Technologies for the Removal of Organic Micropollutants in Drinking Water Treatment

Waterworkshop

Chemistry Department of the Faculty of Sciences

University of Novi Sad

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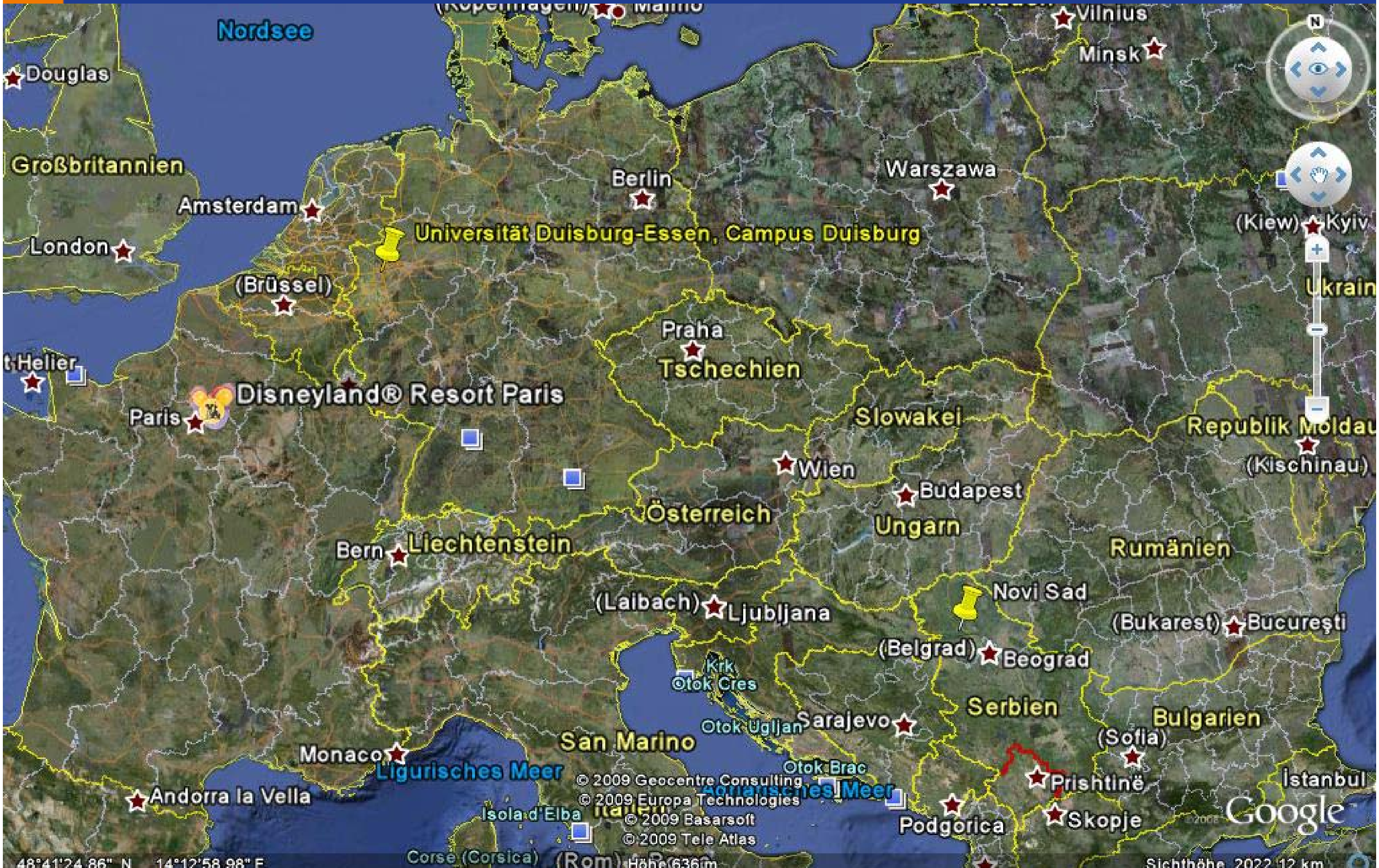
Institute for Energy and Environmental Process Engineering / Water Technology

IWW

IWW Rhenish-Westphalian Institute for Water Research

Where we are?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Google
48°41'24.86" N 14°12'58.98" E
Corse (Corsica)
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Höhe 636 m
Sichthöhe 2022.12 km

Institute for Energy and Environmental Process Engineering Water Technology

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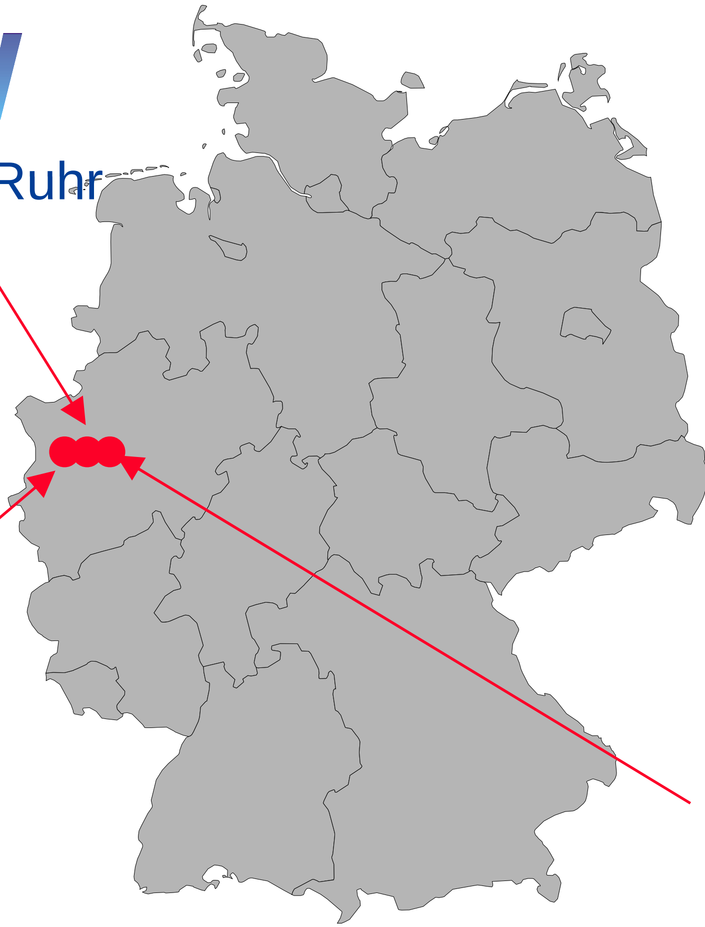
Mülheim an der Ruhr



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Institute for Energy and Environmental Process Engineering
Water Technology

Chair: Professor Dr.-Ing. Rolf Gimbel

- **Research areas**
  - **Membrane Technology**
    - Dr.-Ing. Stefan Panglisch / Dr.-Ing. Ralph Hobby
    - M. Sc. Mathis Keller
    - M. Sc. Grit Hoffmann
    - M. Sc. Anik Deutmarg
  - **Fixed Bed Processes, Sorption Processes**
    - Dr.-Ing. Ralph Hobby
    - Dipl.-Ing. Carsten Bäcker
    - M. Sc. Grit Hoffmann
  - **Artificial Neural Networks (ANN)**
    - Dipl.-Ing. Silke Strugholtz
    - M. Sc. Mathis Keller
  - **Computational Fluid Dynamics (CFD)**
    - M. Sc. Wei Ding
  - **Bioprocess Technology**
    - N. N.
  - **Xenobiotics, Nanoparticles in the Environment**
    - Dr.-Ing. Ralph Hobby
    - Prof. Dr. Ivana Ivancev-Tumbas (Universität Novi Sad)

