Human Stress on Water Quality of the Water Cycle

Fritz H. Frimmel

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„Hier ist sicher noch Bewusstseinsbildung nötig. Unser tatsächlicher Wasserverbrauch ist um eine Vielfaches höher...“ ***Sigmar Gabriel (SPD)***

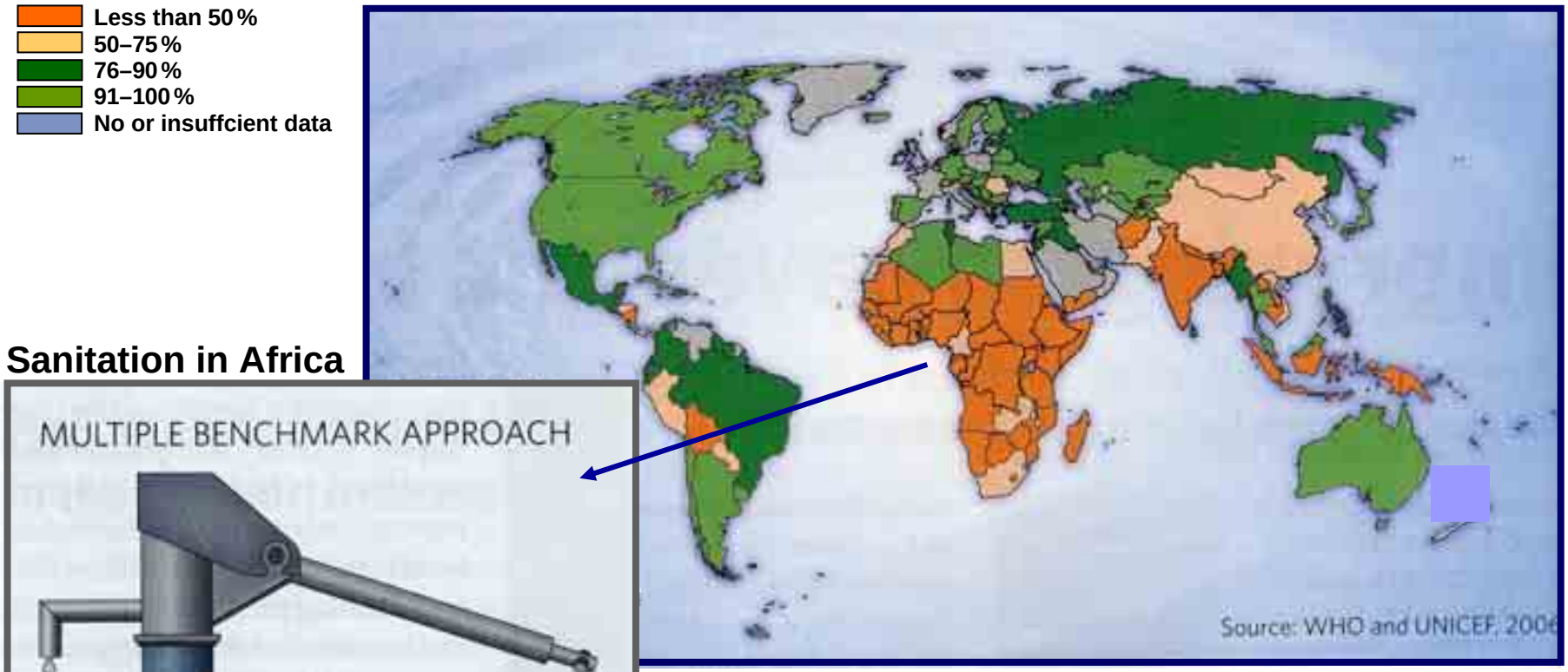
„Wir müssen uns überlegen, ob wir kostbares Trinkwasser weiter als Transportmittel für Fäkalien in unseren Toiletten nutzen wollen...“ ***Uschi Eid (Bündnis 90/Die Grünen)***

„Wasser ist künftiges Krisen- und Kriegsrisiko Nummer eins...“
Christian Ruck (CSU)

„Wassermangel trifft Kinder am härtesten...“
Regine Stachelhaus (Unicef)

Millennium Goal: 15 50 90

Proportion of population with improved sanitation



Nature; 20.03.2008

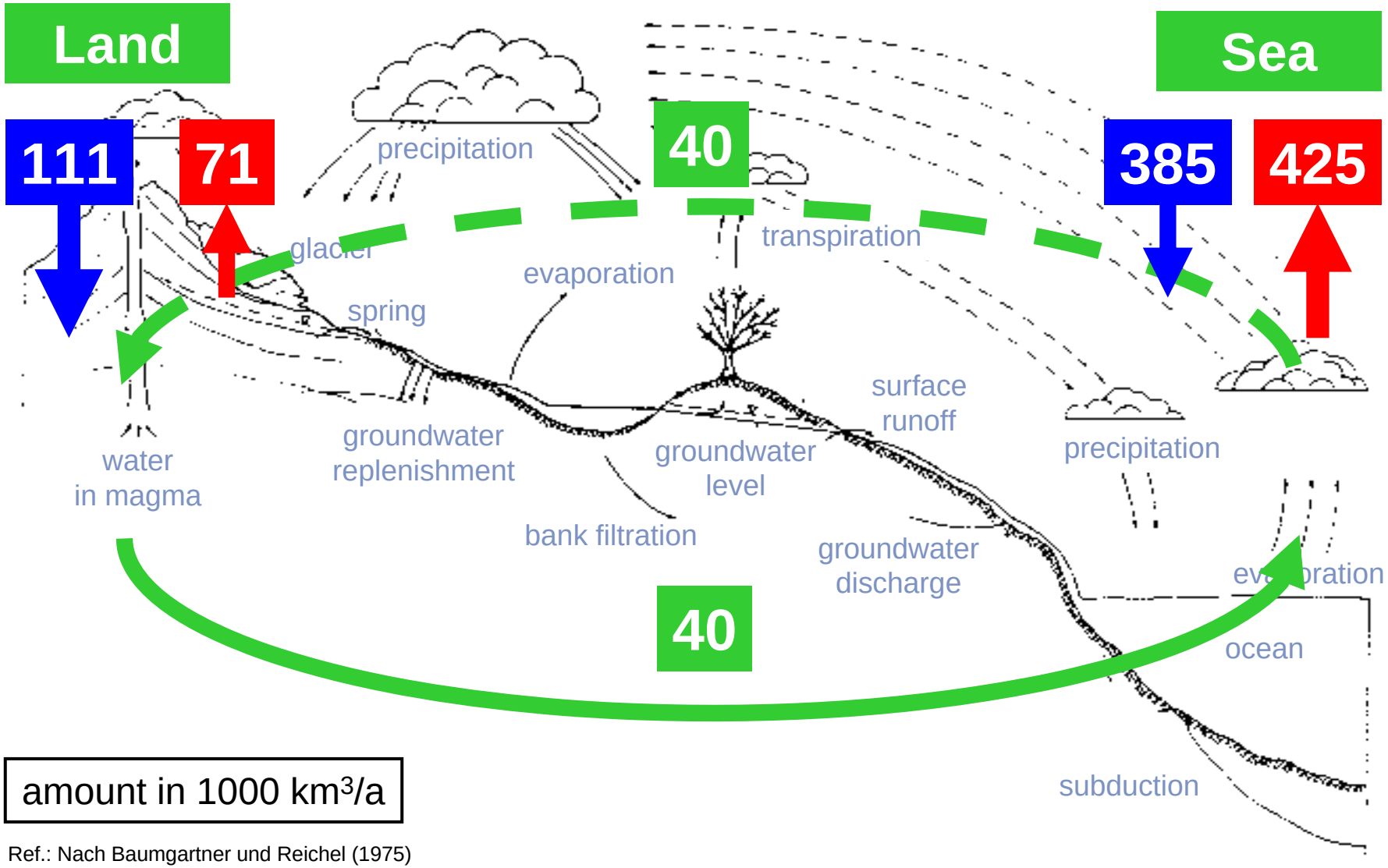
Sanitation in Africa

Proportion of population without access to safe drinking water and improved sanitation:

Target

50 % reduction by 2015 compared to reference status 1990

Water Quantity
Hydrological Cycle and Global Water Balance

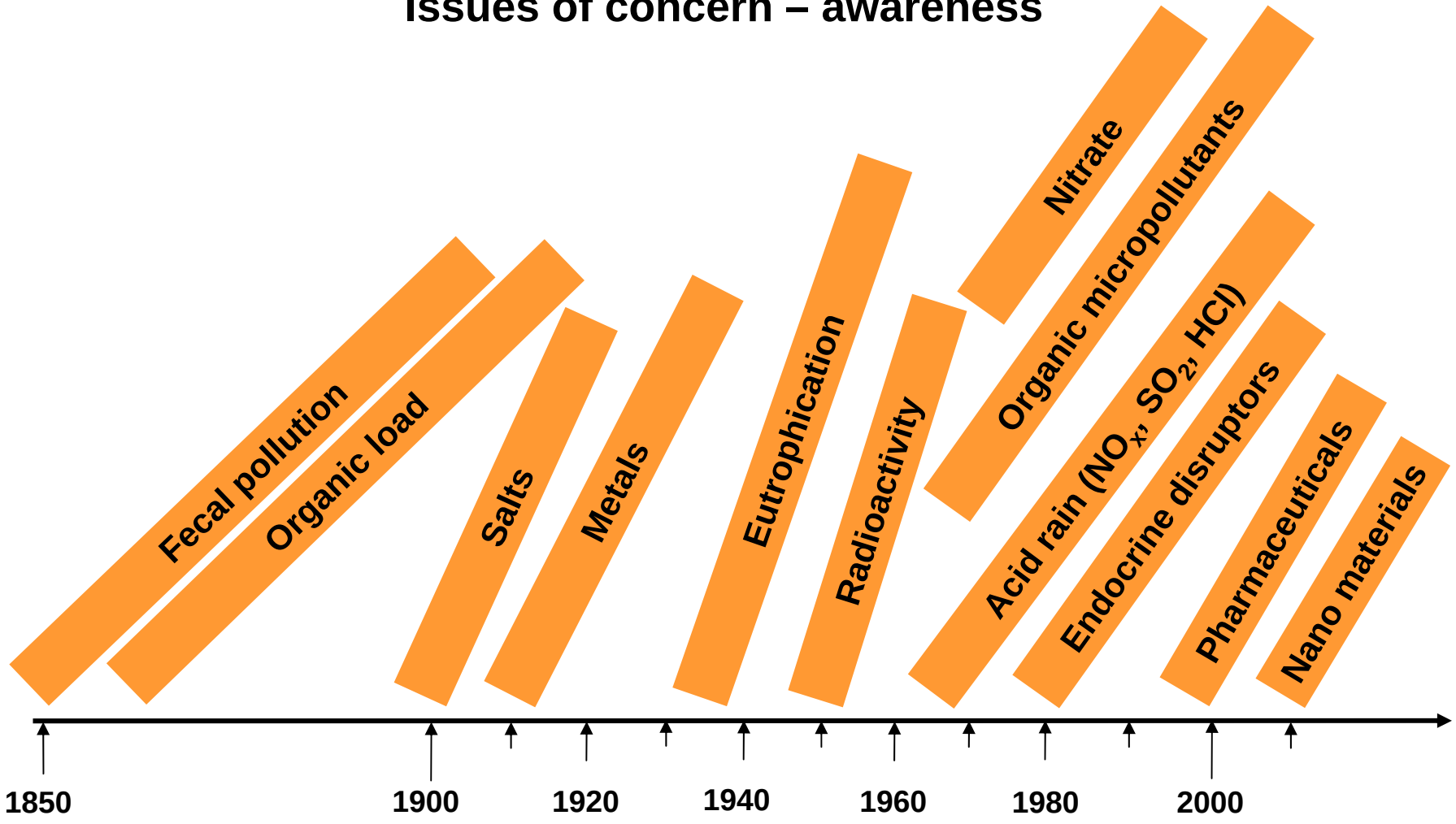


amount in 1000 km³/a

Ref.: Nach Baumgartner und Reichel (1975)
From: http://www.iup.uni-heidelberg.de/institut/studium/lehre/Atmosphaerenphysik/script/WASSER.pdf

Water Pollutants

Issues of concern – awareness



Contents

- Pharmaceuticals
- Endocrine Disruptors
- Colloids and ENPs
- The Way Out


Pharmaceutically active compounds in the water!
Only an analytical challenge?

