

# "Advanced Wastewater Treatment by Nanofiltration and Activated Carbon for High Quality Water Reuse"

Von der Fakultät für Maschinenwesen der Rheinisch-Westfälischen Technischen  
Hochschule Aachen zur Erlangung des akademischen Grades eines  
Doktors der Ingenieurwissenschaften genehmigte Dissertation

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Tag der mündlichen Prüfung: 22.09.2011

Diese Dissertation ist auf den Internetseiten der Hochschulbibliothek  
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## Abstract

Hybrid processes combining activated carbon and nanofiltration have been studied to identify the optimum solution for advanced wastewater treatment in high quality water reclamation and reuse. With a focus on the removal of bulk and trace organic compounds the investigation identified three promising process combinations, namely powdered activated carbon followed by nanofiltration (PAC/NF), granular activated carbon followed by nanofiltration (GAC/NF) and nanofiltration followed by granular activated carbon (NF/GAC). The removal potential was examined in lab and pilot scale for a range of refractory pharmaceuticals and industrial chemicals typically detected in effluent in trace concentrations ranging from ng/L to  $\mu\text{g/L}$ . Fluorescence excitation emission spectroscopy was employed for the investigation of the fate of effluent organic matter. The optimum strategies for operation of the hybrid processes were determined in pilot scale. The experiments were conducted at the Wastewater Treatment Plant Aachen Soers providing an effluent of high quality with low dissolved organic carbon (DOC) concentrations of about 5 mg/L.

In comparison to a single stage NF or a single adsorption stage, all three hybrid processes provide a superior product quality with DOC concentrations clearly below 0.5 mg/L and organic micropollutant concentrations close or below the limit of quantification. If a high degree of salinity removal is not required, nanofiltration-activated carbon hybrid processes can be regarded as a reliable and economic alternative to dual membrane processes (ultrafiltration and reverse osmosis). They are well suited for high-grade water reuse applications.

Due to lower filtration pressures the hybrid processes feature lower energy consumption and produce less problematic concentrates mainly consisting of organics and multivalent ions which can be precipitated. They feature also some advantages in indirect potable reuse applications such as managed aquifer recharge since the salt content of the product water is closer to natural conditions. The optimum combination of nanofiltration and activated carbon depends on local boundary conditions such as size of plant, raw water characteristics and plant location. In the light of growing water scarcity and increasing concerns about organic micropollutants activated carbon treatment in combination with nanofiltration has the potential to be applied in an increasing number of cases.

**Key words:** High quality water reuse, nanofiltration, activated carbon, membrane hybrid processes, organic micropollutants, bulk organic removal

## Zusammenfassung

Verschiedene Hybridverfahren in Kombination von Aktivkohle und Nanofiltration wurden für den Einsatz in der weitergehenden Abwasserbehandlung zur hochwertigen Wasserwiederverwendung untersucht. Mit Schwerpunkt auf der Entfernung von Massenorganik und organischen Spurenstoffen wurden drei vielversprechende Verfahrenskombinationen identifiziert: Pulveraktivkohle gefolgt von Nanofiltration (PAK/NF), granuliert Aktivkohle gefolgt von Nanofiltration (GAK/NF) und Nanofiltration gefolgt von granulierter Aktivkohle (NF/GAK). Die Entfernungsleistung der Prozesse wurde im Labor- und Pilotmaßstab für eine Reihe von refraktären Pharmazeutika und Industriechemikalien studiert, die üblicherweise im Abwasser in Spurenkonzentrationen im Bereich von ng/L bis µg/L nachgewiesen werden. Der Verbleib der Massenorganik von Kläranlagenablauf wurde mittels Fluoreszenz-Spektroskopie betrachtet. Die optimalen Betriebsstrategien zur Umsetzung der Prozesse wurden im Pilotmaßstab bestimmt. Die Versuche wurden auf der Kläranlage Aachen-Soers durchgeführt, deren Ablauf eine hohe Qualität mit DOC-Konzentrationen von etwa 5 mg/L aufweist.

Im Vergleich zu den Einzelverfahren, Nanofiltration oder Adsorption, lieferten alle drei Hybridverfahren deutlich bessere Produktwasserqualität mit DOC-Konzentrationen unterhalb von 0,5 mg/L und organischen Spurenstoffkonzentrationen nahe oder kleiner der Bestimmungsgrenze. Falls eine weitgehende Entsalzung nicht erforderlich ist, bilden Nanofiltration-Aktivkohle-Hybridverfahren eine verlässliche und wirtschaftliche Alternative zu Doppel-Membranverfahren bestehend aus Ultrafiltration und Umkehrosmose, die den Stand der Technik darstellen. Die untersuchten Hybridverfahren sind gut geeignet für den Einsatz in der hochwertigen Wasserwiederverwendung.

Aufgrund der geringeren Filtrationsdrücke weisen die Prozesse einen niedrigeren Energieverbrauch auf und produzieren weniger problematische Konzentrate, die im wesentlichen aus Organika und fällbaren, mehrwertigen Ionen bestehen. Es ergeben sich zudem einige Vorteile bei der indirekten Wiederverwendung von Kläranlagenablauf zur Trinkwassergewinnung, z.B. bei der künstlichen Grundwasseranreicherung, da der Salzgehalt des Produktwassers dem natürlicher Wasser ähnlicher ist als das Permeat von Umkehrosmoseanlagen. Die optimale Kombination von Nanofiltration und Aktivkohle hängt von den lokalen Rahmenbedingungen ab, wie beispielsweise Anlagengröße, Rohwassercharakteristik und Anlagenstandort. Angesichts wachsender Wasserknappheit und der Spurenstoffproblematik hat die Kombination von Aktivkohlebehandlung und Nanofiltration das Potential in einer zunehmenden Zahl von Fällen eingesetzt zu werden.

**Stichworte:** Hochwertige Wasserwiederverwendung, Nanofiltration, Aktivkohle, Membranhybridverfahren, organische Spurenstoffe, Entfernung von Massenorganik

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## Abbreviations and Nomenclature

AC	Activated carbon
ANF	Adsorption filtration followed by nanofiltration
ANN	Artificial neural network
AOI	Adsorbable organic iodine
AOP	Advanced oxidation process
APCI	Atmospheric pressure chemical ionisation
BTA	Benzotriazole
BZF	Bezafibrate
BPA	Bisphenol A
BVT	Bed volumes treated
BW	Backwash
CBM	Carbamazepine
Cap NF	Capillary nanofiltration
CAS	Conventional activated sludge
CD	Constant diffusivity
CF	Cross flow
CLA	Clarithromycin
CLOF	Clofibric acid
COD	Chemical oxygen demand
CP	Concentration polarisation
CR	Chemical recovery (= chemical cleaning)
CSTR	Completely stirred tank reactor
CUR	Carbon usage rate
DIATR	Diatrizoic acid
DBP	Disinfection byproduct
DCF	Diclofenac
DNF	Direct nanofiltration
DOC	Dissolved organic carbon
EBCT	Empty bed contact time
EDC	Endocrine disrupting compound
EDTA	Ethylenediaminetetraacetic acid
EC	European Commission
EE2	17 $\alpha$ -Ethinylestradiol
EEM	Excitation emission matrix
EfOM	Effluent organic matter
EQS	Environmental quality standard
ERY	Erythromycin
ESI	Electrospray ionisation
EU	European Union
FEEM	Fluorescence excitation emission matrix

FI	Fluorescence index
GAC	Granular activated carbon
GPC	Gel permeation chromatography
HPLC	High-performance liquid chromatography
HRT	Hydraulic retention time
IBP	Ibuprofen
ICM	Iodinated contrast media
IOHEX	Iohexol
IOMEPI	Iomeprol
IOPAM	Iopamidol
IPM	Iopromide
IPR	Indirect potable reuse
LC-OCD	Liquid chromatography - organic carbon detection
LC-MS	Liquid chromatography - mass spectrometry
LC-UVD	Liquid chromatography - ultraviolet detection
LCD	Lignite coke dust
LMH	Permeate flux expressed in L/(m <sup>2</sup> ·h)
LOD	Limit of detection
LOQ	Limit of quantification
MAR	Managed aquifer recharge
MBR	Membrane bio-reactor
MF	Microfiltration
MFI	Modified fouling index
MW	Molecular weight
MWCO	Molecular weight cut off
MS	Mass spectrometry
NDEA	N-Nitrosodiethylamine
NDMA	N-Nitrosodimethylamine
NF	Nanofiltration
NFP	Nitrosamine formation potential
NMOR	N-Nitrosomorpholine
NPIP	N-Nitrosopiperidine
NPYR	N-Nitrosopyrrolidine
O&M	Operation and maintenance
PA	Polyamide
PAC	Powdered activated carbon
PEC	Predicted environmental concentration
PEG	Polyethylene glycol
PES	Polyethersulfone
PFOS	Perfluorooctane sulphonic acid
PhAC	Pharmaceutically active compounds
PMMA	Polymethylmethacrylate



PNEC	Predicted no effect concentration
PRIM	Primidone
PTFE	Polytetrafluoroethylene
QSAR	Quantitative structure-activity relationship
QSPR	Quantitative structure-property relationship
RI	Refractory index
RO	Reverse osmosis
ROX	Roxithromycin
RSSCT	Rapid small-scale column test
SAT	Soil aquifer treatment
SCADA	Supervisory control and data acquisition
SD	Standard deviation
SDI	Silt density index
SMP	Soluble microbial product
SMX	Sulfamethoxazole
SPE	Solid phase extraction
SUVA	Specific ultraviolet absorption
TDS	Total dissolved salts
TMP	Transmembrane pressure
TMP	Trimethoprim
TOC	Total organic carbon
UF	Ultrafiltration
UV	Ultraviolet radiation
UVA	Ultraviolet absorption
UV254	Ultraviolet absorption at 254 nm
WFD	Water Framework Directive
WWTP	Wastewater treatment plant

## Notations for Equations

<b>Term</b>	<b>Symbol</b>
Acid dissociation constant	$pK_a$
Area	A
Bed volumes	BV
Concentration of species	c
Density	$\rho$
Diameter	d
Dynamic viscosity	$\eta$
Equilibrium adsorbent-phase concentration of adsorbate	$q_A$
Freundlich adsorption capacity parameter	$K_F$
Freundlich adsorption intensity parameter	n
Length	L
Mass	M
Mass flux of compound	$\dot{m}$
Membrane constant for temperature dependency	U
Octanol water distribution coefficient	$\log D$
Octanol water partition coefficient	$\log K_{ow}$
Permeability	A
Permeate flux	J
Pressure	p
Pressure loss	$\Delta p$
Removal rate / rejection	R
Reynolds number	Re
Temperature	T
Temperature correction factor	TCF
Time	t
Transmembrane pressure	TMP
Velocity	v
Volume	V
Volumetric flow rate	Q

## ACKNOWLEDGEMENTS

This thesis developed over a period of five years during my time at the Department of Chemical Engineering of RWTH Aachen University, mainly in course of the EU project "Reclaim Water - Water reclamation technologies for safe artificial groundwater recharge" (contract number: 018309) and the AiF project "Nanofiltration combined with adsorption on powdered carbon for the removal of trace organic substances from wastewater treatment plant effluent" supported by the German Federal Ministry of Economics and Technology through the German Federation of Industrial Research Associations "Otto von Guericke" (AiF project number 14773 N1). The support of the funding agencies is most gratefully acknowledged.

I am indebted to many people who contributed to the success of this thesis, in particular Prof. Dr.-Ing. Thomas Melin for the supervision of my work and his skilful guidance as well as for giving me the opportunity to conduct this research, collaborate in a number of research projects and grow in an atmosphere of freedom, confidence and responsibility, Prof. Dr.-Ing. Martin Jekel for interesting discussions, inspirations based on his broad experience, and for accepting the task as second examiner, Prof. Dr.-Ing. Matthias Wessling for inspiring insights, very valuable support of my thesis, guidance regarding the nanofiltration experiments and particularly serving as examiner, Prof. Dr.-Ing. Thomas Wintgens for his scientific and practical support and all the opportunities, which developed due to his talents in networking and project development, and Dr. Süleyman Yüce for fruitful discussions and great support at many points. I am very grateful to Dr. Silvio Beier for all his feedback and support in the final compilation of my thesis. I thank all our cooperation partners who supported my thesis, particularly Guido Fink and Dr. Thomas Ternes (BFG, Koblenz), Dr. Saed Baghoth, Dr. Saroj Sharma and Prof. Gary Amy (UNESCO-IHE Delft), Dr. Adriano Joss, Dr. Martin Krauss, Dr. Lubomira Kovalova and Prof. Juliane Hollender (EAWAG), Dr. Mathias Ernst (TU Berlin), Dr. Kai Lehnberg and Prof. Wolfgang Dott (RWTH Aachen University Hospital), as well as Frederik Spenkelink, Dr. Harry Futselaar and Dr. Erik Roesink (Norit X-Flow). I further wish to acknowledge the bachelor, master and diploma students as well as student workers for conducting large parts of the practical work (in chronological order) Markus Linden, Eva Kretschmar, Jochen Herr, Michael Gropp, Le Anh Thu Nguyen, Daniela Schmitz, Fangfang Zhao, Christian Staaks, Raquel Lopez, Christian Rauchholz, Burkhard Ohs, Yong Tian, Rachid Nismy as well as the laboratory staff, explicitly Sybille Hanisch, Sandra Gelbach and Gerd Spalding for high quality analytical work and support of the students. I thank Thomas Zobel and his team for the support during the experiments at the wastewater treatment plant Aachen Soers, and all companies donating the adsorbents we used: Norit Deutschland GmbH, RWE Power, Chemviron and Donau Carbon.

I finally wish to express my gratitude to my father and my mother for all their support and giving me all possible freedom. The biggest supporter of my thesis was my wife Ulrike and I thank her for encouraging me, having tons of patience and for the joyful time between the hours in front of the computer.

Aachen, July 2011



# 1 Introduction

## 1.1 Problem definition

During the last two decades water reuse has become a key element in integrated water resources management under water scarcity conditions. In terms of quantity wastewater treatment plant effluent represents a highly reliable water source but quality aspects prevent high-quality water reuse without advanced water treatment due to the pollution with numerous microbial, organic and inorganic contaminants posing severe health risks (Bixio and Wintgens, 2006, Asano *et al.*, 2007). Water reclamation applications such as indirect or even direct potable reuse target therefore at a complete removal of pathogens and trace contaminants to minimise the risk and reach drinking water quality (Wintgens *et al.*, 2008). As health based criteria for the majority of micropollutants such as pharmaceuticals and endocrine disruptors are not yet established (Kampa *et al.*, 2010) full scale systems apply treatment trains for water reclamation and reuse based on the multi-barrier principle combining several unit processes to remove these unwanted pollutants to the parts-per-trillion level corresponding to the usual detection limit of the analytical methods.

Double membrane processes combining porous membranes with reverse osmosis followed by advanced oxidation represent the state of the art in advanced water treatment for high-quality water reuse (Bixio and Wintgens, 2006; Asano *et al.*, 2007). Most of the large scale systems for planned indirect potable reuse rely on this treatment train. Some prominent examples are the Groundwater Replenishment System in Orange County, CA, the NEWater reclamation plants in Singapore, and the Western Corridor Recycled Water Project in Brisbane, Australia. Although very effective for the elimination of the contaminants, the double membrane process is associated with high capital and operating cost, and involves the use of chlorinated chemicals to suppress membrane fouling. Furthermore cost-efficient methods for the treatment of RO concentrate containing salts, nutrients, disinfection by-products and micropollutants are not yet available. In certain cases, for example in direct potable reuse, the product water might even require a post-treatment such as re-mineralisation.

Against this backdrop, nanofiltration provides an interesting alternative to reverse osmosis with a number of advantages in particular lower rejection of monovalent salts and thus less problematic membrane concentrates (Bellona and Drewes, 2007). The lower operating pressure leads to reduced energy demands of 0.6 - 1.2 kWh/m<sup>3</sup> compared to 1.5 - 2.5 kWh/m<sup>3</sup> with RO (Asano *et al.*, 2007). While nanofiltration builds an excellent barrier against microbial contaminants including viruses on the same level as reverse osmosis (Trussell *et al.*, 2000; Asano *et al.*, 2007) the rejection of certain small-size organic contaminants is often lower than in reverse osmosis systems (Bellona *et al.*, 2004, Yoon and Lueptow, 2005). To achieve a comparable removal of micropollutants, nanofiltration has to be combined with additional separation processes such as adsorption to activated carbon (Verliefde, 2008).

## 1.2 State of the art and knowledge gaps

### 1.2.1 Activated carbon and nanofiltration

As standard method for organics removal, several projects (Snyder *et al.*, 2007; Metzger, 2010; Zwickelpflug *et al.*, 2010) investigated the behaviour and optimisation of activated carbon in effluent treatment. Likewise nanofiltration (NF) was covered in a number of research projects during the last decade, particularly for the removal of micropollutants (*e.g.* Schäfer *et al.*, 2005; Nghiem *et al.*, 2005; Drewes *et al.*, 2008; Verliefde, 2008; Yangali Quintanilla, 2010). Nanofiltration for the removal of organic micropollutants has also been already employed in large scale projects such as at the Méry-sur-Oise water treatment plant (Beros *et al.*, 2003) where nanofiltration ensures the safe removal of pesticides from surface water for drinking water production.

In a comprehensive literature review Bellona *et al.* (2004) identified the main factors affecting the rejection of organic solutes in nanofiltration and reverse osmosis. According to his findings, micropollutant properties characterised by molecular weight, molecular size, acid dissociation constant, octanol-water partition coefficient and diffusion coefficient, as well as membrane properties defined by molecular weight cut-off, membrane pore size, surface charge, hydrophilicity and membrane surface roughness, determine the degree of solute rejection. Verliefde (2008) highlighted the importance of the solute charge. He also proposed to add granular activated carbon after nanofiltration in drinking water treatment to adsorb the compounds poorly retained in nanofiltration.

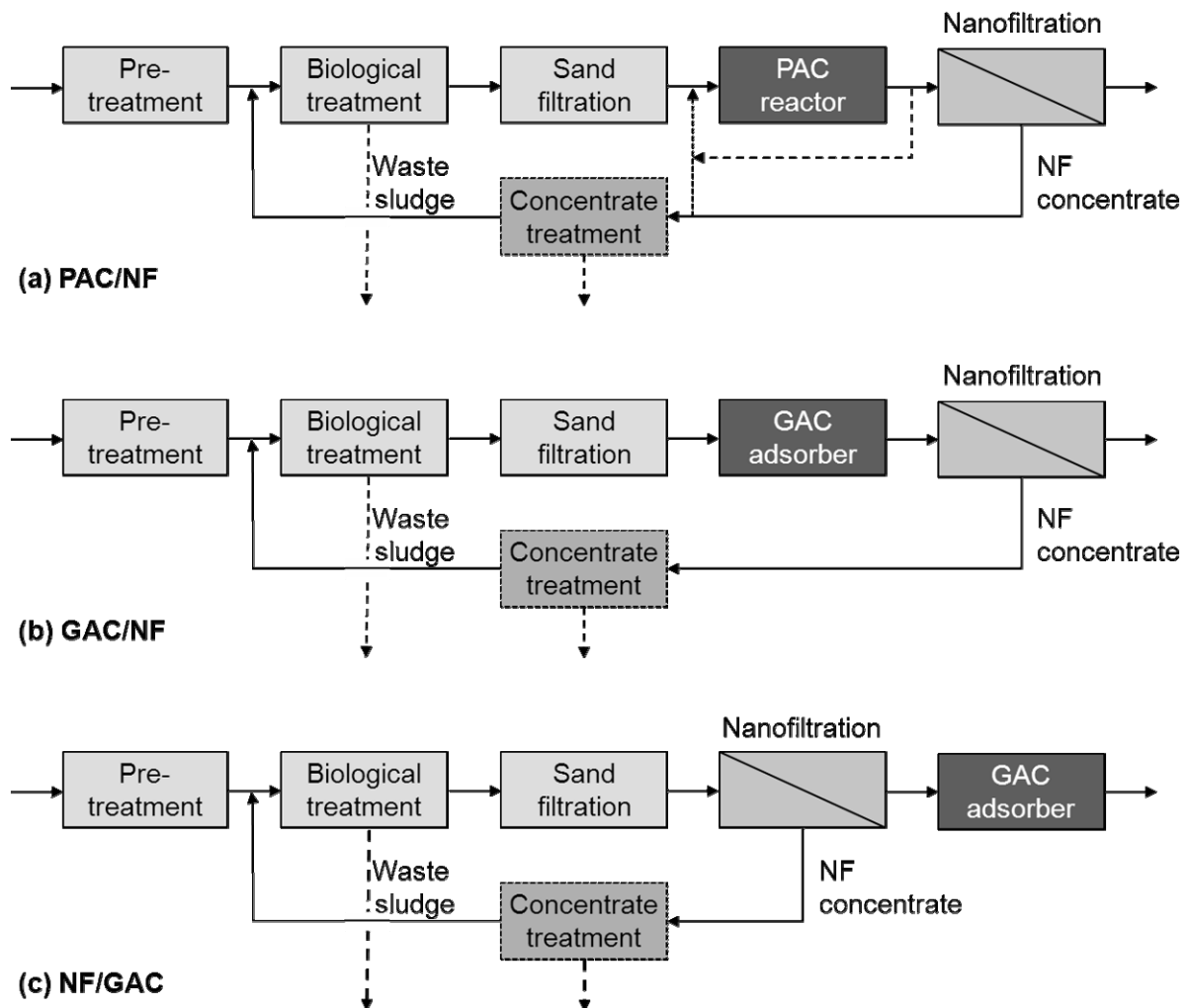
Yangali Quintanilla (2010) further studied the previous work by developing a quantitative structure-activity relationship (QSAR) model combined with an artificial neural network (ANN) model to predict the rejection of organic micropollutants in nanofiltration and reverse osmosis in drinking water treatment and water reuse based on the molecular structure of the target solute. The applicability of the QSAR-ANN model was proven in lab-scale tests. Meanwhile the quantitative structure-property relationship (QSPR) methodology was also successfully transferred to activated carbon (Dickenson and Drewes, 2010). Schrader (2006) investigated direct nanofiltration of effluent from conventional wastewater treatment plants and proved the successful application using spiral-wound modules. Besides a small study on concentrate treatment, his work focused on fouling and anti-fouling strategies due to the high fouling potential of effluent organic matter.

### 1.2.2 Hybrid processes

Ernst (2000) was the first to investigate treatment trains combining nanofiltration and activated carbon for effluent polishing prior to managed aquifer recharge. Using mainly tests at laboratory scale, he identified powdered activated carbon (PAC) and granular activated carbon (GAC) following an 'open' nanofiltration membrane as most efficient and best operable combination. Further biofouling was detected as the main fouling mechanism in

direct nanofiltration and it was concluded that porous membranes should serve as a proper pre-treatment, as long as no fouling resistant or backflushable nanofiltration membranes were available. Since then, several treatment trains combining nanofiltration and activated carbon as shown in Figure 1.1 have been developed in search of optimised hybrid processes and proposed for advanced water treatment:

- PAC/NF process - powdered activated carbon followed by nanofiltration (Meier and Melin, 2005; Meier, 2008),
- GAC/NF process - granular activated carbon followed by nanofiltration (Roorda, 2005), and
- NF/GAC - nanofiltration followed by granular activated carbon (Ernst, 2000; Verliefde, 2008) or NF/PAC if followed by powdered activated carbon (Ernst, 2000)



**Fig 1.1** Treatment trains for high-quality water reuse involving nanofiltration and adsorption to activated carbon

The combination of powdered activated carbon followed by nanofiltration was first applied in landfill leachate treatment (Eltner, 1998; Eilers, 2000; Meier *et al.*, 2002) and later adapted to effluent treatment (Eilers, 2000; Meier and Melin, 2005; Meier, 2008) using capillary

nanofiltration membranes (Futselaar *et al.*, 2002). Investigating the effect of powdered carbon on nanofiltration, Meier (2008) showed that activated carbon particles have a significant influence on the operability, particularly in terms of membrane abrasion, which occurred at high shear rates above  $18,000 \text{ s}^{-1}$ . At lower shear rates particle deposition, mainly the small particle fraction, lead to the formation of a cake layer, which reduced the permeate flux and compromised the solute rejection.

Ernst as well as Meier did not investigate organic micropollutants. Roorda (2005) and Verliefde (2008) touched upon micropollutant removal in activated carbon nanofiltration hybrid processes. A comparative study of the micropollutant removal during the possible process combinations for advanced water treatment as given above has not been performed. Open questions further exist with regard to the long-term behaviour and operability of nanofiltration activated carbon hybrid processes as the previous tests were conducted either in lab- to bench-scale or in pilot scale for shorter periods.

### 1.3 Objective

This thesis aims to identify the optimum process combination of activated carbon and nanofiltration for water reclamation. As all combinations involving nanofiltration can be expected to provide excellent removal of pathogens, the investigation focuses on the removal of organic compounds by the three most promising process combinations, PAC/NF, GAC/NF and NF/GAC. The main objectives are as follows:

- Determination of the capacity of capillary nanofiltration to remove organic micropollutants and identification of the main governing factors.
- Definition of the potential improvement of the organic micropollutant removal by nanofiltration through addition of activated carbon comparing fixed-bed adsorption with powdered carbon.
- Identification of the relevant boundary conditions for the employment of activated carbon, such as carbon usage rate, preferred type of carbon, and influence of bulk organics on the micropollutant removal.
- Elucidation of the fate and removal of effluent organic matter (EfOM) from tertiary effluent during direct nanofiltration compared to activated carbon in combination with nanofiltration applying advanced dissolved organic carbon characterisation methods such as fluorescence excitation-emission spectroscopy.
- Demonstration of the hybrid processes in pilot scale and definition of optimum operation strategies for treatment of waste treatment plant effluent.

### 1.4 Scope and outline of the thesis

The thesis is divided into eight chapters (*cf.* table 1.1). Some of the main chapters are based on peer-reviewed journal publications and conference papers with relevant updates and



additions of previously unpublished data. Following the introduction, chapter 2 sets the scene and describes the scientific and regulatory boundary conditions of the study putting the emphasis on the issue of micropollutants. Chapter 3, 4 and 5 contain the analysis of the applicability of direct capillary NF, PAC/NF, GAC/NF and NF/GAC to remove organic micropollutants from wastewater treatment plant effluent based on experiments in laboratory- and pilot-scale. For these investigations key micro-contaminants were selected known to be refractory in conventional wastewater treatment and hardly biodegradable in natural systems. Chapter 6 investigates the removal of bulk organics in nanofiltration and hybrid activated carbon nanofiltration. Fluorescence excitation emission spectroscopy served as the main method to trace the fate of the different groups in effluent organic matter. Chapter 7 looks into the applicability of capillary nanofiltration for the investigated hybrid processes. It presents relevant findings on fouling behaviour and methods for optimised operation including backflushing as an outstanding feature of capillary nanofiltration. Chapter 8 provides the summary of the thesis presenting a comparison of the investigated treatment trains for high quality water reuse and gives an outlook on promising future research, potential optimisation of the investigated treatment trains and possible areas of application.

**Table 1.1** Outline of the thesis

<b>Chapter</b>	<b>Research focus</b>	<b>Outcomes</b>
1	Brief review of state-of-the-art technologies	Motivation and objectives
2	Background and legal framework for high-quality water reuse	Definition of - treatment requirements - target compounds
3 4 5	Removal of organic micropollutants in - Direct NF - PAC/NF - GAC/NF and NF/GAC	Determination of - removal capacity - process characteristics
6	Fate of bulk organics in nanofiltration activated carbon hybrid processes	Determination of - removal capacity
7	Capillary nanofiltration in hybrid water reclamation processes	Identification of - process stability - operational aspects
8	Conclusions and outlook	Comparison of processes Potential for application Open questions

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activated carbon for the removal of micropollutants from municipal wastewater). Final report of the MicroPoll project, EAWAG on behalf of the Swiss Federal Office for the Environment, Dübendorf, CH, [http://www.eawag.ch/forschung/eng/schwerpunkte/abwasser/strategie\\_micropoll/pak\\_eawag/Abschlussbericht\\_MicroPoll\\_PAK.pdf](http://www.eawag.ch/forschung/eng/schwerpunkte/abwasser/strategie_micropoll/pak_eawag/Abschlussbericht_MicroPoll_PAK.pdf) (accessed 10 June 2011)

## 2 Background

### 2.1 Water reuse

#### 2.1.1 The importance of water reuse

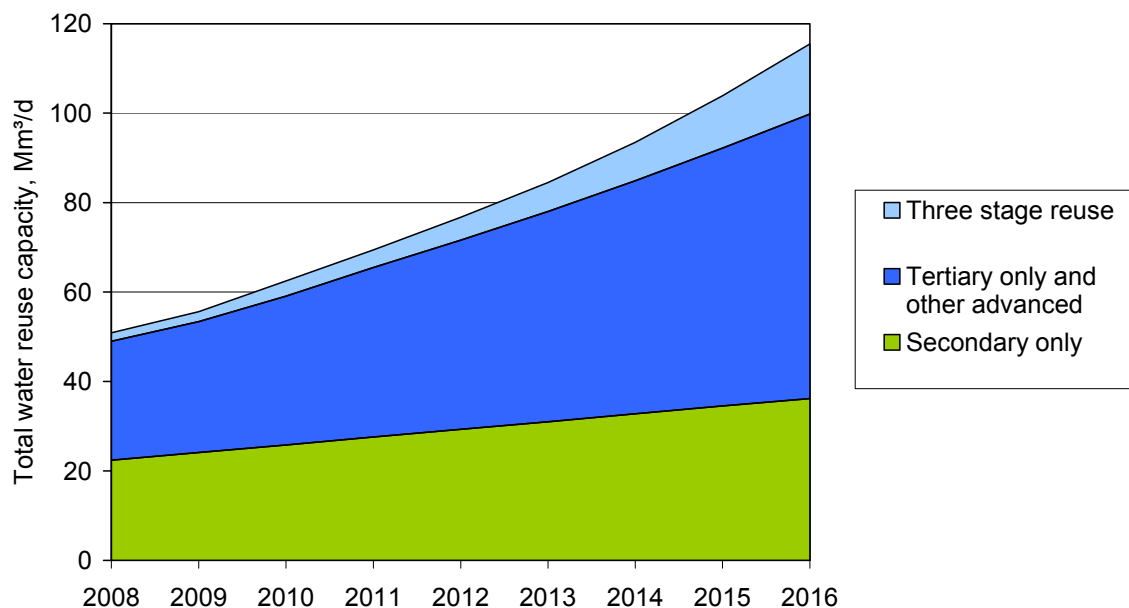
Water scarcity is a global challenge with increased and significant impacts on Europe and many countries worldwide. To date 11% of the European population and 17% of its territory are affected by water scarcity (European Commission, 2007). About 70% of the EU population lives in countries affected by water stress (AQUAREC, 2006). Climate change is exacerbating these global problems, *e.g.* in Australia, Mexico and Southwestern US, as well as in Spain and Cyprus. Ongoing population growth and urbanisation pose additional threat to sustainable water management and safe water supply (Segrave *et al.*, 2007).

The European Commission estimated the economic impacts of drought events in the last 30 last years to be around 100 billion € at EU level (European Commission, 2007). In Europe particularly Mediterranean countries are heavily affected by water scarcity and now prioritise water reuse (EUWI MED, 2007). Alternative water sources such as desalinated seawater and reclaimed water are the answer to these problems whereas water transfers and dams - traditionally used to address increasing demands - become less important due to environmental problems, social implications as well as changing rainfall patterns and long lasting drought periods (GWI, 2009).

After massive investment in energy-intensive desalination mainly in Spain, Israel, Australia, Algeria, and the Gulf region which increased the global production capacity of desalinated water by 67% to 52 million m<sup>3</sup>/d (GWI, 2009), governments are now looking at overall water efficiency and started to prioritise water reclamation and reuse as a solution to water scarcity since water reclamation requires only a third to a fourth of the energy for reverse osmosis (RO) desalination. While the combined approach of seawater desalination and water reuse has proven to be successful in a number of coastal sites such as Barcelona and Singapore, land locked cities have to focus completely on water reuse (Yüce *et al.*, 2012), sometimes even accepting direct potable reuse as practised in Windhoek, Namibia (Menge *et al.*, 2009). With a closed water loop, land locked cities require high-quality water reuse systems mostly based on membrane technology as key barrier. While dense membranes produce permeate of very high quality, the rejected constituents are contained in the membrane concentrate which is typically discharged to the ocean. The Windhoek case where desalination is not yet used also underpins the importance of the control of salinity levels as the ion contents in the supplied water have been slowly rising since the implementation of the reuse schemes. Compared to seawater desalination water reclamation and reuse feature many advantages from the sustainability perspective. GWI (2009) anticipates that the compound annual growth rate at which new water reuse facilities are brought online will reach 18% between 2009 and 2016 due to four main reasons:

- *Growing water scarcity* all over the world, in particular in those countries that depend on non-renewable groundwater resources (North-East China, Central and South-Eastern India, Central Asia, the Gulf, the Mediterranean fringe, Mexico and the Southwestern US)
- *Environmental concerns against traditional water management solutions* (dams and water transfers) support reuse due to the lower use of land and energy and its advantageous effect to the environment such as recharge of aquifers and balancing surface water flows.
- *Financial advantages of water reuse* concepts as the reused water can be marketed and supports the investment in wastewater treatment plants or their upgrading.
- *Decreasing public opposition* to indirect potable reuse (IPR) as successful projects demonstrate the technical and economic feasibility and revealed the positive effects mentioned above.

The strongest growth is expected in the area of high-quality water reuse (*cf.* Figure 2.1) which mostly demands advanced treatment technologies particularly reverse osmosis or nanofiltration membranes as key technology to retain pathogens, bulk and trace organics as well as salts.



**Fig 2.1** Water reuse capacity forecast by treatment grade (GWI, 2009), three stage = dual membrane + AOP

### 2.1.2 Typology

In many arid regions, water reuse has been applied for thousands of years for agricultural irrigation. Due to the lowest quality requirements and high water demands, irrigation has been traditionally prioritised to make use of water of impaired qualities discharged from urban areas. With increasing water scarcity a number of other water reuse applications have been

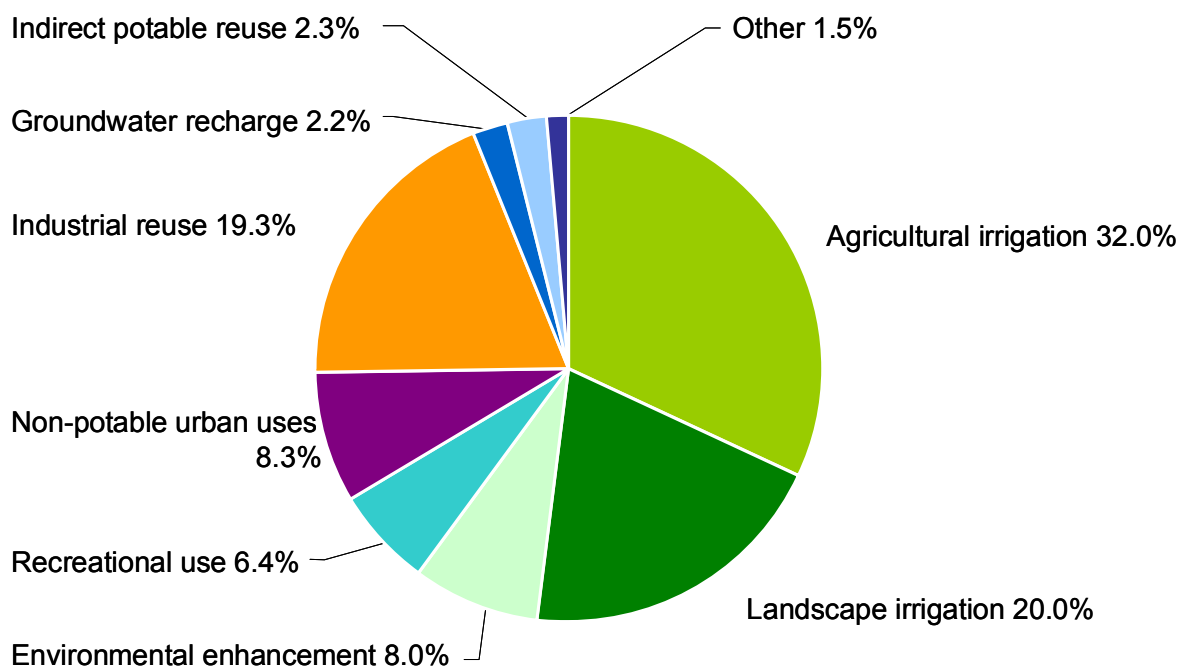
introduced ranging from landscape irrigation and environmental uses to non-potable urban uses and industrial reuse. The highest quality is required for the recharge of aquifers and all applications targeting at different types of potable reuse. Table 2.1 gives an overview of the main water reuse categories, typical applications and related quality requirements.

**Table 2.1** Water reuse categories, examples of applications and quality requirements (modified from Asano *et al.*, 2007)

<b>Reuse category</b>	<b>Typical applications</b>	<b>Quality requirements</b>
Agricultural irrigation	Crop irrigation Commercial nurseries	low to medium
Landscape irrigation	Parks Golf courses Residential	low to medium
Environmental/recreational uses	Streamflow augmentation Fisheries Lakes and ponds	low to medium
Non-potable urban uses	Fire protection Air conditioning Toilet flushing	medium
Industrial recycling and reuse	Cooling water Boiler feed Process water Heavy construction	medium to high
Managed aquifer recharge	Groundwater replenishment Storage Treatment (e.g. SAT) Salt water intrusion barrier Hydrological barrier Soil subsidence control	medium to very high
Indirect potable reuse	Blending in reservoirs Blending in rivers Blending in groundwater	high to very high
Direct potable reuse	Direct pipe to pipe water supply	very high

The current relevance of the different reuse applications can be derived from Figure 2.2. To date about two thirds of the reused water can be attributed to mostly low-grade applications such as irrigation, environmental enhancement and recreational uses. Often economic aspects and high water demands in the target regions drive this type of cascading water use. Another 20% are reused in industrial applications. Still potable and non-potable urban uses as well as groundwater recharge play a relatively small role but are expected to grow rapidly due to a shift to more high-grade water qualities supported by a new water reuse model. GWI (2009) identified a trend towards high-grade water reuse as practised for example in Singapore and explains its background as follows. Instead of agricultural use of reclaimed water, which is often not supported by increased efficiency and thus only leads to an increased water consumption without relieving the pressure on urban water supply, new models for water reuse focuses on the urban water cycle. Accordingly, high quality treated water can on the one

hand be supplied directly to industrial users at a market price recovering the actual costs and on the other hand be returned to the water supply sources such as aquifers or reservoirs. Both measures impact directly on the freshwater demand and help to offset decreasing water availability as observed in many urban areas. This concept is applied in a growing number of cases where integrated urban water management includes high-quality water reclamation as a corner stone to provide water for industrial and drinking water purposes. Relevant examples are the NEWater scheme in Singapore, the Western Corridor in South Queensland, the Southern Californian water management in particular the Los Angeles Edward C. Little facility and Orange County groundwater replenishment scheme, as well as the leading European recycling scheme in Barcelona.



**Fig 2.2** Distribution of global water reuse applications with secondary or higher treatment levels in 2009 by reuse categories (GWI/PUB Water Reuse Inventory, 2009)

### 2.1.3 Key contaminants in water reuse applications

Appropriate management of environmental and public health risks is the key issue in water reuse applications (Asano and Cotruvo, 2004; NRMMC-EPC-AHMC, 2006; Khan and Roser, 2007). Type of hazard and related control measures depend on the water origin and the pollutants. Another main aspect is linked to the exposure to the contaminants during usage of the recycled water. Hence quality requirements are adapted to the specific reuse application and boundary condition (Wintgens *et al.*, 2011). Three classes of constituents are of special concern in water reuse. Health concerns arise primarily from pathogens, *e.g.* enteric viruses, pathogenic bacteria, certain protozoa such as *Giardia* and *Cryptosporidium*, and Helminth eggs (WHO, 2003). Antibiotic resistance genes are a compound class linked to this and are gaining growing attention due to increasing antibiotic resistance challenging modern medical therapy.



Organic constituents of wastewater and stormwater origin are the other main group of contaminants in water reuse. Bulk organics such as effluent organic matter can promote numerous unwanted effects during the advanced water treatment like fouling and clogging due to bacterial growth. Further bulk organics are precursors for the formation of disinfection by-products such as trihalomethanes or nitrosamines. Trace organics including industrial chemicals, pesticides, pharmaceuticals, residual home cleaning chemicals, personal care products and other persistent pollutants are the other main critical and an extremely complex group of organic compounds. It is very complicated to derive scientifically based standards for most of these compounds but due to the absence of these so-called micropollutants in unpolluted natural water sources they are regarded as unwanted contaminants which are to be removed in high-quality reuse applications such as indirect potable reuse.

The third and also very complex compound class is linked to inorganic constituents ranging from heavy metals to salts. Heavy metals are known to have acute or chronic toxic effects on the environment and humans and thus have to be removed. Salinity often has to be controlled to avoid salinisation of water sources and soil. Furthermore inorganic constituents can lead to scaling, *e.g.* in dense membrane systems, or may affect negatively the mineral content of soil. Other main risks and constraints arising from unwanted constituents encompass corrosion, biofilm formation, clogging, staining and foaming which can compromise the acceptability of recycled water.

The complexity of the wastewater contamination and the high risk arising from the broad range of pollutants lead to the development of a very detailed risk assessment and risk management procedure to avoid any negative impact from the usage of recycled water. The Australian Guidelines for Water Recycling (NRMCC–EPHC–AHMC, 2006) defined the following three main principles of sustainable use of recycled water:

- "Protection of public and environmental health is of paramount importance and should never be compromised
- Protection of public and environmental health depends on implementing a preventive risk management approach
- Application of preventive measures and requirements for water quality should be commensurate with the source of recycled water and the intended uses."

## 2.2 Organic micropollutants

The occurrence of organic micropollutants in the aquatic environment, often called 'emerging pollutants' as they became increasingly detectable since the last two decades, have been identified as a global issue. Research has shown the ubiquitous presence of a broad range of pharmaceuticals, personal care products and industrial chemicals in the water cycle, particularly in the effluent of wastewater treatment plants and surface waters in low concentrations from ng/L to µg/L (Ternes, 1998; Heberer, 2002; Kolpin *et al.*, 2002;

Schwarzenbach *et al.*, 2006; Roig, 2010). Pharmaceutical agents of different modes of action such as antibiotics, antiinflammatories, antirheumatics, analgetics, antidepressants, antiepileptics, anti-convulsants, betablockers, contraceptives iodinated contrast media and lipid regulators (Daughton and Ternes, 1999; Snyder *et al.*, 2003; Ternes and Joss, 2006; Roig, 2010) have been detected and it can be expected that with increasingly sensitive analytical methods almost every pharmaceutical agent and its metabolites will be discovered in the aquatic environment and other related compartments such as sediments, soil and sludge. Since the 1990s more than 500 articles were published on pharmaceuticals in the environment covering topics from occurrence, fate and behaviour to risk assessment and toxicity (Roig, 2010).

### **2.2.1 Environmental effects of pharmaceuticals**

Although mostly occurring in concentrations far below their effectiveness in human, these substances are causing concern in water reclamation due to potential hazards for the users and particularly the receiving environmental compartments (Daughton and Ternes, 1999; Roig, 2010). Like all potential toxins, organic micropollutants show dose related effects and risk assessment methodologies have been implemented to predict environmental effects. A simplified risk assessment method is based on the ratio between the predicted environmental concentration PEC and the predicted no-effect concentration PNEC (Ternes and Joss, 2006). If the ratio PEC/PNEC, known as the risk quotient, is above 1, it can be expected that adverse effects are likely to occur. This approach allows an evaluation of the specific environmental or health effect of certain compounds in trace concentrations.

While these investigations are mostly based on acute toxicity data, pharmaceuticals and personal care products are different from conventional organic pollutants as they are designed to cause biological effects on a cellular level. Applied primarily as human or veterinary pharmaceuticals, they can also interact with non target organism and their cellular receptors. Furthermore chronic effects on the environment can occur below the typically investigated acute toxicity (Fent *et al.*, 2006). Due to the higher sensitivity, continuous exposure, multigenerational exposure and potential accumulation along the food chain, effects on aquatic organisms can occur at much lower concentrations than those causing effects in humans as mode of action (Melnick *et al.*, 2002; Fent *et al.*, 2006). De Lange *et al.* (2006) report sublethal effects of pharmaceuticals in the aquatic environment. They detected, for example, a significant decrease in activity as behavioural response of *Gammarus pulex* to fluoxetine and ibuprofen in the range of environmentally occurring concentrations (10 - 100 ng/L). An overview of potential environmental effects of some main pharmaceutical groups is given in Table 2.2.

**Table 2.2** Examples of possible adverse environmental effects of human pharmaceuticals (modified from Sattelberger, 1999 and BLAC, 2003 with information from Fent *et al.*, 2006)

Compound class	Application	Possible or known adverse environmental effects
Analgesics and anti-inflammatory drugs	Pain relief	Side effects on kidneys, proven toxic effect on vultures
Antibiotics	Antimicrobial effects, <i>e.g.</i> bacteriostatics and bactericides	Development of antibiotic resistance <i>via</i> the compound directly or <i>via</i> transfer of antibiotic resistance genes
Psychotropic drugs	Neurological or psychiatric medications, <i>e.g.</i> antiepileptics, antidepressants, anticonvulsants (used as mood stabilisers) Drug abuse, <i>e.g.</i> stimulants opiates	Possibility of neurotoxic effects, alterations of behaviour or enzyme induction
Sex hormones	Sex steroids, <i>e.g.</i> contraceptives, testosterone	Reduced reproductive success, mutation, changes in the gender, <i>e.g.</i> feminisation of fish
Cytostatics	Therapy of cancer and autoimmune diseases	Mutagenicity, carcinogenicity, teratogenicity, infertility

Endocrine disrupting chemicals are one of the most important compound groups and of highest concern within trace organics (Bull *et al.*, 2008). The US EPA (1997) defines an endocrine disrupting compound as "an exogenous agent that interferes with the synthesis, secretion, transport, binding, action or elimination of natural hormones in the body that are responsible for the maintenance of homeostasis, reproduction, development, and/or behavior". Well reported are endocrine disrupting effects of numerous industrial chemicals, *e.g.* plasticisers (phthalates and bisphenol A), surfactants (nonylphenols), flame retardants, pesticides, organohalogenes (dioxin and PCB) and pharmaceuticals such as oral contraceptives (EPA, 2001, Melnick *et al.*, 2002; Snyder *et al.*, 2003; Wise *et al.*, 2011). The most obvious result of endocrine disruption is fish feminisation observed in many streams in Europe and abroad (Öm *et al.*, 2003; Gross-Sorokin *et al.*, 2006; Vigan *et al.*, 2010; Vajda *et al.*, 2011). Some endocrine disruptors show already effects in very low ng/L-concentrations which are close or sometimes even below the limit of quantification. Wenzel *et al.* (1999) report that 17 $\alpha$ -ethinylestradiol (EE2) might cause environmental effects in concentrations below 1 ng/L. Caldwell *et al.* (2008) recommend using 0.35 ng/L as the PNEC for EE2 in surface water. Ecotoxicological and environmental data classify EE2 as being highly relevant to the environment. While conventional sewage treatment plants remove between 50 to 95% of EE2 (Andersen *et al.*, 2003; Johnson *et al.*, 2005; Ternes and Joss, 2006) effluent concentrations may still range in environmentally relevant concentrations.

Bisphenol A (BPA) is another environmentally relevant chemical with endocrine disrupting effects - however not due to its high activity but to the significantly higher effluent concentrations typically in the low  $\mu\text{g/L}$  range. Another group of high concern are cytostatics (Bull *et al.*, 2008) used in the therapy of cancer and autoimmune diseases due to their mutagenicity, carcinogenicity and teratogenicity (Lenz *et al.*, 2007).

### **2.2.2 Technical approaches to address the issue of organic micropollutants**

Following the risk management approach and the legal principle of precautionary environmental and public health protection, multi-barrier concepts are applied to safeguard high quality water reclamation and reuse under all operational standard and emergency conditions (Asano *et al.*, 2007). The multiple barrier approach is a concept of using more than one type of protection or treatment in a series of natural and engineered processes along the water cycle from source water to supplied water to control contamination and increase the robustness of the supply chain. This often includes source protection, multistage treatment, secure distribution system, monitoring and response methods (Page *et al.*, 2011). Membrane systems often represent the key barrier in reuse systems (Bixio and Wintgens, 2006). As explained in chapter 1, their efficiency for pathogen removal is well proven whereas the removal of organic micropollutants and bulk organics is largely depending on the compound properties and the membrane characteristics. Besides membranes, oxidative processes, UV light and activated carbon as well as combinations of these processes are used to remove, degrade and adsorb these contaminants (Snyder *et al.*, 2007).

Supporting these technological end-of-pipe methods are approaches to minimise the discharge of organic micropollutants, *e.g.* through improved source control at known point sources such as treatment of hospital wastewater before indirect discharge into the municipal sewerage, improved disposal of pharmaceutical waste such as collection systems for medicinal products that are unused or have expired, and development of substitutes for identified hazardous compounds to allow phasing-out of toxic compounds (Pronk and Kazner, 2008).

### **2.2.3 Selected organic micropollutants**

There is an ever growing amount of compounds which have been detected and included in fate studies. In a recent, very comprehensive Swiss study on the removal of organic micropollutants from effluent through activated carbon, the fate of more than 50 compounds was investigated (Margot *et al.*, 2011). Although challenging lab capacities and available budgets, this number of included compounds appears still rather small in comparison to the estimated 30,000 organic compounds available on the Swiss market (Margot *et al.*, 2011). In Germany, for example, more than 3,000 active ingredients are licensed as pharmaceuticals and marketed in more than 9,000 preparations (BPI *et al.*, 2006). However, only 120 agents have been detected in the environment (SRU, 2007). Huschek and Krenzel (2003) classified 111 compounds as potentially environmentally relevant based on the quantities sold and the

criteria for environmental risk assessment of the European Medicines Agency (2001). Through metabolites generated through their human metabolism and degradation in the environment the actual number of pharmaceutical related organic micropollutants can be expected to be much higher. Schultz *et al.* (2008) have shown in degradation study of the X-ray contrast media iopromide that it degrades with 12 transformation products some of which were detected also in significant environmental concentrations and are assumed to be very stable to persistent. In the light of these figures it becomes obvious that micropollutant research is still in its infancy and no fate study will be able to investigate 10,000s of compounds. Most of the studies therefore follow the approach to select a number of representative substances, an approach similar to the microbial contaminants in water.

The present study selected 19 compounds of relevance, mainly pharmaceuticals, to investigate the efficiency of nanofiltration in combination with activated carbon to remove organic micropollutants from treated effluent. The compounds were chosen to cover a broad range of compound properties in terms of molecular weight close to the MWCO of the tested membrane, polarity, and charge. All compounds, except 17 $\alpha$ -ethinylestradiol, are known to be present in wastewater in typical concentrations between 100 ng/L and 10  $\mu$ g/L which allows for pilot tests with real concentrations.

An overview of the selected micropollutants is given in Table 2.3. The chemical structures of the selected compounds are given in appendix 1. Roig (2011) presents a comprehensive overview of occurrence and behaviour of pharmaceuticals in conventional wastewater treatment.

The main compound classes covered are industrial chemicals, represented by the complexing agent benzotriazole and the plasticiser bisphenol A, antibiotics (macrolides, sulfonamides and trimethoprim), psychotropic pharmaceuticals (primidone, carbamazepine), antirheumatics and antiphlogistics (diclofenac, ibuprofen), lipid regulators (bezafibrate and clofibrac acid which is a metabolite of the original active agent) and iodinated contrast media. This encompasses a number of top selling pharmaceuticals with known poor degradability. In 2001, the top selling compound in Germany was ibuprofen with an annual consumption of 345 tons/year (SRU, 2007). However, only 1%, equivalent to 3.5 tons leaves the body non-metabolised. Other top sellers are diclofenac (86 tons/year, 70% excretion of non-metabolised agent), sulfamethoxazole (54 tons/year, 33% excretion of non-metabolised agent), and carbamazepine (88 tons/year, 30% excretion of non-metabolised agent) (SRU, 2007). Thus some pharmaceuticals are discharged in amounts of up to 60 tons/year. Based on the average annual wastewater production in Germany of about 5,000 million m<sup>3</sup>, one can expect raw wastewater concentrations of the top selling agents in the range of a few 100 ng/L to several  $\mu$ g/L. Concentrations in this order of magnitude have actually been measured in most cases (Ternes, 1998; SRU, 2007; Roig *et al.*, 2011).

**Table 2.3** Selected organic micropollutants

Compound CAS reg.	Short name	Compound class	MW [g/mol]	pKa **	log K <sub>ow</sub> **	log D pH 7 pH 8	Charge at pH 7
Benzotriazole 95-14-7	BTA	Complexing agent	119.13	0.42; 8.37	1.44	*	0
Bezafibrate 41859-67-0	BZF	Lipid regulator	361.82	3.44	4.25	1.02 0.24	-
Bisphenol A 80-05-7	BPA	Industrial chemical	228.29	9.7	3.32	*	0
Carbamazepine 298-46-4	CBM	Antiepileptic	236.27	0.37; 13.9	2.45	*	0
Clarithromycin 81103-11-9	CLA	Antibiotic (macrolide)	747.96	8.99	3.16	1.17 2.13	+
Clofibric acid 882-09-7	CLOF	Lipid regulator	214.65	3.35	2.57	-0.20 -0.98	-
Diatrizoic acid 117-96-4	DIATR	Contrast medium	613.90	3.40	1.37	-2.23 -3.23	-
Diclofenac 15307-86-5	DCF	Analgesic	296.15	4.15	4.51	1.66 0.74	-
Erythromycin 114-07-8	ERY	Antibiotic (macrolide)	733.93	8.88	3.06	1.17 2.13	+
17 $\alpha$ -Ethinyl- estradiol 57-63-6	EE2	Contra- ceptive	296.41	10.2	4.10	*	0
Ibuprofen 15687-27-1	IBP	Analgesic	206.29	4.47	3.97	1.44 0.44	-
Iohexol 66108-95-0	IOHEX	Contrast medium	821.13	na	-3.05	*	0
Iomeprol 78649-41-9	IOMEPI	Contrast medium	777.07	na	-2.52	*	0
Iopamidol 60166-93-0	IOPAMI	Contrast medium	777.07	na	-2.42	*	0
Iopromide 73334-07-3	IPMI	Contrast medium	791.10	10.2	-2.05	*	0
Primidone 125-33-7	PRIMI	Anti- convulsant	218.26	12.3	0.91	*	0
Roxithromycin 80214-83-1	ROXI	Antibiotic (macrolide)	837.05	8.80	2.75	0.94 1.89	+
Sulfamethoxazole 723-46-6	SMXI	Antibiotic (sulfonam.)	253.28	1.9, 5.60	0.89	-0.53 -1.51	-
Trimethoprim 738-70-5	TMP	Antibiotic	290.32	7.12	0.91	0.56 0.86	+0

\* Log D = Log K<sub>ow</sub>

\*\* according to Ternes and Joss, 2006

na = not available

### 2.2.4 Physicochemical properties

The physicochemical properties of the compounds allow estimating their behaviour in water under different boundary conditions. Besides the basic molecular characteristics such as molecular weight (*cf.* Table 2.3) and size, which govern the rejection in membrane processes mainly, a number of other compound characteristics are used as secondary factors in rejection and adsorption prediction. These factors include the acid dissociation constant  $pK_a$  determining the speciation of the compound at the particular pH. For a monoprotic acid the acid dissociation constant  $pK_a$  is defined as

$$pK_a = pH - \log \frac{[A^-]}{[HA]} \quad (2.1)$$

where HA is the acid in its non-dissociated form and  $A^-$  the dissociated form known as the conjugate base of the acid. At  $pH = pK_a$  50% of the compound is dissociated. Complex molecules such as sulfamethoxazole may feature several ionisable functional groups resulting in more than one  $pK_a$  value (*cf.* Table 2.3). Another important factor is the octanol water partition coefficient  $\log K_{OW}$ . It describes the ratio of concentrations of a compound in octanol and water for a neutral solute or at the pH where the solute is in its neutral form. It is defined as

$$\log K_{OW} = \log \frac{[C]_{oct}}{[C]_{aq}} \quad (2.2)$$

High  $\log K_{OW}$  values (above 2) indicate a high affinity to octanol (= hydrophobicity) while compounds with low  $\log K_{OW}$  values, *e.g.* contrast media, are hydrophilic. Ionisable solutes are however insufficiently described by the  $\log K_{OW}$  as they show a different behaviour when present in their dissociated, typically hydrophilic form (Sangster, 1997). This is reflected in the octanol water distribution coefficient  $\log D$ , which is defined as

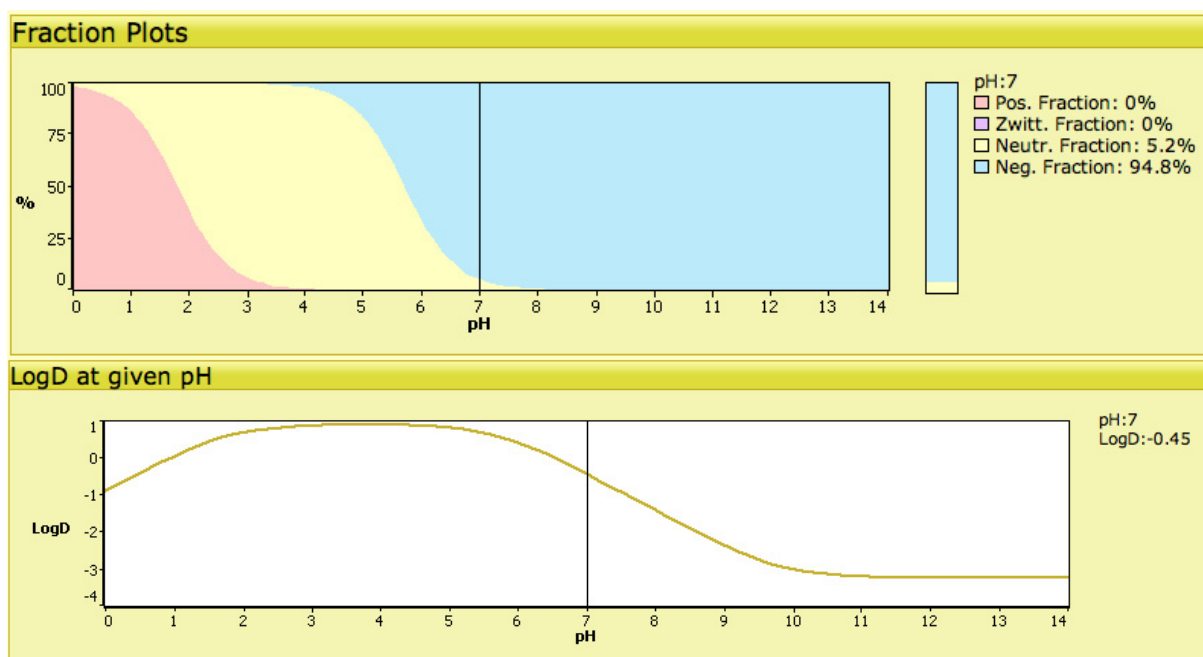
$$\log D = \log \frac{\sum [C_i]_{oct}}{\sum [C_i]_{aq}} \quad (2.3)$$

where the subscript  $i$  corresponds to the ionised and unionised forms. Different experimental and theoretical methods are available to determine the  $\log D$  of a solute. If the solute pH is not far from the  $pK_a$  of the compound, the  $\log D$  can be estimated according to Buchwald and Bodor (1998) to:

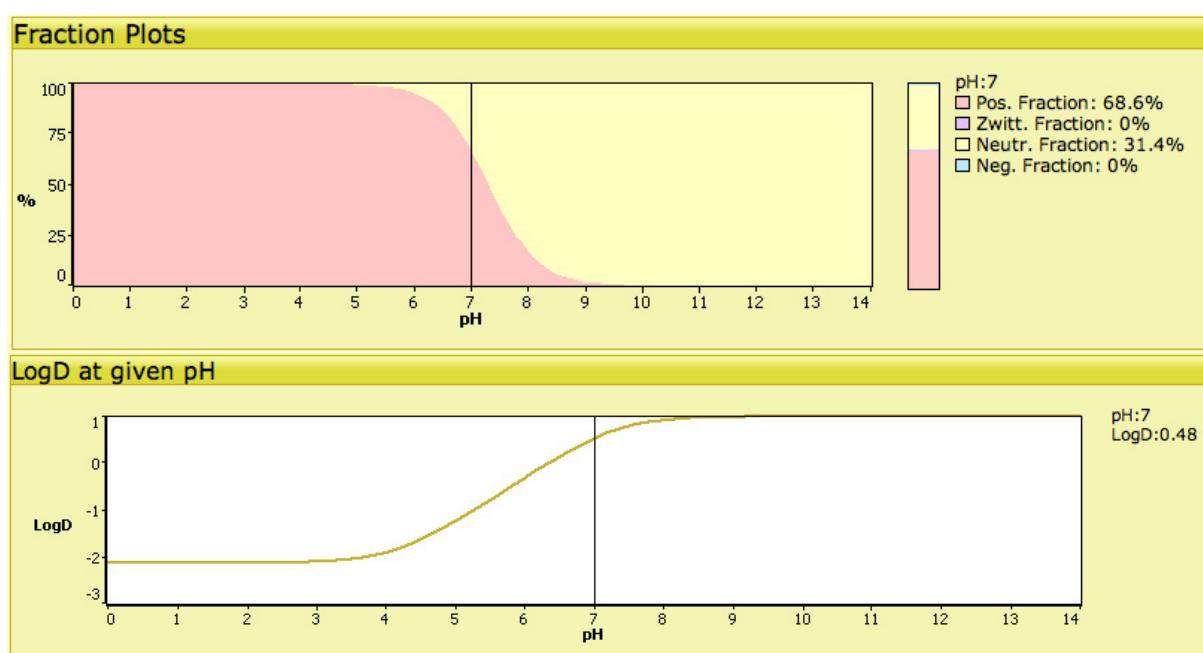
$$\text{for acids: } \log D = \log K_{OW} - \log (1 + 10^{pH - pK_a}) \quad (2.4)$$

$$\text{for bases: } \log D = \log K_{OW} - \log (1 + 10^{pK_a - pH}) \quad (2.5)$$

In other cases the  $\log D$  has to be determined experimentally or can be predicted based on a QSPR approach. The  $\log D$  values in Table 2.3 were calculated with the ADME/Tox Web Software. For compounds with  $pK_a$  close to pH the formulas above were used.



**Fig 2.3** Speciation and log D calculation for sulfamethoxazole (ADME Tox Web software)



**Fig 2.4** Speciation and log D calculation for trimethoprim (ADME Tox Web software)

Figure 2.3 and 2.4 present examples of the speciation of two ionic pharmaceuticals at different pH values and the log D at given pH. While sulfamethoxazole and trimethoprim have similar log  $K_{OW}$  values (0.9) they show a completely different log D behaviour at different pH values.

An overview of the speciation and log D of all ionic micropollutants selected for this investigation is given in appendix 2.



### 2.2.5 Reuse guidelines and legislation

Unlike the United States (EPA, 2004) and Australia (NRMMC–EPHC–AHMC, 2006, 2008, 2009a, 2009b), Europe has not developed specific guidelines for water reuse. However, some member states such as Spain have issued national guidelines (Spanish Official Bulletin, 2007) to promote water reuse and avoid environmental and health risks linked to this. Currently high-quality water reuse including potable reuse is not covered in any legislation of the EU and its member states. For EU member states, the EU directives define the framework for integrated water resources management and environmental quality standards (EQS). The Water Framework Directive (2000) and the Urban Waste Water Treatment Directive (1991) are of particular importance for reuse. Article 12(1) of the Urban Waste Water Treatment Directive states that treated wastewater shall be reused whenever appropriate. However it does not define the required boundary conditions and criteria. A detailed overview of the European legislation with regard to water reuse is given in Hochstrat *et al.* (2008). The most important directive for indirect potable reuse is the Drinking Water Directive (1998). Furthermore, depending on the reuse path the Groundwater Directive (2006) and the future Surface Water Directive (EC, 2006; EC, 2008) define the acceptable EQS to achieve the good chemical status of the respective water bodies. This determines also raw water qualities for drinking water production, in the case of the Surface Water Directive particularly with regard to priority substances according to Annex X of the Water Framework Directive (2000).

