Pharmaceutical Occurrence in Wastewater and Surface Water in *UNESCO Biosphere Reserve Kristianstads Vattenrike*

Regional Report, Kristianstad, Region Skåne, Sweden, 2021
Project: MORPHEUS 2017-2019
Model Areas for Removal of Pharmaceutical Substances in the South Baltic
Interreg South Baltic – 2nd Call, Green Technologies

Erland Björklund - main author
Ola Svahn - co-author
MoLab

KRISTIANSTAD UNIVERSITY
SWEDEN

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

Kristianstad University Sweden

Interreg South Baltic
EUROPEAN UNION
European Regional Development Fund

Contact information
erland.bjorklund@hkr.se

Cover photo
Helge Å river and Kristianstad City, Region Skåne, Sweden.

CONTENT

Summary

Key facts of the MORPHEUS project

Where should we sample?

General about Kristianstads Vattenrike – ”Vattenriket®”

Detailed overview of the three sampling sites

Site specific information on the 3 river areas

- Helge Å river area and Kristianstad WWTP
- Vramsån river area and Tollarp WWTP
- Segesholmsån river area and Degeberga WWTP

Chemical analysis

Sampling

Three wastewater treatment plants (WWTPs) in Kristianstad Municipality, Region Skåne

Results of pharmaceutical analyses

Discussion

- Inlet concentrations (ng/L) of 15 pharmaceuticals in 3 WWTPs
- Inlet chemical load (g/year) of 15 pharmaceuticals in 3 WWTPs
- Outlet concentrations (ng/L) of 15 pharmaceuticals in 3 WWTPs
- Outlet chemical load (g/year) of 15 pharmaceuticals in 3 WWTPs
- The 3 WWTPs ability to reduce pharmaceuticals – removal efficiency (%)
- Recipient concentrations of 15 pharmaceuticals in rivers and lakes in Kristianstad municipality

Final remarks

Supplementary Figures 1-6

Summary

In this project the release of 15 pharmaceuticals from three different WWTPs into three different recipients in Kristianstad Municipality, Region Skåne was investigated. All three WWTPs are situated within the borders of the first UNESCO Biosphere Reserve in Sweden, Kristianstads Vattenrike – "*Vattenriket*®", established in 2005. Pharmaceutical included were:

1. Atenolol
2. Azithromycin
3. Carbamazepine
4. Ciprofloxacin
5. Clarithromycin
6. Diclofenac
7. Erythromycin
8. Estrone
9. Ibuprofen
10. Naproxen
11. Metoprolol
12. Propranolol
13. Oxazepam
14. Paracetamol
15. Sulfamethoxazole

Below is a summary of the major findings of the project.

The three WWTPs

The three WWTPs differed in size with the largest being Kristianstad WWTP treating a yearly wastewater volume of 8 186 000 m^3 from roughly 52 000 people and large food industries, followed by Tollarp WWTP with 361 000 m^3 from 4 790 people and food industry, and finally Degeberga WWTP with 79 000 m^3 from 950 people. Both inlet and outlet wastewater samples were taken at two seasons; winter (February) and summer (August).

Occurrence of pharmaceuticals in WWTPs – inlet and outlet water

Inlet concentrations

The inlet concentrations showed that ibuprofen and paracetamol were present in the highest levels in all three WWTPs ranging between 13 458–307 278 ng/L and 17 364–46 936 ng/L, respectively. Thereafter the top five pharmaceuticals in Kristianstad WWTP were naproxen 1 967 ng/L, atenolol 1 160 ng/L, metoprolol 895 ng/L, carbamazepine 641 ng/L and diclofenac 636 ng/L. Ciprofloxacin was the antibiotic with the highest inlet concentration of 514 ng/L. Tollarp WWTP contained naproxen 938 ng/L, atenolol 907 ng/L, metoprolol 896 ng/L, clarithromycin 612 ng/L and oxazepam 594 ng/L. Apart from clarithromycin, once again ciprofloxacin was the antibiotic with the highest concentration at 444 ng/L. Degeberga WWTP had higher inlet concentrations than the other two WWTPs, possibly due to less dilution in industrial wastewater. These were carbamazepine 5 126 ng/L, ciprofloxacin 4 867 ng/L, naproxen 3 597 ng/L, metoprolol 3 463 ng/L and atenolol 3 328 ng/L. Summer and winter inlet concentrations were compared by taking the average of all summer data and the average of all winter data. In total 10 out of 15 pharmaceuticals showed higher average inlet concentrations during the summer season; in the order of 10% to 257% higher. During the winter season 5 out of 15 pharmaceuticals showed higher average inlet concentrations; in the order of 10% to 731% higher. However, the ciprofloxacin concentration at Degeberga WWTP was exceptionally high (giving the value of 731%), and if excluded the other 4 compounds ranged between 10% to 120% higher in winter time.

Inlet chemical loads

The inlet chemical loads were calculated using the measured average inlet concentrations and knowledge of the yearly volume treated wastewater, in the three WWTPs. The chemical load was estimated to be 599 kg, 25 kg and 23 kg at Kristianstad, Tollarp and Degeberga WWTP, respectively. The majority of this chemical load came from ibuprofen and paracetamol. When excluding these two pharmaceuticals the chemical loads for the other 13 pharmaceuticals were 59 kg, 1.9 kg and 1.9 kg, meaning that ibuprofen and paracetamol together represented more than 90 % of the incoming chemical load.

Outlet concentrations

The outlet concentrations showed that these did not always correlate well with inlet concentrations and was especially pronounced for ibuprofen and paracetamol. Both occurred at inlet concentrations that by far exceeded any of the other pharmaceuticals, while their outlet concentrations in most cases were similar to or lower than the other pharmaceuticals. Thereby the ranking in outlet concentrations differed from the inlet ranking. The top five pharmaceuticals in Kristianstad WWTP outlet water were metoprolol 667 ng/L, ibuprofen 602 ng/L, diclofenac

579 ng/L, naproxen 465 ng/L and carbamazepine 427 ng/L. Erythromycin was the antibiotic with the highest outlet concentration of 270 ng/L. Tollarp WWTP outlet water contained ibuprofen 1 260 ng/L, naproxen 931 ng/L, metoprolol 919 ng/L, oxazepam 699 ng/L and diclofenac 646 ng/L. Clarithromycin, was the antibiotic with the highest outlet concentration of 255 ng/L. Despite that Degeberga WWTP showed higher inlet concentrations than Kristianstad and Tollarp, the outlet concentrations for most pharmaceuticals were not higher. The top five pharmaceuticals were carbamazepine 4 362 ng/L, diclofenac 1 132 ng/L, oxazepam 846 ng/L, metoprolol 216 ng/L and ciprofloxacin 39 ng/L. The summer and winter outlet concentrations were compared by taking the average of all summer data and the average of all winter data. In total 9 out of 15 pharmaceuticals showed higher average outlet concentrations during the winter season in the order of 6% to 282% higher. During the summer season 6 out of 15 pharmaceuticals showed higher average outlet concentrations in the order of 1% to 101% higher.

Outlet chemical loads

The outlet chemical loads in the three WWTPs were estimated to 33 kg, 2.0 kg and 0.5 kg at Kristianstad, Tollarp and Degeberga WWTP, respectively. As shown above, the major chemical inlet load came from ibuprofen and paracetamol. However, excluding these two pharmaceuticals from the calculations gave outlet loads of 28 kg, 1.5 kg and 0.5 kg for Kristianstad, Tollarp and Degeberga WWTP, respectively. Therefore, ibuprofen plus paracetamol now only represented 18%, 33% and 0.05% of the outlet loads. Consequently, ibuprofen and paracetamol were removed to a large extent during the wastewater treatment processes; paracetamol by 99%, and ibuprofen by 97%. Removal efficiency differed much between compounds as exemplified by ciprofloxacin 83%, naproxen 63%, metoprolol 37% and carbamazepine 3%, as an average for all WWTPs at both seasons. When taking the average of all pharmaceutical concentrations during the summer sampling and likewise for the winter sampling, this gave an average removal efficiency of 55% and 32%, respectively. Consequently, there seemed to be a tendency for a better removal efficiency during the summer. There were also tendencies that WWTPs differed in their ability to remove pharmaceuticals. The highest average removal efficiency was seen at Degeberga WWTP with 78% in summer, while the lowest average removal efficiency was seen at Tollarp WWTP with 17% in winter.

The three recipients and sampling points

The three WWTPs released their treated wastewater into three different recipients. Kristianstad WWTP in Hammarsjön lake, which is part of the Helge Å river system, which in turn ends in the Hanöbukten bay of the Baltic Sea. Tollarp WWTP in the Vramsån river, which ends in the Helge Å river. Finally, Degeberga WWTP in the Segesholmsån river, which ends directly in the Hanöbukten bay. The size of the three recipients also varied largely. The Helge Å river system is the largest with an average yearly flow of roughly 56 m^3/s close to the entrance of the Hammarsjön lake and 61 m^3/s at the exit in the Baltic Sea. The Vramsån river and the Segesholmsån river are smaller with average flows of roughly 4.8 m^3/s and 0.8 m^3/s at their exit points in the Helge Å river and the Baltic Sea, respectively. However, the fact that Hammarsjön lake is a more stagnant part of the Helge Å river system than the main flow of the river meant that dilution of the large volume of released wastewater from Kristianstad WWTP was less efficient than for the other two WWTPs which ended directly in the main flow of the Vramsån river and the Segesholmsån river, respectively. The change in pharmaceutical concentrations in the rivers caused by the released wastewater from the WWTPs in the three river systems were studied by taking both upstream and downstream samples in all rivers. In the Helge Å river one upstream and four downstream river sampling points were taken for Kristianstad WWTP to study the pharmaceuticals concentrations in the river all the way to the entrance into the Baltic Sea. In the Vramsån river one upstream and one downstream sampling point for Tollarp WWTP was taken, but since Vramsån river ends in Helge Å river, two of the Helge Å river sampling points were also downstream Tollarp WWTP. In the Segesholmsån river one upstream and two downstream sampling points from Degeberga WWTP were taken, the second point was close to the exit of the river in the Baltic Sea.

Occurrence of pharmaceuticals in recipients – upstream and downstream WWTPs

The Helge Å river system including the Hammarsjön lake.

Upstream Kristianstad WWTP

At the sampling point upstream Kristianstad WWTP in the Helge Å river several pharmaceuticals were identified despite the large size of the river. The concentrations differed somewhat between seasons but 8 compounds could be detected in concentrations above 1.0 ng/L; paracetamol 8.4 ng/L (winter), carbamazepine 7.8 ng/L (summer), naproxen 7.0 ng/L (winter), metoprolol 4.5 ng/L (summer), oxazepam 3.2 ng/L (summer), atenolol 2.5 ng/L (summer), diclofenac 1.4 ng/L (summer) and erythromycin 1.2 ng/L (summer). However, of these, only paracetamol, carbamazepine, metoprolol, oxazepam, atenolol and erythromycin were above their method quantification levels (MQL), while the presence of naproxen and diclofenac was indicative.

Downstream Kristianstad WWTP - Sampling point 1

Sampling point 1 was the entrance point of water into the Hammarsjön lake after the released wastewater had been

running through the 1 500 m channel. When the channel ends the water is pumped from the channel into the lake. This water contained high concentrations since it mainly consists of treated wastewater from the WWTP. 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 reduction of pharmaceuticals in the channel was estimated by comparing these concentrations with the outlet concentrations from Kristianstads WWTP to the channel. Taking the average for all pharmaceuticals gave 50% reduction during winter and 31% reduction during summer. An explanation to this difference might be a larger inflow of external water to the channel during winter than during summer causing a higher degree of dilution. In any case the results show that the 1 500 m channel cannot remove the pharmaceuticals from the water in a satisfying way. Previous studies by us have shown that the sediment of the channel contains very high concentrations of some persistent pharmaceuticals, meaning that the channel becomes an aquatic repository for certain organic contaminants over time.

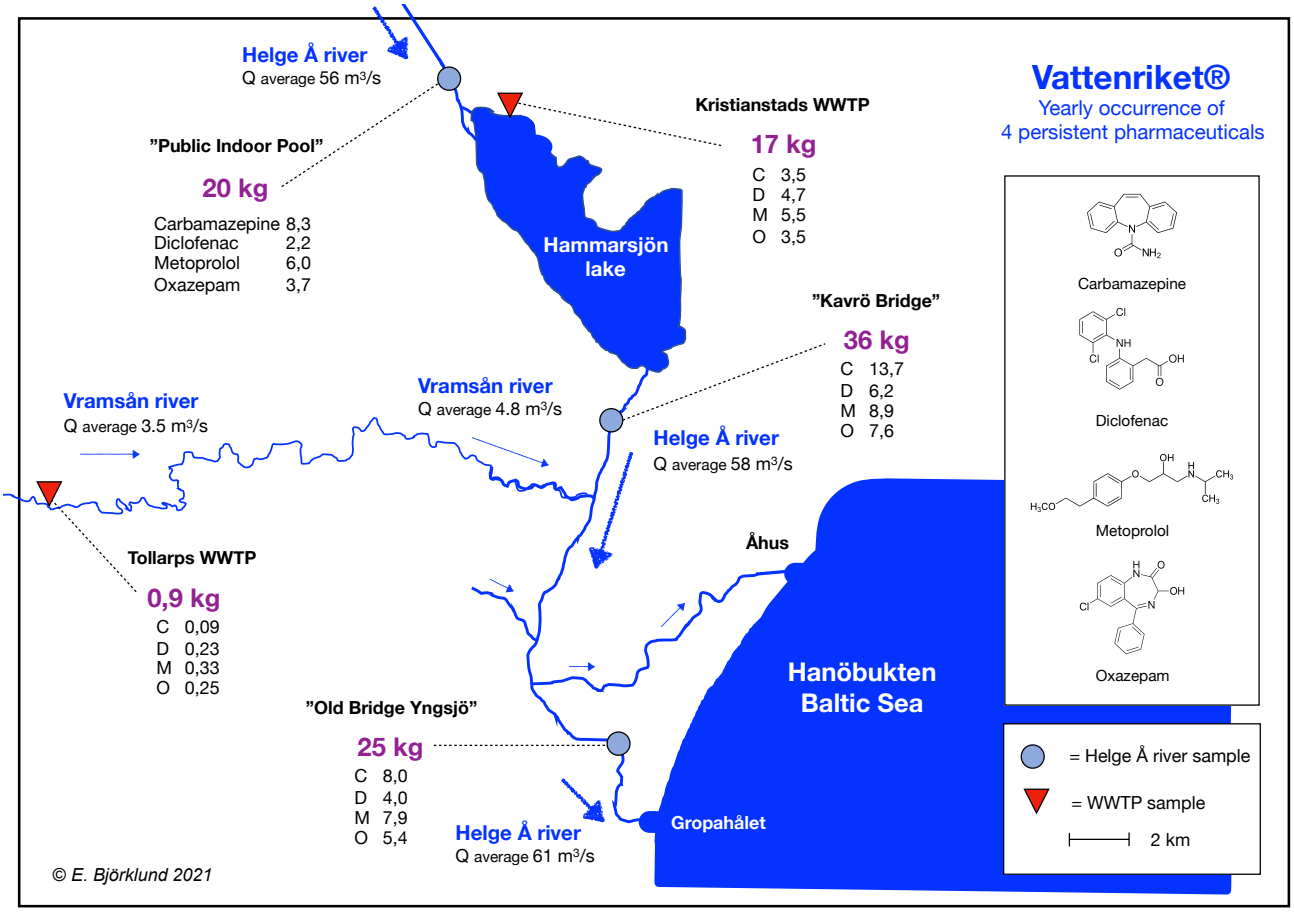
Downstream Kristianstad WWTP - Sampling points 2-4

Sampling points 2-4 were located in: a) the Hammarsjön lake 500 m downstream sampling point 1, b) the Helge Å river ca. 10 km downstream sampling point 1 c) the Helge Å river ca 20 km downstream sampling point 1, close to the exit of the river in the Baltic Sea. The concentrations observed followed a logical trend as the concentrations were lowered downstream in the river system. In Hammarsjön lake, 500 m downstream, 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). The relative decrease in concentrations downstream the entrance point in the lake (sampling point 1) was studied by dividing the entrance concentrations with the concentrations observed in sampling points 2-4. This was done for those six pharmaceuticals that were observed in all three downstream points; carbamazepine, oxazepam, metoprolol, diclofenac, erythromycin and sulfamethoxazole. A tendency of lower concentrations the closer to the outlet in the Baltic Sea the samples were taken was very clear for the summer samples. The average relative decrease at the three sampling points were 25 (500 m), 57 (10 km) and 99 (20 km). The relative concentration decrease was not identical for all pharmaceutical but were still within a factor of 4 for all compounds except one. This difference in relative decrease may indicate that other factors than dilution is at play, since pure dilution ideally would lead to the same relative concentration decrease for all compounds. Noteworthy was also that the difference in relative decrease in concentration between the two sampling points in Helge Å river, situated 10 km (sampling point 3) and 20 km (sampling point 4) downstream the entrance point of pharmaceuticals in the Hammarsjön lake, were quite substantial for many of the compounds, sometimes exceeding a factor of 2. Yet, the summer flow rates at these two sampling points were very similar with values of 24.0 m^3/s (10 km) and 25.3 m^3/s (20 km) giving a factor of only 1.1 higher dilution close to the outlet in the Baltic Sea. This also strongly indicates that factors apart from dilution is causing the larger relative decrease in concentration during the summer sampling between the two sites. Winter samples also had a tendency that the sampling point 500 m downstream in the lake (sampling point 2) showed a lower relative concentration decrease than the sampling point 10 km (sampling point 3) downstream, as also observed during the summer sampling. A major difference however was that the sampling point situated 20 km (sampling point 4) downstream had almost the same relative decrease in concentration as the 10 km point. This was clear when comparing the average relative decrease at the three sampling points which were 87 (500 m), 149 (10 km) and 131 (20 km). This also clearly showed that the relative concentration decrease was larger during winter than during summer for most compounds at all sampling stations. A plausible explanation to this is dilution as the volume of water in the Hammarsjön lake is much larger during the winter than during the summer due to much higher river flows. This was additionally supported by looking at the sampling point 10 km downstream were it could be seen that the relative concentration decrease was larger during winter than during summer. This also seems logical as the flow rate in the Helge Å river during winter and summer sampling were 114 m^3/s and 24 m^3/s, respectively at this point. Notable was also that the decrease in concentrations between sampling points 10 km and 20 km was less pronounced during the winter than during the summer. In the summer period the difference in dilution by the river was calculated to be a factor of 1.1 (above), despite a difference in relative decrease in concentration between sampling points 10 km and 20 km sometimes exceeding a factor of 2, indicating that other processes than dilution are at play in the summer. On the contrary, in the wither, the difference in relative decrease in concentration between these two sampling points most often were just below 1. Comparing the Helge Å river flow rates during the winter sampling showed that they were 114 m^3/s (10 km) and 119 m^3/s (20 km) giving a factor of only 1.04 higher dilution close to the outlet in the Baltic Sea. This shows that dilution may be the main parameter decreasing concentrations in the winter as biotic and abiotic processes most likely are less efficient during the colder period.

Chemical burden in the Hammarsjön lake, the Helge Å river system and the Baltic Sea

The chemical burden released into the Hammarsjön lake, the Helge Å river system and the Baltic Sea was calculated

for four common semi-persistent pharmaceuticals; carbamazepine, diclofenac metoprolol and oxazepam. This was possible by using the determined concentrations and the known water flows in the WWTPs and the river systems. These four pharmaceuticals occurred above their method quantification level (MQL) in the Helge Å river upstream Kristianstad WWTP, which made it possible to estimate the contribution from the Helge Å river into the Hammarsjön lake and compare it to the contribution of pharmaceuticals from Kristianstad WWTP into the same lake. Finally, the amount pharmaceuticals present in the Helge Å river a few kilometres upstream the river outlet in the Baltic Sea was calculated. Overall, this gave a rough picture of the yearly mass flow of these pharmaceuticals in the lower part of the Helge Å river system.



Both Helge Å river itself, upstream Hammarsjön lake and the WWTP at the entrance point into the Hammarsjön lake via the 1 500 m channel contributed to the total load of pharmaceutical. The sum of all four pharmaceuticals was ca. 20 kg from the Helge Å river system (sampling point "Public Indoor Pool") and ca. 17 kg from Kristianstads WWTP. At sampling point "Kavrö Bridge" downstream the Hammarsjön lake the estimated chemical load was calculated to 36 kg. The Vramsån river, which is roughly 10 times smaller than Helge Å river, had a chemical load from Tollarp WWTP of around 1 kg as a sum of the four pharmaceuticals. Further south at sampling point "Old Bridge Yngsjö" the total load was calculated to be 25 kg. A major part of this load will most likely reach the Hanöbukten bay. This study was limited to a summer sample and a winter sample, but with a few more seasonal samples the accuracy of the mass flow analysis could be improved.

The Vramsån river

The Vramsån river showed very low background levels of pharmaceuticals ranging from <MQL to around 6 ng/L. The top three compounds were paracetamol 5.6 ng/L (winter), naproxen 3.6 ng/L (winter) and diclofenac 1.7 ng/L (summer). None of the other pharmaceuticals were detected at concentrations exceeding 1.0 ng/L. The concentrations downstream Tollarp WWTP were higher than upstream. The top three were ibuprofen 30 ng/L (winter), metoprolol 18 ng/L (summer) and diclofenac 18 ng/L (summer). Calculations made showed higher loads in the river than those being released from Tollarp WWTP. This was likely caused by sampling in the river to close to the WWTP outlet (WWTP exit not known) giving to high concentrations due to insufficient dilution, thereby overestimating the river load.

