EFFICIENT TREATMENT OF PHARMACEUTICAL RESIDUE AT SOURCE - EPIC

Millä eroon jäteveden lääkeainejäämistä

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Need

- Existing wastewater treatment processes removes significant amount of micropollutants but not all
- Tertiary treatments are needed
- Technologies for removal of micropollutants
  - Binding (adsorption)
  - Concentrating (membrane filtration)
  - Degrading (oxidation)

Switzerland:

- activated carbon, ozone to remove micropollutants

France (Méry-sur-Oise):

- nanofiltration for removal of pesticides (atrazine, simazine)
- 140000 m^3/day (1.6 m^3/second), 340000 m^2 membranes

Removed or not?

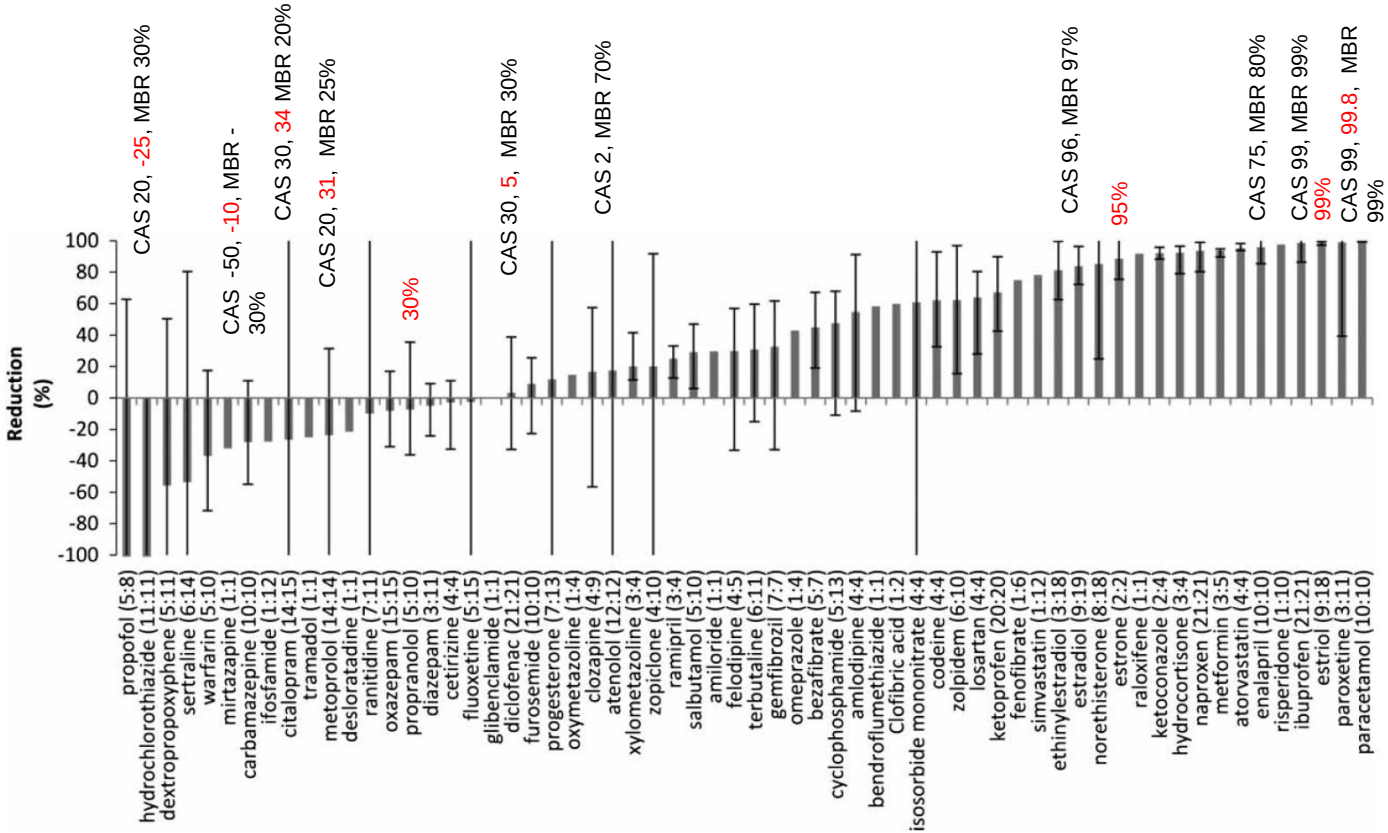


Figure 5 | Median removal efficiency in activated sludge plants with extended nitrogen removal. T-bars indicate standard deviation and numbers within brackets represent – Number of plants used in calculations: Number of plants sampled.

