



Pharmaceutical residues and bromide challenges

- presence in wastewater and recipient and future challenges with ozonation

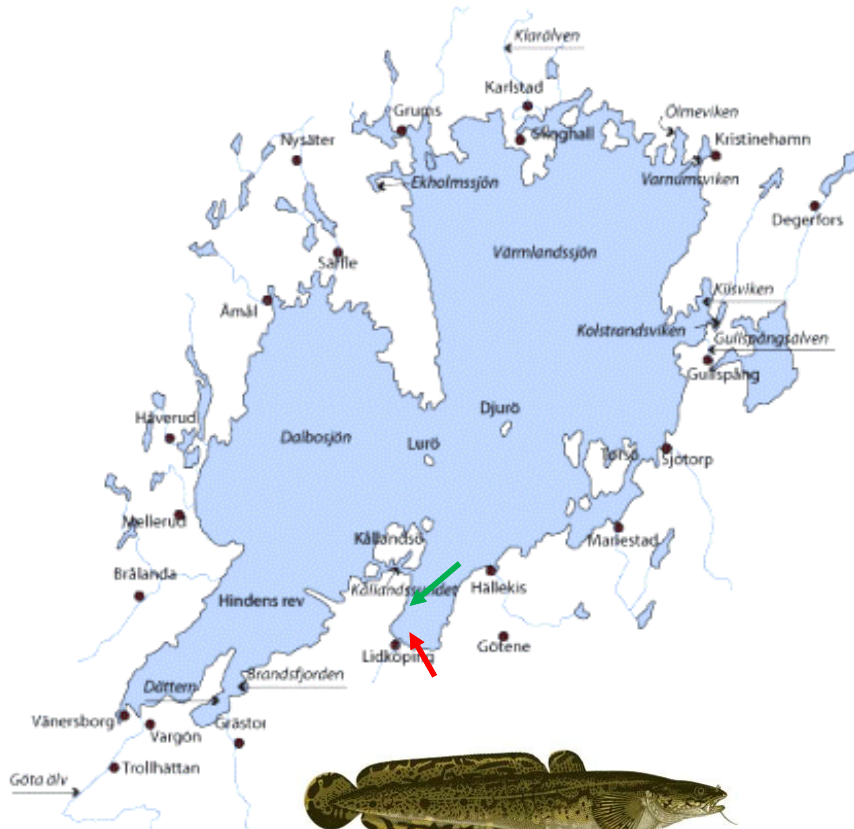


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Agenda for presentation

- Pharmaceutical residues
 1. Swedish legislation
 2. Recommended substances for analysis
 3. Measurements in waste water
- Bromide investigation
 1. Concentration of outgoing water from waste water treatment plant
 2. Concentration of bromide in the drinking water
 3. Identification of potential bromide sources and concentrations
 4. Further work

About Vänern



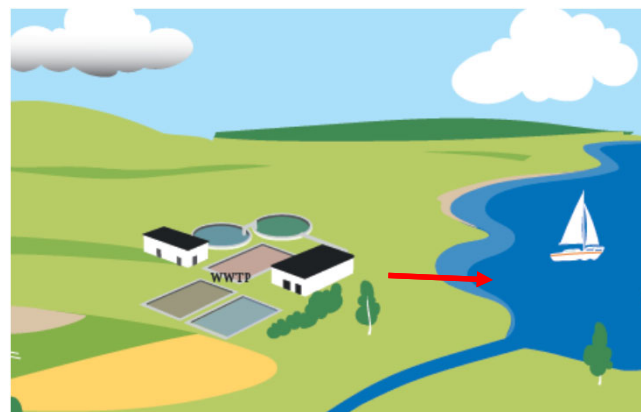
- The largest lake in Sweden, and the third largest lake in Europe. Vänern and the Göta älv supply approximately 800 000 persons with drinking-water
- The chemical and biological status of the lake is very important
 - 38 permanent fishspecies
 - 50 species of birds
- The river Lidan – 93 km, average water flow 19 m³/s



