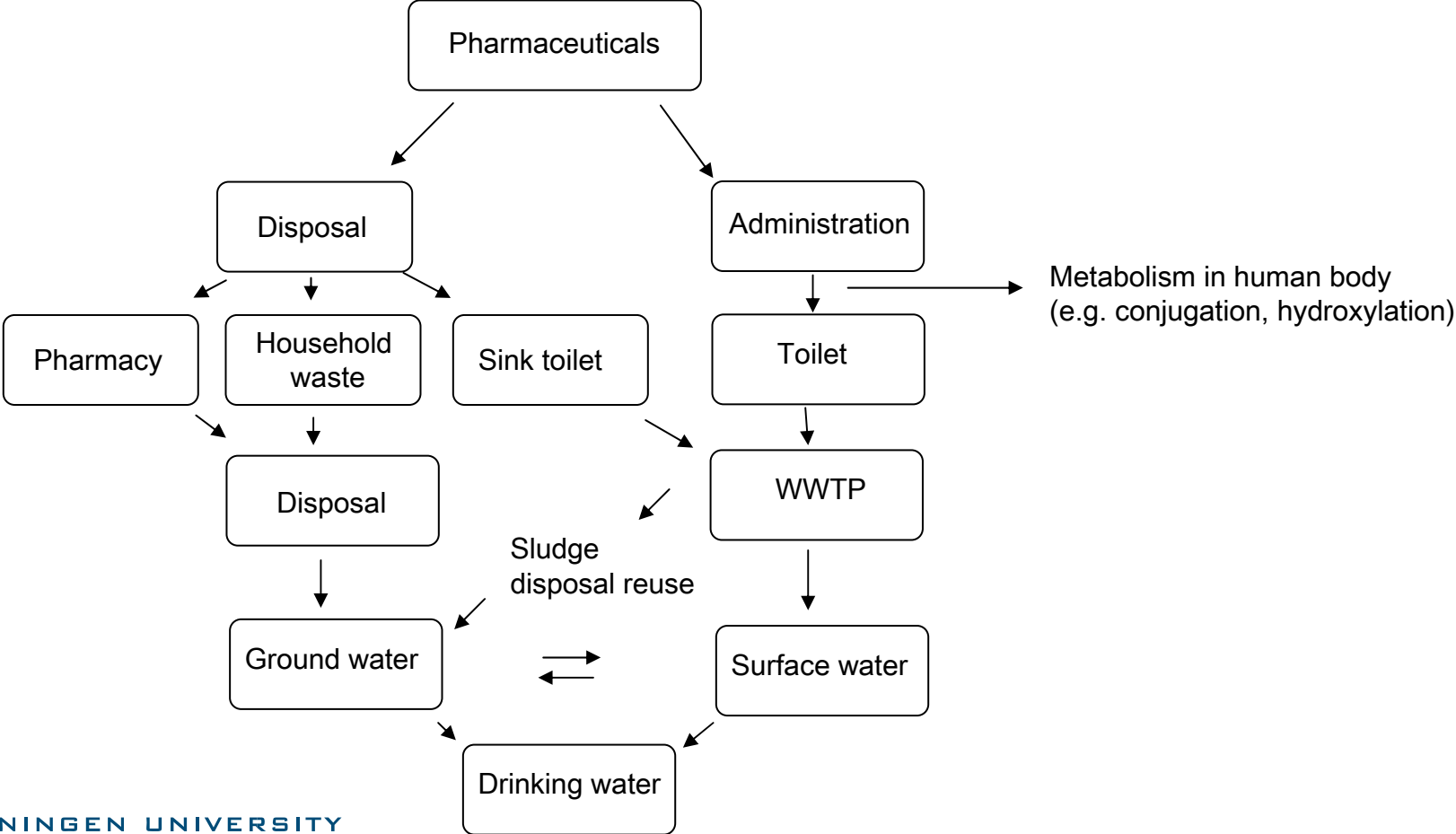




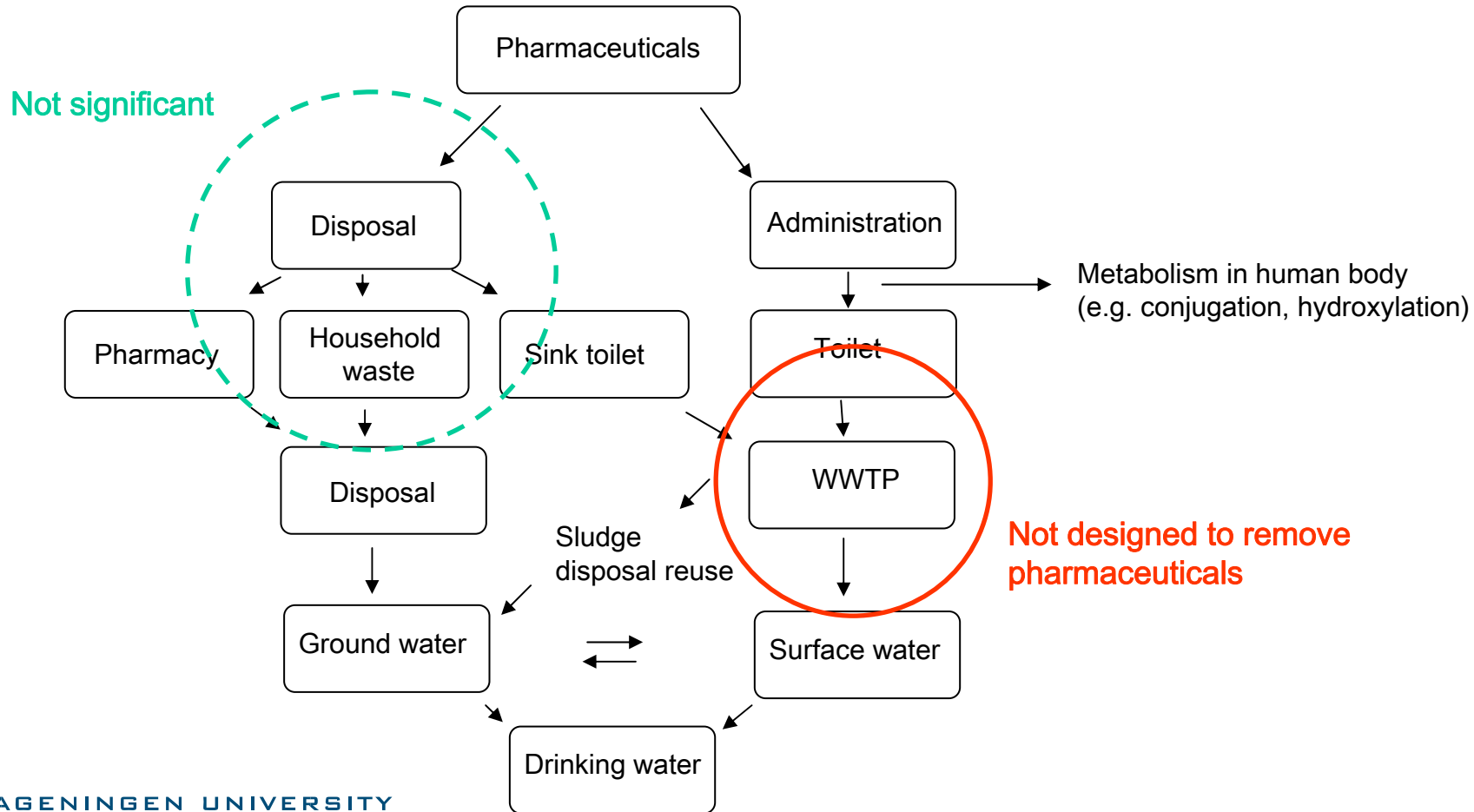
Elimination of pharmaceuticals from concentrated wastewater flows

Katarzyna Kujawa-Roeleveld
