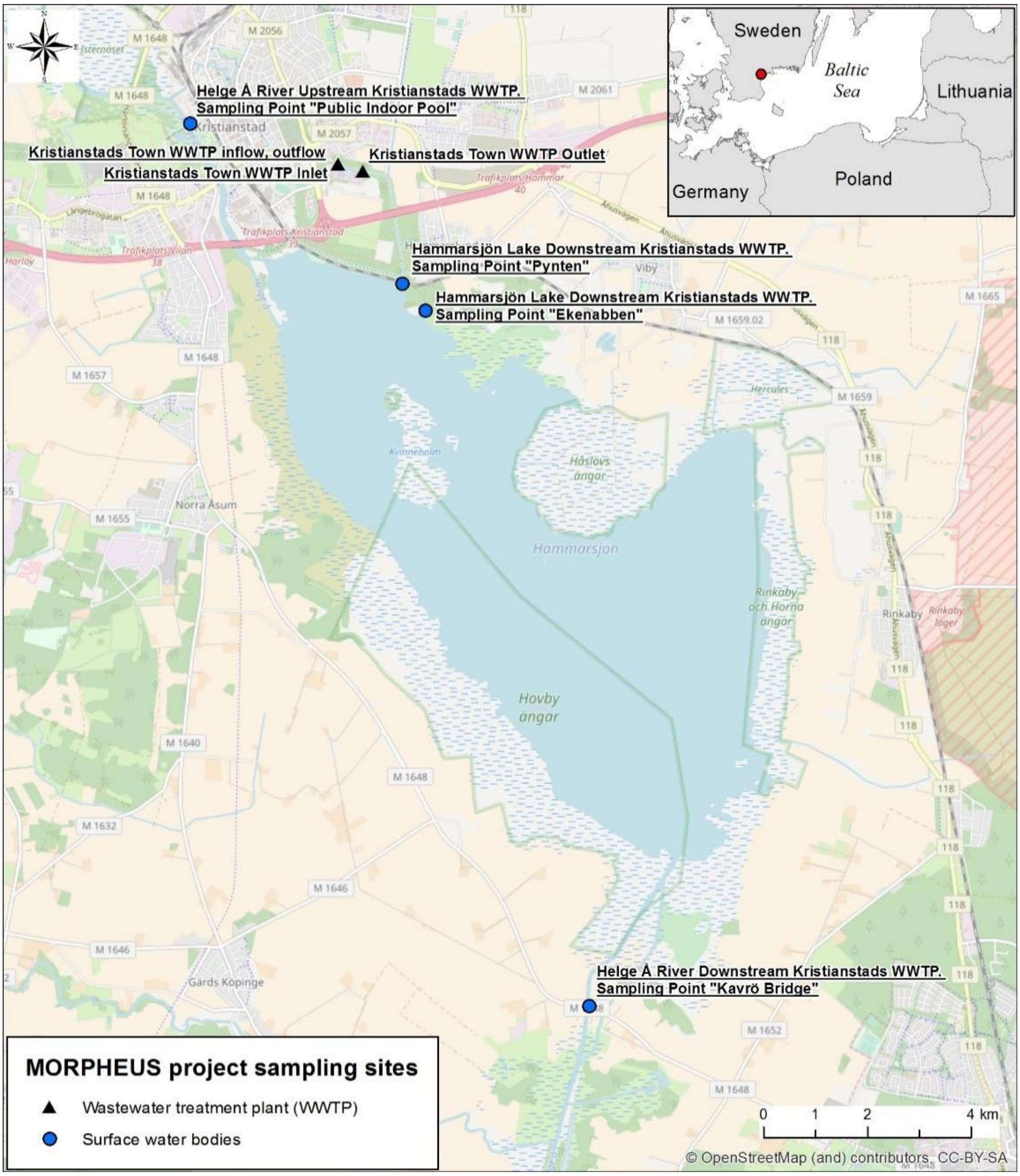
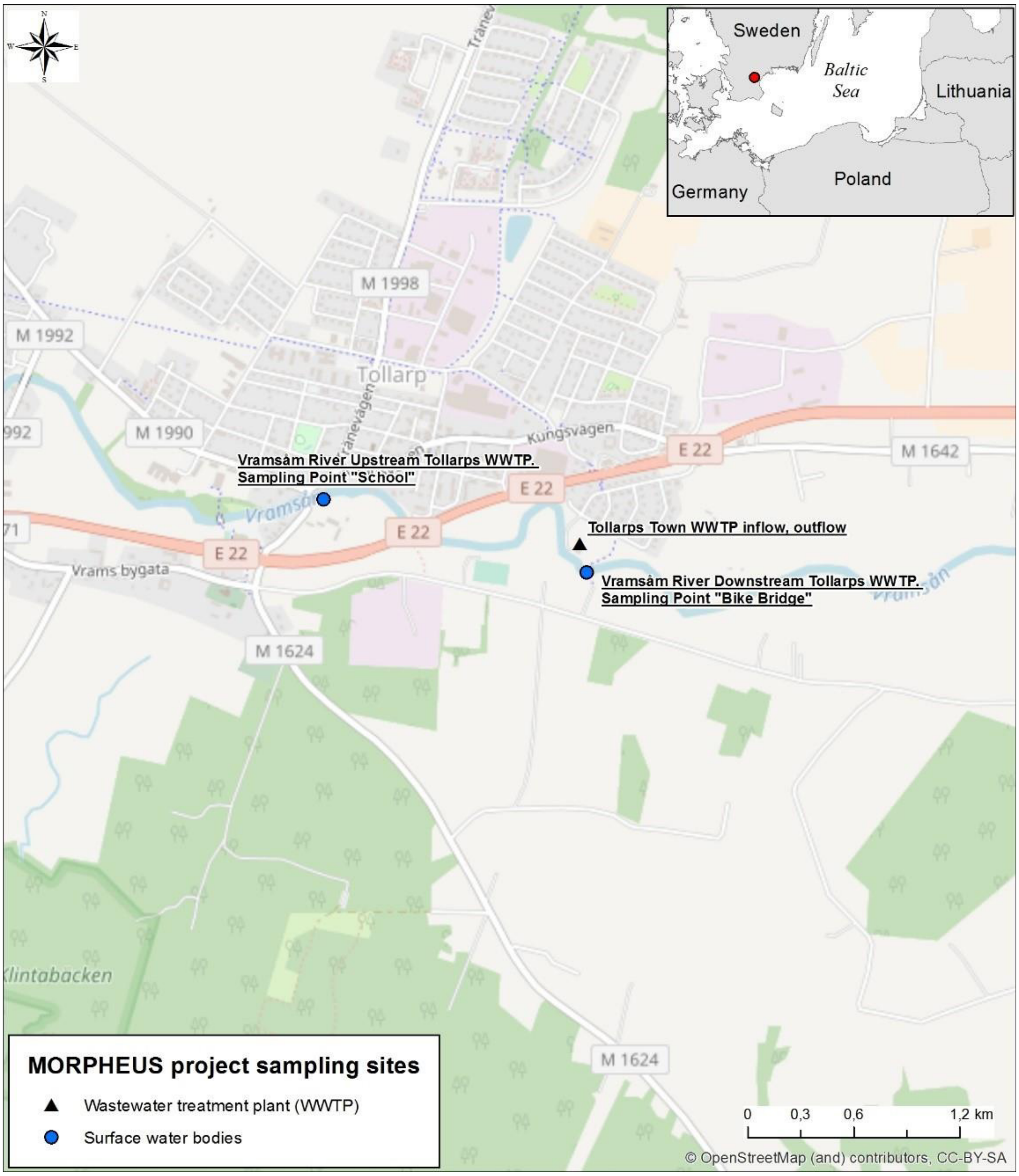


Figure 4.2 General overview of the 3 sampling areas in Region Skåne Sweden in the summer sampling campaign in August 2017. These places were also sampled in February 2018 except for the background point in Forsakarsbacken (SE10), which was excluded in the winter sampling campaign



Helge Å River Upstream Kristianstads WWTP. Sampling Point "Public Indoor Pool"
Kristianstads Town WWTP inflow, outflow
Kristianstads Town WWTP Inlet
Kristianstads Town WWTP Outlet
Hammarsjön Lake Downstream Kristianstads WWTP. Sampling Point "Pynten"
Hammarsjön Lake Downstream Kristianstads WWTP. Sampling Point "Ekenabben"
Helge Å River Downstream Kristianstads WWTP. Sampling Point "Kavrö Bridge"
Sweden
Baltic Sea
Lithuania
Germany
Poland
MORPHEUS project sampling sites
Wastewater treatment plant (WWTP)
Surface water bodies
0 1 2 4 km
© OpenStreetMap (and) contributors, CC-BY-SA


Sweden
Baltic Sea
Lithuania
Germany
Poland
M 1998
M 1992
Tollarp
992
M 1990
Kungsvägen
E 22
M 1642
Vramsån River Upstream Tollarps WWTP.
Sampling Point "School"
Vramsån
Tollarps Town WWTP inflow, outflow
Vramsån River Downstream Tollarps WWTP.
Sampling Point "Bike Bridge"
Vrams bygata
M 1624
Klintabacken
MORPHEUS project sampling sites
Wastewater treatment plant (WWTP)
Surface water bodies
0
0,3
0,6
1,2 km
© OpenStreetMap (and) contributors, CC-BY-SA

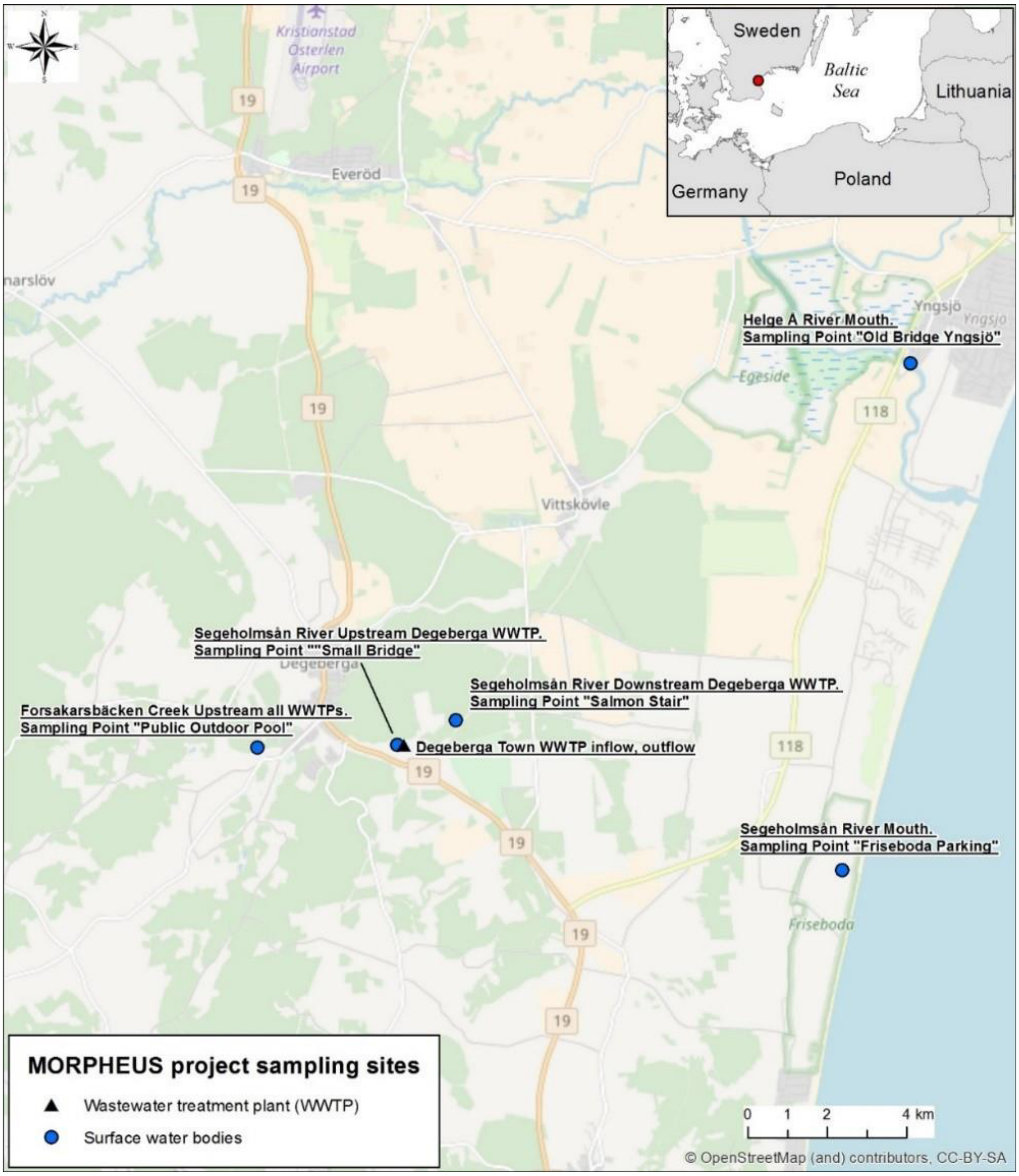


Figure 4.3 A more detailed scheme of sampling locations of the Swedish WWTPs, and in the effluents receiving water bodies

A summary of the types and number of samples in Region Skåne are shown in *Table 4.1*. In total 33 samples were analysed for their content of pharmaceuticals.

Table 4.1 Summary of the types and number of samples in Region Skåne during the summer sampling campaign August 2017 and winter sampling campaign February 2018

Receiving water bodies + WWTP	Season	Upstream	WWTP Inlet	WWTP Outlet	Downstream
Helge Å River + Kristianstad WWTP	Summer	1	1	1	4
	Winter	1	1	1	4
Vramsån River + Tollarp WWTP	Summer	1	1	1	1
	Winter	1	1	1	1
Segesholmsån River + Degeberga WWTP	Summer	1	1	1	2
	Winter	1	1	1	2
Forsakarsbäcken Creek	Summer	1	-	-	-
∑ **Samples of different types**	Summer + Winter	7	6	6	14
∑ **All Samples**			**33 (17 summer, 16 winter)**		

4.4.3. Site-specific information on the WWTPs and receiving water bodies - Sweden

Helge Å river area and Kristianstad WWTP

Helge Å River is a little less than 200 km and has a drainage area of approximately 4,725 km^2 and is one of southern Sweden's largest rivers. In this project samples were taken at the lowest part of Helge å river within the borders of Kristianstad Municipality before the river ends in the Hanöbukten Bay in the Baltic Sea as shown in *Figure 4.4.*

