



# Environmental levels and risks of APIs in Baltic Sea region

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# Three years ago: several knowledge gaps



**Table 1.** An overview of data provided in response to a HELCOM questionnaire on occurrence, sources and pathways of pharmaceuticals in the Baltic Sea region.

Source: Original data.

Country	Production & waste		Sales, Consumption		Monitoring data					
	Production	Waste management	Human	Veterinary	WWTPs	Sludge	Rivers	Sea water	Sediments	Biota
Denmark					•	•	•	•		
Estonia		•	•		•		•	•	•	
Finland	•	•	•	•	•	•	•	•	•	
Germany		•	•	•	•		•	•		
Poland								•		
Russia			•		•			•		
Sweden		•	•		•	•	•	•	•	•



# CWPharma filled in some knowledge gaps

## Human and veterinary consumption of APIs

### Levels of APIs

- Rivers, lakes and Baltic Sea estuaries
- Sediments of Baltic Sea estuaries
- Influent and effluent from WWTPs
- Sewage sludge from WWTPs
- Soils fertilized with sludge or manure
- Coastal waters near fish farms
- Watercourses near pig and poultry farms
- Effluents from manufacturing facilities and hospitals
- Leachates from landfills

### Environmental risks

### Upscaling of screening data to BSR



13 400 data points  
from 226 samples

+

Consumption  
data of 80 APIs



### 10 API groups

- Antibiotics
- Antiepileptics
- Antihypertensives
- Asthma and allergy medications
- Gastrointestinal disease medications
- Hormones
- Metabolic disease medications
- Non-steroidal anti-inflammatory drugs (NSAIDs) and analgesics
- Other cardiovascular medicines
- Psychopharmaceuticals
- Veterinary medicines

# Environmental levels and risks



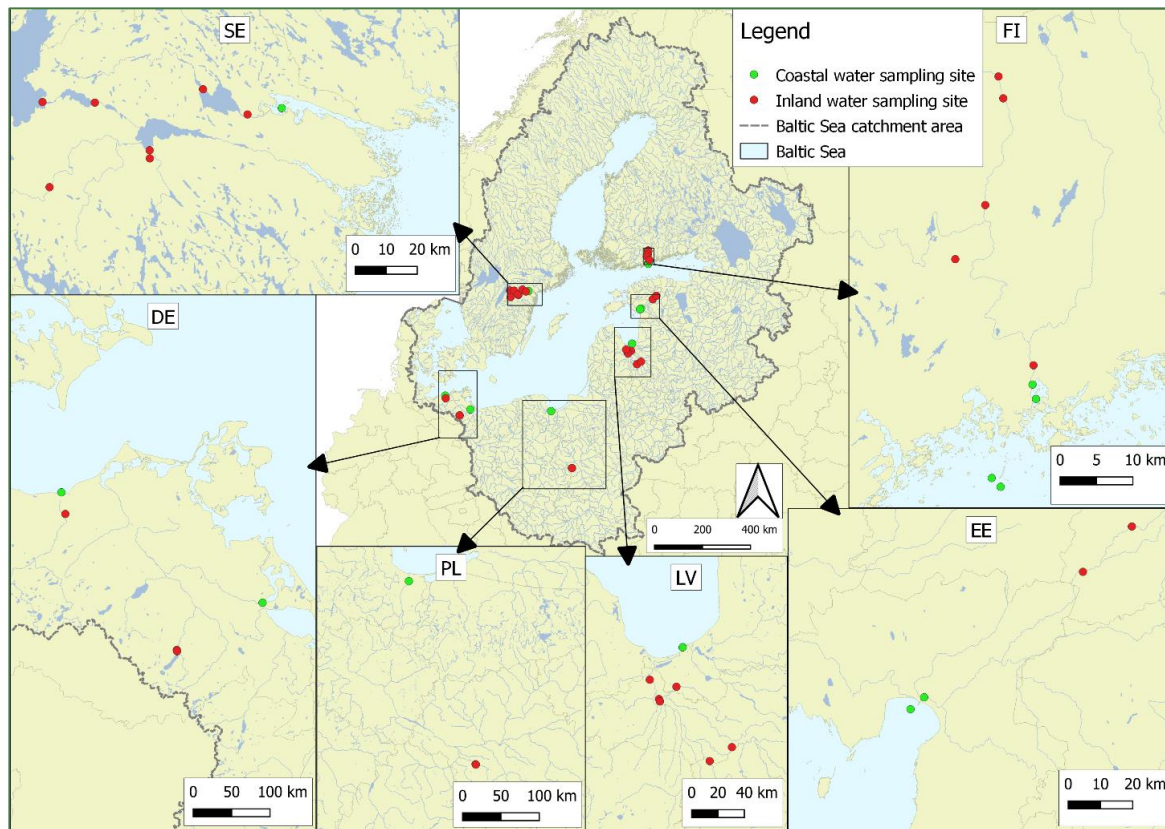
# Case study areas – 6 river basin districts