The Californian regulations issued by California Department of Public Health (CDPH, 2009) are most advanced in defining the requirements and quality standards for high quality water reuse. Currently the Californian water recycling policy aims to increase water recycling significantly by 1.2 billion m<sup>3</sup>/year till 2020 and thereafter by 2.4 billion m<sup>3</sup>/year till 2030. Chapter 7.3 of the Californian Safe Drinking Water Act and related Statutes (CDPH, 2011) covers direct and indirect potable reuse. In the Californian legal context "*direct potable reuse* means the planned introduction of recycled water either directly into a public water system, ..., or into a raw water supply immediately upstream of a water treatment plant. ... *Indirect potable reuse for groundwater recharge* means the planned use of recycled water for replenishment of a groundwater basin or an aquifer that has been designated as a source of water supply for a public water system, ... and ... *surface water augmentation* means the planned placement of recycled water into a surface water reservoir used as a source of domestic drinking water supply" (CDPH, 2011). The California Water Code does not yet define maximum concentration levels and criteria for potable reuse. However, the ongoing regulatory efforts are detailed in §13560. It is requested to adopt criteria for indirect potable reuse for groundwater recharge by 31 December 2013 and furthermore to investigate and report on direct potable reuse by 31 December 2016 (CDPH, 2011). A summary of the currently applied Californian regulation on groundwater recharge can be found in Wintgens *et al.* (2012).

### 2.2.6 Micropollutant legislation

Organic micropollutants are partly covered in European legislation (Ternes and Joss, 2006; Kampa *et al.*, 2011). The Water Framework Directive (WFD) requires good status of water bodies (surface water as well as groundwater) by 2015. The good chemical status is defined through a range of environmental quality standards (EQS) established for chemical substances at European level. The WFD requests a periodic review of the list of hazardous substances to ensure inclusion of new critical compounds. The current list of 33 priority substances (Directive 2008/105/EC) comprises the following classes of contaminants: Alkylphenols, brominated flame retardants, chlorinated alkanes, chlorinated benzenes, selected heavy metals, herbicides, insecticides, and some other biocides, polyaromatic hydrocarbons and tin organics. Further 14 substances including bisphenol A (BPA), ethylenediaminetetraacetic acid (EDTA) and perfluorooctane sulphonic acid (PFOS) are under review as possible priority substances (Directive 2008/105/EC). Besides three other compounds, diclofenac is discussed as additional priority substance for review (Bundesrat, 2011). European law differentiates between priority substances (= harmful) and priority hazardous substances (= extremely harmful), which are a subset of priority substances. Concentrations of priority and priority hazardous substances must meet the EQS by 2015. In addition to this, priority hazardous substances have to be phased out by 2025. Pharmaceuticals are not yet covered in European legislation. Several member states, however, have started to address the issue of trace concentrations of pharmaceuticals in water. Based on the precautionary principle Germany applies 0.1 µg/L as EQS for several emerging micropollutants such as pharmaceuticals in surface waters. In March 2011, the German Federal Council approved the surface water regulation (Bundesrat, 2011) defining EQS for 167 substances and included in addition to the substances of the Directive 2008/105/EC also two pharmaceuticals. They defined an EQS of 0.1 µg/L for sulfamethoxazole and 0.5 µg/L for carbamazepine.

Switzerland has chosen a different approach (Geiger *et al.*, 2009). Based on an ecotoxicological approach, Ort *et al.* (2009) have shown that current diclofenac concentrations in Swiss surface waters are expected to exceed the corresponding water quality criterion of 0.1 µg/L and propose to upgrade WWTPs for further reduction of micropollutants. The Swiss Federal Office for the Environment proposed to modify the Swiss water protection ordinance (and select five indicator compounds, which have to be reduced by 80% during wastewater treatment (*i.e.* conventional treatment plus advanced treatment): Carbamazepine, diclofenac, sulfamethoxazole, benzotriazole and mecoprop (a herbicide). A final decision on the exact procedure, such as identification of relevant WWTPs, monitoring, removal rates etc. is still pending.

The drinking water situation is more complex. For hazardous substances the input to groundwater has to be prevented (= zero input) while for other compounds (*e.g.* salts) the discharge into groundwater has to be limited below the maximum allowable concentrations.

## 2.2.7 Quality requirements for high quality water reuse

Table 2.4 presents an overview of quality requirements for high-quality water reuse (modified from Joss *et al.*, 2009).

**Table 2.4** Comparison of typical concentration of pollutants after biological treatment (Metcalf & Eddy, 1979; Gujer, 1999; Henze *et al.*, 2002; Tchobanoglous, 2003), requirement for indirect groundwater recharge (Bixio and Wintgens, 2006), proposed quality for direct groundwater recharge and drinking water quality requirement (The Council of the European Union, 1998)

Parameter	unit	Secondary effluent	Polishing goal for indirect infiltration	Polishing goal for direct infiltration	Drinking water quality
pH		6.7 - 7.5	7 - 9	>6.5 and <9.5	>6.5 and <9.5
Conductivity	mS/cm	0.7 - 1.2	0.7	<0.7	<2.5
TSS	mg/L	5 - 25			
COD	mg/L	5 - 50	70 - 100	<5	<5
TOC	mgC/L	15 - 40		<0.5 **	
Total N	mgN/L	5 - 40	<5.6	<5.6	
NH <sub>4</sub> <sup>+</sup>	mgN/L	0 - 2	<0.2	<0.4	<0.4
NO <sub>2</sub> <sup>-</sup>	mgN/L	0		<0.4	<0.4
NO <sub>3</sub> <sup>-</sup>	mgN/L	5 - 40	<5.6	<5.6	<11.3
Total P	mgP/L	0 - 1			
PO <sub>4</sub> <sup>3-</sup>	mgP/L	0 - 1			
SO <sub>4</sub> <sup>2-</sup>	mgS/L	20 - 50	30	<30	<250
As	µg/L		5	<10	<10
B	mg/L		0.2	<1.0	<1.0
Cd	µg/L	0.3 - 1.5	3	<5.0	<5.0
Cl-	mg/L	30 - 90	100	<250	<250
Cr	µg/L	20	25	<50	<50
Hg	µg/L		0.5	<1.0	<1.0
Pb	µg/L	10 - 30	5	<25 <10 in 2013	<25 <10 in 2013
Zn	µg/L	40 - 300			
Micropollutants	µg/L	0.001 - 100	<0.1	*	*
NDMA	ng/L		<10	<10	
E. Coli	N/100 mL				0
Enterococci	N/100 mL				0
Faecal coliforms	CFU/100mL	10 <sup>4</sup> - 10 <sup>6</sup>	<10 <sup>4</sup>	0	0
Faecal streptoc.	CFU/100mL	10 <sup>4</sup>		0	0
Helminth ova, Giardia	1/L	200	<1	0	0

\* depending on compound

\*\* Californian standard (if injectant consists to 100% of reclaimed effluent)

## 2.3 State of the art treatment

### 2.3.1 Technological benchmarks in water reuse

For the European water reuse context, Bixio *et al.* (2008) propose five benchmark treatment trains for different reuse applications:

1. *Advanced disinfection* as required in almost all the treatment trains,
2. *“Title 22” benchmark* comprising of coagulation/flocculation, sedimentation, filtration and disinfection step for unrestricted irrigation,
3. *High-quality benchmark* comprising of secondary effluent, MF/UF, RO, and back-up disinfection for high-quality water reuse including managed aquifer recharge, direct and indirect potable reuse, and high-grade process water applications,
4. *“WHO Guidelines” benchmark* consisting of secondary effluent and maturation ponds for unrestricted agricultural irrigation with reclaimed water, and a
5. *“Natural-step” benchmark* covering secondary effluent followed by constructed wetlands with or without maturation ponds intended to meet quality requirements for recreational and environmental uses.

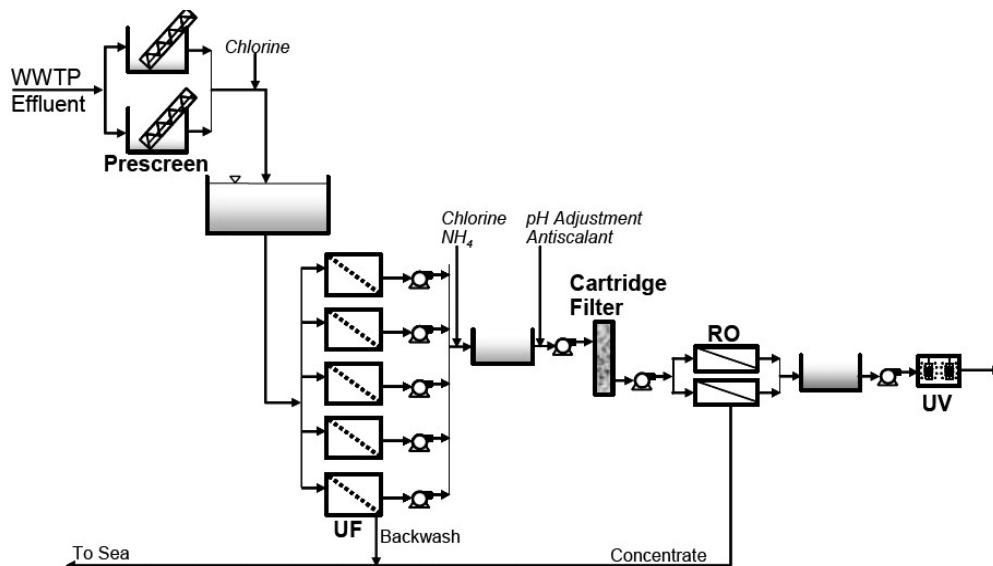
The different treatment trains and full-scale examples are described in the AQUAREC water reuse manual (Bixio and Wintgens, 2006).

### 2.3.2 Dual membrane filtration

Since the pilot studies of the Orange County Water District, double membrane systems followed by AOP are regarded as the benchmark in high-grade water reclamation and reuse. They provide the highest water quality with very low concentrations of organic and inorganic compounds (*cf.* Table 2.5). Reverse osmosis serves here as the main barrier against pollutants. However, as RO membranes are susceptible for fouling, biofouling and scaling, some preventive measures in terms of pre-treatment of the feed water have to be taken to safeguard a stable and economic operation of the RO stage. Figure 2.5 depicts a typical treatment train including the dosage of chemicals such as antifoulants and antiscalants as well as pre-treatment with membranes to reduce bacteria, suspended solids and foulants prior to RO treatment. Many full scale plants rely on additional post-treatment before water reuse to remove small size molecules such as nitrosamines known to be carcinogenic. UV and AOP proved to be very efficient in decomposing NDMA and other small refractory micropollutants.

The Wulpen-Torreele-St. André reclamation scheme represents the most prominent European example where this treatment train is applied. It is operational since July 2002 after pilot tests from 1997-99. In order to reduce the extraction of natural groundwater for potable water production and push back the saline intrusion at the Flemish coast of Belgium, 2.5 million m<sup>3</sup>/year of reclaimed water is infiltrated in the dunes *via* infiltration ponds. The recharged water is recaptured after a minimum residence time of 40 days in the dune aquifer. The recharge system performs as expected and drinking water quality standards are met (Van

Houtte *et al.*, 2012). The product water is softer than it used to be, adding to the comfort of the customers. As given in Figure 2.5 the secondary effluent from the near-by Wulpen WWTP designed for advanced nutrient removal enters the reclamation plant *via* two parallel pre-screens with 1 mm slots. Before entering the effluent holding reservoir, chlorine is added to control bio-growth. From the effluent reservoir, the water flows to five, parallel UF trains equipped with Zenon Zeeweed 500C. UF filtrate enters a holding reservoir after being chloraminated. From there it is pumped to the RO system. Both scale inhibitor and sulfuric acid are injected to control scaling. A third pump can dose  $\text{NaHSO}_3$  to neutralise free chlorine. Before the RO system equipped with DOW Filmtec 30LE-440, the water passes through a cartridge filter of 15  $\mu\text{m}$  pore size. The RO filtrate enters a reservoir from where it is pumped to the infiltration ponds in the dunes. Prior to conveying the RO permeate to the infiltration site, caustic soda is dosed to increase the pH and UV disinfection is possible if required (Bixio and Wintgens, 2006).



**Fig 2.5** Process flow diagram of the Torreele water reclamation plant treating the effluent of the Wulpen WWTP (Van Houtte and Verbauwhe, 2008)

### 2.3.3 Removal capacity

The removal efficacy regarding the main parameters is shown in Table 2.5. The RO product water complies with all requirements of the drinking water guidelines and the applied standards for infiltration (van Houtte *et al.*, 2012). The infiltration water DOC is around 0.5 mg/L. The total volume of recovered water amounts to 3.5 million  $\text{m}^3/\text{year}$  to safeguard full recovery of the infiltrated water and mixing with ambient groundwater (mixing ratio 70%/30%). Conductivity is reduced from 1200  $\mu\text{S}/\text{cm}$  in the effluent to 300  $\mu\text{S}/\text{cm}$  in the recovered water. All pathogens are fully removed. Organic micropollutants were also almost completely rejected by RO. Only NDMA, NMOR and bisphenol A were still detectable. All compounds were removed below the LOQ during MAR. During the investigation period the UV post-treatment was not in operation. Additional removal is therefore attributed to subsoil processes.

**Table 2.5** Average removal rates of contaminants from WWTP effluent and concentrations of the extracted water of the Torreele reclamation plant and St-André aquifer recharge scheme (Kazner *et al.*, 2012)

	UF removal	UF/RO removal	UF/RO/ MAR removal	Extracted water
	%	%	%	
<i>Bulk organics</i>				
COD	29.5	>72.5	>72.5	< 10 mg/L
DOC	26.5	>90.7	76.3	2 mg/L
<i>Standard parameters</i>				
Ammonia (NH <sub>4</sub> -N)	44.6	88.4	70.5	0.20 mg/L
Nitrate (NO <sub>3</sub> -N)	9.6	90.3	96.8	0.37 mg/L
Total Nitrogen	17.5	>82.0	>82.0	< 2 mg/L
Total Phosphorus	27.3	86.4	72.7	0.06 mg/L
<i>Salinity</i>				
Electrical conductivity	14.6	95.4	82.9	247 µS/cm
<i>Microbiological parameters</i>				
Total bacteria count (22 °C)	99.992	99.999	99.994	2.9 CFU/mL
Total bacteria count (37 °C)	99.592	100	99.999	0.17 CFU/mL
Total coliforms	100	100	100	0 CFU/100mL
E.Coli	100	100	100	0 CFU/100mL
Enterococci	99.999	100	100	0 CFU/100mL
Clostridium spores	100	100	99.996	0.1CFU/100mL
Bacteriophages	99.6	100	97.8	450 PFU/mL
<i>Organic micropollutants</i>				
Benzotriazole	-1.0	66.1	>95.8	< 10 ng/L
Carbamazepine	2.7	>99.8	>99.8	< 2 ng/L
Clarithromycin	-48.1	>98.1	>98.1	< 2 ng/L
Diclofenac	-3.5	>99.2	>99.2	< 2 ng/L
Ibuprofen	-19.5	>99.0	>99.0	< 2 ng/L
Naproxen	30.2	>99.6	>99.6	< 2 ng/L
Sulfamethoxazole	3.6	>97.8	>97.8	< 2 ng/L
N-Ac-SMX	-5.9	>96.9	>96.9	< 10 ng/L
Trimethoprim	30.4	>98.2	>98.2	< 2 ng/L
Primidone	15.4	>96.9	>96.9	< 2 ng/L
<i>Contrast media</i>				
Iomeprol	7.7	>99.7	>99.7	< 2 ng/L
Iopromide	18.9	>99.9	>99.9	< 2 ng/L
Diatrizoate	34.4	>99.95	>99.95	< 10 ng/L
AOI	-25.3	94.5	91.8	< 2 ng/L
<i>EDCs</i>				
Estrone E1	24.8	>90.8	>90.8	< 1 ng/L
Bisphenol-A	50.2	68.5	>89.5	< 5 ng/L
<i>DBPs</i>				
N-Nitrosodimethylamine (NDMA)	-7.2	8.5	>85	< 0.7 ng/L

## 2.4 Conclusions

Water reuse is of rapidly increasing importance as key element in integrated water resources management in Europe and other water stressed regions in the world. While low quality reuse applications such as agricultural use have dominated until now, future reuse is expected to focus more on high-grade water reuse applications to quench the thirst of the growing urban areas.

Membrane systems and in particular UF/RO treatment represent the current state of the art in high-grade water reuse, which provides a product water acceptable for all high quality applications such as surface water augmentation, groundwater recharge and other forms of indirect potable reuse.

In high quality reuse, main compounds of concern are pathogenic microorganisms such as protozoa, bacteria and viruses and chemical contaminants, and above all organic contaminants. Alternatives to UF/RO are nanofiltration based treatment trains which provide a comparable removal of pathogens but often not a complete removal of micropollutants. The present investigation therefore focuses on the removal of micropollutants in NF based advanced water treatment. For this purpose a range of prominent refractory pharmaceuticals and other emerging micropollutants have been selected. They represent a very heterogeneous group of contaminants with different physicochemical properties.

In most cases 100 ng/L can be regarded as acceptable threshold value for micropollutants in surface water augmentation. In groundwater recharge and direct reuse, drinking water standards apply which requires preventing the input of hazardous substances. Most probably this will encompass in future also some pharmaceuticals such as diclofenac and certain industrial chemicals such as bisphenol A. From the legal perspective this would mean that these compounds have to be reduced below the limit of detection.

The environmental and public health effects of the so-called emerging pollutants have not yet been evaluated comprehensively on a sound scientific basis. Due to the high complexity, such as due to chronic effects and effects of mixtures and metabolites, and multi-level effects *e.g.* along generations and food chains, the answers to these questions will remain very challenging.

The present investigation will therefore utilise the presently targeted threshold values, *i.e.* 100 ng/L and below limit of detection respectively. However it must be considered that these targets are more politically motivated than scientifically supported.

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## 3 Removal of organic micropollutants from tertiary effluent by direct capillary nanofiltration

### 3.1 Introduction

Dense membrane processes have been shown to retain micropollutants to a high degree depending on solute and membrane characteristics (Bellona *et al.*, 2004; Verliefe, 2008; Yangali Quintanilla, 2010). When applied in water reclamation, reverse osmosis and nanofiltration typically require substantial pretreatment to reduce the fouling and clogging potential of secondary effluent. Critical constituents encompass suspended solids, organics, inorganic substances, *e.g.* iron and manganese, oil, grease, and erosive substances (Celenza, 1999). The methods of pretreatment are selected based on the target compounds and include depth filtration, microfiltration, ultrafiltration, cartridge filters as well as dissolved air flotation (Asano *et al.*, 2007). Besides these physical methods, chemical methods such as pH adjustment, precipitation, disinfection and dosing of antiscalants are used to further reduce the fouling potential regarding biofouling and scaling (Asano *et al.*, 2007). The treatability of feed water by dense membrane processes is typically tested by the silt density index, SDI, (ASTM, 2002) or the modified fouling index, MFI, (Schipper and Verdouw, 1980). Asano *et al.* (2007) report recommended SDI values of 0 - 3 for NF and RO. While typical secondary effluent has SDI values exceeding the recommended values significantly, porous membranes can reduce the SDI to below 2 (Redondo *et al.*, 2001).

Direct nanofiltration is an alternative treatment approach for nanofiltration where the WWTP effluent or other type of raw water receives no additional pre-treatment. It employs in particular capillary membranes (Duin *et al.*, 2000, Futselaar *et al.*, 2002), but was also shown to be applicable to spiral wound membranes when the dissolved oxygen levels of the feed water are kept minimal (Schrader, 2006). Capillary nanofiltration was already developed in the late 1990's (van der Meer and van Dijk, 1997; Frank *et al.*, 2001) but is still in a stage of research and development. It combines capillary ultrafiltration membranes with an active nanofiltration layer providing two treatment steps in one that allow treating impaired water sources. Raw water may contain higher particle loads up to feed concentrations of about 200 mg/L (Futselaar *et al.*, 2002). Until now it was employed in several studies, mainly in drinking water treatment from surface water and effluent polishing (Duin *et al.*, 2000; Futselaar *et al.*, 2002; Futselaar *et al.*, 2003; van der Bruggen *et al.*, 2003; Roorda *et al.*, 2005; Sayed *et al.*, 2007).

This chapter describes the performance of capillary nanofiltration for removing organic micropollutants from tertiary effluent. As outlined in chapter 1, the rejection mechanism of organic micropollutants by nanofiltration membranes is based on interactions between solute and membrane. Three different interaction types are differentiated: size exclusion by steric hindrance, electrostatic interactions and adsorptive interactions (Schäfer *et al.*, 2003; Nghiem

*et al.*, 2004; Verliefde, 2008, Yangali Quintanilla, 2010). The following influencing factors have been identified:

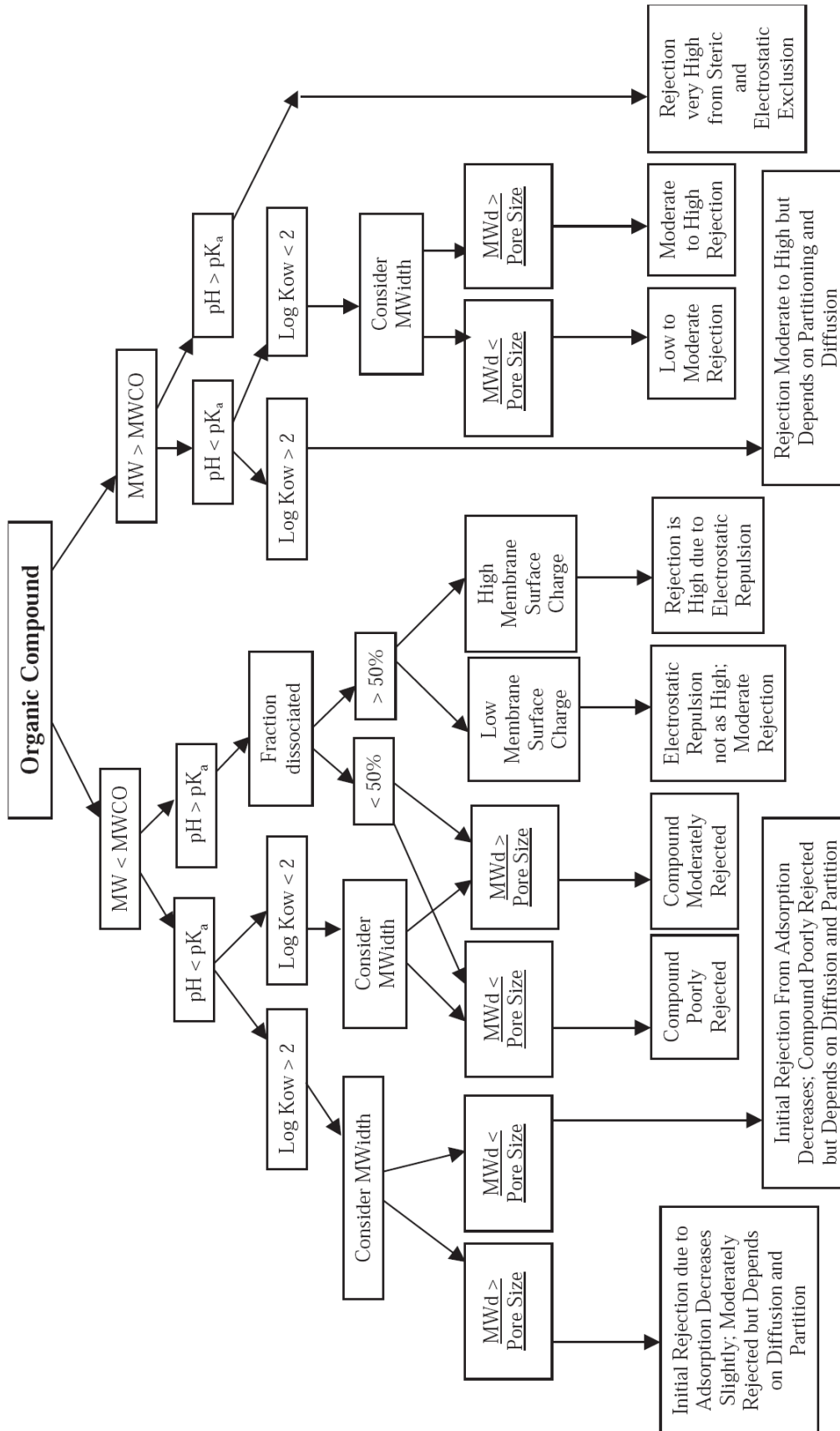
- Membrane properties such as molecular weight cut-off, membrane porosity, membrane morphology, surface charge, and hydrophobicity of the membrane (Bellona *et al.*, 2004, Verliefde, 2008)
- Pollutant properties such as molecular weight, molecular size, solute charge and  $pK_a$ , adsorbability, hydrophobicity and  $\log K_{OW}$  (Bellona *et al.*, 2004, Verliefde, 2008, Yangali Quintanilla, 2010)
- Feed water composition, *e.g.* pH, temperature, and inorganic balance (Verliefde, 2008).

Based on a comprehensive literature review, Bellona *et al.* (2004) proposed a rejection diagram to estimate the micropollutant retention based on solute and membrane properties (*cf.* Figure 3.1).

According to Yangali Quintanilla (2010) the rejection of ionic compounds with negative charge is governed by electrostatic repulsion between the solute and the negatively charged membrane surface. He observed that for neutral compounds whether hydrophilic or hydrophobic, the rejection is mainly influenced by the molecular size characteristics. Yangali Quintanilla further confirmed that the rejection of hydrophilic neutral compounds was poor when their size is smaller than or close to the membrane pore size and hydrophobic neutral solutes ( $\log K_{OW} > 3$ ) are influenced by adsorption effects which dominate the rejection until saturation of the membrane. Additionally, the membrane (surface) properties may be changed due to fouling and thus alter its rejection behaviour (Verliefde, 2008). As a consequence, each compound and membrane pair shows individual rejection patterns.

Most of the nanofiltration studies in micropollutant removal research have been conducted in lab- or bench-scale. However plants in pilot or technical scale can behave differently, as process design and operating conditions such as transmembrane pressure, permeate flux, and recovery (Verliefde, 2008) further influence the rejection of micropollutants. A key phenomenon limiting the rejection in membrane processes is concentration polarisation (Mulder, 2004; Melin, 2007) which can be influenced through a number of operational settings and countermeasures, *e.g.* crossflow velocity, usage of spacer and spacer design, backflush or forward flush cycle and duration, air flush (Salehi, 2008).





**Fig 3.1** Rejection diagram for organic micropollutants during membrane treatment based on solute and membrane properties (adapted from Bellona *et al.*, 2004)

As shown in Figure 3.1, one key aspect of nanofiltration is the partitioning characteristic of the membrane. While porous membranes are typically characterised by the pore size only, the rejection behaviour of dense membranes is mainly determined by the molecular weight cut-off (MWCO) defined as 90% rejection of the smallest molecular weight species. Although a decisive value for the characterisation of membranes, the MWCO is not an absolute factor as it depends on operating conditions and the pore size distribution. According to the pore size distribution, the retention of molecules leads to a typical sigmoidal retention curve, with an either slight or sharp gradient (Verliefde, 2008) influencing the rejection of smaller molecules below the MWCO. Furthermore the MWCO is determined by the operating conditions, as a higher transmembrane pressure might compress the membrane in such a way that the intermolecular space decreases, leading to a lower MWCO. The flow pattern is another factor having impact on mass transfer (Melin, 2007). Generally, a higher crossflow velocity, particularly when kept in the transition phase to turbulent flow, produces a lower MWCO due to a reduction of the concentration polarisation.

This chapter selected different methods and tests to characterise the micropollutant rejection by capillary nanofiltration. Firstly, the rejection of polyethylene glycols was determined under varying operating conditions. Secondly, the retention of a broad range of micropollutants in ambient concentrations as detailed in chapter 2 which cover different compound properties in terms of molecular weight, charge, and hydrophilicity was investigated in short-term pilot tests. Thirdly, lab tests and long-term pilot test employed four main polar persistent compounds to identify main factors influencing the nanofiltration process and gain insight in the long-term behaviour. And fourthly, the rejection of two prominent endocrine disrupting compounds was determined by spiking as their concentrations are usually close to the detection limit of the applied method.

## 3.2 Materials and Methods

### 3.2.1 Selected pharmaceuticals and other micropollutants

Table 3.1 summarises the selected target compounds chosen due to molecular weights close to the MWCO of the membrane and their presence in relevant concentrations. In addition to the compounds in table 3.1, the following substances were analysed but detected in concentrations close to or below the level of quantification ranging from 2 to 10 ng/L depending on the compound: bezafibrate, fenoprofen, florfenicol, ibuprofen, indomethacin, lincomycin, N-acetyl-sulfamethoxazole, naproxen, sulfadimidine, sulfadoxine, sulfamerazine, sulfamethoxine, sulfisoxazole, tiamulin, and trimethoprim. The present investigation selected 17 $\alpha$ -ethinylestradiol (EE2) and bisphenol A (BPA) as endocrine disruptors. Different from the other experiments, the compounds were spiked to the WWTP effluent at concentrations of about 1  $\mu$ g/L to investigate the rejection effects which can hardly be measured reliably at the ambient concentrations of BPA and EE2 which are normally detected in concentrations around 1 ng/L. In lab scale tests with benzotriazole, carbamazepine, sulfamethoxazole and primidone, the compounds were spiked in concentrations between 170 and 3000  $\mu$ g/L.

**Table 3.1** Organic micropollutants selected for direct NF tests

Analytes	Short name	MW g/mol	pK <sub>a</sub>	Log K <sub>ow</sub>	Charge at pH 7	Pilot short	Pilot long	Lab test
Bisphenol A	BPA	228.3	9.7	3.2	0	sp		
Benzotriazole	BTA	119.13	8.37	1.44	0	•	•	sp
Bezafibrate	BZF	361.82	3.44	4.25	-			
Carbamazepine	CBM	236.27	0.37	2.45	0	•	•	sp
Clofibric acid	CLOF	214.65	3.35	2.57	-			
Clarithromycin	CLA	747.95	8.90	3.16	+	•		
Diatrizoic acid	DIATR	613.90	3.4	1.37	-	•		
Diclofenac	DCF	296.15	4.15	4.50	-	•		
Erythromycin	ERY	733.93	8.88	3.06	+	•		
17 $\alpha$ -Ethinylestradiol	EE2	296.4	10.2	4.1	0	sp		
Iohexol	IOHEX	821.14		-3.05	0	•		
Iomeprol	IOMEPR	777.00			0	•		
Iopamidol	IOPAM	777.09		-2.42	0	•		
Iopromide	IPM	791.00	10.2	-2.05	0	•		
Primidone	PRIM	218.25		0.90	0	•	•	sp
Roxithromycin	ROX	837.05	8.80	2.75	+			
Sulfamethoxazole	SMX	253.28	5.60	0.89	-	•	•	sp

(• = analysis of actual concentration, sp = spiking of compound)

### 3.2.2 Sampling and analytical methods

All samples from the pilot tests were taken as 24 h composite samples. An auto sampling unit of MAXX GmbH provided the sampling of the influent and permeate samples with 200 mL each 30 min collected in a 10 L Duran glass bottle and stored at 7 °C. Pharmaceutical concentrations in the feed, permeate and concentrate were analysed by using SPE enrichment prior to LC-MS-MS detection according to methods developed and described by Ternes and Joss (2006) and Ernst *et al.* (2012). The EDCs measurement used a different method with Oasis HLB SPE-cartridges prior to HPLC (Agilent 1100) with a reverse phase column (Thermo HyPurity C18) and detection by an Applied Biosystems triple quadrupole mass spectrometer (API 3000) as described by Lehnberg (2010). All samples were quantified with <sup>13</sup>C or <sup>15</sup>N labelled internal standards. The analytical methods are explained in detail in the appendix.

### 3.2.3 Determination of molecular weight cut-off

A range of polyethylene glycols (Table 3.2) were solved in a concentration of 50 g/L in deionised water as stock solution, and later 150 mL were mixed with 14.8 L of deionised water and 50 mL sodium azide solution (500 mg/L) to suppress biofouling ( $V_{\text{feed, total}} = 15$  L). The NF test unit was flushed four times with deionised water between each test run. The respective feed and permeate samples were analysed with GPC and RI detection. The elugrams were evaluated with the software WinGPC Unity (Polymer Standard Service).

**Table 3.2** Polyethylene glycols used for the MWCO determination

Molecule(s)	MW [g/mol]
Ethylene glycol	62
Diethylene glycol	106
Triethylene glycol	150
Polyethylene glycols	250, 300, 400, 500, 600, 800, 1000

### 3.2.4 Employed membrane

The experiments were run with the capillary nanofiltration membrane NF50 M10 from Norit X-Flow (Futselaar *et al.*, 2002) in different module configurations as given in Table 3.3.

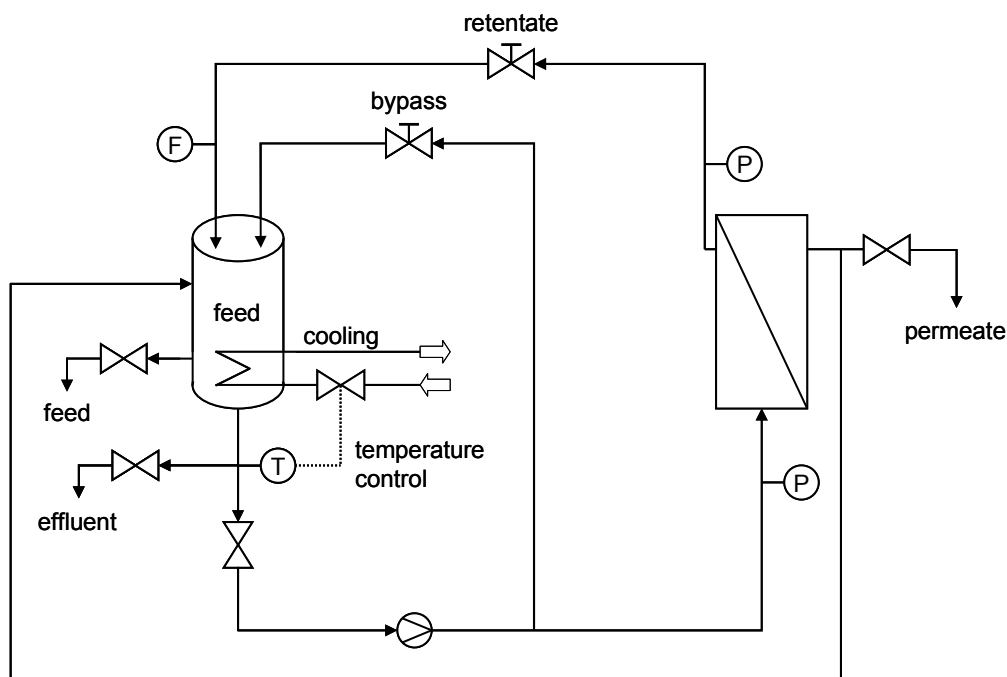
**Table 3.3** Dimensions of tested NF50 M10 modules

	1" module	4" module	8" module
Module type	RX-300	S30-AQ	S225-AQ
Capillary diameter	1.5 mm	1.5 mm	1.5 mm
Module diameter	25 mm	100 mm	200 mm
Module length	300 mm	1047 mm	1537 mm
Membrane area	490 cm <sup>2</sup>	3.6 m <sup>2</sup>	20 m <sup>2</sup>
Employed in	lab-scale tests	pilot tests	pilot tests

All modules were equipped with capillaries of 1.5 mm inner diameter. The membranes are operated in inside-out filtration mode. The composite membrane has a thin active layer of polyamide with a supporting layer of polyethersulfone. According to own tests the clean water permeability was  $12.3 \pm 0.8 \text{ L/m}^2 \cdot \text{h} \cdot \text{bar}$  (demineralised water at  $25 \text{ }^\circ\text{C}$ ). The maximum transmembrane pressure according to the supplier's data is 7 bar. The allowable pH range is 4 to 10 during operation at  $25 \text{ }^\circ\text{C}$  and 3 to 11 during cleaning at max.  $35 \text{ }^\circ\text{C}$ . The temperature range is  $1 - 40 \text{ }^\circ\text{C}$ . The rejection of NaCl is  $35 \pm 5\%$  and of  $\text{MgSO}_4$   $94 \pm 2\%$  (Norit X-Flow, 2006).

### 3.2.5 Nanofiltration test device

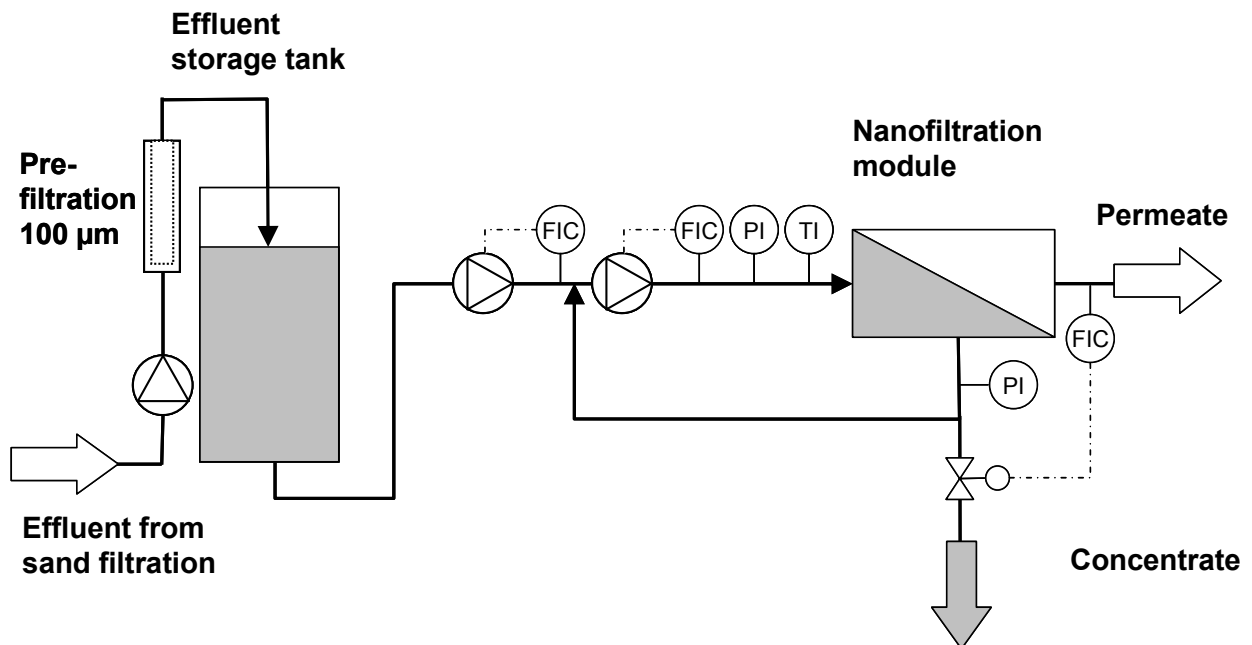
Fig 3.2 shows the schematic of the nanofiltration test device. The lab scale unit accommodates a RX 300 module and operates in crossflow mode. The module contains 40 capillaries of 1.5 mm diameter with a permeable length of the capillaries between the potting of 26 cm. The feed is delivered *via* a high pressure pump to the NF membrane. Operated in recirculation mode the test device allows redirecting retentate and permeate to the feed tank ( $V = 15 \text{ L}$ ). The temperature is kept constant with the help of a cooling circuit in the feed tank. The configuration of the test device incorporates two restrictors to regulate the feed pressure and the crossflow velocity. The crossflow velocity is measured after the restrictor of the retentate. The pressure is measured in front of as well as behind the module. Hence, the transmembrane pressure can be approximated using eq. (3.3). The test device was used for tests with PEG and with benzotriazole, carbamazepine, sulfamethoxazole and primidone. The NF test device was operated for five hours with the micropollutant containing feed prior to taking samples to avoid sorption effects of the weakly sorbing compounds. The pH of the micropollutant experiment was in the range of 8.8.



**Fig 3.2** Experimental set-up of the nanofiltration test device

### 3.2.6 Nanofiltration pilot plant

A schematic diagram of the pilot plant is shown in Fig 3.3. The feed water used for the experiments was the effluent from the WWTP Aachen Soers which was conveyed to a storage tank by a submersible pump. In order to retain coarse particles such as algae from the effluent channel, the water was pre-filtered by a cartridge filter unit equipped with a 100  $\mu\text{m}$  nylon filter element (Contec, Bad Honnef, Germany). The NF pilot plant was operated in feed-and-bleed mode. The nanofiltration unit was fed by two pumps, a centrifugal pump transporting the feed water in the recirculation loop and a booster pump circulating the water in the crossflow loop. All volumetric flow rates were measured by flow meters and controlled by frequency converter controlled pumps linked to a SCADA system operating the pilot unit, all fully automated. The permeate flow was kept constant by a control valve in the concentrate discharge pipe. The SCADA also recorded the standard data, such as pressure, temperature, pH and conductivity measured online as shown in Figure 3.3. The permeate was buffered in a storage tank used as storage for the backflush and sampling point.



**Fig 3.3** Experimental set-up of the NF pilot plant

The NF50 M10 membrane was operated with a transmembrane pressure between 1.5 and 4.0 bar. At the initial phase, the permeate flux ranged between 15 to 25  $\text{L}/\text{m}^2\cdot\text{h}$  and the recovery between 65 and 85 % to determine the optimum operation conditions (*cf.* chapter 8). The flux was then kept constant at 20  $\text{L}/\text{m}^2\cdot\text{h}$  with a recovery of 75%. The membrane was operated in crossflow mode with a crossflow velocity of 1.25 m/s. A backflush was applied every 45 minutes for 1 minute for fouling prevention. The pilot plant treated the effluent from the sand filtration directly for several thousand hours of operation. The pilot tests used 4" and 8" modules. At a flux of 20  $\text{L}/\text{m}^2\cdot\text{h}$  the permeate production is dependent on the module type: 400 L/h for the 8" module and 72 L/h for the 4" module. During the test of the EDC removal,

the selected micropollutants were spiked from a 10 L Duran glass bottle with a peristaltic pump (Ismatec Reglo Analog, Germany) in the stirred effluent storage tank.

### 3.2.7 Selection of operating parameters

Several effects influenced by operating conditions govern the performance of capillary nanofiltration. A crucial aspect for setting the right operating conditions is the mass transfer that is mainly influenced by fluid dynamics and temperature. The temperature affects the viscosity of the aqueous solution, which in turn impacts on fluid dynamics. The Reynolds number  $Re$  is a dimensionless number used to characterise the flow regime. For the flow in a tube,  $Re < 2,300$  is designated to laminar flow pattern (Melin, 2007).  $Re$  is calculated with the following equation:

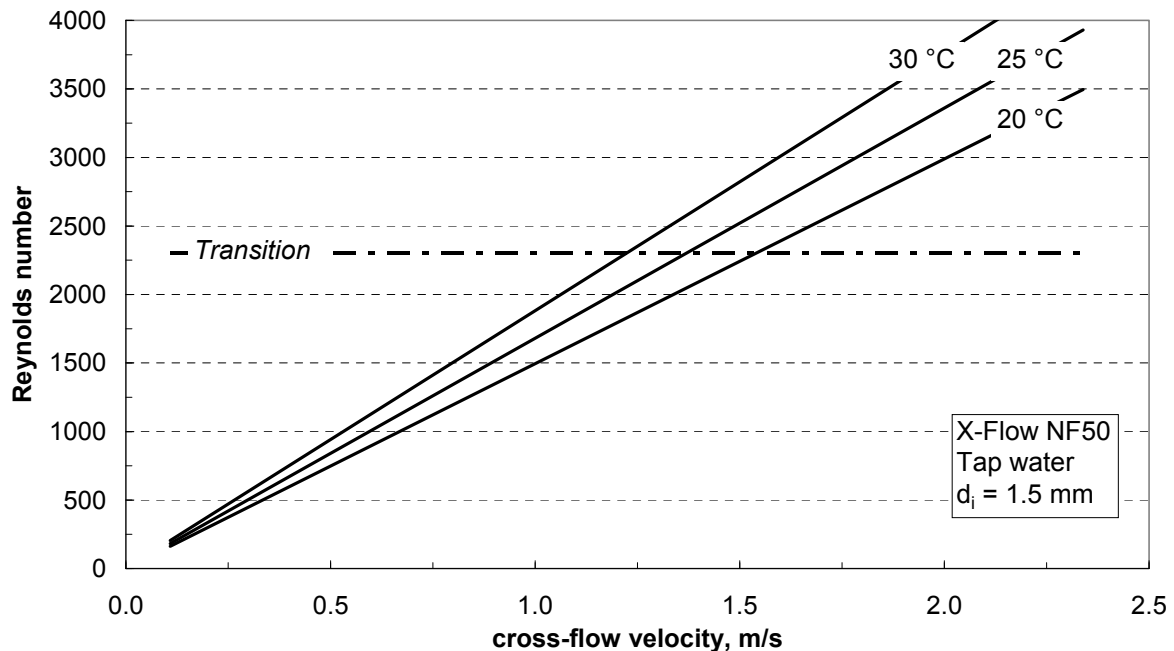
$$Re = \frac{d_h \cdot v \cdot \rho}{\eta} \quad (3.1)$$

where  $d_h$  = hydraulic diameter, m

$v$  = crossflow velocity, m/s

$\rho$  = density of the fluid, kg/m<sup>3</sup>

$\eta$  = dynamic viscosity of the fluid, kg/(m·s)



**Fig 3.4** Reynolds-number *versus* crossflow velocity

Concentration polarisation (CP) is one of the most important factors influencing the rejection of target compounds and the operational performance of the membrane unit (Mulder, 1998). In pressure driven membrane filtration, CP describes the increase in solute, colloid or particle

concentration at the membrane surface on the feed-side and results in deterioration of membrane performance regarding permeability. Furthermore the quality of the permeate decreases as the membrane rejection is governed by the compound concentration at the membrane surface (Ng and Elimelech, 2004; Kim and Hoek, 2005). Improved mass transfer conditions at the membrane induced by feed-spacers and/or higher crossflow velocities can significantly reduce concentration polarisation through an increase in back-transport of rejected solutes into the bulk flow. Salehi (2008) has detected in nanofiltration tests more than a doubling of the rejection of BPA by using a feed-spacer and increasing the feed flow. Thus fluid dynamics are decisive for an optimum rejection of target solutes. Capillary NF does not employ feed spacers, but higher crossflow velocities are applied to counteract CP, preferably in the transition phase from laminar to turbulent flow. Depending on the feed temperature, crossflow velocities between 1.2 and 1.5 m/s are required to operate the membrane in the transition zone between laminar and turbulent flow (*cf.* Fig 3.4). The pressure loss in capillary membranes depends significantly on the diameter as can be seen from the Hagen-Poiseuille equation, which is only valid for laminar flow. The diameter in the denominator has exponential influence on pressure difference. Thus small values result in high pressure loss which limits the capillary diameter and packing density of capillary NF.

$$\Delta p = \frac{v_{\text{cap}} \cdot L \cdot 128 \cdot \eta}{\pi \cdot d_h^4} \quad (3.2)$$

where  $\Delta p$  = pressure loss

$v_{\text{cap}}$  = volumetric flow

$L$  = length of capillary

$d_h$  = hydraulic diameter

Based on the Hagen-Poiseuille equation, it is obvious that the pressure in a capillary membrane is not uniform, but decreases in the direction of flow. The transmembrane pressure describes the average filtration pressure. In the tests the temperature was kept constant at 25°C to suppress temperature influences.

$$TMP = \frac{p_f + p_c}{2} - p_p \quad (3.3)$$

where  $TMP$  = transmembrane pressure

$p_f$  = feed pressure

$p_c$  = concentrate pressure

$p_p$  = permeate pressure

According to the Hagen-Poiseuille law, the real pressure is higher at the beginning of the membrane and lower at the end. The permeate pressure is negligibly small in a single staged NF system with an open outlet as employed in the present pilot and lab tests.



### 3.3 Results and Discussion

#### 3.3.1 Removal rates and permeate quality in pilot tests

*Removal rates.* To evaluate the process performance two different removal rates were used:

Membrane rejection by the nanofiltration membrane

$$R_{mem} = 1 - \frac{c_p}{c_r} \quad (3.4)$$

where  $c_p$  = concentration of compound in the permeate

$c_r$  = concentration of compound in the retentate

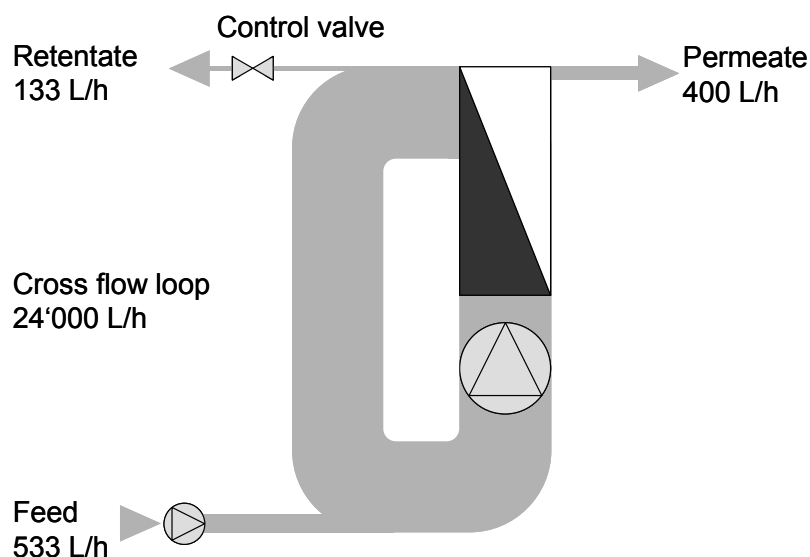
Total removal by the direct nanofiltration process

$$R_{tot} = 1 - \frac{c_p}{c_i} \quad (3.5)$$

where  $c_p$  = concentration of compound in the permeate

$c_i$  = concentration of compound in the influent water (= WWTP effluent, = feed in Figure 3.6)

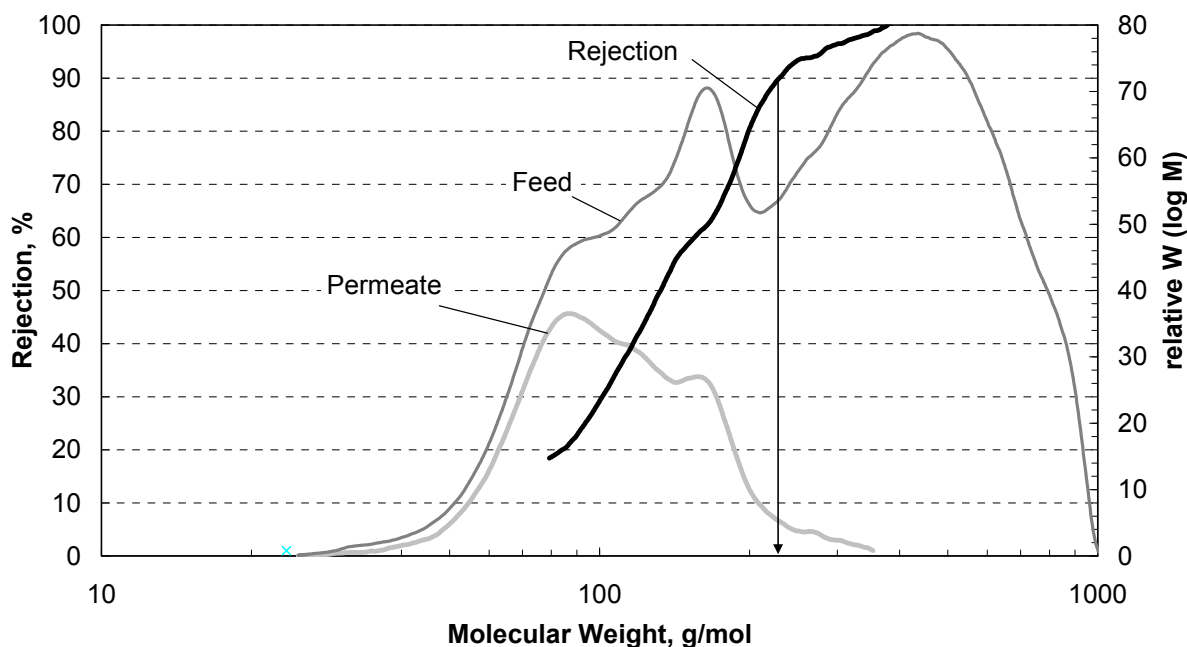
Due to the high crossflow volume (*cf.* Fig 3.5), the concentration of the feed water at the membrane corresponds approximately to the retentate concentration. Thus the membrane rejection can be derived from the ratio of the solute concentration in the permeate to the solute concentration in the retentate.



**Fig 3.5** Volumetric flow rates of the 8" nanofiltration unit at a permeate flux of 20 L/m<sup>2</sup>·h, a recovery of 75% and a crossflow velocity of 1.25 m/s (T = 25 - 30°C)

### 3.3.2 Molecular weight cut-off tests with PEG

The results of the molecular weight cut-off measurements are shown in Fig 3.6 and table 3.4. The average MWCO was  $221 \pm 6$  g/mol. The rejection curve is a sigmoid-like function with a steep incline between 100 and 250 g/mol and a sharp cut-off at 221 g/mol. It fades out reaching 100% rejection at around 400 g/mol.



**Fig 3.6** Molecular weight cut-off measurement for Norit X-Flow NF50 M10 (PEG method)

Table 3.4 shows that pressure and crossflow velocity impact only slightly on the MWCO within the measured ranges. As expected from the theoretical considerations concentration polarisation decreases slightly with increasing crossflow velocity and presumably membrane compression reduced the MWCO with increasing transmembrane pressure (TMP) to some degree.

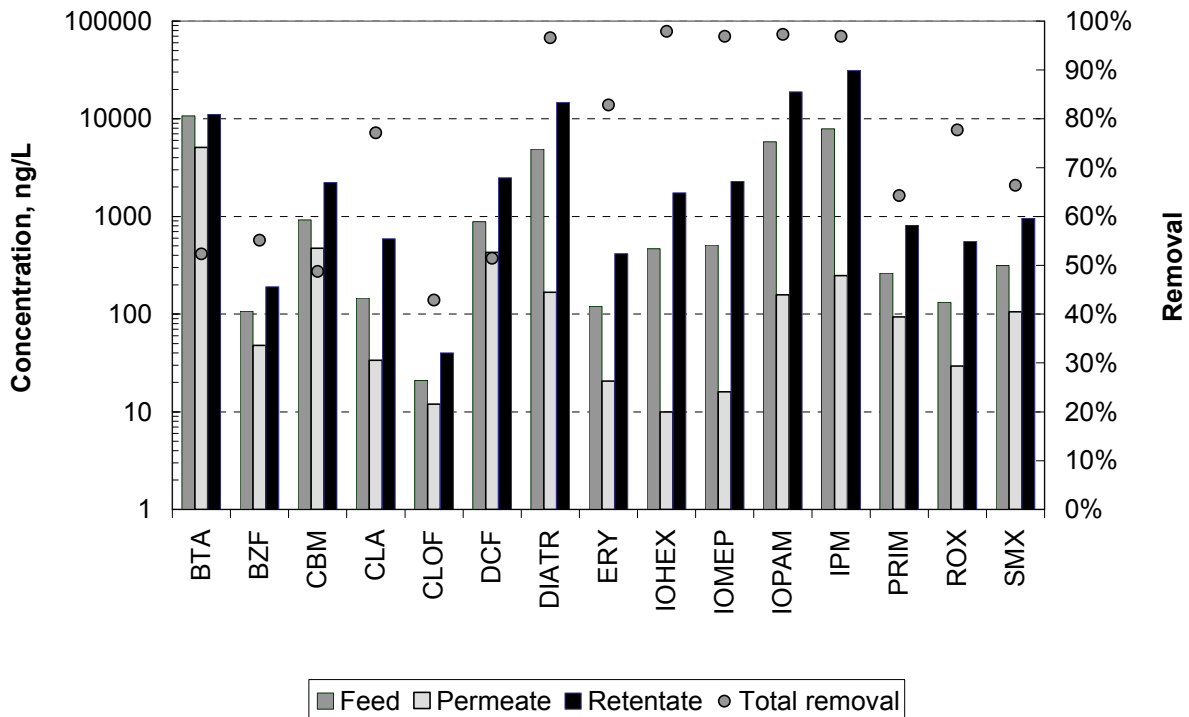
**Table 3.4** MWCO of NF50 M10 *versus* pressure and crossflow velocity (25 °C)

$v$ (m/s)	MWCO (g/mol)	TMP (bar)	MWCO (g/mol)
1.25	225	2.5	226
1.50	223	3.0	221
1.75	221	3.5	217
2.00	220		

#### Permeate quality

Figure 3.7 shows the concentrations of the influent to the NF plant, the permeate and the concentrate. The influent concentrations ranged between 10 to 1  $\mu\text{g/L}$  for benzotriazole and the contrast media and 1 to 0.1  $\mu\text{g/L}$  for the majority of the investigated pharmaceuticals. With removal rates between 40 to 80% for the pharmaceuticals the nanofiltration permeate

failed to reach the targeted concentrations  $\leq 100$  ng/L for many of the micropollutants, e.g. for CBM, DCF, and SMX. Although the removal of the contrast media was significantly higher some of the compounds were detected still in concentrations above 100 ng/L due to the high feed water concentrations. The rejection of benzotriazole was particularly poor reaching only 5.1  $\mu\text{g/L}$  in the permeate.



**Fig 3.7** Concentrations and removal of selected pharmaceuticals for the direct NF pilot test with the capillary NF membrane (permeate flux = 20 L/m<sup>2</sup>·h, recovery = 75%)

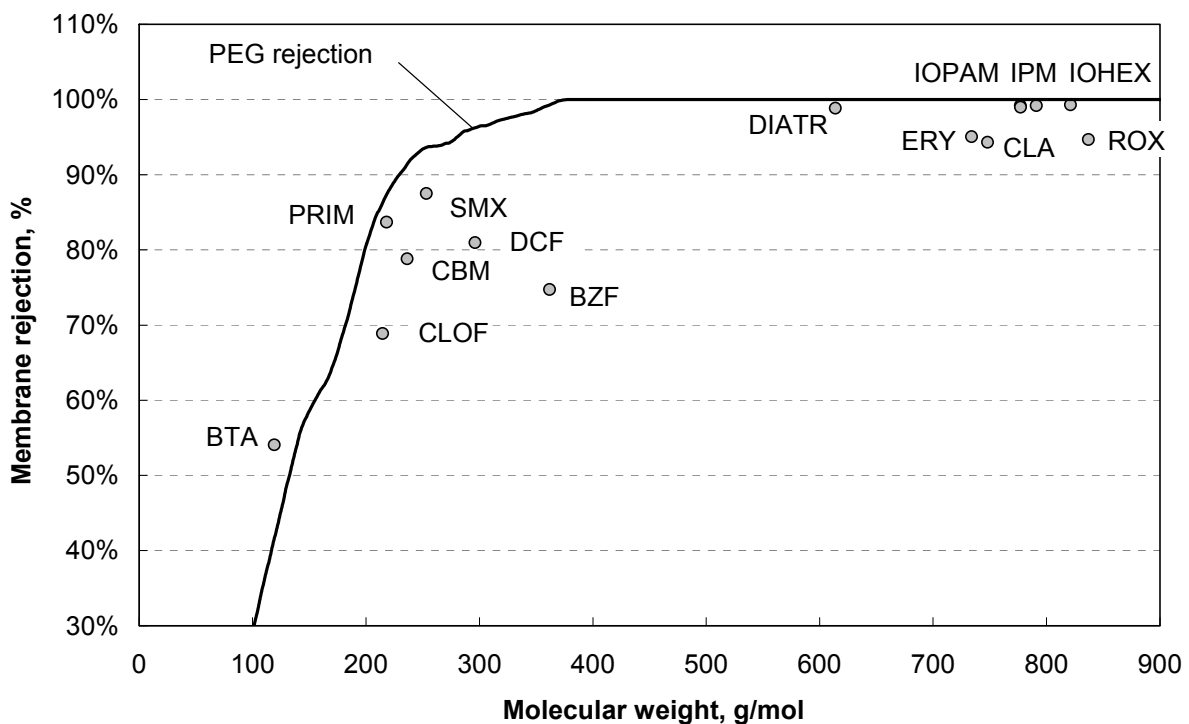
### Retentate concentrations

As the nanofiltration was operated with a recovery of 75%, the concentrations increased up to four times. The majority of the micropollutant concentrations in the retentate rose to levels of 1 to 10  $\mu\text{g/L}$  with some compounds even exceeding 30  $\mu\text{g/L}$ . This underlines the urgent necessity for a sufficient treatment of the NF concentrate as the bulk organic and micropollutant loads remain mostly unchanged in the reject stream, concentrated by a factor of 2 to 4.

### Removal rates

Figure 3.8 depicts the membrane rejection  $R_{\text{mem}}$  of the selected compound in comparison with the PEG rejection curve. Direct nanofiltration showed the expected incomplete removal of small size molecules with molecular weights close to the membrane cut-off. The retention of the small compounds was in the range of 50 to 80%, whereas larger ones as contrast media were retained almost completely. The rejection of the single compounds roughly followed the trend of the PEG curve. While the rejection of some compounds was, however, quite well reflected by the PEG curve, e.g. of BTA, PRIM, and contrast media, several pharmaceuticals were not retained at the expected level. Differences between the measured and the levels expected according to the rejection curve were between < 10 to 25%. The reasons for these

differences are diverse and complex and can be attributed to the specific interactions between the solute and the membrane as explained in the introduction. Electrostatic interaction between the negatively charged membrane and the positively charged macrolides ERY, CLA, and ROX reduce the membrane rejection by about 10%, presumably due to adsorption to the membrane and subsequent partial transport through the membrane. Verliefde *et al.* (2008) demonstrated that the rejection by nanofiltration of betablockers, which are positively charged at neutral pH, could be increased from between 75-90% at neutral pH up to 95-98% by lowering the pH and transferring the compound in the uncharged form.