Use of Pharmaceuticals

Amount of Drugs for Human Use (circ. 2800): circ. 6500 t/a

Antiepileptics
- **Carbamazepine**

Lipid-lowering agents
- **Bezafibrate**
- **Clofibric acid**

Beta blockers
- **Metoprolol**

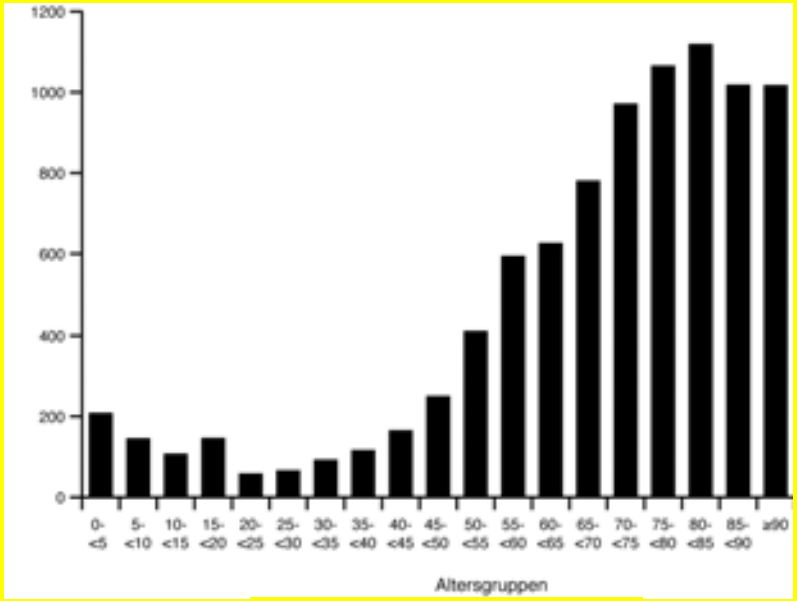
Antiphlogistics
- **Diclofenac**
- **Ibuprofen**

Antibiotics
- **Dehydro-erythromycine**

Diagnostics
- **Iopamidol**
- **Iopromide**

Application versus Age

Defined daily dose (DDD) per insured person



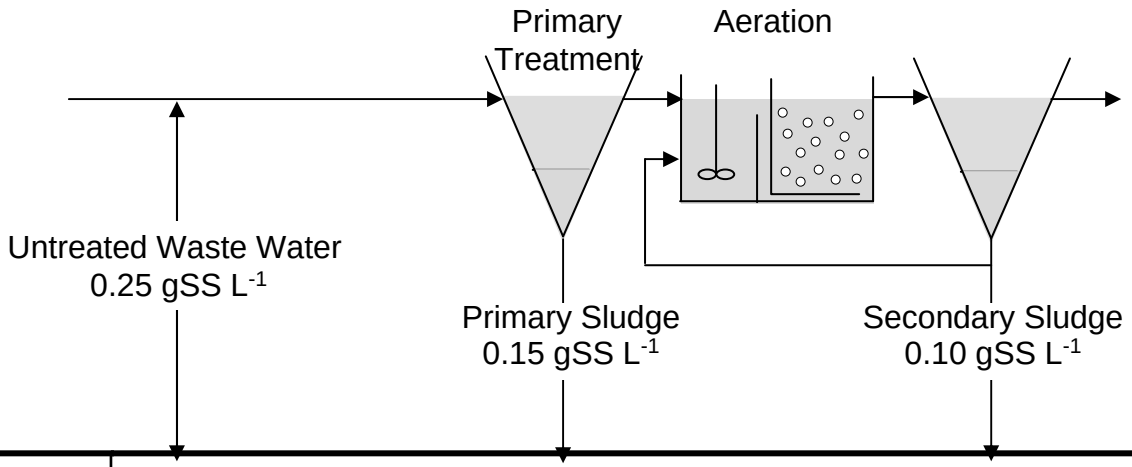
Age class

Prescription Report (2005)

Amount of Drugs for Veterinary Use: circ. 1000 t/a

Antibiotics
- **Sulfonamides**
- **Tetracyclines**

Pharmaceuticals in Wastewater Treatment Plants (WWTP) – Sorption

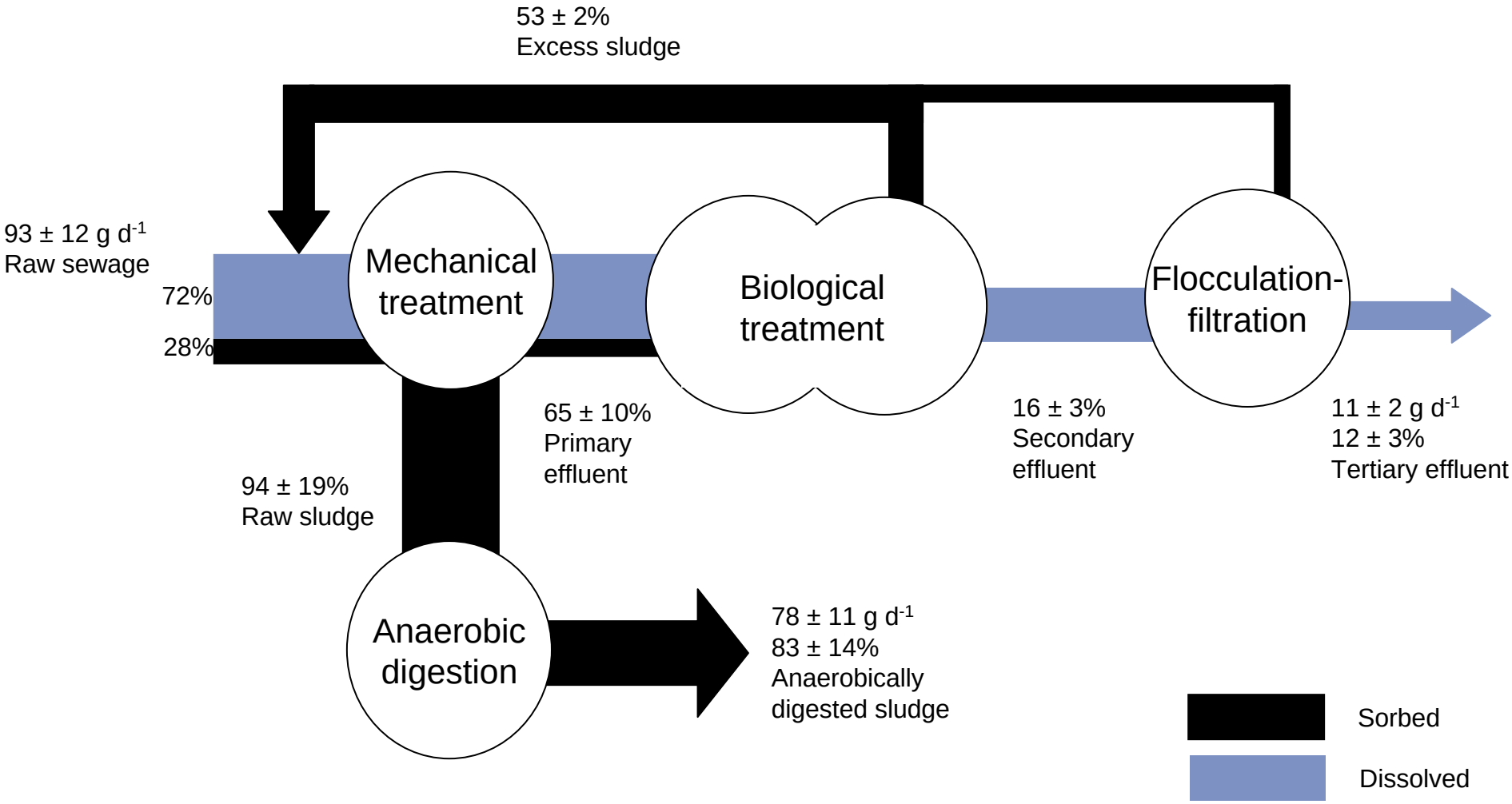


Compound	K_d (L g_{SS}^{-1})	Percentage sorbed, %		
Diclofenac	0.45 / 0.05	10	6	0.5
Estrogen	0.35 / 0.27	8	5	3
Tonalide	5.5 / 2	58	45	17
Norfloxacin	25 / 2	33	23	72

SS – solid substances

Golet et al. 2003; Siegrist et al. 2003; Ternes et al. 2004

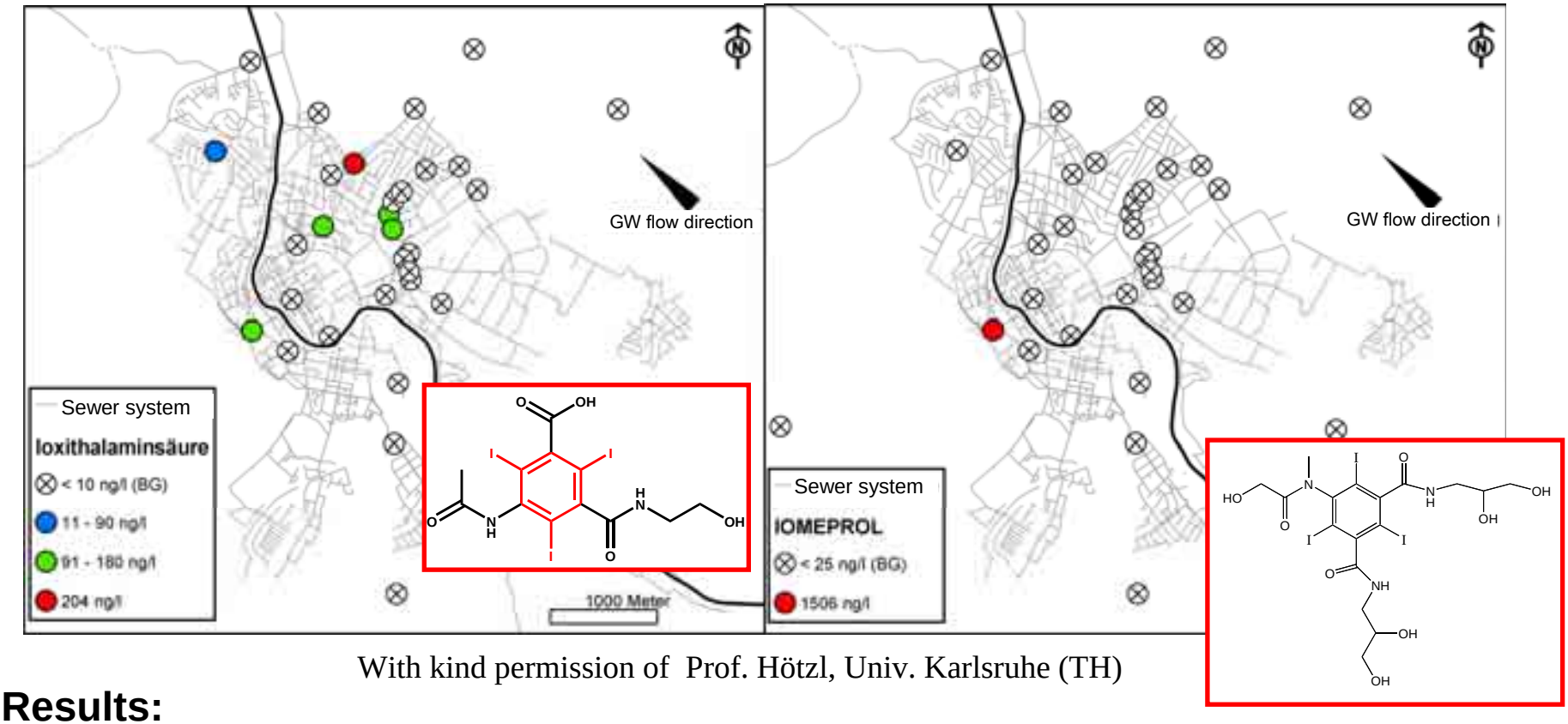
Pharmaceuticals in WWTP – Example Ciprofloxacin (Antibiotics)



