Fate of human pharmaceuticals (PhACs) in source oriented sanitation systems (SOSS)

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Global consumption of human PhACs

- **Globally: 100 000 tons per year**
- **15 g.capita^{-1}.year^{-1}**
- **industrialized countries: 50-150 g.capita^{-1}.year^{-1}**

- **In Europe ~3000 human pharmaceuticals**
- **less than 50 compounds make up 95% of total consumption (US, Sweden, survey)**

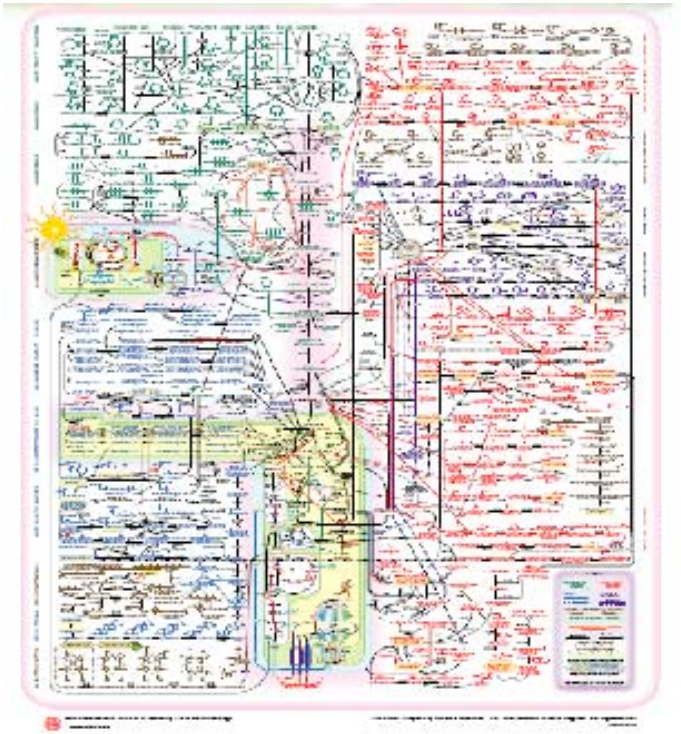
Sources Kummerer, 2004, Sedlak et al., 2005, Stockholm County Council, 2005;

Consumption of PhAC generally increases (personsx1000)

	2002	2006	
A Alimentary track and metabolism	2.910	3.441	↑
B Blood and blood forming organs	1.655	1.944	↑
C Cardiovascular system	2.676	3.630	↑
D Dermatologicals	3.421	3.484	↑
G Genito urinary system and sex hormones	2.774	1.594	
H Systemic hormonal preparations, excl. sex hormones and insulins	828	1.043	↑
J Antiinfectives for systemic use	3.840	4.229	↑
L Antineoplastic and immunomodulating agents	145	221	↑
M Musculo-skeletal system	3.403	3.369	↑
N Nervous system	3.584	3.555	
P Antiparasitic products, insecticides and repellents	144	170	↑
R Respiratory system	3.149	3.481	↑
S Sensory organs	1.785	2.137	↑
V Various	34	60	↑

(CVZ, 2007),

Metabolism of PhAC



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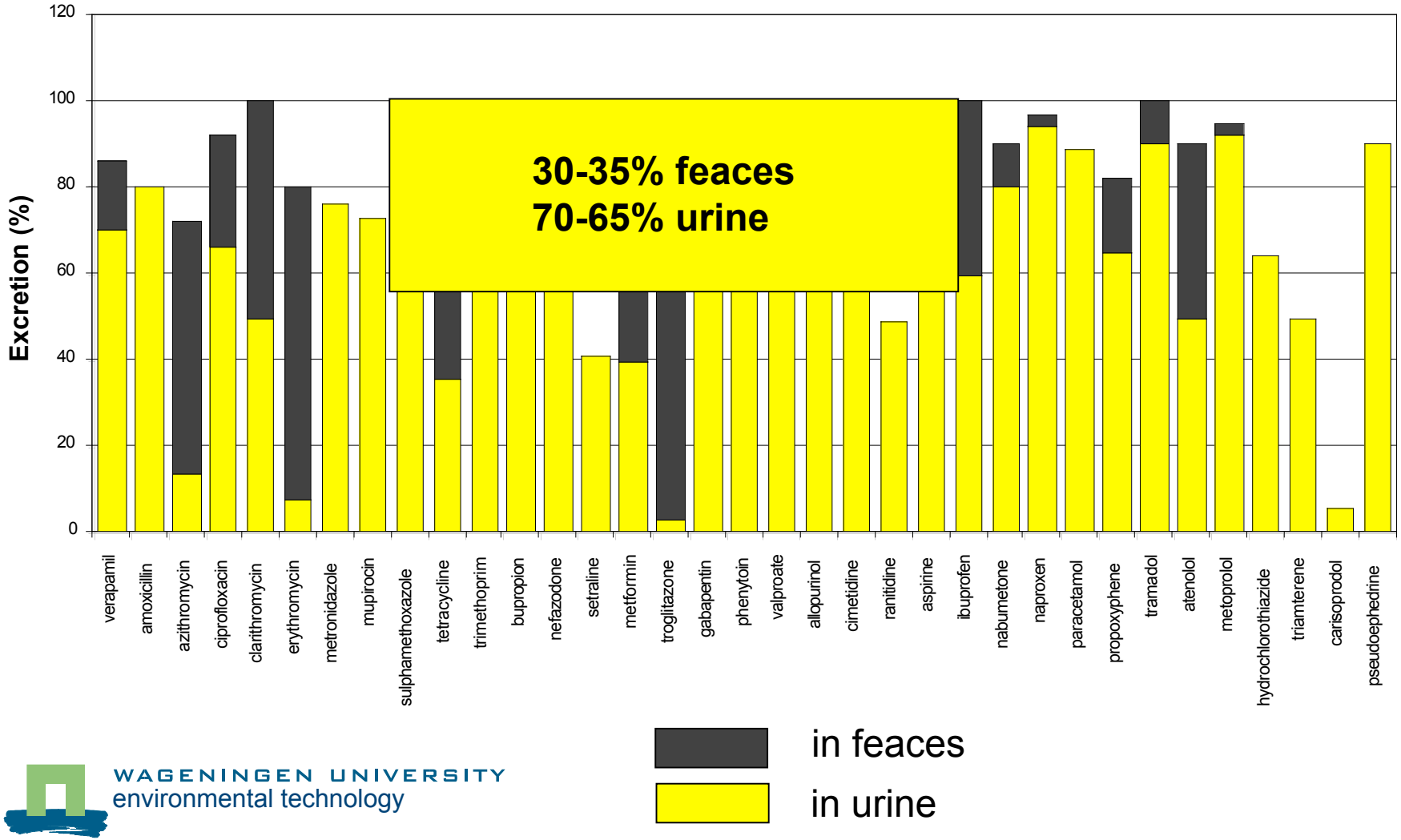
This first-of-its-kind metabolic network builds on the sequencing of the human genome and contains more than 3,300 known human biochemical transformations that have been documented during 50 years of research worldwide.