CAS: conventional activate sludge process
MBR: membrane bioreactor
CAS_EPIC (average 6 plants)

Hydrochlorothiazide
Carbamazepine
Citalopram
Diclofenac
Metoprolol
Atenolol

Approach

The aim was to treat pharmaceutical containing wastewaters in the place where they are formed.

Studied effluents

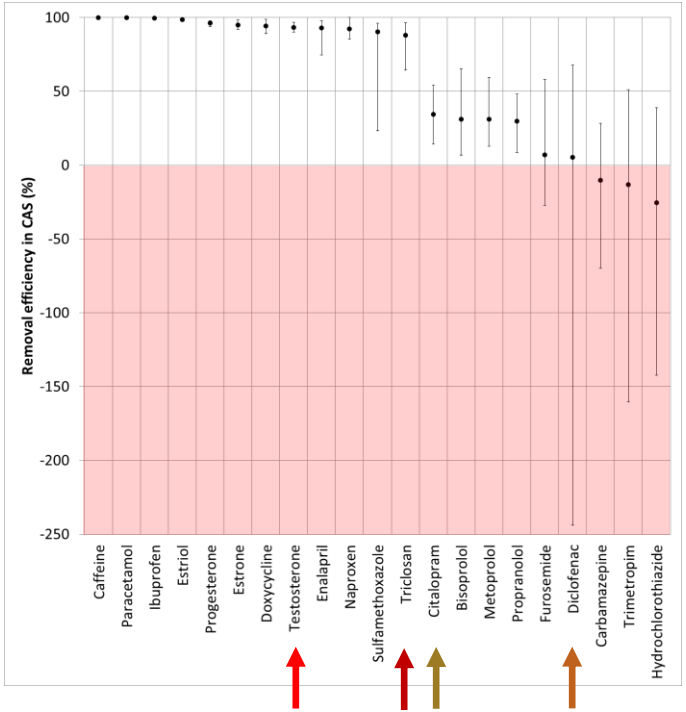
- Waste water from CAS process (Rinnekoti)
- Waste water before CAS process (Rinnekoti)
- Waste water from hospital
- Urine

Studied technologies for removal of micropollutants

- Concentrating (membrane filtration)
- Degrading (oxidation)
- Binding (adsorption)

Removal efficiency in CAS treatment

- EPIC-project, 6 wastewater treatment plants



	Concentration after CAS, µg/L	PNEC value, µg/L	Ratio, -
Paracetamol	0.100	46	0.00
Bisoprolol	0.488	36	0.01
Diclofenac	0.956	0.050	19.12
Doxycycline	0.040	2	0.02
Enalapril	0.024	-	
Furosemide	2.347	142	0.02
Hydrochlorothiazide	2.951	1000	0.00
Ibuprofen	0.086	1	0.09
Carbamazepine	1.228	3	0.49
Caffeine	0.140	-	
Metoprolol	0.737	7	0.10
Naproxen	0.299	0.640	0.47
Propranolol	0.160	0.230	0.70
Citalopram	0.173	0.010	17.33
Progesterone	0.001	-	
Testosterone	0.0010	0.0003	3.85
Triclosan	0.011	0.001	7.50

The predicted No Effect Concentration (PNEC) is the concentration

- PNEC values are not available for all compounds
- Very low concentration limit the accuracy of analysis