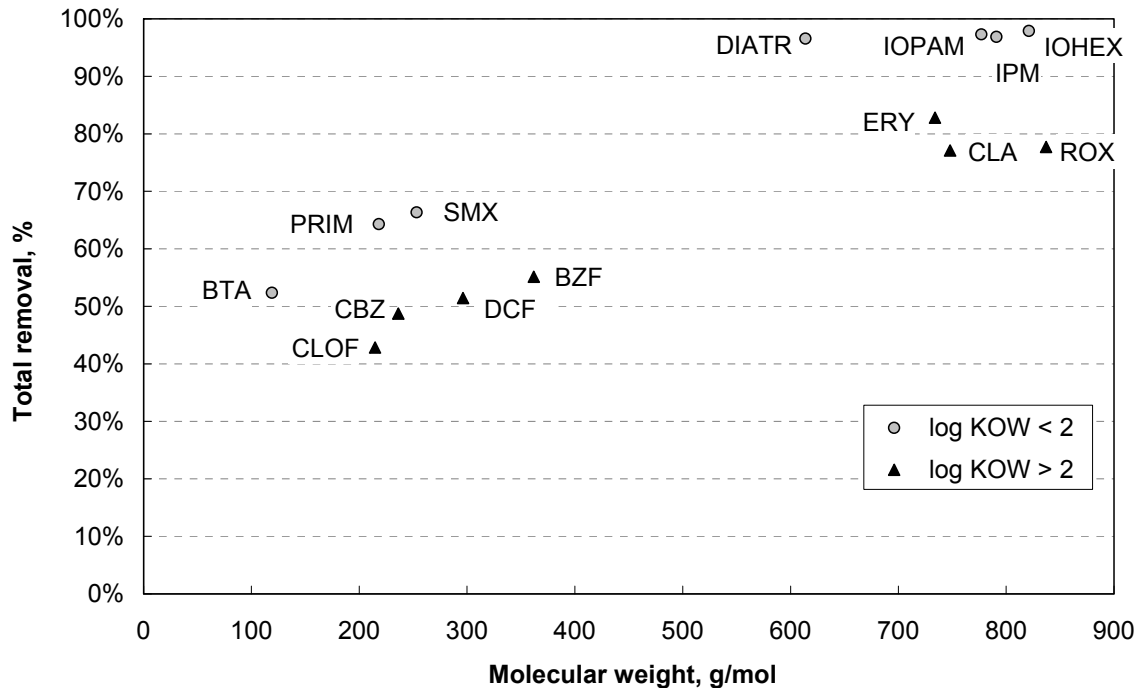
**Fig 3.8** Comparison of the membrane rejection  $R_{mem}$  of selected micropollutants in pilot scale short-term tests with the rejection of PEG (NF50 M10,  $J = 20$  LMH,  $v_{CF} = 1.25$  m/s, recovery = 75%)

The hydrophobicity of the target compound, measured as  $\log K_{OW}$ , was confirmed as second key factor besides the compound charge. In contrast to the previous figure, figure 3.9 shows the total removal  $R_{tot}$  of the selected micropollutants. It was observed that all compounds with a  $\log K_{OW} > 2$  were significantly less retained than the compounds with a  $\log K_{OW} < 2$ . This suggests that the rejection diagram of Bellona *et al.* (2004) is also applicable in capillary nanofiltration. The hierarchy of effects is assumed to be:

1. electrostatic interactions (attraction and repulsion) and adsorptive interactions (hydrophobicity)
2. size exclusion by steric hindrance

Comparing the removal rates of macrolides with contrast media, it is supposed that as soon as a compound sorbs to the membrane surface either due to hydrophobic/hydrophobic adsorption

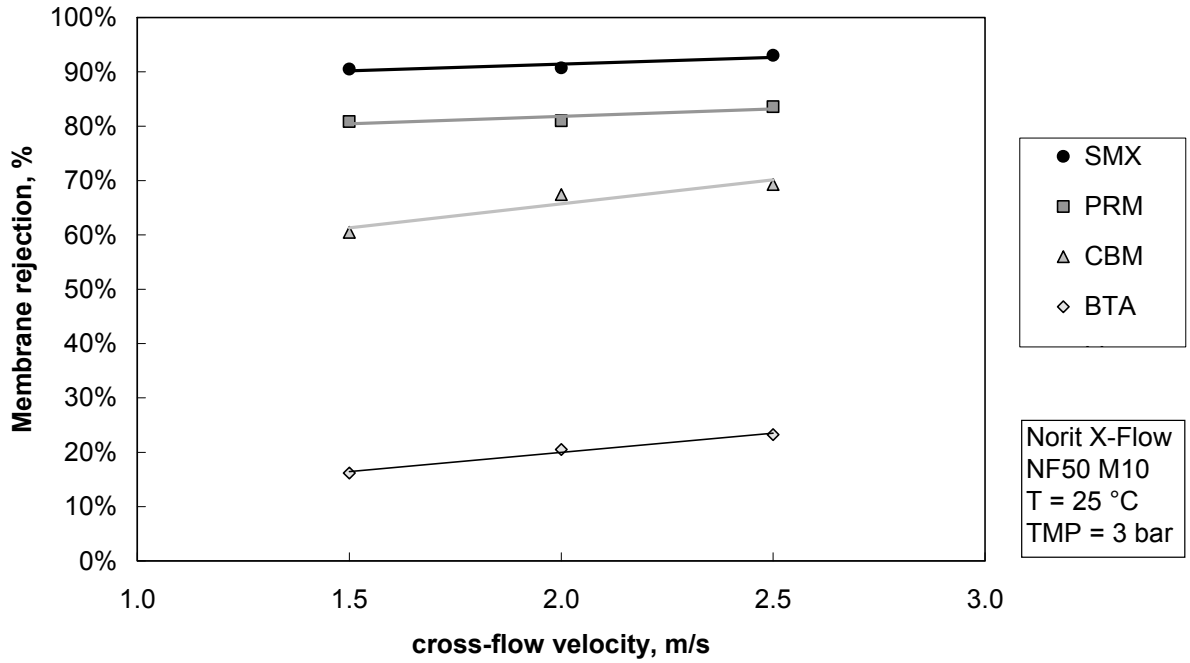
or electrostatic attraction, it can be transported through the membrane even if the molecular weight would suggest a complete rejection.



**Fig 3.9** Total removal  $R_{tot}$  of selected pharmaceuticals by nanofiltration in pilot scale short-term tests depending on molecular weight and  $\log K_{OW}$  (recovery = 75%,  $J = 20$  LMH,  $v_{CF} = 1.25$  m/s)

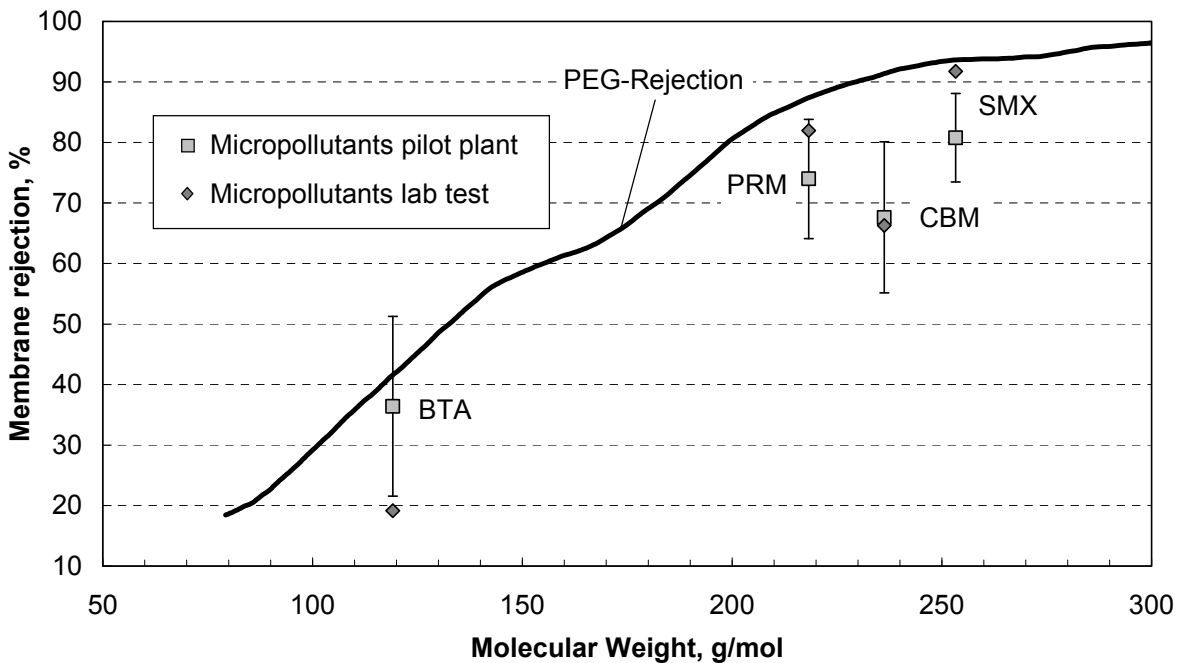
### 3.3.3 Removal rates in laboratory tests

To investigate the influence of the flow regime and crossflow velocity on the rejection of micropollutants in capillary nanofiltration, tests have been conducted using the lab scale nanofiltration test device. In addition, the lab scale test results were used to investigate the transferability of lab test data, which is rapidly available under well controllable conditions, to pilot scale tests. The lab tests employed the four compounds BTA (119 g/mol), PRM (218 g/mol), CBM (236 g/mol) and SMX (253 g/mol). Figure 3.10 shows that there was a slight dependency of the rejection of the investigated substances on the crossflow velocity. The figure shows that higher crossflow velocities lead to a better performance in rejection. Higher crossflow velocities imply flow patterns in the transition phase from laminar to turbulent flow. Less concentration polarisation occurs within this flow pattern finally resulting in enhanced rejection. The test suggests that poorly rejected compounds are more significantly influenced by the flow conditions than compounds rejected  $> 80\%$ . BTA for example was rejected by 16% at 1.5 m/s compared to 23% at 2.5 m/s, while SMX increased only from 91% to 93%. Compared to other effects and influencing factors such as compound properties, the improvement of the retention by high crossflow velocities beyond  $Re = 2300$  is negligibly small.



**Fig 3.10** Rejection of micropollutants against crossflow velocity (recovery = 75%)

The influence of changing transmembrane pressure was assessed separately at constant crossflow velocity. However in contrast to the PEG tests (*cf.* table 3.4), no clear correlation could be observed for the relation of rejection and TMP in the range between two and four bars.

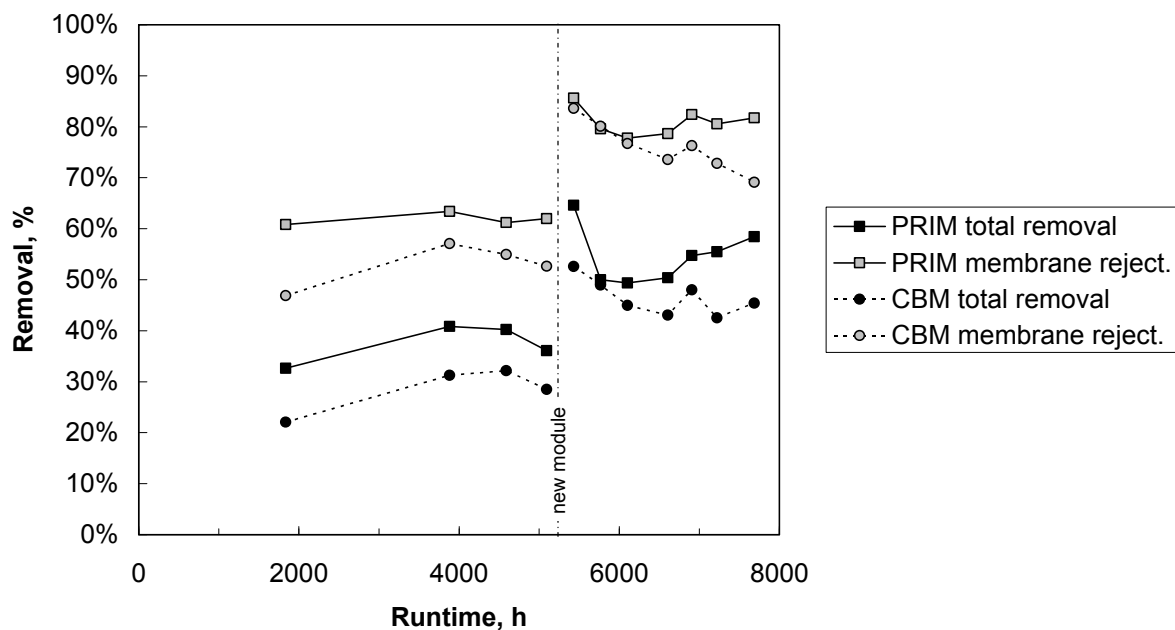


**Fig 3.11** Comparison of the rejection of selected micropollutants in pilot scale (long-term tests) and lab scale test with the rejection of PEG (20 LMH,  $v \sim 1.25$  m/s, recovery = 75%)

Figure 3.11 gives the opportunity to compare the PEG rejection curve with the rejection rates of the selected trace compounds from lab scale tests and long-term pilot tests as shown below. It can be seen from the figure that the pilot test values varied quite strongly. Similar to the observations during the crossflow velocity tests (*cf.* fig 3.10) the variance decreased with increasing retention of the compound. The compound rejection rates were within the range range of values from the long-term pilot tests, however some values deviate more than 10% from the averaged pilot plant values. Finally, it can be summarised that the rejection of PEGs is not transferable to molecules of the same or similar molecular weight but different chemical properties.

### 3.3.4 Investigation of the long-term behaviour in pilot tests

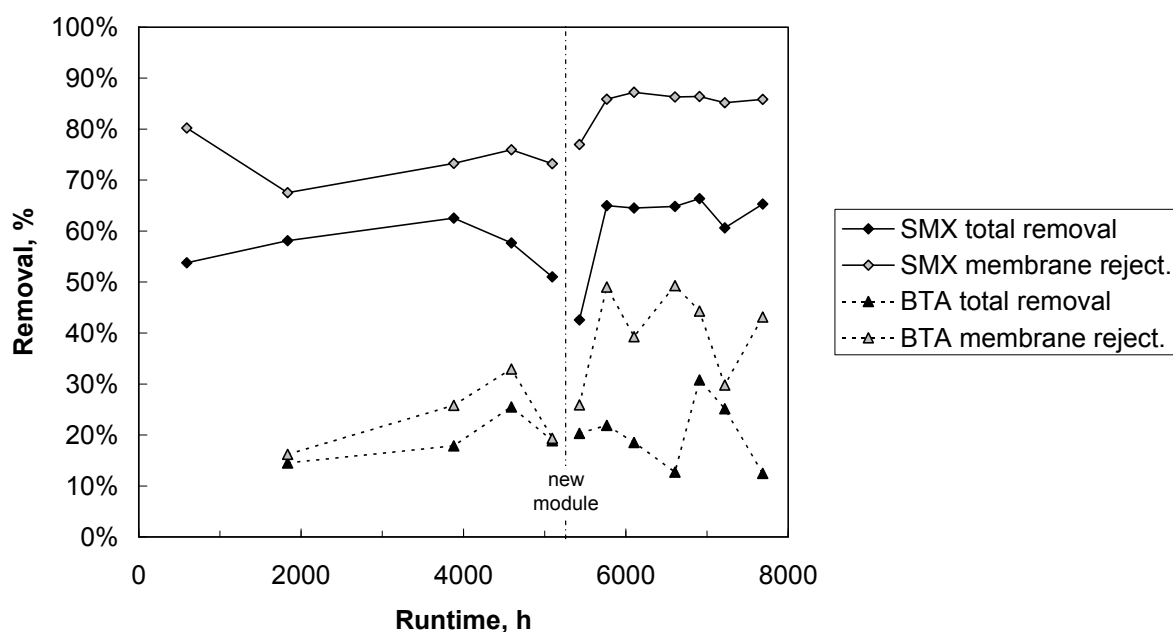
During the NF/GAC tests (*cf.* chapter 5) the 4" nanofiltration unit was operated in direct NF mode for almost 10'000 hours. During this period the plant was equipped with two 4" Norit X-Flow NF50M10 modules.



**Fig 3.12** Long-term removal of primidone and carbamazepine in NF pilot tests (4" module, 20 LMH, 75% recovery)

As shown in Figure 3.12 and 3.13 the rejection behaviour of the membranes was rather stable. The first module was discarded due to irreversible fouling after 5200 hours. The new module exhibited a better rejection of all investigated compounds. This was particularly valid for the retention of PRIM and CBM which was about 15% better than before. While the new module showed high removal rates for CBM and PRIM from the beginning, the rejection of BTA and SMX increased during the first hundred hours after restarting. It is known from literature that fouled membranes reject micropollutants differently. Foulants can cause a cake layer which increases the concentration polarisation (Ng and Elimelech, 2004) and they can alter the compound rejection due to changed membrane surface properties (Xu *et al.*, 2006).

Comparing tertiary effluent with MBR permeate, Kimura *et al.* (2009) showed that foulants modify the surface of the membrane differently depending on the source and composition of the effluent organic matter. Heijman *et al.* (2007) highlighted that bulk organic matter changes the rejection of micropollutants depending on the underlying membrane solute interactions. They observed that the rejection of negatively charged molecules decreased due to reduced repulsion, the rejection of positively charged molecules increased due to reduced attraction and the rejection of neutral molecules remained rather unaffected by fouling. The observations of Heijman *et al.* could explain the increasing rejection of the positively charged benzotriazole after a few hundred hours of operation. However their theory would suggest the opposite for sulfamethoxazole which is negatively charged at neutral pH. A slight decrease was observed for the neutral compounds carbamazepine and primidone.



**Fig 3.13** Long-term removal of sulfamethoxazole and benzotriazole in NF pilot tests (4" module, 20 LMH, 75% recovery)

A complete explanation for varying rejection rates during the long-term experiments could not be derived. It is assumed that variations in rejection can be attributed to changing raw water composition (bulk organics, bivalent ions, etc.), variations of micropollutant concentrations in the raw water, different fouling states of the membrane in terms of the operation time since the last chemical cleaning, membrane aging, temperature effects and development of a fouling layer of different composition (organic fouling, particulate fouling and biofouling). Xu *et al.* (2006) concluded in their fouling study that fouling affects the rejection of organic solutes by NF significantly, possibly by several effects such as hydrophobic adsorption, bridging, chemical binding, affinity, polar interactions and hydrogen bonding. The differences between the two 4" modules from different production series used during the long-term tests suggest that also slight variations in the coating might exist.



### 3.3.5 Adsorption of micropollutants to membrane and plant

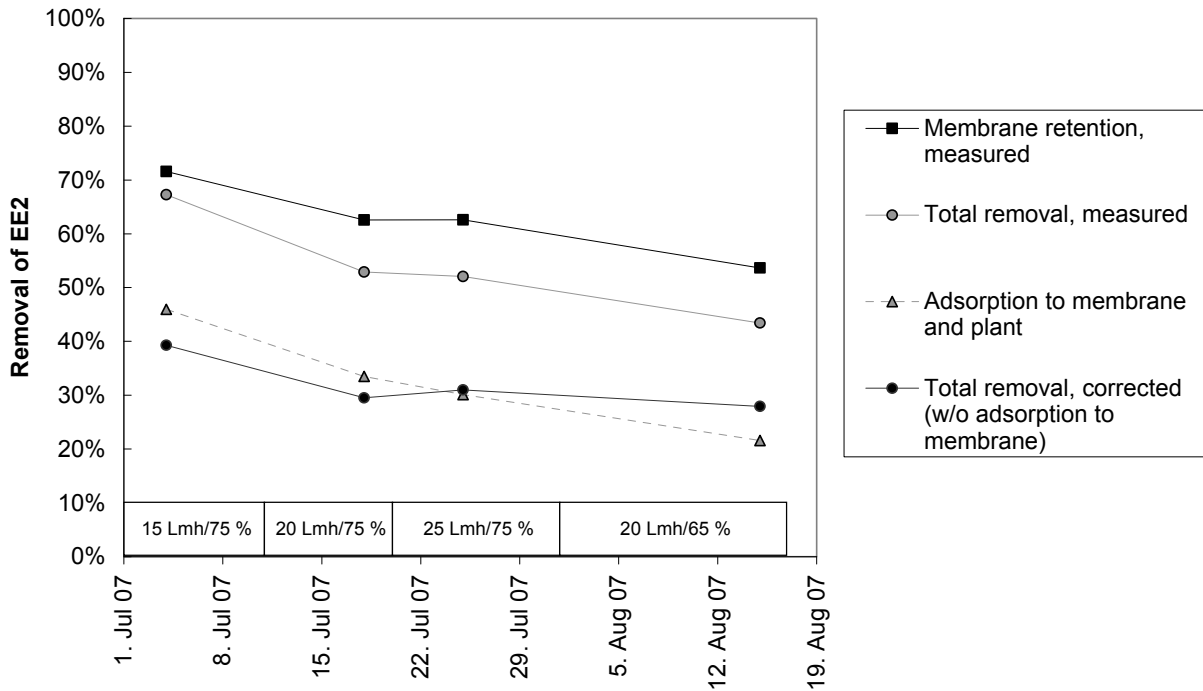
Bisphenol A and 17 $\alpha$ -ethinylestradiol were chosen to study the fate of endocrine disruptors. Details of the study and applied methods are given in Kazner et al. (2008). Different from the other selected compounds investigated above, BPA and EE2 are rather hydrophobic and were expected to sorb strongly to the system as observed in several other EDCs studies (Kimura *et al.*, 2003; Nghiem *et al.*, 2005; Gallenkämper, 2005; Salehi, 2008). After a rapid decrease within the first three hours of the lab scale test, Nghiem *et al.* (2005) measured a rejection of about 40% for BPA by nanofiltration employing the NF270 membrane. While most studies investigated these effects in lab to bench scale, the present tests investigated the rejection behaviour in pilot scale during a run time of 7 weeks with continuous spiking of the target compounds 24 hours before the tests started.

An overview of the results from the direct NF filtration pilot tests is given in table 3.5. The average membrane retention varied largely between -5% and 45% for BPA and between 54 and 72% for EE2 depending on the operating conditions (*cf.* Figure 3.14). A slight decrease of the real total removal was observed when increasing the permeate flux. As described by Nghiem *et al.* (2004 and 2005) it was proven that large amounts of the compounds were sorbed to the membrane and a substantial part of the total removal was due to sorption effects. This was relevant for all selected compounds.

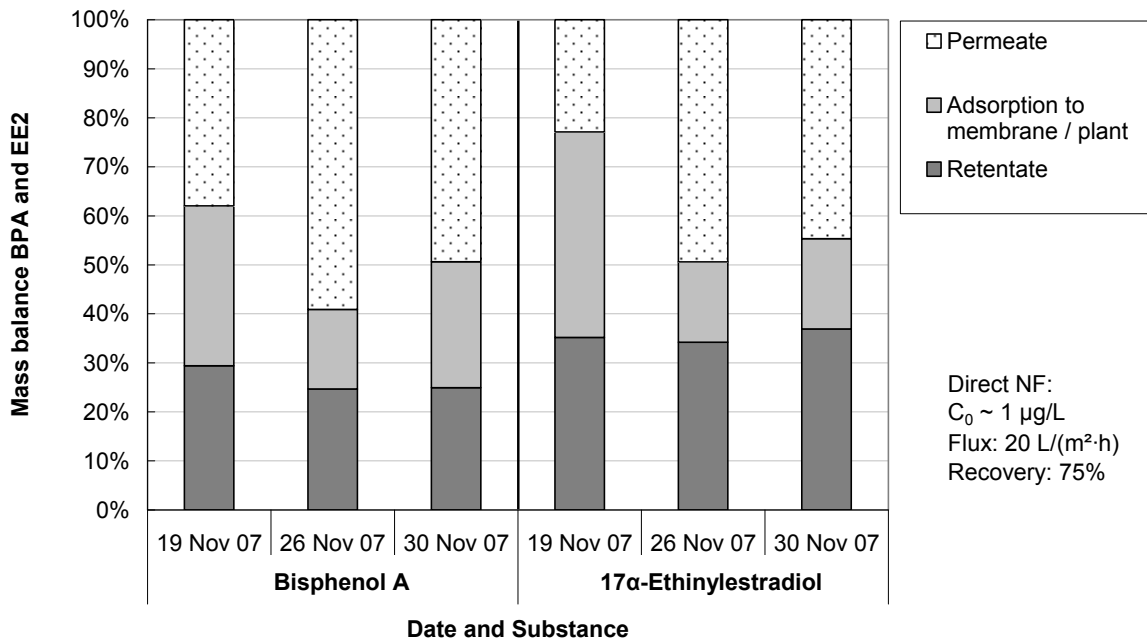
**Table 3.5** General operational parameters and experimental conditions of the direct NF pilot tests and retention of BPA and EE2 ( $R_{tot}^*$  = total removal corrected, without adsorption to NF and plant)

Flux L/(m <sup>2</sup> ·h)	Recovery %	TMP bar	Permeability L/(m <sup>2</sup> ·h·bar)	BPA retention, %			EE2 retention, %		
				$R_{mem}$	$R_{tot}$	$R_{tot}^*$	$R_{mem}$	$R_{tot}$	$R_{tot}^*$
15	75	1.9	8.8	44.5	58.5	17.0	71.6	67.3	39.3
20	75	2.5	10.0	28.8	43.1	9.5	62.6	52.9	29.5
25	75	2.9	8.9	17.0	37.1	5.0	62.6	52.1	31.0
20	65	2.6	8.7	-5.1	35.4	-1.6	53.6	43.4	27.9

Despite the molecular weight above the cut-off of the membrane, the target compounds EE2 (MW = 296 g/mol) and BPA (228 g/mol) showed a relatively low real total removal of 30 to 40% for EE2 and 5 to 17% for BPA (*cf.* table 3.6). Adsorption to the membrane contributed significantly to an apparent total removal between 35 to 60% for BPA and 43 to 70% of EE2. Adsorptive effects dominated over other influencing factors such as flux and transmembrane pressure. Initially slightly higher corrected total removal rates during the 15 LMH tests stabilised during the subsequent experiments.



**Fig 3.14** Average removal of EE2 in direct NF with spiked effluent (spiking conc. ~ 1 µg/L)



**Fig 3.15** Mass balance of BPA and EE2 in long-term spiking test (2 weeks continuous spiking with pre-fouled membrane after chemical cleaning)

The adsorption effects were studied in more detail during continuous spiking for two weeks. Fig 3.15 shows that also during these tests the initially high rejection decreased subsequently. However, balancing of the different fractions suggested that even after two weeks a saturation of the membrane and plant was not fully achieved. The initial adsorption of 30% for BPA and 40% for EE2 diminished and appeared to level off at 10 to 20%. However, an influence from adsorption of the target compounds to colloidal matter cannot be ruled out. The fraction of trace compounds found in the retentate was rather stable at 25% for BPA and around 35% for

EE2. Under changing operation conditions permeate concentrations sometimes exceeded the retentate concentrations presumably due to desorption from the membrane. Based on the test results, it can be expected that in full scale NF plants BPA and EE2 concentrations could exceed feed concentrations as the permeate concentration depends not only on the operation conditions such as flux and transmembrane pressure and the feed water composition such as NOM level and ionic strength (Nghiem *et al.*, 2004) but also on the ever changing equilibrium between adsorption and desorption to the membrane and transport of sorbed compounds through the membrane which can lead to unexpected peaks in the permeate.

### 3.3.6 Comparison of capillary NF to commercially available NF membranes

The table below shows the results of this study in comparison to two standard spiral wound NF membranes. The NF50M10 showed a poorer retention of micropollutants and salts than the NF270 (medium salt retention) and the NF90 (high salt retention). The capillary NF membrane can thus be classified as relatively open.

**Table 3.6** Average total removal rates for different NF membranes (recovery = 75%)

	Unit	NF50M10	NF270	NF90
Membrane type		X Flow capillary	DOW Filmtec flat sheet	DOW Filmtec spiral wound
MWCO		230	400	200
Source		this study	Comerton <i>et al.</i> , 2008	Melin <i>et al.</i> , 2012
<b>Bulk organics</b>				
DOC	%	90 - 95**	*	95
<b>Organic micropollutants</b>				
Carbamazepine	%	50	71	98.7
Diclofenac	%	50	*	99.2
Bezafibrate	%	50	*	88.0
<b>Antibiotics</b>				
Sulfamethoxazole	%	65	90	98.2
<b>Iodinated contrast media</b>				
Iopromide	%	99	*	*
Diatrizoate	%	95	*	99.7
<b>Endocrine disruptors</b>				
17 $\alpha$ -Ethinylestradiol	%	30	77	*
<b>Salinity</b>				
Conductivity	%	15-20	*	85-90
Sulphate	%	70-90	>97 ***	99
Chloride	%	5-20	40-60 ***	85

\* not determined, \*\* *cf.* chapter 6, \*\*\* Supplier data

### 3.4 Conclusions

The molecular weight cut-off (MWCO) of the NF50M10 membrane was determined as 220 to 230 g/mol depending on the operating conditions. The PEG rejection curve did not resemble the rejection of substances with similar molecular weight but different chemical properties.

The selected organic micropollutants were rejected by the investigated capillary nanofiltration to a varying degree as follows:

- Very high rejection of neutral and negatively charged molecules with a molecular weight significantly larger than the MWCO due to electrostatic repulsion and/or steric hinderance, prominent examples are contrast media,
- Lower but still high rejection of positively charged molecules with a molecular weight significantly larger than the MWCO due to a combination of electrostatic attraction and size exclusion, prominent examples are macrolides,
- Rejection of molecules with a molecular weight close to the MWCO in good accordance to the PEG rejection curve, if compounds are hydrophilic ( $\log K_{OW} < 2$ ) irrespective of their charge due to size exclusion, examples are benzotriazole, primidone and sulfamethoxazole,
- Rejection of molecules with a molecular weight close to the MWCO significantly below the PEG rejection curve if compounds are more hydrophobic ( $\log K_{OW} > 2$ ) irrespective of their charge, examples are carbamazepine, diclofenac and clofibrac acid,
- Poor rejection of strong hydrophobic compounds ( $\log K_{OW} > 3$ ), persistent adsorption to the membrane and plant can lead to breakthrough of compounds and permeate concentrations above feed concentrations, examples are bisphenol A and 17 $\alpha$ -ethinylestradiole,

The investigated capillary nanofiltration must be regarded as relatively loose NF rejecting many organic micropollutants typically found in secondary effluent only partially. In comparison to dense nanofiltration membranes (*cf.* table 3.6), it becomes obvious that capillary nanofiltration with the NF50M10 membrane requires post- or pre-treatment, *e.g.* by adsorptive or oxidative processes to reduce the target compounds to the requested levels below 100 ng/L or even below the LOQ (around 1 to 10 ng/L) as mostly applied in indirect potable reuse schemes.

The necessity of high crossflow velocities around 1.2 m/s to counteract concentration polarisation must be seen as a disadvantage of capillary NF when compared to spiral wound modules where membrane spacers prevent concentration polarisation at crossflow velocities in the order of 0.2 m/s.

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## 4 Removal of organic micropollutants from tertiary effluent by powdered activated carbon adsorption in combination with nanofiltration

### 4.1 Introduction

The PAC/NF process combines adsorption to powdered activated carbon (PAC) with nanofiltration. The hybrid process was first applied in treatment of landfill leachate for highly effective removal of organics and inorganics, in particular multivalent ions (Eilers, 2000; Meier *et al.*, 2002). Specific advantages are high recovery rates up to 97%, integrated concentrate treatment and costs somewhat lower than RO treatment (Melin *et al.*, 2005). Subsequently the PAC/NF process was transferred and adapted to treatment of WWTP effluent (Meier and Melin, 2005; Meier, 2008). Previous tests on lab and pilot scale (Meier, 2008) focused on process design with particular emphasis on the selection of the appropriate membrane type, cake layer control and membrane abrasion. Likewise basic performance tests were conducted while the fate of organic micropollutants during PAC/NF has not yet been investigated.

#### 4.1.1 Process design

Figure 4.1 presents the schematic of the PAC/NF process. Powdered activated carbon is dosed to WWTP effluent in a completely stirred tank reactor (CSTR). The suspension is then fed to the crossflow loop of a nanofiltration unit operated in feed and bleed mode. The concentrate contains the organic loaded PAC and the retained inorganic compounds such as sulphate, calcium and magnesium. It can either be recycled to the activated sludge unit or to the CSTR tank with or without retention of the PAC and additional treatment of the inorganic constituents. Alternatively the concentrate can be discharged after PAC removal such as settling and further treatment according to the local requirements.

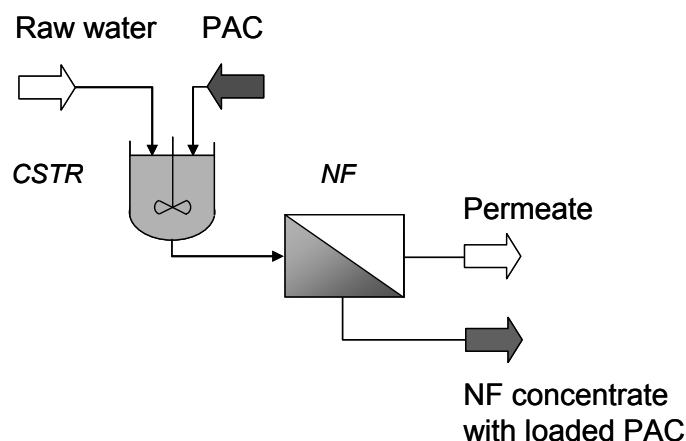


Fig 4.1 Schematic of the PAC/NF process

Especially thanks to advantages concerning the production of high quality water without further pre-treatment as required for reverse osmosis, the PAC/NF process is supposed to have a good potential for water reclamation (Meier and Melin, 2005). PAC adsorption removes many organic micropollutants while some trace compounds such as X-ray contrast media are poorly adsorbable (Ternes and Joss, 2006), but can be well removed by dense membranes (Bellona *et al.*, 2004; Snyder *et al.*, 2007).

Meier *et al.* (2002) summarised the expected advantages of the process combination over single stage membrane processes as follows:

- Better permeate quality as adsorption to PAC provides pre-cleaning of the tertiary effluent resulting in a better permeate quality concerning organic contaminants.
- Higher flux as PAC acts as a filter aid and prevents potential foulants from getting into contact with the membrane.
- Better removal of fouling layer due to non-polar carbon particles embedded in the layer.
- Higher loading of the PAC due to increased concentration of organics in the crossflow recirculation loop of the NF.

In contrast to fixed-bed adsorption, the PAC-dosage can be adjusted to the feed quality. However, in a detailed study of the impact of powdered carbon on nanofiltration at PAC concentrations of 200 to 500 mg/L, Meier (2008) could not confirm reduced fouling and higher fluxes. It was observed that the carbon dosage had a slightly positive impact on membrane fouling only at low permeate fluxes below 20 L/(m<sup>2</sup>·h). At higher fluxes a neutral to slightly increased membrane resistance was detected.

#### 4.1.2 Process operation

From the operational point of view PAC/NF is very complex process. Several factors influence the performance of the PAC/NF process (*cf.* Table 4.1). The most challenging part is the optimisation of the nanofiltration especially regarding the control of the cake layer formation and the fouling phenomena. According to Meier (2008) the formation of a cake layer can hardly be avoided completely and is advantageous to avoid abrasion. The PAC/NF process should be operated at slightly carbon depositing process conditions with shear rates between 6000 and 18000 s<sup>-1</sup> and use hydraulic flushes and chemical cleaning to limit the formation of a cake layer. During previous pilot tests and the experiments presented here, backflush as available in capillary nanofiltration was the main method for cake layer control. Meier and Melin (2005) demonstrated that non-backflushable membranes, such as spiral wound module also with wide spacers, were quickly blocked and therefore cannot be employed in PAC/NF. Theoretical considerations and practical experiments confirmed the importance of the carbon particle size for the formation of the cake layer (Meier, 2008) with fine particles below 0.4 µm depositing preferentially. Scanning electronic microscopy revealed that the membrane was covered by a 30 to 50 µm thick cake layer of particles and agglomerates sized from 0.5 to 3 µm ( $v_{CF} = 1.25$  m/s,  $C_{PAC} = 0.2 - 0.5$  g/L). A reduced

retention of the sulphate from around 96% to 87% was attributed to cake enhanced concentration polarisation as described by Hoek *et al.* (2002) and Hoek and Elimelech (2003).

**Table 4.1** Factors affecting the performance of the PAC/NF process with regard to rejection of organic solutes and economic efficiency (Bellona *et al.*, 2004; Crittenden *et al.*, 2005; Snyder *et al.*, 2007; Schäfer *et al.*, 2005; Yangali Quintanilla, 2010)

	<b>Powdered activated carbon</b>	<b>Nanofiltration</b>
Material properties	Inner surface	MWCO
	Pore size distribution	Porosity
	Particle size distribution	Surface charge
	Raw material and origin	Surface roughness
	Shape	Applicable pH range Resistance against oxidants
Water characteristics	Temperature	Temperature
	pH value	pH value
	Water matrix (bulk organics)	Raw water matrix (foulants)
	Salinity	Ion concentration (e.g. Ca <sup>2+</sup> )
Solute characteristics	log K <sub>OW</sub> and log D	Molecular weight
	Charge (pK <sub>a</sub> )	log K <sub>OW</sub>
	Diffusivity	Charge (pK <sub>a</sub> )
		Molecular size
Operational conditions	Carbon concentration	Permeate flux
	Reactor type	Recovery
	Mixing	Transmembrane pressure
	Contact time (PAC reactor and crossflow recirculation loop)	Crossflow velocity
		Backflush duration and cycle
		Membrane cleaning method
		Dosage of chemicals (e.g. antiscalants)

### Optimisation of PAC/NF for the removal of organic micropollutants

In a system with influences of compound properties, carbon and membrane characteristics a complex interaction develops between the two processes and the specific behaviour of the solute in the respective process. Optimisation of the PAC/NF system for the removal of micropollutants requires:

- A) Good and stable retention of targeted micropollutants, particularly minimisation of the cake layer to limit cake enhanced concentration polarisation during nanofiltration, and
- B) Optimisation of the PAC adsorption for the most critical compounds.

## Membrane selection

The NF membrane should ideally feature high rejection for hardly adsorbable micropollutants to limit the influence from cake-enhanced concentration polarisation. However, high rejection rates for micropollutants require very dense nanofiltration or even RO membranes, which encompass also high rejection rates for inorganic compounds. This may lead to an increased risk of scaling alongside problems associated with the disposal of highly saline NF concentrates, particularly in inland locations. Therefore PAC/NF should prefer medium dense NF membranes allowing good retention of critical micropollutants such as contrast media but only partly rejecting monovalent ions.

## Optimisation of the PAC adsorption

Methods to design and optimise water treatment by powdered activated carbon are well documented in literature (*e.g.* Sontheimer *et al.*, 1988; Crittenden *et al.*, 2005). Selection of the appropriate carbon type is the key factor for the removal of the target solute in a given water matrix. Raw material and activation method determine the porosity and the inner surface of the activated carbon. In effluent polishing, carbon types with a high percentage of mesopores alongside a large inner surface allow a low carbon usage rate. After the selection of the carbon based on the adsorption isotherms for the targeted compounds and water matrix, optimisation addresses the adsorption kinetics. Lehnberg (2010) showed for EE2 and BPA that with increasing PAC concentration the adsorption kinetics improve. Other main influencing factors are the particle size, the porosity, the pore size distribution and the inner surface. While fine PAC is advantageous from the kinetic perspective (Ando *et al.*, 2010; Matsui *et al.*, 2010) it must be considered unfavourable for PAC/NF as particles below 0.4  $\mu\text{m}$  deposit preferentially (Meier, 2008).

### 4.1.3 Objectives

This investigation aims to determine the interplay between powdered activated carbon and nanofiltration in removing organic micropollutants. The key question is which PAC concentration will be required for an overall improved removal of micropollutants by PAC/NF. For this purpose, a pilot PAC/NF plant was operated for polishing tertiary effluent (conventional activated sludge treatment followed by sand filtration) testing PAC concentrations between 10 and 100 mg/L.

## 4.2 Materials and Methods

### 4.2.1 Selected organic micropollutants

Table 4.2 presents an overview of the selected target compounds. The list covers a broad range of substances with molecular weights close to the MWCO (220 - 230 g/mol; PEG method, *cf.* chapter 3.2) and different hydrophobicity from very hydrophilic to hydrophobic. All compounds, except for 17 $\alpha$ -ethinylestradiol (EE2) and bisphenol A (BPA), were

investigated in ambient concentrations between 10 ng/L and 10 µg/L (*cf.* chapter 4.3.1). Due to low ambient concentrations, EE2 and BPA were spiked in specific tests targeted at the removal of endocrine disrupting compounds. In lab scale adsorption tests with benzotriazole, carbamazepine, clofibric acid, ibuprofen, primidone and sulfamethoxazole, the compounds were spiked in initial concentrations of about 250 µg/L.

**Table 4.2** Organic micropollutants selected for PAC/NF tests

Compound	Short name	MW g/mol	pK <sub>a</sub>	Log K <sub>OW</sub>	Log D at pH 8	Charge at pH 7-8	Pilot tests	Iso-therm tests
Benzotriazole	BTA	119.13	8.37	1.44	1.44	0	●	sp
Bezafibrate	BZF	361.82	3.44	4.25	0.24	-	●	sp
Bisphenol A	BPA	228.3	9.7	3.32	3.32	0	sp	
Carbamazepine	CBM	236.27	0.37	2.45	2.45	0	●	sp
Clarithromycin	CLA	747.95	8.90	3.16	2.13	+	●	
Clofibric acid	CLOF	214.65	3.35	2.57	-0.98	-	●	sp
Diatrizoic acid	DIATR	613.90	3.4	1.37	-3.23	-	●	
Diclofenac	DCF	296.15	4.15	4.51	0.74	-	●	
Erythromycin	ERY	733.93	8.88	3.06	2.13	+	●	
17α-Ethinylestradiol	EE2	296.4	10.2	4.10	4.10	0	sp	
Ibuprofen	IBP	206.29	4.47	3.97	0.44	-		sp
Iohexol	IOHEX	821.14		-3.05	-3.05	0	●	
Iomeprol	IOMEPI	777.00		-2.52	-2.52	0	●	
Iopamidol	IOPAMI	777.09		-2.42	-2.42	0	●	
Iopromide	IPMI	791.00	10.2	-2.05	-2.05	0	●	
Primidone	PRIMI	218.25	12.3	0.91	0.91	0	●	sp
Roxithromycin	ROXI	837.05	8.80	2.75	1.89	+	●	
Sulfamethoxazole	SMXI	253.28	5.60	0.89	-1.51	-	●	sp

(● = real concentration, sp = spiking of compound)

#### 4.2.2 General characteristics of the influent water

To evaluate the performance of the PAC/NF-process under realistic conditions regarding the effluent matrix and real trace organic concentrations, a pilot plant has been installed at the WWTP Aachen Soers (460,000 p.e.) treating continuously about 500 L/h of tertiary effluent from the sand filtration. The wastewater treatment plant with advanced biological treatment including nitrogen and phosphorus removal as well as a final sand filtration provides a high quality effluent with an average DOC of  $5.2 \pm 0.9$  mg/L, average COD of  $15.6 \pm 2.3$  mg/L, average conductivity of  $0.97 \pm 0.19$  mS/cm, and mean pH of  $7.7 \pm 0.4$ .

### 4.2.3 Sampling and analytical methods

All samples were taken as 24 h composite samples. An auto sampling unit of MAXX GmbH provided the sampling of the influent and permeate samples with 200 mL each 30 min collected in a 10 L Duran glass bottle and stored at 7 °C. The feed and retentate samples containing PAC were manually produced composite samples removing the carbon directly after sampling with a 0.7 µm glass fibre filter to interrupt adsorption. Pharmaceutical concentrations in the feed, permeate and concentrate were analysed by using SPE enrichment prior to LC-MS-MS detection according to methods developed and described as in Ternes and Joss (2006) and Ernst *et al.* (2012). The EDC measurement used a different method with Oasis HLB SPE-cartridges prior to HPLC (Agilent 1100) with a reverse phase column (Thermo HyPurity C18) and detection by an Applied Biosystems triple quadrupole MS (API 3000) as described in Lehnberg (2010). All samples were quantified with <sup>13</sup>C or <sup>15</sup>N labelled internal standards. The analytical methods are explained in detail in the appendix.

### 4.2.4 Adsorbent

The present tests employed the commercially available powdered activated carbon SAE Super (Norit Deutschland GmbH) due to good results in previous tests (Melin and Meier, 2005) and its application in many other European studies (*e.g.* Metzger, 2010; Zwickenpflug *et al.*, 2010; Margot *et al.*, 2011) which allows comparability of the study results. SAE Super has an inner surface of 1300 m<sup>2</sup>/g (BET method) and a median particle size D<sub>50</sub> of 15 µm with particles ranging from 0.5 to 300 µm. The PAC dosage was varied between 10 and 100 mg/L. The carbon was pre-moistened to a drinking water content of 50% (ETC engineering & technology consulting GmbH, Burgau, Germany) for improved handling and proper mixing.

### 4.2.5 PAC/NF pilot plant

PAC/NF cannot employ standard spiral wound NF modules as high particulate loads from PAC quickly block the module (Meier and Melin, 2005). Based on previous tests (Melin and Meier, 2005) it uses a 1.5 mm capillary Nanofiltration NF50 M10 from Norit X-Flow (Futselaar *et al.*, 2002) in an 8" module and a total membrane area of 20 m<sup>2</sup> (*cf.* Table 3.3). According to PEG tests the molecular weight cut-off of the composite membrane is between 220 and 230 g/mol. It has an active layer of polyamide with a supporting layer of polyethersulfone. With a permeate flux of 20 L/m<sup>2</sup>·h the permeate production was 400 L/h. The membrane was operated in crossflow mode with a crossflow velocity of 1.2 m/s and a recovery of 75%. Backflush with permeate was applied for 1 min every 45 min. The operating conditions in the PAC/NF pilot tests chose shear rates around 6700 s<sup>-1</sup> well below the critical boundary. The transmembrane pressure ranged between 1.5 to 4.0 bar. Contact time in the PAC reactor was 1.2 h and additional 15 min in the crossflow recirculation loop. During the spiking tests, EE2 and BPA were spiked from a 10 L Duran glass stock bottle with an Ismatec Reglo Analog peristaltic pump in the stirred raw water storage tank. A schematic diagram of the pilot plant is shown in Figure 4.2.

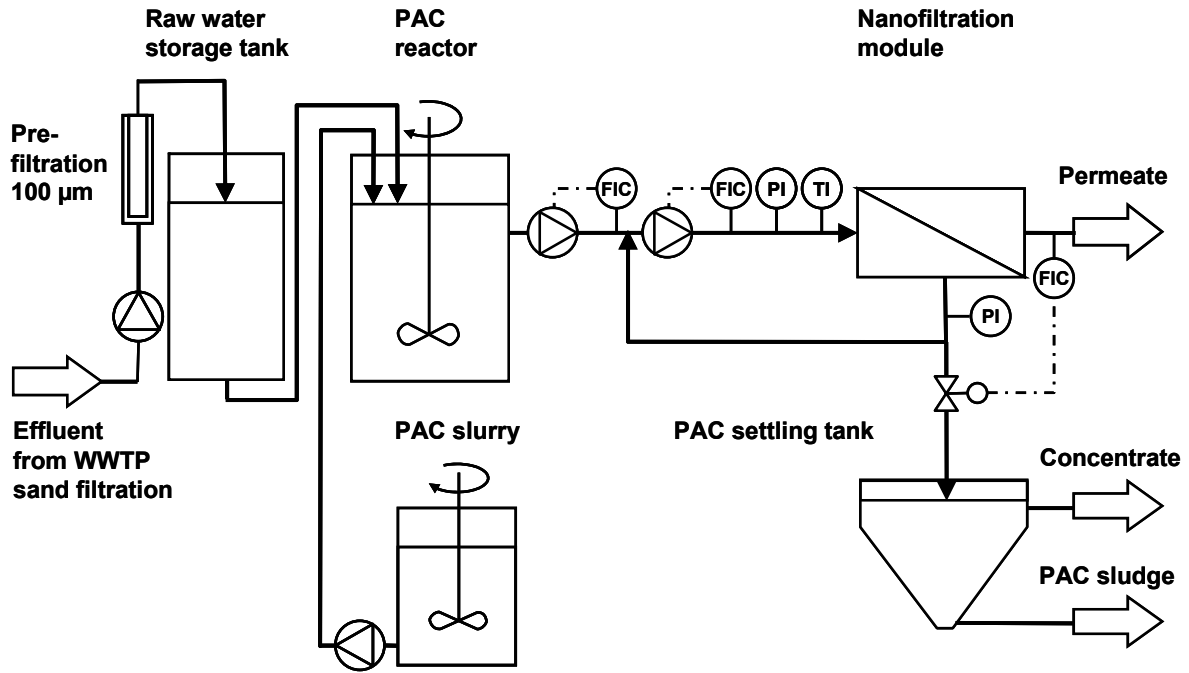


Fig 4.2 Experimental set-up of the PAC/NF pilot plant

#### 4.2.6 Calculation of removal rates

To evaluate the process performance two different removal rates were used:

Adsorptive removal by activated carbon in the first stage

$$R_{ads} = 1 - \frac{c_f}{c_i} \quad (4.1)$$

where  $c_f$  = concentration of compound in the feed water to the NF

$c_i$  = concentration of compound in the influent water (= WWTP effluent)

Membrane rejection by the nanofiltration membrane

$$R_{mem} = 1 - \frac{c_p}{c_r} \quad (4.2)$$

where  $c_p$  = concentration of compound in the permeate

$c_r$  = concentration of compound in the retentate

Total removal by the direct nanofiltration process

$$R_{tot} = 1 - \frac{c_p}{c_i} \quad (4.3)$$

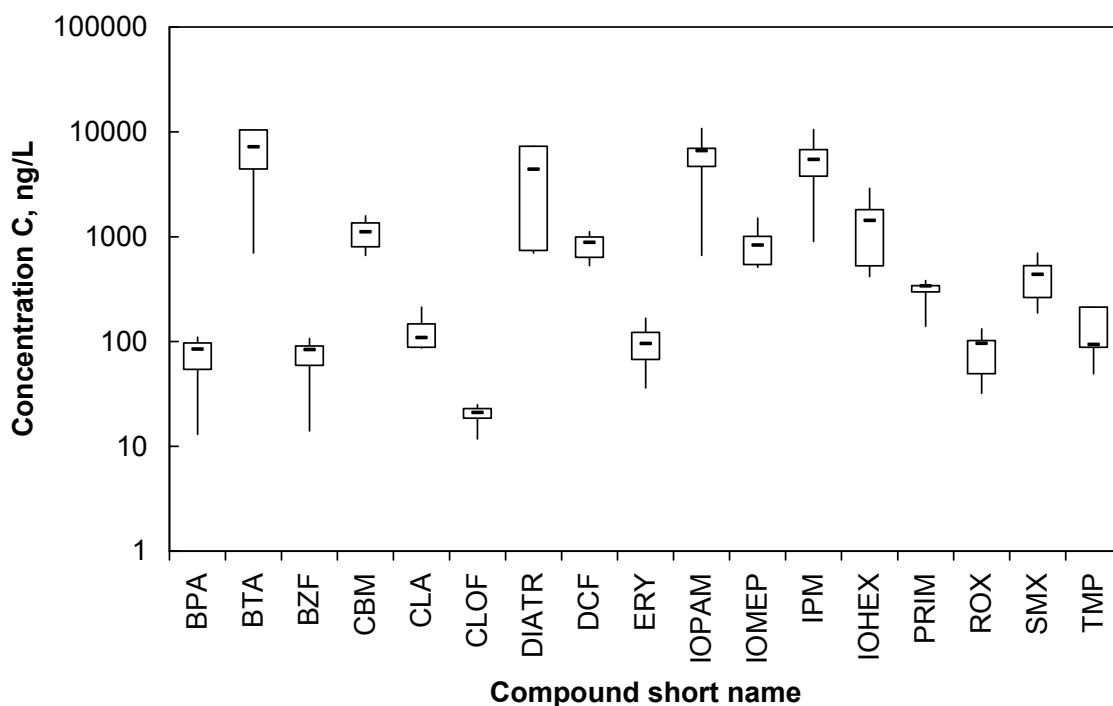
where  $c_p$  = concentration of compound in the permeate

$c_i$  = concentration of compound in the influent water (= WWTP effluent)

## 4.3 Results and discussion

### 4.3.1 Quality of the municipal WWTP effluent

The highest average concentrations were detected for benzotriazole (BTA), carbamazepine (CBM), and the majority of the X-ray contrast media within a range of 1 to 10 µg/L (Figure 4.3). Antibiotics such as macrolides, sulfamethoxazole (SMX) and trimethoprim (TMP), as well as primidone (PRIM), diclofenac (DCF), and iomeprol (IOMEPI) were present in concentrations between 100 to 1000 ng/L. bisphenol A (BPA), bezafibrate (BZF) and clofibric acid (CLOF) were measured in concentrations between 10 and 100 ng/L. The average PAC/NF influent concentrations are given in Table 4.3.



**Fig 4.3** Micropollutant concentrations of the influent to the PAC/NF plant (n =7; min, Q25, median, Q75, max)

### 4.3.2 Permeate quality and total removal in PAC/NF pilot tests

#### Permeate quality

The permeate produced by the PAC/NF process proved to be of very high quality with concentrations  $\leq 100$  ng/L for most of the micropollutants at higher PAC doses (*cf.* Table 4.4). At a dosage of 50 mg/L of PAC, only benzotriazole exceeds the target value of 100 ng/L, while most substances were reduced close to or below the limit of detection (LOD). Without dosage of PAC the permeate concentrations of some substances of concern such as carbamazepine, diclofenac and benzotriazole are significantly higher, in particular BTA: 5.1 µg/L, CBM: 0.47 µg/L, DCF: 0.43 µg/L, and no compound was reduced below the level



of detection. Due to the high influent concentrations and their critical properties in terms of small molecule size or low adsorbability, benzotriazole and diatrizoate are the most critical compounds for removal by the PAC/NF process. Furthermore sulfamethoxazole is critical in PAC/NF treatment but because of the relatively low influent concentrations, low carbon rates could reduce SMX below 100 ng/L.

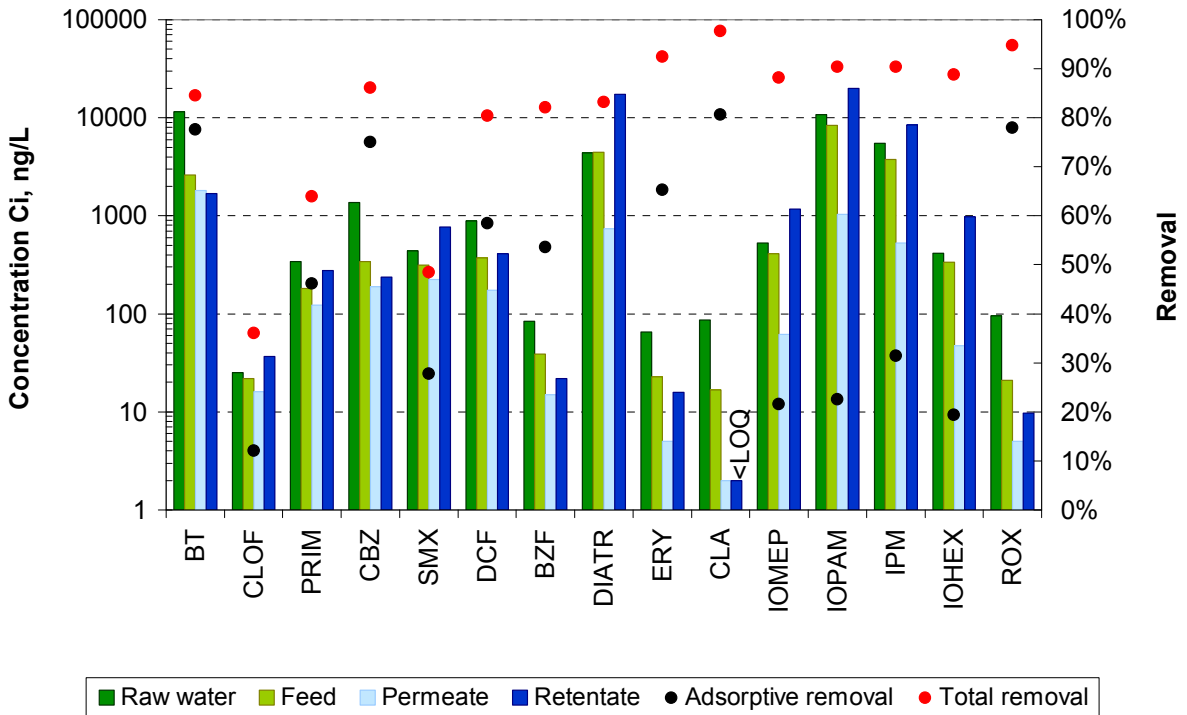
**Table 4.3** Concentrations of micropollutants in influent (= WWTP effluent) and PAC/NF permeate at different PAC doses

Compound	C <sub>influent</sub> ng/L	Concentration in permeate in ng/L at PAC dose of				
		0 mg/L	10 mg/L	25 mg/L	50 mg/L	100 mg/L
Amount of samples	n = 7	n = 1	n = 1	n = 1	n = 1	n = 1
Benzotriazole	9030	5100	1800	192	196	26
Bezafibrate	85	48	15	< 10	< 10	< 10
Carbamazepine	1290	473	189	113	< 2	< 25
Clarithromycin	92	34	< 2	< 25	< 2	< 25
Clofibric acid	19	12	16	< 10	< 10	<10
Diclofenac	825	430	175	84	15	< 10
Diatrizoate	4120	168	739	< 50	na	231
Erythromycin	106	21	< 5	< 10	< 5	< 10
lomeprol	785	16	62	25	25	< 5
lopamidol	6350	158	1035	91	51	29
lopromide	4355	248	527	245	46	<5
lohexol	1200	10	47	50	22	< 5
Primidone	293	94	123	84	24	5
Roxithromycin	95	29	< 5	< 10	< 5	< 10
Sulfamethoxazole	501	106	225	66	84	9

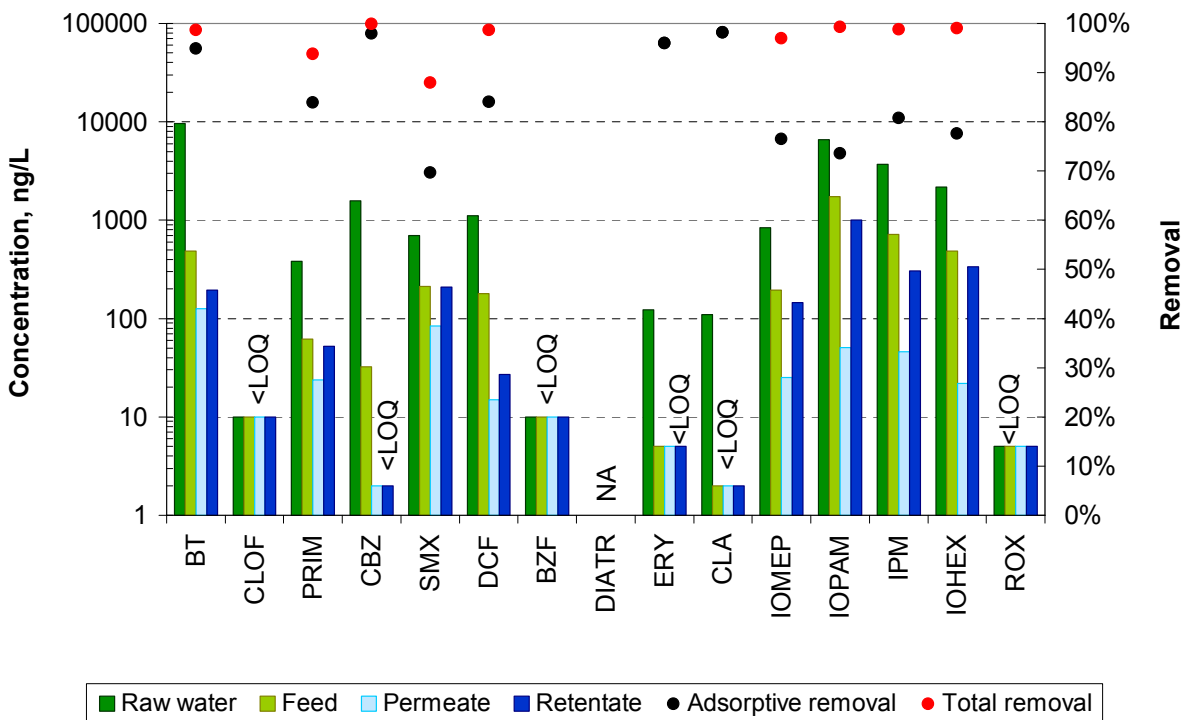
na = not available

#### Total removal of micropollutants by PAC/NF

As explained in the chapter 3, nanofiltration without PAC dosage showed for compounds with molecular weights close to the MWCO an incomplete removal of 40 to 80% while larger molecules such as contrast media were retained almost completely (*cf.* chapter 3, Fig 3.9). Figure 4.4 to 4.7 depict the concentrations of the selected compounds in the influent to the PAC/NF plant, the feed to the NF, the NF permeate and the NF retentate. All concentrations are measured in the liquid phase with the powdered activated carbon filtered off directly after sampling. The second y-axis gives the removal rates with regard to adsorptive removal by PAC in the 1st stage (CSTR) and the total removal by PAC/NF. The compounds given on the x-axis are ordered following their molecular weight as this was shown to be the main criterion in rejection by nanofiltration (compare chapter 3). Table 4.4 presents the total removal rates of the selected compounds.



**Fig 4.4** Concentration and removal rates for selected micropollutants during PAC/NF treatment (10 mg/L PAC)



**Fig 4.5** Concentration and removal rates for selected micropollutants during PAC/NF treatment (50 mg/L PAC)

**Table 4.4** Total removal rates of micropollutants during PAC/NF at different PAC doses

Compound	removal rate at PAC dose of				
	0 mg/L	10 mg/L	25 mg/L	50 mg/L	100 mg/L
Benzotriazole	52.3%	84.5%	95.2%	98.7%	99.4%
Bezafibrate	55.1%	82.1%	>83.1%	na	na
Carbamazepine	48.7%	86.2%	>83.0%	>99.9%	>98.1%
Clarithromycin	77.1%	>97.7%	>88.3%	>98.2%	na
Clofibrac acid	42.9%	36.0%	na	na	na
Diclofenac	51.4%	80.3%	92.4%	98.7%	>98.6%
Diatrizoate	96.6%	83.2%	93.2%	na	95.3%
Erythromycin	82.8%	92.4%	>94.0%	>95.9%	>72.2%
Iomeprol	96.9%	88.2%	97.8%	97.0%	>99.1%
Iopamidol	97.3%	90.4%	97.4%	99.2%	99.6%
Iopromide	96.9%	90.3%	97.7%	98.8%	>99.9%
Iohexol	97.9%	88.8%	92.8%	99.0%	>90.9%
Primidone	64.3%	63.9%	74.4%	93.7%	98.5%
Roxithromycin	77.7%	94.8%	>90.2%	na	>68.8%
Sulfamethoxazole	66.3%	48.5%	68.4%	88.0%	98.0%

na = not available, concentration below level of quantification

Low PAC doses of 10 mg/L as typically applied in drinking water treatment could not improve the removal efficiency significantly (Fig 4.4). Although a small improvement of the total removal was observed for several poorly rejected compounds, the target permeate concentration of 100 ng/L was not reached for more than half of the compounds. Total removal rates varied between < 40% and >98%. Sulfamethoxazole and clofibrac acid were the most problematic compounds with low adsorption and poor total removal.

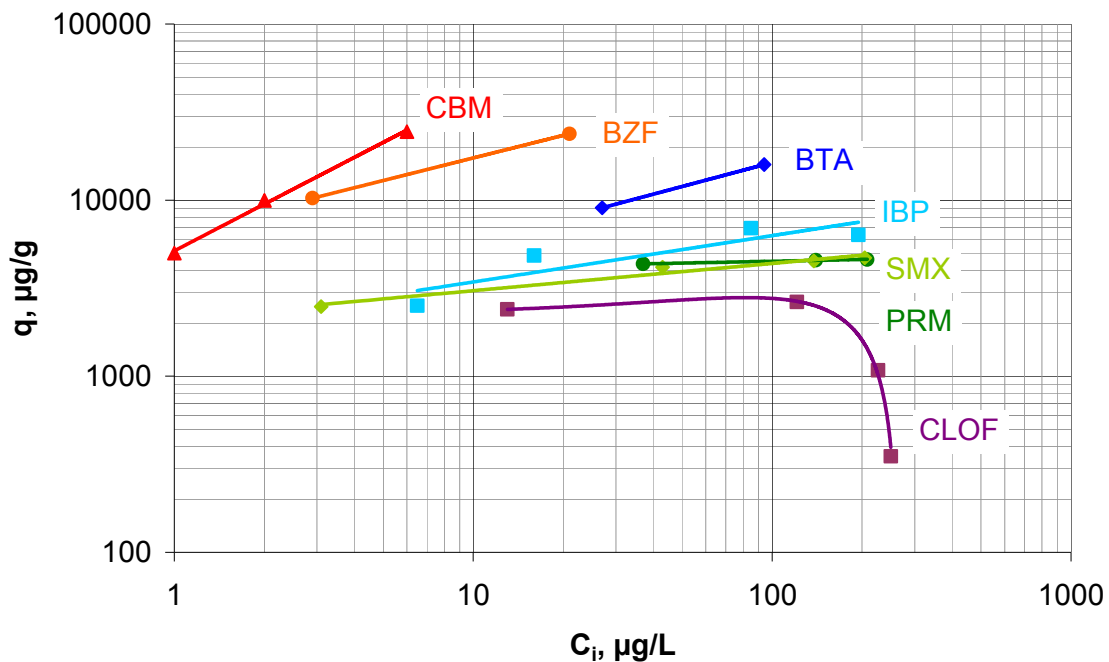
When increasing the PAC concentration to 25 mg/L (Table 4.3 and 4.4), the majority of compounds were removed above 80% and only sulfamethoxazole and primidone remained in the range between 70 to 80%. Most of the compounds were removed below 100 ng/L. However the permeate concentrations of benzotriazole and some contrast media remained slightly above 100 ng/L due to high raw water concentrations of 3 to 11 µg/L requiring removal rates above 99% to achieve the target values.

With a PAC dose of 50 mg/L the total removal increased considerably reaching 88% for sulfamethoxazole (66% without PAC) to >99.9% for carbamazepine (49% without PAC). The process combination demonstrates that poorly adsorbable contrast media are well retained by NF while PAC adsorbs small size molecules. At a carbon dose of 100 mg/L all compounds are removed below 100 ng/L and most of them even below the LOD. Sulfamethoxazole and diatrizoate appear to be the benchmark compounds.

It is noteworthy that a carbon dosage of 10 mg/L deteriorated the removal rates. For instance the high rejection of X-ray contrast media was reduced from >97% (0 mg/L PAC) to 83 – 90% (10 mg/L). This phenomenon attributable to cake enhanced concentration polarisation is discussed in more detail below in chapter 4.3.4.

