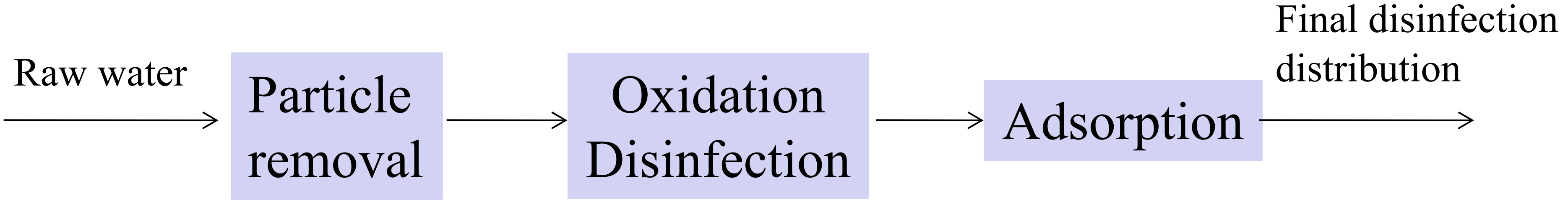
Adsorption processes

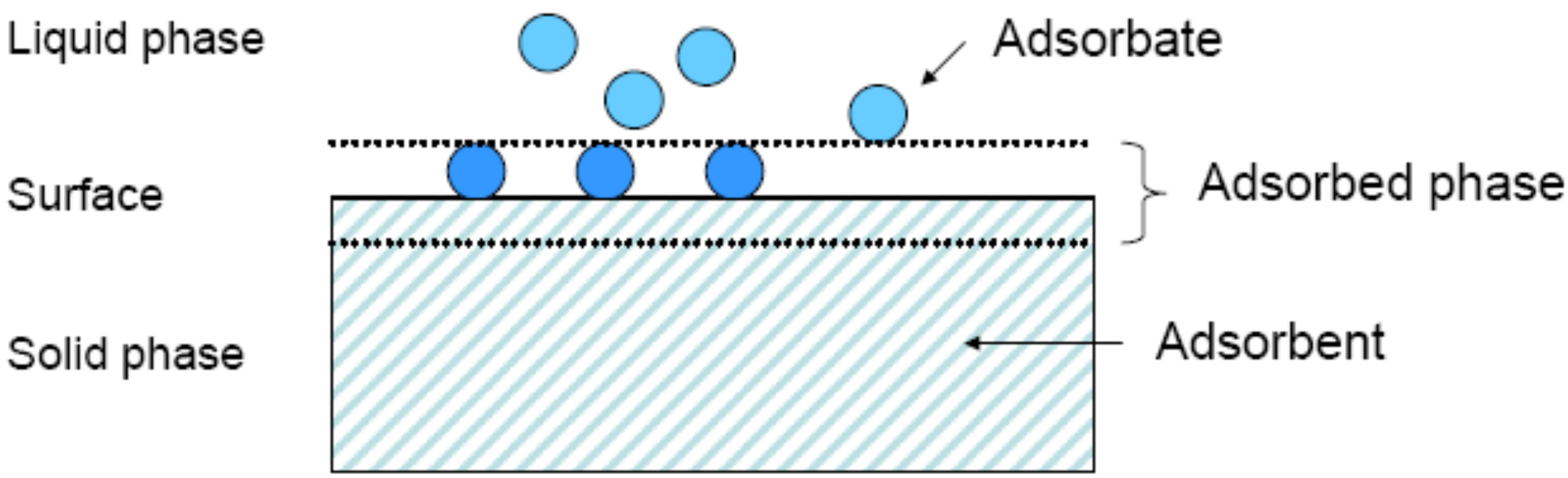
Urs von Gunten

Role of adsorption processes

- Adsorption processes are widely used in water treatment for micropollutant removal
- Zeolites, synthetic polymeric adsorbents, **activated carbon**
- Typically used in process combinations as a polishing treatment



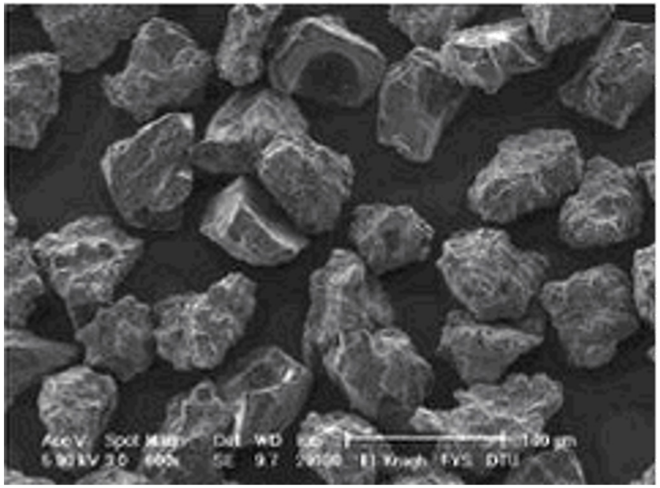
Adsorption processes



Activated carbon

Granular activated carbon (GAC)

Ø 0.5 - 2 mm



Powdered activated carbon (PAC)

Ø 0.04 – 0.07 mm

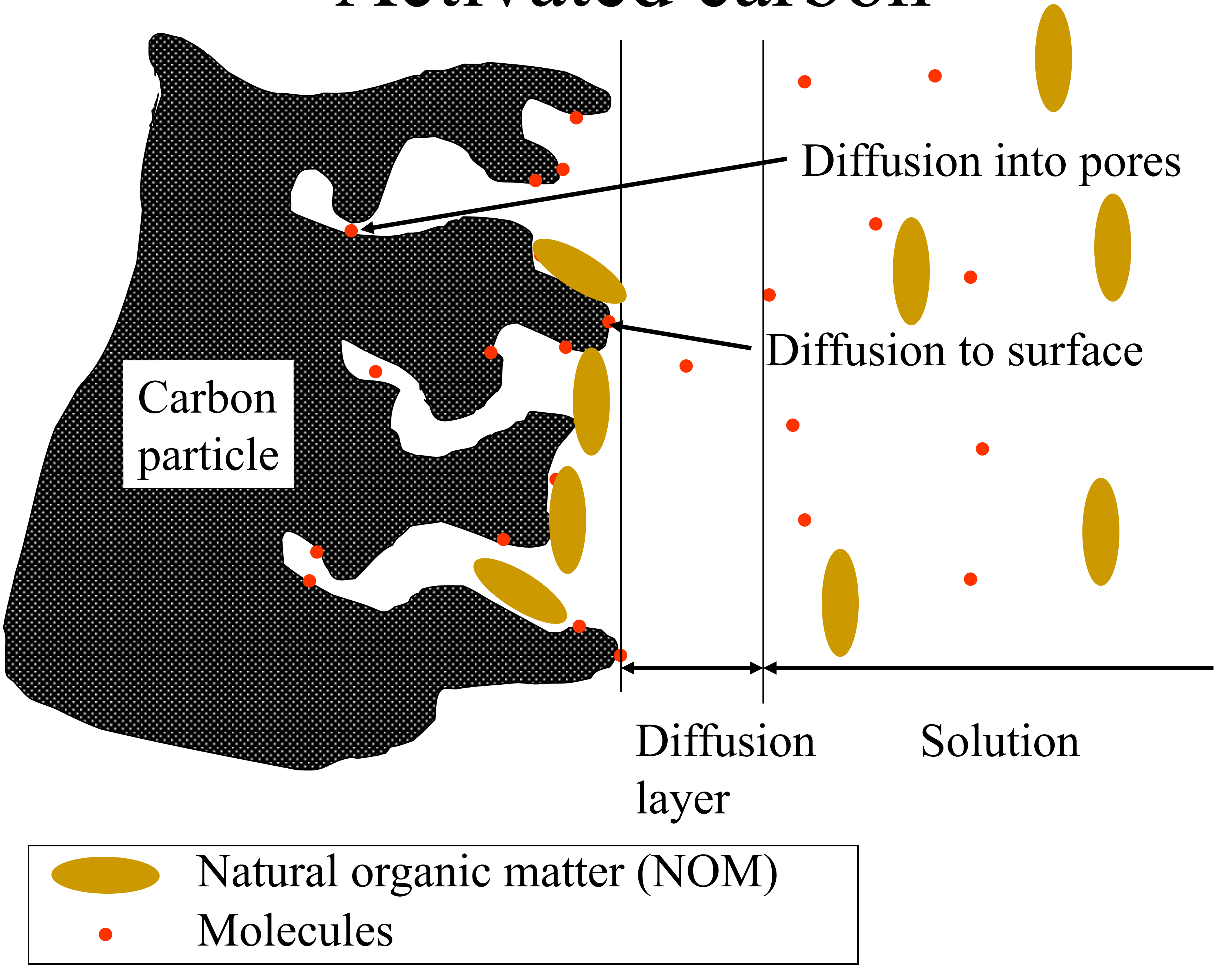
High internal surface areas

400 - >1500 m^2/g

Ca. 10 tennis courts/g

Adsorption capacity up to 0.2g adsorbate/g adsorbent

Activated carbon



Activated carbon

- Deep bed, powdered carbon
- Adsorption processes → kinetics, affinity
- Adsorption can be described by empirical equations
- Langmuir isotherm (not shown here)
- Freundlich isotherm for compound S:

$C_s = K \cdot C_w^{1/n} \rightarrow \log C_s = \log K + 1/n \log C_w$

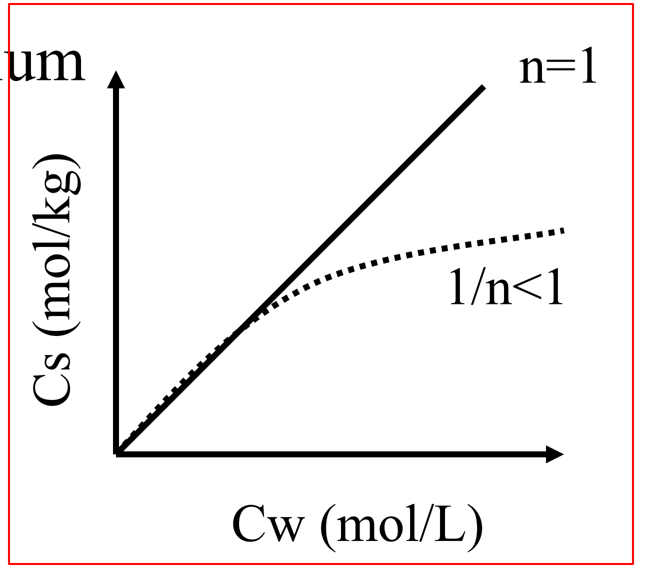
C_s = Amount of S adsorbed per mass unit activated carbon