Comparison of different streams

	Concentration of pharmaceutical compounds in treated streams						
	Urine	Hospital WW	Rinnekoti Influent	Rinnekoti After CAS	Average of 6 MWWTP Influent	Average of 6 MWWTP After CAS	PNEC
	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L
Caffeine	2600	470	250	0.012	174.3	0.14	-
Paracetamol	1400	580	88	<0.05	103	<0.05	46
Ibuprofen	1400	28	7.7	<0.05	15.31	0.086	1
Naproxen	250	1.1	2.2	0.082	3.92	0.299	0.64
Hydrochlorothiazide	18	4.2	1.1	0.83	2.35	2.951	1000
Metoprolol	9.1	0.37	0.36	0.44	1.07	0.737	7.3
Doxycycline	7.5	2	0.21	<0.02	0.69	0.04	2
Bisoprolol	4.7	0.84	0.34	0.18	0.71	0.488	35.6
Citalopram	2.2	0.23	0.34	0.26	0.26	0.173	0.01
Propranolol	1.3	0.21	0.12	0.23	0.23	0.16	0.23
Diclofenac	0.74	0.6	0.052	0.33	1.01	0.956	0.05
Enalapril	0.47	0.31		<0.01	0.34	0.024	-
Furosemide		11	1.5	0.29	2.52	2.347	142
Carbamazepine		0.35	2.3	3.1	1.12	1.228	2.5
Triclosan			0.006			0.011	0.0014
Progesterone		<0.01	<0.01		0.03	0.001	-
Testosterone			0.014		0.02	0.001	0.00026

Analysed pharmaceutical compounds		
	All, µg/L	Without caffeine, µg/L
Urine	5784	3184
Hospital WW	1148	678
Rinnekoti (influent)	354	104
6 MWWTP (influent)	312	136

- No difference between Rinnekoti and other WWTPs
- 6x higher concentration in hospital WW and 30x higher in urine

Concentrations of certain compounds after CAS process exceeded the PNEC-values!
Citalopram, propranolol, diclofenac, carbamazepine, triclosan, testosterone

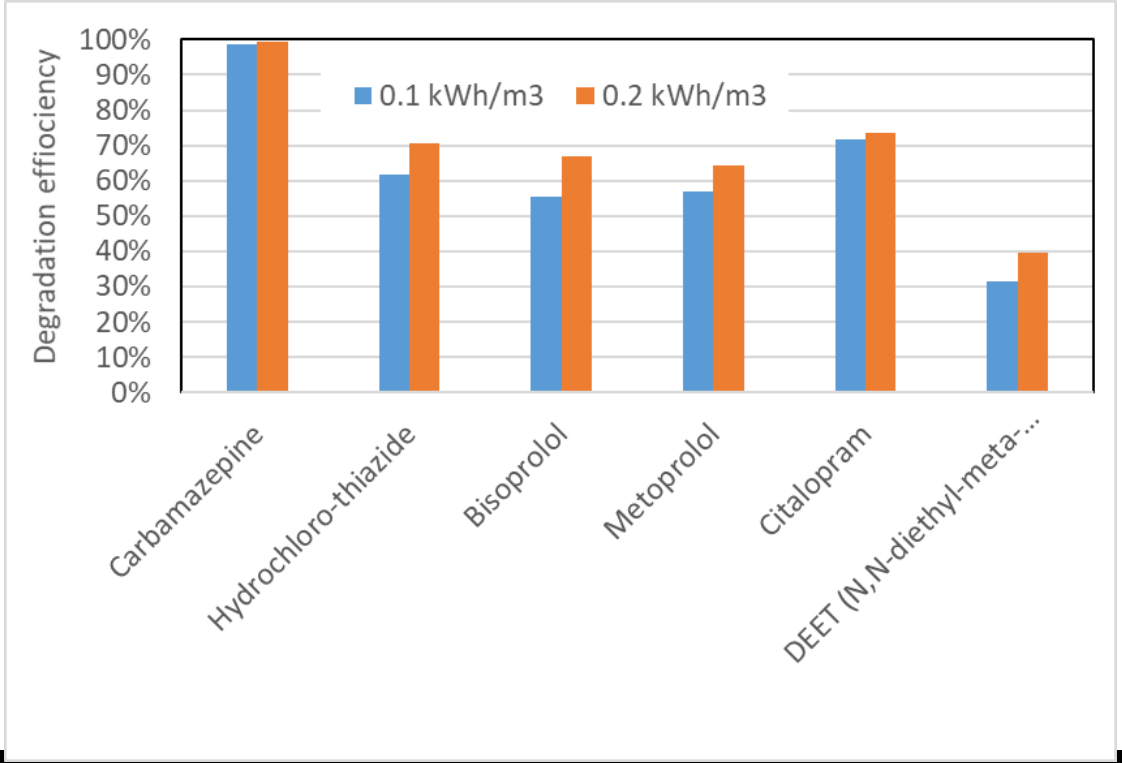
Concentration of pharmaceuticals after membrane filtrations and oxidation