Excretion of PhACs in urine and feaces



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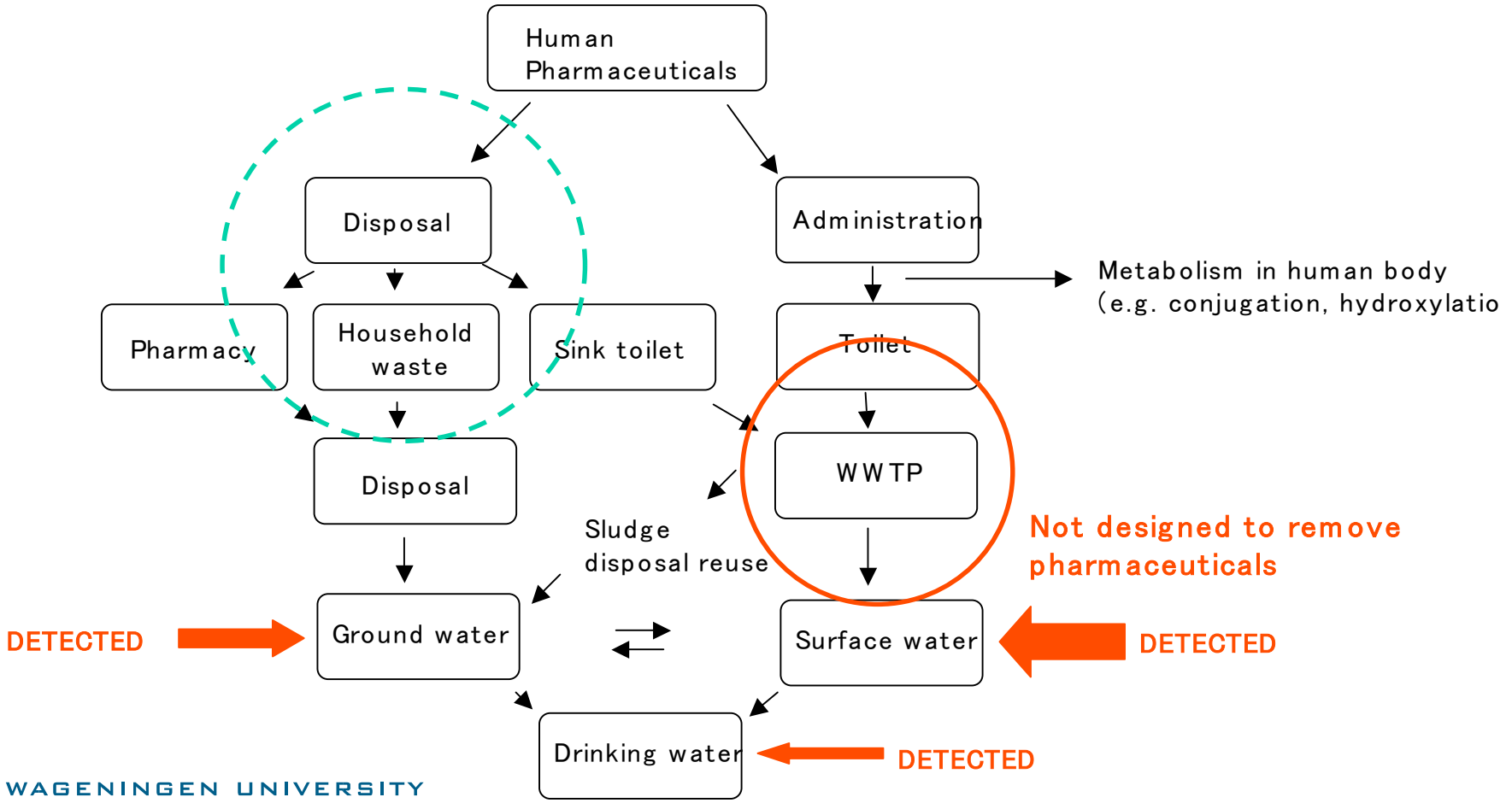
Pathways of human PhAC to aquatic compartments



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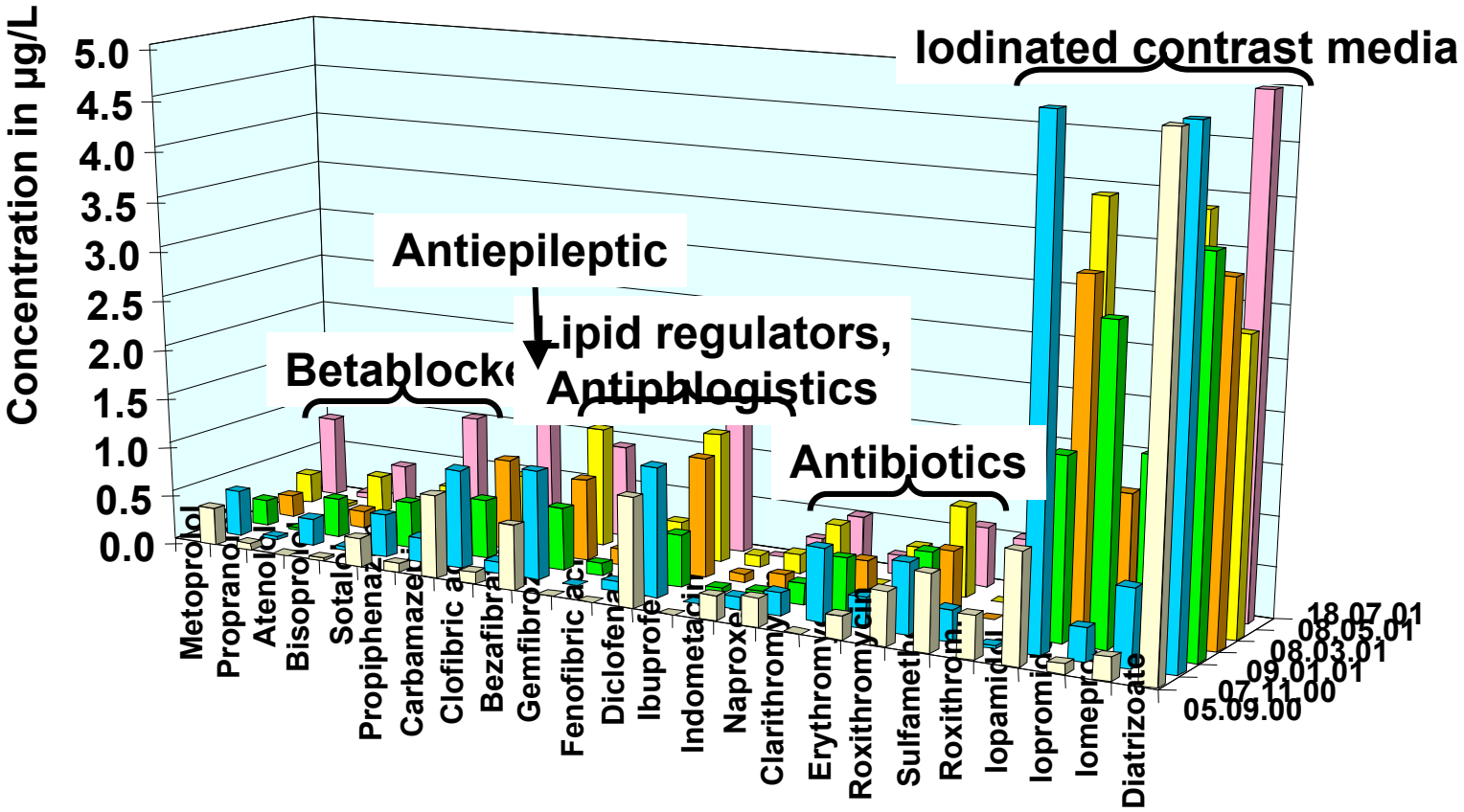
WWTP effluent contains PhACs



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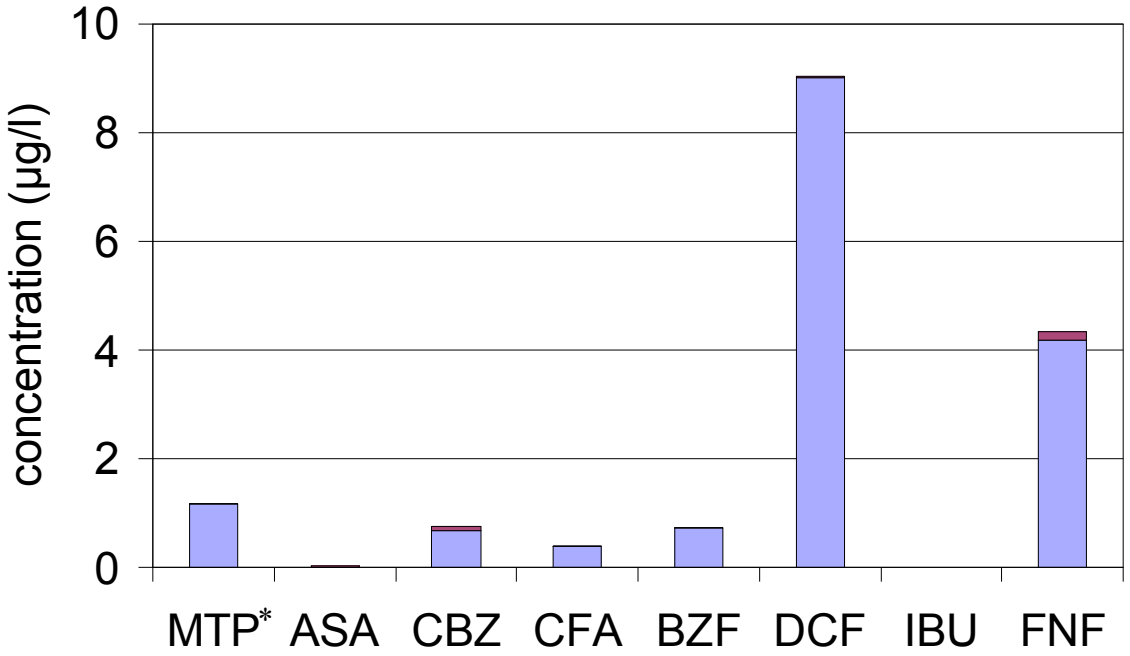
Ternes *et al.*, 2003