Motala ström in Sweden

Vantaa in Finland

Warnow-Peene in Germany

Pärnu in Estonia

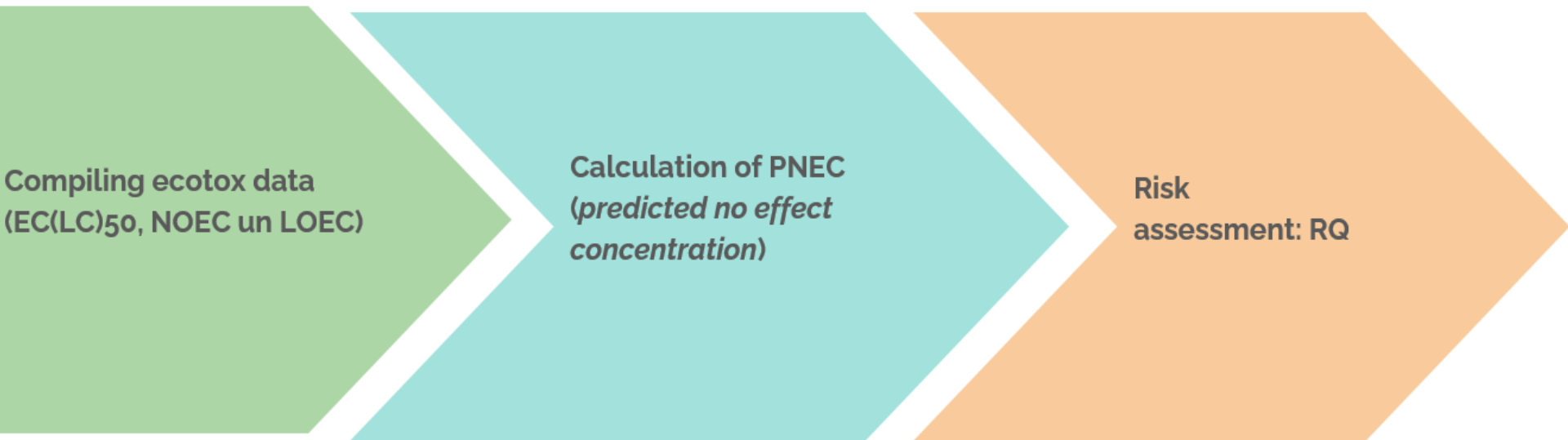


Vistula in Poland

Lielupe and Daugava in Latvia



# Assessment of environmental risks



$$RQ = \frac{PEC(MEC)}{PNEC}$$



### Information sources

Agency for Toxic Substances and Disease Registry database

Cal/Ecotox

Columbia Environmental Research Centre Acute Toxicity Database

ECHA

ECOTOX

EPA

FASS

PAN Pesticide Database

TOXicology Data NETwork

WikiPharma

+ Scientific literature



EC(LC)<sub>50</sub>

NOEC

LOEC





# Assessment of environmental risks I

- No ectox data -> nebivolol and cetirizine
- Additional ecotoxicological tests:
  - bacterial bioluminescence test
  - Algal growth inhibition test
  - *Daphnia magna* immobilization test