Grietje Zeeman
Adriaan Mels

Path of pharmaceuticals to environment (now)



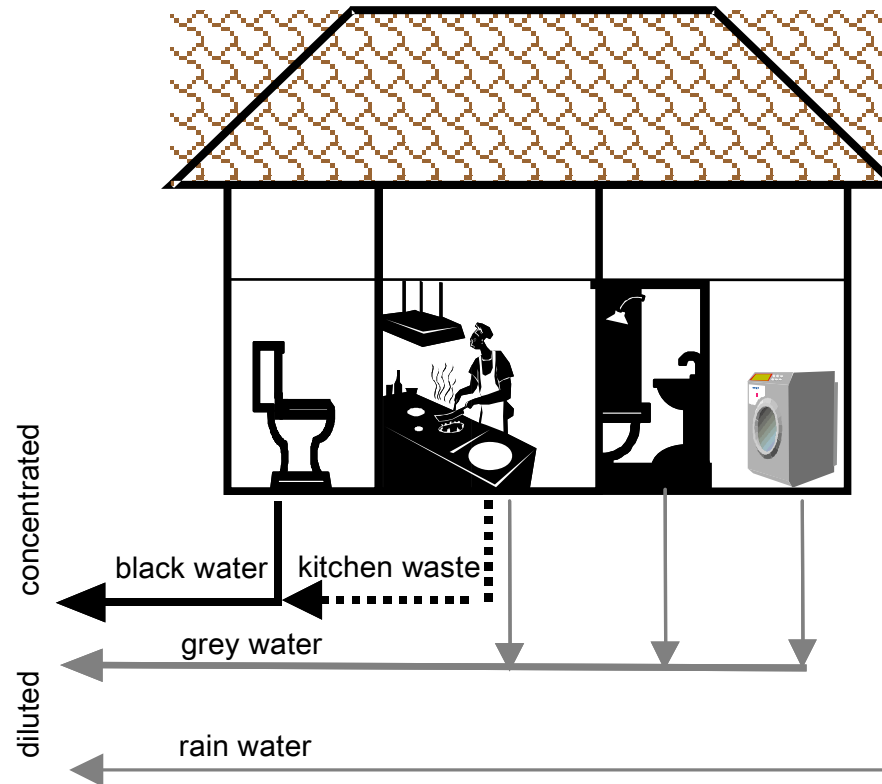
Sewer is a major disposal route



Issue?