WWTP effluent contains PhAC



Activated sludge (late autumn) from the end of low-loaded aeration circuit in WWTP Bennekom (The Netherlands)
Only these 8 compounds were measured (SWITCH) , 6 were detected at low µg/L range

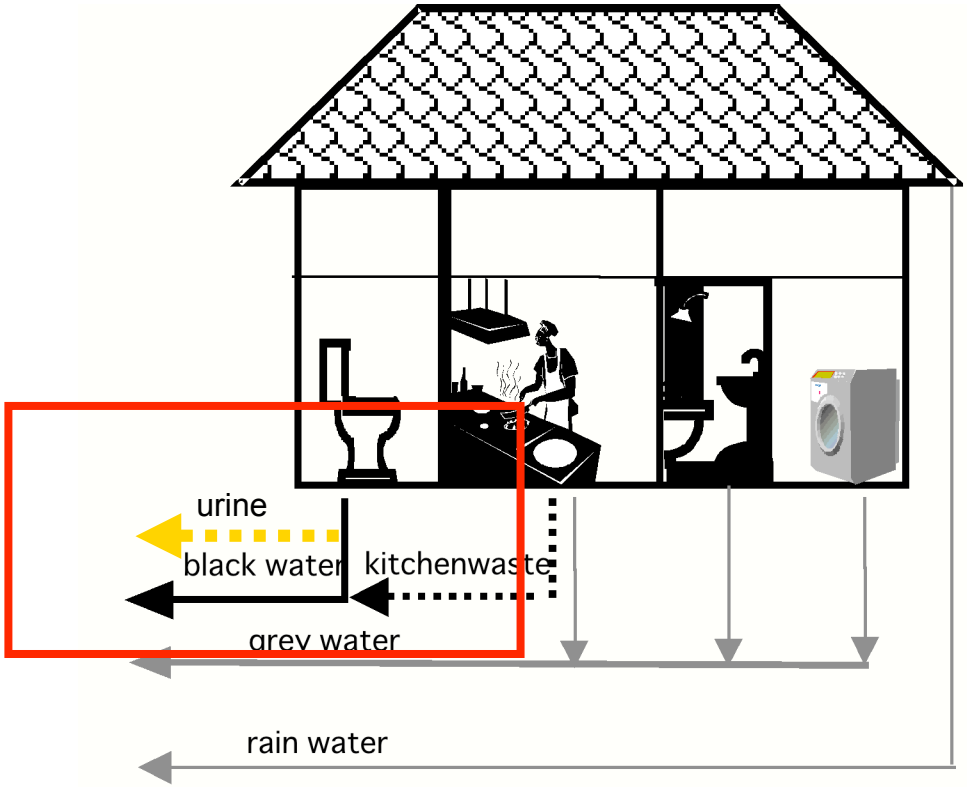
* MTP – metoprolol, ASA – aspirine, CBZ – carbamazepine, CFA – clofibric acid, BZF – bezafibrate, DCF – diclofenac, IBU- ibuprofen, FNF - fenofibrate

Conventional WWT systems are not efficient for PhAC removal, why?

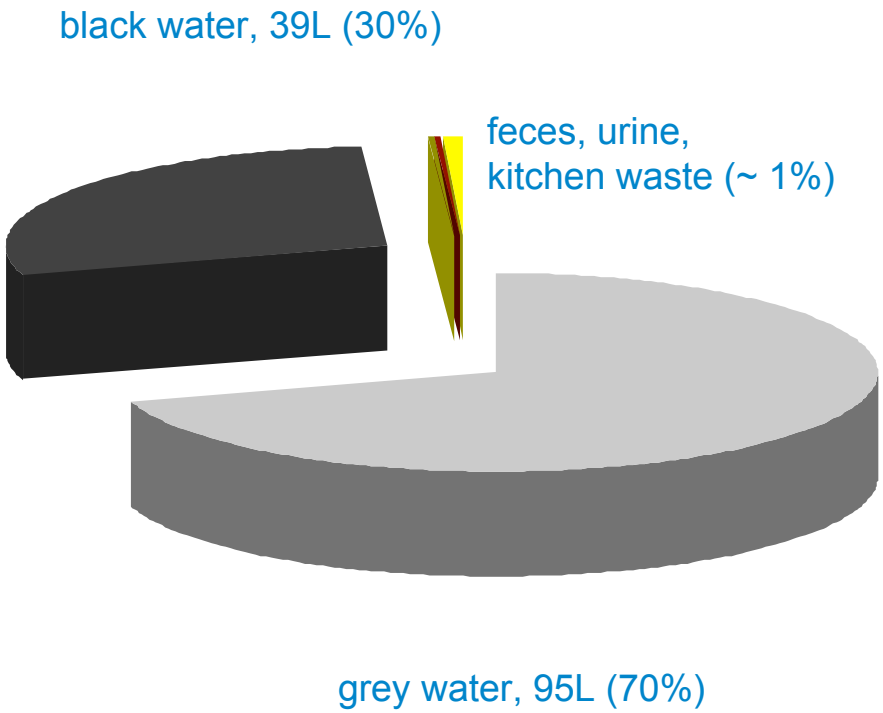
- Nature of the compounds
  - Persistent, very slowly biodegradable
  - Hydrophilic, polar
  - Toxic (?)
  - Not volatile
  - Small concentrations (COD negligible)

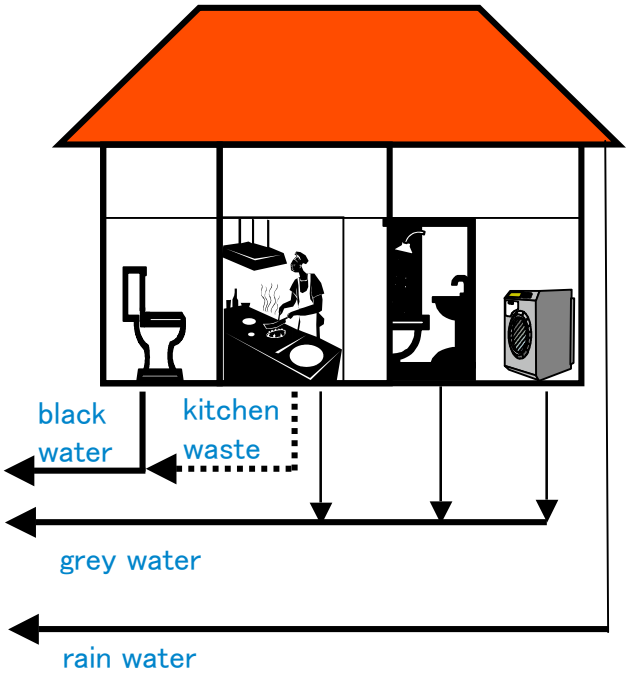
- Characteristics of the plant
  - Processes involved
  - Involved processes conditions are not optimal
  - Adding new process units not necessary now (legislation)

(Re)source oriented sanitation systems



Waste streams at SOSS





Composition concentrated domestic wastewater streams

A human being produces *ca.* 1.5 litres faeces plus urine (= black water) plus kitchen waste wherein:

- *ca*. 90% **of the nitrogen;**
- *ca*. 80% **of the phosphate;**
- *ca*. 80% **of the potassium;**
- *ca*. 70% **of the COD;**
- Main **part of the pathogens;**
- All **excreted PhACs forms (and hormones)!**

2 basic sanitation concepts regarding PHACs ‘rich’ wastewater streams

- Separate collection and treatment of:
  - Urine
  - Black water

Concept I: separate treatment of black water

- all PhACs present
- other pollutants too (difficult matrix)
- other goals (nutrient and energy recovery, pathogens removal) is aimed at
- advanced, multi-stage treatment

- that may guarantee high reduction of PhAC

Concept II: Separate treatment of urine

- complete separation of urine not possible (max 75%)
- 65-70% of excreted PhAC present in urine stream
- not clean stream (COD,N,P,pathogens)
- very small stream, min 1.5 L/p/d
- therefore direct treatment for PhACs sometimes feasible (hot spots)