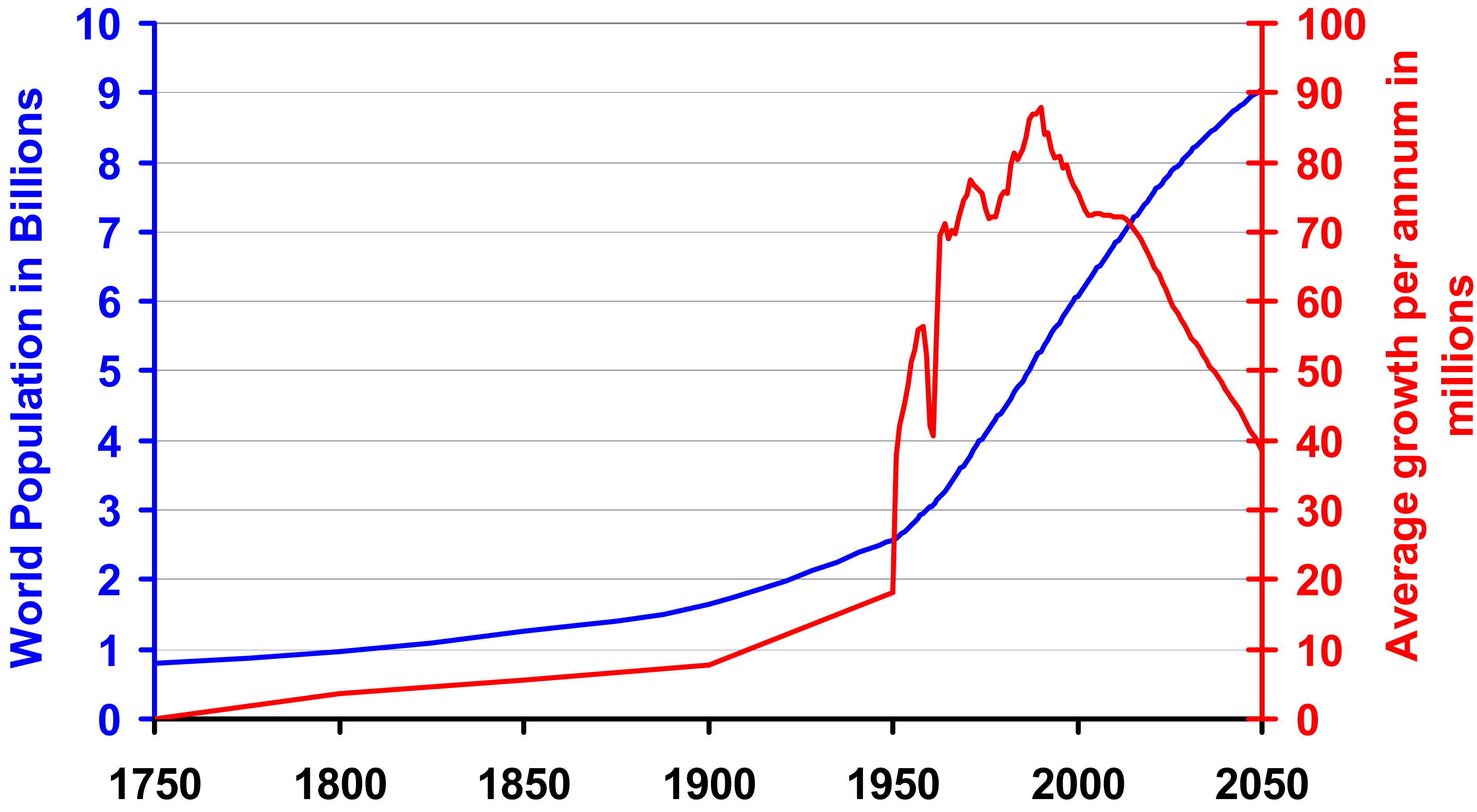
Cooperation with IWW in the Fields of

- **Water Technology (Drinking Water, Industrial Water)**
- **Process Analysis and Analysis of Micropollutants**
- **Applied Microbiology (Hygiene, Biofouling)**

Main Topics

- **Actual problems and challenges of drinking water treatment**
- **Some modern conventional processes**
- **Non-conventional processes**
  - **Oxidation / AOP**
  - **Membrane filtration**
- **Conclusions**

World Population Growth Between 1750 and 2050 (Source Data of the UN 1998)



Trouble Spot of the Global Water Use

- Increasing demand on water with an appropriate quality for irrigation and for supply of industry and communities (drinking water)
- Increasing demand on water supply and waste water discharge in conurbations (megacities, megalopolis)
- Increasing pollution of water resources with anthropogenic compounds
  $\Rightarrow$ xenobiotics, organic micropollutants
- Climatic change
  (especially increasing of extreme dry spells and extreme rain falls)

$\Rightarrow$ The World‘s Water Crisis $\Leftarrow$

Water Technology as Support for the Solution of the World‘s Water Crisis

- Waste water treatment for sustainable water protection
- Waste water treatment for closing water cycles in industry and trade
- Waste water treatment for waste water reuse (e. g. irrigation)
- Treatment of ground water and surface water to produce clean drinking water
- Water treatment for special use (e. g. process water)
- Desalination of brackish water and sea water
- ...

Variety of Substances in Water

Solid Substances

particles, colloids, e. g.

- bacteria
- parasites
- algae
- clay particles
- ...
- viruses

Dissolved Substances

organic subst., high-molecular

organic subst., middle-sized

organic subst., low-molecular

inorganic substances:

ions, polyvalent

ions, monovalent

gases

- Some actual „groups of interfering substances“:
  - too high salt concentration...~ kg / m^3
  - nutrients...~ g / m^3
  - micropollutants
    (e. g. EDCs, PPCPs, Pesticides, several metabilotes,
    industrial chemical products like MTBE, PFT, EDTA)........... ~ µg till mg / m^3
  - persistent pathogens..................................... ~ 1 Particle / m^3 or 10^{-3} ng / m^3
  - in the future nanoparticles?

Some Organic Micropollutants...

Groups of Substances	*Examples*
Hormones , EDCs	**17α-ethinylestradiol, 17β-estradiol, estrone**
Pharmaceuticals (contrast agents)	**Diclofenac, Ibuprofen (both antiphlogistics), Bezafibrate (lipid regulator), Diazepam (tranquilizer), Carbamazepine (anti-epileptic), Iopromide, Iopamidol, Diatrizoic acid**
Personal care products	**Tonalide (AHTN), Galaxolide (HHCB) (musk fragrances)**
Disinfectants	**Triclosan**
Surfactants	**Fluorosurfactants, (Perfluorooctanesulfonic acid (PFOS), Perfluorooctanoic acid (PFOA))**
Flame retardants	**Organophosphates**
Gasoline additives	**Methyl tertiary butyl ether (MTBE),**

Characteristics of “waterworks relevant” and “drinking water relevant” Micropollutants

e. g. some EDCs, PPCPs, Pesticides, several metabilotes, industrial chemical products like MTBE, PFT, EDTA

- Low or none biodegradability
- Chemical stability
- High polarity respectively high water solubility
- Low tendency to adsorb

→ Low or no removal efficiency in soil passage

→ Characteristics of micropollutants are very important for the efficiency of treatment steps

- e. g.
  - water solubility
  - octanol-water partition coefficient (log K_{OW})

Main Topics

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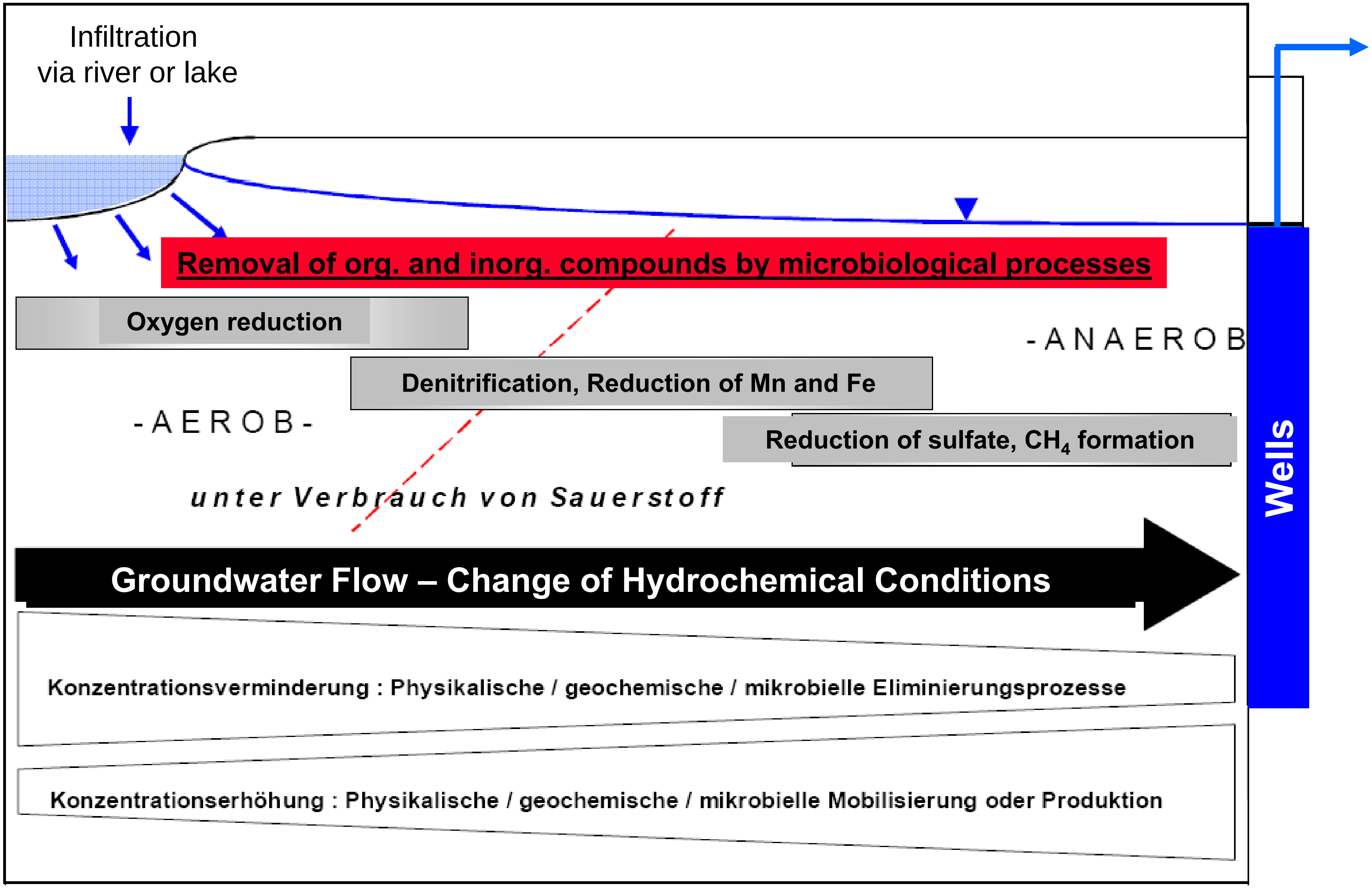
- Conclusions

