Biodegradability of pharmaceuticals in biological systems treating source separated wastewater streams

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SWITCH

Sustainable Water management Improving Tomorrow's Cities' Health

Theme 4: Treatment of Source separated black water and/or urine

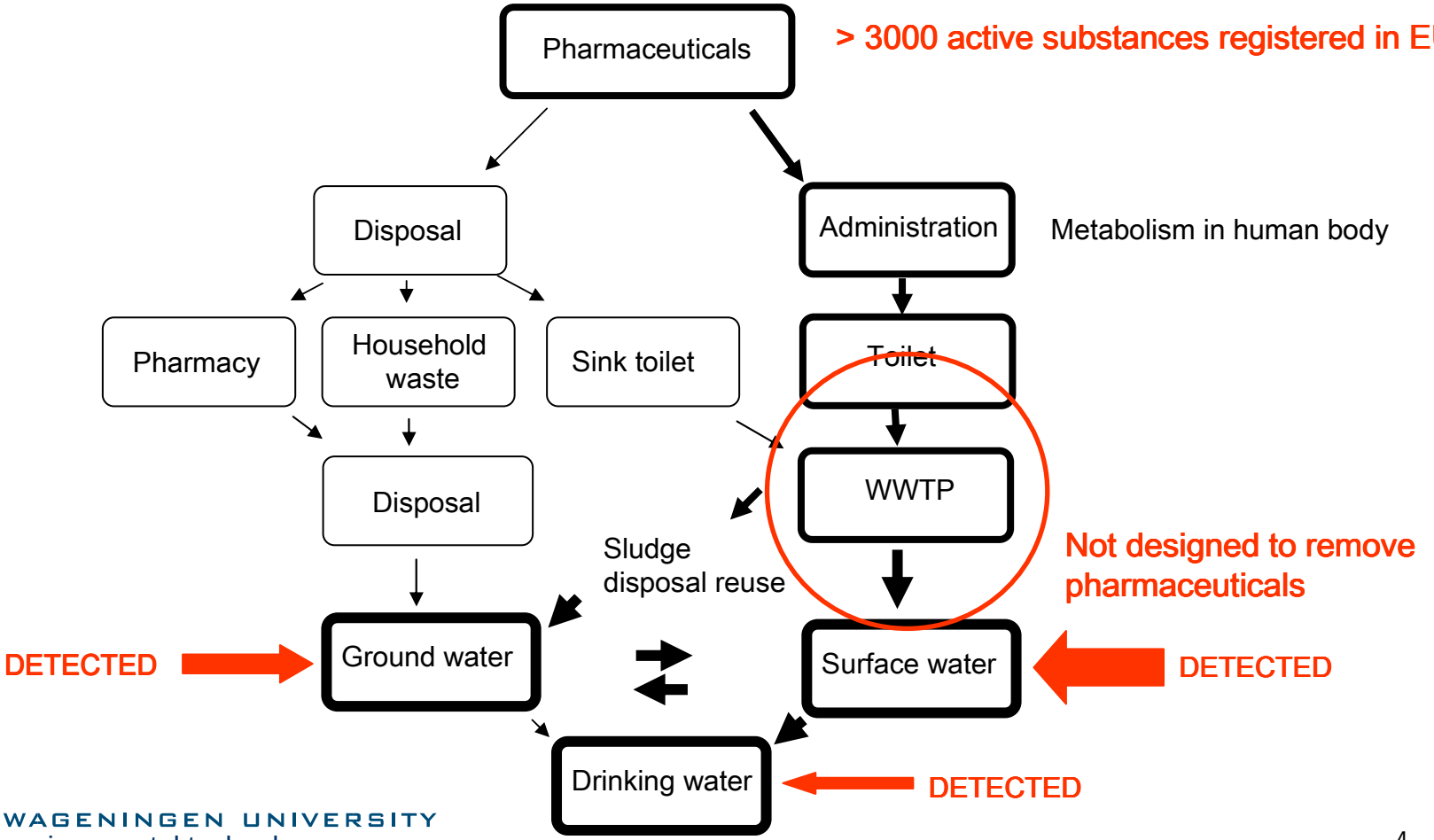
Activity 2: Development of treatment system for removal of pharmaceuticals from urine and black water