### 4.3.3 Adsorptive removal

The adsorbability between the different organic micropollutants varies significantly. Figure 4.6 presents the result of an adsorption isotherm derived for SAE Super with a range of micropollutants spiked to the WWTP effluent in parallel (adsorption after 24 h;  $c_{\text{PAC}} = 0, 10, 25, 50, 100,$  and  $200$  mg/L). While the strongly adsorbing compounds such as CBM, BZF and BTA were removed at a carbon dose of 50 mg/L below the detection limit (ca.  $1 \mu\text{g/L}$ , without SPE) equivalent to >99.5%, the poorer adsorbable compounds (PRM, SMX and IBP) were still detectable at 100 mg/L PAC. For clofibric acid strong competitive effects were observed at low carbon dosages of 10 to 25 mg/L.



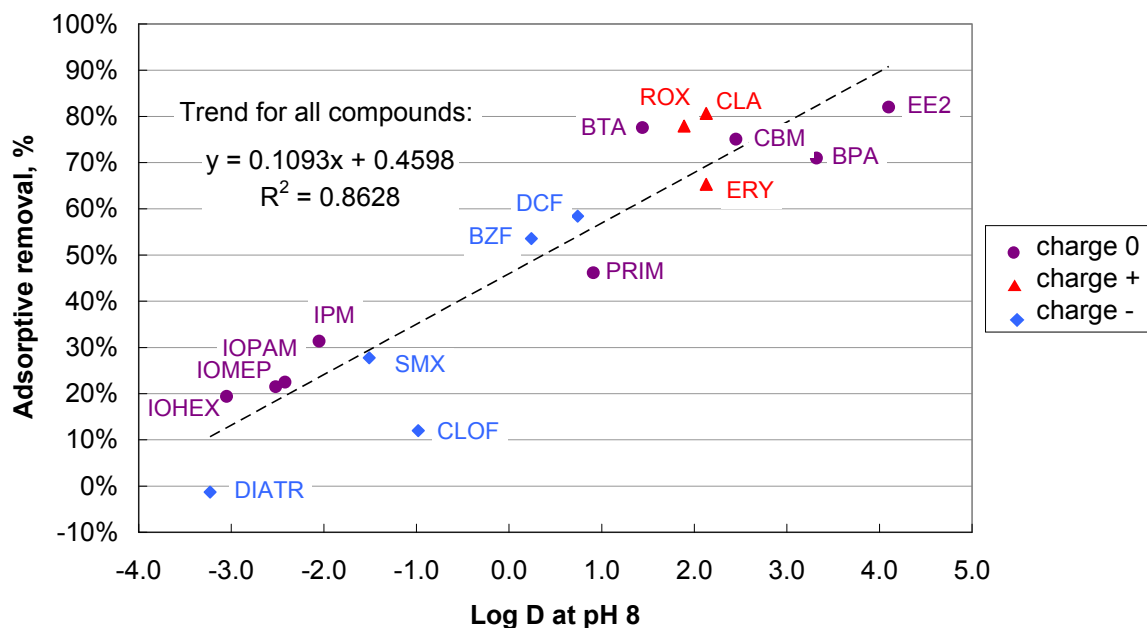
**Fig 4.6** Adsorption isotherms: Comparison of micropollutant adsorption (SAE Super, effluent from WWTP Aachen, parallel spiking of compounds,  $C_{0,i} = 250 \mu\text{g/L}$ ,  $C_{\text{DOC},0} = 8.2 \text{ mg/L}$  incl. spiked compounds)

Based on the results of the PAC/NF pilot tests at a carbon dose of 10 mg/L (*cf.* Figure 4.7), the compounds were grouped in 5 different classes. The results are presented in Table 4.5. The operating conditions of the pilot tests during the PAC dosage of 10 mg/L SAE Super comprised a contact time in CSTR of 1.2 h, a background DOC of  $3.9 \pm 0.6 \text{ mg/L}$ , a pH of  $7.9 \pm 0.2$  and a water temperature of 21 to 24 °C.

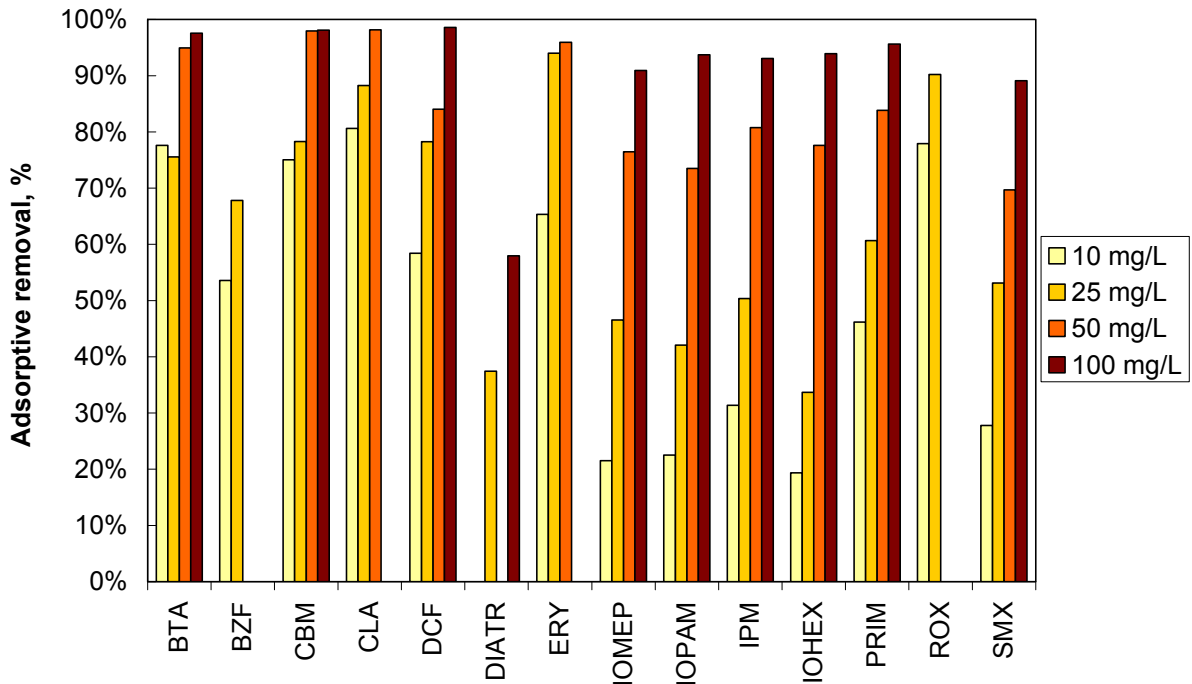
**Table 4.5** Treatment removal categories of selected compounds in PAC adsorption (10 mg/L PAC, contact time 1.2 h, DOC = 3.9 mg/L).

Adsorbability of compound	Removal rate at 10 mg/L PAC (SAE Super)	Example
very good	> 80%	17 $\alpha$ -ethinylestradiol
good	70 - 80%	benzotriazole, bisphenol A, carbamazepine, clarithromycin, roxithromycin, trimethoprim
moderate	50 - 70%	bezafibrate, diclofenac, erythromycin
poor	20 - 50%	iohexol, iomeprol, iopamidol, iopromide, iothalamic acid, naproxen, primidone, sulfamethoxazole
very poor	< 20%	clofibric acid, diatrizoate

Correlating the adsorptive removal at 10 mg/L PAC to the hydrophobicity of the investigated compounds given as log D, a clear trend could be identified (Figure 4.7). Different than expected, the charge of the compounds seemed to play a minor role.

**Fig 4.7** Adsorptive removal of selected micropollutants at 10 mg/L PAC versus Log D at pH 8

An overview of the adsorptive removal rates at different carbon concentrations is given in Figure 4.8. Several critical substances such as SMX and DIATR proved to be poorly adsorbable as even at 100 mg/L only 60 to 90% were sorbed. On the other hand BTA and CBM sorbed already at 50 mg/L to more than 95%.



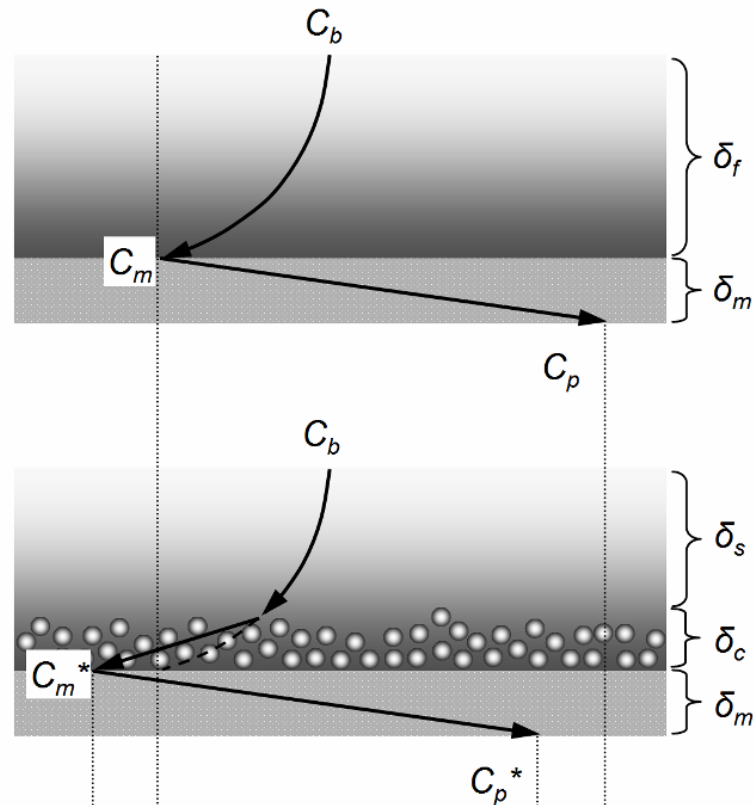
**Fig 4.8** Adsorptive removal of selected micropollutants in CSTR versus PAC dose (SAE Super, 1.2 h contact time in PAC CSTR, ambient micropollutant concentrations,  $DOC_0$ : 3.9 mg/L @ 10 mg/L PAC, 4.9 mg/L @ 25 mg/L PAC, 5.0 mg/L @ 50 mg/L PAC, 5.3 mg/L @ 100 mg/L PAC)

#### 4.3.4 Cake-enhanced concentration polarisation

Cake-enhanced concentration polarisation is a phenomenon well described in literature. It illustrates the additional increase of the concentration of soluble compounds, *e.g.* salt ions, in dense membrane processes such as reverse osmosis due to the formation of a cake layer, *e.g.* from small colloids passing through a MF pre-treatment. The effect of cake-enhanced concentration polarisation is twofold: It increases the concentration of the compound at the membrane surface  $C_m$  and leads to an increased permeate concentration  $C_p$  (*cf.* Fig 4.9).

Furthermore the elevated ion concentration increases the osmotic pressure and the energy requirement in dense membrane filtration. Hoek *et al.* (2002, 2003) applied this model to ion rejection in RO processes and confirmed that cake-enhanced concentration polarisation was the main factor causing a decreased salt rejection and a loss in permeate flux.

Applying this model to the PAC/NF process it becomes obvious that the formed cake layer is more solid than the colloid based layer in the experiments of Hoek *et al.* (2002). As shown by Meier (2008) a carbon based cake layer of 10 to 20  $\mu\text{m}$  can be expected under the applied operating conditions in terms of flux, crossflow velocity, carbon concentration and particle size.

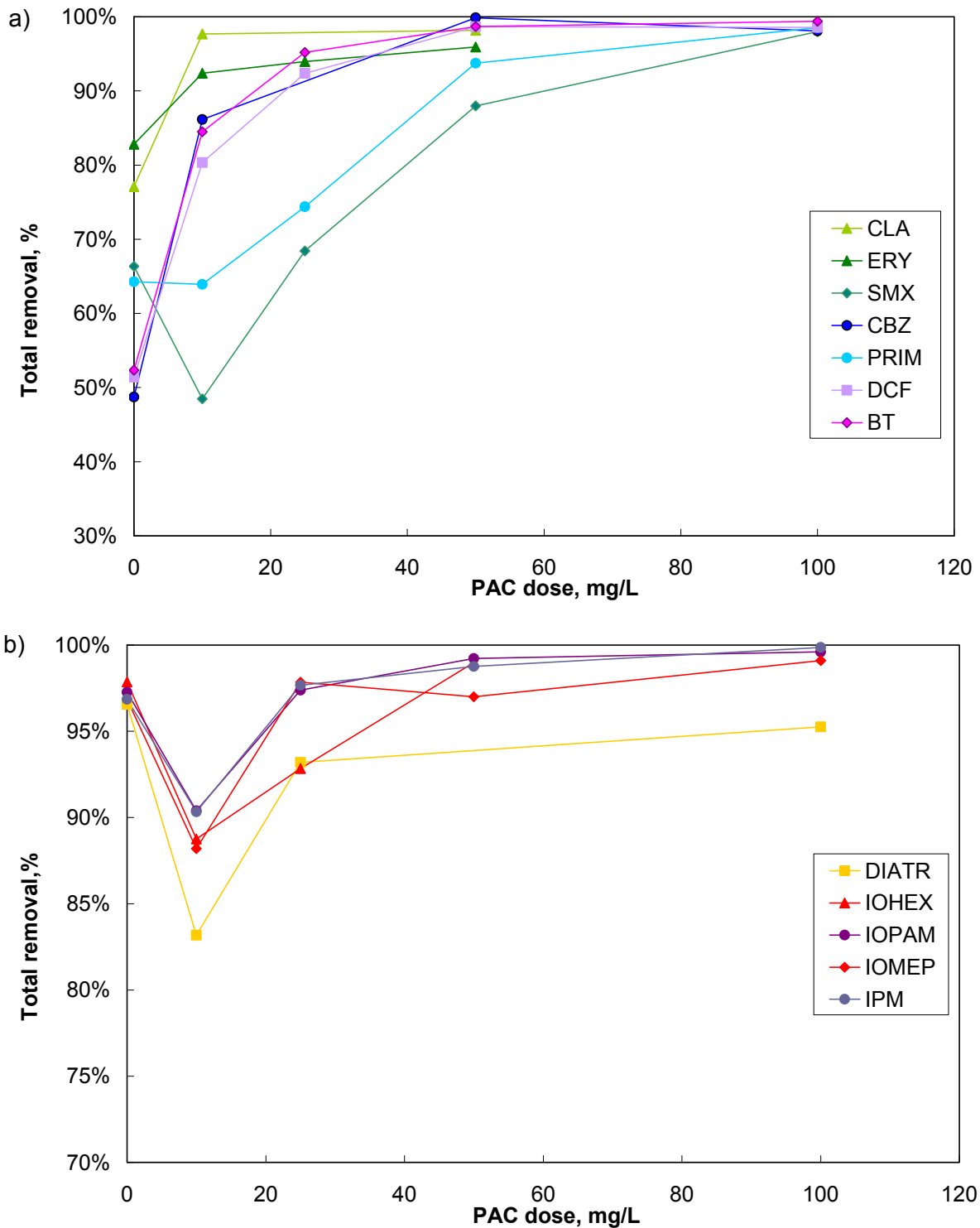


**Fig 4.9** Cake-enhanced concentration polarisation (adapted from Hoek *et al.*, 2002)

The carbon based cake layer leads to several effects relevant for the total removal of target solutes:

1. Increase of concentration of salt ions at the membrane surface ( $C_m^*$ ) and reduced salt rejection,
2. Increase of concentration of bulk and trace organics at the membrane surface ( $C_m^*$ ) and reduced rejection rates for poorly adsorbable compounds.
3. Increase of concentration of well adsorbable compounds leading to increased competitive adsorption and desorption of poorly adsorbable compounds triggering effect number 2

Figure 4.10 illustrates that exactly this phenomenon was observed. While well adsorbable compounds such as benzotriazole or diclofenac show a significantly improved total removal during PAC/NF treatment at low carbon dosage (10 mg/L), the total removal of poorly adsorbable compounds such as sulfamethoxazole decreases first and later recovers at higher carbon dosage. The same effect was detected for the removal of all X-ray contrast media. All investigated contrast media compounds showed a considerable decrease of removal from around 98% to 83-90% although their molecular weights (614-821 g/mol) are significantly above the MWCO of the NF membrane. This demonstrates the importance of the cake enhanced concentration polarisation, in particular at low carbon rates.



**Fig 4.10** Total removal rates *versus* PAC dose for a) antibiotics and acidic compounds and b) contrast media compounds

Likewise the rejection of salts was reduced due to cake-enhanced concentration polarisation. As shown in Table 4.8, the removal of sulphate was reduced from 70-90% to 60-70%, the removal of monovalent ions such as chloride was even stronger effected decreasing from a small retention around 5-20% to values between 5 to -5% depending on the carbon dosage. Figure 4.11 illustrates the impact of the PAC dose on the membrane retention of the selected organic micropollutants. PAC dosage reduced the membrane retention of all compounds. The



reduction from the NF membrane retention without carbon dosage to PAC/NF with 10 mg/L PAC varies between 5% for the well rejected compounds such as contrast media and 60% for the poorly rejected benzotriazole. Although there is a trend of an increasing reduction in membrane retention with decreasing original membrane retention in direct NF, a direct correlation could not be confirmed. In most cases higher PAC doses lead to further decrease in membrane retention. This suggests that addition of PAC to the NF crossflow loop has multiple and complex consequences for the micropollutant removal which are compound specific and depending on the PAC dose. PAC may influence the membrane retention by the following effects:

- Build-up of a carbon based cake layer resulting in increased *concentration polarisation*,
- *Screening of negative surface charge* leading to a reduced rejection of negatively charged solutes and
- *Increased adsorption of compounds* to activated carbon attached to the membrane.

The strongest decrease in retention over the whole range of PAC doses was observed for primidone and sulfamethoxazole. Both compounds are poorly adsorbable, but they are differently charged (SMX negative, PRIM neutral).

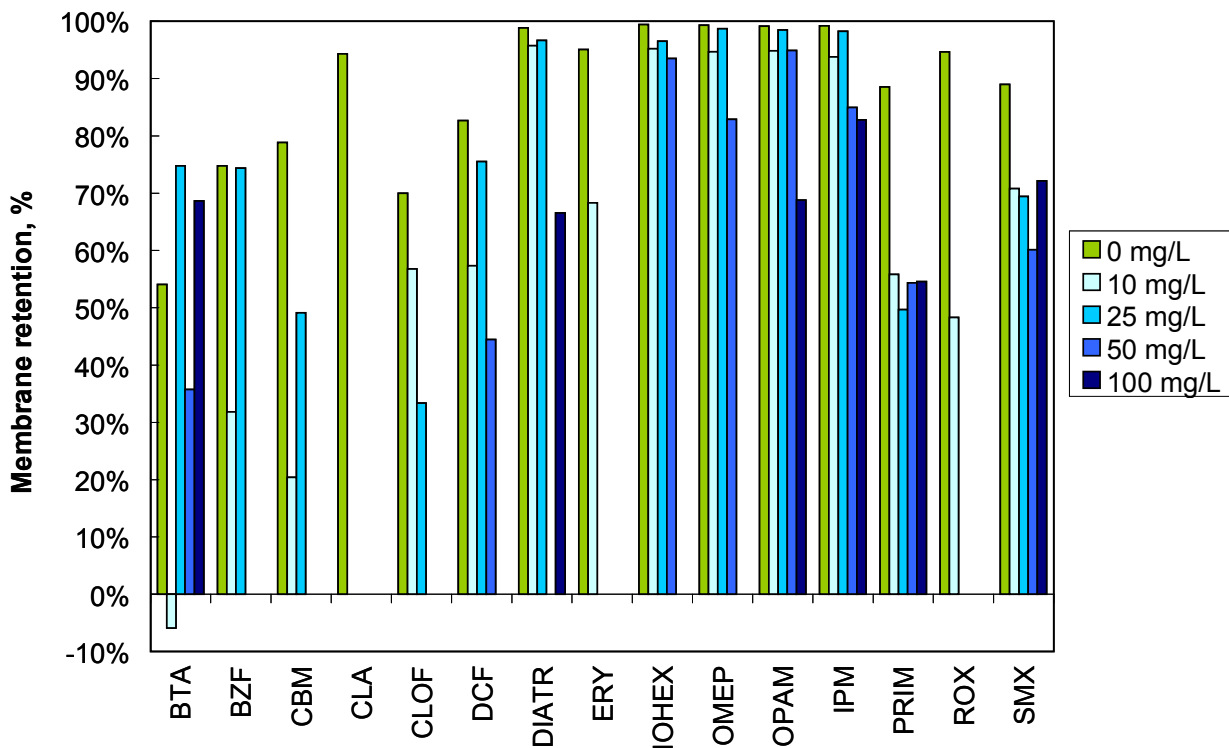
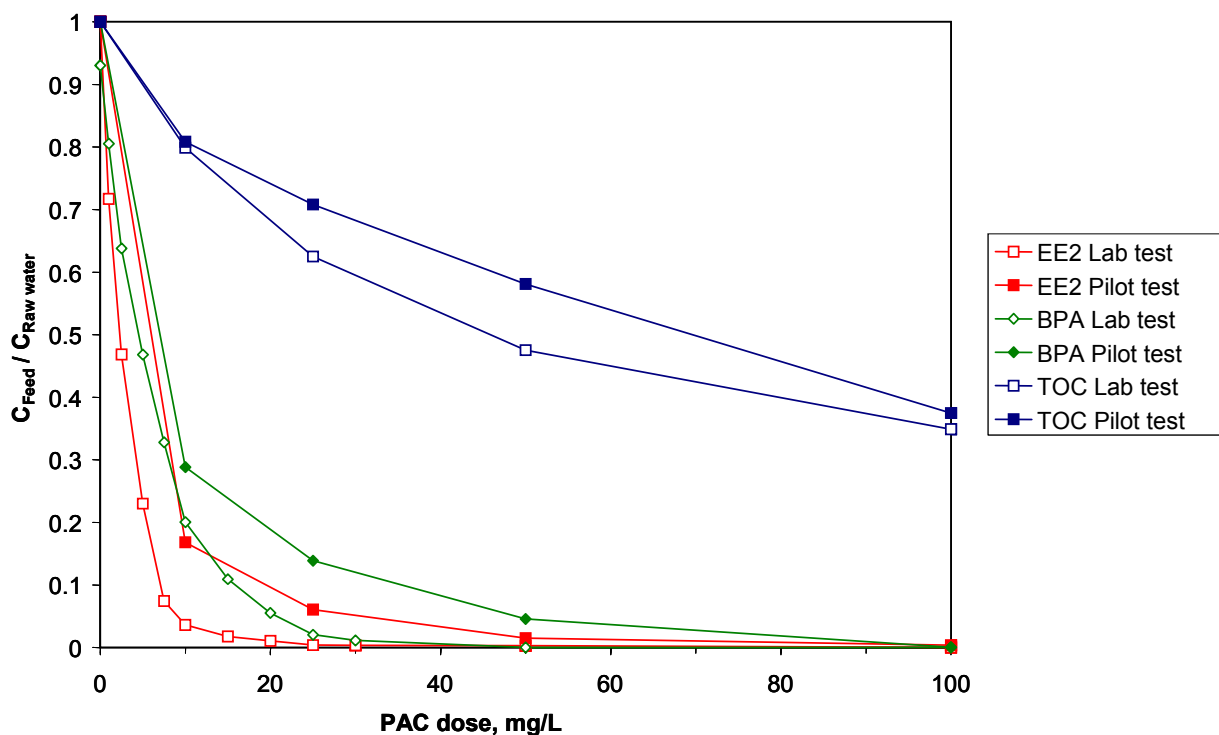


Fig 4.11 Membrane retention *versus* PAC dose

#### 4.3.5 Interplay between adsorption and nanofiltration

As explained in the introduction (*cf.* Table 4.1) the optimisation of PAC/NF has to consider the single treatment steps, *i.e.* PAC adsorption and NF, and the interaction between the two

processes. As described above, cake enhanced concentration polarisation as main impediment of the NF cannot be avoided completely. Optimisation of the adsorption step has to determine in particular the optimum contact time besides the selection of the appropriate carbon type. Lehnberg (2008) showed for EE2 and BPA that with increasing PAC concentration the adsorption kinetics improve. Figure 4.12 illustrates the difference between the lab tests with 24 h contact time and the pilot tests with 1.2 h contact time in the CSTR adsorption tank. For instance, EE2 is sorbed to 83% at a carbon dose of 10 mg/L during the pilot tests while extending the contact time to 24 h increases the removal rate to above 97%. Similar differences are observed for BPA and higher PAC concentrations up to 50 mg/L. The observation from the lab tests of Lehnberg (2008) was confirmed by the pilot tests. Several technical approaches have been proposed to extend the contact time and the retention time of the PAC. Metzger (2010) showed that an increased adsorption could be achieved, if the carbon is recycled within the PAC adsorption unit and subsequently returned to the activated sludge system. This is supported by the observation that the adsorption of some organic micropollutants is not completed after 24 h (Knappe *et al.*, 2007).



**Fig 4.12** Comparison of adsorption of DOC, EE2 and BPA in lab test and pilot test (SAE Super, contact time in lab test 24 h and in pilot test 1.2 h)

### Mass balance

Besides the optimisation of the single treatment steps adsorption and nanofiltration, PAC/NF shows specific removal behaviour for each compound. To further characterise the interplay between the two processes and the importance of the post-adsorption in the NF crossflow loop, mass balances were calculated for DOC representing the bulk organics and selected

micropollutants representing typical compound behaviour using the following balance equations:

$$0 = -\dot{m}_i + \dot{m}_{\text{ads,CSTR}} + \dot{m}_{\text{ads,CF NF}} + \dot{m}_r + \dot{m}_p \quad (4.4)$$

$$0 = -c_i \cdot Q_i + c_{\text{ads,CSTR}} \cdot Q_i + c_{\text{ads,CF NF}} \cdot Q_r + c_r \cdot Q_r + c_p \cdot Q_p \quad (4.5)$$

where  $\dot{m}_i$  = mass flux of compound in the influent water (= WWTP effluent)  
 $\dot{m}_{\text{ads,CSTR}}$  = mass flux of compound adsorbed to PAC in the CSTR  
 $\dot{m}_{\text{ads,CF NF}}$  = mass flux of compound adsorbed to PAC in the NF crossflow loop  
 $\dot{m}_p$  = mass flux of compound in the permeate  
 $\dot{m}_r$  = mass flux of compound in the retentate  
 $c_i$  = concentration of compound in the influent (= WWTP effluent)  
 $c_{\text{ads,CSTR}}$  = concentration of compound adsorbed to PAC in the CSTR  
 $c_{\text{ads,CF NF}}$  = concentration of compound adsorbed to PAC in the NF CF loop  
 $c_p$  = concentration of compound in the permeate  
 $c_r$  = concentration of compound in the retentate  
 $Q_i$  = volumetric flow rate of the influent (= WWTP effluent)  
 $Q_p$  = volumetric flow rate of the permeate  
 $Q_r$  = volumetric flow rate of the retentate

The results of the mass balance are given in Table 4.6. Balancing the DOC it becomes obvious that even at high PAC concentrations about 40% of the bulk organics remain dissolved. Interestingly doubling the PAC dose increased the adsorption in the CSTR stage without major change of the overall adsorption.

As shown in Table 4.7 and in Figure 4.13 and 4.14, five different adsorption-rejection types were identified. Diclofenac exemplifies *type A* where poor to moderate initial removal of the NF quickly increases with PAC dosage due to good adsorbability of the compound. The mass balance reveals that at 25 mg/L PAC 94% of the DCF mass flux are removed. Other compounds following this pattern are BTA, CBM, BPA and EE2. Type A represents the ideal case of PAC/NF showing the maximum improvement in removal. *Type B* (e.g. primidone) varies type A whereas due to poorer adsorbability of the compound a delay in improvement was observed leading to increased removal rates only at higher PAC doses. *Type C, D* and *E* show all compound behaviour with moderate to strong impact of cake enhanced concentration polarisation due to poor to very poor adsorbability of the target solutes. Substantial improvement was achieved at higher PAC doses of about 50 mg/L. Neutral contrast media are examples for type C, ionic contrast media such as diatrizoate represent type D. Sulfamethoxazole and clofibrac acid show the type D behaviour with poor to moderate rejection in NF increasing to removal rates around 90% at 50 mg/L PAC.

**Table 4.6** Mass balance of DOC and selected micropollutants at different PAC doses (\* = compound spiked at 1 µg/L)

Compound	Mass fraction	Mass fraction at PAC dose, %				
		0 mg/L	10 mg/L	25 mg/L	50 mg/L	100mg/L
DOC	m solved, permeate	4.9	7.5	7.3	4.1	4.0
	m solved, retentate	95.1	70.7	56.4	42.3	35.3
	m adsorbed, CSTR	0.0	19.6	29.1	41.9	60.7
	m adsorbed, CF NF	0.0	2.3	7.2	11.7	0.0
Benzotriazole	m solved, permeate	38.2	11.4	3.8	1.0	0.5
	m solved, retentate	59.8	3.9	3.9	0.5	0.5
	m adsorbed, CSTR	0.0	77.6	75.6	94.9	97.5
	m adsorbed, CF NF	0.0	7.1	16.7	3.6	1.5
Bisphenol A *	m solved, permeate	67.9	9.1	3.8	4.6	0.0
	m solved, retentate	32.1	3.5	1.7	0.3	0.2
	m adsorbed, CSTR	0.0	71.2	86.4	95.1	99.8
	m adsorbed, CF NF	0.0	16.1	8.2	0.0	0.0
Carbamazepine	m solved, permeate	38.9	10.2	13.5	0.1	1.4
	m solved, retentate	58.2	4.6	6.9	0.0	0.5
	m adsorbed, CSTR	0.0	75.1	78.3	97.9	98.1
	m adsorbed, CF NF	0.0	10.1	1.3	2.0	0.0
Diclofenac	m solved, permeate	36.9	14.4	6.1	1.0	1.1
	m solved, retentate	67.4	12.2	6.4	0.6	0.4
	m adsorbed, CSTR	0.0	58.5	78.3	84.1	98.5
	m adsorbed, CF NF	0.0	14.9	9.2	14.3	0.0
Diatrizoate	m solved, permeate	2.6	12.4	5.4	NA	3.6
	m solved, retentate	72.6	104.6	42.3	NA	3.5
	m adsorbed, CSTR	0.0	-1.3	37.4	NA	58.0
	m adsorbed, CF NF	0.0	-15.7	14.9	NA	34.9
17 $\alpha$ -Ethinylestradiole *	m solved, permeate	52.9	1.7	0.7	2.2	0.2
	m solved, retentate	47.1	1.4	0.3	0.1	0.0
	m adsorbed, CSTR	0.0	83.2	94.1	89.0	99.6
	m adsorbed, CF NF	0.0	13.7	4.9	8.7	0.1
Iopromide	m solved, permeate	2.4	7.1	1.8	0.9	0.1
	m solved, retentate	94.9	41.2	27.0	2.1	0.2
	m adsorbed, CSTR	0.0	31.4	50.4	80.8	93.9
	m adsorbed, CF NF	0.0	20.3	20.8	16.2	5.8
Primidone	m solved, permeate	27.1	26.5	20.3	4.7	1.1
	m solved, retentate	74.9	21.7	10.5	3.5	0.8
	m adsorbed, CSTR	0.0	46.2	60.7	83.8	95.6
	m adsorbed, CF NF	0.0	5.6	8.5	8.0	2.5
Sulfamethoxazole	m solved, permeate	25.6	37.9	25.1	9.0	1.5
	m solved, retentate	73.5	46.8	21.3	7.6	1.8
	m adsorbed, CSTR	0.0	27.8	53.1	69.7	89.1
	m adsorbed, CF NF	0.0	-12.5	0.5	13.7	7.6

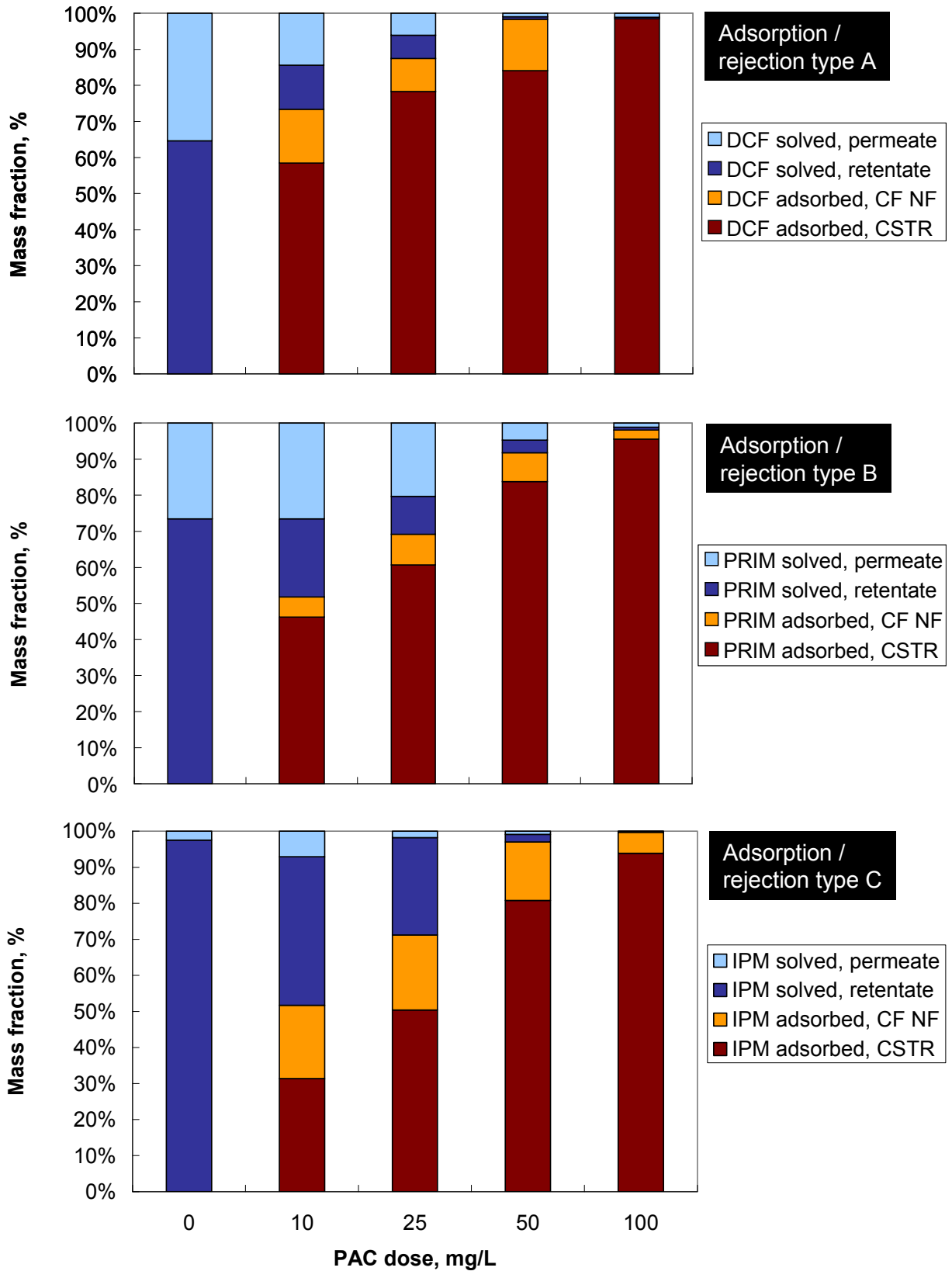
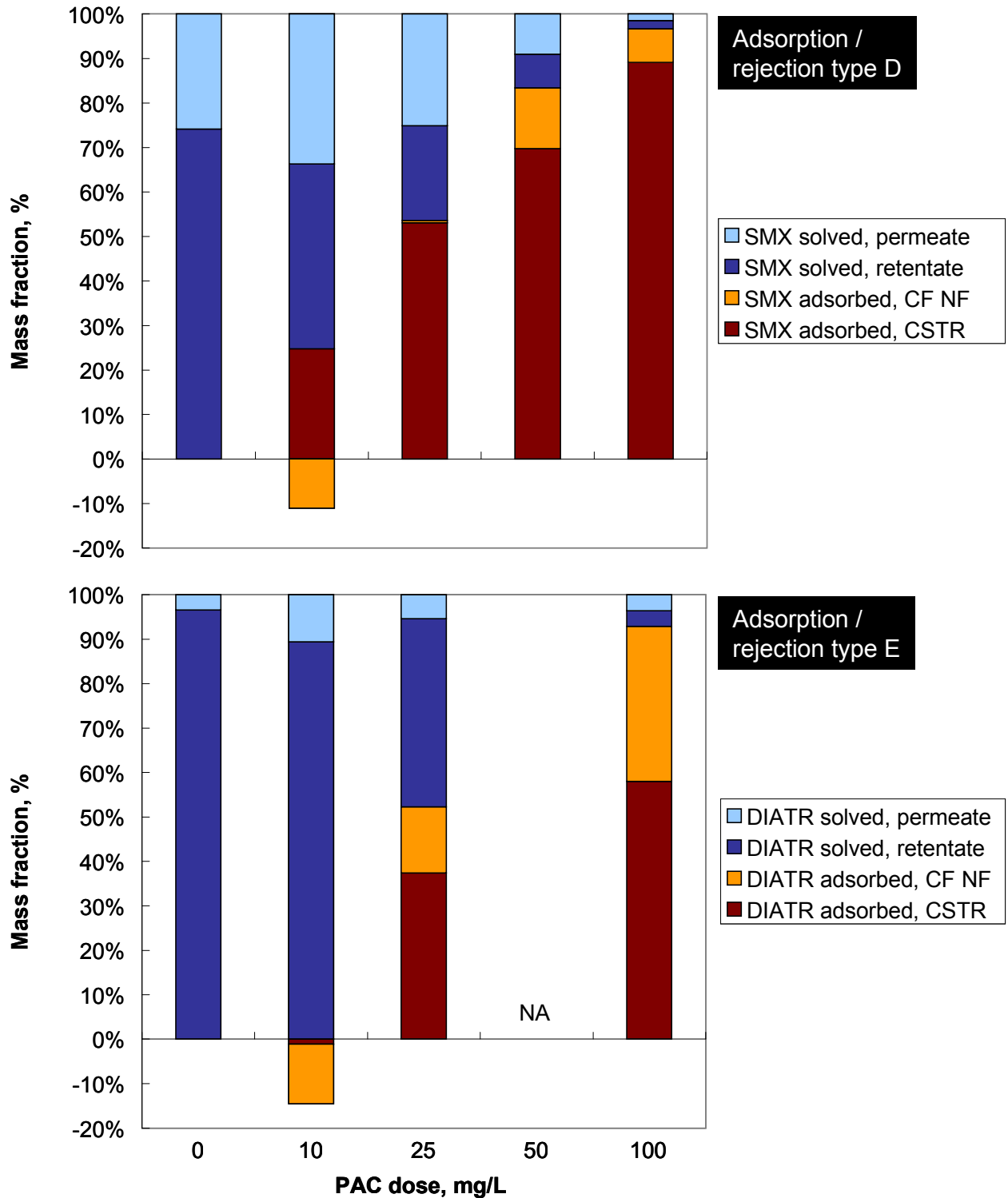


Fig 4.13 Mass balance for A) DCF, B) PRIM and C) IPM at different PAC doses



**Fig 4.14** Mass balance for D) SMX and E) DIATR at different PAC doses (NA = not available)

Comparing the different adsorption rejection types (*cf.* figure 4.13 and 4.14) reveals that the post-adsorption in the crossflow loop can have positive and in some cases very significant impact on the total PAC adsorption, *e.g.* for neutral contrast media. However, at a carbon dosage of 10 mg/L desorption effects were observed for charged compounds with poor adsorbability, *i.e.* log D value < -1, presumably due to competitive adsorption with

compounds of higher adsorbability. This reinforced the effects from cake enhanced concentration polarisation and lead to an overall reduced rejection of the target compound. Even at a PAC dosage of 25 mg/L sulfamethoxazole did not show an increased adsorption in the crossflow post-adsorption stage.

**Table 4.7** Typology of micropollutant behaviour in PAC/NF treatment

Adsorption / rejection type	Adsorbability of compound	Retention of compound by cap NF	Behaviour in PAC/NF	Required PAC dose	Example
A	very good to good	poor to moderate	poor to moderate removal in NF increases rapidly with increasing PAC dose	low to medium	benzotriazole, carbamazepine, diclofenac, bisphenol A, 17 $\alpha$ -ethinylestradiole
B	poor	moderate	moderate removal in NF remains unchanged at low PAC dose and rises continuously at higher PAC dose	medium to high	primidone
C	poor	high	high removal in NF decreases at low PAC dose before it recovers at higher PAC dose	medium	neutral contrast media, e.g. iopromide, iohexole, iopamidole
D	poor	poor to moderate	moderate removal in NF decreases at low PAC dose before it increases at higher PAC dose	high	sulfamethoxazole, clofibric acid
E	very poor	high	high removal in NF decreases at low PAC dose before it recovers at higher PAC dose	medium to high	diatrizoate

#### 4.3.6 Comparison of PAC/NF with PAC and NF treatment

Table 4.8 provides a summary of the removal behaviour of the single treatment systems and their combinations at a PAC dose of 10 and 50 mg/L. While PAC/NF does not clearly improve the removal of bulk organics, it has a very significant impact on the removal of micropollutants. All compounds were removed by 90 to 99.9% at a PAC dose of 50 mg/L. Due to cake enhanced concentration polarisation (Meier, 2008) salinity removal deteriorates.

**Table 4.8** Average rejection rates for direct NF and PAC/NF (NF: Norit X-Flow NF50M10, 75 % recovery, 20 L/m<sup>2</sup>·h, PAC: Norit SAE Super C<sub>DOC,0</sub> = 5 - 6 mg/L)

	Unit mg/L	NF 0	PAC adsorption		PAC/NF	
			10	50	10	50
<b>Bulk organics</b>						
DOC	%	90 - 95	20	50 - 60	90 - 95	90 - 95
<b>Salinity</b>						
Conductivity	%	15 - 20	0	0	12	12
Sulfate	%	70 - 90	0	0	60 - 70	60 - 70
Chloride	%	5 - 20	0	0	3 - 5	-5 - 0
<b>Organic micropollutants</b>						
<i>Complexing agents</i>						
Benzotriazole	%	50	80	95	85	98
<i>Lipid regulators</i>						
Bezafibrate	%	50	55	∅	80	∅
Clofibrac acid	%	40	10	∅	35	∅
<i>Antiphlogistics / analgesics</i>						
Diclofenac	%	50	60	85	80	99
<i>Anti-convulsants/anti-epileptics</i>						
Carbamazepine	%	50	75	98	85	99.9
Primidone	%	65	50	85	55	95
<i>Antibiotics</i>						
Macrolides (CLA, ERY, ROX)	%	80	80	>99	95	>99
Sulfamethoxazole	%	65	30	70	50	90
<i>Iodinated contrast media</i>						
Neutral X-ray contrast media	%	99	20 - 30	75 - 80	90	97 - 99
Diatrizoate	%	95	0	50 *	85	94 *
<i>Endocrine disruptors</i>						
Bisphenol A	%	10	80	90	98	98
17 $\alpha$ -Ethinylestradiol	%	30	70	95	88	94

∅ Concentrations below LOQ

\* Value for 50 mg/L estimated based on removal rates at 25 and 100 mg/L (cf. Table 4.4)



## 4.4 Conclusions

The PAC/NF process combining adsorption on PAC with nanofiltration can be regarded as a reliable treatment concept for the production of high quality recycled water. Removal rates of above 90% for a broad range of pollutants prove that PAC/NF is an alternative to double membrane processes (UF/RO), if a high degree of desalination is not required. It is also an alternative to the combination of GAC and NF as presented by Roorda *et al.* (2005).

PAC/NF further provides combined treatment of the organics in NF concentrate. At PAC doses of about 50 mg/L the selected trace organics were reduced by 1 to 3 log<sub>10</sub> units and effluent organic matter was removed from 5 - 6 mg/L DOC to below 0.5 mg/L (*cf.* chapter 6). The PAC/NF process can provide a high quality permeate from treatment of tertiary effluent reaching concentrations below 100 ng/L or even close to the level of quantification for the relevant organic micropollutants. If intended for indirect potable reuse many of the investigated compounds can further break down in subsequent natural treatment process such as managed aquifer recharge. In a comprehensive literature review, Maeng *et al.* (2011a) confirmed that biodegradation of pharmaceuticals plays a key role in their removal during aquifer recharge and river bank filtration. However some compounds such as carbamazepine are not biodegradable (Laws *et al.*, 2011, Maeng *et al.*, 2011b).

Through selection of the adsorbent and its dosage, the PAC/NF process allows the exact adjustment of the permeate quality according to the site specific requirements with regard to the raw water characteristic and intended use of recycled water. Two factors are crucial for an efficient and stable application of the PAC/NF process:

1. Exact control of the cake layer, which may lead to significant cake enhanced concentration polarisation of poorly adsorbable compounds and thus limit the total removal of target solutes, and
2. Choice of the appropriate adsorbent which should have a high adsorptive capacity for the most critical compounds such as sulfamethoxazole or diatrizoate.

Recent investigations of micropollutant removal from WWTP effluent by PAC revealed that different PAC types have significant differences regarding the adsorptive capacity for poorly adsorbable compounds (*e.g.* sulfamethoxazole) although the inner surface of the PACs was comparable (Grünebaum *et al.*, 2011). In the study of Grünebaum *et al.* (2011) the carbon employed in the present investigation (SAE Super) reached only 50% of the adsorptive capacity of another powdered activated carbon. In a 24-hour batch test with a carbon dose of 25 mg/L and a background DOC of 4.2 mg/L, removal rates for sulfamethoxazole ranged from 35 to 40% (SAE Super) to 80% (Donau Carbon Carbopal AP). This suggests that the required PAC dose could possibly be halved from 50 mg/L to about 25 mg/L with significant impact on the process operation (*cf.* chapter 7) and costs.

In order to maximise the contact time of the activated carbon, further optimisation could be achieved through PAC recycling from the crossflow NF loop to the adsorption reactor and then the excess carbon from the PAC system to the activated sludge system similar to the treatment concept of Metzger (2010). However, desorption effects as observed in low PAC doses during PAC/NF cannot be ruled out completely. Furthermore desorption effects should be also considered when introducing the excess sludge with loaded PAC to the anaerobic digestion system. From the economic point of view it could further be interesting to employ a slightly denser capillary nanofiltration membrane to better retain compounds such as sulfamethoxazole that would allow reducing the carbon dose.

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## 5 Removal of organic micropollutants from tertiary effluent by combinations of granular activated carbon adsorption and nanofiltration

### 5.1 Introduction

Granular activated carbon adsorption (GAC) is the state of the art in removal of DOC and trace contaminants in drinking water treatment (Hobby and Gimbel, 2004; Crittenden *et al.*, 2005; von Gunten *et al.*, 2006). An increasing number of studies have investigated granular and biological activated carbon treatment for the removal of micropollutants and in particular pharmaceuticals from WWTP effluent (*e.g.* Roorda *et al.*, 2005; Snyder *et al.*, 2007; Nowotny, 2009; Beier, 2010; Reungat *et al.*, 2011). At the Goreangab water reclamation plant in Windhoek, Namibia, a combination of BAC and GAC serves as main barrier against organic contaminants (Menge *et al.*, 2009). Granular activated carbon binds the contaminants through adsorption and has to be renewed or regenerated regularly, whereas biological activated carbon sorbs the contaminants, degrades them biologically and generates metabolites which are sometimes very stable.

Granular activated carbon filtration can also be used in combination with nanofiltration either as pretreatment (*i.e.* GAC/NF) to reduce the concentration of bulk and trace organics, suspended solids and bacteria or as posttreatment (*i.e.* NF/GAC) for removing trace organics from NF permeate. In the same way as PAC/NF, nanofiltration and granular activated carbon filtration are expected to act complementary in removing organic micropollutants.

Compared to surface and groundwater, WWTP effluent has high concentrations of organics from different natural, microbial and synthetic sources known as effluent organic matter (EfOM) which causes elevated carbon fouling. DOC concentrations range in secondary effluent between 5 to 20 mg/L (Metcalf & Eddy, 2004). Thus GAC adsorbers require frequent backwashing to prevent growth of a biofilm and transition to biologically active GAC treatment which limits the ability to remove non-degradable trace organics as observed by Snyder *et al.* (2007). Organic fouling and biofouling can therefore compromise the efficiency of GAC. Roorda *et al.* (2005) tested GAC/NF in pilot scale using real secondary effluent. They coupled a GAC filter with a relatively large empty bed contact time of 30 minutes with a capillary nanofiltration unit. They observed several advantages over direct nanofiltration, such as high fluxes (30 L/m<sup>2</sup>·h instead of 10-20 L/m<sup>2</sup>·h) at low TMP, high recovery above 94% without scaling and low brine production (<6%), reduced chemical cleanings (< 1 per month), and slightly improved removal of micropollutants such as carbamazepine and diclofenac at costs similar to direct NF. In NF/GAC the concept is different as NF serves as bulk organic barrier for GAC. Compounds not well rejected by nanofiltration are then more readily adsorbed by the GAC filtration (Heijman *et al.*, 2007). In comparison to effluent GAC, the bed volumes till the filter bed exhaustion are extended significantly (Ernst, 2000).

Furthermore GAC adsorption as posttreatment improves the removal of organic micropollutants significantly (Verliefde *et al.*, 2007; Verliefde, 2008). The NF/GAC process allows an extended and economic operation of the GAC filter and provides a double barrier minimising the potential break-through of trace contaminants (Snyder *et al.*, 2007).

While the general applicability of GAC in water reuse is well documented, long-term behaviour of GAC filtration in combination with nanofiltration, particularly in terms of micropollutant removal has not been investigated. Due to the different water qualities and removal tasks for GAC adsorption, significant differences between GAC/NF and NF/GAC can be expected. The study described here aims to elucidate the optimum process combination in terms of micropollutants removal. The performance and reliability of both process combinations were studied in pilot scale treating municipal WWTP effluent. Supporting lab scale experiments with rapid small-scale column tests (Crittenden *et al.*, 2005) were conducted to identify favourable GAC types and gain further insight in the behaviour of different trace contaminants.

## 5.2 Materials and Methods

### 5.2.1 Selected organic micropollutants

Based on the experiences from previous tests (*cf.* chapter 3 and 4), a range of pharmaceuticals and industrial chemicals typically present in WWTP effluent and representing characteristic compound classes were selected to test the performance of the GAC-NF hybrid processes. Table 5.1 presents an overview of the selected organic micropollutants. The list covers substances with molecular weights close to the MWCO of the NF and compounds which have been shown to be critical in adsorption processes, such as SMX and CLOF.

**Table 5.1** Organic micropollutants selected for GAC-NF tests

Compound	Short name	MW g/mol	pK <sub>a</sub>	Log K <sub>ow</sub>	Log D at pH 8	Charge at pH 7-8	Pilot tests	Lab tests
Benzotriazole	BTA	119.13	8.37	1.44	1.44	0	●	sp
Bezafibrate	BZF	361.82	3.44	4.25	0.24	-		sp
Carbamazepine	CBM	236.27	0.37	2.45	2.45	0	●	sp
Clofibric acid	CLOF	214.65	3.35	2.57	-0.98	-		sp
Ibuprofen	IBP	206.29	4.47	3.97	0.44	-		sp
Primidone	PRIM	218.25	12.3	0.91	0.91	0	●	sp
Sulfamethoxazole	SMX	253.28	5.60	0.89	-1.51	-	●	sp

(● = real concentration, sp = spiking of compound)

During the pilot tests benzotriazole, carbamazepine, primidone and sulfamethoxazole were measured at ambient effluent concentrations. During NF/GAC two samplings further included bezafibrate, clarithromycin, erythromycin, trimethoprim, and X-ray contrast media. The GAC rapid small-scale column tests were conducted with spiked compounds and thus could be extended to other contaminants present in the effluent in ambient concentrations below 100 ng/L (*cf.* chapter 4.3). WWTP effluent, NF permeate and NF concentrate were spiked with the compounds according to table 5.1 in concentrations of 250 µg/L.

### 5.2.2 Sampling and analytical methods

All samples from the pilot plants were taken as 24 h composite samples. An auto sampling unit of MAXX GmbH provided the sampling of the raw water (influent to GAC adsorber or NF feed, respectively), GAC filtrate and NF permeate. Samples of 200 mL were collected automatically every 30 min in a 10 L Duran glass bottle and stored in darkness at 4°C to inhibit microbial growth and to avoid photochemical reaction. The samples from the GAC adsorber at the respective levels and from the NF concentrate were taken manually every two to four hours through sampling valves and also stored in glass bottles at 4°C. The composite samples of these points were produced manually through mixing of the grab samples.

Cuvette tests (Hach Lange) were employed for the analysis of standard parameters such as ammonia, nitrate, phosphate, sulphate, chloride and COD. A Varian Cary 1 E UV/Vis spectrophotometer was used to determine the UV<sub>254</sub>. The samples for DOC measurement were pre-filtered with 0.45 µm filters (Acrodisc, Pall Corporation). TOC and DOC were analysed by a DIMA-TOC 100 total organic carbon analyser (Dimatec Analysentechnik GmbH, Germany).

For the samples of the pilot tests, measurement of micropollutants was performed using SPE enrichment prior to LC-MS-MS detection according to the 'Antibiotics' and 'Acidics' methods developed and described as in Ernst *et al.* (2012). The methods have been transferred to the laboratory of the Department of Chemical Engineering, RWTH Aachen University as described in Yu (2012). Method 1 'Antibiotics' was used for the detection of benzotriazole, primidone, carbamazepine and sulfamethoxazole; method 2 'Acidics' was employed for the measurement of ibuprofen, bezafibrate and clofibric acid. Details of the methods and sample preparation are given in Annex 9.3. A LC with a linear ion trap-quadrupole-mass spectrometer (Thermo Finnigan LXQ; Thermo Scientific, USA) was used for the measurement of trace pollutants with a Hypersil Gold 5 µm column (150 x 2.1 mm, Thermo Scientific) for method 1 and Hypersil Gold aQ 3 µm column (150 x 2.1 mm, Thermo Scientific) for method 2. Injection volume was 20 µl. Method 1 used ESI (electrospray ionisation) and method 2 APCI (atmospheric pressure chemical ionisation). The samples of the RSSCT experiments employed method 1 and 2 without SPE. Table 5.2 presents the LOQ of the methods for the specific compounds.

**Table 5.2** Limit of quantification of the LC/MS measurement at RWTH Aachen University (Thermo Finnigan LXQ, Thermo Scientific)

Compound	Short name	LOQ, µg/L	Method *
Benzotriazole	BTA	10	1
Bezafibrate	BZF	1	2
Carbamazepine	CBM	0.5	1
Clofibric acid	CLOF	1	2
Ibuprofen	IBP	5	2
Primidone	PRIM	5	1
Sulfamethoxazole	SMX	0.5	1

\* cf. Annex 9.3

### 5.2.3 Adsorbents

The experiments used different commercially available granular activated carbons and one extruded activated carbon. The carbons covered a range of different qualities in terms of inner surface, raw materials and grades (virgin carbon *versus* reactivate). Table 5.3 gives an overview of the investigated carbon types.

**Table 5.3** Characteristics of investigated GAC types according to supplier information

Supplier	Product name	Particle diameter mm	Iodine number mg/g	Inner surface m <sup>2</sup> /g	Density after BW kg/m <sup>3</sup>	Price €/kg	Raw material	Comment
Chem- viron	Aquacarb 207C	0.6 - 1.7	1100	1100	530	na	coconut	virgin carbon
	Cyclecarb 201	0.43 - 2.36	775	800	470	0.87	coal	reactivate
	Cyclecarb 401	0.43 - 2.36	900	900	450	1.20	diverse	reactivate
	Filtrisorb 300	0.6 - 2.36	950	950	460	1.70	coal	virgin carbon
Donau Carbon	Epibon A 8x30	0.6 - 2.36	>1100	1200	300	1.65	not available	virgin carbon
	Hydraffin XC30	0.6 - 2.36	950	1000	450	1.45	coal	virgin carbon
Norit	NRS Carbon GA	0.5 - 2.5	850	975	430	1.00	diverse	reactivate
	NRS Carbon EA	0.5 - 2.5	875	1000	360	1.50	diverse	reactivate
	Norit GAC 830 EN	0.6 - 2.36	1000	1100	435	1.90	coal	virgin carbon



Prior to the pilot and the RSSCT tests, all carbons were tested in batch adsorption tests and the optimum carbon types for the respective water selected. Table 5.4 presents the selection for the different test runs.

**Table 5.4** GAC types selected for pre-tests, RSSCT and pilot tests

Product name	Pilot test		WWTP effluent	RSSCT	
	GAC/NF	NF/GAC		NF permeate	NF concentrate
Aquacarb 207C			○	○	○
Cyclecarb 201			○	○	○
Cyclecarb 401			○	○	○ ●
Filtrisorb 300			○ ●	○ ●	○
Epibon A 8X30			○	○ ●	○ ● /▶
Hydraffin XC30			○ ●	○	○
NRS Carbon GA 0.5-2.5	○ ■	○	○ ●	○	○ ●
NRS Carbon EA 0.5-2.5	○	○ ■	○	○ ●	○
Norit GAC 830 EN			○ ●	○ ●	○

○ = used in pre-tests for adsorption isotherms (fine grinded carbon,  $d < 45 \mu\text{m}$ )

■ = used in pilot tests (original carbon, 0.5 - 2.5 mm)

● = used in RSCC tests (grinded carbon, fraction 125 - 250  $\mu\text{m}$ )

▶ = use of carbon pre-loaded during RSSCT of NF permeate

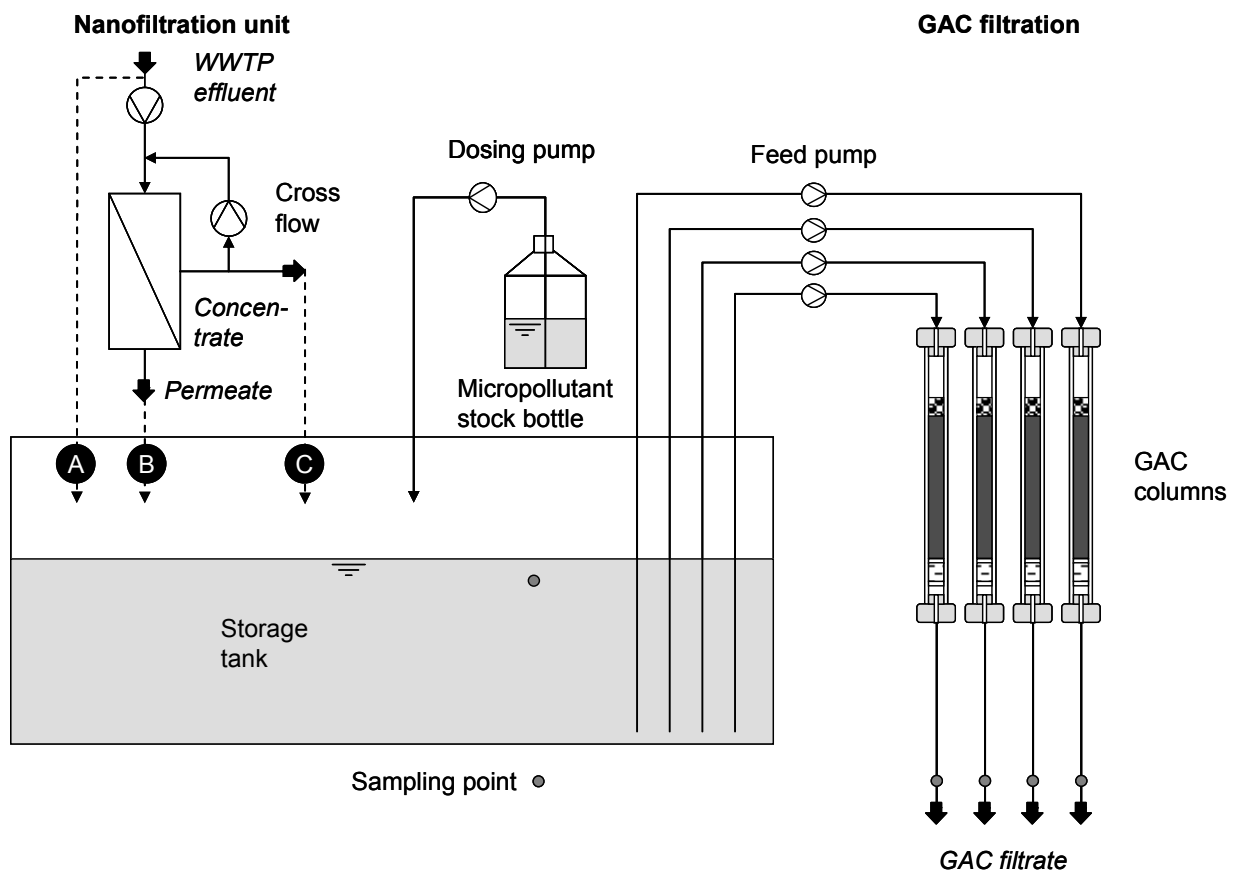
## 5.2.4 Batch adsorption tests

Indicative batch adsorption measurements were conducted with micropollutants spiked in parallel to identify the preferential GAC types. The samples consisting of 190 mL of the respective water sample (effluent, NF permeate and NF concentrate) and 10 mL of the micropollutant stock solution ( $c_i = 5 \text{ mg/L}$  in demin water) were added to a 250 mL flask resulting in an initial concentration of 250  $\mu\text{g/L}$  for each compound. Activated carbon was introduced in the following end-concentrations: 0, 5, 10, 25, 50 and 100 mg/L activated carbon for the tests with NF permeate and 0, 10, 25, 50, 100 and 200 mg/L activated carbon for the tests with NF concentrate and WWTP effluent. The DOC concentration of the NF concentrate after mixing with the spiked trace compounds was 17.0 mg/L, of the WWTP effluent 7.1 mg/L. The bottles were shaken for 24 hours at 160 rpm and a room temperature of ca. 20 °C. After 24 hours the samples were filtered (0.45  $\mu\text{m}$ ) and measured by LC/MS.

## 5.2.5 Rapid Small-Scale Column Tests

The Rapid Small-Scale Column Tests (RSSCT) employed the methodology as described in Crittenden *et al.* (2005). Figure 5.1 shows the experimental set-up. The respective feed water (WWTP effluent, NF permeate, or NF concentrate) was conveyed to the storage tank (Dehoust; HDPE,  $V = 1.1 \text{ m}^3$ ) while the micropollutant stock solution was dosed to the tank

in parallel at a ratio of 1:20 (pump type: Ismatec REGLO Digital MS-CA-2/6-160). The micropollutant stock solution had a single solute concentration  $c_i$  of 5 mg/L solved in demin water in a 10 L Duran glass bottle. With a four channel pump (Ismatec MCP Standard + CA 4) the spiked feed water was pumped to the GAC columns (Götec Labortechnik, Bickenbach, Germany; type: SuperVarioPrep glass column 300-10 „SC“). The daily flow rate was  $4 \times 50.26 \text{ L/d} = 201.0 \text{ L/d}$  (*cf.* Table 5.5). The RSSCT experiments were conducted on site at the WWTP Aachen Soers in parallel to the NF pilot tests, which provided the respective GAC feed water. The materials of the test unit were selected to minimise adsorptive losses. PTFE tubes were used for all connecting lines, Duran glass for the columns and bottles, and PTFE and stainless steel for all connecting parts. The system was equilibrated with a test run to limit adsorption to the equipment. The equipment was cleaned between each test run. The tests started with the cleanest water quality (NF permeate) and then continued with gradually poorer qualities (WWTP effluent and NF concentrate).



**Fig 5.1** Experimental set-up of the rapid small-scale column tests for (A) WWTP effluent, (B) NF permeate, and (C) NF concentrate

The carbon bed in the glass columns consisted of the following five layers (in flow direction): glass beads ( $h = 1 \text{ cm}$ ,  $d_{\text{beads}} = 1 \text{ mm}$ ), activated carbon bed ( $h = 15.6 \text{ cm}$ ), filter 1 (PE,  $d_{\text{pores}} = 80\text{-}120 \text{ }\mu\text{m}$ ), quartz wool ( $h = 1 \text{ cm}$ ) and filter 2 (PTFE,  $d_{\text{pores}} < 100 \text{ }\mu\text{m}$ ). To minimize the impact from the walls and channelling, a column with an inner diameter of 10 mm was chosen equivalent to at least 50 times the carbon diameter (ca.  $200 \text{ }\mu\text{m}$ ) as requested by Crittenden *et al.* (1989).