The Segesholmsån river

The Segesholmsån river contained no detectable levels of pharmaceuticals in the upstream sample except for naproxen at 12 ng/L in the winter sample. Only a few compounds could be found in the downstream samples. In the 500 m downstream sample the top three were carbamazepine 52 ng/L (summer), oxazepam 8.6 ng/L (summer)

and diclofenac 7.8 ng/L (summer), while in the 8 km downstream sampling point, they were carbamazepine 45 ng/L (summer), oxazepam 8.0 ng/L (summer) and diclofenac 7.0 ng/L (summer). Calculating the yearly mass flow analysis showed very good conformity between the WWTP outlet masses and those calculated from river data. The WWTP outlet loads were 345 g of carbamazepine, 89 g of diclofenac, 17 g of metoprolol and 67 g of oxazepam, while river data 500 m downstream were 442 g, 89 g, 17 g and 81 g, respectively. Dividing the river concentrations in the 500 m downstream point with the WWTP outlet concentrations gave factors of 0.0077, 0.0060, 0.0060 and 0.0073 for carbamazepine, diclofenac, oxazepam and metoprolol, respectively. This is very close to the estimated dilution factor of the treated wastewater which was obtained by diving the yearly volume of wastewater eluted from Degeberga WWTP with the yearly flow in the river giving a value of 0.0060. Dilution thereby seems to be a major factor in the observed decrease in river concentrations.

Key facts of the MORPHEUS project

MORPHEUS is a project financed by the European Union Interreg South Baltic Programme for 36 months.

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 2017-2019.

The project has a total of 7 partners from four countries: Sweden, Germany, Poland and Lithuania:

1. Kristianstad University (Lead Partner) – Sweden
2. EUCC – The Coastal Union Germany – Germany
3. University of Rostock – Germany
4. Gdansk Water Foundation – Poland
5. Gdansk University of Technology – Poland
6. Environmental Protection Agency – Lithuania
7. Klaipeda University – Lithuania

The project includes a total of 10 associated partners from these countries.

For additional information on the project and activities please visit the MORPHEUS homepage at: http://www.morpheus-project.eu

Background to MORPHEUS

The background to MORPHEUS is the constant release of pharmaceuticals and other micro-pollutants via WWTPs to the South Baltic Sea.

Objectives of MORPHEUS

The project will combine information on upstream pharmaceuticals consumption patterns (**Work package 3**) with estimates of the downstream discharge of pharmaceuticals from a few selected WWTPs (**Work package 4**) located in the coastal regions Skåne (Sweden), Mecklenburg (Germany), Pomerania (Poland) and Klaipeda (Lithuania). Additionally, an inventory of the status of existing treatment technologies will be made available (**Work package 5**). This information will be gathered in collaboration with personnel at WWTPs and regional as well as national authorities, which are the key target groups of the project.

MORPHEUS will integrate information on pharmaceutical consumption (**WP 3**), existing technologies (**WP 5**), release rates and environmental occurrence (**WP 4**) in coastal regions in the South Baltic. This information will aid WWTPs and authorities in a future implementation of the most suitable advanced treatment technology.

The Regional Report in a MORPHEUS context

This report is a regional report from the Lead Partner at Kristianstads University, under **WP 4.** It presents the occurrence and release of pharmaceuticals from three Swedish WWTPs into three different recipients in Kristianstad Municipality, Region Skåne, all situated within the borders of the first UNESCO Biosphere Reserve in Sweden, Kristianstads Vattenrike – "*Vattenriket*®".

Each of the four regions in Sweden, Germany, Poland and Lithuania have their own data on the occurrence of pharmaceuticals in wastewater and surface waters based on chemical analyses from samples collected in the different regions. The regional results are summarized into a comprehensive report on pharmaceutical chemical burden in the four coastal regions which is **Deliverable 4.1** with the title "*Determination of the Regional Pharmaceutical Burden in 15 Selected WWTPs and Associated Water Bodies using Chemical Analysis*".

Where should we sample?

The County Administrative Board of Skåne, Sweden, in 2014 issued a supervisory guide entitled *"Läkemedelsrester i avloppsvatten"* [Drug residues in wastewater][1], **Figure 1**.

Figure 1. *The supervisory guide "Drug remnants in wastewater" issued by The County Administrative Board of Skåne in 2014".*

The County Board writes that "*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 2.**

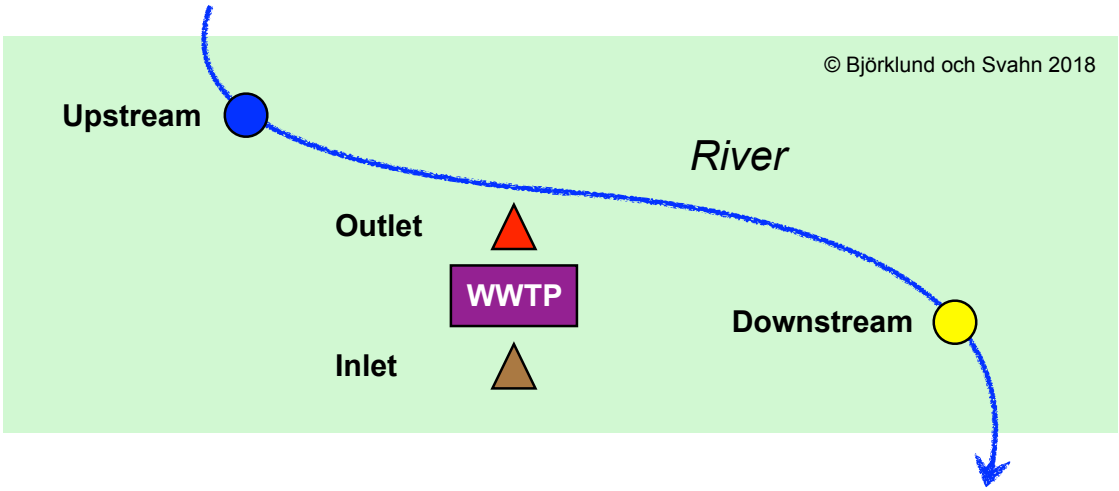


Figure 2. *Three sampling points proposed by the County Administrative Board of Skåne and a fourth sampling point at the wastewater treatment plant's inlet water.*

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 was also included as described in more detail below.

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

General about Kristianstads Vattenrike – ”Vattenriket®”

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®”*[2]. Only five Biosphere Reserves in Sweden are officially recognized by the United Nations agency UNESCO. *”Vattenriket®”* is the oldest of the Swedish biosphere reserves and covers an area of 35 x 35 km (1 040 km^2) which includes a variety of natural environments. This creates a large number of habitats which holds a large diversity of species of which many are red listed. According to the UNESCO program Man and Biosphere it is stated that[3]: “*Biosphere reserves are 'learning places for sustainable development'. They are sites for testing interdisciplinary approaches to understanding and managing changes and interactions between social and ecological systems, including conflict prevention and management of biodiversity. They are places that provide local solutions to global challenges. Biosphere reserves include terrestrial, marine and coastal ecosystems. Each site promotes solutions reconciling the conservation of biodiversity with its sustainable use.*”

On the homepage of “*Vattenriket®*” it is written that (translated from Swedish)[4]: “*Biosphere Reserve Kristianstads Vattenrike is an engine in the municipality's sustainability work. Vattenriket is also an important part of the Kristianstad brand and of creating an attractive municipality with a long-term sustainable living environment. Kristianstad Municipality's roadmap to 2020 emphasizes the importance of a rich nature and healthy ecosystems. It contains sub-goals for maintained and strengthened ecosystem services, strengthened status for endangered species and improved water status in Hanöbukten Bay.*”

In **Figure 3** the area of Kristianstad Municipality and “*Vattenriket®*” is shown together with the three WWTPs investigated in Kristianstad, Tollarp and Degeberga. Additionally, the three recipients Hammarsjön lake/Helge Å river, Vramsån river and Segesholmsån river are shown, which are the receiving water bodies of the three WWTPs, respectively. The occurrence of pharmaceuticals in “*Vattenriket®*” has been examined by the Lead Partner at Kristianstad University in a previous study[5], however the MORPHEUS project will provide a more in-depth knowledge of pharmaceuticals in the Biosphere Reserve.

Figure 3. *General overview of the borders of Kristianstad Municipality, the UNESCO Biosphere Reserve Kristianstads Vattenrike – “Vattenriket®”, the three investigated WWTPs in Kristianstad, Tollarp and Degeberga, and the three recipients Hammarsjön lake/Helge Å river, Vramsån river and Segesholmsån river.*

---

2 https://vattenriket.kristianstad.se/other-languages/english/

3 https://en.unesco.org/node/314143

4 https://vattenriket.kristianstad.se/uppdrag/

5 Pharmaceutical Residues Affecting the UNESCO Biosphere Reserve Kristianstads Vattenrike Wetlands: Sources and Sinks, Archives of Environmental Contamination & Toxicology, 71 (2016) 423–436. Björklund, O. Svahn, S. Bak, S. Oppong Bekoe, M. Hansen

Detailed overview of the three sampling sites

A general overview of the three sampling areas is shown in **Figure 4**. In total three WWTPs ending in three different river systems were sampled. 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 Helge Å river and was assumed to contain no pharmaceuticals.

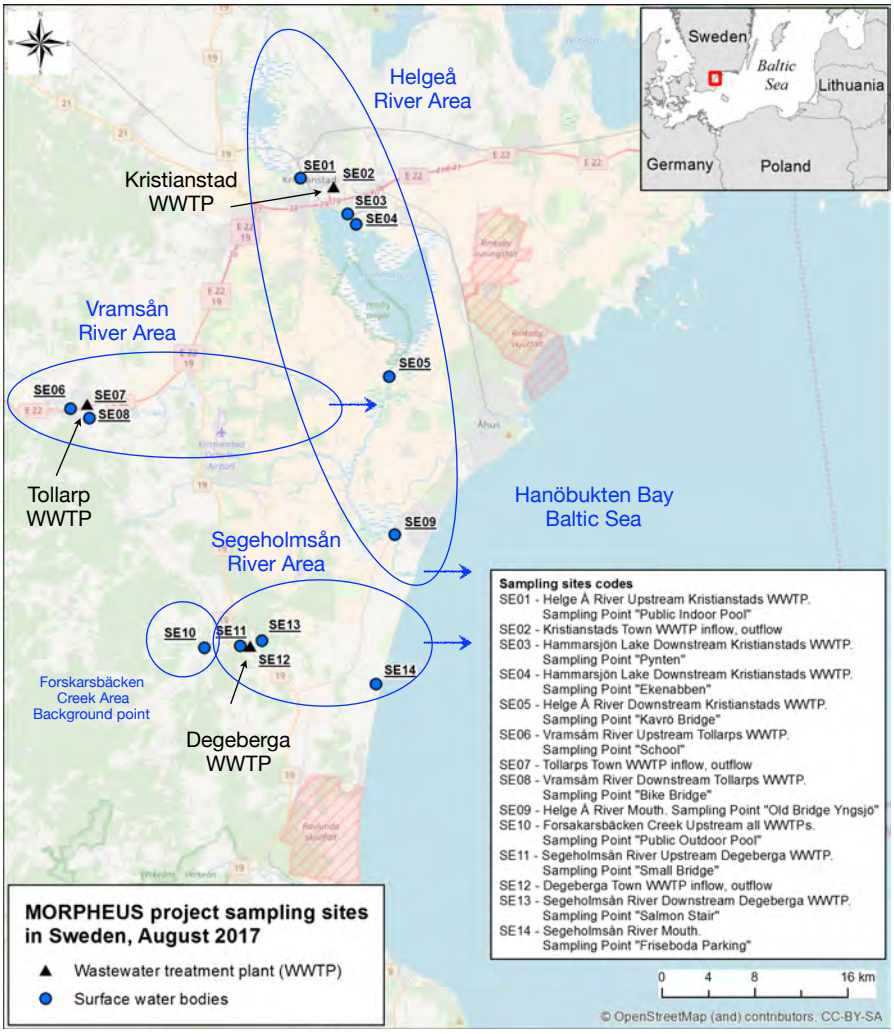


Figure 4. *General overview of the three sampling areas in Kristianstad Municipality, Region Skåne, Sweden in the summer sampling campaign in August 2017. These places were also sampled in February 2018 except for the background point in Forsakarsbäcken (SE10) which was excluded in the winter sampling campaign. All three WWTPs are situated in the UNESCO Biosphere Reserve Kristianstads Vattenrike – "Vattenriket®".*

A summary of the types and number of samples collected is shown in **Table 1**. In total 33 samples were analysed for their content of pharmaceuticals.

Table 1. *Summary of the types and number of samples collected during the summer sampling campaign August 2017 and winter sampling campaign February 2018.*

River Area + 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	-	-	-
Σ Samples of different types	Summer + Winter	7	6	6	14
Σ All Samples		**33**			

Site specific information on the 3 river areas

The three rivers Helge Å river, Vramsån river and Segesholmsån river represents very different rivers, the main difference being size. This is seen by their drainage areas which are approximately 4 725 km^2, 374 km^2 and 64 km^2, respectively. The Helge Å river and the Vramsån river drainage areas are therefore roughly 74 and 6 times larger than the Segesholmsån river drainage area. The length of the three rivers also differ and vary from almost 200 km for Helge Å river, to 55 km and 23 km, for Vramsån river and Segesholmsån river, respectively.

More site-specific information of the three rivers is given below.

Helge Å river area and Kristianstad WWTP

Helge Å river is almost 200 km long and has a drainage area of approximately 4 725 km². It is one of southern Sweden's largest rivers. In this project samples were taken at the lower part of the Helge Å river within the borders of Kristianstad Municipality before the river ends in the Hanöbukten Bay of the Baltic Sea as shown in **Figure 5**.

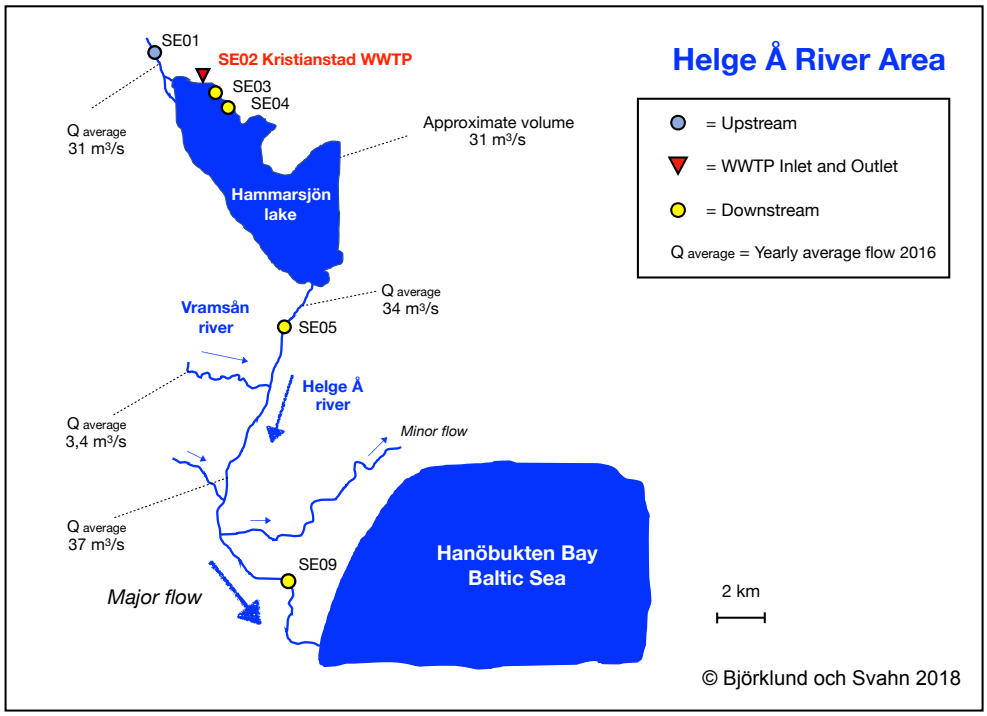


Figure 5. *Sampling points in Helge Å river area, Region Skåne, Sweden. Flow data from the report "Helge Å 2016".*

Overview sampling points in 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 south east of "Pynten" and is a classic recreational area. Two additional downstream sampling points in Helge Å river was taken at "Kavrö Bridge" (**SE05**) ca 10 km downstream **SE03** and "Old Bridge Yngsjö" (**SE09**) ca 20 km downstream **SE03**, which both were surface water samples. Photos of the six different sampling points **SE01**, **SE02**, **SE03**, **SE04**, **SE05** and **SE09** are shown in **Figure S1**. The photos represent the winter sampling campaign in February 2018.

General about Helge å river and Hammarsjön lake

Hammarsjön lake has an estimated volume of 782 000 m³. According to the homepage of *"Vattenriket®"* the entire river and lake system shown in **Figure 5** is only a few decimetres above sea level, and with the seasons the water level varies up to 2 meters[6]. 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. Moreover, just upstream sampling point **SE01** in **Figure 5**, 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 the 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 5** are collected from a recent report called "*Helge Å 2016*"[7], 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 "*WISS – Water Information System Sweden*" as described below.

---

[6] http://www.vattenriket.kristianstad.se/helgea/helgea.php

[7] HELGEÅN 2016 Kommittén för samordnad kontroll av Helgeån by Caroline Svärd och Elisabet Hilding at the company ALcontrol AB. Published 2017-05-08, 42 pages.

Flow of water in Hammarsjön lake and Helge Å river according to "*WISS – 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 5**) there is a large number of data available in WISS and therefore only a few strategically selected points were chosen 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 a) humus rich, brown, sour water from the north, b) nutritious, well-buffered water from the agricultural areas around Hässleholm and Kristianstad, and c) 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.

Based on sampling points **SE01**, **SE05** and **SE09** a total of 3 detailed flow profiles within WISS was selected. As sampling occurred in August 2017 and February 2018 the daily profiles for 365 days surrounding this period was chosen starting 3 months before the summer sampling and ending 3 months after the winter sampling, covering the period 2017-05-01 to 2018-04-30. The resulting flow profiles including the flow at the specific sampling dates are shown in **Figure S2a-c**. From this figure it can be seen that the flow during the selected period is higher than those reported for 2016 ($Q_{average} = 37\ m^3/s$) as indicated in **Figure 5**. The average flow is more in line with the average flow reported for 2014 in the report "*Helge Å 2016*" which was 54 m³/s. It can also 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** (**Figure S2a**), **SE05** (**Figure S2b**) and **SE09** (**Figure S2c**), 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 in **Figure 6**, and also in **Figure 5** above.

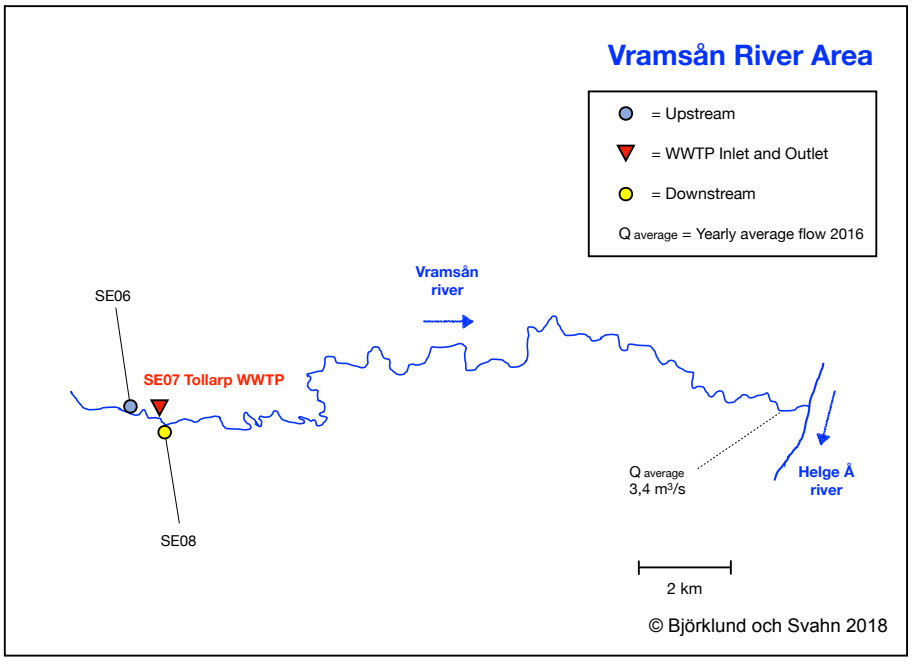


Figure 6. *Sampling points in Vramsån river area, Region Skåne, Sweden. Flow data from the report "Helge Å 2016".*

Overview sampling points in 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 S3**. The photos 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 flow in Vramsån river varies over the year, and the average flow rate for 2016 is presented in **Figure 6**. This figure was collected from the recent report "*Helge Å 2016*" (see above), stating a flow of 3.4 m^3/s, just before Vramsån river becomes part of the Helge Å river and its flow. 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*"

Based on sampling points **SE06** and **SE08** two detailed flow profiles within WISS was selected. The profiles covered the same period as described for Helge Å river above (2017-05-01 to 2018-04-30). The resulting flow profiles including the flow at the specific sampling dates are shown in **Figure S4a-b**. In this figure it can be seen that the outflow of Vramsån river in Helge Å river during the selected period was 4.83 m^3/s which exceeds that reported for 2016 ($Q_{average} = 3.4\ m^3/s$) as indicated in **Figure 6**. Additionally, 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** (**Figure S4a**) and to the outflow in Helge Å river (**Figure S4b**), respectively.