Pharmaceuticals as environmental issue since late ‘90s

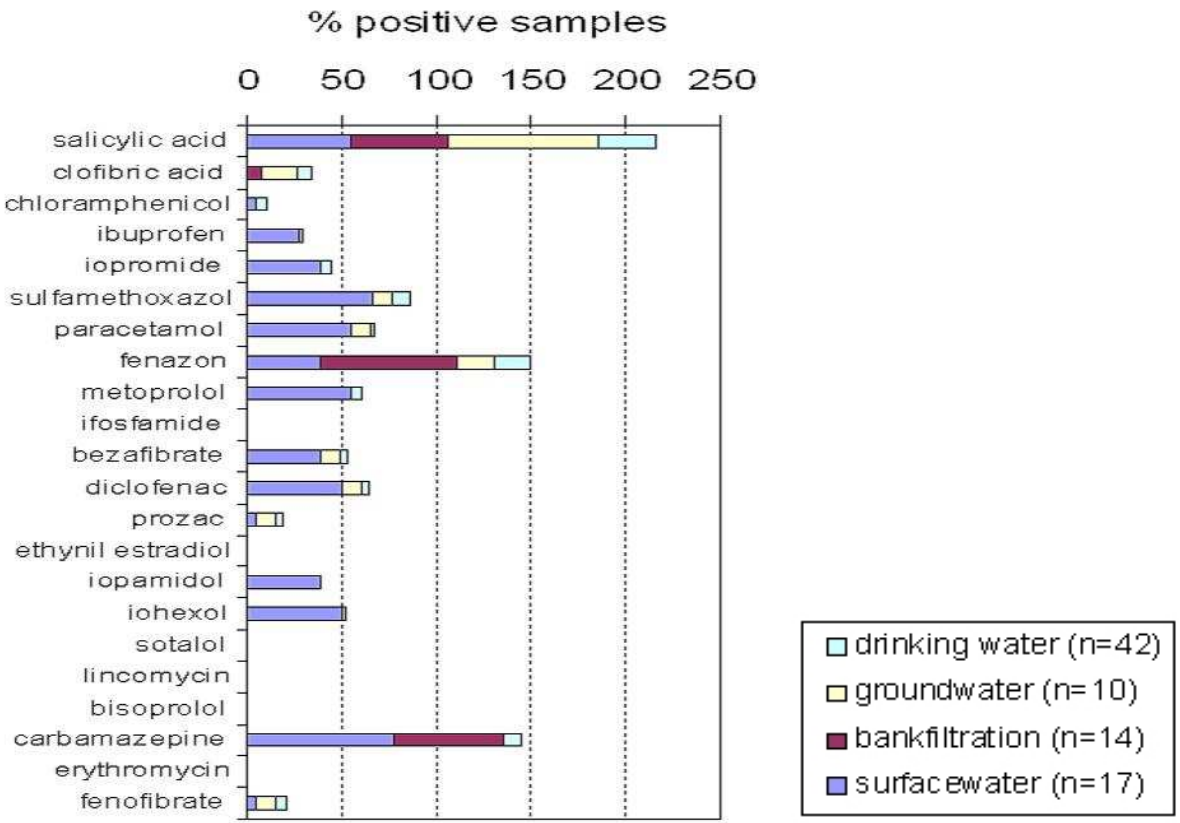
- Detection of low levels of drugs triggered a number of scientific publications, conferences, media stories and research (lots)
- Widely divergent speculations of the potential effects to wildlife - uncertainty on potential chronic effects

- Presence of xenobiotics and especially pharmaceuticals in environment, even at trace concentrations, regardless harmful or not, is not acceptable for a public

How pharmaceuticals reach environment?



Pharmaceuticals are present in drinking water



Source: Versteegh et al., 2007 (RIVM)

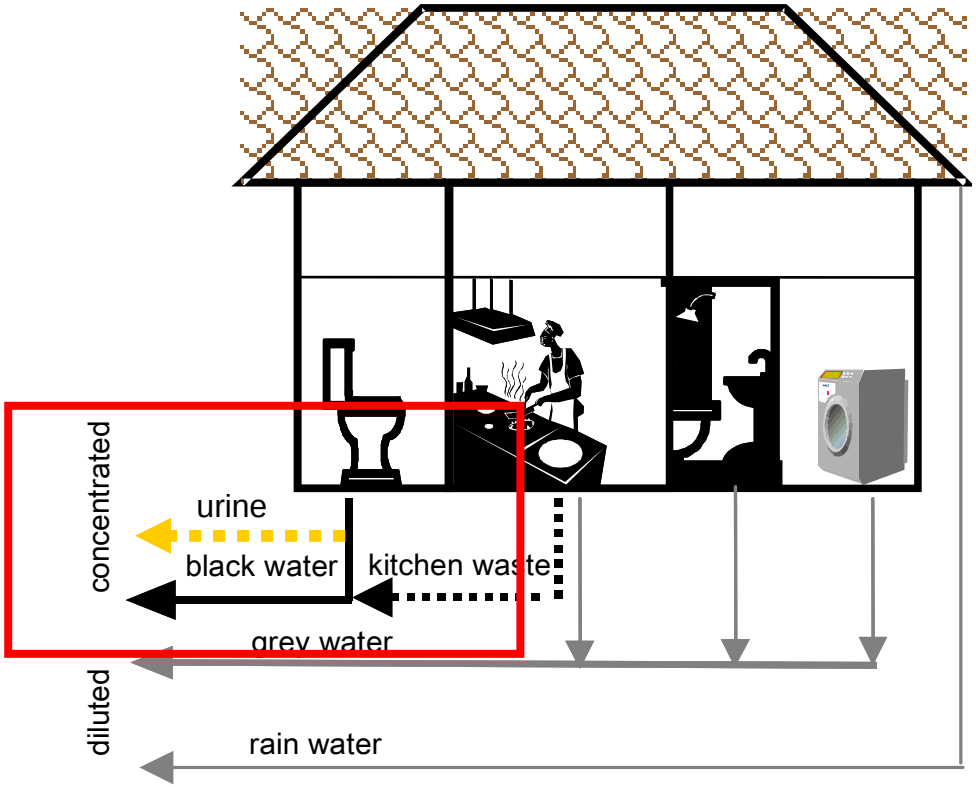
Why current WWTP do not remove PhACs?