		Concentrations after different treatments							
		Urine		Hospital WW		Rinnekoti, raw		Rinnekoti, CAS	
	PNEC		PCD 250 W		PCD 250 W		PCD 250 W		PCD 250 W
		RO	1 kWh/m³	UF+RO	1 kWh/m³	UF+RO	1 kWh/m³	UF + NF	1 kWh/m³
	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L		
Caffeine	-	43	2000	39.50	480	26.0	180.0	0.01	<0.010
Paracetamol	46	16	950	31.50	130	8.60	29.0		
Ibuprofen	1	19	980	1.55	26	1.00	<0,5		
Naproxen	0.64	2.7	190	0.08	0.50	0.20	1.30	0.044	<0.010
Hydrochlorothiazide	1000	0.15	9.5	0.25	4.30	0.16	1.10	0.78	<0.050
Metoprolol	7.3	0.1	6	0.03	0.26	0.04	0.14	0.095	<0.005
Doxycycline	2	<0.20	1.3	<0.020	0.32	<0.020	<0.2		
Bisoprolol	35.6	0.07	2.7	0.06	0.35	0.04	0.20	0.033	<0.010
Citalopram	0.01	0.017	0.76	0.01	<0.10	0.03	0.18	0.027	<0.010
Propranolol	0.23	0.018	0.58	<0.010	<0.10	0.01	<0.1	0.089	<0.010
Diclofenac	0.05	0.014	0.37	0.04	0.08	<0.005	<0.05	0.06	<0.005
Enalapril	-	<0.010	0.24	0.02	0.25				
Furosemide	142			0.61	<0.50	0.10	<0,5	0.088	<0.050
Carbamazepine	2.5			0.02	0.09	0.25	1.50	1.3	<0.005
Triclosan	0.0014					<0.005	<0.5		
Progesterone	-				0.02	<0.005	0.01		
Testosterone	0.00026					0.002	0.01		

Oxidation of CAS treated waste water

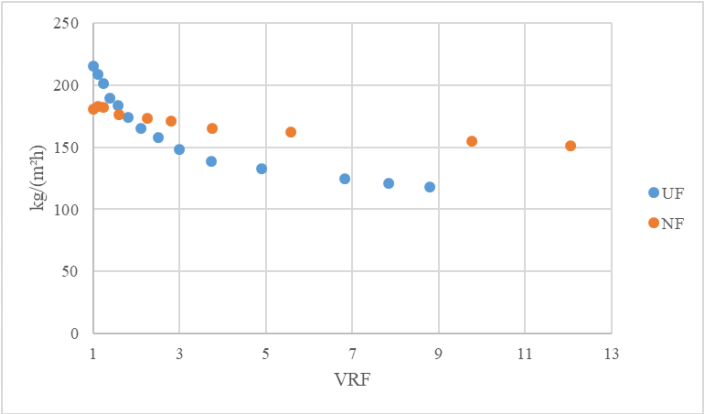
Conductivity	432 µs/cm
COD	33 mg/L
TOC	11 mg/L
Total phosphorous	0.1 mg/L
Total nitrogen	3.3 mg/L

Concentration of pharmaceutical compounds after oxidation less than NPEC values except citalopram (2-3x higher)