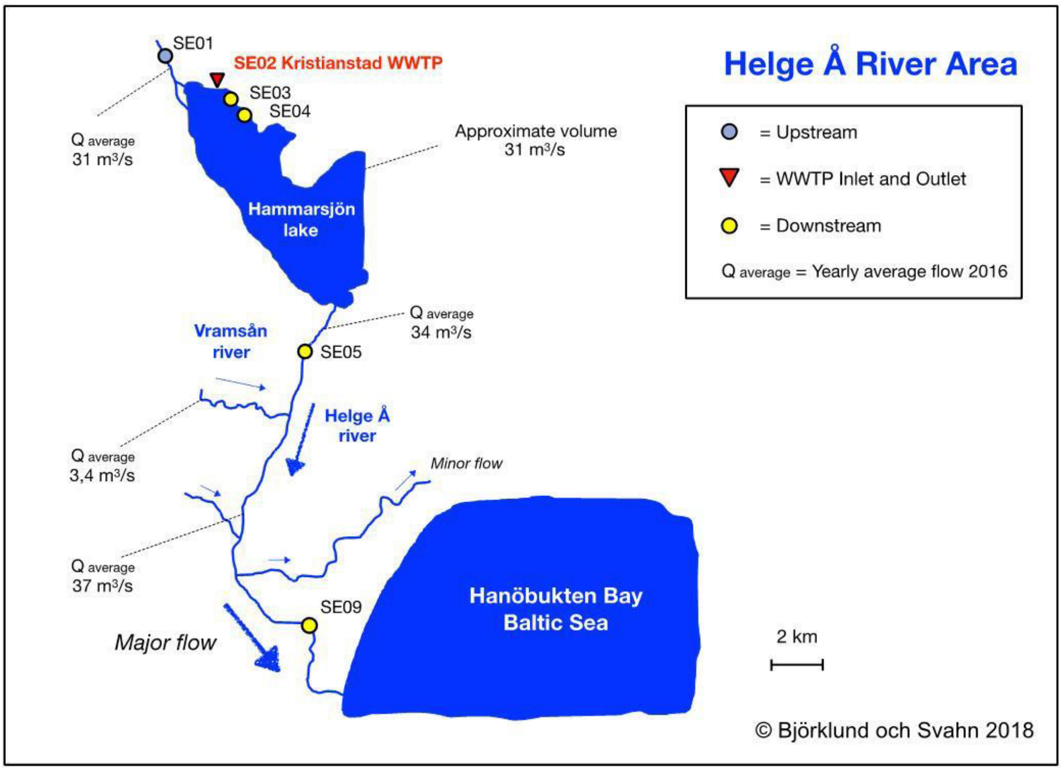


Figure 4.4 Sampling points in Helge Å river area, Region Skåne, Sweden

Overview sampling points Helge Å river and Hammarsjön Lake. Helge Å River feeds into the north-western part of Hammarsjön Lake, and an upstream sample was taken in the river at a place named “Public indoor pool” (SE01). Kristianstad WWTP (SE02) discharges its water in a 1,500 m long excavated canal, which in turn feeds out into Hammarsjön Lake at a point called “Pynten” (SE03). As the WWTP and the channel is below the level of Hammarsjön Lake the water is pumped ca 2 m up into Hammarsjön Lake at “Pynten”. The second downstream point is called “Ekenabben” (SE04) and is situated around 500 m southeast of ‘Pynten” and is a classic recreational area. Two additional downstream sampling points in Helge Å river was taken at “Kavrö Bridge” (SE05) and “Old Bridge Yngsjö” (SE09) which both were surface water samples. Photos of the six different sampling points SE01, SE02, SE03, SE04, SE05 and SE09 are shown in Figure 4.5. The photos represent the winter sampling campaign in February 2018.

Figure 4.5 Photos of the six different sampling points SE01, SE02, SE03, SE04, SE05 and SE09 represent the winter sampling campaign in February 2018

General about Helge å River, Hammarsjon Lake and "Vattenriket". Hammarsjön Lake has an estimated volume of 782,000 m3. The lower part of Helge Å River including Hammarsjön Lake is a unique wetland and was given the status of a UNESCO Biosphere Reserve in 2005, with the name "Vattenriket" . The area holds a great variety of species of which many are red listed. According to "Vattenriket" homepage the entire river and lake system shown in Figure 4.4 is only a few decimetres above sea level, and with the seasons the water level varies up to 2 meters . Furthermore, it can be read that during winter, the water surface usually is one meter above sea level, while in summer, the water level is sometimes so close to the sea surface that the river flows backwards. According to "Vattenriket" homepage just upstream sampling point SE01 in Figure 4.4, the lowest water flow is ca. 5 m3/s, which often occurs in the summer, while the highest water flow is ca. 136 m3/s, occurring in the winter period. Further downstream, the watercourse is obviously larger, but more difficult to measure as the ocean descends and sometimes even penetrates to Hammarsjön Lake. These conditions cause large parts of the lands around Helge Å River to be regularly flooded within the municipality of Kristianstad. The average flow rates for 2016 which are presented in Figure 4.4 are collected from a recent report called "Helge Å 2016" , which includes the average flow rate of 37 m3/s. In this report the authors also stated that 2016 had a substantially lower average flow rate than the average water supply in 2014 and 2015, which were 54 and 43 m3/s, respectively. It was also lower than the average for the period 1982-2015 which was 48 m3/s. More specific information on flow rates is available via the system "W1SS — Water Information System Sweden" as described below.

Flow of water in Hammarsjon Lake and Helge A River according to “I/I/7SS - Water Information System Sweden”. The “WISS – Water Information System Sweden” (in Swedish “VISS – VattenInformationsSystem Sverige”) is a database that has been developed by the Competent Authorities of the Swedish Water Districts, the County Administrative Boards and the Swedish Agency for Marine and Water Management. WISS is today managed by the County Administrative Board of Kalmar. In WISS there are classifications and maps of all Swedish major lakes, rivers, groundwater and coastal waters. In the below text all flow information is collected from WISS. It could be noted that within the Helge Å River area (Figure 4.4) there is a large number of data available in WISS and therefore only a few strategically selected points were selected as outlined below.

In WISS it is stated that Hammarsjön Lake is only 0.7 m above sea level and that Sweden's lowest point is situated in the dried parts of the lake. Hammarsjön Lake has an area of 16.8 km2 and is a very shallow plain lake with a maximum depth of 2.5 m and an average depth of 0.7 m with fast turnover of its water. There have been estimates of 0.0194 years which would correspond to roughly 7 days. The large variations in water levels, an average of 1.4 m, give unusual and significant dynamics to the landscape, with large annual floods. The water consists of a varied mixture of humus rich, brown, sour water from the north, nutritious, well-buffered water from the agricultural areas around Hässleholm and Kristianstad, as well as in Hammarsjön occasionally entering brackish water from the Baltic Sea. Hammarsjön Lake has a rich bird life and is designated as a Ramsar Site and is also a Natura 2000 Site. From the detailed flow profiles it can be seen that the samplings represent very differing flow conditions. The water flow during the winter was 4.3, 4.8 and 4.7 times higher during the winter sampling than during the summer sampling close to SE01, SE05 and SE09, respectively.

Vramsån River area and Tollarp WWTP

Vramsån River has a length of ca 55 km and a drainage area of approximately 374 km2 and is part of the Helge Å River drainage area since it ends in the Helge Å River as shown Figure 4.6 and also in Figure 4.4 above.

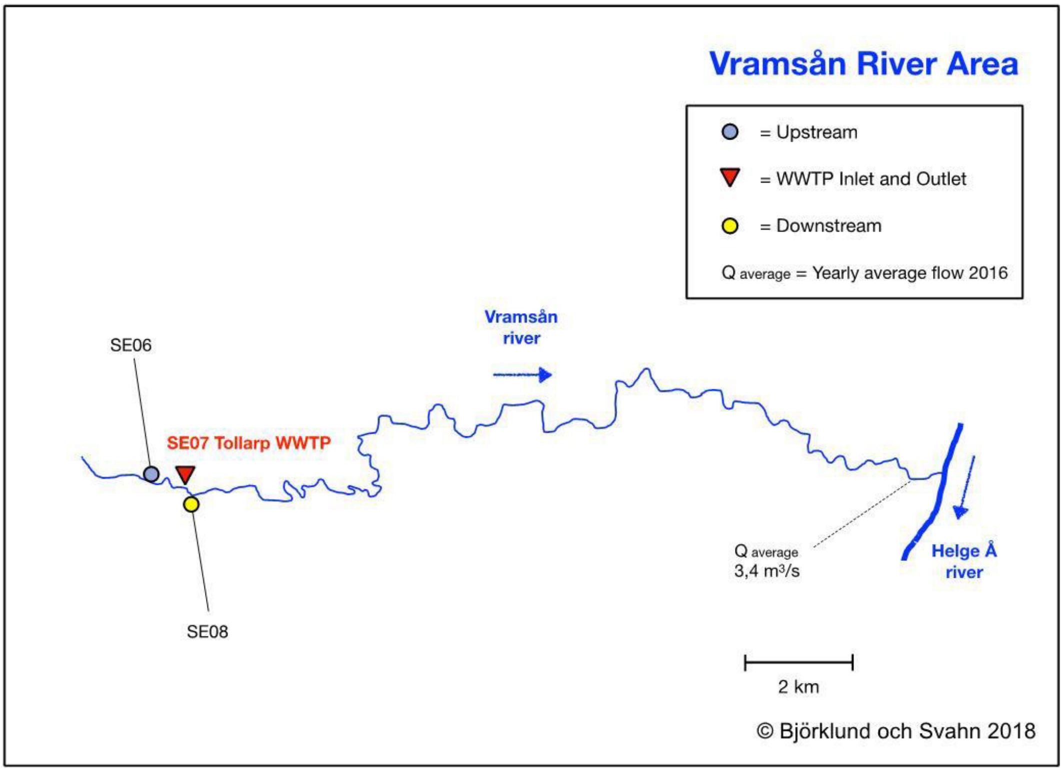


Figure 4.6 Sampling points in Vramsån River area, Region Skåne, Sweden

The flow in Vramsån varies over the year, but the average annual flow in previous studies is approximately 4 m3/s, just before it becomes a part of the Helge Å River.

Overview sampling points Vramsån River. Vramsån is flowing from west to east passing a few small villages. One of the larger villages is Tollarp and a surface sample was taken upstream Tollarp WWTP at a point called “School” (**SE06**). Tollarp WWTP (**SE07**) discharges its water directly into Vramsån River, and a surface sample was taken directly downstream the WWTP at a point called “Bike Bridge” (**SE08**). Photos of the 3 different sampling points **SE06**, **SE07** and **SE08** are shown in **Figure 4.7**. The photos represent both the summer sampling campaign in August 2017 and the winter sampling campaign in February 2018.

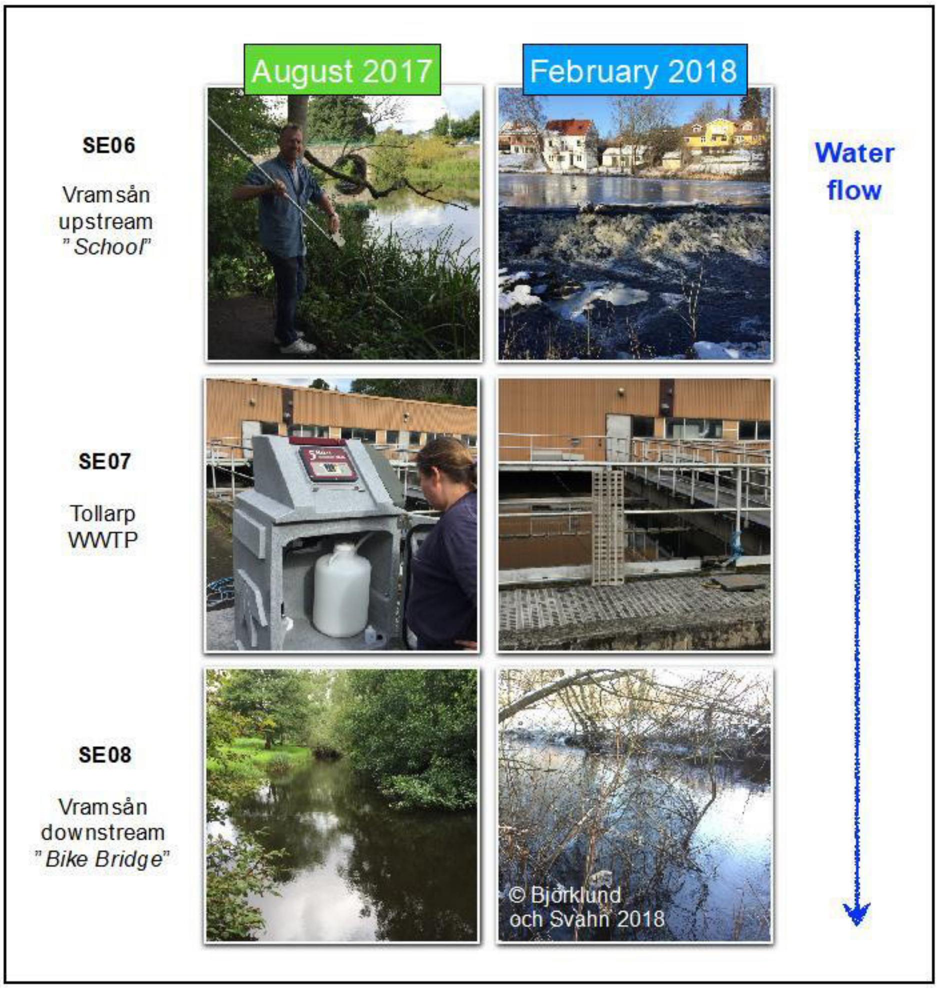


Figure 4.7 Photos of the 3 different sampling points SE06, SE07 and SE08 represent both the summer sampling campaign in August 2017 and the winter sampling campaign in February 2018

General about Vramsån River in "Vattenriket". Vramsån River is part of the UNESCO Biosphere Reserve "*Vattenriket*" just as Helge Å River. Vramsån River is also a Natura 2000 Site. The watercourse has a very winding flow and in a number of places, the river regularly floods the surrounding fields, and the river holds a large number of rare species and is one of Europe's finest place for a number of mussels. The average flow rate of 3.4 m^3/s for 2016 which is presented in Figure 4.6 is collected from the recent report "*Helge Å 2016*" (see above). More specific information on flow rates was gathered via the system "*WISS – Water Information System Sweden*".

Flow of water in Vramsån River according to "*WISS – Water Information System Sweden"*

The samplings represent very differing flow conditions of Vramsån River, where the water flow during the winter was 4.2 and 4.1 times higher during the winter than during the summer at sampling close to **SE06** and **SE08** and to the outflow in Helge Å River, respectively.

Segesholmsån River area and Degeberga WWTP

Segesholmsån River has a length of 23 km and a drainage area of approximately 64 km2 and is a river that ends directly in the Hanöbukten Bay, Baltic Sea as shown in Figure 4.8.

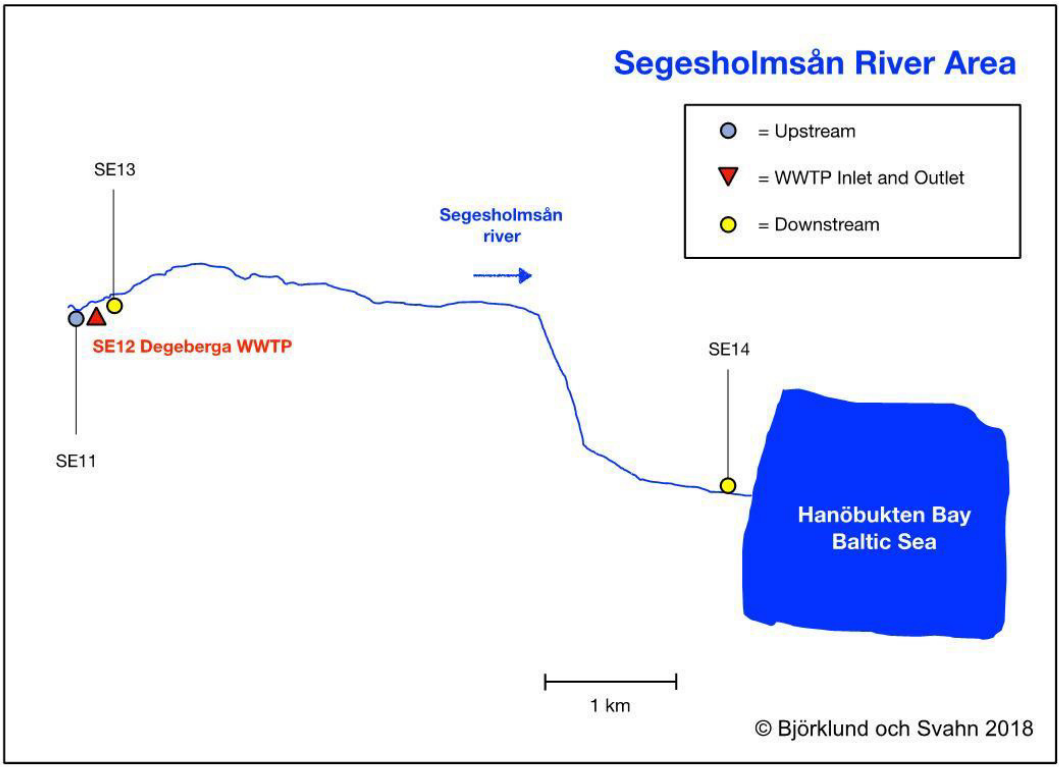


Figure 4.8 Sampling points in Segesholmsån River area, Region Skåne, Sweden

The flow in Segesholmsån is smaller than that of Vramsån and is around 0.6 m^3/s, just before it enters Hanöbukten Bay in the Baltic Sea.