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

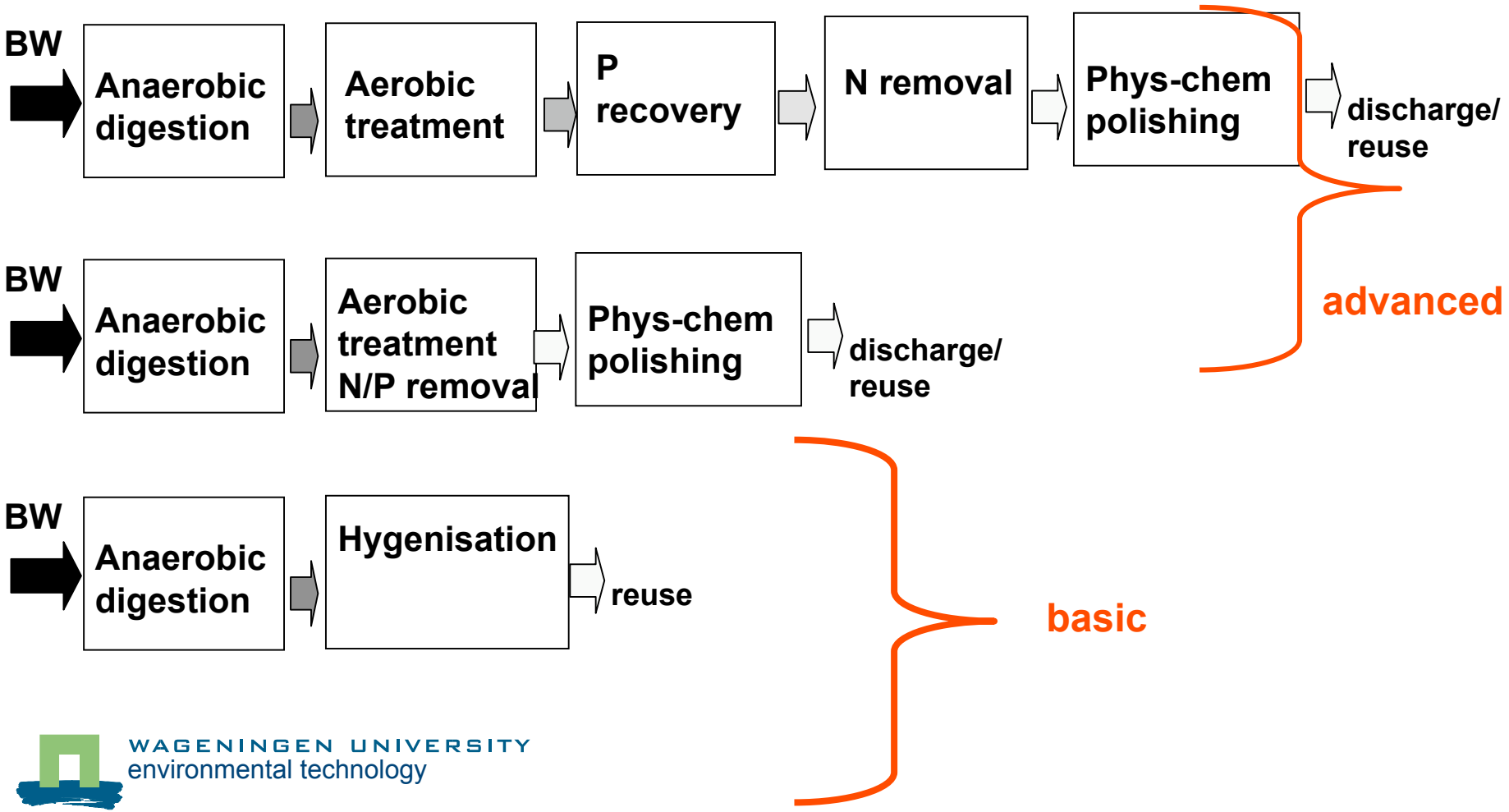
PhAC	Urine	Black water	Influent WWTP
Ibuprofen	80	16	0.016
Metoprolol	5	1	
Carbamazepine)	13	2.7	0.0022

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 toilet, so only 7,5 L black water/person/day is generated
Ibuprofen, DDD = 1.2 g/person/d, excretion 10% in unchanged form of ibuprofen,
Metoprolol DDD = 0.15 g/person/d excretion 5% in unchanged form,
Carbamazepine DDD = 1 g/p/d, excretion 5% in unchanged form

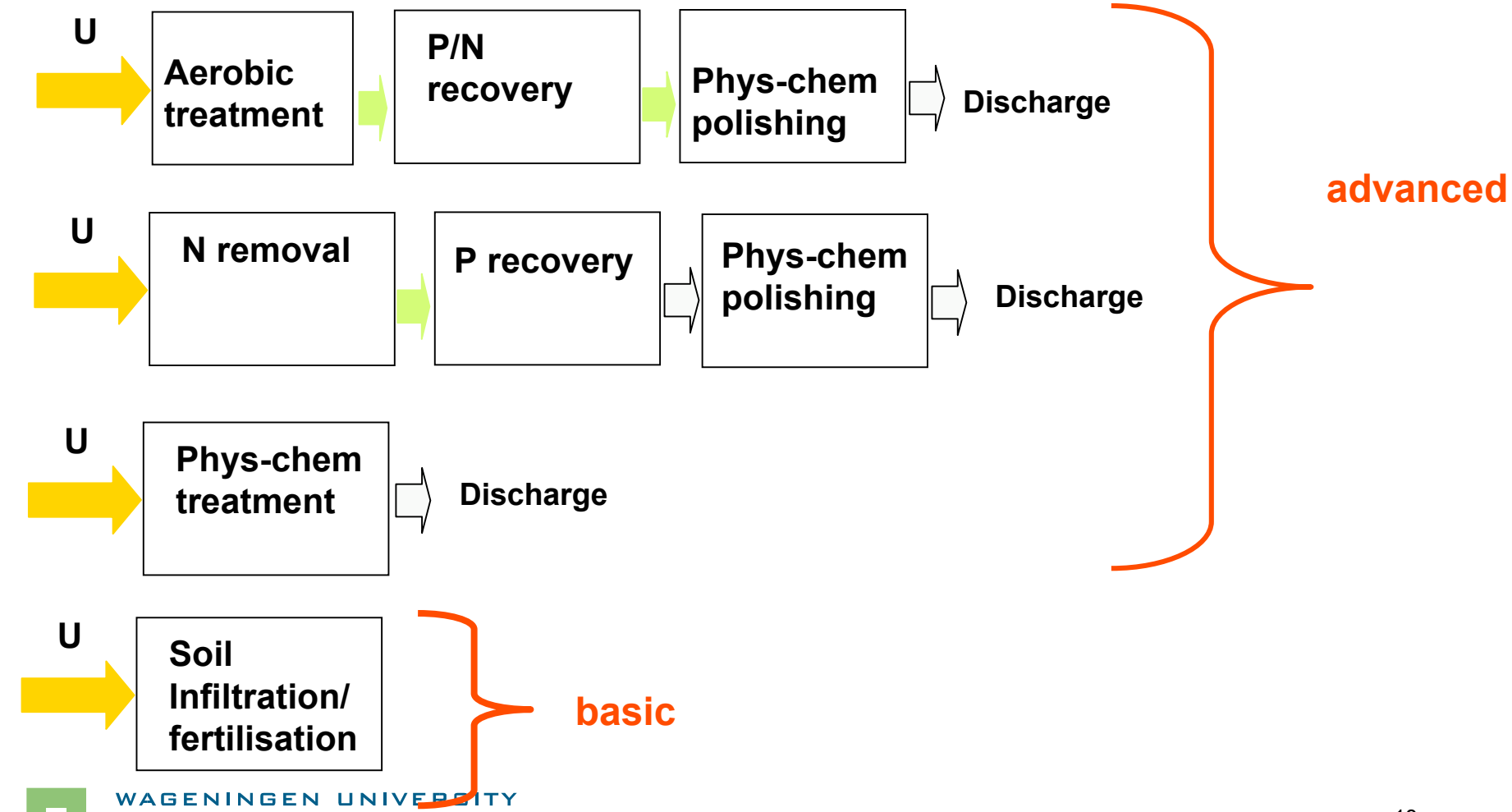
$$C_{\mathrm{PhAC_{individual}}} = \frac{\mathrm{DDD} \quad \mathrm{E}}{\mathrm{V_{ww}}}$$

$$C_{PhAC_{area}} = \frac{DDD \quad E \quad N_{users}}{V_{area\_wastewater}}$$

Black water (BW) treatment configurations



Urine (U) treatment configurations



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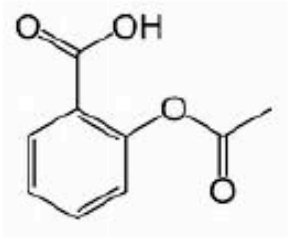
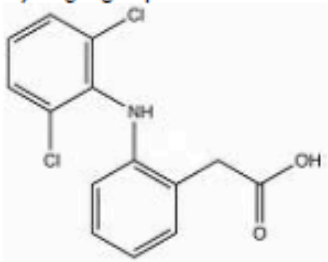
Representative compounds used in SWITCH research

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.