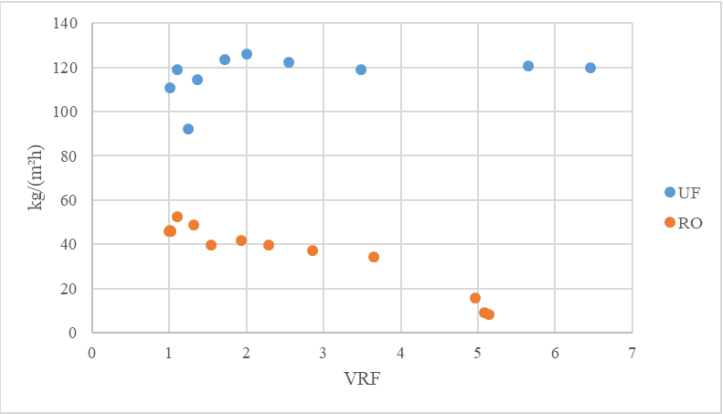


Membrane filtration of CAS treated waste water and untreated waste water

CAS + UF + NF



UF + RO



	TOC, mg/L	Conductivity, mS/cm	Fosfori, mg/L	Nitrogen, mg/L
CAS	5.5	0.46		
CAS + UF + NF	**0.7**	**0.22**		
Raw WW	62	0.82	5.9	44.6
UF + RO	**5.3**	**0.12**	**0.1**	**8.4**
PCD 1 kWh/m³	72	0.78	5.3	42

→ **Drinking water quality?**

→ **Higher purity than after CAS**

Hospital waste water

		Concentration after treatment			Removal efficiency		
	Raw ww	UF	**RO**	PCD 30 W	UF + RO	PCD 250 W	PCD 30 W
	mg/L	mg/L	**mg/L**	mg/L	at 82% water rec.	1 kwh/m^3	1 kwh/m^3
P_{tot}	5.5	3.9	**0.1**	4.6	98.2 %	7 %	16 %
N_{tot}	63	54	**6**	62	90.5 %	0 %	2 %
COD	793	500	**21**	666	97.4 %	13 %	16 %
DOC	200	140	**3**	178	98.5 %	12 %	11 %

- **Direct membrane filtration is promising methods for purification of hospital waste water**
- Direct oxidation degraded significant amount of pharmaceuticals
- Oxidation power / time affect the oxidation efficiency at same energy dose

	UF + RO	PCD 250 W	PCD 30 W
	at 82% water rec.	1 kwh/m^3	1 kwh/m^3
Citolapram	95 %	100 %	100 %
Carbamazepine	95 %	75 %	100 %
Diclofenac	93 %	86 %	100 %
Metoprolol	92 %	30 %	100 %
Bispropol	93 %	53 %	100 %
Ibuprofein	94 %	7 %	50 %
Hydrochlorothiazide	94 %	-2 %	48 %
Enalapril	95 %	19 %	39 %
Metronidazole	98 %	6 %	18 %
Caffeine	92 %	-2 %	19 %
Hydrocortisone	90 %	22 %	18 %
Paracetamol	95 %	78 %	93 %
Doxycycline	>99%	84 %	> 90%
Naproxen	93 %	55 %	> 90%
Citalopram	95 %	> 60%	> 60%

Ajo P., et al. 2018, Hospital wastewater treatment with pilot-scale pulsed corona discharge for removal of pharmaceutical residues, Journal of Environmental Chemical Engineering 6(2) 1569-1577.

Conclusion

- Waste water from Rinnekoti contained the same level pharmaceutical compounds as municipal waste water
- Higher concentration (6 times) was observed in hospital wastewater (especially paracetamol)
- Urine contained 30x more pharmaceuticals than centralized waste waters
- Concentration of several compounds exceeded the PNEC values in CAS treated waste water

Conclusion

Oxidation

- PCD oxidation degraded most of residual pharmaceuticals with as low energy consumption as 0.1-0.2 kWh/m^3 water when waste waters were pretreated by activated sludge process
- Direct oxidation of waste waters or membrane concentrates obviously needs more energy, at least 30 times more
- No effect to the total amount of organic compounds or nutrients

Conclusion

Membrane filtration

- Reverse osmosis retained more than 95% of almost all pharmaceutical compounds
- After CAS process the water quality corresponds to the drinking water quality
- Direct membrane filtration with UF and RO membranes lead to better water quality than CAS process
- Nutrients and DOC are also removed

- **Not only pharmaceuticals but also nutrients, organic compounds, salts etc. need to be taken into account when advanced purification process is selected**