- Nature of the compounds
  - Persistent, very slowly biodegradable
  - Hydrophilic
  - Toxic?
  - Not volatile
  - Small concentrations (COD negligible)
- *Characteristics* of the plant
  - Processes involved
  - Process conditions are not optimal
  - Large streams to deal with (economy)

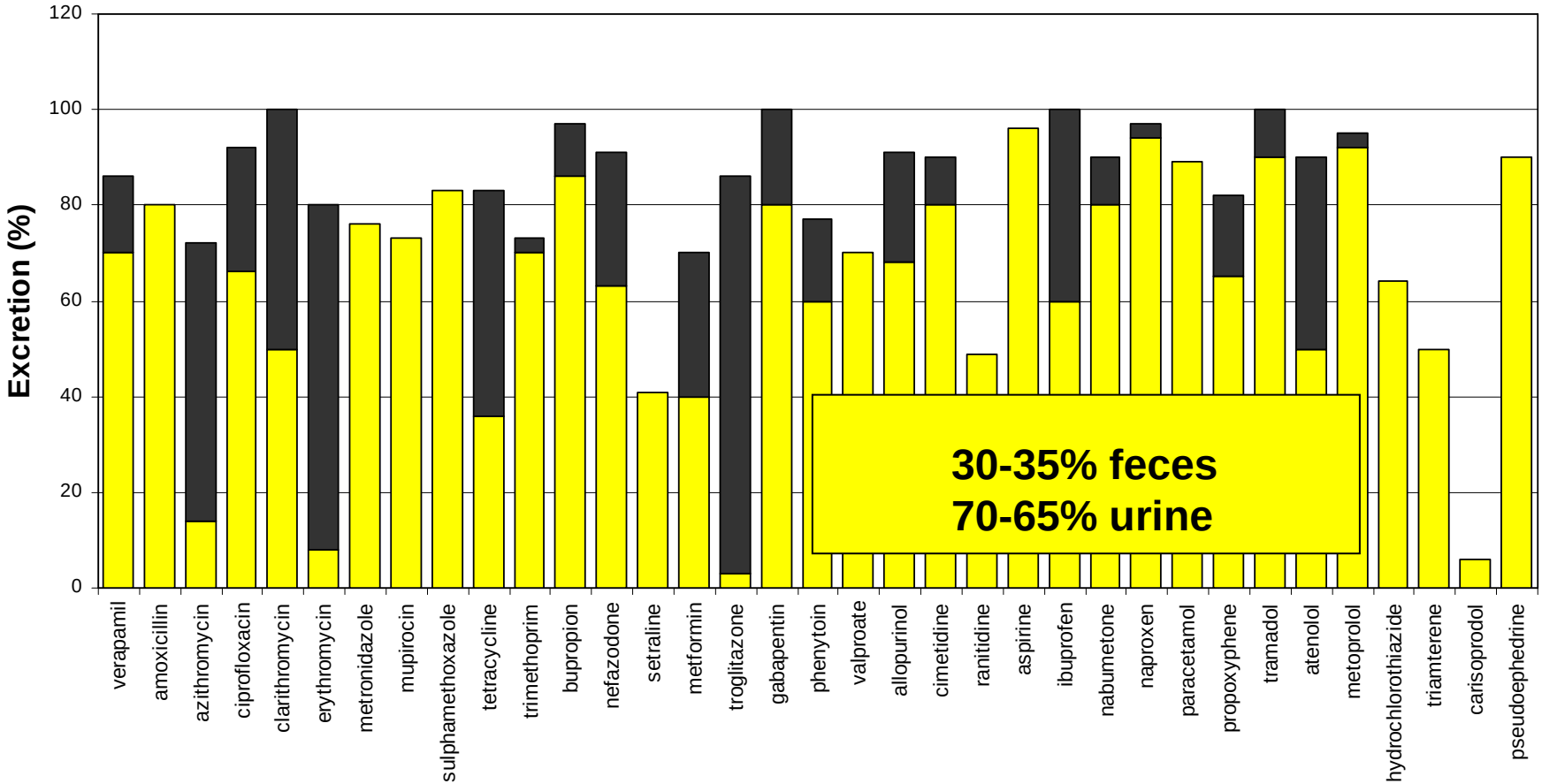
Measures

1. **Upgrading existing treatment systems**
2. **Source separation**
3. **Source control (not up to us but physicians, hospitals, pharmaceutical industry…)**