Overview sampling points Segesholmsån River. Segesholmsån is running from west to east passing a few small villages, where Degeberga is one of them. A surface sample was taken upstream Degeberga WWTP at a point called “Small Bridge” (**SE11**). Degeberga WWTP (**SE12**) discharges its water directly into Segesholmsån River, and a surface sample was taken downstream the WWTP at a point called “Salmon Stair” (**SE13**). A third surface samples was taken further downstream Segesholmsån River inside a nature reserve called Friseboda. The sampling is called “Friseboda Parking” (**SE14**). Photos of the four different sampling points **SE11**, **SE12**, **SE13** and **SE 14** are shown in Figure 4.9. The photos represent both the summer sampling campaign in August 2017 and the winter sampling campaign in February 2018.

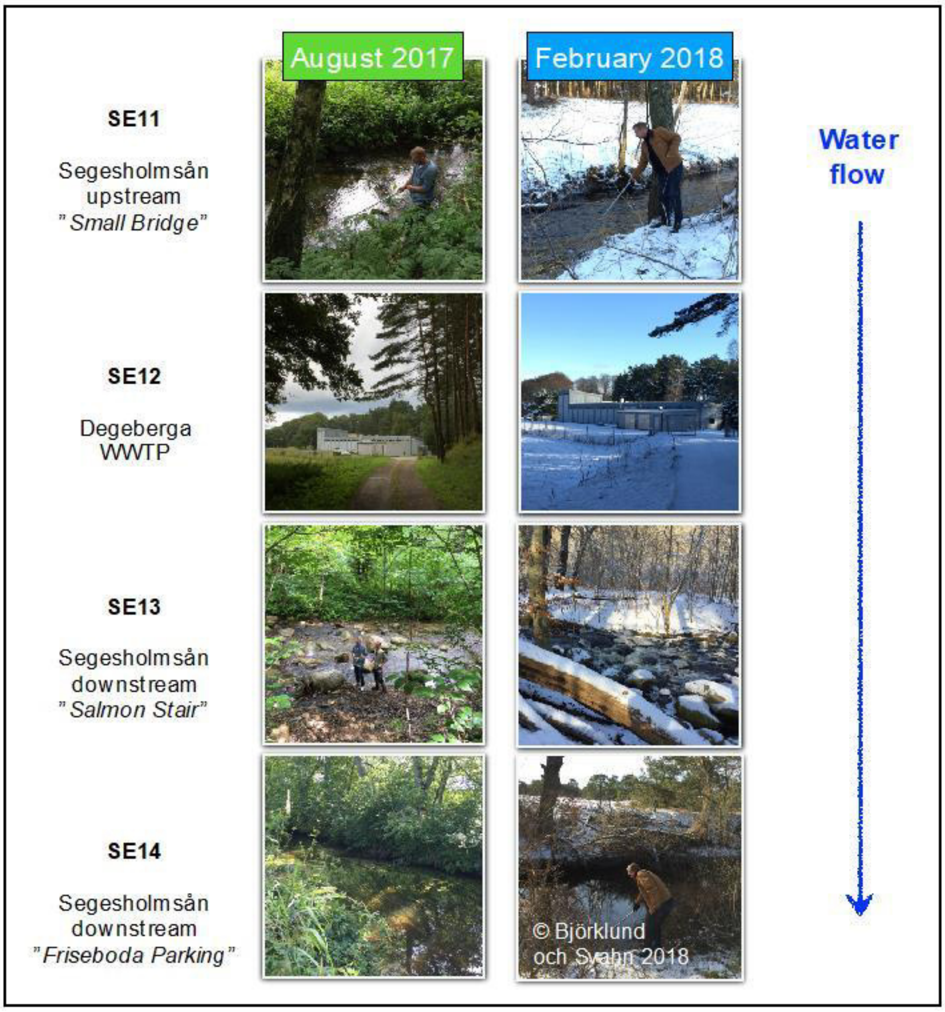


Figure 4.9 Photos of the four different sampling points SE11, SE12, SE13 and SE 14 represent both the summer sampling campaign in August 2017 and the winter sampling campaign in February 2018

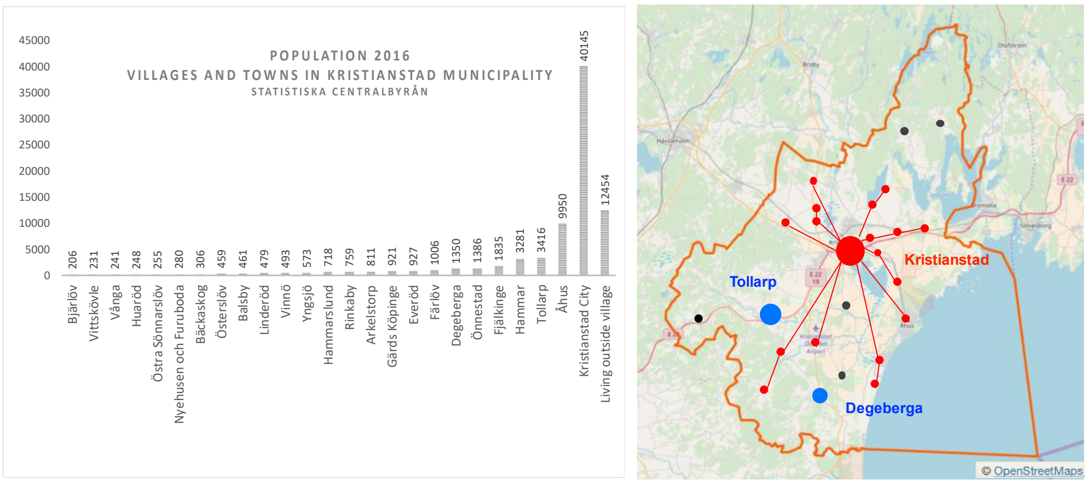
General about Segesholmsån River. Segesholmsån is one of the best-preserved rivers in Region Skåne. It has a relatively undisturbed stream with clean, cold and oxygen-rich water, which contains many sensitive species. The river houses both trout and rare species of caddisflies. More specific information on flow rates was gathered via the system "WISS – Water Information System Sweden". Flow of water in Segesholmsan River according to "WISS- Water Information System Sweden"

Flow of water in Segesholmsån River according to "WISS – Water Information System Sweden"

The sampling occasions clearly represent very differing flow conditions of Segesholmsån River. The water flow during the winter was 3.6 and 4.4 times higher during the winter than during the summer at sampling close to SE11 and SE13 and the outflow in the Baltic Sea SE14, respectively.

4.4.4. Short information on the WWTPs - Sweden

The 3 WWTPs Kristianstad, Tollarp and Degeberga represent different types of plants. One of the main differences is size. As seen from Figure 4.10 Kristianstad WWTP treats water from more than 40,000 people from Kristianstad City but also wastewater from 17 smaller villages which are connected via pipes to Kristianstads WWTP. Tollarp and Degeberga on the other hand have separate and much smaller WWTPs. Finally, marked in dark grey in Figure 4.10, Kristianstad municipality have five very minor and separate WWTPs which are not included in MORPHEUS. Together, Kristianstad, Tollarp and Degeberga WWTP represent a vast majority of all inhabitants that are connected to WWTPs within the borders of Kristianstad Municipality.



Red = small villages connected to Kristianstad WWTP analysed in MORPHEUS
Blue = the villages Tollarp and Degeberga WWTP analysed in MORPHEUS
Grey are WWTPs not connected to Kristianstad WWTP, not analysed in MORPHEUS

© Björklund och Svahn 2018

Figure 4.10 To the left is seen an overview of the number of people in villages with at least 200 inhabitants within Kristianstads municipality 2016 according to official Swedish statistics. To the right is seen the connection of 17 villages via pipes to Kristianstads WWTP (red), Tollarp and Degeberga WWTPs (blue) and minor separate WWTP not connected to Kristianstad WWTP (grey)

WWTPs size, flow and treatment steps. Basic Information about the WWTPs dimensions, volumes of treated water, COD-Cr, BOD_7, N and P vary and is presented in Table 4.2a, while the treatment steps used in each WWTP are shown in a summarized form in Table 4.2b.

In general, the treatment steps in the 3 WWTPs show large similarities, and they all have mechanical, biological and chemical treatment. All 3 WWTPs use $FeCl_3$ in the chemical treatment step. A key difference though is that Kristianstad and Degeberga has a sand filter step while Tollarp does not.

Table 4.2a Basic information about the 3 WWTPs operating parameters in 2016 according to official reports made available by Kristianstads Municipality

Treatment plant	Maximum dimension PE	[1)] Actual number PE	Connected number of residents	[2)] Industry PE	Annual volume m^3	[3)] Daily flow average m^3/day	COD-Cr In kg/year	COD-Cr Out kg/year	BOD_7 In kg/year	BOD_7 Out kg/year	N-tot In kg/year	N-tot Out kg/year	P-tot In kg/year	P-tot Out kg/year	Recipient
Kristianstad, SE02	205,000	118,000	52,000	64,000	8,186,000	22,427	7,218,000	232,000	3,022,000	16,000	399,000	49,100	68,300	565	Hammarsjön Lake Helge Å River
Tollarp, SE07	9,000	4,790	3,000	3,900	361,000	989	267,000	7,400	126,000	1,160	10,300	2,000	1,400	37	Vramsån River
Degeberga, SE12	2,000	950	950	0	79,000	216	63,144	1,186	25,396	119	4,921	1,039	654	13	Segesholmsån River

1) Calculated number based on total incoming BOD7 to the WWTP
2) Calculated number based on total incoming BOD7 from the industries
3) Calculated as annual volume divided by 365 days

Table 4.2b Treatment steps as described in official reports made available by Kristianstads Municipality

Treatment plant	Coarse debris screen	Chamber for sand and grit removal	Primary sedimentation	Biological step	Intermediate sedimentation	Chemical step	Final sedimentation	Polishing step
Kristianstad SE02	Yes	Yes Aerated.	Yes Sludge removed for treatment.	Yes Activated sludge 2 parallel types: N-type, classical E-type, Krauss process	Yes Part of the sludge pumped back to the biological step. Excess sludge removed for treatment.	Yes Flocculation and precipitation by adding $FeCl_3$.	Yes Sedimentation and removal of chemically produced sludge for treatment.	Yes Sand filter.
Tollarp SE07	Yes	Yes	Yes	Yes Activated sludge Contact basin followed by activation basin. Both basins aerated	Yes Part of the sludge pumped back to the biological step. Excess sludge removed for treatment.	Yes Flocculation and precipitation by adding $FeCl_3$.	Yes Sedimentation and removal of chemically produced sludge. The chemically produced sludge is pumped back to the biological step.	No
Degeberga SE12	Yes	Yes Aerated.	–	Yes Activated sludge classical type.	Yes Part of the sludge pumped back to the biological step. Excess sludge removed for treatment	Yes Flocculation and precipitation by adding $FeCl_3$.	Yes Sedimentation and removal of chemically produced sludge. Part of the sludge pumped back to the biological step. Excess sludge removed for	Yes Sand filter.

4.4.5. Sampling procedure - Sweden

All sampling at WWTPs was done in cooperation with the staff at the 3 WWTPs run by Kristianstads Municipality (Associated Partner 9). At Kristianstad WWTP Mr. Sven-Johan Johansson provided assistance, while at Tollarp and Degeberga WWTP Mrs. Susanna Raftmark aided in sampling. All WWTP samples were taken either as grab samples or 24-h samples in 100 mL HDPE bottles depending on what the personnel at the WWTP could accomplish at the time of collection. All surface water samples in rivers and lakes were taken as grab samples in 500 mL HDPE bottles by the lead partners O. Svahn and E. Björklund. Sampling depth was 0.2 m for all surface water samples. All samples were kept frozen at -18°C until analysis. For determination of pharmaceuticals, 50 mL and 500 mL of the collected sample volume was extracted with SPE (solid-phase extraction) for wastewaters and surface waters, respectively.

4.4.6. Results of pharmaceutical analysis – Sweden

Inlet concentrations (Table 4.3):

The inlet concentrations of ibuprofen and paracetamol by far exceeds any of the other pharmaceuticals. Ibuprofen ranged from 13,458-307,278 ng/L (a factor 23), while paracetamol varied from 17,364-46,936 ng/L (a factor 2.7). Especially Degeberga showed very high incoming concentrations as compared to the other WWTPs. Looking at the data in Table 4.3 the summer concentrations of ibuprofen were higher than the winter concentrations. For paracetamol no such trend exists. However, the inlet concentrations were in nearly all cases higher for ibuprofen than for paracetamol at all WWTPs and at both seasons. The one exception was the winter sample in Tollarp where the concentrations of ibuprofen and paracetamol were 13,458 and 17,364 ng/L, respectively. Taking the average summer concentrations of the 3 WWTPs for ibuprofen gave a value of 141,640 ng/L, while the average winter concentration was 64,579 ng/L. Corresponding average summer and winter concentrations for paracetamol were 34,874 ng/L and 27,928 ng/L, respectively.

Another observation was that Degeberga WWTP in general had higher concentrations of ibuprofen and paracetamol than Kristianstad and Tollarp WWTP. The reason for this is not known but might be a consequence of less dilution in Degeberga as Degeberga WWTP has no incoming industrial wastewater. In fact, somewhat higher concentrations were observed for 11 out of 15 investigated compounds at Degeberga WWTP during the summer season and for 11 out of the 15 compounds during the winter season as compared to Kristianstad and Tollarp WWTP.

After ibuprofen and paracetamol, the following top 5 pharmaceuticals at Kristianstads WWTP during the summer were naproxen, atenolol, carbamazepine, metoprolol and diclofenac. The winter inlet concentrations at Kristianstad WWTP followed basically the same pattern, though carbamazepine fell in concentration by a factor of 4, while ciprofloxacin was present at much higher concentrations during the winter than during the summer, increasing by a factor of 17. The decrease in concentration for carbamazepine and increase in concentrations for ciprofloxacin during the winter was also observed at Tollarp WWTP, where the former fell by a factor of 5, and the latter rose by a factor of 2. At Degeberga WWTP the decrease in concentration for carbamazepine during winter was very small, while the increase for ciprofloxacin during winter was very large being a factor 10 higher.

The pattern at Tollarp WWTP is not fully the same as that observed in Kristianstad. Here the top 5 candidates in the summer sample were atenolol, metoprolol, clarithromycin, oxazepam and naproxen. However, both carbamazepine and diclofenac were still present in Tollarp and ranked as 6 and 7 in Tollarp WWTP inlet water, respectively.

Turning to Degeberga WWTP, the 5 top summer pharmaceuticals were the same as those in Kristianstad, but with a somewhat differing order; carbamazepine, atenolol, metoprolol, diclofenac and naproxen.