C_w = Aqueous concentration of S in equilibrium

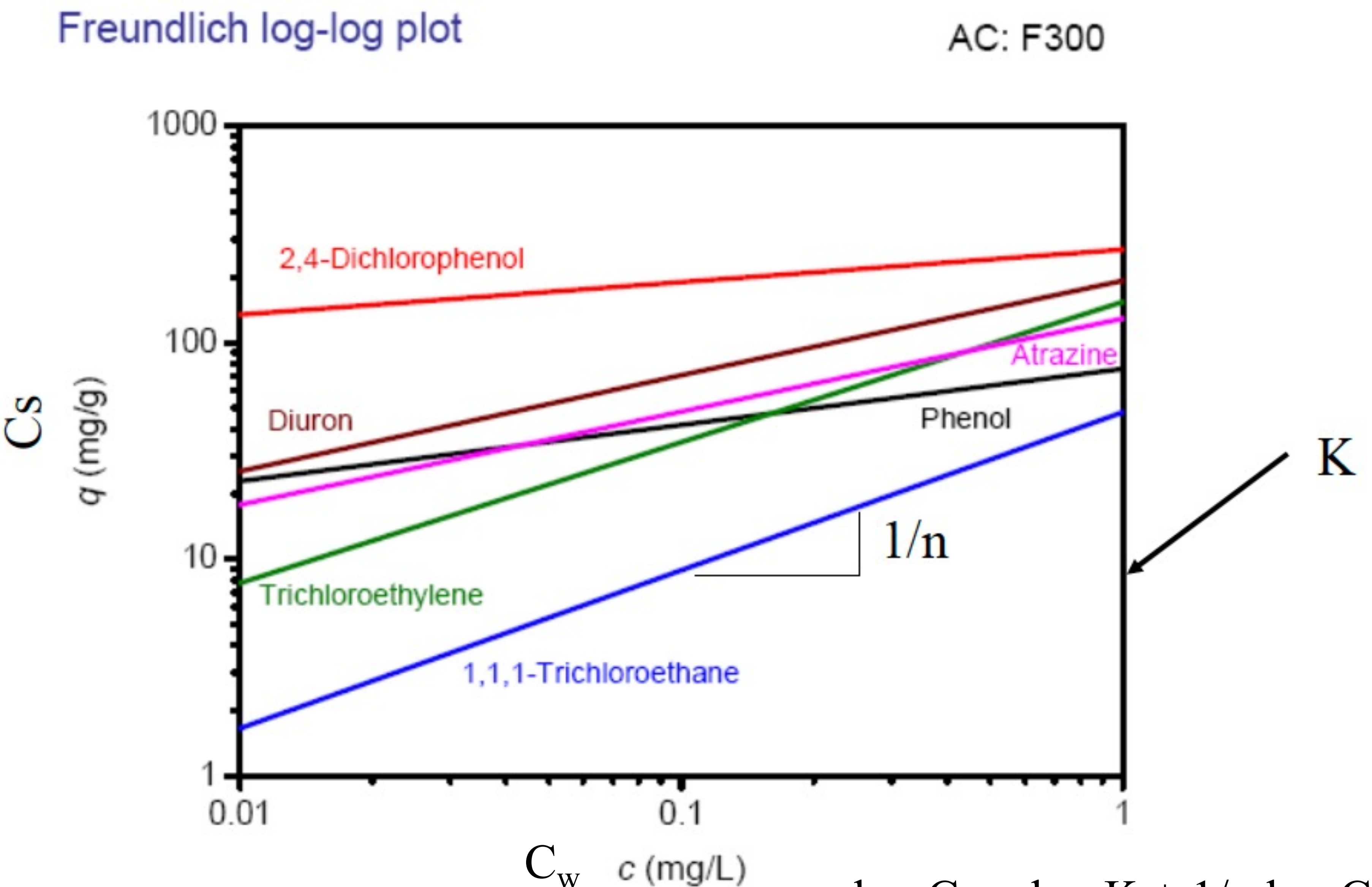
K = Freundlich constant $(mg/g)(L/mg)^{1/n}$

1/n = Freundlich exponent

n=1 or C_w small ⇒ $K = K_d = C_s/C_w$



Adsorption isotherms: Batch tests



$$\log Cs = \log K + 1/n \log C_w$$

Adsorption on activated carbon

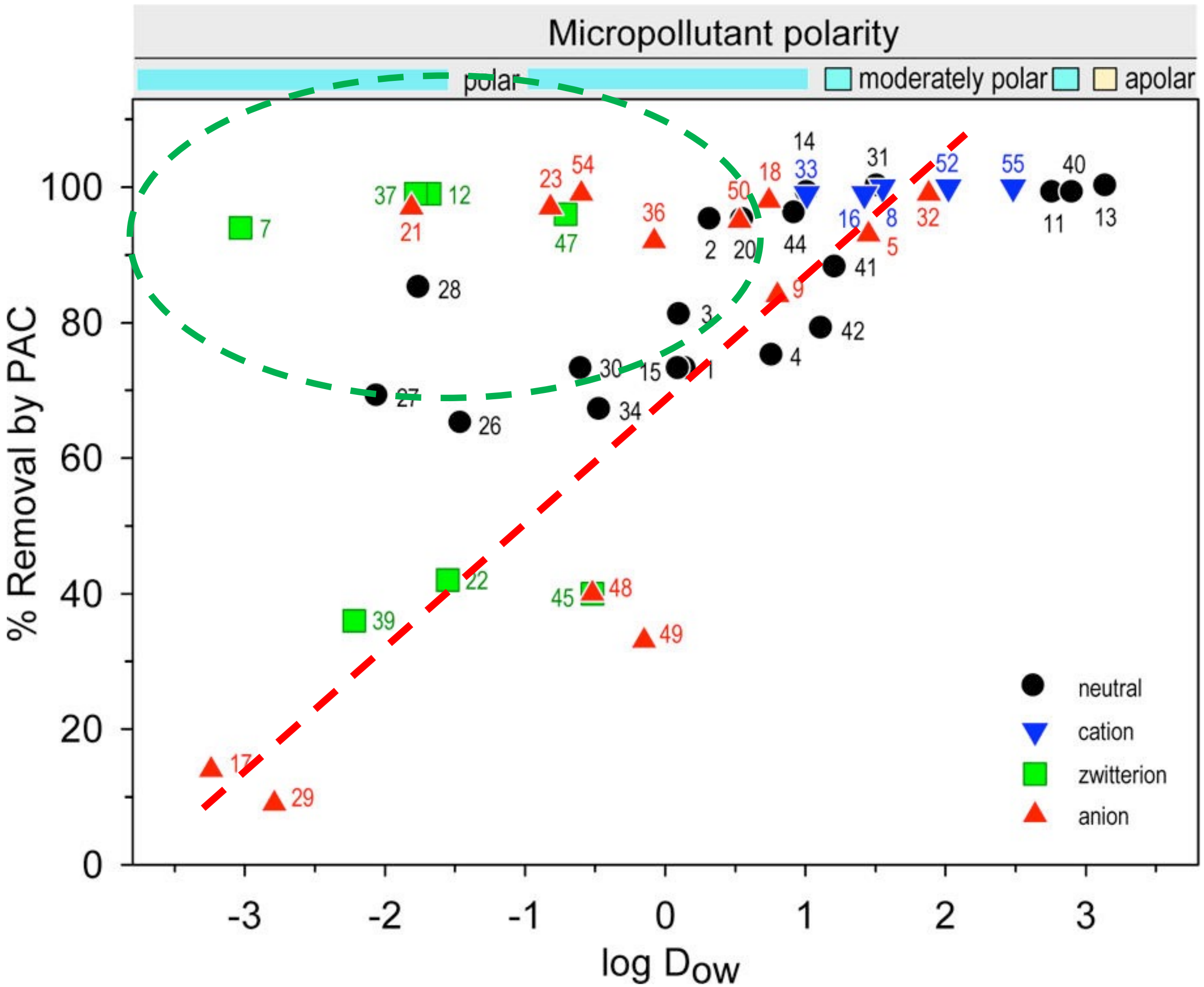
Compound	log K_d [1)]	log K_{ow} [2)]
Methyltertbutylether (MTBE)	1.3	0.94
Chloroform	1.6	0.91
Trichlorethen	2.8	2.4
Tetrachlorethen	3.3	2.9
Atrazin	4.1	2.65
Geosmin	3.9	