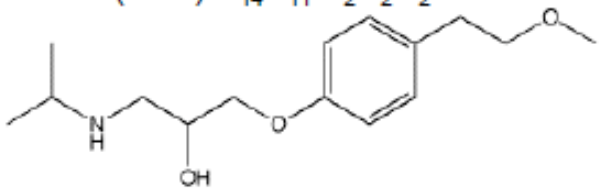
Selected representative compounds



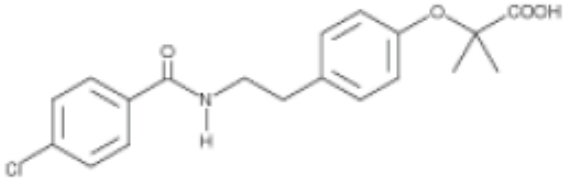
Aspirine (ASA) $C_9H_8O_4$



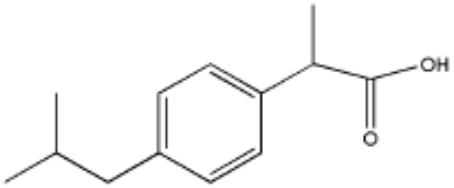
Diclofenac (DCF) $C_{14}H_{11}Cl_2N_2O_2$



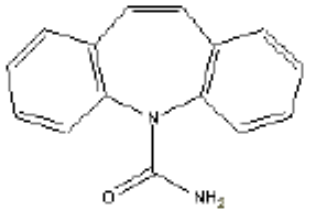
Metoprolol (MTP) $C_{15}H_{25}NO_3$



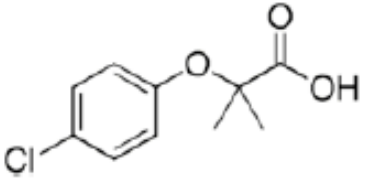
Bezafibrate (BZF)$C_{19}H_{20}ClNO_4$



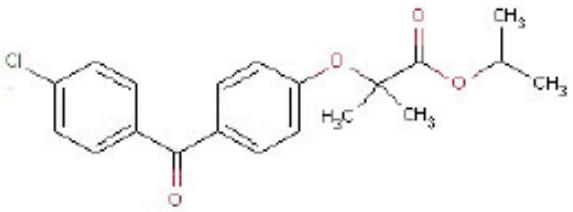
Ibuprofen (IBU) $C_{13}H_{18}O_2$



Carbamazepine (CBZ) $C_{15}H_{12}N_2O$



Clofibric acid (CFA) $C_{10}H_{11}ClO_3$

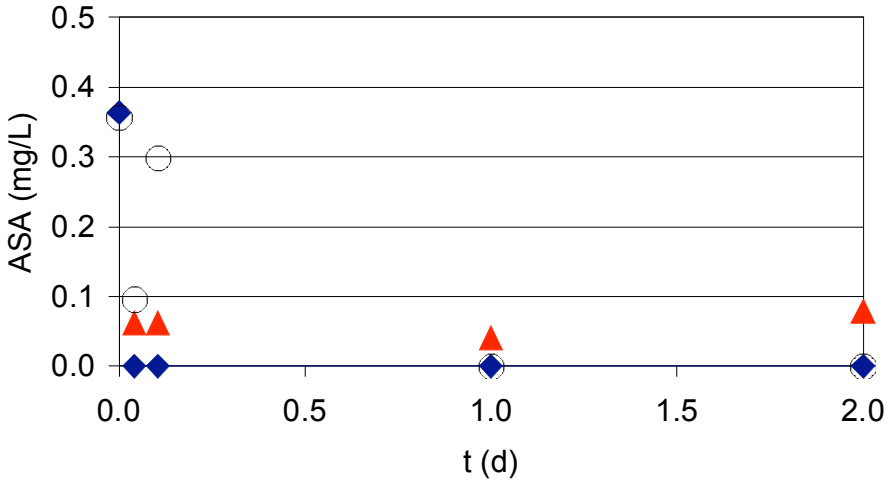


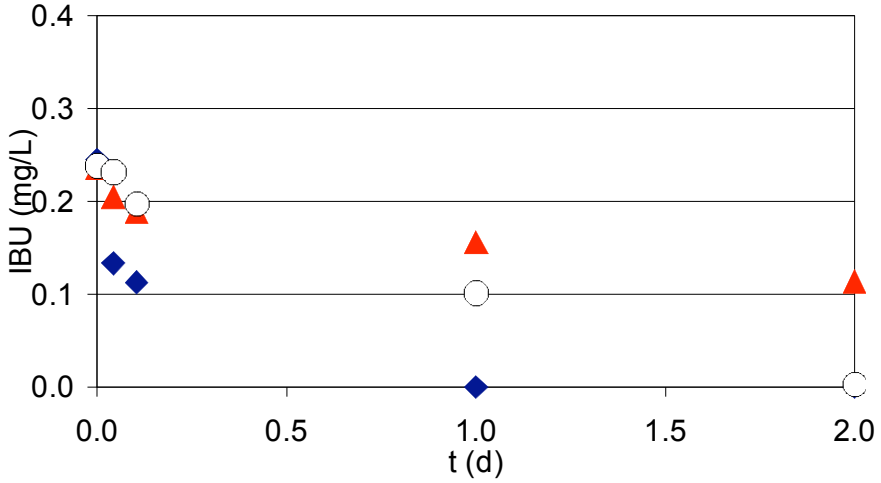
Fenofibrate (FNF) $C_{20}H_{21}ClO_4$

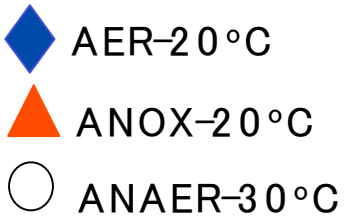
Biodegradability of selected PhACs from concentrated wastewaters

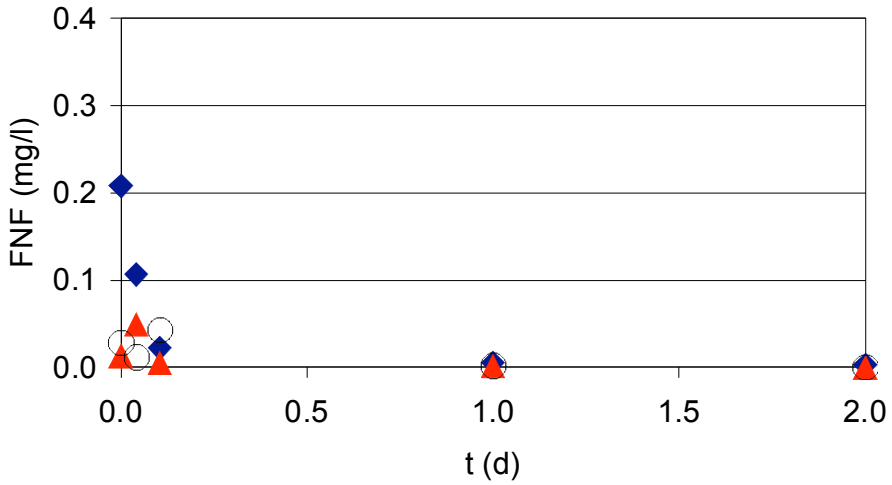
- Selected compounds (8)
- Higher concentrations than in WWTP (calculated based on DDD and excretion rate)
- Different sludge: activated sludge, anaerobic sludge
- Different temperature (T, 10, 20, 30°C)) and redox conditions (aerobic, anoxic, anaerobic)
- Batches: sludge + coctail PhAC at low mg/L+ varying conditions

Results:
Some PhACs can be biodegraded



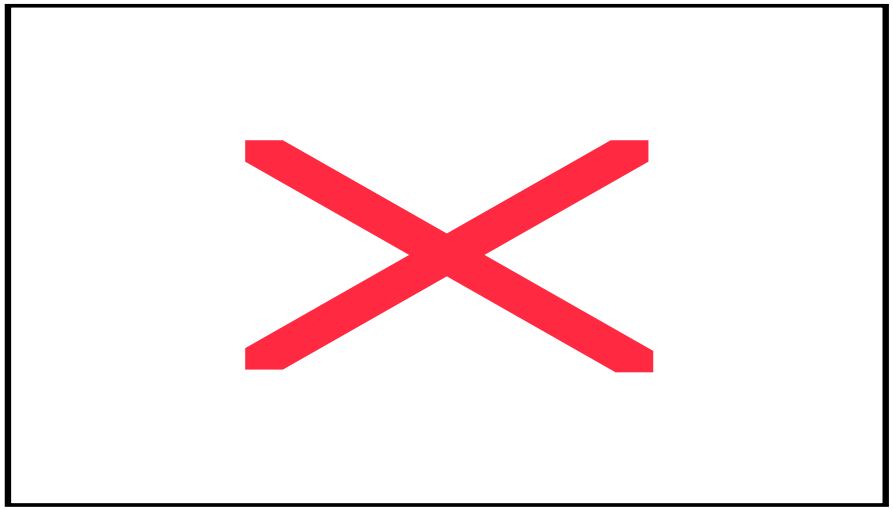






ASA: aspirin,
IBU: ibuprofen,
FNF:fenofibrate

Results: but others not!



