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Sequential biofiltration – a novel concept for enhanced biological attenuation of trace organic compounds during wastewater treatment

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Abstract

The ubiquitous occurrence of a large variety of anthropogenic organic chemicals in the aquatic environment has been subject to the field of water research for many years. Due to their typically low concentrations in the range of ng/L to µg/L these substances are also referred to as trace organic chemicals (TOrCs). Concerns have been raised regarding their potential to cause adverse effects on aquatic ecosystems and human health. Municipal wastewater treatment plants (WWTPs) have been identified as major point sources for the entry of TOrCs into the aquatic environment. Different additional barriers have been discussed to achieve an enhanced elimination of TOrCs from WWTP effluents, including oxidative, adsorptive and membrane-based technologies. While additional biological treatment barriers have gained less attention, recent findings suggested an improved biological degradation of TOrCs under oxic and substrate-limited, so-called oligotrophic conditions. Using a sequential infiltration approach during managed aquifer recharge, previous studies demonstrated that these favorable conditions can be induced in engineered treatment systems. In three overarching research objectives, this dissertation investigated (i) options for the implementation and optimization of a novel biofiltration concept, applicable as an additional above-ground treatment step during municipal wastewater treatment to achieve an enhanced degradation of TOrCs, (ii) tools for an improved characterization of *in situ* redox conditions in biofiltration systems, and (iii) the potential of and the benefits from combining biological with oxidative and/or adsorptive advanced treatment processes.

The novel concept of sequential biofiltration was introduced using two granular media filters operated in series with an intermediate aeration step aiming for favorable oxic and oligotrophic operational conditions in the second filter stage. Results from column experiments conducted at pilot-scale confirmed a reduced substrate availability and predominantly oxic conditions in the second filter stage of the setup. Increased removal of several TOrCs was observed compared to a conventional single-stage biofiltration unit operated at the same overall empty bed contact time (EBCT). Higher removal of several TOrCs at increased EBCTs in the second filter stage indicated that EBCT might play a crucial role in the degradation of certain compounds. Additional experiments aimed at further advancing the feasibility of sequential biofiltration systems by reducing EBCTs in the first filter stage and investigated the pre-treatment of WWTP effluent by coagulation as an option to further decrease the availability of organic carbon during sequential biofiltration. Results indicated that an EBCT reduction in the first filter stage adversely affected process performance regarding the removal of organic bulk parameters and several TOrCs over short-term. However, after an extended adaptation period, comparable performance was observed. The pre-treatment of secondary effluent by coagulation, flocculation, and sedimentation was not found to enhance the performance during sequential biofiltration despite substantial removal of organic bulk parameters during the pre-treatment. However, despite the vast removal of total phosphorous during coagulation,

nutrient limitation was not found to adversely affect the biological performance of the subsequent system.

The biological degradation of many TOrCs is strongly redox dependent. The traditional characterization of redox conditions using the succession of inorganic electron acceptors such as dissolved oxygen and nitrate falls short in accurately describing the critical transition state between oxic (> 1 mg/L O_2) and suboxic (< 1 mg/L O_2) conditions. In an extensive study, the use of the successive *in situ* biological transformation of the iodinated contrast medium iopromide as an intrinsic tracer of prevailing redox conditions in biofiltration systems was investigated under varying substrate conditions. Iopromide degradation in biofiltration systems was monitored by quantifying twelve known biological transformation products formed under oxic conditions. A strong correlation between the consumption of dissolved oxygen and iopromide transformation emphasized the importance of general microbial activity on iopromide degradation. However, results disproved a direct correlation between oxic and suboxic conditions and the degree of iopromide transformation. Results indicated that besides redox conditions also the availability of biodegradable organic substrate affected the degree of iopromide transformation.

Further studies investigated the potential of combining sequential biofiltration, ozonation, and activated carbon adsorption in hybrid systems and focused on synergies between these treatment steps. Results proved that pre-treatment of WWTP effluent using biofiltration resulted in a significant, though limited, decrease in ozone demand for the transformation of several TOrCs characterized by moderate reaction rate constants with ozone. Biological and biological-oxidative pre-treatment resulted in substantially increased lifetimes until the breakthrough of granular activated carbon adsorbers. The improved process efficiency observed during ozonation and adsorption was attributed to the removal and structural alteration of dissolved organic matter during biological or biological-oxidative pre-treatment of the WWTP effluent. Beneficial effects observed in hybrid systems within this study are opposed by increasing process complexity and costs of operation, necessitating critical cost-benefit analyses to evaluate the feasibility of potential applications.

In conclusion, this dissertation highlighted the potential of advanced biological treatment systems to contribute to improved removal of TOrCs during municipal wastewater treatment. Results underlined the importance of operational conditions for successful biotransformation but also demonstrated the strong compound-specific differences in the degradation of different individual substances. Investigated multi-barrier systems demonstrated their high potential to achieve the removal of an extended range of TOrCs with many different physicochemical characteristics. However, full-scale applications of sequential biofiltration and sequential biofiltration-based hybrid systems must undergo critical cost-benefit analyses including site-specific factors to determine feasible and fit for purpose treatment options.

Zusammenfassung

Das Auftreten einer Vielzahl anthropogener organischer Substanzen in nahezu allen Kompartimenten des Wasserkreislaufs ist seit Jahren Gegenstand der Wasserforschung. Aufgrund der häufig niedrigen Konzentrationen (ng/L bis µg/L) werden diese Stoffe auch unter dem Begriff organische Spurenstoffe zusammengefasst. Die weite Verbreitung von Spurenstoffen in der aquatischen Umwelt führte zu Bedenken hinsichtlich eines möglichen human- und ökotoxikologischen Potentials. Kommunale Kläranlagen stellen bedeutende Punktquellen für den Eintrag von Spurenstoffen in die aquatische Umwelt dar. Um eine verbesserte Entfernung dieser Stoffe im Rahmen der Abwasseraufbereitung zu erreichen, stehen adsorptive, oxidative und membranbasierte Reinigungsverfahren in der Diskussion. Weitergehende biologische Behandlungsverfahren erlangten hingegen weniger Aufmerksamkeit. Ergebnisse jüngerer Studien konnten jedoch einen verbesserten biologischen Abbau zahlreicher Substanzen unter oxischen und substrat-limitierten, so genannten oligotrophen Bedingungen zeigen. Mittels eines sequentiellen Infiltrationsansatzes im Rahmen der künstlichen Grundwasseranreicherung konnten diese günstigen Bedingungen auch in technischen Behandlungssystemen eingestellt werden. In drei Schwerpunkten untersuchte diese Dissertation (i) Optionen für die Implementierung und Optimierung eines neuartigen Biofiltrationskonzepts, das als zusätzlicher Behandlungsschritt im Rahmen der kommunalen Abwasserbehandlung einen verbesserten Abbau von Spurenstoffen erreichen kann, (ii) neue Strategien für eine verbesserte *in situ*-Charakterisierung von Redoxbedingungen in Biofiltrationssystemen und (iii) die Vorteile der Kombination verschiedener weitergehender biologischer, oxidativer und/oder adsorptiver Behandlungsverfahren.

Im Rahmen der Studie wurde das Konzept der sequentiellen Biofiltration eingeführt, das zwei in Reihe geschaltete Schüttungsfilter mit einem Zwischenbelüftungsschritt verknüpft, um oxische und oligotrophe Betriebsbedingungen in der zweiten Filterstufe zu realisieren. Ergebnisse aus Säulenversuchen im Pilotmaßstab bestätigten eine reduzierte Substratverfügbarkeit und überwiegend oxische Bedingungen in der zweiten Filterstufe. Im Vergleich zu einem einstufigen Biofiltrationssystem, das bei gleicher Gesamtkontaktzeit (engl.: Empty Bed Contact Time (EBCT)) betrieben wurde, konnte eine verbesserte Entfernung verschiedener Stoffe beobachtet werden. Eine bessere Entfernung mehrerer Substanzen bei erhöhten EBCTs in der zweiten Filterstufe legte nahe, dass die EBCT eine entscheidende Rolle für den Abbau bestimmter Verbindungen spielt. Weitere Experimente zielten darauf ab die technische Umsetzbarkeit sequentieller Biofiltrationssysteme durch Verringerung der EBCT in der ersten Filterstufe zu verbessern und die Vorbehandlung von Kläranlagenablauf durch Koagulation als Option zur weiteren Verringerung der Verfügbarkeit von organischem Kohlenstoff während der sequentiellen Biofiltration zu untersuchen. Die Ergebnisse zeigten, dass eine Verringerung der Kontaktzeit in der ersten Filterstufe die Entfernung organischer Summenparameter und einiger Spurenstoffe kurzfristig negativ beeinflussen kann. Nach längerer Adaption konnte jedoch eine

vergleichbare Entfernungsleistung beobachtet werden. Eine Vorbehandlung des Kläranlagenablaufs mittels Koagulation, Flockung und Sedimentation konnte die Leistung eines nachgeschalteten sequentiellen Biofiltrationssystems trotz deutlicher Entfernung organischer Summenparameter nicht verbessern. Trotz der weitgehenden Entfernung des Gesamtphosphors während der Koagulation konnte jedoch auch keine nachteilige Beeinträchtigung der Leistungsfähigkeit des nachfolgenden biologischen Systems festgestellt werden.

Der biologische Abbau vieler Spurenstoffe ist stark abhängig von den vorherrschenden Redoxbedingungen. Die konventionelle Charakterisierung von Redoxbedingungen unter Verwendung der Abfolge anorganischer Elektronenakzeptoren, wie gelöstem Sauerstoff und Nitrat, ist ungeeignet, um den für den Spurenstoffabbau kritischen Übergangszustand zwischen oxischen (> 1 mg/L O_2) und suboxischen (< 1 mg/L O_2) Bedingungen zu charakterisieren. Im Rahmen dieser Studie wurde untersucht inwiefern die sukzessive biologische Transformation des iodierten Röntgenkontrastmittels Iopromid als intrinsischer Tracer für die vorherrschenden Redoxbedingungen in Biofiltrationssystemen unter verschiedenen Substratbedingungen verwendet werden kann. Der Iopromidabbau wurde durch die Quantifizierung zwölf bekannter biologischer Transformationsprodukte überwacht, deren Bildung in Vorstudien unter oxischen Bedingungen beschrieben wurde. Eine starke Korrelation zwischen der Sauerstoffzehrung und der Iopromidtransformation legte die Bedeutung allgemeiner mikrobieller Aktivität für den Iopromidabbau nahe. Die Ergebnisse konnten jedoch keinen direkten Zusammenhang zwischen oxischen und suboxischen Bedingungen und dem Grad der Iopromidtransformation nachweisen. Die Ergebnisse verdeutlichten, dass die Verfügbarkeit von biologisch verfügbarem Substrat den Grad der Iopromidtransformation beeinflusst.

Weitere Studien untersuchten das Potential der Kombination von sequentieller Biofiltration, Ozonierung und Adsorption an Aktivkohle in Hybridsystemen hinsichtlich möglicher Synergien zwischen den Behandlungsschritten. Ergebnisse zeigten, dass die Vorbehandlung von Kläranlagenablauf mittels Biofiltration zu einer signifikanten, jedoch begrenzten Verminderung des Ozonbedarfs für die Transformation verschiedener Substanzen führte. Die biologische und biologisch-oxidative Vorbehandlung von Kläranlagenablauf bewirkte eine Erhöhung der Standzeit von Aktivkohleadsorbern bis zum Durchbruch der meisten untersuchten Spurenstoffe. Die beobachtete verbesserte Prozesseffizienz, wurde auf die teilweise Entfernung und strukturelle Veränderung gelöster Substanzen des organischen Hintergrunds während der biologischen und biologisch-oxidativen Vorbehandlung zurückgeführt. Die in dieser Studie beobachteten positiven Effekte in Hybridsystemen gehen mit einer zunehmenden Prozesskomplexität und steigenden Betriebskosten einher, die kritische Kosten-Nutzen-Analysen erfordern, um die Umsetzbarkeit möglicher Prozesskombinationen umfassend zu bewerten.

Diese Dissertation konnte das Potential weitergehender biologischer Behandlungssysteme zur verbesserten Entfernung von Spurenstoffen im Rahmen der kommunalen Abwasserbehandlung belegen. Die Ergebnisse unterstrichen die Bedeutung vorherrschender Betriebsbedingungen für die biologische Transformation, zeigten aber auch die deutlichen substanzspezifischen Unterschiede beim Abbau unterschiedlicher Verbindungen. Die Kombination verschiedener Verfahren in Hybridsystemen erwies sich als effektiv um die Entfernung von Spurenstoffen mit verschiedensten physikalisch-chemischen Eigenschaften zu erreichen. Der großtechnischen Anwendung der sequentiellen Biofiltration und der untersuchten Hybridsysteme müssen jedoch kritische Kosten-Nutzen-Analysen unter Beachtung standortspezifischer Faktoren vorausgehen, um geeignete und zweckmäßige Behandlungsoptionen zu identifizieren.

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Abbreviations

4-FAA	*4-Formylaminoantipyrine*
AOC	*Assimilable organic carbon*
ATP	*Adenosine triphosphate*
BDOC	*Biodegradable dissolved organic carbon*
BOD	*Biochemical oxygen demand*
c	*Concentration*
c_0	*Initial concentration*
CFS	*Coagulation, flocculation and sedimentation*
COD	*Chemical oxygen demand*
DEET	*N,N-diethyl-m-toluamide*
DO	*Dissolved oxygen*
DOC	*Dissolved organic carbon*
DOM	*Dissolved organic matter*
EAWAG-BBD-PPS	*EAWAG Biodegradation/Biocatalysis Database Pathway Prediction System*
EPS	*Extracellular polymeric substances*
ESI	*Electrospray ionization*
Fe(III)	*Trivalent iron*
f_k	*Dimensionless iopromide transformation factor*
GAC	*Granular activated carbon*
HPLC	*High-pressure liquid chromatography*
HRT	*Hydraulic retention time*
ID	*Inner diameter*
k	*Pseudo-first-order rate constant*
k_{O3}	*Second-order reaction rate constant with ozone*
k_{OH}	*Second-order reaction rate constant with hydroxyl radicals*
l	*Length*
LC-MS/MS	*Liquid chromatography coupled with tandem mass spectrometry*
LOQs	*Limits of quantitation*
MAR	*Managed aquifer recharge*
MRM	*Multiple reaction monitoring*
N	*Nitrogen*
NOM	*Natural organic matter*
O_2	*Oxygen*
O_3	*Ozone*
PAC	*Powdered activated carbon*
PSA	*Pressure swing adsorption*
RSSCTs	*Rapid small-scale column tests*
SBF	*Sequential biofiltration*
SBF(Air)	*Sequential biofiltration with intermediate aeration*
SBF(O_3)	*Sequential biofiltration with intermediate ozonation*
SMART	*Sequential managed aquifer recharge technology*
SRT	*Solid retention time*
SUVA	*Specific UV absorbance*
t	*Time*
TCEP	*Tris(2-chloroethyl) phosphate*
T_{IOP}	*Dimensionless parameter for the degradation of iopromide*
TOC	*Total organic carbon*
TOrCs	*Trace organic chemicals / Trace organic compounds*
TPs	*Transformation products*
UVA_{254}	*UV absorbance at 254 nm*
v_f	*Filter velocity*
WWTPs	*Wastewater treatment plants*

ΔDO	*Consumption of DO*
ΔDOC	*Consumption of DOC*
ΔUVA_{254}	*Change in* UVA_{254}

1 General introduction

The widespread occurrence of numerous anthropogenic chemicals in water bodies worldwide has been subject of ongoing investigations in the field of water research (Ternes, 1998; Khim et al., 1999; Heberer, 2002; Chiu and Westerhoff, 2010; Hughes et al., 2013; Loos et al., 2013; Sorensen et al., 2015; Sun et al., 2018). Due to their presence at low concentrations in the range of ng/L to µg/L, they are commonly referred to as trace organic chemicals (TOrCs). TOrCs detected in the aquatic environment comprise a large variety of substance classes, including pharmaceuticals, personal care products, pesticides, and industrial chemicals. In a review from 2013, Hughes et al. amounted the number of pharmaceutically active compounds alone, detected in water bodies across the world to be > 200 (Hughes et al., 2013), while the detection of yet unreported compounds is ongoing (e.g. Funke et al., 2015). Concerns have been raised regarding potential adverse effects on aquatic ecosystems and human health. While direct toxic effects on human health seem unlikely (Schriks et al., 2010), negative effects at environmental concentrations have been observed in aquatic organisms (Cleuvers, 2003; Triebskorn et al., 2004; Cuklev et al., 2011; Brodin et al., 2013; Wilkinson et al., 2016). Single compound acute toxicity testings indicated the toxicological relevance of a number of compounds even at low concentrations below 1 mg/L (Petrie et al., 2015), classifying them as potentially very toxic to aquatic organisms according to the EU-Directive 93/67/EEC (Commission of the European Communities, 1996; Petrie et al., 2015). Besides findings proving toxicological effects of certain individual compounds at low concentrations, studies also indicated an elevated toxicological potential caused by combinatory effects in complex mixtures (Cleuvers, 2003, 2004). In addition, the effects of a long-term exposure to a large variety of chemicals present at low concentrations are hardly predictable (Schwarzenbach et al., 2006). In recent years, concerns have been raised regarding a potential correlation between an increase in bacteria exhibiting elevated antimicrobial resistance and the presence of low concentrations of many different antibiotic drugs in the aquatic environment (Taylor et al., 2011; Huerta et al., 2013; Marti et al., 2014).

Municipal wastewater treatment plants (WWTPs) have been identified as major point sources for the discharge of TOrCs into the aquatic environment (Ternes, 1998; Heberer, 2002; Ternes, 2007; Reemtsma et al., 2010; Dong et al., 2015). Technologies applied during conventional wastewater treatment are mostly based on the activated sludge process aiming for optimized biological removal of organic bulk parameters and nutrients. Not being designed for the retention of individual chemicals, the removal of TOrCs in conventionally applied wastewater treatment processes was reported to be strongly compound-dependent (Ternes, 1998; Vieno et al., 2007; Zorita et al., 2009; Falås et al., 2016). While effective mitigation was reported for some compounds due to biotransformation or sorption onto activated sludge flocs, only partial or no removal was found for others (Ternes, 1998; Ternes et al., 1999; Hörsing et al., 2011; Hyland et al., 2012; Falås et al., 2016; Anumol et al., 2016).

To further mitigate the discharge of TOrCs into the aquatic environment, additional, advanced treatment barriers during wastewater treatment are required. Various treatment technologies have demonstrated their potential to effectively mitigate TOrCs from WWTP effluents, including oxidation and adsorption processes, or membrane filtration (Rizzo et al., 2019). Oxidative treatment, by ozone or UV based advanced oxidation processes, has been studied extensively and was identified as a powerful technology for the effective transformation of most TOrCs occurring in WWTP effluent (Huber et al., 2003; Ternes et al., 2003; Huber et al., 2005; Hollender et al., 2009; von Sonntag and von Gunten, 2012; Miklos et al., 2018). The oxidation of TOrCs does typically not yield in compound mineralization but results in the formation of different transformation products (TPs) of often unknown toxicological relevance (Hübner et al., 2013b; Kuang et al., 2013; Favier et al., 2015; Zucker et al., 2018). Besides, the matrix-dependent formation potential of toxic oxidation by-products, such as nitrosamines and bromate demands careful consideration during process design and operation (von Gunten, 2003; Wert et al., 2007; Krasner, 2009; Gerrity et al., 2015; Marti et al., 2015; Sgroi et al., 2016). Oxidation of feed waters containing dissolved organic matter (DOM), typically results in the formation of easily biodegradable organic components, such as aldehydes and ketoacids (Janssens et al., 1985; van der Kooij et al., 1989; Price et al., 1993; Griffini et al., 1999; Ramseier et al., 2011). To achieve biologically stable product water, ozonation is usually followed by post-treatment in biologically active granular media filters (Janssens et al., 1985; Kramer et al., 1993; Hozalski et al., 1995). Biological post-treatment has been reported to also effectively remove several organic oxidation by-products, such as nitrosamines (Yoon et al., 2013; Gerrity et al., 2015; Bacaro et al., 2019). The application of activated carbon in powdered or granular form has been reported as a suitable option for the removal of a broad range of TOrCs from WWTP effluents (Nowotny et al., 2007; Altmann et al., 2016; Benstoem et al., 2017; Kårelid et al., 2017). In contrast to oxidative treatment processes, adsorption results in the removal of compounds without the formation of undesired TPs or disinfection by-products of known or unknown toxicological relevance. Activated carbon has been found to be less effective for the removal of highly polar substances (Kormos et al., 2011; Zietzschmann et al., 2014a; Altmann et al., 2016). Also, the presence of high amounts of DOM in WWTP effluents substantially reduces process efficiency due to competitive adsorption of matrix components (Corwin et al., 2011; Summers et al., 2013; Zietzschmann et al., 2014b, 2016). An effective removal of TOrCs from WWTP effluent can also be achieved by the use of high-pressure membrane systems, equipped with nanofiltration or reverse osmosis membranes (Kim et al., 2005a; Xu et al., 2005; Coday et al., 2014; Fujioka et al., 2015; Taheran et al., 2016). Full-scale applications, however, are opposed by high energy demands and the production of brine solutions, demanding further treatment.

Besides advanced treatment with oxidative, adsorptive or membrane technologies, several studies investigated options for an enhanced removal of TOrCs via additional treatment in biologically active granular media filters during drinking and wastewater treatment (Reungoat et al., 2010; Rattier et al., 2014; Escolà Casas and Bester, 2015; Paredes et al., 2016; Zhang et al., 2017; Sbardella et al., 2018). In addition, many studies dealt with the fate of TOrCs in natural treatment systems such as bank filtration or managed aquifer recharge (MAR) applications (Grünheid et al., 2005; Onesios et al., 2009; Onesios and Bouwer, 2012; Hoppe-Jones et al., 2012; Benotti et al., 2012; Regnery et al., 2015a; Hamann et al., 2016). In general, however, advanced biological treatment options have gained less attention, which might be explained by the fact that the extensive biological processes applied during conventional wastewater treatment often only achieve an unsatisfactory removal of many TOrCs. The evolution of modern wastewater treatment has demonstrated the huge potential of biological processes to achieve an effective removal of various wastewater relevant parameters. While the removal of bulk organic parameters and a reduction of biochemical and chemical oxygen demand was the focus of first activated sludge systems, enhanced removal of nitrogenous and phosphorous nutrients became a driver for process development in the second half of the 20th century (Lofrano and Brown, 2010). The widespread use of anaerobic digestion to produce biogas from waste sludges produced during treatment (Metcalf and Eddy, 2003; McCarty et al., 2011; Shen et al., 2015) or alternative concepts for a more energy efficient removal of nitrogenous components (Hellinga et al., 1998; van de Graaf et al., 1998; Weißbach et al., 2018), represent further examples for the large variety of biological processes already applied during conventional wastewater treatment. In the past, increasing water quality demands or an increased energy efficiency could be achieved, using the vast diversity of naturally occurring microbial activity. By selective adjustment of operational conditions, biological processes were tuned to achieve an optimized process performance. The continued optimization and adaptation of biological wastewater treatment processes in the last century, using the abilities of diverse microbial communities to achieve different treatment goals, motivated the question whether an improved removal of TOrCs could also be achieved in a specifically designed advanced biological treatment step under optimized operational conditions.

Recent studies identified key parameters that were found to have an impact on the biodegradation of many TOrCs. Redox conditions have been shown to have a significant effect on the removal of many different TOrCs. Several authors found increased and accelerated removal of TOrCs in the presence of sufficient dissolved oxygen (Massmann et al., 2008; Baumgarten et al., 2011; Regnery et al., 2015b; Schmidt et al., 2017) while only a few compounds were reported to be preferably degraded under reducing conditions (Wiese et al., 2011; König et al., 2016; Gonzalez-Gil et al., 2019b). Biological TOrC removal was also found to be dependent on the amount and composition of the primary substrate present (Rauch-Williams et al., 2010; Li et al., 2012, 2013, 2014; Alidina et al., 2014). Considering the low concentrations of TOrCs in environmental settings, cometabolism is believed to be the dominant mechanism for biological removal (Kobayashi and Rittmann, 1982; Onesios et al., 2009; Tran et al., 2013). Li et al. (2012) demonstrated that the makeup of the primary substrate present had effects on the structure of investigated microbial communities. Under conditions with a predominantly refractory primary substrate a higher microbial diversity was found to be established than under conditions with higher amounts of easily degradable substrate, also referred to as biodegradable dissolved organic carbon (BDOC). A refractory primary substrate is believed to shape a microbial community capable of expressing enzymes able to utilize even hardly degradable substances (Rauch-Williams et al., 2010). As a consequence, increased removal of TOrCs through cometabolic processes is expected.

Sequential managed aquifer recharge technology (SMART) describes a groundwater recharge concept in which a sequential infiltration approach is used to establish oxic and oligotrophic conditions (Regnery et al., 2016; Hellauer et al., 2017a, 2017b). Source water that might be rich in BDOC is infiltrated in the first infiltration stage. Microbial degradation of BDOC leads to rapid oxygen depletion and increasingly reducing redox conditions. After recovering the water, re-aeration supplies oxygen to the water before it is infiltrated again in a second infiltration stage. After depletion of BDOC in the first filter stage and re-aeration, oxic and oligotrophic conditions are achieved in the second infiltration stage. Regarding the targeted TOrC removal, results indicated significantly improved attenuation of several moderately biodegradable TOrCs compared with conventionally operated MAR systems (Regnery et al., 2016). The findings from Regnery et al. (2016) revealed that a relatively simple change in operation mode is suitable to tune biological systems for enhanced removal of compounds which exhibit a high degree of persistence in other applications. As demonstrated in SMART, the optimization of biological treatment systems for an enhanced removal of poorly degradable substances is possible without necessarily resulting in complex and technology-intensive processes.

In a first objective, this study aimed at investigating the suitability of a novel biofiltration concept to contribute to enhanced mitigation of TOrCs from WWTP effluent. The identification of key parameters for an enhanced biological transformation of TOrCs indicated an unused potential for the optimization of biological systems to achieve an improved removal of TOrCs from the effluents of municipal WWTPs. The promising results obtained in SMART systems motivated the quest for options to utilize the approach in engineered biological above-ground treatment systems which could be applied as an advanced biological treatment step subsequent to conventional wastewater treatment. The study investigated in how far oxic and substrate-limited conditions can also be implemented in systems operated at substantially lower hydraulic residence times compared to those typically applied in MAR applications to achieve an improved biological degradation of TOrCs.

In a second objective, this study investigated an alternative approach for the *in situ* characterization of redox conditions in biofiltration systems. The removal of TOrCs in biological systems has been shown to be highly dependent on redox conditions (Massmann et al., 2008; Baumgarten et al., 2011; Wiese et al., 2011; Regnery et al., 2015b; König et al., 2016). The characterization of aquifer redox conditions as oxic, suboxic and anoxic is based on the presence of the redox indicator species dissolved oxygen, nitrate, sulfate, manganese, and iron as described by McMahon and Chapelle (2008). While this proposed categorization is capable of broadly characterizing redox zonation in aquifer systems, it might not be sensitive enough to accurately describe the transition state between oxic and suboxic conditions, which has been reported to be critical for the degradation of several redox-sensitive compounds (Regnery et al., 2015b). Following the successive transformation of an individual biodegradable compound, might be an alternative for a more sensitive identification of limitations caused by unfavorable redox conditions. Within this study, the well-described transformation of the X-ray contrast medium iopromide under oxic conditions was investigated for its suitability to serve as an intrinsic redox tracer in different biofiltration systems.

In a third objective, combinations of biological, oxidative and adsorptive treatment technologies were investigated for their potential to achieve an optimized removal of TOrCs from WWTP effluents. Compound-specific differences impede the success of single technology-based solutions to achieve complete removal of TOrCs during advanced treatment. The combination of different treatment mechanisms in hybrid systems is an option to broaden the spectrum of compounds addressed during advanced treatment and overcome limitations encountered in single technology-based systems. Three hybrid systems were chosen which present promising process combinations for effective removal of TOrCs with a broad range of characteristics. Besides an expected increase in removal efficacy due to additive effects in the combination of biological with sorptive and/or oxidative treatment steps, also synergies between the individual processes are hypothesized to allow for an increased process efficiency.

2 State of the art

2.1 Advanced biological treatment

2.1.1 Metabolic strategies in the microbial transformation of xenobiotic substances

Mechanisms for the biological degradation of xenobiotic substances can be categorized in metabolic and cometabolic pathways. In heterotrophic organisms, metabolic degradation of organic substrate serves the purpose of maintaining vital functions including the biosynthesis of cell constituents during growth or reproduction while parts of the substrate are used for energy production via oxidation to carbon dioxide and water (Janke and Fritsche, 1985; Fischer and Majewsky, 2014). Complete degradation of xenobiotic organic compounds, including mineralization, is typically linked to metabolic degradation mechanisms (Janke and Fritsche, 1985). Dalton and Stirling (1982) defined cometabolism as "the transformation of a non-growth substrate in the obligate presence of a growth substrate or another transformable compound".

2.1.1.1 Metabolic degradation of xenobiotic compounds

Metabolic degradation has been identified as a responsible mechanism for the biotransformation of xenobiotic compounds in many cases. Studies on the aerobic degradation of various halogenated aliphatic and aromatic hydrocarbons have suggested metabolic pathways as responsible for their attenuation (Cecen et al., 2010). Several authors observed the metabolic degradation of various pharmaceuticals in different pure and mixed cultures (Tran et al., 2013). In batch experiments with activated sludge, Quintana et al. (2005) reported metabolic degradation of ketoprofen when fed as sole carbon source. Other studies suggested metabolic degradation of the compounds ibuprofen, estradiol, N,N-diethyl-m-toluamide (DEET) or acetaminophen in pure cultures at elevated concentrations in the range of mg/L to g/L (Murdoch and Hay, 2005; Rivera-Cancel et al., 2007; Iasur-Kruh et al., 2011). Early studies on the metabolic transformation of xenobiotic compounds have described a metabolic transformation as the result of fortuitous interactions in the case of high structural analogies between xenobiotic compound and natural substrate while pronounced structural differences hinder the direct metabolism of xenobiotic compounds (Janke and Fritsche, 1985). Also, metabolic transformation of xenobiotic compounds has been described to require concentrations that are sufficiently high to serve as a source of energy and promote growth. At low concentrations in the ng/L to µg/L range, the limited conversion of the available substrate has been assumed to not provide sufficient energy for microorganisms to sustain (McCarty et al., 1981; Kobayashi and Rittmann, 1982). Findings from more recent studies, however, indicated that a metabolic pathway in the degradation of xenobiotic compounds might also contribute to the transformation of xenobiotic compounds at lower concentrations. Baumgarten et al. (2011) observed an improved degradation of the antibiotic sulfamethoxazole when concentrations were increased from a few hundred ng/L to a concentration in the low µg/L range. An adaptation of the transformation efficiency to concentration levels speaks in favor of a metabolic pathway. Also, observations of an increasing degradation potential for the artificial sweetener acesulfame, typically present in the µg/L range, in municipal WWTPs over time, as reported by Kahl et al. (2018), indicate the possibility of an adaptation of the metabolic capability of the microbial community to substrate present at low concentrations.

2.1.1.2 Cometabolic degradation of xenobiotic compounds

In cometabolism, the transformation of a xenobiotic substance is the result of gratuitous interactions with rather unspecific enzymes which do not or only indirectly yield energy for growth for the cometabolizing organism (Alexander, 1981; Arp et al., 2001; Rieger et al., 2002; Tran et al., 2013; Fischer and Majewsky, 2014). Cometabolic transformation of xenobiotics often results in the production of stable intermediates, however, additional sequential breakdown of formed intermediates might be carried out in the following by different organisms in microbial associations (Alexander, 1981; Kobayashi and Rittmann, 1982; Janke and Fritsche, 1985; Rieger et al., 2002).

A distinct differentiation between metabolic and cometabolic mechanisms in the degradation of compounds is not feasible in natural systems. In complex microbial communities, metabolic and cometabolic degradation of xenobiotic substances can occur simultaneously, carried out by different species (Cecen et al., 2010) and might be closely interrelated (Fischer and Majewsky, 2014). Also, adaptation to changing living conditions might lead to the development of new metabolic pathways, thus, turning cometabolic into metabolic degradation mechanisms (Fischer and Majewsky, 2014).

For the cometabolic degradation of a non-growth substrate present at low concentrations, Schmidt et al. (1985) proposed degradation kinetics to follow an exponential pseudo-first-order model:

$$\frac{c}{c_0} = \exp(-k * t) \tag{1}$$

Here c_0 is the initial concentration of a non-growth substrate present at low concentrations, c is the concentration after a reaction time t, and k is the compound-specific first-order rate constant. Biodegradation first-order rate constants have been calculated by various authors to describe the kinetics of biological transformation of individual substances (Zearley and Summers, 2012; Burke et al., 2014; Escolà Casas and Bester, 2015; Hallé et al., 2015; Regnery et al., 2015b). Burke et al. (2014), Regnery et al. (2015b) and Schmidt et al. (2017) demonstrated that observed biodegradation rate constants strongly depend on environmental factors, such as redox conditions. Hallé et al. (2015) critically discussed the use of biodegradation rate constants and observed substantial deviations for constants determined in different experimental setups. While the limited transferability of biodegradation rate constants does not allow for accurate predictions in other systems, they still hold valuable information regarding the degradability of different compounds in an individual system.

2.1.2 *The role of the available primary substrate*

Cometabolic conversion of trace organic chemicals (TOrCs) is linked to the extracellular activity of rather unspecific enzymes targeting the primary substrate present. Although extracellular enzymes were reported to catalyze the transformation of a broader variety of substances with similar structures and functional groups, their function is still adapted for interactions with the primary substrate available. Liu et al. (2013) observed varying pathways during the cometabolic degradation of the compound imidacloprid when different types of available primary substrates, sucrose and succinate, were used. The findings were related to the expression of different cofactors. This suggests that the variety of potential cometabolic conversions is governed by the type and structure of the primary substrate available.

The role of type, degradability and amount of available substrate on the cometabolic transformation of TOrCs has been studied extensively in recent years. Substrate-limited, so-called oligotrophic conditions have been described to foster the establishment of slowly growing but highly adaptable microorganisms, capable of expressing a large variety of enzymes and able to shift metabolic pathways to survive in the presence of very little available substrate (Kobayashi and Rittmann, 1982). Rauch-Williams et al. (2010) observed unexpected and pronounced transformation of several substances in the presence of low biodegradable dissolved organic carbon (BDOC) concentrations which was related to a specialized microbial community growing on a refractory carbon substrate. Using high-throughput sequencing tools, Li et al., (2012) demonstrated the influence of dissolved organic carbon (DOC) concentrations on the structure of microbial communities in the infiltration zone of managed aquifer recharge (MAR) systems. The results indicated a correlation between DOC concentrations and the abundance of *Betaproteobacteria* and *Gammaproteobacteria* while the diversity of the microbial community was negatively correlated to DOC concentrations. The authors concluded that the availability of easily degradable substrate selects for fast-growing microbial groups with high substrate conversion while low amounts of easily degradable substrate promote the growth of organisms capable to also use more refractory carbon sources (Li et al., 2012, 2013). In another study, Li et al. (2014) found a correlation between the humic acid content of the primary substrate and the relative abundance of certain microbial groups, such as *Firmicutes*, *Planctomyces*, and *Actinobacteria* which were also suggested to be capable of an increased transformation of xenobiotics. Accordingly, several studies demonstrated an improved degradation of moderately biodegradable TOrCs in the presence of a mainly refractory substrate (Rauch-Williams et al., 2010; Maeng et al., 2012; Alidina et al., 2014; Regnery et al., 2016; Carpenter and Helbling, 2017; Hellauer et al., 2017a; Wolff et al., 2018). In a recent study, however, Hellauer et al. (2019) found no direct correlation between the low concentrations of refractory, humic acid-like substrate and the degradation of investigated TOrCs.

2.1.3 The role of redox conditions in the biological transformation of trace organic chemicals

Biological degradation of xenobiotic compounds has been found to occur under varying redox conditions. Many studies reported prevailing redox conditions to be of utmost importance for the degradation of individual compounds (Massmann et al., 2008; Wiese et al., 2011; Burke et al., 2014; Regnery et al., 2015b; König et al., 2016; Wolff et al., 2018). While the degradation of some compounds was reported to be rather insensitive towards changing redox conditions, others were found to be highly redox-sensitive indicated by decreasing degradation rate constants or even persistence when redox conditions were unfavorable.

During the bioremediation of contaminated sites dehalogenation of chlorinated hydrocarbons was observed under anaerobic conditions via halorespiration (Cecen et al., 2010). Also, dehalogenation of iodinated X-ray contrast media, such as iopromide, iomeprol, and diatrizoate was only observed under reducing conditions (Kalsch, 1999; Drewes et al., 2001; Redeker et al., 2018). Substantial degradation of the highly persistent antiepileptic drug carbamazepine was found to only occur under anaerobic conditions (Wiese et al., 2011; König et al., 2016). Recent studies by Gonzales-Gil et al. demonstrated the effective biological transformation of several TOrCs which could be linked to the enzymatic activity of microorganisms living under anaerobic conditions (Gonzalez-Gil et al., 2017, 2019b). Besides specific enzymes only expressed under anaerobic conditions, some enzymes enable substance transformation under both, aerobic and anaerobic conditions (Wolff et al., 2018; Gonzalez-Gil et al., 2019b).

Despite successful degradation of several xenobiotic compounds under anaerobic conditions, many studies reported elevated and faster transformation in the presence of sufficient dissolved oxygen for numerous compounds (Greskowiak et al., 2006; Massmann et al., 2008; Baumgarten et al., 2011; Liu et al., 2011; Herzog et al., 2014; Regnery et al., 2015b; Schmidt et al., 2017; Castronovo et al., 2017; Henning et al., 2018). The change in system performance when redox conditions change from oxic to suboxic is yet not fully understood. Slight alterations in dissolved oxygen concentration around a critical threshold of about 1 mg/L have been found to significantly affect the removal of various moderately biodegradable TOrCs (Regnery et al., 2015b).

2.1.4 The role of microbial residence time

The role of microbial residence time in the removal of TOrCs has been investigated in various studies. Mansfeldt et al. (2019) reported a positive correlation between microbial residence times and the taxonomic richness and diversity of active organisms. In conventional activated sludge systems the microbial residence time can be expressed by the solid retention time (SRT) which represents the average residence time of activated sludge in a defined system (Metcalf and Eddy, 2003). Several authors observed an elevated transformation of TOrCs at increasing SRTs (Kreuzinger et al., 2004; Clara et al., 2005; Kim et al., 2005b; Maeng et al., 2013). Achermann et al. (2018b) observed compound-specific differences but reported increasing rate constants for transformations including oxidative reactions. Two factors were frequently discussed to explain this observation: i) At elevated SRTs, also slow-growing and more specialized organisms might be able to establish relevant populations, contributing to a higher diversity of the metabolic potential (Clara et al., 2005; Maeng et al., 2013), and ii) lower substrate availability at higher SRTs might be a driver for changes in the expression of enzymes enabling the degradation of an expanded set of substrates (Maeng et al., 2013).

An observed improved degradation of TOrCs at higher SRTs has often been explained by the activity of autotrophic nitrifiers which require elevated SRTs to develop stable populations. Several studies reported improved degradation of various TOrCs under nitrifying conditions, pointing towards a correlation between the activity of ammonia-oxidizing microorganisms and TOrC degradation (Tran et al., 2009; Fernandez-Fontaina et al., 2012; Helbling et al., 2012; Tran et al., 2013). While findings from Men et al. (2017) supported the importance of ammonia oxidizers in the degradation of some compounds, the authors also suggested a potential overestimation of the influence of ammonia-oxidizing bacteria in previous studies, caused by the use of allylthiourea as an inhibitor of ammonia-oxidizing activity. According to Men et al. (2017), allylthiourea might also affect the activity of other enzymes responsible for the degradation of TOrCs, thus leading to an overprediction of the influence of ammonia-oxidizing bacteria during TOrC degradation. Besides the elevated expression of ammonia monooxygenase by nitrifying organisms also increased abundance and diversity of oxidoreductase enzymes at higher SRTs was suggested to contribute to an enhanced oxidative transformation of TOrCs (Achermann et al., 2018b).

Attached growth systems have been described to be beneficial for the establishment of microbial communities with increased TOrC degradation potential compared to suspended growth systems using activated sludge under comparable operational conditions (Falås et al., 2012, 2013; Johnson et al., 2015; Mansfeldt et al., 2019). Here, the higher microbial residence time in biofilm systems was hypothesized to favor the establishment of slow-growing communities and diversified enzymatic degradation pathways and was suggested as a reason for this observation.

2.1.4.1 Biofilms as advantageous modes of microbial life

Biofilms consist of microbial communities that are embedded in a matrix of self-produced extracellular polymeric substances (EPS) (Flemming et al., 2016). Bacteria in biofilm communities profit from numerous advantages compared to the existence as free-living bacterial cells. Bacteria in biofilm communities exhibit increased tolerance towards environmental factors, such as water stress and antimicrobial agents due to the embedment in the EPS matrix (Flemming and Wingender, 2010; Billings et al., 2015). The EPS matrix allows to capture and store substrate and nutrients by sorption processes (Flemming and Wingender, 2010). The proximity of bacterial cells in biofilms enables the use of cell debris after decay and lysis by surviving cells (Pinchuk et al., 2008). Biofilms represent complex networks in which individual bacterial cells profit from synergistic effects during metabolism by exchanging by-products between species (West et al., 2006), by intercellular signaling (Nealson, 1977; Prindle et al., 2015) or by exchanging genetic material (Hansen et al., 2007). The EPS matrix increases the efficiency of extracellular enzymatic activity by retaining them in the biofilm serving different members of the biofilm community by creating a shared external digestion system (Flemming and Wingender, 2010; Tielen et al., 2013). Due to the heterogenic physiological activities, biofilms can exhibit highly diverse living conditions in proximity, resulting in steep gradients in substrate availability, pH or redox conditions (Chang et al., 2015).

2.1.5 Optimization potential for the biological removal of trace organic chemicals

Studies on the biodegradation of TOrCs in engineered and natural treatment systems demonstrate a broad spectrum of compound degradation patterns. The successful biodegradation of an individual substance was suggested to depend on several parameters. Compound-specific structural characteristics seem to determine the high persistence of some substances towards biological degradation. Despite the high persistence of some xenobiotic compounds, many compounds demonstrate susceptibility to biodegradation to a varying extent. Thus, variations in the efficiency of compound degradation in many cases are most likely related to different operational or environmental conditions. Previous studies emphasized the importance of the available primary substrate and its effect on the formation of the microbial community present. A rather refractory character of the primary carbon source was found to induce the establishment of a more diverse microbial community equipped with increased metabolic potential. Besides, the important role of redox conditions for the biotransformation of TOrCs was highlighted by many authors. In conclusion, the establishment of substrate-limited and oxic conditions was proposed to foster the establishment of a microbial community capable of an enhanced TOrC degradation (Rauch-Williams et al., 2010; Li et al., 2012, 2013, 2014; Alidina et al., 2014; Regnery et al., 2015b). In addition, higher diversity and thus increased metabolic potential for the degradation of TOrCs might be found in microbial communities cultivated in attached growth systems with high microbial residence times (Falås et al., 2012, 2013; Johnson et al., 2015; Achermann et al., 2018b; Mansfeldt et al., 2019).

Based on the identification of the beneficial effects of substrate-limited and oxic conditions on the biodegradation of TOrCs, Regnery et al. (2016) introduced the concept of sequential managed aquifer recharge technology (SMART) in which a short riverbank filtration passage is followed by reaeration and a subsequent infiltration step for aquifer recharge.

Depletion of easily degradable substrate during riverbank filtration induced sequential redox conditions resulting in suboxic to anoxic conditions. Recovery and reaeration resulted in increased dissolved oxygen concentrations allowing for oxic conditions. The subsequent infiltration step was then characterized by largely reduced amounts of the available easily degradable substrate resulting in redox conditions to remain oxic throughout the infiltration. While removal of moderately degradable TOrCs was observed during both, riverbank filtration and subsequent infiltration step, the degradation of various compounds was substantially improved during the second infiltration step, suggesting improved operational conditions for biodegradation of TOrCs. Additional studies at bench-scale (Hellauer et al., 2017b) and a different field-site (Hellauer et al., 2017a) demonstrated that stable substrate-limited and oxic conditions can be established during SMART and confirmed an improved degradation of several substances compared to conditions prevailing in conventional MAR settings.

The establishment of favorable substrate and redox conditions in attached growth systems with high microbial residence times might offer the opportunity of optimized biological mitigation of TOrCs, also, from the effluents of municipal WWTPs.

2.1.6 Biofiltration

Biologically active granular media filters have been commonly used in water and wastewater treatment in many different applications and with varying treatment goals. In biofiltration, a granular filter media, such as sand, anthracite or granular activated carbon, serves as a carrier for the establishment of a biofilm on the surface of the filter material. Biofilters represent biological attached growth systems, the establishment of surface-bound biofilms allows for the transformation or mineralization of inorganic and organic water constituents while the water percolates through the filter.

2.1.6.1 Biofiltration – areas of application in water and wastewater treatment

Granular media filtration is an essential treatment step in the production of drinking water from different raw water sources and is efficient to remove particles from the water phase. Unless measures are taken to impair biological activity by frequent disinfection or backwashing, a microbial community will establish on the filter material, even under oligotrophic conditions (Bouwer and Crowe, 1988). Biological activity in rapid and slow sand drinking water filters has the potential to positively affect the effectivity of the treatment process and the product water quality. The consumption of biodegradable dissolved organic matter (DOM) during biofiltration reduces the amount of substrate in the product water and the risk of undesired microbial growth in drinking water distribution systems (Hozalski et al., 1995; Norton and LeChevallier, 2000). Reducing the amount of DOM also lowers the formation potential for undesired and partly toxic disinfection by-products formed during disinfection (Bouwer and Crowe, 1988). Biological activity in biofilters can also contribute to the oxidation of reduced inorganic compounds, such as iron, manganese or ammonia (Bouwer and Crowe, 1988). Besides, biofiltration has the potential to transform individual organic contaminants such as the naturally occurring taste and odor compounds 2-methylisoborneol and geosmin (Namkung and Rittmann, 1987; Shimabuku et al., 2019) or compounds of anthropogenic origin. Drinking water treatment trains applying ozonation are commonly equipped with subsequent biofiltration to remove easily degradable DOM formed during ozonation (Hozalski et al., 1995; van der Kooij et al., 1989; Ramseier et al., 2011).

During wastewater treatment, filtration has been applied to achieve various treatment goals. Tertiary filtration is used to optimize the removal of suspended solids before discharge into receiving streams. Trickling filters are non-submerged granular media filters filled with rocks or plastic carriers and have been successfully applied for nitrification and the biological removal of DOM for a long time (Metcalf and Eddy, 2003). Besides, also submerged biologically active filters with aerated, non-aerated or fluidized filter beds are used for biodegradation of organic matter, nitrification, and denitrification. Recently, studies also investigated the potential of biofiltration as advanced biological treatment step to achieve an improved removal of xenobiotic compounds (Reungoat et al., 2010; Rattier et al., 2014; Escolà Casas and Bester, 2015; Paredes et al., 2016; Zhang et al., 2017; Sbardella et al., 2018).

2.1.6.2 Factors influencing the performance of biofiltration systems

The performance of biofiltration systems depends on a variety of factors. Some of these factors are design parameters and can be modified, such as the type of filter material, the empty bed contact time, and backwash modalities. Other parameters have been shown to have a strong impact on process performance but cannot be addressed in conventional biofiltration setups, such as the amount and activity of the attached biomass, feed water quality and substrate availability, redox conditions, and temperature.

Filter media

Granular filter materials commonly selected for the application in biofilters are sand, anthracite, granular activated carbon (GAC) or combinations of those. Besides offering surfaces for the establishment of biofilm structures, the filter materials also achieve the retention of particles. Besides, also physicochemical interactions between filter material and water constituents can occur, mainly due to sorption. While the impact of sorption on the removal of DOM, inorganic water constituents and TOrCs is low in filters using sand or anthracite as filter media, GAC is known for its high adsorption capacity (Worch, 2012). Typically, GAC filters allow for effective abiotic removal of adsorbing water constituents at the beginning of the operation. With increasing time of operation, concentrations in the effluents increase due to the saturation of the adsorbent material’s adsorption capacity. However, due to the establishment of microbial activity on the GAC, even after complete exhaustion of the adsorption capacity, concentrations of biodegradable compounds or organic bulk parameters in the filter effluent approximate concentrations lower than those found in the filter influent (Worch, 2012). Even after exhaustion of the adsorption capacity, several studies suggested differences in biofilter performance and characteristics between systems operated with GAC and other, non-adsorbing filter media. Several authors observed improved degradation of organic contaminants especially at cold water conditions in biofilters operated with GAC compared to anthracite even after complete exhaustion of the adsorption capacity (Urfer et al., 1997; Emelko et al., 2006). Despite a generally higher external surface area of smaller sand particles, a better biofilm attachment on the irregular surface of GAC was proposed as a potential reason for the differences (Urfer et al., 1997; Emelko et al., 2006). A recent study, however, found higher removal of xenobiotic compounds in biological filtration systems using sand compared to systems operated with exhausted GAC (Shimabuku et al., 2019). Studies investigating the biological activity in sand, anthracite and GAC filters, were not conclusive regarding correlations between the amount of attached biomass and the type of filter material used (Pharand et al., 2014).

Empty bed contact time (EBCT)

The contact time between water and filter material is an important parameter in the operation of biofilters. For simplification, the contact time in technical filtration systems is usually referred to as empty bed contact time (EBCT) which is defined as the ratio of the filter volume and the flow rate. When comparing filters with different filter media porosities, two filters with the same EBCT might exhibit substantially different hydraulic retention times (HRT). Compared to the hydraulic loading rate the EBCT was found to have a stronger impact on process performance in biofiltration systems. Thus, external mass transfer was assumed to be of minor importance for the removal of biodegradable organic matter (Urfer et al., 1997). Several authors reported only little and disproportional additional effect of increasing EBCTs on the removal of biodegradable organic matter above a certain threshold level (Kramer et al., 1993; Hozalski et al., 1995; Zhang and Huck, 1996; Urfer et al., 1997). While the effect of EBCT on the removal of easily biodegradable organic matter was discussed controversially, different studies have reported an improved removal of TOrCs at elevated EBCTs in biofilters (Zearley and Summers, 2012; Hallé et al., 2015; Escolà Casas and Bester, 2015; Paredes et al., 2016).

Filter backwash

Particle deposition and biomass growth adversely affect the permeability of biofilters after some time of continuous operation. To maintain filter permeability, most technical filter systems are equipped with backwash installations using water, air or water and air simultaneously. Due to increased turbulence and shear stress during backwash, adverse effects on the attached biofilm and subsequent filter performance might be expected. Backwash strategies for biofilters aim at removing particles and excess biomass while maintaining the necessary biofilm attached to the filter media (Ahmad et al., 1998). Several studies have investigated the effect of different backwash modes on the attached biomass and filter performance. Despite the disturbance of the biologically active filter bed during backwash, most authors did not observe negative effects of filter backwash with water and air on biofilter performance regarding the removal of easily degradable organic matter or individual substances (Ahmad et al., 1998; Emelko et al., 2006). The use of chlorinated water for backwash, however, was reported to be detrimental to the performance of biologically active filters (Ahmad et al., 1998).

Measures for the biological activity in biofiltration systems

A successfully operating biofilter requires a stable amount of active biomass attached to the surface of the filter media. In the past, different methods were applied to monitor and quantify biomass and/or biomass activity on filter media, however, complex analytical procedures and the necessity to also quantify nonculturable microorganisms impeded data acquisition (Pharand et al., 2014). While methods such as the quantification of phospholipid concentration are regarded as tools to quantify biomass, they do not distinguish between active and inactive biomass. Monitoring the consumption of dissolved oxygen in biological systems is a simple, but indirect, method to characterize microbial activity, indicated by respiration in aerobic systems. Measuring adenosine triphosphate (ATP) was identified as a suitable method to quantify the amount of active biomass in a biological system and has been applied to measure the viable biomass attached to biofilter media (Pharand et al., 2014). As would be expected, the quantification of ATP in drinking water biofiltration systems revealed an impact of water quality on the amount of viable biomass. Thus, increased amounts of biodegradable organic matter also resulted in higher amounts of viable biomass (Pharand et al., 2014). This goes well along with observations of decreasing amounts of viable biomass with increasing filter depth (Pharand et al., 2014). The consumption of easily degradable substrate in the upper filter layers results in less available substrate and thus lower amounts of biomass in the deeper filter layers. Several studies investigated the effect of different filter media (Wang et al., 1995; Urfer et al., 1997; Emelko et al., 2006; Pharand et al., 2014) or the influence of backwash modalities (Miltner et al., 1995; Ahmad et al., 1998; Emelko et al., 2006) on the amount of attached biomass. The relationship between the amount of viable biomass and filter performance is not yet fully understood. While studies using the phospholipid method for biomass quantification could not correlate the removal of biodegradable organic matter to the biomass concentration, limited data is available from studies measuring ATP (Pharand et al., 2014).

Presence of growth substrate

The growth of heterotrophic microorganisms requires the presence of a carbon source that is available for metabolic activity. In water treatment systems natural organic matter (NOM), including groups such as humic substances, hydrophilic acids, carbohydrates, amino acids, and carboxylic acids, serves as the main growth substrate (Volk and LeChevallier, 2000). Representing a complex mixture of many different chemical groups, NOM can be divided into biodegradable organic matter, accessible for biodegradation, and a refractory part, which is not or only hardly biodegradable. Different methods are used to characterize NOM in water samples. The most common analytical approach to characterize

NOM in water is measuring the amount of total organic carbon (TOC) or dissolved organic carbon (DOC), which also contains information regarding the amount of carbon which is, in theory, available for microorganisms. Further differentiation of biodegradable organic matter distinguishes between assimilable organic carbon (AOC) and biodegradable dissolved organic carbon (BDOC) (Servais et al., 1987; van der Kooij et al., 1982). Here, BDOC is composed of the organic carbon fraction in water which can be mineralized by microorganisms. AOC represents a portion of BDOC which can be converted to cell mass (Huck, 1990). Both, BDOC and AOC, are determined by the use of bioassays after sample sterilization. AOC analysis is carried out by relating the growth yield of a test culture incubated with the water sample to the growth yield observed in cultures incubated with a standard growth substrate at known concentrations. Thus, the observed growth of biomass is converted to AOC via calibration. During BDOC analysis, the test water is fed to an inoculum, which is suspended in the water phase or attached on a solid surface. DOC consumption observed during incubation over a period of several days is then referred to as BDOC (Servais et al., 1987; Volk and LeChevallier, 2000). Determining the parameters BDOC and AOC, various studies could demonstrate substantial differences in the biodegradability of different types of feed water NOM (Huck, 1990; Servais et al., 1987; Volk and LeChevallier, 2000). Thus, the sole determination of absolute concentrations of DOC or TOC might be misleading regarding the amount of bioavailable carbon source in water samples. Introduction of the parameters BDOC and AOC enabled an analytical differentiation between biodegradable and non-biodegradable carbon sources, however, time-consuming analytical procedures must be considered a drawback. Woolschlager and Rittmann (1995) also questioned the significance of AOC and BDOC results for characterization of BOM and critically discussed the importance of soluble microbial products and degradation kinetics for different substrates for BDOC determination, and the use of easily degradable carbon sources as a reference, such as acetate, during AOC analysis.