1) Blum et al. 1994, 2) Schwarzenbach et al. 2003

K_d: AC/water distribution coefficient

K_{OW}: Ocatnol/water distribution coefficient

Removal of micropollutants with PAC from a hospital wastewater



PAC: 23 mg/L
pH: 8.8
DOC ca. 7 mg/L

D_{ow}: K_{ow} corrected for acid-base speciation

Kovalova et al. ES&T, 2013

Purposes of an activated carbon filter

Rapid filtration

-Removal of particles typically in preceeding processes

Deep bed adsorber

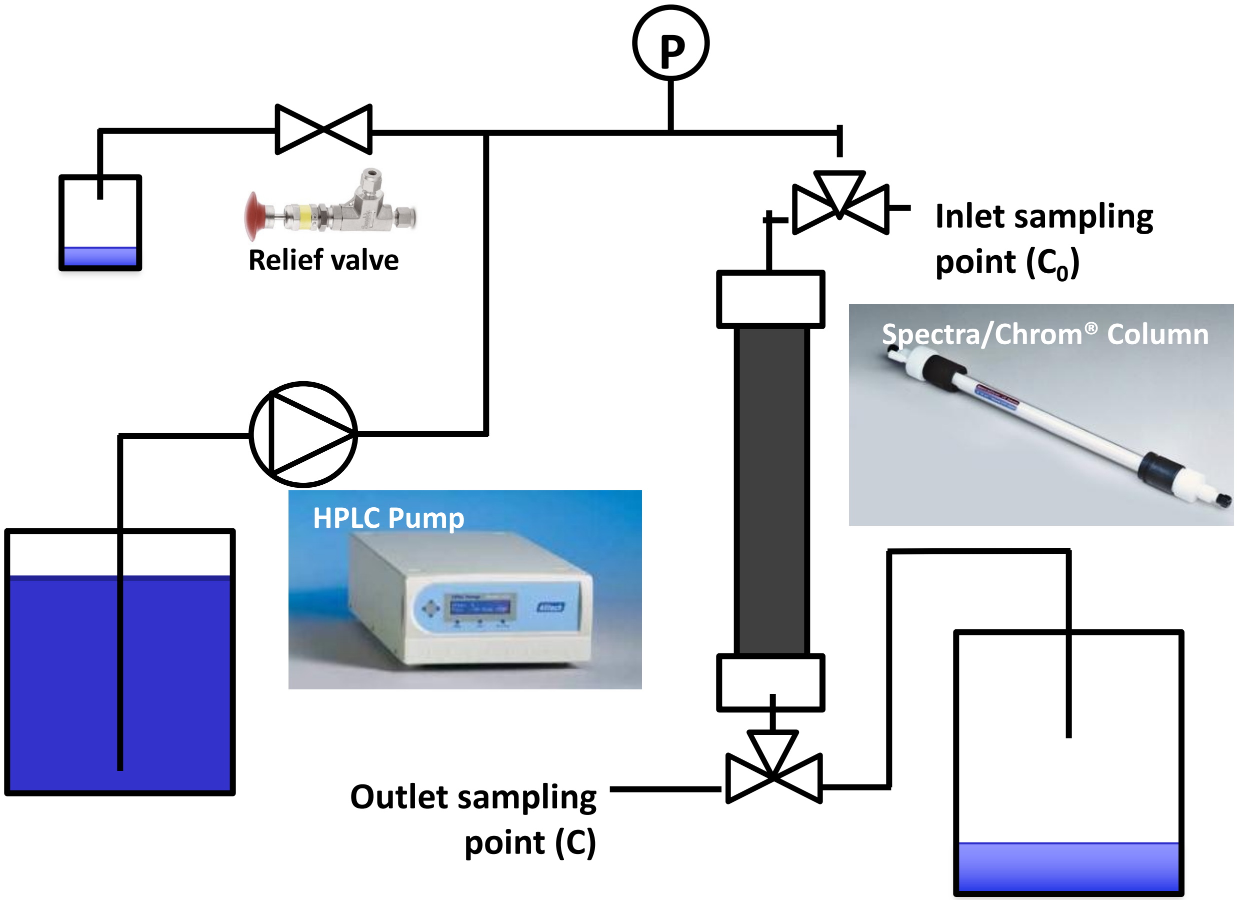
-Elimination of micropollutants

-Adsorption of NOM

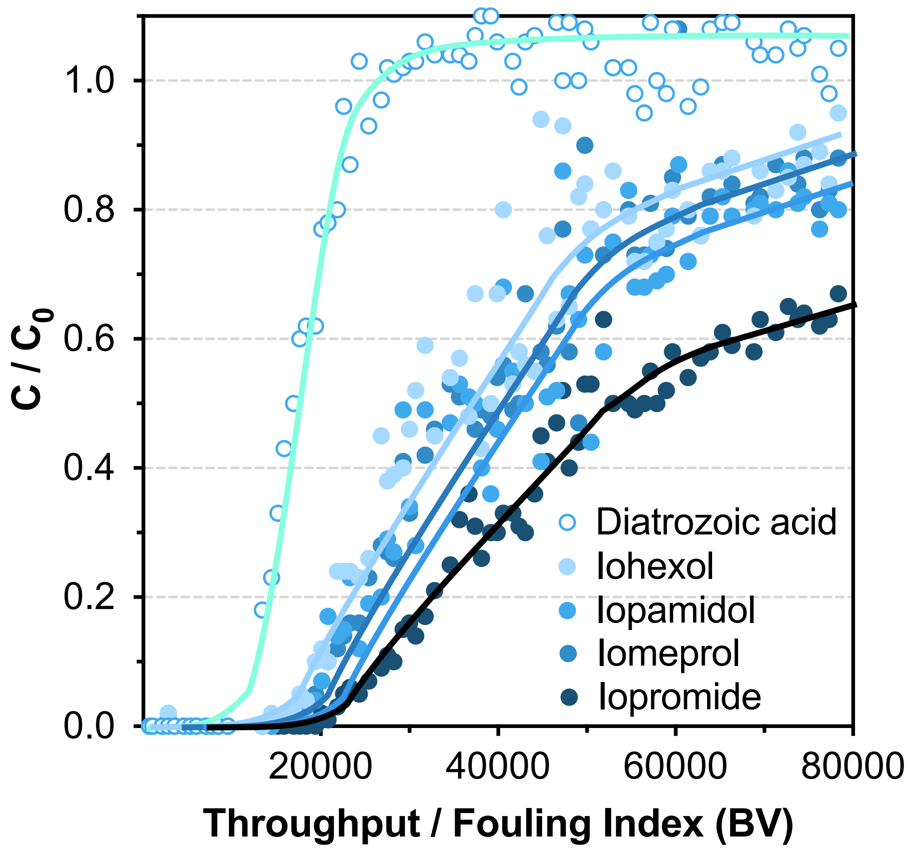
Biological deep bed

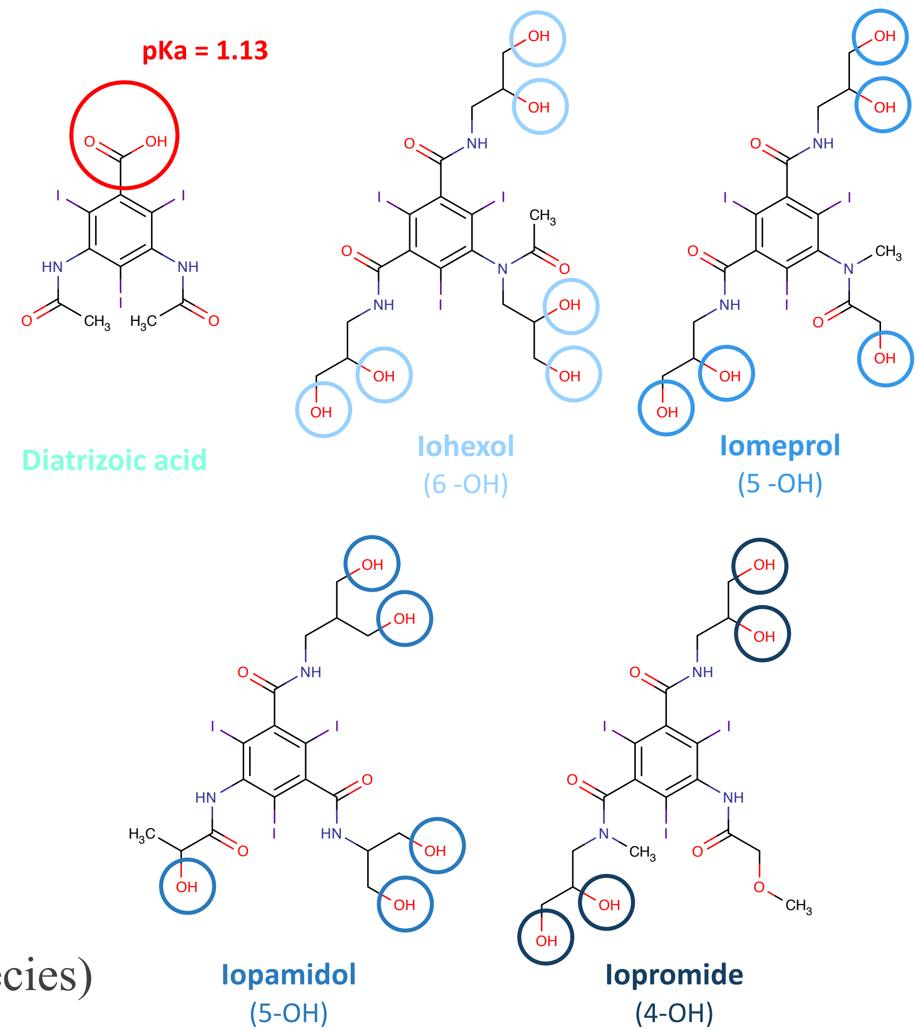
-Biological degradation of AOC and possibly micropollutants

Rapid small-scale column tests



Micropollutant breakthrough - X-ray contrast media



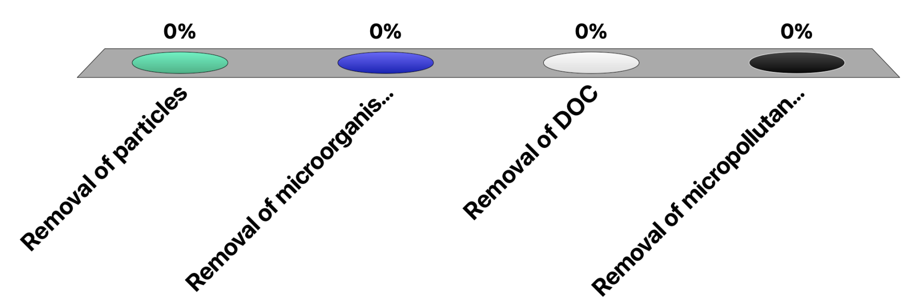


Diatrizoic acid breaks through first (anionic species)