Processes for Drinking Water Treatment

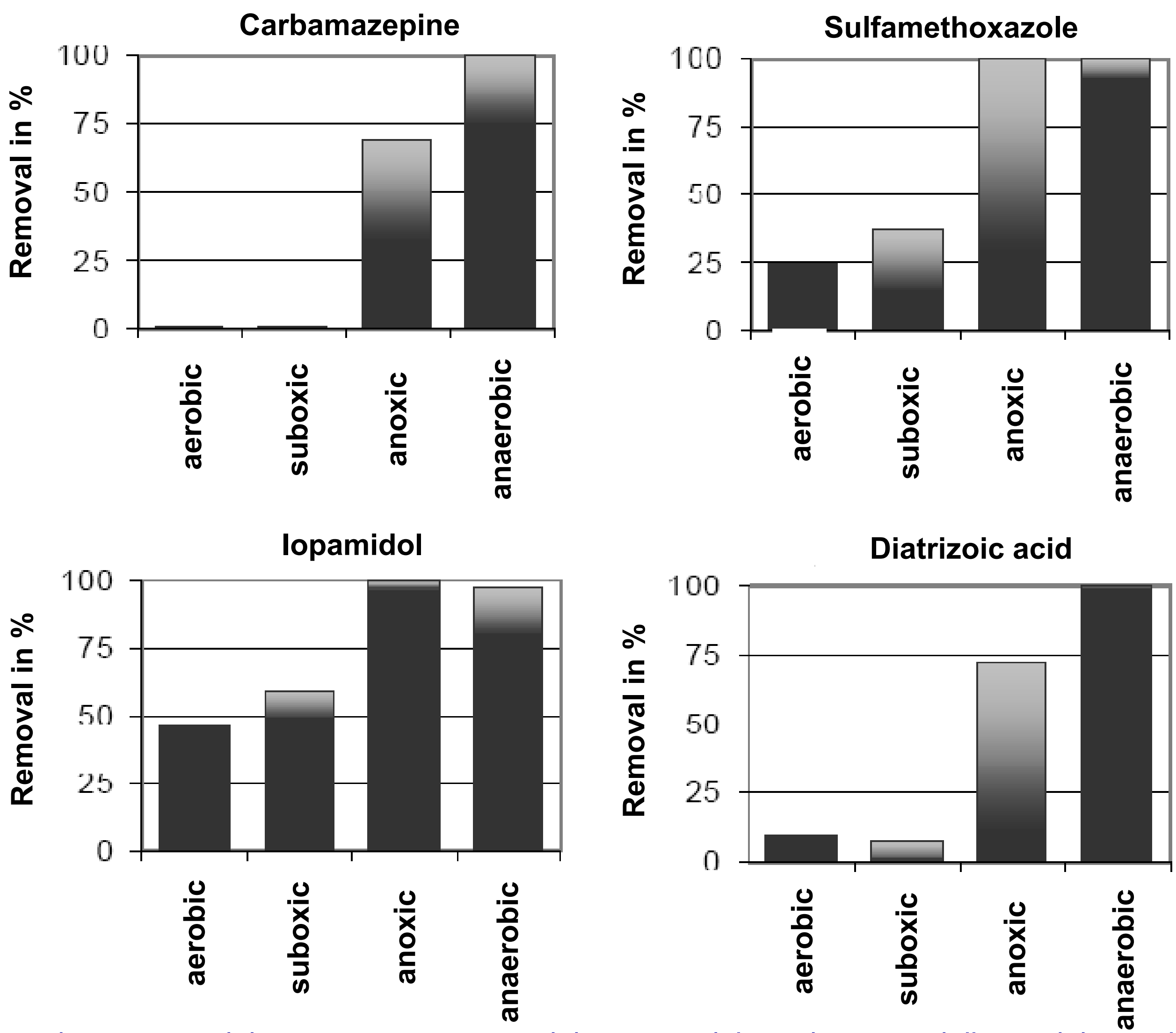
- Bank Filtration
- Aeration
- Flocculation
- Sedimentation
- Rapid Filtration
- Adsorption (GAC)
- Oxidation (Ozonation)
- Advanced Oxidation Processes (AOP)
- Nanofiltration, Low Pressure RO
- Adsorption onto PAC / Micro- , Ultrafiltration

Bank Filtration



Schulte-Ebbert, 2004, modificated

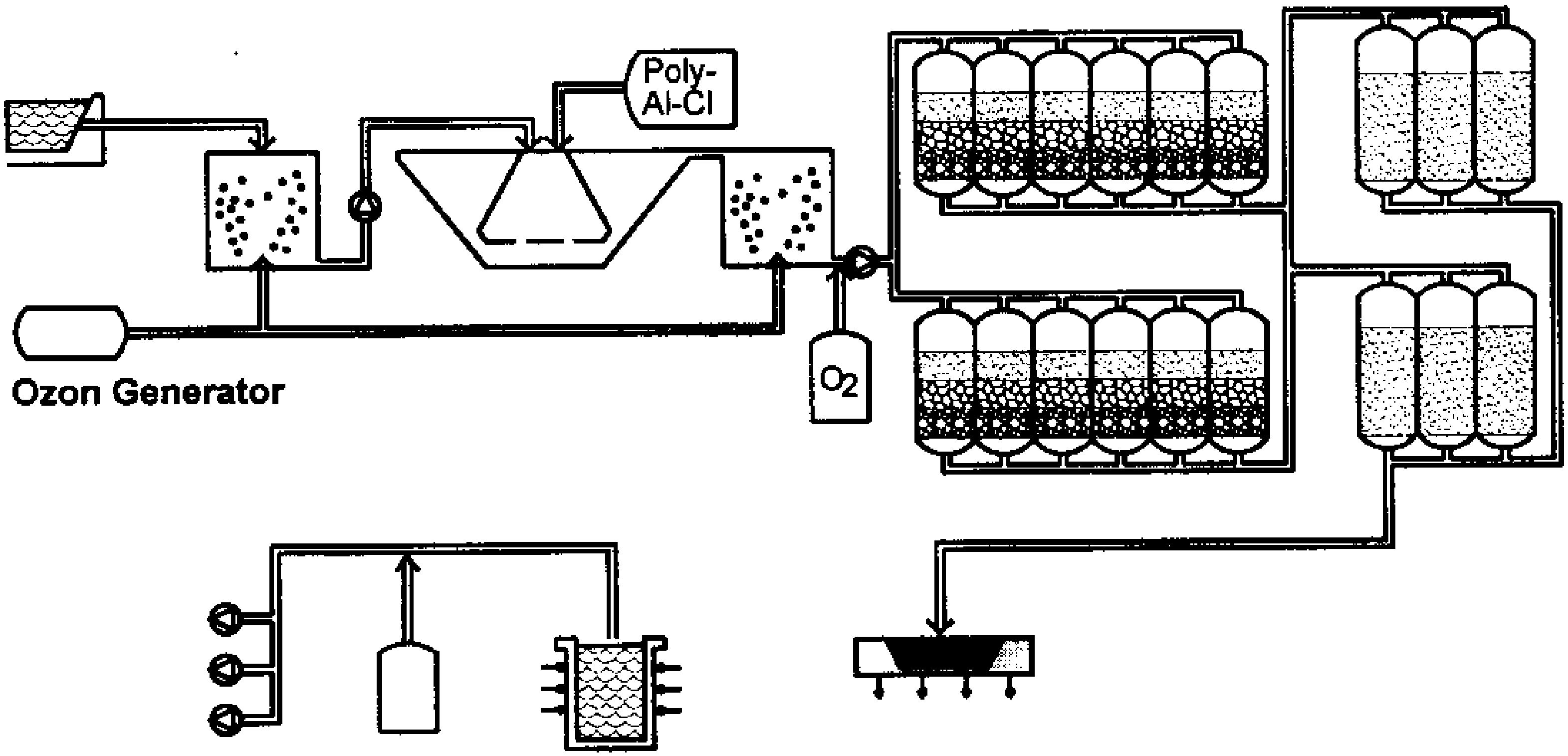
Bank Filtration



Schmidt, Lange (2006): BMBF-Projekt 02WT0280, Kernprojekt B6: Ermittlung der potenziellen Reinigungsleistung der Uferfiltration/ Untergrundpassage hinsichtlich der Eliminierung organischer Schadstoffe unter standortspezifischen Randbedingungen

Modern Treatment of River Water with Conventional Technologies (Example)

River Ruhr | Pre-ozonation | Flocculation | Main-ozonation | DM-Filtration | GAC-Filtration