- **Diffusion from small volume to all ww streams**
- **(ultra) low concentrations**
- **Retrofit of existing plants, feasible?**
- **Effects on aquatic life – there is!**
- **Magnitude, long term effects, synergetic effects - not known**
- **Consumption will only increase**
- **To have solutions before it becomes a ‘real’ issue**
- **...**

Source separation based sanitation



Source separation based sanitation some features

- Separate collection and treatment of concentrated and diluted streams
- Reuse potential: energy, nutrient, water
- Pharmaceuticals and hormones concentrated in small streams
- Relatively high concentrations
- Pathogens idem

Why focus on concentrated flows?

	Urine	Black water	Influent STP	Effluent STP (max found)
Analgesics (e.g. Ibuprofen)	80 000	16 000	16	27
β-blockers (e.g. metoprolol)	5 000	1 000		0.08 – 9.1
Antiepileptics (e.g. carbamazepine)	13 000	2 700	0.25 – 2.2	0.1- 22

In µg/L

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, E 10% unchanged, metoprolol DDD = 0.15 g/p/d 5% unchanged,

carbamazepine 5%, DDD 1 g/p/d

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Source separation based sanitation – source control of pharmaceuticals’ emissions

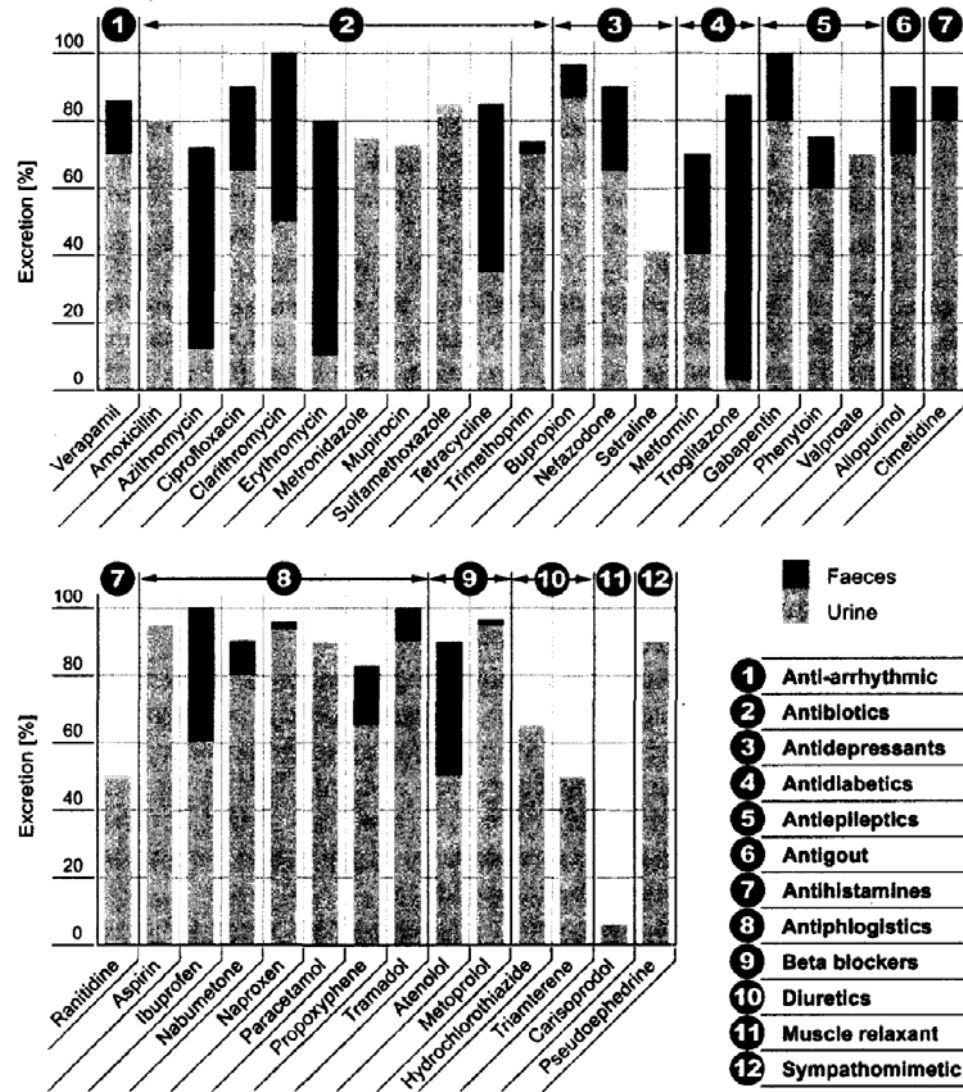
Activity 4.2

- 4.2.1: Selection most important pharmaceutical compounds from various therapeutic groups
(Adaptation and validation of analytical methods)
- 4.2.2: Degradability (fate) of pharmaceutical in different treatment processes
- 4.2.3: Defining wastewater treatment scheme to remove pharmaceuticals from black water/urine

Excretion of pharmaceuticals

- Administration
- Metabolism
- Non-altered pharmaceuticals and metabolites
- Main source urine: 70%
- Second source faeces: 30%

Distribution excreted pharmaceuticals



Selection target compounds, criteria

- Elevated annual prescription rate
- Dose and excretion