Legislation – pharmaceutical residues

WWTP

- no general legislation (yet) regulating the emission of pharmaceutical residues from the WWTP
- when applying for a permit, the permit authority must take into account whether the environmental quality standard (WFD) is exceeded for the parameter in the recipient. It may be a reason to refuse permission



The recipient (lake, river) WFD (Water Framework Directive)

- WFD- ecological status and chemical status (priority substances)
- Sweden has introduced the four pharmaceuticals
 - diclofenac,
 - ciprofloxacin,
 - 17-beta-estradiol and
 - 17-alpha-ethinylestradiol as “*särskilt förorenande ämnen SFÅ*” “special pollutants” for ecological status (physico-chemical) in surface water

[VISS](#)

	Ecological status EQS – SFÄ		Kinnevikén Vänern Surface-water for making drinking water 2017	
	Annual average, µg/l	Maximum Allowable Concentration, µg/l		
Ciprofloxacin		0,1		
Diklofenak	0,1		<0,01	
17-alfa – etinylöstradiol	0,000035			
17-beta-östradiol	0,0004		<0,01	The detection limit for the analyzes higher than the limit

The Swedish EPA's recommended substances for analysis

WFD – Watch List

- 17-Alpha-ethinylestradiol (EE2)
- 17-Beta-estradiol (E2), estrone (E1)
- Macrolide antibiotics (erythromycin, clarithromycin, azithromycin)
- Methiocarb
- Neonicotinoids (imidacloprid, thiacloprid, thiamethoxam, clothianidin, acetamiprid)
- Metaflumizone
- Amoxicillin
- Ciprofloxacin

Substance	Comment	Substance	Comment
Atenolol		Metoprolol	
Carbamazepine		Mutagenicitet	AMES
Ciprofloxacin		Naproxen	
Citalopram		Oxazepam	
Clarithromycin		Paracetamol	
Diclofenac		PFAS-11	
Erythromycin		Propranolol	
Phenolic substances	At least nonylfenol	Sertraline	
Fluconazole		Sulfamethoxazole	
Furosemide		Tramadol	
Ibuprofen		Irimethoprim	
Ketoconazole		Venlafaxine	
Losartan		Zolpidem	
Methotrexate		Estrogenic effects	YES (or cellinjebaserad)

Measurements on incoming and outgoing water, WWTP, 2017

		WWTP incoming ng/l	WWTP outgoing ng/l	Reduction %
Substance	Therapeutic effect			
Paracetamol	Analgesic	295,5	125	58
Amoxicillin	Antibiotics	<0,5	<0,5	
Ampicillin	Antibiotics	<0,5	<0,5	
Benzylpenicillin	Antibiotics	<0,5	<0,5	
Ciprofloxacin	Antibiotics	90	2	98
Clarithromycin	Antibiotics	12	7,4	38
Clindamycin	Antibiotics	14	73	-421
Doxycycline	Antibiotics	6,5	1,3	80
Erythromycin	Antibiotics	6,3	5,8	8
Fusidic acid	Antibiotics	1,8	1,3	28
Linezolid	Antibiotics	4,4	3,6	18
Metronidazole	Antibiotics	21	4,7	78
Moxifloxacin	Antibiotics	<3	<3	
Norfloxacin	Antibiotics	<0,5	<0,5	
Rifampicin	Antibiotics	10	0,5	95
Sulfamethoxazole	Antibiotics	32	8,2	74
Tetracycline	Antibiotics	290	14	95
Trimethoprim	Antibiotics	220	39	82
Warfarin	Anticoagulant	24	14	42
Citalopram	Antidepressant	490	425	13
Fluoxetine	Antidepressant	19	8,6	55
Sertralin	Antidepressant	238,5	28,5	88