Alder et al. 2004

Iodinated X-ray Contrast Agents in Groundwater

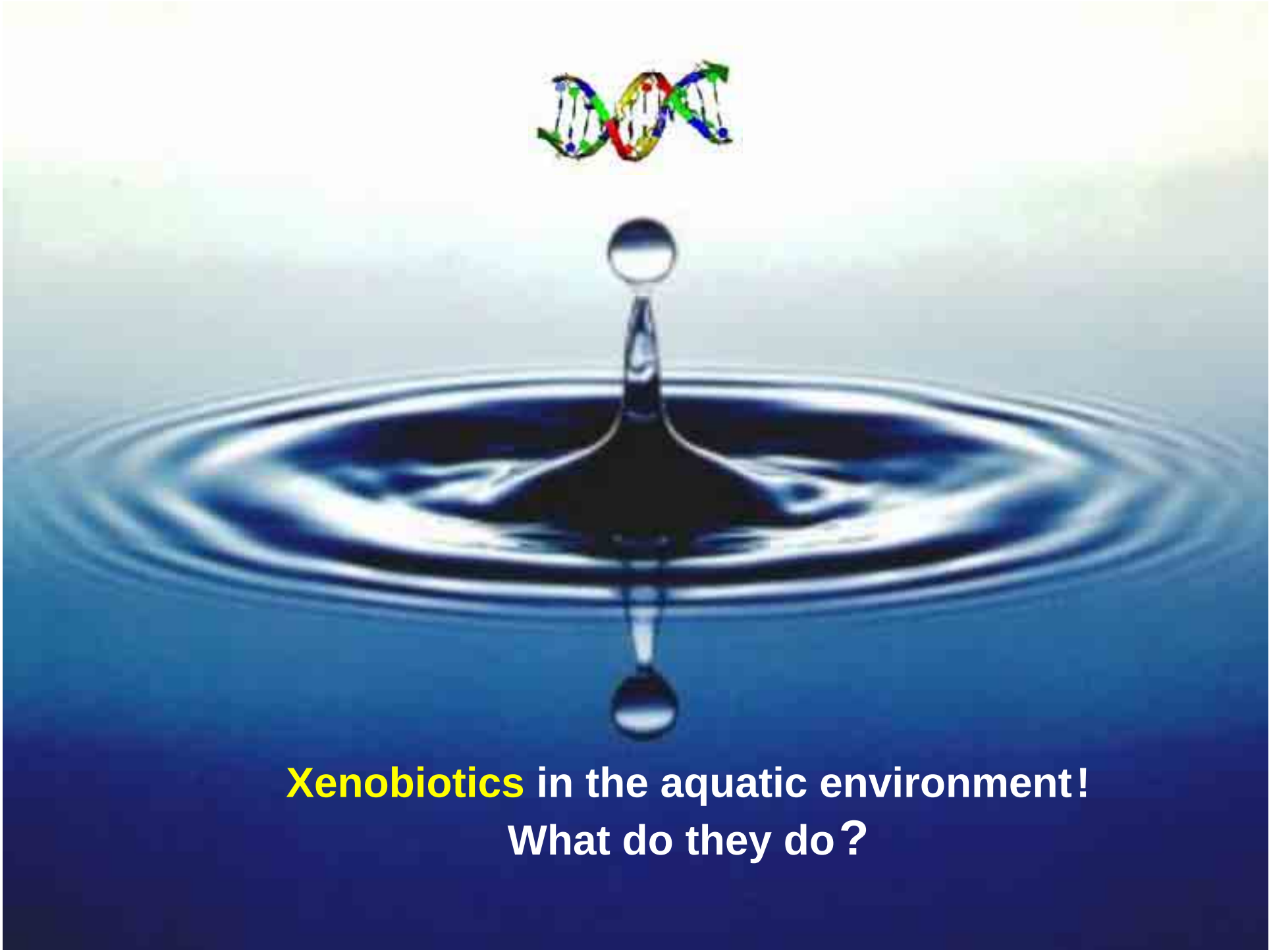
Sampling sites with concentrations of ioxithalamic acid and iomeprol:



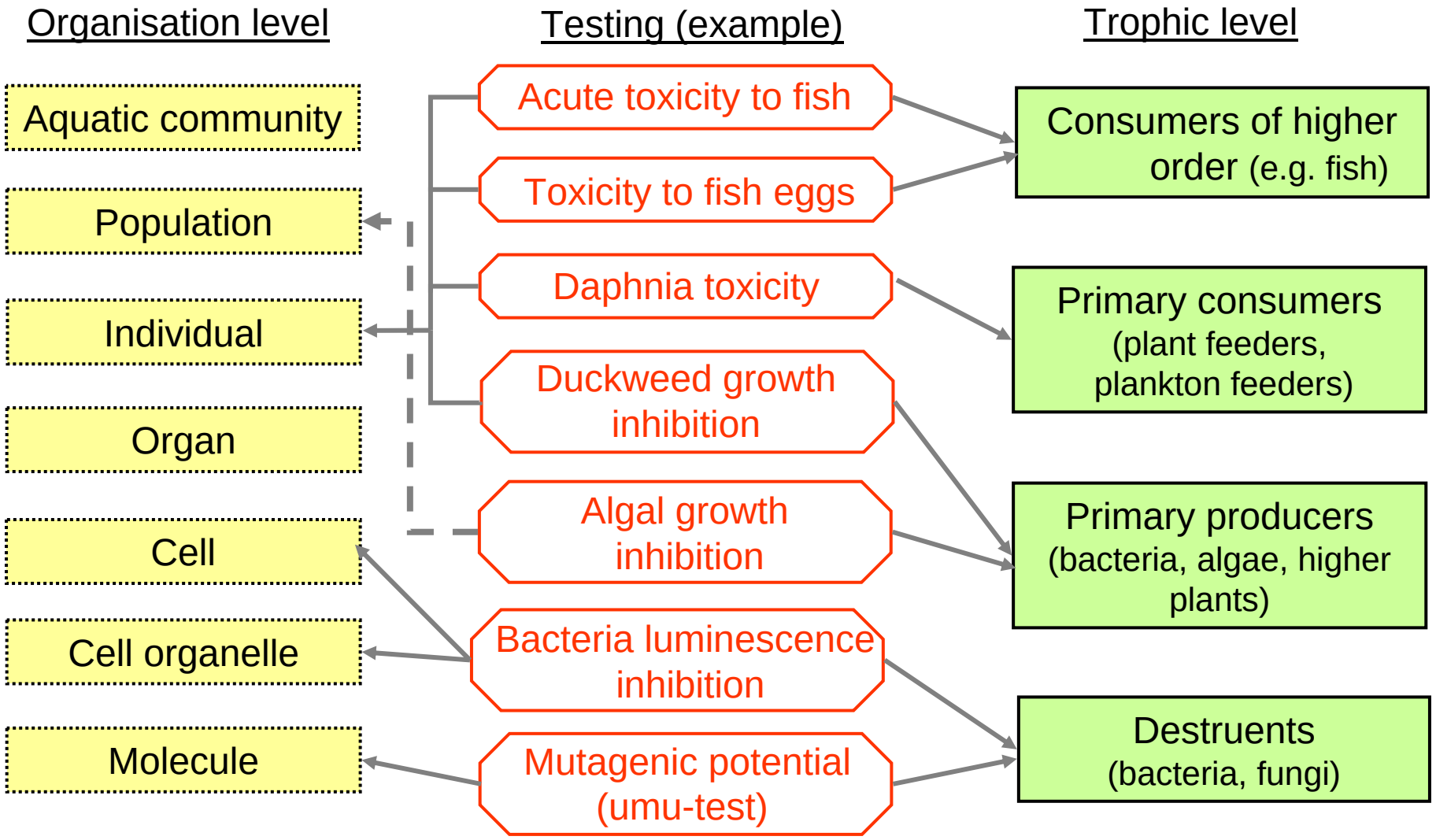
With kind permission of Prof. Hötzl, Univ. Karlsruhe (TH)

Results:

- ➔ Ioxithalamic acid and iomeprol detected only within cities
- ➔ High concentrations of iomeprol due to leaky sewers upstream of sampling site


Xenobiotics in the aquatic environment!
What do they do?

Bioeffects – Testing on Different Levels



Pluta & Rosenberg, 2005

Bioeffects – Example: Endocrine Disruption

Endocrine Disruptor Screening and Testing Advisory Committee (EDSTAC):

An endocrine disruptor is an exogenous chemical substance or mixture that alters the structure or function(s) of the endocrine system and causes adverse effects at the level of the organism, its progeny, populations, or subpopulations of organisms, based on scientific principles, data, weight-of-evidence, and the precautionary principle.