Source separation



Excretion



Moffat et al., 2004

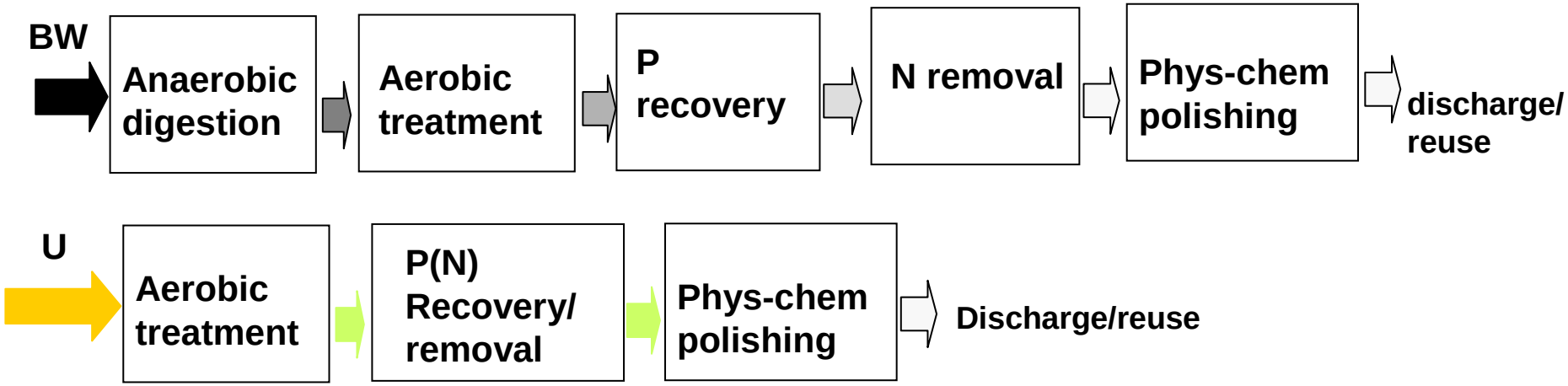
Concentrations pharmaceuticals in urine, black water and sewage (mg/L)

PhAC	Urine	Black water	Influent STP	Effluent STP (max found)
Ibuprofen	80	16	0.016	0.027
Metoprolol	5	1		0.009
Carbamazepine)	13	2.7	0.0022	0.022

Worse case scenario, all people from the target group use the same medication
Undiluted urine, 1.5 L/day/person
Black water collected with vacuum, 7,5 L black water/person/day
Ibuprofen, DDD = 1.2 g/p/d, excretion 10% unchanged,
Metoprolol DDD = 0.15 g/p/d excretion 5% unchanged,
Carbamazepine DDD = 1 g/p/d, excretion 5% unchanged

Difference between conventional- and source separation based sanitation

- Higher PhACs concentrations (different biomass?)
- Different configurations of treatment



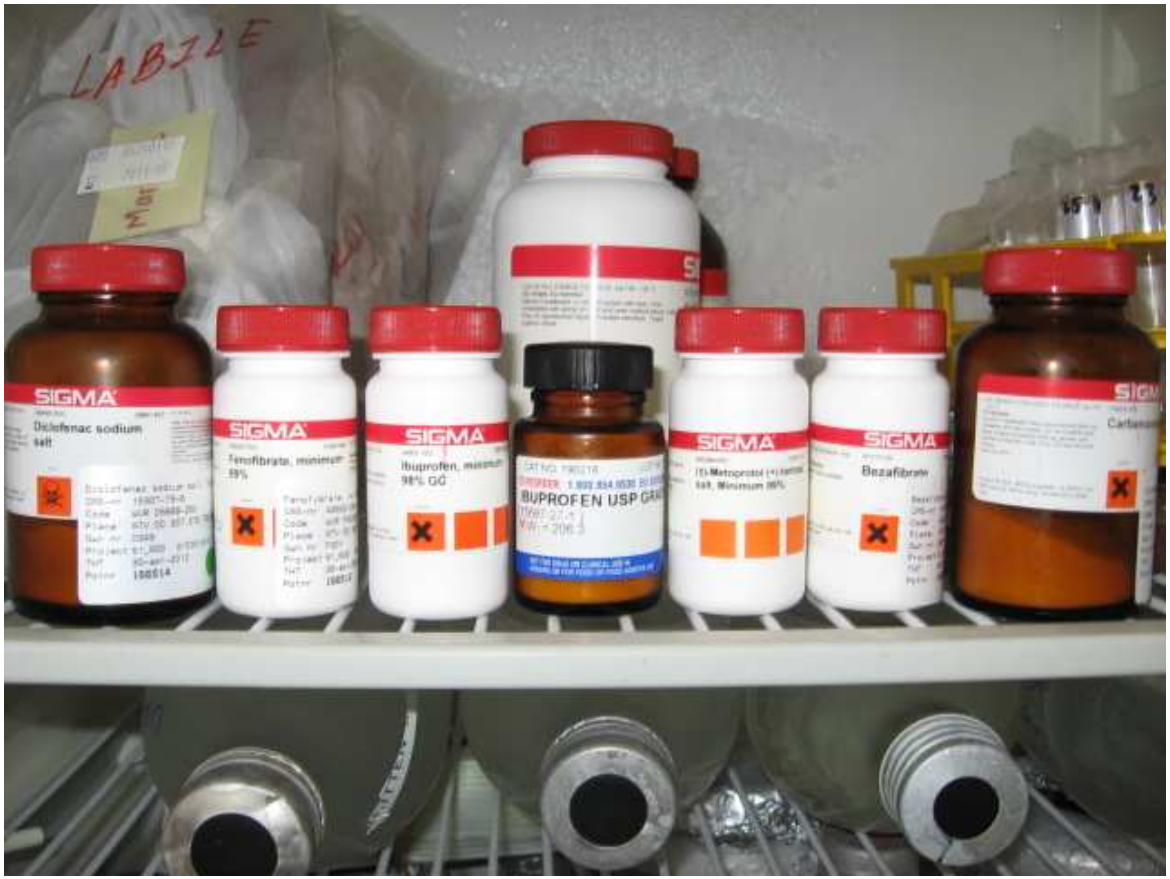
Experimental approach

- Selection representative compounds
- Batch tests
- Different redox conditions (AER, ANOX, AN)
- Different temperatures (10, 20, 30^{o}C)
- Different biomass (AS, anaerobic sludge from black water digester)