Availability of nutrients

Besides an accessible carbon source, also the availability of nutrients, such as nitrogen and phosphorous, is essential to establish and maintain biomass and biological activity in biological treatment systems. Effective nutrient removal in WWTPs might decrease nutrient availability in subsequent biological treatment stages to a degree that is detrimental to microbial growth and activity (Dhawan et al., 2016). In case nutrients are absent or present only at very low concentrations in feed waters, the supplementation of nutrients might be an option to improve the performance of biofiltration systems (Basu et al., 2016; Dhawan et al., 2016). Dhawan et al. (2016) observed a slightly increased removal of DOC after supplementation of nitrogen and phosphorous while no correlation was observed between nutrient addition and biomass quantity and activity measured by phospholipid and ATP analysis. Lauderdale et al. (2012) reported positive effects of nutrient enhancement by the addition of an external phosphorus source on biofilter performance. Besides an improved degradation of contaminants, the authors also reported improved hydraulic characteristics after phosphor supplementation due to a decreased production of EPS. In contrast to Dhawan et al. (2016), Lauderdale et al. (2012) also observed increased biological activity after supplementation of nutrients.

Temperature

Temperature has been identified as an important parameter in the operation of biological filter systems. Several authors could demonstrate that decreasing water temperatures negatively affect the removal of organic bulk parameters, such as TOC, and individual organic contaminants (Price et al., 1993; Emelko et al., 2006; Hallé et al., 2015). Hallé et al. (2015) reported a strong effect of temperature on the removal of TOrCs and proposed the use of compound-specific temperature coefficients to estimate the temperature dependent removal of individual substances. The authors also directly correlated temperature with the necessary EBCT to achieve defined treatment targets. At cold temperatures, also the activity of nitrifying bacteria is limited (Rocher et al., 2012). Measuring phospholipids as a parameter for the amount of viable biomass in biofilters, Emelko et al. (2006) reported decreasing amounts of biomass when temperatures decreased. However, Pharand et al. (2014) did not observe an effect of temperature on the biomass concentrations when using ATP as a parameter to quantify viable biomass. In general, the performance of biological filters using GAC as filter media was found to be less sensitive towards decreasing temperatures (Price et al., 1993; Emelko et al., 2006; Krasner, 2009).

2.2 Oxidative treatment using ozonation

Ozonation has been applied in both, drinking water and wastewater treatment to achieve different treatment goals. In drinking water treatment schemes, ozonation is used for the oxidation of NOM constituents, the removal of taste and odor compounds, and organic chemicals. Ozone also holds the advantage of achieving very effective disinfection for many different pathogens (von Gunten, 2003). In recent years, ozonation has been discussed and implemented as an additional treatment step during municipal wastewater treatment when aiming for improved removal of TOrCs from WWTP effluents (Ternes et al., 2003; Huber et al., 2005; Hollender et al., 2009).

Oxidative reactions during ozonation can be attributed to two mechanisms, the direct reaction with ozone and the indirect reaction with hydroxyl radicals formed during the decomposition of ozone in water and the reaction with matrix components. The direct reaction with ozone is very selective and dependent on the existence of moieties with high electron densities in compounds. Second-order reaction rate constants (k_{O3}) exhibit a wide range over several orders of magnitude (von Sonntag and von Gunten, 2012). Indirect reactions caused by hydroxyl radicals are characterized by low selectivity and generally very high reaction rate constants (k_{OH}). The low selectivity of the indirect reaction also results in the transformation of compounds which are not susceptible to the direct reaction with ozone. The oxidative transformation during ozonation depends on compound-specific reaction rate constants and the oxidant exposure (Lee et al., 2013):

$$\ln \frac{c}{c_0} = -k_{O_3} \int c_{O_3}\, dt - k_{OH} \int c_{OH}\, dt \qquad (2)$$

Ozonation is very effective for the oxidation of many different TOrCs in WWTP effluent (Ternes et al., 2003; Huber et al., 2005; Hollender et al., 2009). However, due to the presence of high amounts of DOM, much of its oxidative potential is lost. This is reflected in the normalization of the applied ozone dosage to DOC concentrations, defined as the specific ozone dosage (mg O_3/mg DOC), which has been demonstrated to be a suitable approach to predict the matrix-dependent transformation of compounds in WWTP effluent (Lee et al., 2013). For the removal of TOrCs from WWTP effluents, usual specific ozone dosages were reported to be in the range of 0.4 to 0.6 mg O_3/mg DOC (Rizzo et al., 2019). Besides organic scavengers, the presence of nitrite substantially reduces the oxidation potential during ozonation and must be accounted for (Stapf et al., 2016).

Oxidation results in the transformation of precursor compounds and does not achieve complete mineralization. Many studies reported an increasing amount of BDOC, caused by the oxidative transformation of DOM during ozonation. Studies indicated a linear correlation between the amount of AOC formed and the specific ozone dose until dosage values of 1 to 2 mg O_3/mg TOC (Janssens et al., 1985; van der Kooij et al., 1989). The increase in BDOC requires biological post-treatment to stabilize the product water (Świetlik et al., 2009; Stalter et al., 2010; Ramseier et al., 2011; Thayanukul et al., 2013). Oxidative reactions with organic and inorganic water matrix constituents also result in the formation of undesired organic and inorganic by-products which might be of toxicological relevance (Griffini et al., 1999; von Gunten, 2003; Wert et al., 2007; Hübner et al., 2013b; Bourgin et al., 2018). While various organic by-products were shown to be sufficiently removed during posterior biological treatment (Hollender et al., 2009; Bourgin et al., 2018), the removal of the inorganic and carcinogenic by-product bromate, has been reported to depend on the presence of sufficient substrate and low concentrations of dissolved oxygen and nitrate (Kirisits et al., 2001; Wang et al., 2018). However, at specific ozone doses usually applied for the removal of TOrCs from WWTP effluent (0.4 to 0.6 mg O_3/mg DOC), the formation of bromate was reported to be limited at bromide concentrations typically present in WWTP effluent (Rizzo et al., 2019).

2.3 Adsorptive treatment using activated carbon

Activated carbon is known for its high porosity and large surface area, enabling interactions and retention of dissolved water constituents. Activated carbon is applied as powdered activated carbon (PAC) with particle sizes < 40 µm or in fixed-bed adsorbers as granular activated carbon (GAC) with grain sizes in the range of 0.5 to 4 mm (Worch, 2012). Adsorption characteristics of activated carbons can vary based on the source material used and the manufacturing process (Zietzschmann et al., 2014a).

The use of activated carbon in water treatment has a long tradition. In drinking water production, activated carbon has been applied to remove taste and odor compounds, and organic pollutants from source waters (Worch, 2012; Summers et al., 2013; Kennedy et al., 2015). Many studies could also demonstrate effective removal of TOrCs from WWTP effluents by the application of activated carbon (Nowotny et al., 2007; Boehler et al., 2012; Altmann et al., 2016; Benstoem et al., 2017). Unlike oxidative treatment, adsorption processes hold the benefit of removing a target substance from the water phase without the formation of undesired by-products of unknown toxicological relevance. Competitive adsorption of DOM reduces the adsorption capacity for compounds primarily targeted during treatment. While in drinking water treatment, removal of NOM holds the benefit of reducing the formation potential of disinfection by-products in subsequent disinfection steps (Worch, 2012), high amounts of DOM present in WWTP effluent strongly reduce the available adsorption capacity and negatively affect process efficiency (Corwin et al., 2011; Boehler et al., 2012; Summers et al., 2013; Zietzschmann et al., 2014b). Especially low and medium weight fractions of DOM were found to have a negative impact on the adsorption capacity of activated carbon for TOrCs (Zietzschmann et al., 2014c, 2016). The adsorption of substances onto activated carbon also depends on compound characteristics, such as hydrophobicity, size, structure, and charge (Worch, 2012). Thus, highly polar compounds show only weak interactions with the activated carbon surface and cannot be effectively removed from the liquid phase.

2.4 Combination of advanced water treatment technologies in hybrid systems

TOrCs present in WWTP effluents exhibit a large variety of chemical properties. Different compound characteristics imply high fluctuations in removal efficiencies for individual compounds during different stages of water treatment. While unpolar or moderately polar compounds might undergo substantial elimination due to sorption during conventional wastewater treatment or advanced treatment applying adsorption onto activated carbon, highly polar compounds remain rather unaffected in the water phase. The efficiency of oxidative removal using ozone is highly dependent on molecule properties. While the formation of hydroxyl radicals also results in unspecific oxidative reactions, the direct oxidation with ozone is highly selective and requires the presence of electron-rich moieties in the targeted molecule. The chemical structure also plays a major role in a molecule’s susceptibility to biodegradation. Microbial degradation can only occur when molecule structure and functional groups enable an enzymatic attack. Even though the variety of enzymatic structures and metabolic activities is highly dependent on environmental or operational conditions, some substances exhibit a generally very high persistence to biological transformation.

Compound-specific differences impede the suitability of single technology-based solutions to achieve complete removal of TOrCs during treatment. The combination of different processes in multi-barrier treatment schemes, also referred to as hybrid systems, is an option to broaden the spectrum of compounds addressed during advanced treatment and overcome limitations encountered in single technology-based systems (Sudhakaran et al., 2013). The removal of TOrCs in multi-barrier treatment systems profits from increased process reliability, which is achieved by redundancy and increased process robustness. Besides increasing the number of contaminants which can be addressed during treatment, also synergies between different treatment steps can be exploited, increasing overall process efficacy and efficiency. Also, process combinations can contribute to abate potential adverse or undesired effects arising during treatment.

Many studies investigated the combination of oxidative and biological treatment options in various applications and with different treatment goals. The coupling of ozonation with posterior biological treatment in engineered biofilters using non-adsorptive filter media, such as sand or anthracite, or soil aquifer treatment has been applied in many different full-scale applications and studied extensively. To remove BDOC and avoid regrowth in distribution systems, biofiltration has been commonly applied after ozonation during drinking water treatment (van der Kooij et al., 1989; Price et al., 1993). The application of ozone for advanced treatment of municipal wastewaters aiming for improved removal of TOrCs is commonly complemented by a subsequent biofiltration step to achieve biologically stabilized product water. Biological post-treatment of ozonated water has also been shown to have the potential to mitigate undesired and potentially toxic oxidation by-products, such as aldehydes and nitrosamines (Kramer et al., 1993; Coffey et al., 1996; Griffini et al., 1999; Krasner, 2009; Gerrity et al., 2015; Bacaro et al., 2019). While the carcinogenic oxidation by-product bromate was found to be stable under oxic conditions, biological transformation was observed under reducing conditions (Kirisits et al., 2001; Hübner et al., 2015a; Wang et al., 2018). Concerning TOrC removal, biological post-treatment can enhance the degradation of compounds which are only partially or not transformed during ozonation. For instance, ozonation only results in a limited transformation of the X-ray contrast medium iopromide which does not react directly with ozone but is only transformed indirectly via the radical pathway (Hollender et al., 2009), whereas biological degradation was observed under suitable conditions (Schulz et al., 2008). In return, ozonation achieves transformation of many compounds which are known for their high persistence to biodegradation, such as the antiepileptic drug carbamazepine (Huber et al., 2005; Hollender et al., 2009). Biological post-treatment has also been found effective to remove certain transformation products originating from the oxidative transformation of TOrCs during ozonation (Hübner et al., 2013b, 2015b). Studies on the effect of ozonation on specific toxicological effects such as endocrine disruption, genotoxicity, antibacterial and antiviral activity, revealed decreased effects after ozonation of WWTP effluent (Huber et al., 2004; Suarez et al., 2007; Dodd et al., 2009; Reungoat et al., 2010; Mestankova et al., 2012). Elevated genotoxicity and non-specific toxicity caused by ozonation was reported in some studies (Rosal et al., 2009; Stalter et al., 2010; Prasse et al., 2012; Magdeburg et al., 2014). Subsequent biofiltration, however, was found effective to further reduce the effects after ozonation (Stalter et al., 2010; Reungoat et al., 2010, 2012).

The combination of ozonation with posterior biological treatment over non-adsorptive filter media is an example for a hybrid system with beneficial additive and synergistic effects. The combination is suitable to increase the overall performance of the treatment scheme, regarding the removal of TOrCs, TOrC transformation products, oxidation by-products, and an improved removal of bulk organic parameters caused by the enhanced biodegradability of DOM constituents after ozonation. When ozonation is complemented with subsequent biofiltration over adsorptive filter media, such as granular activated carbon, additional beneficial effects might occur and are discussed in the following paragraph. The presence of DOM substantially reduces the oxidative potential of ozone for the transformation of TOrCs in secondary WWTP effluents. Improved biological pre-treatment is an option to lower the amounts of DOM, resulting in an improved ozonation efficiency. De Wilt et al. (2018) proposed to use biological pre-treatment to remove degradable organic matter from secondary effluent to increase ozonation efficiency. Decreased ozone demands were observed when feed waters were pre-treated by biofiltration or in natural treatment systems (Hübner et al., 2012; Yoon et al., 2013; Zucker et al., 2015b). Extended biological pre-treatment by biofiltration was also reported to reduce the formation potential of toxicologically relevant oxidation by-products by an improved removal of precursor compounds (Farré et al., 2011; McKie et al., 2015; Marti et al., 2017).

The combination of adsorptive with biological and/or oxidative technologies has the potential to increase process efficacy due to the implementation of an additional treatment barrier and removal mechanism which broadens the spectrum of compounds addressed during advanced treatment. Besides beneficial additive effects caused by combining adsorption with other advanced treatment steps, also synergistic effects might arise. Low efficiency caused by competitive adsorption of DOM components is considered the main drawback in the application of activated carbon for TOrC removal from feed waters rich in DOM (Corwin et al., 2011; Worch, 2012; Summers et al., 2013; Zietzschmann et al., 2014b). Previous research indicated that pre-treatment using other advanced treatment technologies might be an option to lower the negative impact of competitive adsorption on process efficiency. Optimized biological pre-treatment holds promise to reduce the amount of DOM by increasing the degradation or even the mineralization of organic components and might contribute to an improved adsorption capacity for TOrCs. Hozalski et al. (1995) proposed biological pre-treatment via biofiltration as an option to reduce the negative effect of competitive adsorption of organic matter which might result in improved exploitation of adsorption capacity for TOrC removal. The combination of activated carbon with pre-treatment by ozonation might also profit from synergistic effects. While ozonation does not achieve substantial removal of DOM via mineralization, it induces changes in molecule structures resulting in increased polarity. An increase in polarity reduces the adsorbability of organic matrix components and, thus, reduces the impact of competitive adsorption. Zietzschmann et al. (2015) observed an improved adsorption capacity for the removal of TOrCs in WWTP effluent after ozonation which was explained by reduced hydrophobicity, molecular size and aromaticity of water matrix DOM. Thus, the alteration of the structural character of DOM could be an option to achieve increased process efficiency.

Combinations of biological, oxidative and adsorptive advanced treatment technologies have the potential to eliminate a large variety of different TOrCs with a broad range of different physicochemical characteristics. However, combining several treatment steps increases process complexity and necessarily results in higher costs of investment and operation. Besides an application for the removal of TOrCs from WWTP effluents, advanced water treatment hybrid systems might also be applicable in treatment scenarios in which higher water quality standards need to be met.

3 Research significance and hypotheses

The widespread occurrence of trace organic chemicals (TOrCs) in the aquatic environment has been recognized as a potential threat to ecosystems and human health. The establishment of additional and advanced technical barriers in municipal wastewater treatment plants (WWTPs) is necessary to mitigate the entry of TOrCs into the receiving water bodies. Besides established advanced treatment technologies, such as adsorptive or oxidative processes, also the suitability of additional biological treatment, specially designed for an improved TOrC removal, is discussed.

3.1 Objective #1: Development of a novel sequential biofiltration concept that aims for enhanced removal of trace organic chemicals from wastewater treatment plant effluent

Transferring the positive experiences from sequential managed aquifer recharge (SMART) systems into engineered biological above-ground treatment systems, this study's first objective was to develop a novel concept for biofiltration allowing for the establishment of oxic and oligotrophic conditions at drastically reduced empty bed contact times (EBCTs) compared to managed aquifer recharge applications. A biofiltration concept was envisioned which uses the sequential approach applied in SMART. A first filter stage was intended to remove the easily degradable substrate from the feed water allowing for oxic and oligotrophic conditions in the subsequent second filter stage. The operational conditions established during sequential biofiltration (SBF) aim at fostering a microbial community capable of enhanced TOrC removal while EBCTs are in the range of hours compared to days or even weeks in managed aquifer recharge applications.

For the systematic investigation of **Objective #1**, the following hypothesis was tested:

Hypothesis #1: *Enhanced attenuation of moderately biodegradable TOrCs as observed in sequentially operated managed aquifer recharge applications can also be achieved in engineered filtration systems with shortened EBCTs*

To test **Hypothesis #1** a stepwise approach using three sub-hypotheses was proposed. In a first step, the system's ability to establish the targeted operating conditions for enhanced removal of TOrCs was tested. To guarantee oxic and oligotrophic conditions in the second filter stage, sufficient removal of easily degradable substrate must be achieved in the first stage. While an efficient reduction of easily degradable compounds has been observed in managed aquifer recharge applications, the considerably shorter EBCTs in the proposed technical biofiltration systems are challenging. However, an optimized first stage biofilter might be suitable to achieve enhanced removal of easily degradable substrate:

Hypothesis #1.1: *Oxic and oligotrophic conditions can be established with drastically reduced EBCTs compared to managed aquifer recharge applications*

The second step aimed at testing the benefits that arise from the novel SBF approach considering TOrC removal in biofiltration processes. To investigate a potential increase in removal efficiency, system performance had to be compared with a conventional biofiltration unit operated at the same EBCT:

Hypothesis #1.2: *Operating conditions established during sequential biofiltration result in enhanced removal of TOrCs compared to a single-stage biofiltration system with similar EBCTs*

Lastly, the impact of EBCT on TOrC removal under the desired conditions was investigated. While the performance of technical biofiltration systems is believed to not be dependent on EBCT in the first place, EBCT might play a key role once desired operating conditions are established. Especially compounds with low biodegradation rate constants would profit from increased EBCT when oxic and oligotrophic conditions prevail:

Hypothesis #1.3: *EBCT is a key parameter controlling the removal of TOrCs in biofiltration under oxic and oligotrophic conditions*

3.2 Objective #2: Characterization of redox conditions during biofiltration using known iopromide transformation products as intrinsic redox tracers

Monitoring the redox-dependent succession of well-described transformation products of certain indicator compounds could be a suitable strategy to predict redox-sensitive biodegradation of TOrCs in biofiltration systems. Schulz et al. (2008) proposed a transformation pathway for the oxic biodegradation of the iodinated contrast media iopromide and different identified biological transformation products. Muntau et al. (2016) suggested using the abundance of specific known iopromide intermediates for an improved *in situ* characterization of redox conditions relevant for the TOrC degradation efficiency during soil-aquifer treatment

The idea to use iopromide transformation products as intrinsic redox tracers during soil-aquifer treatment motivated the attempt for a better characterization of redox conditions in biofiltration systems with reduced hydraulic retention times.

Systematic investigation of **Objective #2** involved testing of **Hypothesis #2**:

Hypothesis #2: *The use of known iopromide transformation products as intrinsic redox tracers allows for a sensitive characterization of in situ redox conditions in oxic to suboxic environments during biofiltration*

To test **Hypothesis #2** different aspects were to be investigated as expressed in two sub-hypotheses. The correlation between the redox-dependent abundance of certain iopromide transformation products and the removal of other redox-sensitive TOrCs had to be proven:

***Hypothesis #2.1*: The removal efficacy for redox-sensitive TOrCs can be correlated to the formation and fate of different iopromide transformation products**

Given the verification of **Hypothesis #2.1**, monitoring iopromide transformation products would allow for the characterization of operational conditions during SBF and conventional single-stage biofiltration. Assuming predominantly oxic conditions during SBF and oxygen limitations in the deeper zones of a single-stage biofiltration unit, a higher degree of iopromide transformation is expected during SBF. In **Hypothesis #2.2** we proposed:

***Hypothesis #2.2*: The transformation of iopromide indicates improved redox conditions for the removal of redox-sensitive TOrCs during sequential biofiltration compared with single-stage biofiltration**

3.3 Objective #3: Investigation of synergies in sequential biofiltration-based hybrid systems aiming for improved removal of trace organic chemicals from wastewater treatment plant effluent

Combining SBF with intermediate ozonation might result in increased process performance by additive and synergistic effects. Removal of dissolved organic matter (DOM) in the first stage SBF filter would likely result in higher ozonation efficiency due to higher removal of TOrCs at the same ozone dosage applied. At a constant specific ozone dosage, the process would most likely profit from an improved cost-efficiency due to lower energy demands for the production of ozone. The hybridization of SBF and an intermediate ozonation step is believed to allow for a significant reduction of DOM before ozonation, while the second filter stage could serve as the necessary biological post-treatment to remove biodegradable dissolved organic carbon (BDOC) and transformation products formed during ozonation. However, oxic and carbon-limited conditions need to be maintained to support the degradation of non-reactive compounds.

Combining SBF with subsequent Granular activated carbon (GAC) filtration might have the potential to significantly reduce competitive adsorption. The biodegradation of a substantial portion of DOM during SBF might increase TOrC adsorption capacities in equilibrium and might result in prolonged GAC filter lifetimes. SBF aims for the establishment of carbon starving conditions resulting in the depletion of BDOC in the first filter stage. Conditions established in the second filter stage might even be suitable to induce the removal of more refractory DOM constituents. The removal of biodegradable DOM fractions will result in a reduction of competitive adsorption. Replacing the intermediate aeration with pressurized air by an oxidation step using ozone could further decrease the amount of competitive adsorbing DOM. BDOC formed during ozonation would most likely be consumed in the second filter stage resulting in even lower amounts of background DOM present in the GAC filter. An increase in polarity of remaining DOM after ozonation could furthermore decrease the adsorbability of DOM.

To scrutinize the potential of SBF-based hybrid systems, **Objective #3** was split into two main hypotheses (**Hypotheses #3** and **#4**). The first main hypothesis dealt with the combination of SBF and intermediate ozonation. Regarding potential benefits we hypothesized:

Hypothesis #3*: The use of sequential biofiltration with an intermediate ozonation step allows for a reduced ozone demand without jeopardizing the establishment of oxic and oligotrophic conditions in the second filter stage*

For a detailed investigation **Hypothesis #3** was further split into two sub-hypotheses. The first sub-hypothesis addressed the effect of the first stage biofilter on the efficiency of the ozonation step. By reducing the amount of DOM present, an increased efficiency of TOrC removal was expected during ozonation compared to the ozonation of untreated secondary effluent:

Hypothesis #3.1: *Biodegradation of BDOC in the first stage of a sequential biofiltration setup results in a significantly lower ozone demand for the reduction of TOrCs compared with untreated WWTP effluent*

The second sub-hypothesis focused on the effects intermediate ozonation would have on the targeted oligotrophic conditions in the second filter stage. We assumed:

Hypothesis #3.2: *The establishment of oxic and oligotrophic conditions in the second filter stage is not endangered by intermediate ozonation*

The second main hypothesis addressed a hybrid system composed of SBF with intermediate aeration or ozonation and subsequent GAC filtration. An advanced biological treatment step before GAC filtration was supposed to increase the efficiency of the adsorption step due to reduced competitive adsorption of background DOM. We hypothesized:

Hypothesis #4: *Sequential biofiltration with intermediate aeration using air or ozone increases the efficiency of subsequent granular activated carbon filtration by reducing competitive adsorption of background organic matter*

For a detailed investigation also **Hypothesis #4** was further split into two sub-hypotheses. In a first sub-hypothesis, the effect of SBF on the adsorbability of TOrCs and DOC in equilibrium was addressed:

Hypothesis #4.1: *The pre-treatment of secondary effluent by sequential biofiltration reduces competitive adsorption of DOC and results in a higher adsorption capacity for TOrCs in equilibrium*

A second sub-hypothesis focused on the impact a pre-treatment by SBF would have on the breakthrough behavior in small-scale columns. We assumed that:

<u>Hypothesis #4.2</u>: *The pre-treatment of secondary effluent by sequential biofiltration with intermediate aeration or ozonation significantly increases granular activated carbon filter lifetimes for TOrC removal*

3.4 Structure of the dissertation

This thesis has a cumulative structure and comprises a collection of five articles that were published or are in preparation for publication in peer-reviewed journals (section 10.1.1 contains an overview and states author contributions). Each publication is presented as an individual chapter in which the work on the formulated research objectives is demonstrated. In the following, the structure of the dissertation is introduced and summarized in Figure 3-1.

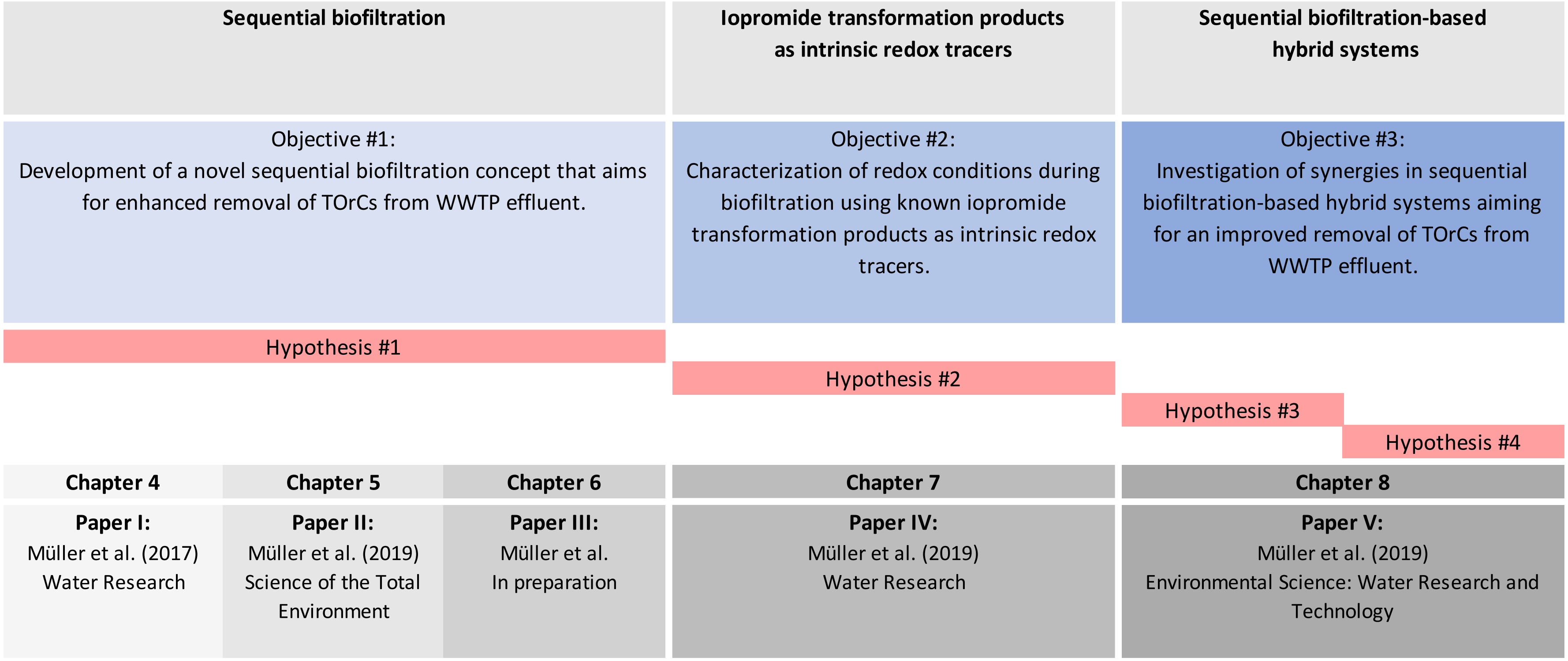
The works carried out related to research **Hypothesis #1**, *"Enhanced attenuation of moderately biodegradable TOrCs as observed in sequentially operated managed aquifer recharge applications can also be achieved in engineered filtration systems with shortened EBCTs"*, are described in Chapters 4 to 6. Chapter 4 introduces the concept of sequential biofiltration (SBF), and its derivation from sequential managed aquifer recharge. The chapter contains a detailed description of the pilot-scale system and a characterization of the start-up period and describes elaborate monitoring which was performed to properly characterize the operational conditions, especially regarding the manipulation of redox conditions and substrate availability, as suggested in **Hypothesis #1.1**. To test **Hypothesis #1.2**, the performance of an SBF system was further compared to a conventional, single-stage biofilter, operated at the same overall empty bed contact time (EBCT). Additional short-term testings aimed at the investigation of the impact of EBCT in the first filter stage of an SBF system on system performance. To test **Hypothesis #1.3**, the impact of the EBCT in the second filter stage of an SBF system was tested in long-term experiments in test columns operated in parallel.

Chapter 5 describes efforts to further optimize the SBF concept. Following up on the experiments described in Chapter 4, the impact of shorter EBCTs in the first filter stage was investigated over longer periods. Pre-treatment of the WWTP effluent by sweep floc coagulation using elevated concentrations of Fe(III) salts was investigated as an option to further decrease substrate availability. Besides, the compatibility of enhanced phosphorous removal caused by sweep flocculation with subsequent SBF was investigated.

Results presented in Chapter 6 validate the results obtained for **Hypotheses #1.1**, **#1.2** and **#1.3** in Chapter 4 by monitoring the degradability of an extended set of indicator TOrCs in sequential and single-stage biofiltration systems. Sampling in different column depths enabled an improved characterization of compound degradation profiles in the different columns. Pseudo-first-order rate constants were determined to compare degradation kinetics in column systems with different operational conditions regarding EBCT, substrate availability and redox conditions.

Chapter 7 presents investigations to test **Hypothesis #2**, "*The use of known iopromide transformation products as intrinsic redox tracers allows for a sensitive characterization of in situ redox conditions in oxic to suboxic environments during biofiltration". The chapter presents an approach for an alternative characterization of *in situ* redox conditions during biofiltration using known transformation products of the X-ray contrast medium iopromide as intrinsic redox tracers. To test **Hypotheses #2.1** and **#2.2**, the investigations involved column experiments with SBF systems operated at different EBCTs and a conventional, single-stage biofilter. The investigation also aimed at linking the successive transformation of iopromide to the initial transformation of other biodegradable indicator TOrCs.

Chapter 8 presents investigations to test **Hypothesis #3**, *"The use of sequential biofiltration with an intermediate ozonation step allows for a reduced ozone demand without jeopardizing the establishment of oxic and oligotrophic conditions in the second filter stage."* and **Hypothesis #4,** *"Sequential biofiltration with intermediate aeration using air or ozone increases the efficiency of subsequent granular activated carbon filtration by reducing competitive adsorption of background organic matter"*. Different SBF-based process combinations were tested for their suitability to achieve enhanced removal of TOrCs from WWTP effluents, including SBF with intermediate ozonation, and SBF with or without intermediate ozonation combined with subsequent activated carbon filtration. Here, investigations focused on synergistic effects between the treatment steps. To test a potential beneficial effect of biological pre-treatment on ozonation efficiency, as suggested in **Hypothesis #3.1**, ozonation experiments were carried out in semi-batch. Testing **Hypothesis #3.2**, column experiments were conducted to investigate the effect of pre-ozonation on oxic and oligotrophic operational conditions during subsequent biofiltration. The effect of biological pre-treatment on the adsorption capacity of activated carbon for TOrCs in equilibrium, as addressed in **Hypothesis #4.1**, was investigated using batch tests. Effects of biological or biological-oxidative pre-treatment on the breakthrough behavior of activated carbon adsorbers, as suggested by **Hypothesis #4.2** were investigated using rapid small-scale column tests.



Sequential biofiltration			**Iopromide transformation products as intrinsic redox tracers**	**Sequential biofiltration-based hybrid systems**
Objective #1: Development of a novel sequential biofiltration concept that aims for enhanced removal of TOrCs from WWTP effluent.			Objective #2: Characterization of redox conditions during biofiltration using known iopromide transformation products as intrinsic redox tracers.	Objective #3: Investigation of synergies in sequential biofiltration-based hybrid systems aiming for an improved removal of TOrCs from WWTP effluent.
Hypothesis #1			Hypothesis #2	Hypothesis #3 Hypothesis #4
Chapter 4	**Chapter 5**	**Chapter 6**	**Chapter 7**	**Chapter 8**
Paper I: Müller et al. (2017) Water Research	**Paper II:** Müller et al. (2019) Science of the Total Environment	**Paper III:** Müller et al. In preparation	**Paper IV:** Müller et al. (2019) Water Research	**Paper V:** Müller et al. (2019) Environmental Science: Water Research and Technology

Figure 3-1: Structure of the dissertation

4 Sequential biofiltration – a novel approach for enhanced biological removal of trace organic chemicals from wastewater treatment plant effluent

The following chapter presents investigations related to ***Hypothesis #1:*** *Enhanced attenuation of moderately biodegradable trace organic chemicals as observed in sequentially operated managed aquifer recharge applications can also be achieved in engineered filtration systems with shortened empty bed contact times.*

Besides a detailed description of the sequential biofiltration (SBF) pilot-scale system and a characterization of the start-up period, results from extensive monitoring are presented which was carried out to properly characterize the operational conditions, especially regarding the targeted manipulation of redox conditions and substrate availability, as suggested in **Hypothesis #1.1**. To test **Hypothesis #1.2**, the performance of an SBF system was further compared to a conventional, single-stage biofilter, operated at the same overall empty bed contact time (EBCT). Short-term testings aimed at the investigation of the impact of EBCT in the first filter stage of an SBF system on system performance. To test **Hypothesis #1.3**, the impact of the EBCT in the second filter stage of an SBF system was tested in long-term experiments in test columns operated in parallel.

The chapter has been published with editorial changes as follows:

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Author contributions: Johann Müller, Uwe Hübner and Jörg E. Drewes developed the research objective and designed the experiment. Johann Müller constructed the experimental setup, conducted the experiments and the analyses and wrote the paper. Jörg E. Drewes and Uwe Hübner supervised the study and reviewed the manuscript. All authors approved the final version of the manuscript.

Sequential biofiltration – a novel approach for enhanced biological removal of trace organic chemicals from wastewater treatment plant effluent

Abstract

Recent studies revealed the benefits of oligotrophic and oxic conditions for the biological removal of many trace organic chemicals (TOrCs) during soil-aquifer treatment. These findings indicate an unused tuning potential that might also be applicable in engineered biofiltration systems with drastically reduced hydraulic retention times for an enhanced mitigation of TOrCs during wastewater treatment. This study introduces the novel approach of sequential biofiltration (SBF) for the advanced treatment of secondary effluent using two granular media filters operated in series with an intermediate aeration step aiming for oxic and oligotrophic conditions in the second filter stage. Results from the experiments conducted at pilot-scale confirm a reduced substrate availability and predominantly oxic conditions in the second filter stage of the SBF setup. An increased removal of several TOrCs was observed in an SBF system as compared to a conventional single-stage biofiltration unit operated at the same overall empty bed contact time (EBCT). Short-term tests with varying EBCTs in the first filter stage revealed a high degree of system robustness of TOrC mitigation when confronted with sudden hydraulic load variations. Higher removal of several TOrCs at increased EBCTs in the second filter stage indicates that EBCT might play a crucial role for the degradation of certain compounds.

4.1 Introduction

The occurrence of trace organic chemicals (TOrCs), such as pharmaceutical residues, industrial chemicals and personal care products at low concentrations in all parts of the water cycle has been subject to extensive studies in the field of water research (Ternes, 2007; Benotti et al., 2009; Dong et al., 2015). While ecotoxicological effects were reported in several studies, direct toxic effects on human health seem unlikely (Schriks et al., 2010; National Research Council, 2012), however, little is known about potential adverse effects arising from long-term exposures to trace amounts of many different chemicals (Cuklev et al., 2011; Stuart et al., 2012; Brodin et al., 2013; Wilkinson et al., 2016).

Wastewater treatment plants (WWTPs) have been identified as major point sources for the discharge of TOrCs into the aquatic environment (Ternes, 2007; Dong et al., 2015). Processes applied in conventional wastewater treatment are mostly based on activated sludge systems aiming for an effective biological removal of bulk organic parameters and nutrients. However, these processes often fall short to achieve efficient reduction of TOrCs which often exhibit a high degree of persistence during treatment (Joss et al., 2006; Vieno et al., 2007; Falås et al., 2016).

In recent years, many studies have investigated different technologies for their applicability as advanced treatment options for the removal of TOrCs during water treatment. Most studies dealing with advanced treatment technologies focused on sorption onto activated carbon, different oxidation processes such as ozonation or UV based advanced oxidation processes and membrane filtration. Adsorptive and oxidative processes and high-pressure membrane filtration have been shown to be effective for the removal of many different TOrCs from WWTP effluent. Drawbacks of these technologies, however, are increasing costs of operation, reduced efficiencies due to the high competition of organic matter present, the formation of undesired by-products, or insufficient rejection of low-molecular compounds (von Gunten, 2003; Fujioka et al., 2012; Zietzschmann et al., 2014b; Sgroi et al., 2016). In contrast, advanced biological treatment systems have received less attention. This might be due to the fact that biological TOrC removal during the treatment in conventional WWTPs is often limited (Joss et al., 2006; Vieno et al., 2007; Falås et al., 2016) and highly dependent on their susceptibility to biodegradation considering typical operating conditions of conventional activated sludge systems. In the light of unsatisfactory removal rates during conventional wastewater treatment, biological processes might appear as unsuitable options for an improved removal of TOrCs.

While experiences with engineered biological above-ground systems for the aim of TOrC removal are rare, many studies have examined the fate of TOrCs in natural treatment systems such as managed aquifer recharge applications (Grünheid et al., 2005; Onesios et al., 2009; Benotti et al., 2012; Onesios and Bouwer, 2012; Hoppe-Jones et al., 2012; Regnery et al., 2015a; Hamann et al., 2016). Recent studies identified key parameters that were found to be favorable for biological TOrC removal. Redox conditions have been shown to have a significant effect on the removal of many different TOrCs. Several authors reported an increased and accelerated removal of TOrCs in the presence of sufficient levels of dissolved oxygen (DO) (Baumgarten et al., 2011; Massmann et al., 2008; Regnery et al., 2015b) while only few compounds were reported to exhibit higher removal under reducing conditions (Wiese et al., 2011; König et al., 2016). Considering the low concentrations of TOrCs in environmental settings, many studies suggest cometabolism to be the dominant mechanism for biological removal (Onesios et al., 2009; Tran et al., 2013). Observed dependency of biological TOrC removal on the concentration and composition of the available organic carbon support this assumption (Li et al., 2012, 2013, 2014; Alidina et al., 2014). However, other authors reported threshold values (Wiese et al., 2011) and extended adaptation periods (Baumgarten et al., 2011) suggesting the importance of metabolic activity for the degradation of TOrCs. Li et al. (2012) applied next-generation high-throughput sequencing and revealed that the makeup of the primary substrate present affects the structure and function of investigated microbial communities. Under conditions with a predominantly refractory primary substrate a higher microbial diversity was found to be established than under conditions characterized by higher amounts of easily degradable substrate (Li et al., 2012, 2013, 2014; Alidina et al., 2014). A more refractory primary substrate is believed to shape a biocommunity by triggering an upregulation of enzymes which are able to transform even hardly degradable substances. As a consequence, an increased removal of TOrCs has been reported under carbon-starving conditions (Alidina et al., 2014).

These findings indicate that the biodegradation of TOrCs is highly dependent on proper environmental conditions. The establishment of oxic redox conditions and oligotrophic primary substrate conditions measured as biodegradable dissolved organic carbon (BDOC) suggests an unused tuning potential for the biological removal of compounds which exhibit a higher degree of persistence in conventional biological treatment systems.

Translating these favorable conditions into an engineered solution has resulted in sequential managed aquifer recharge technology (SMART), in which a sequential infiltration approach is used to establish oxic and oligotrophic conditions during groundwater recharge (Regnery et al., 2016). A source water which might be rich in BDOC is infiltrated in a first infiltration step. Microbial degradation of BDOC leads to rapid oxygen depletion and increasingly reducing redox conditions. After recovery of the water, passive re-aeration supplies oxygen to the water before it is infiltrated again in a second infiltration stage. After depletion of BDOC in the first filter stage and re-aeration, oxic and oligotrophic conditions can be maintained in the second infiltration stage. Regarding the targeted TOrC removal, results indicated significantly improved attenuation of several TOrCs compared to conventionally operated managed aquifer recharge systems (Regnery et al., 2016). The findings from Regnery et al. (2016) revealed that this relatively simple change in operating conditions is suitable to tune biological systems for an enhanced removal of compounds which exhibit a high degree of persistence in conventional WWTPs and managed aquifer recharge applications. Sequential infiltration techniques during aquifer recharge prior to drinking water production have also been used in waterworks in Germany (e.g. Echthausen, Halingen) and France (Flins-Aubergenville), often in combination with other treatment processes. Major objectives were to optimize removal of organic carbon and to minimize sludge production and oxidant demand in drinking water filters, but also an improved removal of organic contaminants was recognized.

As demonstrated in SMART, the optimization of biological treatment systems for an enhanced removal of substances which undergo only limited mitigation during conventional managed aquifer recharge is possible without necessarily resulting in the employment of energy-intensive processes. The promising results obtained in SMART systems motivated the quest for options to utilize the approach in engineered biological above-ground treatment systems which could be applied as advanced treatment steps subsequent to conventional wastewater treatment.

Transferring the positive experiences from SMART into engineered biological above-ground treatment systems, this study's objective was to develop a novel concept for biofiltration allowing for the establishment of oxic and oligotrophic conditions while empty bed contact times (EBCTs) are drastically reduced compared to managed aquifer recharge applications. A biofiltration concept is envisioned which uses the sequential approach applied in SMART. A first filter stage is intended to remove easily degradable substrate from the feed water allowing for oxic and oligotrophic conditions in a subsequent second filter stage. By establishing these conditions, we hypothesize that enhanced attenuation of several TOrCs, as observed in SMART applications, can also be achieved in engineered filtration systems with shortened EBCTs.

4.2 Materials and methods

4.2.1 Experimental setup

The experimental setup consisted of five filter columns at pilot-scale operated under saturated top-down flow conditions. Two backwashable filter columns (A1 and A2, filter bed length (l) = 1 m, inner diameter (ID) = 0.15 m) were operated with anthracite as filter material with grain sizes ranging from 1.4 to 2.5 mm (Everzit N type II, Evers GmbH, Germany). Three columns (S1, S2 and S3, l = 0.95 m, ID = 0.10 m) were filled with technical sand with grain sizes ranging from 0.2 to 1.0 mm (Euroquarz GmbH, Germany) and were inoculated with 5 % aquifer material originating from a river bank filtration site. Two-stage sequential biofiltration trains consisted of a first stage anthracite and a second stage sand filter operated in series. An intermediate aeration basin resupplied oxygen to the water treated in the first filter stage using compressed air. Figure 4-1 exemplarily shows the setup of a SBF train as used within this study. All filter trains were fed with fully nitrified tertiary effluent from a WWTP located in Garching, Germany. TOrCs that were investigated in this study were not spiked to the system but were present in the tertiary effluent used. Peristaltic pumps were used to deliver the water to the column systems. Column EBCTs were set by adjusting the flowrates at the column outlets. To prevent filter clogging due to the deposition of particulate matter during operation, columns A1 and A2 were backwashed gently, using pressurized air and drinking water. The frequency of backwashing events varied due to differing feed water characteristics but was in the range of 4 to 6 weeks. After backwash events, the system was given at least 7 days for re-equilibration before sampling.

4.2.2 Operational conditions

Operational conditions and settings were varied in order to investigate the different aspects addressed in this study. After the adjustment of new conditions, filters were operated at least 8 weeks before sampling to allow for equilibration. This did not apply for the experiments discussed in section 4.3.4 in which the effect of sudden variations in hydraulic loading rates on the first filter stage was investigated in short-term testings.

- For system characterization and monitoring of the establishment of biological activity (section 4.3.1), data from two SBF systems (A1+S1 and A2+S2) are shown. First stage filters A1 and A2 were operated at an EBCT of 90 min, second stage filters S1 and S2 were operated at an EBCT of 200 min.

- To compare a SBF system to a single-stage biofilter (section 4.3.2), the flow rate of the first stage filter A2 was adjusted to operate with an overall EBCT of 290 min, while the SBF system was not changed (A1: 90 min; S1: 200 min).
- To investigate the influence of the EBCT in the second stage filter (section 4.3.3), three SBF systems were operated (A1+S1, A1+S2, A1+S3). While first stage filter A1 was operated at an EBCT of 90 min, second stage filters S1, S2 and S3 were operated at EBCTs of 200, 1,000 and 2,000 min respectively.
- To investigate the effect of sudden load variations on the first stage filter of the SBF system (section 4.3.4) two SBF systems (A1+S1 and A2+S2) were operated in parallel. While EBCTs in A1 were varied (30, 45, 60, 90, 150 min), EBCTs in A2 (90 min) and S1 and S2 (both 200 min) were held constant.

A detailed overview of all experimental conditions and a timeline are given in Figure SI-1 and Table SI-1.

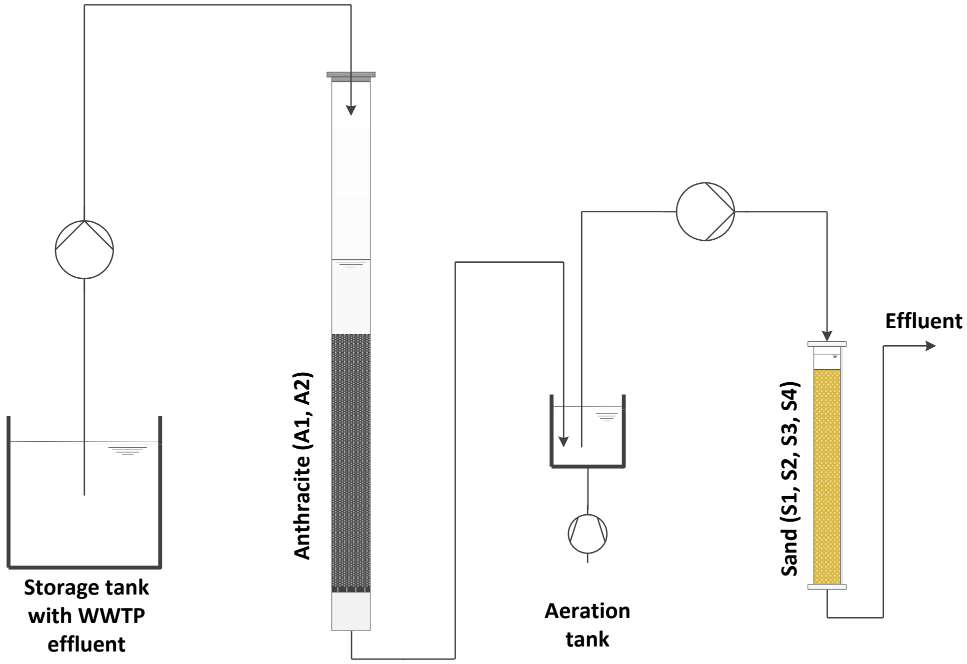

Figure 4-1: Exemplary setup of a sequential biofiltration (SBF) train.

4.2.3 Sample collection and analysis

For ammonia, nitrate, organic bulk parameters and TOrC analyses corresponding water samples were collected at the inlet and outlet of the filter columns accounting for the hydraulic retention time. Samples for ammonia, nitrate and organic bulk parameters were collected in pre-rinsed amber glass bottles to minimize analyte losses due to sorption or photo-degradation. Performance of BDOC and dissolved organic matter removal in the biofiltration systems was assessed by monitoring changes in UV absorbance at 254 nm (UVA_{254}) and DOC. Samples were filtered immediately after sampling using 0.45 µm cellulose acetate membrane filters. Analysis of UVA_{254} was carried out on the same day of sampling, DOC samples were acidified to a pH of 2 using hydrochloric acid, stored at 4°C and analyzed within three days after sampling. For UVA_{254} measurements a DR 6000 UV/vis Spectrophotometer (HACH, Germany) was used, DOC analyses were carried out using a vario TOC cube (elementar, Germany). The specific UV absorbance (SUVA) was calculated as the ratio of the UV absorbance at 254 nm (1/m) and the DOC concentration (mg/L). Samples for the analysis of TOrCs were collected in pre-rinsed 20 mL amber glass bottles and closed with PTFE-lined caps. Samples were processed according to the method described below. If the measurement could not be carried out within three days after sampling, samples were stored at -20°C. Redox conditions in the filtration systems were monitored by measuring dissolved oxygen (DO), ammonia and nitrate concentrations. A PreSens Fibox 4 was used to determine DO concentrations in the inlet and outlet and at different heights of the columns (A1, A2: 10, 30, 50, 70, 90 cm; S1, S2, S3: 10, 30, 50, 70 cm). The system was equipped with a flow-through cell (FTC-PSt3, PreSens, Germany) for the determination of DO concentrations at different heights of the anthracite filters and in the inlet and outlet of the filters whereas sand filters were equipped with oxygen sensor spots (SP-PSt3, PreSens, Germany) allowing for non-invasive oxygen measurements. Cuvette tests and a DR 6000 UV/vis Spectrophotometer were used to determine concentrations of ammonia (LCK 304, HACH-Lange, Germany) and nitrate (LCK 339, HACH-Lange, Germany) in the inlet and outlet of selected filter columns immediately after sampling.

4.2.4 Analysis of trace organic compounds

Trace organic compounds were measured using liquid chromatography coupled with tandem mass spectrometry (LC-MS/MS) with direct injection. Isotope dilution was used to account for matrix suppression and instrument variability following a method described by Vanderford and Snyder (2006).

Prior to measurement, 1,900 µL of sample were spiked with 100 µL of an aqueous 10 ppb isotope labelled standard mix, filtered using 0.22 µm PVDF membrane filters, and stored in 2 mL amber glass vials. Calibration standards were prepared covering a calibration range from 1 to 10,000 ppt. A Knauer PLATINBLUE UHPLC unit (Knauer, Germany) consisting of a degasser, a binary pump, an autosampler, a column oven (column temperature set to 30° C) and an analytical column (XSelect HSS T3 (particle size 2.5 µm; 2.1 x 100 mm), Waters, Germany) were used for the chromatographic separation of the analytes. An injection volume of 100 µL was used for the direct injection of the samples. Mass spectrometric analyses were carried out using a QTRAP 5500 or a TQUAD 6500 mass spectrometer (SCIEX, USA) in positive and negative electrospray ionization (ESI) mode. Binary gradient methods were used to deliver two mobile phases for analyses in ESI positive (A: water containing 0.2 % formic acid; B: acetonitrile) and negative mode (A: water containing 2 mM ammonium acetate; B: acetonitrile) at a flowrate of 0.5 mL/min.

For identification and quantitation, a minimum of two characteristic MS/MS transitions were selected for natural analytes and one for the corresponding isotope labelled standards.

Method detection limits and limits of quantification (LOQs) were determined in drinking water matrix based on a method described by Ripp (1996). Nine standard replicates were prepared at different concentration levels (10, 25, 50, 100, 250, 500, 1,000, 2,500, 5,000 ppt). The standard deviation within a set of replicates was determined and the estimated signal to noise ratio was calculated as mean value over standard deviation. Method detection limits were calculated using the standard deviation of a set of replicates for which the estimated signal to noise ratio was between 2.5 and 10, multiplying it with the student t-value for nine replicates. LOQs were calculated as ten times the standard deviation of the set of replicates identified as described before. In addition to that, the minimum ratio between the signal in standard and blank was set to be at least ten for the quantifier and three for the qualifier transition. To guarantee the conservative nature of the stated values, LOQs in use were set to the next standard concentration level above the calculated LOQs.

More detailed information on chromatographic gradients can be found in Table SI-2. Table SI-3 summarizes compound specific chromatographic retention times, MS settings, such as selected transitions, collision cell and source parameters (declustering potential, collision energy, cell exit potential), and LOQs used in this study.

4.2.5 Definition of redox conditions

Redox conditions are classified based on DO and nitrate measurements according to definitions from Regnery et al. (2015b) and McMahon and Chapelle (2008). Filters with effluent DO above 1 mg/L are defined as oxic. Suboxic conditions are characterized by DO concentrations below 1 mg/l but only limited nitrate reduction (< 0.5 mg N/L) whereas anoxic conditions are present when nitrate reduction exceeds 0.5 mg N/L.

4.2.6 Statistical analysis

Two-tailed, paired Student's t-tests were used to assess the statistical significance of observed differences between two related data sets. In the following, a significant difference was observed if $p < 0.05$. The standard deviation was used as a measure of variability.

4.3 Results and discussion

4.3.1 System characterization and establishment of biological activity

To characterize system performance and the establishment of biological activity during the maturation period, organic bulk parameters and the removal of selected TOrCs were monitored. Increasing biological activity in the filter systems was indicated by increasing removal of DOC and UVA_{254} within the first 100 days (Figure 4-2). After 100 days of operation columns A1 and A2 yielded a mean removal of 21 ± 7 % of the influent DOC and a mean reduction of 10 ± 3 % of influent UVA$_{254}$. After passing through columns S1 and S2, 34 ± 6 % of the influent DOC and 16 ± 3 % of the influent UVA$_{254}$ were removed. Comparing the removal of DOC and UVA$_{254}$ in the first and second filter stage, significantly higher removal was observed in first stage columns A1 and A2 which might be explained by a decreased availability of easily degradable substrate in second stage filters S1 and S2. In deeper zones of columns A1 and A2, oxygen concentrations occasionally were found to be well below 1 mg/L, depending on variations in feed water characteristics. Columns S1 and S2 could be characterized as oxic (> 2 mg/L) even though EBCTs in the second filter stage were more than a two-fold higher than in the first filter stage. Denitrification was not observed at any time with nitrate concentrations remaining at a stable level throughout the study (data not shown).