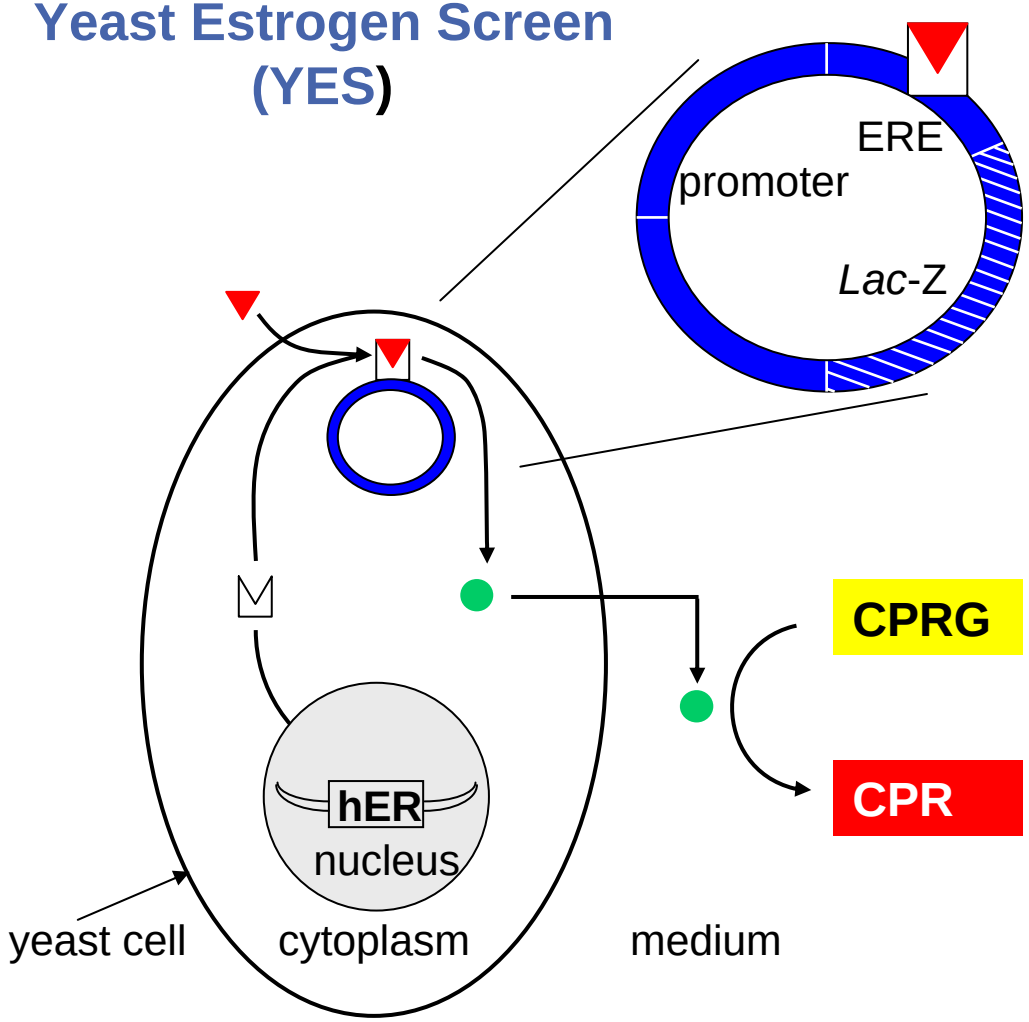
EDSTAC final report, 1996

Classes of estrogenic endocrine disruptors:

- natural hormones, e.g. 17β-estradiol (E2), estrone (E1), estriol (E3)
- synthetic hormones, e.g. 17α-ethinylestradiol
- phyto- and mycoestrogens, e. g. genistein, zearalenone
- xenoestrogens, e.g. 4t-octylphenol, bisphenol A

Bioeffects – Testing Estrogenic Activity

Yeast Estrogen Screen (YES)



- estrogen
- estrogen receptor
- activated receptor
- β -galactosidase

hER:	human estrogen receptor gene
ERE:	estrogen responsive element
lac-Z:	reporter gene
CPRG:	chlorophenol red-β-D-galactopyranoside

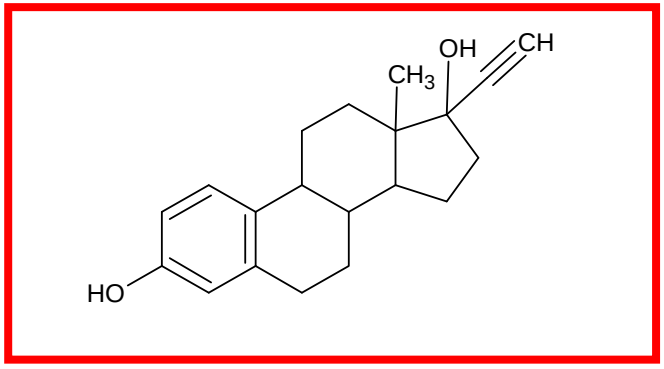
sensitivity:
c (E2) = 10^{-11} mol/L (2.7 ng/L)

[1]Routledge, E. J., Sumpter, J. P. (1996), Environ. Toxicol. Chem. 15, 241-248

Bioeffects – Example: Ecotoxic Effect of EE2

EE2 = 17α-Ethinyl estradiol, active agent of „ the pill “ (contraceptive)

- Endocrine disruptor
- Concentrations in wastewater effluent and in the receiving water course: ng/L-range
- Proposed quality standard: 0.03 ng/L (European Water Framework Directive) (extremely low because of high biological potency)
- Conc. ≥ 0.32 ng/L: Reduced fertilization rate of fish eggs (Flathead Minnow)!
- Conc. ≥ 3.2 ng/L: No eggs, no male fish!
- Exceedance of quality standard in many waters => action is needed!




The nano-age.
Only sun-shine?

Engineered Nanoparticles (ENP)

Metal oxides and metals

TiO_2	Pigment, photo catalyst
Iron oxides	Pigment, pharmaceuticals, medical applications
ZnO / ZrO_2	Surface hardener
SiO_2	Additive for polymers
Ag / Au	Catalysts, electronic devices

Quantum dots

CdTe / GaAs	Semiconductors, electronic devices

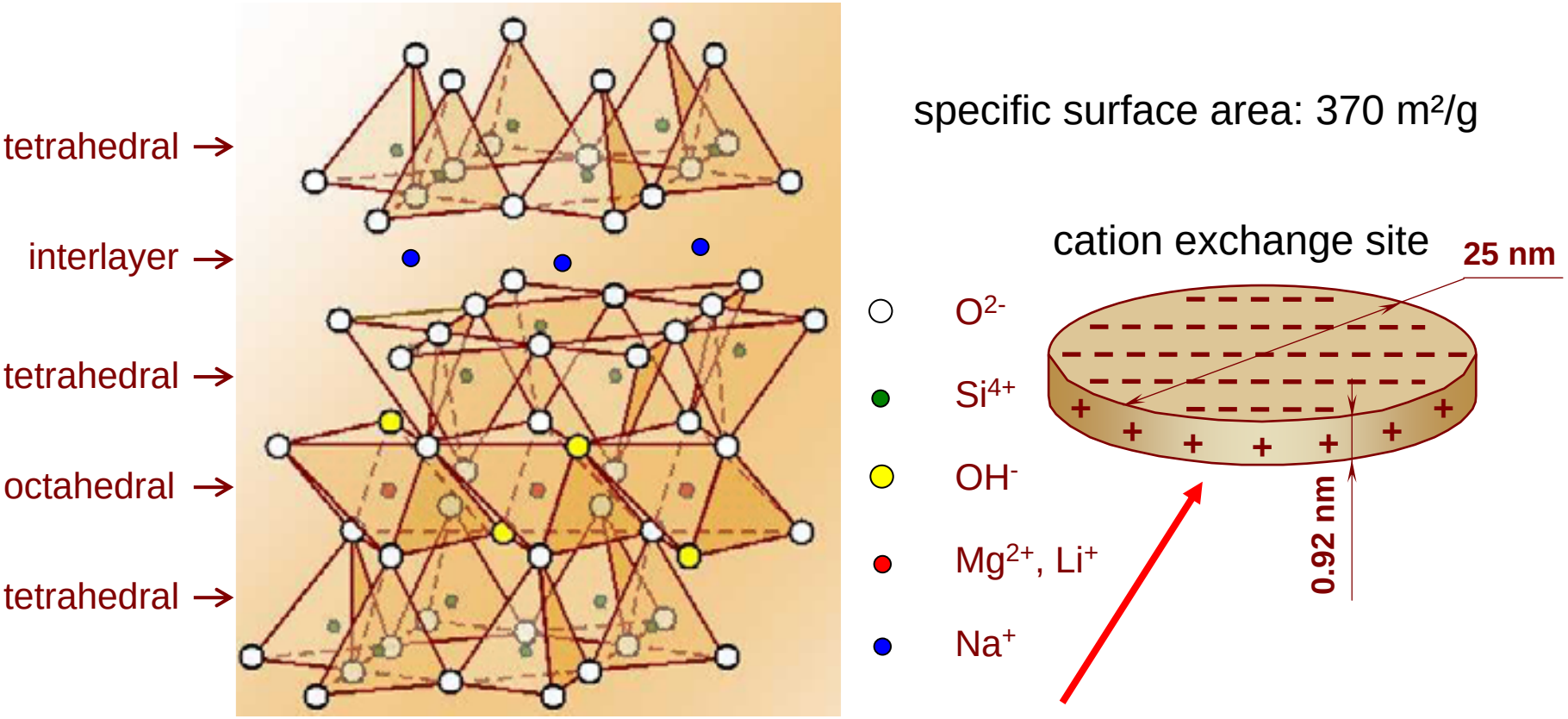
Carbon based nanomaterials (CBN)

Black carbon	Additive in wheels, pigment
Fullerenes	Additive in grease
Nano tubes	Additive in polymers, accumulators and liquid fuel-cells

Engineered Nanoparticles – Example Laponite

Laponite: synthetic tree layer clay mineral

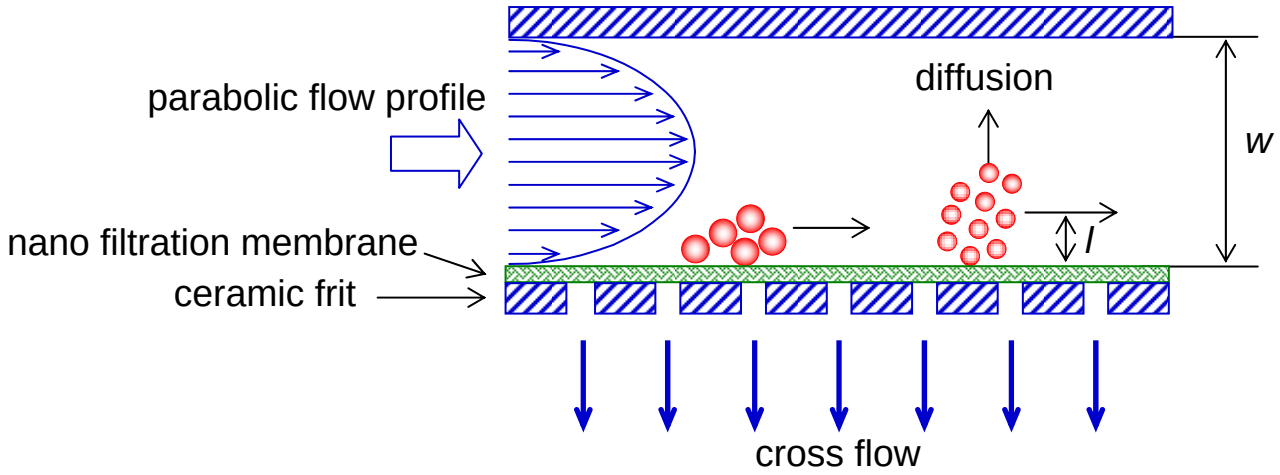
empirical formula: $Na^{+}_{0.7}[(Si_8Mg_{5.5}Li_{0.3})O_{20}(OH)_4]^{0.7-}$



positive potential: ionisation and/or protonation of lateral hydroxyl groups

negative potential: partial substitution of the Mg^{2+} ions by Li^{+} ions in the octahedral layer