Segesholmsån river area and Degeberga WWTP

Segesholmsån river has a length of 23 km and a drainage area of approximately 64 km^2. The river ends directly in the Hanöbukten Bay, Baltic Sea as shown in **Figure 7**.

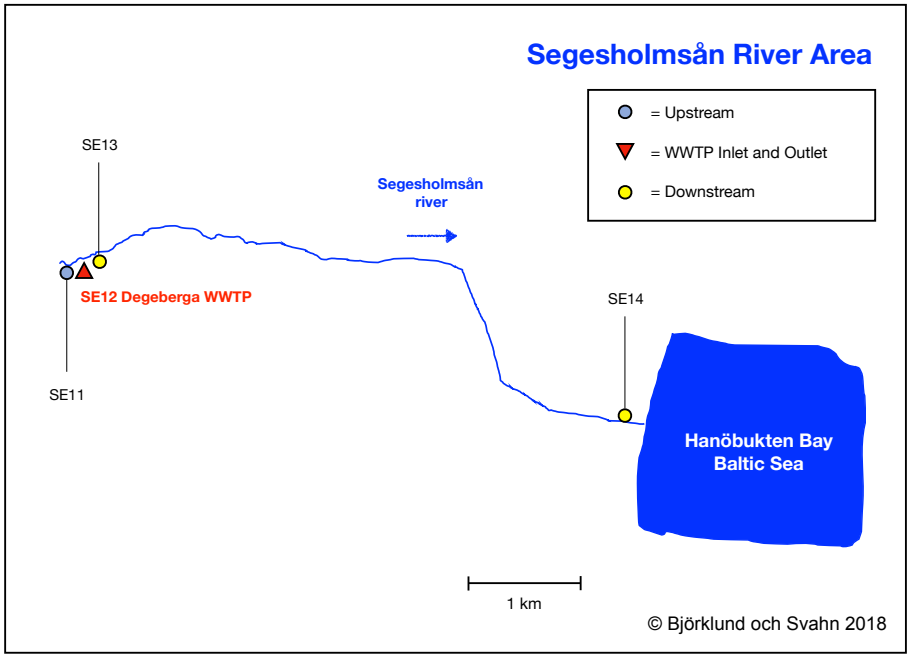


Figure 7. *Sampling points in Segesholmsån river area, Region Skåne, Sweden.*

Overview sampling points in Segesholmsån river.

Segesholmsån river 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**) ca. 500 m downstream. A third surface samples was taken further downstream Segesholmsån river inside a nature reserve called Friseboda. The sampling is called "Friseboda Parking" (**SE14**) ca 8 km downstream. Photos of the four different sampling points **SE11**, **SE12**, **SE13** and **SE 14** are shown in **Figure S5**. The photos 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. The flow in Segesholmsån river is smaller than that of Vramsån river and is around 0.6 m^3/s, just before it enters Hanöbukten Bay in the Baltic Sea. More specific information on flow rates was gathered via the system "*WISS – Water Information System Sweden*".

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

Based on sampling points **SE11**, **SE13** and **SE14** a total of two detailed flow profiles within WISS was selected. The profiles covered the same period as described for Helge Å river above (2017-05-01 to 2018-04-30). The resulting flow profiles including the flow at the specific sampling dates are shown in **Figure S6a-b**. In this figure it can be seen that the outflow of Segesholmsån river in Hanöbukten Bay during the selected period was 0.783 m^3/s. The sampling occasions also 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** (**Figure S6a**) and the outflow in the Baltic Sea **SE14** (**Figure S6b**), respectively.

Chemical analysis

Analysing pharmaceuticals in polluted water, which in some cases occur at very low concentrations, requires special analysis methods based on a technique called liquid chromatography combined with tandem mass spectrometry (LC-MS/MS). In this project a flexible and robust method developed by O. Svahn and E. Björklund in the chemical analysis laboratory **MoLab**, Kristianstad University, Sweden was applied[8,9]. 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[10]. 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 2** together with their Method Quantification Limits (MQL).

Table 2. *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 hormones
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

[8] 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. Björklund

[9] Tillämpad miljöanalytisk kemi för monitorering och åtgärder av antibiotika- och läkemedelsrester i Vattenriket, Svahn 2016 [Applied environmental analytical chemistry for monitoring and measures regarding antibiotics and drug residues in Vattenriket, Svahn 2016]

[10] 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.

Sampling

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.

Three wastewater treatment plants (WWTPs) in Kristianstad Municipality, Region Skåne

The 3 WWTPs in Kristianstad, Tollarp and Degeberga represent different types of plants. One of the main differences is size. As seen from **Figure 8** 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 8**, Kristianstad municipality have several 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 and UNESCO Biosphere Reserve "*Vattenriket*®". In the next section a more comprehensive overview of the three WWTPs included in MORPHEUS is outlined.

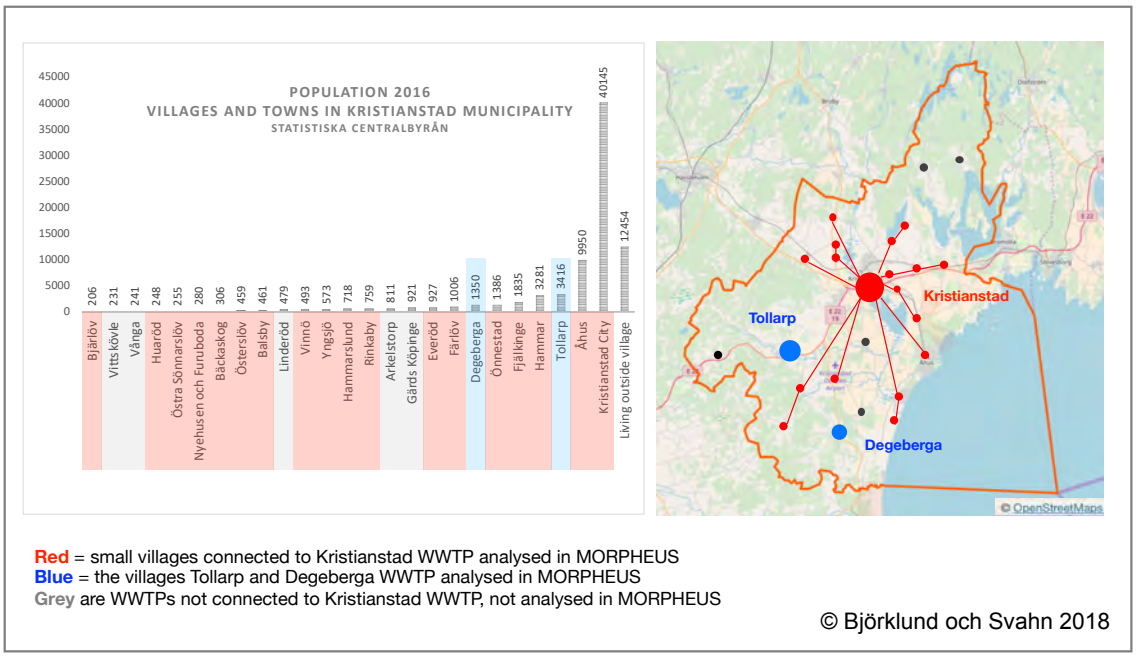


Figure 8. *To the left is seen an overview of the number of people in villages with at least 200 inhabitants within Kristianstads municipality 2016 according to official Swedish statistics. To the right is seen the connection of 17 villages via pipes to Kristianstads WWTP (red), Tollarp and Degeberga 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 3**, while the treatment steps used in each WWTP are shown in a summarized form in **Table 4**.

Table 3. *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 BOD_7 to the WWTP
2) Calculated number based on total incoming BOD_7 from the industries
3) Calculated as annual volume divided by 365 days

Table 4. *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 treatment.	Yes Sand filter.

The annual volume treated water in 3 WWTPs varied from 79 000 m^3 in Degeberga to 8 186 000 m^3 in Kristianstad. The relative size of the WWTPs based on annual volumes of treated water, assigning Degeberga WWTP a value of 1, thereby varies with a factor of 104 as seen in **Figure 9**.

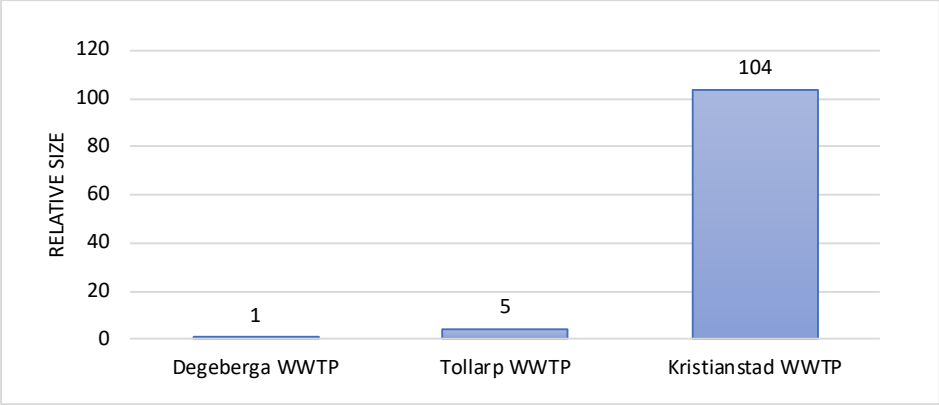


Figure 9. *The relative size of the WWTPs based on annual volumes of treated water based on Degeberga WWTP assigned a value 1 corresponding to approx. 79 000 m^3 treated water/year.*

The daily and hourly flow of water varied from 216 m^3/day (9.0 m^3/h) at Degeberga WWTP to 22 427 m^3/day (934 m^3/h) at Kristianstad WWTP, respectively; a factor of 103. The actual number of PE is also very different, from 915 PE in Gärds Köpinge WWTP to 118 000 PE in Kristianstad WWTP; a factor of 129. Both Kristianstad and Tollarp WWTP have a large component of industrial water, while Degeberga WWTP only has wastewater from households.

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 have a sand filter step while Tollarp does not.

Results of pharmaceutical analyses

In total 15 pharmaceuticals were investigated as shown in **Table 2** above. The results from the chemical analyses are shown in **Table 5** and **Table 6** below. **Table 5** shows inlet and outlet concentrations from the 3 WWTPs, while **Table 6** shows upstream and downstream surface water concentrations in rivers and lakes. The summarized concentration data (ng/L) in **Table 5** and **Table 6** are discussed and graphically presented in the following sections, as well as calculations of the total chemical burden in g/year.

Table 5. *Inlet and outlet concentrations in ng/L of 15 pharmaceuticals from 3 WWTPs operated by Kristianstad Municipality; Kristianstad WWTP, Tollarp WWTP and Degeberga WWTP. These 3 WWTPs are labelled sampling points SE02, SE07 and SE12, and their geographical locations are shown in Figure 5, Figure 6 and Figure 7, respectively, while an overview of all 3 WWTPs is shown in Figure 4. Samples were collected at two seasons; Summer (August 2017) and Winter (February 2018). In this table, the WWTPs are listed in order of size while pharmaceuticals are listed in alphabetical order. Samples were taken by personnel at the WWTP and sample type differed somewhat between the WWTPs and between seasons. The method quantification limits (MQL) are shown in Table 2. 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	Inlet concentrations						Outlet concentrations					
	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

Table 6. *Upstream and downstream concentrations in ng/L of 15 pharmaceuticals in 3 rivers; Helge Å river, Vramsån river and Segesholmsån river. Their geographical locations are shown in Figure 5, Figure 6 and Figure 7, respectively, while an overview of all 3 rivers is shown in Figure 4. Samples were collected at two seasons; Summer (August 2017) and Winter (February 2018) as well as upstream and downstream the 3 WWTPs presented in Table 5. The method quantification limits (MQL) are shown in Table 2. 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. Carbamazepine, diclofenac, metoprolol and oxazepam are highlighted as the mass load into the Hammarsjön lake, the Helge Å river system and the Baltic Sea is calculated in this report.*

Compound	Forsakars-bäcken Creek		Helge Å river										Vramsån river				Segesholmsån river					
	Summer & Winter																					
	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*	-	-	-	-	-	-

Discussion

In the following sections the results from the chemical analyses (**Table 5** and **Table 6)** are discussed and in some cases compared to a recent study from Region Scania called *LUSKA 2017* covering 8 Scanian WWTPs investigated in April 2017[11] .

Inlet concentrations (ng/L) of 15 pharmaceuticals in 3 WWTPs

The presence of pharmaceuticals in the wastewater is shown in **Figure 10a-c**, where compounds are sorted from the highest to the lowest based on the inlet water concentration in Kristianstads WWTP during the summer sampling campaign. Outlet concentrations are shown in **Figure 12a-c** in a later section using the same scale for an easier comparison.

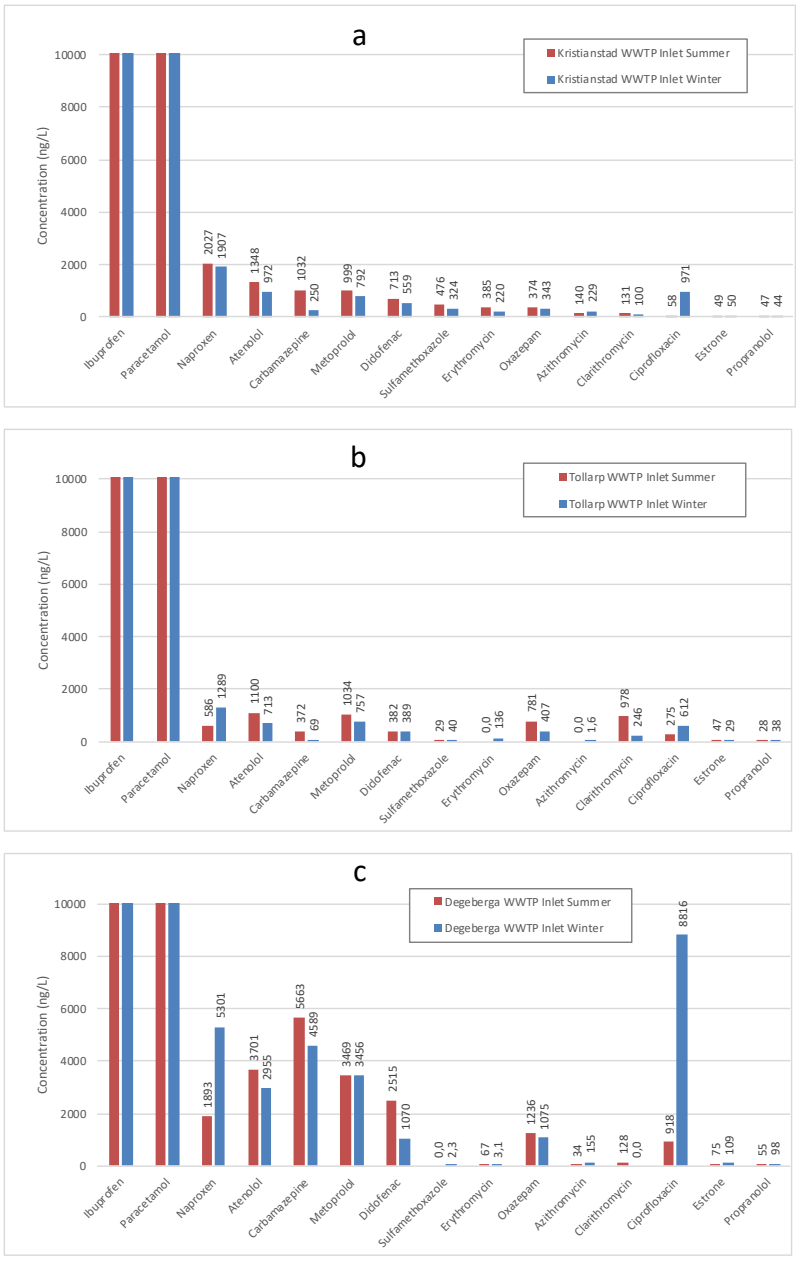


Figure 10. *Inlet concentrations (ng/L) of 15 pharmaceuticals at Kristianstad (a), Tollarp (b) and Degeberga (c) WWTP during summer and winter sampling. In this figure all pharmaceuticals are sorted according to the inlet water concentration at Kristianstads WWTP during the summer sampling campaign 2017, from the highest to the lowest concentration. For additional information see text.*

[11] 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.

Inlet concentrations – ibuprofen and paracetamol

In **Figure 10a-c** the inlet concentrations of ibuprofen and paracetamol by far exceeds any of the other pharmaceuticals and are therefore not visual in the figure.

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). Corresponding ibuprofen data from *LUSKA 2017* was 4 939-37 144 ng/L (a factor 7.5), while paracetamol was not investigated. Especially Degeberga showed very high incoming concentrations as compared to the other WWTPs and to *LUSKA 2017*. Looking at the data in **Table 5** 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 (**Figure 10a-c**).

Inlet concentrations – naproxen, atenolol, carbamazepine, metoprolol, diclofenac and oxazepam

Figure 10a shows the inlet concentrations for Kristianstad WWTP listed from highest to lowest based on the summer sampling campaign 2017. 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 (**Figure 10b**). 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 (**Figure 10c**).

The pattern at Tollarp WWTP is not fully the same as that observed in Kristianstad as seen from **Figure 10b**. 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 in **Figure 10c**, the 5 top summer pharmaceuticals were the same as those in Kristianstad, but with a different order; carbamazepine, atenolol, metoprolol, diclofenac and naproxen. **Figure 10c** also clearly shows the general trend of higher inlet concentrations in Degeberga than in Kristianstad WWTP (**Figure 10a**) and Tollarp WWTP (**Figure 10b**) as all figures use the same scale on the y-axis.

Looking in more detail at individual pharmaceuticals and their potential seasonal variation based on the order presented in **Figure 10a** and concentration data in **Table 5** leads to a few observations.

Naproxen had a concentration range from 586-5 301 ng/L (a factor 9.0) and *LUSKA 2017* was in the same range from 1 059-4 353 ng/L (a factor 4.1). 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. Atenolol was not analysed in *LUSKA 2017*.

Carbamazepine had concentrations between 69-5 663 ng/L (a factor 82) while in *LUSKA 2017* they ranged from 57-1 179 ng/L (a factor 21). Especially Degeberga showed very high incoming concentrations as compared to the other WWTPs and to *LUSKA 2017*. 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) and in the same range as in *LUSKA 2017* that were between 747-2 196 ng/L (a factor 2.9). 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) which was close to *LUSKA 2017* with concentrations between 486-1 059 ng/L (a factor 2.2). 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) which can be compared to *LUSKA 2017* having concentrations between 88-418 ng/L (a factor 4.8). 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.

Inlet concentrations – estrone and propranolol

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. In *LUSKA 2017* estrone varied between 12-68 ng/L (a factor 5.7). 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. Propranolol was not analysed in *LUSKA 2017*.

Inlet concentrations – antibiotics

Antibiotics is a group of special concern and their inlet concentrations are shown separately in **Figure 11**. This figure is identical in structure to **Figure 14** below, which shows corresponding outlet concentrations of antibiotics.

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) which can be compared to the concentration interval of 48-871 ng/L (a factor 18) in *LUSKA 2017*. 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 which is close to *LUSKA 2017* ranging from 63-625 ng/L (a factor 9.9). 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. Azithromycin was not analysed in *LUSKA 2017*.

Clarithromycin ranged in concentration from below MQL to 978 ng/L as compared to *LUSKA 2017* with a concentration range from below MQL to 293 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 which can be compared to *LUSKA 2017* with concentrations in the interval below MQL to 686 ng/L. The average summer and winter concentrations in this study were 151 ng/L and 119 ng/L, respectively.