- Specific mode of action, environmental risks
- Persistency during ww treatment (low and high)
- Abundance in environment
- Availability of analytical methods

Users (*1000) per ATC group (NL)

	2001	2002	2003	2004	2005
A alimentary tract and metabolism	2.831	2.899	3.002	2.767	3.032
B Blood and blood forming organs	1.641	1.655	1.663	1.667	1.720
C Cardiovascular system	2.606	2.684	2.759	2.910	3.080
D Dermatologicals	3.412	3.421	3.465	3.192	3.200
G Genito urinary system and sex hormones	2.824	2.784	2.703	1.418	1.437
H Systematic hormonal preparations	787	828	854	890	947
J Antiinfectives for systematic use	3.884	3.840	3.826	3.775	3.978
L Antineoplastic and immunomodulating agents	134	145	157	169	184
M Musculo-skeletal system	3.442	3.403	3.423	3.322	3.182
N Nervous system	3.590	3.605	3.597	3.344	3.385
P Antiparasitic agents, insecticides, repellents	137	144	148	160	163
R Respiratory system	3.094	3.158	3.064	3.033	3.155
S Sensory organs	1.777	1.786	1.802	1.759	1.787
V Various	33	34	36	40	43

Users (*1000) per ATC group (NL)

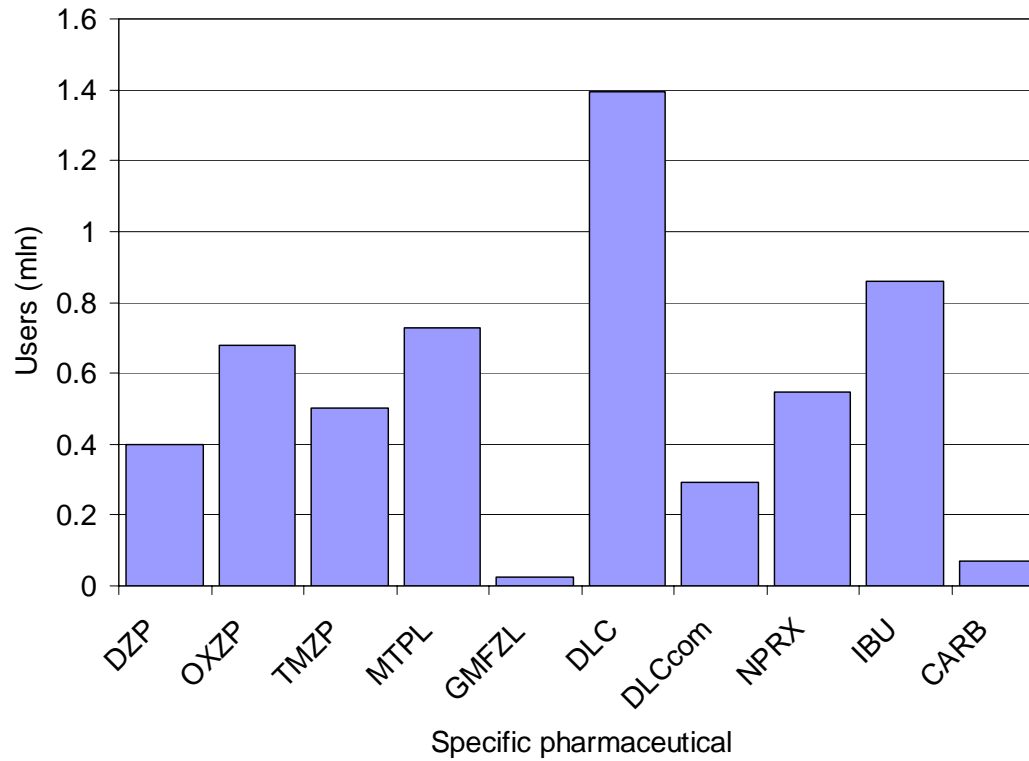
	2001	2002	2003	2004	2005
A Alimentary tract and metabolism	2 831	2 899	3 002	2 767	3032
B Blood and blood forming organs	1 641	1 655	1 663	1 667	1 720
C Cardiovascular system	2 606	2 684	2 759	2 910	3 080
D Dermatologicals	3 412	3 421	3 465	3 192	3 200
G Genito urinary system and sex hormones	2 824	2 784	2 703	1 418	1 437
H Systematic hormonal preparations	787	828	854	890	947
J Antiinfectives for systematic use	3 884	3 840	3 826	3 775	3 978
L Antineoplastic and immunomodulating agents	134	145	157	169	184
M Musculo-skeletal system	3 442	3 403	3 423	3 322	3 182
N Nervous system	3 590	3 605	3 597	3 344	3 385
P Antiparasitic agents, insecticides, repellents	137	144	148	160	163
R Respiratory system	3 094	3 158	3 064	3 033	3 155
S Sensory organs	1 777	1 786	1 802	1 759	1 787
V Various	33	34	36	40	43