Asymmetrical Flow Field Flow Fractionation (AF^4)



separation is based on the hydrodynamic diameter of the analyte particles

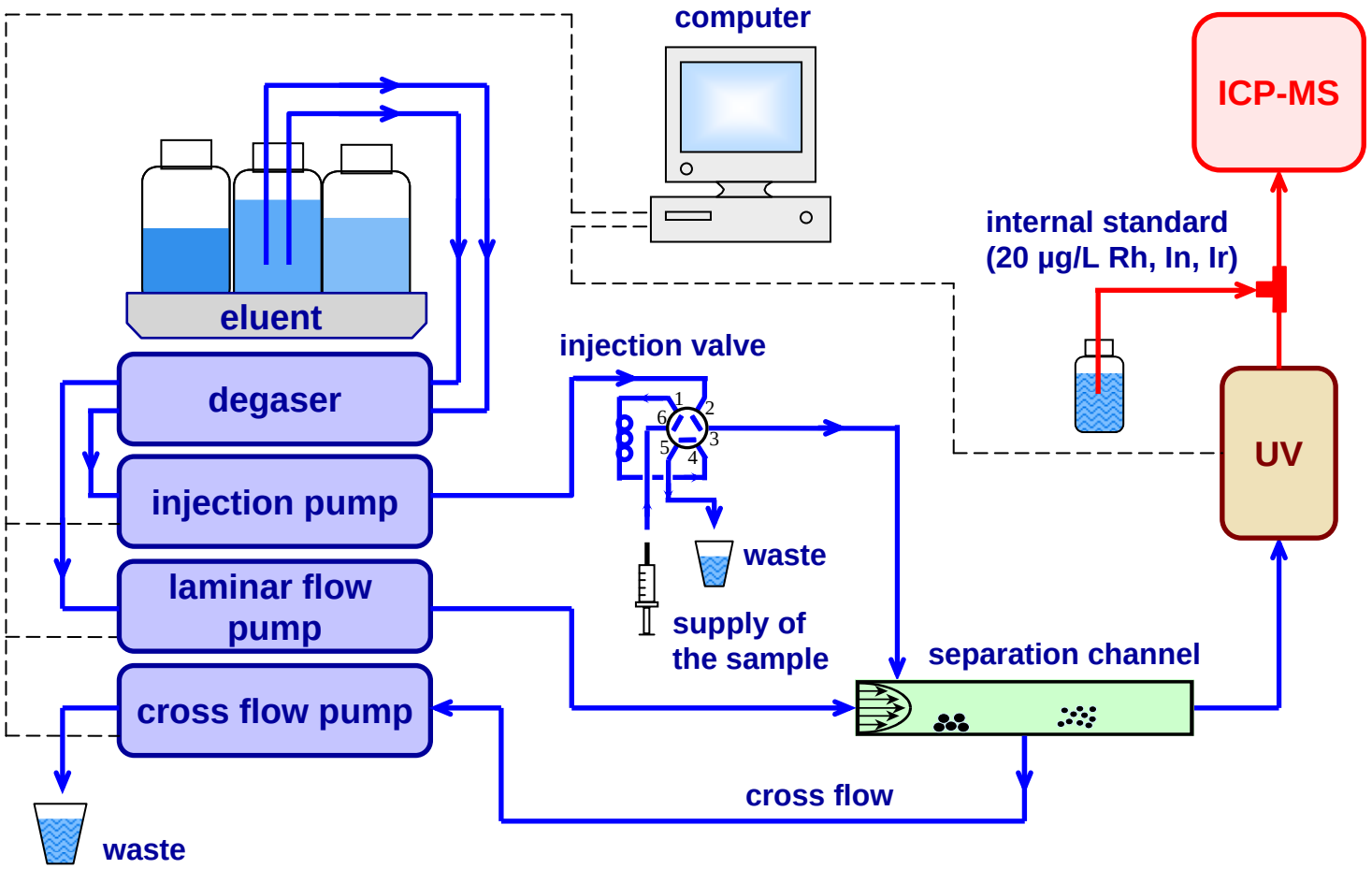
retention parameter

$$\lambda_{AFFFF} = \frac{l}{w} = \frac{kTV^0}{3\pi\eta\dot{V}_c d w^2}$$

k	Boltzmann constant
T	absolute temperature
V^0	geometric volume of the channel
η	dynamic viscosity of the fluid
$\dot{V}_c$	volumetric rate of cross flow
d	hydrodynamic diameter of the particle
w	channel thickness