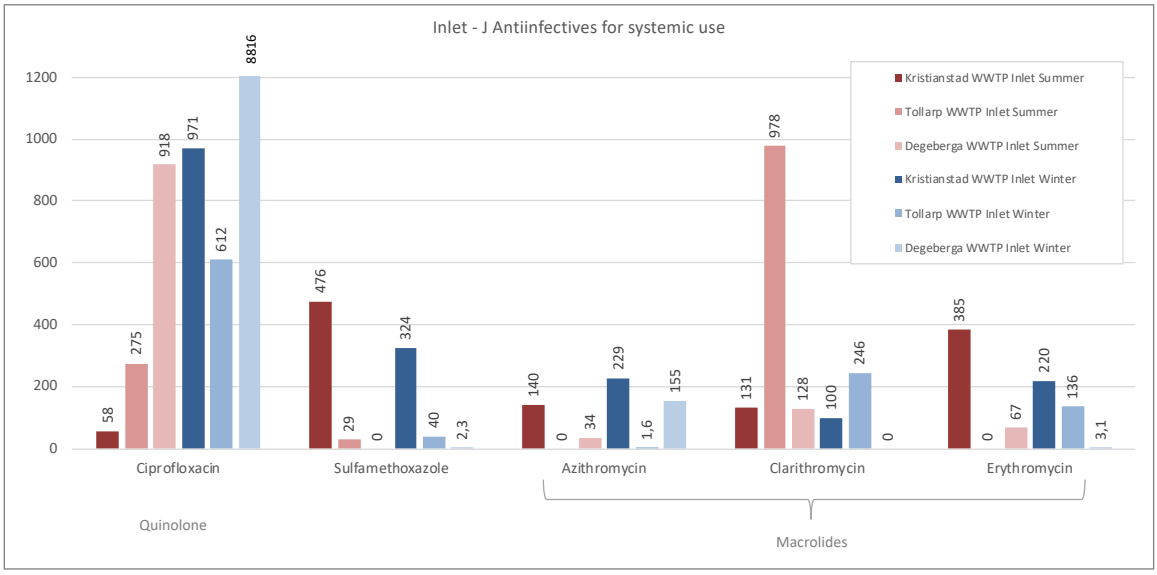


Figure 11. *Inlet concentrations (ng/L) of 5 antibiotics at Kristianstad, Tollarp and Degeberga WWTP during summer and winter sampling. To simplify comparison this figure is visualized in the same scale as Figure 14 below which has the same general structure but shows antibiotic outlet concentrations for the same WWTPs. For additional information see text.*

Summary seasonal average inlet concentrations of 3 WWTPs

In order to identify any potential differences in inlet concentrations between seasons the average of all summer concentrations and of all winter concentrations at the 3 WWTPs for each pharmaceutical were calculated (same as those discussed in the section above). These average concentrations are summarized in **Table 7** below.

Table 7. *Average inlet concentrations in ng/L of the 15 pharmaceuticals in the 3 WWTPs operated by Kristianstad Municipality; Kristianstad WWTP, Tollarp WWTP and Degeberga WWTP These 3 WWTPs are labelled sampling points SE02, SE07 and SE12, and their geographical locations are shown in Figure 5, Figure 6 and Figure 7, respectively, while an overview of all 3 WWTPs is shown in Figure 4. Samples were collected at two seasons; Summer (August 2017) and Winter (February 2018). The highest concentration is marked in the colour of the season. The last column shows how many percent higher the highest season concentration obtained is in relation to the lowest season concentration.*

	Seasonal Average Inlet Concentrations 3 WWTPs		Percentual difference
Compound	Summer	Winter	(%)
Ibuprofen	141 640	64 579	119
Paracetamol	34 873	27 928	25
Carbamazepine	2 356	1 636	44
Atenolol	2 050	1 546	33
Metoprolol	1 834	1 668	10
Naproxen	1 502	2 832	89
Diclofenac	1 203	672	79
Oxazepam	797	608	31
Ciprofloxacin	417	3 466	731
Clarithromycin	412	115	257
Sulfamethoxazole	168	122	38
Erythromycin	151	119	26
Azithromycin	58	128	120
Estrone	57	62	10
Propranolol	44	60	37

In total 10 out of 15 pharmaceuticals showed higher average inlet concentrations during the summer season than during the winter season; ibuprofen, paracetamol, carbamazepine, atenolol, metoprolol, diclofenac, oxazepam, clarithromycin, sulfamethoxazole and erythromycin. For these pharmaceuticals the summer inlet concentrations were in the order of 10% to 257% higher.

During the winter season 5 out of 15 pharmaceuticals showed higher average inlet concentrations; naproxen, ciprofloxacin, azithromycin, estrone, propranolol. For these pharmaceuticals the summer inlet concentrations were in the order of 10% to 731% higher. However, the ciprofloxacin value in the small Degeberga WWTP was very high, and if excluding this compound, the other compounds ranged from being 10% to 120% higher.

Overall, the data shows a slight tendency towards higher concentrations for a majority of the pharmaceuticals in the inlet water during the summer period.

Inlet chemical load (g/year) of 15 pharmaceuticals in 3 WWTPs

An estimate of the chemical load of pharmaceuticals into each individual WWTP expressed as g/year was calculated based on the incoming concentrations (**Table 5**) and the knowledge of the total volume of treated wastewater/year (**Table 3**). 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 8**.

Table 8. *Average inlet concentrations in ng/L of the 15 pharmaceuticals and inlet chemical load (g/year) at each of the 3 WWTPs operated by Kristianstad Municipality; Kristianstad WWTP, Tollarp WWTP and Degeberga WWTP. These 3 WWTPs are labelled sampling points SE02, SE07 and SE12, and their geographical locations are shown in Figure 5, Figure 6 and Figure 7, respectively, while an overview of all 3 WWTPs is shown in Figure 4. The compounds are sorted from highest to lowest based on inlet concentrations at Kristianstad WWTP. For details of calculations see text.*

Compound	Average Inlet Concentrations Summer + Winter (ng/L)			Inlet Chemical Load (g/year)		
	Kristianstad SE02	**Tollarp** SE07	**Degeberga** SE12	**Kristianstad** SE02	**Tollarp** SE07	**Degeberga** SE12
Ibuprofen	44 859	33 997	230 472	367 217	12 273	18 207
Paracetamol	21 007	30 719	42 477	171 960	11 090	3 356
Naproxen	1 967	938	3 597	16 100	338	284
Atenolol	1 160	907	3 328	9 495	327	263
Metoprolol	895	896	3 463	7 329	323	274
Carbamazepine	641	220	5 126	5 244	80	405
Diclofenac	636	386	1 792	5 203	139	142
Ciprofloxacin	514	444	4 867	4 210	160	384
Sulfamethoxazole	400	35	1.2	3 278	12	0.1
Oxazepam	358	594	1 155	2 934	214	91
Erythromycin	302	68	35	2 473	24	2.8
Azithromycin	185	0.8	94	1 511	0.3	7.5
Clarithromycin	115	612	64	944	221	5.1
Estrone	49	38	92	405	14	7.2
Propranolol	45	33	76	372	12	6.0
Total chemical load in g/year				598 673	25 229	23 435
Total chemical load in kg/year				599	25	23
Total chemical load in g/year excl. ibuprofen and paracetamol				59 497	1 866	1 872
Total chemical load in kg/year excl. ibuprofen and paracetamol				59	1.9	1.9

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. From **Table 8** it is also clear that 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 ibuprofen and paracetamol.

Outlet concentrations (ng/L) of 15 pharmaceuticals in 3 WWTPs

The outlet concentrations from the 3 WWTPs are shown in **Figure 12a-c**. In this figure all pharmaceuticals are once again sorted from the highest to the lowest based on the inlet water concentration to Kristianstads WWTP during the summer sampling campaign, in the same way as for inlet water concentrations in **Figure 10a-c** above. The first observation to be made is that the inlet concentrations shown in **Figure 10a-c** were not very well correlated with outlet concentrations for all of the pharmaceuticals. This is most evident for ibuprofen and paracetamol which both occur at inlet concentrations exceeding the other pharmaceuticals by tenths to thousand folds, yet their outlet concentrations were in most cases similar to or lower than the other compounds. The lack of correlation between inlet and outlet concentrations is caused by differences in the WWTPs ability to remove various pharmaceuticals from wastewater. These differences are discussed separately below in the section presenting removal efficiencies for the various WWTPs.

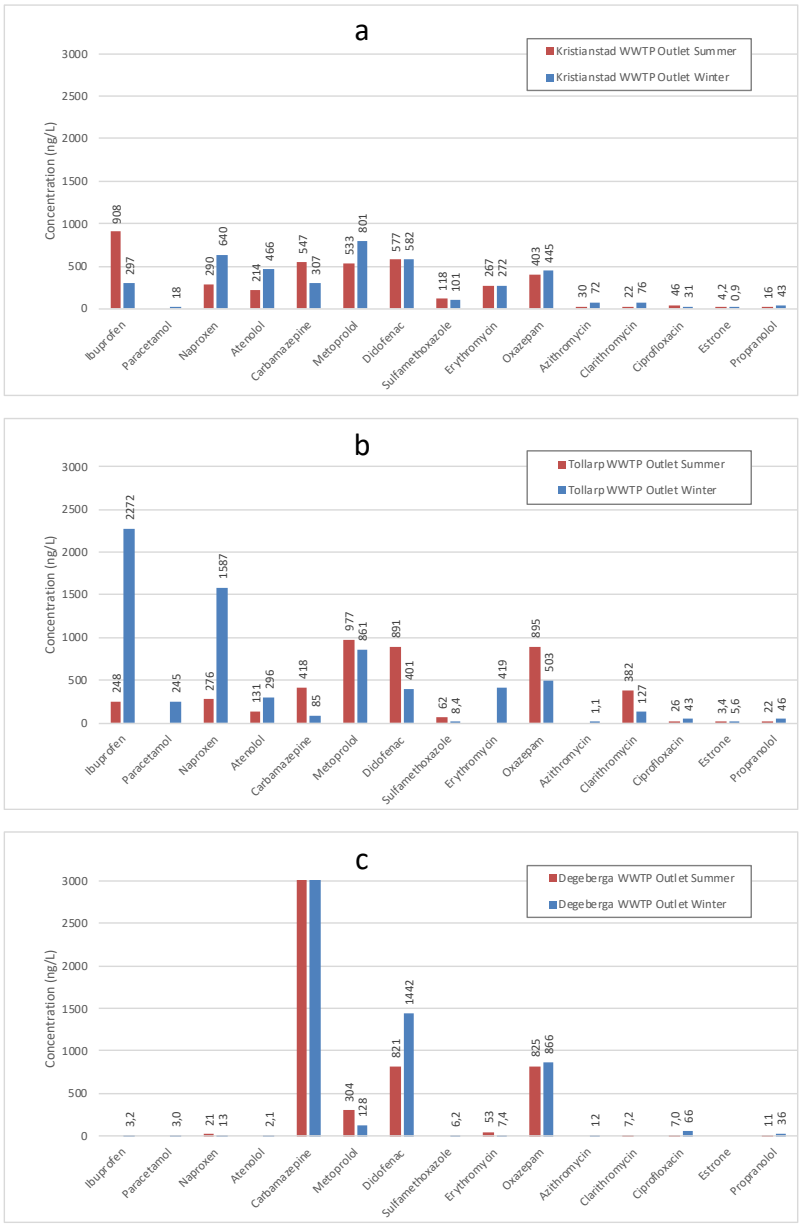


Figure 12. *Outlet concentrations (ng/L) of 15 pharmaceuticals at Kristianstad (a), Tollarp (b) and Degeberga (c) WWTP during summer and winter sampling. In this figure all pharmaceuticals are sorted according to the inlet water concentration at Kristianstads WWTP during the summer sampling campaign 2017, from the highest to the lowest concentration as in Figure 10 above. Figure 10 and 12 are equally scaled for an easier comparison. For additional information see text.*

In order to get an overview of which pharmaceuticals that were released to the highest extent to the receiving recipient the concentrations were ranked from highest to lowest at each WWTP and during each season as shown in **Figure 13 a-f**. For a better overview the compounds were also grouped by horizontal lines into three groups based on their concentration level for each WWTP and season. The groups were >100 ng/L, 10-100 ng/L, and <10 ng/L. The pharmaceuticals are shortly discussed successively according to the outlet concentrations at Kristianstads WWTP during the summer sampling campaign in **Figure 13a** and concentration data in **Table 5**, except for the antibiotics which are discussed separately at the end of this section.

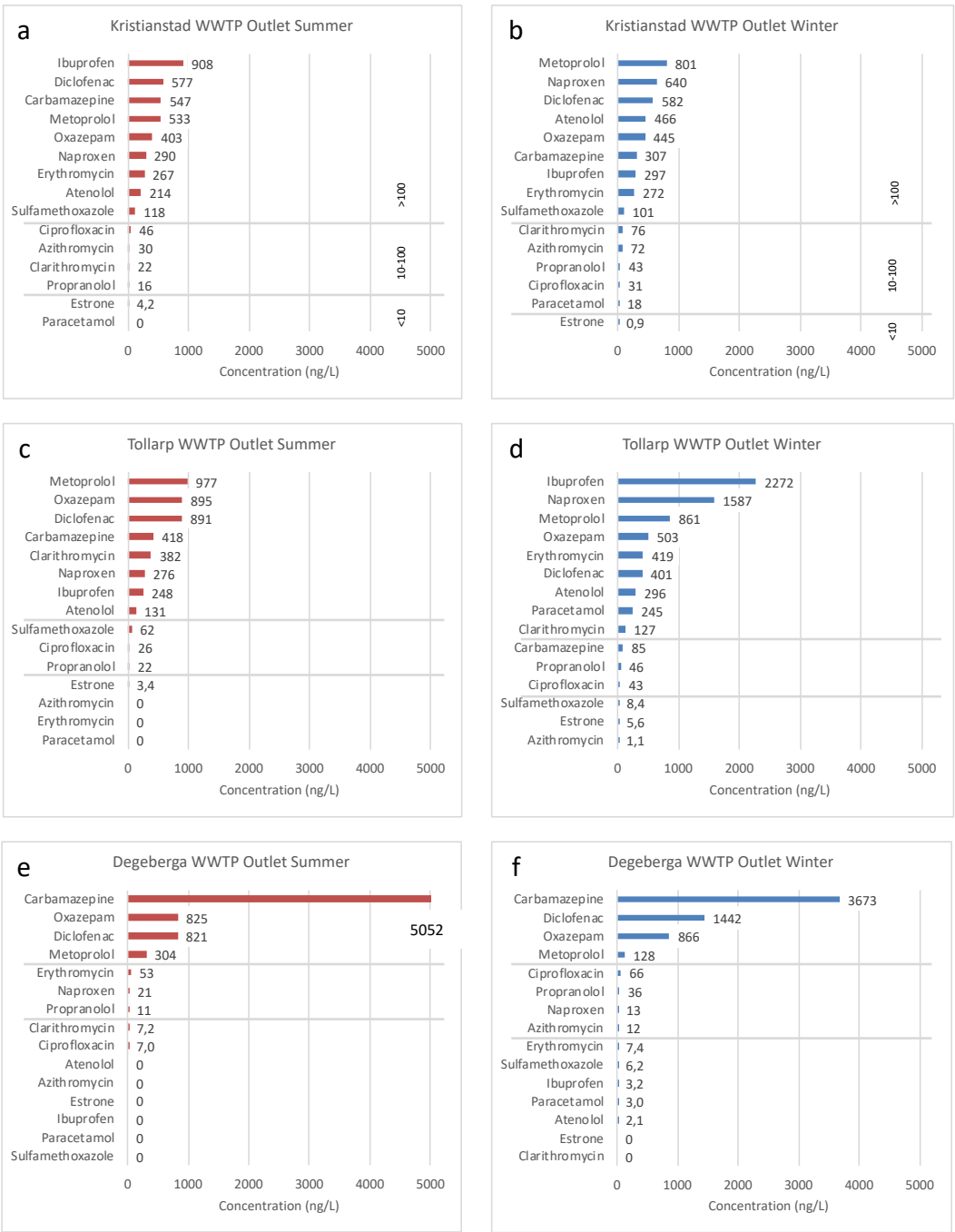


Figure 13. *Outlet concentrations (ng/L) of 15 pharmaceuticals at Kristianstad WWTP summer (a) and winter (b), Tollarp WWTP summer (c) and winter (d), and Degeberga WWTP summer (e) and winter (f). In this figure the pharmaceuticals are sorted according to the outlet water concentration at each WWTP and season, from the highest to the lowest concentration. Figure a-f are all scaled equally. For additional information see text.*

Outlet concentrations – all pharmaceuticals except antibiotics

Ibuprofen was present at outlet concentrations ranging from below MQL to 2 272 ng/L meaning a very large variation. This corresponds well with *LUSKA 2017* which showed concentrations below MQL and 1 158 ng/L. Looking at the data in **Table 5** 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) which was very close to the interval found in *LUSKA 2017* of between 442-1 117 ng/L (a factor 2.5). 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. Corresponding interval in *LUSKA 2017* was 139-699 ng/L (a factor 5.0). 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) which was very close to the *LUSKA 2017* study. 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) and was of the same size as *LUSKA 2017* with concentrations between 692-1 433 ng/L (a factor 2.1). 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) while *LUSKA 2017* had an interval from 95-475 ng/L (a factor 5.0). 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. *LUSKA 2017* ranged from 119-1 430 ng/L (a factor 12). 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. Atenolol was not analysed in *LUSKA 2017*.

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 an 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. Propranolol was not analysed in *LUSKA 2017*.

Estrone was present at very low concentrations in all outlet waters and varied between below MQL and 5.6 ng/L. Outlet concentrations in *LUSKA 2017* varied between 1-63 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. Paracetamol was not analysed in *LUSKA 2017*.

Outlet concentrations – antibiotics

As mentioned above antibiotics are a group of special concern and their outlet concentrations are shown separately in **Figure 14**. For a simpler comparison this figure is identical in structure to **Figure 11** above which shows corresponding inlet concentrations of antibiotics.

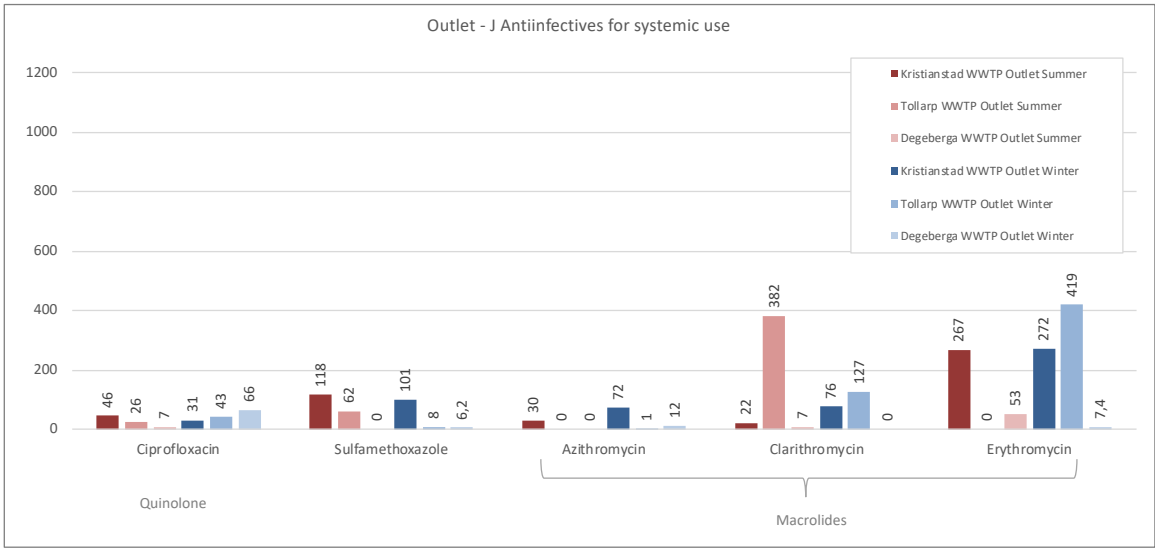


Figure 14. *Outlet concentrations (ng/L) of 5 antibiotics at Kristianstad, Tollarp and Degeberga WWTP during summer and winter sampling. To simplify comparison this figure is visualized in the same scale as Figure 11 above which has the same general structure but shows antibiotic inlet concentrations for the same WWTPs. For additional information see text.*

Ciprofloxacin ranged in concentration from 7-66 ng/L (a factor 9.4) and it varied less than the inlet concentrations. In *LUSKA 2017* outlet concentration were below MQL. 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, while *LUSKA 2017* ranged below MQL to 281 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. Azithromycin was not analysed in *LUSKA 2017*.

Clarithromycin ranged in concentration from below MQL to 382 ng/L as compared to *LUSKA 2017* ranging below MQL and 213 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 and *LUSKA 2017* had an interval between 1-640 ng/L. No seasonal trend was obvious and the average summer and winter concentrations were 107 ng/L and 233 ng/L, respectively.

Summary seasonal average outlet concentrations of 3 WWTPs

In an attempt to detect any potential differences in outlet concentrations between seasons the average of all summer concentrations and of all winter concentrations at the 3 WWTPs for each pharmaceutical were calculated in the section above. These average concentrations are summarized in **Table 9** below.

Table 9. *Average outlet concentrations in ng/L of the 15 pharmaceuticals in the 3 WWTPs operated by Kristianstad Municipality; Kristianstad WWTP, Tollarp WWTP and Degeberga WWTP These 3 WWTPs are labelled sampling points SE02, SE07 and SE12, and their geographical locations are shown in Figure 5, Figure 6 and Figure 7, respectively, while an overview of all 3 WWTPs is shown in Figure 4. Samples were collected at two seasons; Summer (August 2017) and Winter (February 2018). The highest concentration is marked in the colour of the season. The last column shows how many percent higher the highest season concentration obtained is in relation to the lowest season concentration.*

	Seasonal Average Outlet Concentrations 3 WWTPs		Percentual difference
Compound	Summer	Winter	(%)
Carbamazepine	2,006	1,355	48
Diclofenac	763	808	6
Oxazepam	708	605	17
Metoprolol	605	597	1
Ibuprofen	385	857	122
Naproxen	196	747	282
Clarithromycin	137	68	101
Atenolol	115	255	122
Erythromycin	107	233	119
Sulfamethoxazole	60	38	56
Ciprofloxacin	26	47	77
Propranolol	16	42	158
Azithromycin	10	28	171
Estrone	3	2	15
Paracetamol	0	89	48

In total 9 out of 15 pharmaceuticals showed higher average outlet concentrations during the winter season than during the summer season; diclofenac, ibuprofen, naproxen, atenolol, erythromycin, ciprofloxacin, propranolol, azithromycin and paracetamol. For these pharmaceuticals the winter outlet concentrations were in the order of 6% to 282% higher.