Disinfection | Well | Infiltration

The „Mülheim Process“

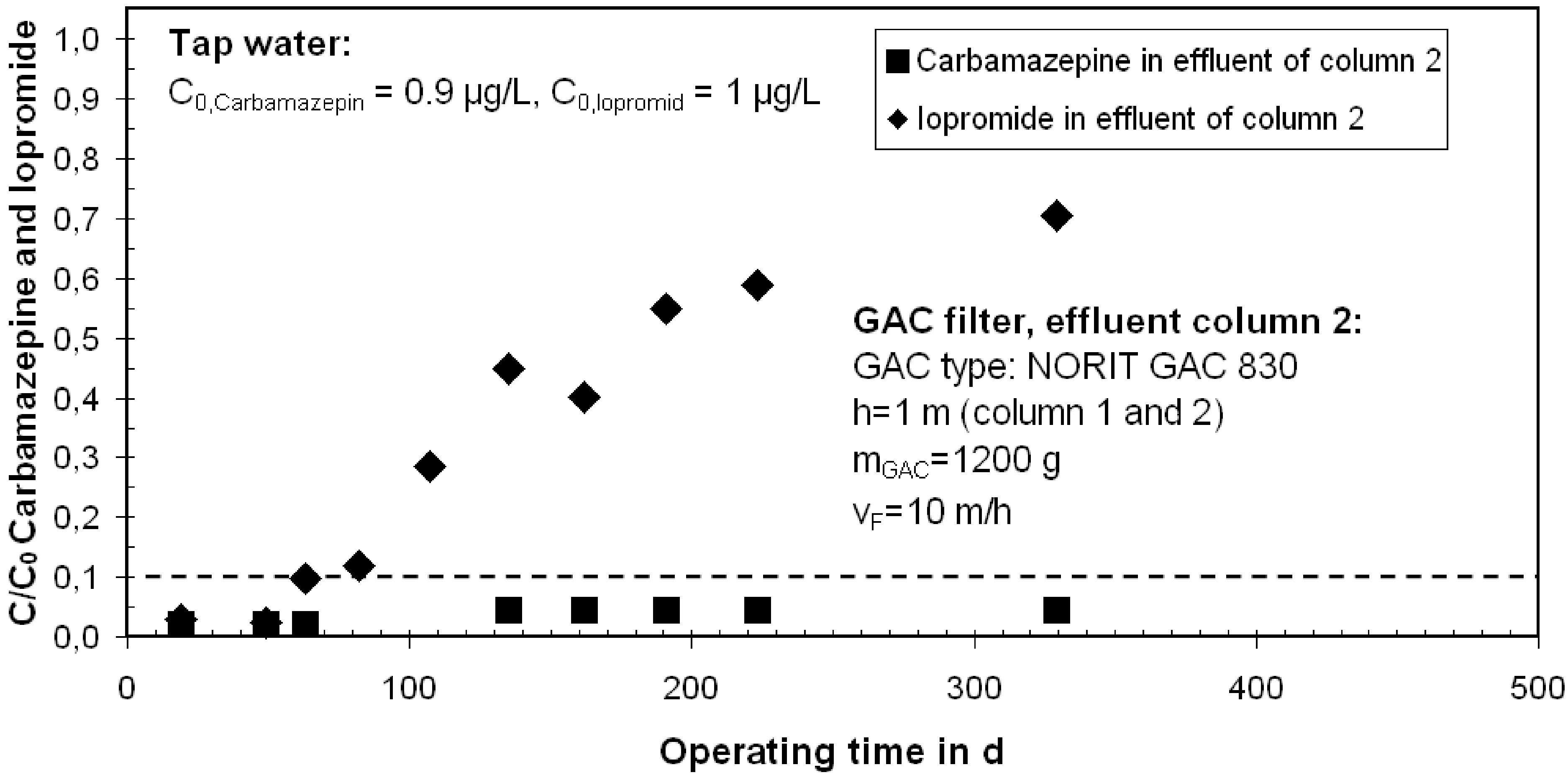
⇒ Multibarrier System ⇐

Removal of Micropollutants by Conventional Processes I

Adsorption on Activated Carbon

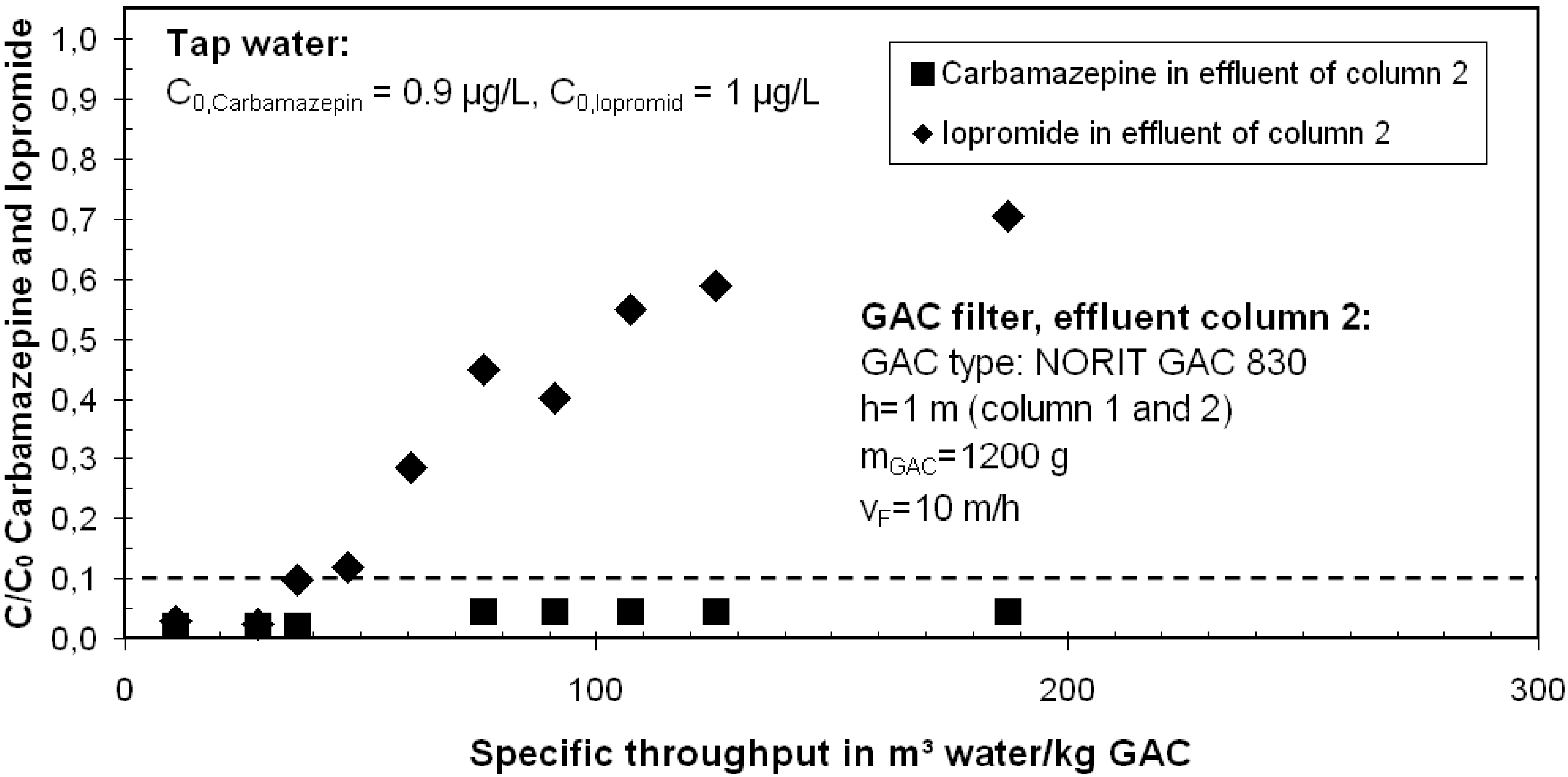
- usual for the removal of organic micropollutants
- high removal efficiency for non-polar substances
- log K_{OW} suitable indicator for
  - non-polar substances
  - substances without heterocyclic or aromatic bound nitrogen
  - log $K_{OW} > 3$ (→ removal efficiency 75 – 100 %)
- operation time of GAC filters dependent on sorption behaviour of micropollutants!

GAC Process



Tap water:
C0,Carbamazepin = 0.9 µg/L, C0,Iopromid = 1 µg/L
Carbamazepine in effluent of column 2
Iopromide in effluent of column 2
GAC filter, effluent column 2:
GAC type: NORIT GAC 830
h=1 m (column 1 and 2)
mGAC=1200 g
vF=10 m/h
C/C0 Carbamazepine and Iopromide
1,0
0,9
0,8
0,7
0,6
0,5
0,4
0,3
0,2
0,1
0,0
0
100
200
300
400
500
Operating time in d

GAC Process



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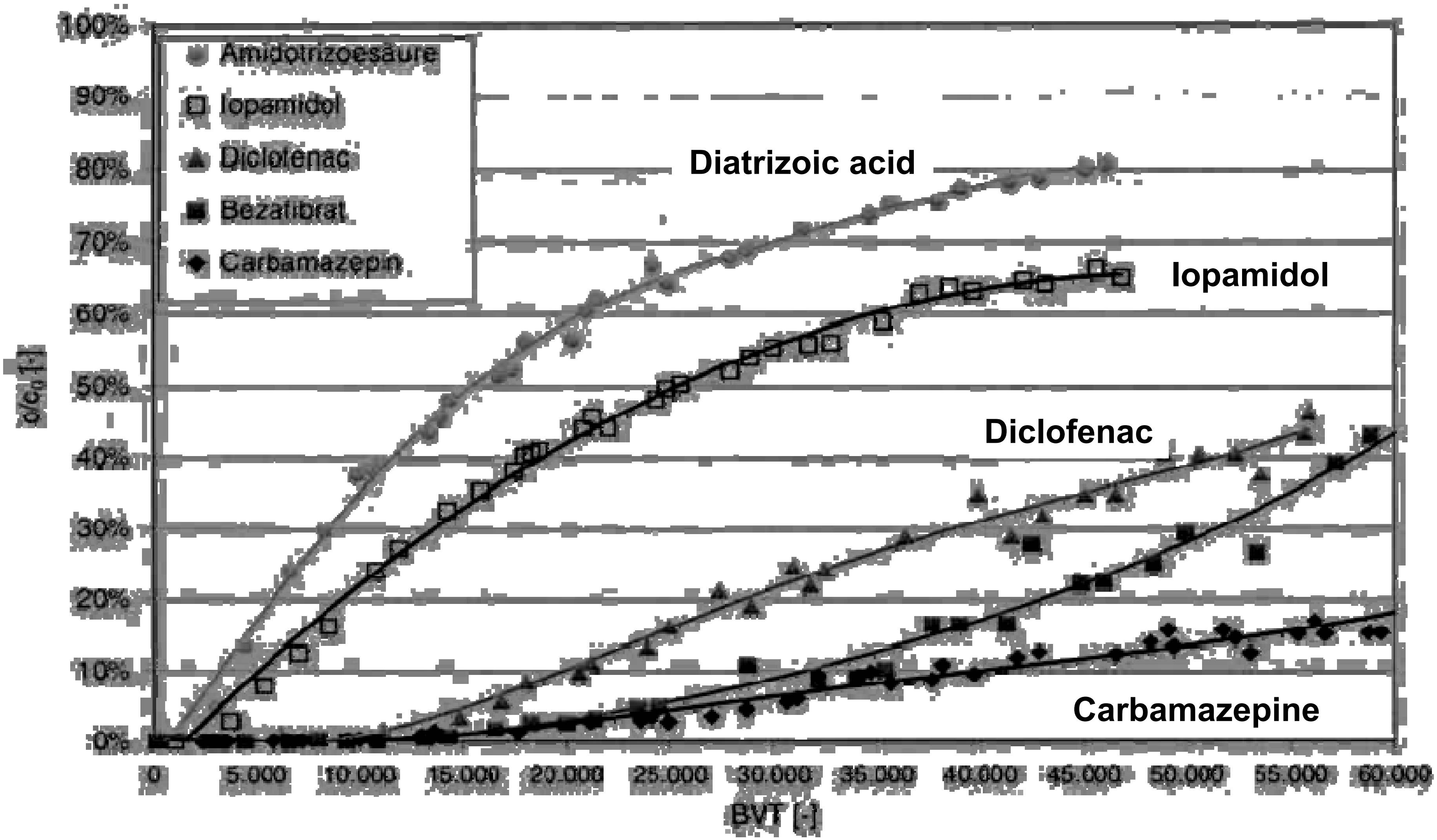
GAC type: NORIT GAC 830
h=1 m (column 1 and 2)
mGAC=1200 g
vF=10 m/h
C/C0 Carbamazepine and Iopromide
1,0
0,9
0,8
0,7
0,6
0,5
0,4
0,3
0,2
0,1
0,0
0
100
200
300
Specific throughput in m³ water/kg GAC