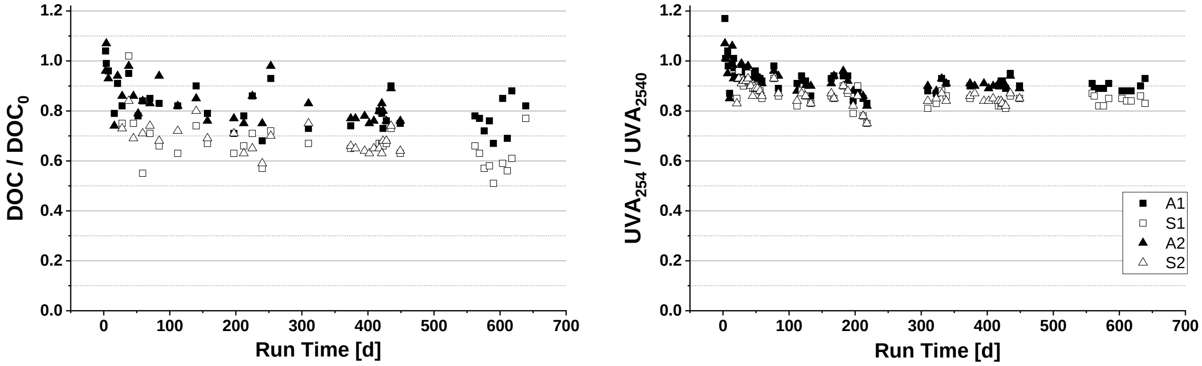

Figure 4-2: Relative residual concentration of DOC and UVA$_{254}$ in SBF systems (normalized to feed concentration in corresponding WWTP effluent samples) during 639 days of operation; data shown for two SBF systems, each comprised of a first stage filter (A1, A2) and a second stage filter (S1, S2); EBCTs in A1 and A2 90 min, in S1 and S2 200 min; mean values in WWTP effluent: DOC 6.9 ± 1.8 mg/L (n = 31), UVA$_{254}$ 13.4 ± 2.9 1/m (n = 37).

The removal of four exemplarily chosen TOrCs during the first 639 days of operation revealed compound specific differences in system performance and microbial adaptation (Figure 4-3). During the first 310 days of system operation the corrosion inhibitor benzotriazole showed only little removal in first stage filters A1 and A2 (9 ± 7 %) whereas attenuation steadily increased in second stage columns S1 and S2 until a relatively stable overall removal of 82 ± 10 % was achieved after approximately 150 days. Benzotriazole removal in filters A1 and A2 slightly improved to 32 ± 12 % between day 310 and day 639 of operation. However, major removal of benzotriazole was restricted to transformation in filters S1 and S2. Feed water composition seemed to have an impact on benzotriazole removal. Day 435 of operation was characterized by unusually high DOC concentrations in the filter influent causing rapid DO depletion and a drop in benzotriazole removal efficiency in first and second stage filters. In most cases, however, the sequential approach proved suitable to buffer varying feed water characteristics and allow for a rather stable overall removal of benzotriazole.

System adaptation for the removal of the beta blocker metoprolol was found to be rather slow, especially in second stage filters S1 and S2 (Figure 4-3). Compared to benzotriazole, less distinct differences were observed within the first 500 days between the two filter stages. Recent data, however, indicate increasing biodegradation in the second filter stage resulting in an increased overall removal (56 ± 7 %).

The nonsteroidal anti-inflammatory drug diclofenac was found to show only limited removal in the SBF system (Figure 4-3). After 200 days of system operation overall removal was unstable and fluctuating between 5 and 40 %. Poor removal of diclofenac in the sequential system contradicts the results obtained during SMART from Regnery et al. (2016). Here diclofenac was found to be highly susceptible to degradation under oxic and oligotrophic conditions. Other than for benzotriazole and metoprolol, only little additional removal of diclofenac was observed in the second stage filters.

For the anti-epileptic drug carbamazepine, no removal could be observed in both filter stages which goes well along with results found in various other studies confirming the high persistence of carbamazepine (Vieno et al., 2007; Zearley and Summers, 2012; Hallé et al., 2015).

For the two nonsteroidal anti-inflammatory drugs ibuprofen and naproxen (data not shown) the adaptation period was found to be short in both filter stages. Instantaneous and complete removal was observed for ibuprofen in first stage columns A1 and A2. Naproxen was removed completely and instantaneously in second stage filters S1 and S2, degradation in first stage columns A1 and A2 increased steadily until substantial removal was observed after 300 days (66 ± 7 %).

While the removal of the bulk organic parameters DOC and UVA_{254} was relatively constant after a maturation phase of about 100 days, adaptation phases for several TOrCs proved to be longer. Evaluating the adaptation of a biofiltration system designed for TOrC removal solely upon the removal efficiency for bulk organic parameters might therefore lead to false assumptions.

To evaluate the biodegradation of TOrCs in granular media filters, compound retention due to sorption must be considered a potential cause for observed attenuation effects. For the system at hand, however, a major contribution of sorption to the overall removal of compounds appears unlikely. In laboratory-scale column studies using anthracite as filter material, Rattier et al. (2014) found no significant removal for 33 TOrCs when columns were inhibited with sodium azide. Results from column studies conducted by Bertelkamp et al. (2014) using technical sand as filter material showed only negligible abiotic removal of 17 investigated TOrCs. The removal patterns of benzotriazole and carbamazepine over time support these observations (Figure 4-3). Carbamazepine has been reported to be susceptible to retardation by sorption under certain conditions (Mersmann et al., 2002;

Chefetz et al., 2008). However, the data acquired suggest no significant degree of retardation of carbamazepine throughout the experiments. The removal pattern of benzotriazole indicates increasing removal efficiencies in the first and second stage filters over time which is typical for biodegradation but untypical for sorption.

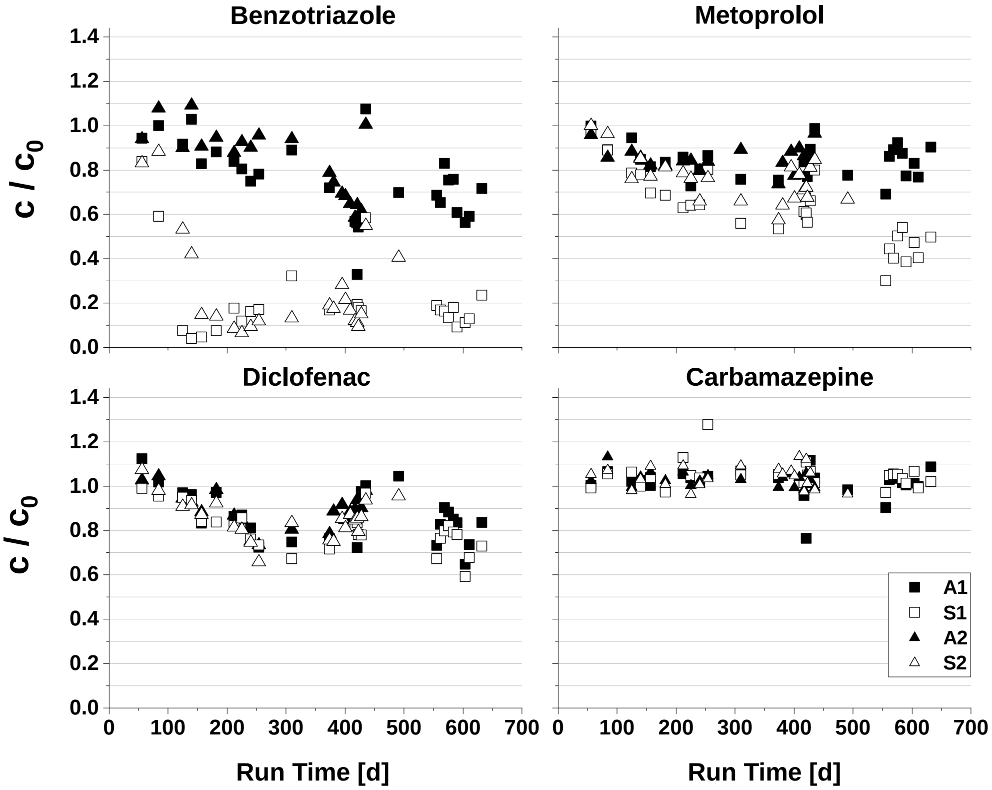

Figure 4-3: Long-term monitoring of the removal of benzotriazole, metoprolol, diclofenac and carbamazepine during 639 days of operation in the sequential biofiltration system. Data display removal normalized to the concentrations measured in WWTP effluent used as feed water to filters A1 and A2, both operated at an EBCT of 90 min. Second stage filters S1 and S2 were operated at an EBCT of 200 min.; c_0 [ng/L]: benzotriazole 4,890 ± 1,510; metoprolol 410 ± 310; diclofenac 1,700 ± 720; carbamazepine 410 ± 100.

Although the sand in the second stage filters was inoculated with biologically active aquifer material, no distinctively higher removal of DOC and UVA_{254} was observed at the beginning of the operation when compared to the first stage filters which were not inoculated. Advantages in adaptation for TOrC removal in the second compared to the first stage columns due to the inoculum in the beginning of the operation cannot be excluded, considering the faster adaptation of second stage filters S1 and S2 for the removal of various compounds such as benzotriazole, naproxen and ibuprofen. After the first year of operation, however, a stable removal of these compounds could also be observed in first stage filters A1 and A2 leading to the assumption that the effect of the inoculum could be neglected in the following. The seed inoculum might have helped to outweigh the lack of primary substrate in the second filter stage, needed to establish microbial activity in a rather short period.

4.3.2 Comparison of conventional single-stage and sequential biofiltration

The different modes of operation affect DO consumption and bulk organic removal in the filter systems. The DO profiles in both, single-stage biofilter A2 and first stage filter A1 of the SBF system indicate rapid DO depletion due to simultaneous BDOC degradation (Figures 4-4a and 4-5a). The DO data suggest that microbial activity leading to BDOC and DO consumption correlates well with the travel time in the systems but is rather independent from the filter bed depth. This might indicate a rather homogeneous distribution of microbial activity over the full length of filters A1 and A2, possibly fostered by the regular backwash events which induce slight vertical mixing of the filter bed. However, to verify this hypothesis additional analyses of the microbial community in different depths of filters A1 and A2 are necessary. DOC data exhibit insignificantly increased DOC consumption in column A2 compared to A1 (2.0 ± 0.5 mg/L and 1.9 ± 0.7 mg/L DOC) even though contact times are a threefold higher in column A2 (Figure 4-5). This indicates that DOC consumption in both anthracite filters is rather independent from EBCT but is influenced by other factors such as prevailing redox conditions. A simplified mass balance for the consumption of DO and DOC was calculated, assuming a stoichiometric ratio of 1 mole O_2/mole C (2.7 mg DO/mg DOC) for complete DOC mineralization. The mass balance for A2 and A1 shows values slightly higher than the stoichiometric ratio (3.5 ± 1.2 and 3.0 ± 0.9 mg DO/mg DOC) which might be due to additional consumption of DO for the oxidation of double bonds or aromatic structures without leading to mineralization. UVA_{254} data reveal significantly higher reduction in A2 compared to A1 (1.8 ± 0.1 and 1.4 ± 0.2 1/m UVA_{254}). Fast consumption of BDOC and DO depletion within the first 90 min of EBCT results in suboxic conditions in deeper zones of A2 whereas the intermediate aeration in the SBF system leads to an increase in DO concentration close to saturation. The DO consumption in the second stage filter S1 decreases with increasing column depth reaching DO concentrations of approximately 5 mg/L in the column effluent (Figure 4-4a) The stagnation of DO consumption in the deeper zones of second stage filter S1 can be explained by decreased availability of easily degradable substrate. The DOC consumption in both filters supports this assumption. Though filter S1 operates at a higher EBCT than A1, consumption of DOC and UVA_{254} is significantly reduced (0.9 ± 0.7 mg/L DOC; 0.7 ± 0.3 1/m UVA_{254}). Comparing the overall reduction of bulk organic parameters in the sequential and single-stage system, significantly higher DOC and UVA_{254} removal was noticed in the SBF system (45 % and 12 %, respectively) though overall EBCTs are similar. This can be explained by DO limitations in the deeper zones of single-stage column A2 whereas oxic conditions leading to more favorable conditions for organic matter transformation are provided in the SBF system due to the intermediate aeration.

Regarding changes in dissolved organic matter characteristics during the treatment SUVA can be used to qualitatively monitor changes in aromaticity (Weishaar et al., 2003). SUVA values reveal an increasing aromaticity throughout the process (Figure 4-5c), supporting the assumption that preferably non-aromatic dissolved organic matter constituents are removed during biodegradation (Hansen et al., 2016). A slight but significant incline was found for SUVA values from WWTP effluent to the values found in the effluent of filters A1, A2 and S1. Similar DOC consumption but significantly higher UVA_{254} removal in A2 compared to A1 are also reflected in slightly higher SUVA values found in the effluent of A2.

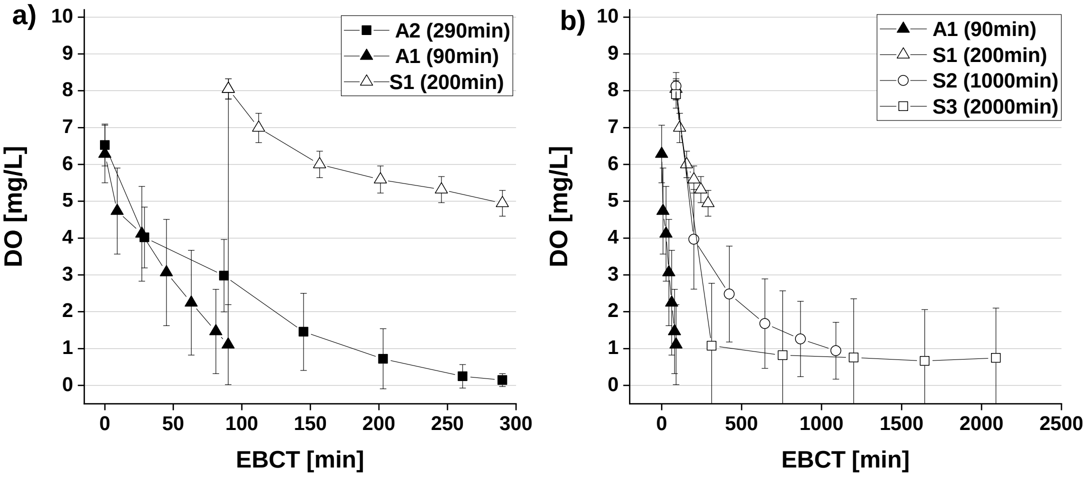

Figure 4-4: DO profiles (n = 11) a) in single-stage filter A2 and SBF system (A1+S1) at a similar overall EBCT of 290 min and b) in SBF with different EBCTs in the second stage filters S1, S2 and S3 (200, 1,000, 2,000 min). EBCT in the first stage filter A1 was held constant at 90 min.

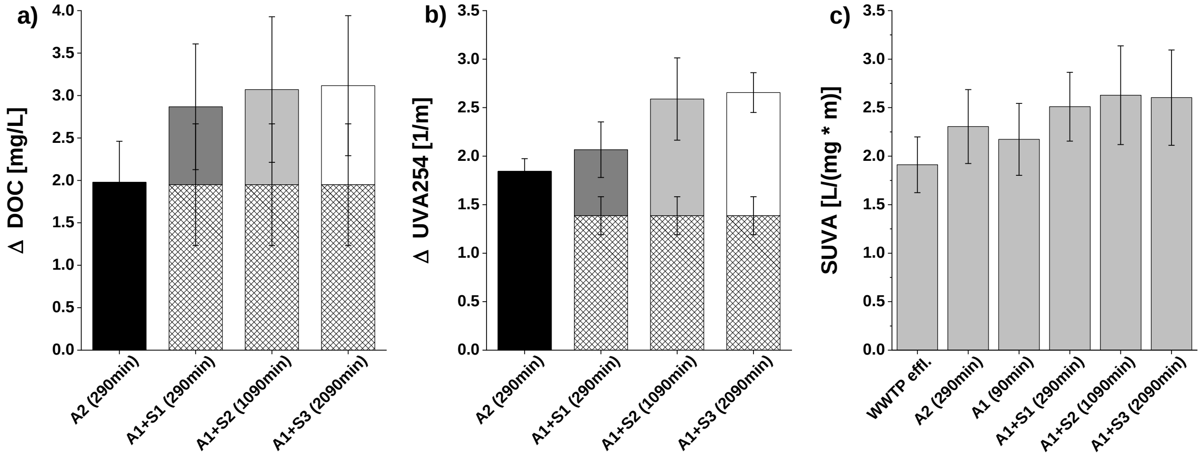

Figure 4-5: Consumption of a) DOC and b) UVA_{254} in single-stage and SBF systems at varying EBCTs in the second stage filters S1, S2 and S3 (200, 1,000, 2,000 min) and c) SUVA in WWTP and filter effluents; mean influent values: DOC 7.1 ± 1.0 mg/L, UVA_{254} 12.9 ± 0.7 1/m; n = 9.

To compare the removal of TOrCs during sequential and single-stage biofiltration, a set of indicator TOrCs was monitored. Although contained in the analytical method, the following compounds are not further considered during this investigation: caffeine and iopromide were found in only three out of nine WWTP effluent samples (caffeine 350 ± 40 ng/L, iopromide 260 ± 140 ng/L) and were always removed below LOQ in the effluents of A1 and A2. Detected concentrations for the compounds phenytoin and TCEP in the WWTP effluent were always found to be below LOQ. The compounds naproxen, gemfibrozil, and ibuprofen were not measured during this investigation.

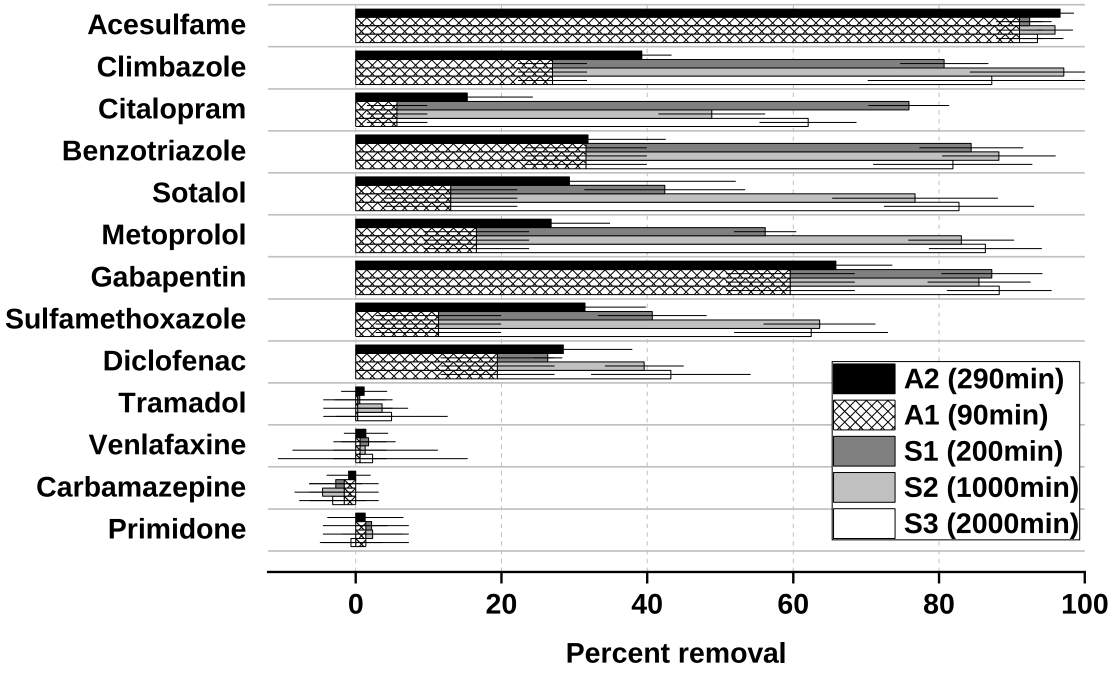

Figure 4-6: TOrC removal during SBF and single-stage biofiltration; data show filter effluents normalized to corresponding WWTP effluent, SBF data shown for different EBCTs in second stage filters S1, S2 and S3 (200, 1,000 and 2,000 min); c_0 [ng/L]: acesulfame 2,440 ± 450. climbazole 140 ± 20, citalopram 160 ± 30, benzotriazole 4,310 ± 230, sotalol 63 ± 14, metoprolol 230 ± 30, gabapentin 1,970 ± 210, sulfamethoxazole 130 ± 50, diclofenac 1,300 ± 350, tramadol 250 ± 10, venlafaxine 320 ± 30, carbamazepine 400 ± 40, primidone 81 ± 18; n = 9 (acesulfame n = 6).

Regarding TOrC attenuation in the two systems substantial differences were observed (Figure 4-6). Despite higher EBCTs in column A2 compared with A1, comparable removal efficiencies were found for the targeted contaminants. The threefold increase in EBCT in A2 compared to A1 did not result in substantially higher TOrC removal. Comparing the single-stage and sequential biofiltration systems, both at overall EBCTs of 290 min, significantly higher removal in the latter for the compounds climbazole, citalopram, benzotriazole, metoprolol, gabapentin, and sulfamethoxazole was observed. No improved removal could be measured for diclofenac. Tramadol, venlafaxine, carbamazepine, and primidone (not shown) were persistent in both, the single-stage and the sequential system.

Lower TOrC removal in single-stage filter A2 can be linked to unfavorable environmental conditions for the microbial degradation of refractory compounds. The presence of easily degradable organic matter in the upper layers of the filter results in rapid DO depletion and predominantly suboxic conditions in the deeper zones of the filter (Figure 4-4a) which have been described to be disadvantageous for the microbial degradation of many TOrCs (Massmann et al., 2008; Baumgarten et al., 2011; Regnery et al., 2015b).

4.3.3 Variation of empty bed contact time in the second filter stage

The results presented above limit a direct correlation between EBCT and TOrC removal efficiency when comparing two different biofiltration systems (Figure 4-6). To investigate the influence of EBCT on TOrC removal under the conditions established in the second filter stage, three SBF systems were operated in parallel while maintaining a constant EBCT of 90 min in the first stage filter A1 and varying EBCTs in second stage filters S1, S2 and S3 (i.e., 200; 1,000; 2,000 min).

Increased EBCTs in second stage columns S1, S2 and S3 were found to have a slight but not significant effect on the removal of DOC (Figure 4-5a). Interestingly, the reduction of UVA_{254} in FS2 seems to be more dependent on EBCT, thus, consumption of UVA_{254} was significantly elevated at the higher EBCTs of 1,000 and 2,000 min (1.2 ± 0.4 and 1.3 ± 0.2 1/m compared to 0.7 ± 0.3 1/m at 200 min) (Figure 4-5b). Higher removal of UVA_{254}, however, indicates an increased conversion of aromatic moieties which could be attributed to an adapted microbial community with an increased capability of transforming also refractory aromatic structures while complete mineralization is not achieved. The degradation of these rather complex dissolved organic matter constituents might be more dependent on EBCT which could explain enhanced UVA_{254} removal at higher EBCTs in the second filter stage. Higher EBCTs and increased UVA_{254} consumptions resulted in stabilized SUVA values in the effluents of columns S2 and S3 (Figure 4-5c). (Regnery et al., 2016) found disproportional removal of UVA_{254} during the second infiltration stage in a full-scale SMART application resulting in declining SUVA values. However, this was not observed in the second stage filters used in this study.

DO concentration profiles acquired in the second stage columns with EBCTs of 1,000 and 2,000 min exhibit increased DO consumptions compared to the second stage filter operated at 200 min (Figure 4-4b). While DO concentrations in filter S1 with an EBCT of 200 min indicated stable oxic conditions throughout the column, filters S2 and S3 operated at EBCTs of 1,000 and 2,000 min exhibited significantly lower and fluctuating DO concentrations. Especially filter S3 was characterized by rapid DO depletion and predominantly suboxic conditions. Here, DO consumption stagnated at low concentration levels which likely depended on variations in feed water quality. The significantly increased DO consumption is also reflected in the mass balance for the consumed DO and DOC in the second stage columns which revealed substantially lower values in filter S1 (2.6 ± 3.2 mg DO/mg DOC) compared to the columns S2 and S3 (4.7 ± 5.4 and 4.1 ± 5.0

mg DO/mg DOC respectively). The reason for the observed increased DO consumption at higher EBCTs in the second filter stage remained unclear. DO profiles acquired in columns S1, S2 and S3 (Figure 4-4b) might indicate increased microbial activity in the upper layers of the columns. At higher EBCTs of 1,000 and 2,000 min in S2 and S3 this stratification might have caused the observed differences in DO profiles due to varying residence times in the zones with high microbial activity. Also, the elevated removal of UVA_{254} in columns S2 and S3 (Figure 4-5b) might be correlated to an additional consumption of DO for the oxidation of double bonds or aromatic structures without leading to complete mineralization, which could explain the observed slightly higher DOC consumption.

Regarding the removal of TOrCs in the second filter stage, increased removal efficiencies at higher EBCTs were found for metoprolol, sulfamethoxazole and diclofenac (Figure 4-6). Regarding the successful removal of diclofenac and sulfamethoxazole as described by Regnery et al. (2016) during SMART, results of this study indicate that EBCT might play a critical role for the attenuation of these compounds, even if desired oligotrophic conditions are established. Prolonged EBCTs in the second stage, however, did not result in further removal of other degradable compounds such as benzotriazole, citalopram, climbazole, and gabapentin. The compounds tramadol, venlafaxine and carbamazepine that showed high persistence before did not exhibit higher removal at increased EBCTs in the second filter stage. However, regarding the depletion of DO in columns S2 and S3 at EBCTs of 1,000 and 2,000 min (Figure 4-4b), the results have only limited significance for the potential removal of compounds at higher EBCTs under oligotrophic and oxic conditions. The increased but still incomplete removal of diclofenac, metoprolol and sulfamethoxazole and the persistence of other compounds might also be attributed to DO limitations in the columns. Regnery et al. (2016) observed vast removal of diclofenac, sulfamethoxazole and other compounds in the second infiltration stage of SMART when oxic conditions could be maintained during hydraulic retention times of two weeks and more. Besides DO limitations also the absence of certain microbial strains must be considered a potential reason for the lacking degradation and might explain observed differences in comparison with other studies regarding the removal of some compounds.

4.3.4 Effects of short-term hydraulic loading rate variations in the first filter stage on sequential biofiltration performance

Different studies have shown that EBCT is a key factor influencing the performance of biofiltration systems (LeChevallier et al., 1992; Hallé et al., 2015). In full-scale WWTPs, however, hydraulic fluctuations cannot be avoided and might therefore adversely affect the performance of a biofiltration treatment step. The concept of sequential biofiltration demands for the establishment of oxic and oligotrophic conditions in a sequential filter

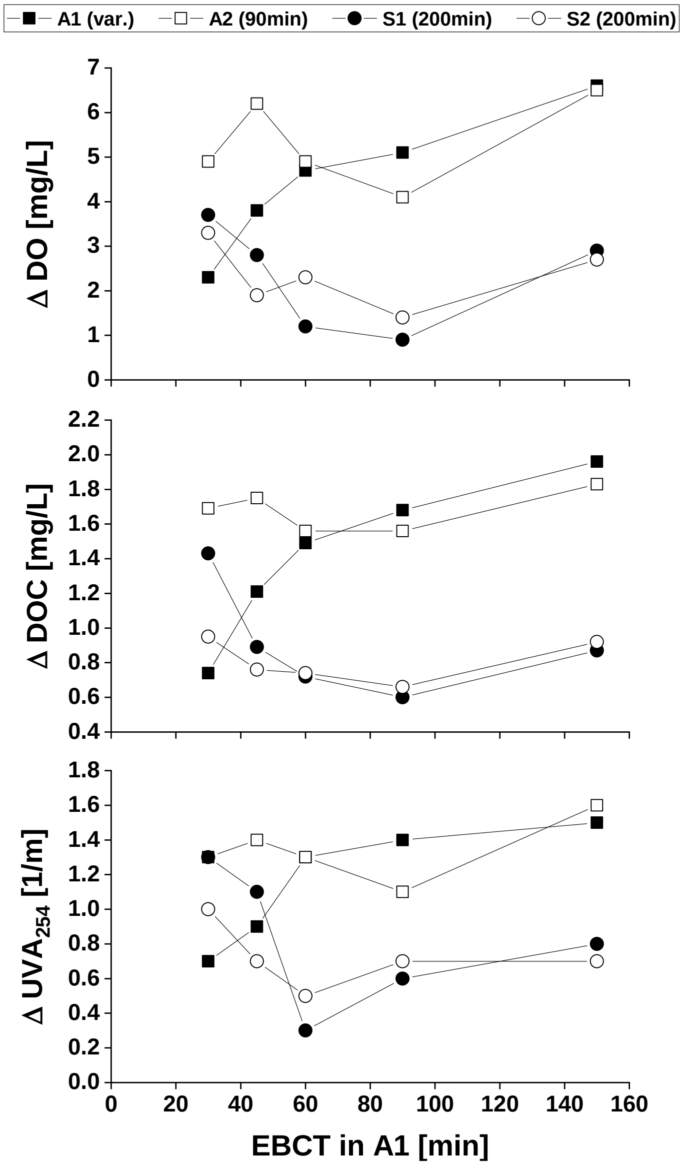

Figure 4-7: Effect of short-term variation of EBCT in first stage filter A1 on DO, DOC and UVA$_{254}$ consumption in first and second stage of an SBF system. EBCT of A1 was varied between 30 and 150 min. EBCT of A2 was held constant at 90 min. Second stage filters S1 and S2 were held constant at an EBCT of 200 min. Data from one sampling event. Mean influent values: DOC 7.0 ± 0.5 mg/L, UVA$_{254}$ 13.8 ± 0.7 1/m, DO [mg/L]: A1 6.9 ± 0.9, A2 7.0 ± 0.6, S1 6.0 ± 1.7, S2 5.1 ± 0.3; n = 5.

stage. For the establishment of these conditions the efficient removal of BDOC in the first stage filter is crucial.

To investigate the effect of hydraulic load variations and varying EBCTs in the first filter stage on the system performance, short-term tests were performed. Two sequential biofiltration trains were operated in parallel. In one train (A1+S1) the EBCT in the first filter stage was varied between 30, 45, 60, 90, and 150 min. The second train (A2+S2) was operated as a reference train with a constant EBCT of 90 min in the first filter stage. Columns S1 and S2 were operated at an EBCT of 200 min. After adjustment of the different EBCTs in column A1 the system was run at least 72 h before sampling.

The results of the short-term tests indicate an influence of reduced EBCT in the first filter stage on the consumption of DO, DOC and UVA$_{254}$ during SBF (Figure 4-7). The reference system (A2+S2) which was operated at a constant EBCT allowed to account for variations in feed water quality Figure 4-7, empty symbols). At EBCTs of 45 and 30 min, less DOC, UVA$_{254}$, and DO was consumed in A1 compared to the reference column A2. The results indicate a decrease in BDOC removal efficiency in the first filter stage leading to an increase of easily degradable substrate in the second filter stage. This is supported by the elevated consumption of DOC, UVA_{254}, and DO in column S1 at EBCTs of 45 and 30 min in column A1. An EBCT of 30 min in A1 even resulted in higher overall consumption of DO, DOC and UVA_{254} in S1 compared to A1. At EBCTs of 60 and 90 min in A1,

differences between the two compared SBF trains were less distinct. At the considerably higher EBCT of 150 min in A1, no increased consumption of DO, DOC and UVA_{254} could be observed. This stagnation of consumption, however, might also be linked to DO depletion in A1 (0.1 mg/L DO in the filter effluent) leading to unfavorable conditions for further removal of DOC and UVA_{254}.

To assess the effect of varying EBCTs in column A1 on TOrC removal the occurrence of several indicator TOrCs in the filter influents and effluents was monitored. Concentrations of the compounds caffeine, iopromide, phenytoin, TCEP, ibuprofen, and gemfibrozil in the WWTP effluent were always found to be below LOQ during the investigation. Results for the removal of sulfamethoxazole in the compared SBF systems were found to be contradictory to other results acquired during this study and are therefore not further discussed. At the time of the investigation the compounds climbazole, citalopram, sotalol, tramadol, and venlafaxine were not yet included in the analytical method.

The changes in substrate availability over a short period in S1 did not result in significant changes in the filter performance concerning TOrC removal (Figure 4-8). Though substrate availability in S1 increased with decreasing EBCTs in A1, redox conditions could still be characterized as oxic with effluent DO concentrations above 3.9 mg/L except for the EBCT of 150 min in A1 (DO concentration in the effluent of S1: 0.5 mg/L).

The results concerning the consumption of DO, DOC and UVA_{254} and the removal of TOrCs (Figures 4-7 and 4-8) have only limited significance concerning long-term operation at the tested EBCTs in the first filter stage. Longer adaptation periods at shorter EBCTs would probably induce a higher biomass density in the first filter stage due to the increased substrate loading rate. Consequently, this could result in increased BDOC and potentially also TOrC removal. The performed testings with varying hydraulic loading rates, however, indicate that even without longer adaptation periods oxic conditions in the second filter stage could be maintained and overall removal was not affected by changed EBCTs in the first filter stage for most TOrCs.

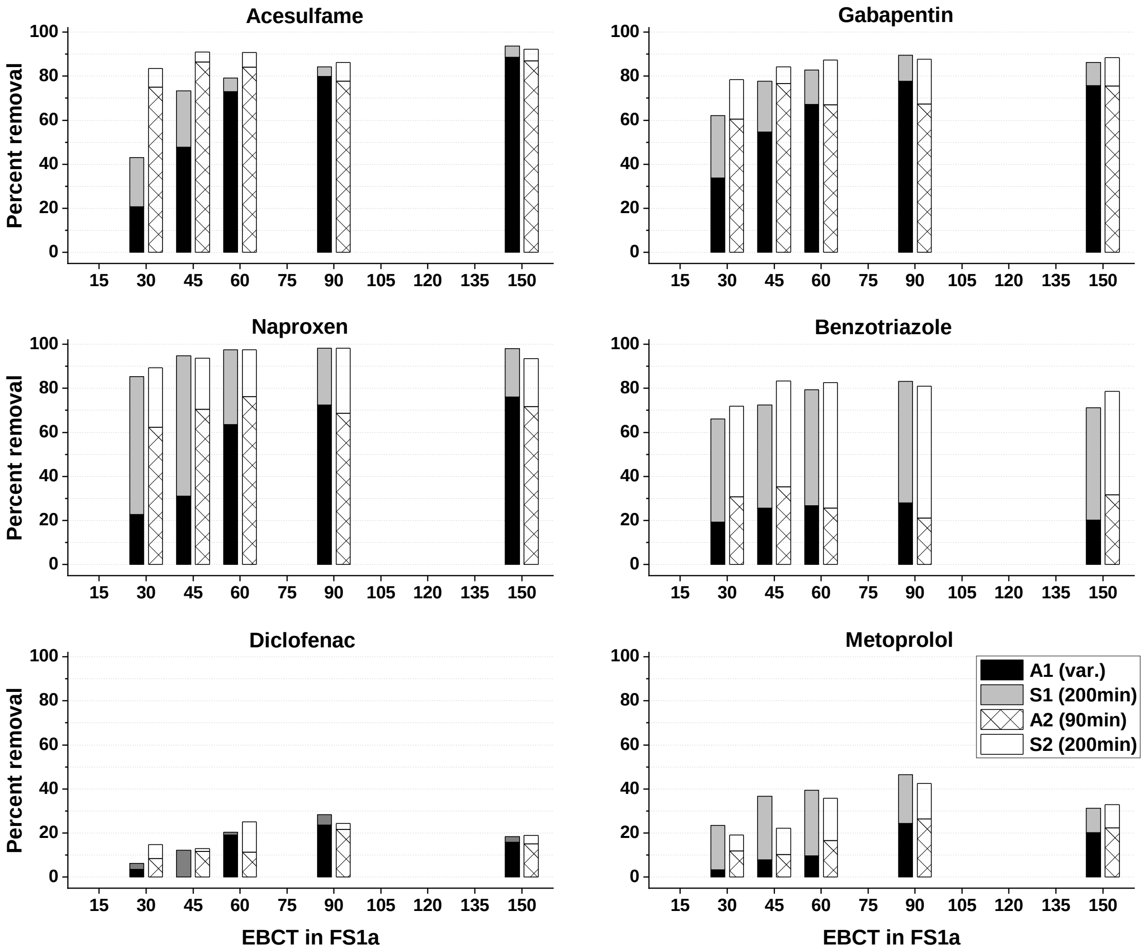

Figure 4-8: Effect of short-term variation of EBCT in the first filter stage on the removal of selected TOrCs. EBCT of column A1 was varied (30, 45, 60, 90, 150 min). EBCT of A2 was held constant at 90 min. Second stage filters S1 and S2 were held constant at an EBCT of 200 min. Data from one sampling event. c_0 [ng/L]: acesulfame 3,440 ± 710, gabapentin 1,820 ± 170, naproxen 240 ± 30, benzotriazole 4,090 ± 170, diclofenac 1,450 ± 250, metoprolol 240 ± 30; n = 5.

4.4 Conclusions

Results from testings at pilot-scale support the hypothesis of an enhanced biological removal of several TOrCs from secondary effluent in a technical sequentially operated biofiltration system. It could be demonstrated that a sequential biofiltration system consisting of two biofilters operated in series with an intermediate aeration step was suitable to establish favorable oxic and substrate limited conditions in the second filter stage. Short-term tests with varying EBCTs in the first filter stage proved system robustness and tolerance to sudden load variations. While the consumption of DO, DOC, UVA_{254}, and some TOrCs in the first filter stage decreased at lower EBCTs, oxic conditions could still be maintained throughout the second filter stage and no adverse effect on the overall removal of TOrCs was observed. Compared to travel times applied in the first infiltration step of sequential managed aquifer recharge applications, the results verified that a biofilter with drastically reduced hydraulic retention times was capable of establishing the desired operational conditions in a subsequent filter stage.

The comparison of a sequential biofiltration system with a conventionally operated single-stage biofilter with the same overall EBCT revealed a higher removal efficiency for organic bulk parameters (DOC and UVA_{254}) as well as for several TOrCs such as citalopram, climbazole, benzotriazole, gabapentin, metoprolol, and sulfamethoxazole. The findings emphasized the importance of predominant operational conditions in the considered biological processes.

Long-term testings with varying EBCTs in the second filter stage of the sequential biofiltration setup were carried out to investigate the influence of EBCT on system performance under oxic and oligotrophic conditions. Preliminary results showed no significant additional consumption of DOC but a significantly elevated consumption of UVA_{254} and DO depletion at higher EBCTs of 1,000 and 2,000 min, suggesting operational conditions characterized as oligotrophic but suboxic in the deeper zones of the filters. Better degradation of diclofenac, metoprolol and sulfamethoxazole at higher EBCTs in the second filter stage, suggested that EBCT might influence system performance once oligotrophic conditions prevailed and oxic conditions could be maintained over a longer time in the system.

Findings of this study suggested that a two-stage infiltration with an intermediate aeration step as used during sequential managed aquifer recharge, is a viable option to also tune the TOrC removal performance in engineered biological above-ground filters, which could serve as an advanced treatment step subsequent to conventional wastewater treatment. Low energy and maintenance costs make sequential biofiltration an economical alternative to other advanced treatment technologies such as adsorption onto activated carbon or advanced oxidation processes for the removal of biodegradable TOrCs. Compared to adsorption onto activated carbon sequential biofiltration offers the benefit of also removing biodegradable polar compounds, such as acesulfame and gabapentin, which show only unsatisfactory removal during adsorption while the formation of undesired disinfection by-products, potentially formed during ozonation and advanced oxidation processes can be avoided. While an enhanced biological removal of various TOrCs could be demonstrated, the high persistence of some TOrCs to biodegradation, even under the targeted operational conditions, remains a drawback for the establishment of exclusively biological treatment options. Also, even though a substantial removal of various TOrCs could be shown at drastically reduced hydraulic retention times compared to managed aquifer recharge applications, physical footprint requirements remain a critical factor when considering potential full-scale applications. The optimization of the system's hydraulic retention time is therefore inevitable to make the concept of sequential biofiltration a viable alternative for advanced onsite-treatment during wastewater treatment.

Acknowledgements

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5 Role of reduced empty bed contact times and pre-treatment by coagulation with Fe(III) salts on the removal of trace organic compounds during sequential biofiltration

The following chapter presents investigations related to ***Hypothesis #1:*** *Enhanced attenuation of moderately biodegradable trace organic chemicals as observed in sequentially operated managed aquifer recharge applications can also be achieved in engineered filtration systems with shortened empty bed contact times.*

This chapter presents results from a study investigating the option to combine sequential biofiltration (SBF) with pre-treatment by coagulation with Fe(III) salts in order to further reduce the amount of the available easily degradable substrate and reduce the consumption of dissolved oxygen to allow for stable oxic conditions in the filter system. In addition, the effect of reduced empty bed contact times in the first filter stage on system performance was investigated over longer time periods. The investigations targeted at potential options for an optimization of the SBF system.

The chapter has been published with editorial changes as follows:

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Author contributions: Johann Müller, Uwe Hübner and Jörg E. Drewes developed the research objective. Leonardo Titzschkau and Johann Müller designed the experiment and constructed the experimental setup. Silvia Levai, Nikolina Popović, Dragan Carevic and Leonardo Titzschkau conducted the experiments and the analyses. Johann Müller wrote the paper. Jörg E. Drewes, Uwe Hübner Silvia Levai, Nikolina Popović, Dragan Carevic and Leonardo Titzschkau reviewed the manuscript. Jörg E. Drewes and Uwe Hübner supervised the study. All authors approved the final version of the manuscript.

Role of reduced empty bed contact times and pre-treatment by coagulation with Fe(III) salts on the removal of trace organic compounds during sequential biofiltration

Abstract

Sequential biofiltration (SBF) has been demonstrated to be a promising approach to achieve enhanced biological removal of various trace organic compounds (TOrCs) from wastewater treatment plant (WWTP) effluents by establishing oxic and carbon-limited conditions. This study investigated options to further advance the feasibility of SBF systems by reducing empty bed contact times (EBCTs). Additional experiments were conducted to investigate the pre-treatment of WWTP effluent by coagulation as an option to further decrease the organic carbon availability during SBF. Results indicated that an EBCT reduction in the first filter stage from 90 to 45 and 30 min adversely affected process performance regarding the removal of organic bulk parameters and several TOrCs over short-term. However, after an extended adaptation period of ten weeks comparable performance was observed in two SBF systems with first stage filters operated at EBCTs of 90 and 45 min. The pre-treatment of secondary effluent by coagulation, flocculation and sedimentation was not found to enhance the performance of an SBF system despite substantial removal of organic bulk parameters during the pre-treatment. However, despite the vast removal of total phosphorous during coagulation, nutrient limitation was not found to adversely affect the biological performance of the subsequent SBF system.

5.1 Introduction

The ubiquitous occurrence of trace organic chemicals of anthropogenic origin, such as pharmaceuticals, personal care products and industrial chemicals in the aquatic environment, has been subject to extensive studies in the field of water research (Putschew et al., 2000; Ternes, 2007; Buerge et al., 2009; Chen et al., 2016). Typically occurring at trace concentrations in the range of ng/L to µg/L, these contaminants are also referred to as trace organic compounds (TOrCs). While negative impacts on human health seem unlikely at present (Schriks et al., 2010), TOrCs have been reported to have potential adverse effects in aquatic ecosystems (Cuklev et al., 2011; Brodin et al., 2013; Wilkinson et al., 2016). Municipal wastewater treatment plants (WWTPs) have been identified as main point sources for the entry of TOrCs into the aquatic environment (Ternes, 1998; Heberer, 2002).

To improve the removal of TOrCs in WWTPs, several advanced treatment options have been proposed. Many studies have shown the great potential of oxidation processes, such as ozonation or the adsorption onto activated carbon for the removal of a wide range of contaminants (Huber et al., 2003, 2005; Hollender et al., 2009; Corwin and Summers, 2012; Altmann et al., 2016; Sbardella et al., 2018). In addition, there are also many studies reporting enhanced degradation of TOrCs in natural treatment systems. Despite their high persistence to biodegradation during conventional activated sludge treatment, effective biological removal of some of these compounds was reported during soil-aquifer treatment or river bank filtration (Drewes et al., 2003; Schittko et al., 2004; Hübner et al., 2012; Hamann et al., 2016). Previous studies investigating the degradation efficiency of TOrCs in natural treatment systems identified oxic redox conditions and oligotrophic or carbon-limited conditions to positively enhance the degree of attenuation (Baumgarten et al., 2011; Hoppe-Jones et al., 2012; Li et al., 2012, 2013, 2014; Regnery et al., 2015b).

Sequential biofiltration (SBF) uses two filter stages operated in series with an intermediate aeration to establish oxic and carbon-limited conditions during granular media filtration of WWTP effluent (Müller et al., 2017). A first filter stage aims to reduce the amount of easily degradable carbon in the treated water. After reaeration, filtration in the second filter stage takes place under carbon-limited conditions, also reducing consumption of dissolved oxygen and thus, allowing for oxic redox conditions. Previous studies revealed an increased TOrC removal potential during SBF treatment compared to a single-stage biofilter operated at the same empty bed contact time (EBCT) (Müller et al., 2017). SBF systems profit from a low process complexity and are low in maintenance. The treatment does not result in the continuous production of waste streams or the formation of potentially toxic disinfection by-products, also no addition of chemicals or a frequent replacement of filter materials is required.

A factor limiting applications of SBF systems as optional advanced biological treatment steps after conventional wastewater treatment are the relatively large footprints of a full-scale system. While second stage filters might be designed as low-maintenance and low-cost slow sand filters, first stage filters need to be equipped with backwash capabilities, increasing also the costs of investment. A reduction of EBCT, thus, would be desirable especially in the first filter stage. However, the removal of easily biodegradable organic matter in the first filter stage is key to the establishment of the desired oxic and carbon-limited conditions in the second filter stage.

Coagulation using metal-based coagulants such as Fe(III) salts is a well-established water treatment process aiming for the reduction of colloidal and dissolved organic matter and advanced phosphorous removal in different water matrices (Matilainen et al., 2010; Bunce et al., 2018). Where establishing low carbon conditions is desired, pre-treatment of WWTP effluent by coagulation prior to feeding it into the SBF system could be a possible additional option to remove dissolved organic matter (DOM) from the aqueous phase. DOM removal during enhanced or sweep floc coagulation, induced by the addition of elevated concentrations of Fe(III) salts (Crozes et al., 1995; Ghernaout and Ghernaout, 2012), might reduce the amount of easily degradable organic carbon, enhancing carbon-limited conditions which were proposed to be favorable for an increased degradation of TOrCs (Li et al., 2012, 2013, 2014). Also, additional removal of phosphorous can be regarded beneficial to further increase the effluent quality and prevent eutrophication stress in receiving surface water bodies.

This study investigated options suitable to optimize the concept of SBF. In a first experimental campaign, the influence of reduced EBCTs on the removal of bulk organic matter and trace organic chemicals was investigated. Additional experiments were conducted to assess the effect of pre-treatment via sweep floc coagulation.

5.2 Materials and methods

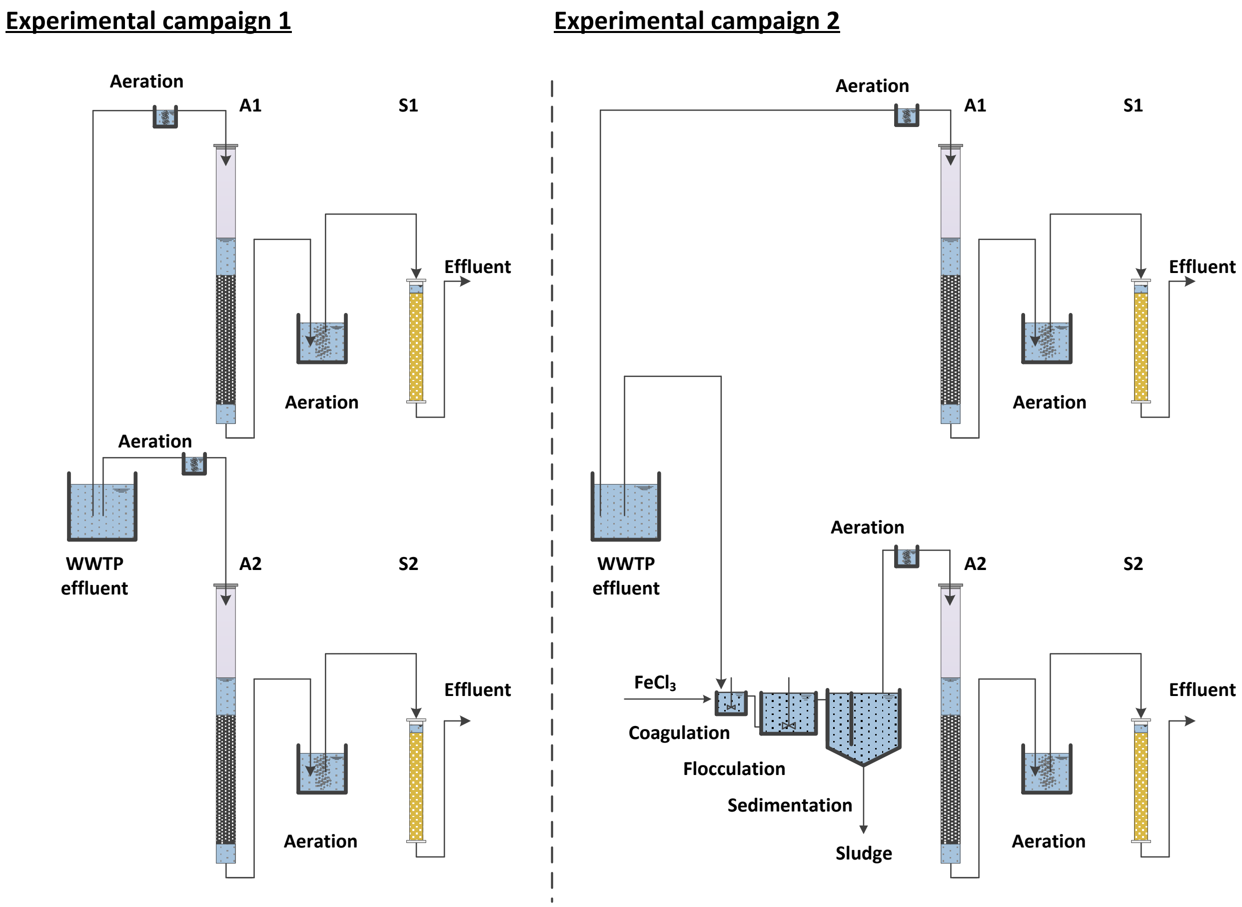
5.2.1 Experimental setup

5.2.1.1 Sequential biofiltration

For the experiments, two sequential biofiltration (SBF) systems were operated in parallel (A1+S1, A2+S2) (Figure 5-1). Each SBF system consisted of an anthracite column (A1, A2; length (l): 1.05 m; inner diameter (ID): 0.15 m) and a subsequent sand column (S1, S2; l: 0.95 m; ID: 0.1 m) operated in series under saturated top-down flow conditions. The anthracite in the filter columns was characterized by grain sizes ranging from 1.4 to 2.5 mm (Everzit N type II, Evers GmbH, Germany). The sand used in columns S1 and S2 was technical sand with grain sizes ranging from 0.2 to 1.0 mm (Euroquarz, Germany), initially inoculated with 5 % aquifer material from a river bank filtration site. Intermediate aerated containers served to resupply dissolved oxygen to the effluents of columns A1 and A2 using pressurized air. Columns A1 and A2 could be backwashed using air and tap water to maintain filter permeability. Water was fed via peristaltic pumps to the filter columns at flowrates which corresponded to the desired empty bed contact time (EBCT). SBF systems were fed with fully-nitrified tertiary effluent of the WWTP Garching, Germany (31,000 PE), after pre-aeration with pressurized air. Indicator TOrCs were not spiked to the water but were present at ambient concentrations. Prior to the experiments described in this study, the biofiltration systems were in operation for over 30 months.

5.2.1.2 Enhanced coagulation, flocculation and sedimentation (CFS)

WWTP effluent was fed into a coagulation tank (Volume (V): 1 L) at a flowrate of 500 mL/min using a peristaltic pump. Ferric chloride solution (35 %) was added to the coagulation tank using a high precision peristaltic pump, adjusting a Fe(III) concentration of 30 mg/L. To promote rapid distribution, the coagulation tank was completely mixed at high mixing rates using an overhead stirrer. After coagulation the water was directed into a flocculation tank (V: 5 L) and mixed at low mixing speed with an overhead stirrer to promote floc growth. Upon flocculation, the suspension was conveyed into a sedimentation tank (V: 33 L) to separate most flocs formed from the water phase via sedimentation. Periodic removal of flocculation sludge was carried out every three hours using a peristaltic pump. The supernatant, clear of visible flocs, was then fed into column A2.



Experimental campaign 1

Experimental campaign 2

Figure 5-1: Experimental setups used during experimental campaigns 1 and 2. EBCTs: Experimental campaign 1: A1: 90 min, S1, S2: 200 min, A2: 90, 45, 30 min; Experimental campaign 2: A1, A2: 45 min; S1, S2: 200 min.

5.2.2 *Operational conditions*

Results presented in this study were obtained from two independent experimental campaigns (Figure 5-1).

- During the first experimental campaign, the effect of different EBCTs in the first stage anthracite filter on system performance was investigated (Figure 5-1, left). A reference system (A1+S1) was operated at constant EBCTs in columns A1 (90 min) and S1 (200 min). In the test system (A2+S2) the EBCT in column S2 was operated at a constant EBCT (200 min) while column A2 was varied from 90 min (phase I) to 45 min (phase II), 30 min (phase III) and back to 45 min in phase IV and held constant for at least three weeks before sampling. Both SBF systems were fed with WWTP effluent.

- During the second campaign, the effect of pre-treating WWTP effluent by enhanced coagulation, flocculation and sedimentation (CFS) on the performance of an SBF system was investigated (Figure 5-1, right). Here, reference system A1+S1 was fed with WWTP effluent while test system A2+S2 was fed with WWTP effluent pre-treated by CFS. EBCTs during the second experimental campaign were set to 45 min in columns A1 and A2 and to 200 min in columns S1 and S2.