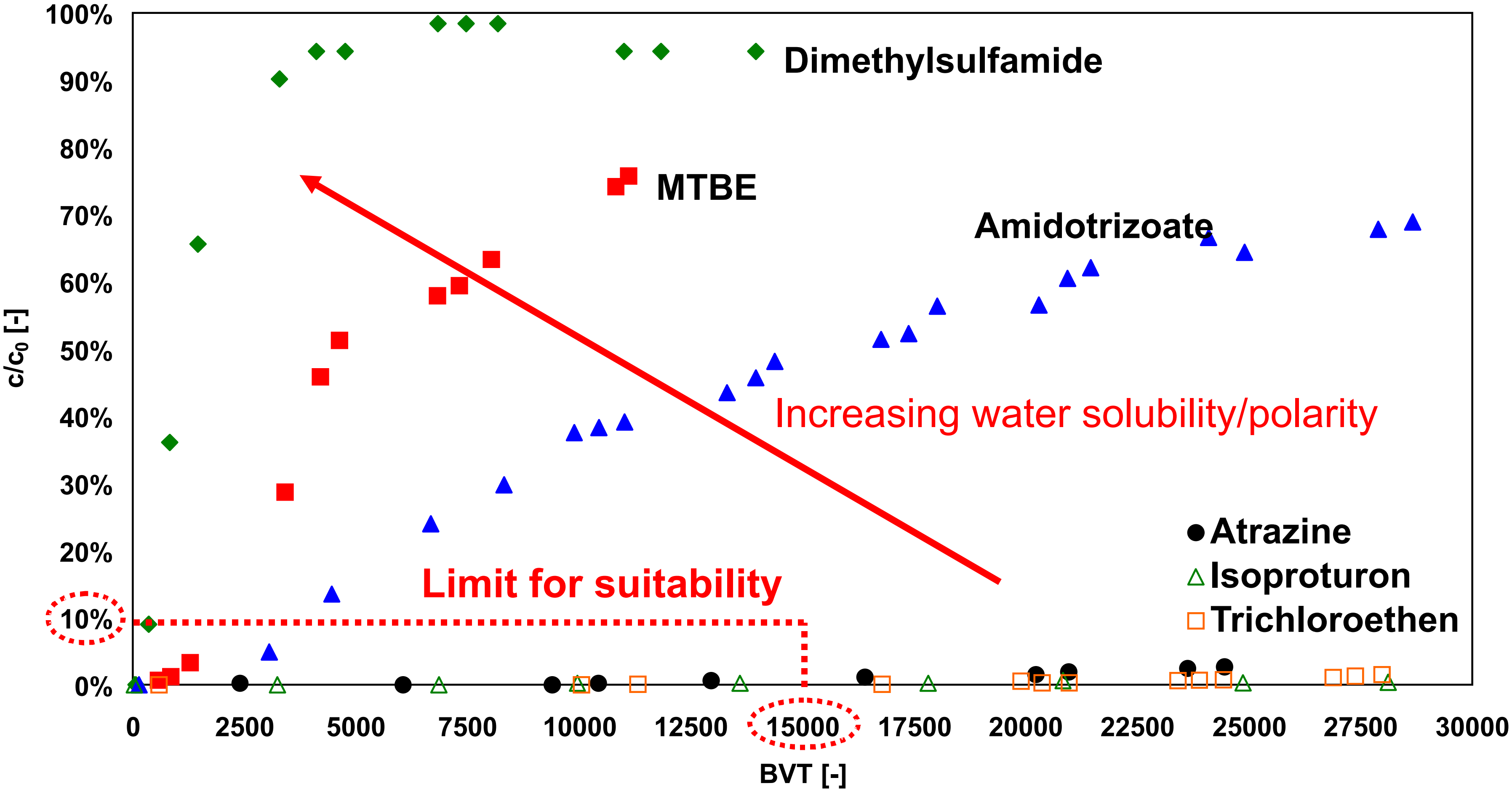
Possible relation between adsorption and the number of hydroxyl groups (-OH).

The main purpose of the application of activated carbon is..

A. Removal of particles
B. Removal of microorganisms
C. Removal of DOC
D. Removal of micropollutants



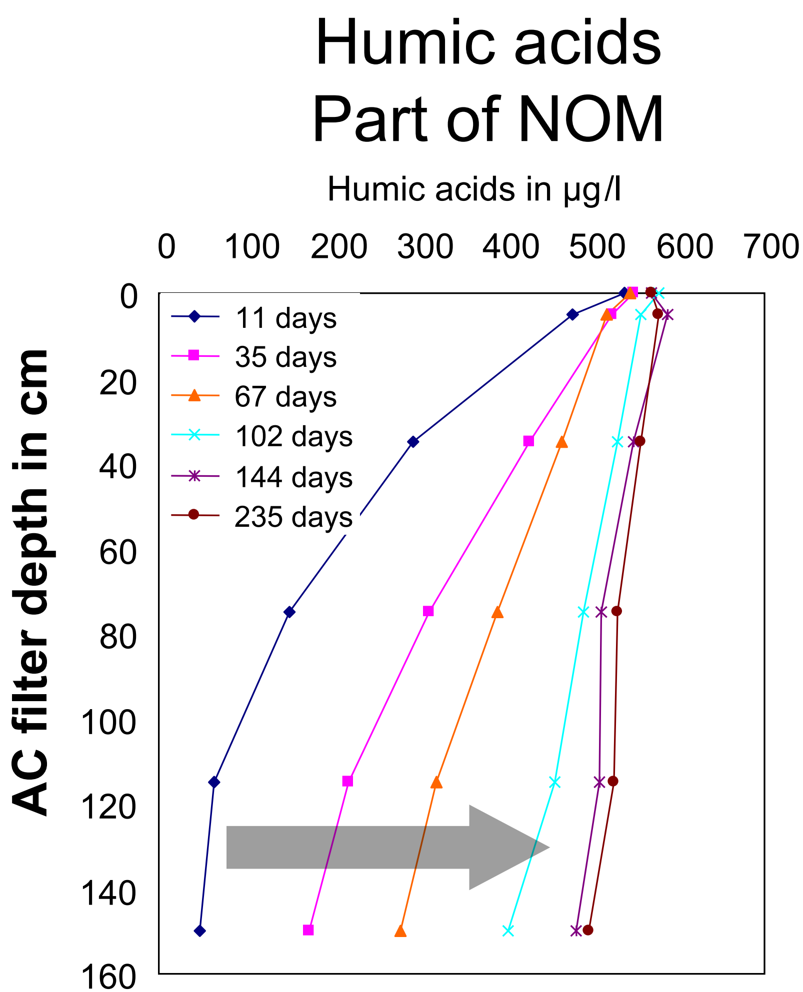
Standard Laboratory tests with small-scale activated carbon filters: Breakthrough of selected compounds

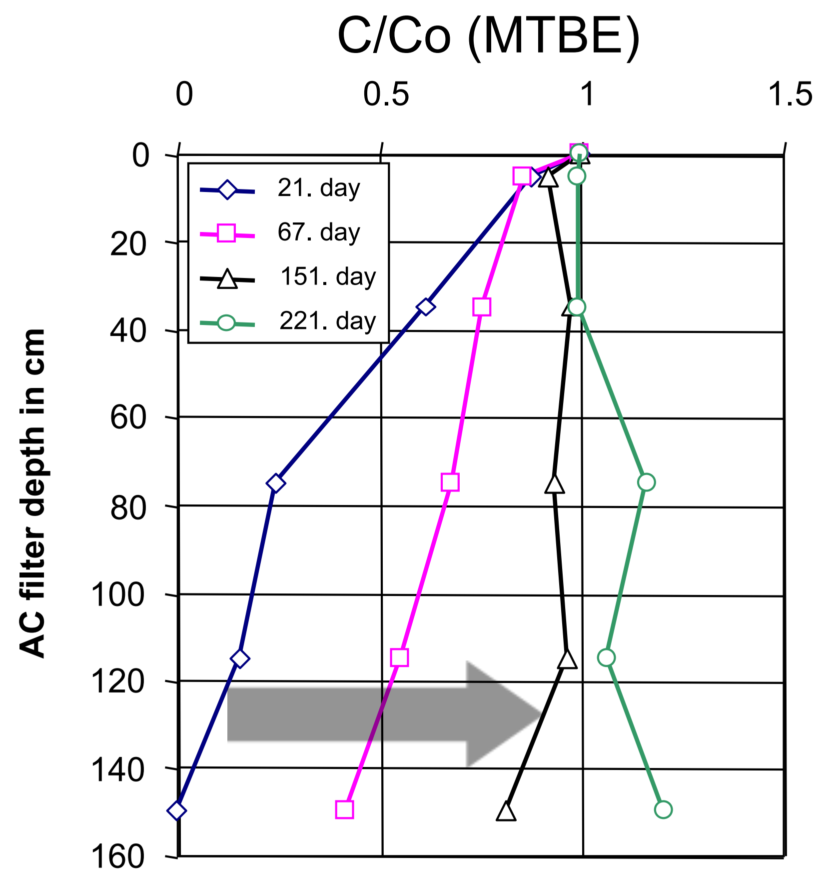


8 mL/min, diameter of filter 10 mm, amount carbon F300: 1.6g, average grain diameter 385 µm, EBCT ≈ 25 s, inlet concentration 25 µg/L, tap water Karlsruhe

TZW, Karlsruhe, 2006

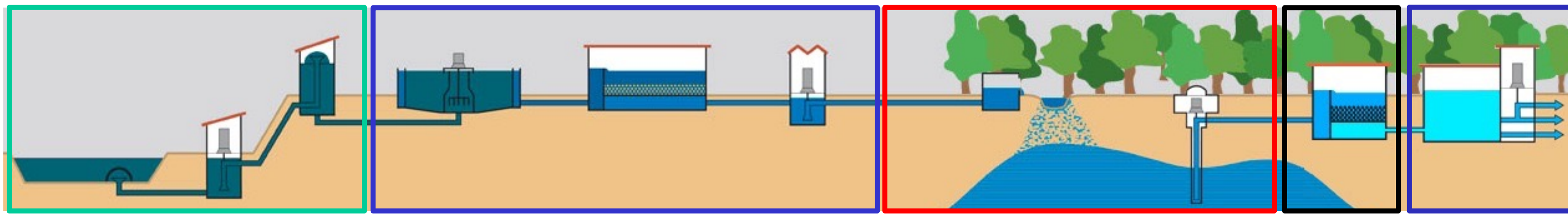
Behaviour of humic acids and MTBE in a pilot plant activated carbon filter (Lengg, Zürich)