		WWTP incoming ng/l	WWTP outgoing ng/l	Reduction %
Substance	Therapeutic effect			
Amlodipine	Antihypertensive	128	4,55	96
Atenolol	Antihypertensive	3150	1800	43
Bisoprolol	Antihypertensive	390	320	18
Hydrochlorothiazide	Antihypertensive	1550	1250	19
Metoprolol	Antihypertensive	2000	1650	18
Propranolol	Antihypertensive	150	155	-3
Ramipril	Antihypertensive	30,5	14	54
Diclofenac	Anti-inflammatory	1300	980	25
Ibuprofen	Anti-inflammatory	13500	45,5	100
Ketoprofen	Anti-inflammatory	645	76,5	88
Naproxen	Anti-inflammatory	6000	114	98
Risperidone	Antipsychotic	<1,9	<1,9	
Ranitidine	Antiulcer	315	170	46
Terbutaline	Asthma medication	33,5	17	49
Furosemide	Diuretic	2600	1450	44
etinylöstradiol	Hormone			
östradiol	Hormone	9,9	<LOD	
östron	Hormone	73	0,9	99
Östrogena effekter		17	0,07	100
Simvastatin	Lipid-regulating	165	16,6	90
Carbamazepine	Sedative	690	670	3
Oxazepam	Sedative	835	705	16
Caffeine	Stimulant	116500	375	100

µg/l	EQS – SFÄ Ecological status		2017 Recipient	2017 WWTP
	Annual average,	Maximum Allowable Concentration,	Kinneviken, Vänern Surface-water for making drinkingwater	Treated wastewater WWTP (incoming)
Ciprofloxacin		0,1		0,002 (0,090)
Diklofenak	0,1		<0,01	0,98 (1,3)
17-alfa – etinylöstradiol	0,000035			Detected but uncertain analyzes
17-beta-östradiol	0,0004		<0,01 The detection limit for the analyzes higher than the limit	<LOD (0,01)

Next step -

Major study of pharmaceutical residues, PFAS and some other organic pollutants

- Sampling will take place in Sweden's three largest lakes; Vänern, Vättern and Mälaren
- Collaboration between three societies for water conservation, the Swedish University of Agriculture (SLU), the Swedish Agency for Marine and Water Management, municipalities and the EU project LIFE IP Rich Waters.
- Sampling 4 times during 2019-2020
 - Lidköping WWTP
 - Spiken WWTP
 - Lockörn water treatment
- 85 pharmaceutical substances
- 13 PFAS
- 7 Industrial chemical
- 2 pesticides
- 7 other substances (parabens, artificial sweetener, stimulants)



Investigation of bromide

- Bromide + Ozone → Bromate
- Bromate is cancerogenic
 - Proposal: <50 µg/l as environmental quality standard
 - Drinking water concentration limit of 10 µg/l in Sweden
- MBBR can not reduce bromate.
- If Bromide exists, there are three ways to avoid bromate formation in the ozonation reactor:
 - Lower the ozone dose
 - Add hydrogen peroxide or altering pH
 - Eliminate bromide source from the inlet stream.

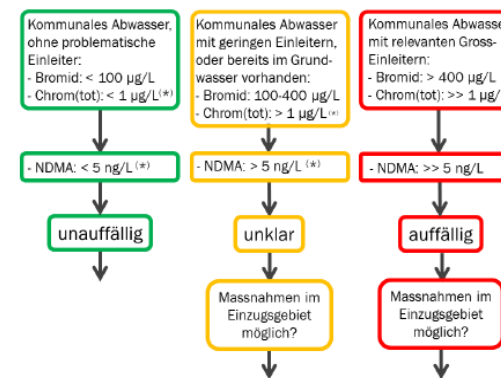
Analysis of bromide upstream!

1. Waste water out from the WWTP 2017

- Outgoing water from the Waste water treatment plant contains relatively high levels of bromide.
- According to recommendations from Switzerland the concentrations are in the upper Yellow zone.
- Dose of 0.4-0.6 gO₃/gDOC render around 3% bromate yield (C_{bromate}/C_{bromide})

→ Need to continue the bromide investigation!

Bromide		
	Date	µg/l
Out from Waste water plant	2017-04-26	350
	2017-04-27	360
	2017-04-28	290
	2017-05-02	280
	2017-05-03	300
	2017-05-04	350
	2017-05-05	250
	Average:	311



(*) oder gemäss Bestimmungsgrenze der gängigen analytischen Methoden.