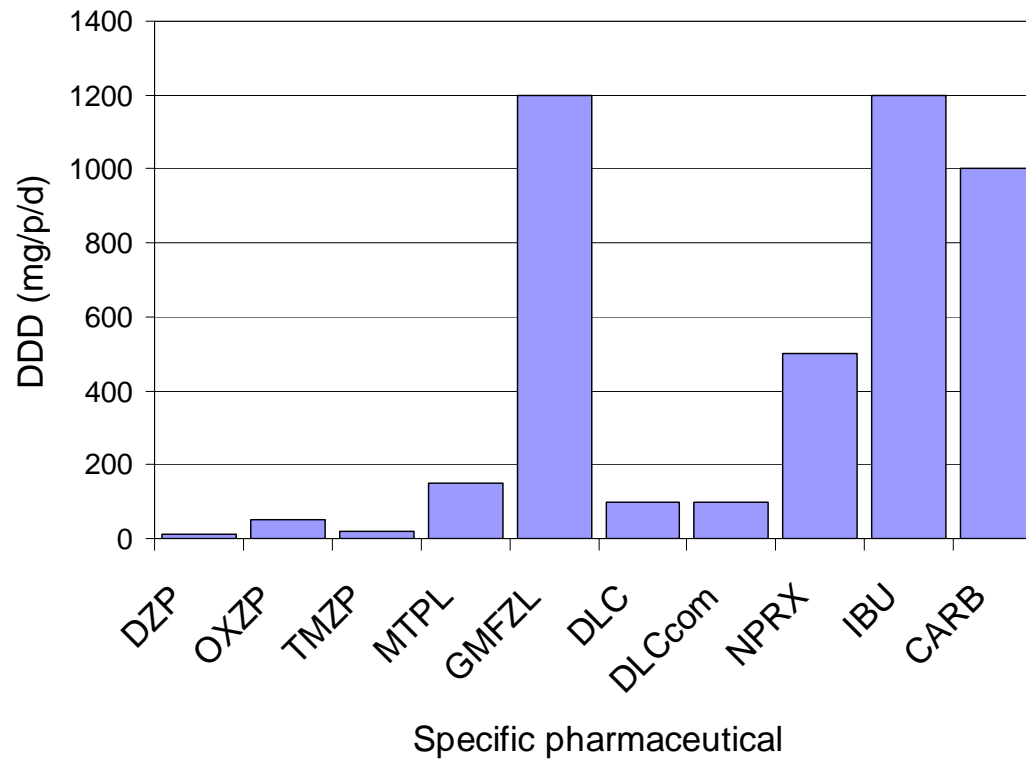
Short list

- diazepam, oxazepam, temazepam,
- metoprolol
- gemfibrozil
- diclofenac
- naproxen
- ibuprofen
- carbamazepine