Breakthrough curves of different pharmaceuticals (incl. contrast agents) in GAC-Filter test



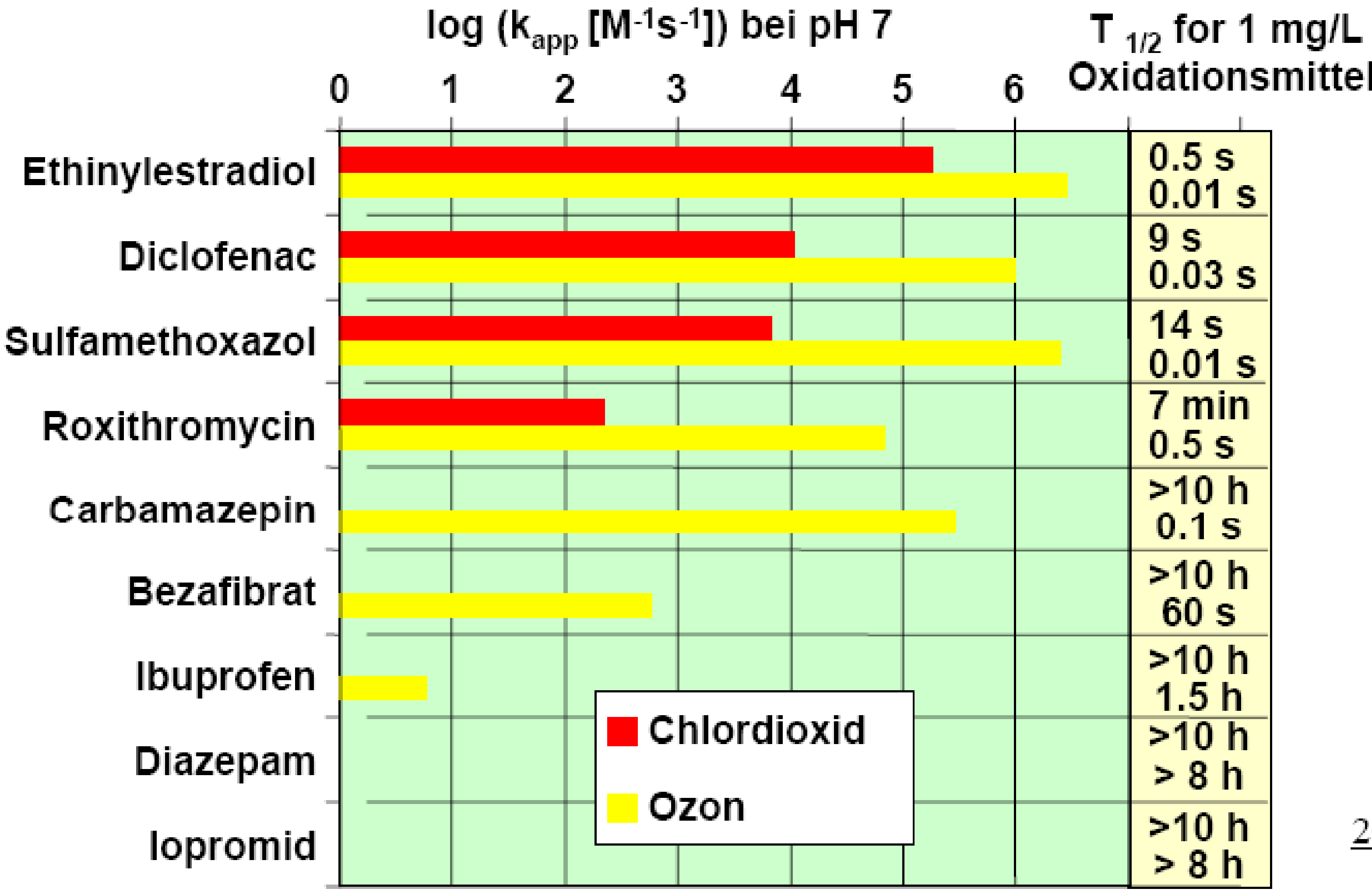
Quelle: Marcus, 2005

Removal of Micropollutants by Conventional Processes II

Oxidation with Ozone (as O_3)

- usually addition of approx. 1-2 mg O_3 per mg DOC
- ozone (as O_3) reacts selectively with substances which can be easily oxidised.
- the degradation rate for micropollutants depends strongly on the type of substance and ambient conditions (e. g. pH).

Rate Constant and Half Life Period (for 1 mg/L Ozone) for Some Pharmaceuticals Reacting with O_3 und ClO_2 (pH = 7)



Huber et al., 2005, Water Res.

Source: Ternes, 2006

Removal of Micropollutants by Conventional Processes III

Oxidation with Ozon (radical formation)

- during ozonation formation of highly reactive OH-radicals, which react non-selectively and their rate constants are between 10^7 and 10^9 L/(mol s)
- concentration ratio of OH-radicals and ozone (usually ~ 10^{-9}) is too low
- concentration ratio can be increased by Advanced Oxidation Processes (AOP) up to ~ 10^{-6}

Main Topics

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Removal of Micropollutants by AOP

- Rate constants for the reaction of ozone respectively OH-radicals with pharmaceuticals (Huber et al. 2003, Baus et al. 2007)

Wirkstoff	k_{O3} in L/(mol s)	k_{OH} in L/(mol s)
Diclofenac	$1{,}0 \times 10^6$	$7{,}5 \times 10^9$
Sulfamethoxazol	$2{,}5 \times 10^6$	$5{,}5 \times 10^9$
Ibuprofen	9,6	$7{,}4 \times 10^9$
Iopromid	< 0,8	$3{,}3 \times 10^9$
MTBE	0,14	$1{,}9 \times 10^9$
ETBE	1,98	$(2{,}80 +/- 0{,}38) \times 10^9$

  - AOP
    - O_3/H_2O_2 (Peroxon-Process)
    - UV/O_3
    - UV/H_2O_2
    - $Fe(II)/H_2O_2$ (Fenton-Process)
  - Radicals react non-selectively. But especially hydrogen carbonate ions and the natural organic matter act as scavengers

- Removal in % of pharmaceuticals in Lab experiments using ozone and hydrogen peroxide(data from Zwiener und Frimmel, 2000)

	in destilliertem Wasser	in Oberflächenwasser		
	O_3	O_3/H_2O_2		
Wirkstoff	1mg/l	1/0,4 mg/l	3,7/1,4 mg/l	5/1,8 mg/l
Clofibrinsäure	8	21,8	92,1	97,7
Ibuprofen	12	29,2	94	99,4
Diclofenac	96,8	99,4	99,5	99,9

Some Critical Aspects Concerning O_3-Oxidation or Photolysis

- **Using ozone**
  - possible formation of substances, which may cause more problems due to their toxicity and removal efficiency than the substances in the raw water before the oxidation step (e. g. NDMA)
  - by-product formation (e. g. bromate, less with the Peroxon-Process)
- **Using UV**
  - high energy consumption (more than by the use of NF and RO for TDS < 5,000 mg/L)

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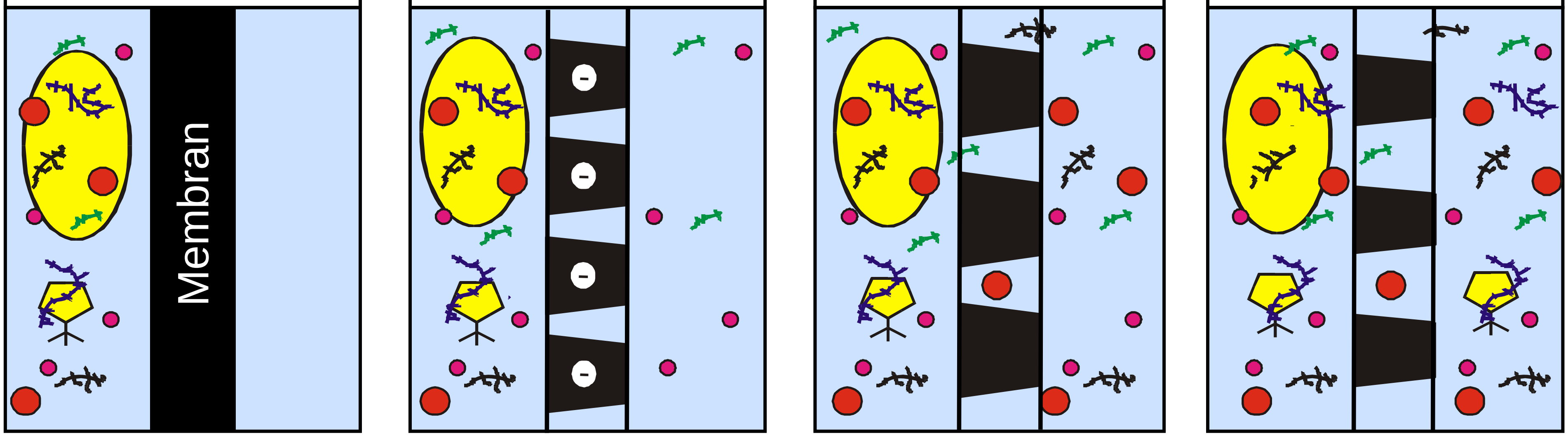
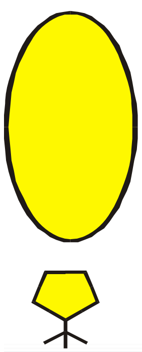
Principle of Membrane Filtration Processes