5.2.3 Sample collection and analytical methods

Corresponding liquid samples for the analysis of dissolved organic carbon (DOC), UV absorbance at 254 nm (UVA_{254}), ammonia, nitrite, nitrate and indicator TOrCs were taken from column inlets and outlets and analyzed according to methods described in Müller et al. (2017) (see Tables SI-4 and SI-5 for concentrations observed in WWTP effluent and limits of quantitation (LOQs)). Measurement of dissolved oxygen (DO) was carried out in column influents, effluents and at different heights of the columns as described in Müller et al. (2017). In addition, during flocculation experiments, samples for the analysis of total dissolved iron and total phosphorous were taken before and after treatment by CFS. Total phosphorous was analyzed using cuvette tests LCK 349 (Hach-Lange, Germany) and a DR6000 spectrophotometer (Hach-Lange, Germany). Total iron concentrations were determined by atomic absorption spectroscopy using an Agilent AA240FS (LOQ 50 µg/L) after sample filtration and acidification with nitric acid (DIN 38406-32:2000-05).

5.2.4 Definition of redox conditions

Redox conditions were classified following definitions proposed by Regnery et al. (2015) and McMahon and Chapelle (2008) and were determined based on measurements of DO and nitrate. Filter columns were characterized as oxic if DO concentrations in effluents were exceeding 1 mg/L. Lower DO concentrations accompanied by limited reduction of nitrate (< 0.5 mg N/L) were defined as suboxic, whereas anoxic conditions were characterized by nitrate reduction > 0.5 mg N/L.

5.2.5 Statistical analysis

The statistical significance of differences observed between related data sets was tested using Student’s t-tests and two-tailed Student’s t-tests. In the following, a statistically significant difference implies $p < 0.05$. Standard deviations were used as measures of variability.

5.3 Results and discussion

System characterization involved monitoring of redox indicators DO and nitrate. Ammonia and nitrite concentrations were measured to exclude nitrification as a relevant cause of DO consumption in the filter columns. In the following, DO consumption was also used as a proxy for general microbial activity in the column systems. The removal of organic bulk parameters DOC and UVA_{254} was monitored to characterize the consumption of organic substrate and the removal of DOM. Redox conditions were always characterized as oxic with DO concentrations > 1 mg/L in filter effluents during all experiments. Denitrification indicated by nitrate concentration reduction of > 0.5 mg/L N was not observed. Ammonia and nitrite concentrations in WWTP effluent close to the LOQ excluded nitrification as a relevant cause for DO consumption in the column systems. Details on WWTP effluent characteristics during the experimental campaigns can be found in Tables SI-4 and SI-5.

System performance to degrade TOrCs was monitored by measuring a list of 21 indicator compounds representing different degrees of biodegradability. Concentrations for 14 of those were found to exceed a threshold of 3.5 x LOQ in more than 50 % of the analyzed WWTP effluent samples. Among them, the compounds carbamazepine, tramadol and venlafaxine demonstrated high persistence in all investigated systems, indicated by a removal below 15 %, and are not further discussed in this study. Tables SI-5, SI-6 and SI-7 summarize data on WWTP effluent concentrations and removal efficiencies of all investigated compounds.

5.3.1 Process characterization and removal of organic bulk parameters and trace organic chemicals under different empty bed contact times in the first filter stage

Parallel operation of a well-equilibrated system (A1+S1), operated under stable operational conditions, served as a reference for the test system (A2+S2) to rule out environmental factors as responsible for observed changes in system performance. After changing the EBCT in column A2 during phases I, II and III, the system was equilibrated for three weeks. While continuous sampling was carried out also during the equilibration period to acquire data in time series (Figures 5-2 and 5-4), the data used for comparison of trains A1+S1 and A2+S2 was acquired during three sampling campaigns after the three weeks of adaptation (Figures 5-3 and 5-5). During phase IV, the equilibration period was extended to ten weeks before data for comparison were collected during seven sampling campaigns.

5.3.2 Characterization of reference train A1+S1

Data from system A1+S1 revealed fluctuating process performance regarding the removal of organic bulk parameters and TOrC degradation even under stable operational conditions, especially in first stage filter A1. For instance, a significant drop in DO consumption from 6.0 ± 0.4 mg/L in column A1 was observed in phase I to 3.4 ± 0.6 mg/L in phase IV (Figures 5-2a and 5-3a). Fluctuating DO consumption was accompanied by a decline in the consumption of the organic bulk parameters DOC (phase I: 2.3 ± 0.9 mg/L; phase IV: 1.0 ± 0.4 mg/L) and UVA_{254} (phase I: 1.4 ± 0.5 1/m; phase IV: 0.8 ± 0.3 1/m) (Figure 5-3a, b and c, respectively). Standard deviations observed for DOC consumption also indicated fluctuations in BDOC availability at different sampling events within the same experimental phase. Also, the degradation of certain TOrCs in column A1 was found to fluctuate strongly over time (Figure 5-4). During the study the degradation of gabapentin was found to decline (phase I: 80 ± 2 % to phase IV: 35 ± 9 %) following the trend observed for DO consumption, a phenomenon already observed in a previous study (Müller et al., 2019). Instable removal in A1 was also found for 4-formylaminoantipyrine (4-FAA) while metoprolol degradation remained rather consistent. Fluctuating removal of gabapentin in column A1 was compensated by degradation occurring in the second stage column S1, causing the overall degradation in system A1+S1 to remain stable. In contrast overall removal of 4-FAA in system A1+S1 seemed to be stronger affected by fluctuations in degradation in column A1 due to less compensation in column S1. Reasons for the varying consumption of DO and organic substrate and the degradation of certain TOrCs remained unclear. Differences in feed water composition are considered to potentially contribute to differences, however, time series data for DOC, UVA_{254} and specific UV absorbance (SUVA) in WWTP effluent indicate a rather constant feed water quality (7.6 ± 1.5 mg/L, 14.4 ± 0.7 1/m and 1.9 ± 0.2 L/mg*m, respectively (Figure SI-2)).

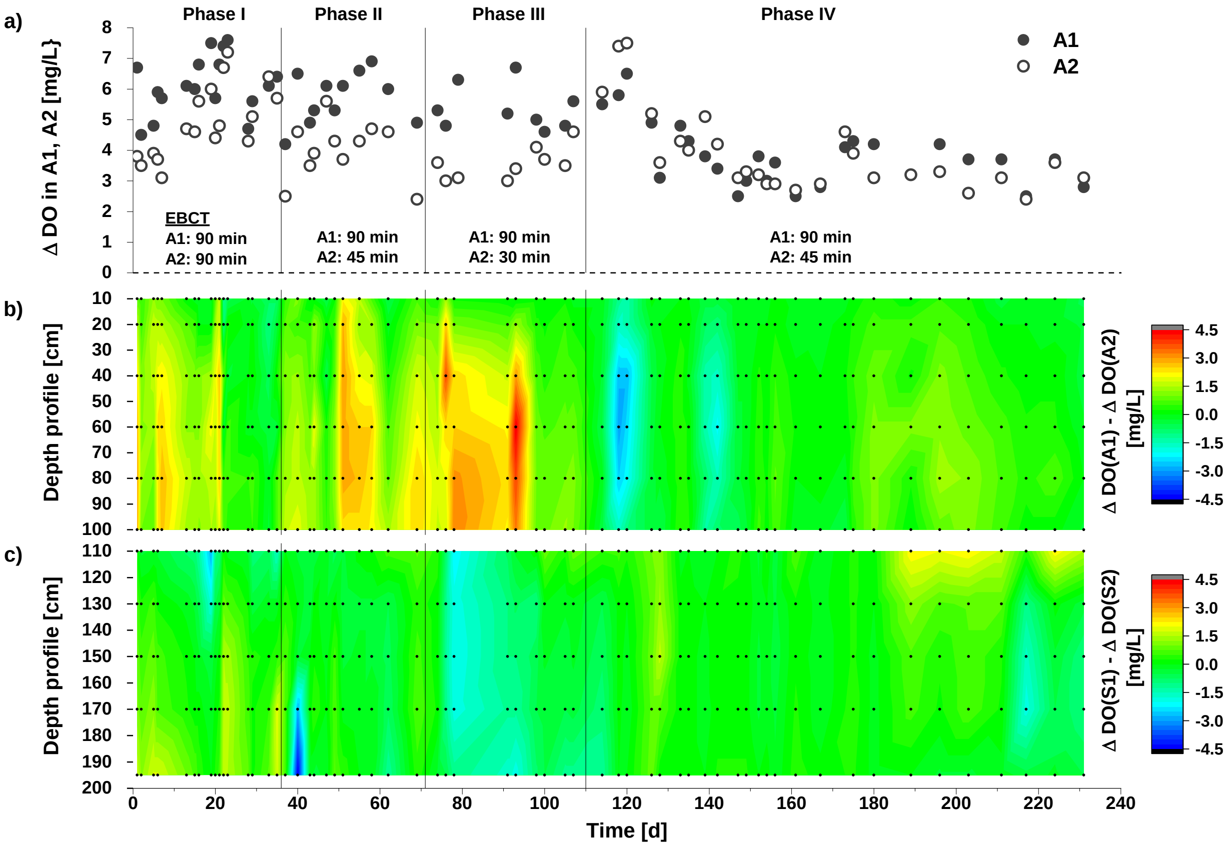


Figure 5-2: a) DO consumption ($DO_{influent}$ - $DO_{effluent}$, n = 63) over time in filters A1 (serving as reference at constant EBCT of 90 min) and A2 (varying EBCTs of 90, 45, 30 and 45 min from phases I to IV). b), c): Differences in the depth profiles of DO consumption in columns A1 and A2 (b)), and S1 and S2 (c)) in response to changing EBCTs in filter A2 over time (n = 63). Black dots indicate positions of sampling ports and frequency of sampling.

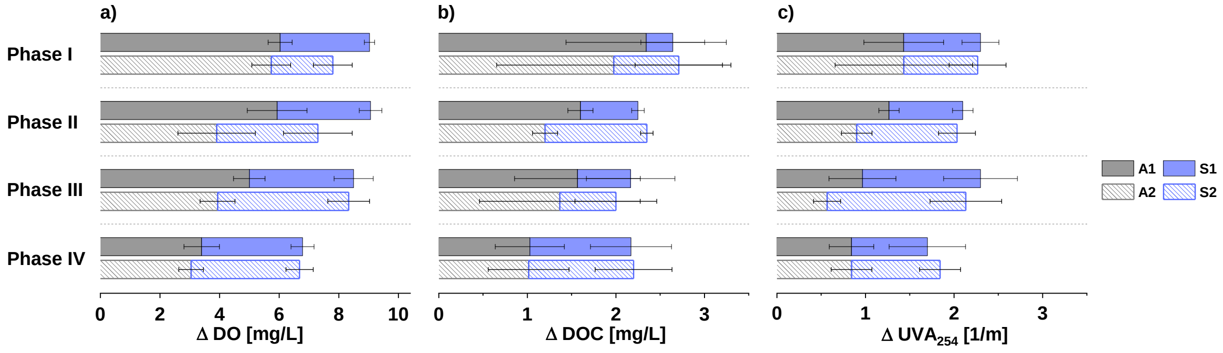


Figure 5-3: Change of a) DO, b) DOC and c) UVA_{254} in SBF systems A1+S1 and A2+S2 at varying EBCTs in A2. Data for phases I to III was taken after an adaptation period of three weeks (n = 3); data acquisition in phase IV after ten weeks of adaptation (n = 7). See Table SI-4 for initial concentrations in WWTP effluent samples.

5.3.3 *Impact of empty bed contact time in first stage filter on system performance*

Monitoring DO, DOC, UVA_{254}, and indicator TOrCs revealed differences in organic carbon utilization and TOrC degradation in reference train A1+S1 and test train A2+S2 during the experimental phases. During phase I both trains, A1+S1 and A2+S2, were operated under the same operational conditions with an EBCT of 90 min in first stage anthracite filters and of 200 min in second stage sand filters. Data from phase I suggested comparable organic carbon utilization in both trains, indicated by only insignificant differences in the consumption of DO, DOC and UVA_{254} (Figure 5-3). Comparable behavior was also observed for the removal of most investigated TOrCs (Figures 5-4 and 5-5; Table SI-6). Table SI-6 summarizes differential changes of DO, DOC and UVA_{254} and removal efficiencies for all investigated compounds and lists details on the significance of observed differences. Data from phase II indicated lower consumption of DO, DOC and UVA_{254} in column A2 after reducing the EBCT to 45 min. Significantly lower consumption of DO and UVA_{254} was also found after further reducing the EBCT in A2 to 30 min during phase III. Reduced consumption of DO, DOC and UVA_{254} in column A2 compared to reference column A1 indicated less substrate utilization at lower EBCTs. Lower substrate consumption in A2 during phases II and III was accompanied by an increased utilization in column S2, compensating for fluctuating DOC concentrations and UVA_{254} values in A2 effluent. Reduced substrate utilization in column A2 during phases II and III was likely related to the increased substrate loading rate after reducing the EBCT. An increased substrate loading rate causes a sudden increase in organic carbon availability and triggers biomass growth, also in deeper filter layers (Carlson and Amy, 1998; Chaudhary et al., 2003). Increases in biomass density, however, might be restricted by different factors. Limited growth rates, especially in biofilm systems require sufficient time for system adaptation before the biomass density matches the changed substrate availability in the system. The maximum biomass density in biofilm systems might also be limited by operational parameters, such as increased washout of biomass due to higher sheer forces at increased hydraulic loading rates. Although biomass concentrations were not directly determined in this study, results from experimental phase IV indicate the importance of a sufficient adaptation period. While for phases I, II and III system adaptation conditions were held constant over three weeks before sampling, the system was operated under stable conditions for ten weeks before sampling during phase IV. Although the EBCT in A2 during phases II and IV were set to 45 min, no significant difference was found between reference train A1+S1 and A2+S2 after the extended adaptation period in phase IV.

Degradation of the three exemplarily chosen TOrCs gabapentin, metoprolol and 4-FAA in systems A1+S1 and A2+S2 during the experimental phases I to IV demonstrated compound specific differences (Figures 5-4 and 5-5). Figure 5-4 presents the percent removal of gabapentin, metoprolol and 4-FAA during the experimental phases I to IV. As discussed above, the removal of the compounds gabapentin and 4-FAA fluctuated also in reference system A1+S1 which was operated at constant EBCT settings, indicating the relevance of additional factors in the degradation of TOrCs. Thus, system performance in test system A2+S2 must be compared to the time-dependent removal in A1+S1 to investigate adaptation or changed degradation performance. While gabapentin removal in A2 seemed to decrease with decreasing EBCT in phases II and III, the same was observed in reference column A1. In the initial phase after reduction of EBCT in filter A2 from 90 to 45 (phase II, days 40 to 50) and from 45 to 30 min (phase III, days 80 to 90), data indicated less removal of gabapentin in filter A2 compared to reference filter A1. This difference, however, diminished rapidly indicating a short adaptation period for gabapentin removal in A2 despite lower EBCTs. While no effect of EBCT was found for the degradation of gabapentin in column A2 after a short adaptation period of three weeks, slightly lower transformation of metoprolol and 4-FAA was observed in column A2 compared to reference column A1 (Figure 5-5). In the case of 4-FAA, second stage filter S2 was found to compensate the differences in 4-FAA degradation in trains A1+S1 and A2+S2 as also observed for DOC and UVA_{254} consumption. Slightly but significantly increased removal of metoprolol was found in reference system A1+S1 during all experimental phases. Differences in metoprolol degradation in systems A1+S1 and A2+S2 during phases I, II and III, however, were found to remain rather stable and, thus, revealed to be independent from the EBCT adjusted in column A2. When compared to reference column A1, metoprolol degradation in column A2 indicated a negative effect of EBCT reduction over short-term in phases II and III (Figures 5-4 and 5-5). After an extended adaptation period of ten weeks, however, similar removal of metoprolol was observed in columns A1 and A2. The importance of system adaptation could also be observed in the degradation of 4-FAA. While degradation in phases II and III was substantially lower in column A2 compared to reference column A1, an extended adaptation period resulted in improved degradation of 4-FAA in column A2. After adaptation for ten weeks, degradation in column A2 even slightly exceeded degradation in reference column A1 in phase IV.

Monitoring DO consumption in compared systems was identified as a useful tool to reveal differences in system performance and to follow system adaptation. Heat maps illustrate differences in DO consumption in different depths of first (Figure 5-2b) and second stage filters (Figure 5-2c) in systems A1+S1 and A2+S2 over time. Results indicated lower DO consumption in column A2 after reduction of EBCT in phases I, II and III which could be attributed to the changed hydraulic loading rate. The reduction of the EBCT in A2 to 30 min induced the strongest observed differences in DO consumption in columns A1 and A2. Here, the change in EBCT seemed to even affect substrate availability in second stage column S2 which was indicated by higher DO consumption compared to reference column S1. Differences initially observed after changes of EBCT in column A2 were found to diminish during adaptation. Especially after a longer adaptation period, as used in phase IV, DO consumption patterns in systems A1+S1 and A2+S2 converged.

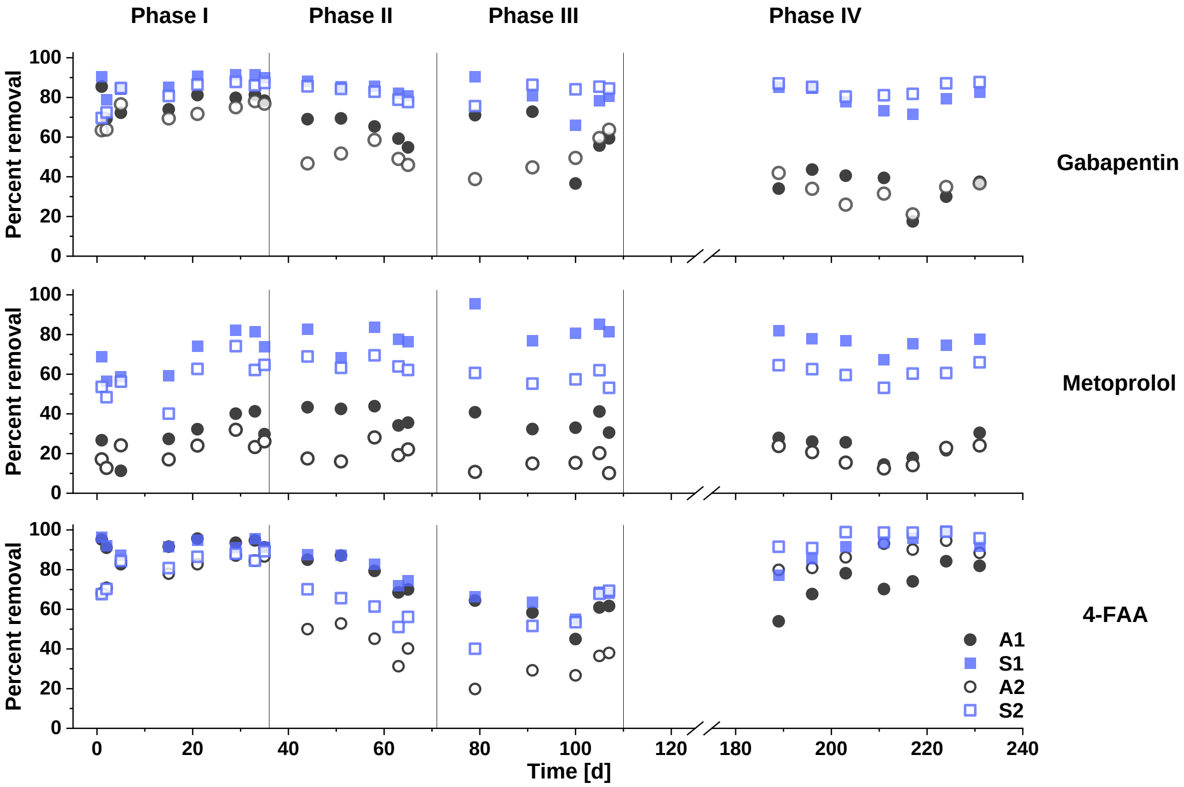


Figure 5-4: Cumulative removal of compounds gabapentin, metoprolol and 4-FAA in systems A1+S1 and A2+S2 over time. Displayed removal related to concentrations found in WWTP effluent (see Table SI-5 for initial concentrations found in WWTP effluent samples).

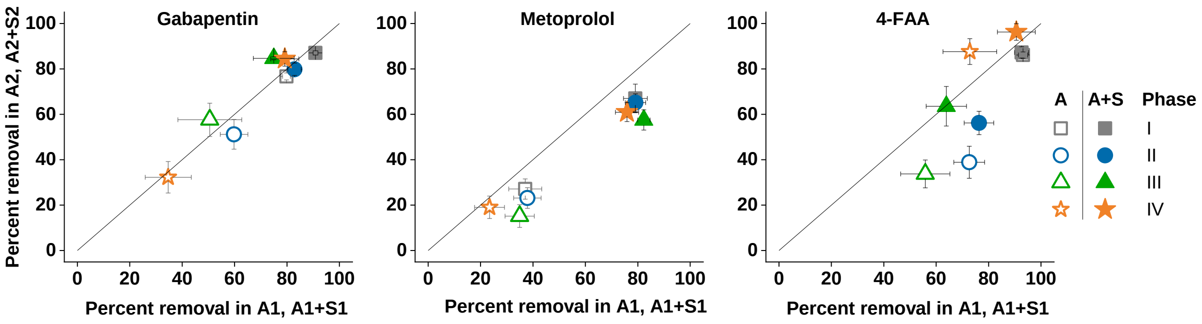


Figure 5-5: Comparison of cumulative removal of gabapentin, metoprolol and 4-FAA in SBF systems A1+S1 and A2+S2 at varying EBCTs in A2. Data for phases I to III was taken after an adaptation period of three weeks (n = 3); data acquisition in phase IV after ten weeks of adaptation (n = 7). Displayed removal related to concentrations found in WWTP effluent (see Table SI-5 for initial concentrations found in WWTP effluent samples).

Results indicated that reductions of EBCT from 90 to 45 and 30 min in the first filter stage might have adverse effects on the performance of SBF systems without sufficient system equilibration affecting substrate removal in the first filter stage which is key for the desired substrate limited conditions in the second filter stage. Also, TOrC removal in the first filter stage might decrease in response to a shorter EBCT. After longer system adaptation at an EBCT of 45 min, however, no negative impact of the reduced first stage filter EBCT was observed. Thus, given sufficient adaptation, a reduction of EBCTs in first stage filters of SBF systems is considered possible without substantial performance losses. Reduced EBCTs in first stage filters imply lower footprints of filter units and thus, increase the feasibility of a potential full-scale installation. However, results of this study could not identify a minimum EBCT necessary to maintain a comparable system performance as observed in the reference system.

5.3.4 Flocculation as a pre-treatment step before sequential biofiltration

Data for the comparison of reference system A1+S1 with test system A2+S2 was acquired during a three-week sampling campaign with collection of eight sample sets. Before the campaign, systems were operated under stable conditions for eight weeks to allow for system adaptation.

5.3.4.1 Effect of coagulation and flocculation on feed water quality

Dosing of 30 mg/L Fe(III) to WWTP secondary effluent resulted in a decrease in pH from 7.5 ± 0.3 to 6.8 ± 0.4 (n = 5). Iron concentrations in the influent of column A2 after flocculation were very low (71 ± 15 µg/L; n = 4) indicating almost complete transformation of dosed Fe(III) to insoluble components with subsequent precipitation. Total phosphorous concentrations of 0.4 ± 0.1 mg/L (n = 9) in WWTP effluent were reduced below the LOQ (50 µg/L) in all investigated samples after coagulation.

Significant decreases in UVA$_{254}$ (32 ± 4 %; ΔUVA$_{254}$ 4.0 ± 0.6 1/m; n = 8) and DOC (10 ± 1 %; ΔDOC 0.8 ± 0.2 mg/L; n = 3) concentration indicated substantial reduction of DOM in WWTP effluent during enhanced coagulation (Figure 5-6). Elevated removal of UVA_{254} indicated preferential removal of DOM constituents with higher aromaticity.

Despite the strong impact of CFS on DOM content and structure, no significant removal of TOrCs was observed during the experiments (Figure 5-7). These observations are in accordance with results from several studies (Westerhoff et al., 2005; Vieno et al., 2006) while some authors reported higher removal even at substantially lower coagulant doses (McKie et al., 2016).

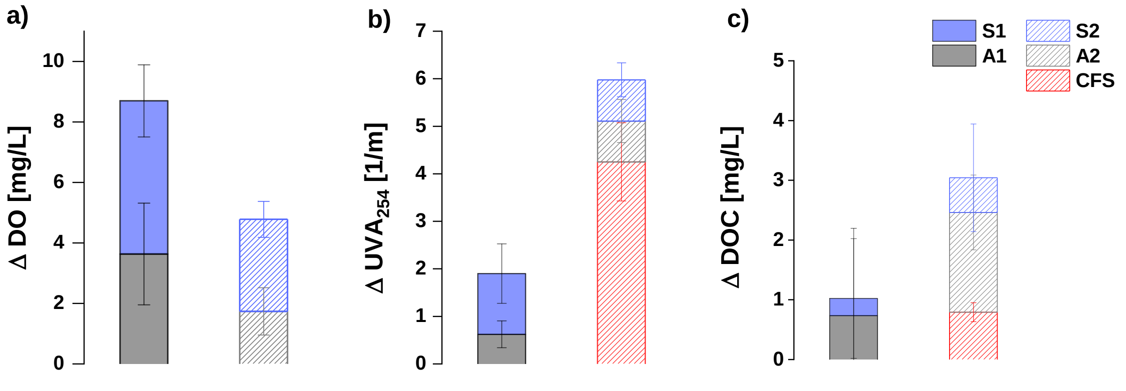


Figure 5-6: Consumption of a) DO, b) UVA_{254} and c) DOC in SBF systems A1+S1 and A2+S2 fed with WWTP effluent with (A2+S2) and without (A1+S1) pre-treatment by enhanced coagulation, flocculation and sedimentation (CFS) (n = 8; DOC: n = 3).

5.3.4.2 *Impact of enhanced coagulation on subsequent sequential biofiltration*

Aeration of the WWTP effluent with and without pre-treatment by CFS resulted in comparable pH values in both feed waters (Influent A1: 8.0 ± 0.4; Influent A2: 7.8 ± 0.4). The increase in pH especially in the WWTP effluent after CFS could be explained by stripping of CO_2 from the aqueous phase during aeration. The comparison of the reference system A1+S1, fed with WWTP effluent, with system A2+S2, fed with WWTP effluent after CFS, revealed differences in DO consumption and the removal of bulk parameters (Figure 5-6). DO consumption in columns A2 and S2 was significantly lower compared to the reference columns A1 and S1. Lower DO consumption in system A2+S2 was accompanied by the observed substantial removal of bulk parameters during CFS, indicated especially by reduced UVA_{254} values. Thus, lower DO consumption could be interpreted as a hint towards lower amounts of available substrate and less substrate consumption in system A2+S2. This interpretation, however, was not supported by results obtained for the consumption of UVA_{254} and DOC in the two systems (Figure 5-6). Despite higher DO consumption in reference column A1, differential changes of UVA_{254} and DOC in column A2 was found to even slightly, not significantly, exceed the changes observed in column A1. The differential change of UVA_{254} in second stage filters, however, indicated slightly but significantly higher removal in reference column S1. The obtained results do not allow for an assessment of the impact of CFS as a pre-treatment on the amount of biodegradable substrate present in the influent of SBF systems. While reduced DO consumption supported the hypothesis of successful growth substrate removal in the feed water, results for the bulk parameters UVA_{254} and DOC indicated that mostly non-degradable DOC was removed by CFS.

Monitoring the degradation of indicator TOrCs in systems A1+S1 and A2+S2 did not reveal distinct differences in system performance (Figure 5-7). Table SI-7 summarizes the collected data on TOrC removal as observed during the study. The results do not support the hypothesis of an improved removal of TOrCs during SBF after pre-treatment of WWTP effluent by CFS. For most compounds, the results even suggested slightly higher removal in the reference system A1+S1.

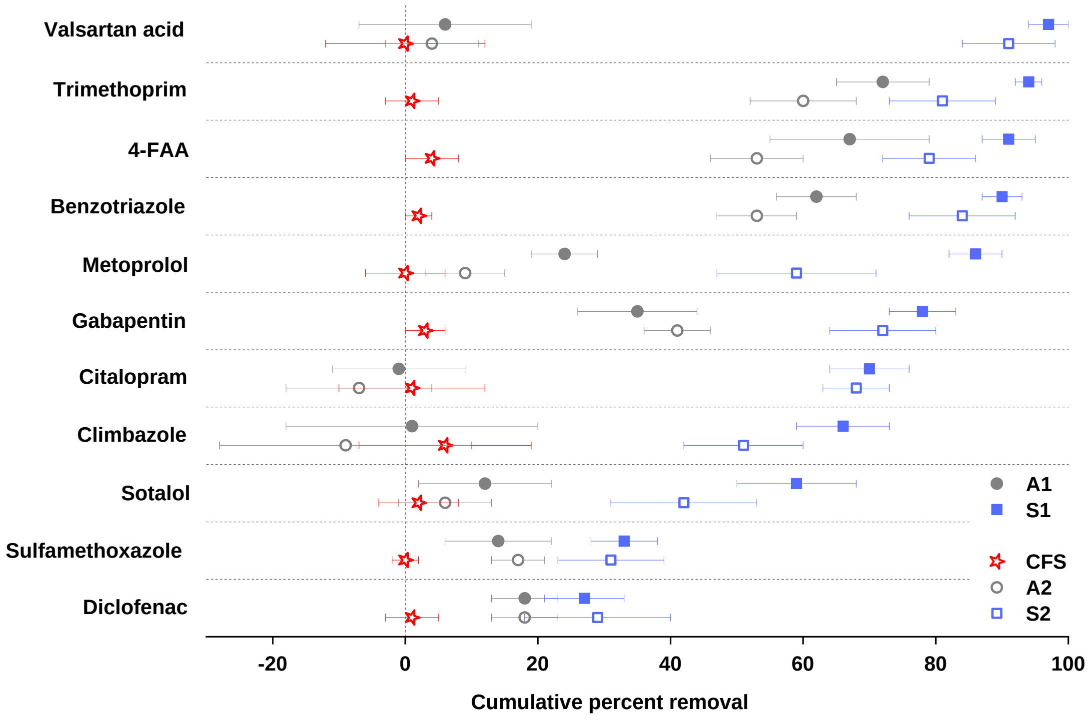


Figure 5-7: Percent removal of indicator TOrCs in SBF systems fed with WWTP effluent without (A1+S1) and with (A2+S2) pre-treatment by enhanced coagulation, flocculation and sedimentation (CFS) (n = 8). Displayed removal related to concentrations found in WWTP effluent (see Table SI-5 for TOrC concentrations found in WWTP effluent samples). Table SI-7 summarizes data on the removal of all investigated compounds.

The removal of DOM during enhanced coagulation, and thus, the reduction of potentially bioavailable organic carbon did not result in an increased degradation of TOrCs in the SBF system. Also, elevated DO concentrations did not have a positive effect on TOrC degradation. During the experiments, redox conditions were characterized as fully oxic in both systems, A1+S1 and A2+S2. Although no improved transformation of TOrCs was observed in test system A2+S2 during the experiments, a beneficial effect of pre-treatment might still be expected when increased amounts of easily degradable substrate were present in the WWTP effluent. In this case, pre-treatment by CFS might lower DO consumption and thus keep redox conditions always oxic during treatment in the SBF system.

It remained unclear, however, to what extent the DOM removed during CFS was part of the biodegradable substrate in the WWTP effluent. Results showed a strong reduction of UVA_{254} which is an indicator for rather aromatic, thus, rather refractory DOM constituents. Comparable or even higher removal of bulk parameters UVA_{254} and DOC in system A2+S2 seemed to contradict an effective limitation of easily degradable substrate by CFS. These findings support observations from other studies suggesting preferential removal of hydrophobic, high molar mass fractions of DOM during coagulation while rather hydrophilic, low molar mass constituents are removed to a lesser extent (Matilainen et al., 2010).

The complete removal of total phosphorous during CFS might be considered a potential limitation for the biological activity in the subsequent biofilters. Removal of total phosphorous below LOQ (50 µg/L), as observed during this study at the applied high Fe(III) concentrations, might inhibit microbial growth in subsequent biological systems. Several studies demonstrated the importance of nutrient availability for the performance of biofiltration systems (Lauderdale et al., 2012; Dhawan et al., 2016). Lauderdale et al. (2012) and Dhawan et al. (2016) reported C:N:P molar ratios of 100:10:1 to be beneficial for microbial activity in environmental systems. However, the results obtained for the removal of TOrCs in systems A1+S1 and A2+S2 did not support the assumption of a generally lower removal efficiency caused by reduced microbial activity in system A2+S2 which was fed with WWTP effluent pre-treated by CFS.

Considering feasibility aspects, the application of CFS systems at full-scale would be opposed by footprint requirements and increased OPEX and CAPEX. Results indicated that sweep floc coagulation, as tested within this study, had no positive effect on TOrC removal, benefits of an application were limited to an improved nutrient removal. An enhanced removal of total phosphorous, however, could also be achieved by direct filtration at lower coagulant concentrations and lower CAPEX (Bunce et al., 2018).

5.4 Conclusions

Results from this study demonstrated that the combination of sequential biofiltration (SBF) with coagulation, flocculation and sedimentation can be a viable option for enhanced removal of trace organic compounds (TOrCs) and total phosphorus from secondary treated effluents of municipal wastewater treatment plants (WWTPs), even at significantly lower empty bed contact times (EBCTs) than reported in previous studies for SBF.

Short-term reductions of the EBCT in first stage filters resulted in reduced removal of easily degradable substrate and lower TOrC degradation in the first filter stage but after longer adaptation periods, a reduction of the EBCT in first stage filters from 90 to 45 min resulted in comparable process performance regarding substrate removal and TOrC degradation. These results indicated that a reduction of the EBCT in first stage filters might be an option to increase system feasibility by lowering necessary physical footprints. Minimum required EBCT, however, need to be determined during long-term evaluation of continuously operated pilot-scale filters.

In addition, pre-treatment of WWTP by enhanced coagulation, flocculation and sedimentation (CFS) prior to SBF was investigated as an option to reduce the amount of easily degradable substrate and thus, to facilitate the establishment of substrate limited and oxic conditions during SBF. Besides efficient removal of phosphorus and a significant reduction of organic bulk parameters UVA_{254} and DOC during CFS, higher dissolved oxygen concentrations could be achieved in the SBF system fed with the pre-treated WWTP effluent. While pre-treatment by coagulation was not found to increase TOrC degradation in a subsequent SBF system, results indicate that SBF systems could be combined with coagulation to also achieve an enhanced removal of phosphorous.

Acknowledgements

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6 Revealing the transformation of trace organic chemicals in sequential biofiltration systems using profile sampling and first-order biodegradation rate constants

The following chapter presents investigations related to ***Hypothesis #1:*** *Enhanced attenuation of moderately biodegradable trace organic chemicals as observed in sequentially operated managed aquifer recharge applications can also be achieved in engineered filtration systems with shortened empty bed contact times.*

The investigations presented in the following chapter aimed for a better understanding of the degradation of trace organic chemicals (TOrCs) in biofiltration systems. This involved extensive monitoring of the fate of an extended set of TOrCs and the operational conditions over column depth to allow for an improved characterization of compound degradation in conventional and sequential biofiltration systems.

The following chapter is a manuscript in preparation for publication.

Müller, J., Jewell, K., Hermes, N., Ternes, T.A., Drewes, J.E., Hübner, U., 2019. Revealing the transformation of trace organic chemicals in sequential biofiltration systems using profile sampling and first-order biodegradation rate constants.

Revealing the transformation of trace organic chemicals in sequential biofiltration systems using profile sampling and first-order biodegradation rate constants

6.1 Introduction

The presence of a broad spectrum of anthropogenic chemicals in the aquatic environment at low concentrations in the ng/L to µg/L range has been subject to extensive research activities (Putschew et al., 2000; Ternes, 2007; Buerge et al., 2009; Chen et al., 2016). Due to their occurrence at trace concentrations in the range of ng/L to µg/L these contaminants are also referred to as trace organic chemicals (TOrCs). Due to the typically low concentrations, a direct toxicological relevance for human health was reported unlikely for the vast majority of TOrCs (Schriks et al., 2010), however, studies demonstrated various adverse effects on aquatic organisms (Cuklev et al., 2011; Brodin et al., 2013; Wilkinson et al., 2016). Also, potential chronic or combinatory effects caused by the long-term exposure to a large variety of different chemicals cannot be ruled out (Cleuvers, 2003, 2004; Schwarzenbach et al., 2006). Municipal wastewater treatment plants (WWTPs) have been identified as major point sources for the entry of TOrCs into the aquatic environment (Ternes, 1998; Heberer, 2002). Designed for an effective removal of organic bulk parameters and nutrients, conventional WWTPs often fall short in effectively mitigating individual chemicals (Joss et al., 2006; Vieno et al., 2007; Falås et al., 2016). As a consequence, many individual chemicals undergo only partial removal and are discharged into the receiving waterbodies.

To improve the TOrC removal capabilities of WWTPs, different treatment technologies have been discussed to serve as additional barriers. Oxidative treatment, using ozonation or other advanced oxidation processes is known to be effective for the transformation of many different substances (Huber et al., 2003, 2005; Hollender et al., 2009). Adsorptive treatment, mainly using activated carbon in powdered or granular form, has been demonstrated to allow for the retention of many TOrCs (Corwin and Summers, 2012; Altmann et al., 2016; Sbardella et al., 2018). Other studies demonstrated that an effective retention of TOrCs can also be achieved using high pressure membrane systems, such as reverse osmosis or nanofiltration (Kim et al., 2005a; Fujioka et al., 2015).

While only limited or varying removal efficiencies were found for many compounds during conventional biological wastewater treatment applying the activated sludge process (Falås et al., 2016), an enhanced degradation could be demonstrated under optimized operational conditions in natural and engineered treatment systems (Regnery et al., 2016; Hellauer et al., 2017a; Müller et al., 2017). Here, especially the prevailing redox conditions and the availability of easily degradable substrate were found to influence the degree of compound transformation. While effective biodegradation of some compounds was observed also under reducing conditions (Wiese et al., 2011; König et al., 2016; Gonzalez-Gil et al., 2017), many studies reported an improved and accelerated transformation of TOrCs under oxic redox conditions (Massmann et al., 2008; Baumgarten et al., 2011; Regnery et al., 2015b). The amount and composition of available primary substrate was reported to shape the microbial community present. Substrate-limited, so-called oligotrophic conditions were reported to induce the establishment of a highly diverse microbial community (Li et al., 2012, 2013, 2014), possibly equipped with a higher metabolic potential also for the degradation of substances characterized by an increased persistence in other systems.

Previous studies aimed at optimizing the biodegradation of TOrCs in natural and engineered treatment systems. In sequential managed aquifer recharge technology (SMART), a two-stage infiltration with an intermediate aeration step is used to induce oxic and oligotrophic conditions during the second infiltration step. Several studies could demonstrate an improved degradation of moderately degradable TOrCs using SMART compared to conventional, single-stage infiltration systems (Regnery et al., 2016; Hellauer et al., 2017a, 2017b). The concept of sequential biofiltration (SBF) (Müller et al., 2017), transferred the sequential infiltration approach used in SMART into a biological above-ground treatment systems, applicable as an option for onsite treatment to achieve an enhanced biodegradation of TOrCs from WWTP effluents. Results from a previous study demonstrated an improved degradation of several moderately degradable TOrCs during SBF when compared to a single-stage biofilter operated at the same empty bed contact time (EBCT) (Müller et al., 2017).

While previous studies could demonstrate the enhanced removal of several compounds in SBF systems by comparing influent and effluent concentrations of SBF and single-stage biofiltration systems, a more detailed characterization of the process is needed, including the elucidation of degradation kinetics under different operational conditions.

Previous studies have used exponential pseudo-first order rate constants to describe the relationship between the degradation of TOrCs and the hydraulic residence time in natural and engineered biological filtration systems:

$$\frac{c(EBCT)}{c_0} = \exp(-k * EBCT) \tag{3}$$

Here, c_0 represents the initial concentration of the feed water, *c(EBCT)* is the concentration after a defined *EBCT*, and *k* is the compound-specific first-order biodegradation rate constant.

Analyzing data obtained from studies at managed aquifer recharge sites, Wiese et al. (2011) investigated biodegradation kinetics for TOrCs, including the possibility of using first-order biodegradation rate constants to describe observed concentration decays. Zearley and Summers (2012) and Hallé et al. (2015) determined first-order rate constants for the degradation of different TOrCs in drinking water filters. In a lab-scale column study simulating managed aquifer recharge, Regnery et al. (2015b) determined rate constants to compare the transformation of TOrCs under different redox conditions. The previous studies indicated that determined rate constants are strongly dependent on the prevailing redox conditions (Wiese et al., 2011; Regnery et al., 2015b). Rate constants were found to vary substantially when determined in different investigated systems (Hallé et al., 2015). The occurrence of compound specific threshold concentrations at which no further degradation is observed was reported in several studies (Wiese et al., 2011; Gonzalez-Gil et al., 2018, 2019a) and might complicate the determination and the application of rate constants. Also, decreasing biomass concentrations with increasing filter depth in biological filtration (Pharand et al., 2014), result in a stratification of biological activity and might impair the fit and the determination of rate constants. However, the calculation of biodegradation rate constants might be a tool to compare the degradation efficiency in controlled biological filtration systems under defined operational conditions.

In this study, the fate of a set of 53 indicator compounds in biofiltration column systems was monitored in detail via extensive profile sampling. The results were used to compare the biodegradation of TOrCs in three SBF systems and one conventional, single-stage biofiltration system. Sampling in different column depths was carried out to reveal new insights into the characteristics of TOrC transformation in biofiltration systems. The determination of rate constants might allow for the comparison of degradation efficiencies in different filter stages of SBF systems, independent from EBCT in the operated columns.

6.2 Materials and methods

6.2.1 Experimental setup

This study involved experiments with biofiltration columns using a setup at pilot-scale, as described by Müller et al. (2017). Two columns, A1 and A2 (filter bed length (l) = 1 m; inner diameter = 0.15 m), were filled with anthracite EVERZIT N type II (Evers GmbH, Germany; grain sizes 1.4 to 2.5 mm) and were equipped with backwash utilities, allowing for filter backwash with air and water. Three columns S1, S2 and S3 (l = 0.95 m; ID = 0.1 m) were filled with technical sand (Euroquarz GmbH, Germany, grain sizes 0.2 to 1.0 mm) which was initially inoculated with 5 % aquifer material from a riverbank filtration site to promote the establishment of biological activity in the beginning of the operation. Columns A1 and A2 were operated at EBCTs of 90 and 290 min, Columns S1, S2 and S3 were operated at EBCTs of 200, 1,000 and 2,000 min, respectively. Three sequential biofiltration (SBF) trains (A1+S1, A1+S2, A1+S3) consisted of an anthracite and a sand column operated in series with an intermediate aeration basin. Besides, anthracite column A2 was operated as a conventional, single stage biofilter. The biofiltration setup was fed with fully nitrified effluent from the WWTP Garching, Germany, using peristaltic pumps. Targeted EBCTs in the individual filter columns were achieved by adjusting the flow rates, measured at the column outlets.

6.2.2 Sample collection and analysis

Collection of liquid samples and determination of dissolved oxygen (DO) concentrations involved sampling in filter inlets, outlets and at sampling ports, installed in different column depths. Anthracite columns A1 and A2 were equipped with sampling ports in depths of 10, 20, 40, 60 and 80 cm. In sand columns S1, S2 and S3 sampling ports were installed in depths of 10, 30 and 70 cm. Liquid samples were analyzed for the parameters dissolved organic carbon (DOC), UV absorbance at 254 nm (UVA_{254}), ammonia and nitrate. The parameters were measured according to methods described in Müller et al. (2017). Besides, the concentrations of a set of indicator trace organic chemicals (TOrCs) was monitored using a method described in detail in Hermes et al. (2018) and Müller et al. (2019).

Samples were collected during a three-week sampling campaign with a total of five sampling events. Collection of corresponding samples was carried out during a three-weeks sampling campaign with a total of five sampling events. During three sampling events, liquid samples were collected from filter influents, effluents, and from sampling ports located at different column depths. During two sampling events, liquid samples were only collected from filter influents and effluents.

6.2.3 Characterization of redox conditions

Redox conditions were categorized as oxic, suboxic or anoxic based on categorizations introduced by McMahon and Chapelle (2008) and Regnery et al. (2015). Thus, redox conditions in filter columns are defined as oxic when DO concentrations in filter effluents are > 1mg/L. Partly suboxic conditions are defined by DO concentrations < 1mg/L in filter effluents and minor nitrate reduction (< 0.5 mg N/L) whereas anoxic conditions are defined by nitrate reduction exceeding 0.5 mg N/L.

6.2.4 Calculation of pseudo-first-order rate constants

Pseudo-first-order rate constants were calculated to determine the time-dependent degradation of TOrCs in the columns. A determination of the porosities of the used filter media revealed values of $\varepsilon = 0.40$ for sand and $\varepsilon = 0.43$ for anthracite. The comparable porosities suggested a similar relation between EBCT and HRT in filters operated with anthracite and sand. Therefore, in this study the EBCT was used as time variable. An exponential fitting procedure was used (software Origin 2019, function “non-linear fit Exp1p2”) to model concentrations normalized to column influents and to determine exponential pseudo-first-order rate constants, k, according to equation *(3)*.

6.3 Results and discussion

6.3.1 Characterization of redox conditions and substrate availability

Data for the characterization of redox conditions and the removal of organic bulk parameters were already presented and discussed in detail in a previous study (Müller et al., 2019). In brief, redox conditions in columns A1, A2, S1 and S2 could be characterized as oxic during the sampling campaign with DO concentrations above 1 mg/L in all column effluents. Redox conditions in column S3 could be characterized as partially suboxic, with DO concentrations below 1 mg/L after an EBCT of 715 min. Anoxic redox conditions indicated by relevant reduction of nitrate were observed at no time. DO consumption in anthracite column A1 (ΔDO 4.1 ± 0.2 mg/L) was observed to be lower than in column A2 (ΔDO 6.2 ± 0.4 mg/L), operated at a higher EBCT. Compared to DO consumption in column S1 (ΔDO 2.1 ± 0.1 mg/L), elevated consumption was also observed in columns S2 and S3 (ΔDO 4.7 ± 0.3 and 8.0 ± 0.2 mg/L) operated at higher EBCTs.

The consumption of DOC and the change in UVA_{254} was used to characterize substrate availability and degradation in the systems. Higher EBCTs in A2 compared to A1 were proposed as a cause for a slightly increased consumption of DOC (ΔDOC 1.4 ± 0.3 and 1.2 ± 0.2 mg/L) and changes in UVA_{254} (ΔUVA_{254} 1.2 ± 0.1 and 0.9 ± 0.1 1/m). Treatment in sand column S1 increased the overall consumption of DOC and changes in UVA_{254} in system A1+S1 (ΔDOC 1.6 ± 0.4 mg/L and ΔUVA_{254} 1.4 ± 0.1 1/m). Higher EBCTs in columns S1 and S2, increased the overall consumption of DOC and changes in UVA_{254} in systems A1+S2 and A1+S3 (ΔDOC 2.0 ± 0.3 and 2.2 ± 0.5 mg/L; ΔUVA_{254} 1.9 ± 0.3 and 1.9 ± 0.3 1/m).

Figures SI-3, SI-4 and SI-5 illustrate observed DO profiles, DOC concentrations and changes in UVA_{254} in all operated column systems.

6.3.2 Removal of trace organic chemicals

To investigate the fate of TOrCs in the operated column systems a total of 53 different indicator substances were monitored. To increase significance, only 47 substances were further analyzed for which concentrations in the WWTP effluent exceeded 3.5 x LOQ during all five sampling campaigns. High persistence indicated by poor removal below 25 % in all column systems was found for 24 substances which were not further analyzed. The remaining 23 compounds were found to be moderately (removal 25 to 70 %) or even well biodegradable (removal > 70 %). Table SI-8 summarizes details on all compounds measured during the sampling campaign and their removal in the column systems.

While the following analysis included only compounds which were susceptible to biodegradation, different degradation patterns were identified during the investigations. In general, observations revealed varying degradability in the different operated filter columns, a varying extent of degradation, and, for some compounds, the influence of reformation after initial degradation. Figure 6-1 displays degradation patterns of the four exemplarily chosen substances acesulfame, mecoprop, furosemide and citalopram. The degradation of acesulfame is characterized by steep initial gradients in the anthracite columns A1 and A2, while no further degradation seems to result from treatment in sand filters S1, S2 and S3. Despite the rapid initial removal, concentrations of acesulfame stagnated at concentration levels considerably above the LOQ. Limited removal of mecoprop was observed in columns A1 and A2. Here, treatment in sand columns S1, S2 and S3 resulted in rapid transformation below LOQ. The degradation of furosemide over time exhibited stable removal in both column types, indicated by a smooth exponential decay with increasing EBCT and a removal below LOQ in the sand columns. A very different pattern was found for citalopram. After substantial decay in anthracite filters A1 and A2, rapid initial degradation occurred in the sand columns. However, in columns S2 and S3, which were operated at higher EBCTs of 1,000 and 2,000 min, increasing concentrations in the deeper filter layers indicated reformation of citalopram.

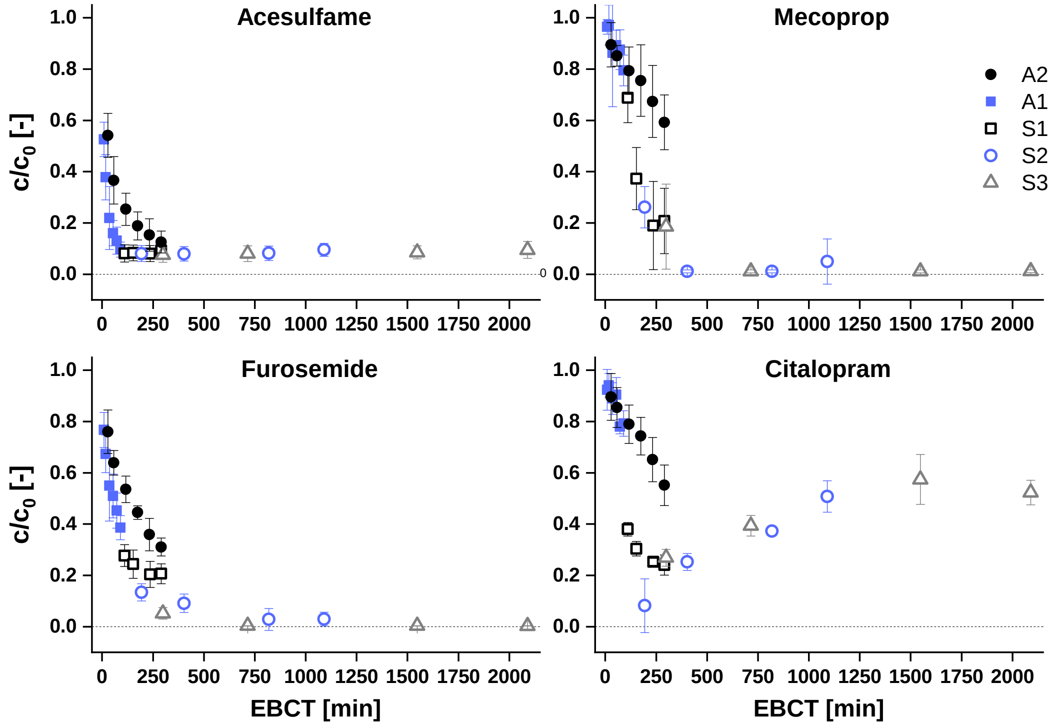

Figure 6-1: Concentrations of exemplarily chosen indicator TOrCs during conventional, single-stage biofiltration (A2) and sequential biofiltration (A1+S1; A1+S2; A1+S3) normalized to concentrations found in WWTP effluent; n = 3–5.

The degradation patterns observed for the four compounds displayed in Figure 6-1 are representative for the behavior of most investigated biodegradable substances observed in this study. Rapid initial degradation in filters A1 and A2, as observed for acesulfame, was also found for other compounds, such as clarithromycin, gabapentin, N,N-diethyl-meta-toluamide (DEET) or valsartan. The occurrence of threshold concentrations could be demonstrated for several compounds. Interestingly, threshold concentrations were mainly found for substances which exhibited rapid degradation in anthracite filters. Besides acesulfame, a similar pattern was also observed for DEET and gabapentin. After initial degradation in anthracite filters, characterized by steep gradients, very limited or even no further removal was observed after reaching a certain extent of degradation. Results indicated that this threshold level was rather independent from whether further treatment occurred in anthracite or in sand columns. Thus, removal of acesulfame in column A2, operated at an EBCT of 290 min did not exceed removal in column A1, operated at an EBCT of 90 min. Also, additional treatment in sand filters after reaeration and over substantially longer EBCTs did not result in a further degradation. For the degradation of TOrCs in biological systems at low concentrations, cometabolic transformation has often been referred to as the dominant transformation mechanism (Quintana et al., 2005; Rauch-Williams et al., 2010; Tran et al., 2013). Assuming a solely cometabolic mechanism, changing concentration levels cannot explain the stagnation of degradation. Gonzales-Gil et al. proposed the reversibility of enzymatic reactions as a potential reason for the phenomenon of threshold concentrations (Gonzalez-Gil et al., 2018, 2019a). At low concentrations, a thermodynamic equilibrium between transformation of the parent compound and the back-transformation of a dominant transformation product might result in stable concentrations. According to Gonzalez-Gil et al., the occurrence of threshold concentrations might thus be explained by thermodynamic equilibrium rather than by kinetic factors. This assumption, however, demands for additional investigations including the confirmation of an accumulation of primary transformation products. Highly specific enzymatic interactions in the degradation of different TOrCs are also indicated by the fact that other compounds, such as furosemide, are removed below the LOQ without exhibiting detectable threshold concentrations. This, however, might also be explained by lower reaction rate constants responsible for the back-transformation, resulting in lower equilibrium concentrations below the LOQ. Also, consecutive transformation of first metabolites might explain that threshold concentrations are not observed for all compounds. Other studies proposed a depletion of primary substrate as a potential cause for residual threshold concentrations in natural treatment systems (Baumgarten et al., 2011; Wiese et al., 2011). Assuming that also metabolic transformation might be responsible for or at least contribute to the degradation of certain compounds, residual concentrations might also result from a lower threshold for the feasibility of metabolic transformation. In the case of acesulfame, a recent study by Kahl et al. (2018) suggested that biodegradation pathways might evolve over time which might also enable the development of targeted metabolic activity for the degradation.