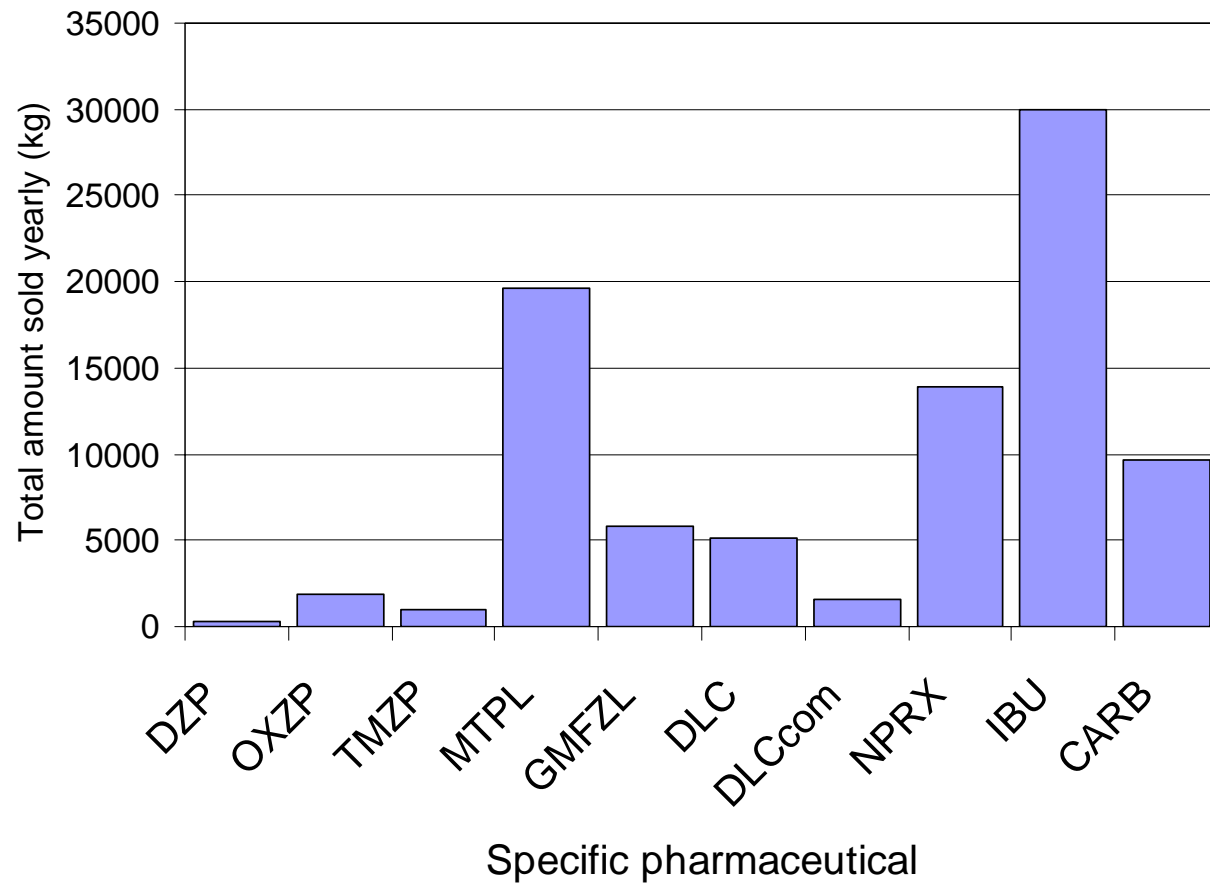
Users (NL)



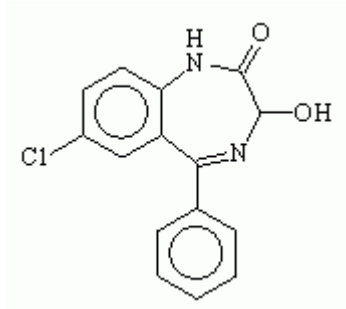
Differences in DDDs



Consumption of specific compounds (NL)