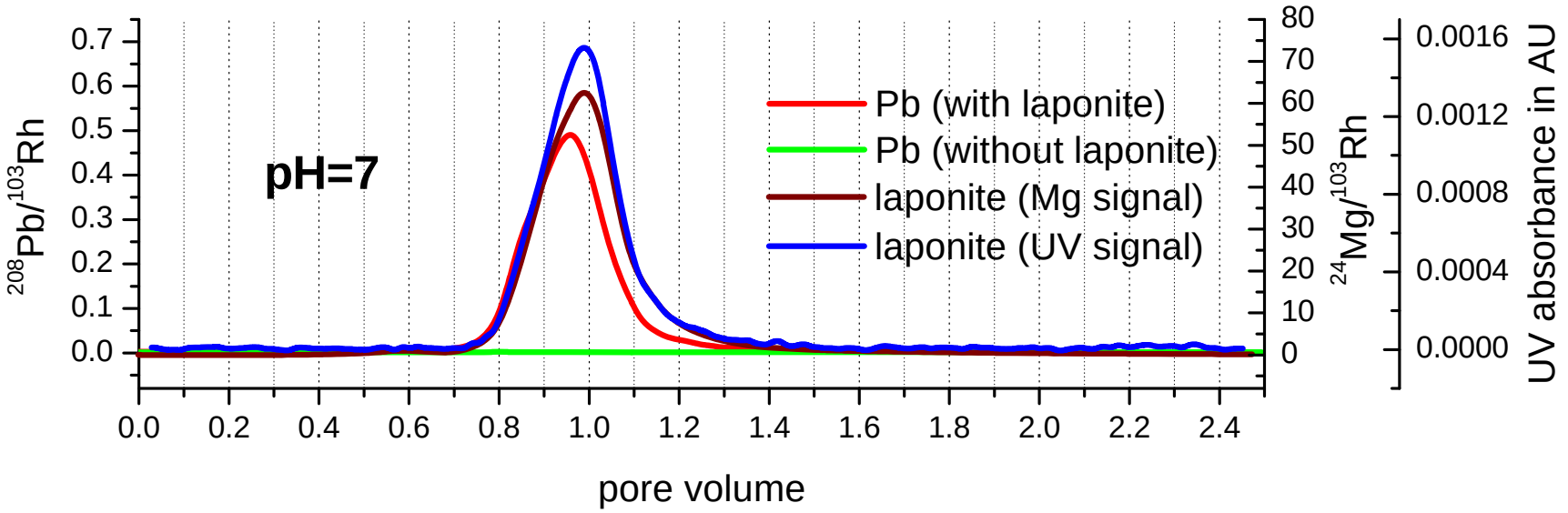
Studying the Role of Nanoparticles

Coupling: **Asymmetrical flow field flow fractionation (AF^4)** **+** **ICP-MS**



Studying the Role of Nanoparticles

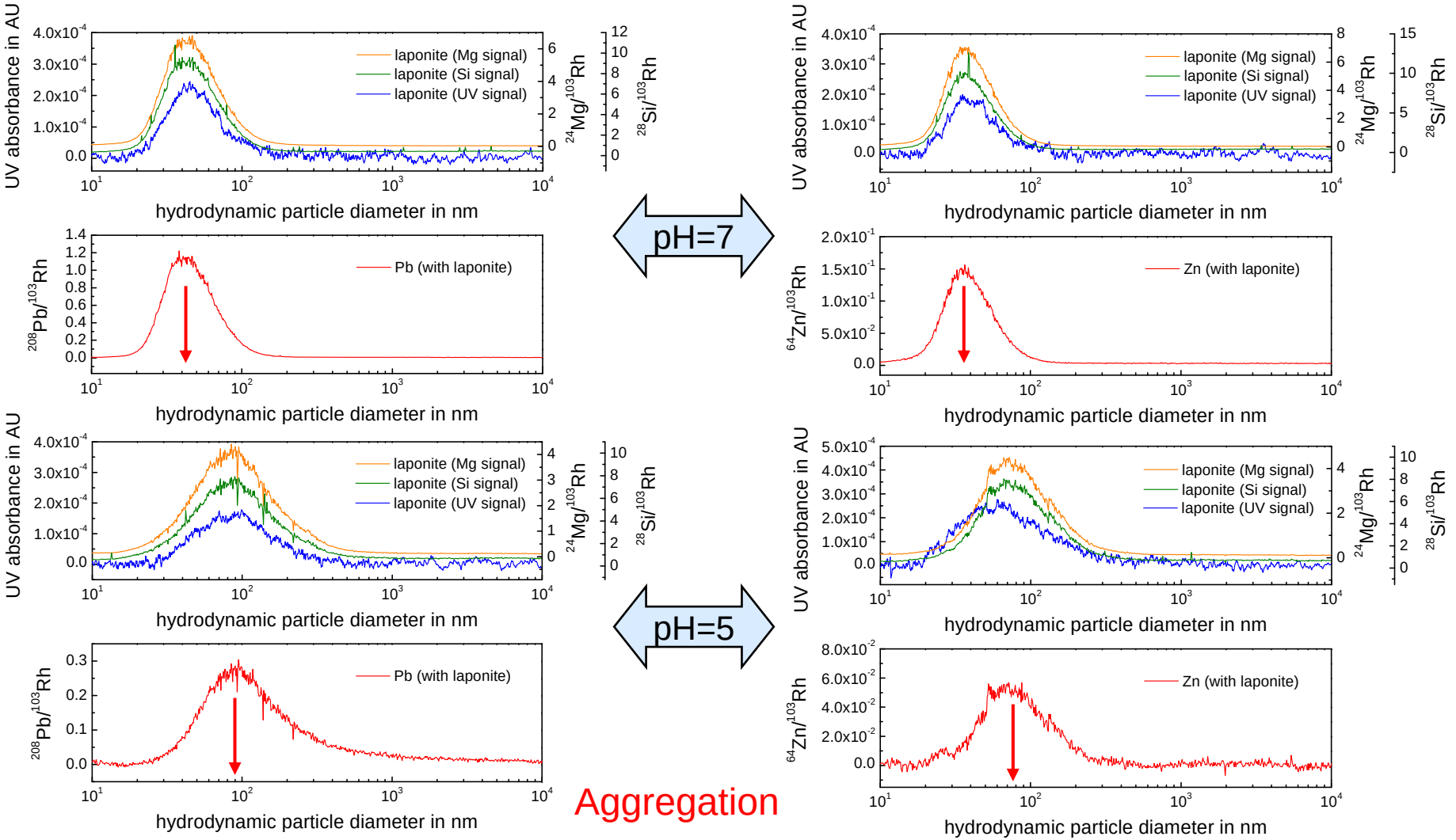
Vehicle Function



Recoveries:
UV: 54 %
Pb (with laponite): 3.3 %

Laponite:	**200 mg/L**
***c*(Pb):**	**10 µmol/L**
Flow Rate:	**1 mL/min**

Studying the Role of Nanoparticles

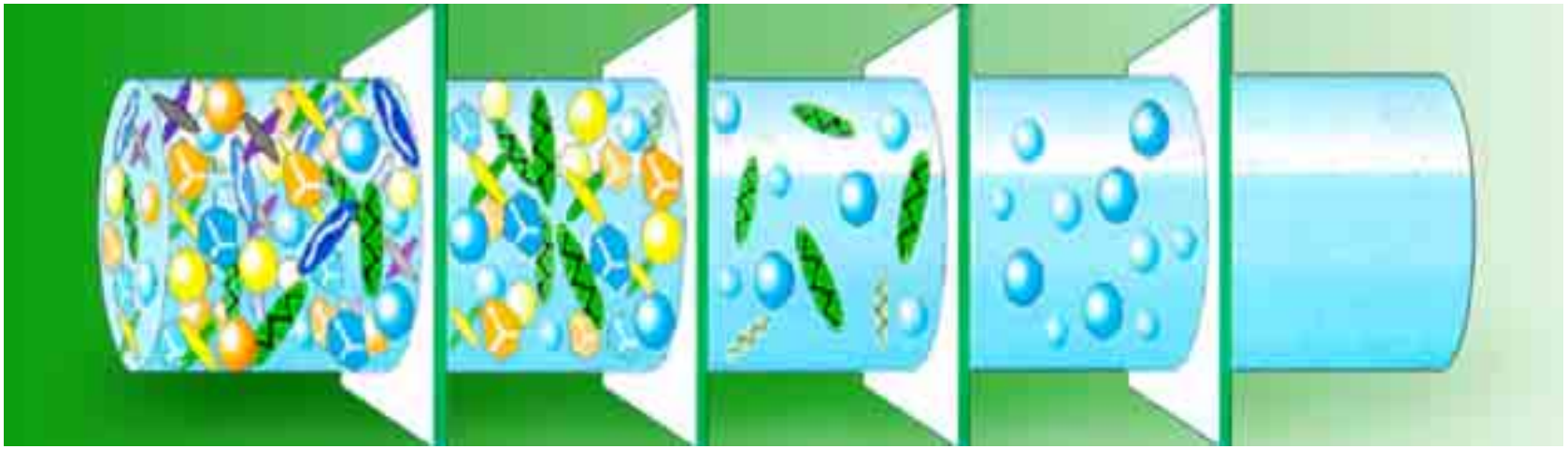


The Way Out:

- Separation
- Degradation
- Biotransformation

Separation – Membrane Filtration

Microfiltration	Ultrafiltration	Nanofiltration	Reverse Osmosis
> 0,1 µm > 500.000 Da	0,1 – 0,01 µm 1 - 500 kDa	0,01 – 0,001 µm 100 - 1.000 Da	< 0,001 µm < 100 Da



Suspended Particles

Colloids, Turbidity

Emulsions

Macro-molecules

Bacteria, Cells

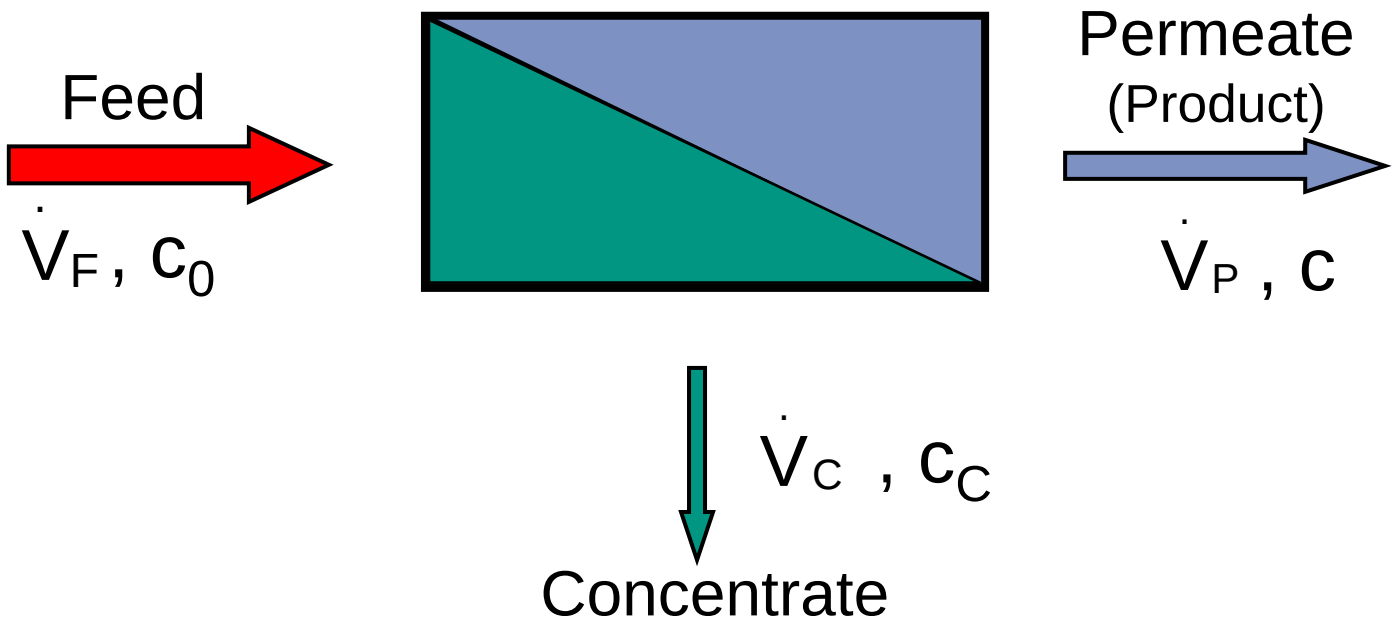
Viruses

Proteins

Low-molecular – weight organic compounds

Ions

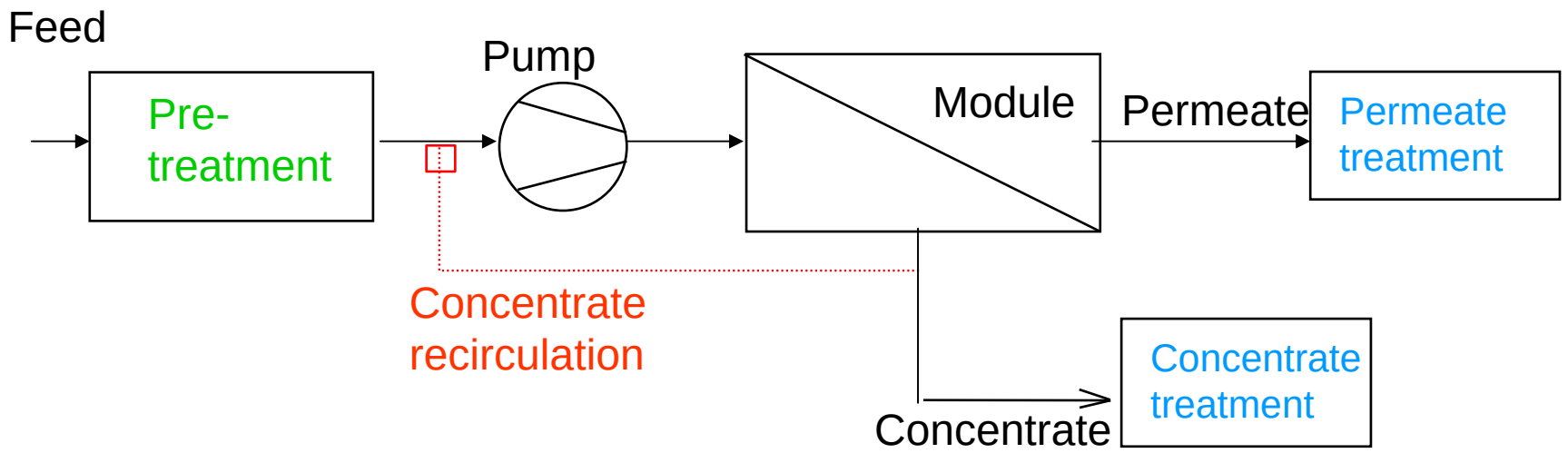
Membrane Separation: Principle



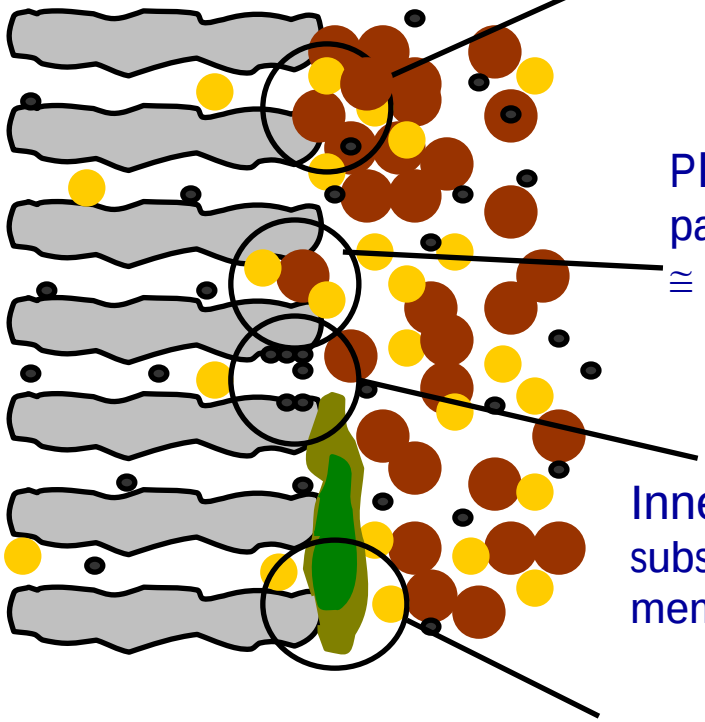
Rejection coefficient $\boldsymbol{R} = (c_0 - c)/c_0$

Separation – Membrane Filtration

Plant scheme



Membrane Filtration – Fouling



Layer formation:
adsorption, compaction,
inclusion, precipitation

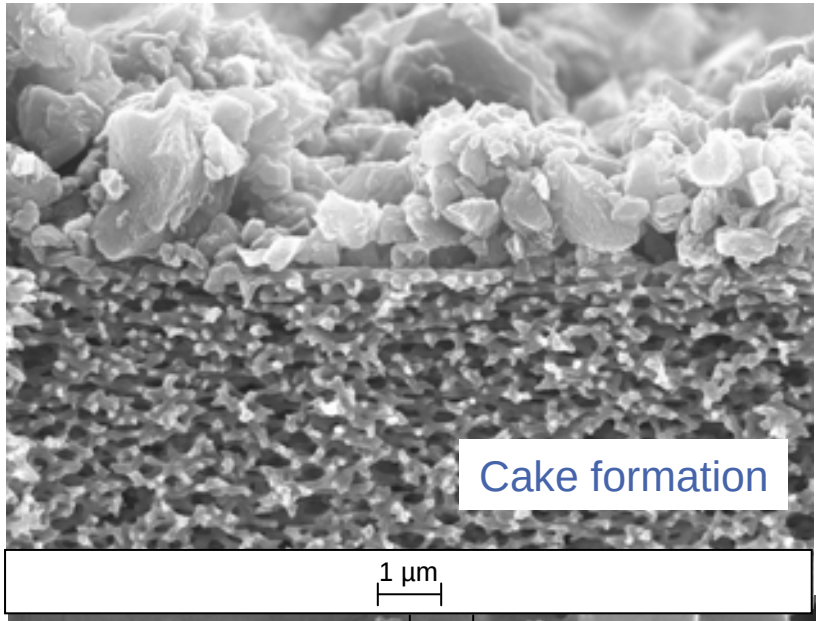
Plugging of pores:
particle diameter
≅ pore diameter