Infiltration field Hardwald BL

Artificial groundwater recharge: Hardwald, Basselland



1. River Rhine pumping station

2. Pre-treatment
(Sedimentation / Rapid sand filtration)

Particle removal

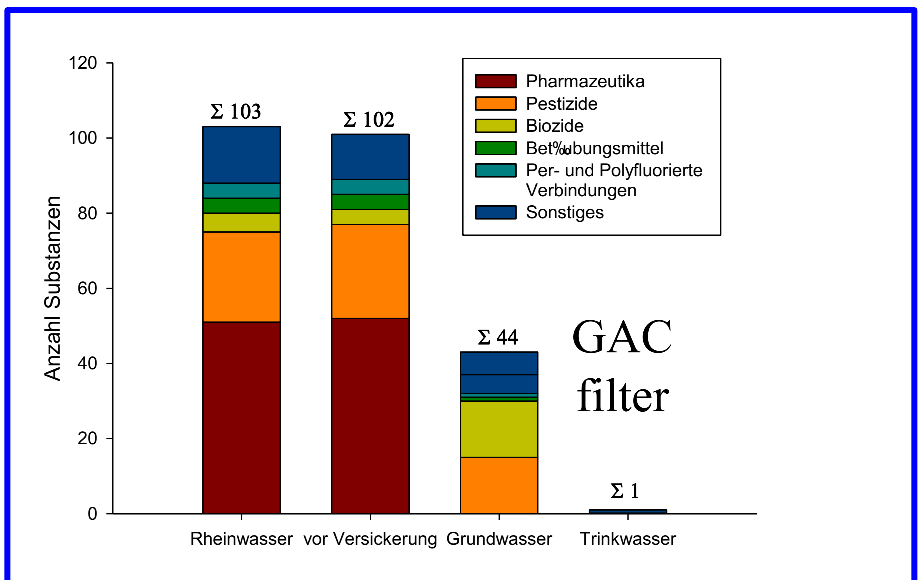
3. Artificial recharge
(Hardwald forest)

Biological treatment

4. GAC filter

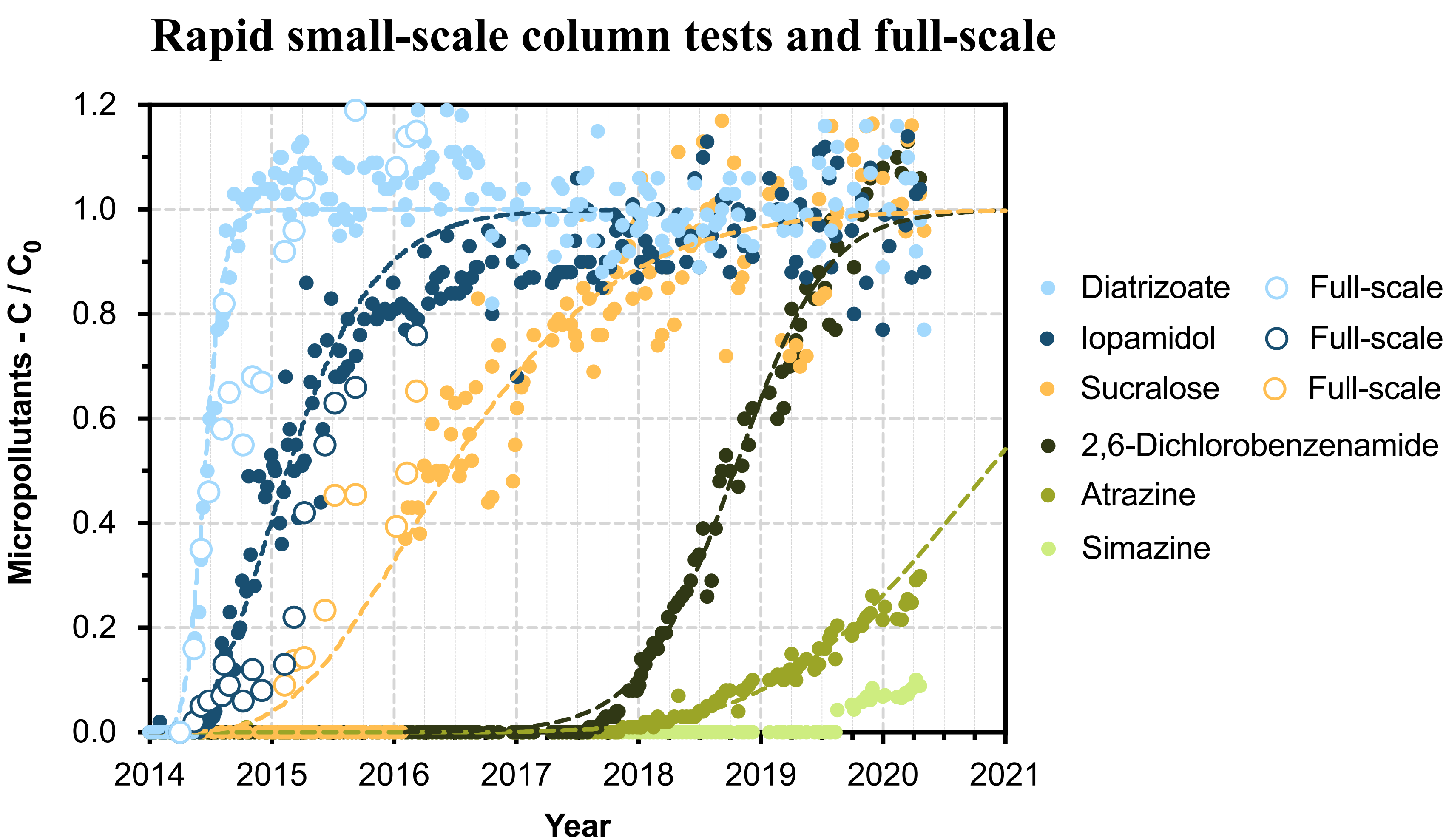
5. UV-Disinfection Distribution

Physical-chemical post-treatment

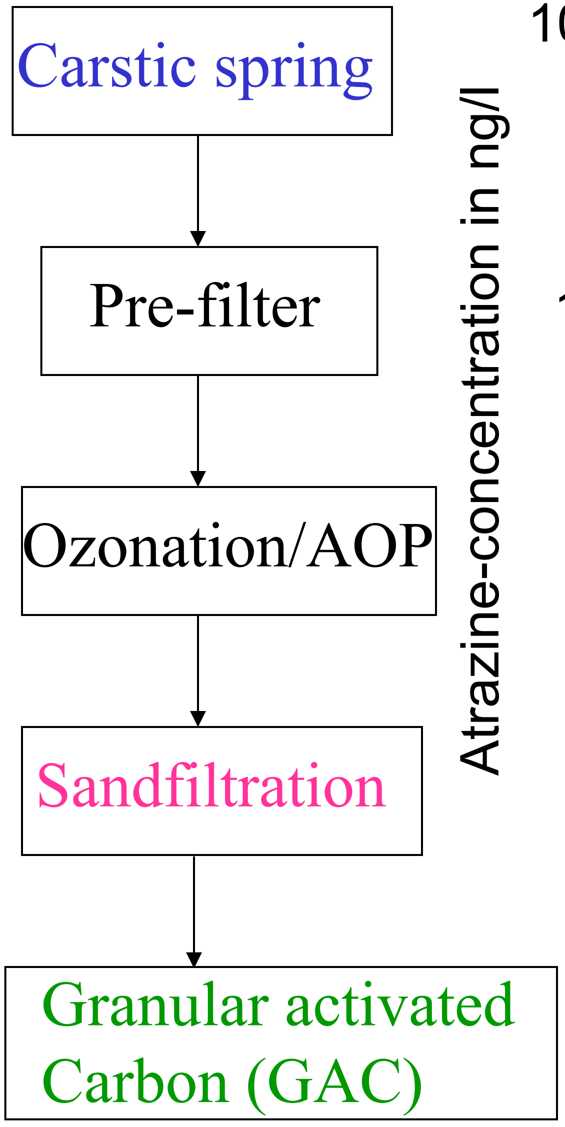


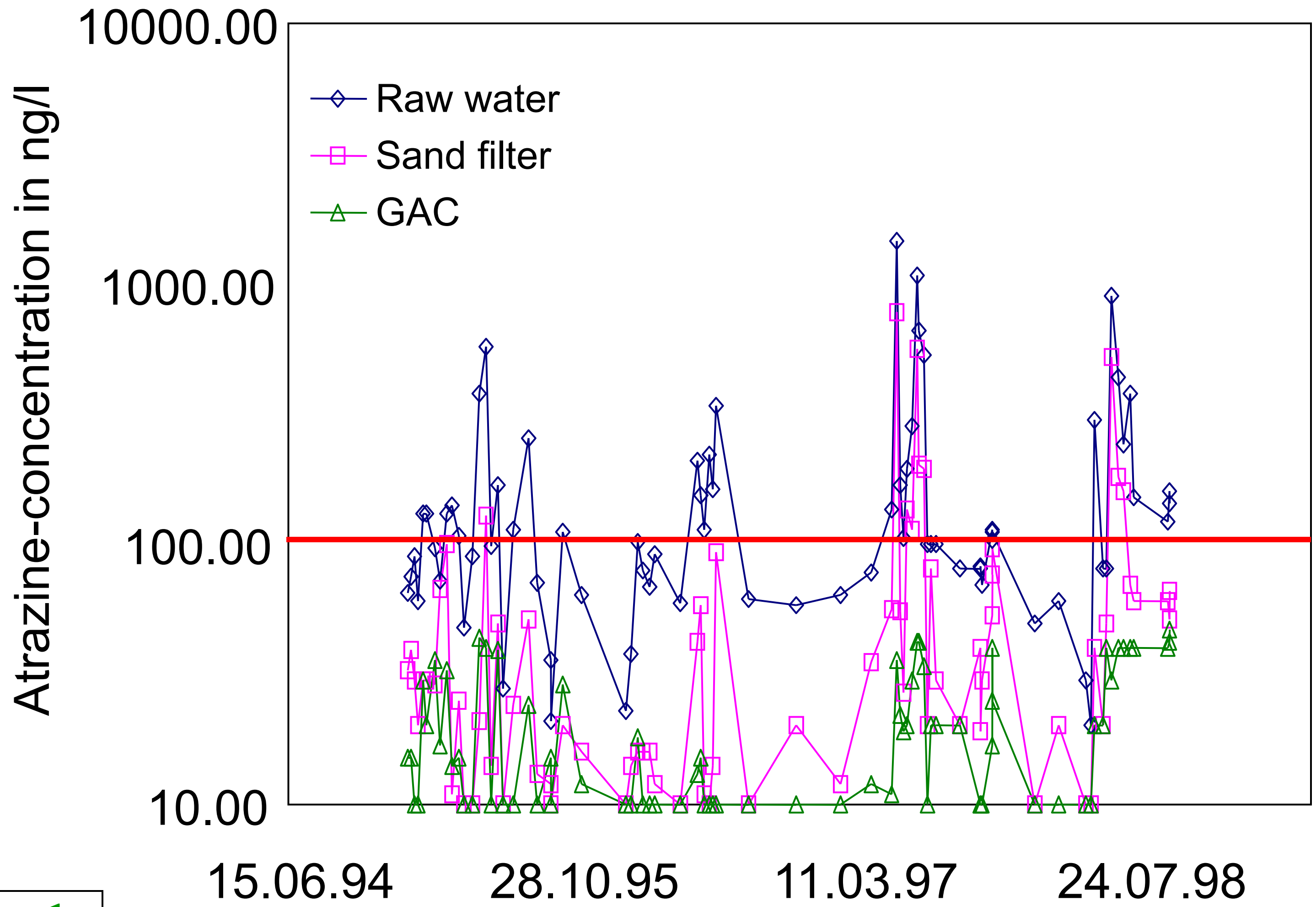
Rhine river	DOC 1.66 mg/L
Sandfilter	DOC 1.54 mg/L
Groundwater	DOC 0.55 mg/L