Substans	Typ
C _{Bromid} ≤ 100 µg/l	No limitation if Z _{spec} ≤ 0,7 g O ₃ /g DOC
100 µg/l < C _{Bromid} ≤ 150 µg/l	No limitation if Z _{spec} ≤ 0,5 g O ₃ /g DOC, For higher Z _{spec} , bromate formation need to be evaluated
C _{Bromid} < 150 µg/l	Bromate formation should be evaluated from case to case.

2. Drinking water 2017

Drinking water i Lidköping: ca 90 % from Vänern and 10 % from Råda (ground water)

→ The bromide does not come from the drinking water.

However, the ozonation plant cannot be running if only water from Råda is used

Bromide		
Sampling site	Date	µg/l
Lake water	2017-06-21	12
Lake water	2017-06-21	11
Råda	2017-06-21	290
Råda	2017-06-21	300
Drinking water	2017-06-21	14
Drinking water	2017-06-21	13
Drinking water	2017-06-21	20
Average drinking water:		16

3. Identification of areas where bromide may exist

Bromide might come from the following three industrial activities:

- Incineration plant
- Leachate from the landfill
- Smaller metal industry, Kinnegrip

Pump station, for comparison with domestic water

- New built area, little in leakage
- Ca 110 households
- Proper flow measurements

Incoming water to the WWTP for mass balances



Results from the bromide analysis

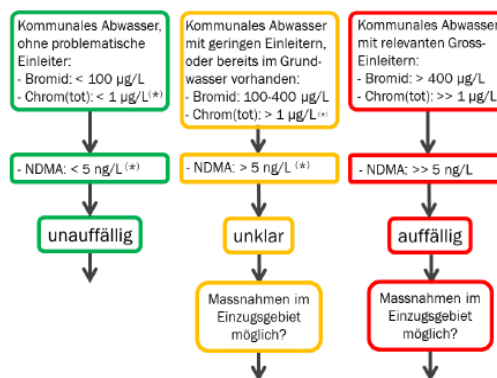
Different results from previously year

- In WWTP 2019: 423 µg/l
- Out WWTP 2017: 311 µg/l

Leachate stands for 15 %

Sampling site	Mass % of In WWTP
Incineration plant	0,09
Leachate	15
Metal industry	1,3
Pump station	0,04

If Leachate would be removed it would reduce the bromide concentration from 423 µg/l to 362 µg/l → in the yellow zone.



(*) oder gemäss Bestimmungsgrenze der gängigen analytischen Methoden.

Sampling site	Date	µg/l	Flow m3/d
Incineration plant	2019-05-15	210	24
Incineration plant	2019-05-16	120	24
Incineration plant	2019-05-17	120	24
Average Incineration plant*		150	24
Leachate from landfill	2019-05-14	13000	37
Leachate from landfill	2019-05-15	16000	34
Leachate from landfill	2019-05-16	16000	43
Average Leachate from landfill		15000	38
Metal industry	2019-02-22	4500	20
Metal industry	2019-03-18	1900	36
Metal industry	2019-04-16	1600	22
Metal industry	2019-05-21	520	21
Average Metal industry		2130	24,75
Pump station	2019-05-14	57	31
Pump station	2019-05-15	41	28
Pump station	2019-05-16	50	27
Average Pump station		49	29
In WWTP	2019-05-14	460	9548
In WWTP	2019-05-15	380	9057
In WWTP	2019-05-16	430	9326
Average In WWTP		423	9310

*The flow from the incineration plant is an average value from a two month flow measurement from 2017



4. Further investigations

Bromide investigations

- Comparing concentrations in and out from WWTP
- Western port area
- Eastern port area
- Hospital

Other compounds recommended to measure:

- NDMA (N-nitrosodimetylamin)
- Chromium → Chromate

Exposure tests of the waste water with reference values and different specific ozone doses