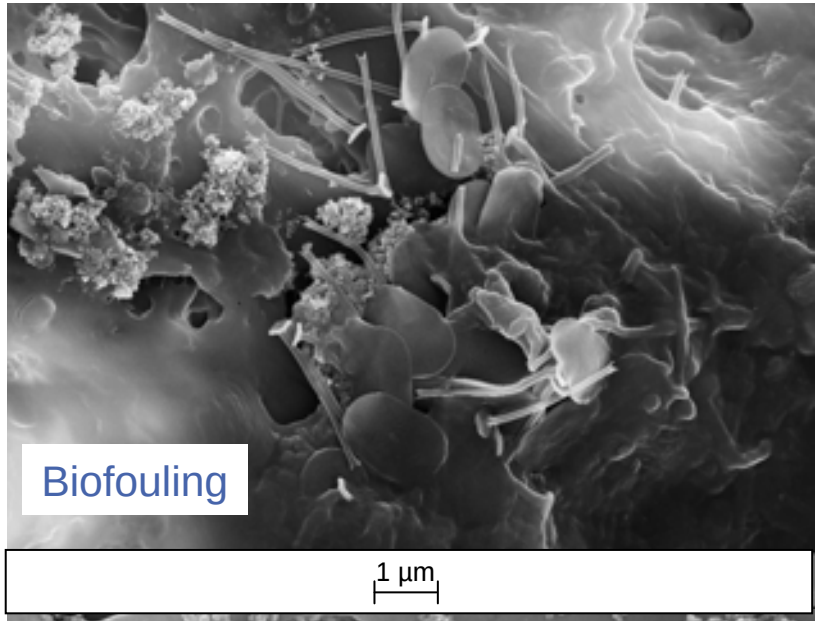
Inner adsorption:
substances with affinity to
membrane material

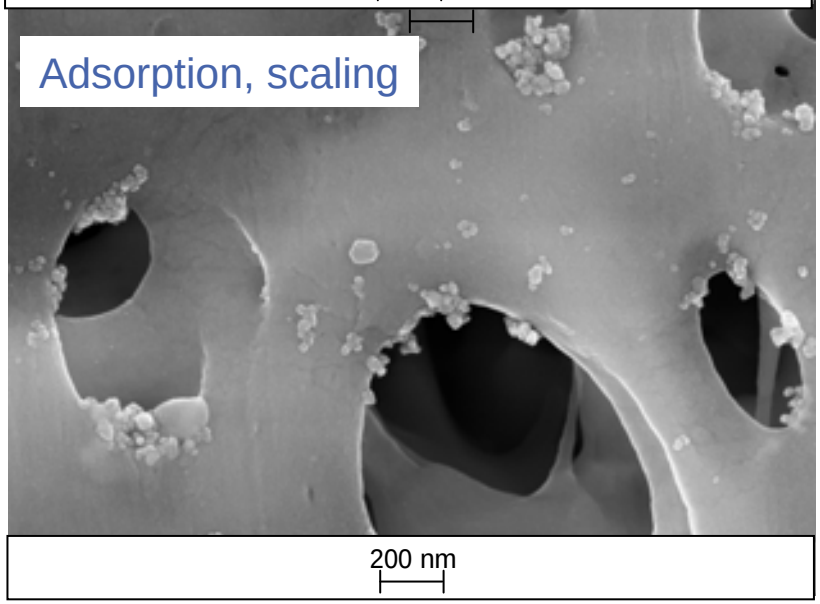
Biofouling:
microorganisms in a film of
extracellular polymeric substances (EPS)

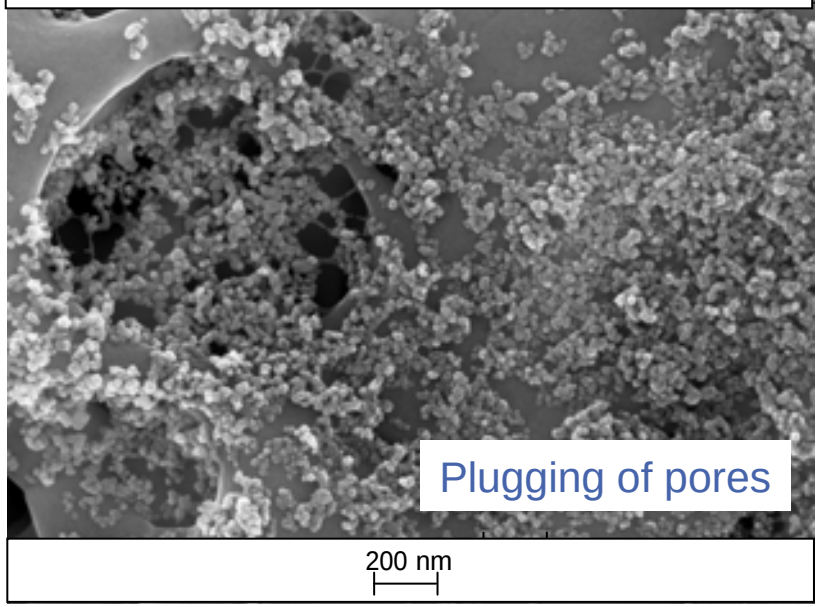
Decrease of performance

Membrane Filtration – Fouling









Saravia, F. et al., 2009

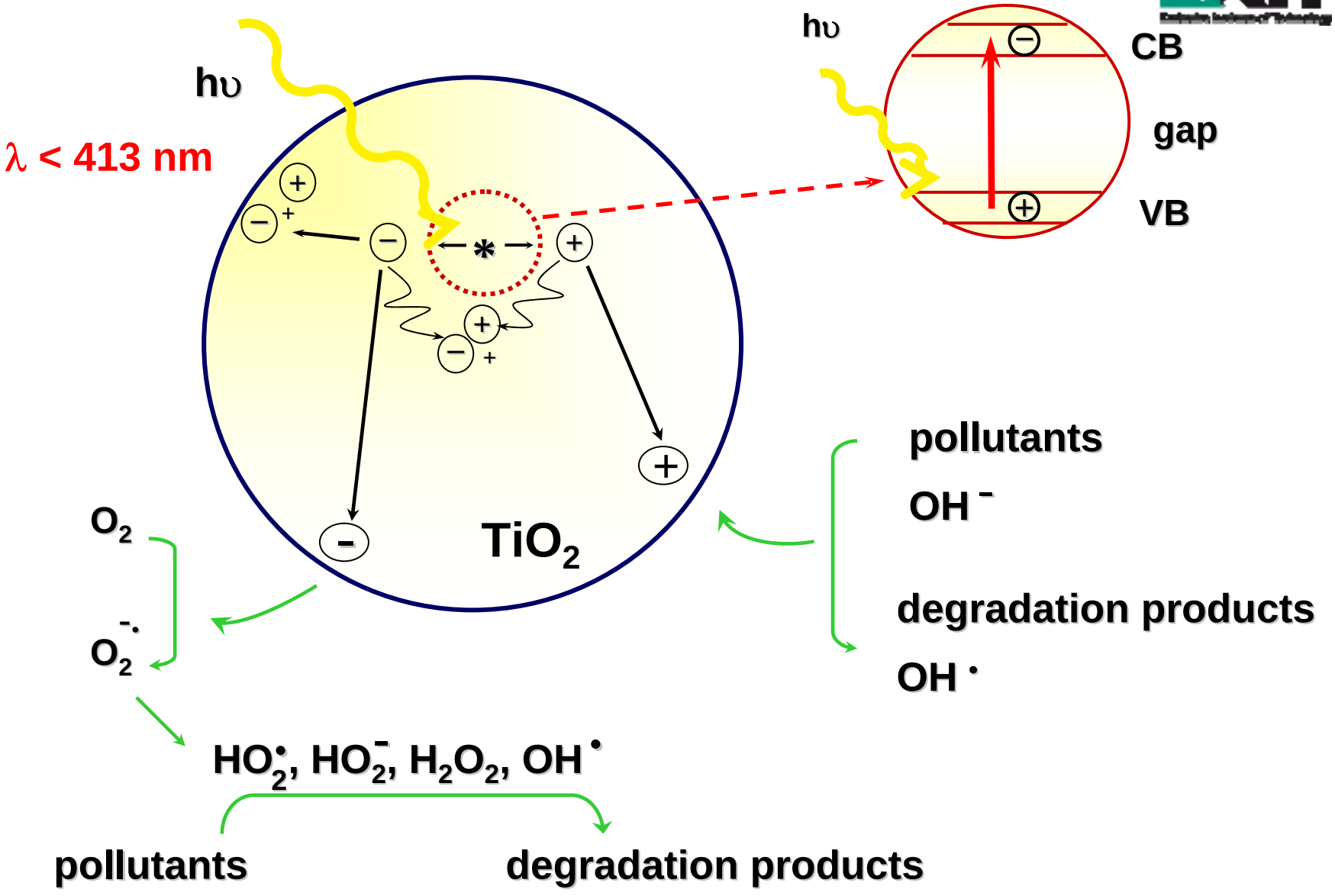
Degradation – Advanced Oxidation Processes (AOP)

Combination processes involving OH• Radicals

- ultraviolet radiation/hydrogen peroxide — UV/H_2O_2
- ultraviolet radiation/ozone — UV/O_3
- ozone/hydrogen peroxide — O_3/H_2O_2
- Fenton reagent — Fe^{2+}/H_2O_2
  photo Fenton reaction — $UV/Fe^{2+}/H_2O_2$
- ultraviolet radiation/titanium dioxide catalyst — UV/TiO_2
- high-energy radiation (vacuum UV, γ-radiation, fast electrons)