During the summer season 6 out of 15 pharmaceuticals showed higher average outlet concentrations; carbamazepine, oxazepam, metoprolol, clarithromycin, sulfamethoxazole and estrone. For these pharmaceuticals the summer outlet concentrations were in the order of 1% to 101% higher.

Overall, the data shows a slight tendency towards higher concentrations for a majority of the pharmaceuticals in the outlet water during the winter period.

Outlet chemical load (g/year) of 15 pharmaceuticals in 3 WWTPs

An estimate of the chemical load of pharmaceuticals released to the recipient from each individual WWTP expressed as g/year was calculated based on the outgoing concentrations (**Table 5**) and the knowledge of the total volume of treated wastewater/year (**Table 3**). 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 10**.

Table 10. *Average outlet concentrations in ng/L of the 15 pharmaceuticals and outlet chemical load (g/year) at each of the 3 WWTPs operated by Kristianstad Municipality; Kristianstad WWTP, Tollarp WWTP and Degeberga WWTP. These 3 WWTPs are labelled sampling points SE02, SE07 and SE12, and their geographical locations are shown in Figure 5, Figure 6 and Figure 7, respectively, while an overview of all 3 WWTPs is shown in Figure 4. The compounds are sorted from highest to lowest based on outlet concentrations at Kristianstad WWTP. For details of calculations see text.*

Compound	Average Outlet Concentrations Summer + Winter (ng/L)			Outlet Chemical Load (g/year)		
	Kristianstad SE02	**Tollarp** SE07	**Degeberga** SE12	**Kristianstad** SE02	**Tollarp** SE07	**Degeberga** SE12
Metoprolol	667	919	216	5 462	332	17
Ibuprofen	602	1 260	1.6	4 931	455	0.1
Diclofenac	579	646	1132	4 743	233	89
Naproxen	465	931	17	3 808	336	1.4
Carbamazepine	427	251	4 362	3 496	91	345
Oxazepam	424	699	846	3 471	252	67
Atenolol	340	213	1.0	2 785	77	0.1
Erythromycin	270	210	30	2 207	76	2.4
Sulfamethoxazole	109	35	3.1	896	13	0.2
Azithromycin	51	0.5	5.8	415	0.2	0.5
Clarithromycin	49	255	3.6	401	92	0.3
Ciprofloxacin	39	35	36	316	13	2.9
Propranolol	30	34	24	242	12	1.9
Paracetamol	9.2	123	1.5	76	44	0.1
Estrone	2.5	4.5	0.0	21	1.6	0.0
Total chemical load in g/year				33 269	2 028	528
Total chemical load in kg/year				33	2.0	0.5
Total chemical load in g/year excl. ibuprofen and paracetamol				28 262	1 528	527
Total chemical load in kg/year excl. ibuprofen and paracetamol				28	1.5	0.5

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 2 000 g/year (>2kg/year). Sulfamethoxazole, azithromycin, clarithromycin, ciprofloxacin and propranolol were released to between 200-1 000 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 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 10**. As previously seen from **Table 8** above it was shown that 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, **Table 10**. 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.

The 3 WWTPs ability to reduce pharmaceuticals – removal efficiency (%)

The information available on both inlet and outlet concentrations in **Table 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 11 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.

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

As shown in **Table 11**, 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. To get a first rough estimate of the 3 Scanian WWTPs ability to remove pharmaceuticals the average of all 3 WWTPs removal efficiency at both seasons was calculated from the data in **Table 11** (n=6). The results are shown in **Figure 15** below. In **Figure 15** the average removal efficiency obtained from 7 WWTPs (n=7) investigated in *LUSKA 2017* are also indicated in light grey for comparison, as well as the removal efficiency data from a *Swedish National Screening 2011*[12] covering 4 WWTPs (n=4), marked in light blue.

[12] IVL (2011) Results from the Swedish National Screening Programme 2010. Subreport 3. Pharmaceuticals; 56 pages

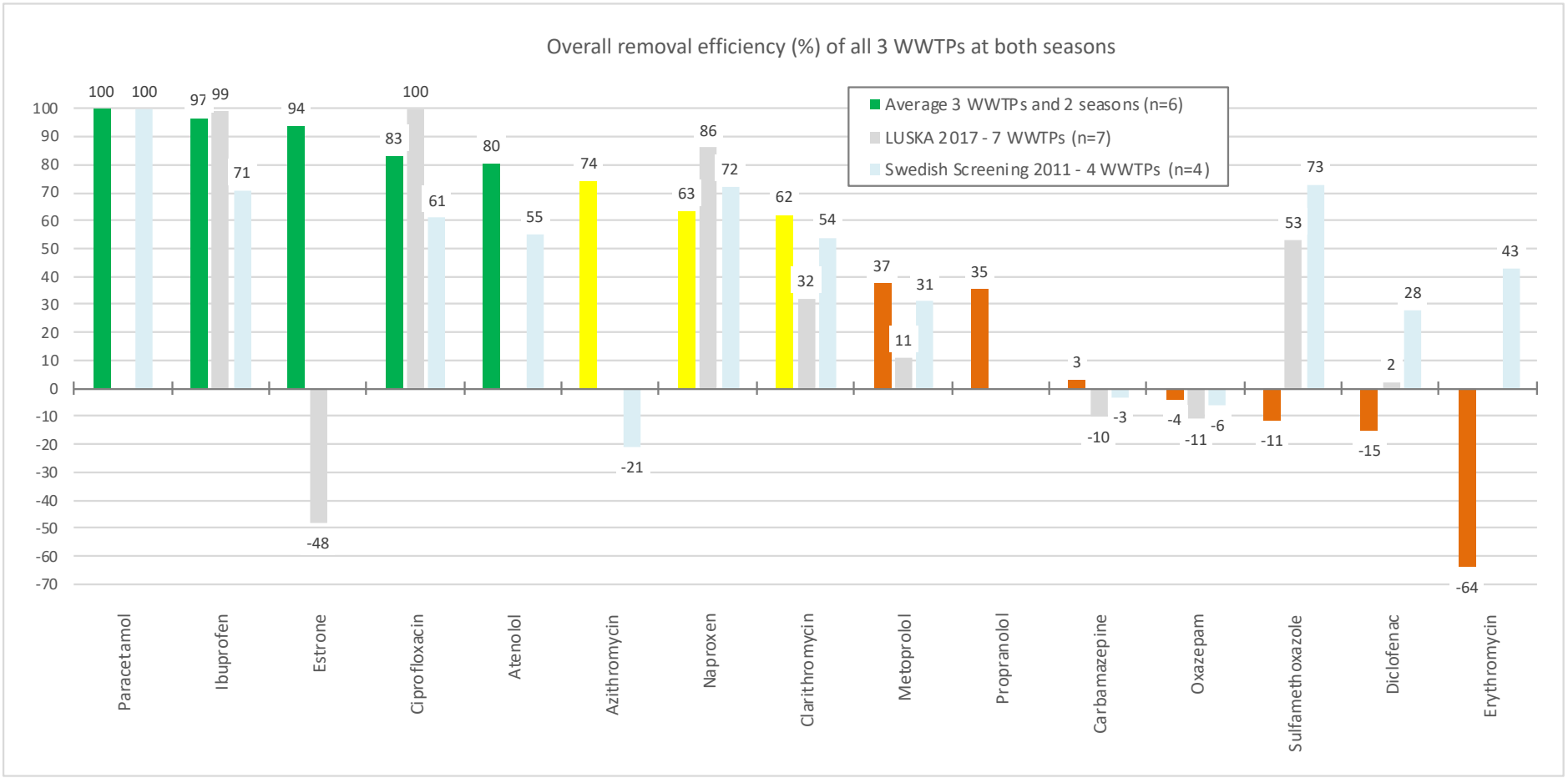


Figure 15. *Overall removal efficiencies (%) for all 3 WWTPs at both season (n=6). Data from Table 11 above. The removal efficiencies for this study is marked in either green, indicating >80% removal, yellow indicating 50-80% removal and orange <50% removal. The removal efficiencies are compared to the average removal efficiency obtained from 7 WWTPs (n=7) investigated in LUSKA 2017 (light grey), and from 4 WWTPs (n=4) in a Swedish National Screening 2011covering 4 WWTPs (light blue). For additional information see text.*

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. The two heart medicines metoprolol and propranolol, on the other hand, are only removed to a limited extent. Likewise, carbamazepine, oxazepam and diclofenac are (in)famous for their persistence and large tendency to pass WWTPs basically unaltered.

In order to reveal any possible differences in removal efficiency between seasons, the average of all 3 summer values as well as all 3 winter values were calculated and presented in **Figure 16**. The pharmaceuticals are sorted from highest to lowest removal efficiency based on the summer values.

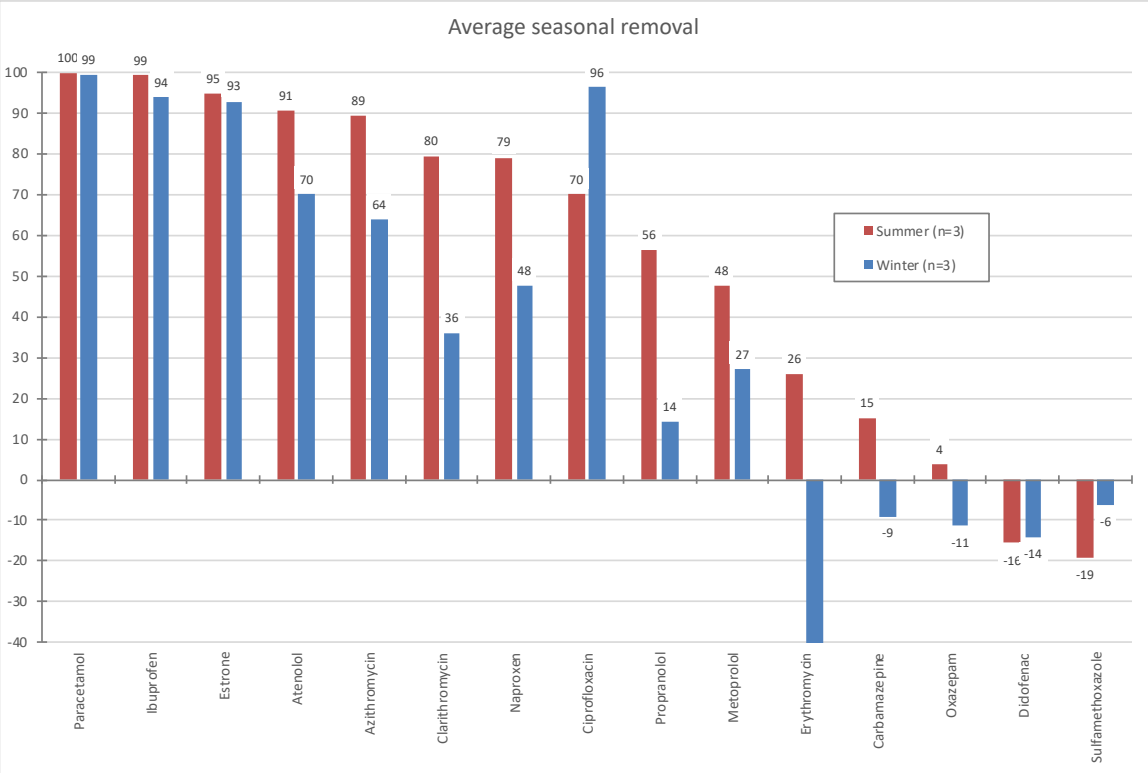


Figure 16. *Average seasonal removal efficiencies for the 3 WWTPs at summer (n=3) and winter (n=3) conditions. Data from Table 11 above. For additional information see text.*

Taking the average value of all pharmaceuticals for all summer values as well as for all winter values gives a total removal efficiency of 55% and 32%, respectively. There seem to be a tendency for a better removal efficiency during the summer season at the selected WWTPs.

Finally, each individual WWTPs ability to reduce pharmaceuticals was estimated by taking the average of all pharmaceuticals removal efficiencies for each WWTP at each season in **Table 11** (average of each column separately) and the results are shown in **Figure 17** below.

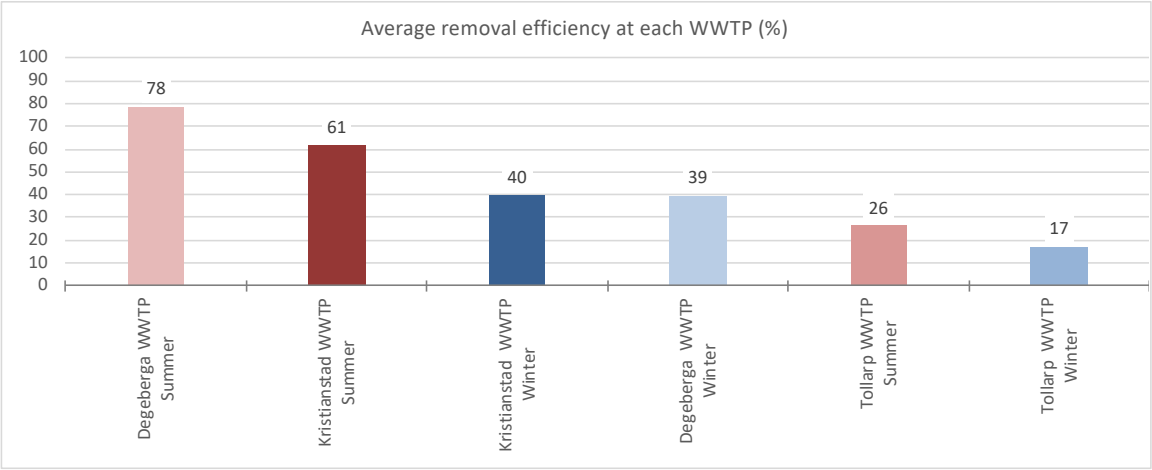


Figure 17. *Average removal efficiency for each WWTP at each season. Summer values are shown in red colours and winter values in blue colours. Data from Table 11 above. For additional information see text.*

In **Figure 17** it can be seen that for each of the 3 WWTPs the removal efficiency value is higher during summer than during winter. It also becomes clear that Degeberga and Kristianstad WWTP are showing removal efficiencies that are much closer to each other than to Degeberga at both seasons. During summer Degeberga and Kristianstad has a removal efficiency above 60% while in winter it is close to 40% at both WWTPs. Corresponding values in Tollarp are 26% and 17%, respectively.

Recipient concentrations of 15 pharmaceuticals in rivers and lakes in Kristianstad municipality

The pharmaceutical concentrations found in the rivers and lakes upstream and downstream the 3 WWTPs are presented in **Table 6** above for Helge Å, Vramsån and Segesholmsån rivers. The concentrations are visualized for each river system in **Figure 18a-f, Figure 19a-d** and **Figure 20a-d**, based on the therapeutic classification shown in **Table 2** above.

Helge Å river (Kristianstad WWTP)

The Helge Å river pharmaceutical concentrations are shown in **Figure 18a-f**. The upstream point "Public indoor pool" (**SE01** in **Figure 5**) contains very low background levels of pharmaceuticals ranging from <MQL to around 8 ng/L. The top 3 compounds above their MQL were paracetamol 8.4 ng/L (*N – Nervous system*), carbamazepine 7.8 ng/L (*N – Nervous system*) and metoprolol 4.5 ng/L (*C – Cardiovascular system*). 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 of 24.2 m^3/s and 105 m^3/s during the summer and winter sampling campaign, respectively (**Figure S2a**), 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 (J) pharmaceuticals are present at very low levels close to or below MQL (**Figure 18a-b**). Looking at outlet concentrations (**Table 5**) none of these, except Erythromycin occur at very high concentrations which fits with the identified concentrations in the upstream point.

Cardiovascular system (C) pharmaceuticals shows that atenolol was present at 2.5 ng/L during the summer but below MQL in the winter (**Figure 18c-d**). 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 5**) as well as the removal efficiencies of the three cardiovascular pharmaceuticals (**Figure 16**) these findings seem logical.

Musculo-skeletal system (M) pharmaceuticals have concentrations below or close to MQL for all compounds (**Figure 18e-f**).

Nervous system (N) are present above MQL in nearly all cases except paracetamol during the summer

sampling (**Figure 18g-h**). Carbamazepine occur at concentrations around 8 ng/L and oxazepam between 1-3 ng/L at sampling point **SE01**. Both compounds are hard to degrade (**Figure 16**) and also occur at relatively high concentrations in wastewater from all types of WWTPs (**Table 5**), which may explain their occurrence in the upstream point.

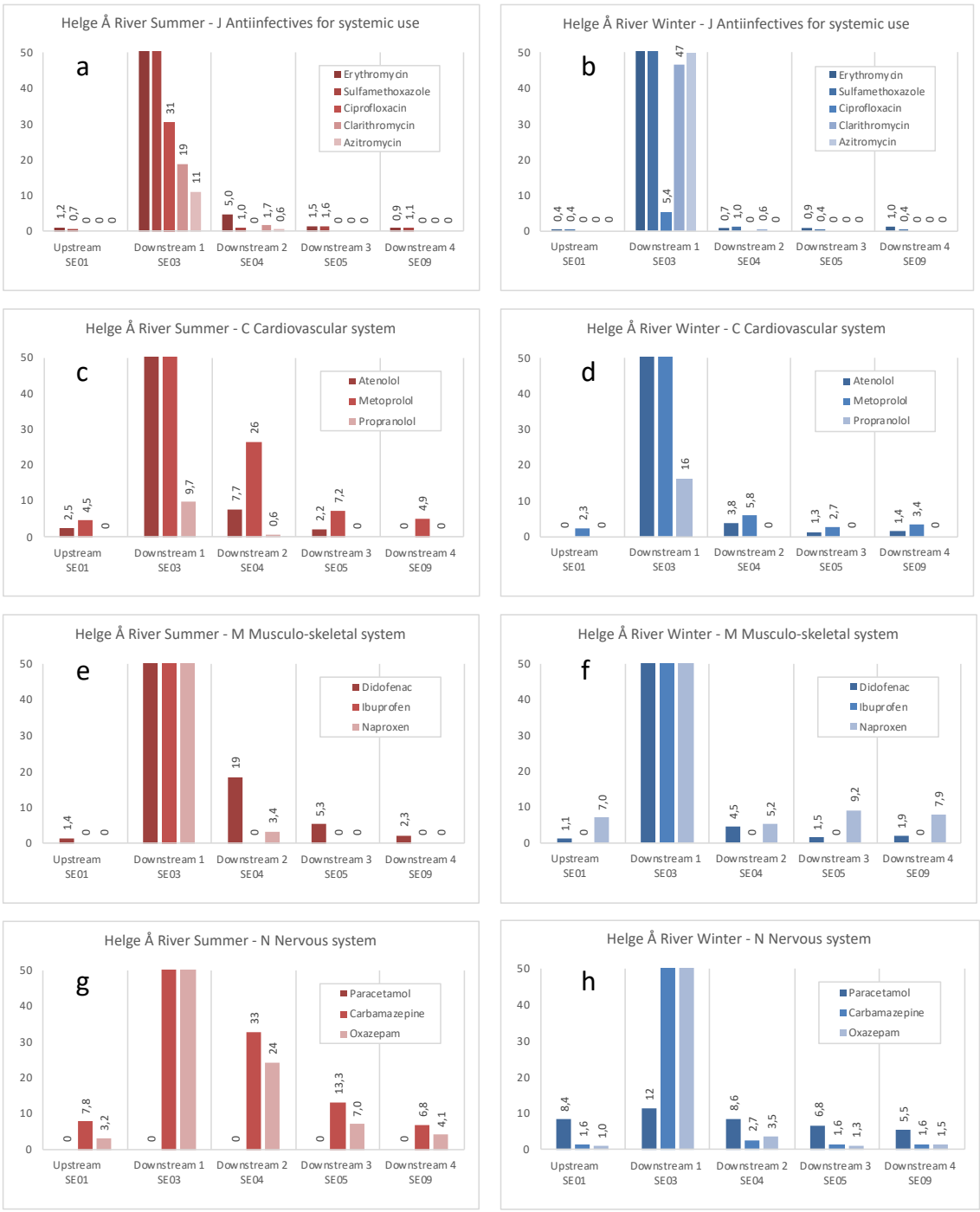


Figure 18. *Concentration of pharmaceuticals (ng/L) in the Helge Å river system including Hammarsjön lake, upstream and downstream Kristianstad WWTP. Summer concentrations are shown in red in Figure a, c, e and g, while winter concentrations are shown in Figure b, d, e and f. Sampling points SE01, SE03, SE04, DSE05 and SE09 are shown in Figure 5 above, and the concentrations are taken from Table 6. For additional information see text.*

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 point downstream Kristianstad WWTP. As seen in **Table 6** and **Figure 18** 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), 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.