The relevance of the reversibility of enzymatic transformation is also demonstrated by the example of citalopram. Unlike a stabilization of concentrations at a certain threshold level, as observed for acesulfame, here, a drastic increase in concentration could be observed after substantial initial transformation, resulting in fluctuating concentrations. The effect was only observed in sand filters S2 and S3, operated at higher EBCTs, whereas concentrations in column S1 steadily decreased. Similar behavior could be observed for diphenhydramine. The results support findings from Gonzalez-Gil et al. (2019b) who observed reformation of citalopram after an initial decrease in experiments using enzymatic assays with enzymes extracted from anaerobic sludge. Gonzales-Gil et al. explained the observation by a reversibility of enzymatic reactions involved in the degradation of citalopram, an effect they also observed for other compounds, such as clarithromycin and climbazole. A similar pattern for clarithromycin and climbazole, however, was not found in this study which might be explained by different transformation pathways under oxic conditions. Also, a reformation of sulfamethoxazole related to back-transformation of the main transformation-product N^4-acetylsulfamethoxazole, as described by other studies (Göbel et al., 2005; Achermann et al., 2018a) was not observed in this study. Back-transformation might be caused by the same enzymes responsible for the initial degradation, as proposed by Gonzalez-Gil et al. (2019a) but could also be carried out by different enzymes in the deeper layers of the column.

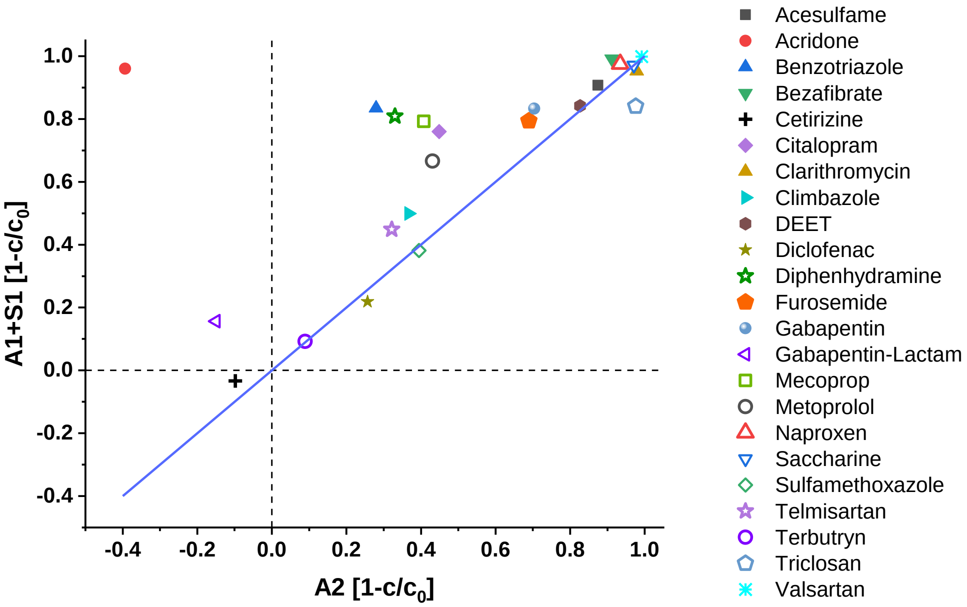

Figure 6-2: Removal of compounds in A2 and in SBF system A1+S1.

Preferential removal in sand filters S1, S2 and S3, as observed for mecoprop, was also found for other compounds, such as acridone and benzotriazole. The preferential removal of compounds in sand filters indicates a beneficial effect of changed operational conditions after pre-treatment in A1. Here, a different microbial community might profit from the substrate-limited and oxic conditions as proposed by several studies (Li et al., 2012, 2013, 2014; Alidina et al., 2014; Regnery et al., 2015b). Benefits of the sequential biofiltration approach compared to conventional, single-stage biofiltration, as demonstrated in a previous study (Müller et al., 2017), could also be observed in this study. An improved degradation of several moderately degradable compounds was observed in SBF system A1+S1 when compared to single stage biofilter A2, operated at the same EBCT of 290 min (Figure 6-2). For most compounds, however, removal in both systems was comparable. Also, degradation of the compounds diphenhydramine and citalopram, which both indicated higher removal in system A1+S1, was found to be reversible, as discussed above. Little differences in process performance between single stage biofilter A2 and SBF system A1+S1 might be related to oxic redox conditions in both systems during the sampling campaign. In a previous study (Müller et al., 2017) single stage filter A2 was characterized by partly suboxic redox conditions which might have impaired the degradation of compounds. To assess the removal of indicator substances in systems A1+S2 and A1+S3, also the increased EBCTs in sand columns S2 and S3 must be taken into account when comparing degradation performance in different systems.

6.3.3 Determination of pseudo-first-order rate constants

The determination of pseudo-first-order rate constants might be a viable option to characterize and compare the degradation of indicator compounds in biofiltration systems, especially when operated at different EBCTs. Rate constants k were calculated according to equation *(3)* for all operated columns A2, A1, S1, S2 and S3 (Table 6-1). The quality of the exponential fit used to determine k values was expressed by the coefficient of determination (R^2). In the following discussion only those k values were considered for which R^2 was > 0.45. A broad variety was found for the quality of fit, depending on the investigated compound and also the described column. Figure 6-3 exemplarily displays concentrations of acesulfame, mecoprop and furosemide at different EBCTs normalized to concentrations detected in column influents and illustrates the exponential fit used for the determination of rate constants.

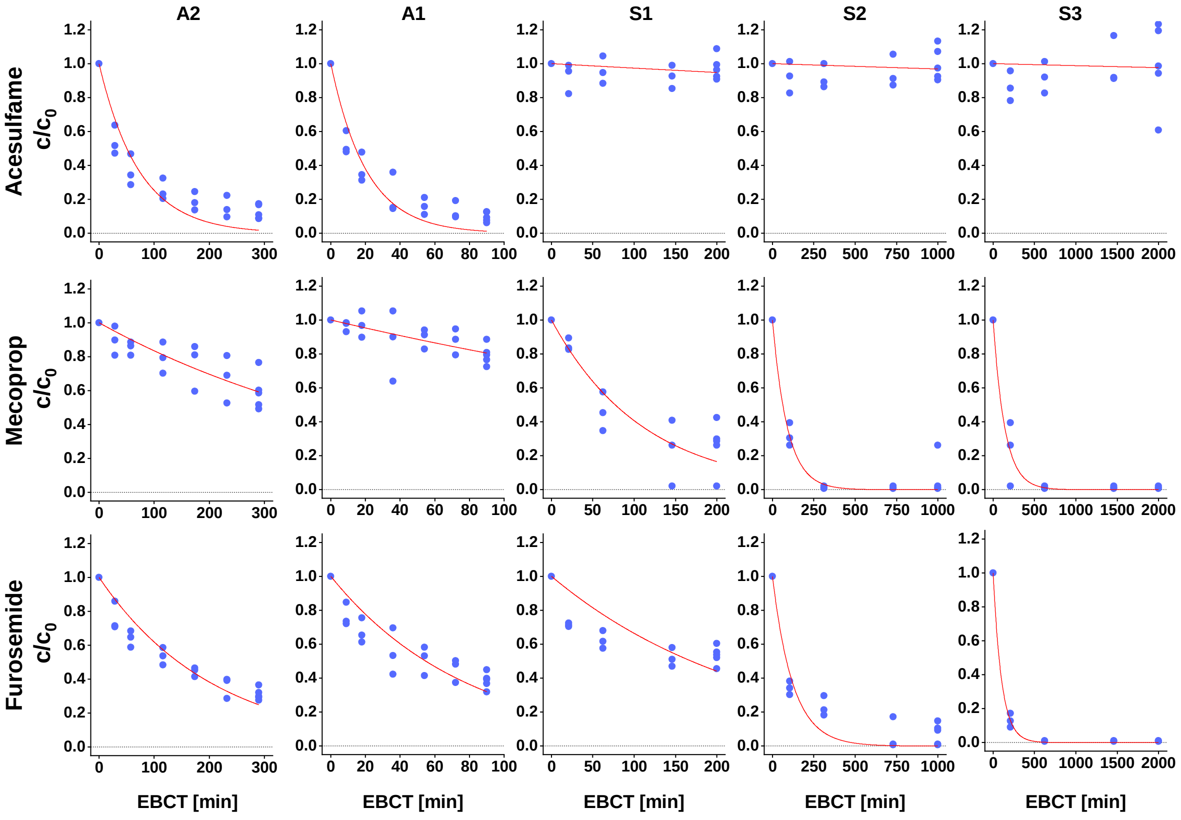

Figure 6-3: Degradation of exemplarily chosen TOrCs in operated columns and exponential fit ($c/c_0 = \exp(-k*EBCT)$). Concentrations normalized to column influents. Concentrations observed in WWTP effluent (c_0 for A1 and A2) and percent removal values in filter systems are summarized in Table SI-8.

Figure 6-4 summarizes and compares calculated rate constants in columns A1 and A2 and indicates higher degradation rates in A1 compared to A2 for most investigated compounds. While DO concentrations in deeper column layers were higher than in column A2, both columns could be characterized as oxic throughout the experimental campaign (Figure SI-3), which excludes unfavorable redox conditions as a cause for the observed differences. Different hydraulic loading rates might, in theory, affect external mass transfer by influencing the thickness of the water boundary layer. Thus, a decreased thickness of the boundary layer at higher hydraulic loading rates could decrease mass transfer resistance. However, several studies reported external and internal mass transfer to be of minor importance in biofiltration systems while degradation kinetics of biodegradable compounds were mainly controlled by reaction rates (Wang and Summers, 1996; Gagnon and Huck, 2001; van der Kooij et al., 2013). Reasons for the noticeable differences between the anthracite filters remained unclear.

Figure 6-4b compares rate constants determined in filter columns A1 and S1, thus, in the first and second stage filters of an SBF system. Hypothesizing optimized operational conditions for the degradation of TOrCs established in S1, faster degradation with higher rate constants could be expected. The comparison indicates higher rate constants for several compounds, such as acridone, benzotriazole, mecoprop and citalopram. While rapidly removed in both columns, also bezafibrate and naproxen exhibited higher removal rates in column S1. On the contrary, rate constants for diclofenac, sulfamethoxazole, DEET and acesulfame could only be calculated for column A1, due to little additional removal and high variation indicated by low or even negative R^2 values obtained for curve fitting of data in column S1 (see Table 6-1). As discussed above, threshold concentrations for some of these compounds might explain these observations. The potential impact of threshold concentrations impairs the comparability of results obtained in columns A1 and S1. While results indicated that removal only occurs in column A1, no conclusions could be drawn regarding theoretical rate constants in sand filters in the presence of higher concentrations of these substances. Assuming solely cometabolic degradation mechanisms, the differences between concentrations in the inlet of columns A1 and S1 should not affect the degradation patterns in the columns. However, previous studies indicated that even at low concentration ranges of ng/L to µg/L, slightly elevated concentration levels might induce a more efficient transformation (Baumgarten et al., 2011).

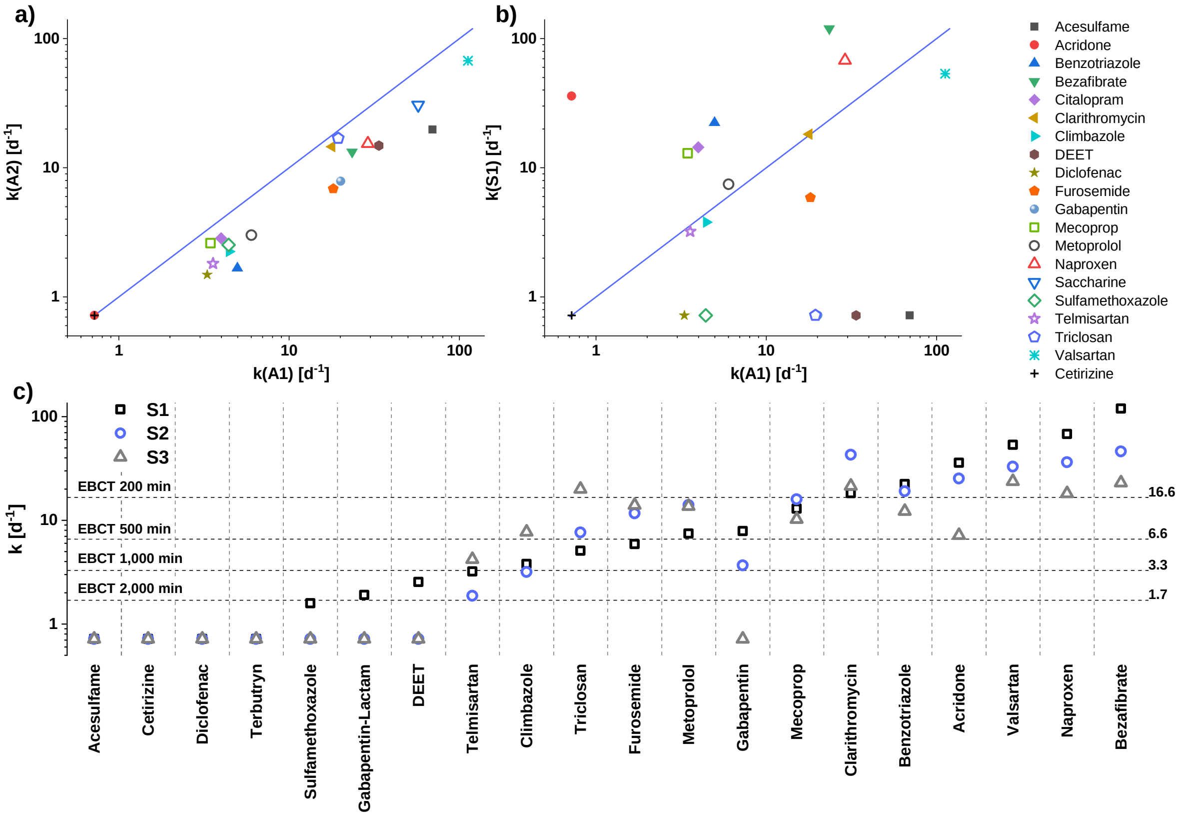

Figure 6-4: Pseudo-first-order rate constants k for investigated TOrCs; comparison between columns a) A1 and A2; b) A1 and S1 and c) S1, S2 and S3; c): horizontal lines indicate minimum k values to achieve removal of 90 % at EBCTs of 200, 500, 1,000 and 2,000 min. Asterisks indicate removal below LOQ at the first sampling port of columns S2 and S3.

A comparison of rate constants determined for the degradation of compounds in sand filters S1, S2 and S3, operated at EBCTs of 200, 1,000 and 2,000 min, is illustrated in Figure 6-4c. In general, a similar trend could be observed for rate constants of different compounds in sand filters. However, the results also exhibited substantial differences, especially for well degradable substances, such as acridone, naproxen and bezafibrate. Here, determined rate constants were found to decrease with increasing EBCT in the columns (k(S1) > k(S2) > k(S3)). This observation can, most likely, be linked to the different EBCTs between the column inlet and the first sampling port located at a column depth of 10 cm. Thus, lower rate constants determined in columns S2 and S3 compared to column S1 might simply originate from lower resolution over EBCT. The example of bezafibrate illustrates the effect (Figure 6-5). Although removal below LOQ was observed already at the first sampling port in a depth of 10 cm in columns S2 and S3, rate constants determined for degradation in columns S1, S2 and S3 differed substantially. This effect might also complicate the comparison of rate constants determined in different studies and might be a cause of a high variability.

Compared to studies in batch systems, vertical gradients in biofiltration columns complicate the interpretation of acquired data. The validity of rate constants has been reported to be closely related to prevailing operational conditions. Previous studies proved that redox conditions have a great impact on compound degradation and determined rate constants (Wiese et al., 2011; Regnery et al., 2015b; Schmidt et al., 2017). Also, substrate availability has the potential to alter the degradation performance of biological systems (Rauch-Williams et al., 2010; Alidina et al., 2014; Li et al., 2014). The inhomogeneity of operational conditions in vertical flow systems might affect the degradation of individual substances, often characterized by highly compound specific degradation patterns. Besides decreasing concentrations of primary substrate and DO, also biomass density decreases with increasing column depth (Wang et al., 1995; Carlson and Amy, 1998; Pharand et al., 2014; Carpenter and Helbling, 2017).

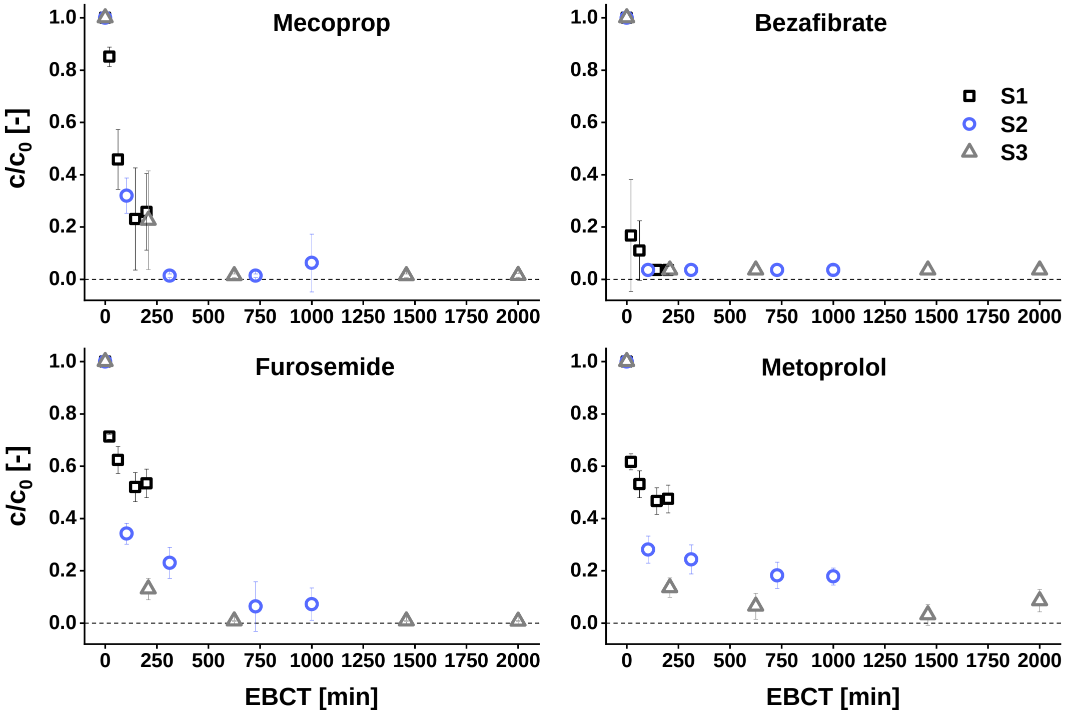

Figure 6-5: Concentrations of exemplarily chosen indicator TOrCs in sand filters S1, S2 and S3 normalized to concentrations found in column inlets; n = 3–5.

In Figure 6-5, the degradation of mecoprop, bezafibrate, furosemide and metoprolol in sand filters S1, S2 and S3 is illustrated. The degradation of mecoprop over EBCT reveals similar behavior in all three sand columns. This is also indicated by the relatively small differences between the calculated rate constants (Figure 6-4c; Table 6-1). In contrast, the degradation of furosemide and metoprolol over EBCT revealed differences. After comparable EBCTs (100 to 300 min), the highest degradation was observed in column S3 followed by S2 and S1. Here, residence time in the top layer of the columns was positively correlated with degradation. Differences in degradation efficacy in column top layers are likely related to an increased microbial activity in response to higher concentrations of available substrate. Elevated DO and DOC consumption in top layers of column S3 supports this assumption

(Figures SI-3 and SI-4) and indicates accumulation of microbial activity in column top layers. The effect was already demonstrated in a previous study and suggests that the degradation of some compounds correlates well with DO consumption (Müller et al., 2019). Several studies observed that at higher hydraulic loading rates, the transport of BDOC into deeper filter layers induced increased microbial activity in deeper zones (Carlson and Amy, 1998; Carpenter and Helbling, 2017). In this study, however, elevated degradation observed in top layers of columns S2 and S3, was not outweighed by further degradation in the deeper layers of column S1. The examples of furosemide and metoprolol illustrate the limitations of pseudo-first order rate constants in precisely describing the degradation behavior in column systems characterized by vertical gradients of microbial activity. Despite comparably high R^2 values determined for the fit to metoprolol degradation in S2 and S3, the k value suggests slightly faster degradation in column S2 (Table 6-1). As described above, however, the data actually indicated a more rapid degradation in the top layers of column S3.

Table 6-1: Pseudo-first-order reaction rate constants for 23 biodegradable indicator compounds. Asterisks indicate insufficient exponential fit (R^2 < 0.45) or very low rate constants (< 0.7 d^{-1}). Concentrations for saccharine detected in the effluent of A1 were too low (< 3.5 x LOQ) to calculate rate constants in columns S1, S2 and S3.

Compound	**A2**		**A1**		**S1**		**S2**		**S3**	
	k [d^{-1}]	**R^2**	**k [d^{-1}]**	**R^2**	**k [d^{-1}]**	**R^2**	**k [d^{-1}]**	**R^2**	**k [d^{-1}]**	**R^2**
Acesulfame	19.8	0.90	69.7	0.93	0.7*	-0.11	0.7*	-0.13	0.7*	-0.06
Acridone	0.7*	0.65	0.7*	0.45	35.8	0.89	25.3	0.97	7.2	0.92
Benzotriazole	1.7	0.94	5.0	0.7	22.3	0.86	19.1	0.84	12.2	0.82
Bezafibrate	13.2	0.94	23.4	0.90	119.5	0.95	46.1	1.00	23.1	1.00
Cetirizine	0.7*	-0.62	0.7*	-0.23	0.7*	0.22	0.7*	0.61	0.7*	0.59
Citalopram	2.9	0.85	4.0	0.65	14.4	0.63	0.7*	-0.65	0.7*	-0.51
Clarithromycin	14.6	0.95	17.8	0.84	18.2	0.84	42.7	0.75	21.4	0.49
Climbazole	2.2	0.91	4.4	0.86	3.8	0.66	3.2	0.54	7.7	0.25
DEET	14.9	0.90	33.7	0.92	2.5	0.35	0.7*	0.28	0.7*	0.02
Diclofenac	1.5	0.79	3.3	0.81	0.7*	0.09	0.7*	0.51	0.7*	0.80
Diphenhydramine	1.9	0.83	2.6	0.29	48.7	0.73	20.5	-1.46	0.7*	-0.48
Furosemide	6.9	0.91	18.2	0.82	5.9	0.64	11.7	0.94	14.1	1.00
Gabapentin	7.9	0.88	20.2	0.83	7.9	0.37	3.7	0.49	0.7*	0.40
Gabapentin-Lactam	0.7*	-0.14	0.7*	0.10	1.9	0.69	0.7*	0.61	0.7*	0.64
Mecoprop	2.6	0.73	3.5	0.45	12.9	0.88	16.0	0.98	10.3	0.98
Metoprolol	3.0	0.80	6.0	0.65	7.5	0.53	14.1	0.82	13.6	0.98
Naproxen	15.4	0.93	29.1	0.91	67.7	0.91	36.3	0.98	18.2	0.98
Saccharine	30.7	0.97	57.4	0.76	-		-		-	
Sulfamethoxazole	2.5	0.93	4.4	0.62	1.6	0.34	0.7*	0.43	0.7*	0.21
Telmisartan	1.8	0.95	3.6	0.84	3.2	0.76	1.9	0.77	4.2	0.75
Terbutryn	0.7*	0.39	0.7*	0.11	0.7*	0.00	0.7*	0.26	0.7*	0.09
Triclosan	16.9	0.96	19.4	0.66	5.1	0.25	7.6	0.96	20.0	0.99
Valsartan	67.4	1.00	112.4	0.98	53.4	0.96	33.0	0.99	23.8	1.00

Results obtained in this study indicated a limited benefit of higher EBCTs in second stage filters of SBF systems on the degradation of TOrCs. Horizontal lines in Figure 6-4c illustrate minimum rate constants necessary to theoretically achieve 90 % degradation at EBCTs of 200, 500, 1,000 and 2,000 min in second stage sand filters. As indicated in Figure 6-4c, lower rate constants necessitate higher EBCTs to achieve a defined treatment target. However, several of the compounds with low rate constants in sand filters S1, S2 and S3, such as acesulfame, DEET or gabapentin were well removed in the first stage anthracite filter A1 (Tables 6-1 and SI-8). In addition, results indicated that degradation in columns S2 and S3 mainly occurred in column top layers, whereas little additional transformation was observed in the deeper column layers. Therefore, the feasibility of systems with high EBCTs, and thus, higher footprints, must be discussed critically.

6.4 Conclusions

This study aimed at a better characterization of the removal of trace organic chemicals (TOrCs) in wastewater treatment plant effluent using advanced biological treatment by monitoring the degree of TOrC degradation in different column depths of biofiltration and sequential biofiltration (SBF) systems. Besides, the study investigated the suitability of using pseudo first-order rate constants to describe observed degradation kinetics using the empty bed contact time (EBCT).

Results indicated compound-specific differences in the observed degradation patterns. While 24 of 47 compounds exhibited high persistence (removal < 30 %) in all operated systems, moderate (removal 30 to 70 %) and good (removal > 70 %) degradability was observed for 6 and 17 compounds, respectively. Biodegradable compounds showed different removal patterns. Fast transformation, independent of the investigated column system, was observed for several compounds, such as acesulfame and furosemide. Other compounds, such as mecoprop, revealed more effective transformation in second stage filters of the SBF system. For some compounds, such as citalopram, substantial reformation was observed after initial transformation. The occurrence of threshold concentrations was observed for various compounds.

Pseudo-first-order rate constants from cometabolic degradation of TOrCs contain valuable information about the degradability of substances in a biological system. Provided a good fit of the model to observed experimental data and a sufficiently high resolution over EBCT, rate constants could also be used to scale biological systems to achieve an envisioned treatment target. However, results from this study also revealed the limitations of the concept. Pseudo-first-order rate constants are not suitable to determine the effect of threshold concentrations. Also, their transferability might be limited in particular in inhomogeneous systems, such as vertical flow columns or filters when operational parameters, such as hydraulic loading rates, vary.

7 Capturing the oxic transformation of iopromide – A useful tool for an improved characterization of predominant redox conditions and the removal of trace organic compounds in biofiltration systems?

The following chapter presents investigations related to **Hypothesis #2**, "*The use of known iopromide transformation products as intrinsic redox tracers allows for a sensitive characterization of in situ redox conditions in oxic to suboxic environments during biofiltration*".

The chapter presents results from a study investigating an approach for an alternative characterization of in-situ redox conditions during biofiltration using known transformation products of the X-ray contrast medium iopromide as intrinsic redox tracers. **Hypotheses #2.1** and **#2.2** were tested using column experiments including sequential biofiltration systems operated at different empty bed contact times and a conventional, single-stage biofilter. The investigation also aimed at linking the successive transformation of iopromide to the initial transformation of other biodegradable compounds.

The chapter has been published with editorial changes as follows:

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Author contributions: Johann Müller, Uwe Hübner, Jörg E. Drewes, Kevin S. Jewell and Thomas A. Ternes developed the research objective and designed the experiment. Johann Müller conducted the experiments and carried out a part of the analyses. Nina Hermes and Manoj Schulz carried out LC-MS/MS analyses for the quantification of trace organic compounds and iopromide transformation products. Johann Müller wrote the paper. Uwe Hübner, Jörg E. Drewes, Kevin S. Jewell and Thomas A. Ternes reviewed the manuscript. Uwe Hübner and Jörg E. Drewes supervised the study. All authors approved the final version of the manuscript.

Capturing the oxic transformation of iopromide – A useful tool for an improved characterization of predominant redox conditions and the removal of trace organic compounds in biofiltration systems?

Abstract

The biological degradation of many trace organic compounds has been reported to be strongly redox dependent. The traditional characterization of redox conditions using the succession of inorganic electron acceptors such as dissolved oxygen and nitrate falls short in accurately describing the critical transition state between oxic and suboxic conditions. Novel monitoring strategies using intrinsic redox tracers might be suitable to close that gap. This study investigated the potential use of the successive biological transformation of the iodinated contrast medium iopromide as an intrinsic tracer of prevailing redox conditions in biofiltration systems. Iopromide degradation in biofiltration systems was monitored by quantifying twelve known biological transformation products formed under oxic conditions. A novel dimensionless parameter (T_{IOP}) was introduced as a measure for the successive transformation of iopromide. A strong correlation between the consumption of dissolved oxygen and iopromide transformation emphasized the importance of general microbial activity on iopromide degradation. However, results disproved a direct correlation between oxic (> 1 mg/L O_2) and suboxic (< 1 mg/L O_2) conditions and the degree of iopromide transformation. Results indicated that besides redox conditions also the availability of biodegradable organic substrate affects the degree of iopromide transformation. Similar behavior was found for the compounds gabapentin and benzotriazole, while the oxic degradation of metoprolol remained stable under varying substrate conditions.

7.1 Introduction

Widespread occurrence of pharmaceuticals, industrial chemicals, and personal care products at low concentrations in various water bodies, referred to as trace organic compounds (TOrCs), has been subject to numerous studies in the field of water research (Ternes, 2007; Benotti et al., 2009; Dong et al., 2015). Since their removal during conventional treatment is often limited, effluents from municipal wastewater treatment plants (WWTPs) are considered major point sources for the entry of TOrCs into the aquatic environment. Treatment processes like activated carbon adsorption or ozonation have been shown to serve as effective barriers for an improved removal or transformation of many of these compounds (Huber et al., 2003; Jekel et al., 2013). Recent studies also emphasize the potential of advanced transformation in biofiltration processes under optimized operational conditions (Regnery et al., 2016; Müller et al., 2017; Hellauer et al., 2017a).

The transformation of TOrCs in biological systems has been shown to strongly depend on predominant redox conditions (Wiese et al., 2011; Regnery et al., 2015b). While few compounds were reported to be preferably degradable under reducing conditions (Wiese et al., 2011; König et al., 2016; Ghattas et al., 2017), many studies have shown an improved removal of various moderately biodegradable TOrCs when oxic conditions prevail (Massmann et al., 2008; Baumgarten et al., 2011; Regnery et al., 2015). Regnery et al. (2015) demonstrated the sensitivity of biological TOrC removal in biologically-active porous media systems to slight changes in redox conditions, where rate constants decreased significantly from oxic to suboxic and anoxic conditions.

Traditional characterization of redox conditions in natural systems is based on monitoring the ecological succession of the inorganic electron acceptors dissolved oxygen, nitrate, sulfate, manganese and iron (McMahon and Chapelle, 2008). While using this categorization allows to broadly characterize redox zonation in aquifer systems it might not be sensitive enough to accurately describe the transition state between oxic and suboxic conditions or prevalent conditions at the pore scale where biotransformation occurs. In addition, the determination of low dissolved oxygen concentrations is often challenging since oxygen-free sampling is difficult (Muntau et al., 2016). Novel monitoring concepts might be more suitable to predict redox-sensitive biodegradation of TOrCs in biofiltration systems.

Iopromide, a tri-iodinated benzoic acid derivate used as a X-ray contrast agent, can be detected in many water bodies affected by the discharge of municipal WWTP effluents (Putschew et al., 2000; Ternes and Hirsch, 2000; Kormos et al., 2011; Xu et al., 2017). Biological transformation of iopromide during conventional activated sludge treatment and in managed aquifer recharge systems, such as riverbank filtration and soil aquifer treatment, was observed in many studies (Schittko et al., 2004; Batt et al., 2006; Ternes et al., 2007; Schulz et al., 2008; Kormos et al., 2011; Muntau et al., 2016; Redeker et al., 2018). Transformation of iodinated X-ray contrast agents typically does not result in mineralization of the parent compounds but involves the formation of numerous iodinated transformation products (Kalsch, 1999; Schulz et al., 2008; Kormos et al., 2010, 2011). Only under anaerobic conditions deiodination was observed (Drewes et al., 2001; Schittko et al., 2004; Redeker et al., 2018).

Schulz et al. (2008) proposed a transformation pathway for the biological degradation of iopromide under oxic conditions identifying a total of 12 different iodinated transformation products (TPs) (Figure 7-1). Kormos et al. (2011) categorized these 12 iopromide TPs in three phases according to their appearance during complete transformation using controlled batch experiments. Iopromide TPs of phase I (TP 805 A, TP 805 B, TP 819) include TPs which are formed in the beginning of the transformation. Degradation of phase I TPs leads to the formation of phase II intermediates (TP 817 A, TP 731 A, TP 731 B, TP 729 A, TP 787 A), which eventually are further transformed into more persistent phase III TPs (TP 701 A, TP 701 B, TP 759, TP 643). Further degradation of the final phase III TP 643 under oxic conditions was not observed (Schulz et al., 2008).

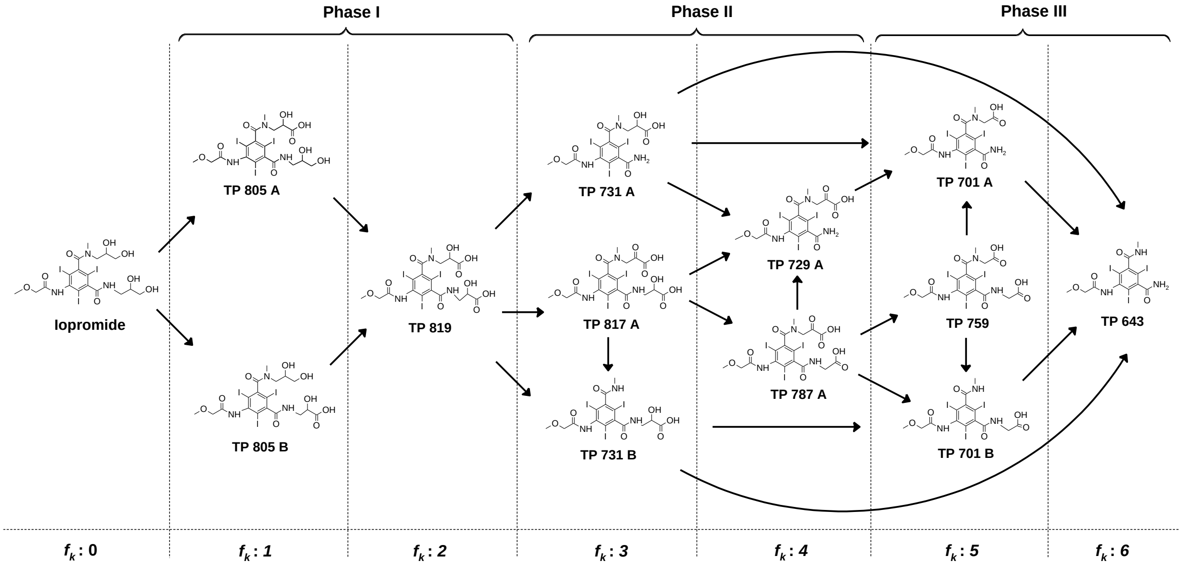

Figure 7-1: Proposed pathway for the oxic transformation of iopromide (adapted from Schulz et al. (2008)) with defined transformation phases I, II and III and defined dimensionless transformation factors f_k. Details on the definition of transformation factors f_k can be found in section 7.3.5.

Muntau et al. (2016) proposed monitoring the succeeding stages of TPs during the oxic biodegradation of iopromide as defined by Schulz et al. (2008) and Kormos et al. (2011), as an approach for an *in situ* characterization of prevalent redox conditions during short-term soil-aquifer treatment. Following up on findings from Scholz et al. (2008) and Muntau et al. (2016), this study attempted to investigate the potential of using intermediates of the biological transformation of iopromide under oxic conditions for a more precise characterization of operational redox conditions in technical biofiltration systems applied as advanced biological treatment steps subsequent to conventional wastewater treatment. In addition, the influence of other operational and environmental parameters, such as empty bed contact time and substrate availability, on the step-wise transformation of iopromide was investigated by introducing a novel dimensionless parameter (T_{IOP}) as a measure for the successive iopromide transformation.

7.2 Materials and methods

7.2.1 Experimental setup

Biofiltration column studies were conducted using an experimental setup at pilot-scale using filter columns as described by Müller et al. (2017). Sequential biofiltration (SBF) trains were comprised of an anthracite column as first and a sand column as second stage filter. Oxygen was resupplied to the first stage filter effluent using an intermediate aeration basin fed with compressed air. An additional anthracite filter was operated as a single-stage biofilter. Fully nitrified tertiary effluent from the WWTP Garching, Germany, was fed to the filter trains using peristaltic pumps. Two backwashable filter columns (A1 and A2, filter bed length (l) = 1 m, inner diameter (ID) = 0.15 m) were filled with anthracite (Everzit N type II, Evers GmbH, Germany; grain sizes 1.4 to 2.5 mm) and three columns

(S1, S2, S3; l = 0.95 m, ID = 0.10 m) were operated using sand as filter material (Euroquarz GmbH, Germany; grain sizes 0.2 to 1.0 mm). Sand filters were initially inoculated with 5 % aquifer material from a riverbank filtration site to accelerate the establishment of biological activity in second stage filters in the beginning of the operation. Filter columns were operated for over 22 months under varying operational conditions prior to conducting the experiments presented in this study. To assure the presence of sufficient iopromide in the tertiary effluent, in line dosing of an aqueous stock solution (3 mg/L) was used to adjust a concentration of 30 µg/L in the influent water using high precision peristaltic pumps. Although iopromide concentrations of more than 10 µg/L in tertiary effluents were reported (Ternes and Hirsch, 2000), a concentration of 30 µg/L must be considered exceptionally high. Spiking of iopromide, however, was inevitable to allow for the sufficient abundance of iopromide TPs. Other investigated TOrCs were not spiked to the system but were present in the tertiary effluent.

7.2.2 Operational conditions

Investigations were carried out during two experimental campaigns. Elevated iopromide concentrations were adjusted four weeks before the start of the experimental campaigns to allow for system adaptation prior to sampling. Empty bed contact times (EBCTs) in the column systems were held constant for over six months before the start of the first experimental campaign.

- During the first experimental campaign three SBF systems were operated. SBF systems consisted of a first filter stage (A1) operated at an EBCT of 90 min and three second stage filters operated in parallel at EBCTs of 200, 1,000 and 2,000 min (S1, S2, S3). In addition, column A2 was used as a single-stage conventional biofilter as a reference to SBF system A1+S1 and operated at the same total EBCT of 290 min.
- During the second experimental campaign two SBF systems (A1+S1; A1+S3) were used and operated at unchanged EBCTs compared to the first experimental campaign. To manipulate prevailing redox conditions in column S3 a hydrogen peroxide solution was added to the column influent via a high precision peristaltic pump. Thus, assuming stoichiometric decomposition of hydrogen peroxide to dissolved oxygen (DO) with a ratio of 2:1, an additional 5 mg/L DO were supplied. Dilution due to dosing of hydrogen peroxide was less than 2 % and considered negligible. Previous studies demonstrated that in the absence of UV irradiation no degradation of TOrCs or dissolved organic matter compounds due to chemical degradation caused by hydrogen peroxide alone occurred (Kitis and Kaplan, 2007; Miklos et al., 2018).

Detailed information on the system setup used during both experimental campaigns is given in the Supplementary Information (Figure SI-6).

7.2.3 Sample collection and analysis

Liquid samples for the analysis of dissolved organic carbon (DOC), UV absorbance at 254 nm (UVA_{254}), TOrCs and iopromide TPs were taken from inlets, outlets and from different depths of the filter columns which were equipped with sampling ports at different depths (A1, A2 (10, 20, 40, 60, 80 cm); S1, S2, S3 (10, 30, 70 cm)). Ammonia and nitrate were measured in inlet and outlet samples. Analysis of ammonia, nitrate, DOC, UVA_{254} and DO measurements at different depths of the columns were carried out according to methods described in Müller et al. (2017).

7.2.4 Analysis of trace organic compounds

The analytical method for the quantification of 54 TOrCs (pharmaceuticals, ingredients of personal care products, industrial chemicals, herbicides, fungicides, sweeteners) investigated during the first experimental campaign is described in detail in Hermes et al. (2018). Samples were filtered using 0.45 µm cellulose acetate membrane filters. The analysis involved liquid chromatography coupled with tandem mass spectrometry with electrospray ionization (LC-ESI-MS/MS) and direct-injection of 80 µl sample. Split into two detection methods, the analysis was performed on a high-pressure liquid chromatography (HPLC) unit 1260 Infinity Series equipped with a Zorbax Eclipse Plus C18 column (150 mm x 2.1 mm, 3.5 µm, Agilent Technologies) coupled to a TripleQuad mass spectrometer (6500+, Sciex). A water-acetonitrile gradient was used; for detection method 1, the aqueous phase was acidified with 0.1 % formic acid while detection method 2 was acidified with 0.1 % acetic acid. Analysis was performed in scheduled multiple reaction monitoring (MRM) mode using deuterium labelled surrogates as internal standards for the quantification of all analytes. Detailed information on MRM transitions and assignment of internal standard to the analytes and validation parameters can be found in Hermes et al. (2018).

During the second experimental campaign LC-ESI-MS/MS measurements in ESI-positive mode were carried out to analyze a reduced set of 11 different indicator compounds using a method described by Müller et al. (2017).

Details on limits of quantitation (LOQs) and inlet concentrations for both experimental campaigns can be found in Tables SI-9 and SI-10.

7.2.5 Analysis of iopromide transformation products

All chemicals were LC/MS grade, labeled and analytical standards were purchased from Dr. Ehrenstorfer GmbH or Toronto Research Chemicals Inc. Iopromide TPs were isolated from batch experiments via semi-preparative HPLC (Schulz et al., 2008). Calibration samples were prepared in Milli-Q water with an internal standard concentration of 10 µg/L and an analyte concentration range from 0.1 to 100 µg/L. 1 mL of filtered column samples were spiked with internal standard (iopromide-d3) to 10 µg/L. Recoveries were determined in spiked samples with concentrations of 10 and 100 µg/L.

The analysis of iopromide and its TPs was carried out by direct injection of 50 µL sample into a LC-ESI-MS/MS system using an Agilent 1260 LC system, equipped with an Eclipse Plus C18 column coupled by ESI in positive ionization mode to a Sciex Triple Quad 6500+ mass spectrometer following a method described by Schulz et al. (2008). Chromatographic and MS conditions, LOQs and recoveries are listed in Tables SI-11 and SI-12.

7.2.6 Definition of redox conditions

The classification of redox conditions followed definitions proposed by Regnery et al. (2015) and McMahon and Chapelle (2008) and were based on the measurement of DO and nitrate. Columns characterized by effluent DO concentrations above 1 mg/L are defined as oxic. DO concentrations below 1 mg/L with limited nitrate reduction (< 0.5 mg N/L) are defined as suboxic. Anoxic conditions are characterized by nitrate reduction exceeding 0.5 mg N/L.

7.3 Results and discussion

7.3.1 Characterization of redox conditions based on the conventional redox parameters dissolved oxygen and nitrate

Redox conditions during the first experimental campaign were revealed as oxic in most operated columns except for column S3 which was characterized by elevated DO consumption and predominantly suboxic redox conditions. Anoxic redox conditions, indicated by substantial reduction of nitrate, were not observed (data not shown). DO profiles in SBF systems A1+S1 and A1+S2 (Figure 7-2c, b), exhibited rapid DO consumption in first stage filter A1 (ΔDO 4.1 ± 0.2 mg/L). After reaeration limited and slower consumption was observed in second stage filters S1 and S2 (ΔDO 2.1 ± 0.1 and 4.7 ± 0.3 mg/L, respectively) despite substantially higher EBCTs compared to column A1. For column S3 DO concentrations below 1 mg/L were found after an EBCT of 715 min while complete DO depletion (ΔDO 8.0 ± 0.2 mg/L) was observed after an EBCT of 1,500 min (DO concentrations < 0.1 mg/L) (Figure 7-2d). Single-stage biofilter A2 (EBCT 290 min) was characterized by elevated DO consumption compared to filter A1 (EBCT 90 min) while redox conditions in the column could still be characterized as oxic with DO concentrations of 1.2 ± 0.2 mg/L in the filter effluent (Figure 7-2a). No difference was found in total DO consumption in SBF system A1+S1 and reference column A2 (ΔDO 6.2 ± 0.2 and 6.2 ± 0.4 mg/L).

The second experimental campaign was characterized by substantially increased DO consumption in the investigated column systems A1+S1 and A1+S3 (Figure 7-2e, f). Similar to the first experimental campaign, reduction of nitrate was not observed. Average DO concentrations indicated suboxic conditions at an EBCT of 72 min in column A1 while a total DO consumption of 7.7 ± 0.2 mg/L was observed. Columns S1 and S3 exhibited entirely oxic redox conditions while an increase of DO consumption was found for column S1 (ΔDO 3.4 ± 0.1 mg/L) compared to the first sampling campaign. Assuming complete decomposition of hydrogen peroxide a total of 8.9 ± 1.9 mg/L DO were consumed in column S3 (see section 7.2.2). It can be assumed that the addition of hydrogen peroxide prevented the establishment of suboxic zones in the deeper layers of column S3.

7.3.2 Removal of organic bulk parameters

Consumption of biodegradable dissolved organic carbon (BDOC) in the column systems was indicated by increasing DO consumption and successive removal of the organic bulk parameters DOC and UVA_{254}. Concentrations of ammonia in the tertiary effluent below the limit of detection (0.015 mg NH_4-N/L) and stable nitrate concentrations excluded nitrification as a relevant cause for DO consumption (data not shown). Profile sampling suggested high microbial activity in the top 10 cm of second stage filters S1, S2 and S3 indicated by disproportionate consumption of DOC, DO (Figure 7-2c, b, d), and UVA_{254} (Figure SI-7c, b and d). Though pronounced biological activity in the upper filter layers was also found for columns A1 and A2, a rather homogeneous consumption was observed in the deeper layers of filters A1 and A2 indicating the presence and degradation of BDOC in the entire column system. It is assumed that frequent backwashing events in columns A1 and A2 are causing some degree of mixing of the filter material, preventing distinct stratification of biological activity as observed in filters S1, S2 and S3.

During the first experimental campaign the tertiary effluent was characterized by DOC concentrations of 5.8 ± 0.4 mg/L (n = 5) and UVA_{254} values of 10.5 ± 0.2 1/m (n = 4). Treatment by anthracite filters A1 and A2 resulted in removal of DOC (ΔDOC 1.2 ± 0.1 and 1.4 ± 0.3 mg/L) and UVA_{254} (ΔUVA_{254} 0.9 ± 0.1 and 1.2 ± 0.1 1/m) (Figure SI-8). Slightly higher removal in column A2 can be explained by the threefold higher EBCT compared to column A1. The comparison of reference column A2 with SBF system A1+S1 reveals slightly higher removal of DOC and UVA_{254} in the latter (1.6 ± 0.4 mg/L; 1.4 ± 0.1 1/m). However, no substantial difference in removal was observed which is supported by the comparable DO consumption observed in both systems (see section 3.1). Higher EBCTs in second stage filters of SBF systems A1+S2 and A1+S3 were found to increase the consumption of DOC (ΔDOC 2.0 ± 0.3 and 2.2 ± 0.5 mg/L) and UVA_{254} (ΔUVA_{254} 1.9 ± 0.3 and 1.9 ± 0.3 1/m) (Figure SI-8). Despite additional BDOC removal in second stage filters, especially at higher EBCTs in S2 and S3, first stage filter A1 proved to allow for an effective removal of BDOC considering the comparably short EBCT. To calculate a simplified DO mass balance, a stoichiometric ratio of 1 mole O_2/mole C is assumed (2.7 mg DO/mg DOC) for complete mineralization of DOC. DO mass balances revealed elevated DO consumption in all columns which could only partially be traced back to DOC consumption. Thus, elevated values were found for anthracite filters A1 and A2 (3.9 ± 0.6 and 5.0 ± 0.8 mg DO/mg DOC respectively, n = 5) and for sand filters S1, S2 and S3 (4.1 ± 1.4, 6.1 ± 1.8 and 8.1 ± 3.4 mg DO/mg DOC, respectively, n = 5). The reason for the substantially elevated DO consumption, especially in columns S2 and S3, remained unclear.

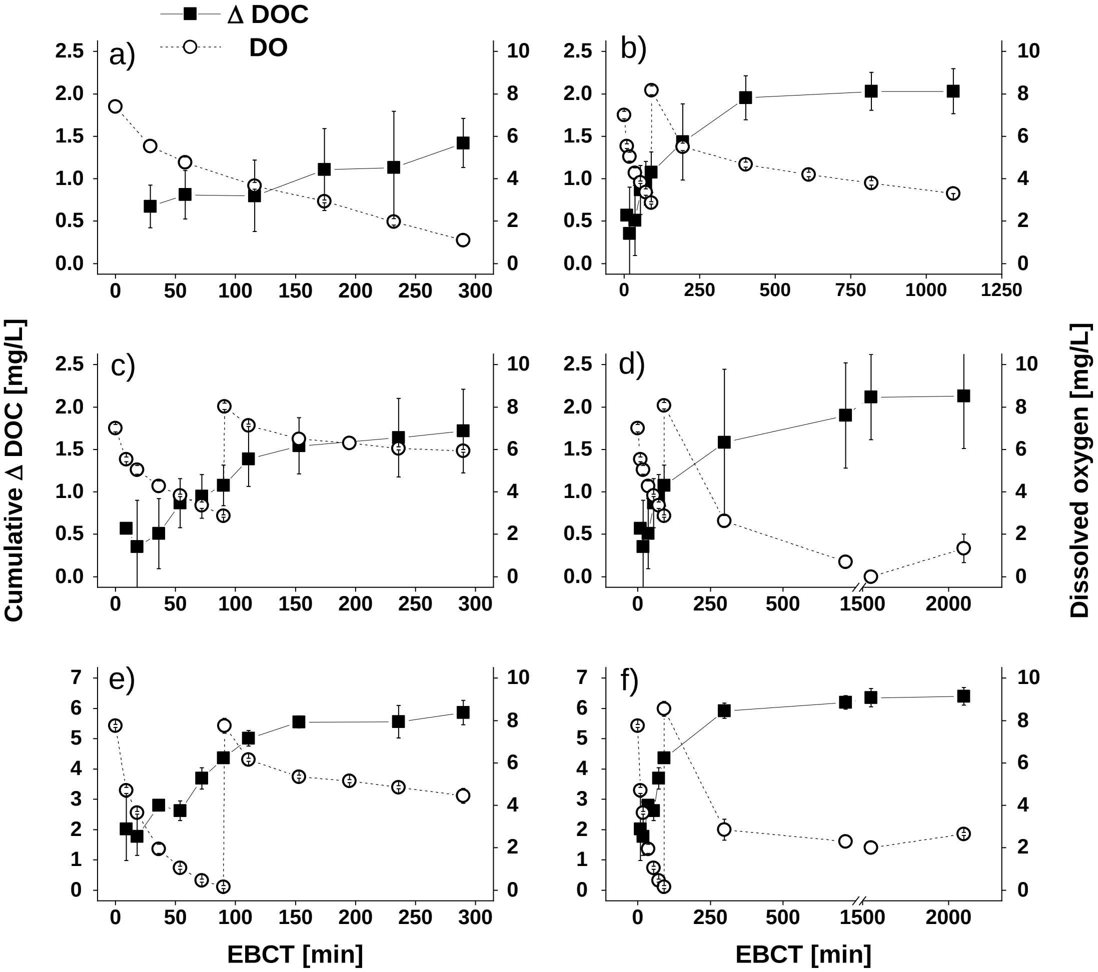

Figure 7-2: DOC consumption and DO concentration profiles during first (a) A2; b) A1+S2; c) A1+S1; d) A1+S3) (DOC_0: 5.3 ± 0.3 mg/L; n = 3) and second experimental campaign (e) A1+S1; f) A1+S3) (DOC_0: 9.7 ± 0.2 mg/L; n = 2). Figure SI-9 displays data over column depths.

Feed water characteristics of the second experimental campaign varied strongly from those observed during the first sampling campaign with DOC concentrations of 9.0 ± 0.9 mg/L (n = 4) and a UVA_{254} of 15.8 ± 0.8 1/m (n = 5). Consequently, removal of BDOC in A1 increased substantially compared to the first experimental campaign, indicated by elevated consumption of DOC and UVA_{254} (ΔDOC 3.4 ± 1.2 mg/L; ΔUVA_{254} 2.2 ± 0.1 1/m) (Figure SI-8). Despite the high removal in column A1, increased consumption was also found in columns S1 and S3 resulting in higher overall BDOC consumption in systems A1+S1 (ΔDOC 4.7 ± 1.4 mg/L; ΔUVA_{254} 3.1 ± 0.1 1/m) and A1+S3 (ΔDOC 5.2 ± 1.4 mg/L; ΔUVA_{254} 4.4 ± 0.4 1/m) (Figure SI-8). Compared to the first experimental campaign, DO mass balances for columns A1 and S1 show higher accordance with the stoichiometric ratio (2.5 ± 0.9 and 2.6 ± 0.5 mg DO/ mg DOC respectively, n = 4). Accounting for the additional DO supply due to the dosing of hydrogen peroxide, the DO consumption in column S3 (5.0 ± 0.7 mg DO/ mg DOC, n = 4) was higher than the stoichiometric value.

Differences in feed water characteristics during the first and second experimental campaign are underlined by changes in the specific UV absorbance (SUVA) during treatment (Figure SI-8). Slightly higher average SUVA values in tertiary effluent during the first experimental campaign (2.0 ± 0.1 L/mg*m) speak to a higher aromaticity of dissolved organic matter compared to the second experimental campaign (1.8 ± 0.2 L/mg*m) (both n = 4). Only slight changes in SUVA were observed after treatment in SBF system A1+S1 during the first experimental campaign (2.3 ± 0.3 L/mg*m) whereas comparatively stronger changes were found during the second experimental campaign (3.1 ± 0.3 L/mg*m) pointing to preferred removal of aliphatic compounds.

7.3.3 Removal of trace organic chemicals

TOrC removal during the first experimental campaign was investigated by monitoring a list of 54 indicator substances (Table SI-9). Out of these, 50 were present in the tertiary effluent with concentrations above 3.5 x LOQ at least in three out of five sampling campaigns. High persistence, indicated by removal below 25 % in all systems, was found for 24 out of these 50 compounds which will not be further discussed. A total of 26 compounds were considered susceptible to biodegradation indicated by removal above 25 % in at least one of the investigated systems. In general, sorption must be considered a potential cause for the removal of compounds in granular media filters. However, studies on the degradation of TOrCs in biological filtration systems using anthracite and sand as filter materials reported negligible abiotic removal for most compounds (Bertelkamp et al., 2014; Rattier et al., 2014). Also results from a previous study using the experimental setup at hand did not point to sorption as a relevant cause for TOrC removal (Müller et al., 2017). Several studies, however, reported a strong affinity of triclosan to sorb onto soil and sediments especially when higher amounts of soil organic matter are present (Wu et al., 2009; Karnjanapiboonwong et al., 2010; Onesios and Bouwer, 2012). Although elevated amounts of organic matter are not expected in the technical sand and anthracite used in the biofiltration columns, a contribution of sorption to the removal of triclosan cannot be ruled out.