Available data	Assessment factor
Up to 8 acute test results	AF=1000
Up to 2 chronic test results	AF=100
At least 3 chronic test results, from 3 trophic levels	AF=10



# Assessment of environmental risks II

$$PNEC_{water} = LCL(HC_5),$$

where  $LCL(HC_5)$  is the lower confidence interval (LCL) of hazardous concentration for 5% of species (HF5).

$$PNEC_{sediment} = PNEC_{water} * (0.783 + 0.0217 * K_{oc}), \uparrow$$

where  $K_{oc}$  is the organic-carbon partition coefficient

- For hydrophilic substances (i.e.  $\log K_{ow} < 3$ )
- For hydrophobic substances (i.e.  $\log K_{ow} \geq 3$ )

$$PNEC_{soil} = \frac{K_{oc} * PNEC_{water}}{85},$$

where 85 is the conversion factor taking into account normalized fraction of organic carbon in soil (0.02) and the bulk density of wet soil ( $1700 \text{ kg/m}^3$ )

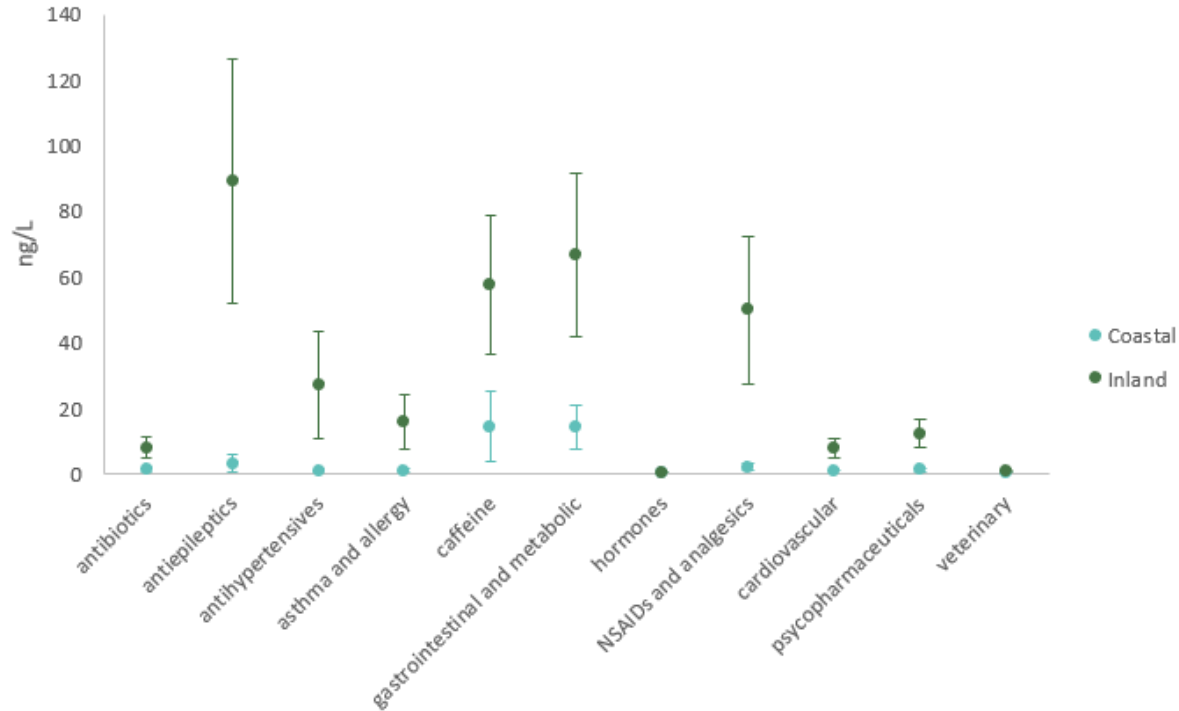


# Results



# Environmental levels in surface waters

- Each sample contained: 8–49 of 63 analysed APIs.
- Sum concentration: 0.0018–12  $\mu\text{g/L}$ .
- Most frequently detected: carbamazepine, tramadol, diclofenac, cetirizine, venlafaxine and citalopram.
- Highest concentrations: telmisartan, metformin and diclofenac (2.2–2.8  $\mu\text{g/l}$ ).