Naproxen had a concentration range from 586-5,301 ng/L (a factor 9.0). Inlet concentrations in Kristianstads were very similar during summer and winter, while larger differences were seen at Tollarp and Degeberga, with the highest concentrations occurring during winter time. Taking the average value of all 3 WWTPs during summer gave a concentration of 1,502 ng/L, while the average winter concentration was 2,832 ng/L.

Atenolol ranged from 713-3,701 ng/L (a factor 5.2) with only a small tendency of higher summer concentrations. The average summer and winter concentration for the 3 WWTPs were 2,050 ng/L and 1,546 ng/L, respectively.

Carbamazepine had concentrations between 69-5,663 ng/L (a factor 82). Especially Degeberga showed very high incoming concentrations as compared to the other WWTPs. Just as for atenolol there was a small tendency of higher summer concentrations. The average summer and winter concentration for the 3 WWTPs were 2,356 ng/L and 1,636 ng/L, respectively.

Metoprolol ranged between 757-3,469 ng/L (a factor 4.6). Summer and winter concentrations were very close, but somewhat higher during the summer as was the case for atenolol and carbamazepine. The average summer and winter concentration for the 3 WWTPs were 1,834 ng/L and 1,668 ng/L, respectively.

Diclofenac ranged in concentrations from 382-2,515 ng/L (a factor 6.6). Kristianstad and Tollarp WWTP had very similar seasonal concentrations while Degeberga had a summer concentration that was 2.5 times higher than the winter concentration. The average summer and winter concentration for the 3 WWTPs were 1,203 ng/L and 672 ng/L, respectively.

Oxazepam had concentrations ranging from 407-1,236 ng/L (a factor 3.0). Kristianstad and Degeberga WWTP had very similar seasonal concentrations while Tollarp had summer concentration 1.9 times higher than the winter concentration. The average summer and winter concentration for the 3 WWTPs were 797 ng/L and 608 ng/L, respectively.

Except for some of the antibiotics (discussed separately below), the two compounds estrone and propranolol were always occurring at the lowest concentrations of all the investigated pharmaceuticals.

Estrone ranged from 29-109 ng/L (a factor 3.8), with no clear tendency of seasonal variation. The average summer and winter concentration for the 3 WWTPs were 57 ng/L and 62 ng/L, respectively.

Propranolol ranged from 28-98 ng/L (a factor 3.5), with a minor tendency of higher winter concentrations. The average summer and winter concentration for the 3 WWTPs was 44 ng/L and 60 ng/L, respectively.

Ciprofloxacin belongs to the group of quinolones and is a broad-spectrum antibiotic and ranged in concentration from 58-8,816 ng/L (a factor 152). In case the very high value of 8,816 ng/L at Degeberga winter sampling was excluded, the concentration range is very similar, as seen from the second highest value which is 971 ng/L giving a new factor of 16.7. The inlet concentrations vary to a large extent between the WWTPs, but a general trend was that winter concentrations were higher than summer concentrations by a factor 3.6, 10.5 and 9.6 for Kristianstad, Tollarp and Degeberga WWTP, respectively. The average summer and winter concentration for the 3 WWTPs were 417 ng/L and 3,466 ng/L, respectively.

Sulfamethoxazole is administered as a combination preparation together with trimethoprim and belongs to the group of sulphonamides antibiotics which inhibits the synthesis of folic acid in bacteria. For sulfamethoxazole there was also a large variation in incoming concentrations ranging from below MQL to 476 ng/L. There was a trend that the larger the WWTP the larger the inlet concentration. However, the variation between seasons seemed limited. The average summer and winter concentration for the 3 WWTPs were 168 ng/L and 122 ng/L, respectively.

Azithromycin, clarithromycin and erythromycin are all antibiotics of the type macrolides with a chemical structure that is very similar to each other. The macrolides are used to treat various types of bacterial infections. For the macrolides, Kristianstad WWTP shows the most constant incoming concentrations with only small differences between summer and winter samples. Both Tollarp and Degeberga WWTP show large differences between both the macrolides as well as between seasons. However, the difference in inlet concentrations between these two WWTPs is also large, with no clear pattern. Looking at each macrolide individually gives the following trends. Azithromycin ranged in concentration from below MQL to 229 ng/L with average summer and winter concentrations of 58 ng/L and 128 ng/L, respectively. Clarithromycin ranged in concentration from below MQL to 978 ng/L. The average summer and winter concentrations in this study were 412 ng/L and 115 ng/L, respectively. Erythromycin ranged in concentration from below MQL to 385 ng/L. The average summer and winter concentrations in this study were 151 ng/L and 119 ng/L, respectively.

Outlet concentrations (Table 4.3):

Ibuprofen was present at outlet concentrations ranging from below MQL to 2,272 ng/L meaning a very large variation. Looking at the data in Table 4.3 there is no clear trend that either of the seasonal concentrations of ibuprofen are higher than the other, even though the average summer and winter concentration for the 3 WWTPs were 385 ng/L and 857 ng/L, respectively. This is caused by a high winter concentration at Tollarp WWTP.

Diclofenac had a concentration range from 401-1,442 ng/L (a factor 3.6). Outlet concentrations in Kristianstads were very similar during summer and winter, while some differences were seen at Tollarp and Degeberga. Overall there was no obvious difference between seasons and taking the average value of all 3 WWTPs during summer and winter gave a concentration of 763 ng/L and 808 ng/L, respectively.

Carbamazepine showed a very large range from 85-5,052 ng/L (a factor 59) with only a tendency of higher summer concentrations. Especially Degeberga WWTP showed very high outlet concentrations and excluding these gave a concentration interval of between 85-418 ng/L (a factor 4.9). The reason for the very high concentrations observed in Degeberga is not known. Overall the average summer and winter concentration for the 3 WWTPs were 2,006 ng/L and 1,355 ng/L, respectively.

Metoprolol had concentrations ranging from 128-977 ng/L (a factor 7.6). In general, there was no clear difference between seasons. The average concentration for all 3 WWTPs during summer and winter gave concentrations of 605 ng/L and 597 ng/L, respectively.

Oxazepam had a concentration range from 445-895 ng/L (a factor 2.0). Outlet concentrations at Kristianstad and Tollarp were very similar during summer and winter, while some differences were seen at Degeberga. Overall the release of oxazepam from all WWTPs and all seasons were relatively constants. The average concentration of all 3 WWTPs during summer and winter were 708 ng/L and 605 ng/L, respectively.

Naproxen showed outlet concentrations as low as 13 ng/L up to 1,587 ng/L (a factor 122) revealing a very large variation. For Kristianstad and Tollarp WWTP there was a clear trend that winter concentrations were higher while Degeberga showed very low concentrations in general (21 ng/L during summer and 13 ng/L during winter). Average summer and winter concentration for the 3 WWTPs were 196 ng/L and 747 ng/L, respectively.

Atenolol showed outlet concentrations from below MQL up to 466 ng/L, and consequently varied to a large extent. Just as was the case for naproxen above both Kristianstad and Tollarp WWTP showed a clear trend that winter concentrations were higher while Degeberga showed very low concentrations (below MQL during summer and 2.1 ng/L during winter). The average summer and winter concentration for the 3 WWTPs were 115 ng/L and 255 ng/L, respectively.

Propranolol varied in concentration from 11-46 ng/L (a factor 4.2). For this compound there was a clear trend that summer concentrations were lower than winter concentrations. The summer concentrations varied between 11-22 ng/L (factor 2.0) with and average concentration for the 3 WWTPs of 16 ng/L. Winter concentrations varied between 36-46 ng/L (a factor 1.3) with an average concentration of 42 ng/L.

Estrone was present at very low concentrations in all outlet waters and varied between below MQL and 5.6 ng/L. No clear trend on differences between seasons could be seen, and average summer concentration for the 3 WWTPs was 2.5 ng/L while the average winter concentrations was 2.2 ng/L.

Paracetamol was present at outlet concentrations ranging from below MQL to 245 ng/L, showing a large variation. For this compound, just as for propranolol above there was a clear trend that summer concentrations were lower than winter concentrations. The summer concentrations were all below MQL, while the winter concentrations varied between 3.0-245 ng/L (a factor 82) with an average concentration of 89 ng/L.

Ciprofloxacin ranged in concentration from 7-66 ng/L (factor 9.4) and it varied less than the inlet concentrations. There was no clear trend that concentrations differed with season. The average summer concentration for the 3 WWTPs was 26 ng/L, while the winter concentration was 47 ng/L.

Sulfamethoxazole had a variation in outgoing concentrations from below MQL ng/L to 118 ng/L. There was a trend that the larger the WWTP the larger the outlet concentration. A seasonal variation was not obvious though, and the average concentration for the 3 WWTPs was 60 ng/L during summer and 38 ng/L during winter.

Azithromycin range in concentration from below MQL to 72 ng/L. There was a tendency towards higher outlet winter concentrations. The average summer and winter concentrations for the 3 WWTPs were 10 ng/L and 28 ng/L, respectively. Clarithromycin range in concentration from below MQL to 382 ng/L. There was no clear trend of seasonal differences. The average summer and winter concentrations were 137 ng/L and 68 ng/L, respectively. Erythromycin ranged in concentration from below MQL to 419 ng/L. No seasonal trend was obvious and the average summer and winter concentrations were 107 ng/L and 233 ng/L, respectively.

Table 4.3 Seasonal inlet, outlet concentrations in WWTPs. Pharmaceuticals that were not detected are indicated as "-". In some cases, concentrations just below MQL were found with a clear peak identified and, in such cases, an indicative value in "grey italic" is shown

	Inlet concentrations in ng/L						**Outlet concentrations in ng/L**					
Compound	**Summer**			**Winter**			**Summer**			**Winter**		
	Kristianstad SE02 24 h	**Tollarp** SE07 grab	**Degeberga** SE12 grab	**Kristianstad** SE02 24 h	**Tollarp** SE07 24 h	**Degeberga** SE12 grab	**Kristianstad** SE02 24 h	**Tollarp** SE07 grab	**Degeberga** SE12 grab	**Kristianstad** SE02 24 h	**Tollarp** SE07 24 h	**Degeberga** SE12 grab
Atenolol	1,348	1,100	3,701	972	713	2,955	214	131	-	466	296	2.1
Azithromycin	140	*0.4*	34	229	1.6	155	30	*0.6*	*0.7*	72	1.1	12
Carbamazepine	1,032	372	5,663	250	69	4,589	547	418	5,052	307	85	3,673
Ciprofloxacin	58	275	918	971	612	8,816	46	*26*	*7.0*	31	43	66
Clarithromycin	131	978	128	100	246	*0.4*	22	382	7.2	76	127	*0.8*
Diclofenac	713	382	2,515	559	389	1,070	577	891	821	582	401	1,442
Erythromycin	385	-	67	220	136	3.1	267	-	53	272	419	7.4
Estrone	49	47	75	50	29	109	4.2	3.4	-	0.9	5.6	*0.1*
Ibuprofen	63,107	54,536	307,278	26,611	13,458	153,666	908	248	-	297	2,272	*3.2*
Naproxen	2,027	586	1 893	1,907	1,289	5,301	290	276	21	640	1,587	13
Metoprolol	999	1,034	3 469	792	757	3,456	533	977	304	801	861	128
Propranolol	47	28	55	44	38	98	16	22	11	43	46	36
Oxazepam	374	781	1,236	343	407	1,075	403	895	825	445	503	866
Paracetamol	22,528	44,075	38,018	19,485	17,364	46,936	-	-	-	18	245	3.0
Sulfamethoxazole	476	29	-	324	40	2.3	118	62	-	101	8.4	6.2

Results of chemical analysis – Swedish water bodies (Table 4.4):

The pharmaceutical concentrations found in the rivers and lakes upstream and downstream the 3 WWTPs are presented in Table 4.4.

Helge Å river (Kristianstad WWTP). The first observation to be made is that the upstream point "Public indoor pool" (SE01) contains very low background levels of pharmaceuticals ranging from <MQL to around 8 ng/L. The top 3 compounds were paracetamol 8.4 ng/L, carbamazepine 7.8 ng/L and naproxen 7.0 ng/L. The reason for this upstream occurrence is most likely that a number of WWTPs exist upstream Kristianstad WWTP. Even though Helge Å river is relatively large with a flow if 24.2 m^3/s and 105 m^3/s during the summer and winter sampling campaign, respectively, dilution and environmental degradation seem not to result in a complete removal of all pharmaceuticals from the river. Looking at the individual groups at the upstream sampling point SE01 shows the following trends:

Antiinfectives for systemic use pharmaceuticals are present at very low levels close to or below MQL. Looking at outlet concentrations (Table 4.3) none of these, except Erythromycin occur at very high concentrations which fits with the identified concentrations in the upstream point.

Cardiovascular system pharmaceuticals show that atenolol was present at 2.5 ng/L during the summer but below MQL in the winter. Metoprolol could be detected at both seasons; 4.5 ng/L (summer) and 2.3 ng/L (winter). Finally, propranolol was below MQL at both seasons. Looking at the inlet and outlet concentration data (Table 4.3) these findings seem logical.

Musculo-skeletal system pharmaceuticals have concentrations below or close to MQL for all compounds.

Nervous system pharmaceuticals are present above MQL in nearly all cases except paracetamol during the summer sampling. Carbamazepine occur at concentrations around 8 ng/L and oxazepam at 1-3 ng/L at sampling point SE01. Both compounds are hard to degrade and also occur at relatively high concentrations in wastewater from all types of WWTPs (Table 4.3), which may explain their occurrence in the upstream point.

As described previously Kristianstad WWTP (SE02) discharges its water in a 1,500 m long excavated canal, which in turn feeds out into Hammarsjön Lake at a point called "Pynten" (SE03). Thus, sampling point SE03 is the first downstream point Kristianstad WWTP. The concentrations at this point are very high. The reason for this is that the water at SE03 to a very large extent consists of treated wastewater. In total 8 compounds had concentrations exceeding 100 ng/L (0.1 µg/L); ibuprofen 696 ng/L (summer), diclofenac 389 ng/L (summer), metoprolol 388 ng/L (winter), carbamazepine 330 ng/L (summer), naproxen 296 ng/L (winter), oxazepam 249 ng/L (summer) and atenolol 245 ng/L (winter) and erythromycin 167 ng/L (summer). The two principal ways the pharmaceutical concentrations may have been reduced at sampling point SE03 are either by a small dilution by a minor water inflow from a small trench ending in the 1,500 m channel, or by various biotic and abiotic degradation processes occurring during the transport of water through the channel.

Turning to the three other downstream sampling points we find "Ekenabben" (SE04) which is situated around 500 m south east of "Pynten" (SE03), sampling point "Kavrö Bridge" (SE05) which is around 10 km downstream "Ekenabben" (SE04) in the Helge Å river (Figure 5) and sampling point "Old Bridge Yngsjö" (SE09) which is roughly 20 km downstream "Ekenabben" (SE04) close to the outlet in the Hanöbukten bay, Baltic Sea. By looking at the concentrations there is a logical trend that the concentrations are decreasing to a large extent between point SE03 to SE04. At

"Ekenabben" (SE04) in Hammarsjön lake the highest observed concentrations were carbamazepine 33 ng/L (summer), metoprolol 26 ng/L (summer), oxazepam 24 ng/L (summer), diclofenac 19 ng/L (summer), paracetamol 8.6 ng/L (winter), atenolol 7.7 ng/L (summer), naproxen 5.2 ng/L (winter), and erythromycin 5.0 ng/L (summer). Thereafter the concentrations are falling further in sampling point SE05 once the pharmaceuticals have reached all the way downstream Hammarsjön Lake and into the major flow of the Helge Å River, though the decrease is not as pronounced as between sampling points SE03 and SE04. A reason for the decrease in concentration between the different points is likely caused by dilution since the turnover time of the waterbody in Hammarsjön Lake is very short (see above detailed description of Hammarsjön Lake) and a large flow in the Helge Å river.