The removal of compounds in the reference column A2 and in SBF system A1+S1, operated at the same overall EBCT of 290 min (Figure 7-3), confirms an improved degradation of some biodegradable substances during SBF (e.g., benzotriazole, gabapentin-lactam, gabapentin, diphenhydramine, metoprolol and mecoprop) supporting results from a previous study (Müller et al., 2017). However, for several biodegradable compounds no substantial difference in removal efficiency was found between both systems (e.g., acesulfame, bezafibrate). Potentially higher removal of compounds during SBF is attributed to different operational conditions. Extensive degradation of BDOC aligned by DO consumption in a single-stage filter potentially leads to rapid DO depletion, resulting in suboxic or even anoxic zones while SBF systems allow for rather oligotrophic conditions and higher DO concentrations in second stage filters. The first experimental campaign, however, was characterized by the presence of low amounts of BDOC in the tertiary effluent used as feed water. Despite substantially higher DO concentrations in SBF system A1+S1, redox conditions in A2 could still be characterized as oxic (see section 7.3.1). Thus, the positive effect of the SBF approach on redox conditions might have been of minor importance during the first sampling campaign. Improved removal of some compounds in system A1+S1 might be explained by a potentially different microbial community in second stage filter S1, which adapted to stable oligotrophic conditions and was not disturbed by backwashing events. Improved removal of moderately degradable compounds under oligotrophic conditions by an adapted microbial community has been reported by several studies for similar systems (Li et al., 2012, 2013, 2014; Alidina et al., 2014).

The effect of increased EBCTs on the removal of TOrCs in second stage filters S1, S2 and S3 revealed compound specific differences. An improved removal at higher EBCTs in second stage filters indicated the importance of kinetic effects for the degradation of some compounds (e.g. metoprolol and telmisartan) (Figure 7-3). Other compounds exhibited rapid degradation and little to no differences were found by extending the retention time (e.g. azithromycin). This also accounts for compounds approaching threshold values above the LOQ such as benzotriazole. Here, increased EBCTs did not yield an improved removal.

During the second experimental campaign 11 compounds were monitored which were also analyzed during the first campaign. Out of these 11 compounds 8 were considered for further discussion excluding substances which exhibited high persistence or very low and unsteady concentrations in the tertiary effluent according to the procedure described above. Table SI-10 summarizes details on all compounds measured during the second experimental campaign of this study. A comparison of the removal of 8 biodegradable compounds in systems A1+S1 and A1+S3, measured during both experimental campaigns, revealed comparable and even slightly increased overall removal efficiencies during the second experimental campaign in system A1+S1, run at the same operational settings as before. The manipulation of redox conditions in the second stage filter of system A1+S3 revealed no clear effect on TOrC removal. Although oxic conditions prevailed throughout the whole length of second stage column S3, no substantial changes in TOrC removal were observed (see Figure SI-10). Given the generally higher amounts of BDOC present during the second campaign, however, it is assumed that without the addition of hydrogen peroxide redox conditions in column S3 would have turned suboxic which potentially might have affected the removal of redox-sensitive TOrCs. The analysis of compounds in the first stage filter A1 exhibited higher removal during the second experimental campaign for most compounds. In the case of benzotriazole, removal in filter A1 increased from 26 % during the first to 70 % during the second experimental campaign. Despite substantially higher presence of BDOC during the second experimental campaign (see section 7.3.2) the removal of some biodegradable TOrCs was comparable or even higher compared to the first campaign.

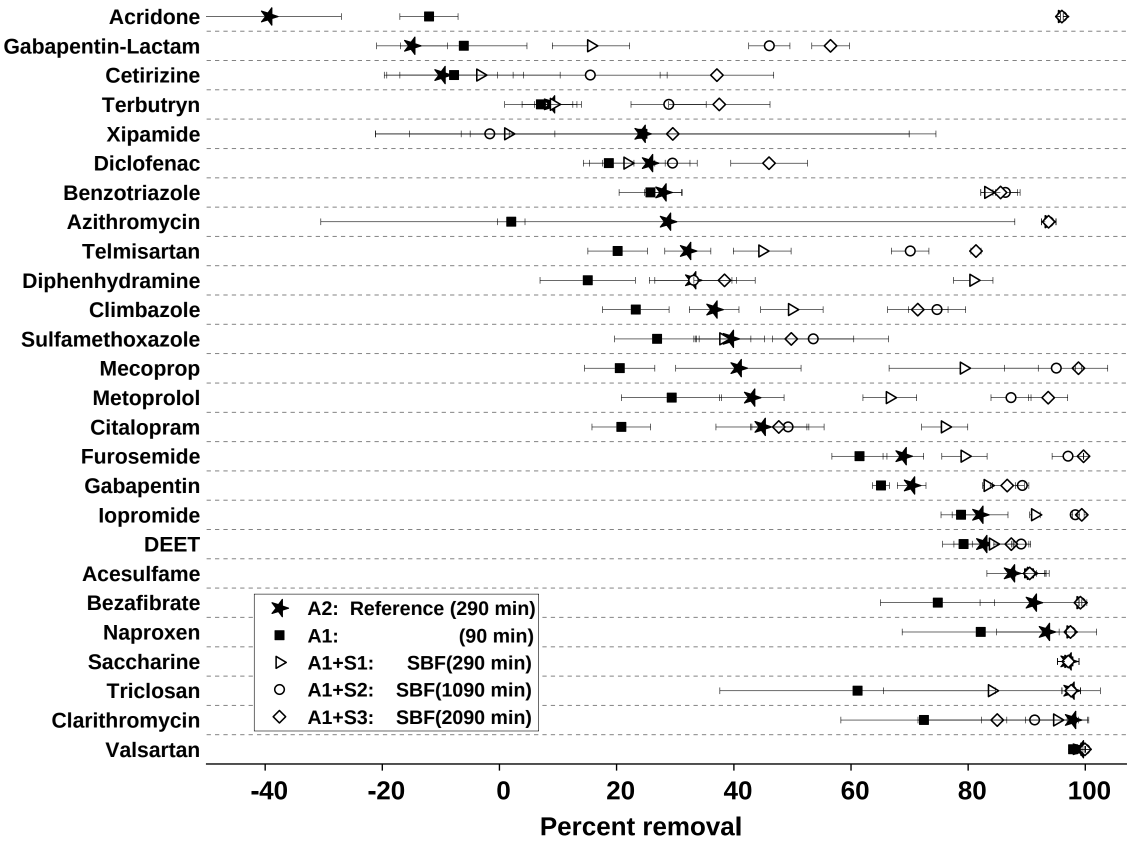

Figure 7-3: Cumulative removal of trace organic compounds in operated systems during first experimental campaign (n = 5); Detailed information on inlet concentrations can be found in Table SI-9.

7.3.4 Transformation of iopromide

This study attempts to link the transformation of iopromide and the occurrence of its TPs in biofiltration systems to operational parameters such as EBCT and operational conditions such as prevailing local redox conditions and substrate availability.

Transformation of iopromide in the operated biofiltration systems was found to closely follow the pathway proposed by Schulz et al. (2008) (Figure 7-1), indicated by a molar mass balance closed up to 90 ± 17 %. More detailed information on molar concentrations and recoveries for all sampling ports can be found in Figures SI-11 and SI-12 and Table SI-14. While all identified TPs were detected at different stages during the sampling campaigns with concentrations above the LOQ, abundances of individual TPs varied greatly. Assuming the determination of all relevant TPs during the transformation of iopromide in the pathway proposed by Schulz et al. (2008) and an almost closed mass balance, molar concentrations of iopromide and individual TPs will be given as relative abundances in proportion to the sum of molar concentrations of iopromide and its 12 TPs found in every sample, following an approach proposed by Engelhardt et al. (2014). The relative abundance for a specific TP (TP_k) is defined as:

$$relative\ abundance\ (TP_k)\ =\ \frac{c(TP_{k,sample})\ [mol]}{\sum_{k\,=\,0}^{12} c\left(TP_{k,sample}\right)[mol]} * 100\ [\ \%] \qquad (4)$$

Here, the concentration of iopromide in a sample is referred to as $c(TP_{0,sample})$. The transformation pathway of iopromide followed a similar pattern in all investigated column systems regarding the successive formation of TPs. The comparison of the iopromide transformation observed in this study and by Schulz et al. (2008) revealed differences in the abundances of several phase II and phase III TPs.

Schulz et al. (2008) reported TP 731 A and TP 731 B to be major phase II representatives, whereas no substantial formation of both products was found during this study. Also, major formation of phase III representatives TP 701 B and TP 643 as found by Schulz et al. (2008), was not observed during this study (Figure 7-4, Table SI-14). Different experimental setups used in both studies might have caused the different TP abundances. While experiments were conducted in biofiltration columns in this study at low iopromide concentrations, Schulz et al. (2008) conducted batch experiments with soil from a wastewater irrigation site and substantially higher iopromide concentrations (1 g/L).

Rapid transformation of iopromide and its intermediates was observed in all column systems during both experimental campaigns. Investigations of iopromide transformation in the conventional single-stage filter A2 and SBF system A1+S1 during the first experimental campaign revealed no distinct differences in the overall performance (Figure 7-4). Despite a seemingly faster degradation of iopromide during the first stage filter A1 compared to filter A2, similar relative abundances were found for iopromide and its TPs in the effluents of both systems after an overall EBCT of 290 min. During the second stage column S1, changes in gradients after the first 10 cm indicate slower transformation in the deeper layers of the column. Findings from columns S2 and S3 (Figure SI-13) support the assumption of elevated transformation in the top layers of second stage filters. In column S2, the upper 10 to 30 cm dominated the formation of phase II and phase III TPs while slower but noticeable transformation was observed until the column outlet, mainly due to transformation of remaining phase I TPs. Column S3 exhibited an even more pronounced concentration of transformation reactions in the upper layers of the column. Here, the passage through the first 10 cm resulted in a drastically changed distribution of iopromide intermediates with relative abundances of iopromide and phase I TPs decreasing from over 70 to 10 % and phase III TPs 759 and 701 A increasing from less than 10 to over 60 %.

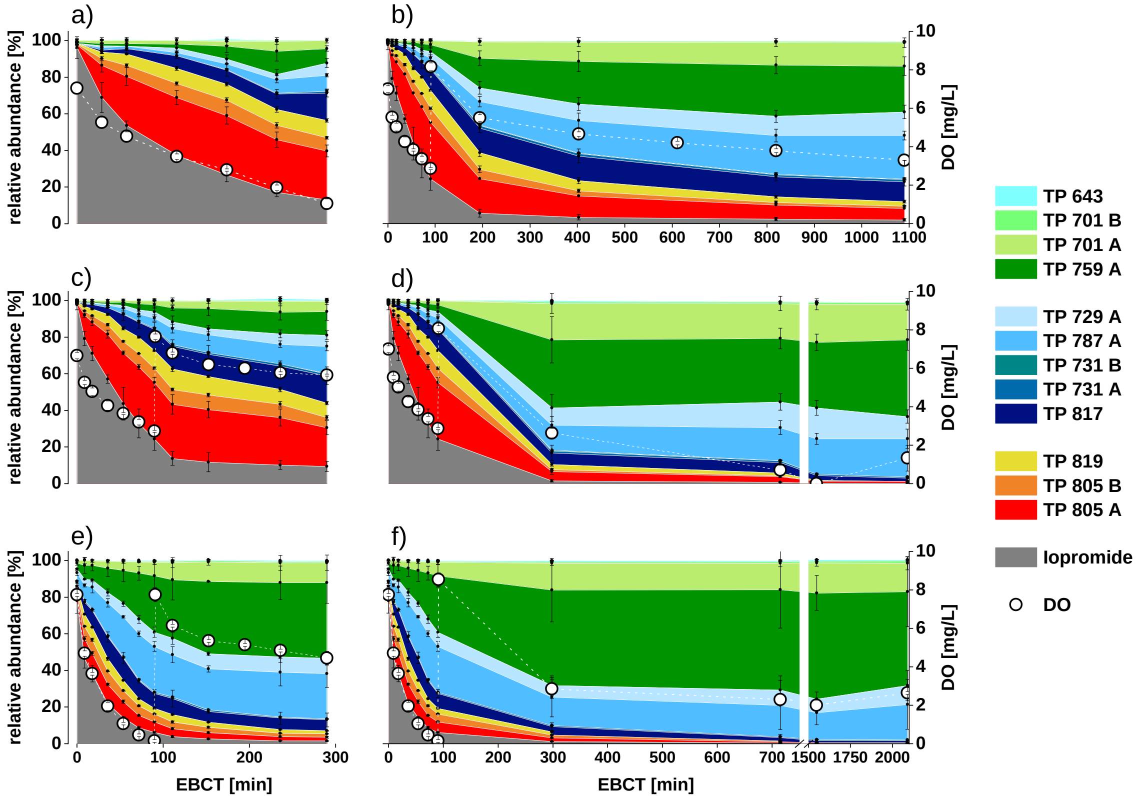

Figure 7-4: Relative abundances (see equation (4)) of iopromide and iopromide transformation products and DO concentration in column systems during first (a) A2; b) A1+S2; c) A1+S1; d) A1+S3; n = 3) and second experimental campaign (e) A1+S1; f) A1+S3; n = 2). Figure SI-13 displays data over column depths. See Table SI-14 for further information on molar concentrations of iopromide and iopromide transformation products.

Further transformation in the deeper filter layers was restricted to transformation of remaining phase I TPs and phase II TP 817. Stable relative abundances of formed phase III TPs 759 and 701 A became noticeable in both columns, S2 and S3. Besides their persistence to further degradation, also their formation seemed hindered in deeper filter layers and their relative abundances appeared to mostly depend on the formation during the passage through the top filter layers.

Results from SBF systems A1+S1 and A1+S3 operated during the second experimental campaign revealed increased and more rapid iopromide transformation. Relative abundances of iopromide and phase I TPs (19 %), phase II TPs (42 %), and phase III TPs (39 %) in the effluent of first stage filter A1 indicated a more advanced transformation compared to those observed during the first experimental campaign (72 %, 21 % and 6 %, respectively) despite the presence of partly suboxic conditions in deeper filter layers. Due to substantially higher transformation already in column A1, the contribution of second stage columns S1 and S3 to the overall transformation is smaller than during the first experimental campaign. However, additional transformation was also observed here, especially in column S3. As noted during the first experimental campaign, major transformation occurred in top layers of columns S1 and S3 (Figure SI-13). Also, after complete transformation of iopromide and phase I TPs in S3, the distribution of phase II and phase III TPs remained stable and rather similar to the one observed during the first sampling campaign.

Except for second stage filter S3 during the first and deeper layers of first stage filter A1 during the second experimental campaign, oxic conditions were present in all operated columns. While no additional transformation of iopromide intermediates was observed in the deeper and suboxic layers of column S3 during the first experiment, the same was observed in column S2 which was characterized by entirely oxic conditions. In addition, the manipulation of redox conditions to entirely oxic conditions in column S3 by adding hydrogen peroxide during the second experimental campaign also did not trigger additional transformation in deeper column layers. More advanced transformation during the second experimental campaign as noted in system A1+S3 was also observed in system A1+S1 which was operated at the same operational conditions as during the first campaign. Redox conditions in the deeper zones of second stage filters seemed to have little impact on the overall transformation of iopromide. No conclusion could be drawn regarding the effects of suboxic or anoxic conditions in the top layers of the columns which were found to largely contribute to the overall transformation.

7.3.5 Transformation of iopromide and select trace organic chemicals as a function of different operational parameters

Similar trends for DO consumption and iopromide transformation were observed (Figures 7-4 and SI-13). As DO consumption in the filtration systems is attributed to aerobic respiration during BDOC degradation, it can be regarded as a proxy for microbial activity. Further investigations targeted potential correlations between iopromide transformation and parameters indicating microbial activity, such as DO consumption, and the EBCT. The dimensionless parameter T_{IOP} was introduced to assess the degree of iopromide transformation in a sample based on the relative abundance of investigated iopromide TPs. To account for the transformation stage of a specific TP_k, dimensionless factors f_k, ranging from 0 to 6, were defined. Factors f_k reflect the theoretical number of transformation steps necessary during the formation of a specific TP_k from iopromide according to the pathway proposed by Schulz et al. (2008). While degradation steps within the proposed pathway are comprehensible, the existence of instable intermediates cannot be ruled out. Such intermediates with potentially short half-lifes or present only at very low concentrations are not accounted for in the proposed scheme. The assignment of factors to specific TPs according to the degree of transformation is illustrated in Figure 7-1.

T_{IOP} is defined as:

$$T_{IOP} = \sum_{k=0}^{12} \left(\frac{\text{relative abundance } (TP_k)[\,\%]}{100\ \%} * f_k \right) \tag{5}$$

Potential T_{IOP} values range from a minimum of 0, when only iopromide is present in a sample, to a maximum of 6, indicating complete transformation of iopromide and its TPs into the final TP 643 for which no further biological transformation has been observed in previous studies (Schulz et al., 2008).

The results presented in Figure 7-5a illustrate iopromide transformation, as T_{IOP}, as a function of EBCT in all operated systems during both experimental campaigns. When compared to results obtained for relative abundances of different TPs (Figure 7-4), T_{IOP} values appear suitable to illustrate successive iopromide transformation. Rapid iopromide transformation within the first 100 min is followed by declining transformation approaching maximum T_{IOP} values of 4.5 to 5 in column S3 samples. An increased T_{IOP} gradient in column A1 during the second experimental campaign reflects faster transformation compared to the first experimental campaign. Also, increased transformation in top layers of filters S1, S2 and S3 is mirrored in the T_{IOP} values. T_{IOP} values from column A1 and the upper layers of second stage columns S1, S2 and S3 during the first experimental campaign suggest a linear correlation of T_{IOP} values and EBCT in zones with elevated microbial activity.

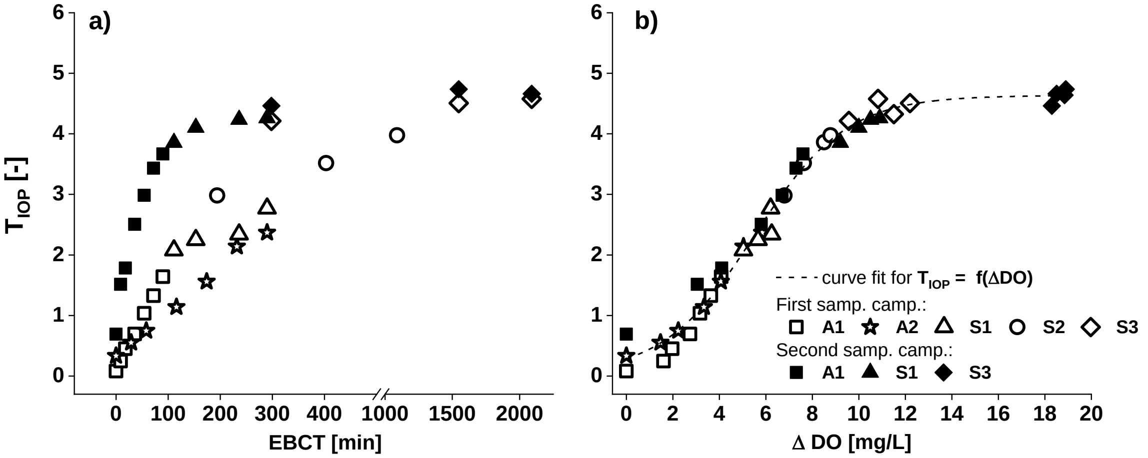

Figure 7-5: Mean cumulative iopromide transformation in samples expressed as T_{IOP} (see equation (5)) as a function of empty bed contact time (a)) and mean cumulative DO consumption (b)) in different systems during both experimental campaigns.

Positive correlations between T_{IOP} values and ΔDO also indicate an influence of the presence of sufficient BDOC and microbial activity on iopromide transformation until maximum T_{IOP} values of 4.5 to 5 are reached (Figure 7-5b). After reaching this threshold level, additional DO consumption did not result in further increasing T_{IOP} values. Despite substantial differences in BDOC removal, gradients of $T_{IOP}/\Delta DO$ curves show high accordance during both experimental campaigns. No noticeable difference was observed in SBF systems A1+S1 and single-stage filter A2, underlining that SBF did not yield an improved transformation of iopromide when operated at the same EBCT. Given the strong correlation between T_{IOP} and DO consumption, however, higher transformation in an SBF system could be expected if higher amounts of BDOC were present causing oxygen depleted conditions to prevail in filter A2 and limit the overall BDOC consumption.

To investigate whether the strong linear correlation between the T_{IOP} and DO consumption also applies to the initial transformation of iopromide and other compounds, the removal of iopromide, gabapentin, metoprolol and benzotriazole was plotted as a function of ΔDO (Figure 7-6). The dashed lines indicate changes of T_{IOP} from Figure 7-5b for comparison. Vast removal of gabapentin was observed in the systems during the first and second experimental campaign. The removal of iopromide and gabapentin as a function of ΔDO was characterized by steep initial gradients indicating rapid transformation especially in anthracite filters A1 and A2. While almost complete transformation was observed for iopromide, a threshold removal of around 90 % was approached at higher ΔDO values for gabapentin. Uniform curve shapes indicated similar degradation mechanisms in the first and second filter stage. Higher removal of iopromide and gabapentin in filter A1 was found during the second experimental campaign suggesting beneficial effects of elevated BDOC concentrations on the removal.

A linear correlation between metoprolol removal and DO consumption in anthracite filters A1 and A2 was found during the first and second experimental campaign. Increased removal of metoprolol in upper layers of second stage filters S1, S2 and S3 was indicated by an offset which was not observed for the initial transformation of iopromide and gabapentin or for the T_{IOP}. Metoprolol degradation was found to steadily increase in second stage filters with increasing EBCTs during the first campaign whereas stagnating removal was observed during the second campaign in column S3 without achieving complete transformation of the parent compound. Differing slopes were found for metoprolol removal as a function of ΔDO in both campaigns while the overall removal in filters A1 and S1 was rather similar. The transformation pattern for metoprolol as a function of ΔDO suggests an independence of general microbial activity indicated by DO consumption in second stage columns S1, S2 and S3.

Increased removal in the upper layers of second stage filters S1, S2 and S3 was also observed for benzotriazole during the first experimental campaign. Here, the increase in removal efficiency was even more pronounced. Benzotriazole removal in filter A1 was substantially higher during the second campaign with only minor contribution of second stage filter S1 to the overall removal suggesting the presence of increased amounts of

BDOC had a beneficial effect on benzotriazole degradation in filter A1. Less additional removal of benzotriazole in second stage filters S1 and S3 is likely due to the increased degradation in filter A1 with removal values close to those also observed as threshold removal values during the first experimental campaign.

The uniform shape of the curves for the T_{IOP} and the removal of iopromide and gabapentin as a function of ΔDO, with no noticeable differences between filters A1 and A2 and filters S1, S2 and S3, suggests that both, iopromide transformation over several transformation levels and gabapentin degradation depend on microbial activity which is directly related to DO consumption. Removal of metoprolol and benzotriazole as a function of ΔDO revealed a different pattern, especially during the first experimental campaign. Here, changes in curve shapes implied that besides DO consumption also other factors affected the degradation of these compounds. This might be interpreted as a hint towards different removal mechanisms during the biodegradation of certain compounds. While an elevated DO consumption related to higher BDOC consumption during the second experimental campaign seems to have enhanced the transformation of iopromide, gabapentin and benzotriazole, no such dependence was found for metoprolol.

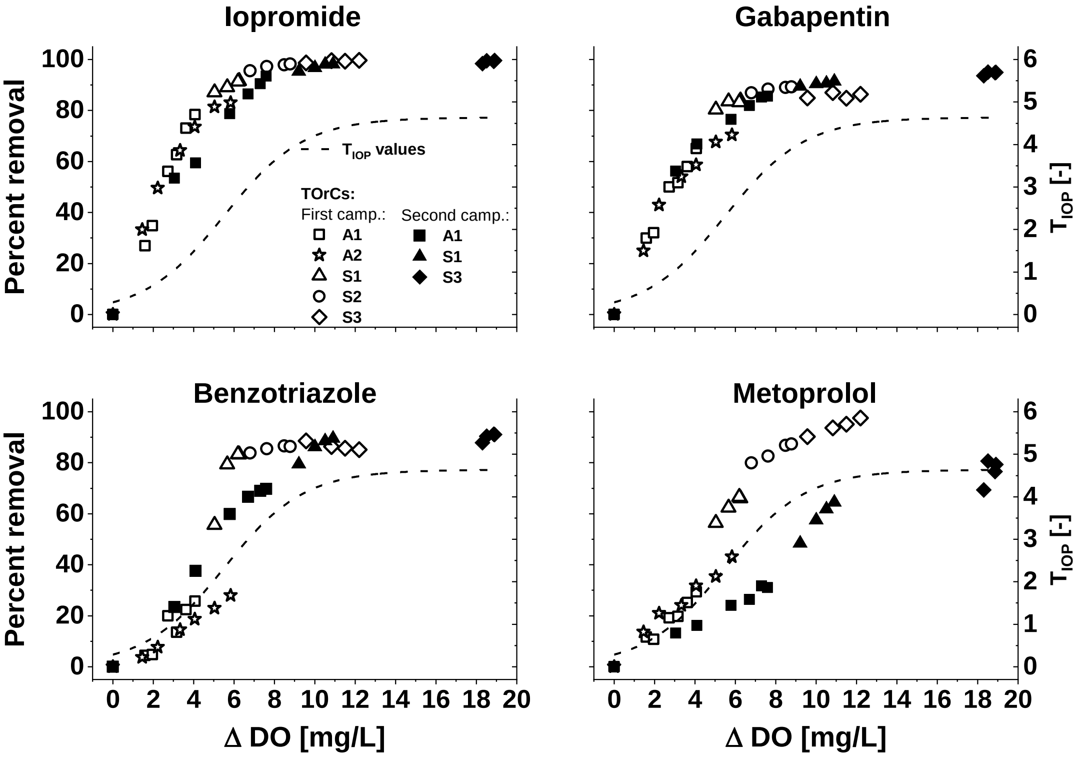

Figure 7-6: Mean removal of iopromide, gabapentin, metoprolol and benzotriazole as a function of mean cumulative DO consumption during first (n = 3) and second experimental campaign (n = 2) and fitted curve for T_{IOP} as a function of ΔDO (see Figure 7-5b).

Results obtained during this study demonstrate the complexity of mechanisms involved in the biotransformation of individual chemicals. While transformation efficiencies for iopromide, gabapentin and benzotriazole could be linked to DO consumption, no such effect was observed for the removal of metoprolol. Different transformation efficiencies for the compounds iopromide, gabapentin, metoprolol and benzotriazole are considered due to differences in the capability of the enzymatic system present to carry out the initial compound dependent transformation steps. A better knowledge of the mechanisms underlying the initial transformation is needed to better understand the differences observed for the individual compounds. Hints on potential mechanisms involved in the degradation of individual compounds might be drawn from studies focused on the experimental identification of transformation products and from pathway prediction tools such as the EAWAG Biodegradation/Biocatalysis Database Pathway Prediction System (EAWAG-BBD-PPS) (Ellis et al., 2008).

Schulz et al. (2008) proposed the oxidation of primary hydroxyl groups as initial transformation step in the oxic degradation of iopromide. Pathway prediction using the EAWAG-BBD-PPS prediction supports these findings (rules bt0001 and bt0003).

Henning et al. (2018) reported gabapentin-lactam to be the quantitatively most relevant transformation product of gabapentin under oxic conditions. The transformation was described to involve an intramolecular amidation step. Huntscha et al. (2014) reported hydroxyaromatic structures to be major transformation products formed during the initial transformation of benzotriazole. The steps involved in the formation of the main transformation products found for gabapentin and metoprolol by Henning et al. (2018) and Huntscha et al. (2014) could not be retraced using the EAWAG-BBD-PPS.

Rubirola et al. (2014) identified metoprolol acid as the dominant transformation product from the oxic degradation of metoprolol. According to the EAWAG-BBD-PPS the formation of metoprolol acid is initiated by the hydration of an ether group (rule bt0023) in a side chain of the molecule followed by the oxidation of the formed primary alcohol and a carboxylation step (rules bt0001 and bt0003).

Studies on the identification of biological transformation products and metabolic pathway prediction illustrate the variety of potential mechanisms contributing to the initial transformation of the investigated compounds iopromide, gabapentin, metoprolol and benzotriazole. The variety of mechanisms involved in the initial transformation might have caused the different transformation patterns observed for the investigated compounds. The reasons for the different transformation efficiencies and the dependence on factors such as the presence of BDOC, however, demand further investigation.

7.4 Conclusions

This study aimed at investigating the potential of using the abundance of specific transformation products from the successive biological degradation of the X-ray contrast medium iopromide to allow for a more sensitive characterization of redox conditions in oxic to suboxic biofiltration systems.

- Results presented in this study do not support a direct correlation between oxic and suboxic conditions and the degree of iopromide transformation or the abundance of specific iopromide transformation products. A stagnation of the transformation process in the biofiltration systems was found to occur also under oxic conditions, ruling out redox conditions to be the only dominant factor during the degradation.
- A strong correlation between iopromide transformation and DO consumption suggested cometabolic processes in the presence of sufficient BDOC as responsible for the biological degradation of iopromide.
- Differences in the dependence of the initial biological transformation of the compounds gabapentin, benzotriazole and metoprolol on the DO consumption pointed to compound-specific degradation mechanisms in the investigated biofiltration systems.

Acknowledgements

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8 Investigating synergies in sequential biofiltration-based hybrid systems for the enhanced removal of trace organic chemicals from wastewater treatment plant effluents

The following chapter presents investigations related to **Hypothesis #3**, *"The use of sequential biofiltration with an intermediate ozonation step allows for a reduced ozone demand without jeopardizing the establishment of oxic and oligotrophic conditions in the second filter stage."* and **Hypothesis #4,** *"Sequential biofiltration with intermediate aeration using air or ozone increases the efficiency of subsequent granular activated carbon filtration by reducing competitive adsorption of background organic matter"*.

Different process combinations based on sequential biofiltration (SBF) were tested for their suitability to achieve enhanced removal of trace organic chemicals (TOrCs) from wastewater treatment plant effluents, including SBF with intermediate ozonation, and SBF with or without intermediate ozonation combined with subsequent activated carbon filtration. The investigations focused on synergistic effects between the treatment steps. To test a potential beneficial effect of biological pre-treatment on ozonation efficiency, as suggested in **Hypothesis #3.1**, ozonation experiments were carried out using an experimental setup in semi-batch. Testing **Hypothesis #3.2**, column experiments were conducted to investigate the effect of pre-ozonation on oxic and oligotrophic operational conditions during subsequent biofiltration. The effect of biological pre-treatment on the adsorption capacity of activated carbon for TOrCs in equilibrium, as addressed in **Hypothesis #4.1**, was investigated using batch tests (see also section 10.7). Effects of biological or biological-oxidative pre-treatment on the breakthrough behavior of activated carbon adsorbers, as suggested by **Hypothesis #4.2** were investigated using rapid small-scale column tests.

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Author contributions: Johann Müller, Uwe Hübner and Jörg E. Drewes developed the research objective and designed the experiment. Johann Müller constructed the experimental setup, conducted the experiments and the analyses and wrote the paper. Jörg E. Drewes and Uwe Hübner supervised the study and reviewed the manuscript. All authors approved the final version of the manuscript.

Investigating synergies in sequential biofiltration-based hybrid systems for the enhanced removal of trace organic chemicals from wastewater treatment plant effluents

Abstract

Combinations of biological, oxidative and adsorptive advanced treatment technologies in hybrid systems hold promise to result in an improved mitigation of trace organic chemicals (TOrCs) from municipal wastewater treatment plant (WWTP) effluents. This study investigated potential process combinations including sequential biofiltration, ozonation and activated carbon adsorption and focused on synergies between these treatment steps. Results proved that pre-treatment of WWTP effluent using biofiltration resulted in a significant decrease in ozone demand for the transformation of TOrCs characterized by moderate reaction rate constants with ozone. At similar ozone doses the transformation of TOrCs was increased up to 25 % when WWTP effluent was pre-treated by biofiltration compared to the transformation observed in WWTP effluent without pre-treatment. This was explained by the removal of dissolved organic matter during biofiltration (21 ± 3 % DOC and 11 ± 3 % UVA_{254}) reducing the competition for ozone. For 12 out of 14 investigated TOrCs biological and biological-oxidative pre-treatment using sequential biofiltration with intermediate aeration or ozonation resulted in a substantial, up to 3-fold increase in treated filter bed volumes until a 10 % breakthrough of granular activated carbon adsorbers was observed. Also here, the improved process efficiency was explained by the removal and structural alteration of dissolved organic matter during biological or biological-oxidative pre-treatment of the WWTP effluent.

8.1 Introduction

The presence of trace concentrations (ng/L to µg/L) of a large variety of anthropogenic chemicals in water bodies across the world, also referred to as trace organic chemicals (TOrCs), has been subject to extensive investigations in the field of water research. While a comprehensive assessment of potential adverse effects of TOrCs on human health is still lacking (Schriks et al., 2010), various studies reported effects on aquatic organisms and ecosystems (Cuklev et al., 2011; Brodin et al., 2013; Wilkinson et al., 2016; Kellner et al., 2016). Effluents of municipal wastewater treatment plants (WWTPs) which are discharged into receiving streams, have been identified as main point sources for the introduction of TOrCs to the aquatic environment (Ternes, 2007; Dong et al., 2015). The conventional activated sludge process is the backbone of conventional municipal wastewater treatment and has been successfully applied for decades for the effective mitigation of bulk organic substances and nutrient removal. While various TOrCs undergo effective mitigation during conventional activated sludge treatment, others exhibit high persistence and are not or only partially removed (Joss et al., 2006; Falås et al., 2016). To improve the capability of WWTPs to reduce TOrC emissions, additional treatment barriers are required.

Different technologies have proven their efficacy in removing TOrCs from WWTP effluents. Oxidative treatment technologies using ozonation or advanced oxidation processes are among the frequently discussed and applied options. Ozonation is very effective for the oxidation of many different TOrCs in WWTP effluents (Ternes et al., 2003; Huber et al., 2005; Hollender et al., 2009). Studies also demonstrated the potential of ozone to reduce various specific toxic effects, such as endocrine disruption, genotoxicity, antibacterial and antiviral activity. During the ozonation of WWTP effluent, however, much of the oxidative potential is lost due to the presence of high amounts of dissolved organic matter (DOM) and potentially elevated concentrations of nitrite (Lee et al., 2013; Lee and von Gunten, 2016). Also, the formation of undesired by-products of which some might be toxicologically relevant (Griffini et al., 1999; von Gunten, 2003; Wert et al., 2007; Hübner et al., 2013b; Bourgin et al., 2018) and of easily degradable substrate, also referred to as biodegradable dissolved organic carbon (BDOC), requires biological post-treatment (Świetlik et al., 2009; Stalter et al., 2010; Ramseier et al., 2011; Thayanukul et al., 2013).

Adsorption using activated carbon in powdered or granular form, has been demonstrated to be effective for the mitigation of a broad range of different TOrCs (Corwin and Summers, 2012; Worch, 2012). Studies also reported a reduction of specific and non-specific toxicity after activated carbon treatment (Reungoat et al., 2011; Prasse et al., 2015). Highly polar compounds, however, show only weak interactions with the surface functions of activated carbon and thus, cannot be properly removed from the aqueous phase. Also, the high amount of DOM present in the WWTP effluent strongly competes for available adsorption sites and negatively affects the process efficiency (Corwin et al., 2011; Summers et al., 2013; Zietzschmann et al., 2014b).

The concept of sequential biofiltration (SBF) uses two-stage sequential granular media filtration with intermediate aeration for the selective adjustment of redox and substrate conditions during biofiltration (Müller et al., 2017). This engineered biological above-ground treatment system with optimized operational conditions for the biodegradation of TOrCs was found to achieve an increased removal of various compounds compared to a single-stage biofilter operated at the same empty bed contact time (EBCT) (Müller et al., 2017). However, even under improved operational conditions, no or only limited removal was observed for highly persistent compounds.

The combination of several advanced treatment processes in a hybrid process holds the potential to improve the overall process performance by taking advantage of additive and synergistic effects. The removal of a broader range of compounds with different characteristics can be expected when multiple barriers are installed in series. Besides such additive effects, also synergistic effects between the processes might positively affect the overall process performance. In an optimized arrangement of different advanced treatment technologies, hybrid systems potentially profit from an increased process efficiency, sustainability and lower costs of operation and might be a viable alternative to single technology-based advanced treatment.

The potential of combining ozonation and biological activated carbon filters or non-adsorptive biological media filtration has been recognized before (Sanchez-Polo et al., 2006; Reungoat et al., 2010; Gerrity et al., 2011; Hübner et al., 2012; Reungoat et al., 2012; Hübner et al., 2013b; Sudhakaran et al., 2013; Yoon et al., 2013; de Wilt et al., 2018; Van Aken et al., 2019). Yet, benefits from process combinations were mainly attributed to additive effects allowing for the removal of a broader range of compounds due to the use of different process mechanisms (Sudhakaran et al., 2013). Implementing ozonation with subsequent granular activated carbon (GAC) filtration offers the removal of compounds that are not susceptible to oxidation but tend to adsorb. Biological media filtration after ozonation was also described as a necessary step to remove BDOC and undesired oxidation by-products formed during ozonation (Griffini et al., 1999; Krasner, 2009; Bourgin et al., 2018; Bacaro et al., 2019). Biofiltration using sand or GAC as filter media was also described effective in reducing specific and non-specific toxicity after ozonation (Reungoat et al., 2010; Stalter et al., 2010; Reungoat et al., 2012; Prasse et al., 2015). Besides the many comprehensive studies on TOrC removal using these treatment technologies, less attention has been paid to potential synergies increasing process efficiency.

Such potential benefits include the reduction of ozone demand and the extension of adsorber run-times while practicing biological pre-treatment. Hübner et al. (2012) demonstrated a decreased ozone demand for the ozonation of surface water after bank filtration. De Wilt et al. (2018) also reported a decreased ozone demand for WWTP effluent after pre-treatment in an additional biological step. Biofiltration prior to ozonation has also been reported effective in reducing precursors for the formation of various oxidation by-products. Sudhakaran et al. (2013) reported extended adsorber run-times when using engineered natural treatment systems prior to adsorption due to the removal of competing DOC. In addition, Zietzschmann et al. (2015) reported the increase in polarity of remaining DOM after ozonation, decreasing the general adsorbability of DOM and positively affecting the adsorption capacity for TOrCs.

This study aimed at investigating the TOrC removal potential in sequential biofiltration-based hybrid systems combining sequential biofiltration with an intermediate aeration, ozonation, and/or posterior adsorption onto activated carbon step to target removal of a broad range of TOrCs. Besides an evaluation of the expectable improved removal efficacy in such multi-barrier systems, this work focused on synergistic effects between unit processes resulting in an increased efficiency of applied unit operations.

8.2 Materials and methods

8.2.1 Experimental setup

8.2.1.1 Sequential biofiltration with intermediate aeration (SBF(Air)) and intermediate ozonation (SBF(O_3))

Sequential biofiltration studies were conducted using an experimental setup at pilot-scale documented in a previous study (Müller et al., 2017). A backwashable filter column (column A, filter bed length (l) = 1 m, inner diameter (ID) = 0.15 m) was filled with anthracite (Everzit N type II, Evers GmbH, Germany; grain sizes 1.4 to 2.5 mm) and operated at an EBCT of 45 min. Two columns (S1 and S2, l = 0.95 m, ID = 0.10 m) were filled with technical sand (Euroquarz GmbH, Germany; grain sizes 0.2 to 1.0 mm) and both operated at an EBCT of 200 min. Sampling ports at different heights (0, 10, 20, 40, 60, 80, 100 cm) allowed the acquisition of dissolved oxygen (DO) profiles in column A. Besides the measurement of DO concentrations in the influent and effluent of columns S1 and S2, DO sensor spots at different depths (10, 30, 50, 70 cm) allowed for non-invasive determination of DO concentrations. Anthracite column A served as first and sand columns S1 and S2 as second stage filters composing two sequential biofiltration trains (A+S1 and A+S2). All filters were operated in top-down flow under saturated conditions. A system overview can be found in Figure 8-1. The biofiltration setup was located indoors, experiments were conducted at room temperature.

Filter A was fed with fully nitrified tertiary effluent of the WWTP Garching, Germany, at a rate of 24 L/h using a peristaltic pump. Compressed air was used to resupply oxygen to the effluent of column A before feeding it to column S1. Remaining effluent of column A was collected in a storage tank prior to ozonation. Ozonated effluent of column A was then fed into column S2. In the following, systems A+S1 and A+S2 will be referred to as SBF(Air) and SBF(O_3).

The biofiltration setup was operated with WWTP secondary effluent for over three years before the start of the experiments and thus could be considered well adapted. Intermediate ozonation treatment was initiated more than four months before the start of the sampling campaign. System settings were held constant for four months prior to the sampling campaign. During three months of sampling campaign, samples were collected on a weekly basis.

8.2.1.2 Pilot-scale ozonation experiments in semi-batch

Ozonation of a batch of column A effluent was carried out twice a week using an ozonation unit at pilot-scale. For the generation of ozone, a G-PSA system (Sewec Ozon, Germany) with a maximum ozone production capacity of 150 g/h was used. The system was equipped with a pressure swing adsorption (PSA) module, allowing for oxygen enrichment, thus, pressurized air could be used as feed gas. A volume of 500 to 1,000 L of column A effluent was collected over two days in a 1 m^3 stainless steel storage tank. For ozonation, water was withdrawn from the storage tank using a centrifugal pump at a flowrate of 4 m^3/h. At a gas flow of 0.65 m^3/h, the ozone gas was introduced into the liquid phase using a venturi injection system in side stream. After passing through a static mixer the gas water phase was introduced into a closed 1 m^3 stainless steel reactor, equipped with a venting valve (Mankenberg, Germany) avoiding overpressure and allowing for continuous discharge of the gas phase which was directed to an ozone destruction unit to remove residual ozone. After ozonation of a batch, the ozonated water was stripped with oxygen for one hour to remove residual ozone from the water phase and residual ozone from the headspace of the reactor. After ozonation, the water was stored in a gastight flexible PVC storage tank (0.5 m^3) and was continuously fed to column S2 via a peristaltic pump. Once a week, the storage tank was filled and rinsed with tap water which was treated with very high ozone concentrations, to avoid excessive formation of biofilm.

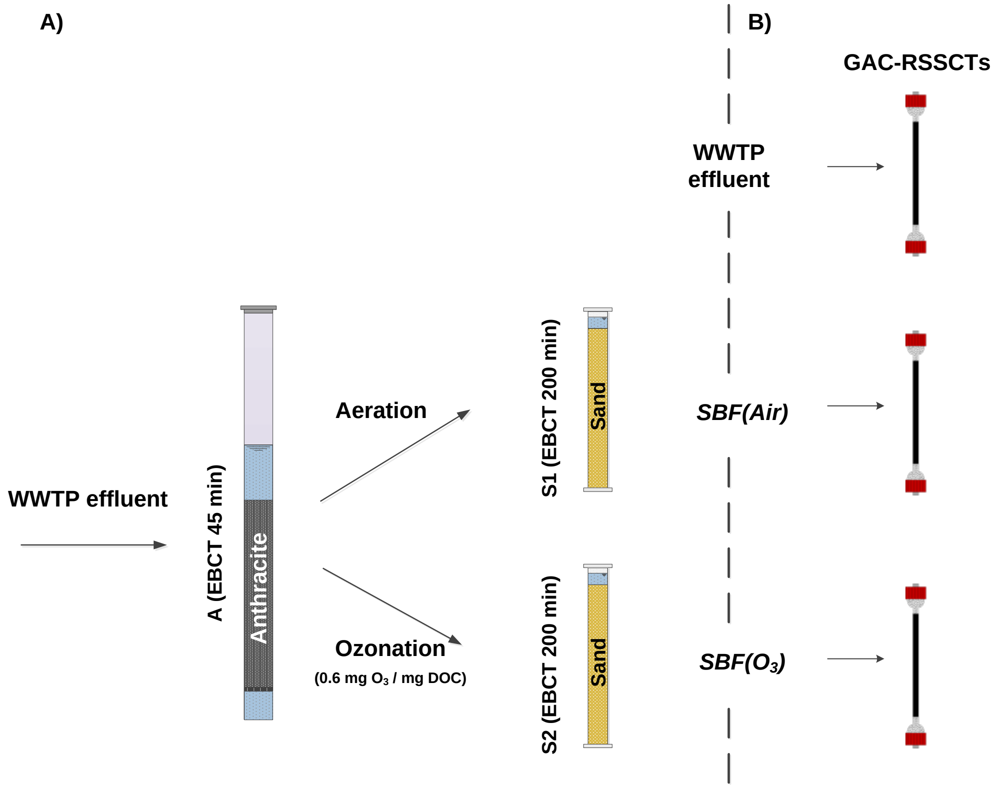

Figure 8-1: Experimental setup: A) Continuously operated systems SBF(Air) and SBF(O_3) at pilot-scale; B) Short-term tests with GAC-RSSCTs fed with WWTP effluent and effluents of systems SBF(Air) and SBF(O_3).

For the ozonation of column A effluent a specific ozone dose of 0.6 mg O_3/mg DOC was targeted. To account for variations in feed water characteristics, the UV absorbance at 254 nm (UVA_{254}) was measured prior to ozonation and DOC values were estimated using a UVA_{254}/DOC correlation (see Figure SI-14). The ozone concentration of the in-gas was adjusted accordingly and monitored via an ozone gas phase analyzer (BMT 964, BMT Messtechnik GmbH, Germany). For the comparison of systems SBF(Air) and SBF(O_3), TOrCs were not spiked to the water but ambient concentrations were considered present in the tertiary effluent from the WWTP.

8.2.1.3 Bench-scale ozonation experiments in semi-batch

In order to investigate the effect of different ozone dosages on the removal of TOrCs in WWTP effluent with and without pre-treatment by biofiltration, additional bench-scale ozonation experiments in semi-batch were conducted with WWTP effluent and column A effluent. An ozone generator (BMT 803 BT, BMT Messtechnik GmbH, Germany) with a maximum ozone production capacity of 8 g/h was used for the experiments. A stirred glass reactor (2.5 L) was used to treat sample volumes of 2 L. Ozone concentrations in the in-gas and off-gas of the reactor were measured with ozone gas phase analyzers (BMT 964, BMT Messtechnik GmbH, Germany). The in-gas was added at a gas flow rate of 0.8 L/min and an ozone concentration of 10 mg/L. After targeted ozone doses were delivered, samples were stripped with pure oxygen to remove dissolved ozone from the liquid phase.

For the experiments, corresponding samples of WWTP effluent and column A effluent were collected. Concentrations of selected TOrCs in both water matrices were fortified by 1,000 to 2,000 ng/L using an aqueous stock solution with a mix of indicator compounds before ozonation. Fortification was used to investigate the effect of biological pretreatment for a larger set of substances. The indicator compounds covered a broad range of reactivities with ozone (see Table SI-15). Chemicals included in the mix were atenolol, antipyrine, benzotriazole, caffeine, carbamazepine, diclofenac, gabapentin, iopromide, metoprolol, phenytoin, primidone, sulfamethoxazole, tris(2-chloroethyl) phosphate (TCEP), and venlafaxine.

8.2.1.4 Rapid small-scale column tests

Rapid small-scale column tests (RSSCTs) allow for the prediction of full-scale adsorber performance in a rapid assessment and at low costs (Crittenden et al., 1986, 1991). Three RSSCTs were conducted to investigate the effect of biological and biological-oxidative pre-treatment of WWTP effluent on the breakthrough behavior of TOrCs in GAC adsorbers. RSSCT columns were designed and operated according to the constant diffusivity approach (Crittenden et al., 1986, 1991). To avoid excessive head loss during the operation and to reduce the column length, the hydraulic loading of the RSSCTs was reduced, ensuring a Reynolds number of > 1, as proposed by Crittenden et al. (1991). To reduce the particle size and obtain an average particle diameter of 250 µm, GAC (CycleCarb 401, Chemviron) was grinded with a ball mill and sieved using woven wire mesh sieves with nominal apertures of 200 and 300 µm (Retsch, Germany). RSSCT columns with GAC bed lengths of 6 cm were constructed in glass columns (l = 30 cm; ID = 1 cm). GAC beds were supported by thin layers of glass wool, 1 mm glass beads were used to fill up the void volume of the columns. EBCTs in the RSSCTs were adjusted to 22 s by adjusting the hydraulic loading delivered to the column. Assuming the validity of the constant diffusivity RSSCT approach, RSSCTs were designed to mimic the breakthrough behavior of a full-scale GAC adsorber (average GAC grain size = 2 mm; l = 1 m; reactor volume = 785 L) operated at an EBCT of 24 min.

For RSSCT investigations, corresponding samples of WWTP effluent, SBF(Air) effluent and SBF(O_3) effluent were collected before the experiments. The TOrCs spiking mix (1,000 to 2,000 ng/L) was slightly different to ozonation experiments and included the compounds atenolol, carbamazepine, citalopram, diclofenac, iopromide, metoprolol, phenytoin, primidone, sulfamethoxazole, tramadol, and trimethoprim.

8.2.2 Sample collection and analysis

Redox conditions in biofiltration systems were characterized by the acquisition of DO profiles in column in- and effluents and at different depths of the columns using installed sampling ports and non-invasive DO sensor spots. In addition, ammonia, nitrite and nitrate concentrations were monitored in filter in- and effluents. For the characterization of dissolved organic matter, organic bulk parameters DOC and UV absorbance at 254 nm (UVA_{254}) were measured. Details on the applied methods can be found in Müller et al. (2017).

Several approaches for the direct determination of BDOC concentrations by the use of bioassays were described in previous studies (Servais et al., 1987; Volk and LeChevallier, 2000). However, time-consuming analyses must be considered a drawback. Also, the significance of the results has been discussed critically (Woolschlager and Rittmann, 1995). In this study, BDOC concentrations were not quantified directly. Instead, a rather qualitative estimation, was conducted by monitoring the consumption of DOC and UVA_{254} in the biofiltration systems as a proxy for BDOC.

Removal of TOrCs during the experiments was investigated by monitoring a list of 21 indicator compounds using liquid chromatography coupled to a tandem mass spectrometer (LC-MS/MS) with isotope dilution. The set of indicator compounds was chosen to cover a broad range of susceptibility to removal during different advanced treatment steps. The limits of quantitation (LOQs) and concentrations in WWTP effluent found for the indicator compounds can be found in Table SI-15. Further method details are documented in Müller et al. (2017).

Performances of systems SBF(Air) and SBF(O_3) was monitored during 10 sampling campaigns. The effect of biological pre-treatment on the ozonation efficiency was investigated during four ozonation batch tests. The effect of pre-treatment on the breakthrough behavior in GAC-RSSCTs was investigated in one experiment.

8.2.3 Characterization of redox conditions

The classification of redox conditions in filter columns was based on measured concentrations of DO and nitrate as proposed by Müller et al. (2017) according to definitions from Regnery et al. (2015) and McMahon and Chapelle, (2008). Thus, filters were defined as ‘oxic’ when DO concentrations above 1 mg/L were found in filter effluents. Columns with DO concentrations in filter effluents below 1 mg/L accompanied by limited nitrate removal (< 0.5 mg N/L) were defined as ‘suboxic’ whereas columns with nitrate reduction exceeding 0.5 mg N/L were considered ‘anoxic’.

8.2.4 Statistical analysis

The statistical significance of differences observed between two related data sets was tested using two-tailed paired Student’s t-tests. Differences were considered statistically significant if $p < 0.05$. Standard deviations were used as measures of variability.

8.3 Results and discussion

8.3.1 Sequential biofiltration with intermediate ozonation

8.3.1.1 Characterization of redox conditions

Systems SBF(Air) and SBF(O_3) were characterized by oxic redox conditions at all times during the operation. Despite substantial DO consumption, DO concentrations remained well above 1 mg/L in all column effluents. The DO profile for system SBF(Air) was characterized by a rapid and seemingly linear decrease of DO in column A suggesting increased DO consumption due to microbial activity also in deeper layers of the filter (Figure 8-2a, b). Resupply of DO via the intermediate aeration allowed for increased DO concentrations in the influent of column S1. The DO profile in column S1 was characterized by slower DO consumption mainly restricted to the upper half of column S1 with little additional DO consumption in deeper column layers (Figure 8-2a, c). Despite differing curve shapes, no significant difference was found for the total DO consumption in columns A and S1 (5.3 ± 0.9 and 6.1 ± 1.0 mg/L). However, the asymptotic shape of the DO consumption as a function of EBCT in column S1 indicated a reduced availability of BDOC in the deeper layers of the column compared to column A which is also supported by the comparable DO consumption at a substantially higher EBCT in column S1. In system SBF(O_3) intermediate ozonation allowed for DO concentrations above 20 mg/L in the influent of column S2. Column S2 exhibited a DO consumption pattern which was comparable to the one observed in column S1 (Figure 8-2a, d). Despite stronger fluctuations in the upper layers of the column, also here, the main DO consumption was restricted to the upper column layers. Only little additional DO consumption was observed in the deeper zones of the column. Despite substantially higher DO concentrations in the influent of column S2 compared to column S1 (23.4 ± 4.4 and 8.0 ± 0.5mg/L), no significant difference was found for the DO consumption in both columns (5.4 ± 0.9 and 6.1 ± 1.0 mg/L).