AER–20°C

ANOX–20°C

ANAER–30°C

CBZ: carbamazepine,
CFA: clofibric acid

Biodegradation of PhACs in SWITCH research

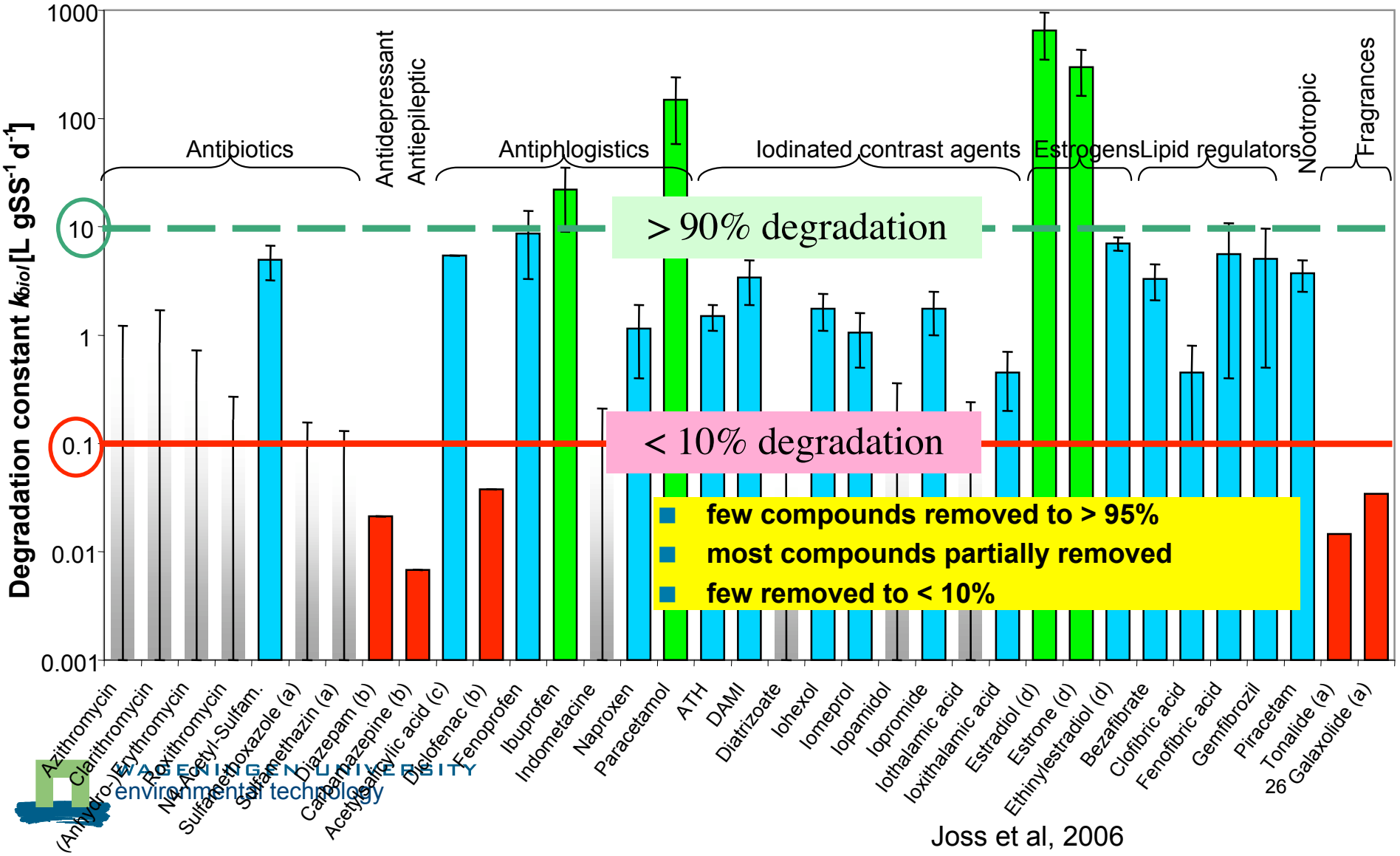
	Aerobic 20°C	Aerobic 10°C	Anoxic 20°C	Anoxic 10°C	Anaerobic 30°C	
ASA	+++	+++	++	++	+	I
FNF	+++	++	++	++	+	
IBU	++	++	+	+	+	
MTP	++	+	+	-	-	II
BZF	+/-	+/-	+	-	-	
DCF	+/-	+/-	-	-	-	
CBZ	-	-	-	-	-	III
CFA	-	-	-	-	-	

(+++) - readily, (++) - good, (+) fairly, (+/-) - degraded when conditions are optimised, (-) - no observed degradation under any conditions

* MTP – metoprolol, ASA – aspirine, CBZ – carbamazepine, CFA – clofibric acid, BZF – bezafibrate, DCF – diclofenac, IBU- ibuprofen, FNF - fenofibrate

Classification of PhAC's

- Group I: will be removed in a biological system
- Group II: will be partially removed in biological systems; process optimisation (redox, SRT, HRT, X, T···) may enhance the removal
- Group III: will be not removed in any biological system; advanced physical–chemical step(s) will be necessary to eliminate these compounds from WWTP effluents


Degradation constant k_{bio}[L gSS^{-1} d^{-1}]
1000
100
10
1
0.1
0.01
0.001
Antibiotics
Antidepressant
Antiepileptic
Antiphlogistics
Iodinated contrast agents
Estrogens
Lipid regulators
Nootropic
Fragrances
> 90% degradation
< 10% degradation
few compounds removed to > 95%
most compounds partially removed
few removed to < 10%
Azithromycin
Clarithromycin
(Anhydro-)Erythromycin
Roxithromycin
N-Acetyl-Sulfam.
Sulfamethoxazole (a)
Sulfamethazin (a)
Diazepam (b)
Carbamazepine (b)
Acetylsalicylic acid (c)
Diclofenac (b)
Fenoprofen
Ibuprofen
Indometacine
Naproxen
Paracetamol
ATH
DAMI
Diatrizoate
Iohexol
Iomeprol
Iopamidol
Iopromide
Iothalamic acid
Ioxithalamic acid
Estradiol (d)
Estrone (d)
Ethinylestradiol (d)
Bezafibrate
Clofibric acid
Fenofibric acid
Gemfibrozil
Piracetam
Tonalide (a)
26 Galaxolide (a)
Joss et al, 2006
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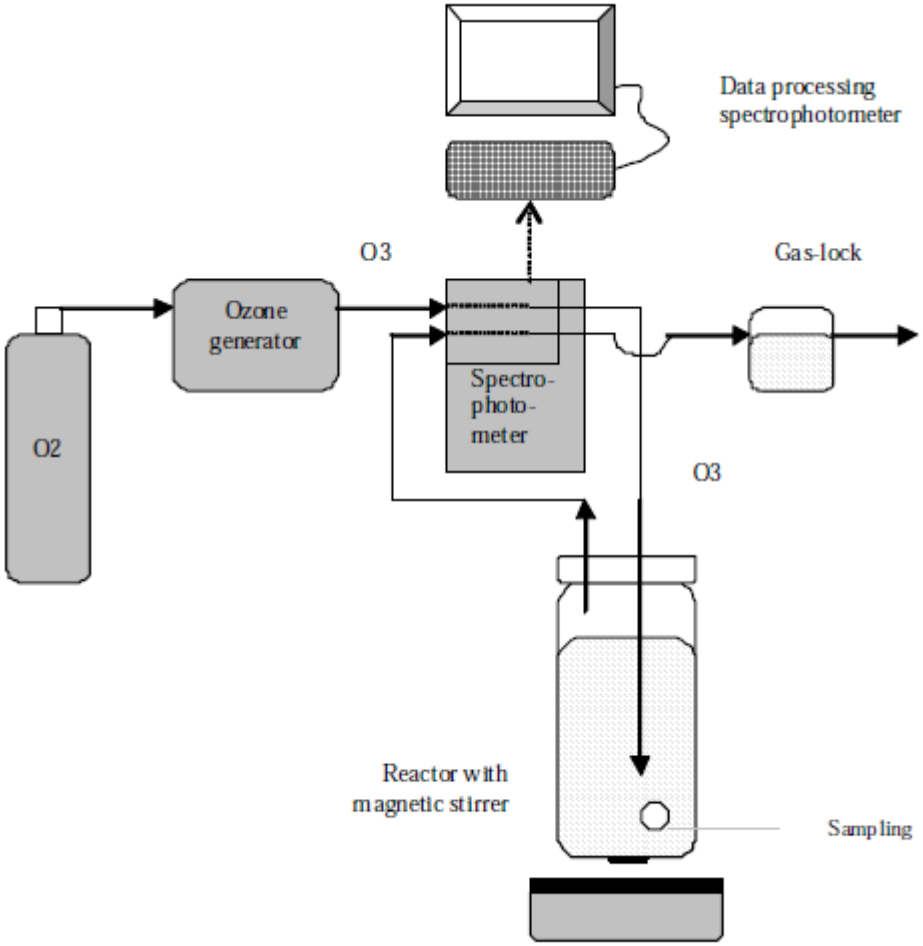
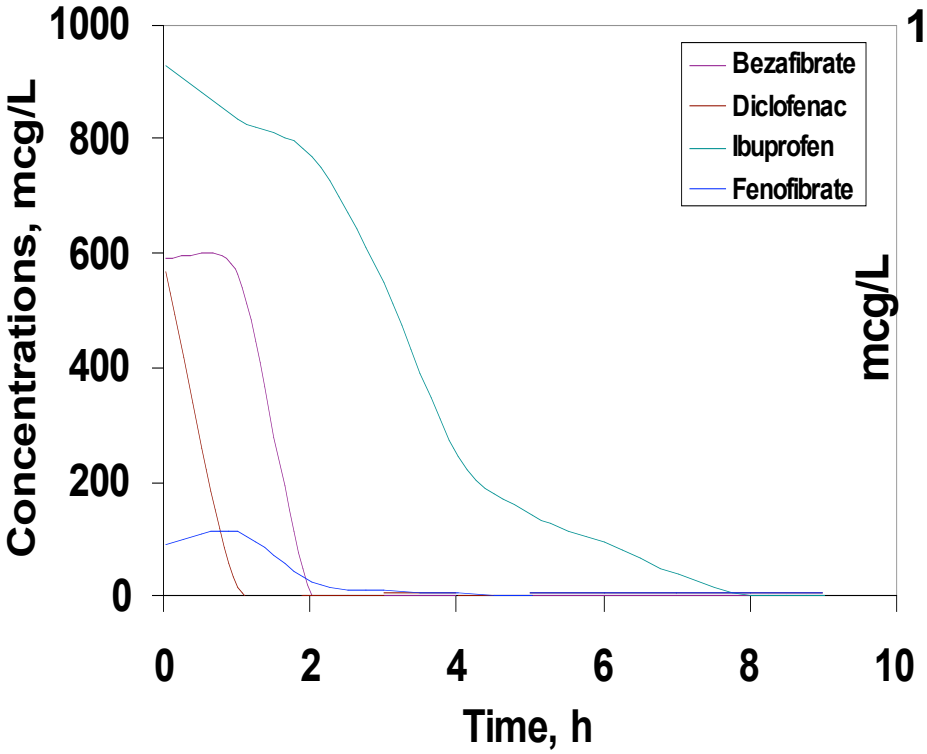
Physical-chemical post-treatment of biologically treated concentrated ww streams