By comparing the outlet concentrations from Kristianstad WWTP (**SE02**) in **Table 5** with the concentrations obtained in Hammarsjön lake at "Pynten" (**SE03**) in **Table 6** a rough estimate of the removal efficiency of the 1 500 m channel could be calculated using the same formula as used to calculate removal efficiencies in the WWTPs. The results are shown in **Figure 19**.

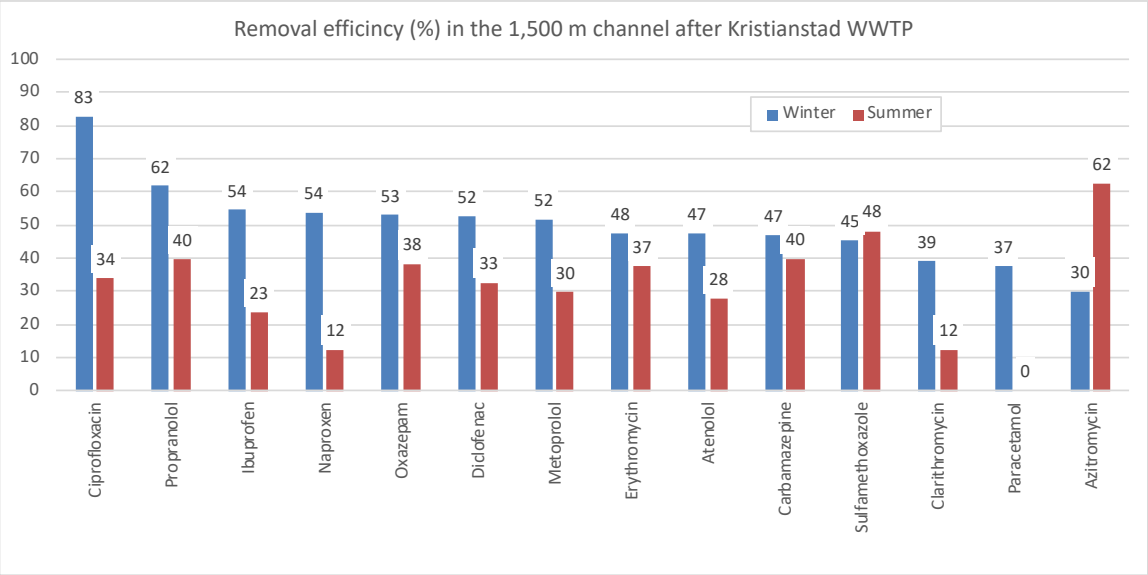


Figure 19. *Seasonal removal efficiencies (%) of pharmaceuticals in the 1 500 long channel downstream Kristianstad WWTP, into which the treated wastewater from Kristianstad WWTP is released. Data are from Table 5 and Table 6 (sampling points SE02 and SE03). For additional information see text.*

The results indicate that the removal efficiency seems higher in the channel during the winter period. Taking the average for all pharmaceuticals gives a value of 50% during winter and 31% during summer. The reason for this difference is not known, but one explanation might be a larger inflow of external water from the trench to the channel during winter than during summer causing a higher degree of dilution. The results also point to the fact that channels and ponds only have a limited effect on the removal of pharmaceuticals from the water. In previous studies we have investigated the sediment of the channel and found very high concentrations of some persistent pharmaceuticals therein. This means that the channel becomes an aquatic repository for organic contaminants over time.

Turning to the three other downstream sampling points we find "Ekenabben" (**SE04**) which is situated around 500 m south east of "Pynten" (S**E03**), 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 in **Figure 18** 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 above their MQLs 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) 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. To study the relative decrease in concentrations in sampling points **SE04**, **SE05** and **SE09** as compared to sampling point **SE03**, a small calculation was done by dividing the **SE03** concentrations with the **SE04**, **SE05** and **SE09** concentrations, respectively. The results are seen in **Figure 20a-b** for both summer and winter sampling. It should be noted that calculations were only made for those six compounds that were detected in all sampling points.

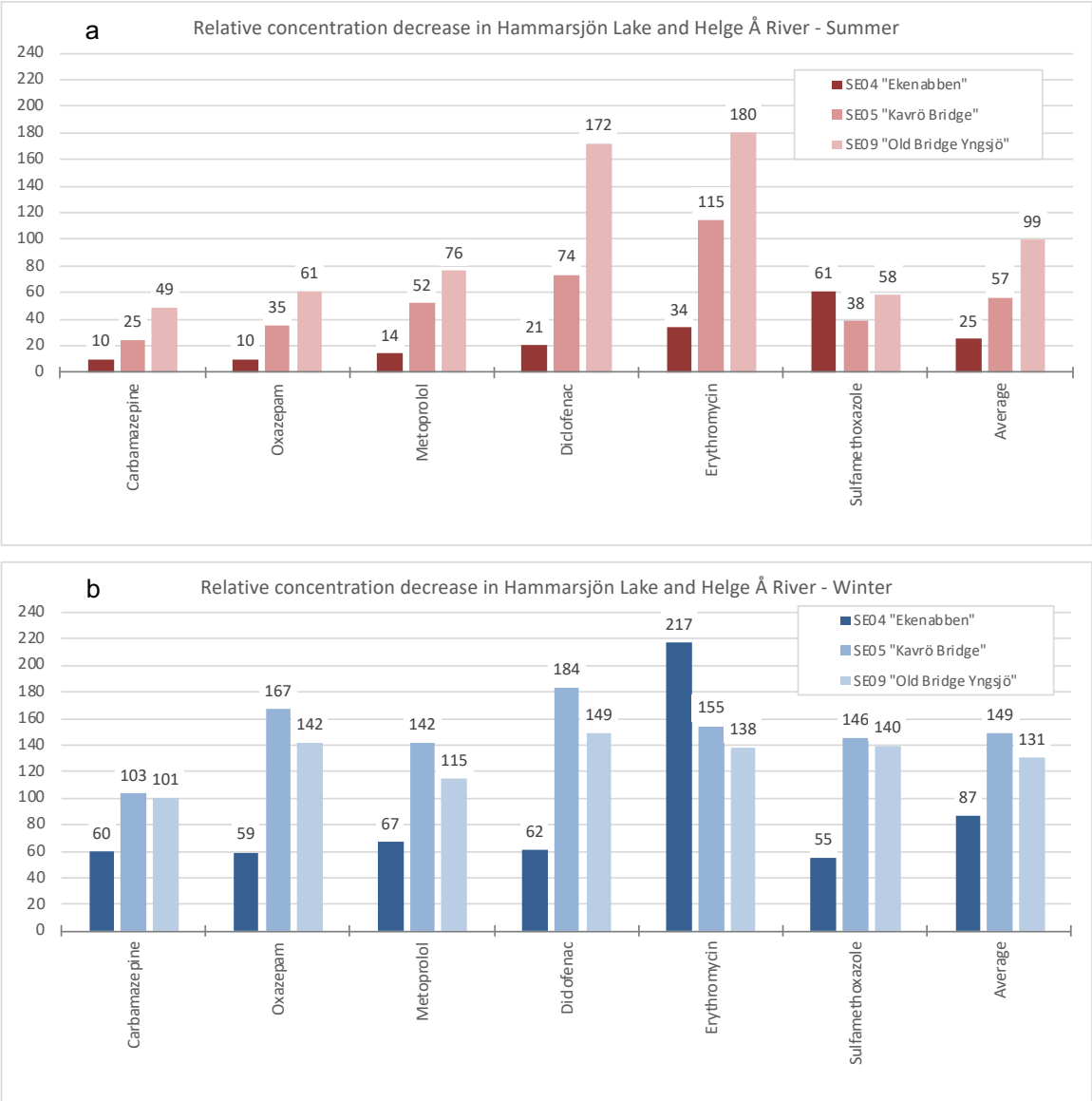


Figure 20. *Relative decrease in concentrations for sampling points "Ekenabben" SE04, "Kavrö Bridge" SE05 and "Old Bridge Yngsjö" SE09 obtained by dividing the SE03 concentrations with the SE04, SE05 and SE09 concentrations, respectively from Table 6. Results are shown for summer concentrations (a) and winter concentrations (b).*

The summer samples show a clear tendency of being lower the closer to the outlet in the Baltic Sea the samples are taken. Even though the relative concentration decrease is not identical for each pharmaceutical at the different samples they are still within a factor of 4 for all compounds except sulfamethoxazole. The fact that the relative concentration decrease is not identical for all compounds may indicate that other factors than dilution is at play, since pure dilution ideally would lead to the same relative concentration decrease for all compounds. An interesting note is also that the difference in relative decrease in concentration between sampling point **SE09** and **SE05** is quite substantial for many of the compounds, sometimes exceeding a factor of 2. However, comparing the summer flow rates at the two sampling points **SE09** and **SE05** shows that during the summer sampling these were

very similar with values of 25.3 m^3/s and 24.0 m^3/s, respectively (**Figure S2b-c**). This gives a factor of only 1.1 higher dilution close to the outlet in the Baltic Sea, and supports that other factors contribute to the larger relative decrease in concentration between the two sites during summer.

Turning to the winter sampling there is once again a tendency that sampling point **SE04** has a lower relative concentration decrease than **SE05** as was also observed during the summer sampling. A difference though is that sampling point **SE09** has nearly the same relative decrease in concentration as **SE05**. A general observation of interest is that the relative concentration decrease is larger during winter than during summer for most compounds at all sampling stations **SE04**, **SE05** and **SE09**. Looking at sampling point **SE04** which is situated 500 m downstream sampling point **SE03** the relative concentration decrease for carbamazepine during the winter is 6.0 times higher (60/10) than during the summer. Corresponding values are 5.9, 4.8, 3.0 and 6.4 for oxazepam, metoprolol, diclofenac and erythromycin, respectively. Sulfamethoxazole did not follow this pattern. We do not know if this is caused by an increased dilution during winter, but it may be a plausible explanation as the volume of water in the Hammarsjön lake is much larger during the winter than during the summer at sampling point **SE04** due to higher river flow. This may find support by looking at sampling point **SE05** located around 10 km downstream sampling point **SE03** were it can be seen that relative concentration decreases once again is larger during winter than during summer for carbamazepine, oxazepam, metoprolol, diclofenac, erythromycin and sulfamethoxazole, being 4.1, 4.8, 2.7, 2.5, 1.3 and 3.8, respectively. By comparing the differences in flow rate in the Helge Å river at point **SE05** during winter and summer sampling shows that these are 114 m^3/s and 24 m^3/s, respectively (**Figure S2b**). This means that the flow rate is 4.8 times higher during the winter than during the summer which might explain the higher degree of concentration decrease in the Helge Å river during the winter.

Another observation from **Figure 18** is that the actual decrease in concentrations between sampling points **SE05** and **SE09** is less pronounced during the winter than during the summer for compounds that can be identified at both places. The difference in dilution by the river during the summer was calculated to be a factor of 1.1 above, despite a difference in relative decrease in concentration between sampling point **SE09** and **SE05**, sometimes exceeding a factor of 2 during the summer. This might indicate that other processes than dilution are more pronounced in the summer period. During the winter, on the other hand, the difference in relative decrease in concentration between sampling point **SE09** and **SE05** was in most cases just below 1. Comparing the winter flowrates at the two sampling points **SE09** and **SE05** shows that during the winter sampling these were 119 m^3/s and 114 m^3/s for **SE09** and **SE05**, respectively (**Figure S2b-c**). This leads to a factor of only 1.04 higher dilution close to the outlet in the Baltic Sea. In contrary to the summer this indicates that dilution may be the main cause of decreasing concentrations during winter as other types of biotic and abiotic process could be less efficient during the colder period.

Based on the data obtained, an estimate of the actual chemical burden released into *Vattenriket*® and into to the Baltic sea was calculated and summarized for four common, and relatively persistent pharmaceuticals; carbamazepine[13,14], diclofenac[15,16], metoprolol[17,18] and oxazepam[19,20].

---

13 Environmental fate of naproxen, carbamazepine and triclosan in wastewater, surface water and wastewater irrigated soil — Results of laboratory scale experiments, Science of the Total Environment 538 (2015) 350–362, Durán-Álvarez, J., Prado, B., González, D., Sánchez, Y., Jiménez-Cisneros B.

14 Pharmaceutical residues are widespread in Baltic Sea coastal and offshore waters – Screening for pharmaceuticals and modelling of environmental concentrations of carbamazepine, Science of the Total Environment, 633 (2018) 1496-1509. Björlenius, B., Ripszám, M., Haglund, P. Lindberg, R., Tysklind, M., Fick, J.

15 Temporal Variation of Chemical Persistence in a Swedish Lake Assessed by Benchmarking, Environmental Science & Technology, 4 (2015) 9881–9888, Zou, H., Radke, M., Kierkegaard, A., McLachlan, M.

16 Degradation of the pharmaceuticals diclofenac and sulfamethoxazole and their transformation products under controlled environmental conditions, Science of the Total Environment 557–558 (2016) 257–267, Poirier-Larabie, S., Segura, P., Gagnona, C.

17 Kinetics and Degradation Products for Direct Photolysis of â-Blockers in Water, Environmental Science & Technology 41 (2007) 803–810, Liu, Q., Williams, H.

18 The degradation and persistence of five pharmaceuticals in an artificial climate incubator during a one year period, Royal Society of Chemistry, Advances, 7 (2017) 8280–8287, Yin, L., Ma, R., Wang, B., Yuan, H., Yu, G.

19 Aqueous Phototransformation of Diazepam and Related Human Metabolites under Simulated Sunlight, Environmental Science % Technology, 46, (2012) 4749–4756, West, C., Rowland, S.

20 Long-Term Persistence of an Anxiolytic Drug (Oxazepam) in a Large Freshwater Lake, Environmental Science & Technology, 49 (2015) 10406–10412, Klaminder, J., Brodin, T., Sundelin, A., Anderson, N., Fahlman, J., Jonsson, M., Fick, J.

The environmental degradation half-lives these pharmaceuticals sometimes range from weeks to months[21,22]

These four pharmaceuticals were in most cases present above their MQL in all sampling points (**SE01**, **SE02**, **SE03**, **SE04**, **SE05** and **SE09**) at all times (summer and winter), thereby giving a rough picture of the yearly mass flow of these compounds in this lower part of the Helge Å river system. They are indicated in purple in **Table 6**.

Starting with the upstream point **SE01** the four pharmaceuticals have the following upstream concentrations in Helge Å river; carbamazepine 7.8 ng/L (summer) and 1.6 ng/L (winter), diclofenac 1.4 ng/L (summer) and 1.1 ng/L (winter), metoprolol 4.5 ng/L (summer) and 2.3 ng/L (winter) and oxazepam 3.2 ng/L (summer) and 1.0 ng/L (winter). This gives average concentrations of 4.70 ng/L, 1.25 ng/L, 3.40 ng/L and 2.10 ng/L, respectively. Using average flowrates at point **SE01** (see **Figure S2a**) of 56.1 m^3/s we end up with the following calculations:

- **SE01**: 56 100 L/s = 1 769 169 600 000 L/year

Carbamazepine: 0.00000000470 g/L gives 8 315 g/year or ca. 8.3 kg/year

Diclofenac: 0.00000000125 g/L gives 2 211 g/year or ca. 2.2 kg/year

Metoprolol: 0.00000000340 g/L gives 6 016 g/year or ca. 6.0 kg/year

Oxazepam: 0.00000000210 g/L gives 3 715 g/year or ca. 3.7 kg/year

The outlet amounts from Kristianstad WWTP (**SE02**) were calculated above (**Table 10**) and gave:

- **SE02**: 3.5 kg of carbamazepine, 4.7 kg diclofenac, 5.5 kg of metoprolol 3.5 kg oxazepam.

Turning to point **SE03** which is the entrance point of the channel into Hammarsjön lake the same approach was applied assuming that the volume water entering the Hammarsjön lake primarily consisted of the treated wastewater from Kristianstad WWTP which was 8 186 000 000 L per year. It should be noted though that this volume may be larger since there is an unknown volume of water flowing into the channel. Consequently, the estimated loads are possibly underestimated. The measured concentrations at point **SE03** were; carbamazepine 330 ng/L (summer) and 163 ng/L (winter), diclofenac 389 ng/L (summer) and 277 ng/L (winter), metoprolol 375 ng/L (summer) and 388 ng/L (winter) and oxazepam 249 ng/L (summer) and 209 ng/L (winter). This gives average concentrations of 246.5 ng/L, 333.0 ng/L, 381.5 ng/L and 229.0 ng/L, respectively. We thereby end up with the following calculations:

- **SE03**: 8 186 000 000 L/year

Carbamazepine: 0.0000002465 g/L gives 2 018 g/year or ca. 2.0 kg/year

Diclofenac: 0.000000333 g/L gives 2 725 g/year or ca 2.7 kg/year

Metoprolol: 0.0000003815 g/L gives 3 123 g/year or ca. 3.1 kg/year

Oxazepam: 0.0000002290 g/L gives 1 875 g/year or ca. 1.9 kg/year

- **SE04** was situated 500 m downstream along the coastline of the Hammarsjön lake, the flow was not known and no calculations could be made.

SE05 was situated 10 km downstream the entrance point of the channel into Hammarsjön lake. The average flow rate of the Helge Å river was 58.2 m^3/s (**Figure S2b**) and the measured concentrations were; carbamazepine 13.3 ng/L (summer) and 1.6 ng/L (winter), diclofenac 5.3 ng/L (summer) and 1.5 ng/L (winter), metoprolol 7.2 ng/L (summer) and 2.5 ng/L (winter) and oxazepam 7.0 ng/L (summer) and 1.3 ng/L (winter). This gives average concentrations of 7.45 ng/L, 3.40 ng/L, 4.85 ng/L and 4.15 ng/L, respectively. We thereby end up with the following calculations:

---

[21] Behaviour and fate of nine recycled water trace organics during managed aquifer recharge in an aerobic aquifer, Journal of Contaminant Hydrology 122 (2011) 53–62, Patterson, B., Shackleton, M., Furness, A., Bekele, E., Pearce, J., Linge, K., Busetti, F., Spadek, T., Toze, S.

[22] A fugacity model assessment of ibuprofen, diclofenac, carbamazepine, and their transformation product concentrations in an aquatic environment, Environmental Science and Pollution Research 26 (2019) 328–341, Nurmi, T., Kiljunen, T., Knuutinen, J.

- **SE05**: 58 200 L/s = 1 835 395 200 000 L/year

Carbamazepine: 0.00000000745 g/L gives 13 673 g/year or ca. 13.7 kg/year

Diclofenac: 0.00000000340 g/L gives 6 240 g/year or ca. 6.2 kg/year

Metoprolol: 0.00000000485 g/L gives 8 902 g/year or ca. 8.9 kg/year

Oxazepam: 0.00000000415 g/L gives 7 617 g/year or ca. 7.6 kg/year

SE09 was situated 20 km downstream the entrance point of the channel into Hammarsjön lake. The average flow rate of the Helge Å river was 60.6 m^3/s (**Figure S2c**) and the measured concentrations were; carbamazepine 6.8 (summer) and 1.6 ng/L (winter), diclofenac 2.3 ng/L (summer) and 1.9 ng/L (winter), metoprolol 4.9 ng/L (summer) and 3.4 ng/L (winter) and oxazepam 4.1 ng/L (summer) and 1.5 ng/L (winter). This gives average concentrations of 4.20 ng/L, 2.10 ng/L, 4.15 ng/L and 2.80 ng/L, respectively. This gives the following calculations:

- **SE09**: 60 600 L/s = 1 911 081 600 000 L/year

Carbamazepine: 0.00000000420 g/L gives 8 027 g/year or ca. 8.0 kg/year

Diclofenac: 0.00000000210 g/L gives 4 013 g/year or ca. 4.0 kg/year

Metoprolol: 0.00000000415 g/L gives 7 931 g/year or ca. 7.9 kg/year

Oxazepam: 0.00000000280 g/L gives 5 351 g/year or ca. 5.4 kg/year

To better see the mass flow analysis the values are graphically shown in **Figure 21**.