Representative compounds

Pharmaceutical	Therapeutic group	Log Kow	Hydrophilic / hydrophobic	pKa value at T = 20 $^0C^2$	k_{biol} for CAS (L/ gSS/d)
Aspirin	anti-inflammatory	1.426	hydrophilic	3.5	n.a.
Ibuprofen	anti-inflammatory	3.481	Moderately hydrophobic	4.5-5.2	21–35
Diclofenac	anti-inflammatory	0.7-4.5 (pH)	varying	4.15	<0.1
Metoprolol	β – blocker	1.9	hydrophilic	9.7	n.a.
Carbamazepine	anti-epileptic	2.69	Moderately hydrophobic	<1, 13.9	n.a.
Clofibric acid	lipid regulating	2.57	Moderately hydrophobic	3.0	0.3–0.8
Bezafibrate	lipid regulating	4.25	hydrophobic	3.6	2.1–3.0
Fenofibrate	lipid regulating	5.19	hydrophobic	n.a.	n.a.

Representative compounds

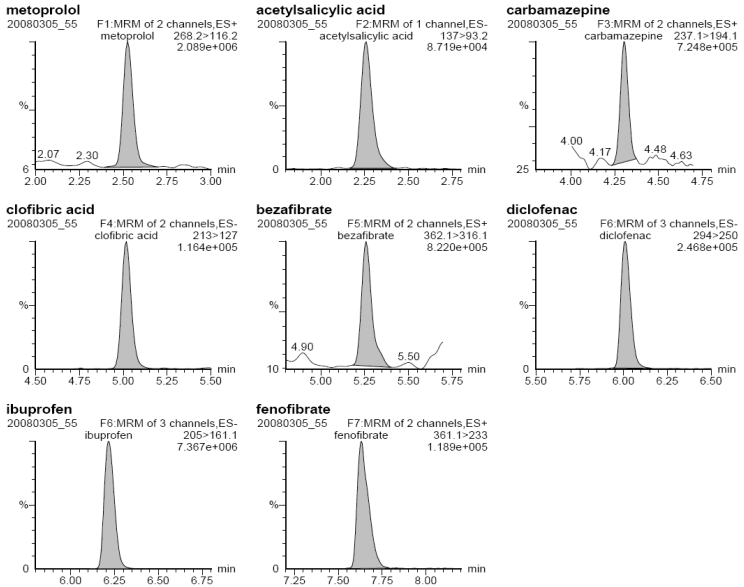


Batches

- Volume 1 L (AER, ANOX), 0.4-0.6 L (AN)
- Brought to required redox
- Spiked with a ‘coctail of 8 compounds’ low mg/L range
- Samples taken in time intervals (t_{max} =70 days)
- Controls (water +PhACs)

Sampling and analysis

- Mixed sample
- Liquid/sludge separated
- Conservation: chloroform and storage at –75^{o}C
- Sent to a specialised laboratory (LC(MS)^{2}) for analysis (National Institute for Public Health and the Environment (RIVM), Laboratory for Food and Residue Analysis)



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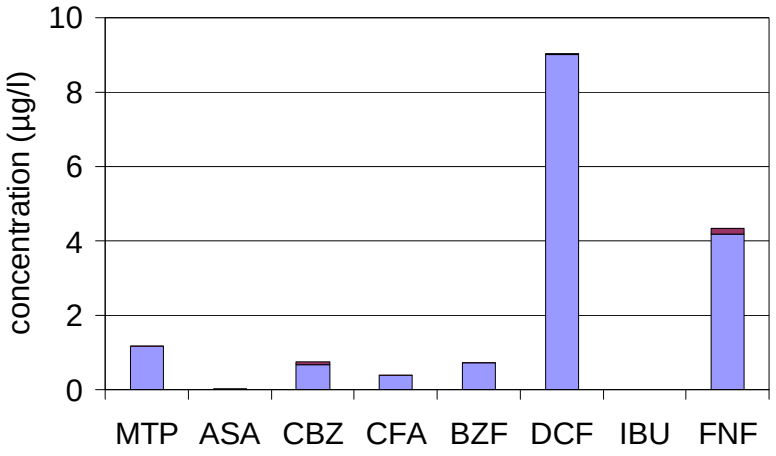
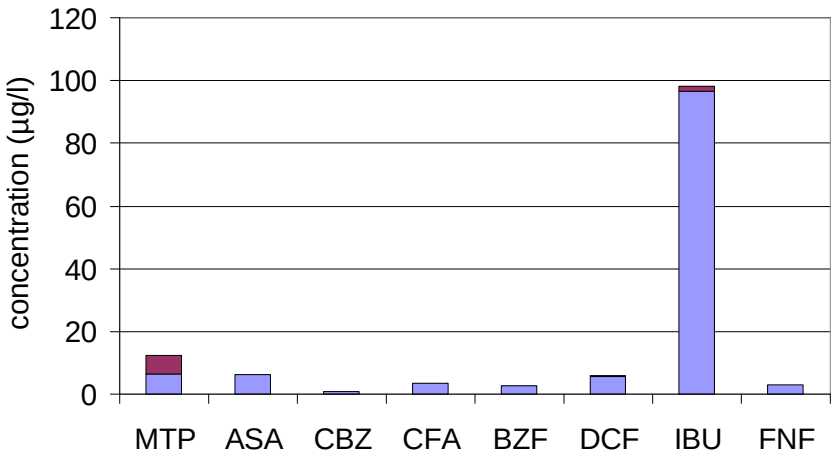
Results
Background concentrations in used media