Based on the data obtained an estimate of the actual chemical burden released into the Hammarsjön Lake and the downstream Helge Å river system and into to the Baltic was summarized for three of the more persistent and omnipresent compounds, carbamazepine and oxazepam and diclofenac. These compounds were all also present in all sampling points (SE01, SE02, SE03, SE04, SE05 and SE09) at all times (summer and winter). This gives a rough picture of the yearly mass flow of these compounds in the river system.

Vramsån River (Tollarp WWTP). The upstream point "School" (SE06) contains very low background levels of pharmaceuticals ranging from <MQL to around 6 ng/L. The top 3 compounds were paracetamol 5.6 ng/L, naproxen 3.6 ng/L and diclofenac 1.7 ng/L. None of the other pharmaceuticals were detected at concentrations exceeding 1.0 ng/L. The source of these low background concentrations is not known, since no WWTP exists upstream Tollarp WWTP. One explanation is that they originate from single households and farms releasing their wastewater into the river. It is also interesting to note the similarities between the top 3 candidates in the Vramsån river and the top 3 compounds in Helge Å river (described above), which were paracetamol 8.4 ng/L, carbamazepine 7.8 ng/L and naproxen 7.0 ng/L, showing similarities between the two river systems. Only carbamazepine was substantially lower in the Vramsån river with a concentration just above the MQL of 0.2 ng/L. Diclofenac, which was number 3 in the Vramsån river with a concentration of 1.7 ng/L, also occurred at similar concentrations upstream in the Helge Å river system as shown above.

Tollarp WWTP (SE07) discharges its water directly into Vramsån River, and a surface sample was taken downstream the WWTP at a point called "Bike Bridge" (SE08). Looking at the various classes shows the following downstream situation:

Antiinfectives for systemic use are present at low concentrations. The highest observed concentrations were clarithromycin 5.6 ng/L (summer) and 1.8 ng/L (winter), erythromycin 3.8 ng/L (winter) and sulfamethoxazole 1.2 ng/L (summer).

Cardiovascular system pharmaceuticals shows that metoprolol had the highest concentrations with 18 ng/L (summer) and 11 ng/L (winter). Atenolol had concentrations of 3.2 ng/L (winter) and 2.5 ng/L (summer), while propranolol could not be detected. This relation between the three drugs was also seen downstream Kristianstad WWTP sampling point SE05.

Musculo-skeletal system pharmaceuticals show that ibuprofen has the highest concentration of 30 ng/L (winter), while it could not be identified in the summer sample. Next comes naproxen with a winter value of 16 ng/L but, just as for ibuprofen, it could not be detected in the summer sample. Finally, diclofenac could be identified at both seasons, just as was observed in the Helge Å river system above. The observed concentrations were 18 ng/L (summer) and 6.1 ng/L (winter).

Overall the trend for these three pharmaceuticals were similar between the Vramsån river and the Helge Å river system (point SE05).

Nervous system pharmaceuticals shows that oxazepam has the highest concentration of 16 ng/L (summer) and 6.0 ng/L (winter). This is followed by carbamazepine 8.8 ng/L (summer) and 1.3 ng/L (winter). Finally, paracetamol has a winter value of 7.6 ng/L while the compound could not be detected in the summer sample. Also for this group of compounds there are some similarities with the Helge Å river system (point SE05).

Segesholmsån River (Degeberga WWTP). The upstream point "Small Bridge" (SE11) contains no detectable levels of pharmaceuticals. Only naproxen could be quantified at 12 ng/L in the winter sample.

Degeberga WWTP (SE12) discharges its water directly into Segesholmsån river, and a surface sample was taken downstream the WWTP at two points called "Salmon Stair" (SE11) ca. 500 m downstream and "Friseboda Parking" (SE14) ca 8 km downstream. Looking at the various classes shows the following downstream situation:

Antiinfectives for systemic use pharmaceuticals could not be identified at all in the winter sample, while traces of erythromycin were observed in both summer samples.

Cardiovascular system pharmaceuticals could not be found in any of the winter samples while metoprolol was the only compound identified in the summer samples at 2.6 ng/L (SE13) and 2.9 ng/L (SE14).

Musculo-skeletal system pharmaceuticals show that only diclofenac could be identified in the downstream samples. Sampling point SE13 had 7.8 ng/L (summer) and 5.7 ng/L (winter), while sampling point SE14 had 7.0 ng/L (summer) and 2.0 ng/L (winter).

Nervous system pharmaceuticals shows that paracetamol could not identified in any sample. Both carbamazepine and oxazepam was present in all samples, however. Carbamazepine had had 52 ng/L (summer) and 14 ng/L (winter) in sampling point SE13, while sampling point SE14 had 45 ng/L (summer) and 4.4 ng/L (winter). For oxazepam sampling point SE13 had oxazepam values of 8.6 ng/L (summer) and 3.7 ng/L (winter), while sampling point SE 14 had values of 8.0 ng/L (summer) and 1.4 ng/L (winter).

All three river systems contained atenolol, metoprolol, diclofenac, carbamazepine and oxazepam downstream the WWTPs, in both summer and winter sample. In general, the concentrations of the compounds were higher in the summer samples than in the winter sample. Some of these are consumed on a regular basis such as the heart medicines and the higher concentrations in the summer might be related to less dilution in the rivers, due to much less flow in the summer. Ibuprofen, naproxen and paracetamol were clearly higher in the winter samples than in the summer samples. One explanation could be dramatically higher consumption in the winter period; however this is not verified by consumption data. In order to cause increased concentrations in the river the consumption must be very high in order to also overcome the increased dilution in the river due to increased flow.

Table 4.4 Seasonal variations of concentrations in the receiving waters. Pharmaceuticals that were not detected are indicated as "-". In some cases, concentrations just below MQL were found with a clear peak identified and, in such cases, an indicative value in "grey italic" is shown

Compound	Forsakarsbäcken Creek		Helge Å river										Vramsån river				Segesholmsån river					
	Summer & Winter, ng/l																					
	Background Value		Kristianstad WWTP										Tollarp WWTP				Degeberga WWTP					
			Upstream		Downstream								Upstream		Downstream		Upstream		Downstream			
	SE00		SE01		SE03		SE04		SE05		SE09		SE06		SE08		SE11		SE13		SE14	
Atenolol	*1.1*	NA	2.5	-	155	245	7.7	3.8	2.2	*1.3*	-	*1.4*	-	-	2.5	3.2	-	-	-	-	-	-
Azithromycin	-	NA	-	-	11	50	*0.6*	-	-	-	-		-	-	-	-	-	-	-	-	-	-
Carbamazepine	-	NA	7.8	1.6	330	163	33	2.7	13.3	1.6	6.8	1.6	0.8	0.2	8.8	1.3	-	-	52	15	45	4.4
Ciprofloxacin	-	NA	-	-	31	5.4	-	-	-	-	-		-	-	-	-	-	-	0.6	-	-	-
Clarithromycin	-	NA	-	-	19	47	1.7	*0.6*	-	-	-		-	-	5.6	1.8	-	-	-	-	-	-
Diclofenac	*0.5*	NA	*1.4*	*1.1*	389	277	19	4.5	5.3	1.5	2.3	*1.9*	1.7	*0.7*	18	6.1	-	-	7.8	5.7	7.0	2.0
Erythromycin	-	NA	1.2	0.4	167	143	5.0	0.7	1.5	0.9	0.9	1.0	-	-	-	3.8	-	-	0.6	-	0.7	-
Estrone	-	NA	-	0.3	7.2	1.1	-	0.3	-	0.2	-	0.3	-	0.2	0.7	0.3	-	-	0.3	0.2	0.5	0.3
Ibuprofen	-	NA	-	-	696	135	-	-	-	-	-		-	-	-	30	-	-	-	-		-
Naproxen	-	NA	-	7.0	254	296	*3.4*	*5.2*	-	9.2	-	*7.9*	-	*3.6*	-	16	-	12	-	-	-	-
Metoprolol	-	NA	4.5	2.3	375	388	26	5.8	7.2	2.7	4.9	3.4	*0.8*	*0.6*	18	11	-	-	2.6	-	2.9	-
Propranolol	-	NA	-	-	9.7	16	*0.6*	-	-	-	-		-	-	-	-	-	-	-	-	-	-
Oxazepam	-	NA	3.2	1.0	249	209	24	3.5	7.0	1.3	4.1	1.5	1.0	*0.3*	16	6.0	-	-	8.6	3.7	8.0	1.4
Paracetamol	-	NA	-	8.4	-	12	-	8.6	-	6.8	-	5.5	-	5.6	-	7.6	-	-	-	-	-	-
Sulfamethoxazole	-	NA	*0.7*	*0.4*	61	55	*1.0*	*1.0*	1.6	*0.4*	1.1	*0.4*	-	-	1.2	*0.4*	-	-	-	-	-	-

4.4.7. Calculated chemical load in Swedish WWTPs and removal rates

Chemical load from the WWTPs (Table 4.5).

An estimate of the **inlet chemical load** of pharmaceuticals into each individual WWTP expressed as g/year was calculated based on the incoming concentrations and the knowledge of the total volume of treated wastewater/year. The volumes of wastewater treated in litres (L) were 8,186,000,000 L, 361,000,000 L and 79,000,000 L at Kristianstad, Tollarp and Degeberga WWTP, respectively. The inlet concentrations used for this calculation were the average of the summer inlet concentration and the winter inlet concentration for each WWTP, which was multiplied by the total volume treated. The results are shown in Table 4.5.

The total chemical inlet loads at Kristianstad WWTP varied from 367,217 g/year (367 kg) of ibuprofen to 372 g/year (0.37 kg) of propranolol. Ibuprofen was also the pharmaceutical with the highest inlet chemical load at Tollarp and Degeberga WWTP with values of 12,273 g/year (12 kg) and 18,207 g/year (18 kg). The order of inlet chemical loads from highest to lowest showed some similarities between the 3 WWTPs. The second highest compound at all WWTPs was paracetamol with values of 171,960 g/year (172 kg), 11,090 g/year (11 kg) and 3,356 g/year (3.3 kg) at Kristianstad, Tollarp and Degeberga WWTP, respectively. However, some differences can also be seen between the larger WWTP at Kristianstad and the two smaller WWTPs.

By summing up all of the inlet chemical loads the total incoming amounts of pharmaceuticals in the 3 WWTPs could be estimated to 598,673 g/year (599 kg), 25,229 g/year (25 kg) and 23,435 g/year (23 kg) at Kristianstad, Tollarp and Degeberga WWTP, respectively. The majority of this chemical load is coming from ibuprofen and paracetamol. Excluding these two pharmaceuticals from the calculations gives chemical loads of 59 kg, 1.9 kg and 1.9 kg for Kristianstad, Tollarp and Degeberga WWTP, respectively, meaning that more than 90 % of the load is coming from these two compounds.

An estimate of the **outlet chemical load** of pharmaceuticals released to the recipient from each individual WWTP expressed as g/year was calculated based on the outgoing concentrations and the knowledge of the total volume of treated wastewater/year. The volumes of wastewater treated in litres (L) were 8,186,000,000 L, 361,000,000 L and 79,000,000 L at Kristianstad, Tollarp and Degeberga WWTP, respectively. The outlet concentrations used for this calculation were the average of the summer outlet concentration and the winter outlet concentration for each WWTP, which was multiplied by the total volume treated. The results are seen in Table 4.5.

The total chemical outlet loads at Kristianstad WWTP varied from 5,462 g/year (5.5 kg) of metoprolol to 21 g/year (0.021 kg) of estrone. Metoprolol was followed by ibuprofen, diclofenac, naproxen, carbamazepine, oxazepam, atenolol and erythromycin, which all were release to the channel and Hammarsjön Lake at amounts exceeding 2000 g/year (>2kg/year). Sulfamethoxazole, azithromycin, clarithromycin, ciprofloxacin and propranolol were released to between 200-1000 g/year (0.2-1.0 kg/year), while finally the amounts of paracetamol and estrone were less than 100 g/year (0.1 kg/year). At Tollarp the compounds ranged from ibuprofen 455 g/year to azithromycin 0.2 g/year. The trend in amount released compounds in Tollarp was similar to that shown in Kristianstad. Clarithromycin and paracetamol, though showed a somewhat higher occurrence in Tollarp, while azithromycin showed a very low occurrence relative to Kristianstad. At Degeberga the release pattern was different for many of the compounds, some being relatively higher and some lower than at Kristianstads WWTP.

By adding all the outlet chemical loads, the total chemical burden of pharmaceuticals to the receiving recipient from the 3 WWTPs can be estimated to 33,269 g/year (33 kg), 2,028 g/year (2.0 kg) and 528 g/year (0.5 kg) at Kristianstad, Tollarp and Degeberga WWTP, respectively, Table 4.5. As it was shown above, the majority of the chemical inlet load was coming from ibuprofen and paracetamol, representing 90 % of the amount. From an outlet point of view the scenario is somewhat different. By excluding these two pharmaceuticals from the calculations give chemical outlet loads of 28,262 g, 1,528 g and 527 g for Kristianstad, Tollarp and Degeberga WWTP, respectively. Consequently, ibuprofen and paracetamol now only represent 18%, 33% and 0.05% of the outlet load at the 3 WWTPs, respectively. This demonstrates once again that these two compounds are being removed to a large extent during the treatment processes. A more thorough comparison of the removal efficiencies of the 3 WWTPs is given below.

Table 4.5 Average inlet and outlet chemical loads(g/year) at each of the 3 WWTPs

	Inlet Chemical Load (g/year)			Outlet Chemical Load (g/year)		
Compound	**Kristianstad** SE02	**Tollarp** SE07	**Degeberga** SE12	**Kristianstad** SE02	**Tollarp** SE07	**Degeberga** SE12
Atenolol	9,495	327	263	3,808	336	1.4
Azithromycin	1,511	0.3	7.5	316	13	2.9
Carbamazepine	5,244	80	405	3,471	252	67
Ciprofloxacin	4,210	160	384	2,207	76	2.4
Clarithromycin	944	221	5.1	242	12	1.9
Diclofenac	5,203	139	142	2,785	77	0.1
Erythromycin	2,473	24	2.8	401	92	0.3
Estrone	405	14	7.2	76	44	0.1
Ibuprofen	367,217	12,273	18,207	5,462	332	17
Metoprolol	7,329	323	274	3,496	91	345
Naproxen	16,100	338	284	4,743	233	89
Oxazepam	2,934	214	91	415	0.2	0.5
Paracetamol	171,960	11,090	3,356	4,931	455	0.1
Propranolol	372	12	6.0	21	1.6	0.0
Sulfamethoxazol	3,278	12	0.1	896	13	0.2
Total chemical load in g/year	598,673	25,229	23,435	33,269	2,028	528
Total chemical load in kg/year	599	25	23	33	2.0	0.5

Removal rates (Table 4.6)

The information available on both inlet and outlet concentrations in Table 4.5 above provided the possibility to calculate the removal efficiency of the 3 WWTPs. The removal efficiency expressed as percentage of pharmaceuticals removed in the WWTP was calculated as follows:

• Removal efficiency = ((Inlet conc. — Outlet conc.) / Inlet conc.) * 100 %

Table 4.6 presents the removal efficiency of the various substances at the different WWTPs during both summer and winter season. The results are sorted from highest to lowest based on the removal efficiency at Kristianstad WWTP during the summer period. Pharmaceuticals reduced >80 % are marked in green, between 50-80 % in yellow, and lastly <50 % in orange.

As shown in Table 4.6, the reduction of some compounds such as paracetamol was very high (green, >80%) while several compounds only were removed to a limited extent (orange, <50%). Some substances even show a negative reduction, which has been observed many times in other investigations.