### Dimensioning

The RSSCT were performed according to the constant diffusivity model of Crittenden *et al.* (1986). The down scaling procedure was developed using dispersed-flow pore and surface diffusion model (Crittenden *et al.*, 1986). The simulated contact time was 10 min. Details of the RSSCT parameters are shown in table 5.5. The targeted runtime of maximum 60'000 bed volumes equals to 14.7 d of operation in the RSSCT.

**Table 5.5** Test parameters of the RSSCT

Parameter	Unit	Value
Volumetric flow rate $Q_{SC}$	ml/min	34.9
Selected carbon particle fraction (after grinding) $d_{P,min} - d_{P,max}$	$\mu\text{m}$	125 - 250
Diameter of the small-scale column $d_{SC}$	cm	1.01
Area of the small-scale column $A_{SC}$	$\text{cm}^2$	0.79
Height of the small-scale column $h_{SC}$	cm	15.60
Volume of the small-scale column $V_{SC}$	$\text{cm}^3$	12.25
Superficial velocity (hydraulic loading) of the small-scale column $v_{SC}$	m/h	26.7 *
Empty bed contact time $EBCT_{SC}$	s	21 *

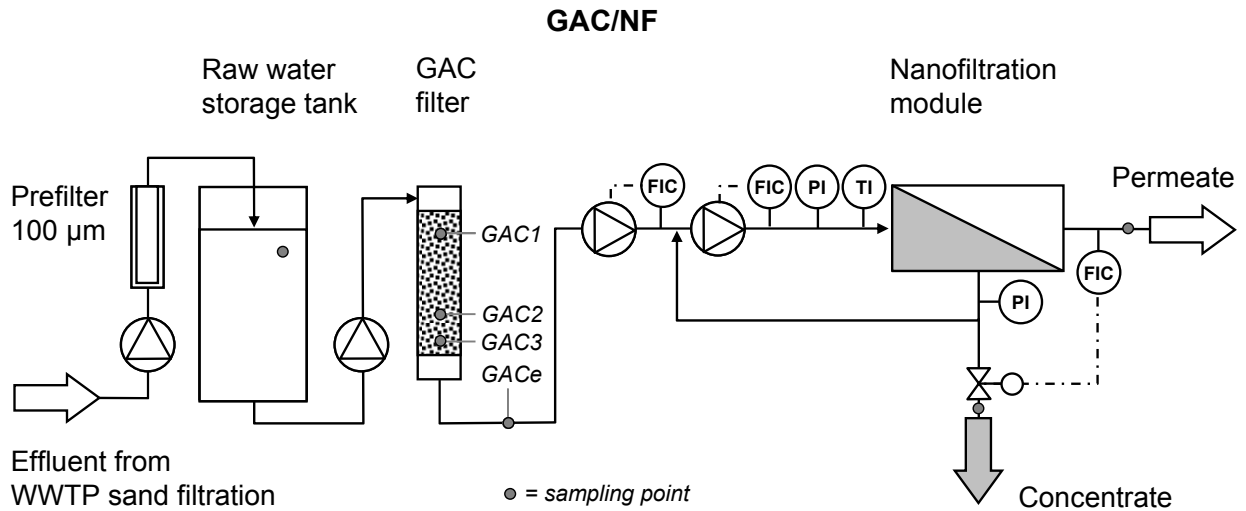
\* Calculated with CD RSSCT design

### 5.2.6 Pilot tests

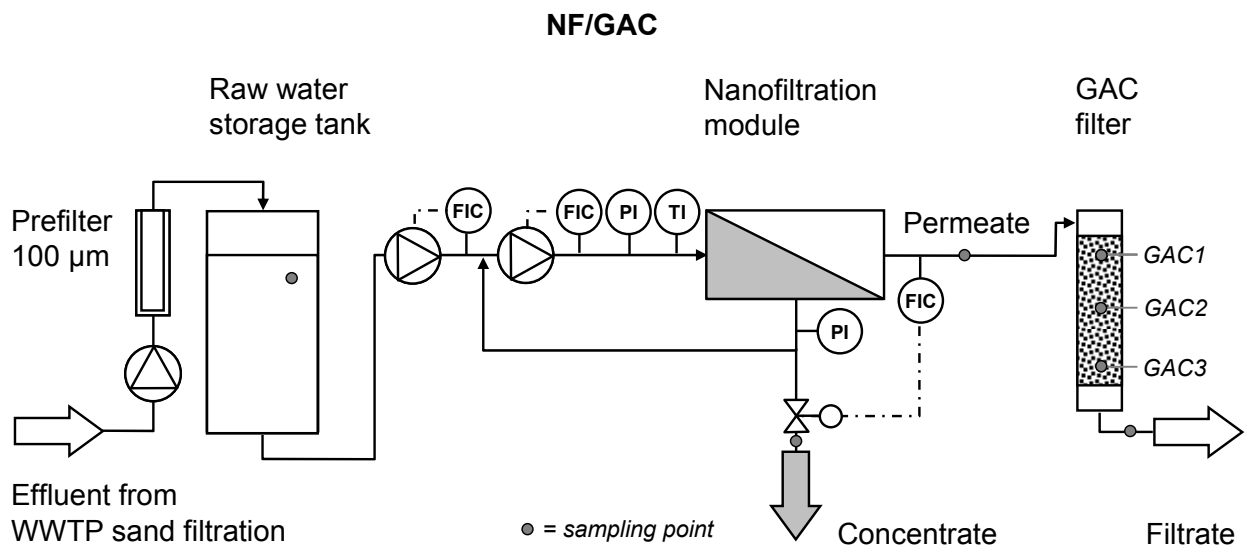
To investigate the performance of the GAC/NF and the NF/GAC process, a pilot plant was installed at the WWTP Aachen Soers. The pilot plant comprised two main units, the GAC adsorber and the nanofiltration. The GAC column (PMMA;  $h = 1500$  mm;  $d_i = 235$  mm) was partially filled with NRS Carbon GA 0.5-2.5 for the GAC/NF tests and NRS Carbon EA 0.5-2.5 for NF/GAC test. To sample the column at different levels it was equipped with sampling valves at 5 levels (50, 150, 450, 700, and 1450 mm). During GAC/NF the carbon was filled up to a bed height of 525 mm (EBCT ~15 min). The sampling valves along the GAC filter allowed observing the removal along the carbon bed whereas GAC 1 indicated the flow distance after 2.1 min, GAC 2 after 10.7 min and GAC 3 after 13.6 min. During NF/GAC the bed height was 850 mm (EBCT ~30 min) with sampling points at 5, 15 and 25 min. To avoid the growth of algae in the GAC column and storage tanks, the pilot plant was placed in a dark, windowless container.

Figure 5.2 presents the schematic of both experimental set-ups. The nanofiltration unit was equipped with a Norit X-Flow NF50M10 membrane in a 4" module configuration. The test employed the same pilot plant as described in chapter 3.2.6. The test were conducted with a permeate flux of  $20 \text{ L/m}^2\cdot\text{h}$  and permeate production of  $72 \text{ L/h}$ . The membrane was operated in crossflow mode with a crossflow velocity of  $1.2 \text{ m/s}$  and a recovery of 75%. Backflush with permeate was applied for 5 min every 30 min. The transmembrane pressure ranged between 1.5 to 4.7 bar (details are given in chapter 7).

a)



b)



**Fig 5.2** Experimental set-up of the GAC/NF (a) and NF/GAC pilot plant (b)

The runtime of the NF/GAC plant reached almost 10,000 h during May 2008 and September 2009. The plant availability was 80% with interruptions mainly due to computer problems, which were fixed in November 2009, and failure of auxiliary units such as the compressor and the submersible feed pump. Downtime for chemical recovery was about 4%. The GAC/NF plant was operated for about 3 months (1700 hours) from October to December 2009. The plant availability was 90% with interruptions due to chemical cleaning and minor technical issues with the SCADA system. In average, chemical cleaning was performed every 3 weeks. During operation no chemicals such as antiscalants or antifoulants were added.

### 5.2.7 Calculation of removal rates and bed volumes

To evaluate the process performance two different removal rates were used:

Adsorptive removal by GAC

$$R_{ads} = 1 - \frac{c_{fi}}{c_i} \quad (5.1)$$

where  $c_{fi}$  = concentration of compound in the GAC filtrate

$c_i$  = concentration of compound in the influent water (= WWTP effluent)

Total removal of the GAC/NF process

$$R_{tot,GAC/NF} = 1 - \frac{c_p}{c_i} \quad (5.2)$$

where  $c_p$  = concentration of compound in the NF permeate

$c_i$  = concentration of compound in the influent water (= WWTP effluent)

Total removal of the NF/GAC process

$$R_{tot,NF/GAC} = 1 - \frac{c_{fi}}{c_i} \quad (5.3)$$

where  $c_{fi}$  = concentration of compound in the GAC filtrate

$c_i$  = concentration of compound in the influent water (= WWTP effluent)

The typical unit for the evaluation of GAC filtration is bed volume. According to an empty bed contact time of 15 minutes, 1 hour equals to 4 bed volumes. Time series based figures are therefore depicted with bed volumes treated (BVT) to indicate the performance evaluation over time.

Bed volumes

$$BV = \frac{t_{filtered}}{EBCT} \quad (5.4)$$

where  $t_{filtered}$  = total runtime of filter

EBCT = empty bed contact time of the GAC filter

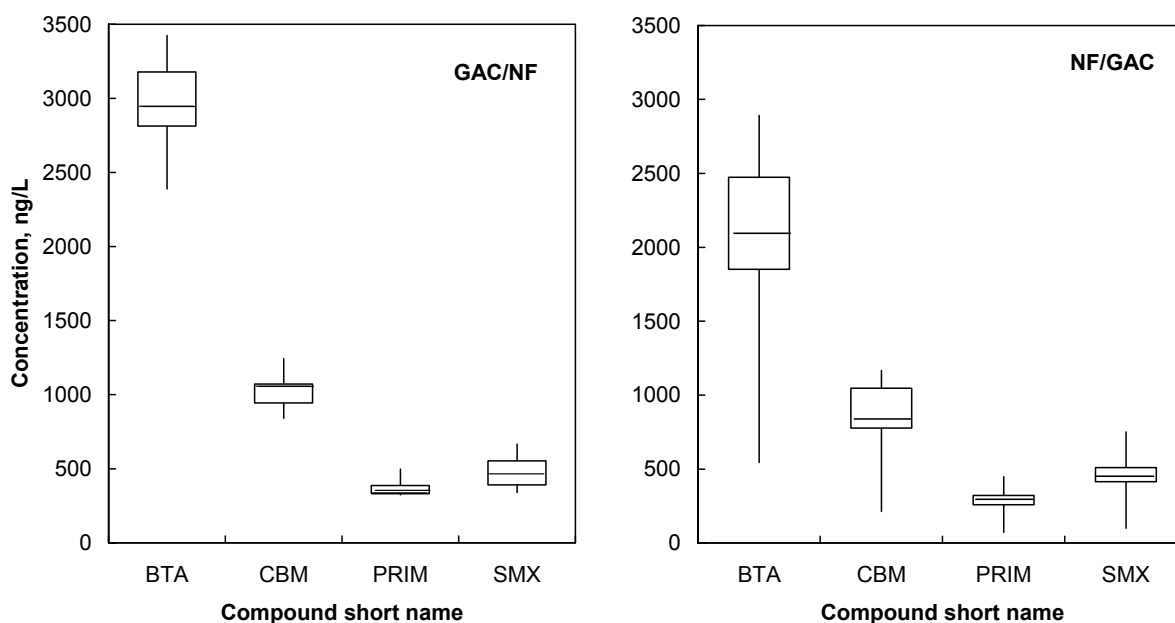
## 5.3 Results and discussion

### 5.3.1 Quality of the influent to the pilot plants

For a realistic performance evaluation of the GAC/NF and the NF/GAC processes, the pilot plant have been operated at the WWTP Aachen Soers (460,000 p.e.) treating continuously about 100 L/h of tertiary effluent from the sand filtration. The wastewater treatment plant with biological nutrient removal and a final sand filtration provided an effluent of rather high quality. During the three months of the GAC/NF pilot study, the effluent from the sand filter had an average DOC of  $5.2 \pm 0.6$  mg/L, average COD of  $15.5 \pm 2.0$  mg/L, average conductivity of  $0.88 \pm 0.22$  mS/cm, and mean pH of  $7.8 \pm 0.3$ . During the NF/GAC tests which ran for almost 15 months, the average concentrations of the effluent from the sand filter amounted to  $5.0 \pm 0.7$  mg/L for DOC,  $14.5 \pm 2.1$  mg/L for COD,  $0.99 \pm 0.22$  mS/cm for electrical conductivity, and  $7.9 \pm 0.2$  for the pH. The average micropollutant concentrations are given in Table 5.6 and Figure 5.3. Highest concentrations were measured for BTA followed by CBM, SMX and PRIM.

**Table 5.6** Average raw water concentrations during the GAC/NF and NF/GAC pilot tests

	Concentration ng/L			
	Benzotriazole	Carbamazepine	Primidone	Sulfamethoxazole
Influent to GAC/NF	$2962 \pm 347$	$1024 \pm 135$	$370 \pm 63$	$479 \pm 124$
Influent to NF/GAC	$2090 \pm 667$	$832 \pm 305$	$274 \pm 101$	$448 \pm 194$



**Fig 5.3** Micropollutant concentrations of the influent to the GAC/NF (left) and NF/GAC (right) pilot plant (n = 7 and 11; min, Q25, median, Q75, max)

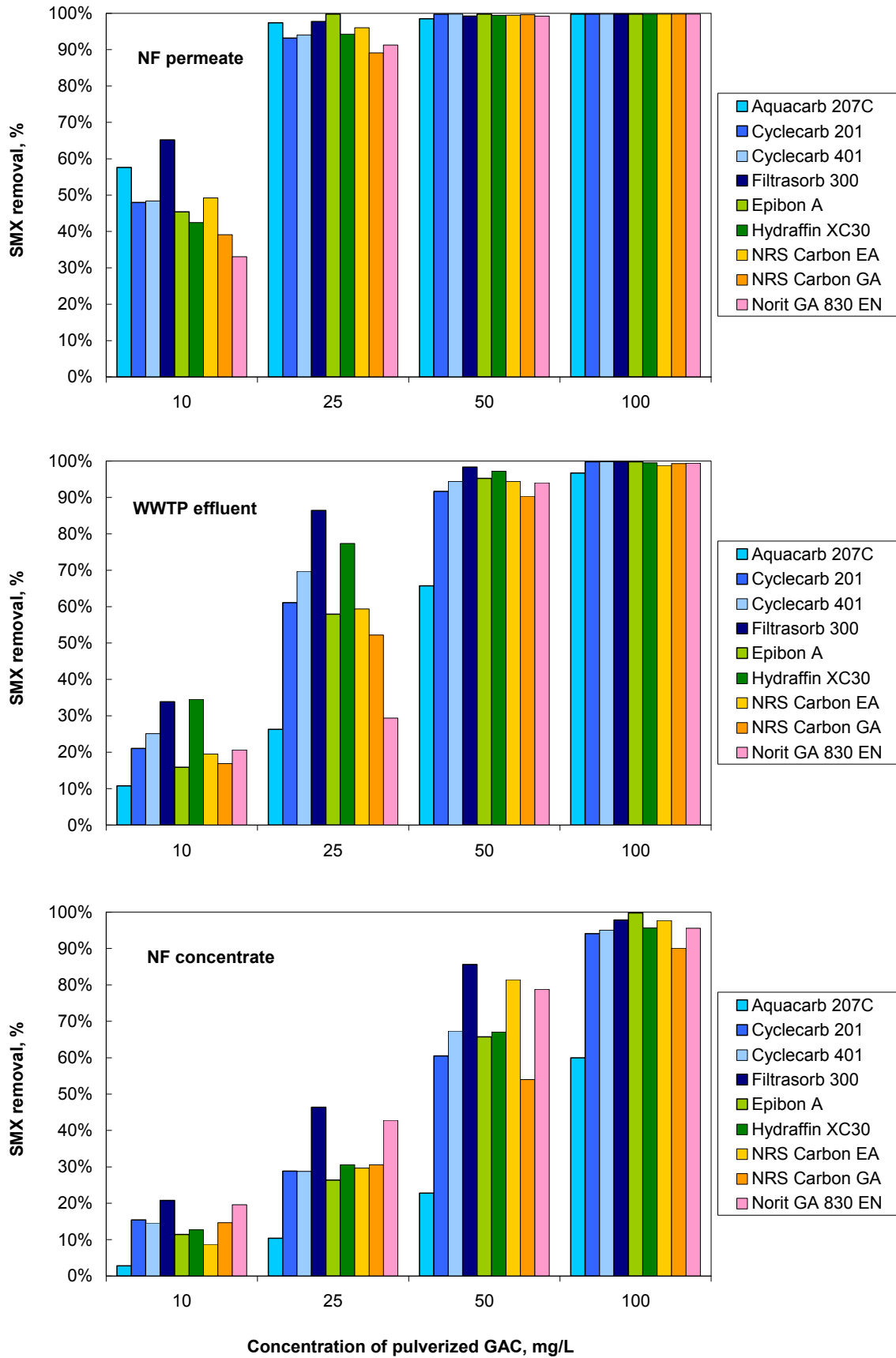
### 5.3.2 Pre-tests for carbon selection

Pre-tests were conducted with nine GAC types representing different raw materials such as coal, coconut, and mixed materials, as well as virgin carbon and reactivates, and carbon types with different porosities and surface areas (*cf.* Table 5.3 and 5.4). The finely pulverised GAC was tested in batch tests with the respective spiked waters (*cf.* chapter 5.2.4). Besides DOC, sulfamethoxazole and clofibric acid proved to be the benchmark compounds with poorest adsorbability. As SMX is of highest relevance and found in high concentrations of about 0.5 to 1 µg/L, it was identified as main criterion for the carbon selection.

Table 5.7 and Figure 5.4 show the test results for SMX. Targeting at the highest efficiency, adsorptivity and economic aspects determined the choice of four carbons for each RSSCT experiment with NF permeate (very low DOC), WWTP effluent (moderate DOC) and NF concentrate (high DOC). It is noteworthy that the carbon types chosen for the RSSCT experiment cannot be regarded as superior to the carbons not selected. It became obvious that the characteristics of the carbons are targeted for specific applications such as drinking water (low DOC) or effluent (high DOC). Thus every carbon has a preferential use. For the experiments with the NF concentrate, one preloaded carbon was tested by RSSCT to identify the potential of post-adsorption of a high surface carbon, if directly reused for concentrate treatment. The experimental results show that the removal efficiency depends on the one hand as expected, on the adsorbates and the GAC type, and on the other hand also strongly on the water matrix (*cf.* Fig. 5.4). As shown in Figure 5.5 the individual pollutants can be arranged in the following order of decreasing adsorbability: bezafibrate ~ carbamazepine > benzotriazole > ibuprofen ~ primidone > sulfamethoxazole > clofibric acid.

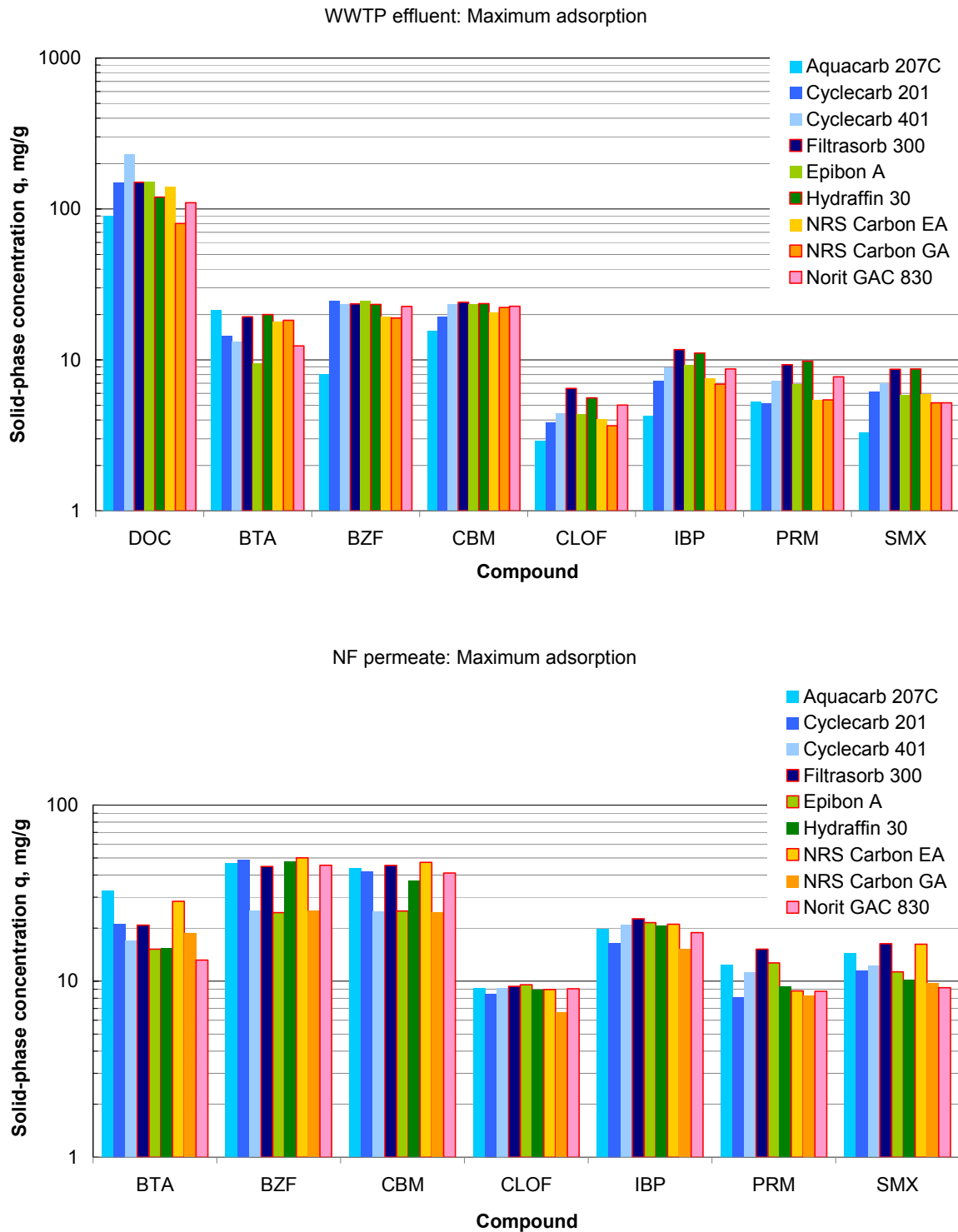
**Table 5.7** DOC and SMX removal rates (in %) at 10mg/L GAC in batch adsorption test (carbon selected for RSSCT marked in grey, reactivates in italics)

	DOC		Sulfamethoxazole		
	WWTP effluent	NF concentrate	NF permeate	WWTP effluent	NF concentrate
Aquacarb 207C	12.7	9.8	57.6	10.8	2.8
<i>Cyclecarb 201</i>	20.8	9.4	48.0	21.0	15.4
<i>Cyclecarb 401</i>	26.7	8.3	48.4	25.1	14.6
Filtrisorb 300	28.3	13.5	65.2	33.9	20.8
Epibon A 8x30	18.0	8.7	45.8	15.9	11.4
Hydraffin XC30	24.0	7.9	42.5	34.5	12.7
<i>NRS Carbon EA 0.5-2.5</i>	19.7	8.2	49.2	19.5	8.7
<i>NRS Carbon GA 0.5-2.5</i>	10.3	7.0	39.1	16.9	14.7
Norit GAC 830 EN	15.1	6.7	33.1	20.6	19.6



**Fig 5.4** Batch adsorption test: Comparison of GAC concentration *versus* SMX removal for NF permeate, WWTP effluent and NF concentrate (DOC = 1.4; 7.2; 17 mg/L)





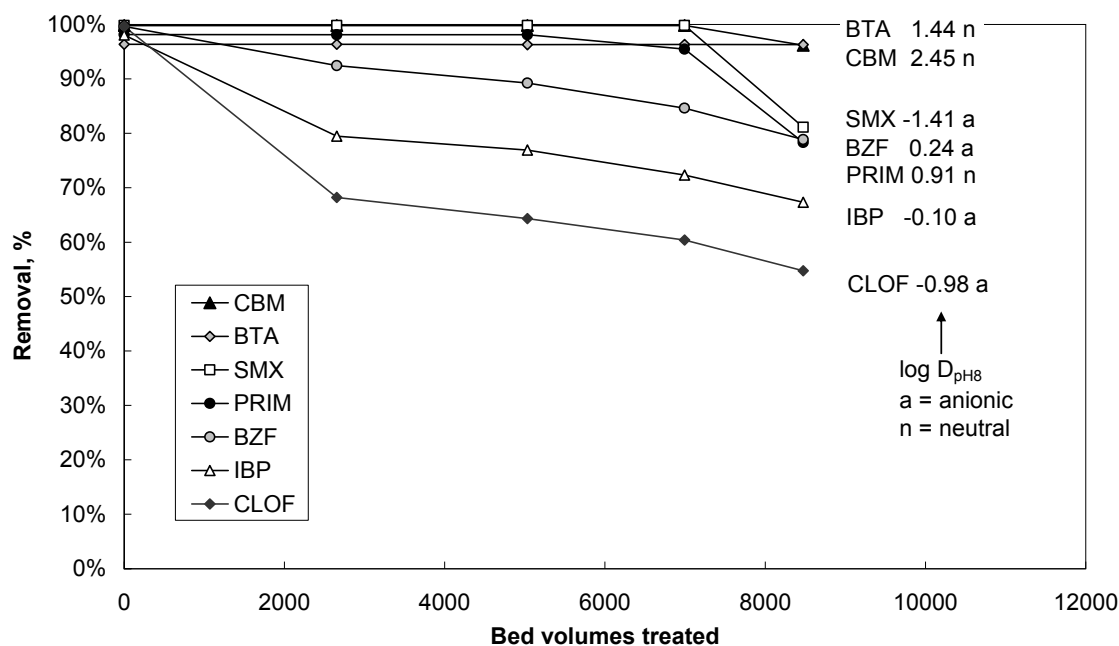
**Fig 5.5** Maximum solid-phase concentrations of selected compounds ( $C_{MP,i} = 250 \mu\text{g/L}$ ) measured during batch adsorption tests (top: NF permeate; bottom: WWTP effluent)

### 5.3.3 GAC for effluent treatment

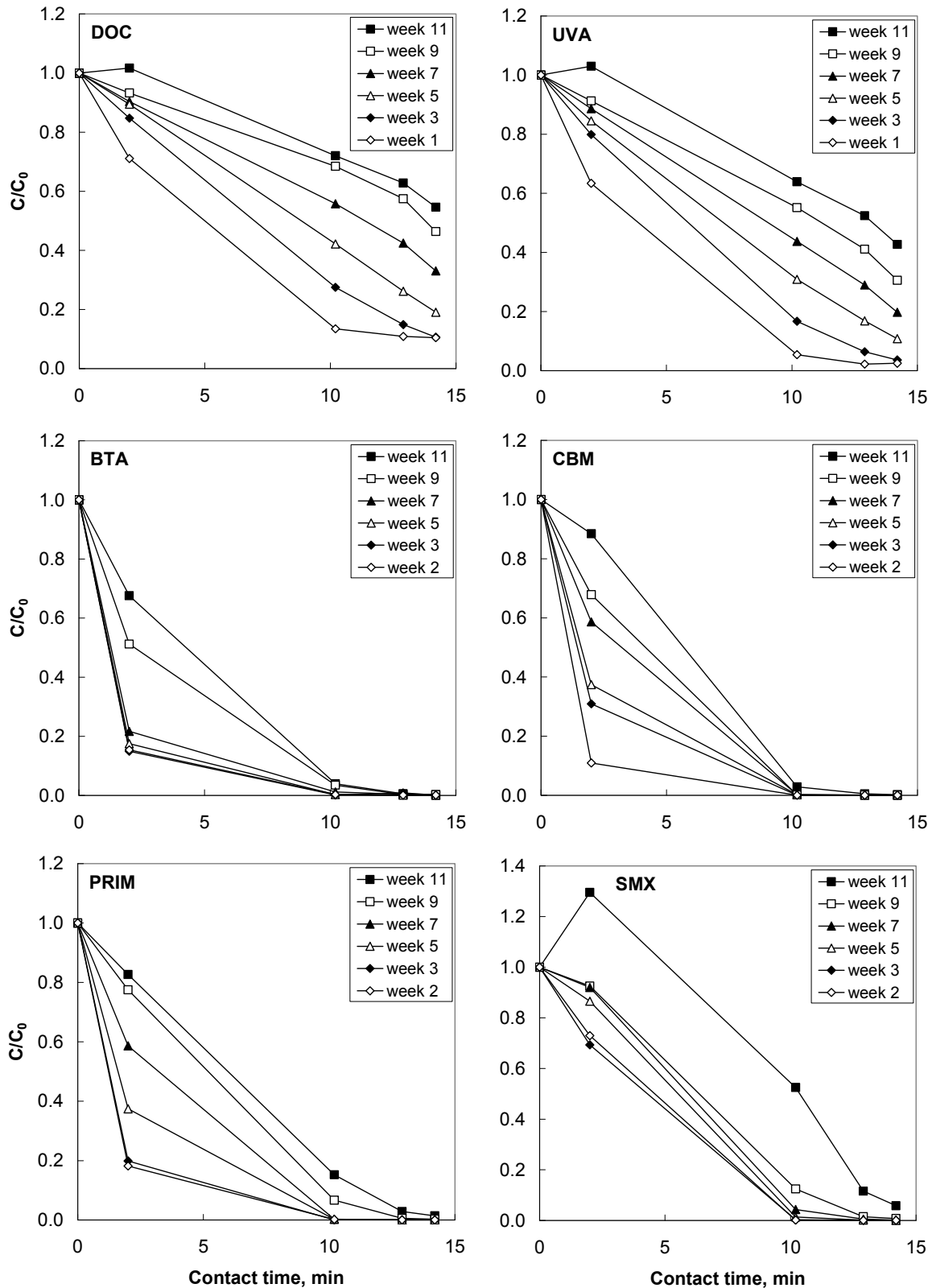
In the GAC/NF configuration, GAC treats the WWTP effluent directly and removes bulk and trace organics to a high degree as explained above. The GAC bed volumes to breakthrough were investigated in a pilot scale and with small-scale columns.

#### Pilot-scale evaluation

A GAC pilot column treated real WWTP effluent for a period of three months. Empty bed contact time was chosen to 15 min. The pilot test employed an inexpensive reactivate (NRS Carbon GA) with moderate adsorptivity. Figure 5.6 shows the progressive loading of the GAC column. A rapid exhaustion of the column was observed at the upper sampling level (2 min). DOC, UVA and sulfamethoxazole reached already 70% breakthrough after 1 to 2 weeks. While a continuous progression of the mass transfer zone was measured for bulk organics, sulfamethoxazole remained stable before it suddenly started to break through at week 11. The removal dropped from initially 30% to -30% indicating that SMX was released by competitive adsorption. Slightly deviating from the pre-tests, benzotriazole showed the best adsorptivity and was better removed than carbamazepine and primidone that behaved similarly. After 6700 bed volumes a 50 to 60% breakthrough of the bulk organics was measured. However the micropollutants were still removed at the filter outlet level although at the 10- and 13-minute-level compounds already started to break through. The RSSCT with the same carbon showed a similar breakthrough pattern after 7000 BVT with SMX suddenly increasing after being stable for several thousand BVT. Likewise, primidone, carbamazepine and benzotriazole showed similar behaviour as in pilot scale. In contrast to the pre-test, ibuprofen was poorly adsorbable on a level comparable to clofibric acid.



**Fig 5.6** RSSCT using spiked WWTP effluent (NRS Carbon GA; EBCT = 10 min equivalent in full-scale)



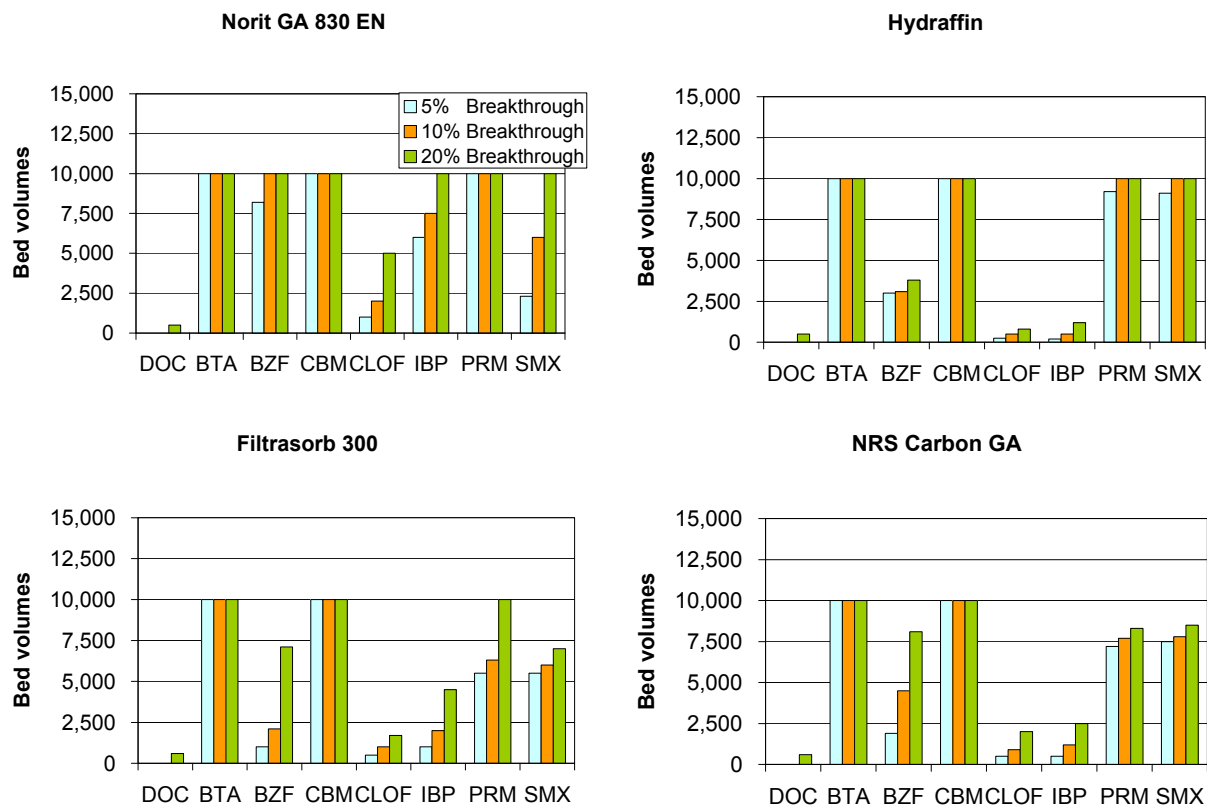
**Fig 5.7** Concentration profiles of bulk organics and selected micropollutants during GAC pilot tests (Norit NRS Carbon GA; week 11 = 6700 bed volumes treated; influent concentrations of pollutants according to table 5.6, contact time equivalent to respective sampling ports)

### Rapid small-scale column tests with WWTP effluent

The RSSCT experiments investigated three virgin carbons from different suppliers and one reactivated GAC. The inner surface ranged from 950 to 1100 m<sup>2</sup>/g.

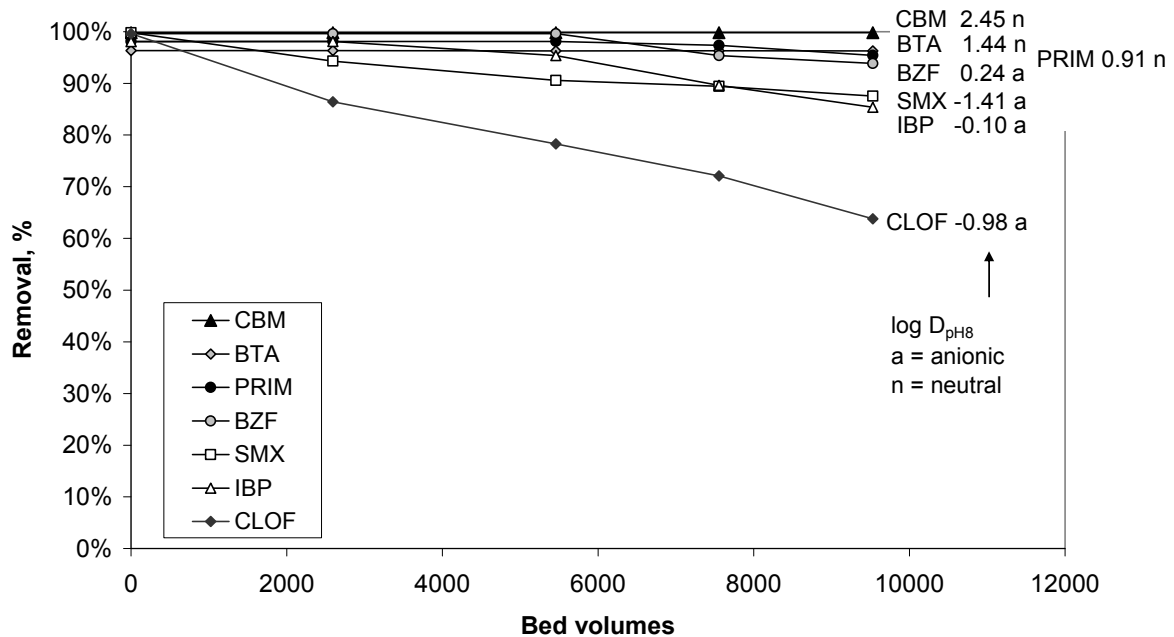
Figure 5.8 presents a comparison of the bed volumes treated till breakthrough of the target compounds. The tests were stopped after 10000 BVT due to increasing blocking of the test columns. Although the general characteristics of the virgin carbons were similar, *e.g.* surface area and source material, significant differences were observed. All carbons removed BTA and CBM almost completely till 10000 BVT. Also PRIM was very well removed by GA 830 and Hydriffin, and to lesser extent by F300 and NRS GA. GA 830 and F300 removed SMX till 6000 BVT, Hydriffin till >10000 BVT, and NRS GA until 7700 BVT. Poorest adsorption was detected for CLOF and IBP showing a 10% breakthrough already after 500-2000 BVT (CLOF) and 500-7500 BVT (IBP) respectively.

All carbon types showed weaknesses in the adsorption of certain compounds. In general neutral compounds were much better adsorbed. The removal of charged solutes varied significantly between the different carbon types and between the different substances for the respective carbon.



**Fig 5.8** RSSCT for WWTP effluent: Bed volumes to breakthrough of DOC and micropollutants ( $v_F = 5$  m/h and EBCT = 10 min equivalent in full scale)

The long-term behaviour of the RSSCT is shown in Figure 5.6 and 5.9. The direct comparison of the breakthrough curves of a virgin carbon with a reactivated reveals the differences in quality more significantly. Except for CLOF, the virgin carbon removed all compounds at least by 85% until 10000 BVT, whereas the adsorptivity of the reactivated decreased quicker and reached between 70 and 95% after 8500 BVT. Log D proved to be the key factor for the differences in adsorption between the neutral solutes as well as between most of the charged solutes. Only SMX sorbed better than expected from the log D value and the pre-tests.



**Fig 5.9** RSSCT using spiked WWTP effluent (GA 830 EN; EBCT = 10 min equivalent in full-scale)

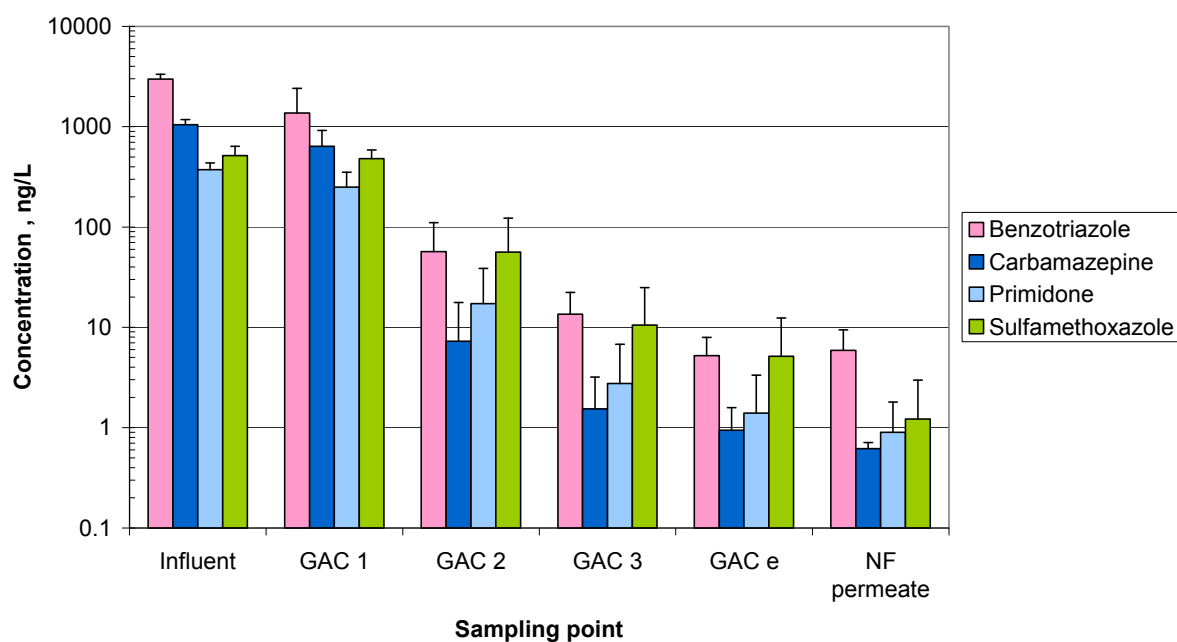
### 5.3.4 GAC/NF treatment

The pilot tests used the effluent from the GAC filter as characterised in figure 5.7 as feed for the nanofiltration. It is obvious that the almost complete removal of micropollutants did not challenge the NF unit. As the micropollutants were already almost completely removed by the GAC filter, NF showed only little additional effect. The total removal of SMX, PRIM and CBM was stable on a very high level between 99.8 to 99.9%. Due to the small molecular size, BTA removal was governed by the GAC filter and NF showed no additional effect. Overall the performance of the GAC/NF process is very high and reaches levels of RO systems (Snyder *et al.*, 2007). A potential early breakthrough of diatrizoate and neutral contrast media (which were not considered in these tests) could safely be counteracted by the NF post-treatment as shown earlier in direct NF (*cf.* chapter 3). Moreover NF is a very good barrier to pathogens including viruses. Table 5.8 and figure 5.10 show the average concentrations and removal rates of the GAC filter and the GAC/NF plant. EfOM as well as multivalent ions such as phosphate and sulphate were removed to a high degree, while monovalent ions *i.e.*

chloride and nitrate were not retained. Nitrate was even detected in slightly elevated concentrations, most probably due to the Donnan effect.

**Table 5.8** Average concentrations and removal rates for DOC and selected pharmaceuticals for GAC/NF (runtime 1700 hours, GAC NRS Carbon GA)

Parameter	GAC influent	GAC effluent	NF permeate	GAC removal	GAC/NF removal
	mg/L	mg/L	mg/L	%	%
<i>Bulk organics</i>					
DOC	5.24	1.54	<0.17	70.6	>96.8
<i>Nutrients</i>					
Ammonium (NH <sub>4</sub> -N)	0.09	0.06	0.03	33.3	66.7
Nitrate (NO <sub>3</sub> -N)	5.2	5.6	5.9	-7.7	-13.5
P total	0.05	0.04	0.001	20.0	98.0
<i>Salinity</i>					
EC	882	861	778	2.4	11.8
Chloride	79	77	77	2.5	2.5
Sulphate	59	59	16	0	72.9
<i>Micropollutants</i>					
	µg/L	µg/L	µg/L		
Benzotriazole	2.990	<0.0052	<0.0059	>99.8	>99.8
Carbamazepine	1.046	<0.0009	<0.0006	>99.9	>99.9
Primidone	0.373	<0.0014	<0.0009	>99.6	>99.8
Sulfamethoxazole	0.515	<0.0051	<0.0012	>99.0	>99.8



**Fig 5.10** Average concentrations of selected micropollutants in GAC/NF along the treatment train (NRS Carbon GA 0.5 - 2.5, sampling points acc. to Fig. 5.2a)

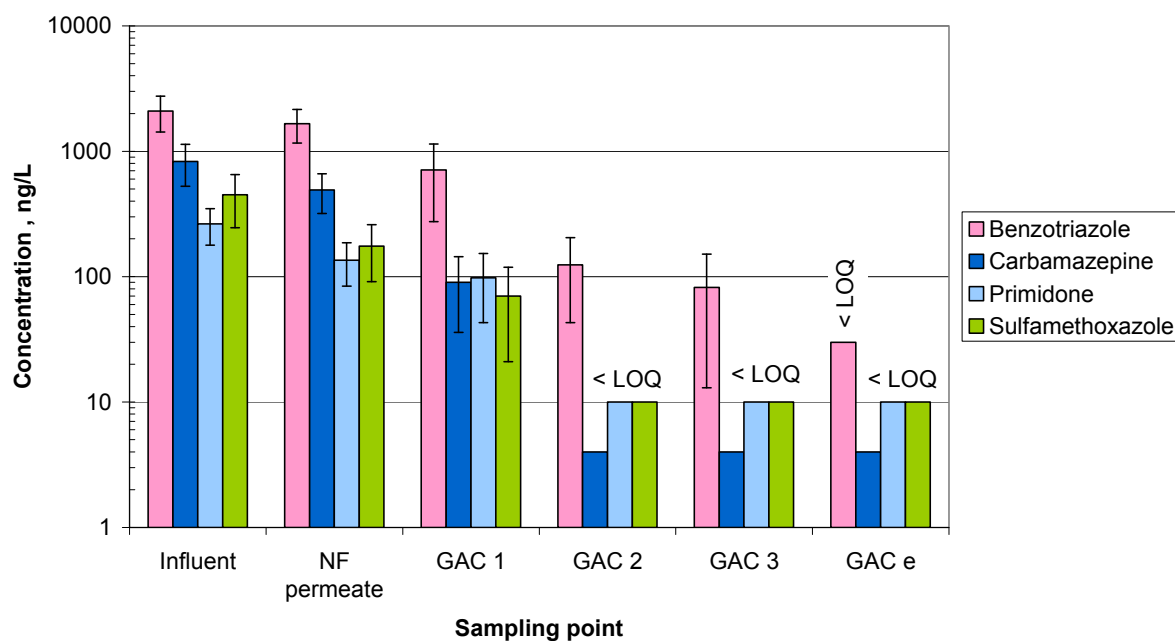
### 5.3.5 NF/GAC pilot tests

The NF/GAC process has been investigated in pilot scale for 16 months which translates to bed volumes of about 19000 BVT (*cf.* chapter 5.2.6). The average concentrations and removal rates are presented in table 5.9. The removal of bulk organics and micropollutants reached a very high level. Effluent-DOC was removed by 95% to concentrations below 0.3 mg/L. All GAC filtrate concentrations of the selected micropollutants were below the limit of quantification after GAC posttreatment, while the NF provided only partial rejection of solutes with molecular weight close to the MWCO of the membrane (*cf.* chapter 3). Salinity and nutrient removal was characterised by the typical low removal of monovalent ions.

**Table 5.9** Average concentrations and removal rates for DOC and selected pharmaceuticals for NF/GAC (runtime 9500 hours, GAC NRS Carbon EA)

Parameter	NF feed	NF permeate	GAC filtrate	NF removal	NF/GAC removal
	mg/L	mg/L	mg/L	%	%
<i>Bulk organics</i>					
DOC	4.98	0.46	0.24	90.8	95.2
<i>Nutrients</i>					
Ammonium (NH <sub>4</sub> -N)	0.09	0.03	0.02	66.7	77.8
Nitrate (NO <sub>3</sub> -N)	5.7	5.6	6.0	1.8	-5.3
P total	0.09	0.03	0.03	66.7	66.7
<i>Salinity</i>					
EC	978	836	826	14.5	15.5
Chloride	160	164	159	-2.5	0.6
Sulphate	65	15	14	76.9	78.5
<i>Micropollutants (n = 11)</i>					
	µg/L	µg/L	µg/L		
Benzotriazole	2.090	1.660	<0.030	20.6	>99.8
Carbamazepine	0.831	0.490	<0.004	41.0	>99.9
Primidone	0.263	0.135	<0.004	48.7	>99.8
Sulfamethoxazole	0.449	0.175	<0.010	61.0	>99.8
<i>Micropollutants (n = 2)</i>					
Bezafibrate	0.079	0.017	<0.010	78.5	>87.3
Clarithromycin	0.116	<0.005	<0.005	>95.7	>95.7
Erythromycin	0.145	<0.010	<0.010	>93.1	>93.1
Sulfamethoxazole	0.718	0.332	<0.010	53.8	>98.6
Trimethoprim	0.101	0.048	<0.005	52.5	>95.0
Diatrizoate	1.416	0.030	<0.010	97.9	>99.3
Iohexol	0.138	<0.010	<0.010	>92.8	>92.8
Iomeprol	0.427	0.005	<0.010	98.8	>97.7
Iopamidol	3.566	0.064	<0.010	98.2	>99.7
Iopromide	1.850	0.029	<0.025	98.4	>98.6

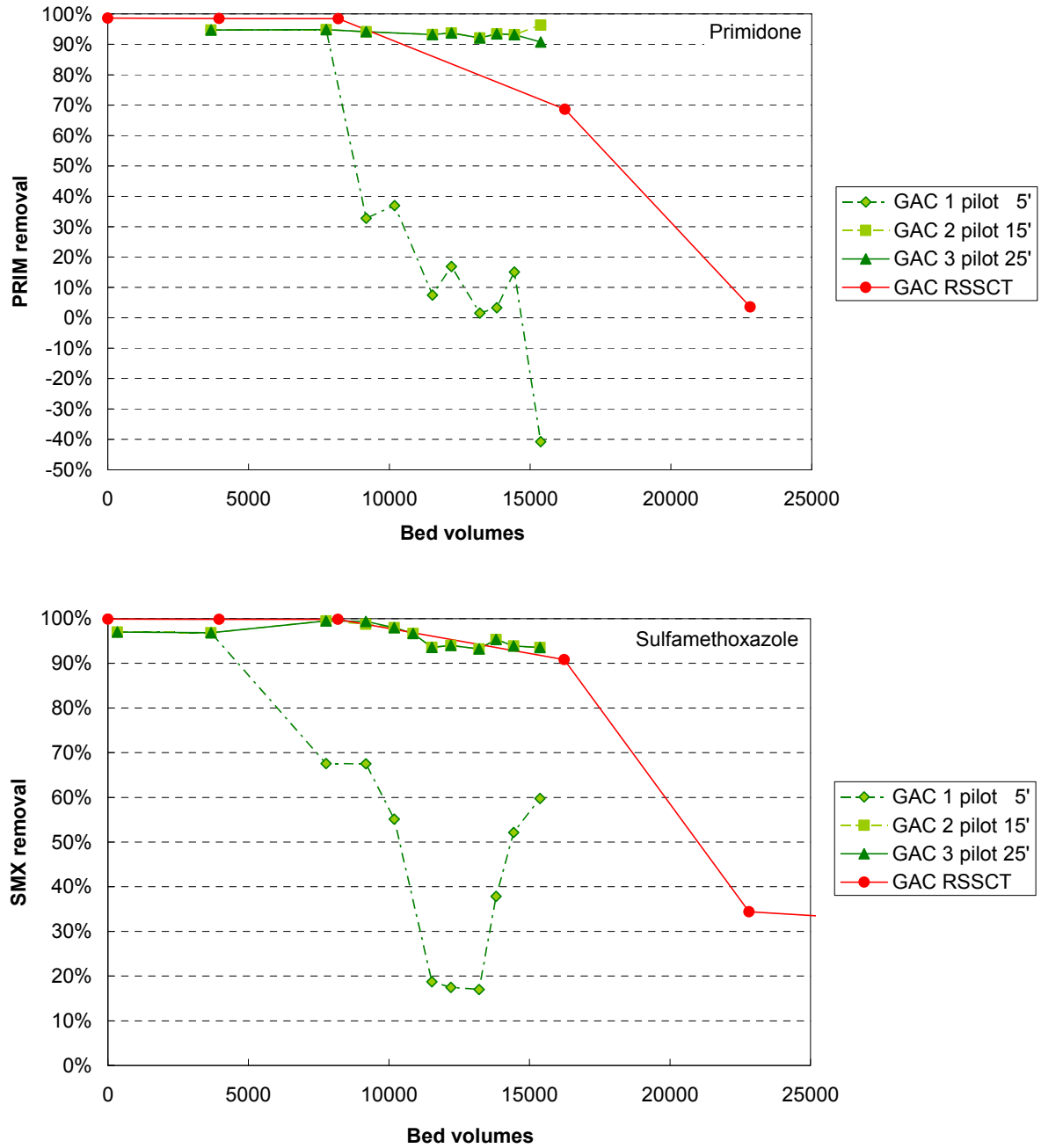
As shown in Figure 5.11 the GAC filter removed the investigated micropollutants mainly in the first half of the filter. The concentrations of carbamazepine, primidone and sulfamethoxazole were already below the limit of quantification at point GAC 2 (15 min). Due to high influent concentrations and poor removal in nanofiltration, benzotriazole was still present in the NF permeate in concentrations of 1 to 2  $\mu\text{g/L}$  and proved as benchmark compound requiring a removal of about two  $\log_{10}$  units. Benzotriazole was detectable until point GAC 3 (25 min.), but likewise removed below the limit of quantification in the GAC effluent.



**Fig 5.11** Average concentrations of selected pharmaceuticals in NF/GAC along the treatment train (NRS Carbon EA 0.5 - 2.5, sampling points acc. to Fig. 5.2b)

Figure 5.12 presents a comparison of the micropollutant elimination in pilot test and RSSCT for primidone and sulfamethoxazole. The RSSCT with a contact time equivalent to 10 minutes in full scale resembles the behaviour of the pilot fixed-bed adsorber well. The RSSCT graph was in-between the 5 and 15 minutes values of the pilot column. The pilot column was progressively exhausted in level GAC 1 until 12000 to 14000 BVT. Then the primidone concentrations started to exceed the influent concentrations, most probably due to competitive adsorption. An opposite effect was observed for sulfamethoxazole, where the removal rates increased again and recovered from 20% to 60%. It is assumed that the removal was due to biodegradation by bacteria which needed about 1 year to establish as reported in some soil column studies (Hein, 2011).





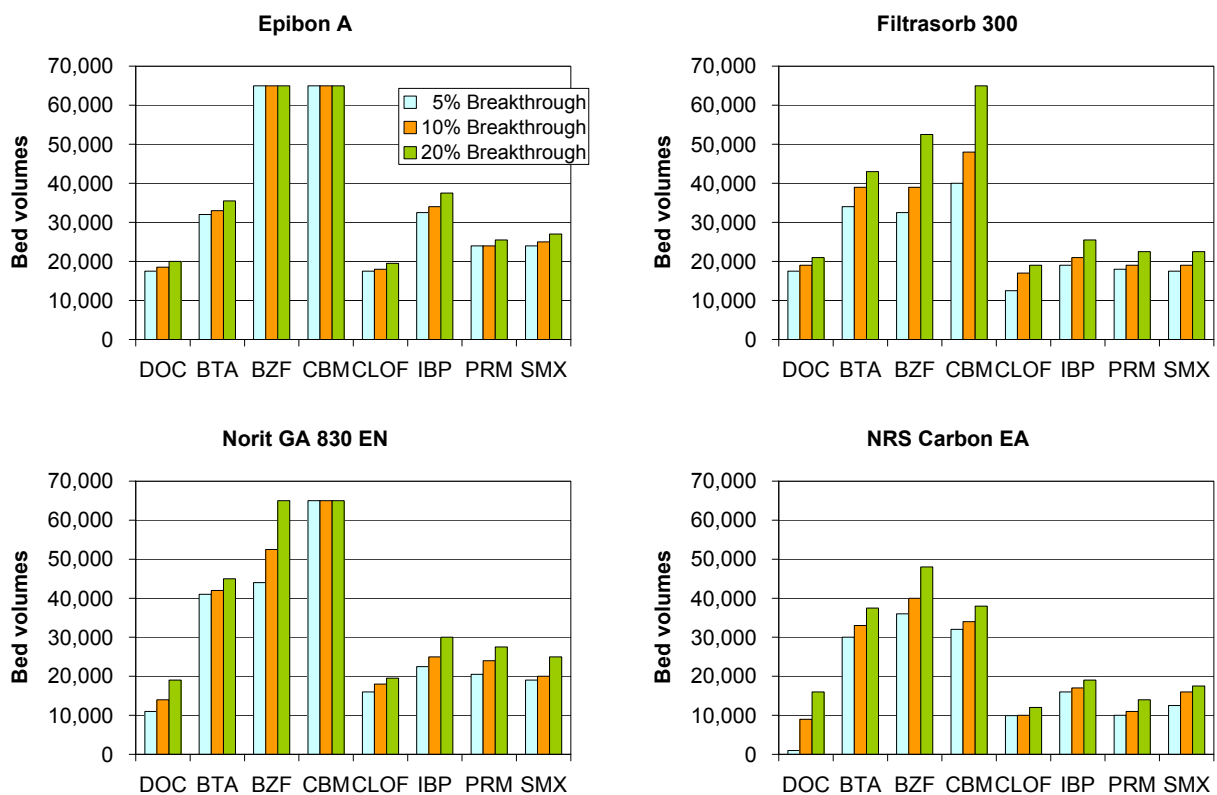
**Fig 5.12** Comparison of primidone and sulfamethoxazole removal in pilot test (GAC 1, 2, and 3) and rapid small scale column test (RSSCT, contact time equivalent to 10 min in full scale)

### Rapid small-scale column tests with NF permeate

Three high-grade drinking water carbons and one reactivant (extruded carbon) were selected for the RSSCT with NF permeate. The inner surface of the activated carbons ranged from 950 to 1200 m<sup>2</sup>/g. The tests were conducted for 65000 BVT (= 1.2 years, EBCT 10 min). All carbons showed very good removal of all target solutes until 10000 to 15000 BVT (Fig. 5.13). As shown in Table 5.10, the target compounds can be grouped in different classes (Snyder *et al.*, 2007b). Three groups can be identified for the bed volumes to 10% breakthrough of the target compounds. Epibon A and GAC 830 EN could adsorb even critical compounds such as CLOF to 90% almost up to 20000 BVT compared to 10000 BVT for the NRS EA. The performance of F300 was between the high-grade virgin carbons and the extruded reactivant.

**Table 5.10** GAC bed volumes to 10% breakthrough of target solutes in NF permeate

	Epibon A	F300	GAC 830 EN	NRS Carb EA
> 50,000 BVT	BZF, CBM		BZF, CBM	
20,000 - 50,000 BVT	BTA, IBP, PRIM, SMX	BTA, BZF, CBM, IBP	BTA, IBP, PRIM, SMX	BTA, BZF, CBM
< 20,000 BVT	CLOF, DOC	CLOF, PRIM, SMX, DOC	CLOF, DOC	CLOF, IBP, PRIM, SMX, DOC

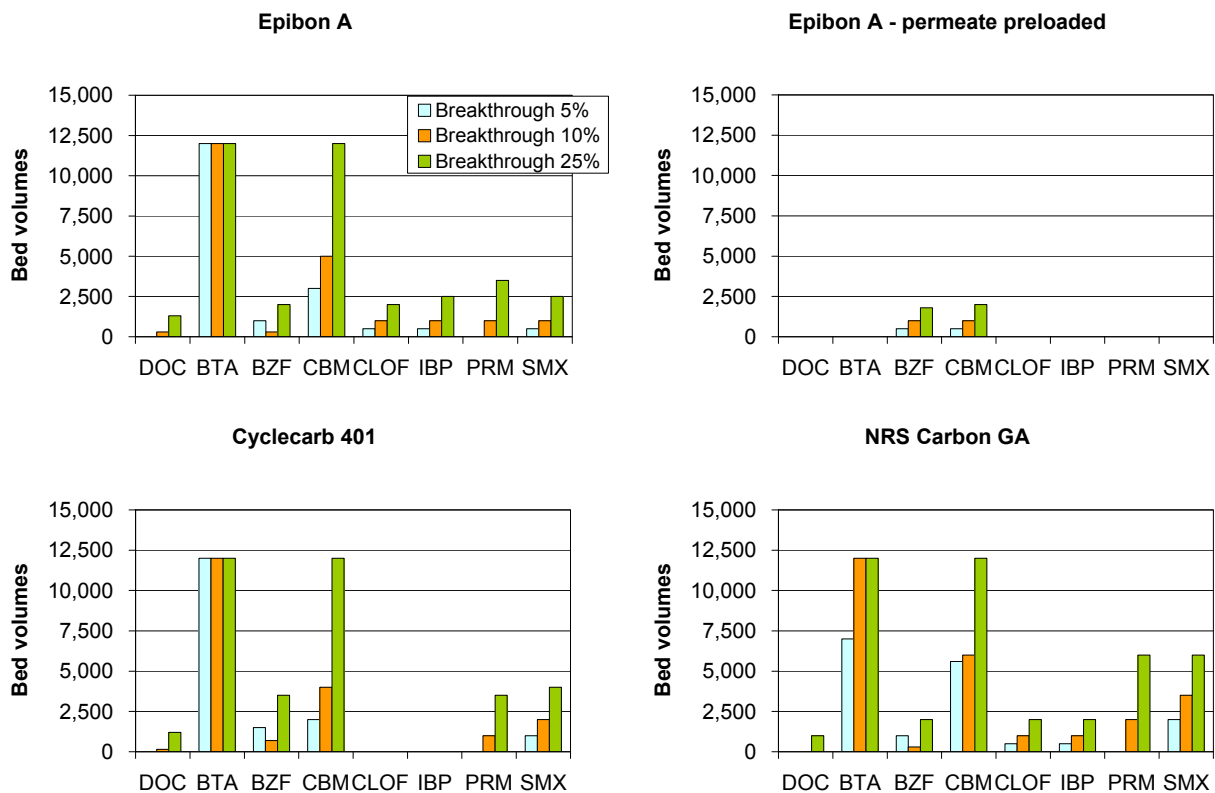


**Fig 5.13** RSSCT for NF permeate: Bed volumes to breakthrough of DOC and micropollutants ( $v_F = 5$  m/h and EBCT = 10 min equivalent in full scale)

### Rapid small-scale column tests with NF concentrate

In contrast to the NF concentrate during PAC/NF and GAC/NF, the concentrate of NF/GAC still contains elevated concentrations of micropollutants, bulk organics and inorganic compounds. The RSSCT experiments with NF concentrate investigated the adsorption in this additional treatment step for posttreatment of the concentrate. In the light of the high organic content and the low requirements two reactivates and one high-grade carbon were selected. In addition the same carbon preloaded from treatment of NF permeate was tested to investigate potential reuse.

Figure 5.14 depicts the bed volumes till breakthrough of the target solutes. In comparison to the low DOC in NF permeate, the high DOC in concentrate reduced the adsorptivity of the carbons significantly. Carbamazepine for instance break through to 10% already after 5000 BVT, while it was still well removed after 65000 BVT when treating NF permeate. Reusing the preloaded carbon did also not prove successful. The reactivated carbons which are generally rich in mesopores showed overall good removal behaviour. The bed volumes to 10% breakthrough for critical compounds such as SMX reached, however, only 1000 to 3000 BVT. The RSSCT tests prove that EfOM rich waters require pretreatment prior to GAC filtration to reduce the carbon fouling. In order to reduce the DOC pretreatment could be provided by biological activated carbon or ozonation.