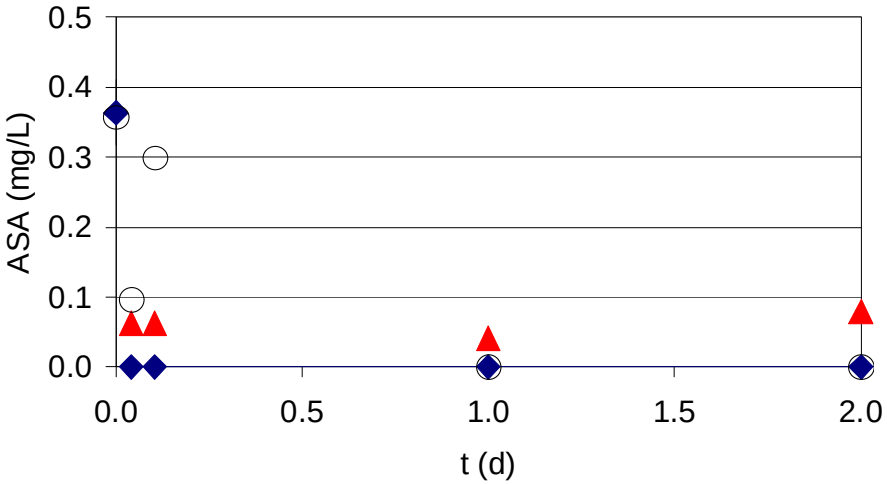
Activated sludge (autumn, winter) end of aeration circuit

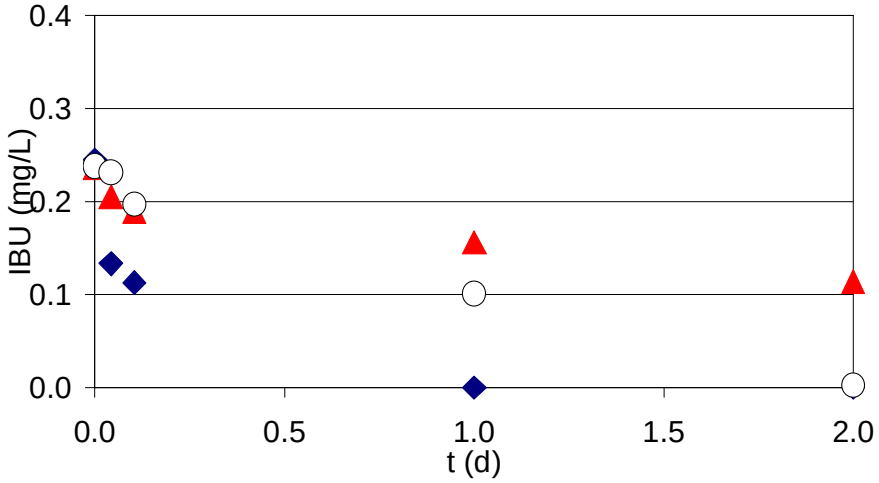


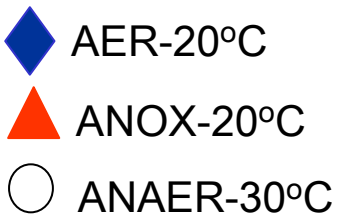
Anaerobic sludge (treating concentrated BW)

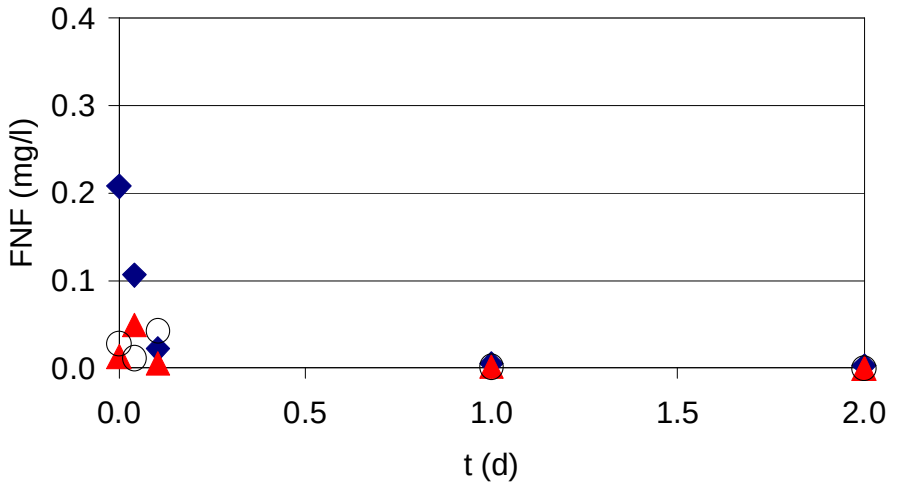


Biodegradability (aspirin, ibuprofen, fenofibrate)