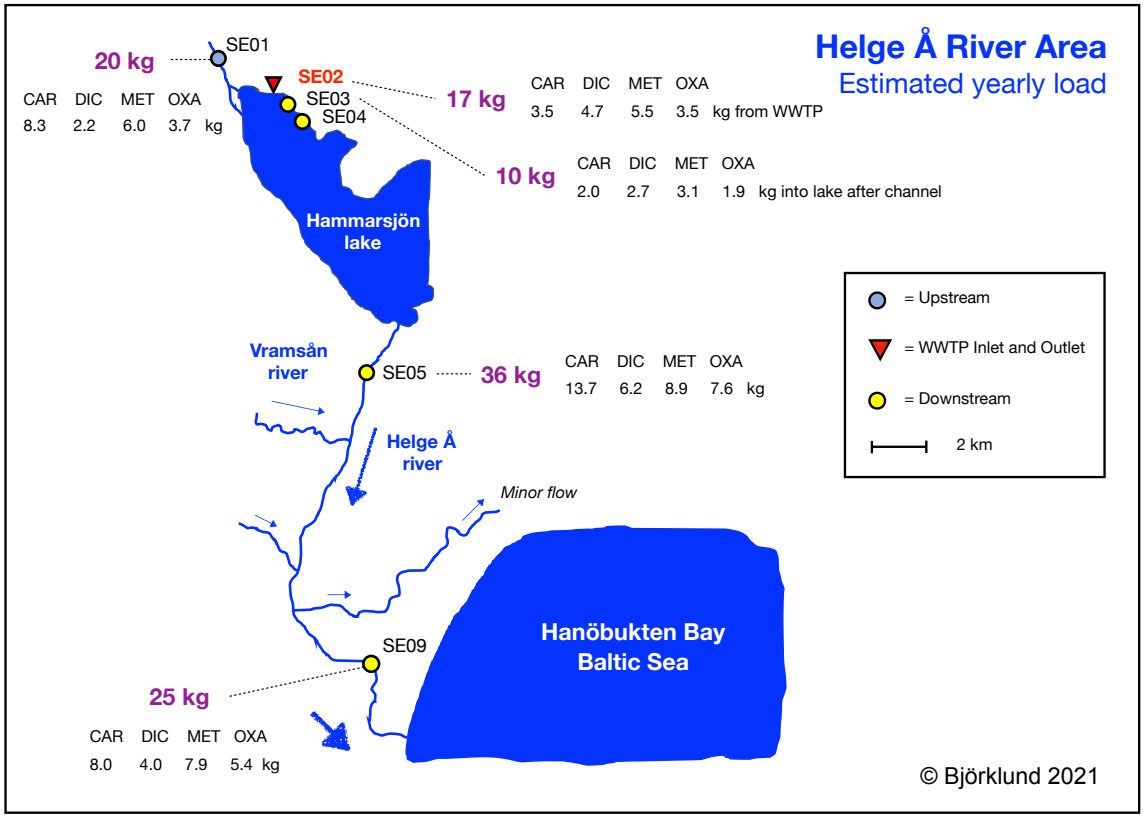


Figure 21. *Estimated mass flow analysis of carbamazepine (CAR.), diclofenac (DIC), metoprolol (MET) and oxazepam (OXA) and for sampling points "Kristianstad WWTP" SE02, "Channel" SE03, "Kavrö Bridge" SE05 and "Old Bridge Yngsjö" SE09. See text for details on calculations.*

From this figure there are several things to be noted. First of all, both Helge Å river itself (**SE01)**, Kristianstad WWTP (**SE02)** and the entrance point in Hammarsjön lake via the 1 500 m channel (**SE03)** contribute to the total load of pharmaceutical to the Hammarsjön lake. Taking carbamazepine as an example ca 8.3 kg enters via Helge Å river (**SE01**) and 2.0 kg via the channel (**SE03**), giving a

total estimate of ca. 10.3 kg carbamazepine. However, the contribution from the channel may well be underestimated as discussed above. The total chemical burden of all four pharmaceuticals from Helge Å river (**SE01**) and Kristianstads WWTP (**SE02**) into the channel (which is part of *Vattenriket*®) adds up to 37.4 kg. The total burden into Hammarsjön lake from Helge Å river and the entrance point of the channel into the lake adds up to 29.9 kg.

In the Helge Å river 10 km downstream (**SE05)** the total estimate load was ca. 13.7 kg, 6.2 kg, 8.9 kg and 7.6 kg for carbamazepine, diclofenac, metoprolol and oxazepam, respectively. Summing these amounts gives a total value of 36.4 kg. This figure is close to the 37.4 kg found by adding Helge Å river (**SE01**) and Kristianstad WWTP (**SE02**), but somewhat higher than the sum of 29.9 kg found by adding Helge Å river (**SE01**) and the channel inlet (**SE03**). Even though the mass balance is not exactly matching, there is a very logical trend. The total burden from upstream Helge Å river (**SE01**) is 20.2 kg, while Kristianstad WWTP (**SE02**) and the channel inlet to the lake (**SE03**) are estimated to 17.2 kg and 9.7 kg, respectively. Overall, the contribution of the four semi-persistent pharmaceuticals is roughly 20 kg (2/3 of the burden) from Helge Å river (**SE01**) and ca. 10 kg (1/3 of the burden) from the WWTP via the inlet to the lake (**SE02**, **SE03**). However, as pointed out above the inlet flow to the lake might be somewhat underestimated since it could contain additional water apart from the treated wastewater from the WWTP. Probably the chemical load to the lake is somewhere in the range 10-15 kg. If the higher load is applied this would mean that the contribution to the total load to the Helge Å river from the WWTP would be 15 kg / (15 + 20 kg) = 0.43 or ca 40%. In any case there is a clear trend that there are increased amounts downstream Helge Å river (**SE05**) after the load from the WWTP has been added. These concentrations and amounts thereafter further decreases 20 km downstream (**SE09**) with a total load of 25.3 kg as a sum of all four pharmaceuticals. From this sampling point there is only around 3 km to the entrance of the Helge Å river into the Hanöbukten bay. This means that much of this load will be discharged into the Baltic Sea every year.

In should be noted that in this project only two samplings (summer and winter) could be performed and the measured concentrations were in some cases in the low ng/L range. Applying a better resolution to the river system by taking more samples at regular intervals e.g., once a month for 12 months would likely improve the precision of the mass flow analysis. Understanding the chemical burden from WWTPs in sensitive aquatic lakes and river systems is of key importance and fully in line with requests made by the Swedish EPA in a recent report[23]. The Swedish EPA states that we need to identify such vulnerable recipients in order to take appropriate action when upgrading existing WWTPs with advanced treatment technologies.

Vramsån river (Tollarp WWTP)

The Vramsån river pharmaceutical concentrations are shown in **Figure 22a-d**. The figure shows that the upstream point "School" (**SE06** in **Figure 6**) contains very low background levels of pharmaceuticals ranging from <MQL to around 6 ng/L. The top 3 compounds above their MQL were paracetamol 5.6 ng/L (*N – Nervous system*), oxazepam 1.0 ng/L (*N – Nervous system*) and carbamazepine 0.8 ng/L (*N – Nervous system*). 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 (*N – Nervous system*), carbamazepine 7.8 ng/L (*N – Nervous system*) and metoprolol 4.5 ng/L (*C – Cardiovascular system*), showing similarities between the two river systems. Finally, diclofenac had a concentration in Vramsån of 1.7 ng/L which is just below the MQL of 2.1 ng/L. Diclofenac also occurred at similar concentrations upstream in the Helge Å river system as shown above with concentrations in the range 1.1-1.4 ng/L.

[23] Avancerad rening av avloppsvatten för avskiljning av läkemedelsrester och andra oönskade ämnen. Behov, teknik och konsekvenser. Redovisning av ett regeringsuppdrag. Naturvårdsverket Rapport 6766, April 2017, 88 pages.

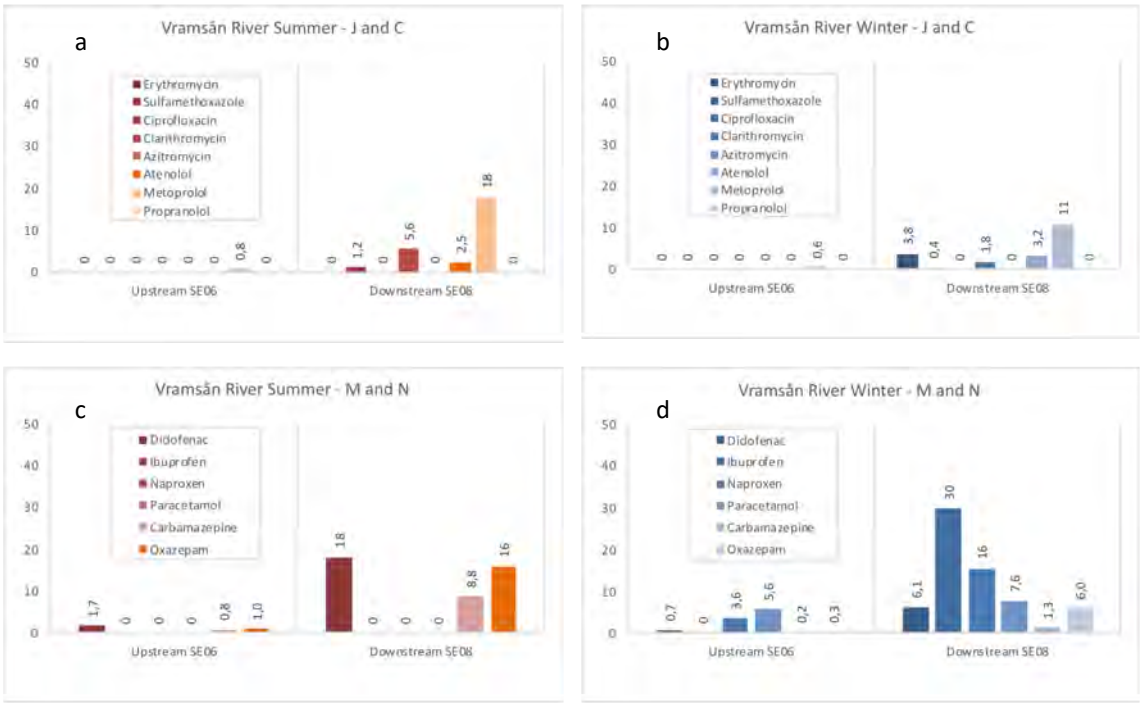


Figure 2. *Concentration of pharmaceuticals (ng/L) in the Vramsån river system, upstream and downstream Tollarp WWTP. Summer concentrations are shown in red in Figure a, c, while winter concentrations are shown in Figure b, d. Sampling points SE06, SE08 are shown in Figure 6 above, and the concentrations are taken from Table 6. For additional information see text.*

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 (**Table 6**):

Antiinfectives for systemic use (J) 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 (C) pharmaceuticals show 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** (**Figure 18c-d**).

Musculo-skeletal system (M) 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 (**SE05**).

Nervous system (N) 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 (**SE05**).

The downstream point **SE08** in the Vramsån river contained carbamazepine, diclofenac, metoprolol and oxazepam in both the summer and the winter samples and the chemical load was calculated in the same way as for the Helge Å river above.

Staring with the amounts released from Tollarp WWTP (**SE07**) these were calculated to be 91 g of carbamazepine, 233 g of diclofenac, 332 g of metoprolol and 252 g of oxazepam (**Table 10**).

At upstream point **SE06** the concentrations were relatively low, and in some cases below the MQL. The results were; carbamazepine 0.8 ng/L (summer) and 0.2 ng/L (winter), diclofenac 1.7 ng/L (summer) and 0.7 ng/L (winter), metoprolol 0.8 ng/L (summer) and 0.6 ng/L (winter) and oxazepam 1.0 ng/L (summer) and 0.3 ng/L (winter). This gives average concentrations of 0.5 ng/L, 1.2 ng/L, 0.7 ng/L and 0.65 ng/L, respectively. This gives the following loads:

- **SE06**: 3 510 L/s = 110 691 360 000 L/year

Carbamazepine: 0.0000000005 g/L gives 55 g/year or ca. 0.06 kg/year

Diclofenac: 0.0000000012 g/L gives 133 g/year or ca. 0.13 kg/year

Metoprolol: 0.0000000007 g/L gives 77 g/year or ca. 0.08 kg/year

Oxazepam: 0.00000000065 g/L gives 72 g/year or ca. 0.07 kg/year

At point **SE08** situated downstream Tollarp WWTP the average flow rate of the Vramsån river was 3.51 m^3/s (**Figure S4a**) and the measured concentrations were; carbamazepine 8.8 ng/L (summer) and 1.3 ng/L (winter), diclofenac 18 ng/L (summer) and 6.1 ng/L (winter), metoprolol 18 ng/L (summer) and 11 ng/L (winter) and oxazepam 16 ng/L (summer) and 6.0 ng/L (winter). This gives average concentrations of 5.1 ng/L, 12.1 ng/L, 14.5 ng/L and 11.0 ng/L, respectively. We thereby end up with the following calculations:

- **SE08**: 3 510 L/s = 110 691 360 000 L/year

Carbamazepine: 0.0000000051 g/L gives 564.5 g/year or ca. 0.56 kg/year

Diclofenac: 0.0000000121 g/L gives 1 339 g/year or ca 1.3 kg/year

Metoprolol: 0.0000000145 g/L gives 1 605 g/year or ca. 1.6 kg/year

Oxazepam: 0.000000011 g/L gives 1 218 g/year or ca. 1.2 kg/year

It can be seen that the calculated amounts using two different strategies do not fit very well. Using the river flow data and river concentrations gives total amounts that are 6.2, 5.7, 4.8 and 4.8 times larger than WWTP loads. One reason for this could be that the exact release point of the wastewater into the river was not known and that the sampling point **SE08** was very close to the actual WWTP. The distance was probably less than 100 m causing insufficient dilution in the river. This in turn leads to somewhat too high river concentrations as compared to a sampling point further downstream. This is further supported by the good correlations observed for the Segesholmsån river below where the sampling points were situated 500 m and 8 km downstream Degeberga WWTP.

Segesholmsån river (Degeberga WWTP)

The Segesholmsån river pharmaceutical concentrations are shown in **Figure 23a-d**. The figure shows that the upstream point "Small Bridge" (**SE11** in **Figure 7**) 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" (**SE13**) ca. 500 m downstream and "Friseboda Parking" (**SE14**) ca 8 km downstream. Looking at the various classes shows the following downstream situation (**Table 6**):

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

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

Musculo-skeletal system (M) 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 (N) pharmaceuticals show that paracetamol could not be identified in any sample. Both carbamazepine and oxazepam was present in all samples, however. Carbamazepine had concentrations

of 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).

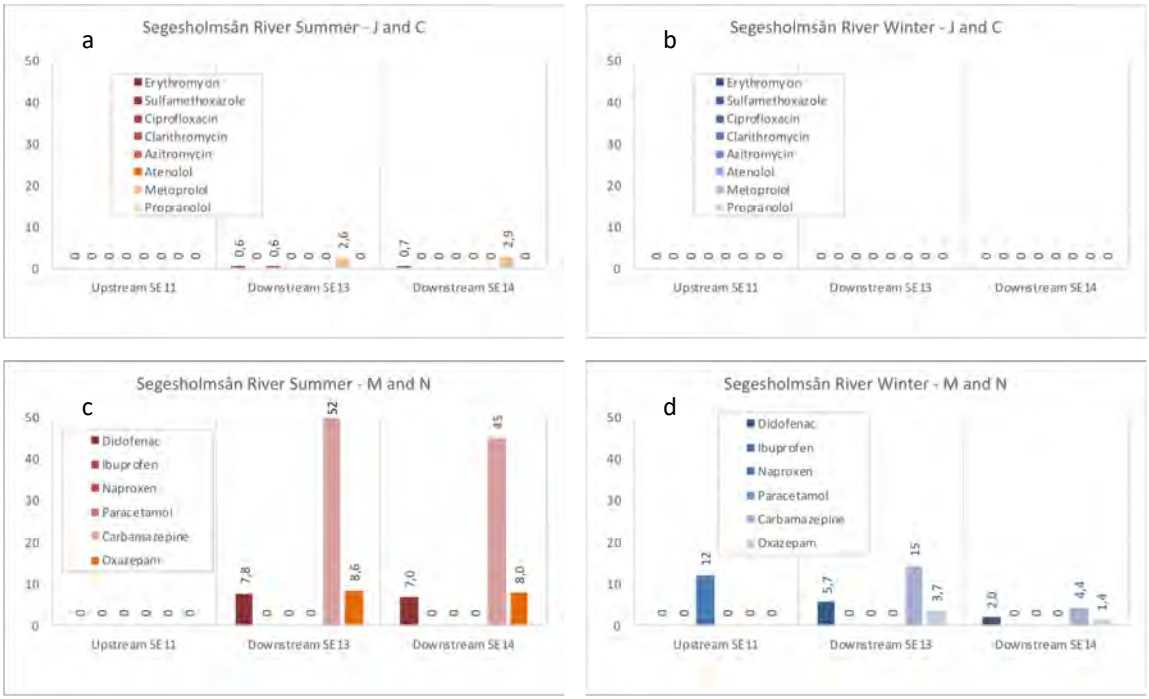


Figure 23. *Concentration of pharmaceuticals (ng/L) in the Segesholmsån river system, upstream and downstream Degeberga WWTP. Summer concentrations are shown in red in Figure a, c, while winter concentrations are shown in Figure b, d. Sampling points SE11, SE13 and SE14 are shown in Figure 7 above, and the concentrations are taken from Table 6. For additional information see text.*

The amounts released from Degeberga WWTP (**SE12**) were calculated above (**Table 10**) to be 345 g of carbamazepine, 89 g of diclofenac, 17 g of metoprolol and 67 g of oxazepam.

At point **SE13** situated ca 500 m downstream Degeberga WWTP the average flow rate of the Segesholmsån river was 0.419 m^3/s (**Figure S6a**) and the measured concentrations were; carbamazepine 52 ng/L (summer) and 15 ng/L (winter), diclofenac 7.8 ng/L (summer) and 5.7 ng/L (winter), metoprolol 2.6 ng/L (summer) and not detected (winter) and oxazepam 8.6 ng/L (summer) and 3.7 ng/L (winter). This gives average concentrations of 33.5 ng/L, 6.75 ng/L, 1.30 ng/L and 6.15 ng/L, respectively. We thereby end up with the following calculations:

SE13: 419 L/s = 13 213 584 000 L/year

Carbamazepine: 0.0000000335 g/L gives 442 g/year or ca. 0.44 kg/year

Diclofenac: 0.00000000675 g/L gives 89 g/year or ca. 0.09 kg/year

Metoprolol: 0.00000000130 g/L gives 17 g/year or ca 0.02 kg/year

Oxazepam: 0.00000000615 g/L gives 81 g/year or ca. 0.08 kg/year

The concentrations measured in the river multiplied by the average yearly flow correlates well with the calculated released amounts from the WWTP. The relation between the loads from the WWTP and those identified in the reiver were 0.78, 1.00, 1.00 and 0.82 for carbamazepine, diclofenac, metoprolol and oxazepam, respectively. Such correlations were also good for the Helge Å system above at several downstream points. In contrast to this stands the Vramsån river above, which further supports the fact the sampling was done to close to the WWTP in Tollarp.

At point **SE14** situated ca 8 km downstream Degeberga WWTP the average flow rate of the

Segesholmsån river was 0.783 m^3/s (**Figure S6b**) and the measured concentrations were; carbamazepine 45 ng/L (summer) and 4.4 ng/L (winter), diclofenac 7.0 ng/L (summer) and 2.0 ng/L (winter), metoprolol 2.9 ng/L (summer) and not detected (winter) and oxazepam 8.0 ng/L (summer) and 1.4 ng/L (winter). This gives average concentrations of 24.75 ng/L, 4.50 ng/L, 1.45 ng/L and 4.70 ng/L for carbamazepine, oxazepam and diclofenac, respectively. We thereby end up with the following calculations:

SE14: 783 L/s = 24 692 688 000 L/year

Carbamazepine: 0.00000002475 g/L gives 611 g/year or ca. 0.61 kg/year

Diclofenac: 0.00000000450 g/L gives 111 g/year or ca. 0.11 kg/year

Metoprolol: 0.000000000145 g/L gives 36 g/year or ca. 0.36 kg/year

Oxazepam: 0.0000000047 g/L gives 116 g/year or ca. 0.12 kg/year

The concentrations measured in the river multiplied by the average yearly flow in the river once again correlated relatively well with the calculated released amounts from the WWTP. The relation between the loads from the WWTP and those identified in the reiver were 0.56, 0.80, 0.47 and 0.58 for carbamazepine, diclofenac, metoprolol and oxazepam, respectively.

An additional comparison was made between the outlet concentrations from Degeberga WWTP and the downstream concentrations for carbamazepine, diclofenac, metoprolol and oxazepam by dividing the latter with the former to get an estimate of the dilution. The average outlet concentrations for Degeberga WWTP were 4 363 ng/L carbamazepine, 1 132 ng/L diclofenac, 216 ng/L metoprolol, 846 ng/L oxazepam, (**Table 10**), while the average downstream concentrations were 33.5 ng/L, 6.75 ng/L, 1.30 ng/L and 6.15 ng/L for the four pharmaceuticals (**SE13**). This gives a relation of 0.0077, 0.0060, 0.0060 and 0.0073, respectively. By diving the yearly volume of wastewater eluted from Degeberga WWTP with the yearly flow in the river we get the following calculation: 79 000 m^3 / 13 213 584 m^3 = 0.0060. This is very close to the above calculated values. From these figures it seems justified to state that dilution is the primary means the pharmaceutical concentrations are reduce in Segesholmsån river before entering the Baltic Sea. However, the dilution might vary over the year as the relation between the volume released wastewater and the flow rate of the river vary with season. This will also lead to peak concentrations in the river, especially in the summer period when the water flow in the river sometimes is very low.

Final remarks

The data presented in this report aids in the general understanding of how the release of pharmaceuticals and antibiotics from specific WWTPs will distribute in a large river system and can serve as a scientific background on where to take action to reduce this release. It also provides specific new knowledge on the occurrence, distribution and load of pharmaceutical residues within the first Biosphere Reserve established in Sweden; Kristianstads Vattenrike – "*Vattenriket*®". These data could hopefully aid in reducing the chemical load to "*Vattenriket*®" and thereby help to better protect these unique and precious wetlands in the south of Sweden.

Kayaking in the Helge Å river (left) and a view of the wetlands as seen from Naturum Vattenriket[24] (right). In both photos Kristianstad town is visible in the background showing the close contact between the city and nature.