**Fig 5.14** RSSCT for NF concentrate: Bed volumes to breakthrough of DOC and micropollutants ( $v_F = 5$  m/h and EBCT = 10 min equivalent in full scale)

### 5.3.6 Cost comparison

As shown above GAC can be combined with NF in different modes. In zero liquid discharge systems, the treatment of concentrates has to be considered as well. The costs for the carbon in the following applications of GAC and PAC will be compared subsequently:

- GAC pretreatment prior to NF (GAC/NF)
- NF with GAC posttreatment (NF/GAC) including treatment of NF concentrate by GAC filtration
- PAC adsorption followed by nanofiltration (PAC/NF)

For the cost comparison the following minimum removal rates were used:

GAC prior to NF:	$\eta = 90 \%$
GAC after NF:	$\eta = 90 \%$
GAC for NF concentrate:	$\eta = 75 \%$
PAC prior to NF:	$\eta = 90 \%$

The performance of the different GAC types was quantified in term of the carbon usage rate (CUR) calculated as follows (Crittenden *et al.*, 2005):

$$CUR = \frac{M_{GAC}}{V_L} = \frac{\rho_{GAC} \cdot V_F}{V_L} = \frac{\rho_{GAC}}{BV} \quad (5.5)$$

where

CUR	= carbon usage rate until regeneration	[kg/m <sup>3</sup> ]
M <sub>GAC</sub>	= mass of GAC	[kg]
t <sub>bk</sub>	= runtime to breakthrough	[h]
Q	= flow rate to GAC filter	[m <sup>3</sup> /h]
V <sub>L</sub>	= treated water volume at t = t <sub>bk</sub>	[m <sup>3</sup> ]
	= Q · t <sub>bk</sub>	
ρ <sub>GAC</sub>	= apparent density of GAC after backwash	[kg/m <sup>3</sup> ]
V <sub>F</sub>	= volume of the GAC filter	[m <sup>3</sup> ]
BVT	= bed volumes to breakthrough	[-]

The GAC adsorber has to be dimensioned for the compound with the earliest breakthrough considering the relevance of the respective compound in terms of the real raw water concentrations instead of the spiked concentrations as applied in the RSSCT experiments. Compounds in low concentrations are expected to be sufficiently removed by a partial adsorption to AC and the retention through NF. This applies to BZF, CLOF and IBP. Thus BTA, CBM, PRIM and SMX are considered design relevant. In all tests, SMX showed the quickest breakthrough of the design relevant compounds. For the evaluation of the most relevant compounds the bed volumes till 10% breakthrough of SMX (WWTP effluent and NF permeate) and 25% breakthrough (NF concentrate) were derived from the experimental data (Table 5.11). The specific costs for the respective GAC type were calculated from the carbon usage rate until regeneration (CUR) and the price according to table 5.3. The data for the

density after backwash and the carbon price are based on supplier information. Table 5.11 and 5.12 present the overview of the experimental results and the cost comparison based on the specific carbon costs to breakthrough.

**Table 5.11** GAC bed volumes to breakthrough of target solutes in treatment of effluent, permeate and concentrate

<b>GAC for effluent treatment</b>			<b>10% breakthrough at</b>			
Name	$C_{real}$ µg/L	relevant	Hydraffin BVT	NRS GA BVT	Filtrisorb 300 BVT	Norit GA 830 BVT
BTA	2.090	yes	> 10,000	> 10,000	> 10,000	> 10,000
BZF	0.060	no	3,100	4500	2,100	> 10,000
CBM	0.830	yes	> 10,000	> 10,000	> 10,000	> 10,000
CLOF	0.016	no	500	900	1,000	2,000
IBP	0.013	no	500	1,200	2,000	7,500
PRIM	0.270	yes	> 10,000	7,700	6,300	> 10,000
SMX	0.450	yes	10,000	7,800	6,000	6,000

<b>GAC for NF permeate</b>			<b>10% breakthrough at</b>			
Name	$C_{real}$ µg/L	relevant	Epibon A BVT	NRS EA BVT	Filtrisorb 300 BVT	Norit GA 830 BVT
BTA	1.660	yes	33,000	33,000	39,000	42,000
BZF	0.013	no	> 65,000	40,000	39,000	52,500
CBM	0.490	yes	> 65,000	34,000	48,000	> 65,000
CLOF	0.008	no	18,000	10,000	17,000	18,000
IBP	0.004	no	34,000	17,000	21,000	25,000
PRIM	0.140	yes	24,000	11,000	19,000	24,000
SMX	0.180	yes	25,000	16,000	19,000	20,000

<b>GAC for NF concentrate</b>			<b>25% breakthrough at</b>		
Name	$C_{real}$ µg/L	relevant	Epibon A BVT	NRS GA BVT	Cyclecarb 401 BVT
BTA	2.790	yes	> 12,000	> 12,000	> 12,000
BZF	0.150	no	3,500	2,000	
CBM	1.680	yes	> 12,000	> 12,000	> 12,000
CLOF	0.041	no	2,000	2,000	
IBP	0.027	no	2,500	2,000	
PRIM	0.560	yes	3,500	6,000	3,500
SMX	0.970	yes	2,500	6,000	4,000

**Table 5.12** Carbon usage rate and specific carbon costs to breakthrough of target solutes in treatment of effluent, permeate and concentrate

<b>GAC for effluent treatment</b>		Hydraffin	NRS GA	F300	Norit GA
Density after backwash	[kg/m <sup>3</sup> ]	500	500	460	450
BVT at 10% breakthrough	[-]	10,000	7,800	600	6,000
CUR	[kg/m <sup>3</sup> ]	0.05	0.06	0.08	0.08
GAC price	[€/kg]	1.45	1.00	1.70	1.90
Specific carbon costs	[€/m <sup>3</sup> ]	0.073	0.064	0.130	0.143
incl. 33% concentrate recycle	[€/m <sup>3</sup> ]	0.096	0.085	0.173	0.190
<b>GAC for NF permeate</b>		Epibon A	NRS EA	F 300	Norit GA
Density after backwash	[kg/m <sup>3</sup> ]	300	410	460	450
BVT at 10% breakthrough	[-]	25,000	16,000	19,000	20,000
CUR	[kg/m <sup>3</sup> ]	0.01	0.03	0.02	0.02
GAC price	[€/kg]	1.65	1.50	1.70	1.90
Specific carbon costs	[€/m <sup>3</sup> ]	0.020	0.038	0.041	0.043
<b>GAC for NF concentrate</b>		Epibon A	NRS GA	C 401	
Density after backwash	[kg/m <sup>3</sup> ]	300	500	450	
BVT at 10% breakthrough	[-]	2,500	6,000	4,000	
CUR	[kg/m <sup>3</sup> ]	0.12	0.08	0.11	
GAC price	[€/kg]	1.65	1.00	1.20	
Specific carbon costs	[€/m <sup>3</sup> ]	0.198	0.083	0.135	
related to the product water	[€/m <sup>3</sup> ]	0.066	0.028	0.045	

**GAC treatment of WWTP effluent (GAC/NF)**

Depending on the carbon type, a 10% breakthrough of SMX was detected between 6,000 and 10,000 bed volumes. Based on a zero-liquid-discharge concept, the specific carbon demand was increased by 33% equivalent to the additional water volume from the concentrate recycling. This reflects a complete recycle of the NF concentrate at a 75% recovery of the NF plant. Considering the 33% recycle of NF concentrate the specific carbon costs range from 8.5 Cent/m<sup>3</sup> (NRS Carbon GA) to 19.0 Cent/m<sup>3</sup> (Norit GA 830 EN). The lowest cost was detected for a reactivated.

**GAC treatment of NF permeate (NF/GAC)**

The GAC filter showed a 10% breakthrough of SMX at 16,000 to 25,000 BVT when processing NF permeate. The specific GAC costs ranged from 2.0 (Epibon A) to 4.3 Cent/m<sup>3</sup> (Norit GA 830 EN). The lowest costs were observed for a drinking water carbon.

**GAC treatment of NF concentrate**

A 25% breakthrough of SMX was observed between 2,500 and 6,000 BVT. According to the specific percentage the specific GAC costs are reduced to 33% for the determination of the

costs to be added to the NF permeate treatment costs. This reflects that only a fourth of the NF feed is retained as concentrate. Related to the product water (filtrate from NF/GAC), the specific GAC costs vary between 2.8 Cent/m<sup>3</sup> (NRS Carbon GA) and 6.6 Cent/m<sup>3</sup> (Epibon A).

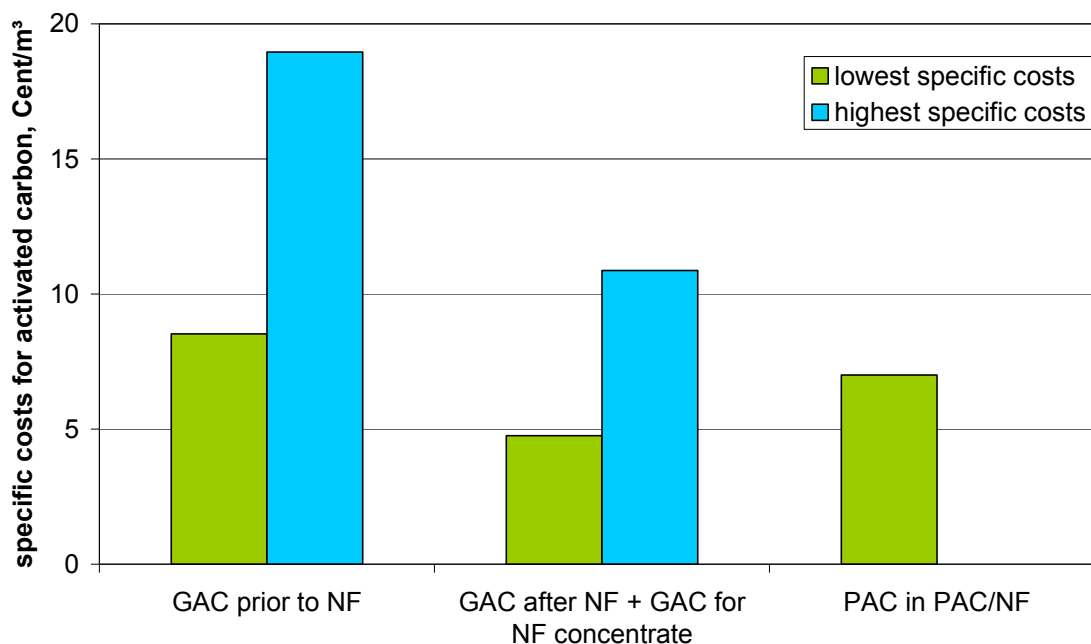
### Summary of the cost comparison

The overview below does not contain the capital cost and the O&M costs besides the carbon costs. The costs are calculated based on the usage of fresh carbon. Depending on the size and location of the plant, reactivation of the carbon may lead to cost reductions. Table 5.13 shows that in GAC pretreatment the specific carbon costs are about twice as high as in GAC post-treatment including a separate treatment of the NF concentrate.

**Table 5.13** Comparison of the carbon costs in GAC/NF and NF/GAC

Process	lowest specific carbon costs	carbon type
GAC/NF	8.5 Cent/m <sup>3</sup>	NRS Carbon GA
NF/GAC		
NF permeate	2.0 Cent/m <sup>3</sup>	Epibon A
NF concentrate	2.8 Cent/m <sup>3</sup>	NRS Carbon GA
Total cost	4.8 Cent/m <sup>3</sup>	

Figure 5.15 presents the comparison of the lowest and highest specific cost for the activated carbon in the investigated process combinations. NF/GAC can provide the lowest costs while PAC/NF and GAC/NF are on a similar cost level.



**Fig 5.15** Comparison of specific carbon costs in GAC/NF, NF/GAC and PAC/NF

## 5.4 Conclusions

NF-GAC hybrid processes provide water of highest quality with DOC concentrations below 0.5 mg/L and concentrations of organic micropollutant below the limit of quantification. In the light of the known high rejection of pathogens by NF membranes and the slight removal of salinity, GAC/NF and NF/GAC can be regarded as good alternate treatment train for high-grade water reuse applications. Although nanofiltration as such is already an efficient water recycling technology, the addition of granular activated carbon features some advantages, in particular with regard to an improved removal of small size pharmaceuticals and industrial chemicals as shown earlier by Verliefde *et al.* (2007) and Roorda *et al.* (2005). The present study revealed the following key insights in the longterm behaviour of the investigated processes:

- GAC adsorption for advanced treatment of WWTP effluent can provide a very good removal of most of the refractory micropollutants. However, high effluent-DOC concentrations can limit the carbon efficiency. With an empty bed contact time of 15 min it can be expected that micropollutants break through after 7000 to 10000 bed volumes depending on the carbon characteristics. From the economic and operational point of view it appears advantageous to employ a reactivated carbon with a large degree of mesopores and high inner surface as this seems to be more resilient against competitive effects from bulk organics. The appropriate carbon type should be selected based on tests using a representative effluent. All carbon types showed properties which can be beneficiary under specific boundary conditions.
- Coupling GAC with NF posttreatment can upgrade the water quality in particular regarding pathogens, multivalent ions and large micropollutants, *e.g.* iodinated contrast media.
- GAC adsorption following nanofiltration showed very stable removal results over a period of more than a year. Removal of bulk organics prior to GAC filtration produced an influent water quality comparable to drinking water treatment. For these applications a long runtime of the adsorber can be accomplished, particularly if high-grade drinking water carbons are employed. This could also be required to obtain authorisation for managed aquifer recharge according to drinking water standards.
- The combination of NF/GAC exceeds the performance of GAC/NF in terms of DOC removal, which was stable at around 98%, and also in terms of the achievable bed volumes which were well above 20,000 for NF/GAC compared to about 7,000 for GAC/NF.

Both hybrid processes feature also advantages in managed aquifer applications as the salt content of the product water is closer to natural conditions and could be treated more easily on-site. RSCCT experiments proved successful for carbon selection, while pilot scale studies revealed good and complex results but took long time for investigation. RSSCT tests can be used to determine the maximum achievable bed volumes which are expected to be above 20,000 for a minimum 90% removal in NF/GAC.



## 5.5 References

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## 6 Tracking effluent organic matter in activated carbon nanofiltration hybrid processes

### 6.1 Introduction

Effluent from wastewater treatment plants contains a broad range of bulk and trace organic compounds, which are often referred to as effluent organic matter (EfOM). It is composed of soluble microbial products (SMP) derived from biological wastewater treatment, allochthonous natural organic matter (NOM) such as humic and fulvic acids originating from runoff and leaching of vegetable debris from terrestrial sources within the watershed and remaining anthropogenic trace organics (Drewes *et al.*, 2006; Amy, 2008). The compounds in EfOM range from low to high molecular weight up to several ten thousand g/mol. Bulk organics in EfOM are composed of polysaccharides, proteins, aminosugars, nucleic acids and cell compounds besides NOM derived compounds such as humic and fulvic acids (Rebhuhn *et al.*, 1971; Barker *et al.*, 2000). In water reclamation processes bulk organics largely influence the fouling of membranes (Schäfer, 2001; Amy, 2008) and adsorbents with all its technical and economic implications, contribute to soil clogging (Bouwer 2002) and are the precursors of disinfection by-products (Oliver, 1983; Singer, 1993).

High-quality water reuse such as managed aquifer recharge with direct injection in aquifers requires therefore also a very high water quality regarding EfOM (Bouwer, 2002; Toze *et al.*, 2005). The Californian Department of Public Health has set the strictest standard for EfOM in reclaimed water for indirect potable reuse *via* groundwater recharge of maximum 0.5 mgDOC/L (CDPH, 2008). Dual membrane processes followed by advanced oxidation are the state of the art for advanced water treatment to comply with these requirements (Bixio and Wintgens, 2006; Asano *et al.*, 2007). Nanofiltration and activated carbon are alternative processes to this, which allow reaching comparable low concentration levels.

Numerous standard and novel methods are available for the characterisation of bulk organic matter in water samples (Amy, 2008). Dissolved organic carbon (DOC) and UVA absorbance at 254 nm (UVA 254) are the typical standard parameters. The specific UVA (SUVA) derived from these standard parameters is calculated by dividing the UVA absorbance by the concentration of DOC. The SUVA reveals the relative amounts of aromatic compounds and allows an insight in the nature of the organic matter. Samples rich in humic substances show SUVA values above 4 L/(mg·m), while low SUVA values below 2 L/(mg·m) indicate carbon sources from effluent with a lower proportion of humic substances and more hydrophilic properties (Amy *et al.*, 2006).

A determination of the molecular weight by size exclusion chromatography with DOC (SEC-DOC) or UVA (SEC-UVA) detection is often applied to identify the fate of the main bulk

organic groups during water treatment. The method is also known as LC-OCD (Huber, 1998). To identify the polarity distribution of the organic matter ion exchange resin are used. A very sensitive method to investigate and monitor transformations of dissolved organic matter is fluorescence excitation-emission spectroscopy (Hudson *et al.*, 2007), which gives a 3-dimensional fingerprint of the water sample known as fluorescence excitation-emission matrix (FEEM). FEEMs show typically main peaks of humic-like substances derived from NOM and protein-like substances derived from microbial origin (Hudson *et al.*, 2007). On the basis of FEEM, the fluorescence index can be determined by the ratio of fluorescence intensities at emission 450 and 500 nm at excitation 370 nm (McKnight *et al.*, 2001). It represents another tool to trace NOM origin of EEM samples.

The investigation presented in this chapter aims to elucidate the fate and removal of bulk organics from tertiary effluent during adsorption to different activated carbon types ranging from powdered to granular activated carbon, direct nanofiltration and nanofiltration activated carbon hybrid processes taking PAC/NF as an example. The study employs standard characterisation methods such as DOC and UVA as well as advanced methods such as size exclusion chromatography and fluorescence excitation-emission matrix (FEEM) spectroscopy (Baker, 2001, Her *et al.*, 2003).

## **6.2 Materials and methods**

### **6.2.1 Raw water quality**

To evaluate the performance of nanofiltration and activated carbon nanofiltration hybrid processes under realistic conditions pilot studies have been conducted at the WWTP Aachen Soers (460,000 p.e.) treating continuously tertiary effluent for several months. The wastewater treatment plant with advanced biological treatment including nutrient removal as well as a final sand filtration already provides a high quality effluent with an average DOC of  $5.2 \pm 0.9$  mg/L, average COD of  $15.6 \pm 2.3$  mg/L, average conductivity of  $0.97 \pm 0.19$  mS/cm, and an average pH of  $7.7 \pm 0.4$ .

### **6.2.2 Characterisation of organic matter**

A MAXX SP III auto sampler provided the sampling of the 24 h composite samples with 200 mL collected every 30 min in a 10 L Duran glass bottle and stored at 7 °C. The samples with activated carbon were taken as manually produced composite samples, removing the PAC directly after sampling with a 0.45 µm filter to interrupt the adsorption process. TOC and DOC were analysed on a DIMA-TOC 100 total organic carbon analyser (Dimatec Analysentechnik GmbH, Germany). For DOC measurement the samples were pre-filtered with 0.45 µm Acrodisc filters from Pall Corporation. A photometer of Varian Company, Model Cary 1 E was used for the measurement of UVA 254.

### 6.2.3 Advanced bulk organic characterisation

Specific characterisation of the bulk organics was performed by LC-OCD and LC-UVD respectively as published in Meier and Melin (2005).

The FEEM spectroscopy was performed using a FluoroMax-3 spectrofluorometer from Horiba Jobin Yvon Inc., USA, with a xenon lamp as excitation source at the laboratory of UNESCO-IHE. The adapted protocol was based on work by Westerhoff *et al.* (2001). Depending on the DOC concentration the filtered samples were diluted to about 1 mg/L of DOC with 0.01M KCl solution with an adjusted pH of ~2.8 using HCl. The samples were measured at room temperature around 20 °C with the following range of wavelengths: Excitation: 240-450 nm in 10 nm intervals and Emission: 290-530 nm in 2 nm intervals. The sample EEMs were corrected by subtraction of the blank EEM (0.01 KCl, pH of 2.8 using HCl) to remove raman scatter peaks.

### 6.2.4 Adsorbents

Four commercially available carbon types were tested: Norit SAE Super, Norit NRS GA 0.5-2.5, Norit NRS EA 0.5-2.5 (Norit, Amersfoort, The Netherlands) and lignite coke dust "Herdofenkoks Super" (RWE Power - Rheinbraun Brennstoff, Frechen, Germany). The four carbons were selected to cover a representative range of types applicable to NF/AC hybrid processes. The granular and extruded activated carbons were grinded to fine dust with a particle size below 45 µm by a Retsch MM301 ball mill. Table 6.1 summarises the properties of the studied adsorbents.

**Table 6.1** Characteristics of the selected adsorbents (original size before grinding in brackets)

Adsorbent	Activated carbon type	Surface area m <sup>2</sup> /g	Particle size d <sub>50</sub> µm	Raw material	Price €/kg
Norit SAE Super	powdered	1300	15	diverse	1.35
Norit NRS GA 0.5-2.5	granular (recycled)	975	< 45 (1300)	diverse	1.00
Norit NRS EA 0.5-2.5	extruded (recycled)	1000	< 45 (1280)	diverse	1.50
RWE LCD	lignite coke dust	300	24	lignite	0.35

### 6.2.5 Adsorption isotherms and kinetics

To allow a better evaluation of the adsorption processes and for optimisation of the treatment trains investigated in pilot scale, laboratory tests were conducted to determine adsorption isotherms and adsorption kinetics of DOC for the selected adsorbents. Adsorption isotherm experiments were conducted in 500 mL DURAN glass bottles containing different amounts of carbon. All glassware was rinsed twice with ultrapure water and acetone, and subsequently dried at 105 °C. The adsorbents used in lab-scale tests were dried in an oven for 24 hours at

105°C and cooled down in a desiccator prior to the tests. Each amount of carbon was weighed by means of aluminium foil. 250 mL of the WWTP effluent sample was measured with a measuring cylinder. The carbon was transferred into the glass bottle and any remaining particles were washed off with the sample water. The content of the flasks was shaken at 190 rpm and 20°C for 24 hours. Samples were filtered with Pall IC Acrodisc filters (0.45 µm) and analysed with the respective methods. Kinetics experiments were performed at the RWTH Aachen University Hospital by Dr. Kai Lehnberg and Dr. Lubomira Kovalova in the course of a joint research project. The tests were conducted in 1L Erlenmeyer flasks containing the respective amount of carbon and run with a duplicate. The contents of the flasks were shaken at 100 rpm and 20°C. At the respective time points, samples were taken by syringe and were immediately filtered by a syringe filter (0.45 µm Acrodisc filters, Pall Corporation).

### **6.2.6 PAC/NF pilot plant**

The tests were conducted in pilot scale supported by lab tests. The PAC/NF pilot plants used for this study is explained in detail in Chapter 3 and 4 for its operation in direct NF without carbon dosage and with carbon dosage as PAC/NF.

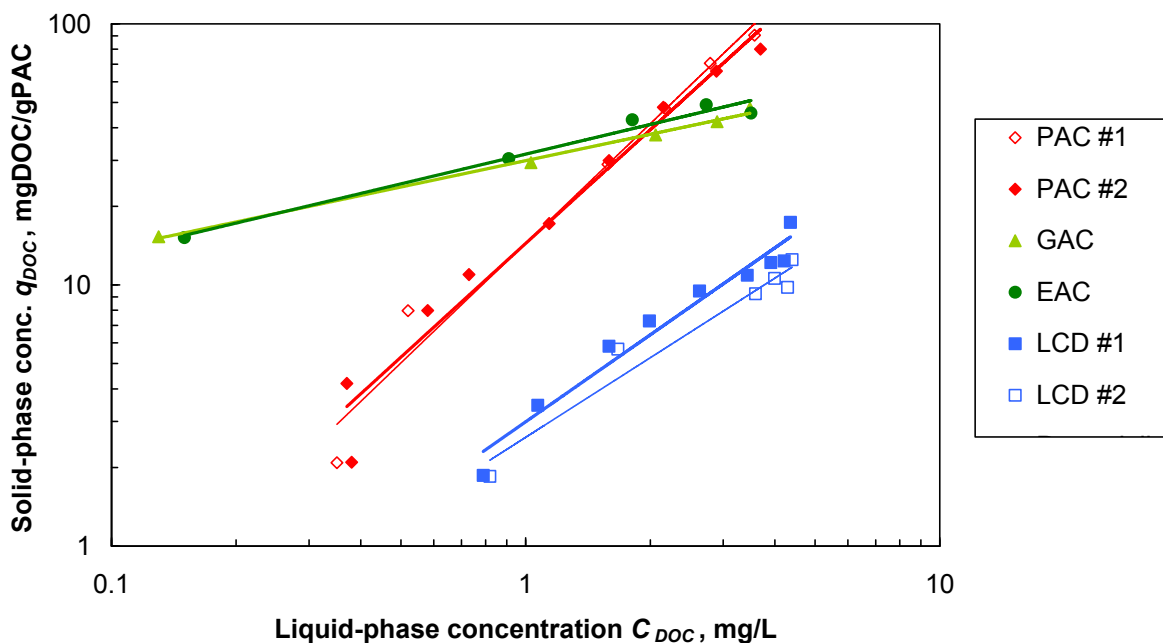
The plant was operated with a contact time in the PAC reactor of 1.25 hours. The capillary NF was operated in crossflow mode with a recovery of 75% and a specific permeate flux of 20 L/(m<sup>2</sup>·h).

## 6.3 Results and discussion

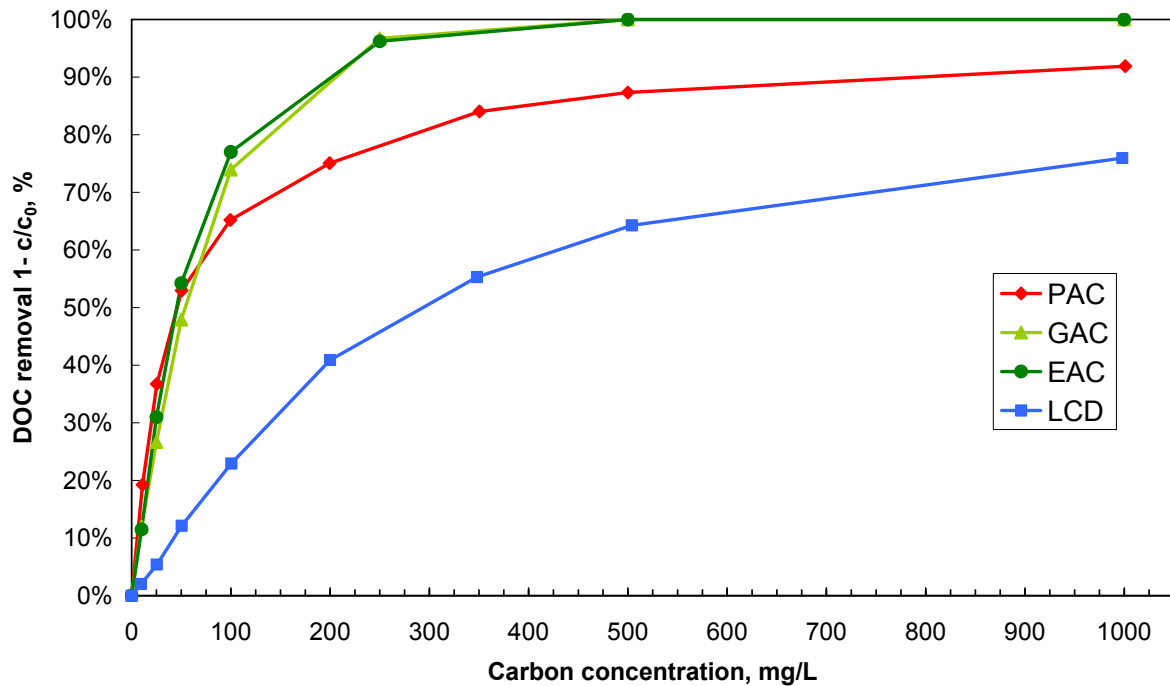
### 6.3.1 Adsorption of dissolved organic carbon

#### Adsorption isotherms

Figure 6.1 and 6.2 show the adsorption characteristics of the selected adsorbents for the WWTP effluent used for the pilot and laboratory tests. The finely pulverised GAC and EAC exhibited the highest adsorption capacity for DOC. Up to a dosage of 50 mg/L, PAC had a similar adsorption capacity, but did not reach at higher dosages comparable levels. This was also reflected in the adsorption isotherms. While at high DOC concentrations very high loadings of about 100 mg/g were measured, a steep decrease of the loading was observed at lower equivalent concentrations. In comparison, GAC and EAC had a significantly flatter slope indicating a more balanced adsorption capacity and high removal rates at low concentrations of the adsorbate. According to the producer, both carbon types, which are recycled, have a high proportion of mesopores. At a dose of 50 mg/L, all three activated carbons adsorbed already 50% of the DOC. It is noteworthy that GAC and EAC fully adsorbed the DOC at high carbon dosage. In contrast, PAC did not exceed a maximum adsorptive removal of around 90%. Reflecting the low surface area of 300 m<sup>2</sup>/g compared to 1,300 m<sup>2</sup>/g for the employed PAC, lignite coke dust adsorbed around 50% of the DOC first at a dosage of 350 mg/L corresponding to a sevenfold higher dosage, and reached a maximum adsorptive removal of 75%. The slope of the LCD isotherm was slightly less than that of PAC.



**Fig 6.1** Adsorption isotherms of DOC for effluent from WWTP Aachen Soers (initial concentrations and Freundlich parameters are given in table 6.2, PAC and LCD series #1 and #2 of duplicates)



**Fig 6.2** Adsorption of DOC *versus* carbon dose (effluent from WWTP Aachen Soers, initial concentrations are given in table 6.2)

Table 6.2 gives an overview of the Freundlich isotherm parameters according to the Freundlich isotherm equation written in the following form:

$$q_A = K_F C_A^n \quad (6.1)$$

where  $q_A$  = equilibrium adsorbent-phase concentration of adsorbate A,  
mg adsorbate/g adsorbent

$C_A$  = equilibrium concentration of adsorbate A in solution, mg/L

$K_F$  = Freundlich adsorption capacity parameter, (mg/g)/(mg/L)<sup>n</sup>

$n$  = Freundlich adsorption intensity parameter, unitless

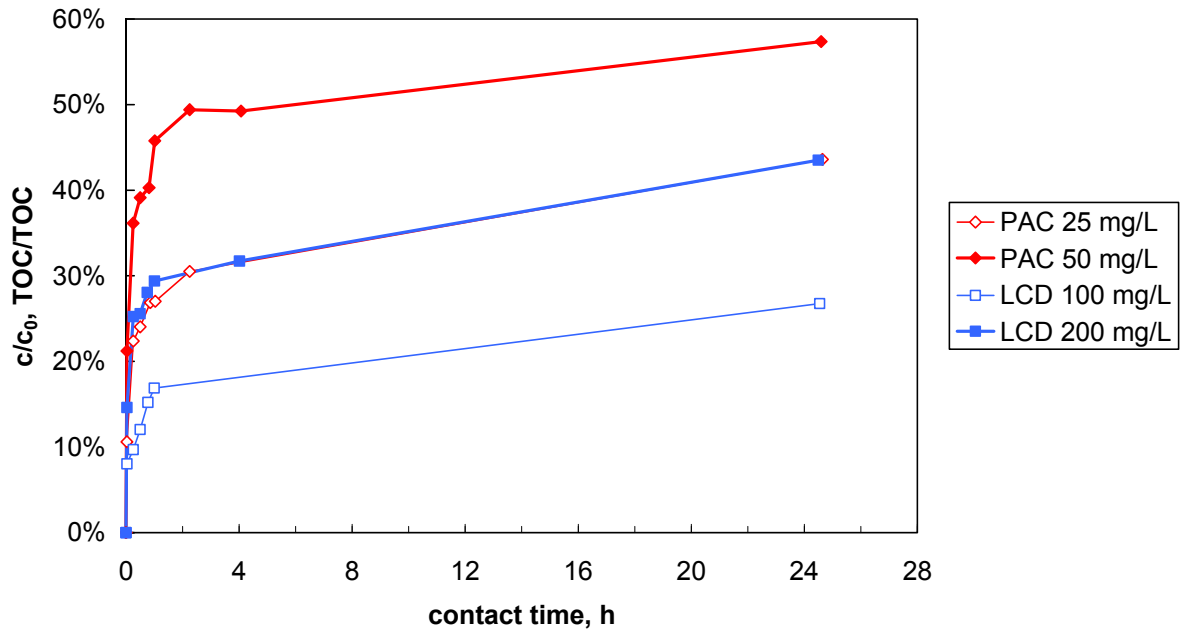
**Table 6.2** Freundlich isotherm parameters of DOC for PAC, GAC, EAC and LCD (t = 20 °C, 24 h contact time, 190 rpm)

Adsorbent	Initial concentration	Freundlich coefficient	Freundlich exponent	Coefficient of determination
	$C_0$ mg/L	$K_F$	$n$	$R^2$
PAC	4.5	14.44	1.521	0.973
	4.5	14.42	1.446	0.966
GAC	4.0	29.93	0.336	0.996
EAC	4.0	31.69	0.378	0.976
LCD	4.5	2.99	1.107	0.960
	4.5	2.61	1.013	0.954

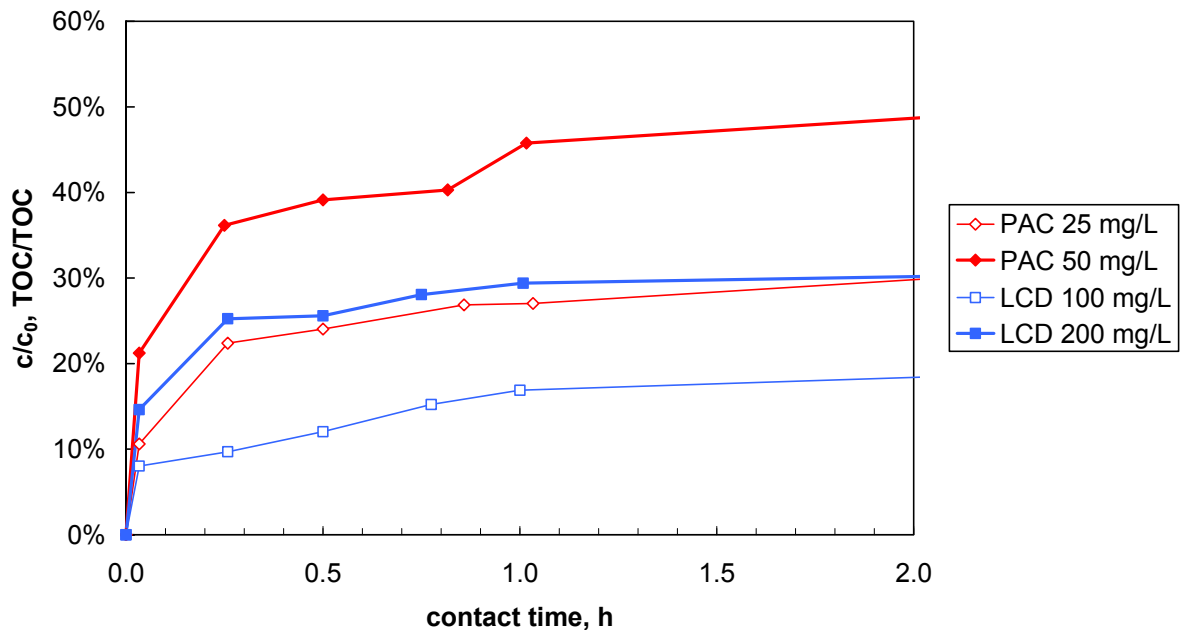
### Adsorption kinetics



In laboratory experiments the adsorption kinetics of PAC and LCD were investigated. After 24 h the adsorptive removal reached the same levels as in the isotherm tests (*cf.* Figure 6.3). That means that for example PAC could remove 44% of the dissolved organic matter at a carbon dose of 25 mg/L and 57% at a concentration of 50 mg/L (see Figure 6.4). At 100 mg/L LCD, a DOC removal of 27% was measured which increased at 200 mg/L to 44%.

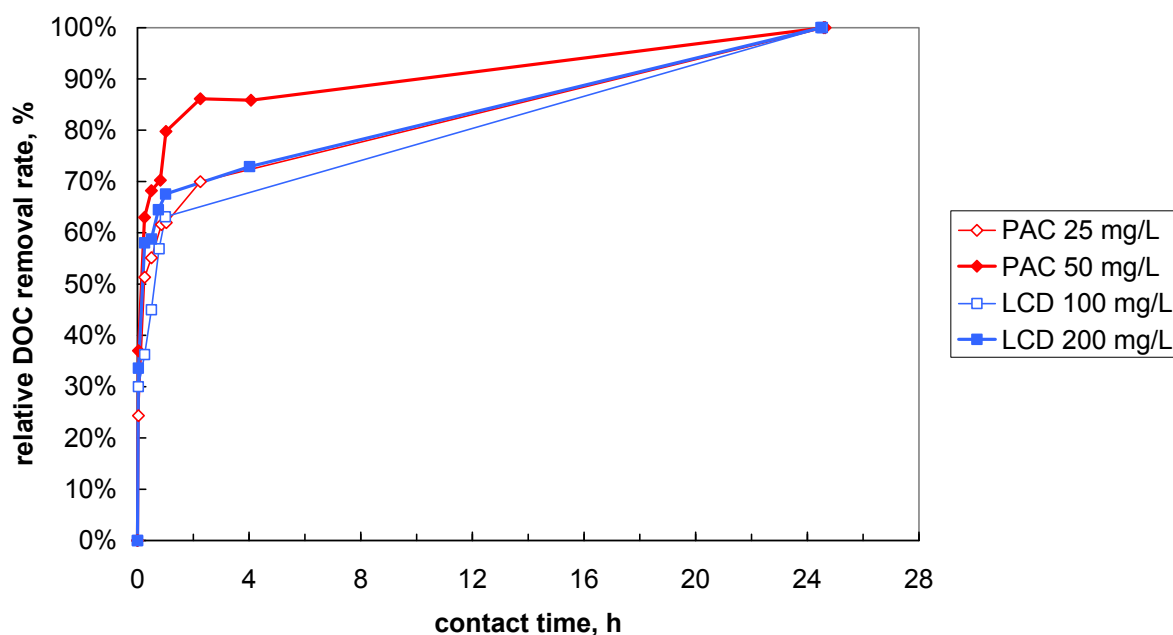


**Fig 6.3** Kinetic of DOC-adsorption during 24 h contact time (effluent from WWTP Aachen Soers,  $c_0 = 6.0$  mg/L)



**Fig 6.4** Kinetic of DOC-adsorption during the first 2 h contact time (effluent from WWTP Aachen Soers,  $c_0 = 6.0$  mg/L)

In all experiments a rapid increase in DOC removal was observed during the first 2 hours, which levelled out after that. The steepest increase was observed during the first 20 minutes (see Figure 6.4). If the maximum adsorption achieved after 24 hours is set to 100%, then the DOC adsorption is revealed more clearly as the relative DOC removal rate (see Figure 6.5). Within the first hour around 60 to 80% of the maximum adsorption was already achieved. This, however, remains below the adsorption kinetics of micropollutants (Melin *et al.*, 2008). Here values of up to 90% were detected. For both carbon types, a clear trend of a faster DOC adsorption at a higher carbon concentration was observed. This means that in full scale applications, aiming at the lowest carbon dosage the contact time should be as long as possible to fully utilise the capacity of the PAC.



**Fig 6.5** Relative DOC removal rate during 24 h contact time (effluent from WWTP Aachen Soers,  $c_0 = 6.0$  mg/L)

### 6.3.2 Removal of dissolved organic carbon in activated carbon nanofiltration hybrid processes

Table 6.3 shows the average concentrations of DOC and UVA as well as the respective SUVA values at the different sampling points. The average removal rates are given in Table 6.4. Direct NF provided already permeate of high quality with DOC concentrations of around 0.3 mg/L and a total DOC removal of 93%. Low doses of powdered activated carbon between 10 to 25 mg/L lead to a slightly deteriorated NF permeate quality. The total DOC removal dropped to 90%. By dosing 50 to 100 mg/L PAC the total DOC removal was again increased to 94 to 95% with average DOC concentrations in the permeate below 0.3 mg/L. In comparison, the GAC based hybrid processes, GAC/NF and NF/GAC, performed better and reached DOC removal rates of 95 to 99%.

**Table 6.3** Average DOC and UVA concentrations, and SUVA values during pilot tests of DNF, PAC/NF, GAC/NF and NF/GAC

Parameter		WWTP effluent	NF feed	NF permeate
<b>DNF</b>				
DOC	mg/L	4.81 ± 0.73	-	0.34 ± 0.12
UVA	cm <sup>-1</sup>	0.128 ± 0.018	-	0.011 ± 0.007
SUVA	L/(mg·m)	2.68 ± 0.20	-	4.65 ± 2.05
<b>PAC/NF 10 mg/L</b>				
DOC	mg/L	3.89 ± 0.62	3.13 ± 0.30	0.39 ± 0.10
UVA	cm <sup>-1</sup>	0.117 ± 0.015	0.089 ± 0.014	0.015 ± 0.003
SUVA	L/(mg·m)	3.03 ± 0.10	2.85 ± 0.16	3.84 ± 0.18
<b>PAC/NF 25 mg/L</b>				
DOC	mg/L	4.87 ± 0.75	3.46 ± 0.63	0.48 ± 0.08
UVA	cm <sup>-1</sup>	0.131 ± 0.011	0.086 ± 0.015	0.017 ± 0.002
SUVA	L/(mg·m)	2.70 ± 0.20	2.49 ± 0.03	3.62 ± 0.17
<b>PAC/NF 50 mg/L</b>				
DOC	mg/L	5.09 ± 0.17	2.97 ± 0.19	0.29 ± 0.05
UVA	cm <sup>-1</sup>	0.142 ± 0.020	0.073 ± 0.004	0.012 ± 0.001
SUVA	L/(mg·m)	2.96 ± 0.07	2.46 ± 0.10	4.30 ± 0.65
<b>PAC/NF 100 mg/L</b>				
DOC	mg/L	5.29 ± 0.54	2.08 ± 0.43	0.25 ± 0.07
UVA	cm <sup>-1</sup>	0.149 ± 0.011	0.040 ± 0.007	0.009 ± 0.001
SUVA	L/(mg·m)	2.82 ± 0.10	1.92 ± 0.07	3.65 ± 0.59
<b>GAC/NF week 1</b>				
DOC	mg/L	4.60	0.48	0.05
UVA	cm <sup>-1</sup>	0.136	0.003	0.001
SUVA	L/(mg·m)	2.96	0.71	2.20
<b>GAC/NF week 11</b>				
DOC	mg/L	5.90	3.20	0.29
UVA	cm <sup>-1</sup>	0.157	0.067	0.007
SUVA	L/(mg·m)	2.66	2.09	2.52
		WWTP effluent	NF permeate	GAC filtrate
<b>NF/GAC</b>				
DOC	mg/L	5.02 ± 0.74	0.41 ± 0.13	0.25 ± 0.10
UVA	cm <sup>-1</sup>	0.138 ± 0.015	0.014 ± 0.002	0.003 ± 0.002
SUVA	L/(mg·m)	2.76 ± 0.23	3.67 ± 1.01	1.34 ± 0.72

**Table 6.4** Average removal rates of DOC and UVA during NF, PAC and GAC treatment (PAC/NF: contact time = 1.13 h + 0.12 h; GAC in GAC/NF: EBCT = 0.25 h; GAC in NF/GAC: EBCT = 0.5 h)

Parameter	Removal 1st stage	Removal 2nd stage	Total removal
<b>DNF</b>			
DOC mg/L	93.0%	-	93.0%
UVA cm <sup>-1</sup>	91.0%	-	91.0%
<b>PAC/NF 10 mg/L</b>			
DOC	19.6%	87.6%	90.0%
UVA	23.9%	83.4%	87.4%
<b>PAC/NF 25 mg/L</b>			
DOC	29.1%	86.3%	90.2%
UVA	34.2%	80.1%	86.9%
<b>PAC/NF 50 mg/L</b>			
DOC	41.7%	90.3%	94.3%
UVA	48.5%	83.2%	91.4%
<b>PAC/NF 100 mg/L</b>			
DOC	60.7%	87.9%	95.2%
UVA	73.3%	77.6%	94.0%
<b>GAC/NF week 1</b>			
DOC	89.6%	89.6%	98.9%
UVA	97.5%	67.6%	99.2%
<b>GAC/NF week 11</b>			
DOC	45.8%	90.9%	95.1%
UVA	57.3%	89.1%	95.4%
<b>NF/GAC</b>			
DOC	91.8%	39.0%	95.0%
UVA	89.9%	78.6%	97.8%

Except for the low dose PAC/NF process, all processes were able to eliminate the DOC stably below the targeted DOC concentration of 0.5 mg/L.

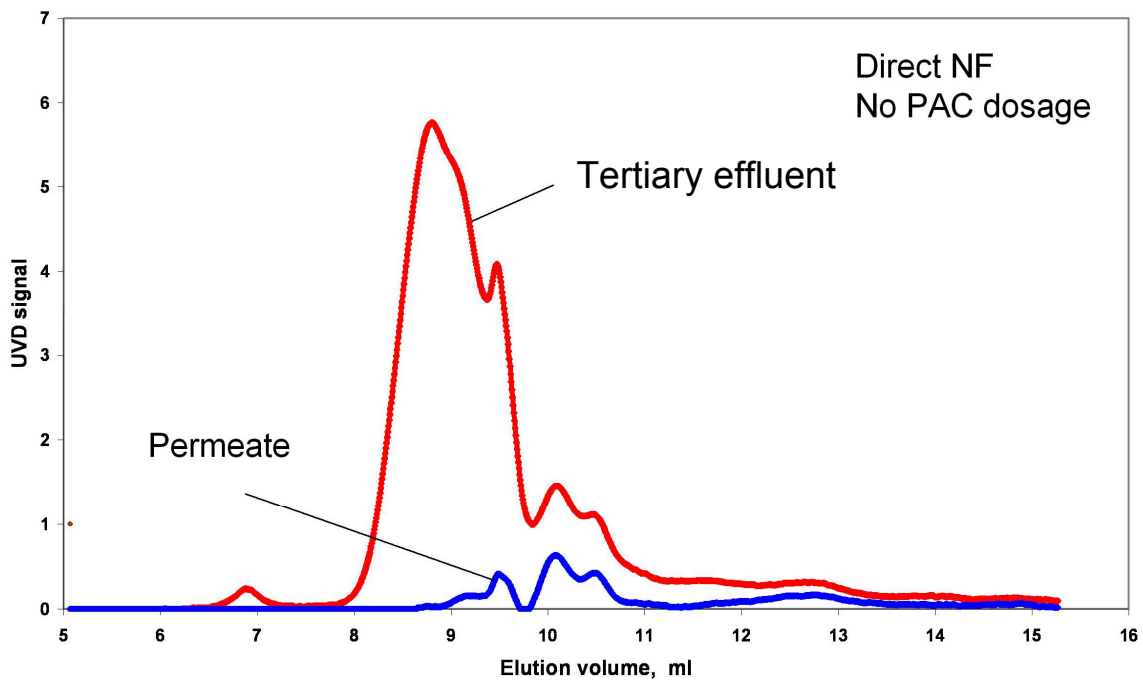
In direct NF and PAC/NF, the organic fraction detected by UVA was removed slightly worse than the DOC, whereas in GAC based hybrid processes UVA was eliminated slightly better. The different removal rates for DOC and UVA indicated that UV relevant molecules such as humic substances possess a higher affinity to adsorb to PAC, GAC and EAC, quite independent from the concentration of the organic matter. The average SUVA in the effluent of the WWTP used as influent for the pilot tests ranged between 2.7 and 3.0 L/(mg·m). It was above the typical effluent value of 2 L/(mg·m) and proved a relatively high share of humic compounds, which were preferentially removed during adsorption and reduced the SUVA. The average SUVA after PAC varied between 2.9 and 1.9 L/(mg·m) depending on the PAC

dose. After nanofiltration, which is known to efficiently remove high molecular weight soluble microbial products (SMPs) well, the SUVA increased again to around 4 L/mg·m indicating a higher aromaticity on a very low DOC level. In contrast the GAC based processes provided a final product water of very low aromaticity on a very low level. The SUVA values around 1.3 to 2.5 L/(mg·m) show that the water has a wastewater history although the concentration levels are far below typical DOM levels of drinking water.

### 6.3.3 Size exclusion chromatography

#### Nanofiltration

Size exclusion chromatography (SEC) for direct nanofiltration without dosage of powdered activated carbon showed as expected an incomplete rejection of low molecular weight neutrals and acids while large molecules such as proteins and humic substances were removed to a very high degree (Fig 6.6).

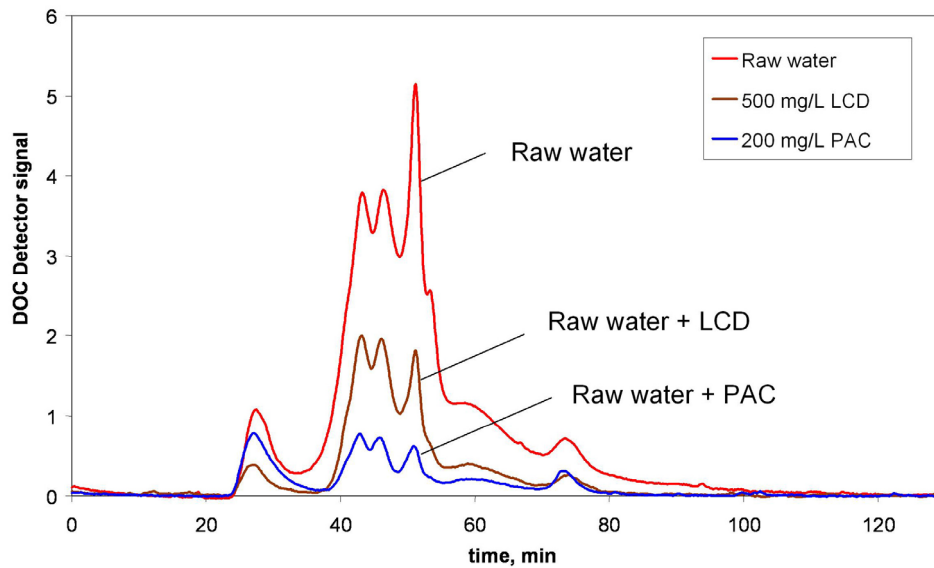


**Fig 6.6** Size exclusion chromatograms for the removal of direct nanofiltration

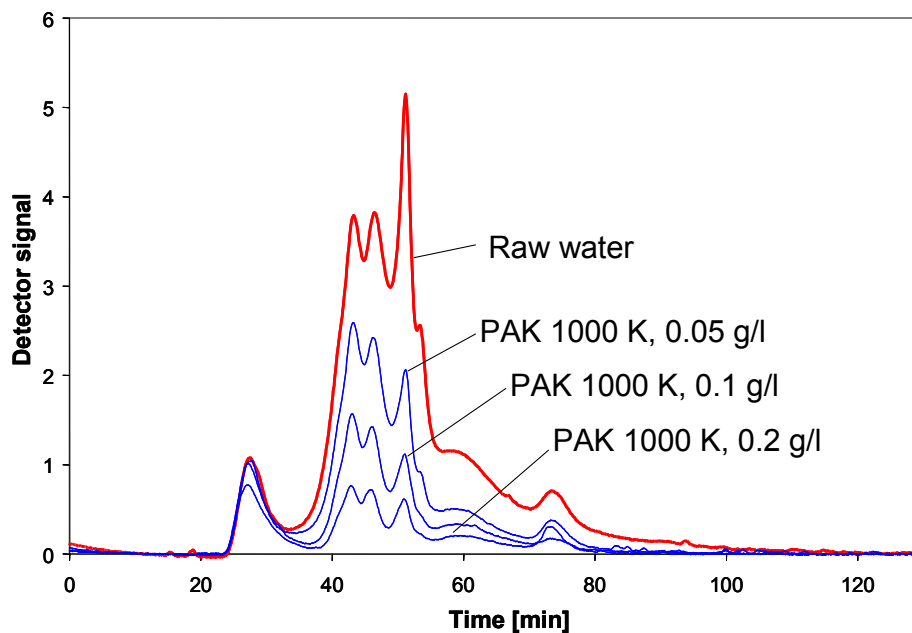
#### Adsorptive removal

Figure 6.7 depicts the different adsorption characteristics of the powdered activated carbon *versus* lignite coke dust. The pore size distribution of lignite coke dust allowed a better adsorption of the fouling relevant high molecular weight substances - at very high adsorbent concentration, whereas powdered activated carbon primarily removed humic substances and small size molecules (*cf.* Figure 6.8). The tests proved the importance of the carbon properties

for the selective removal of certain EfOM groups. Thus an optimised adsorption step prior to NF has the potential to reduce compounds problematic for nanofiltration.



**Fig 6.7** Size exclusion chromatograms for the adsorptive removal by PAC and LCD (adapted from Meier and Melin, 2005)

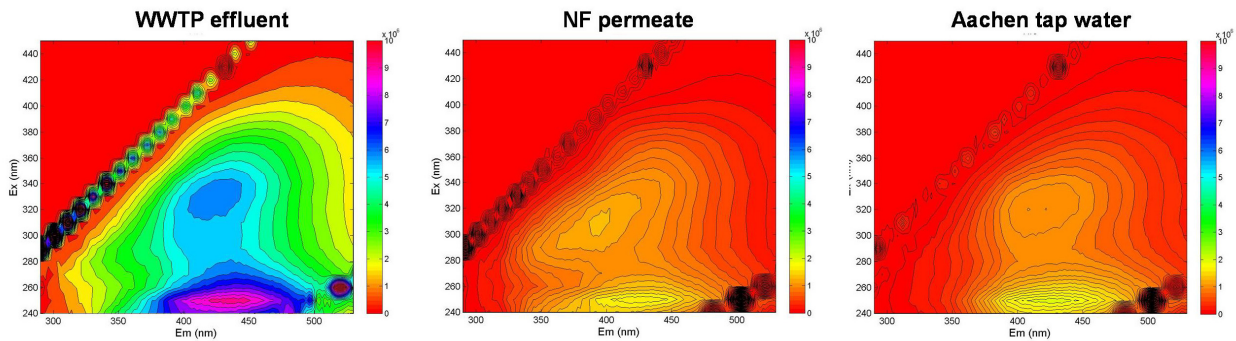


**Fig 6.8** Size exclusion chromatograms for the adsorptive removal by different PAC concentrations (adapted from Meier and Melin, 2005)

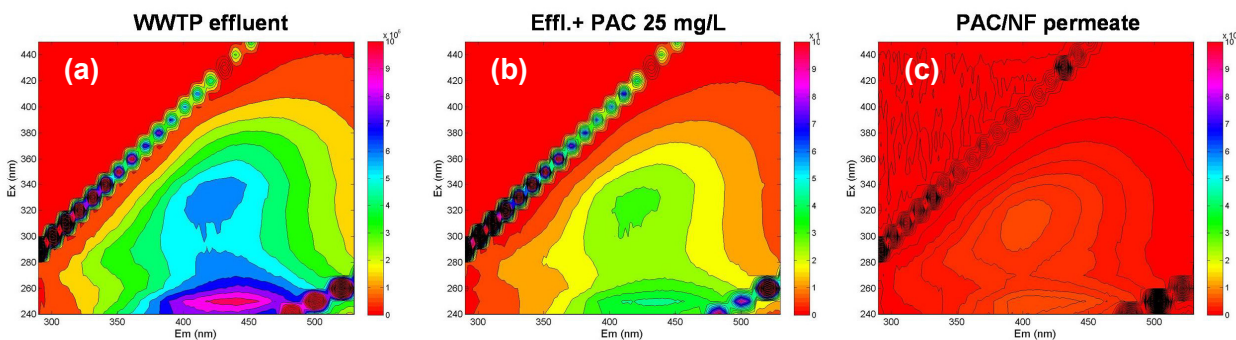
The impact of PAC, LCD and GAC on the operation and performance of the nanofiltration will be investigated in the next chapter (chapter 7). A significant reduction of NF foulants was only observed in GAC/NF as long as the GAC absorber retained the effluent-DOC to a high degree.

### 6.3.4 Fluorescence EEM spectroscopy

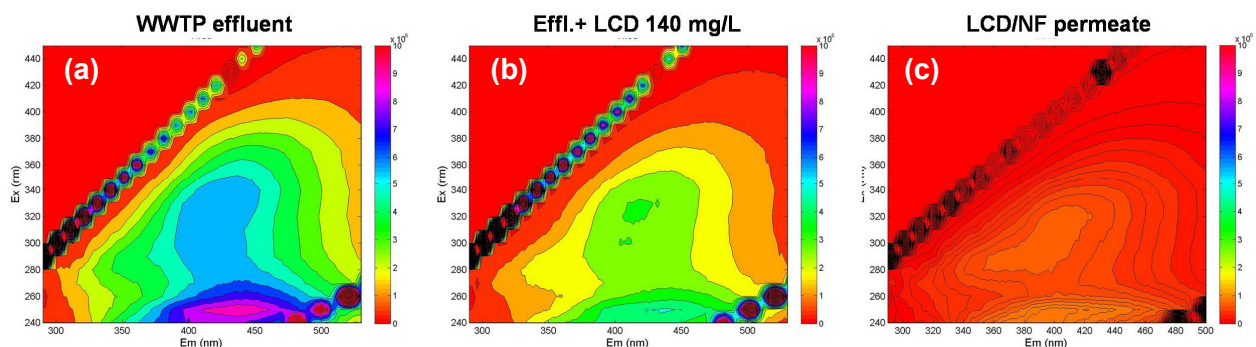
Water samples used for the EEM measurements presented in Fig 6.9 to Fig 6.13 were taken on five different days but showed a similar composition of the WWTP effluent used as raw water for the pilot unit and laboratory tests.



**Fig 6.9** Fluorescence EEMs for direct NF treatment compared to Aachen tap water (DOC: effluent: 5.2 mg/L, permeate: 0.3 mg/L, tap water: 0.5 mg/L details *cf.* Table 6.5)



**Fig 6.10** Fluorescence EEMs for the PAC/NF treatment (PAC dosage 25 mg/L; DOC: effluent: 5.7 mg/L, after PAC: 4.0 mg/L, permeate: 0.3 mg/L, details *cf.* Table 6.5)



**Fig 6.11** Fluorescence EEMs for the LCD/NF treatment (LCD dosage 140 mg/L; DOC: effluent: 5.6 mg/L, after LCD: 4.5 mg/L, permeate: 0.4 mg/L, details *cf.* Table 6.5)

All raw water assays exhibited dominating fulvic- and humic-like peaks at  $E_m/E_x = 440/250$  nm and  $424/340$  nm respectively and intensities of  $9.6$  to  $10.0 \times 10^6$  and  $6.2$  to  $6.4 \times 10^6$ . Long slopes from the peaks towards the lower excitation/emission range indicated the presence of protein-like substances typical for wastewater influenced samples. A clear third peak as often

detected in wastewater was, however, not observed. The protein-like intensity at Em/Ex 320/280 ranged from 1.5 to  $2.3 \times 10^6$ . The relatively small polyprotein peak in the UVD chromatogram (fig 6.6) showed little recognition of the peak of polymeric compounds typically measured (fig 6.7), suggesting that the effluent samples contained more polysaccharides than proteins.

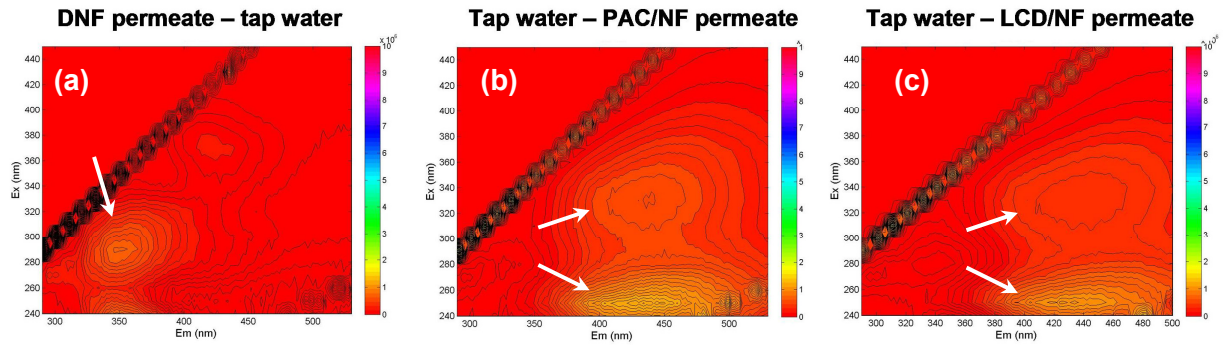
**Table 6.5** DOC and UVA average concentrations, SUVA and removal rates

Parameter	Raw water	Adsorption		PAC/NF	
	$C_{\text{wwtp effluent}}$	$R_{\text{adsorptive}}$	$C_{\text{Feed}}$	$R_{\text{total}}$	$C_{\text{Permeate}}$
<b>Direct NF (without PAC)</b>					
DOC	4.6 mg/L	-	-	93.4 %	0.3 mg/L
UVA 254	$0.126 \text{ cm}^{-1}$	-	-	90.0 %	$0.0126 \text{ cm}^{-1}$
SUVA	2.7 L/mg·m	-	-	-	4.2 L/mg·m
<b>PAC/NF with 25 mg/L PAC</b>					
DOC	5.7 mg/L	29.8 %	4.0 mg/L	94.7 %	0.3 mg/L
UVA 254	$0.136 \text{ cm}^{-1}$	34.6 %	$0.089 \text{ cm}^{-1}$	90.4 %	$0.0130 \text{ cm}^{-1}$
SUVA	2.4 L/mg·m	-	2.2 L/mg·m	-	4.3 L/mg·m
<b>PAC/NF with 140 mg/L LCD</b>					
DOC	5.4 mg/L	18.5 %	4.4 mg/L	92.6 %	0.4 mg/L
UVA 254	$0.133 \text{ cm}^{-1}$	28.6 %	$0.126 \text{ cm}^{-1}$	88.0 %	$0.0160 \text{ cm}^{-1}$
SUVA	2.5 L/mg·m	-	2.2 L/mg·m	-	4.0 L/mg·m

### Direct nanofiltration

Fig 6.9 illustrates the shift of the humic-like peak from Em/Ex = 430/330 to 390/310 nm with an intensity of  $1.3 \times 10^6$  towards the protein-like substances through the removal of the humics by nanofiltration. The fulvic-like peak at Em/Ex = 430/250 nm was reduced to an intensity of  $1.8 \times 10^6$ , but not significantly shifted. The DOC was reduced from 5.2 to 0.3 mg/L. The comparison with the Aachen tap water showed similar intensities of the drinking water with peaks at 420/330 nm ( $1.1 \times 10^6$ ) and 430/250 nm ( $2.0 \times 10^6$ ) which were more confined without the influence from protein-like compounds (Fig 6.9c). Although in the same range of intensities the position and extension of the NF permeate peaks demonstrated the wastewater history of the NF permeate. The differential plot of the FEEM from the DNF permeate minus the Aachen tap water (*cf.* Fig 6.12a) revealed the protein-like peak at 350/280 nm with an intensity of  $2.6 \times 10^5$  one order of magnitude lower than the protein-like peak of the effluent sample.





**Fig 6.12** FEEM differential plots of difference in DOM between tap water and permeates ( $\Delta\text{DOC} = 0.1 - 0.2 \text{ mg/L}$ )

a: NF permeate (fig 6.9b) – Aachen tap water (fig 6.9c)

b: Aachen tap water (fig 6.9c) – PAC/NF permeate (fig 6.10c)

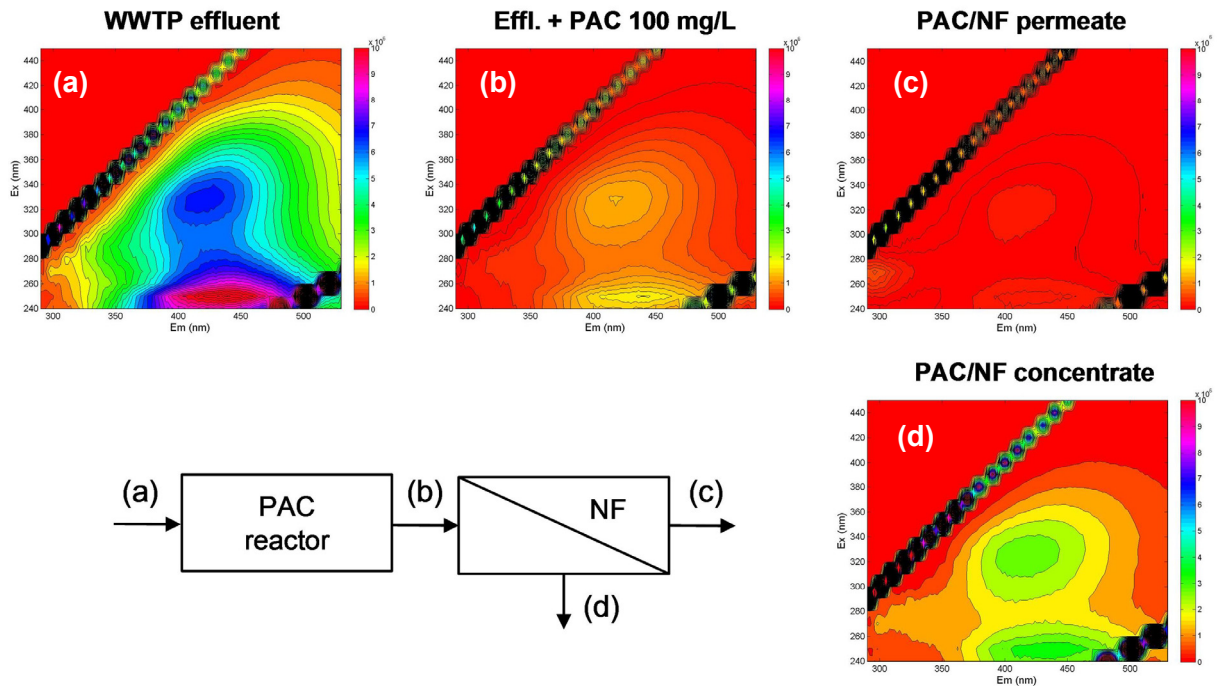
c: Aachen tap water (fig 6.9c) – LCD/NF permeate (fig 6.11c)

### PAC combined with NF

Fig 6.10 shows the series of EEM spectra with the effect of PAC dosage of 25 mg/L Norit SAE Super. While reducing the peaks from  $6.4 \times 10^6$  to  $3.1 \times 10^6$  ( $\text{Em}/\text{Ex} = 420/330 \text{ nm}$ ) and  $10.0 \times 10^6$  to  $4.5 \times 10^6$  ( $430/250$ ), PAC did not shift the peaks and only partly removed the protein-like wastewater indicators. The PAC/NF permeate showed the highest quality of all samples measured. The peaks at  $\text{Em}/\text{Ex} = 400/310$  and  $408/250$  with intensities of  $5.8 \times 10^5$  and

$7.1 \times 10^5$  (Fig 6.10c) were well below the Aachen drinking water. Still some of the protein-like substances remained in the permeate. The differential plot of the FEEM from the Aachen tap water minus the PAC/NF permeate (*cf.* Fig 6.12b) showed mainly humic-like compounds, which were detected at higher level in the tap water.