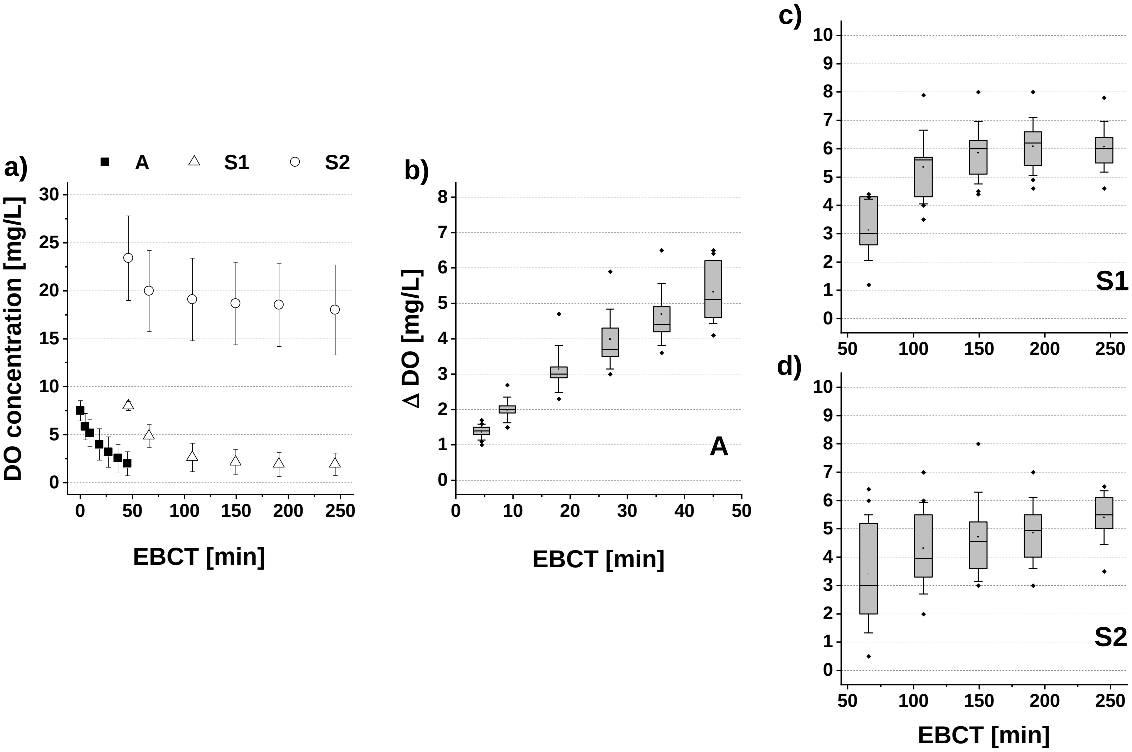

Figure 8-2: Dissolved oxygen (DO) concentration profile (a)) and consumption (b), c), d)) in columns A, S1 and S2 as a function of empty bed contact time (EBCT) (n = 10).

8.3.1.2 Removal of organic bulk parameters

The presence and removal of BDOC in columns A, S1 and S2 was followed by monitoring the organic bulk parameters DOC and UVA_{254} (Figure 8-3a, b). No significant differences in removal of DOC and UVA_{254} in columns A and S1 indicated the presence of BDOC in both filter stages of system SBF(Air) (ΔDOC 1.8 ± 0.5 and 1.4 ± 0.5 mg/L; ΔUVA_{254} 1.1 ± 0.4 and 0.9 ± 0.4 1/m). These findings are supported by the comparable results observed for DO consumption in both columns (see section 8.3.1.1). The pattern for DO consumption in columns A and S1 indicated major BDOC consumption to occur over the full length of column A and in the upper layers of column S1 (Figure 8-2b, c) resulting in BDOC depleted conditions in deeper layers of filter S1. The effect of ozonation on bulk parameters DOC and UVA_{254} supported findings from other studies and relates to the specific character of ozone reactions. While ozonation did not achieve substantial mineralization of organic matter, the selective reaction with electron rich moieties results in structural changes and mainly affects chromophores. Thus, only minimal (still significant) removal of DOC (ΔDOC 0.3 ± 0.1 mg/L) is aligned by substantial removal of UVA_{254} (ΔUVA_{254} 3.4 ± 0.7 1/m). Ozonation has been reported to increase the amount of BDOC by breaking up complex molecules increasing the biodegradability of organic matter (Hammes et al., 2006). Findings from this study, however, only show insignificantly increased

BDOC removal in column S2 after intermediate ozonation (ΔDOC 1.9 ± 0.5 mg/L; ΔUVA_{254} 1.1 ± 0.2 1/m) compared to column S1 after intermediate aeration which is also supported by the comparable total DO consumption found in both columns (see section 8.3.1.1).

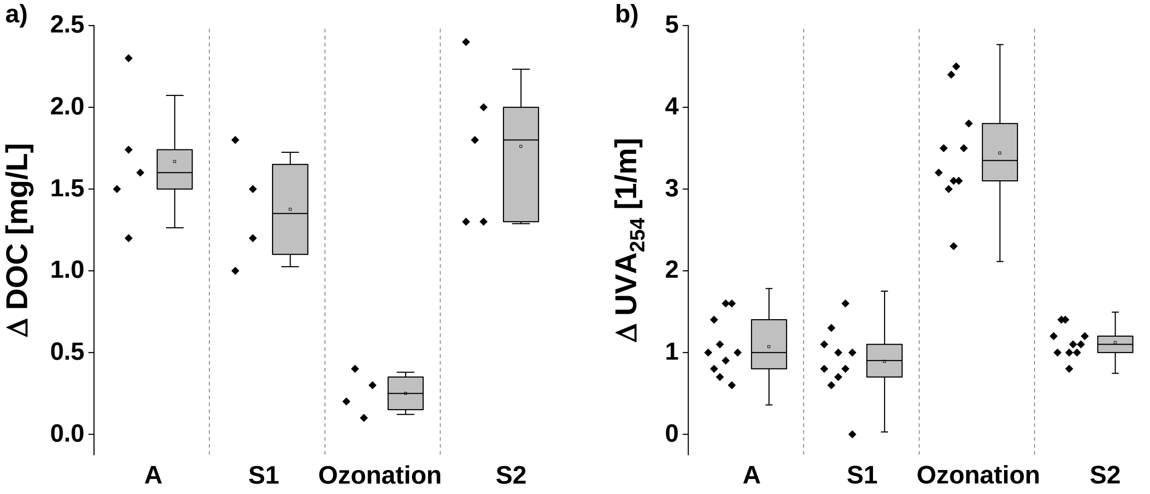

Figure 8-3: Consumption of bulk parameters DOC (a)) and UVA_{254} (b)) in filtration columns A, S1 and S2 and during ozonation. WWTP effluent: DOC 7.2 ± 0.9 mg/L (n = 4–5); UVA_{254} 12.6 ± 1.2 1/m (n = 10).

8.3.1.3 Removal of trace organic chemicals in systems SBF(Air) and SBF(O_3)

The TOrC removal potential in systems SBF(Air) and SBF(O_3) was investigated by monitoring a list of 21 indicator compounds. Out of these, 15 compounds will be further discussed which were found to be present in the secondary effluent during at least 3 out of 10 sampling campaigns at concentrations > 3.5 x LOQ. When concentrations were decreased below the LOQ during treatment, concentration values for the calculation of removal rates were set to 0.5 x LOQ.

The cumulative removal of indicator TOrCs in systems SBF(Air) and SBF(O_3) revealed expected compound specific differences (Figure 8-4a). The average overall removal of most indicator compounds in systems SBF(Air) and SBF(O_3) was characterized by relatively low standard deviations, indicating a high process stability. The compounds 4-formylaminoantipyrine (4-FAA), valsartanic acid, benzotriazole gabapentin and metoprolol proved to be well biodegradable (> 70 %) in system SBF(Air). Moderate removal (30 to 70 %) was found for compounds sotalol, citalopram, climbazole, sulfamethoxazole and diclofenac whereas primidone, venlafaxine, tramadol and carbamazepine exhibited high persistence. Column S1 of system SBF(Air) substantially contributed to an improved removal of well and moderately degradable compounds such as valsartanic acid, metoprolol, sotalol and citalopram. Here, filter S1 accounted for > 50 % of the overall removal. Currently, studies are carried out to determine first-order rate constants to allow for a comprehensive comparison of compound degradation in first and second stage filters during SBF.

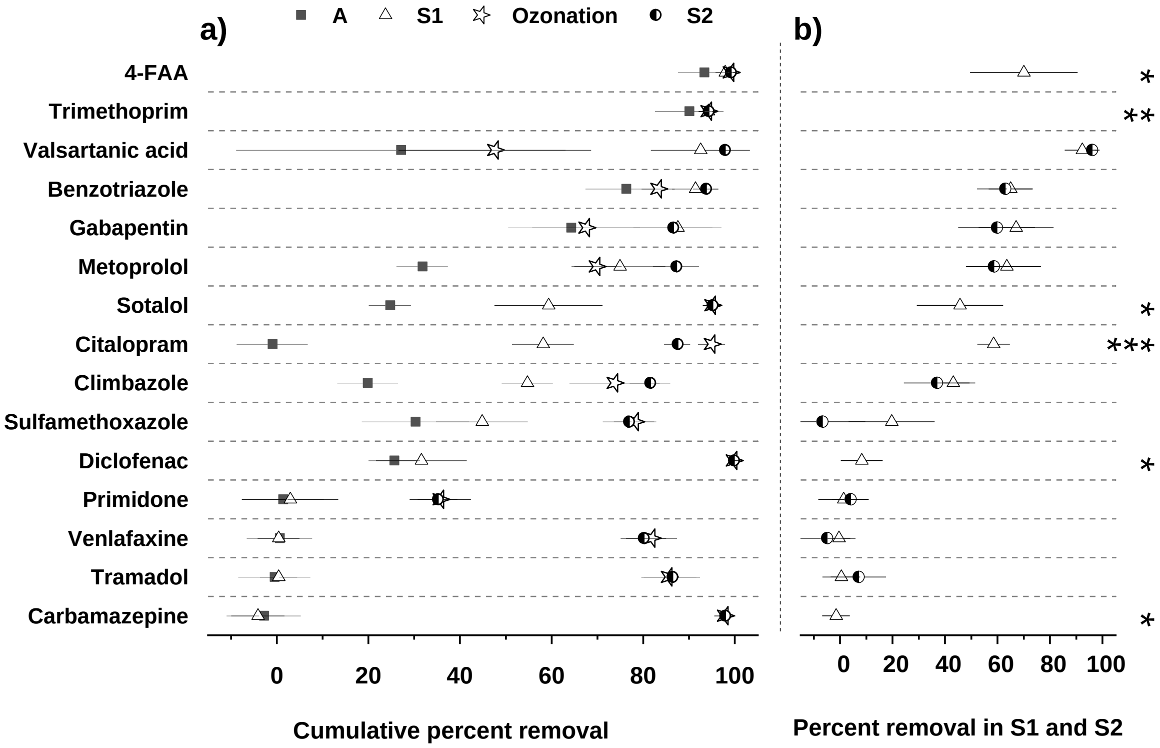

Figure 8-4: a) Cumulative removal of indicator compounds in systems SBF(Air) and SBF(O_3); b) Removal of indicator compounds in filters S1 and S2 of treatment trains SBF(Air) and SBF(O_3); asterisks indicate concentrations < 3.5 x LOQ after *ozonation or **treatment in column A. Citalopram concentrations in column S2 effluent were significantly higher than after ozonation; n = 10.***

In system SBF(O_3), substantial oxidative transformation during ozonation, contributing to > 50 % of the overall transformation, was observed for the compounds citalopram, carbamazepine, venlafaxine, tramadol, primidone, diclofenac, sotalol, climbazole, and sulfamethoxazole. For the compounds carbamazepine, tramadol and venlafaxine which were found to be highly persistent in system SBF(Air), ozonation contributed to > 95 % of the overall transformation in system SBF(O_3). Similarly, effective oxidative transformation was also observed for citalopram which was found to be moderately biodegradable in system SBF(Air). Main transformation of 4-FAA, trimethoprim, valsartanic acid, benzotriazole, gabapentin and metoprolol could be related to biodegradation, also in system SBF(O_3). While 4-FAA and trimethoprim have been reported to rapidly react with ozone (Hollender et al., 2009; Favier et al., 2015), effective biodegradation was already observed in column A. In contrast valsartanic acid, benzotriazole and gabapentin react poorly with ozone, thus, limited removal can be linked to the reaction with hydroxyl radicals. Here, biodegradation proves to be an effective barrier for the mitigation of such compounds which are less susceptible to oxidative reactions.

8.3.2 Synergistic effects in process combinations including sequential biofiltration, ozonation and adsorption onto activated carbon

8.3.2.1 Effect of intermediate ozonation on the biodegradation of TOrCs in second stage filters

Besides the expected improved removal of indicator compounds in system SBF(O_3) compared to SBF(Air) due to the addition of an oxidative treatment barrier, investigations also targeted a potentially different removal efficiency in column S2 after intermediate ozonation. Figure 8-4b displays the removal of indicator TOrCs in filters S1 and S2 related to the concentrations found in the column inlets. Results indicated no significant differences in the removal of most compounds in columns S1 and S2. The transformation of gabapentin was slightly, still significantly, increased in column S1 compared to column S2 (69 ± 14 and 55 ± 19 %). Significant reformation of compounds after oxidation was observed for sulfamethoxazole (S1: 22 ± 17; S2: -9 ± 19 %) and citalopram (S1: 59 ± 6; S2: -226 ± 194 %) in column S2 which was most likely caused by a back-transformation of instable oxidative transformation products into the parent compounds. Similar effects for sulfamethoxazole and citalopram have been observed in previous studies (Achermann et al., 2018a; Gonzalez-Gil et al., 2019a). Gonzalez-Gil et al. proposed that the reversibility of certain enzymatic transformations might be responsible for this effect. However, the results indicated no distinct influence of the pretreatment of column A effluent via intermediate aeration or ozonation on the biological degradability of most indicator compounds in filters S1 and S2. Substantially higher DO concentrations in column S2 (Figure 8-2a) did not cause an alteration of the biotransformation efficiency of TOrCs in column S2 after ozonation. Column S1, however, was also characterized by DO concentrations well above 1 mg/L, thus, operational conditions in both columns could not be distinguished based on different redox conditions according to the definitions proposed (see section 8.2.3). Also, structural changes in the DOM present after ozonation and a decrease in aromaticity, as indicated by an elevated ΔUVA_{254} (Figure 8-3b), did not seem to affect the microbial community's ability to remove TOrCs.

8.3.2.2 Effect of biological pre-treatment on ozonation efficiency

To investigate whether SBF(O_3) hybrid systems benefit from an increased ozonation efficiency compared to the direct ozonation of WWTP effluent, ozonation experiments were conducted in semi-batch mode applying two different ozone doses (3 and 5 mg/L O_3) to WWTP effluent and the corresponding effluent of column A.

Treatment in column A resulted in a removal of 21 ± 3 % DOC (WWTP effluent: 7.4 ± 1.3; A effluent: 5.8 ± 1.1 mg/L; n = 4) and 11 ± 3 % UVA_{254} (WWTP effluent: 14.1 ± 1.2; A effluent: 12.5 ± 0.9 1/m; n = 4). Biological pre-treatment achieved a partial reduction of potential scavenging effects caused by DOM and allowed, at similar ozone doses, for higher specific ozone doses compared to the direct ozonation of WWTP effluent. Thus, ozone doses of 3 and 5 mg/L translated into specific ozone doses of 0.4 ± 0.1 and 0.7 ± 0.1

mg O_3/mg DOC in WWTP effluent and 0.5 ± 0.1 and 0.9 ± 0.2 mg O_3/mg DOC in column A effluent.

The compounds carbamazepine, diclofenac, sulfamethoxazole and venlafaxine exhibited a removal of > 90 % in both waters already at the lower ozone dose of 3 mg/L O_3 and are not further discussed here. Fast oxidative transformation of these compounds, as observed during this study, is in accordance with findings from other studies at comparable specific ozone doses and is attributed to their high second-order rate constants with ozone (see Table SI-15) (Hollender et al., 2009; Lee et al., 2013; Zucker et al., 2018). The flame-retardant TCEP exhibited high persistence also at the higher ozone dose of 5 mg/L O_3 (< 5 % removal in both water matrices), which is in accordance with other studies (Lee et al., 2013). Thus, TCEP is not further discussed for the comparison of ozonation efficiencies in the compared water matrices.

Results obtained for the indicator compounds pointed to a slightly improved transformation efficiency at similar ozone doses when WWTP effluent was pre-treated by biofiltration (column A) instead of directly ozonating the corresponding WWTP effluent (Figure 8-5). Significantly improved removal after biological pre-treatment of WWTP effluent in column A at both investigated ozone doses was observed for the compounds atenolol, benzotriazole and caffeine.

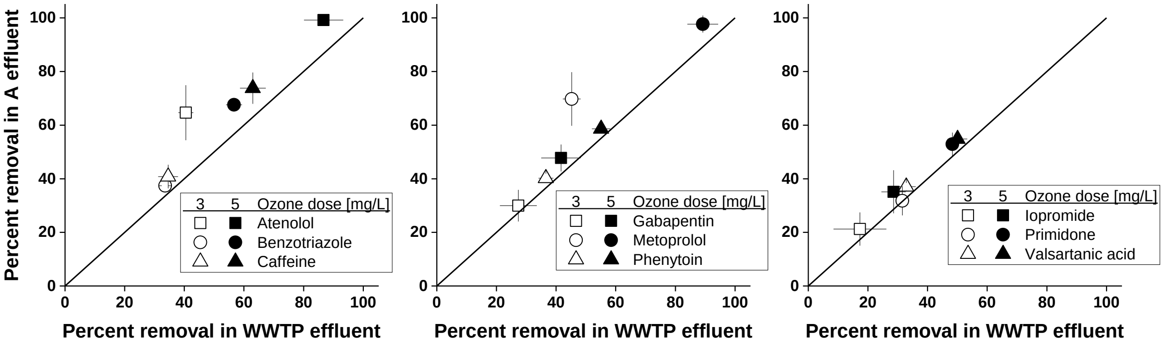

Figure 8-5: Percent removal of selected indicator compounds by ozonation in WWTP effluent and in the effluent of column A (n = 4).

Significantly improved removal of metoprolol, phenytoin and valsartanic acid was found in column A effluent at the lower ozone dose of 3 mg/L O_3 and for gabapentin at the higher ozone dose of 5 mg/L O_3. Improvements in removal efficiencies > 10 % were observed for atenolol, benzotriazole, caffeine and metoprolol. Maximum differences were found for metoprolol and atenolol (up to 25 % higher removal in column A effluent). No significantly improved removal was found for primidone and iopromide which are known for their limited susceptibility to reactions with ozone (Huber et al., 2003; Hollender et al., 2009; Lee et al., 2013).

Increased ozonation efficiency in column A effluent was linked to partial degradation of BDOC during biofiltration resulting in reduced scavenging effects caused by DOM. The removal efficiency for compounds with high second-order rate constants with ozone (i.e., carbamazepine, diclofenac, sulfamethoxazole, venlafaxine; see Table SI-15) were not affected by the biological pre-treatment. No substantial differences were also observed for compounds with low second-order rate constants for the reaction with ozone (i.e., primidone, iopromide, phenytoin, gabapentin) which are mainly transformed via secondary oxidation by OH radicals formed during the decomposition of ozone. A significant effect of pre-treatment by biofiltration on ozonation efficiency was mainly restricted to compounds with medium second-order rate constants (i.e., atenolol, caffeine, metoprolol, benzotriazole). Here, the removal of organic scavengers seemed to have an influence on the ozonation efficiency.

8.3.2.3 Effect of biological and biological-oxidative pre-treatment on the efficiency of a posterior adsorption step

Experiments with GAC-RSSCTs aimed at investigating potential beneficial effects on the breakthrough behavior of TOrCs in a GAC adsorber when WWTP effluent was pre-treated via the biological and biological-oxidative processes SBF(Air) and SBF(O_3). To evaluate the removal efficiency of RSSCTs, the following classification was applied: Poorly adsorbing (10 % breakthrough after < 5,000 bed volumes treated (BVT)), moderately adsorbing (10 % breakthrough after 5,000 to 15,000 BVT), and well adsorbing (10 % breakthrough after > 15,000 BVT).

Results indicated different removal efficiencies for individual compounds in the operated RSSCTs. Differences in compound adsorbability were identified as one reason for the observations. Thus, the highly polar compounds gabapentin and iopromide, known for their low adsorbability onto activated carbon (Nowotny et al., 2007; Altmann et al., 2016), were categorized as poorly adsorbable in all three RSSCTs, whereas benzotriazole proved to be well adsorbable during all experiments, supporting findings from other studies (Figures 8-6 and SI-15) (Zietzschmann et al., 2014b; Altmann et al., 2016).

The comparison of the breakthrough curves obtained from RSSCTs fed with WWTP effluent and effluents of systems SBF(Air) and SBF(O_3) indicated that biological or biological-oxidative pre-treatment of WWTP effluent did affect the efficiency of the posterior adsorption step. RSSCTs fed with effluents from systems SBF(Air) and SBF(O_3) exhibited an improved retardation of all compounds, except for gabapentin for which instantaneous breakthrough was observed in all test columns (Figures 8-6 and SI-15). Table 8-1 summarizes the effect of pre-treatment on the breakthrough behavior of the investigated compounds. Results also indicated differences in the breakthrough behavior of several compounds depending on the type of pre-treatment. Especially for rather moderately adsorbable compounds, such as sulfamethoxazole, primidone, diclofenac and phenytoin the adsorption capacity of the RSSCTs was found to be in the following order: WWTP effluent < SBF(Air) effluent < SBF(O_3) effluent.

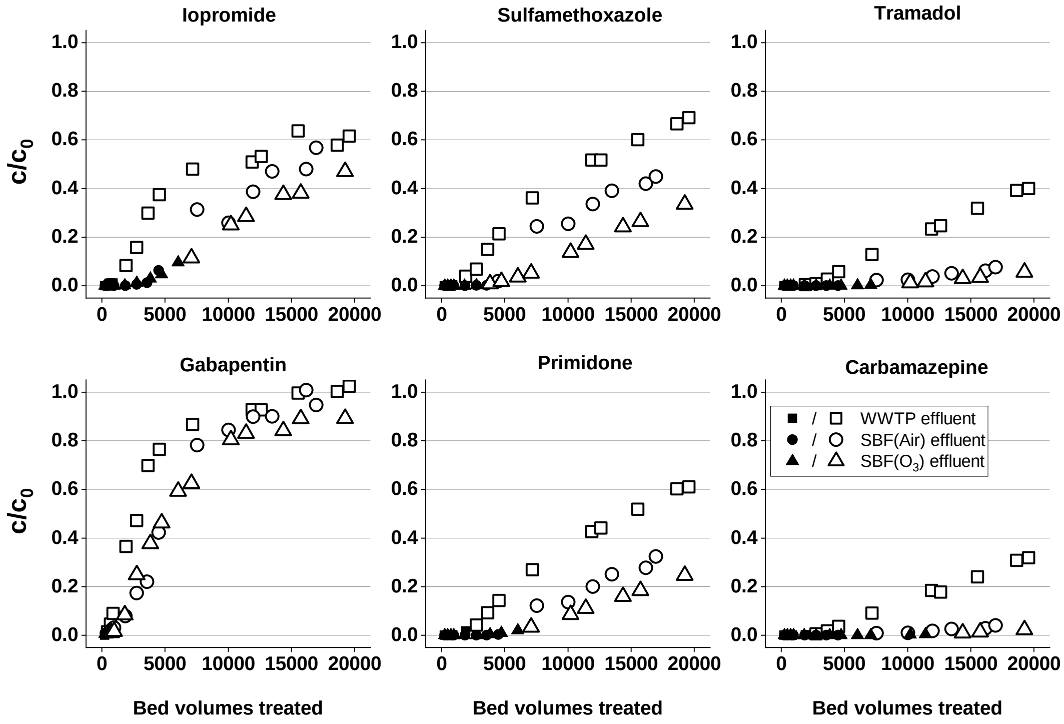

Figure 8-6: Breakthrough curves for a selection of compounds from RSSCTs fed with WWTP effluent and effluent of systems SBF(Air) and SBF(O_3). Full symbols indicate values < LOQ, empty values indicate values > LOQ. Breakthrough curves for all remaining investigated compounds are illustrated in Figure SI-15.

The increased adsorption capacity for TOrCs in RSSCTs fed with the effluents of SBF(Air) and SBF(O_3) is most likely caused by the removal of BDOC during biofiltration, reducing the impact of competitive adsorption and allowing for substantially prolonged filter lifetimes until breakthrough of the target compounds. While only little additional BDOC consumption after ozonation was found in filter S2 of system SBF(O_3) compared to filter S1 of system SBF(Air) (see section 8.3.1.2), differences were observed in the breakthrough behavior indicating an improved retention of several TOrCs in the RSSCT fed with effluent from system SBF(O_3). Besides a slightly increased removal of BDOC in system SBF(O_3), also a reduced adsorbability of the DOM due to structural changes caused by the ozonation as proposed by Zietzschmann et al. (2015) could be responsible for an improved adsorption capacity. The preferential attack of electron-rich moieties during ozonation causes a decrease in aromaticity of the DOM during ozonation (see section 8.3.1.2). Interactions between aromatic moieties and surface structures of activated carbon, however, are known to be relevant mechanisms during adsorption (Worch, 2012). Thus, structural changes aligned by a decrease in aromaticity during ozonation might have caused a lower adsorbability of DOM constituents present in the effluent of SBF(O_3) compared to the effluent of SBF(Air) and contributed to an increased adsorption capacity for TOrCs.

Table 8-1: Categorization of investigated compounds according to observed breakthrough behavior in RSSCT columns fed with WWTP secondary effluent, SBF(Air) effluent and SBF(O_3) effluent. “-“: breakthrough of 10 % c_0 after < 5,000 BVT; “0”: breakthrough of 10 % c_0 after 5,000 to 15,000 BVT; “+”: breakthrough of 10 % c_0 after > 15,000 BVT.

	Atenolol	Benzotriazole	Carbamazepine	Citalopram	Diclofenac	Gabapentin	Iopromide	Metoprolol	Phenytoin	Primidone	Sulfamethoxazole	Tramadol	Trimethoprim	Valsartanic acid
WWTP effluent	○	○	○	○	−	−	−	○	−	−	−	○	○	−
SBF(Air) effluent	+	+	+	+	○	−	−	+	○	○	○	+	+	○
SBF(O_3) effluent	+	+	+	+	+	−	−	+	+	○	○	+	+	○

8.3.3 Implications for the use of hybrid systems for enhanced removal of trace organic compounds

Results presented in sections 8.3.1 and 8.3.2 demonstrate the potential of combining the unit processes SBF, ozonation and activated carbon adsorption for a more comprehensive attenuation of TOrCs. Integrating multiple barriers with different removal mechanisms to a hybrid system benefits from an increased effectivity to remove a wider range of TOrCs with different characteristics. The effective removal of various compounds during SBF supported findings from a previous study (Müller et al., 2017) and confirmed the suitability of advanced biological treatment systems to contribute to an improved removal of TOrCs (see section 8.3.1.3). The high persistence to biodegradation of some compounds, such as carbamazepine and primidone, however, demands the application of other treatment technologies to achieve effective attenuation. Ozonation proved to be effective in removing several compounds which were not or not effectively removed during solely biological processes (i.e., carbamazepine, tramadol, venlafaxine, diclofenac) (see section 8.3.1.3). Adsorption onto GAC also was found to be effective in removing various non-biodegradable compounds, especially in the beginning of the operation (see section 8.3.2.3). Despite the strengths of oxidative and adsorptive unit treatment steps, especially the compound gabapentin demonstrated the merits of biological treatment systems. While ozonation and adsorption fell short to substantially mitigate gabapentin, vast removal was achieved during SBF (see section 8.3.1.3). While this study focused on the removal of a set of indicator compounds, many authors also reported beneficial additive effects in the combination of oxidative and biological or biological-adsorptive treatment processes. Post-treatment in biologically active sand or GAC filters was reported effective in removing various organic oxidation by-products, formed during ozonation (Kramer et al., 1993;

Coffey et al., 1996; Griffini et al., 1999; Bourgin et al., 2018; Bacaro et al., 2019), and resulted in a reduction of specific and non-specific toxicity (Stalter et al., 2010; Reungoat et al., 2010, 2012).

Besides an improved overall TOrC removal due to additive effects caused by the combination of several unit treatment steps, hybrid systems also take advantage of synergistic effects between individual treatment steps when designed wisely. Synergistic effects identified during this study were mainly related to the partial removal or structural alteration of DOM. Results indicated only a limited, but still significant, improvement of ozonation efficiency for several TOrCs when installed as an intermediate oxidation step between the first and the second filter stage of a SBF system compared to the direct ozonation of WWTP effluent (see section 8.3.2.2). In our study, such positive effects on the ozonation efficiency were only noted for compounds with moderate reactivity towards ozone. For WWTP effluents containing significant amounts of nitrite, however, biological pre-treatment in the first stage filter might also help to reduce the negative impact of nitrite peaks present in the WWTP effluent on ozone demand. This has been demonstrated in a previous study (Zucker et al., 2015). While not investigated in this study, biofiltration prior to ozonation might also have the potential to remove precursors for the formation of various toxicologically relevant oxidation by-products (Farré et al., 2011; Marti et al., 2017; McKie et al., 2015). The pre-treatment of WWTP effluent by SBF(Air) and SBF(O_3) proved to substantially prolong the lifetime of a posterior GAC adsorber for adsorbable compounds compared to the direct treatment of WWTP effluent which is likely attributed to the removal of BDOC during biofiltration (section 8.3.2.3). Also, structural changes in DOM caused by ozonation might have contributed to an improved adsorption capacity, as suggested by Zietzschmann et al. (2015). Intermediate aeration and ozonation did not seem to have different effects on the biodegradation of TOrCs in second stage filters of SBF systems.

Additive and synergistic effects were found for all investigated hybrid systems. Their applicability, however, must be evaluated by considering cost-benefit aspects. Besides an improved removal efficacy for TOrCs of the investigated unit processes, also increased process complexity, space requirements, and costs of operation must be considered. The final assessment of the suitability of a treatment scheme will strongly depend on site-specific factors, such as WWTP effluent characteristics and treatment requirements. Despite a slightly improved ozonation efficiency for the removal of some TOrCs in system SBF(O_3), observed beneficial effects of the biological pre-treatment on the overall performance, were rather limited. Biological or biological-oxidative treatment prior to adsorption proved to substantially increase the efficiency of GAC adsorbers. The combination of SBF(Air) with posterior adsorption onto GAC can thus be regarded a suitable combination of different unit processes. When combining SBF(O_3) with posterior adsorption, even higher GAC filter lifetimes were observed.

The optimized utilization of synergistic effects between unit treatment processes might be a measure to reduce costs for the operation of additional treatment technologies in some cases. However, critical cost-benefit analyses are necessary to evaluate the feasibility of additional treatment steps when hybrid systems are considered for full-scale application.

8.4 Conclusions

This study investigated combinations of different advanced treatment technologies to optimize the removal of trace organic chemicals (TOrCs) during wastewater treatment. Investigated treatment technologies included sequential biofiltration (SBF), designed for an improved biological removal of TOrCs, ozonation and adsorption onto activated carbon. Experiments at lab- and pilot-scale targeted an increased process efficacy caused by the application of various removal mechanisms. In addition, synergistic effects between unit operation steps resulting in an improved efficiency of individual treatment processes were investigated.

- Advanced biological treatment using a SBF system with an intermediate aeration (SBF(Air)) proved successful to remove various well and moderately biodegradable TOrCs while ozonation and activated carbon adsorption achieved transformation or retention of most investigated non-biodegradable compounds.
- The integration of multiple barriers with different removal mechanisms in hybrid systems allowed for the removal of an extended range of compounds with varying characteristics.
- SBF achieved the removal of easily biodegradable constituents of dissolved organic matter, resulting in a partial removal of DOC and UVA_{254}.
- SBF with an intermediate ozonation step (SBF(O_3)) benefitted from a slightly improved ozonation efficiency of TOrCs compared to the direct ozonation of WWTP effluent which was attributed to the partial removal of organic scavengers in the first filter stage.
- The pre-treatment of WWTP effluent in biological and biological-oxidative systems SBF(Air) and SBF(O_3) causing partial removal and structural alteration of the background organic matter was shown to substantially increase the adsorption capacity for TOrCs during posterior granular activated carbon adsorbers which is expressed in prolonged filter lifetimes until breakthrough.
- While synergies in hybrid systems hold promise to improve overall process efficiency, critical cost-benefit analyses are necessary to evaluate the feasibility of the combination of several additional treatment steps.

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgements

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9 Discussion

In three overarching research objectives and specified in four derived research hypotheses (Chapter 3), this study investigated (i) options for the implementation and optimization of a novel biofiltration concept, applicable as an additional treatment step during municipal wastewater treatment to achieve an enhanced degradation of trace organic chemicals (TOrCs), (ii) tools for an improved characterization of *in situ* redox conditions in biofiltration systems, and (iii) the potential of and the benefits from combining biological with oxidative and/or adsorptive advanced treatment steps.

In research **Objective #1**, this study investigated options to make use of previously identified key parameters and infiltration strategies used in sequential managed aquifer recharge (SMART) applications to develop an advanced above-ground biological treatment step capable of an improved removal of TOrCs from wastewater treatment plant (WWTP) effluents. In Chapter 4, the concept of sequential biofiltration (SBF) was introduced which aims to establish favorable operational conditions for the enhanced biotransformation of TOrCs by using a sequential infiltration approach combined with an intermediate aeration step. Chapter 5 presented attempts to further develop and improve the system regarding necessary empty bed contact times (EBCTs) and the effect of pre-treatment via sweep flocculation using Fe(III) salts on system performance. Chapter 6 presented a study in which the fate of indicator compounds in single-stage and sequential biofiltration systems was investigated in detail by using depth profile sampling and the determination of pseudo-first-order rate constants. Research **Objective #2** tested an alternative tool for the characterization of *in situ* redox conditions during biofiltration which are crucial for the biodegradation of redox-sensitive TOrCs. Chapter 7 presented investigations in which the possibility of an improved characterization of suboxic to oxic redox conditions by following the successive and well-described transformation of the X-ray contrast medium iopromide was tested. The third research **Objective #3** targeted to investigate options for the combination of SBF systems with ozonation and/or activated carbon filtration. Here, investigations mainly focused on the identification of synergistic effects evolving between the different applied technologies combined in hybrid treatment systems (Chapter 8).

Based on the results presented in Chapters 4 to 8, the following sections contain a comprehensive discussion of the different aspects addressed in this study. This involves the critical discussion of the proposed approaches and a critical assessment regarding factors potentially limiting their applicability. This section also aims to identify future research needs and to provide recommendations for the practical implementation.

9.1 Sequential biofiltration – enhanced biodegradation of trace organic chemicals in wastewater treatment plant effluents

Research **Hypothesis #1** targeted the question of whether an improved degradation of moderately degradable TOrCs, as observed in sequential managed aquifer recharge applications, could be transferred into an above-ground treatment system operated at drastically reduced EBCTs. The detailed investigation of **Hypothesis #1** involved the characterization of operational conditions during SBF, a comparison of system performance in SBF and single-stage biofiltration systems, and an assessment of the EBCT as a control parameter under the desired oxic and substrate-limited conditions.

9.1.1 Operational conditions during sequential biofiltration

To establish the desired oxic and carbon-limited, so-called oligotrophic conditions, during SBF, the first filter stage must achieve vast removal of easily degradable substrate, often approximated by the amount of biodegradable dissolved organic carbon (BDOC). After depletion of a substantial part of BDOC, the second filter stage is then characterized as carbon-limited, the reduced availability of substrate also results in decreasing consumption of dissolved oxygen (DO) which causes redox conditions to remain oxic. Results presented in Chapter 4 indicated that the treatment of WWTP effluent in the first filter stage of the SBF system resulted in effective substrate removal as indicated by decreasing DOC concentrations and UVA_{254} values. Despite substantially higher EBCTs in second stage filters (200; 1,000; 2,000 min) compared to the first stage filter (90 min), DOC consumption in the first filter stage accounted for > 70 % of the overall DOC reduction. Higher EBCTs in second stage filters did not induce substantial additional consumption of DOC. While observations in Chapter 4 indicated an efficient removal of most BDOC in the first filter stage, results presented in Chapter 5 suggested fluctuations in process performance and a varying BDOC removal efficiency over longer periods. Figure 9-1 displays data from long-term monitoring of DOC concentrations in WWTP effluent and DOC consumption in an SBF system operated at constant EBCTs. DOC in WWTP effluent fluctuated between 5 and 10 mg/L with a mean concentration of 7.3 ± 1.3 mg/L (n = 60). Mean DOC consumption in first stage filter A1 was significantly higher (two-paired t-test; $p < 0.05$) than in second stage filter S1 (1.7 ± 0.8 and 0.9 ± 0.6 mg/L, respectively) (Figure 9-1a and b), indicating that around 70 % of total BDOC removal observed in the SBF system occurred in the first filter stage. Moderate positive correlations between DOC concentrations in WWTP effluent and observed DOC consumptions in both filter stages indicated that the availability of BDOC was related to the total amount of DOC contained in WWTP effluent (Figure 9-1c). The positive correlation between DOC concentrations in WWTP effluent and DOC consumption in the second filter stage also indicates that the first stage filter only achieved a partial removal of BDOC. Despite pre-treatment in the first filter stage, substrate availability in the second filter stage could still be related to the quality of the WWTP effluent fed to the system. Effective removal of BDOC in the first filter stage could also be observed at reduced EBCTs of 45 min, as reported in Chapter 5.

Given sufficient time for adaptation, system optimization regarding EBCT did not have detrimental effects on system performance. Tolerance of BDOC removal performance in biofiltration systems towards changes in EBCT has been reported before in other studies (LeChevallier et al., 1992; Hozalski et al., 1995; Hallé, 2010; Basu et al., 2016). Findings presented in Chapter 5 indicated the possibility of further optimization of the SBF system by reduction of EBCTs in the first filter stage.

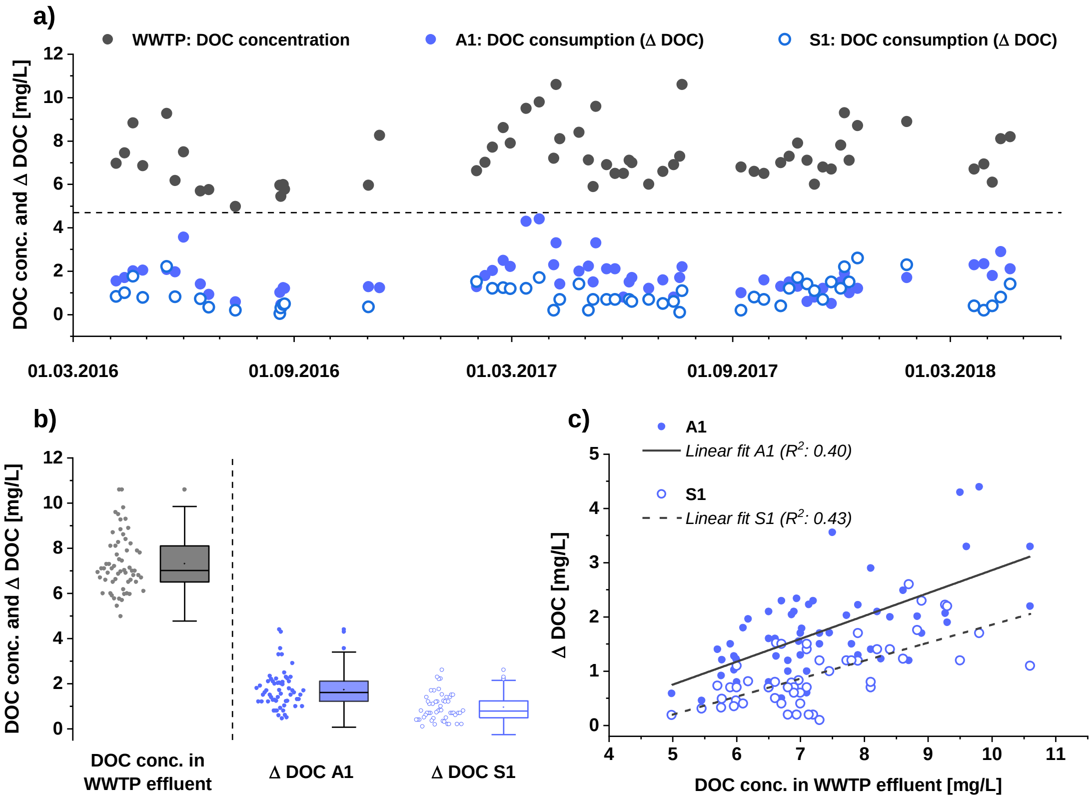

Figure 9-1: a), b) DOC concentration in WWTP effluent during more than two years of system operation (n = 60); DOC consumption (ΔDOC) in first (A1) and second stage filter (S1) of an SBF system operated at EBCTs of 90 and 200 min; c) Correlation between DOC concentration in WWTP effluent and ΔDOC in filters A1 and S1.

Partial removal of available substrate in the first filter stage followed by intermediate aeration proved effective to realize stable oxic redox conditions throughout the second filter stage (effluent DO concentrations > 1 mg/L). Results obtained in Chapters 4 to 8, indicated stable oxic conditions in the reference SBF system, operated at an EBCT of 45 or 90 min in the first and 200 min in the second filter stage. In contrast, a single-stage biofilter, operated at an overall EBCT of 290 min exhibited rapid consumption of DO and the formation of suboxic zones in the deeper layers of the filter bed, as indicated by results presented in Chapter 4. Results presented in Chapter 6 and 7, however, demonstrated that redox conditions could also remain oxic in the single-stage biofilter operated at an EBCT of 290 min. Thus, redox conditions in single-stage biofilters proved highly dependent on fluctuations in WWTP effluent quality. The direct comparison between an SBF system and a single-stage biofilter highlighted the benefit of the sequential system regarding the establishment of stable oxic and substrate-reduced conditions. However, results presented in Chapter 4 also indicated an elevated DO consumption in second stage filters when operated at higher EBCTs of 1,000 and 2,000 min. Here, substantial additional DO consumption even resulted in the formation of suboxic zones. The additional DO consumption could not be explained by the additional mineralization of DOC. The reasons for the additional consumption of DO remained unclear. Despite very low DO concentrations in deeper zones of second stage filters operated at higher EBCTs, anoxic conditions, indicated by nitrate reduction were not observed throughout the study. Here, the lack of available BDOC might have prevented denitrifying activity.

Results presented in this study indicated that SBF systems allow for the manipulation of operational conditions regarding substrate availability and redox conditions. Despite the possibility of fluctuations in BDOC removal efficiency, the treatment in the first filter stage allowed for stable substrate-limited and oxic conditions in a second stage filter operated at an EBCT of 200 min, while single-stage biofilters might partly turn suboxic. Thus, **Hypothesis #1.1** could be accepted.

9.1.2 Degradation of trace organic chemicals during sequential biofiltration

Results presented in Chapters 4 to 8 underlined the potential of advanced biological treatment systems to achieve increased degradation of TOrCs present in WWTP effluent. As demonstrated by the results presented in Chapter 4, additional removal of several compounds could be achieved during SBF but also during conventional, single-stage biofiltration. Compound-specific differences were shown to determine the general susceptibility to biodegradation, transformation kinetics and the degree of transformation. While some compounds were found to undergo substantial removal, others revealed high persistence in all operated biological systems.

The beneficial effect of a sequential infiltration approach combined with an intermediate aeration step on the removal of various moderately degradable TOrCs was reported in Chapter 4. The comparison of an SBF system with a conventional, single-stage biofilter operated at the same overall EBCT of 290 min, revealed significantly improved transformation of several moderately degradable compounds in the SBF system, such as climbazole, citalopram, benzotriazole, sotalol, metoprolol, gabapentin, and sulfamethoxazole. The findings emphasized the importance of prevailing operational conditions on system performance. During SBF, elevated removal of bulk parameters DOC and UVA_{254} was achieved while redox conditions remained oxic. Results presented in Chapter 6 underlined an improved degradation of several moderately degradable compounds in the SBF system. Differences, however, were less pronounced, which might be attributed to a different quality of WWTP effluent during sampling indicated by lower DOC and DO consumption in both systems. Lower substrate availability caused redox conditions to remain oxic also in the single-stage biofilter. The findings reported in Chapter

4, 5 and 6 proved increased process stability in SBF systems. An improved degradation of several moderately degradable compounds resulted in the acceptance of **Hypothesis #1.2**.

Process stability and reliability in achieving a defined treatment goal are key factors in the evaluation of a novel technology. To allow for the stable and continuous achievement of a defined treatment target, a process should exhibit a high degree of robustness towards the variation of operational conditions. Results presented in Chapter 5 indicate high stability of TOrC degradation in SBF systems. Long-term monitoring demonstrated fluctuating removal efficiencies in the effluents of first stage filters for different TOrCs and organic bulk parameters DOC and UVA_{254}, whereas lower fluctuations and comparably stable levels of the removal efficiency was observed after the second filter stage. By buffering fluctuations in first filter stage effluent qualities, the second filter stage substantially contributed to process robustness of the SBF system.

The impact of EBCT in second stage filters on the effectivity of TOrC degradation was investigated in Chapters 4, 6 and 7. Results presented in Chapter 4 demonstrated the effect of increased EBCT on TOrC removal in second stage filters. Increased degradation of several compounds, such as sotalol, metoprolol, sulfamethoxazole, and diclofenac, was found at elevated EBCTs of 1,000 and 2,000 min in second stage filters compared to a reference filter operated at an EBCT of 200 min. The increased degradation, however, was found disproportional to the drastic increase in EBCT by the factor of 5 or even 10. Despite the removal of BDOC in the first filter stage, elevated DO consumption was observed in the test column operated at an EBCT of 2,000 min resulting in low DO concentrations and oxic to suboxic redox conditions in the deeper filter layers. Although additional DO consumption in the filter operated at an EBCT of 2,000 min was observed, a positive effect of increased EBCTs on the degradation of some but not all moderately degradable compounds was found. Results from depth profile samplings in second stage filters presented in Chapters 6 and 7 revealed that residence time in column top layers had an impact on the overall degradation of several compounds, whereas little additional degradation was observed in deeper zones of the columns operated at higher EBCTs of 1,000 and 2,000 min. As demonstrated in Chapters 6 and 7, threshold concentrations were observed for several compounds. Here, an increase of EBCT in second stage filters could not improve the overall degradation. The findings reported in Chapters 4, 6 and 7 resulted in the partial acceptance of **Hypothesis #1.3**.

Despite an effective degradation of various moderately degradable TOrCs during SBF, several compounds revealed high persistence to microbial degradation. While some compounds, such as carbamazepine and primidone, are known for their low susceptibility to biodegradation, effective degradation of others has been observed in previous studies under the desired oxic and oligotrophic conditions. Diclofenac was reported to be well degraded under oxic and oligotrophic conditions (Regnery et al., 2015b, 2016; Hellauer et al., 2017b, 2018), whereas only limited removal could be observed in this study. Also, the compounds venlafaxine and tramadol were reported to be well degradable under the desired conditions (Hellauer et al., 2018), while high persistence was found in this study. Only partial removal of diclofenac might be explained by comparably low hydraulic retention times used in SBF systems, while results from other studies were often acquired in systems with hydraulic retention times in the range of days or even weeks. The high persistence of tramadol and venlafaxine, however, might rather be explained by the absence of certain microbial strains and the absence of enzymes capable of an initial attack. Some compounds, such as acesulfame or benzotriazole, generally categorized as well degradable in the operated systems, were found to approach threshold concentrations at which no further, or only very limited additional removal was observed. Recent studies suggested that the potential reversibility of certain enzymatic reactions might be responsible for this effect (Gonzalez-Gil et al., 2018, 2019a).

9.1.3 Practical aspects related to the applicability of sequential biofiltration

Results from this study demonstrated that SBF systems are capable of an improved biological removal of various moderately degradable TOrCs from WWTP effluents. The implementation of SBF systems for advanced wastewater treatment, however, must be based on a comprehensive assessment including benefits of the treatment but also drivers for costs of investment and operation, and process limitations.

Considering the removal of TOrCs from WWTP effluents the study could show that SBF systems are capable of an enhanced transformation of several compounds compared to conventional biological wastewater treatment or single-stage biofiltration. A share of the investigated compounds, however, exhibited high persistence also in the SBF systems. Thus, the efficacy of advanced biological treatment using SBF systems is highly compound dependent. This, however, is also the case for other non-biological advanced treatment technologies, such as ozonation or activated carbon adsorption and must be considered a general drawback of single-technology based treatment options

SBF systems benefit from a low process complexity and could be operated with little effort and without the need for sophisticated process control. Apart from the equipment of first stage filters with backwash installations, the construction of SBF systems can be considered rather simple, fail-safe and holds little risk potential. Low system complexity only requires limited expertise unlike other advanced treatment technologies, such as ozonation. Thus, SBF systems might offer a favorable option for advanced treatment in small WWTPs with limited personnel. Treatment does not result in the continuous production of waste or the formation of potentially toxic oxidation by-products. The concept of SBF presents a self-sustaining treatment option without the need for chemical addition or material replacement. It, however, holds the option for extension by combination with other treatment steps, such as pre-treatment by coagulation for enhanced phosphorous removal (Chapter 5) or the implementation of pre- or intermediate ozonation (Chapter 8). Besides improved biodegradation of TOrCs during SBF, the treatment also achieves improvement of other water quality parameters. Consumption of BDOC and oxidation of reduced nitrogen compounds will result in lower values for biochemical and chemical oxygen demand (BOD and COD) and might reduce costs for effluent discharge fees. Product water might profit from reduced turbidity and reduced siltation potential due to improved physical retention of suspended solids during filtration. Granular media filtration of WWTP effluent also holds the benefit of improving the hygienic quality of the product water by contributing to the removal of pathogens (Aronino et al., 2009; Bauer et al., 2011; Seeger et al., 2016).

Potential limitations hindering the use of SBF systems are the high footprints necessary for the installation, the high sensitivity towards the quality of the WWTP effluent used for filtration, and little process flexibility. Considering the large volumes of water treated in full-scale municipal WWTPs, elevated hydraulic residence times necessary for the achievement of a defined treatment goal translate into reactor designs with large footprints. Pilot-scale investigations carried out during this study tested different EBCTs in first and second stage filters. Investigations in first stage filters were carried out at EBCTs of 90, 45 and 30 min (Chapter 5). In the second stage filters EBCTs of 200, 1,000 and 2,000 min were tested (Chapter 4). For a defined EBCT, the reactor volume is proportional to the flow of water to be treated. For a given EBCT and a corresponding reactor volume, the required surface area is inversely proportional to the reactor height. However, decreasing surface area by manipulation of filter height and infiltration rate is restricted by practical aspects, limiting the maximum filter height. Figure 9-2 illustrates the simple relationship between EBCT and area footprint per flow rate for different filter bed heights of 1, 1.5 and 2 m. At a defined reactor volume and flow rate the filter velocity is a function of the filter cross-section. To a limited extent, the necessary footprint can be reduced by increasing the reactor height. Required footprints for the realization of filtration systems with EBCTs of several hours must be considered the main drawback of SBF systems. The application of SBF systems in larger WWTPs treating high volumes of wastewater and located in densely populated urban or industrial areas is most likely not feasible due to the lack of available space. In less densely populated areas with smaller WWTPs, space requirements might not be a limiting factor. To give an overview, Table 9-1 summarizes calculated footprints of SBF first and second stage filters for EBCTs of 30, 45 and 90 min in the first filter stage and 200 min in the second filter stage for exemplarily selected filter bed heights and different flow rates. Calculated filter velocities, v_f, illustrate that the first filter stage can be categorized between slow sand filtration (0.05 to 0.3 m/h) and rapid sand filtration (around 10 m/h), whereas filter velocities qualify the second filter stage as slow sand filtration. A further reduction of EBCTs, especially in the first filter stage of SBF systems would be desirable to promote the applicability of the SBF concept. Given a sufficiently long adaptation period, results from Chapter 5 indicated that a reduction of the EBCT does not necessarily result in decreasing process performance. Also previous studies reported that the performance of biofiltration systems often tolerates reductions of EBCT to a certain extent (Kramer et al., 1993; Hozalski et al., 1995; Zhang and Huck, 1996; Urfer et al., 1997). SBF second stage filters were operated at substantially higher EBCTs compared to the first filter stage. However, the absence of backwash installations allows for a simpler design. Also, the combination of a technical first filter with a low-tech and low-maintenance second infiltration stage, such as planted soil filters, might be an option for the realization of higher EBCTs without necessarily demanding large technical reactor volumes.

Table 9-1: Filter velocity (v_f) and reactor footprint (A) for exemplary chosen EBCTs, filter bed heights, and treated flow rates in first (FS1) and second stage filters (FS2).

	EBCT	**Height**	**v_f**	**A**	**A [m^2] for different flows**		
	min	m	m/h	$m^2/(m^3/d)$	200 [m^3/d]	2,000 [m^3/d]	20,000 [m^3/d]
FS1	30	1.5	3	0.014	3	28	278
	45	1.5	2	0.021	4	42	417
	90	1.5	1	0.042	8	83	833
FS2	200	1.0	0.3	0.139	28	278	2778

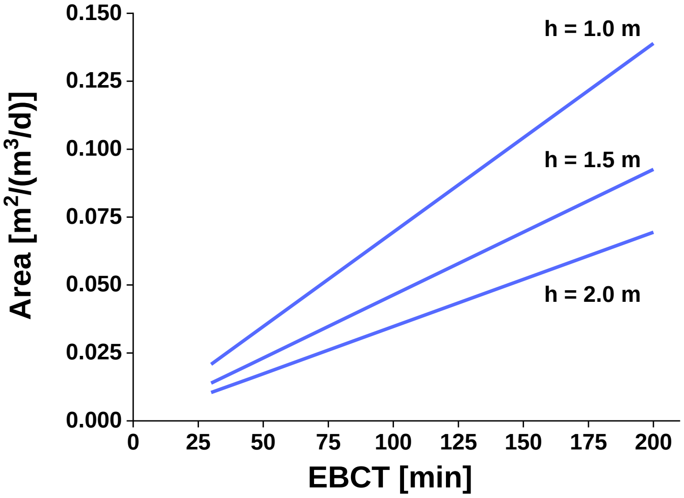

Figure 9-2: Relationship between reactor footprint normalized to treated flow and EBCT for different filter heights.

The quality of the secondary or tertiary effluent fed into SBF systems has a substantial impact on operational conditions and system performance. SBF first stage filters are designed to reduce the amount of available substrate in the feed water via oxic mineralization of BDOC, allowing for substrate limited and oxic conditions in second stage filters. When assuming a simplified mass balance for the conversion of BDOC into CO_2 with a stoichiometric ratio of 1 mole O_2/mole C for complete mineralization, 2.7 mg DO are consumed for the mineralization of 1 mg C. Assuming a water temperature of 15 °C and atmospheric pressure, the maximum solubility of DO in water is approximately 10 mg/L. Thus, the maximum amount of BDOC degradation via oxic respiration amounts to

3.7 mg BDOC/L assuming exclusive DO consumption for BDOC mineralization. Under realistic conditions, however, DO concentrations in the influent of SBF systems will be substantially lower and will not exceed 6 to 8 mg DO/L, limiting the amount of DO available for BDOC consumption. As denitrification was observed at no time during the study, BDOC degradation using nitrate as terminal electron acceptor was excluded as a relevant mechanism for the consideration. However, the formation of stable anoxic conditions in the presence of elevated BDOC concentrations might induce BDOC degradation under denitrifying conditions. Besides BDOC, also other reduced water constituents might significantly contribute to DO consumption. The presence of reduced nitrogen components represents another major sink for DO in the system. Complete oxidation of ammonia to nitrate consumes 2 moles O_2/mole NH_4-N, which translates to 4.6 mg DO/mg NH_4-N. The mass balance illustrates the need for complete nitrification as an indispensable precondition for the application of SBF systems. Due to the intermediate aeration step, SBF systems can supply more DO for treatment than conventional, single-stage biofiltration systems. However, to allow for stable oxic conditions in the second filter stage, pre-treatment during conventional wastewater treatment processes must generate feed water which is poor in DO consuming water constituents, such as elevated concentrations of BDOC or reduced nitrogen components.