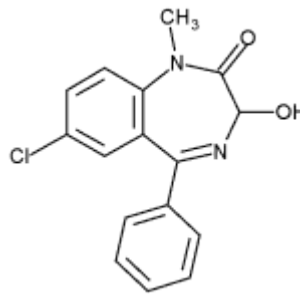


Hypnotics, sedatives, anxiolytics, amnestics, anticonvulsants



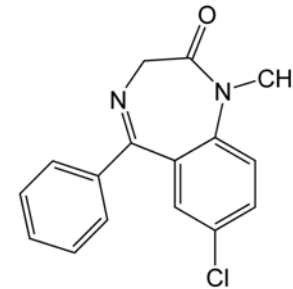
Oxazepam

$C_{15}H_{11}ClN_2O_2$
286,713 g/m
DDD 50 mg



Temazepam,

$C_{16}H_{13}ClN_2O_2$
300,7 g/m
DDD 20 mg

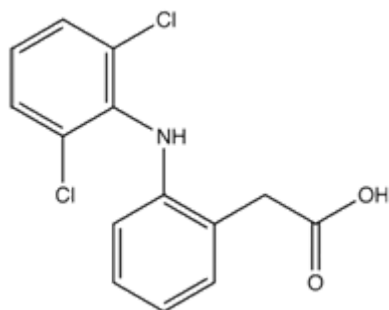


Diazepam

$C_{16}H_{13}ClN_2O$
284.7 g/m
DDD 10 mg

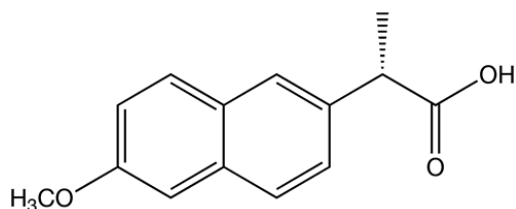
Environmental fate little described

NSAIDs and anti-epileptic



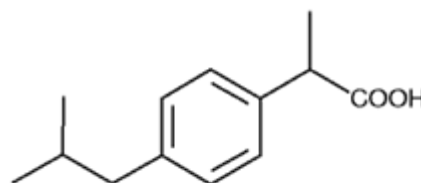
Diclofenac

$C_{14}H_{11}ClN_2O_2$
286,713 g/mol
DDD 100 mg
B 5-45%
S < 5%



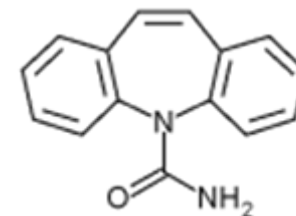
Naproxen

$C_{14}H_{14}O_3$
230,259 g/mol
DDD 500 mg
B 55-85%
S < 5%



Ibuprofen

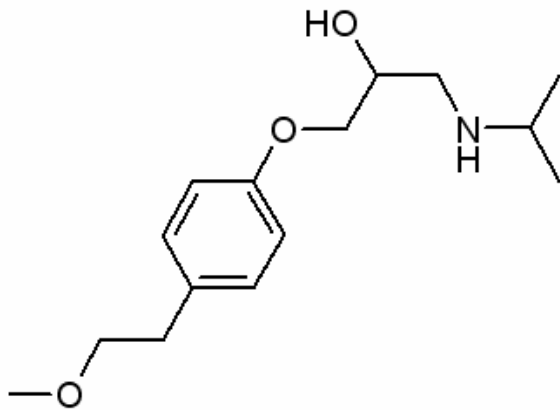
$C_{16}H_{13}ClN_2O$
206.3 g/mol
DDD 1200 mg
B 90 – 100%
S < 5%



Carbamazepine

$C_{15}H_{12}N_2O$
236.27 g/mol
DDD 1000 mg
B < 40%
S < 5%

Beta-blockers and lipid lowering agents



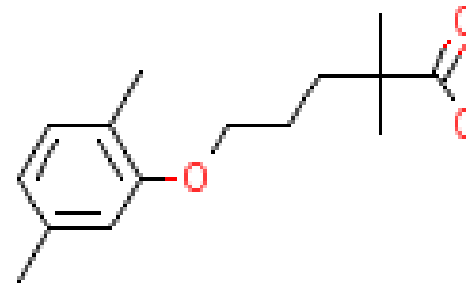
Metoprolol

$C_{15}H_{25}NO_3$

beta1 receptor blocker

267,364 g/mol

DDD 150 mg



Gemfibrozil

$C_{16}H_{13}ClN_2O_2$

250,333 g/mol

DDD 1200 mg

Removal mechanisms during ww treatment

- Sorption (K_d) ?
- (Bio)degradation (k_{biol})
- ~~Volatilisation (K_H)~~

Biological treatment

For various compounds different parameters, microorganisms and removal mechanisms may be rate limiting

Biological treatment

- Sludge age – crucial parameter for removal of pharmaceuticals?
- Availability of co-substrate
- Fraction inert material in the sludge
- Temperature
- Mass transfer limitation
- Availability of electron acceptors (redox)

Biological treatment

- Sludge age – crucial parameter for removal of pharmaceuticals?
- Availability of co-substrate
- Fraction inert material in the sludge
- Temperature
- Mass transfer limitation
- Availability of electron acceptors (redox)
 - » Most information from full scale measurements

Biodegradability batch tests

- Different sludge (inoculum) e.g. non-nitrifying AS, AS of long SRT, MBR, biofilm
- With pure substrate (pharmaceutical)
- With co-substrate (urine, black water)
- Two temperatures
- Different sludge dilution
- Aerobic, anoxic, anaerobic
- Abiotic processes

Oxidation - ozone

- Partial oxidation of refractory COD
- Complete mineralisation economically not feasible and formation of unwanted inorganic by-products
Again post-treatment required (sand filtration)
- Most pharmaceuticals react readily with ozone
- (Partial disinfection)

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- Complete mineralisation economically not feasible and formation of unwanted inorganic by-products
Again post-treatment required (sand filtration)
- Most pharmaceuticals react readily with ozone
- Partial disinfection

» Much to be done!

AOP (O_3/H_2O_2 ; UV/ H_2O_2 ; Fe^{2+}/H_2O_2)

- Unselective (oxidation capacity lost)
- Partial oxidation
- O_3/H_2O_2 ; UV/ H_2O_2 comparable results expected

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- Unselective (oxidation capacity lost)
- Partial oxidation
- O_3/H_2O_2 ; UV/ H_2O_2 comparable results expected
 - » much to be done

Oxidation batch tests

- Choice oxidant
- Oxidant dose
- Pure substrate
- Effect of wastewater matrix
- Transformation, degradation or mineralisation?