# Risky substances in surface waters

## Lakes & rivers

Compound	API group	PNEC (ng/L)	Number of samples above LOQ exceeding PNEC
<b>Estrone</b>	Hormone	0.008	14/55 <sup>a)</sup>
<b>Clarithromycin</b>	Antibiotic	3.9	25/55
<b>Norethisterone</b>	Hormone	0.50	23/55
<b>Diclofenac</b>	NSAID	85.2	19/55
<b>Ofloxacin</b>	Antibiotic	20.4	8/55
<b>Emamectin</b>	Veterinary	1.0	2/55 <sup>b)</sup>
<b>Sum of tetracycline and doxycycline</b>	Antibiotic	36.9 (doxycycline)	1/55
<b>Metformin</b>	Metabolic disease	1350	1/55
<b>Mometasone</b>	Asthma and allergy	14	1/55

a) 31/55 samples were non-detects, but LOQ > PNEC

b) LOQ > PNEC in two samples



# Risky substances in surface waters

## Coastal waters

Compound	API group	PNEC (ng/L)	Number of samples above LOQ exceeding PNEC
<b>Estrone</b>	Hormone	0.008	14/26 <sup>a)</sup>
<b>Emamectin</b>	Veterinary	1.0	5/26 <sup>b)</sup>
<b>Clarithromycin</b>	Antibiotic	3.9	1/26
<b>Norethisterone</b>	Hormone	0.50	4/26

a) 12/26 samples were non-detects, but LOQ > PNEC

b) LOQ > PNEC in three samples



# Environmental levels in sediments

- Each sample contained: 13–27 of 64 analysed APIs.
- Sum concentration: 37 to 188  $\mu\text{g}/\text{kg dw}$ .
- Most frequently detected (DF=100 %): metformin, tramadol, oxazepam, risperidone, and caffeine.
- Highest concentrations: paracetamol, xylometazoline and metformin (60–85  $\mu\text{g}/\text{kg dw}$ ).

Compound	API group	PNEC ( $\mu\text{g}/\text{kg dw}$ )	Number of samples above LOQ exceeding PNEC
<b>Metformin</b>	Metabolic disease	1.6	10/10
<b>Paracetamol</b>	NSAID	1.3	7/10
<b>Ciprofloxacin</b>	Antibiotic	6.7	6/10
<b>Sum of tetracycline and doxycycline</b>	Antibiotic	0.037 (doxycycline)	5/10 <sup>a)</sup>
<b>Estrone</b>	Hormone	0.0002	4/10 <sup>b)</sup>
<b>Norethisterone</b>	Hormone	0.0044	2/7 <sup>c)</sup>
<b>Clarithromycin</b>	Antibiotic	0.41	3/10
<b>Emamectin</b>	Veterinary	0.31	3/10
<b>Ofloxacin</b>	Antibiotic	0.93	2/10
<b>Diclofenac</b>	NSAID	0.47	1/10

a) 5/10 samples non-detects, but LOQ > PNEC

b) 6/10 samples non-detects, but LOQ > PNEC

c) 5/7 samples non-detects, but LOQ > PNEC



# Environmental levels in soils fertilised with sludge or manure

- Each sample contained: 18-25 of 63-64 analysed APIs.
- Sum concentration: 15 –166 µg/L µg/kg dw.
- Most frequently detected (DF=100 %): trimethoprim (0.059–0.25 mg/kg d.w.) , paracetamol (1.4–28 mg/kg d.w.), tramadol (0.31–1.5 mg/kg d.w.) , risperidone (0.079–0.40 mg/kg d.w.) and fenbendazole (0.40–1.7 mg/kg d.w.).