In general, the removal efficiencies obtained in this study shows a similar pattern as compared to the two previous Swedish studies. Both ibuprofen and paracetamol are known from a number of published studies to be removed to a large extent, as are ciprofloxacin and atenolol. Likewise, carbamazepine, oxazepam and diclofenac are (in)famous for their persistence and large tendency to pass WWTPs basically unaltered.

Table 4.6 Percentage reduction of studied pharmaceuticals in 3 Scanian WWTPs. Green indicates >80 % reduction, yellow 50-80 % reduction and orange <50 % reduction. In this table, the WWTPs are listed in order of size while the pharmaceuticals are listed from highest to lowest removal efficiency based on the summer sampling at Kristianstad WWTP. For details of calculations see text

	Kristianstad	**Tollarp**	**Degeberga**	**Kristianstad**	**Tollarp**	**Degeberga**
Compound	**Summer**			**Winter**		
Atenolol	84	88	100	52	58	100
Azithromycin	79		100	69	30	92
Carbamazepine	47	-12	11	-23	-24	20
Ciprofloxacin	20	91	99	97	93	99
Clarithromycin	83	61	94	24	48	
Diclofenac	19	-133	67	-4	-3	-35
Erythromycin	31		21	-24	-209	-136
Estrone	91	93	100	98	81	100
Ibuprofen	99	100	100	99	83	100
Metoprolol	47	6	91	-1	-14	96
Naproxen	86	53	99	66	-23	100
Oxazepam	-8	-15	33	-30	-24	19
Paracetamol	100	100	100	100	99	100
Propranolol	66	23	80	1	-21	63
Sulfamethoxazole	75	-114		69	79	-167

5. Data evaluation and interpretation

5.1. Pollution load comparison in four coastal regions

Basic information about the 15 WWTPs in four coastal regions - volumes of treated water, average inlet and outlet pharmaceutical load and removal efficiency are shown in a summarized form in **Tables 5.1**, **5.2, and 5.3**. The data of the chemical load of pharmaceuticals into each individual WWTP expressed as kg/year were taken from countries reports presented above.

The annual volume treated wastewater in 15 WWTPs varied from 64 662 m^3 in Satow, Germany to 33 929 670 m^3 in Gdansk, Poland. This also partly determined the distribution of the pharmaceutical loads. The total average annual inlet chemical load of 15 pharmaceuticals varied from 11,5 kg in Nida settlement, Lithuania to 18840 kg in Gdansk WWTP, Poland.

Ibuprofen form the highest load in all WWTPs inlets, reaching almost 50 000 kg or 90 percent of total load. The second highest compound was **Paracetamol**, which contributed 2164 kg or 4 % of the total load. **Azithromycin** ranked third contributing 569 kg (1,1%) to all WWTPs. Other chemicals accounted for less than one percent of the total influent load.

The amount of pharmaceutical loads in effluent/treated wastewater is shown in Table 5.2. Both, **Ibuprofen** and **Paracetamol** which occur in large amounts in inlets, were almost completely removed during wastewater treatment process, e.g. **Ibuprofen** and **Paracetamol** were detected only in 5 and 10 WWTPs respectively and in small quantities, both with less than 1% of the total effluent load. The top 4 pharmaceuticals present at the highest loads in WWTP effluents were **Diclofenac**, **Azithromycin**, **Metoprolol** and **Carbamazepine**. The highest average load of 178 kg or 30 % of total load was calculated for the anti-inflammatory drug **Diclofenac**. **Azithromycin** with 126 kg (21%) takes the second place. **Metoprolol** and **Carbamazepine** contribute 100 kg (16,8%) and 92 kg (15,4%) to the total effluent load, respectively. **Clarithromycin** and **Sulfamethoxazole**, each contribute slightly above 24 kg or 4,1% of the total load. The remaining amounts of drugs varies about one percent, which is from 0,7 to 10 kg each.

Table 5.3 below provide calculated removal efficiencies of all 15 WWTPs. The removal efficiency expressed as percentage of pharmaceuticals removed in the WWTP was calculated as follows: removal efficiency = (average inlet load — average outlet load) / average inlet load) * 100 %.

Pharmaceuticals reduced >90 % are **Paracetamol**, **Ibuprofen** and **Estrone** (except Tollarp WWTP), between 70-90 %: **Ciprofloxacin** (except Nida WWTP), **Atenolol**, **Naproxe**n (except Nida and Tollarp WWTPs), **Azithromycin** (with exception of Nida, Jastrzębia-Góra and Tollarp WWTPs). All other compounds were only removed to a limited extent. Some substances – **Oxazepam**, **Erythromycin** even showed a negative reduction, which has been observed many times in other investigations.

Average load elimination efficiency for each WWTP showed best results in Laage and Kretinga WWTPs, reaching about 75 % removal of all pharmaceuticals load entering the sewage treatment plants.

In order to compare different sized WWTPs inlet and outlet loads, several parameters of the wastewater treatment plants were selected (volume treated wastewater, load, number of connected residents, actual number PE). Selected parameters were divided by relative numbers/factors, such as: average inlet/outlet load in kg per one million m³ of wastewater; 1000 connected inhabitants and 1000 PE, see **Table 5.4** and **Figure 5.1**.
A first look at the inlet load in kg per one million m³ of wastewater shows quite large differences, ranging from as low as 50.0 kg at Nida, Lithuania, to as high as 1730 kg at Krakow, Germany. This is a factor of almost 35 different. By instead looking at outlet load in kg per one million m³ of wastewater the values range from 2.83 kg at Nida to 10.25, which is only a factor of 3.6 different. Consequently, the outlet load expressed as kg kg per one million m³ of wastewater differs less than outlet load. By taking the average value of all outlet loads of all 15 WWTPs we get an average outlet value of 5.39 kg pharmaceuticals per one million m³ of wastewater in WWTPs surrounding the South Baltic Sea. By doing this countrywise the following release loads are obtained; 4,00 kg (Lithuania), 6,04 kg (Germany), 6,08 kg (Poland) and 5,46 kg (Sweden). These figures can be compared to a previous Swedish study conducted for 8 WWTPs in Region Skåne in 2017 which showed a release of roughly 4 kg pharmaceuticals per one million m³ of wastewater[3]. Even though the analysed set og pharmaceuticals were not identical, the most essential occurring at high concentrations were similar.

The average inlet loads per 1000 residents varies between 8.41 kg at Tollarp (Sweden) to 110.46 kg at Krakow (Germany), which is a factor 13 different, which is somewhat lower than for inlet load in kg per one million m³ of wastewater. Outlet loads in kg per 1000 residents, shows a variation from 0.28 kg at Laage (Germany) and Swarzewo (Poland) to 0.84 kg at Palanga (Lithuania). This is a factor 3.00 which is lower than the variation when applying load expressed as kg kg per one million m³ of wastewater. The average outlet loads for all 15 WWTPs is 0.46 kg per 1000 resident. Countrywise this can be calculated to be: 0.50 kg (Lithuania), 0,40 kg (Germany), 0.36 kg (Poland) and 0.62 kg (Sweden).

When taking the average inlet load in kg per 1000 PE the values varies between 5.07 kg at Kristianstad (Sweden) to 70.52 kg at Krakow (Germany). This is a factor 14 different which is similar to the value obtained using 1000 residents.

[3] LUSKA – Pharmaceuticals Emissions from Scanian Wastewater treatment plants in 2017 - A development and collaborative project at Kristianstad University, Svahn, O. and Björklund E, Kristianstad University. Report, 60 pages.

The average outlet load in kg per 1000 PE ranges from 0.07 kg at Swarzewo (Poland) to 0.56 kg at Degeberga (Sweden), giving a factor of 8 in difference. This is a larger variation than using outlet per 1000 residents. The average outlet per 1000 PE for all 15 WWTPs can be calculated to 0.31 kg which is lower than the value of 0.46 kg per 1000 residents, which is expected since the number of actual residents always are lower than the number of PE except for Tollarp where they are equal.

Relative data showed quite large difference in inlet load trends in all WWTPs, while outlet loads seemed to vary less. The differences in outlet concentrations might be explained by different consumption, different removal efficiency but most likely also differences in for example amount of wastewater coming from households and industry at the various WWTPs. One example is the three Swedish WWTPs. If we calculate the ratio between the actual burden in PE based on BOD_7 and the actual number of residents, we get 2,269, 1,579 and 1,000 for Kristianstad, Tollarp and Degeberga, respectively. These different ratios are explained by the fact that much of the water at Kristianstad comes from large food industries which gives a PE of 118.000 while the actual number of residents connected are only 52000. In Tollarp there is also a food industry connected giving PE of 4790 while only 3000 residents are connected. Finally, Degeberga has the same number of PE as residents which is 950. Consequently, the lowest outlet load in kg per 1000 PE is lowest in Kristianstad (0.28 kg) and highest in Degeberga (0.56 kg). However, when normalizing to number of 1000 residents, the outlet loads are very similar, with values of 0.64, 0.68 and 0.56 kg for Kristianstad, Tollarp and Degeberga, respectively. Therefore, using actual number of residents most likely will give a better comparison between WWTPs. Similar trends were seen also for the other region, though not as pronounced.

Table 5.1 Average (summer + winter) inlet load in four coastal regions WWTPs

	LT Average Inlet Load, kg/a				DE Average Inlet Load, kg/a				PL Average Inlet Load, kg/a				SE Average Inlet Load, kg/a		
	Klaipeda	**Palanga**	**Kretinga**	**Nida**	**Rostock**	**Laage**	**Krakow**	**Satow**	**Gdansk-Wschod**	**Gdynia-Debogorze**	**Swarzewo**	**Jastrzębia-Góra**	**Kristianstad**	**Tollarp**	**Degeberga**
Atenolol	1.66	0.39	0.3	0.01	10.21	0.07	0.05	0.04	4.94	3.53	0.3	0.07	9.50	0.33	0.26
Azithromycin	4.19	0.43	0.55	0	28.32	0.78	1.81	0.39	265.31	247.72	15.35	4.09	1.51	0.00	0.01
Carbamazepine	6.5	0.75	0.23	0.07	13.91	0.42	0.72	0.07	67.69	37.43	4.06	0.66	5.24	0.08	0.41
Ciprofloxacin	4.33	0.3	0.33	0	6.87	0.08	0.18	0.02	56.15	49.1	7.8	1.17	4.21	0.16	0.38
Clarithromycin	20.19	1.78	3.84	0.05	9.13	1.2	0.76	0	100.04	64.35	10.91	0.76	0.94	0.22	0.01
Diclofenac	40.99	5.5	6.16	0.81	50.42	1.19	1.03	0.26	104.69	76.24	12.97	1.65	5.20	0.14	0.14
Erythromycin	1.32	0.1	0.43	0	2.62	0.11	0.06	0	1.76	0.7	0.11	0.02	2.47	0.02	0.00
Estrone	1.25	0.18	0.15	0.01	1.22	0.01	0.02	0	2.4	1.65	0.19	0.02	0.41	0.01	0.01
Ibuprofen	2198.41	193.19	386.58	8.21	9683.76	83.96	427.81	82.98	17 127	16 957	2 252.21	387.1	367.22	12.27	18.21
Metoprolol	20.71	3.32	2.86	0.16	43.77	0.97	1.58	0.3	37.6	21.98	1.69	0.46	7.33	0.32	0.27
Naproxen	15.37	2.94	2.48	0.03	12.63	0.05	1.09	0.41	104.23	78.31	6.49	1.36	16.10	0.34	0.28
Oxazepam	0.84	0.11	0.11	0.01	0.46	0	0.01	0	0.88	0.55	0.05	0.01	2.93	0.21	0.09
Paracetamol	130.82	24.82	28.69	2.12	198.63	2.18	2.54	0.85	946.66	680.12	109.61	22.67	171.96	11.09	3.36
Propranolol	0.17	0.01	0.01	0	1.3	0.02	0.03	0	1.24	0.73	0.09	0.02	0.37	0.01	0.01
Sulfamethoxazole	13.04	1.26	0.49	0	15.81	0.11	0.18	0.14	20.06	14.7	1.3	0.74	3.28	0.01	0.00
∑	**2459.80**	**235.08**	**433.22**	**11.50**	**10079.06**	**91.15**	**437.87**	**85.46**	**18840.65**	**18234.11**	**2423.13**	**420.8**	**598.68**	**25.23**	**23.43**
∑∑	**54 400**														
Ibuprofen, % of total WWTP load	89.4	82.2	89.2	71.4	96.1	92.1	97.7	97.1	90.9	93.0	92.9	92.0	61.3	48.6	77.7

Table 5.2 Average (summer + winter) outlet load in four coastal regions WWTPs

	LT Average Outlet Load, kg/a				DE Average Outlet Load, kg/a				PL Average Outlet Load, kg/a				SE Average Outlet Load, kg/a		
	Klaipeda	**Palanga**	**Kretinga**	**Nida**	**Rostock**	**Laage**	**Krakow**	**Satow**	**Gdansk-Wschod**	**Gdynia-Debogorze**	**Swarzewo**	**Jastrzębia-Góra**	**Kristianstad**	**Tollarp**	**Degeberga**
Atenolol	0.37	0.05	0.02	0	1.95	0.01	0.01	0.01	1.54	0.53	0.03	0.02	2.79	0.08	0.00
Azithromycin	0.96	0.11	0.02	0.01	1.37	0.02	0.13	0	63.3	56.08	2.12	1.4	0.42	0.00	0.00
Carbamazepine	6.87	1.02	0.24	0.04	16.03	0.29	0.66	0.04	39.57	20.47	2.05	0.82	3.50	0.09	0.35
Ciprofloxacin	0.04	0.01	0.01	0	1.2	0.02	0.01	0	2.28	2.05	0	0.03	0.32	0.01	0.00
Clarithromycin	10.58	1.03	0.39	0.04	2.4	0.31	0.32	0	5.61	3.02	0.35	0.05	0.40	0.09	0.00
Diclofenac	31.66	5.45	4.4	0.36	30.62	0.41	0.64	0.08	57.18	37.35	3.5	1.01	4.74	0.23	0.09
Erythromycin	1.2	0.08	0.07	0	2.24	0.02	0.1	0	2.35	1.14	0.1	0.02	2.21	0.08	0.00
Estrone	0.02	0.01	0.01	0	0	0	0	0	0.11	0.14	0.003	0.001	0.02	0.00	0.00
Ibuprofen	0	0	0	0	0	0.01	0.09	0.12	0	0	0	0	4.93	0.46	0.00
Metoprolol	16.14	2.63	0.86	0.16	21.48	0.15	0.55	0.09	31.96	19	1.14	0.26	5.46	0.33	0.02
Naproxen	0.65	0.1	0.12	0.01	1.21	0	0.02	0.01	2.87	0.89	0.09	0.03	3.81	0.34	0.00
Oxazepam	1.01	0.14	0.09	0.01	0.47	0	0.01	0	1.18	0.76	0.06	0.02	3.47	0.25	0.07
Paracetamol	0	0	0.01	0.01	0.12	0	0	0.01	0.13	0.24	0.04	0.004	0.08	0.04	0.00
Propranolol	0.16	0.01	0	0	1.27	0.01	0.03	0	1.37	0.75	0.07	0.01	0.24	0.01	0.00
Sulfamethoxazole	6.93	0.34	0.08	0	4.49	0.02	0.03	0.03	6.71	4.24	0.3	0.13	0.90	0.01	0.00
∑	**76.60**	**10.97**	**6.32**	**0.65**	**84.85**	**1.27**	**2.6**	**0.39**	**216.16**	**146.66**	**9.85**	**3.81**	**33.27**	**2.03**	**0.53**
∑∑	**596**														
Diclofenac, % of total WWTP load	**41.3**	**49.7**	**69.6**	**55.4**	**36.1**	**32.3**	**23.8**	**20.5**	**26.5**	**25.5**	**35.5**	**26.5**	**14.2**	**11.3**	**17.0**