Activated carbon – Breakthrough of micropollutants (compared to iodinated contrast agents)



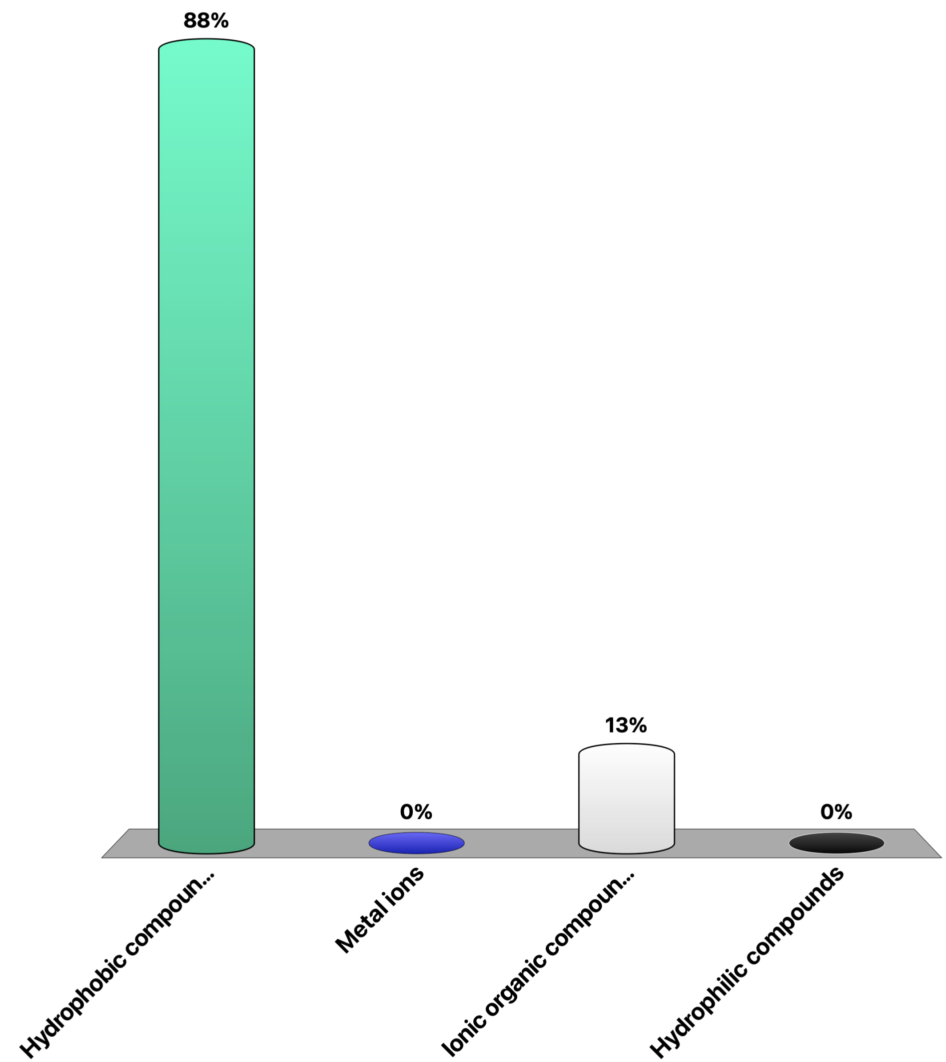
Long-term behavior of the atrazine concentration in the water treatment plant Le Betteraz, Porrentruy JU



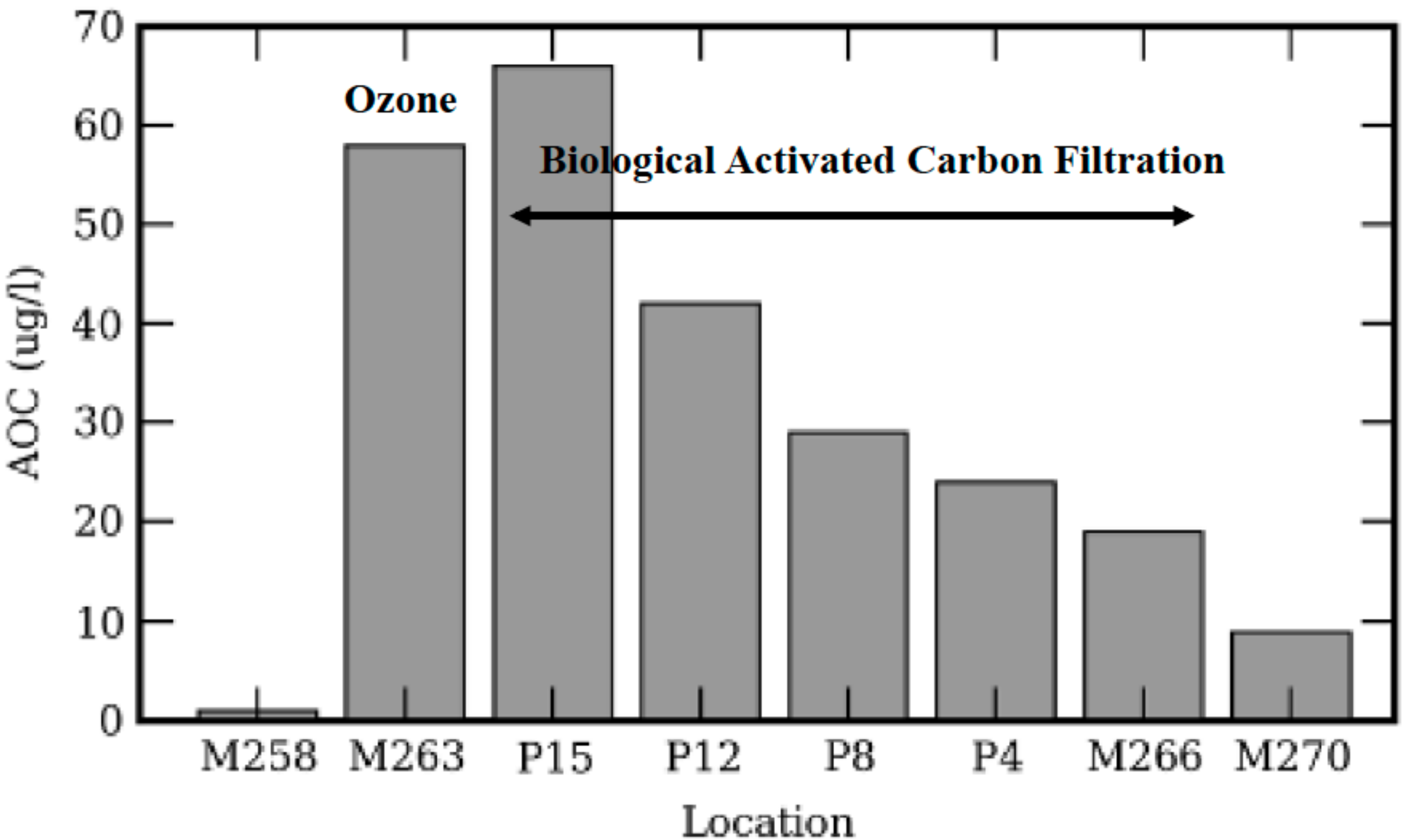


Activated carbon is well suited for the removal of..

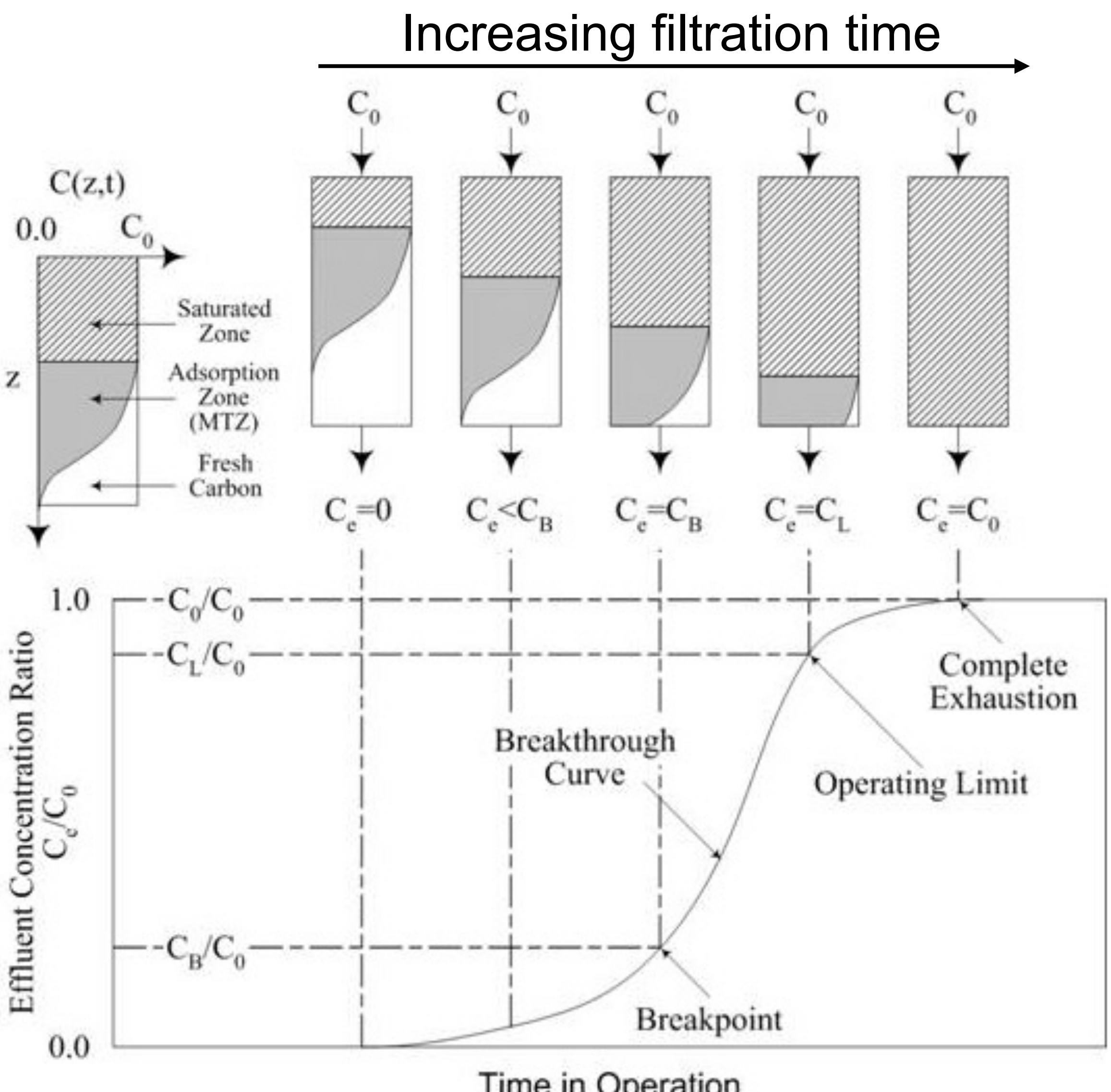
A. Hydrophobic compounds
B. Metal ions
C. Ionic organic compounds
D. Hydrophilic compounds