When dosing 100 mg/L PAC the humic-like peaks were already significantly reduced through adsorption from initially  $6.7 \times 10^6$  to  $1.3 \times 10^6$  ( $\text{Em}/\text{Ex} = 428/340 \text{ nm}$ ) and  $1.1 \times 10^7$  to  $1.8 \times 10^6$  ( $\text{Em}/\text{Ex} = 446/250 \text{ nm}$ ). The intensities in the permeate were  $2.1 \times 10^5$  and  $2.9 \times 10^5$  for the humic-like compounds and  $2.0 \times 10^5$  for the protein-like compounds. These values were one order of magnitude below the tap water which had 1 to  $2 \times 10^6$  for the humic-like compounds and  $2.0 \times 10^5$  for the protein-like compounds. The concentrate from PAC/NF as shown below exhibited intensities of 2.8 to  $3.8 \times 10^6$  (humic-like compounds) and  $1.4 \times 10^6$  (protein-like compounds).



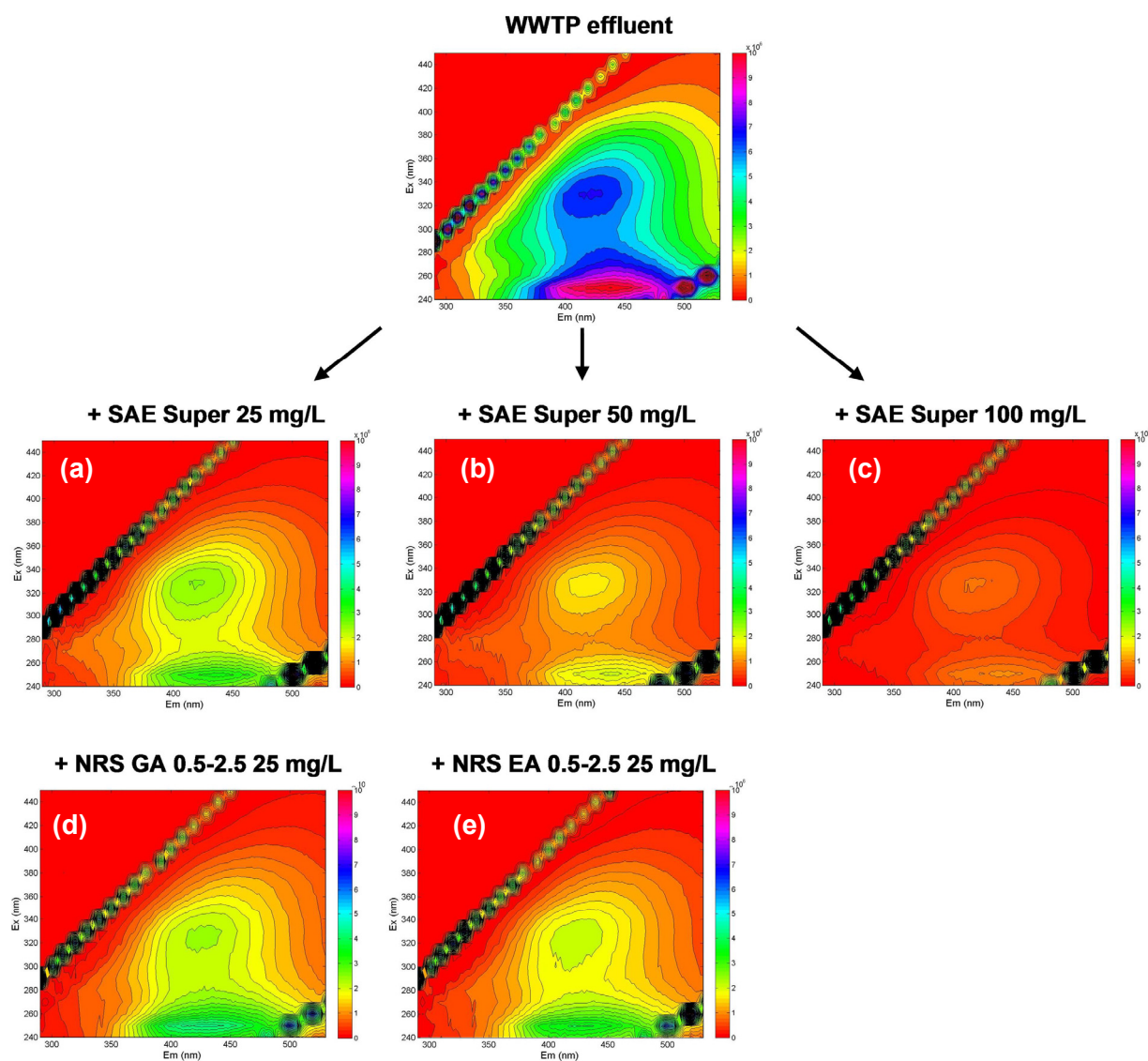
**Fig 6.13** Fluorescence EEMs for PAC/NF treatment (PAC dosage 100 mg/L; DOC: WWTP effluent: 5.2 mg/L, after PAC: 0.6 mg/L, permeate: 0.2 mg/L; contact time PAC reactor: 1.2 h, CF loop: 0.25 h)

### LCD combined with NF

When applying lignite coke dust (Fig 6.11), organic matter was removed similarly as in the case of PAC. The broad peaks of the permeate sample at  $Em/Ex = 400/250$  and  $392/300$  with intensities of  $9.5 \times 10^5$  and  $7.1 \times 10^5$  were below the drinking water but exhibited stronger shifts towards the protein-like compounds. Other than expected from the adsorption pattern of LCD (Fig 6.7) that showed a higher removal of the high molecular weight fraction, more wastewater derived protein-like compounds remained in the LCD/NF permeate (Fig 6.11c).

### Comparison of different adsorbents

Fig 6.14 illustrates the influence of different types of adsorbents and their concentration on the removal of the humic-like and protein-like compounds. While PAC gradually removed more humic and protein-like compounds by increasing the carbon dosage, changing the adsorbent type from powdered to granular or extruded activated carbon altered the specific removal pattern clearly. The specific removal of the respective peaks revealed this even clearer (*cf.* Fig 6.16).

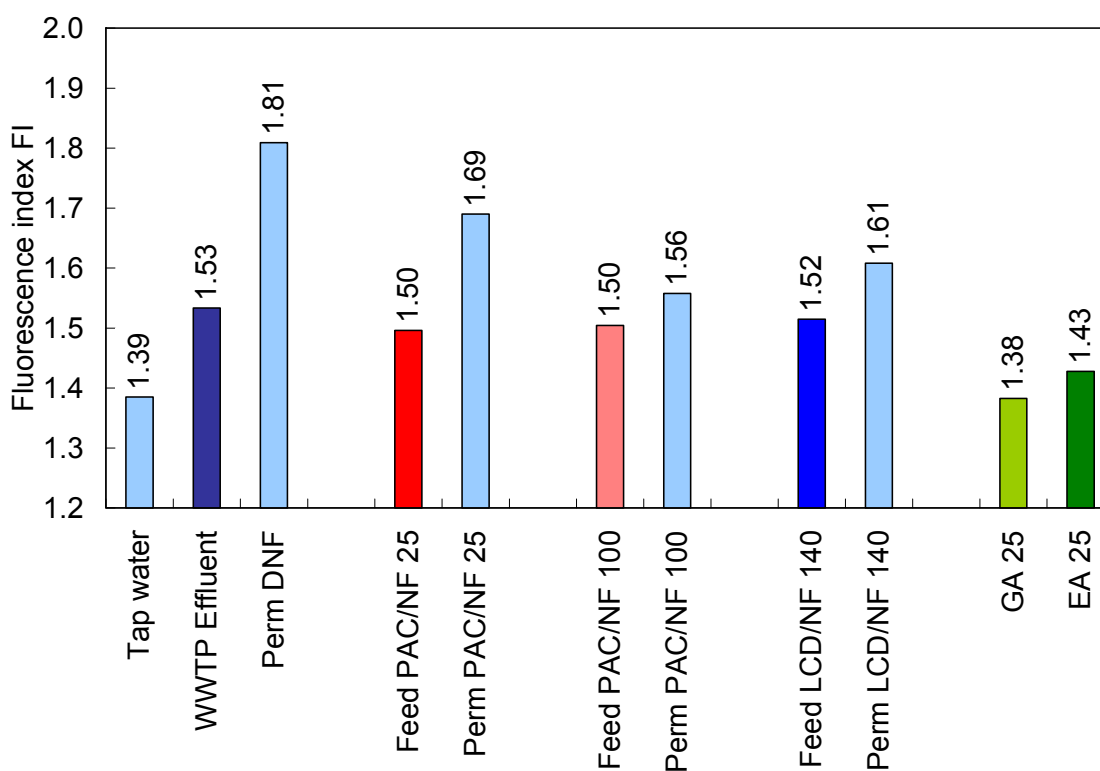


**Fig 6.14** Fluorescence EEMs for different dosages of powdered activated carbon (a: 25 mg/l; b: 50 mg/L; c: 100 mg/L;  $\text{DOC}_0 = 4.5 \text{ mg/L}$ ; batch adsorption test, 24 h contact time) compared to alternative activated carbon treatment methods (d: granular activated carbon; e: extruded activated carbon)

### Fluorescence index

On the basis of FEEM, the fluorescence index (FI) can be determined by the ratio of fluorescence intensity at emission 450 and 500 nm at excitation 370 nm (McKnight *et al.*, 2001). It represents another tool to trace NOM origin of EEM samples.

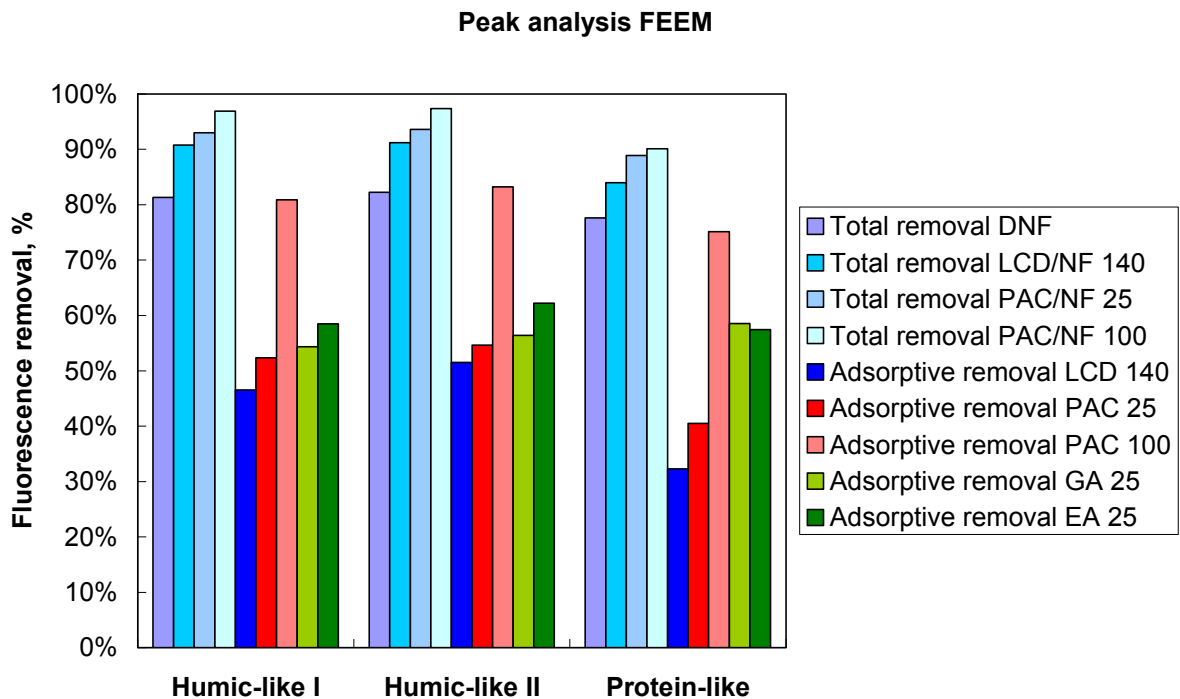
The FI of the WWTP effluent varied between 1.50 and 1.59. The FI increased significantly during direct nanofiltration (1.81) indicating that the remaining organic matter has a high share of the autochthonous compounds on a very low DOC level ( $< 0.5$  mg/L). With increasing activated carbon dosage the FI of the PAC/NF permeate decreased and reached levels similar to the WWTP effluent. All values reflect organic matter in the transition area between allochthonous NOM and EfOM of autochthonous (microbial) origin known to be in the range of 1.7 to 2.0. The FI of the tap water sample (1.39) showed the typical allochthonous (terrestrial) signature (1.3 to 1.4). Treatment with granular and extruded activated carbon rich in mesopores was able to reduce the FI to a typical allochthonous characteristic although the DOC was only reduced by 30% (*cf.* fig 6.3).



**Fig 6.15** Fluorescence index of different water samples from Aachen tap water, WWTP effluent, direct NF, PAC/NF, and adsorption (numbers signify the carbon dose in mg/L, feed PAC/NF = effluent + PAC prior to NF, Perm = permeate, Conc = concentrate)

### Peak Analysis

Fig 6.16 shows the removal of the three main compound groups detected by FEEM. While the humic-like substances I and II were removed by 81 to 82% in direct NF, protein-like compounds decreased by 78%. In adsorptive removal, the differences between humic-like compounds and protein-like compounds were even more pronounced with up to 20% difference for LCD. Granular and extruded activated carbon, however, showed no significant difference between the adsorption of humic-like and protein-like compounds. In comparison to the bulk DOC (*cf.* fig 6.3) the removal of fluorescence exceeded the DOC removal significantly, *e.g.* 25 mg/L PAC adsorbed 30% of the DOC, but more than 50% of the humic-like substances and still 41% of the protein-like substances. This indicates that a large amount of non adsorbable or poorly adsorbable compounds is not detected by FEEM. It is assumed that these are for example polysaccharides which have been shown to be poorly adsorbable by PAC.



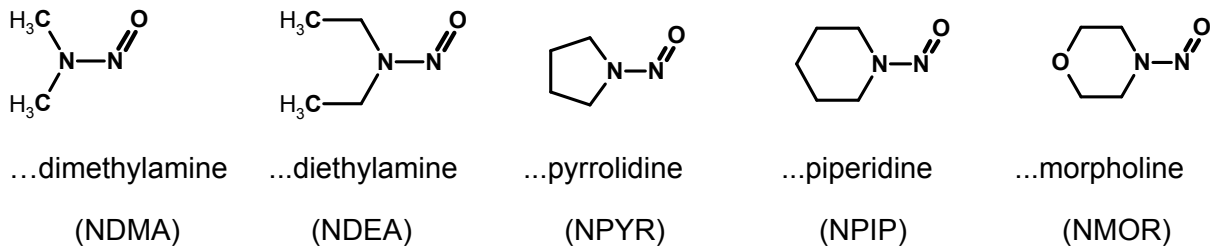
**Fig 6.16** Removal rates of bulk organic fractions during NF and PAC/NF

In PAC/NF, the total removal of the humic-like compounds was comparable to the removal of the bulk DOC above 90%. The removal of protein-like compounds was, however, between 84 to 90%. This confirms the observation of the other parameters such as FI and SUVA, which also indicated that humic-like substances are removed slightly better than bacteria derived compounds.

### 6.3.5 Nitrosamine formation potential

Based on the method of Mitch *et al.* (2004), a nitrosamine formation potential (NFP) test (Krauss *et al.*, 2010) was performed for a few selected samples at EAWAG by Dr. Martin Krauss. The analytical procedure for the selected nitrosamines (Fig 6.17) followed the method of Krauss and Hollender (2008).

N-Nitroso...



**Fig 6.17** Structural formulas of the investigated nitrosamines

The wastewater treatment plant effluent and the PAC/NF permeate treatment were analysed for nitrosamines, which are of particular concern in water reuse due to their high carcinogenic potential. NDMA, NDEA and NMOR were detected in low concentrations between 1.5 and 6.7 ng/L below the Californian standard for NDMA, NDEA and NDPA of 10 ng/L. There was no significant change in concentration during the PAC/NF treatment, which does not involve any chlorinated chemicals. NDMA and the other nitrosamines are known to be hardly adsorbable. NF could also not retain the compounds due to their low molecular weight significantly below the MWCO. The PAC/NF treatment was able to reduce the nitrosamine formation potential comparably to the DOC removal by 90 to 95% for NDMA, NPYR and NPIP (*cf.* Table 6.6).

**Table 6.6** Nitrosamine concentration and removal during PAC/NF treatment and nitrosamine formation potential ( $C_{PAC} = 50$  mg/L)

compound	DBP concentrations			Nitrosamine formation potential			
	MW g/mol	WWTP effluent ng/L	PAC/NF permeate ng/L	Removal %	WWTP effluent ng/L	PAC/NF permeate ng/L	Removal %
NDMA	74.1	5.8 ± 0.0	6.7 ± 0.0	- 14 %	465 ± 3.5	22 ± 3.2	95 %
NDEA	102.1	1.7 ± 0.5	1.5 ± 0.0	14 %	1.4 ± 1.1	2.0 ± 0.4	- 41 %
NPYR	100.1	< 1	< 1	-	16.5 ± 1.7	0.5 ± 0.1	97 %
NPIP	114.1	-	-	-	8.2 ± 0.3	0.8 ± 0.1	90 %
NMOR	116.1	3.7 ± 0.2	3.8 ± 0.4	- 3 %	0.4 ± 0.5	-	-

## 6.4 Conclusions

Direct nanofiltration as well as activated carbon combined nanofiltration hybrid processes can produce high-quality water from tertiary effluent. DOC values below 0.5 mg/L and removal rates above 90 % confirm the excellent quality suitable for direct injection. Differences in the remaining organic matter can be detected with advanced characterisation methods such as size exclusion chromatography with DOC and UV detection as well as fluorescence EEM. Combining both methods allow precise observation of the fate of specific bulk organic groups. Direct nanofiltration partly rejected the molecules with low molecular weights and exhibited FEEM spectra with a distinct wastewater impact.

As PAC tends to adsorb the humic and fulvic substances as well as smaller size molecules while LCD adsorbs more of the larger molecules such as polysaccharides, PAC can be regarded as more advantageous than LCD to counterbalance deficits of the membrane. Combining PAC with NF produced permeate of highest quality with regard to bulk organics. The PAC/NF process allows the fairly accurate adjustment of the permeate quality according to the site specific requirements through proper selection of the adsorbent and the dosage. Small PAC concentrations resulted in a slight decrease of NOM removal. At higher concentrations above 25 mg/L, the total removal of DOC was stably increased to 95%. An even higher removal of DOC including wastewater derived protein-like compounds can be achieved through combining nanofiltration with GAC or EAC treatment when the selected adsorbents are rich in mesopores. The tested recycled carbon types proved to be very efficient over the entire range of bulk organic compounds.

The PAC kinetics tests underlined the importance of a sufficient contact time. A steep increase of the loading was observed during the first two hours, particularly within the first hour reaching around 60 to 80% of the maximum adsorption. The contact time should therefore be kept at least between one and two hours to achieve an acceptable carbon loading.

Although the permeate DOC values of direct NF and PAC/NF indicate a quality better than the original tap water, FEEM reveals even in very low organic matter concentrations the history of the water. Reaching levels below 0.5 mg/L DOC and removing , activated carbon nanofiltration hybrid processes can be regarded as a viable alternative to UF/RO. Although PAC/NF does not remove NDMA and other nitrosamines, the nitrosamine formation potential is significantly reduced (> 90 to 95%). NDMA concentrations above 10 ng/L might require a post-treatment with AOP like in dual membrane treatment. Further NDMA removal can occur during SAT and MAR (Drewes *et al.*, 2009)

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## 7 Capillary nanofiltration in hybrid water reclamation processes

### 7.1 Introduction

Capillary nanofiltration combines capillary ultrafiltration with nanofiltration (Frank *et al.*, 2001; Futselaar *et al.*, 2002; Verberk and van Dijk, 2006). While featuring the typical properties of dense nanofiltration membranes such as high rejection of bivalent ions, pathogens and organics, the use of capillaries has the advantage that higher solid loads can be processed at reduced risk of feed channel blockage. Operational strategies to control concentration polarisation, cake layer formation and fouling comprise forward flushing (Futselaar *et al.*, 2003), air sparging (Futselaar *et al.*, 2003; Verberk and van Dijk, 2006) and backflush of the module. These particular properties allow new applications in surface water treatment, polishing of WWTP effluent and industrial processes.

Capillary nanofiltration (Cap NF) behaves differently from spiral wound nanofiltration membranes. Due to the absence of feed spacers Cap NF concentration polarisation effects are more pronounced. Verberk and van Dijk (2006) have shown that the required Reynolds numbers are about a factor 10 higher than in spiral wound NF to counteract concentration polarisation on the same level. High shear stress to break up laminar flow can mainly be generated by high crossflow velocities or air sparging.

In hybrid capillary nanofiltration processes involving activated carbon, the operational conditions are even more complex than in a single stage direct NF. Particularly PAC/NF is a very challenging process from the operational point of view. This chapter focuses on preferential process conditions for Cap NF to avoid excessive cake layer formation, feed channel blockage and abrasive effects which can impair the NF performance significantly. Besides the characteristics of the particulates such as size distribution (Meier, 2008), the main factors to control the cake layer and limit abrasion are the crossflow velocity, backflush and chemical cleaning procedures. An overview of potential strategies is given in Table 7.1.

**Table 7.1** Strategies for cake layer control in PAC/NF

Strategy	Measure	Applicability / impact
Proactive	Crossflow velocity	- Abrasion at crossflow velocities > 1.5 m/s - Costs
	Air Flush	- Abrasion due to locally high velocities
	Backflush	- Detachment of active layer - Fibre breakage
Reactive	Chemical cleaning	- Membrane aging - Costs

Meier (2008) determined by modelling that particles in the range of 0.01 to 8  $\mu\text{m}$  will deposit on the membrane at fluxes between 15-20  $\text{L}/\text{m}^2\cdot\text{h}$  and shear rates between 2000 and 10000  $\text{s}^{-1}$ . In the cake layer of membranes operated at conditions comparable to the pilot tests of this study he detected particles of a size from 0.5 to 3  $\mu\text{m}$ .

While the importance of the carbon particle size and the shear rate is well proven, it can be assumed that the development and the thickness of the carbon cake layer is further influenced by secondary effects such as adsorbability of the carbon to the membrane surface. Carbon adsorption to the membrane surface is assumed to be governed by membrane properties such as surface roughness, surface charge, and the membrane material as well as changes in the membrane surface due to fouling effects. These include fouling by organic and inorganic molecules attached to the membrane and combinations of these *e.g.* through bridging, which describes the attachment of negatively charged humic acids to the negatively charged NF surface *via* bivalent positively charged ions such as calcium and magnesium. The control of the cake layer thus requires a targeted set of methods addressing the main process limitations. Meier (2008) concluded that as long as PAC with particles below 5  $\mu\text{m}$  is used in PAC/NF the formation of a cake layer cannot be avoided because high crossflow velocities as counter measures would lead to membrane abrasion.

Fouling and biofouling pose major obstacles for long term operation of NF systems. Thus fouling control and in some cases scaling control are the main issues from an operational perspective besides cake layer control. Recent studies investigated the preferential operational settings of direct NF systems for fouling control, such as the influence of an air flush and forward flush (Bonné *et al.*, 2002; Schrader, 2006), of coagulation as pre-treatment (Schrader, 2006), of an electric field (Schrader, 2006) and the influence of the raw water conditions (Schrader, 2006).

The objective of the investigation presented in this chapter is the definition of the optimum operation strategies of the tested hybrid processes, *i.e.* direct NF, PAC/NF, and GAC/NF, for treatment of waste treatment plant effluent. For a good transferability of the results, tests are conducted in pilot scale. The analysis of the main strategies for an optimised operation of the NF encompasses the determination of the critical flux, optimum PAC dose or GAC bed volumes, and chemical cleaning methods as well as backflush strategies to minimise cake layer formation and fouling.

## 7.2 Materials and Methods

### 7.2.1 Pilot units

The experiments were run with the NF50 M10 membrane supplied by X-Flow in 4" and 8" modules with a capillary diameter of 1.5 mm and an area of 3.6 m<sup>2</sup> and 20 m<sup>2</sup> respectively. The membrane was installed in two pilot plants as shown below in Figure 7.1.

Details on the experimental set-up of the pilot units are given in chapter 3 (direct NF tests), chapter 4 (PAC/NF tests) and chapter 5 (GAC/NF tests). The processes mentioned above have been tested with different plants. PAC/NF was investigated with the 8" installation and operated over a period of more than 2 years. The 4" installation served for the investigation of NF/GAC and GAC/NF with a runtime of 17 months and 3 months, respectively.

The membrane was operated in crossflow mode with a crossflow velocity of 1.2 m/s. The recovery was set at 75% according to the typical values applied in dense membrane filtration (Asano *et al.*, 2007). For additional cake layer control a backwash was applied. The optimum operational conditions have been studied in the present investigation.



**Fig 7.1** Fully automated 4" pilot plant (left) and 8" pilot plant (right) for capillary NF tests at WWTP Aachen Soers

### 7.2.2 Feed water characteristics

The pilot plants were set up at the WWTP Aachen processing the secondary effluent from sand filtration with the general characteristics as given above in Table 7.2. The WWTP effluent is characterised by low DOC concentrations and relatively low salinity of around 900  $\mu\text{S}/\text{cm}$ . The final treatment stage of the full scale WWTP is a sand filtration which reflects in low solids and moderate bacteria concentrations.

**Table 7.2** General characteristics of the feed water (effluent WWTP Aachen-Soers, Meier and Melin, 2005)

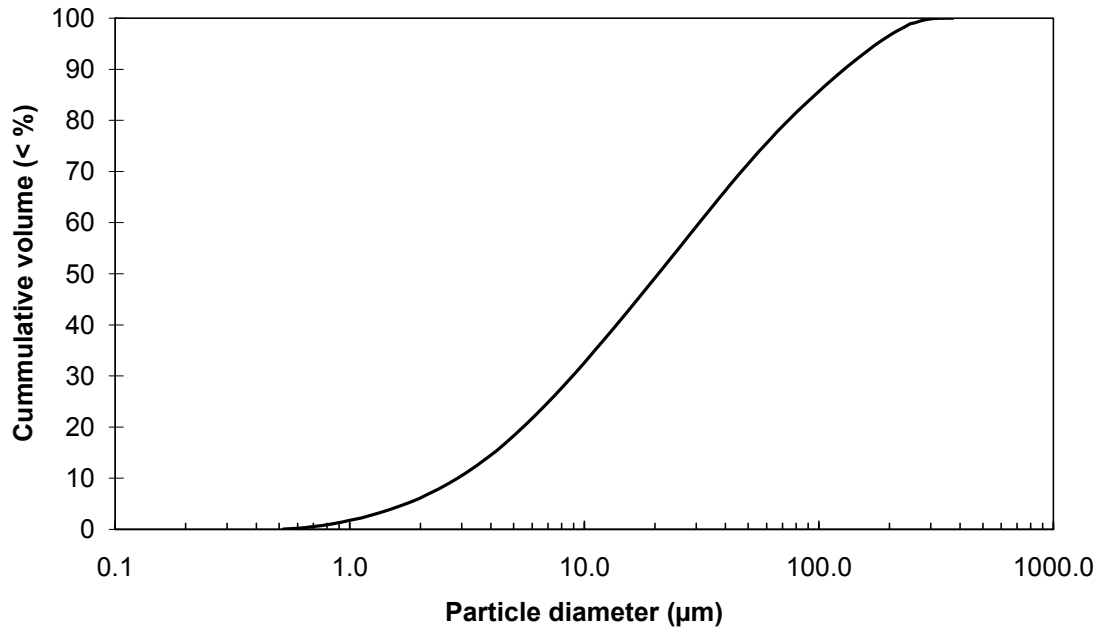
Parameter	Unit	Average	Standard deviation
Escherichia coli	-/100 mL	$1.0 \cdot 10^3$	$1.5 \cdot 10^3$
Total coliforms	-/100 mL	$8.7 \cdot 10^3$	$7.5 \cdot 10^3$
CFU (22°C)	-/ mL	$7.2 \cdot 10^3$	$2.6 \cdot 10^4$
CFU (37°C)	-/ mL	$1.2 \cdot 10^3$	$2.3 \cdot 10^3$
Iron	mg/L	< 0.048	-
Ca <sup>2+</sup>	mg/L	44.6	5.4
Mg <sup>2+</sup>	mg/L	8.8	1.7
DOC	mg/L	5.2	1.7
Turbidity	NTU	0.36	0.18
SDI	-	5.6	-
MFI	-	86	-

### 7.2.3 Adsorbents

The tests employed commercially available carbon types as shown in Table 7.3. Figure 7.2 presents the particle size distribution of SAE Super. It becomes clear that a relatively large fraction of the carbon (ca. 25%) is below 5  $\mu\text{m}$  increasing the risk of cake layer formation.

**Table 7.3** Characteristics of the selected adsorbents

Adsorbent	Activated carbon type	Surface area m <sup>2</sup> /g	Particle size d <sub>50</sub> $\mu\text{m}$	Raw material	Price €/kg
Norit SAE Super	powdered	1300	15	diverse	1.35
RWE LCD	lignite coke dust	300	24	lignite	0.35
Norit NRS GA 0.5-2.5	granular (recycled)	975	1300	diverse	1.00



**Fig 7.2** Particle size distribution for Norit SAE Super (supplier data)

#### 7.2.4 Performance criteria

To characterise the process performance the following parameter were used.

Transmembrane pressure

$$TMP = \Delta p - p_p = \frac{p_f + p_c}{2} - p_p \quad [\text{bar}] \quad (7.1)$$

where  $\Delta p$  = average feed pressure loss during filtration

$p_f$  = feed pressure

$p_c$  = concentrate pressure

$p_p$  = permeate pressure

The experiments with the pilot plants were conducted at varying temperatures in a range between 20 and 30°C. To compare the different data the influence from temperature was considered by the temperature correction factor TCF according to Verberk and van Dijk (2006)

$$TCF = \exp^{U[1/(T+273)-1/(T_{ref}+273)]} \quad (7.2)$$

where  $U$  = constant indicating the temperature dependency of the membrane

$T$  and  $T_{ref}$  = temperature and reference temperature, respectively

The constant  $U$  considers the temperature dependency of the membrane including the effects from changing water viscosity. Temperature correction with the viscosity only was not

satisfactory. The value for the constant U was found to be 4200 for the 4" NF membrane and 2100 for the 8" NF membrane. The reference temperature in all tests was 25°C.

The temperature corrected transmembrane pressure  $TMP_{TC}$  is then

$$TMP_{TC} = \frac{TMP}{TCF} \quad [\text{bar}] \quad (7.3)$$

The membrane water permeability is derived from permeate flux and transmembrane pressure and serves as parameter for evaluation of the membrane filtration performance:

$$\text{Permeability } A = \frac{J}{TMP} \quad [\text{L}/(\text{m}^2 \cdot \text{h} \cdot \text{bar})] \quad (7.4)$$

where J = permeate flux [L/(m<sup>2</sup>·h); simplified LMH]  
 =  $Q_p / A_{\text{membrane}}$



## 7.3 Results and Discussion

### 7.3.1 Critical flux

Initial tests with direct nanofiltration focused on the determination of a sustainable flux. In a test with the 8" pilot plant (backflush 1 min every 45 min) three different set points were studied over a total period of one month. During the 15 LMH filtration phase a low increase of 0.02 bar/d was detected. It increased to 0.06 bar/d when operated at a permeate flux of 20 LMH. When raising the flux to 25 L/(m<sup>2</sup>·h) a steep increase of the TMP was observed within a few days (Figure 7.3) on a significantly higher TMP level. In repeated filtration cycles after chemical cleaning the TMP increase was even more pronounced. PAC doses in the range of 10 to 200 mg/L confirmed a critical flux at about 20 L/(m<sup>2</sup>·h). For further optimisation of the process the permeate flux was kept at 20 L/(m<sup>2</sup>·h).

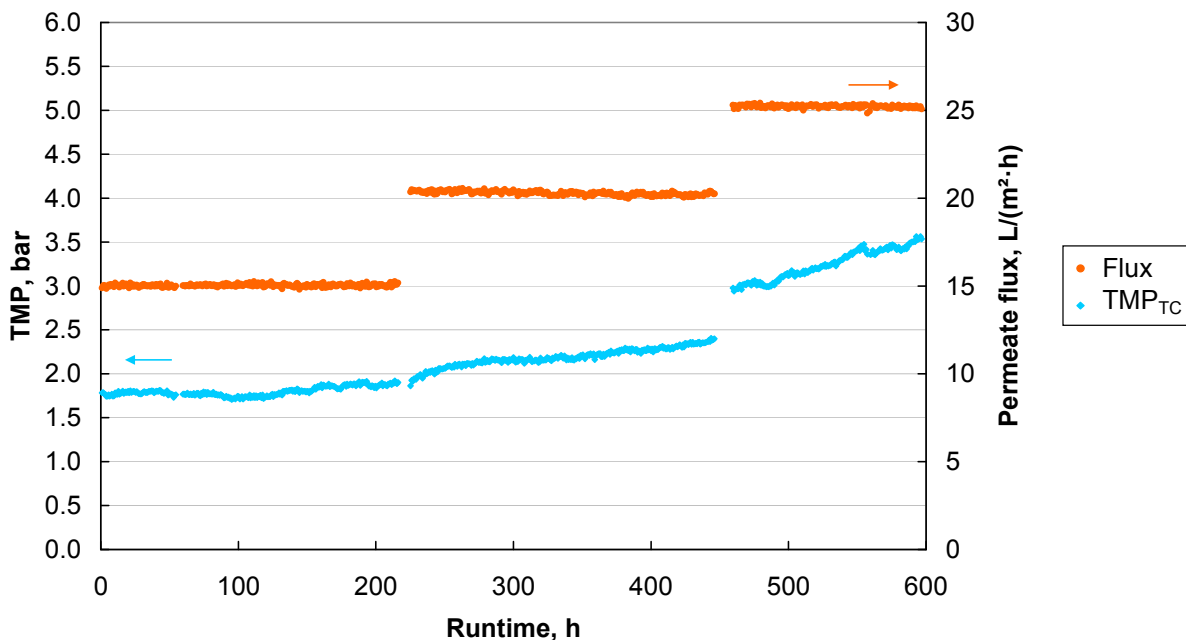


Fig 7.3 Direct NF: Determination of critical flux

### 7.3.2 Transmembrane pressure

According to the supplier the maximum pressure for the NF50 M10 is limited to seven bar. The feed pressure during the tests was kept below 6 bar and chemical cleanings were conducted to recover the fouled membrane (details of the procedure are given below). The transmembrane pressure (TMP) typically ranged between 1.5 to 3.7 bar (Table 7.4 and 7.5). In phases of direct NF, variation of the flux showed an increase from an average of 1.7 bar at 15 L/(m<sup>2</sup>·h) and 2.1 bar at 20 L/(m<sup>2</sup>·h) to above 3 bar at 25 L/(m<sup>2</sup>·h). The TMP at 25 L/(m<sup>2</sup>·h) during PAC dosage was even higher ranging between 3 to 3.5 bar (data not shown). Carbon doses were varied between 10 and 50 mg/L PAC and 50 and 200 mg/L LCD. The average

TMP varied between 2.3 and 2.8 bar at carbon doses between 10 and 200 mg/L. When applying PAC, the average TMP was thus always above the TMP during the direct NF phases without PAC dosage, presumably due to the cake layer formation and concomitant effects such as increased concentration polarisation and fouling. Increasing concentration LCD showed a slightly improved permeability, presumably due to increasing adsorbance of foulants.

**Table 7.4** General experimental conditions and results of the PAC/NF pilot tests

Carbon dose mg/L	Carbon type	Flux L/(m <sup>2</sup> ·h)	Recovery %	TMP bar	Permeability L/(m <sup>2</sup> ·h·bar)
0	-	15	75	1.7 ± 0.1	8.8 ± 0.4
0	-	20	75	2.1 ± 0.2	9.4 ± 0.7
0	-	25	75	3.3 ± 0.3	7.6 ± 0.8
10	PAC	20	75	2.3 ± 0.2	8.8 ± 0.4
25	PAC	20	75	2.8 ± 0.2	7.2 ± 0.3
50	PAC	20	75	2.7 ± 0.2	7.4 ± 0.4
50	LCD	20	75	2.7 ± 0.1	7.4 ± 0.3
100	LCD	20	75	2.6 ± 0.2	7.7 ± 0.6
200	LCD	20	75	2.5 ± 0.2	8.0 ± 0.4

The impact of the PAC addition on the DOC fractions has been investigated in a former study (Meier, 2008) by means of LC-OCD analysis (Liquid chromatography with organic carbon detection) indicating that the potential foulants are sorbed to the carbon and when high carbon doses above 500 mg/L are administered they can be removed almost completely. Figure 7.4 illustrates that low carbon doses cannot reduce membrane foulants sufficiently and instead lead to a larger TMP increase about twofold that of the direct NF. At a PAC dose of 50 mg/L, however, where a DOC removal of 50 to 60% was observed (*cf.* chapter 6), a reduced increase of the TMP could be observed similar to direct NF. Higher carbon doses in the range of 100 to 200 mg/L again resulted in an increased TMP similar to the low concentrations. This confirms that on the one hand the carbon based cake layer formation has a greater influence on the pressure development than the potential adsorption of organic foulants to the activated carbon and that on the other hand about 200 mg/L in the crossflow recirculation loop (equivalent to 50 mg/L PAC dose at 75% recovery) are a reasonable limit of PAC dosage, both from the operational as from the technical perspective.

When operated in parallel as direct NF the 8" and 4" plants did not show completely identical behaviour. The average daily TMP<sub>TC</sub> increase varied between 0.05 bar/d and 0.10 bar/d in the 8" installation while in the 4" plant the average daily TMP<sub>TC</sub> increase during direct NF was between 0.10 and 0.15 bar/d. The 4" plant also required a longer backflush period to sustain stable operation (*cf.* chapter 7.3.5). Figure 7.5 shows the diurnal variation of the

transmembrane pressure which directly mirrors the water temperature. The temperature corrected TMP reveals the real pressure increase which developed with a constant gradient. During each filtration cycle the TMP rose about 0.25 bar and was almost fully recovered by backflushing.

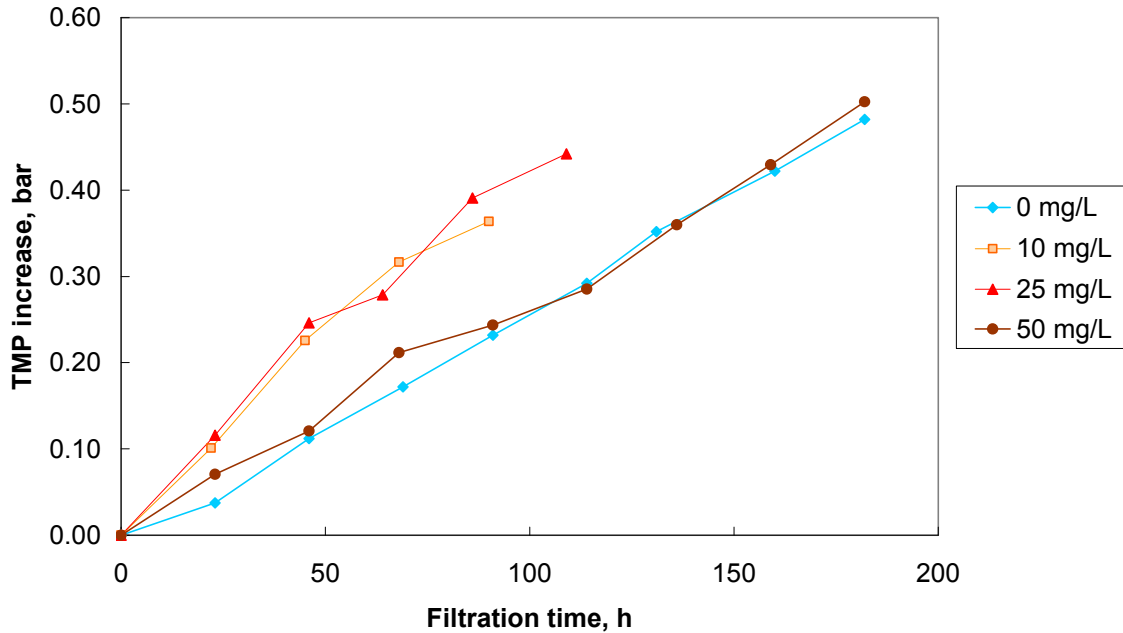


Fig 7.4 PAC/NF: Specific increase of TMP<sub>TC</sub> for different PAC doses vs. direct NF

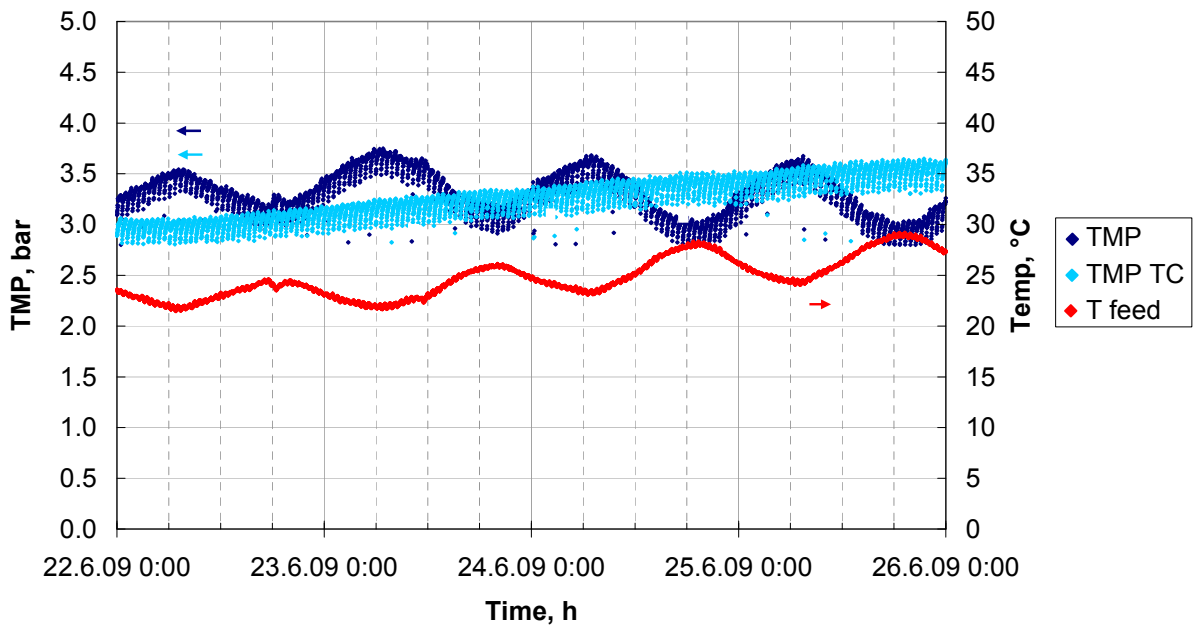
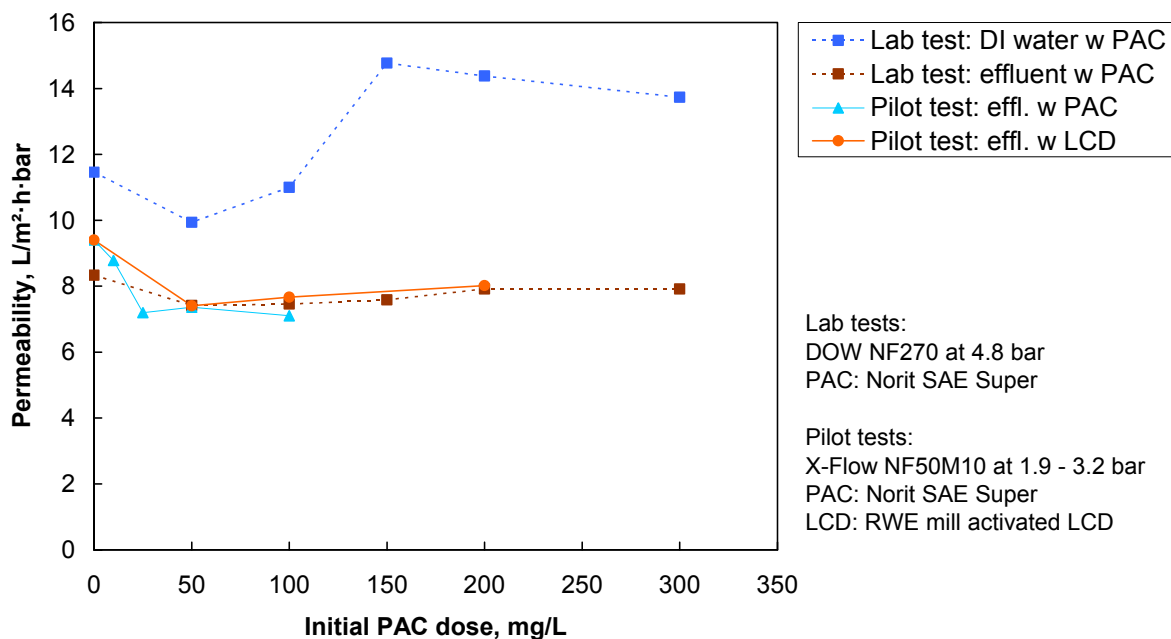


Fig 7.5 Direct NF (4" plant): Diurnal variation of transmembrane pressure versus feed water temperature and increase of temperature corrected TMP

### 7.3.3 Water permeability

The water permeability quickly dropped from an initial clean water permeability of about 12 L/(m<sup>2</sup>·h·bar) (*cf.* chapter 3) to about 8 to 9 L/(m<sup>2</sup>·h·bar) in direct NF mode. As shown in table 7.4 it ranged between 7 to 9 L/(m<sup>2</sup>·h·bar) when applying PAC. Meier (2008) observed a decrease down to 6 L/(m<sup>2</sup>·h·bar) at high carbon doses and long-term operation with progressive irreversible fouling. Veríssimo *et al.* (2005) report of novel capillary membranes with coatings other than the PA coated PES membrane tested here. In their investigation they observed high permeabilities between 10 to 20 L/(m<sup>2</sup>·h·bar) for new coating materials, however at somewhat lower rejection rates (membrane retention for MgSO<sub>4</sub> ca. 80%). When coating denser membranes the final permeability was in the range of 6 to 10 L/(m<sup>2</sup>·h·bar). This confirms that the NF50 M10 can be regarded as sound compromise between rejection (membrane retention for MgSO<sub>4</sub> 94-96%) and permeability. Roesink *et al.* (2011) reported that improved capillary NF membranes are available. Key aspects of the new membranes are environmentally friendly coating methods and improved rejection behaviour.



**Fig 7.6** Average permeability during lab scale and pilot scale experiments

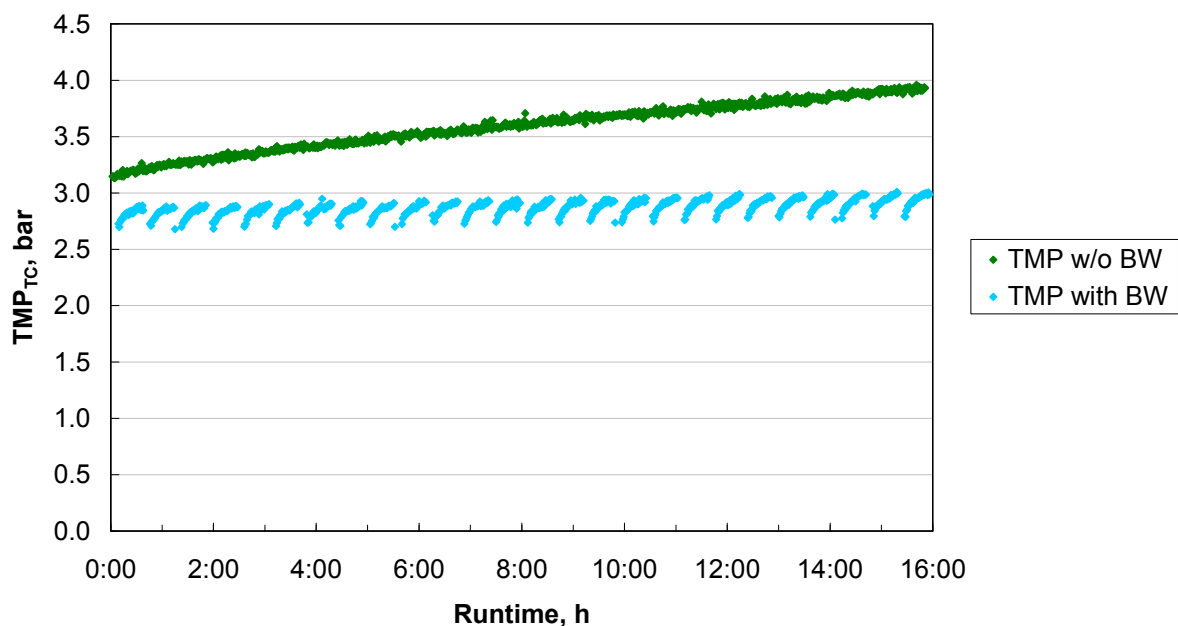
Parallel lab tests of the permeability changes by means of a test cell (type GN10-400, Berghof membrane technology GmbH) employed NF 270 membranes as this membrane type has properties similar to the NF50 M10 which is not available as flat sheet. Both lab scale and pilot scale experiments detected a decrease of permeability depending on the carbon dose with reductions of up to 25% at carbon doses between 10 and 300 mg/L (*cf.* Figure 7.6 and Table 7.3). Despite a significant adsorption of the raw water bulk organics (1.25 h contact time) especially at high PAC doses, no significant decrease of permeability loss was observed. Lab scale testing proved to give a good indication of the pilot plant performance. In lab scale tests with demineralised water, higher carbon doses lead to an unexpected permeability increase which might be due to changed hydrophilicity or surface charge.

### 7.3.4 Crossflow velocity

Crossflow velocities of 1.0 to 1.2 m/s were shown to be sufficient to avoid concentration polarisation effects in direct NF (*cf.* chapter 3). In PAC/NF crossflow is not only required to minimise concentration polarisation (*cf.* chapter 5) but also to control the cake layer. Variation of the crossflow velocity between 1.0 and 1.5 m/s showed no significant influence on the permeability during PAC/NF. Higher CF velocities may lead to membrane abrasion and are not economic. It can be concluded that crossflow as main strategy has to be supported by additional operational strategies such as backflush and the selection of appropriate carbon types with small fine particle fraction.

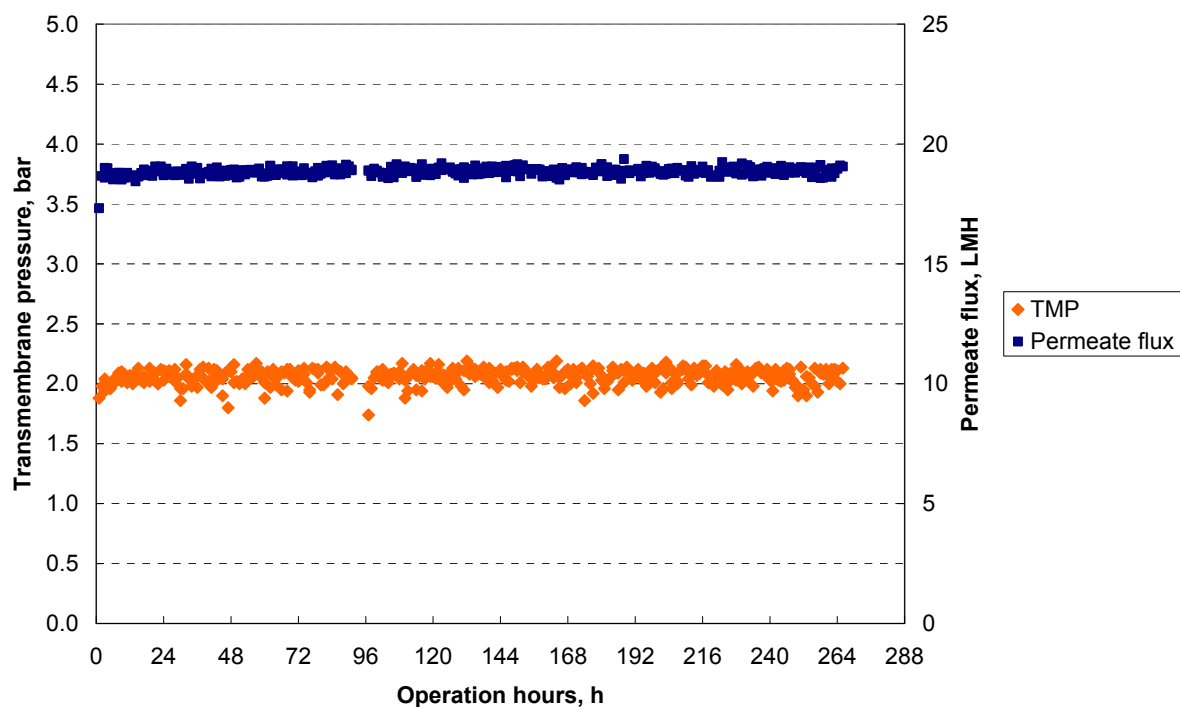
### 7.3.5 Backflush cycle and duration

Backflushing is created by a flow reversal through increasing the pressure on the permeate side to lift the feed side cake or fouling layer off which can then be swept away by the crossflow. It is a standard method in ultra- and microfiltration. Backflush in capillary NF is limited by the risk of detachment of the thin active layer and fibre breakage. In contrast to porous membrane filtration, in particular ceramic membranes where harsh backflushing can quickly and effectively remove fouling and cake layers of PAC or coagulants (Lehman and Liu, 2009; Kommineni *et al.*, 2010; Panglisch *et al.*, 2010), capillary NF has to apply a gentle backflushing regime. It can be enhanced by chemicals to address specific operational issues such as scaling. The present study applied backflushing with different filtration and backflush cycles to further reduce the demand for frequent chemical cleaning. Figure 7.7 depicts a direct comparison of the TMP increase in Cap NF with and without backflush. The applied backwash reduced the pressure increase by 90%.



**Fig 7.7** Influence of backflush in direct NF (4" plant): Comparison of TMP<sub>TC</sub> with backflush (30'/5.5') vs. TMP<sub>TC</sub> without backflush (20 LMH, 75% recovery)

During the long-term direct NF and PAC/NF experiments with the 8" plant backwash procedure with a total duration of ca. 1 min was applied every 45 min as follows: depressurised pause of 5 s; depressurised forward flush with 1 m/s for 5 s; two backflush pulses with a pressure of 1 bar, and depressurised forward flush with 1 m/s for 45 s. As this backwash method was not able to fully counteract fouling (*cf.* Figure 7.4) the backflush duration and cycle was further investigated. To keep the TMP during PAC/NF constant, high backwash frequencies and long flushing periods have been tested. Figure 7.8 presents the test of the extended 3 min backwash procedure with a PAC dose of 50 mg/L. The 10min / 3 min cycle the plant was operated without pressure increase. The cycle duration was gradually increased to 35 min with 3 min backwash procedure while the TMP could be kept constant.



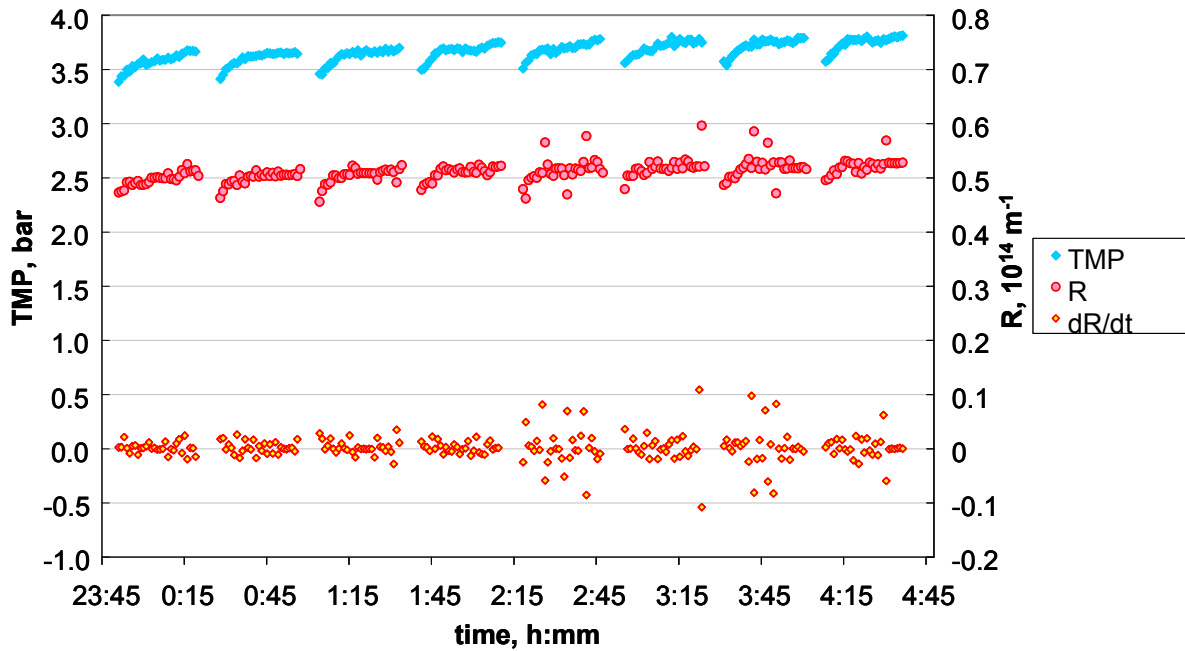
**Fig 7.8** PAC/NF performance at high backflush frequency (10 min / 3 min)

Presumably due to a slightly different flow regime and smaller dimensions, the 4" installation was more susceptible to fouling than the 8" plant and required longer backflush durations to safeguard sustainable operation. In tests at the beginning of the long-term experiments a cycle of 30 min / 5.5 min was identified as stable long-term filtration mode.

### 7.3.6 Membrane resistance

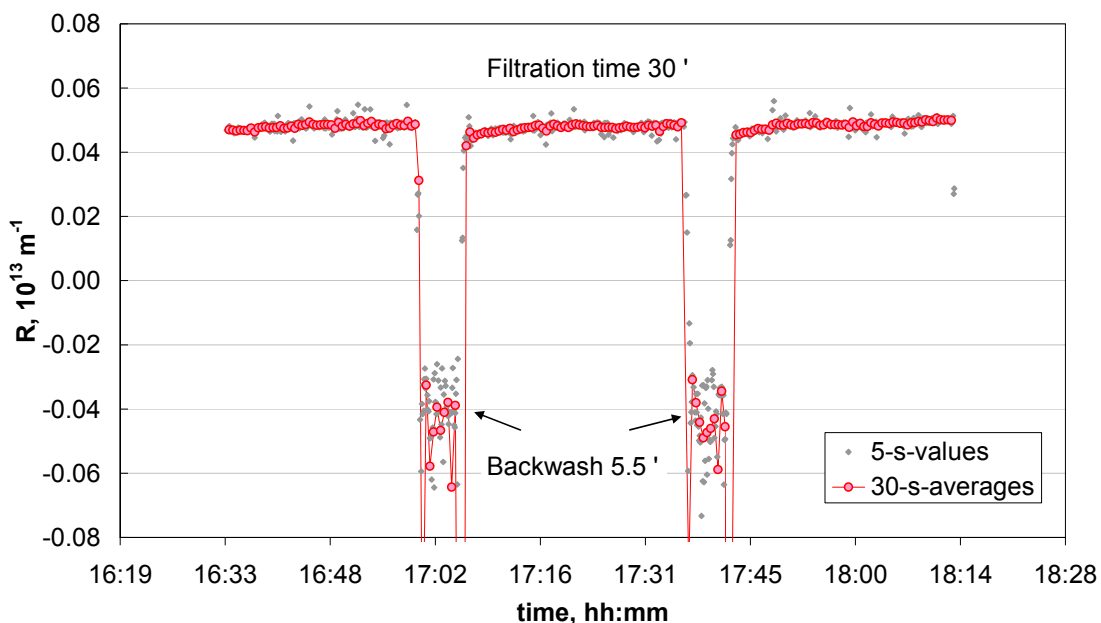
In a detailed analysis of direct nanofiltration, TMP and membrane resistance was studied on the filtration cycle scale. Figure 7.9 illustrates the parallel increase of the pressure and the resistance with time. The absolute change in membrane resistance was rather small. The TMP and resistance increased rapidly at the beginning of each filtration cycle and were then slightly rising till the next backwash. The curves of the TMP and R resemble those from other backwashable membrane systems such as ultrafiltration. Variations in resistance were caused

by swinging within the control system, *e.g.* flow metering and pump frequency, which could not be completely dampened.



**Fig 7.9** Direct NF (4" plant): Transmembrane pressure and resistance

A further point of interest concerned the dynamic behaviour of the membrane resistance during backwash. The question was whether the membrane resistance during backflush is different from the resistance during regular filtration. The backwash was conducted with reduced pressure and flux to prevent any detachment of the active layer. Yet the resistance in reverse direction corresponded to resistance during forward filtration.

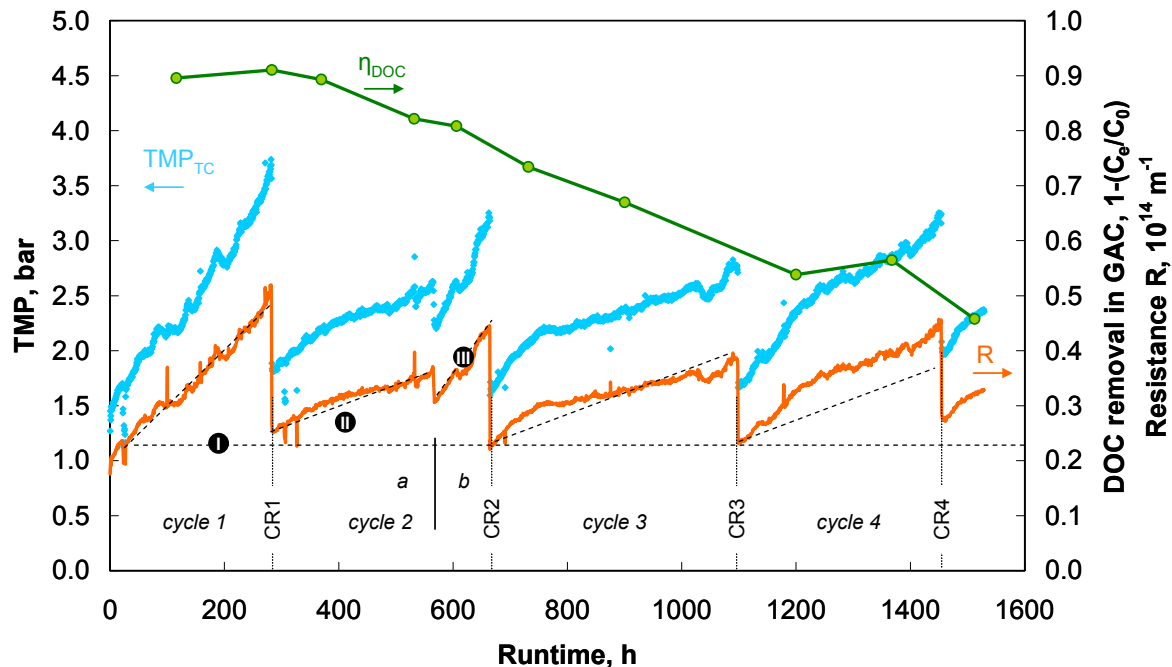


**Fig 7.10** Direct NF (4" plant): Dynamic of resistance during backflush

### 7.3.7 Fouling reduction through GAC pretreatment

Roorda *et al.* (2005) reported that GAC pretreatment prior to Cap NF would reduce membrane fouling significantly and minimise pressure increase in treatment of WWTP effluent. They operated an 8" pilot unit with an 30 min EBCT GAC filter at a large Dutch WWTP. After a rapid decrease from 10 L/(m<sup>2</sup>·h·bar) to around 7 L/(m<sup>2</sup>·h·bar), the filtration was stable for 5 days.