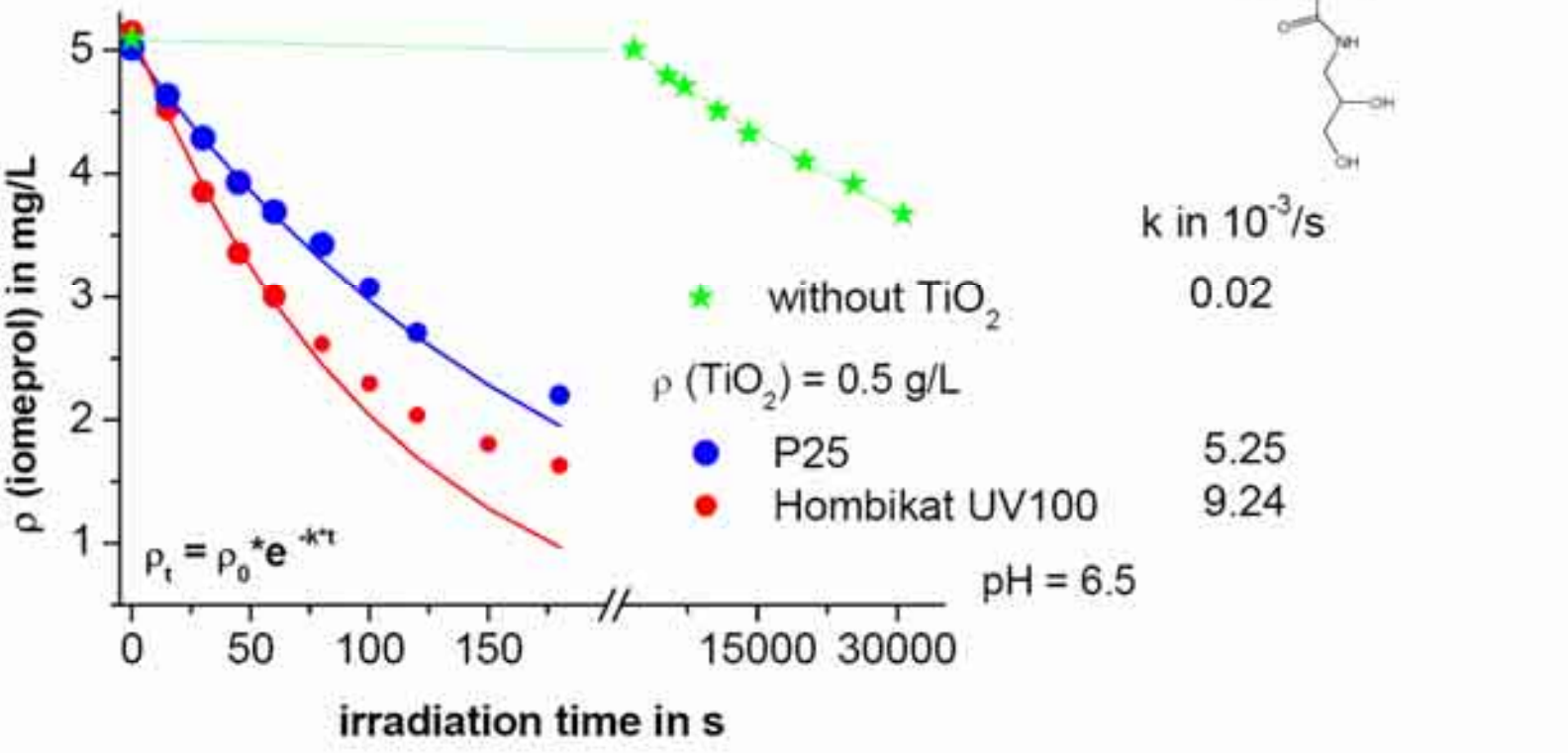
Molec. + OH• → $Molec._{ox}$

AOP – Principle of Photocatalysis



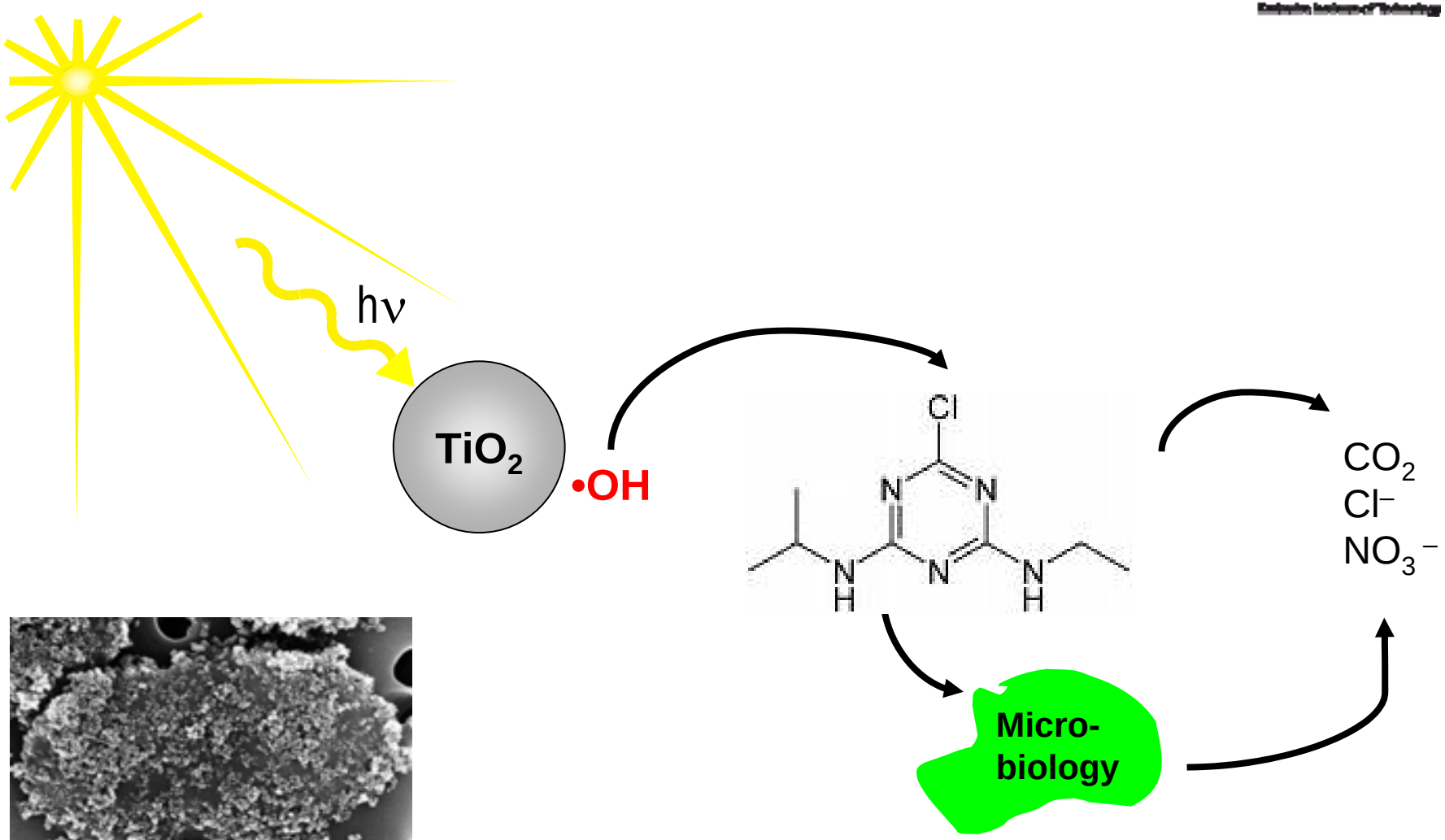
AOP – Photochemical and Photocatalytical Degradation of Iomeprol

Comparison - Hombikat UV100 – P25
Photolysis - Photocatalysis



Doll, T. E., Frimmel, F. H. (2005)

AOP – Degradation and Biotransformation

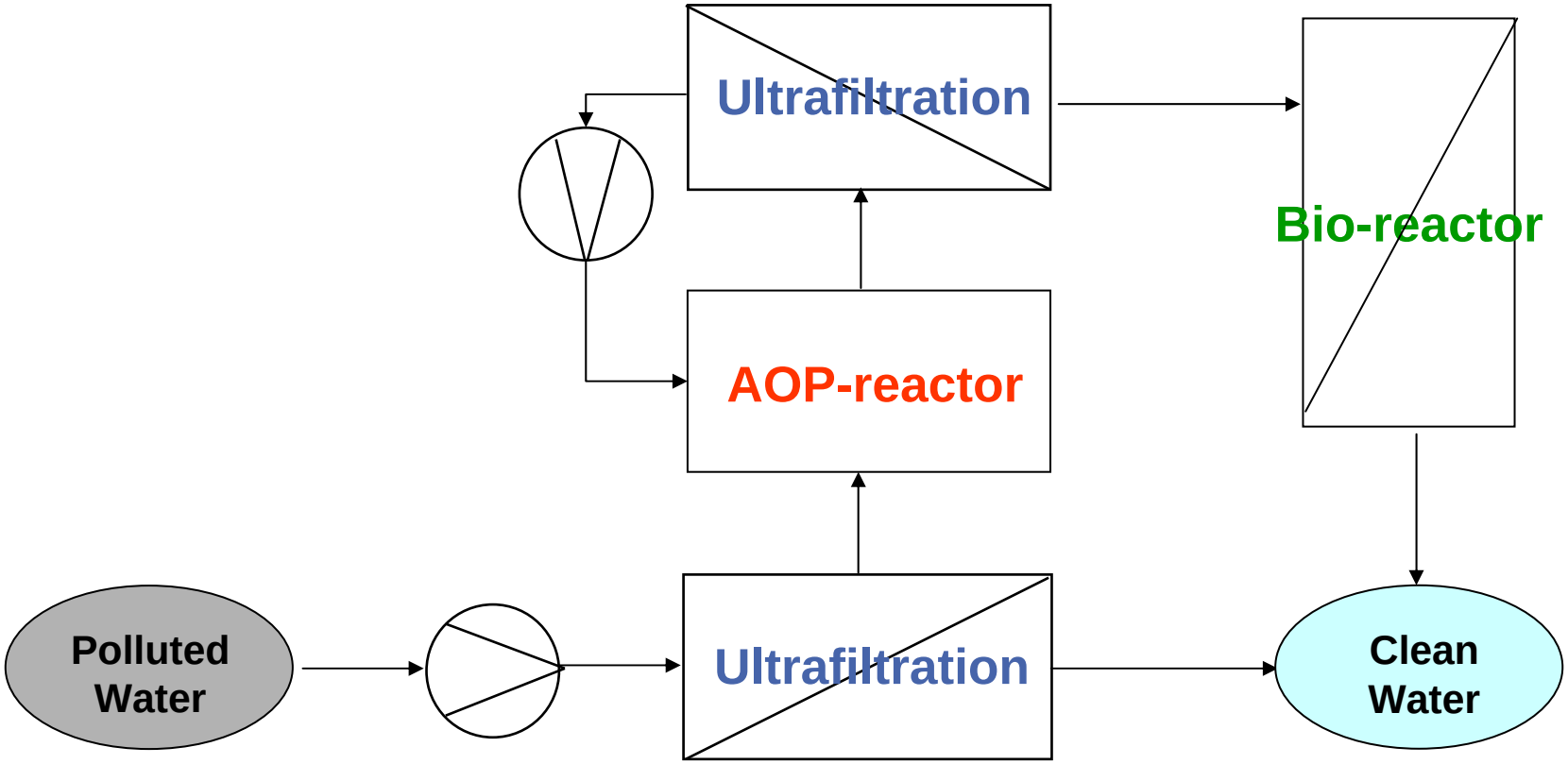


100 nm

Schwegmann, H. et al., 2009

Hybrid Processes

Plant scheme



Biotransformation

Biodegradation: Well-established for reduction of organic load, nitrogen and phosphorus in wastewaters. Typical: high cell densities.

Biodegradation of xenobiotics: Enhancement by **bioaugmentation**

Addition of new genetic capabilities to an existing microbial community

Addition of:
Bacterial strains carrying **chromosomically encoded genes** required for the biodegradative pathway

Problem:
Outcompetition of introduced strains by indigenous micro-organisms

or

Addition of:
Donor organisms carrying **catabolic genes** located on **mobile genetic elements** (plasmids, transposons)

Advantage:
Plasmid exchange between donor organism and indigenous micro-organisms
„horizontal gene transfer“

Example: Plasmid pNB2, encoding genes necessary for 3-dichloroaniline degradation

Bathe, S., Schwarzenbeck, N., Hausner, M., 2005

Conclusions

- Water is irreplaceable for life and culture
- The use of water leads to conflicts
- Science has to define the hot spots for water quality in the water cycle
- Technology has to meet nature to save life on earth in the sense of sustainability

Acknowledgements

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