Flow Direction

Reverse Osmosis (RO)	Nanofiltration (NF)	Ultrafiltration (UF)	Microfiltration (MF)
no pores	$d_{pore} \approx 1$ nm	$d_{pore} \approx 10\text{-}50$ nm	$d_{pore} \geq 50$ nm
$\Delta p = 5 - 100$ bar	$\Delta p = 3 - 10$ bar	$\Delta p = 0.1 - 5$ bar	$\Delta p = 0.1 - 2$ bar

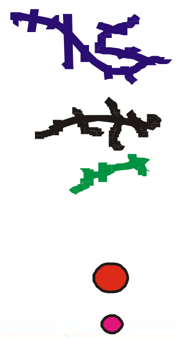




Solid Substances

particles, colloids, e. g.

- bacteria
- parasites
- algae
- clay particles
- viruses

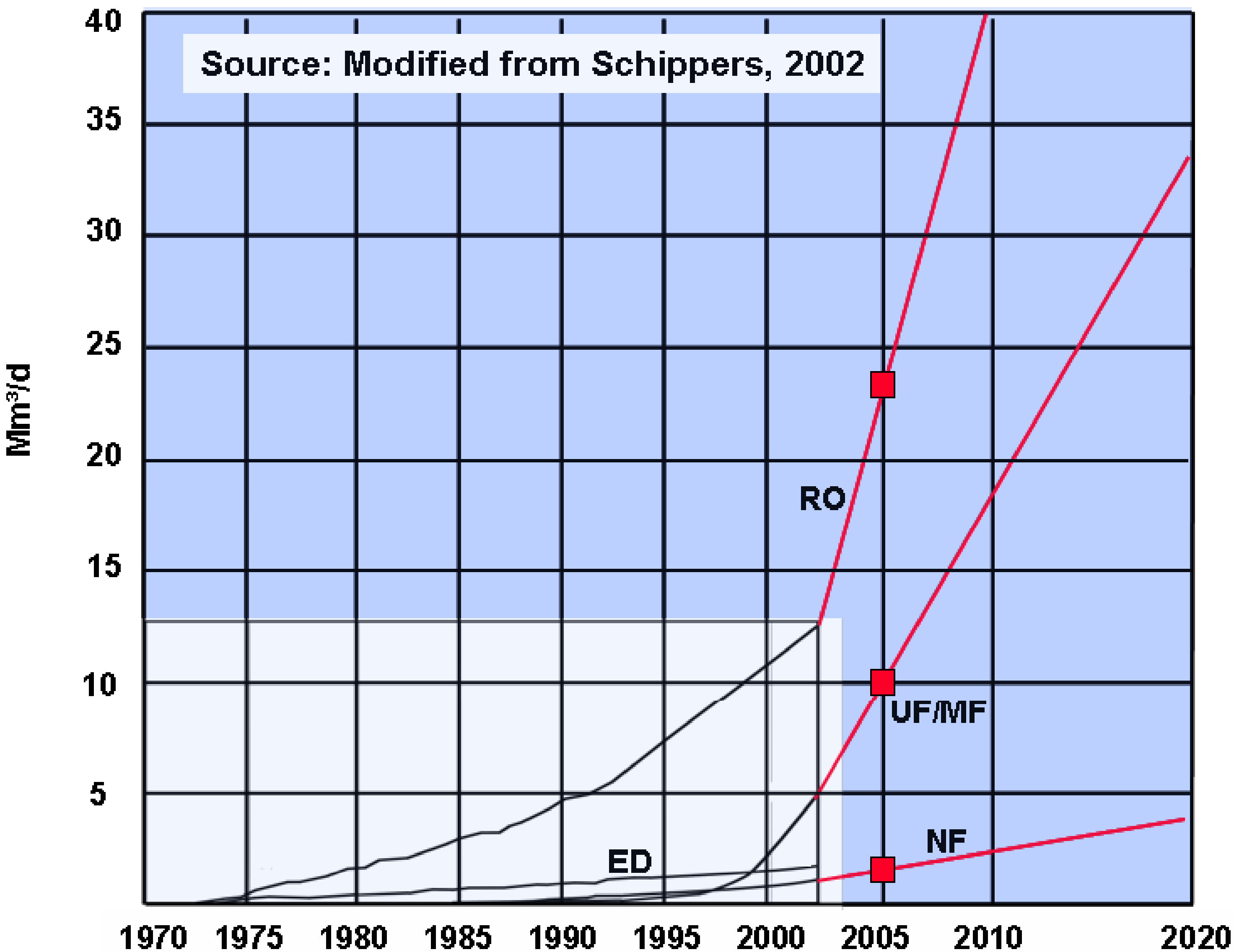


Dissolved Substances

organic subst., high-molecular
organc subst., middle-sized
organic subst. low-molecular

inorganic substances:
ions, polyvalent
ions, monovalent

Development of DW Membrane Filtration Plants Worldwide

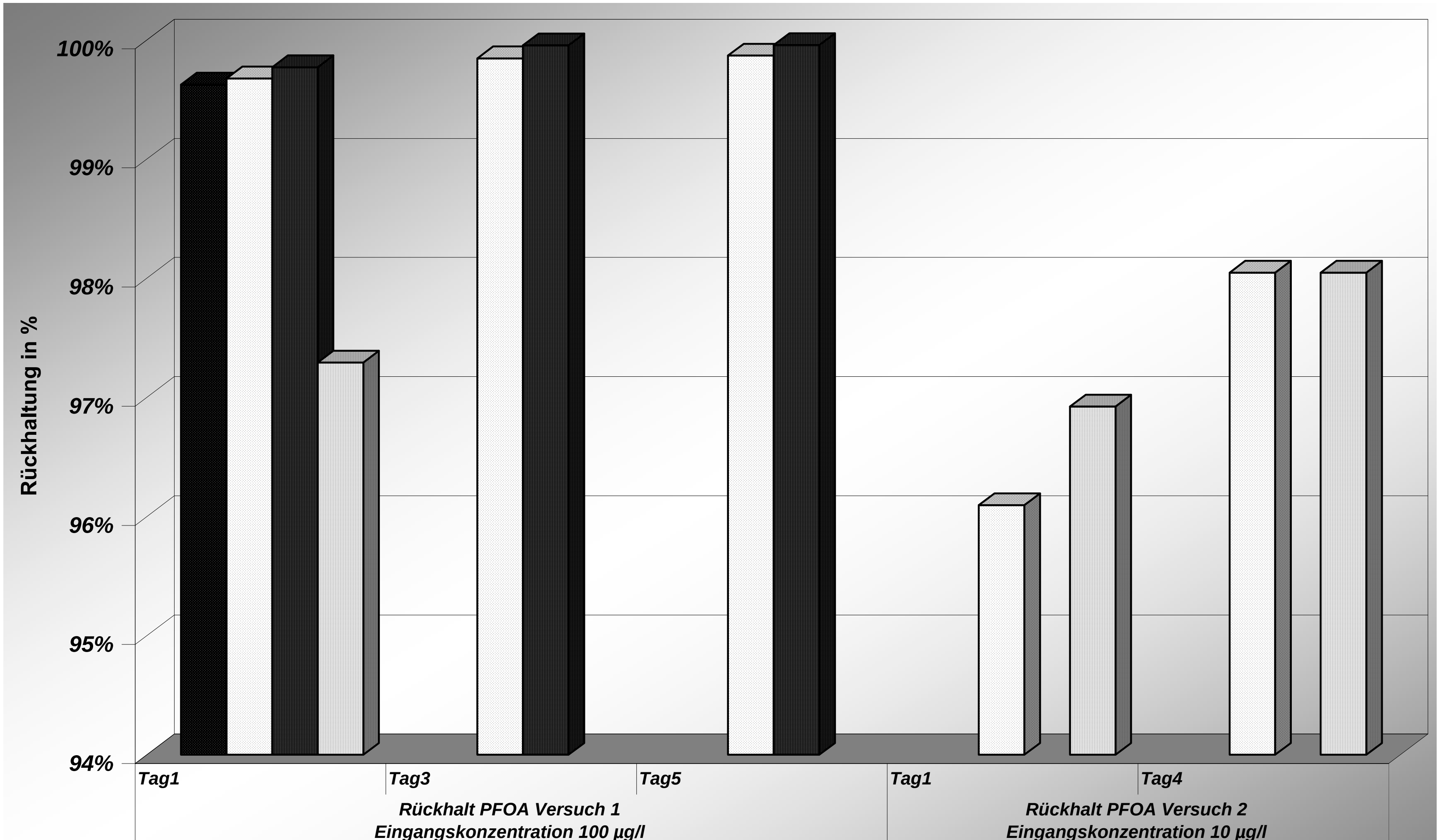


Applications of the Membrane Processes

Main Applications

- RO: Desalination of seawater and brackish water
- NF/LPRO: Removal of hardness, sulfate, colour, NOM (Natural Organic Matter), increasingly org. micropollutants (LPRO=Low Pressure Reverse Osmosis)
- UF/MF: Removal of suspended and colloidal substances, esp. microorganisms, in future possibly desinfection
- (UF/MF in combination with PAC $\Rightarrow$ Removal of organic micropollutants)

LPRO/NF-Results with Polyfluorinated Tensides (PFOA)



	Tag1	Tag3	Tag5	Tag1	Tag4
BW30	99,6				
XLE	99,7	99,8	99,9	96,1	98,0
NF 90	99,8	99,95	99,96		
NF 270	97,3			96,9	98,05

Possibilities and Limits of LPRO / NF...