The GAC/NF process was tested for 3 months at the Aachen WWTP. Figure 7.11 and Table 7.5 illustrate the performance of the GAC filter and the NF unit. The GAC filter with an EBCT of 15 min removed DOC on a high level during the first three weeks. In contrast to the expected low fouling in the subsequent NF stage, a rapid TMP increase was observed during the initial operation phase. It is assumed that this increase was due to washout of GAC fine dust from the adsorber, also most of the dust was removed before through washing of the carbon. This must be regarded as a significant shortcoming of GAC/NF. After the first chemical cleaning the TMP was significantly lower, but rose sharply after a longer interruption of operation which might have resulted in enhanced biofouling. During the third cycle membrane operation was very stable at low increase rates of 0.06 bar/d. With continuing loading of the GAC filter bed and corresponding reduction of DOC removal the fouling increased again and reached almost the level of non-pre-treated water.



**Fig 7.11** Transmembrane pressure and resistance *versus* removal of DOC in GAC adsorber (CR = chemical recovery)

The test confirmed the improved operability of NF when the feed water is GAC pre-treated. However sufficient contact time in the GAC filter should be considered to avoid frequent replacement of the carbon. The contact time of the study of Roorda *et al.* (2005) appears reasonable and might suffice for a 3 to 4 month runtime of the GAC filter equivalent to 5000



to 6000 bed volumes with an EBCT of 30 min. The GAC should be pre-treated to remove any fine dust prior to the NF treatment.

**Table 7.5** General operational parameters and experimental conditions of the GAC/NF pilot tests

Cycle	Duration	TMP <sub>TC</sub> range	TMP <sub>TC</sub> increase	DOC removal in GAC	Comment
	hours	bar	bar/d		
1	280	1.4 - 3.7	0.20	90%	Initial washout of fine GAC dust
2 a	300	1.8 - 2.6	0.06	90 - 80%	
2 b	70	2.3 - 3.3	0.34	80%	Restart after interruption of 2.5 days
3	430	1.7 - 2.7	0.06	80 - 60%	
4	350	1.7 - 3.2	0.10	60 - 45%	

### 7.3.8 Chemical cleaning

Chemical cleaning was important for a stable long-term operation of all investigated hybrid processes. Several chemicals and cleaning regimes were tested. While no single chemical such as caustic soda or hydrogen peroxide was efficient, combinations and various durations of chemical cleaning steps were investigated and successfully applied. Chemical cleaning was performed in average every 2 weeks.

The membrane supplier recommends cleaning within a pH range of 3 to 11. Strong oxidants especially sodium hypochlorite and free chlorine must not be used due to their detrimental effects to the active PA layer. During cleaning the temperature was kept below 40°C. The following procedure employing specific cleaning agents (Ecolab P3 Aquaclean series) was developed for the 8" pilot installation to recover the permeability almost completely.

Step 1: Enzymatic cleaning (ENZ/HCL) at neutral pH, t = 60 min

Step 2: Oxidative cleaning (H<sub>2</sub>O<sub>2</sub>/LAC) at caustic pH (< 11), t = 120 min

Step 3: Acid cleaning (ACS) at pH 3.5 – 4, t = 45 min

Step 4: Caustic cleaning (SAL) at pH 11, t = 45 min

A clear water rinsing for 10 minutes was used between the cleaning steps.

For the 4" installation the chemical cleaning procedure was modified. Chemical cleaning with caustic and acidic agents was applied automatically every two weeks. About every one to two months the NF membrane had to be cleaned manually in a more intense procedure with enzymatic, oxidative (H<sub>2</sub>O<sub>2</sub>), acidic and caustic cleaning steps as described above.

### 7.3.9 Operational stability

Overall the NF showed a very stable performance without any unintentional interruptions. Interruptions were mainly due to pumping problems and malfunctions of the SCADA system. The operation of the PAC/NF process was more challenging. Optimised operation would require an additional modification of the PAC, *e.g.* in terms of removal of the fine particles fraction. Once capillaries were blocked it was hardly fully recoverable as shown in Figure 7.12. Blocking was either inside the feed channels or at the entrance of the capillary caused by large PAC particles or other inert materials such as discard. To avoid feed channel blockage the carbon was later pre-filtered by a fine screen to retain particles larger than 300  $\mu\text{m}$ .



**Fig 7.12** PAC/NF: Partial blocking of capillaries on the influent side of the NF module (After approx. 3000 operating hours, condition after backflushing)

In the harsh pilot testing environment the modules typically reached a runtime of 6000 to 8000 hours before the first integrity problem occurred. The membranes with broken fibres or other defects were not fixed. In full scale plants employing 8" module with around 3300 fibres broken capillaries can be sealed to enable reuse of the module.

Fibre breakage was very problematic in PAC/NF as activated carbon quickly passed to the permeate side and then tended to block the membranes from the permeate side during backflush. Full scale applications would therefore require an automatic shut-off coupled with sensitive turbidity or particle measurement for integrity monitoring.

Table 7.6 gives an overview of the different operational regimes in comparable pilot studies. In direct NF air sparging can further improve the flow regime. Roorda *et al.* (2005) showed that with better pre-treatment the recovery could be increased. This has to be determined on a case-to-case basis depending on the respective water quality to avoid scaling and irreversible fouling, particularly from silica.

**Table 7.6** Comparison between different pilot studies on direct NF treatment of WWTP effluent (adapted and modified from Schrader, 2006)

	Unit	Duin (2000)	Roorda (2005)	Schrader (2006)	This study
Pretreatment		none	adsorbent	none	200 µm screen + adsorbent
Type of membrane		3" capillary Storck	8 " capillary X-Flow	4 " SW NF 270 DOW Filmtec	4" and 8 " capNF X-Flow
Recovery	%	80%	94%	85%	75-85%
CF velocity	m/s	0.5	1.0	0.1	1.2
Operational pressure	bar	4.0	4.0	3.5	1.5 - 4
Permeability	L/m <sup>2</sup> ·bar·h	6.25	7.0	8.2	6 - 10
Cleaning					
- Airflush/FF/BW		2 hour	30-45 min	2 hour	30-45 min
- Acid		1/ week	1/day	1/week	1/10days
- Alkaline/other		1/ week	1/3 weeks	1/week	1/10days
Total runtime module		3 months	1-2 months	1 month	up to 1 year

## 7.4 Conclusions

Capillary nanofiltration opens up new operational possibilities in dense membrane filtration which are particularly well suited for impaired water qualities such as WWTP effluent. It can be employed in different combinations for high quality water reclamation. For all applications with different levels of contamination of the feed water optimised strategies were identified which enable sustainable operation as demonstrated over periods of months up to a year. Backflushing can be used as method to adapt to changing water conditions. However it should be limited to save valuable permeate and operate the plant with a high net flux. High frequency or extended backflushing can safeguard stable operation of particle-rich as well as high fouling feed solutions.

Table 7.7 summarises the importance of the respective interventions for the optimisation of the different hybrid processes. The critical flux was determined to be around 20 to 25 L/(m<sup>2</sup>·h). All hybrid processes requires a high crossflow velocity typically in the range of 1 to 1.5 m/s. It has been shown in other studies that air sparging can further contribute to improved mixing conditions and increase the turbulence so that the crossflow velocity could be reduced. PAC/NF, however, should not employ air sparging to avoid locally increased shear stress beyond the abrasion limit.

**Table 7.7** Optimisation of the operational performance

<b>Process</b>	<b>1<sup>st</sup> priority</b>	<b>2<sup>nd</sup> priority</b>	<b>3<sup>rd</sup> priority</b>
Direct NF	crossflow velocity and permeate flux	backflush, forward flush and/or air sparging	chemical recovery
PAC/NF	crossflow velocity and permeate flux	backflush	proper selection of carbon type, particle distribution, PAC dose
GAC/NF	crossflow velocity and permeate flux	proper selection of GAC type, contact time and achievable bed volumes	Air sparging, backflush, forward flush

In hybrid processes with activated carbon proper selection of carbon type and optimisation of the adsorption step plays a key role to benefit from the additional pretreatment. Even in PAC/NF where activated carbon introduces an additional operational challenge, optimised adsorption can reduce organic fouling and improve the overall performance of the NF. A powdered activated carbon concentration of 50 mg/L was identified as optimum dose to minimise fouling. At a recovery of 75% the effective concentration in the crossflow loop is then increased to 200 mg/L which is also regarded by the manufacturer as long-term maximum particle concentration of the capillary NF membrane. GAC pretreatment can reduce

the DOC significantly and reduce macromolecules from EfOM known as critical membrane foulants. A runtime of up to 6000 bed volumes was identified as limit to safeguard sufficient DOC removal. Fouling rates depend on both organic and particle contents.

All investigated hybrid processes are promising methods for high quality water treatment. While the general applicability was proven, further process optimisation has to be continued in particular regarding energy consumption, concentrate disposal and chemical consumption. Fouling rates can further be reduced by flocculation prior to adsorption as proposed by Shon *et al.* (2004). In PAC/NF the development of the carbon cake layer can still be regarded as the main impediment. The cake layer seems to be of complex nature and might consist of inorganics such as bivalent ions in combination with organic foulants, bacteria and small size particles which tend to deposit in the cake layer. Also biofouling might influence the permeability of the formed cake layer. The study also indicates that operational and design parameters, *e.g.* permeate flux and carbon dose have to be selected according to the specific raw water quality and product water quality requirements.

An issue beyond the operational level of system optimisation was the insufficient lifetime of the modules, which is a problem of general concern in nanofiltration (van der Bruggen *et al.*, 2008a, 2008b). Due to high investment costs the membrane costs largely determine the overall treatment costs. The observed reduced durability of about one year could be attributed to the extreme and unstable operation conditions of a typical pilot installation. Avoiding extreme conditions with pressures close to the limits should extend the lifetime significantly. Also novel more robust membranes can contribute to an extended membrane lifetime just as reduced use of chemicals.

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## 8 Synthesis and outlook

In this thesis hybrid processes combining activated carbon and nanofiltration have been studied to identify the optimum solution for advanced water treatment in water reclamation and reuse. With a focus on the removal of bulk and trace organic compounds the investigation identified three promising process combinations, namely powdered activated carbon followed by nanofiltration (PAC/NF), granular activated carbon followed by nanofiltration (GAC/NF) and nanofiltration followed by granular activated carbon (NF/GAC). The removal potential was examined in lab and pilot scale for a range of refractory pharmaceuticals and industrial chemicals typically detected in effluent in trace concentrations. Fluorescence excitation emission spectroscopy was employed for the investigation of the fate of effluent organic matter. The optimum strategies for operation of the hybrid processes were determined in pilot scale. The experiments were conducted at the WWTP Aachen Soers providing an effluent of high quality with low DOC concentrations of about 5 mg/L.

### 8.1 Comparison of alternative combinations of nanofiltration and activated carbon

All investigated activated carbon nanofiltration hybrid processes provide very high quality product water with dissolved organic carbon concentrations clearly below 0.5 mg/L and organic micropollutant concentrations close or below the limit of quantification. This complies with the strict Californian standard. If a high degree of salinity removal is not required, nanofiltration-activated carbon hybrid processes can be regarded as a reliable and economic alternative to dual membrane processes (UF/RO). Due to lower filtration pressures the hybrid processes feature lower energy consumption and produce less problematic concentrates mainly consisting of organics and multivalent ions which can be precipitated. They feature also some advantages in indirect potable reuse applications such as managed aquifer recharge since the salt content of the product water is closer to natural conditions.

#### 8.1.1 Removal rates

In comparison to a single stage NF or a single adsorption stage, all three hybrid processes provide a superior product quality. In NF/GAC and GAC/NF the removal of the selected micropollutants was slightly better than in PAC/NF (Table 8.1). Overall each of the investigated hybrid processes can treat WWTP effluent to a quality suitable for high quality water reuse applications. If higher rejection rates for salts are required, NF/GAC and GAC/NF can employ tighter NF membranes than the investigated capillary nanofiltration membrane. The PAC/NF process requires the use of a backwashable nanofiltration system such as the investigated capillary nanofiltration. The optimum carbon dose was determined at 50 mg/L using the PAC type SAE Super. In the light of the overall excellent product water quality with only slight differences between the respective hybrid processes, the process selection could be made on the basis of the cost effectiveness and operational performance.

Rapid small scale column tests showed that GAC types with a high percentage of mesopores are favourable for applications with high DOC concentrations whereas waters with low DOC such as NF permeate allow the use of high-grade drinking water GAC to maximise the runtime of the filter.

**Table 8.1** Removal rates of activated carbon, nanofiltration and hybrid processes for key contaminants in water reuse

	PAC***	PAC	Cap NF	PAC/NF	PAC/NF	GAC/NF	NF/GAC
PAC dose/BVT	10mg/L	50 mg/L	0 mg/L	10 mg/L	50 mg/L	< 7000	20000
<i>Bulk organics</i>							
DOC	20%	50-60%	90-95%	90-95%	90-95%	90-95%	>95%
<i>Micropollutants</i>							
Benzotriazole	80%	95%	50%	85%	98%	>99.8%	>99.8%
Primidone	50%	85%	65%	55%	95%	>99.8%	>99.8%
Carbamazepine	75%	98%	50%	85%	99.9%	>99.9%	>99.9%
Sulfamethoxazole	30%	70%	65%	50%	90%	>99.8%	>99.8%
Macrolides	80%	>99%	80%	95%	>99%	>99%*	>98%
Contrast media	20-30%	75-80%	99%	90%	97-99%	>99%*	>99%
Diatrizoate	0%	50%	95%	85%	94%	>99%*	>99%
<i>Salts</i>							
Conductivity	-	-	15-20%	12%	12%	12%	15-20%
Sulfate	-	-	>75%	60-70%	60-70%	>70%	>75%
Chloride	-	-	5-20%	3-5%	-5 - 0%	3%	5-20%
<i>Pathogens**</i>	-	-	>6 log	>6 log	>6 log	>6 log	>6 log

\* qualified estimation, not investigated in detail

\*\* Asano *et al.*, 2007, NRMCC–EPHC–NHMRC, 2008.

\*\*\* SAE Super, other carbon types might deviate in rejection rates

The advanced analytical methods for characterisation of the bulk organics revealed that the product water from AC-NF processes is better than typical drinking water since most of the soluble microbial products are removed alongside the typical drinking water humic substances. Fluorescence spectrometry proved to be a very powerful tool allowing to detect wastewater borne bulk organic substances in samples with DOC concentrations below the limit of quantification (<140 µg/L).

### 8.1.2 Comparison with other alternative processes

AC-NF hybrid processes compete with PAC/UF and PAC/MF as well as with double membrane processes, *i.e.* UF/RO, which is the benchmark process in high-grade water reuse (Table 8.2) applied in all major indirect potable reuse schemes in the US, Australia and Singapore. The removal of all key contaminants occurs in AC-NF hybrid processes on a level comparable to UF/RO. The looser membrane however retains less salts and monovalent ions

such as nitrate, so that AC-NF hybrid processes cannot be employed, if severe salinity problems prevail in the catchment area. Similar to UF/RO, AC-NF processes present a double barrier for key contaminants. While UF/RO provides a double barrier for pathogens, AC-NF processes feature a double barrier for organic compounds. If a natural post-treatment such as managed aquifer recharge is foreseen, remaining contamination in particular NDMA can be well removed during the soil passage. Typical European wastewater also has lower nitrosamine concentrations close to the strict Californian recommendation for recharge so that an AOP posttreatment will not be necessary in most cases. Powdered activated carbon combined with porous membranes is a good alternate process for effluent polishing, if the advantages of nanofiltration such as removal of organics and multivalent ions are not required. However PAC/UF and PAC/MF are no multi-barrier systems.

**Table 8.2** Technical performance of activated carbon, nanofiltration and hybrid processes

Critical parameter	UF	NF	PAC	GAC	PAC/UF	PAC/NF	GAC/NF	NF/GAC	UF/RO
<i>Removal</i>									
Bulk organics	0	++	+	++	++	+++	+++	+++	+++
Organic micropollutants	–	+(+)	+(+)	++	++	++	+++	+++	+++
Microbial parameters	+++	+++	–	–	+++	+++	+++	+++	+++
Salts	–	++	–	–	–	+	++	++	+++
Fouling	0	0	+	–	+	+	++	0	++

Legend: +++ excellent, ++ very good, + good, 0 moderate, – poor

### 8.1.3 Treatment of NF concentrate

One main advantage of the PAC/NF and GAC/NF process is the significant reduction of trace organics in the NF concentrate. Direct NF generates a concentrate with about fourfold elevated micropollutant concentrations reaching levels up to 30 µg/L at a recovery of 75%. A PAC dosage of 50 mg/L reduced the micropollutant concentrations in the liquid phase of the concentrate below the feed concentrations.

In contrast to activated carbon pre-treatment in PAC/NF and GAC/NF, NF/GAC does not contribute to concentrate treatment. In cases where a high recovery is desired or the discharge of the NF concentrates is not possible due to local conditions, additional treatment of the NF concentrate should be foreseen, *e.g.* with a second GAC filter, which enables to return the concentrates to the WWTP. Low grade GAC with a high percentage of mesopores was found to be advantageous for these applications.

## 8.2 Operational aspects

The capillary NF showed a very stable performance without any unintentional interruptions in all process combinations. The operational strategy of the NF can be adapted to the respective raw water quality and hybrid process type. Pretreatment with GAC provided the best feed water quality and reduced the fouling rates. When aiming at an optimised performance of the GAC filter, NF/GAC is superior to the pre-treatment with activated carbon. After almost 20,000 bed volumes bulk and trace organics were still removed stably. It was not necessary to backflush the filter. The operation of the PAC/NF process was the most challenging. The cake layer control was identified as the operational key issue to limit increased concentration polarisation and reduce the transmembrane pressure. Frequent backflushing at the expense of reduced net fluxes proved to have the best potential for a stable operation of PAC/NF.

From the operational perspective NF/GAC was the most favourable combination, but requires a good feed water quality to allow for direct NF. For the treatment of poorer raw water qualities GAC/NF and PAC/NF are good alternatives. Further PAC/NF has still a high optimisation potential to reduce the carbon usage through recycling within the PAC/NF unit and the surplus carbon back to the activated sludge system, as developed by Metzger (2010) for PAC treatment of WWTP effluent.

**Table 8.3** Advantages and disadvantages of the PAC/NF process and the NF/GAC process

	<b>PAC/NF process</b>	<b>GAC/NF process</b>	<b>NF/GAC process</b>
Advantages	Adjustable carbon dose	Combined concentrate treatment	Reduced cake layer formation
	Adsorption on increased concentration level	Adsorption on influent concentration level	Employment of various NF modules
	Combined concentrate treatment	Reduced fouling Employment of various NF modules Separate optimisation of NF and AC	Separate optimisation of NF and AC No fouling of GAC filter Reactivation of GAC
Disadvantages	Carbon cake layer formation	High fouling of GAC filter	No treatment of concentrate
	Increased waste production	Frequent replacement of GAC	Design of GAC filter for maximum load
	No carbon reactivation	Limited reactivation of GAC	

### 8.3 Economic evaluation

From the financial point of view the presented pilot studies do not indicate strong differences in costs for the three hybrid processes as the overall costs are mainly driven by the operational and capital costs for the nanofiltration and to a minor degree by the carbon price and consumption. However, the specific costs for the activated carbon treatment are significantly lower in NF/GAC than in PAC/NF and GAC/NF. Due to a number of constraints any detailed estimation at this stage is hampered by significant uncertainties, such as lack of experience in full scale application, variation of costs due to site specific aspects (*e.g.* plant size, quality upgrading requirement) and future development (*e.g.* optimised membrane characteristics and increased competition lowering specific NF membrane prices)

Furthermore the main question for an optimised implementation of a process with dense membranes remains the disposal of the concentrates and the achievement of high recoveries requiring an optimum embedding of the NF and AC process in the overall wastewater treatment concept. Thus cost comparisons for NF in combination with AC treatment options have to be done on the basis of the case specific boundary conditions. A rough cost estimate indicates treatment costs with PAC/NF, GAC/NF and NF/GAC of about 0.43 to 0.73 €/m<sup>3</sup>.

The applied capillary NF membrane implies investment costs in the range of 2000 – 2500 € per 20 m<sup>2</sup> module for medium to large full scale plants. Thus the specific price ranges between 100 and 125 €/m<sup>2</sup>. With a Lang factor of 3 to 5, a specific design permeate flux of 25 L/(m<sup>2</sup>·h), and an average flow of 70 %, the specific investment costs for a full scale plant varies between 20,000 and 42,000 €/(m<sup>3</sup>/h). Based upon an average depreciation of 10 %/year the specific capital costs range between 0.23 and 0.48 €/m<sup>3</sup>. The operational costs largely depend on the local boundary conditions in terms of labour and energy costs. The operational costs can be estimated to 0.20 to 0.25 €/m<sup>3</sup> (Meier, 2008) including PAC dosage of 50 mg/L (= 0.06 €/m<sup>3</sup>). GAC costs can be slightly lower but higher investment costs are required for the GAC installation. The total costs can therefore be estimated to range between 0.43 and 0.73 €/m<sup>3</sup>.

Energy consumption for NF depends on several factors, such as plant size, raw water salinity, plant configuration, type of NF membrane and module, and the raw water temperature. In the drinking water plant at Mery-sur-Oise near Paris, the NF consumed a mean of 0.35 kWh/m<sup>3</sup> and varied between 0.27 in summer and 0.50 kWh/m<sup>3</sup> in winter. The specific energy consumption for AC-NF hybrid processes can be estimated based upon full scale RO and NF water reclamation references. According to this the energy consumption should range between 0.5 and 1.0 kWh/m<sup>3</sup>.

## 8.4 Conclusion

Activated carbon-nanofiltration hybrid processes are promising alternatives to existing treatment trains. They are well suited for high-grade water reuse applications. The present study demonstrated the feasibility of all three processes and identified advantages and disadvantages of the processes. The optimum combination of nanofiltration and activated carbon depends on local boundary conditions such as size of plant, raw water characteristics and plant location. In the light of growing water scarcity and increasing concerns about organic micropollutants activated carbon treatment in combination with nanofiltration could be applied in an increasing number of cases with appropriate boundary conditions.

Future applications should be embedded in integrated wastewater treatment concepts including concentrate treatment. Particularly combinations with membrane bioreactors are interesting options for innovative sustainable water recycling solutions.

## 8.5 Recommendations for future research and outlook

- The highest importance should be given to the clear definition of the legal boundary conditions for indirect potable reuse. Based on a scientific environmental and public health approach, threshold values should be defined to avoid over-engineered systems for "complete" removal of trace contaminants, mainly driven by analytical capacities and less by sound science.
- The future application of the investigated treatment concepts would also require the development of integrated solutions including treatment of membrane concentrates and enabling recovery of valuable resources, *e.g.* nutrients and energy.
- The effect of concentrated salts from NF concentrates, such as sulphate, calcium and magnesium, on the activated sludge system should also be further investigated to decide which ratio of brine to raw wastewater is still acceptable without negative impact from increased salinity on the operation, materials and biology of the WWTP.
- Integrated treatment concepts should also be compared from the sustainability perspective in terms of carbon footprint, water footprint and resource impact.
- Further optimisation potential can be expected if the PAC pretreatment would be operated with extended contact time and carbon recirculation as developed by Metzger (2010) for PAC treatment of effluent. If the PAC would be settled prior to the NF, cake layer formation could be limited. Further improvement of PAC/NF could also be achieved through the employment of PAC without the fine carbon fraction to minimise cake layer formation.
- With new NF membranes becoming available and the option to tailor made NF membranes for specific range of applications, further optimisation of the investigated processes could be accomplished.

## 8.6 References

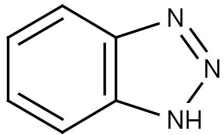
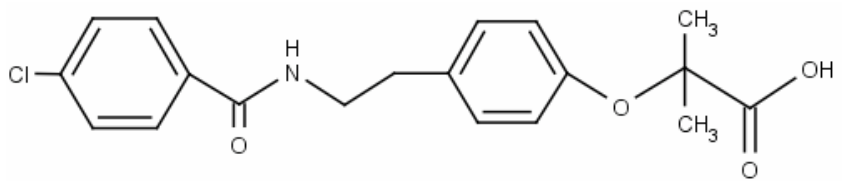
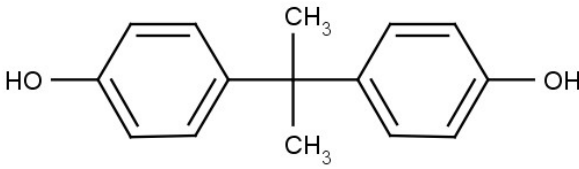
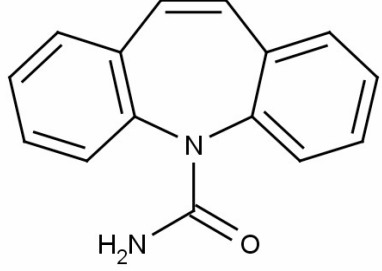
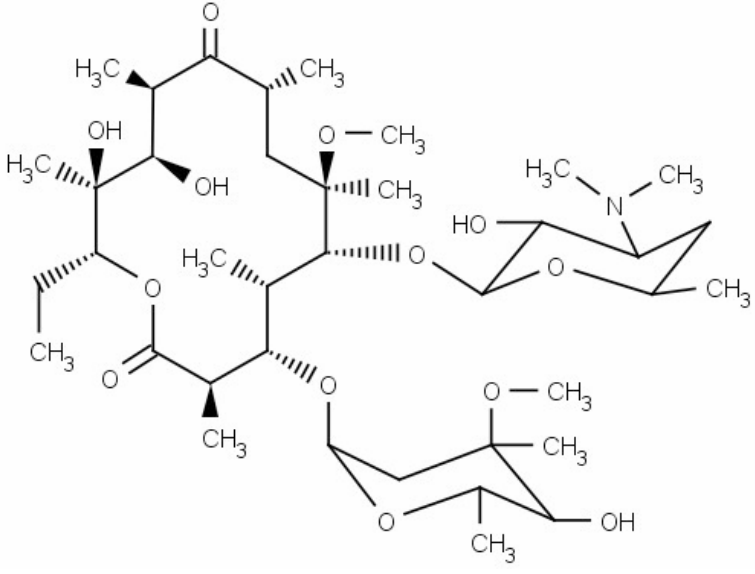
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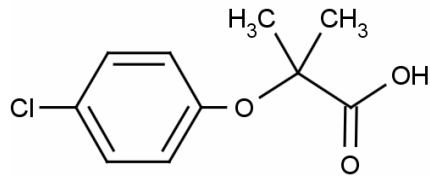


## Appendices

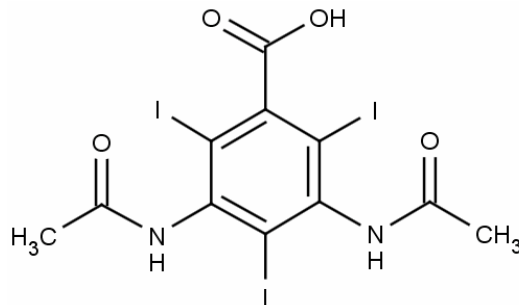
### A1 Chemical structure of selected micropollutants

Benzotriazole 95-14-7	
Bezafibrate 41859-67-0	
Bisphenol A 80-05-7	
Carbamazepine 298-46-4	
Clarithromycin 81103-11-9	

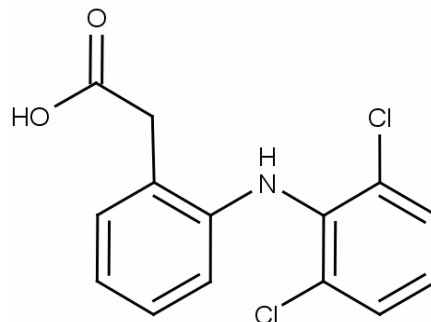
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882-09-7



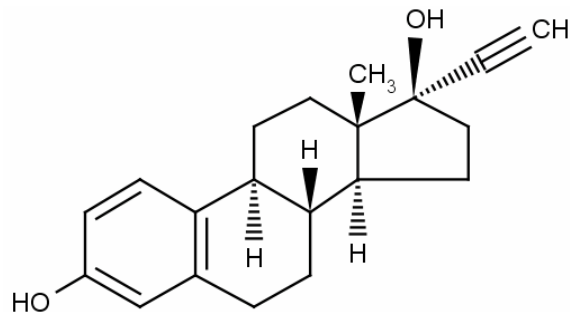
Diatrizoic acid  
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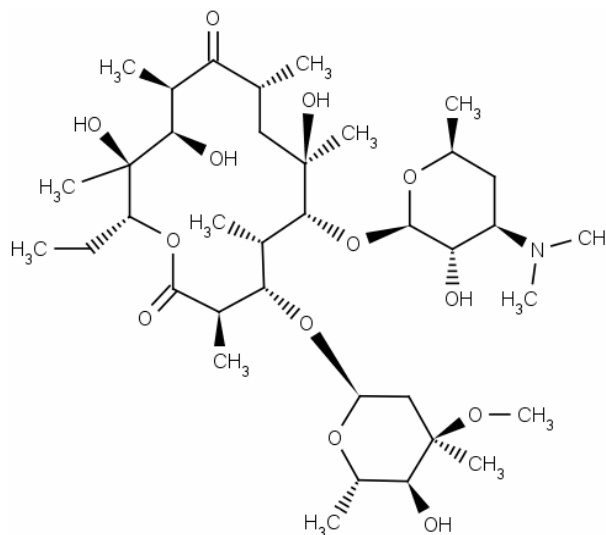
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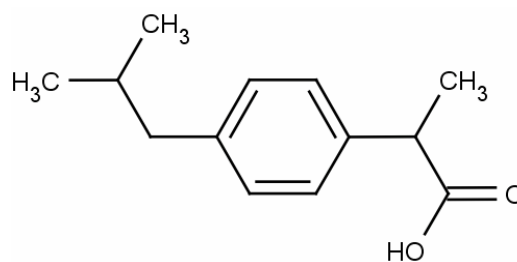
17 $\alpha$ -Ethinylestradiol  
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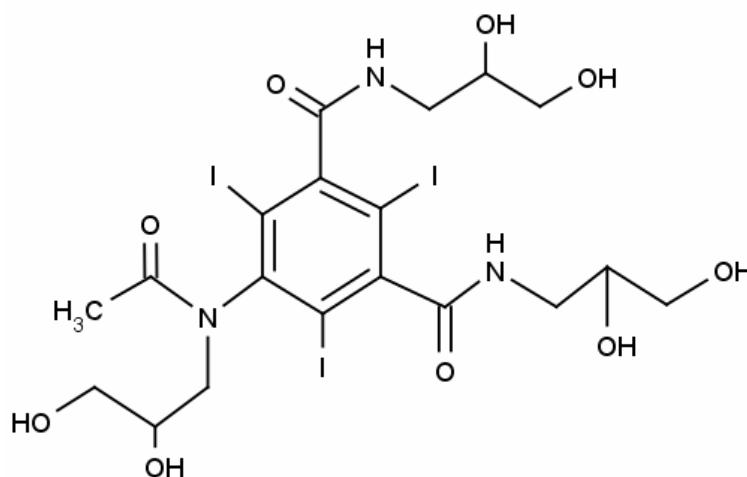
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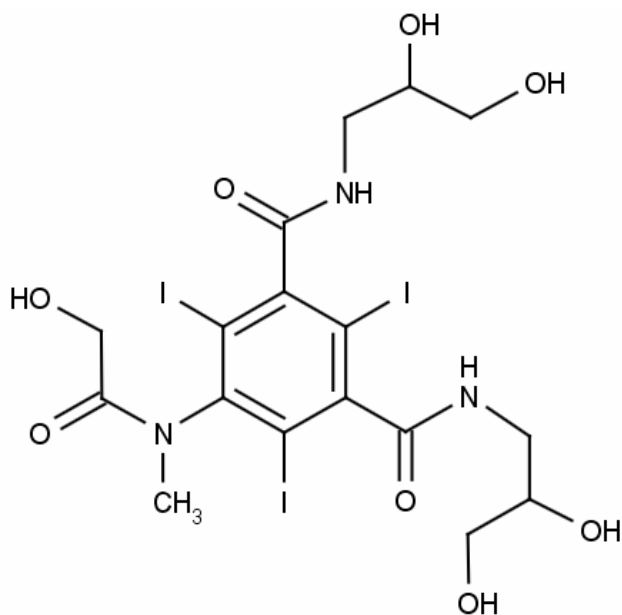
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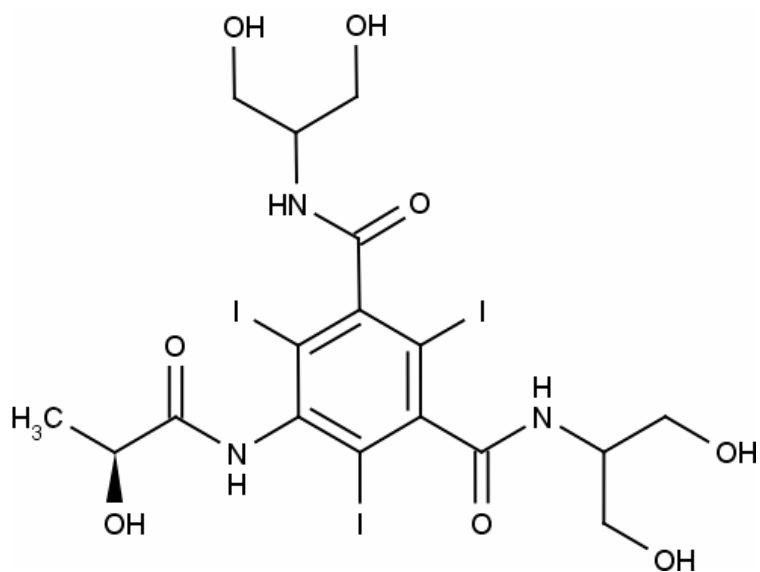
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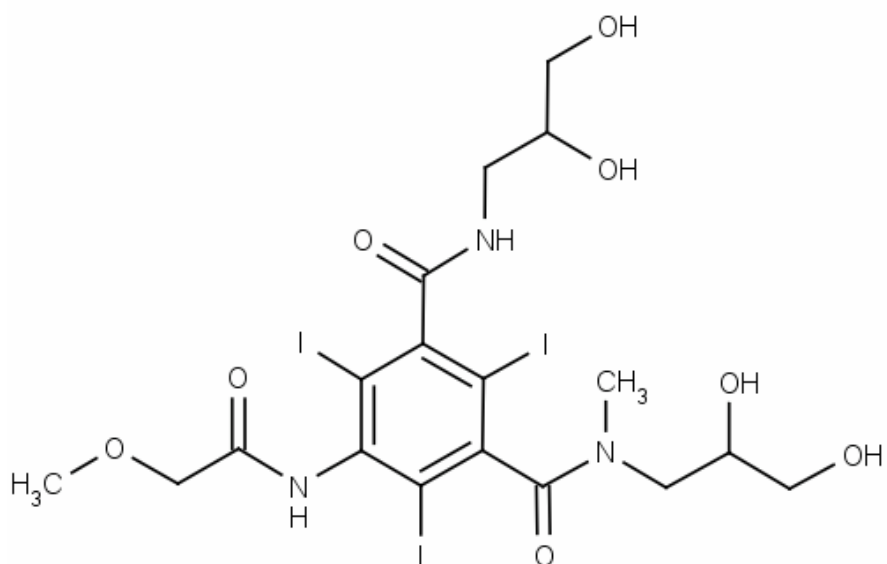
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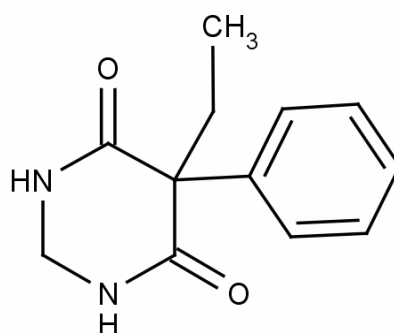
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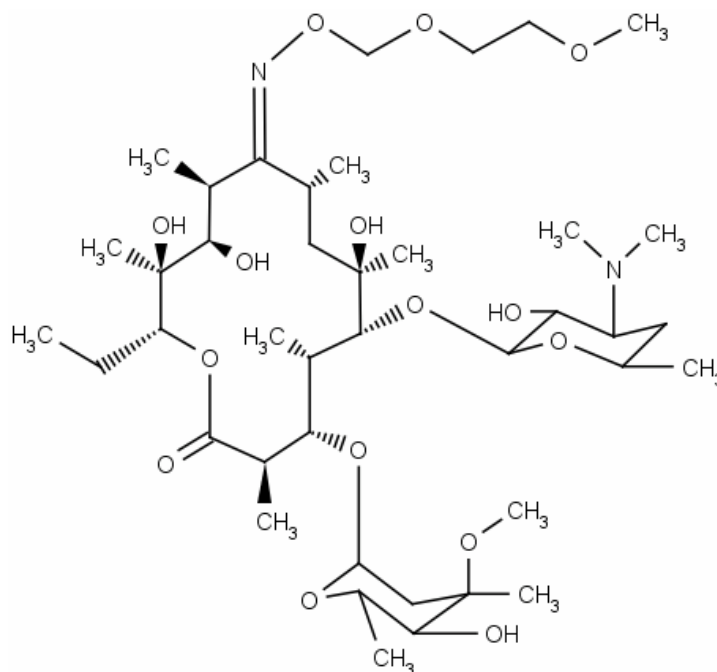
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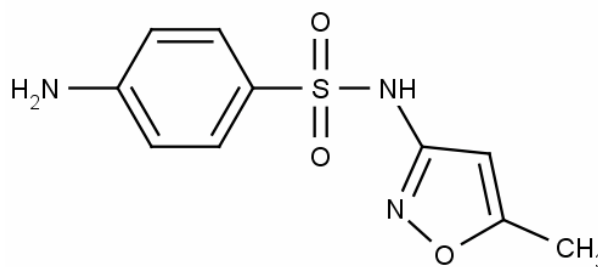
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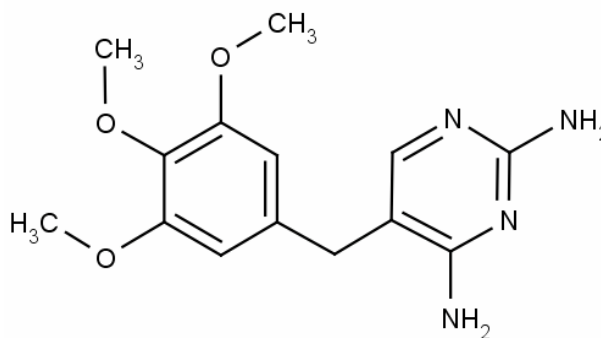
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Sulfamethoxazole  
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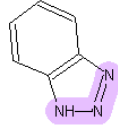
Trimethoprim  
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## A2 Speciation and log D of selected ionic micropollutants

Benzotriazole  
95-14-7

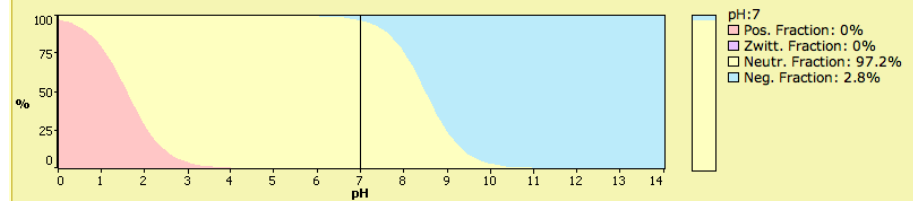
### Predicted Values - pKa and Ion fractions



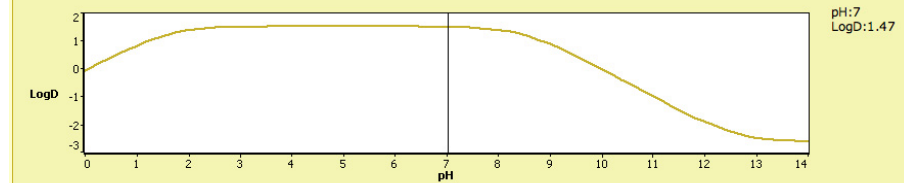
SMILES: N1N=NC2=C1C=CC=C2

Strongest pKa(Acid): **8.50+/-0.50**  
Strongest pKa(Base): **1.60+/-0.50**  
Number of ionizable groups: **1**

### Fraction Plots

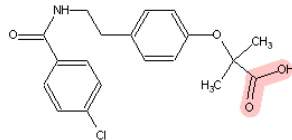


### LogD at given pH



Bezafibrate  
41859-67-0

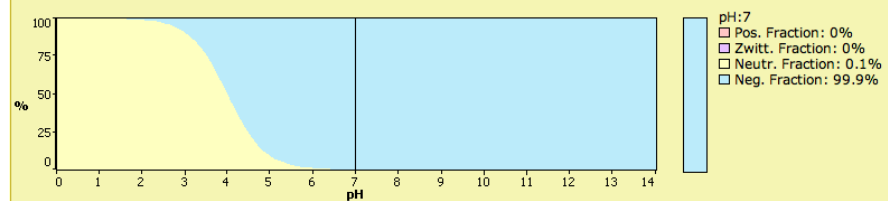
### Predicted Values - pKa and Ion fractions



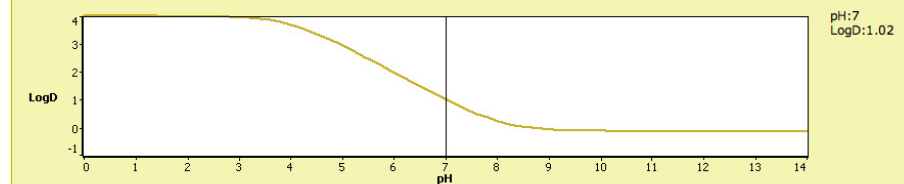
SMILES: CC(C)(OC1=CC=C(CCNC(=O)C2=CC=C2)C=C1)C(=O)O

Strongest pKa(Acid): **4.00+/-0.50**  
Strongest pKa(Base): **No Base pKa**  
Number of ionizable groups: **1**

### Fraction Plots

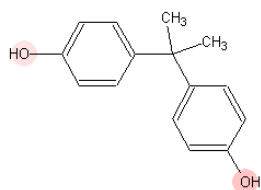


### LogD at given pH



Bisphenol A  
80-05-7

Predicted Values - pKa and Ion fractions

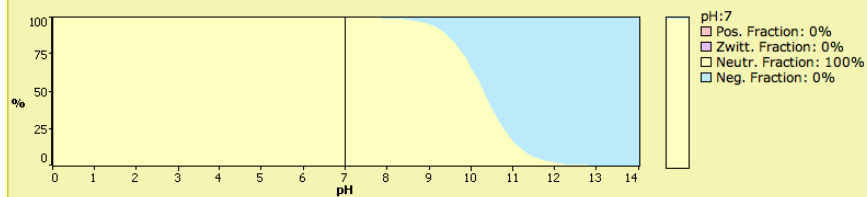


SMILES: CC(C)(C1=CC=C(O)C=C1)C1=CC=C(O)C=C1

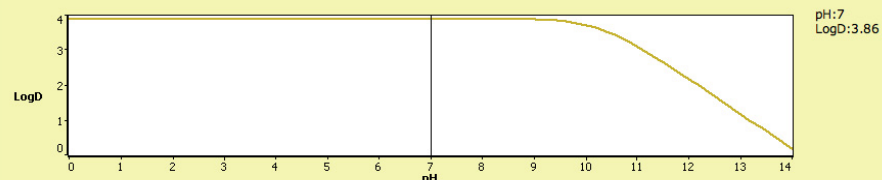


Strongest pKa(Acid): **10.30 +/- 0.50**  
 Strongest pKa(Base): **No Base pKa**  
 Number of ionizable groups: **2**

Fraction Plots

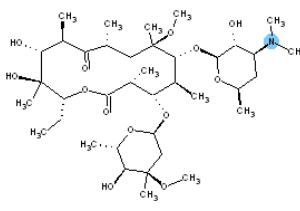


LogD at given pH



Clarithromycin  
81103-11-9

Predicted Values - pKa and Ion fractions

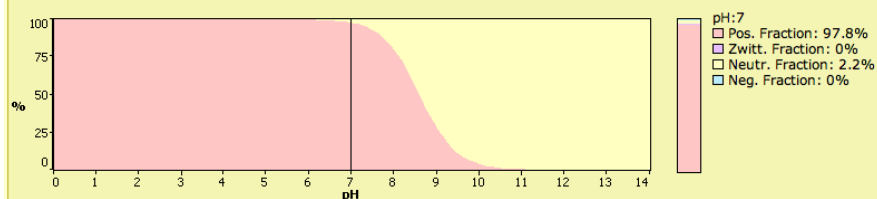


SMILES:

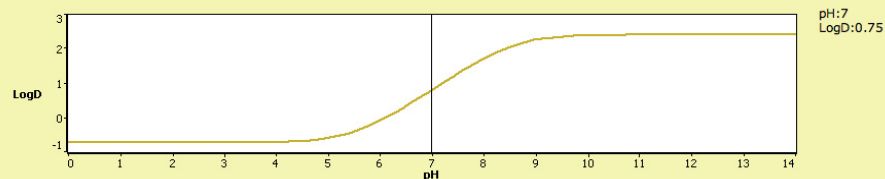


Strongest pKa(Acid): **No Acid pKa**  
 Strongest pKa(Base): **8.60 +/- 0.50**  
 Number of ionizable groups: **1**

Fraction Plots

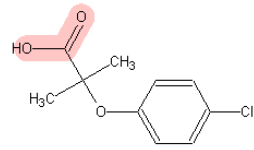


LogD at given pH



Clofibric acid  
882-09-7

Predicted Values - pKa and Ion fractions

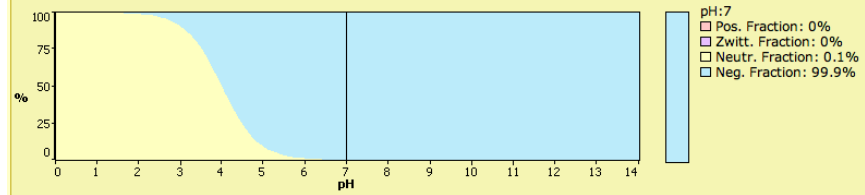


SMILES:

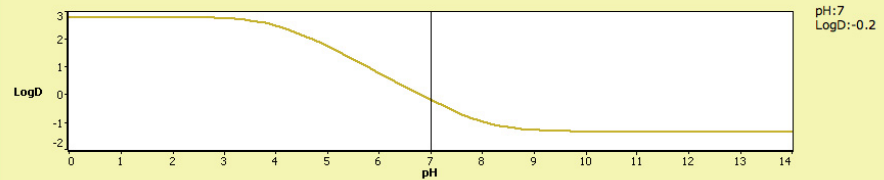


Strongest pKa(Acid): **4.00+/-0.50**  
Strongest pKa(Base): **No Base pKa**  
Number of ionizable groups: **1**

Fraction Plots

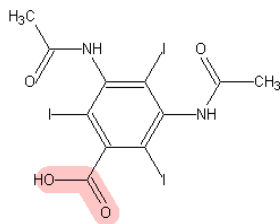


LogD at given pH



Diatrizoic acid  
117-96-4

Predicted Values - pKa and Ion fractions

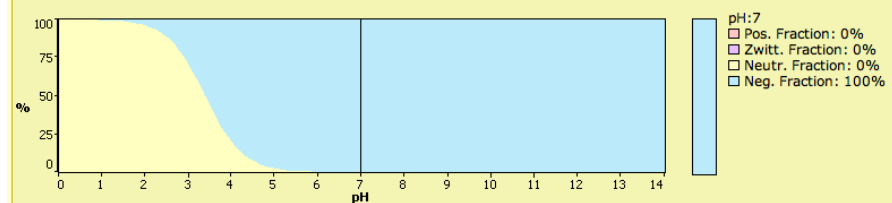


SMILES:

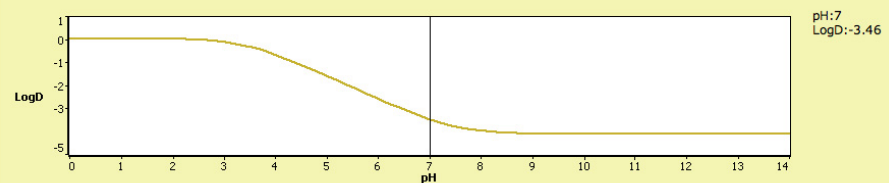


Strongest pKa(Acid): **3.40+/-0.50**  
Strongest pKa(Base): **No Base pKa**  
Number of ionizable groups: **1**

Fraction Plots



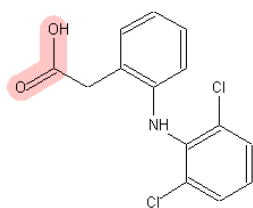
LogD at given pH





Diclofenac  
15307-86-5

#### Predicted Values - pKa and Ion fractions

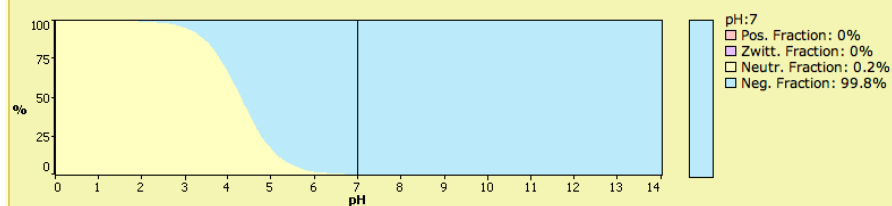


Strongest pKa(Acid): **4.30 +/- 0.50**  
Strongest pKa(Base): **No Base pKa**  
Number of ionizable groups: **1**

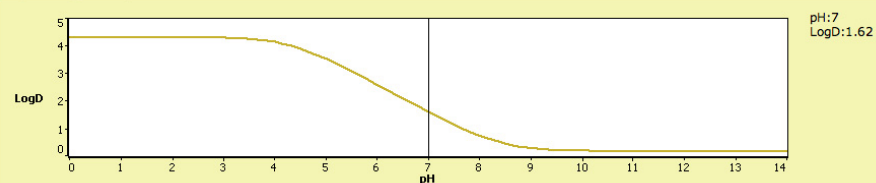
SMILES:



#### Fraction Plots

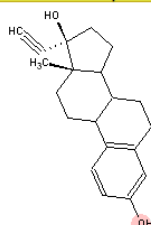


#### LogD at given pH



17 $\alpha$ -Ethinylestradiol  
57-63-6

#### Predicted Values - pKa and Ion fractions

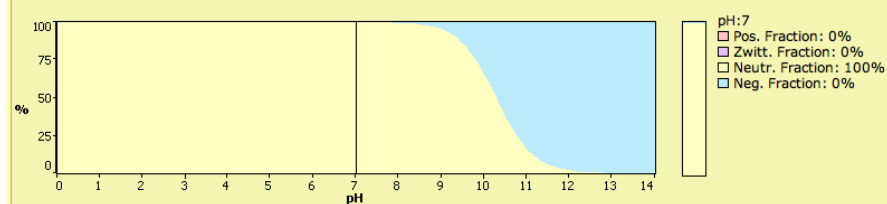


Strongest pKa(Acid): **10.30 +/- 0.50**  
Strongest pKa(Base): **No Base pKa**  
Number of ionizable groups: **1**

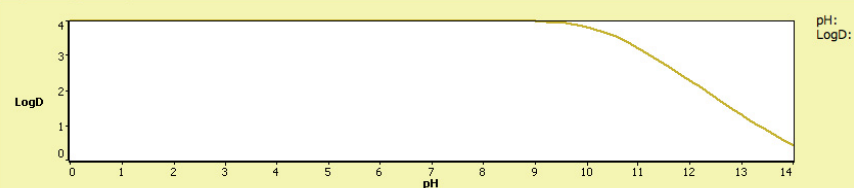
SMILES: [H][C@@]12CC[C@@](O)(C#C)[C@@]



#### Fraction Plots

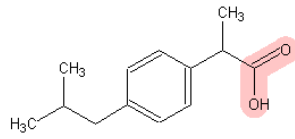


#### LogD at given pH



Ibuprofen  
15687-27-1

### Predicted Values - pKa and Ion fractions

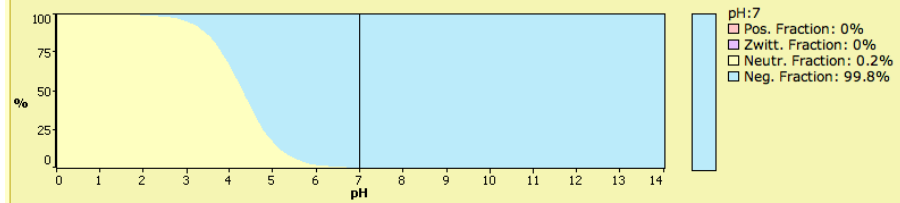


Strongest pKa(Acid): **4.30+/-0.50**  
Strongest pKa(Base): **No Base pKa**  
Number of ionizable groups: **1**

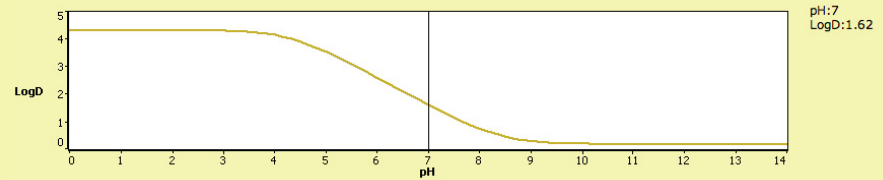
SMILES:



### Fraction Plots

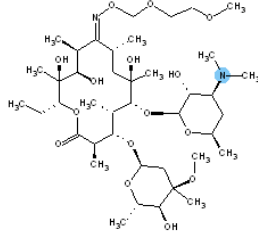


### LogD at given pH



Roxithromycin  
80214-83-1

### Predicted Values - pKa and Ion fractions

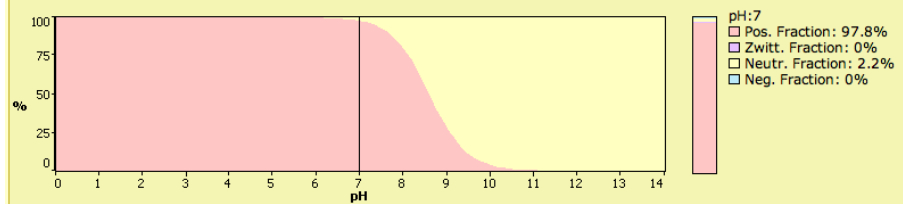


Strongest pKa(Acid): **No Acid pKa**  
Strongest pKa(Base): **8.60+/-0.50**  
Number of ionizable groups: **1**

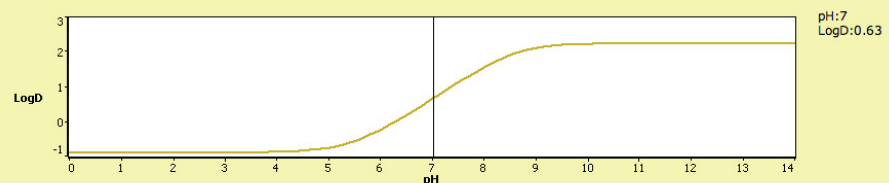
SMILES:



### Fraction Plots

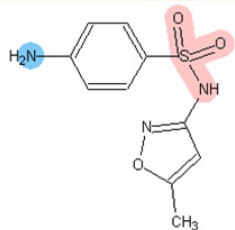


### LogD at given pH



Sulfamethoxazole  
723-46-6

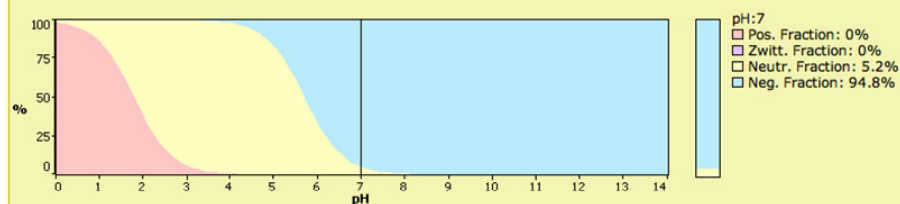
Predicted Values - pKa and Ion fractions



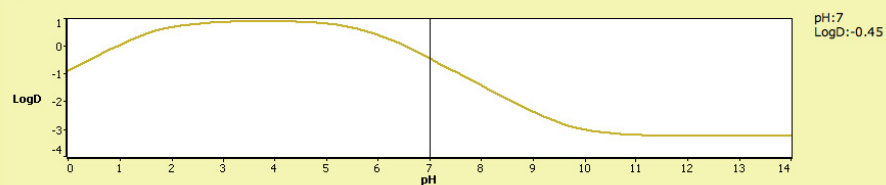
Strongest pKa(Acid): **5.70+/-0.50**  
Strongest pKa(Base): **1.80+/-0.50**  
Number of ionizable groups: **2**

SMILES: CC1=CC(NS(=O)(=O)C2=CC=C(N)C=C2)=C1

Fraction Plots

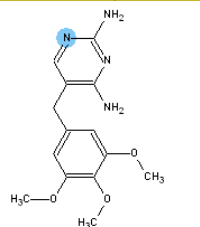


LogD at given pH



Trimethoprim  
738-70-5

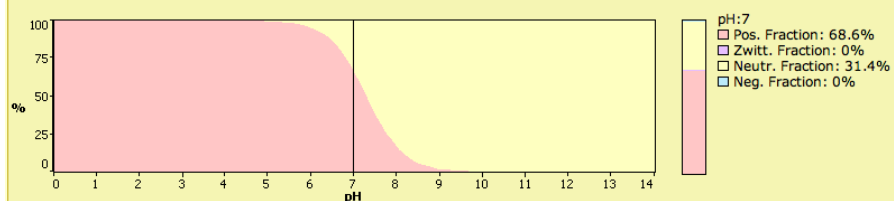
Predicted Values - pKa and Ion fractions



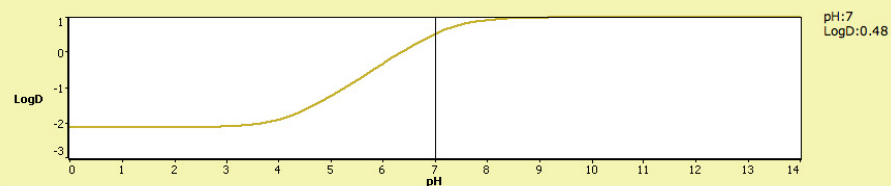
Strongest pKa(Acid): **No Acid pKa**  
Strongest pKa(Base): **7.30+/-0.50**  
Number of ionizable groups: **1**

SMILES: COC1=CC(CC2=C(N)N=C(N)N=C2)=C(OC)C(OC)=C1

Fraction Plots

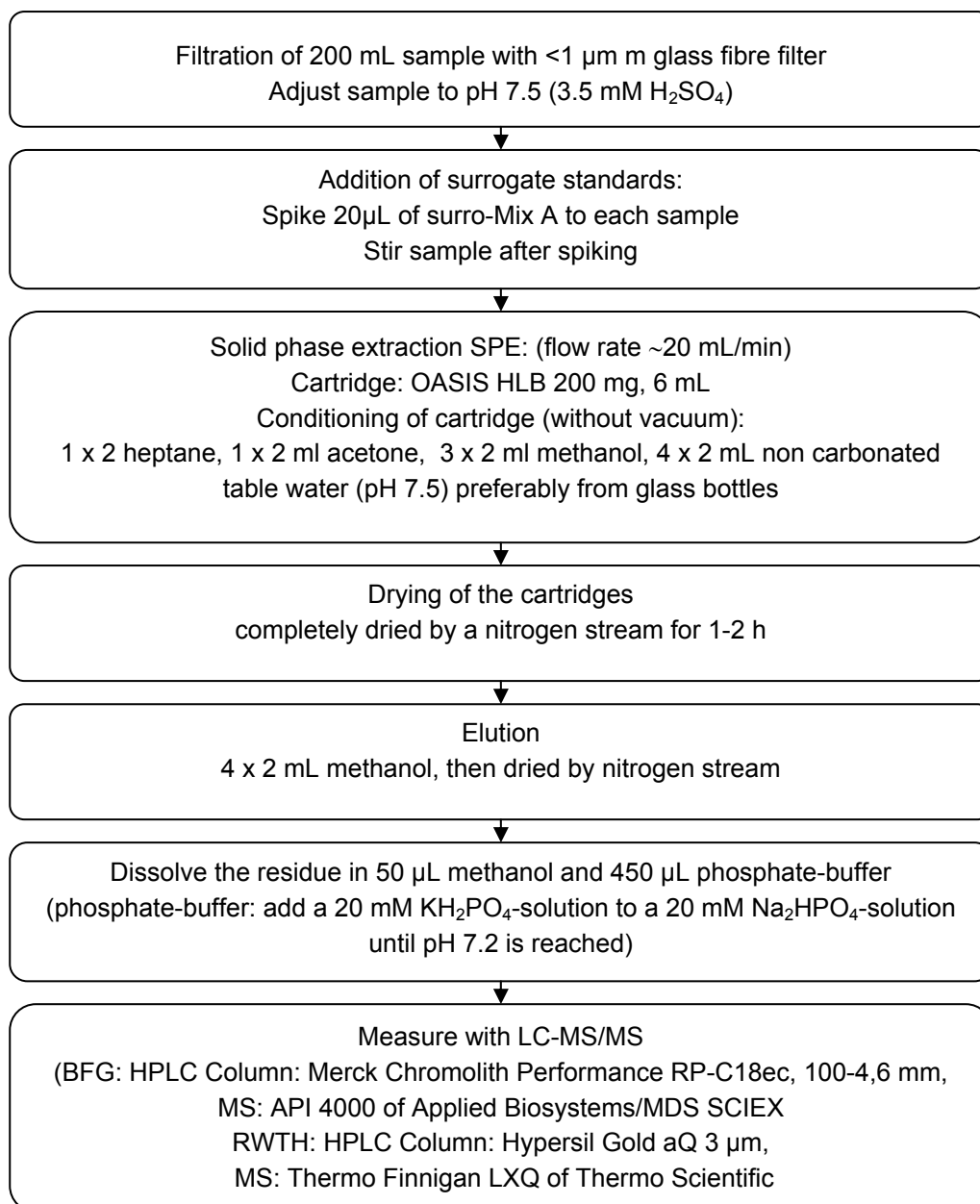


LogD at given pH



### A3 Analytical methods for organic micropollutants

Method 1 “Antibiotics” for simultaneous determination of antibiotics, carbamazepine, primidone, bisphenol A and benzotriazol (adapted from Ernst *et al.*, 2012)



#### Reference:

Ernst M., Hein A., Krauss M., Fink G., Hollender J., Ternes T., Jørgensen C., Jekel M. and McArdell C. (2012) Water quality analysis: Sensing, fate and behaviour of selected trace organic pollutants at different managed aquifer recharge sites. In: C. Kazner, T. Wintgens and P. Dillon (eds.) *Water Reclamation Technologies for Safe Managed Aquifer Recharge*. IWA Publishing, London, UK.

Method 2 for determination of iodinated contrast media und acidic drugs (adapted from Ernst *et al.*, 2012)