	Number of analysed APIs	Number of APIs above LOQ in soil samples	Detection rate in soil samples (%)	APIs conc. below 1 µg/kg d.w.	APIs conc. below 10 µg/kg d.w.	Detection rate below 10 µg/kg d.w. (%)
<b>Estonia (EST1), October 2018</b>	64	16	25	14	16	100
<b>Estonia (EST2), October 2018</b>	63	18	28	15	16	89
<b>Germany, May 2018</b>	64	20	31	13	18	90
<b>Latvia, June 2018</b>	63	25	40	18	22	89
<b>Sweden (SWE1), June 2018</b>	63	16	25	12	15	94
<b>Sweden, (SWE2), June 2018</b>	63	19	30	15	16	84



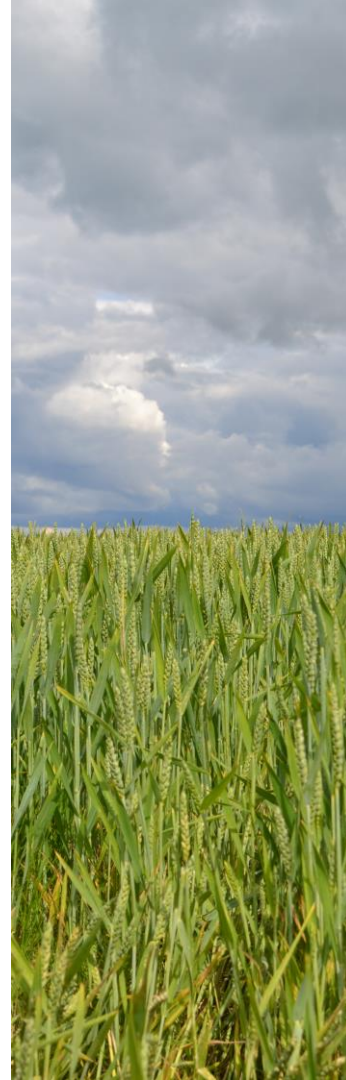


# Environmental levels in soils fertilised with sludge or manure

- Highest concentrations:
  - hydrochlorothiazide (110 µg/kg dw),
  - norfloxacin, paracetamol, estrone (15-30 µg/kg d.w.)
- No clear difference between the soils fertilized by manure or sludge

Compound	API group	PNEC (µg/kg dw)	Number of samples above LOQ exceeding PNEC
<b>Paracetamol</b>	NSAID	0.25	6/6
<b>Metformin</b>	Metabolic disease	0.30	5/6
<b>Ivermectin</b>	Veterinary	0.004	1/6 <sup>a)</sup>
<b>Estrone</b>	Hormone	0.0001	1/6 <sup>a)</sup>
<b>Ofloxacin</b>	Antibiotic	0.49	1/6 <sup>a)</sup>
<b>Diclofenac</b>	NSAID	0.22	1/6
<b>Ciprofloxacin</b>	Antibiotic	3.6	1/6

a) 5/6 samples non-detects, but LOQ > PNEC



# Conclusions - environmental levels & risks

**APIs were detected in all** the studied rivers, lakes, coastal waters, sediments and soils.

**12 APIs were found in levels that pose an environmental risk**

- **Hormones: estrone and norethistrone,**
- **Antibiotics: clarithromycin, ciprofloxacin, ofloxacin, and the sum of tetracycline and doxycycline,**
- **NSAID and analgesic: diclofenac and paracetamol,**
- **Veterinary medicines: emamectin and ivermectin,**
- **Metabolic disease medicine: metformin,**
- **Asthma and allergy medicine: mometasone.**

**The sums of risk quotients were high indicating an urgent need to decrease the loading and the environmental levels of APIs.**



# Thank you!



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