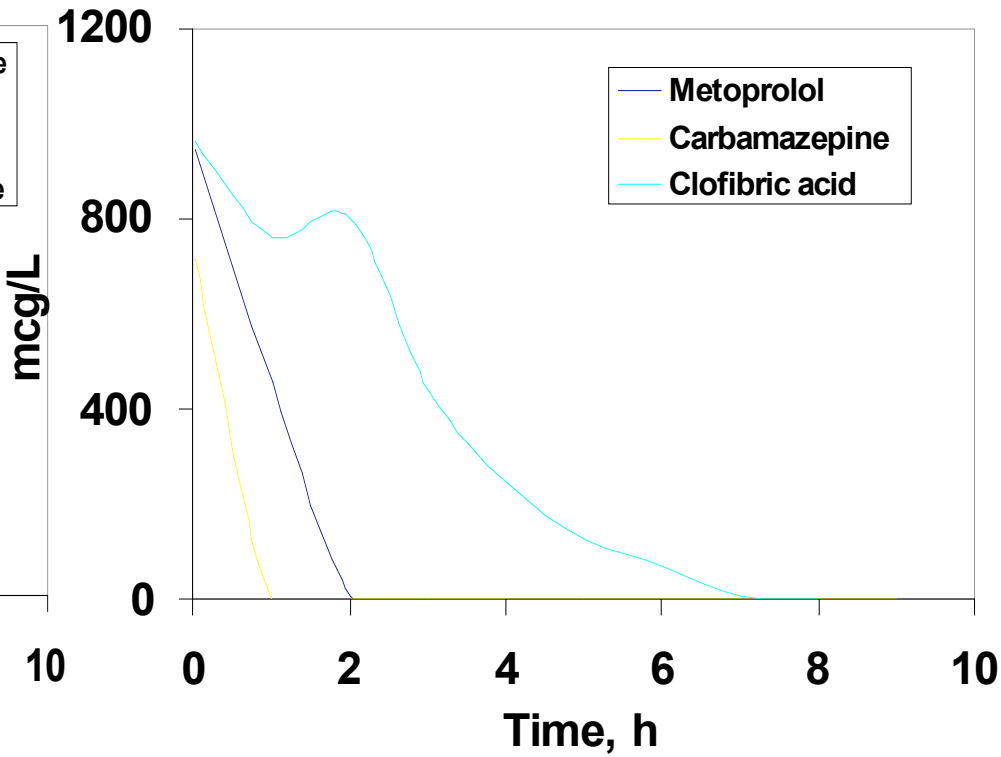
- Ozone
- Activated carbon
- Nanofiltration
- Electrodialysis
- Combined oxidation processes (O_3, UV, H_2O_2)
- …new proceses?

Ozonation of medium containing elevated levels of PhACs



Ozonation PhACs + water





- All compounds ultimately removed
- No matrix interference

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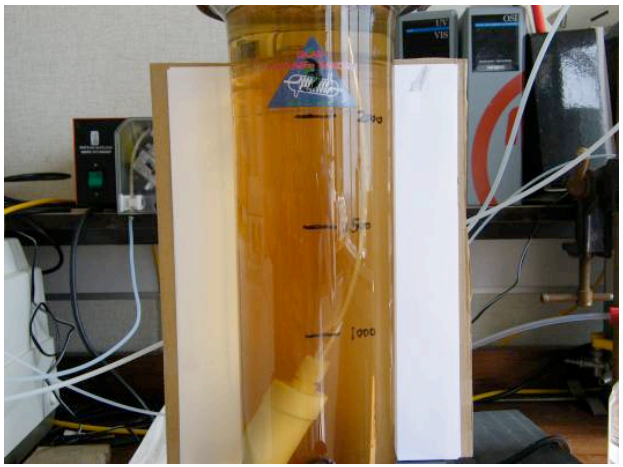
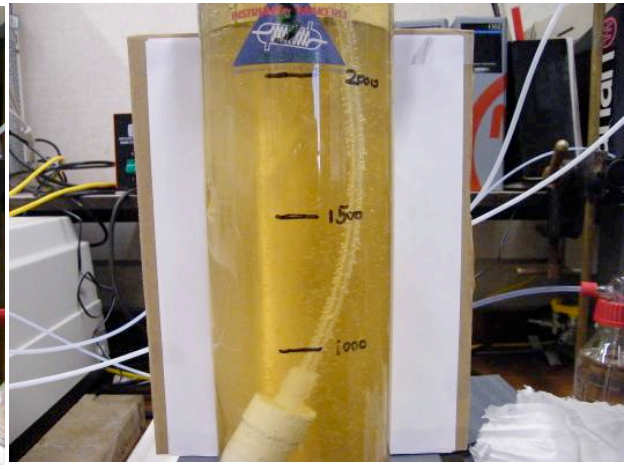
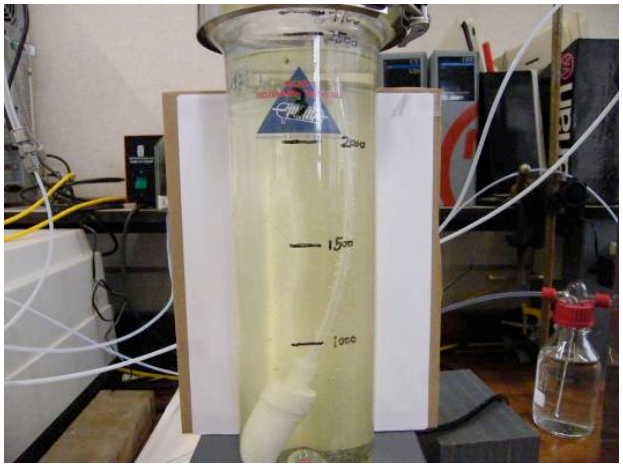
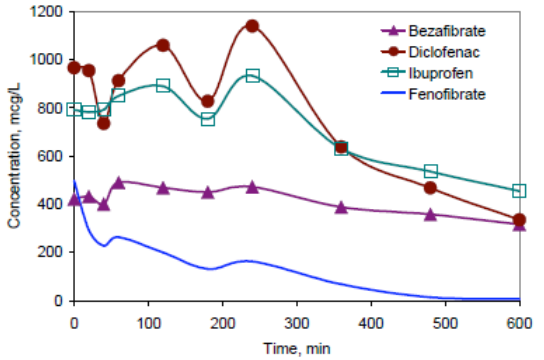
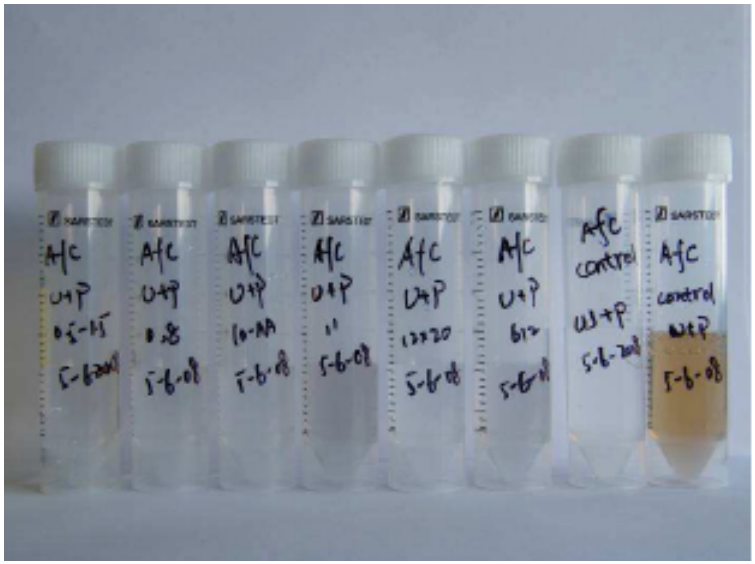
Ozonation urine + PhACs