Erland Björklund

Dalby, 2021-01-31

[24] https://vattenriket.kristianstad.se/naturum/

Supplementary Figures 1-6

Figure S1

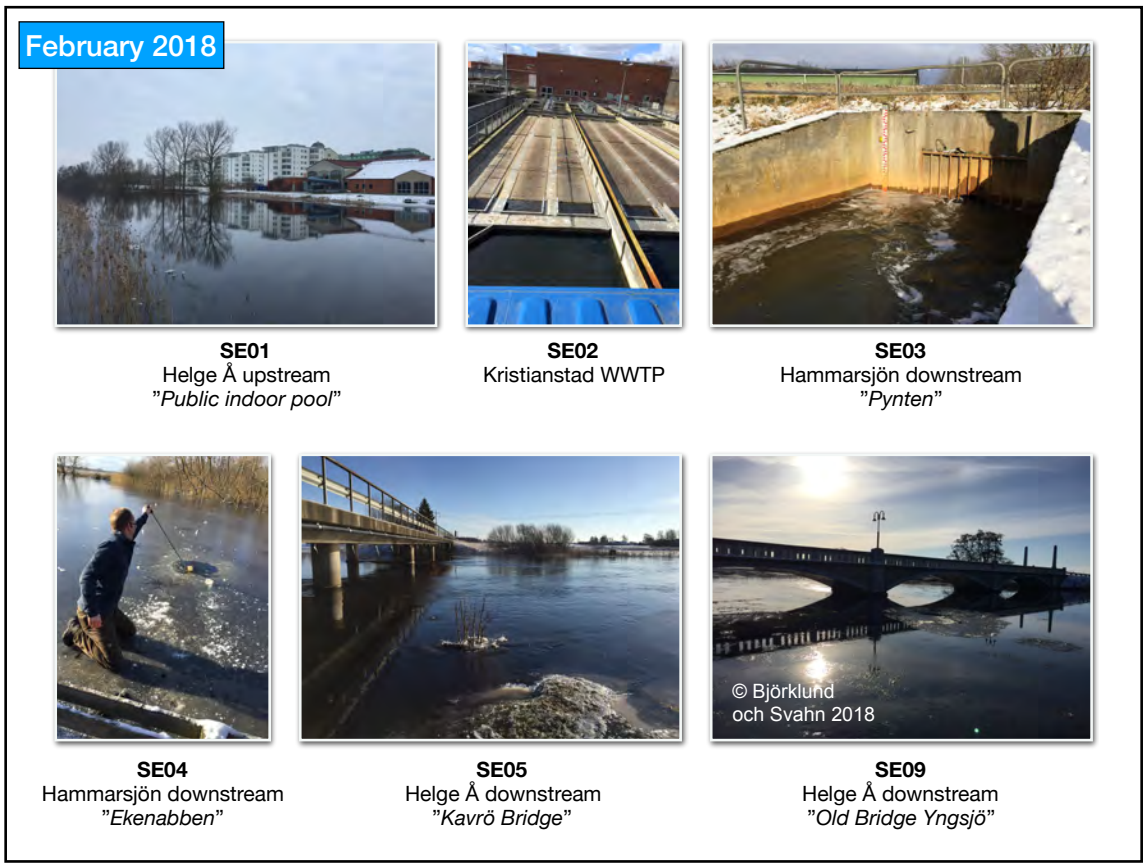


Figure S1. *Photos of the six different sampling points SE01, SE02, SE03, SE04, SE05 and SE09 in Helge Å river area, Region Skåne, Sweden. Photos: Erland Björklund except SE04, Ola Svahn.*

Figure S2

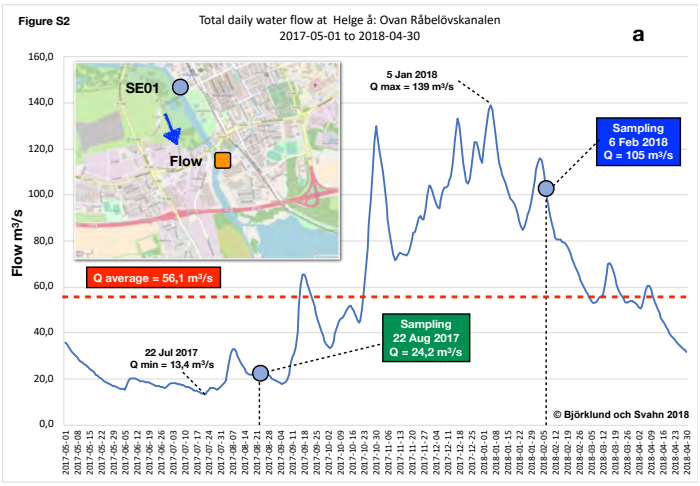
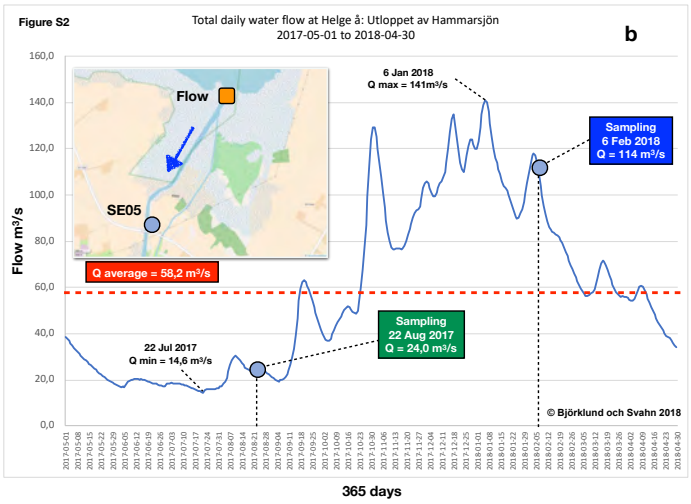


Figure S2a. *Flow data for Helge Å River at three different positions close to sampling point SE01 (a), SE05 (b) and SE09 (c) during the period 2017-05-01 to 2018-04-30. All data from the open database "WISS – Water Information System Sweden"*



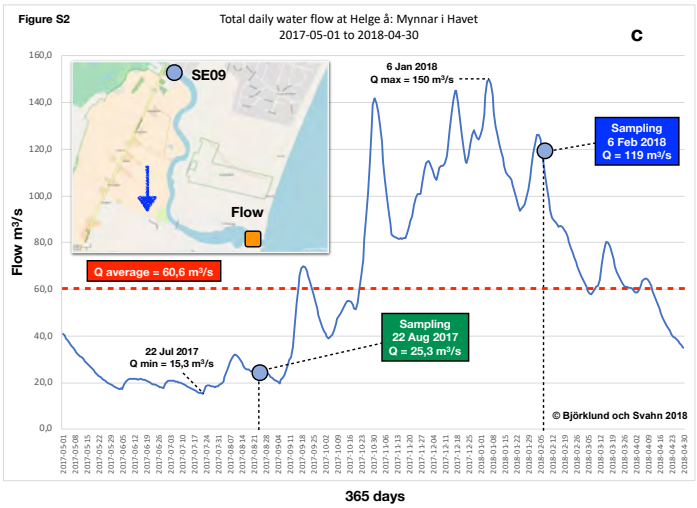


Figure S3

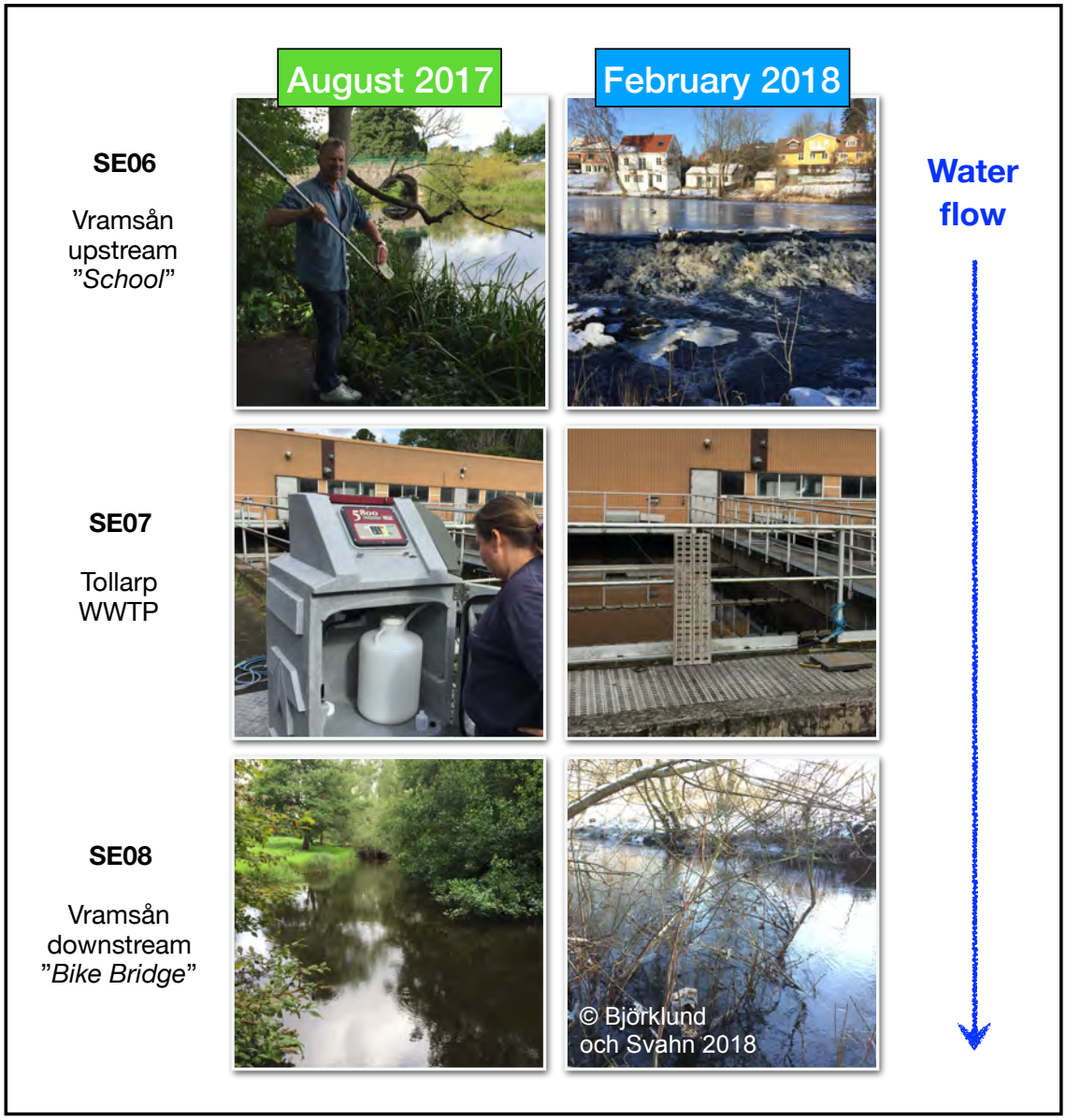


Figure S3. *Photos of the three different sampling points SE07, SE08 and SE09, in Vramsån river area, Region Skåne, Sweden. Photos: Erland Björklund.*

Figure S4

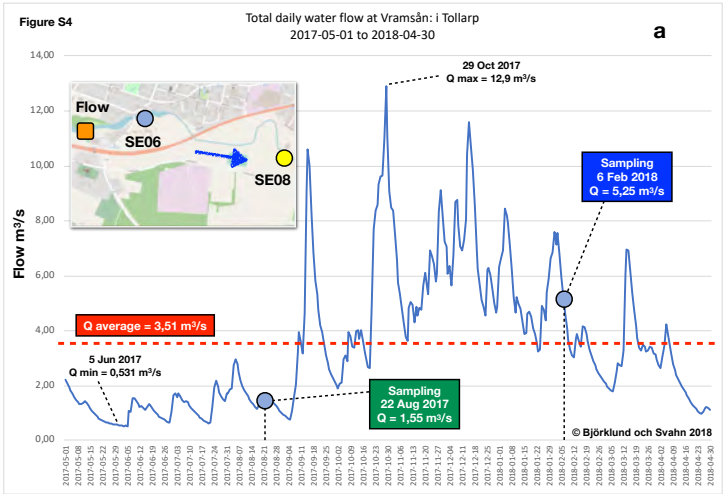


Figure S4. *Flow data for Vramsån River at two different positions related to sampling point SE06 and SE08 (a) and to the outflow of Vramsån River in Helge Å River (b) during the period 2017-05-01 to 2018-04-30. All data from the open database "WISS*

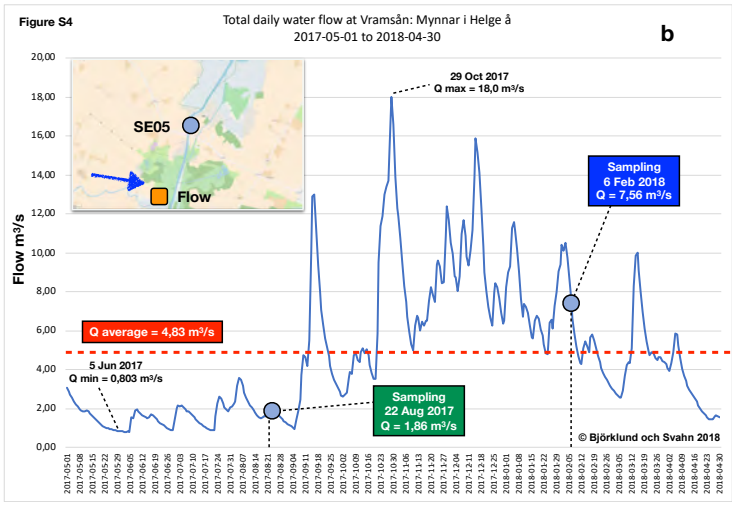


Figure S5

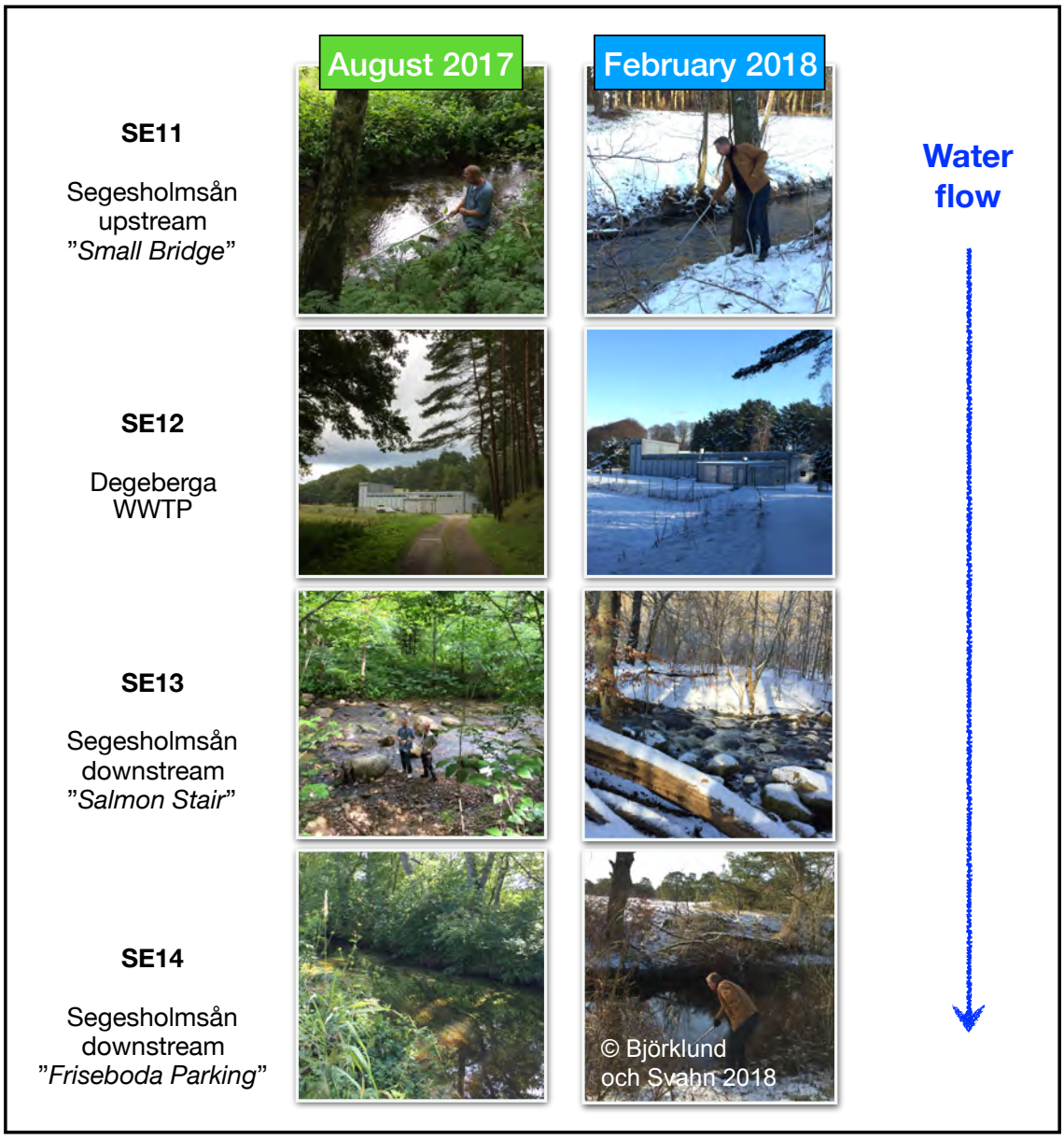


Figure S5. *Photos of the four different sampling points SE11, SE12, SE13 and SE14, in Segesholmsån river area, Region Skåne, Sweden. Photos: Erland Björklund.*

Figure S6

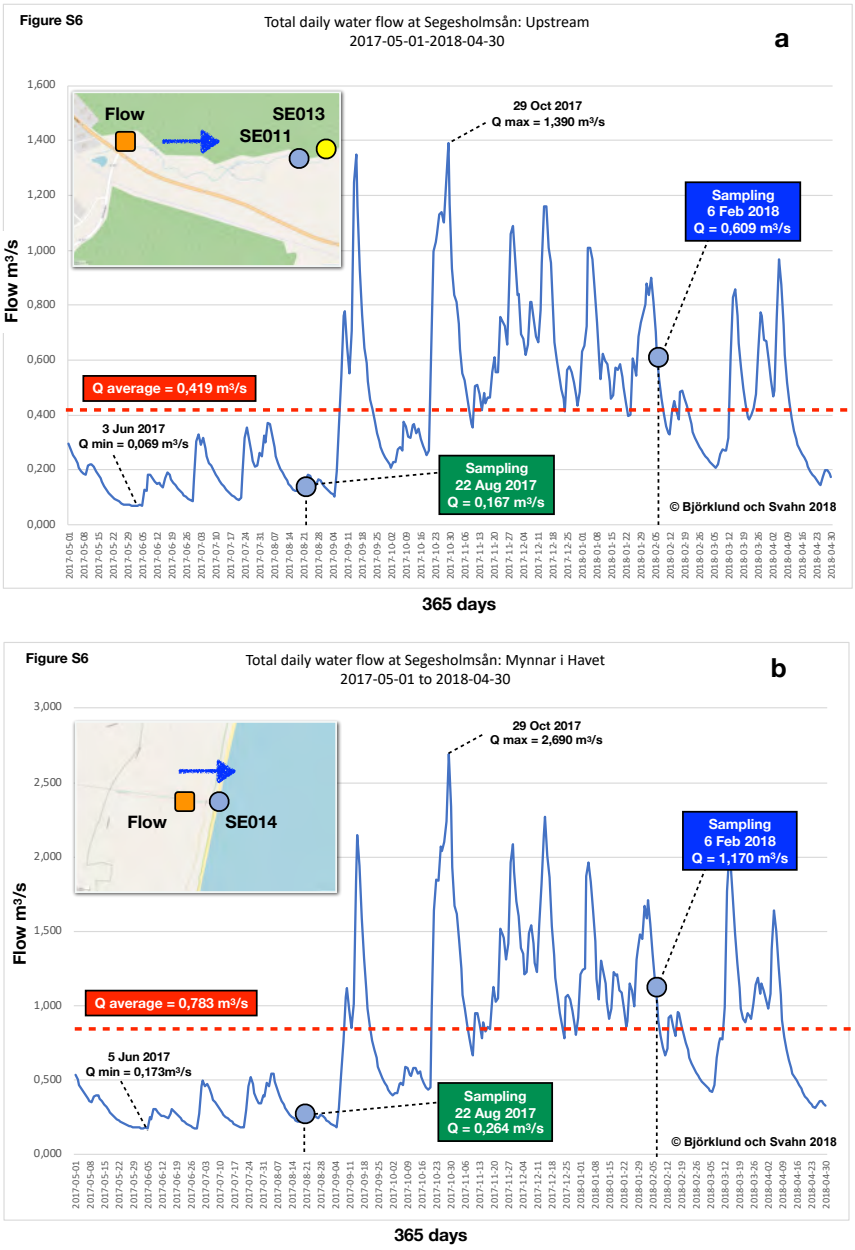


Figure S6. *Flow data for Segesholmsån River at two different positions close to sampling point SE011 and SE13 (a) and SE14 (b) during the period 2017-05-01 to 2018-04-30. All data from the open database "WISS – Water Information System Sweden"*


H
KR