*Table 5.3 Average (summer + winter) pharmaceuticals removal rate in four coastal regions WWTPs. Removal efficiency = (inlet load – outlet load)/inlet load*100. In the table "0,0" means that pharmaceuticals were not detected or rounded quantity not exceeds one hundredth (0,01) of a kilogram*

	LT Average efficiency of removal, % (summer + winter)				**DE Average efficiency of removal, % (summer + winter)**				**PL Average efficiency of removal, % (summer + winter)**				**SE Average efficiency of removal, % (summer + winter)**		
	Klaipeda	**Palanga**	**Kretinga**	**Nida**	**Rostock**	**Laage**	**Krakow**	**Satow**	**Gdansk-Wschod**	**Gdynia-Debogorze**	**Swarzewo**	**Jastrzębia-Góra**	**Kristianstad**	**Tollarp**	**Degeberga**
Atenolol	77.7	87.0	92.2	83.8	80.9	85.7	80.0	75.0	68.8	85.0	90.0	71.4	70.7	76.5	100.0
Azithromycin	77.0	74.3	96.5	-79.9	95.2	97.4	92.8	100.0	76.1	77.4	86.2	65.8	72.5	33.3	93.3
Carbamazepine	-5.7	-35.7	-2.0	43.8	-15.2	31.0	8.3	42.9	41.5	45.3	49.5	-24.2	33.3	-13.8	14.8
Ciprofloxacin	99.0	96.9	96.2	65.3	82.5	75.0	94.4	100.0	95.9	95.8	100.0	97.4	92.5	91.9	99.2
Clarithromycin	47.6	41.8	89.8	12.3	73.7	74.2	57.9	0.0	94.4	95.3	96.8	93.4	57.5	58.4	94.1
Diclofenac	22.8	1.1	28.6	55.1	39.3	65.5	37.9	69.2	45.4	51.0	73.0	38.8	8.8	-67.6	37.3
Erythromycin	8.5	20.5	84.3	-75.0	14.5	81.8	-66.7	0.0	-33.5	-62.9	9.1	0.0	10.8	-216.7	14.3
Estrone	98.8	94.3	95.3	98.5	100.0	100.0	100.0	0.0	95.4	91.5	98.4	95.0	94.8	88.6	100.0
Ibuprofen	100.0	100.0	100.0	100.0	100.0	100.0	100.0	99.9	100.0	100.0	100.0	100.0	98.7	96.3	100.0
Metoprolol	22.1	20.6	69.8	-4.5	50.9	84.5	65.2	70.0	15.0	13.6	32.5	43.5	25.5	-2.8	93.8
Naproxen	95.8	96.6	95.3	58.0	90.4	100.0	98.2	97.6	97.2	98.9	98.6	97.8	76.3	0.6	99.5
Oxazepam	-19.5	-30.9	16.4	-47.9	-2.2	0.0	0.0	0.0	-34.1	-38.2	-20.0	-100.0	-18.3	-17.8	26.4
Paracetamol	100.0	100.0	100.0	99.7	99.9	100.0	100.0	98.8	100.0	100.0	100.0	100.0	100.0	99.6	100.0
Propranolol	9.1	53.6	69.5	-150.0	2.3	50.0	0.0	0.0	-10.5	-2.7	22.2	50.0	34.9	0.0	68.3
Sulfamethoxazole	46.9	73.3	83.4	-114.3	71.6	81.8	83.3	78.6	66.6	71.2	76.9	82.4	72.7	-8.3	-100.0
∑	780.1	793.4	1115	144.98	883.8	1126.9	851.3	832	818.2	821.2	1013.2	811.3	830.7	218.2	941
Average, %	52.0	52.9	74.3	9.7	58.9	75.1	56.8	55.5	54.5	54.7	67.5	54.1	55.4	14.5	62.7

Table 5.4 Calculated comparative pharmaceuticals inlet and outlet loads in the four coastal regions WWTPs

Parameters	LT WWTPs comparative parameters				DE WWTPs comparative parameters				PL WWTPs comparative parameters				SE WWTPs comparative parameters		
	Klaipeda	Palanga	Kretinga	Nida	Rostock	Laage	Krakow	Satow	Gdansk-Wschod	Gdynia-Debogorze	Swarzewo	Jastrzębia-Góra	Kristianstad	Tollarp	Degeberga
Q m³/a	15 100 000	2 879 000	1 471 000	230 000	16 894 000	321 000	253 000	80 000	33 930 000	20 180 000	2 250 000	610 000	8 186 000	361 000	79 000
Q mil. m³/a	15.10	2.88	1.471	0.23	16.894	0.321	0.253	0.08	33.93	20.18	2.25	0.61	8.186	0.361	0.079
Aver. inlet load, kg	2459.8	235.08	433.22	11.5	10079.06	91.15	437.87	85.46	18840.65	18234.11	2423.13	421.8	598.68	25.23	23.43
Aver. outlet load, kg	76.6	10.97	6.32	0.65	84.85	1.27	2.6	0.39	216.16	146.66	9.85	3.81	33.27	2.03	0.53
Aver. inlet load, kg/mil m³	162.90	81.65	294.51	50.00	596.61	283.96	1730.71	1068.25	555.28	903.57	1076.95	691.48	73.13	69.89	296.58
Aver. outlet load, kg/mil m³	5.07	3.81	4.30	2.83	5.02	3.96	10.28	4.88	6.37	7.27	4.38	6.25	4.06	5.62	6.71
Number of connected residents	170 000	13 000	19 150	1 714	235 645	4 516	3 964	1 303	571 350	360 000	35 668	10 000	52 000	3 000	950
Factor of connected 1000 residents	170	13	19.15	1.714	235.645	4.516	3.964	1.303	571.35	360	35.668	10	52	3	0.95
Aver. inlet load kg per 1000 residents	14.47	18.08	22.62	6.71	42.77	20.18	110.46	65.59	32.98	50.65	67.94	42.18	11.51	8.41	24.66
Aver. outlet load kg per 1000 residents	0.45	0.84	0.33	0.38	0.36	0.28	0.66	0.30	0.38	0.41	0.28	0.38	0.64	0.68	0.56
Actual number PE (BOD_7)	210 070	19 945	28 727	3 130	342 483	12 658	6 209	1 303	742 521	476 000	149 000	12 540	118 000	4 790	950
Factor of PE per 1000 PE	210.07	19.945	28.727	3.13	342.483	12.658	6.209	1.303	742.521	476	149	12.54	118	4.79	0.95
Aver. Inlet load kg per 1000 PE	11.71	11.79	15.08	3.67	29.43	7.20	70.52	65.59	25.37	38.31	16.26	33.64	5.07	5.27	24.66
Aver. Outlet load kg per 1000 PE	0.36	0.55	0.22	0.21	0.25	0.10	0.42	0.30	0.29	0.31	0.07	0.30	0.28	0.42	0.56
Number of PE divided by actual number of residents	1,236	1,534	1,500	1,826	1,453	2,803	1,566	1,000	1,300	1,322	4,177	1,254	2,269	1,597	1,000

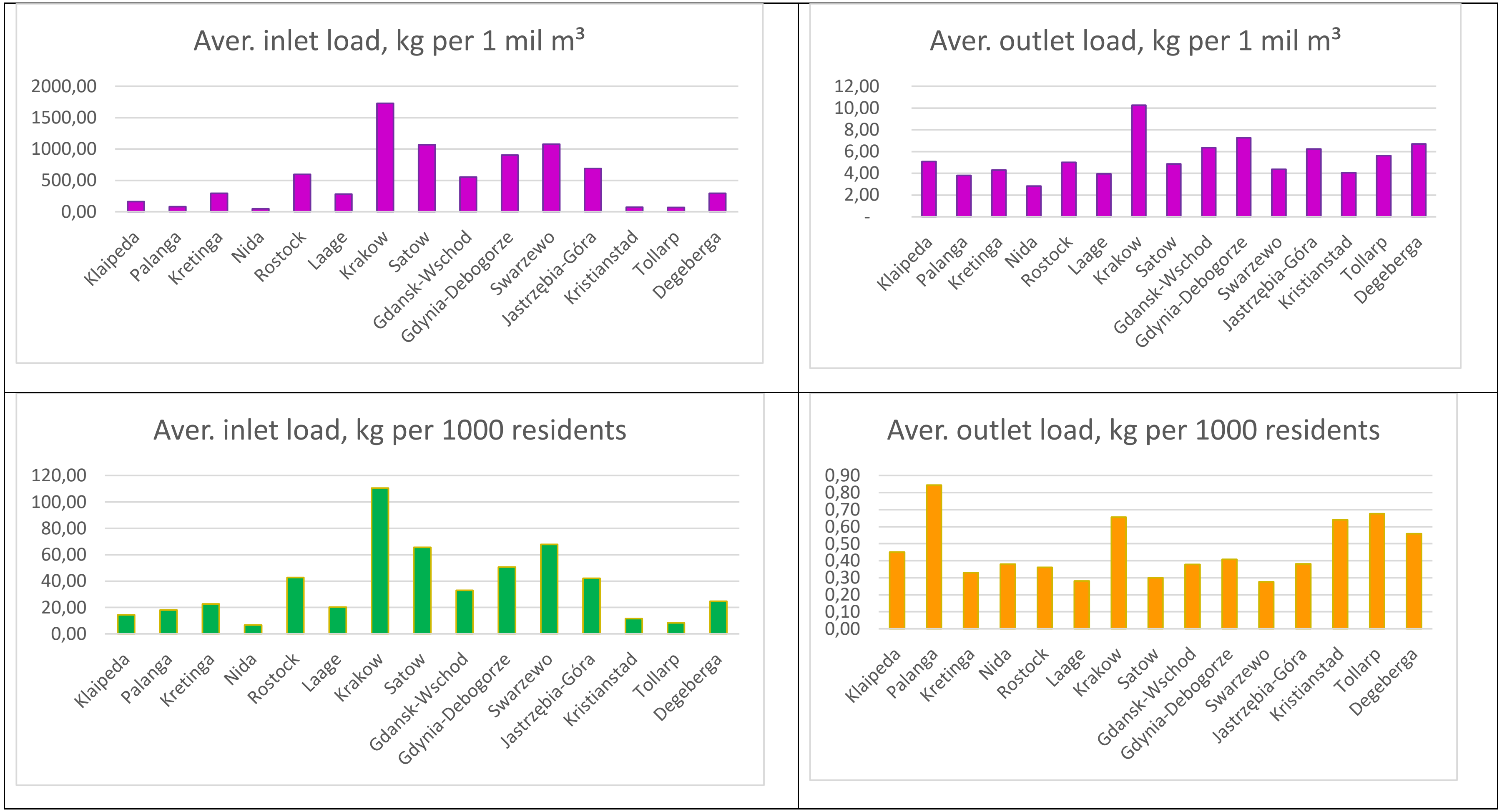


Figure 5.1 Visualization of WWTPs inlet and outlet comparable data

5.2. Status of receiving water bodies

5.2.1. Marine waters

Marine water samples were taken in **Poland**:

- from the Gdansk Bay near the outlet of Gdansk-Wschod WWTP (surface and bottom water layers),
- from the Puck Bay near the outlet of Gdynia-Debogorze WWTP (surface and bottom water layers) and
- from the Baltic Sea near the outlet of Swarzewo WWTP (surface and bottom water layers)

and in **Lithuania**:

- in the Baltic Sea near the outlet of the Palanga WWTP (bottom water layer) and at monitoring station (B-1) as a background concentration.

Summer and winter samples were taken, except of monitoring station (B-1) and bottom water sample near the Swarzewo WWTP, which were taken only in summer.

Concentrations of oxazepam, ciprofloxacin, atenolol, propanolol, naproxen and ibuprofen were below the Method Quantification Limit (MQL) in all samples.

Concentrations of the other pharmaceuticals were higher in summer than in winter, except for paracetamol where concentration above the MQL – 1.2 ng/L was detected only in one sample in winter near the WWTP Swarzewo outlet in the Baltic Sea (PL). Other pharmaceuticals with concentrations above the MQL in winter time were: erythromycin – 0.6 ng/L, sulfamethoxazole – 1.9 ng/L, and diclofenac – 2.4 ng/L in bottom water of Gdansk Bay, and azithromycin – 1.1 ng/L in the surface water of Buck Bay.

Summer concentrations of pharmaceuticals in marine water are presented in Figure 5.2. The highest concentrations of pharmaceuticals were found in the Gdansk Bay near the outlet of Gdansk-Wschod WWTP with the highest average concentration of carbamazepine in summer – 20.6 ng/L. This compound was above the MLQ in all marine samples, the average concentration in summer was 8.9 ng/l, in winter – 3.1 ng/L. The highest concentration of diclofenac was also found in the surface water of Gdansk Bay in summer – 22.1 ng/L.

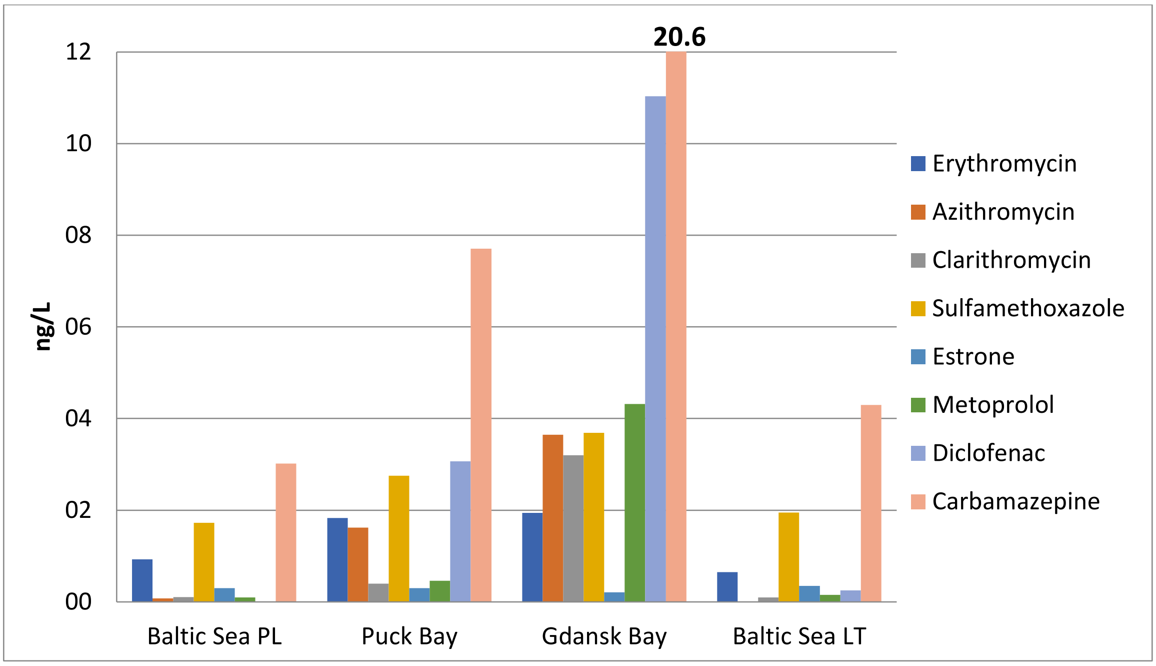


Figure 5.2 Average concentrations of pharmaceuticals in marine samples taken in summer 2017

Higher concentrations of pharmaceuticals were detected in **transitional waters** of Lithuania – in the Klaipeda Strait and in the Curonian Lagoon. The same substances as in the marine water of Lithuania were detected in the water of Klaipėda Strait. Additionally, clarithromycin - up to 6.5 ng/L, diclofenac - up to 15.2 ng/L, paracetamol - up to 14 ng/L, ibuprofen - up to 23.1 ng/L and metoprolol - up to 8.8 ng/L were detected in Klaipėda Strait.