Formation and elimination of assimilable organic carbon (AOC) during water treatment: Role of Biological Activated Carbon (BAC)



Concentration profiles and breakthrough for GAC filters: Mass transfer zone (MTZ)



http://purewaterlab.org/pwl_net/labs/D2_Process_Units/D2L4_Activated_Carbon/Mass_Transfer_Zone.html

Empty bed contact time (EBCT)

$$EBCT = \frac{V_F}{Q} = \frac{A_F L}{v A_F} = \frac{L}{v}$$

V_F: volume occupied by adsorber media including porosity volume, m^3

Q: flow rate to adsorber, m^3/h

A_F: adsorber area available for flow, m^2

L: adsorber media depth, m

v: superficial flow velocity (Q/A_F), m/h

Range of EBCTs: 5-60 min for GAC

Water treatment, Principles and Design, MWH 2005

Specific throughput and carbon usage rate

Specific throughput: volume fed to adsorber divided by mass of GAC m^3/kg

$$\text{Specific throughput} = \frac{Qt_b}{M_{GAC}} = \frac{V_F t_b}{EBCT \times M_{GAC}} = \frac{V_F t_b}{EBCT \times \rho_F V_F} = \frac{t_b}{EBCT \times \rho_F}$$

L treated water / g GAC

$$Q = \frac{V_F}{EBCT}$$

M_{GAC}: mass of GAC, kg

t_b: time to breakthrough (treatment objective is exceeded)

ρ_F: adsorber density or filter bed density, kg/m^3 ($\rho_F = M_{GAC}/V_F$)

Carbon usage rate (CUR)

$$CUR = \frac{M_{GAC}}{Qt_b} = \frac{1}{\text{specific throughput}}$$

g GAC / L treated water

Water treatment, Principles and Design, MWH 2005

Maximum specific throughput and carbon usage rate

When the adsorbate reaches the end of the filter, it is completely saturated.

This corresponds to the maximum specific throughput or the smallest carbon usage rate. All the adsorbate fed is adsorbed in the column and the adsorption capacity is in equilibrium with the influent concentration.

$$QC_{inf}t_b = M_{GAC}q_e(C_{inf})$$

$q_e(C_{inf})$: adsorbent-phase concentration of the adsorbate at location z in equilibrium with the influent concentration, mg adsorbate/ mg adsorbent

$$\text{Maximum specific throughput} = \frac{Qt_b}{M_{GAC}} = \frac{q_e(C_{inf})}{C_{inf}}$$

$$\text{Minimum CUR} = \frac{M_{GAC}}{Qt_b} = \frac{C_{inf}}{q_e(C_{inf})}$$

Water treatment, Principles and Design, MWH 2005

GAC running time

For an influent concentration C_{inf} and a target effluent concentration C_{eff}, the following equation can be formulated:

$$QC_{inf}t_b = Q\int_0^{t_b} C_{eff}\,dt + q_c M_{GAC}$$

q_c: average adsorbent-phase concentration of adsorbate in GAC column, mg adsorbate/ g adsorbent

C_{eff}: effluent liquid phase concentration at time t, mg/L

Specific throughput:

$$\frac{Qt_b}{M_{GAC}} = \frac{Q\int_0^{t_b} C_{eff}\,dt}{C_{inf}M_{GAC}} + \frac{q_c}{C_{inf}}$$

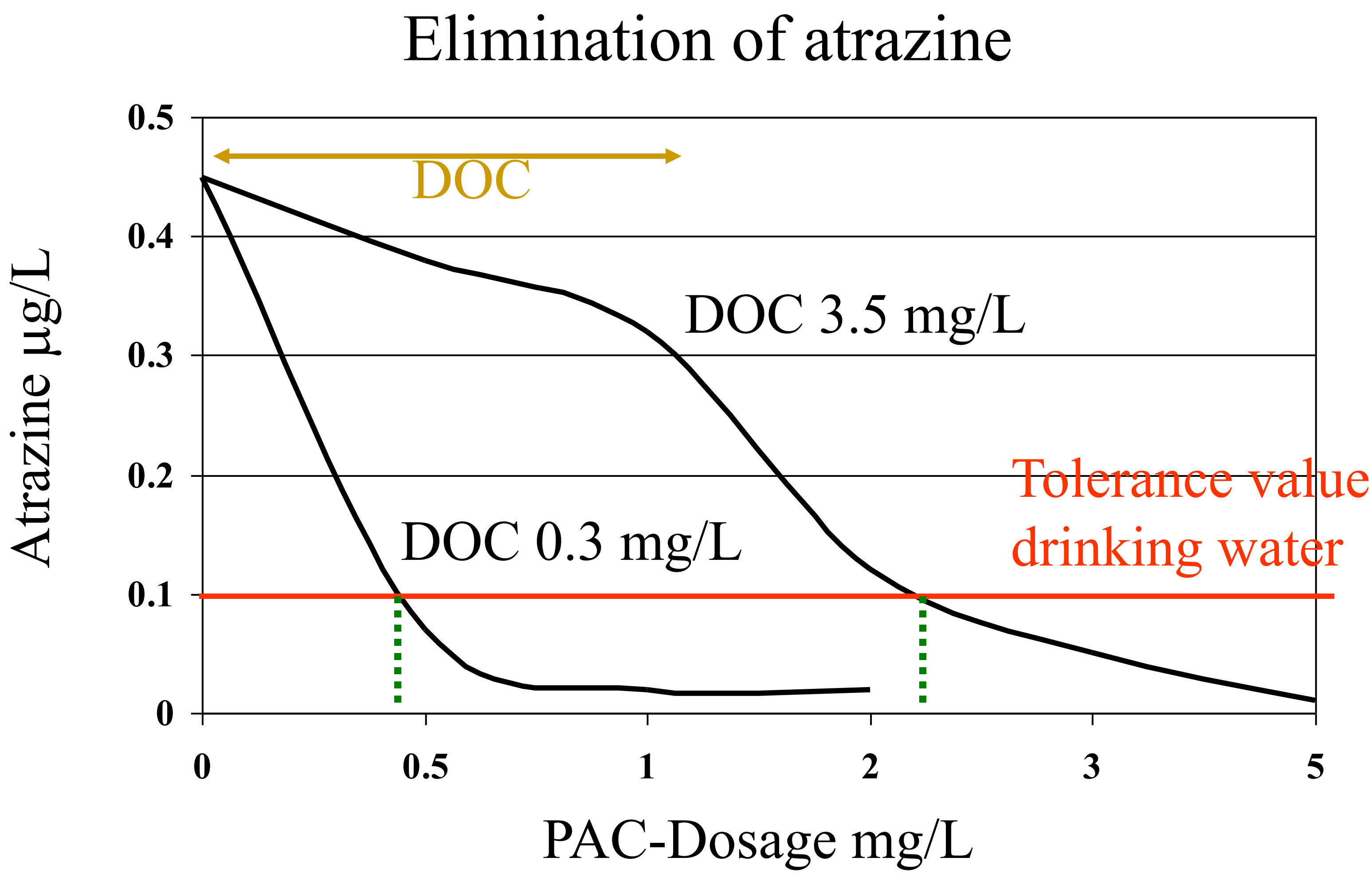
$$\text{if } C_{eff} \ll C_{inf} \Rightarrow \frac{Qt_b}{M_{GAC}} = \frac{q_c}{C_{inf}}$$

When the mass transfer zone is much smaller than the EBCT, $q_c \approx q_e$

$q_e = K \times (C_{inf})^{1/n}$

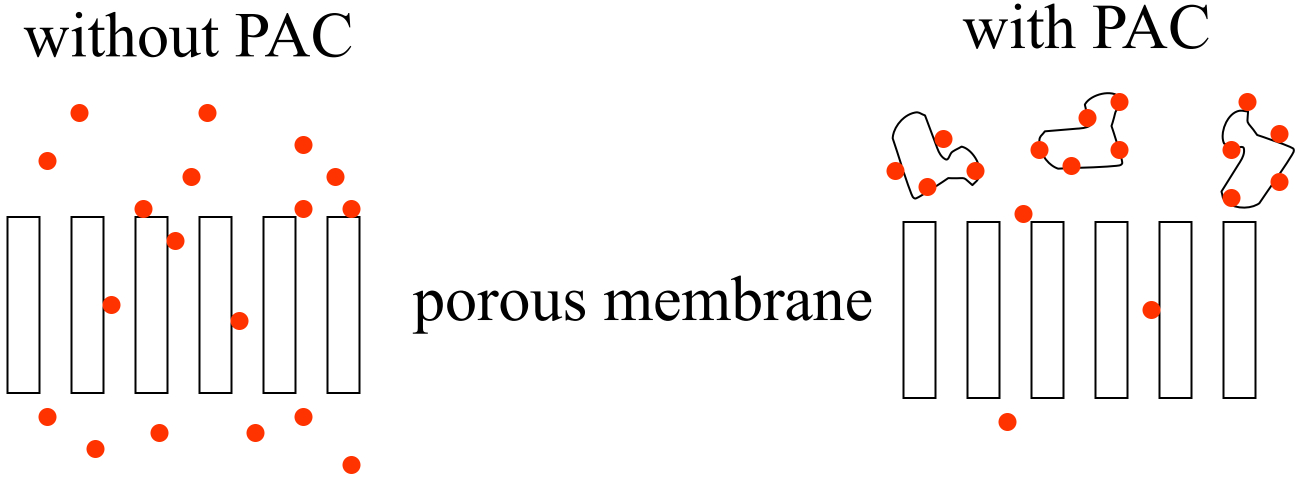
Water treatment, Principles and Design, MWH 2005