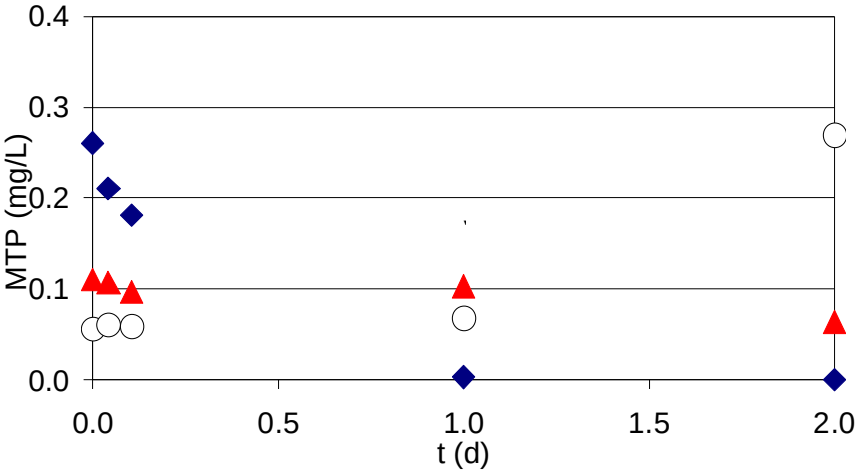


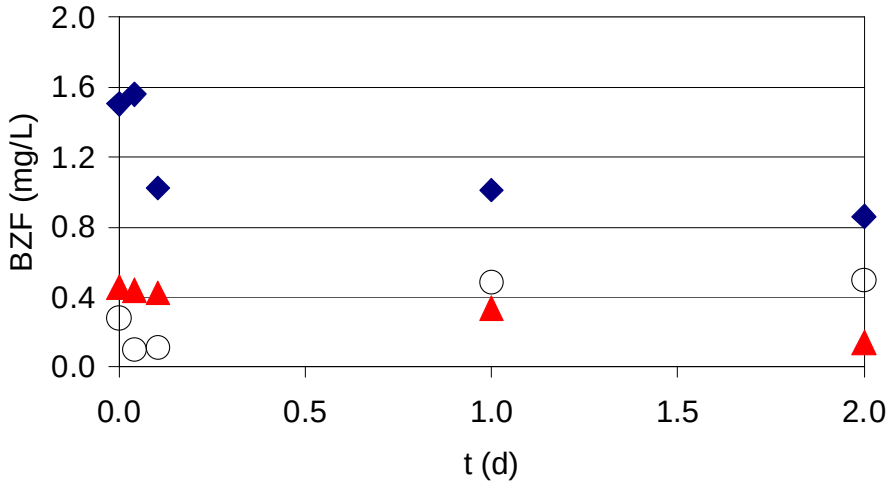


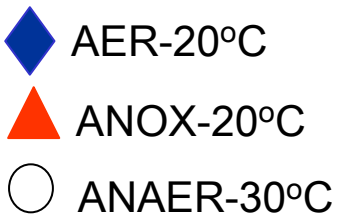


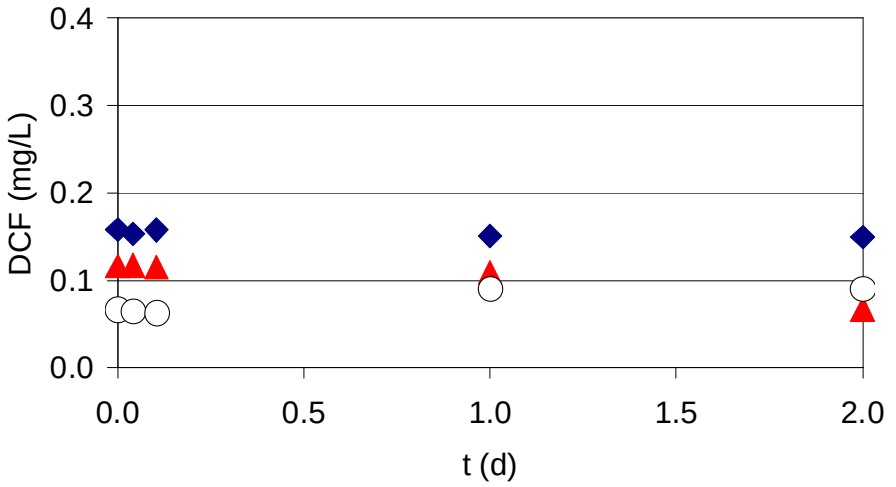


Biodegradability (metoprolol, bezafibrate, diclofenac)