Figure 5.3 shows a comparison of average concentrations (near the outlet and downstream) in Klaipėda Strait in summer and winter samples. Concentrations of carbamazepine, erythromycin and sulfamethoxazole were higher in summer, concentrations of clarithromycin, diclofenac, ibuprofen, metoprolol and paracetamol were notably higher in winter probably due to flue season.

In the water of the Curonian Lagoon near Nida only five pharmaceuticals at low concentrations were detected: carbamazepine, clarithromycin, diclofenac, estrone and paracetamol.

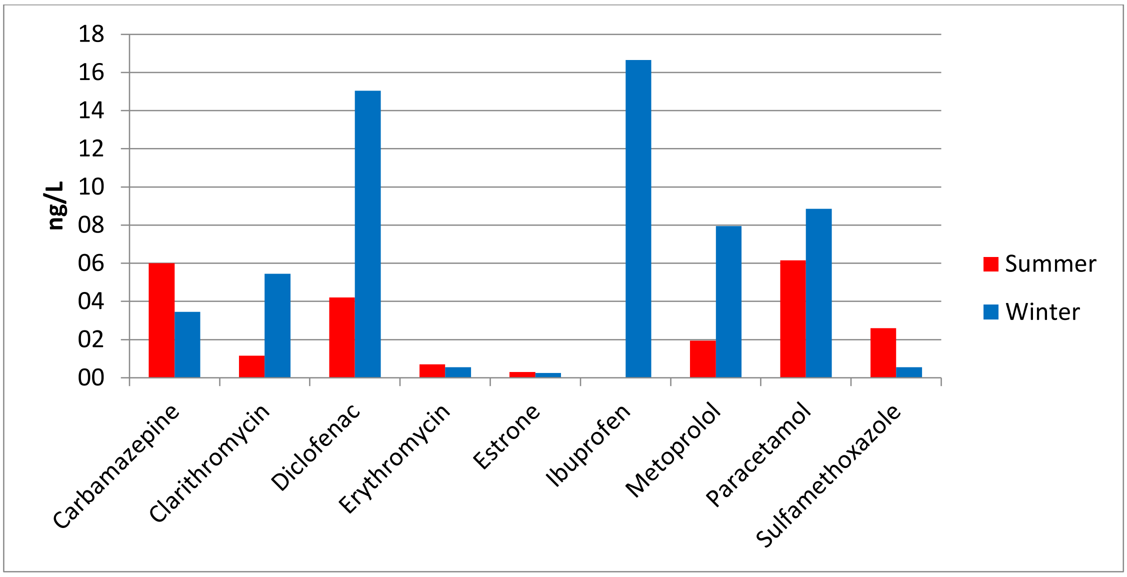


Figure 5.3 Average concentrations of pharmaceuticals in Klaipėda Strait (Lithuania) in summer 2017 and winter 2018

5.2.2. Rivers

In **Germany,** samples were taken in Warnow river (WWTP Rostock), in Recknitz river (WWTP Laage), in small ditch/stresam (WWTP Krakow) and in Mühlenbach stream (WWTP Satow).
In **Lithuania,** samples were taken in Tenžė river (Kretinga WWTP) and in the mouth Akmena-Danė river (only in summer).
In **Poland,** samples were taken in Czarna Wda river (WWTP Jastrzębia-Góra) and in the mouth of Vistula river.
In **Sweden,** samples were taken in Helge Å river (Kristianstad WWTP), in Vramsån river (Tollarp WWTP) and in Segesholmsån river (Degeberga WWTP).
The concentrations of pharmaceuticals were measured upstream the WWTPs, near the outlet of the WWTP (only in Lithuania) and downstream of WWTPs to evaluate the impact of discharged wastewater to the concentration of pharmaceuticals in water.
In all waterbodies the **upstream** concentrations were much lower then downstream. For example for diclofenac, upstream concentrations were 1.6 times lower in Czarna Wda river in winter (upstream concentration – 27.3 ng/L) and 920 times lower in a small ditch upstream WWTP Krakow (upstream concentration – below the MQL). The highest concentration of diclofenac up to 55.2 ng/L was found in the upstream sample of Czarna Wda river in summer, as well as for the pharmaceuticals carbamazepine – 52.4 ng/L, clarithromycin – 3.6 ng/L and metoprolol – 11.1 ng/L. In the Segesholmsån river upstream of Degeberga WWTP in summer the concentrations of all pharmaceuticals were below the MQL.
Small streams/ ditches could be distinguished with high pharmaceutical concentrations **downstream** treated wastewater discharge points (Figure 5.4). The highest average (summer and winter) concentrations of diclofenac (875 ng/L) and carbamazepine (528 ng/L) were observed in the small ditch/stream downstream Krakow WWTP, the highest average concentration of metoprolol (382 ng/L) was found in the outlet discharge point for Kristianstad WWTP in lake

Hammarsjön, the highest average concentration of clarithromycine (38 ng/L) was found in the river Tenžė downsteam Kretinga WWTP. This could be explained by low flow in streams and, at the same time, low dilution rate.
Concentration of pharmaceuticals in the **river mouths** were not high: carbamazepine concentration ranged from 8.3 ng/L in winter to 37.7 ng/L in summer in the Vistula river mouth and was the highest of all pharmaceuticals measured. In Akmena-Danė the concentration of carbamazepine was also the highest – 9.9 ng/L. Diclofenac concentration in Akmena-Danė was 8.5 ng/L, in Vistula river it was lower and ranged from 4.1 ng/L in summer to 5.7 ng/L in winter. Concentration of clarithromycin and metoprolol were below the MQL, while in Akmena-Danė they were 3.4 ng/L and 4.2 ng/L respectively. The average concentration of sulfametoxazole in Vistula river was 4.6 ng/L, while in Akmena-Danė – the concentration was only 1.9 ng/L. In Akmena-Danė paracetamol was detected at a concentration of 7 ng/L, while in Vistula river mouth paracetamol concentrations were below the MQL.

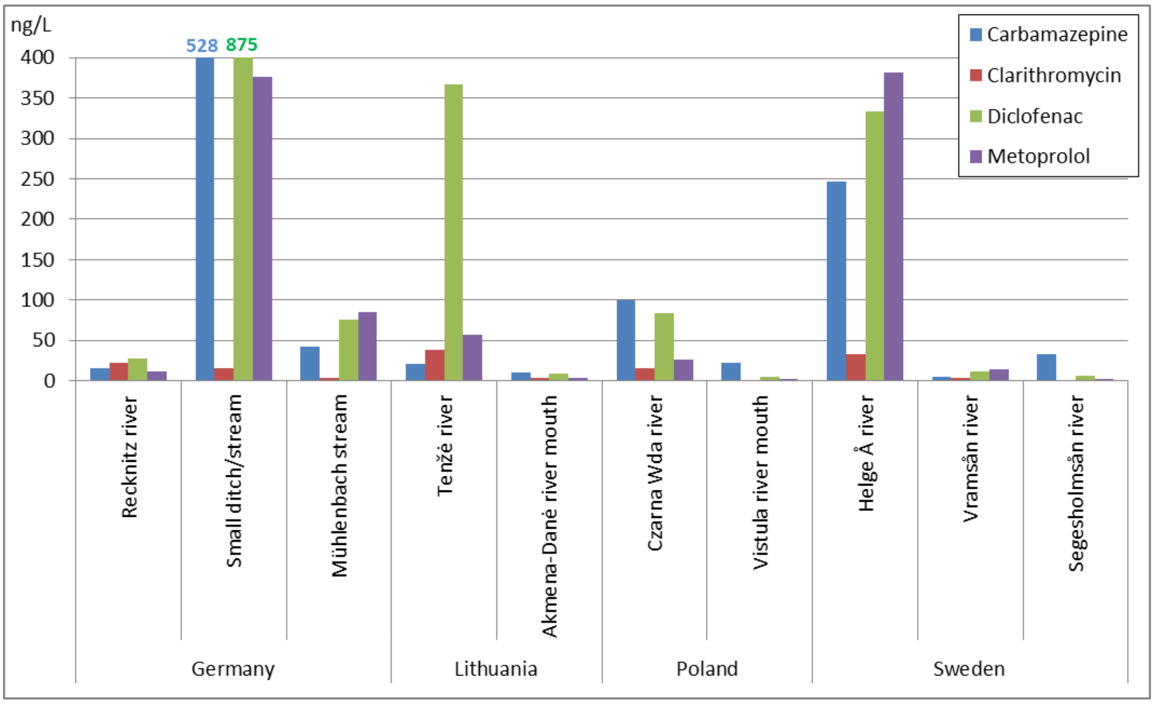


Figure 5.4 Average concentrations (summer and winter) of Carbamazepine, Clarithromycin, Diclofenac and Metoprolol in rivers, streams or ditches in Germany, Lithuania, Poland and Sweden downstream of the WWTPs

The concentration of pharmaceuticals in the waterbodies depends on different factors like consumption rate of the medicines in the area, size of the WWTP, removal efficiency of the WWTP, water flow of the receiving river etc. Average concentrations of the 4 pharmacuticals carbamazepine, clarithromycin, diclofenac and metoprolol at the inlet and outlet of WWTPs and at the downstream of receiving river are shown in the Figure 5.4. Four small-medium size WWTPs were chosen for the comparison: WWTP Tollarp with 3 000 of connected residents, WWTP Laage with 4 516 of connected residents, WWTP Jastrzębia-Góra with about 10 000 of connected residents and WWTP Kretinga with 19 150 connected residents.

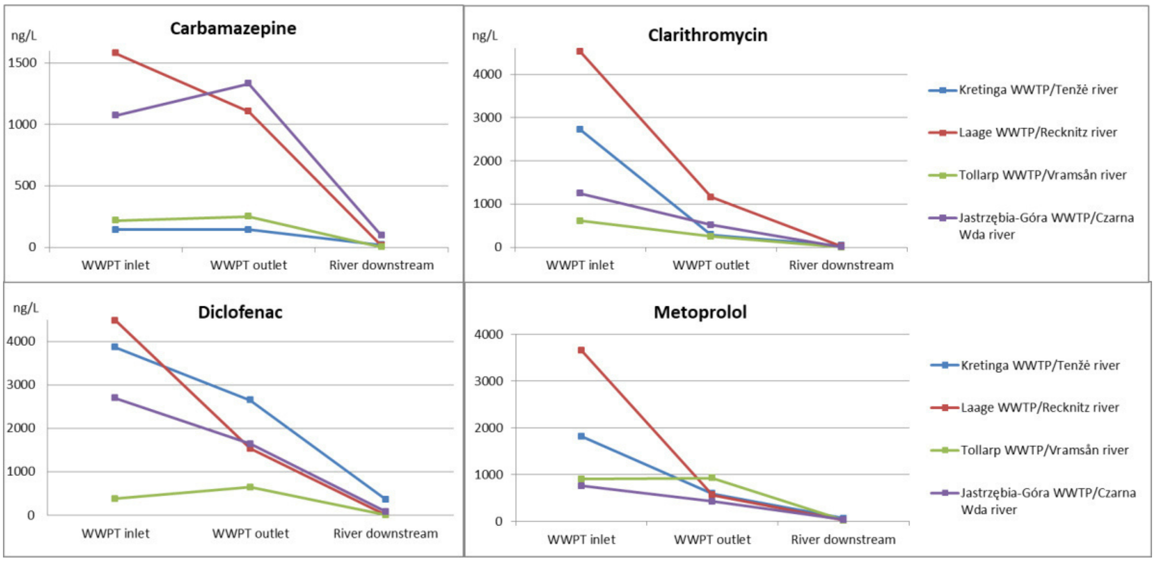


Figure 5.5 Average concentrations (summer and winter) of Carbamazepine, Clarithromycin, Diclofenac and Metoprolol at the inlet and outlet of WWTPs and at the downstream of receiving rivers

Figure 5.5 shows that concentrations of pharmaceuticals at the inlet and outlet of WWTPs do not correlate with the number of connected residants to the WWTP. The higest inlet concentration of all four pharmaceuticals was at the Laage WWTP, which has only 4 516 of connected residents. High concentrations of clarithromycin, diclofenac and metoprolol were measured in the inlet of Kretinga WWTP, which has the highest number of residents of the four WWTPs, although the inlet concentration of carbamazepine was lowest in Kretinga WWTP. Inlet concentrations of pharmaceuticals strogly depend on the consumption rate of the population in the area (see Deliverable 3.1).

The removal rates of pharmaceuticals at the WWTPs are different for the different compounds. For example, the highest average removal efficiency of diclofenac was at Laage WWTP – 65.5 %, at Jastrzębia-Góra WWTP it was 38.8 %, at Kretinga WWTP 28.6 %, at Tollarp WWTP it was negative -67.6 % (see Chapter 5.1).

Downstream concentrations of pharmaceuticals in receiving rivers also depend on the flow of the river. For example, the average flow of Recknitz river and Vramsån river are similar – 3.1 and 3.4 m^3/s respectively, and the concentrations of diclofenac - 15.7 and 12.1 ng/L and metoprolol - 11.4 and 14.5 ng/L in the downstream of both rivers are also similar. Concentrations of carbamazepine - 15.7 and 5.1 ng/L and clarithromycin – 22.7 and 3.7 ng/L also do not differ too much. The flow of Tenžė river is only 0.58 m^3/s. The downstream concentration of pharmaceuticals in the water of Tenžė river are much higher: diclofenac – 367 ng/L; metoprolol – 56.9 ng/L; carbamazepine – 21.5 ng/L; clarithromycin – 38.3 ng/L. All these factors should be taken into account during the assessment of the concentration of pharmaceuticals in receiving waterbodies.

6. Conclusions

Pharmaceuticals are released into the environment during various stages of the product lifecycle – manufacturing, consumption and waste disposal. The main sources of pharmaceuticals in the freshwater and marine environment are the excretion of bioactive substances consumed by humans (via urine and faeces) as well as the incorrect disposal of unused medical products. Consequently, the main pathway of human consumed pharmaceuticals to the marine environment is via direct discharges of effluents from municipal wastewater treatment plants in coastal areas as well as via rivers carrying effluents from inland WWTPs.

More information is still needed to understand and evaluate certain pharmaceuticals as regards to their environmental concentrations and the resulting levels of risk. Today local and regional monitoring of pharmaceuticals in the environment is very limited, especially in the eastern Baltic, but also in many parts of Germany and Sweden. Knowing more about the concentrations of pharmaceuticals in the environment would allow environmental risk assessments to be improved and measures to be more focused, especially if monitoring could be extended to better cover certain parts of the environment that is known to be vulnerable. In this monitoring it is of outmost importance to cooperate with stakeholders and possible policy options to mitigate such impacts.

Monitioring results are highly relevant in prioritization at which WWTPs society should start to take action for the introduction of an advanced/fourth wastewater treatment step, and by linking these monitioring data to consumption, current treatment technologies and chemical load estimations we can better understand were the environmental impact is most pronounced.

Project partners

Kristianstad University, SE
www.hkr.se

Gdansk Water Foundation, PL
www.gfw.pl

EUCC
The Coastal Union Germany, DE
www.eucc-d.de

Gdansk University of Technology, PL
www.pg.edu.pl

University of Rostock, DE
www.auf.uni-rostock.de

Environmental Protection Agency, LT
www.gamta.lt

Klaipeda University, LT
www.ku.lt

MORPHEUS
Model Areas for Removal of Pharmaceutical Substances in the South Baltic

EU STRATEGY FOR THE BALTIC SEA REGION
FLAGSHIP

Interreg
South Baltic

EUROPEAN UNION

European Regional Development Fund