Powdered activated carbon: influence of NOM



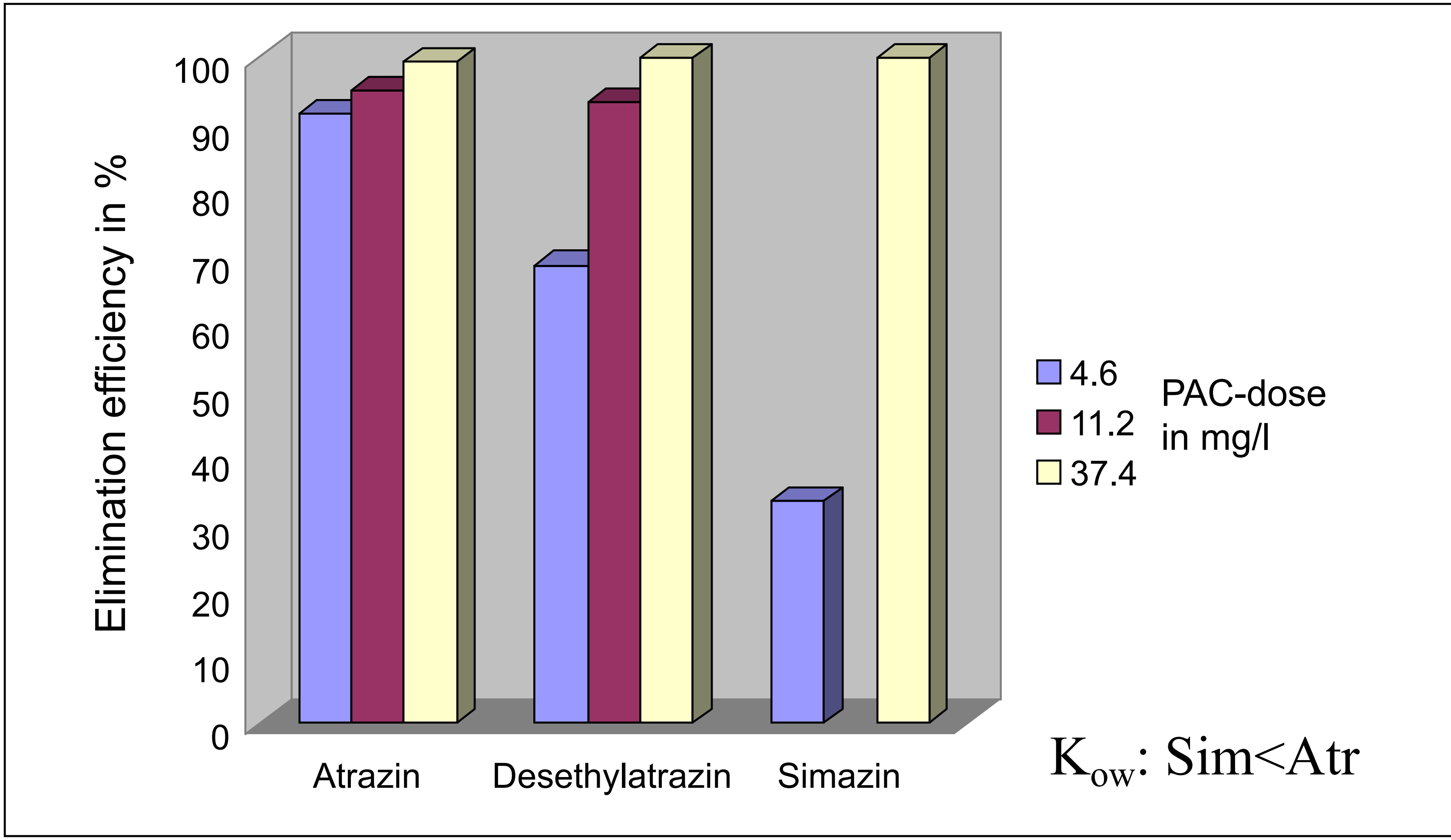
Combination of PAC with membranes

- Adsorption of chemicals on particles
- larger pores in membranes (UF) → smaller pressure (≤ 5 bar)



- Dosage on demand
- Simultaneous removal of NOM

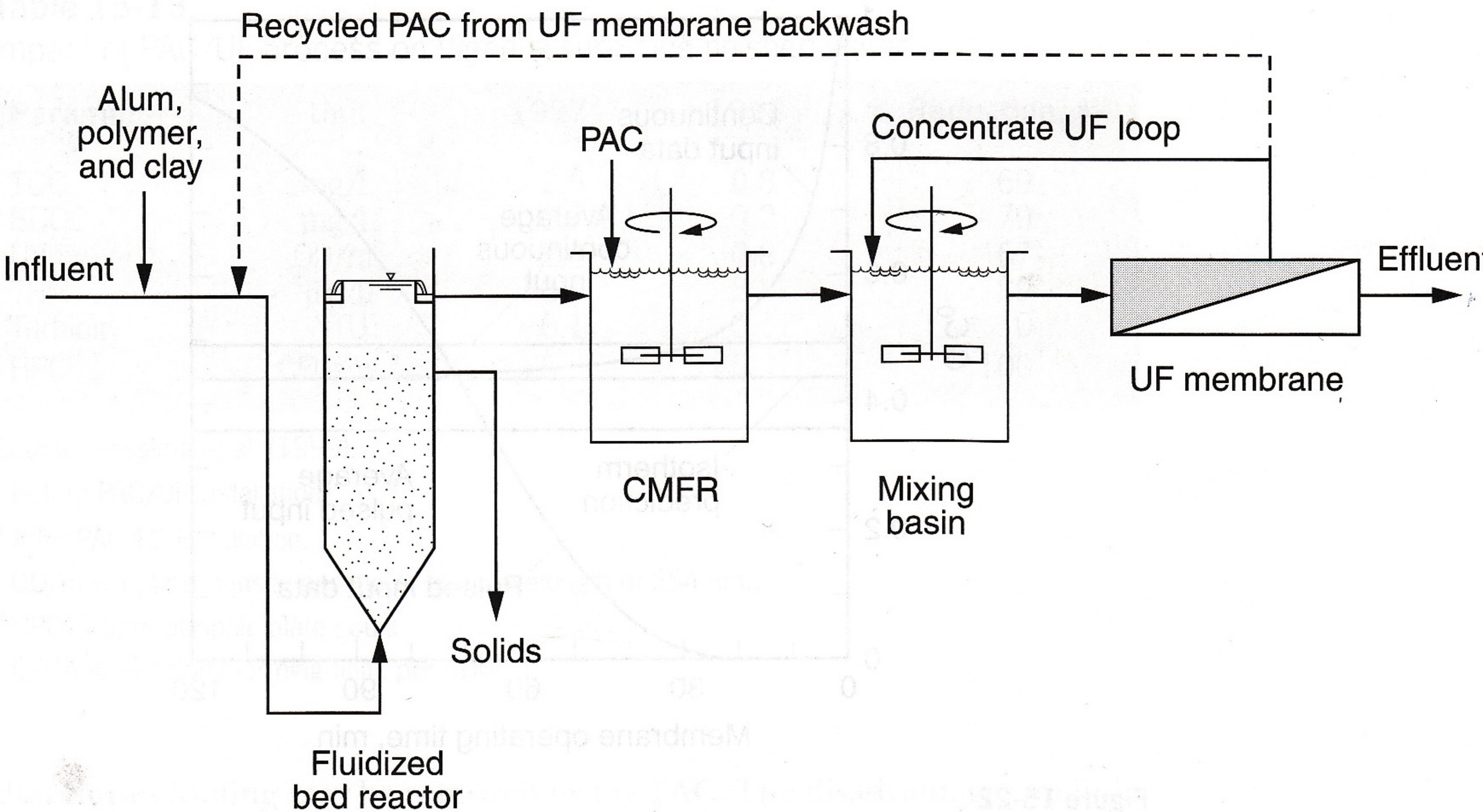
Elimination of pesticides by ultrafiltration combined with powdered activated carbon (PAC)



Ultrafiltration only → no elimination !

PAC injection system, water supply Lausanne, Lutry

PAC – Ultrafiltration (Vigneux sur Seine, F)



Water treatment, Principles and Design, MWH 2005

Water quality parameters for PAC/UF process (Vigneux sur Seine)

Parameter	Before PAC/UF installation	After PAC/UF installation	Reduction, %
TOC mg/L	2.6	0.8	69
BDOC mg/L	0.7	0.2	70
Optical density 1/m	2.4	0.8	67
THM formation μg/L	73	8	89
Turbidity NTU	0.1	0.1	0
Colony forming units 1/mL	5	0	100

Comparison GAC/PAC

Parameter	**Granular Activated Carbon (GAC)**	**Powdered Activated Carbon (PAC)**
Main uses	• Control of toxic organic compounds in groundwaters • Barrier against micropollutants in surface waters (e.g. taste and odor) • Control of DOC	• Seasonal control of micropollutants (e.g. taste and odor, pesticides)
Advantages	• Can be regenerated • Lower carbon usage rate per volume of water treated compared to PAC	• Easily added to existing coagulation for occasional control of organics
Disadvantages	• Need contactors and infrastructure for regeneration • Previously adsorbed compounds can desorb	• Hard to regenerate and recover from sludge • Higher carbon usage rate per volume water treated compared to GAC

Conclusions

- Two forms of AC application: granular activated carbon filters and powdered activated carbon
- Activated carbon can be used as a polishing treatment to remove micropollutants; mostly integrated into multi-step treatment
- Adsorption of micropollutants can be described by empirical adsorption laws, affinity depends on hydrophobic character
- DOM competes with adsorbates and reduces the adsorption capacity
- GAC is often used as biological filtration step: BAC