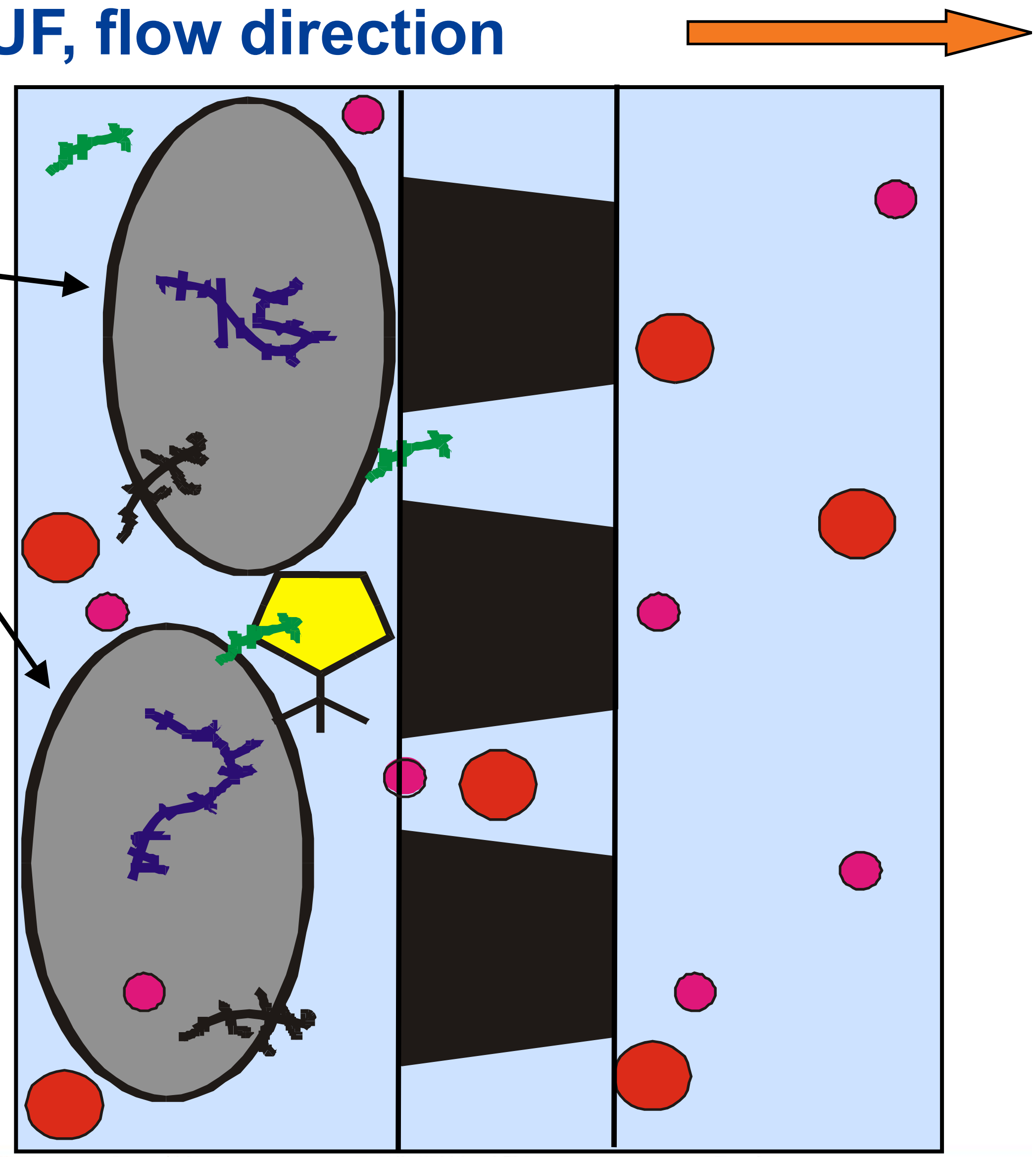
- **Xenobiotics – also polar, persistent ones – are usually very good removable (e. g. Pesticides, PPCPs, PFT, MTBE, EDTA, different metabolites…)**
- **But: low retention of very small and uncharged molecules like Trichloroethene, Chloroform, NDMA (also using LPRO)**
- **Using „real“ NF the retention of substances with molecular weights between approx. 200 und 400 g/mole is strongly dependent on:**
  - **membrane material and membrane structure**
  - **substance!!!**
  - **water matrix**
- **Permeate is not comparable to the raw water with regard to the chemical composition**
- **Characteristics with regard to corrosion behaviour of the permeate are usually influenced negatively $\Rightarrow$ Post Treatment!**

... Possibilities and Limits of LPRO / NF

- Effective pretreatment step for particle removal necessary (no backwashing of spiral wounded modules)
- Recovery only approx. 80 % (maximum 90 %) due to avoiding of scaling (clogging of the membrane)
- In the concentrate are high concentrations of the retained pollutants (factor 5 – 10) and normally anti-scalants (10 – 50 mg/L)
- Total costs (without pre- and post-treatment) are approx. 30-50 Cent/m³
- Application may be more economical, if several conventional treatment steps can be replaced

Principle of the PAC / UF combination

UF, flow direction



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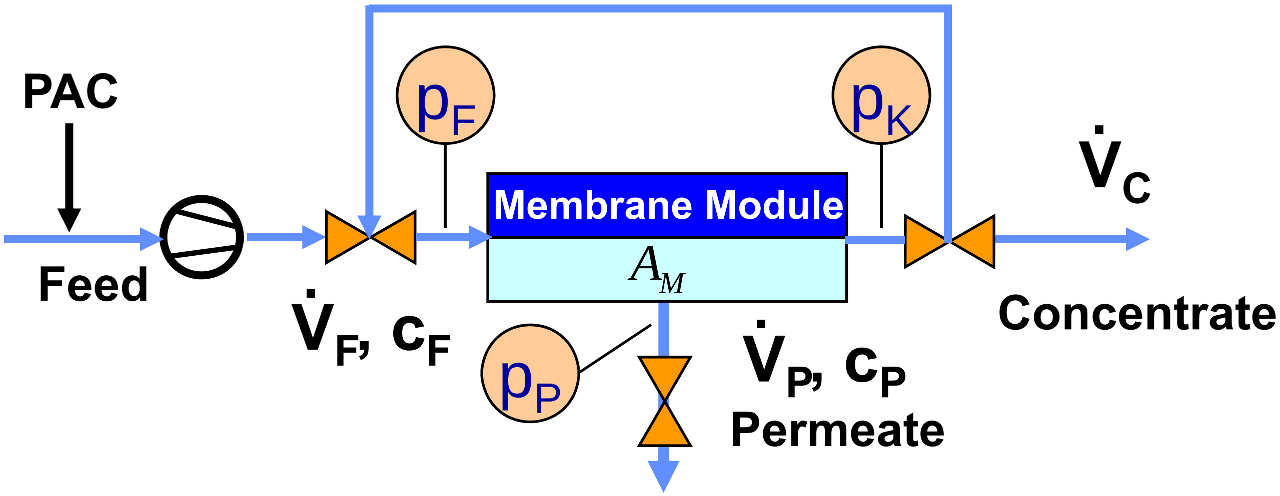
organic subst., high-molecular
organic subst., middle- sized
organic subst., low-molecular

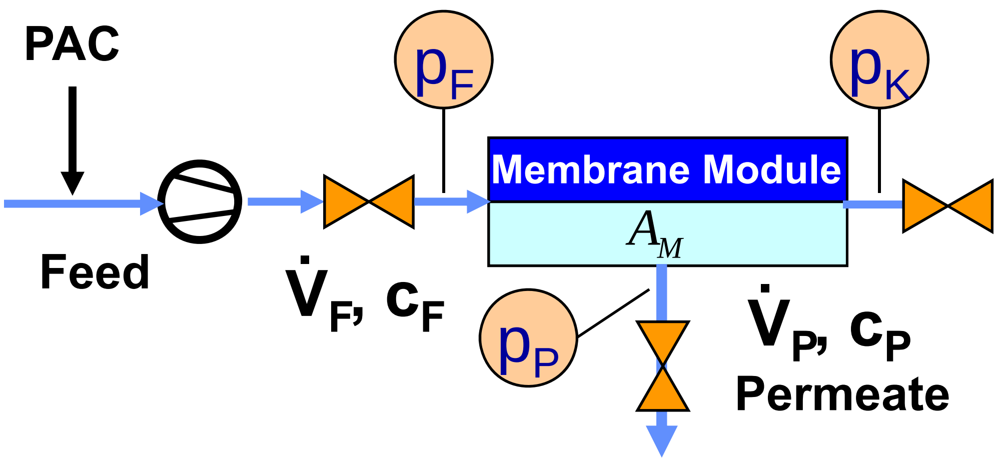
Inorganic subst.:

ions, polyvalent
Ions, monovalent

Use of PAC with Pressure Driven Membrane Filtration



<u>Cross-Flow-Mode</u>
(e. g. Cristal® process)
high energy consumption

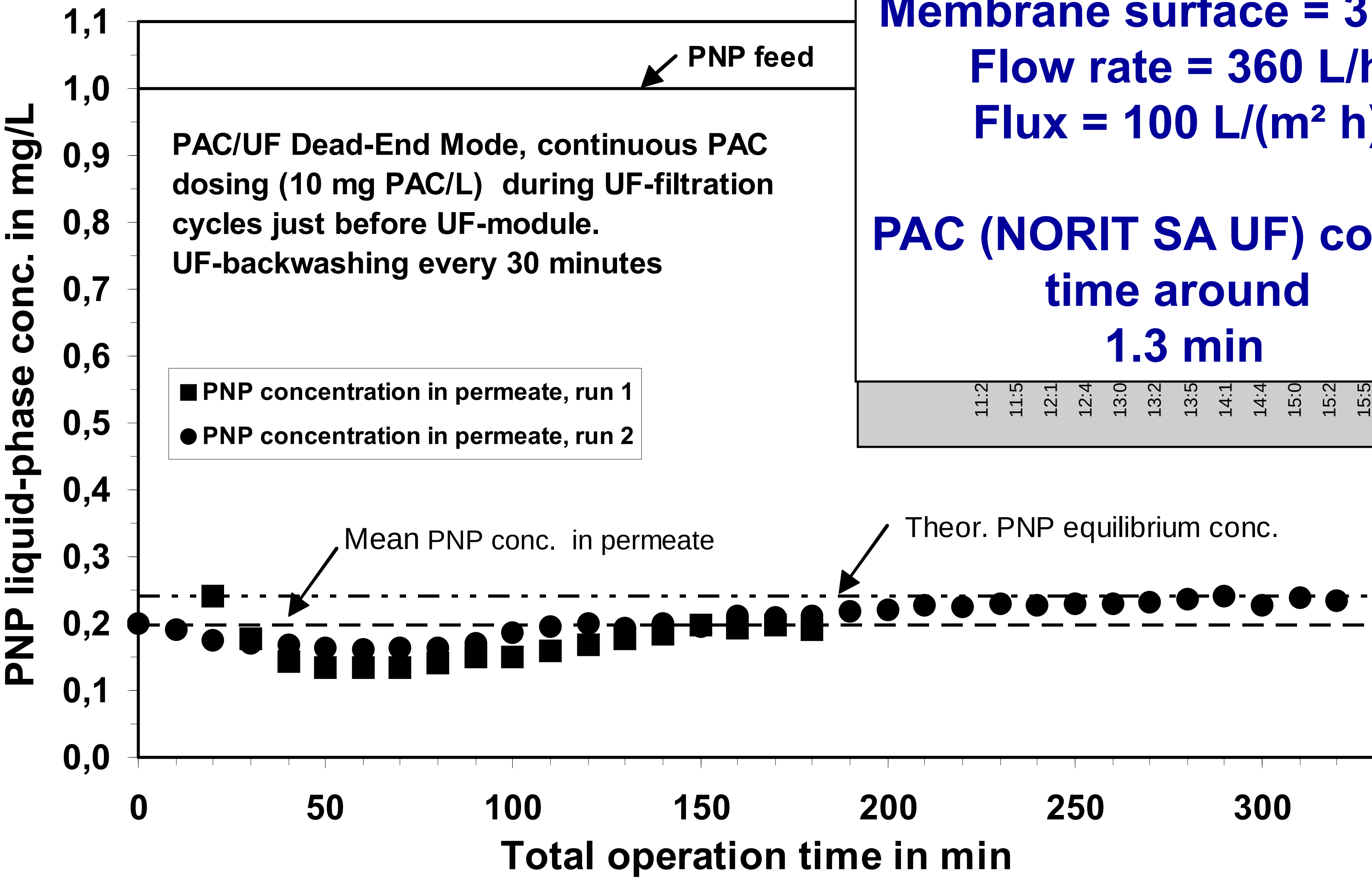


<u>Dead-End-Mode</u>
low energy consumption

Removal of PNP with PAC/UF in Dead-End-Mode

Polym. cap. membrane,
d = 0.8 mm, L = 1.2 m
Membrane surface = 3.6 m²
Flow rate = 360 L/h
Flux = 100 L/(m² h)

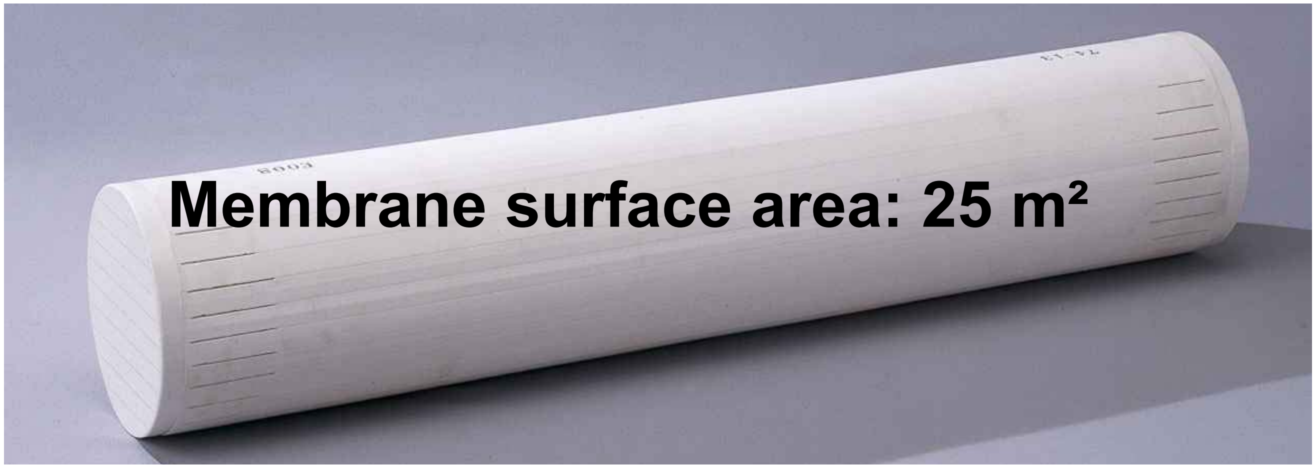
PAC (NORIT SA UF) contact time around 1.3 min

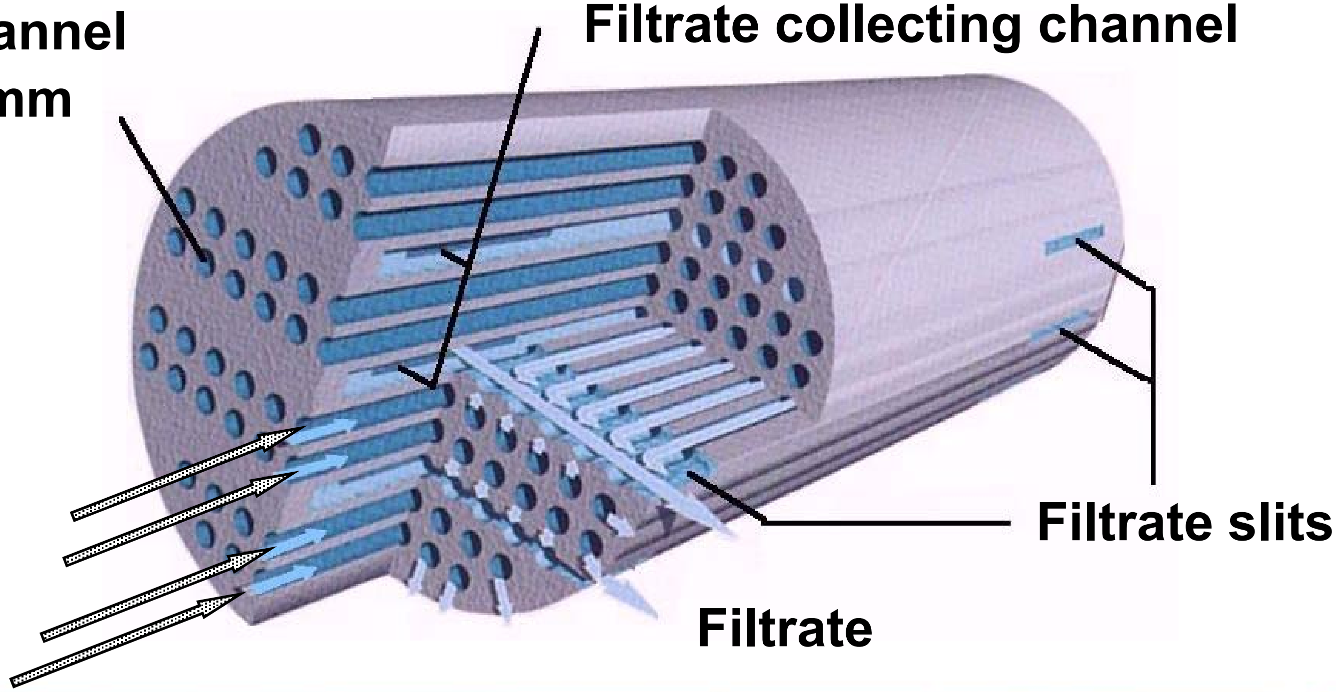


Polymer Membranes versus Ceramic Membranes

- Today low pressure membrane market for DW production is absolutely dominated by <u>polymeric membranes</u>
  - Strength: quite reasonable price
  - Weakness: relatively low mechanical stability, low tolerance against chemicals
- In manyfold industrial solid-liquid separation processes <u>ceramic membranes</u> are well established
  - Strength: high mechanical stability (also at high temperatures), highly resistant against chemicals, high permeability, intensive backwashing and cleaning processes possible
  - Weakness: relatively high price
- In Japan exist about 40 DWTP with <u>ceramic membranes</u> (the largest one with approx. 1,600 m^3/h)

NGK Insulators Ltd. Ceramic MF-Membrane (Material: Al_2O_3)





Main Topics

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Conclusions

- With modern drinking water treatment technologies we can remove nearly all pollutions down to non-relevant concentrations (absolute zero will be impossible!)

but

- our primary objective should always be to protect our water resources! This will allow us to keep the drinking water as natural as possible

Many thanks for your attention!