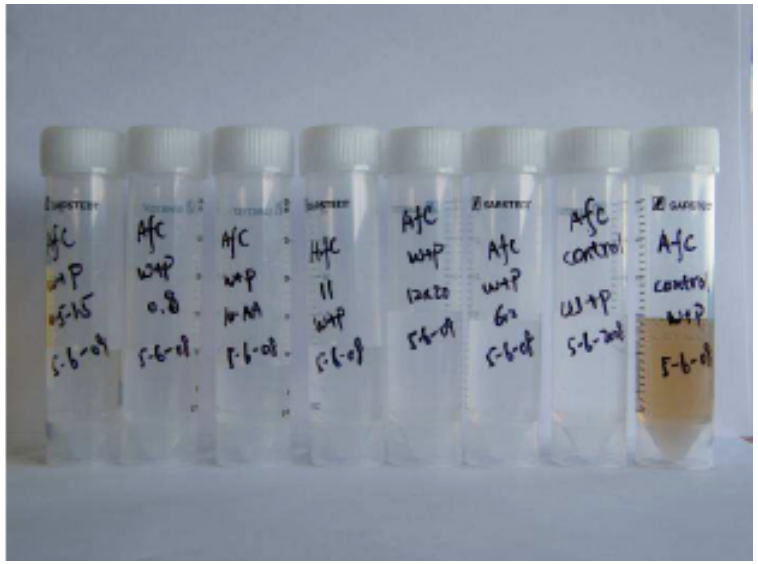




- Takes longer at the same O_3 dosis (matrix)
- Removal of PhAC
- Removal of colour



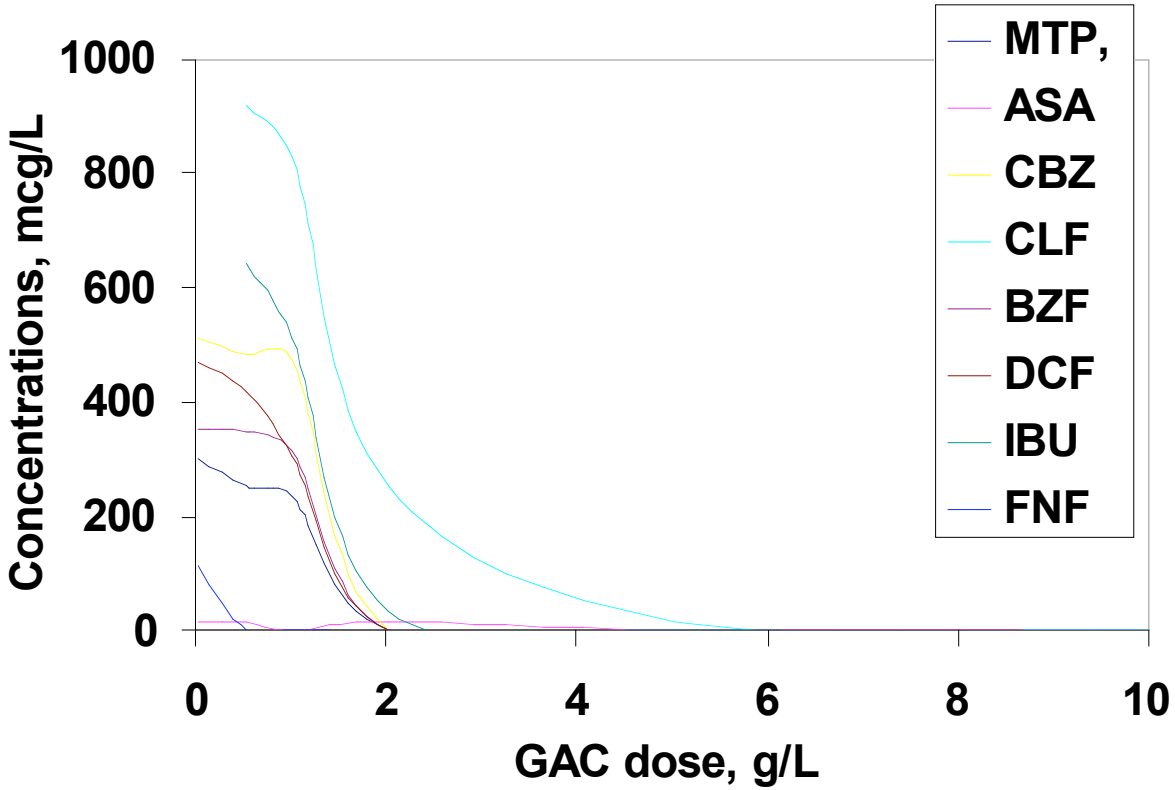
Granular activated carbon sorption of PhACs from urine





- Removal of colour
- Removal of contaminants (a. o. PhAC)

Granular activated carbon and PhACs



- All tested compounds disappeared from water phase (absorbed to activated carbon)
- For polar compounds more GAC is needed

Conclusions: ozonation of PhACs

- All selected PhACs are all potentially well oxidized by ozone
- Matrix slows down or even inhibits process of oxidation of most of pharmaceuticals at applied low O_3 dose
- To lower matrix effect and optimise ozonation a pre-treatment of concentrated wastewater streams (e.g. biological, filtration) is needed

Conclusions: ozonation of PhACs

- For biologically treated wastewater with dissolved organic carbon (DOC) up to 23 mgDOC/L, an ozone dose of 2 to 10 mgO_3/L should be sufficient to remove majority of pharmaceuticals to 90-99% **(Huber 2003) (Ternes 2003)**
- For concentrated streams much higher ozone doses are need to significantly remove micro-pollutants (1 gO_3/l)

Conclusions: sorption of PhACs on GAC

- Sorption on granular activated carbon (GAC) occurred for all tested pharmaceuticals.
- For more polar compounds such as clofibric acid (CFA) a higher dosis of GAC was required.

Overall conclusions

- Sorption on activated carbon and ozonation, are appropriate techniques to remove pharmaceutical compounds from various water matrixes.
- For economical reasons the sequence of the processes and implementation of pre-treatment techniques should be considered for more concentrated wastewater streams such as urine or black water

Research WUR-ETE/Leaf on PhAC

- SWITCH EU (removal of PhAC from concentrated streams)
- STOWA/SWITCH EU (urine as fertiliser: fate of PhAC in soil)
- STOWA (direct physical-chemical treatment of urine for PhAC removal)
- PILLS/SLIK EU/KRW (hospital wastewater treatment)
- PhD thesis (de Mes, 2007, de Graaff, 2010)