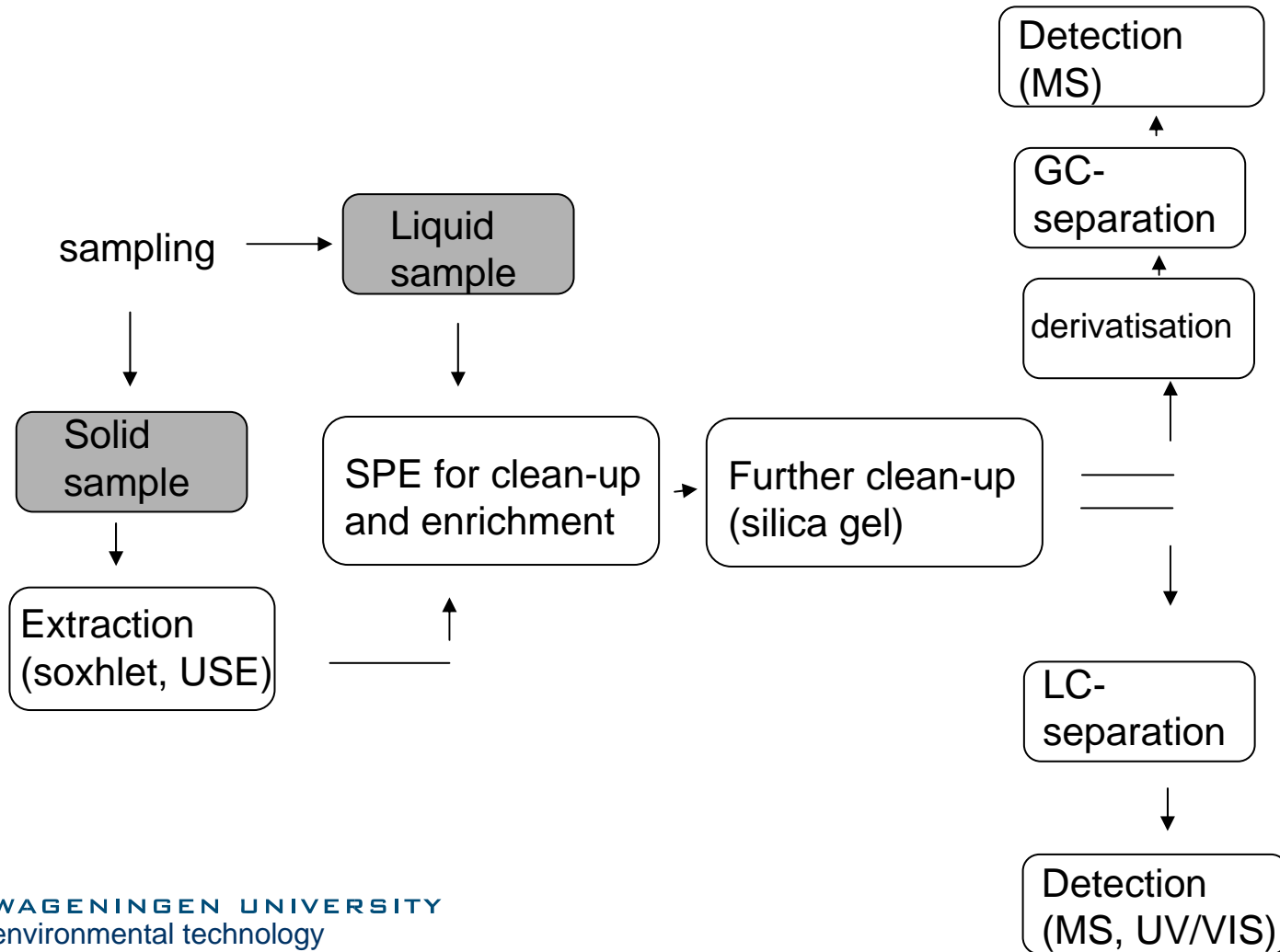
Confirmation: complete systems

- Confirmation batch findings
- Mass balances (in, eff, excess sludge, etc.)
- Include Metabolites (retransformation)

Sophisticated analytical techniques such as LC/MS/MS are needed for correct quantification of pharmaceuticals in environmental matrices

- elevated polarity
- low concentration, low MW
- complex matrix
- trace levels

Analytical multiple step approach



Planning

	Feb 2007	Feb 2008	Feb 2009
Report 'fate of human pharmaceuticals in a wastewater treatment'. Selection representative compounds			
Biodegradability of selected compounds			
Post treatment to remove non-biodegraded compounds. Definition of an 'efficient' treatment system.			



Thank you!