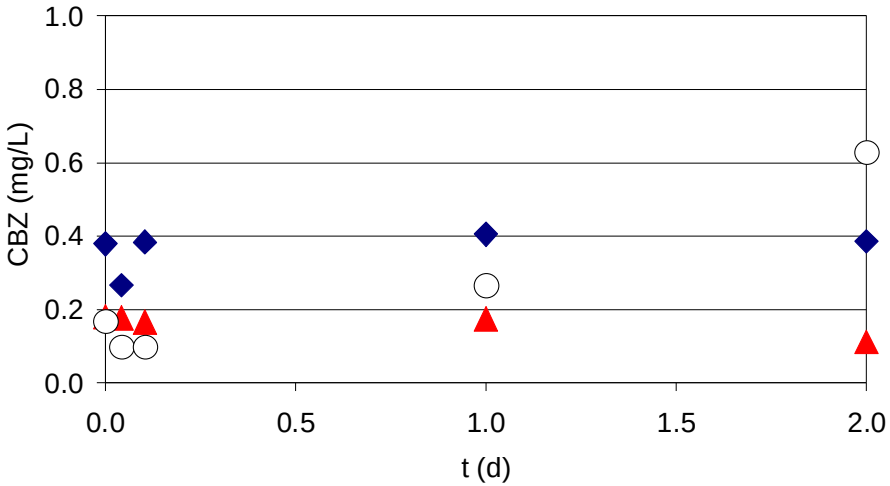


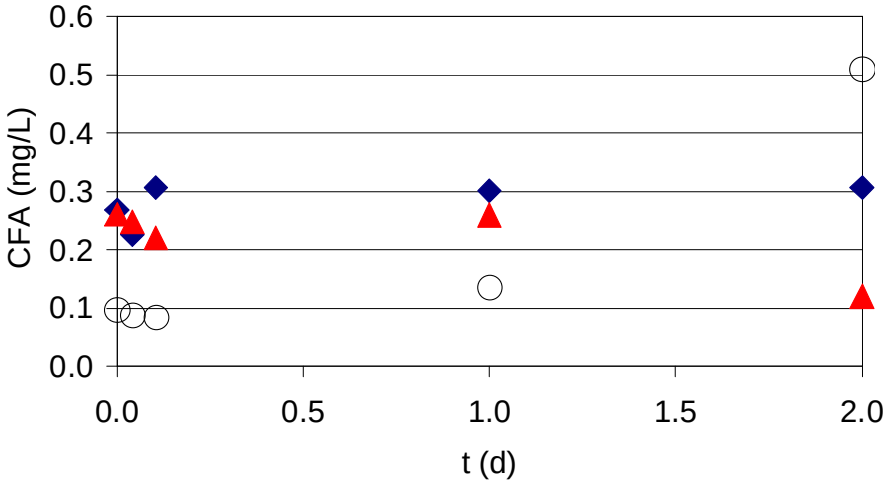






Biodegradability (carbamazepine, clofibric acid)





AER-20ºC

ANOX-20ºC

ANAER-30ºC

Biodegradation kinetic

PhAC	Test	k_{biol} (L/gTS/d) range
ASA	AER-20	37.3 -43.9
	AER-10	15.9 -17.5
	AN-30	0.111- 0.127*
FNF	AER-20	3.74 - 4.46*
	AN-30	0.031- 0.035*
IBU	AER-20	0.874 - 1.07
	AER-10	0.952 - 1.06
	ANOX-10	0.103 - 0.119
	AN-30	0.024 - 0.026
MTP	AER-20	0.569 - 0.691
	AER-10	0.192 - 0.205
BZF	AER-20	0.038 - 0.043
	ANOX-20	0.111 - 0.120

Summary of results

	Aerobic 20°C	Aerobic 10°C	Anoxic 20°C	Anoxic 10°C	Anaerobic 30°C
ASA	+++	+++	++	++	+
FNF	+++	++	++	++	+
IBU	++	++	+	+	+
MTP	++	+	+	-	-
BZF	+/-	+/-	+	-	-
DCF	+/-	+/-	-	-	-
CBZ	-	-	-	-	-
CFA	-	-	-	-	-

Classification of PhAC's

- Group 1: will be removed in a biological system
- Group 2: will be partially removed in biological systems; process optimisation (redox, SRT, HRT, X, T…) may enhance the removal
- Group 3: will be not removed in any biological system; advanced physical-chemical step(s) will be necessary

Conclusions

- Classification is needed covering the whole class of PhACs based on extended knowledge already gained (tests already performed, phys.-chem. characteristic (pKa, log K_{ow}, chem. structure)
- Identification of the third group (how big, how relevant environmentally)
- Invest in research into advanced physical-chemical methods (chemical oxidation (O_3 and AOPs), photolysis, tight membrane filtration, activated carbon); optimization of processes`, especially in respect to concentrated (pre)-treated flows

Acknoledgments

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- The National Institute for Public Health and the Environment (RIVM), Laboratory for Food and Residue Analysis is greatly acknowledged for development and performance of the analytical part of PhACs.

Thank you!