While the low complexity is a benefit of SBF applications, reduced flexibility must be considered a disadvantage. At a constant incoming flow, little operational parameters can be used to react to fluctuations in feed water quality. A dynamic process control option, such as increasing the ozone dose during ozonation in response to varying organic bulk parameter or scavenger concentrations, does not exist. When active aeration is used, however, monitoring of the DO consumption in the filters could be used to control the aeration intensity, and thus, influence the DO availability in the system.

9.2 The transformation of iopromide: an alternative tool for the characterization of redox conditions in biofiltration systems?

Hypothesis #2 investigated the possibility of using known transformation products (TPs) from the successive transformation of the X-ray contrast medium iopromide for improved characterization of *in situ* redox conditions in biofiltration systems. In general, results presented in Chapter 7 suggested that following the successive transformation of iopromide is not a suitable approach for improved characterization of redox conditions. A correlation between the degree of iopromide transformation or the abundance of certain iopromide TPs and the prevalent redox conditions was not found. Results indicated a stagnation of iopromide transformation at a certain degree, independent of the prevalence of oxic or suboxic redox conditions. The introduction of a dimensionless iopromide transformation factor, T_{IOP}, revealed a strong correlation between iopromide transformation and general microbial activity, indicated by the DO consumption. Based on the findings presented in Chapter 7, main **Hypothesis #2** could not be accepted.

Investigations carried out also tested for a correlation between the successive oxic transformation of iopromide and the degradation of other redox-sensitive TOrCs, such as gabapentin, benzotriazole, and metoprolol. Results presented in Chapter 7 could not prove a direct correlation between the formation of certain iopromide TPs and the initial transformation of other investigated compounds. While similar patterns could be demonstrated for the initial transformation step of iopromide and gabapentin, different behavior was observed for benzotriazole and metoprolol. The results indicated a strong influence of different compound-specific removal mechanisms, also for compounds generally referred to as "redox-sensitive". Based on the findings presented in Chapter 7, **Hypothesis #2.1** could not be accepted.

Findings contradicting a hypothesized correlation between iopromide transformation and redox conditions also led to the rejection of **Hypothesis #2.2**. Monitoring iopromide transformation was not a suitable strategy to identify potentially improved redox conditions in SBF systems when compared to conventional, single-stage biofiltration systems.

Although findings of this study did not allow for the identification of a redox dependence in the transformation of iopromide, a dependence is still considered possible and even likely. The transformation pathway, as identified by Schulz et al. (2008), can mainly be attributed to metabolic activities involving oxygenase enzymes that catalyze oxidation reactions with molecular oxygen. Thus, a positive correlation between the presence of DO and iopromide transformation seems probable. Prevalent redox conditions during this study did also not allow for the investigation of iopromide transformation under exclusively oxic, suboxic or anoxic conditions but depended on the complex dynamics of vertical flow systems. While anoxic conditions were observed at no time during the investigation, oxic and suboxic redox conditions followed a gradient in the columns. Thus, column top layers were characterized by oxic conditions while suboxic conditions only occurred in deeper column zones and at higher EBCTs. Besides a stratification of redox conditions, however, also the availability of BDOC followed a vertical gradient. Thus, effects observed during the experiments cannot simply be attributed to a single parameter but must be discussed with regard to the multiple factors potentially involved. While oligotrophic conditions were identified as beneficial for the degradation of many TOrCs (Rauch-Williams et al., 2010; Maeng et al., 2012; Alidina et al., 2014; Li et al., 2014; Wolff et al., 2018), the presence of higher BDOC concentrations increases general microbial activity. If the cometabolic transformation of an individual compound can be carried out by enzymes present under BDOC rich conditions, an elevated enzymatic activity at higher BDOC concentrations will also induce an elevated transformation of the compound. Stratification of microbial activity in biofiltration systems has been demonstrated before in many studies (Wang et al., 1995; Emelko et al., 2006; Pharand et al., 2014; Carpenter and Helbling, 2017). The strong correlation between the observed DO consumption and the transformation factor, T_{IOP}, during two experimental campaigns with very different amounts of the available substrate, speaks in favor of a positive effect of BDOC-induced microbial activity on the transformation of iopromide.

9.3 Sequential biofiltration-based hybrid systems

Combinations of sequential biofiltration, ozonation, and granular activated carbon (GAC) filtration hold the potential of eliminating an extended spectrum of TOrCs with varying characteristics. Besides the investigation of an expected improved removal of TOrCs due to the integration of biological, oxidative and adsorptive removal mechanisms, the study focused on potential synergistic effects between the different treatment technologies used. The operation of hybrid systems, integrating several treatment technologies, is a viable option for the improvement of process efficacy. Following a multi-barrier approach, hybrid systems incorporate different removal mechanisms and address a broader spectrum of contaminants. Provided a wise process selection and design, hybrid systems also profit from synergistic effects, as demonstrated in this study. However, improved process performance is opposed by increased complexity and higher costs of investment, operation, and maintenance. Thus, enhanced removal of TOrCs from WWTP effluents using hybrid systems must undergo critical assessment regarding the plausibility and feasibility of proposed process combinations.

9.3.1 Sequential biofiltration with intermediate ozonation (SBF(O_3))

Hypothesis #3 addressed the combination of sequential biofiltration with an intermediate ozonation step and investigated potential beneficial effects of reducing the amount of competing dissolved organic matter (DOM) on ozonation efficiency. Besides, the effect on operational conditions in the second filter stage after ozonation was investigated. Results presented in Chapter 8 demonstrated the strong potential of biological-oxidative processes for the transformation of many TOrCs indicated by the beneficial complementary degradation of different individual substances. Compounds, such as carbamazepine, venlafaxine, and tramadol, which exhibited high persistence during biological treatment in conventional SBF with intermediate aeration (SBF(Air)) did undergo an effective oxidative transformation during SBF with intermediate ozonation (SBF(O_3)). Some TOrCs which are characterized by lower reactivity with ozone, such as gabapentin or benzotriazole, were effectively degraded in first and second stage filters of the SBF system. While additive effects, improving the overall removal treatment efficacy in process combinations were expected beforehand, specific synergistic effects in SBF(O_3) systems were proposed to result from the removal of biodegradable DOM in the first filter stage. At the same ozone dose, higher specific ozone doses would result after biological pre-treatment of WWTP effluent in the first SBF filter stage. Results presented in Chapter 8 indicated significant, but limited, improvements in ozonation efficiency for the transformation of compounds with medium ozone second-order rate constants, such as atenolol, benzotriazole, caffeine, and metoprolol. For these compounds, pre-treatment of WWTP effluent in the first filter stage resulted in an improved ozonation efficiency, indicated by 10 to 25 % higher removal at the same ozone doses of 3 and 5 mg/L. The degradation of 21 ± 3 % of DOC in the first filter stage caused a reduction of DOM competing with TOrCs for oxidation and resulted in increased specific ozone doses, allowing for a slightly elevated transformation of several TOrCs. Although the improvements in observed ozone transformation efficiency were limited and were found to be highly compound-dependent, the results proved a statistically significant beneficial effect which can be related to synergies between sequential biofiltration and ozonation. Based on the findings presented in Chapter 8, **Hypothesis #3.1** could be accepted.

The main objective of sequentially operated biofiltration systems, as proposed within this study, is the establishment of oxic and substrate-limited conditions in a second filter stage. When combining SBF systems with other advanced treatment technologies, investigations must elucidate in how far these desired operational conditions are affected. Many studies reported the formation of easily biodegradable substrate, referred to as BDOC, as a result of ozonation (Janssens et al., 1985; van der Kooij et al., 1989; Hozalski et al., 1995; Griffini et al., 1999; Hammes et al., 2006). The oxidation of large and complex molecules induces a partial breakdown into smaller molecule fractions which are characterized by increased bioavailability. The integration of an intermediate ozonation step in SBF(O_3) systems might, thus, jeopardize the establishment of substrate-limited conditions in the second filter stage. As a result of potentially elevated amounts of easily degradable substrate, also increased DO consumption could result, endangering oxic redox conditions in the second filter stage. Results presented in Chapter 8, however, did not reveal the formation of significant amounts of additional BDOC during ozonation, indicated by a comparable consumption of organic bulk parameters DOC and UVA_{254} in second stage filters with intermediate aeration and intermediate ozonation. Ozonation resulted in a DO oversaturation after treatment, thus, DO concentrations after ozonation were substantially higher compared to those found after aeration. DO consumption at comparable levels, however, was found in second stage columns of both systems, SBF(Air) and SBF(O_3). Despite the strong impact of ozonation on DOM components with electron-rich moieties, as indicated by the strong effect on UV absorbance and the decrease in specific UV absorbance (SUVA), the bioavailability of DOM during second stage filtration was not affected. Results did also not reveal distinct differences in the capability of TOrC transformation in second stage filters after intermediate aeration or ozonation. Based on the findings presented in Chapter 8, **Hypothesis #3.2** could be accepted.

The plausibility of the SBF(O_3) approach demands critical discussion. Results of this study demonstrated that SBF(O_3) systems allow for slight increases in ozonation efficiency due to the removal of BDOC in the first stage filter, supporting findings from other studies (Hübner et al., 2012; Yoon et al., 2013; de Wilt et al., 2018). Granular media filtration before ozonation also holds the potential to reduce the ozone demand caused by particulate organic matter in WWTP effluent, as reported by other studies (Zucker et al., 2015a). Thus, SBF(O_3) first stage filtration might buffer varying particle removal efficiencies during secondary clarification and might contribute to a more stable ozone demand. In the case of unstable nitrification during preceding conventional treatment, first stage biofiltration might serve as a buffer to reduce nitrite-induced scavenging via additional nitrification. While substantial additional nitrification of relevant amounts of nitrite was not observed during this study, other studies reported effective nitrification in biofilters (Andersson et al., 2001; Zucker et al., 2015b). The observed slightly improved ozonation efficiency in the transformation of some TOrCs, as observed during this study, might not justify the installation of a filtration step before ozonation. As demonstrated in Chapter 8, ozonation results in DO oversaturation of treated water, supplying large amounts of DO for the oxic degradation of BDOC. Unless BDOC concentrations in treated WWTP effluents are substantially higher, or substantially more BDOC is formed during ozonation, DO oversaturation will allow for oxic conditions throughout a subsequent biofiltration step even if WWTP effluent is ozonated without pre-treatment by biofiltration. BDOC removal in top layers of a post-ozonation biofilter results in the establishment of a vertical substrate gradient. Assuming sufficiently long EBCTs, operational conditions in deeper filter layers could most likely also be characterized as oxic and oligotrophic without the need for an additional aeration or ozonation step and a subsequent second stage filter. The combination of ozonation with subsequent biofiltration has been investigated in many studies and was successfully realized in many different applications at pilot- and full-scale (Sanchez-Polo et al., 2006; Hollender et al., 2009; Reungoat et al., 2010, 2012; Zhang et al., 2017; Bourgin et al., 2018). In these applications, however, subsequent biological treatment after ozonation mainly focused on the removal of BDOC formed during ozonation, which is also reflected in rather short EBCTs. Potential advantages of SBF(O_3) systems over the direct ozonation of WWTP effluent followed by conventional, single-stage biofiltration strongly depend on site-specific factors and characteristics of the WWTP effluent treated. At elevated BDOC concentrations and peaks of ammonia and nitrite, pre-treatment in the first stage filter could potentially contribute to process stabilization and an increased ozonation efficiency.

9.3.2 Combining sequential biofiltration with posterior adsorption onto activated carbon

The combination of sequential biofiltration, with intermediate aeration or ozonation, with a posterior adsorption step using GAC filters, was tested as an additional hybrid system in **Hypothesis #4**. Results presented in Chapter 8 revealed the beneficial effect of biological or biological-oxidative pre-treatment on the breakthrough behavior of most investigated compounds. Degradation of BDOC in SBF systems resulted in reduced amounts of DOM competing for adsorption sites on GAC and prolonged filter lifetimes until defined breakthrough threshold values were reached in the filter effluents. Isotherm tests supported observations of an improved adsorbability after pre-treatment in SBF systems by increased adsorption capacity for different indicator TOrCs in equilibrium. The investigation of DOC isotherms and the characterization of DOC adsorbability conducting an adsorption analysis with AdsAna 1.5, suggested that besides the removal of non-adsorptive DOM components, also a general reduction of DOM components with varying adsorptive properties were partially removed by biological pre-treatment in the SBF(Air) system (additional information given in SI-section 10.7). Results from Chapter 8 supported a proposed beneficial effect of pre-treatment of WWTP effluent via SBF(Air) on the adsorption capacity of GAC for TOrCs and led to the acceptance of **Hypothesis #4.1**. The observed improvement in breakthrough behavior was even more pronounced in GAC test columns receiving water pre-treated by SBF(O_3). Only insignificantly additional BDOC consumption during SBF(O_3) second stage filtration indicated that in this case, not only BDOC removal was the reason for the effect. Instead, additional increases in filter lifetimes were proposed to be related to structural changes in DOM, caused by the ozonation, resulting in a higher general polarity and reducing the adsorbability of DOM (Prasse et al., 2015). Similar effects of ozonation on DOM adsorbability had been described before by Zietzschmann et al. (2015). Pre-treatment of WWTP effluent by both, SBF(Air) and SBF(O_3), resulted in an increase of GAC filter lifetimes and thus to an acceptance of **Hypothesis #4.2**. The combination of SBF systems with subsequent GAC filtration was found to profit from synergistic effects caused by the removal or structural alteration of DOM competing for adsorption sites on GAC.

Treatment of WWTP effluent via SBF(Air) or SBF(O_3) before GAC filtration holds the potential for an improved process efficacy and efficiency making use of additive and synergistic effects. Improved adsorption capacity was observed in isotherm and rapid small scale column test (RSSCT) experiments after pre-treatment via SBF(Air) and SBF(O_3) which was related to the removal and structural alteration of WWTP effluent DOM. Experiments using RSSCTs are a useful tool to predict the breakthrough behavior of target compounds in full-scale adsorbers or to compare the breakthrough behavior in adsorbers when fed with different feed waters. The experimental approach includes the reduction of GAC particle sizes using scaling factors to allow for the fast prediction of breakthrough behavior within several days or few weeks (Crittenden et al., 1986, 1991). The approach does not allow for the prediction of the effect of biological activity in GAC filter systems which will establish over time and might positively affect process efficacy via additional biodegradation of compounds. The establishment of biofilms on particle surfaces, however, might also reduce the adsorption capacity by blocking the fine pores of GAC particles, reducing the accessibility of the particle’s inner surface structure. A similar effect on GAC has been observed to be caused by the presence of DOM (Summers et al., 1989; Corwin et al., 2011). Results from RSSCT experiments cannot predict the effects of changes in feed water composition on breakthrough behavior. Also, the negative effect of potentially necessary filter backwashes on location and shape of the mass transfer zone cannot be modeled using RSSCT experiments. Although synergistic effects might be less pronounced in full-scale applications, the direct comparison of the adsorption behavior in equilibrium and in RSSCT experiments indicates benefits of biological and biological-oxidative pre-treatment.

9.3.3 Perspectives for the implementation of hybrid systems including advanced biological, oxidative and adsorptive treatment

Sequential biofiltration-based hybrid systems tested within this study proved to be very effective in removing a broad range of chemicals and were found suitable to overcome limitations of single technology-based advanced treatment processes. Besides, system combinations were found to profit from synergies, increasing the efficiency of the integrated technologies. However, when discussing means to reduce the discharge of TOrCs into the aquatic environment, the realization at full-scale is opposed by increasing costs for investment, operation and maintenance, and large system footprints.

Besides the use of SBF-based hybrid systems for enhanced removal of TOrCs from WWTP effluents to reduce their discharge into the aquatic environment, also other fields of applications could be considered in which increased water quality requirements justify and necessitate elaborate advanced treatment and increased costs.

Water reclamation scenarios, including direct or indirect potable reuse, are examples in which stringent treatment goals for chemical and hygienic water quality have to be met. To achieve highly reliable and robust treatment processes, multi-barrier approaches need to be applied to generate a water quality that is protective to public health (Gerrity et al., 2013; National Research Council, 2012). While Full Advanced Treatment, including ultrafiltration, reverse osmosis and advanced oxidation processes has often been considered as a standard in planned direct and indirect potable reuse applications, also treatment schemes without energy-intensive and cost- intensive high-pressure membranes have been investigated and applied (Gerrity et al., 2013). Here, especially combinations of ozonation and biofiltration have been proposed as suitable and cost-efficient elements in advanced treatment schemes applicable in potable reuse scenarios (Reungoat et al., 2010; Gerrity et al., 2013; Gifford et al., 2018; Bacaro et al., 2019). Thus, novel hybrid systems, incorporating biological, oxidative and adsorptive treatment might be suitable elements in such treatment schemes, in which elevated process complexity is justified by higher water quality demands. Treatment schemes for water reclamation could profit from the integration of optimized biological treatment barriers by an increased process effectivity and efficiency. As infectious diseases caused by waterborne pathogens pose the highest risk for human health, efficient and reliable removal of pathogens is paramount (National Research Council, 2012). While effective removal of a broad variety of different TOrCs in the investigated hybrid systems could be demonstrated in this study, future studies need to determine process performance regarding the elimination of microbial parameters.

9.4 Outlook and future research needs

9.4.1 Comprehensive process evaluation including transformation products and toxicity assessment

The focus of this study was the investigation of novel treatment strategies, including biological, oxidative and adsorptive technologies to achieve an improved removal of TOrCs from the effluent of municipal WWTPs. Process performance was judged based on the removal or transformation of a set of indicator compounds. While adsorptive technologies achieve a physical removal of the compounds from the water phase, biological and oxidative processes result in the formation of transformation products (TPs). The widespread use of LC-MS/MS instruments enables highly sensitive and specific analytical methods for the detection of target compounds in trace concentrations even without pre-concentration with method detection limits often in the low ng/L range. Due to the high specificity of the method, however, even marginal changes in molecule structure result in non-detection, while essential parts of the parent compound might not undergo any changes. The identification of TPs formed during biological and oxidative processes and their occurrence in environmental samples was demonstrated for many substances and in numerous studies. The findings demonstrated that initial transformation of many compounds is followed by the formation of TPs, which can exhibit increased persistence and stability towards transformation (e.g. Schulz et al., 2008; Funke et al., 2015; Castronovo et al., 2017; Zucker et al., 2018), whereas further transformation was proposed for others (Hübner et al., 2013a). After the initial transformation of the parent compound during advanced biological or oxidative treatment, the fate of TPs often depends on their susceptibility to biodegradation in subsequent treatment stages or the aquatic environment. In this study, the well-described biological transformation of the X-ray contrast medium iopromide was followed after Schulz et al. (2008) identified and isolated relevant TPs, enabling also the quantitative analysis (Chapter 7). In the case of iopromide, multi-stage transformation ends after the formation of TP643, for which no further degradation has been observed under oxic conditions. Also, the reformation potential of biological TPs, as observed for citalopram and diphenhydramine in this study (Chapter 6) needs further discussion and investigation. While an elaborate analysis of TPs formed during treatment processes proposed in this study was not feasible, questions remain regarding their potential to cause adverse effects in the environment.

In the context of process evaluation, the use of bioanalytical tools has become of increasing importance in recent years. Bioanalytical tools offer complementary information to chemical water analysis and were found suitable to indicate non-specific and specific toxicological activity of complex mixtures (Macova et al., 2010; Reungoat et al., 2010; Prasse et al., 2015). Applied to different water matrices or before and after investigated processes, the use of *in vivo* and *in vitro* toxicity tests is an option to reveal beneficial or detrimental effects of treatment processes. In this way, also potential adverse effects of TPs formed during treatment could be identified. Studies on the effect of ozonation on specific effects such as endocrine disruption, genotoxicity, antibacterial and antiviral activity, revealed decreased effects after ozonation of WWTP effluent (Huber et al., 2004; Suarez et al., 2007; Dodd et al., 2009; Reungoat et al., 2010; Mestankova et al., 2012). Elevated genotoxicity and non-specific toxicity caused by ozonation was reported by some studies (Rosal et al., 2009; Stalter et al., 2010; Prasse et al., 2012; Magdeburg et al., 2014), while the opposite was reported by others (Reungoat et al., 2010, 2012). Subsequent biofiltration, however, was found effective to further reduce most effects after ozonation (Reungoat et al., 2010; Stalter et al., 2010; Reungoat et al., 2012). While little reduction of effects was observed in sand filters without pre-ozonation, treatment in GAC filters proved effective to reduce non-specific toxicity and different specific toxic effects (Reungoat et al., 2011; Prasse et al., 2015). Further approaches, such as effect-directed analysis attempt to link bioanalytical tools and chemical analysis to identify toxicants causing effects in complex mixtures (Brack, 2003; Burgess et al., 2013; Prasse et al., 2015).

This study proposed options for advanced biological treatment and the combination of biological, oxidative and adsorptive treatment steps for enhanced removal of TOrCs from WWTP effluents. However, an extensive investigation of the formation and fate of biological and oxidative TPs was not within the scope of this study. Also, an investigation of specific or non-specific toxicity could not be carried out. Both aspects require further investigation and might be addressed in future studies.

9.4.2 Improvements of microbial water quality in proposed treatment systems

Besides improving the chemical water quality by enhancing the reduction of organic bulk parameters, nutrients and TOrCs, the investigated treatment concepts might also be promising options to improve the microbial water quality by effective mitigation of pathogens. The extent to which pathogens, such as bacteria, viruses, and protozoa have to be reduced from feed waters, highly depends on the intended use of the product water. While in some regions an improvement of the microbial water quality in WWTP effluents might be desirable to ensure bathing water quality in receiving streams (e.g. in Bavaria, Germany (Huber and Popp, 2005)), substantially higher standards need to be met when water reclamation scenarios for direct or indirect potable reuse are considered. Here, treatment schemes in place must be highly reliable in achieving vast reduction of hygienically relevant organisms which are detrimental to human health and must meet stringent water quality requirements as specified in regulatory guidelines, such as the Californian Code of Regulations, Title 22, or the Australian Guidelines for Water Recycling (NRMMC/EPHC/NHMC, 2006, 2008; CDPH, 2009). In recent years, the detection of antibiotic-resistant bacteria and resistance genes in environmental samples, has raised concerns regarding their potential impact on human health by reducing the success of infectious disease treatment (Pärnänen et al., 2019). Effluents of WWTPs have been proposed as point sources for the entry of antibiotic microbial resistance into the aquatic environment and additional treatment has been discussed as an option to reduce associated risks (Berendonk et al., 2015).

While this study did not focus on the removal of pathogens or antibiotic microbial resistance, current studies at the Chair of Urban Water Systems Engineering at the Technical University of Munich aim to investigate the efficiency of the proposed treatment systems to achieve an improvement of microbial water quality parameters.

9.4.3 Technological advances and feasibility studies

Results obtained in this study highlighted the potential of an integration of advanced biological processes in wastewater treatment schemes. The investigations also identified parameters potentially suitable to further optimize system performance. An optimization of SBF systems might involve a further decrease of EBCTs, especially in the first stage filter, allowing for smaller footprints of full-scale applications. Continuous monitoring of DO concentrations in the filter systems might represent an option for improved process control and enable the adjustment of energy-intensive aeration to the DO demand in the system, improving process efficiency. While the feasibility of hybrid systems proposed in this study was critically discussed, results obtained also indicated the strengths of multi-barrier systems. Further development of hybrid systems might involve the optimized integration of several treatment mechanisms in one treatment step rather than operating several treatment steps in series. The use of different filter media, such as GAC, in SBF systems, might be an option to also achieve the removal of non-biodegradable compounds. The feasibility of full-scale applications of SBF or SBF-based hybrid systems for the advanced treatment of municipal WWTP effluents strongly depends on the scenario for application and needs further discussion, taking into account the specific treatment requirements, site-specific characteristics and costs for investment, maintenance and operation.

10 Supplementary information

10.1 List of topic related publications

10.1.1 Peer-reviewed journal articles and author contributions

Müller, J., Drewes, J.E., Hübner, U., 2017. Sequential biofiltration – A novel approach for enhanced biological removal of trace organic chemicals from wastewater treatment plant effluent. Water Research. 127, 127–138.
https://doi.org/10.1016/j.watres.2017.10.009

Author contributions: Johann Müller, Uwe Hübner and Jörg E. Drewes developed the research objective and designed the experiment. Johann Müller constructed the experimental setup, conducted the experiments and the analyses and wrote the paper. Jörg E. Drewes and Uwe Hübner supervised the study and reviewed the manuscript. All authors approved the final version of the manuscript.

Müller, J., Levai, S., Titzschkau, L., Popović, N., Carevic, D., Drewes, J.E., Hübner, U., 2019. Role of reduced empty bed contact times and pre-treatment by coagulation with Fe(III) salts on the removal of trace organic compounds during sequential biofiltration. Science of the Total Environment. 685, 220–228.
https://doi.org/10.1016/j.scitotenv.2019.05.361

Author contributions: Johann Müller, Uwe Hübner and Jörg E. Drewes developed the research objective. Leonardo Titzschkau and Johann Müller designed the experiment and constructed the experimental setup. Silvia Levai, Nikolina Popović, Dragan Carevic and Leonardo Titzschkau conducted the experiments and the analyses. Johann Müller wrote the paper. Jörg E. Drewes, Uwe Hübner Silvia Levai, Nikolina Popović, Dragan Carevic and Leonardo Titzschkau reviewed the manuscript. Jörg E. Drewes and Uwe Hübner supervised the study. All authors approved the final version of the manuscript.

Müller, J., Jewell, K. S., Schulz, M., Hermes, N., Ternes, T.A., Drewes, J.E., Hübner, U., 2019. Capturing the oxic transformation of iopromide – A useful tool for an improved characterization of predominant redox conditions and the removal of trace organic compounds in biofiltration systems? Water Research. 152, 274–284.
https://doi.org/10.1016/j.watres.2018.12.055

Author contributions: Johann Müller, Uwe Hübner, Jörg E. Drewes, Kevin S. Jewell and Thomas A. Ternes developed the research objective and designed the experiment. Johann Müller conducted the experiments and carried out a part of the analyses. Nina Hermes and Manoj Schulz carried out LC-MS/MS analyses for the quantification of trace organic compounds and iopromide transformation products. Johann Müller wrote the paper. Uwe Hübner, Jörg E. Drewes, Kevin S. Jewell and Thomas A. Ternes reviewed the manuscript. Uwe Hübner and Jörg E. Drewes supervised the study. All authors approved the final version of the manuscript.

Müller, J., Drewes, J.E., Hübner, U., 2019. Investigating synergies in sequential biofiltration-based hybrid systems for the enhanced removal of trace organic chemicals from wastewater treatment plant effluents. Environmental Science: Water Research & Technology. http://dx.doi.org/10.1039/C9EW00181F

Author contributions: Johann Müller, Uwe Hübner and Jörg E. Drewes developed the research objective and designed the experiment. Johann Müller constructed the experimental setup, conducted the experiments and the analyses and wrote the paper. Jörg E. Drewes and Uwe Hübner supervised the study and reviewed the manuscript. All authors approved the final version of the manuscript.

Hermes, N., Jewell, K.S., Schulz, M., **Müller, J.**, Hübner, U., Wick, A., Drewes, J.E., Ternes, T.A., 2019. Elucidation of removal processes in sequential biofiltration (SBF) and soil aquifer treatment (SAT) by analysis of a broad range of trace organic chemicals (TOrCs) and their transformation products (TPs). Water Research. 163, 114857. https://doi.org/10.1016/j.watres.2019.114857

Author contributions: Nina Hermes, Kevin Jewell, Thomas A. Ternes, Manoj Schulz, Uwe Hübner and Jörg E. Drewes developed the research objective and designed the experiment. Nina Hermes and Manoj Schulz conducted the sampling at the field-site. Johann Müller conducted the biofiltration pilot-scale experiments and carried out a part of the analyses. Nina Hermes and Manoj Schulz carried out LC-MS/MS analyses for the quantification of trace organic compounds and iopromide transformation products. Nina Hermes wrote the paper. Uwe Hübner, Jörg E. Drewes, Johann Müller, Kevin S. Jewell, Arne Wick and Thomas A. Ternes reviewed the manuscript. All authors approved the final version of the manuscript.

10.1.2 Manuscript in preparation

Müller, J., Jewell, K., Hermes, N., Ternes, T.A., Drewes, J.E., Hübner, U., 2019. Revealing the transformation of trace organic chemicals in sequential biofiltration systems using profile sampling and first-order biodegradation rate constants. Manuscript in preparation.

10.1.3 Contribution in German

Müller, J., Drewes, J.E., Hübner, U., Sequentielle Biofiltration zur Entfernung anthropogener Spurenstoffe aus dem Ablauf kommunaler Kläranlagen. Mitt. Umweltchem Ökotox 23 (3), 2017, 77-79

10.2 First author contributions to national and international conferences

Müller, J., Villamayor, L., Hübner, U., Drewes, J. E. (2015). Aufbau und Einlaufphase eines sequentiellen biologischen Filtersystems zur Entfernung von Spurenstoffen aus dem Ablauf kommunaler Kläranlagen., „Wasser 2015 – Jahrestagung der Wasserchemischen Gesellschaft“, 11.–13.05.2015, Schwerin, Germany.

Müller, J., Villamayor, L., Kunkel, U., Hübner, U., Ternes, T. A., Drewes, J. E. (2015). Sequential biofiltration for enhanced removal of trace organic compounds during water reclamation., “IWA International Conference on Water Reclamation and Reuse”, 05.–09.07.2015, Harbin, China.

Müller, J., Kunkel, U., Hübner, U., Ternes, T. A., Drewes, J. E (2016). Sequentielle Biofiltration zur Entfernung anthropogener Spurenstoffe aus dem Ablauf kommunaler Kläranlagen., „Wasser 2016 – Jahrestagung der Wasserchemischen Gesellschaft“, 02.–04. 05.2016, Bamberg, Germany.

Müller, J., Schulz, M., Hermes, N., Hübner, U., Ternes, T. A., Drewes, J. E. (2017). Charakterisierung der Redoxbedingungen in biologischen Filtrationssystemen mithilfe bekannter Iopromid-Transformationsprodukte., „Wasser 2017 – Jahrestagung der Wasserchemischen Gesellschaft“, 22.–24.05.2017, Donaueschingen, Germany.

Müller, J., Hübner, U., Drewes, J. E. (2017). Introducing sequential biofiltration hybrid systems for enhanced removal of chemicals of emerging concern and pathogens during water reclamation., “IWA International Conference on Water Reclamation and Reuse”, 23.–27.07.2017, Long Beach, USA.

Müller, J., Hübner, U., Drewes, J. E. (2018). Hybridsysteme: Optimierte Spurenstoffentfernung aus dem Ablauf kommunaler Kläranlagen durch Kombination von sequentieller Biofiltration mit adsorptiven und oxidativen Verfahren., „Wasser 2018 – Jahrestagung der Wasserchemischen Gesellschaft“, 07.–09.05.2018, Papenburg, Germany.

10.3 Supplementary information for Chapter 4

Sequential biofiltration – a novel approach for enhanced biological removal of trace organic chemicals from wastewater treatment plant effluent

Supplementary information

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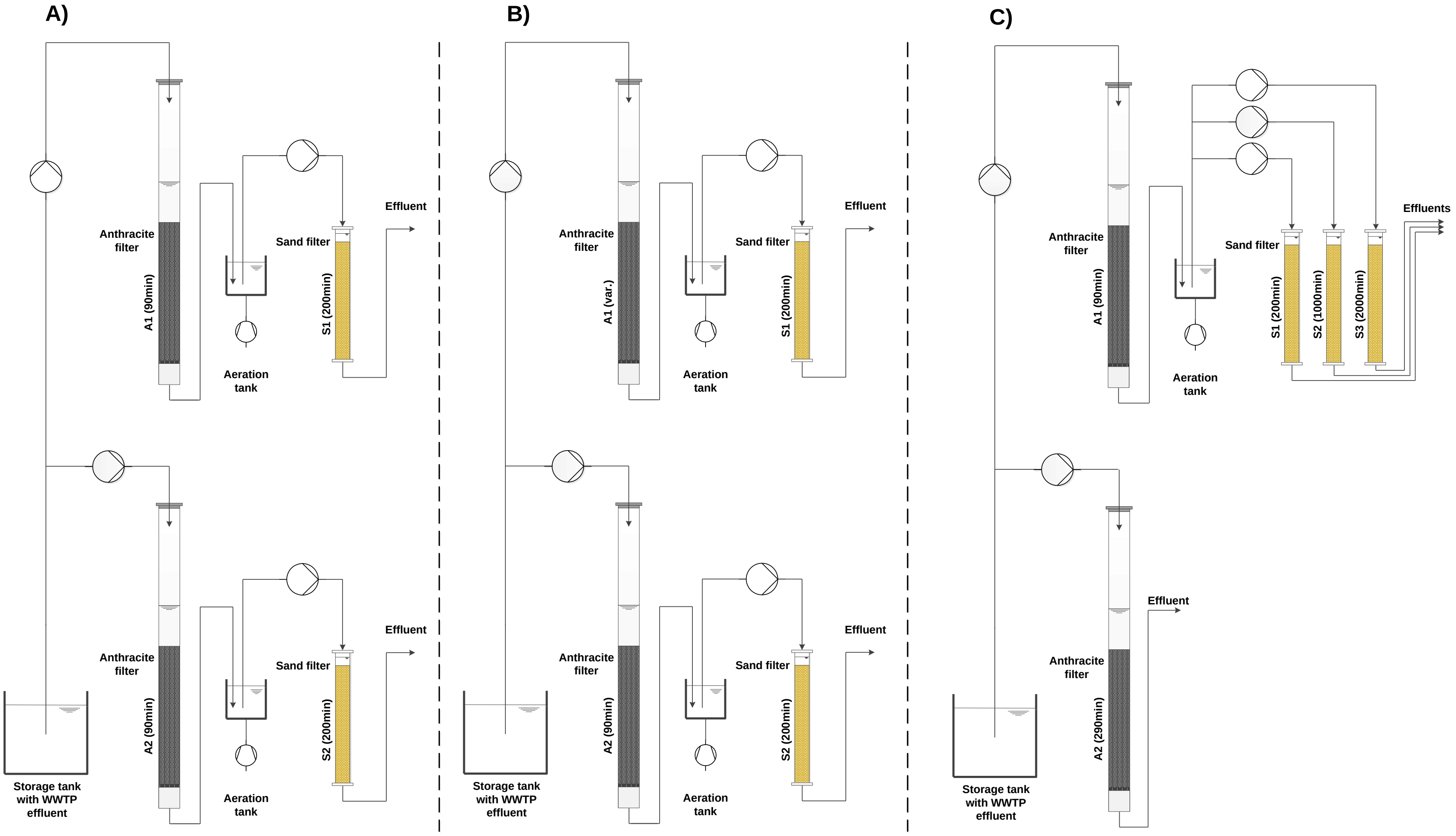

Figure SI-1: Overview over all experimental setups and configurations used in phases A), B) and C) during the study (see Table SI-1).

Table SI-1: Summary of experimental setups, configurations and duration of experiments in months (M) after the start of operation.

	Summary of experimental setups
A)	***Results presented in section 3.1***
A1+S1	Columns A1 (EBCT 90 min) and S1 (EBCT 200 min) operated in series with intermediate aeration. Data shown generated in M 1-12 and 14-21.
A2+S2	Columns A2 (EBCT 90 min) and S2 (EBCT 200 min) operated in series with intermediate aeration. Data shown generated in M 1-15.
B)	***Results presented in section 3.4***
A1+S1	Columns A1 (EBCT varying: 150, 90, 60, 45, 30 min) and S1 (EBCT 200 min) operated in series with intermediate aeration. Data shown generated in M 12-14
A2+S2	Columns A2 (EBCT 90 min) and S2 (EBCT 200 min) operated in series with intermediate aeration. Data shown generated in M 12-14
C)	***Results presented in section 3.2 and 3.3***
A1+S1	Columns A1 (EBCT 90 min) and S1 (EBCT 200 min) operated in series with intermediate aeration. Data shown generated in M 16-21.
A1+S2	Columns A1 (EBCT 90 min) and S2 (EBCT 1000 min) operated in series with intermediate aeration. Data shown generated in M 15-21.
A1+S3	Columns A1 (EBCT 90 min) and S2 (EBCT 2000 min) operated in series with intermediate aeration. Data shown generated in M 15-21.
A2	Column A2 (EBCT 290 min) operated as a single-stage biofilter. Data shown generated in M 15-21.

Table SI-2: LC gradient details (ESI positive mode: A: water containing 0.2 % formic acid and B: acetonitrile; ESI negative mode: A: water containing 2 mM ammonium acetate and B: acetonitrile).

Run time [min]	**Mobile phase A [%]**	**Mobile phase B [%]**
ESI positive		
0	98	2
1	98	2
12	0	100
12.5	98	2
18	98	2
ESI negative		
0	98	2
1	98	2
7.4	10	90
9.5	10	90
10	98	2
15	98	2

Table SI-3: Compound-specific LC retention times, MS/MS parameters and LOQs.

Analyte	**Retention time [min]**	**Precursor mass [Da]**	**Fragment mass [Da]**	**Declustering potential [V]**	**Collision energy [eV]**	**Cell exit potential [V]**	**Limit of Quantification [ppt]**
ESI positive							
Benzotriazole	4.7	120.4	65.0	111	29	10	50
			92.1	111	23	10	
Benzotriazole-d4		123.9	69.1	111	31	8	-
Caffeine	4.5	195.1	138.0	61	25	16	250
			110.0	61	31	12	
Caffeine-^{13}C3		198.1	140.0	106	25	16	
Carbamazepine	7.1	237.0	179.0	131	47	10	10
			165.0	131	57	14	
Carbamazepine-d8		245.0	202.0	121	29	16	-
Citalopram	6.7	325.1	109.0	86	31	12	5
			262.1	86	27	30	
Citalopram-d6		331.1	109.0	76	33	12	-
Climbazole	7.3	293.1	197.0	41	21	22	5
			225.0	41	19	26	
Climbazole-d4		297.1	201.0	46	23	24	-
Diclofenac	9.3	296.0	214.0	41	47	13	25
			250.0	41	19	18	
Diclofenac-d4		300	218.0	120	47	13	-
Gabapentin	4.0	172.1	154.0	61	19	10	10
			137.0	61	23	10	
Gabapentin-d10		182.1	164.0	76	19	14	-
Iopromide	3.8	791.7	572.9	106	33	26	100
			559.0	106	43	24	
Iopromide-d3		794.8	575.9	146	35	26	-
Metoprolol	5.2	268.1	116.0	171	25	14	25
			191.0	171	25	14	
Metoprolol-d7		275.4	123.0	186	25	12	-
Phenytoin	7.2	253.0	182.1	81	23	20	10
			104.0	81	43	12	
Phenytoin-d10		263.1	192.1	71	25	22	-

Primidone	5.2	219.0	162.0	101	17	10	25
			119.0	101	23	10	
Primidone-d5		224.0	167.0	96	17	14	-
Sotalol	3.7	273.1	213.0	1	25	24	5
			255.1	1	15	24	
Sotalol-d6		279.1	261.1	36	17	24	-
Sulfamethoxazole	6.0	254.0	156.0	86	21	12	10
			108.0	86	31	14	
Sulfamethoxazole-d4		258.0	160.0	106	23	14	-
Tris(2-chloroethyl) phosphate (TCEP)	7.5	284.9	223.0	36	17	26	100
			161.0	36	21	18	
TCEP-d12		297.0	232.0	51	19	26	-
Tramadol	5.3	264.2	58.0	41	85	6	5
			56.0	41	49	8	
Tramadol-d3-^{13}C		268.2	58.0	36	51	8	-
Venlafaxine	5.8	278.1	121.1	91	35	12	25
			58.0	91	20	18	
Venlafaxine-d6		284.6	64.0	120	47	13	-
ESI negative							
Acesulfame	1.9	161.9	81.9	-15	-18	-11	10
			77.9	-15	-42	-9	
Acesulfame-d4		165.9	85.9	-140	-20	-9	-
Gemfibrozil	7.0	249.0	121.0	-60	-20	-9	10
			127.0	-60	-14	-11	
Gemfibrozil-d6		255.0	121.0	-120	-20	-11	-
Ibuprofen	6.1	205.1	158.9	-10	-8	-21	25
			161.1	-10	-10	-15	
Ibuprofen-d3		208.1	164.1	-20	-8	-7	-
Naproxen	5.2	229	170.0	-5	-20	-15	10
			185.1	-5	-10	-17	
Naproxen-d3		232.1	188.1	-10	-10	-17	-

10.4 Supplementary information for Chapter 5

Optimizing sequential biofiltration: Role of reduced empty bed contact times and pre-treatment by coagulation with Fe(III) salts on the removal of trace organic compounds during sequential biofiltration

Supplementary information

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Table SI-4: Characteristics of tertiary wastewater treatment plant effluent used during experimental campaigns.

Parameter	*Exp. campaign 1*	*n*	*Exp. campaign 2*	*n*	*LOQ*
UVA_{254} [1/m]	14.6 ± 3.1	28	12.7 ± 0.8	8	-
DOC [mg/L]	7.5 ± 1.7	28	8.2 ± 1.0	3	0.1
Ammonia [mg N/L]	0.065 ± 0.068	9 (19 samples < LOQ)	0.079 ± 0.068	5 (3 samples < LOQ)	0.015
Nitrite [mg N/L]	0.083 ± 0.064	8 (9 samples < LOQ)	0.035	2	0.015
Nitrate [mg N/L]	12.6 ± 3.7	28	9.4 ± 0.7	3	5.0
Total phosphorous [mg P/L]	-	-	0.4 ± 0.1	8	0.05
pH	7.9 ± 0.2	20	7.5 ± 0.3	8	-

Table SI-5: Characteristics of tertiary wastewater treatment plant effluent used during experimental campaigns.

Indicator compounds (concentrations in ng/L)					
	Exp. campaign 1	*Present > 3.5 x LOQ*	*Exp. campaign 2*	*Present > 3.5 x LOQ*	*LOQ*
4-FAA	470 ± 170	25/25	440 ± 110	8/8	10
Antipyrine	20 ± 10	3/25	20 ± 10	1/8	10
Atenolol	30 ± 10	1/25	30 ± 10	2/8	10
Benzotriazole	5810 ± 860	25/25	5940 ± 470	8/8	50
Caffeine	80 ± 40	1/25	40 ± 20	0/8	50
Carbamazepine	490 ± 70	25/25	440 ± 30	8/8	5
Citalopram	250 ± 200	25/25	140 ± 30	8/8	5
Climbazole	180 ± 170	25/25	80 ± 20	8/8	5
Diclofenac	1320 ± 360	25/25	1000 ± 90	8/8	5
Gabapentin	1400 ± 480	25/25	1040 ± 100	8/8	2.5
Iopromide	320 ± 360	11/25	-	0/8	50
Metoprolol	290 ± 50	25/25	250 ± 30	8/8	2.5
Phenytoin	10 ± 10	3/25	-	0/8	5
Primidone	70 ± 30	4/25	40 ± 10	0/8	25
Sotalol	60 ± 20	24/25	40 ± 10	8/8	5
Sulfamethoxazole	300 ± 80	25/25	230 ± 90	8/8	5
TCEP	150 ± 100	6/25	70 ± 40	0/8	50
Tramadol	270 ± 60	25/25	190 ± 40	8/8	5
Trimethoprim	30 ± 10	22/25	50 ± 20	8/8	5
Valsartan acid	3460 ± 590	25/25	3390 ± 1110	8/8	5
Venlafaxine	400 ± 50	25/25	400 ± 130	8/8	2.5

Table SI-6: Performance of SBF systems A1+S1 and A2+S2 at varying EBCTs in column A2. Summary of cumulative consumption of UVA$_{254}$, DOC and DO and percent removal in filter stages A and A+S in both systems. Asterisks indicate significant differences for columns A1/A2 and S1/S2 for TOrC removal during phases I – IV. Phases I – III: n = 3; phase 4: n = 7.

		Phase I				**Phase II**				**Phase III**				**Phase IV**			
	Column	*A1*	*A2*	*S1*	*S2*	*A1*	*A2*	*S1*	*S2*	*A1*	*A2*	*S1*	*S2*	*A1*	*A2*	*S1*	*S2*
	EBCT [min]	*90*	*90*	*200*	*200*	*90*	*45*	*200*	*200*	*90*	*30*	*200*	*200*	*90*	*45*	*200*	*200*
Consumption	*UVA$_{254}$ [1/m]*	1.4 ± 0.5	1.4 ± 0.8	2.3 ± 0.6	2.3 ± 1.1	1.3 ± 0.1	0.9 ± 0.2	2.1 ± 0.0	2.0 ± 0.2	1.0 ± 0.4	0.6 ± 0.2	2.3 ± 0.8	2.1 ± 0.5	0.8 ± 0.3	0.8 ± 0.2	1.7 ± 0.6	1.8 ± 0.4
	DOC [mg/L]	2.3 ± 0.9	2.0 ± 1.3	2.6 ± 0.6	2.7 ± 1.1	1.3 ± 0.5	1.1 ± 0.3	1.6 ± 1.2	1.0 ± 2.3	1.6 ± 0.7	1.4 ± 0.9	2.2 ± 1.0	2.0 ± 1.0	1.0 ± 0.4	1.0 ± 0.5	2.2 ± 0.5	2.2 ± 0.4
	DO [mg/L]	6.0 ± 0.4	5.7 ± 0.7	9.0 ± 0.6	7.8 ± 0.7	5.9 ± 1.0	3.9 ± 1.3	9.1 ± 1.3	7.1 ± 2.3	5.0 ± 0.5	3.9 ± 0.6	8.5 ± 1.1	8.3 ± 1.3	3.4 ± 0.6	3.0 ± 0.4	6.8 ± 0.8	6.7 ± 0.7
Percent removal (non-persistent; > 15 %)	*4-FAA*	93 ± 2*	86 ± 1*	93 ± 3*	87 ± 3*	73 ± 6*	39 ± 7*	76 ± 6*	56 ± 5*	56 ± 9*	34 ± 6*	64 ± 8*	64 ± 9*	73 ± 10*	88 ± 6*	91 ± 7	96 ± 4
	Benzotriazole	77 ± 1*	60 ± 1*	91 ± 1	85 ± 5	63 ± 2*	39 ± 3*	79 ± 1*	85 ± 1*	59 ± 5*	46 ± 5*	90 ± 2*	95 ± 1*	47 ± 8*	57 ± 4*	87 ± 3	90 ± 1
	Citalopram	42 ± 10*	28 ± 5*	83 ± 2	73 ± 5	36 ± 6*	15 ± 3*	80 ± 2	76 ± 2	24 ± 2*	-5 ± 4*	73 ± 3	69 ± 1	7 ± 13	6 ± 19	83 ± 3*	76 ± 4*
	Climbazole	41 ± 7	34 ± 7	61 ± 1	47 ± 4	30 ± 2*	17 ± 2*	61 ± 3*	46 ± 1*	2 ± 16	-11 ± 16	37 ± 10	28 ± 8	9 ± 11	11 ± 19	43 ± 7	45 ± 10
	Diclofenac	32 ± 4	23 ± 6	35 ± 4	24 ± 8	25 ± 5*	16 ± 3*	29 ± 7*	18 ± 5*	18 ± 4	18 ± 3	23 ± 3	20 ± 2	6 ± 2	7 ± 2	11 ± 2	9 ± 2
	Gabapentin	80 ± 2	77 ± 2	91 ± 1	87 ± 1	60 ± 5*	51 ± 7*	83 ± 3	80 ± 3	51 ± 12	58 ± 7	75 ± 8	85 ± 1	35 ± 9	32 ± 7	79 ± 5	84 ± 3
	Metoprolol	37 ± 6	27 ± 5	79 ± 5*	67 ± 6*	38 ± 5*	23 ± 5*	79 ± 4*	65 ± 4*	35 ± 6*	15 ± 5*	82 ± 2*	58 ± 4*	23 ± 6*	19 ± 5*	76 ± 4*	61 ± 4*
	Sotalol	26 ± 3	18 ± 5	54 ± 2	45 ± 6	16 ± 8	14 ± 12	47 ± 3	41 ± 4	18 ± 5	13 ± 6	54 ± 6	43 ± 7	26 ± 21	24 ± 19	72 ± 19	57 ± 14
	Sulfamethoxazole	55 ± 2	41 ± 5	61 ± 3	55 ± 4	43 ± 7*	19 ± 10*	52 ± 8*	50 ± 9*	30 ± 3*	-2 ± 2*	41 ± 7*	44 ± 5*	16 ± 6	19 ± 5	60 ± 4	60 ± 4

	Trimethoprim	93 ± 3	93 ± 3	-	-	90 ± 1*	62 ± 1*	92 ± 3*	92 ± 3*	88*	75*	94*	94*	86 ± 9	80 ± 13	89 ± 2	84 ± 16
	Valsartan acid	38 ± 18*	-24 ± 16*	97 ± 2*	27 ± 15*	37 ± 9*	-9 ± 4*	92 ± 5*	72 ± 10*	9 ± 26*	-16 ± 6*	87 ± 17*	68 ± 40*	-8 ± 9	7 ± 7	91 ± 4*	94 ± 1*
Percent removal (persistent;< 15 %)	*Carbamazepine*	-1 ± 4	-2 ± 1	-5 ± 7	-4 ± 2	0 ± 6	3 ± 3	2 ± 2	1 ± 3	1 ± 3	2 ± 1	-2 ± 2	1 ± 3	0 ± 4	-2 ± 6	-1 ± 6	-1 ± 6
	Tramadol	2 ± 4	1 ± 3	3 ± 3	0 ± 2	10 ± 13	11 ± 14	10 ± 13	11 ± 14	-5 ± 1	-3 ± 2	-5 ± 3	-5 ± 2	-1 ± 4	-2 ± 5	-1 ± 4	0 ± 3
	Venlafaxine	1 ± 2	2 ± 3	2 ± 3	1 ± 2	1 ± 5	3 ± 5	4 ± 4	4 ± 5	1 ± 6	0 ± 3	-1 ± 5	0 ± 4	-1 ± 4	-1 ± 4	1 ± 5	0 ± 3

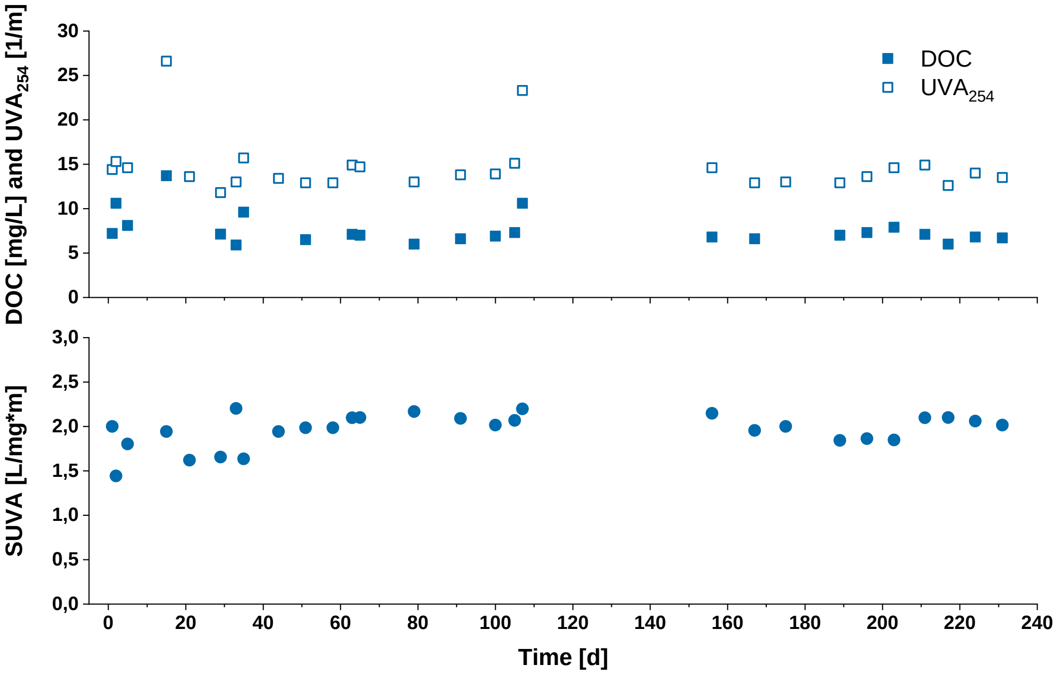

Figure SI-2: Dissolved organic carbon (DOC) concentrations, values for UVA_{254} (above) and SUVA (below) found in WWTP effluent over time during experiments assessing the impact of different EBCTs in first stage filters of SBF systems.

Table SI-7: Performance of SBF systems A1+S1 and A2+S2. WWTP effluent fed to system A2+S2 was pre-treated by coagulation, flocculation and sedimentation (CFS) applying a Fe(III) dose of 30 mg/L. Summary of consumption of UVA_{254} (n = 8), DOC (n = 3) and DO (n = 8) and cumulative percent removal of indicator TOrCs by CFS and in systems A1+S1 and A2+S2.

		A1	***S1***	***CFS***	***A2***	***S2***
	EBCT [min]	*90*	*200*	*-*	*90*	*200*
Consumption	*UVA_{254} [1/m]*	0.6 ± 0.3	1.3 ± 0.6	4.3 ± 0.8	0.9 ± 0.5	0.9 ± 0.4
	DOC [mg/L]	0.7 ± 1.5	0.3 ± 1.0	0.8 ± 0.2	1.7 ± 0.6	0.6 ± 0.9
	DO [mg/L]	3.6 ± 1.7	5.1 ± 1.2	-	1.7 ± 0.8	3.0 ± 0.6
Percent removal (non-persistent; > 15 %)	*4-FAA*	67 ± 12	91 ± 4	4 ± 4	53 ± 7	79 ± 7
	Benzotriazole	62 ± 6	90 ± 3	2 ± 2	53 ± 6	84 ± 8
	Citalopram	-1 ± 10	70 ± 6	1 ± 11	-7 ± 11	68 ± 5
	Climbazole	1 ± 19	66 ± 7	6 ± 13	-9 ± 19	51 ± 9
	Diclofenac	18 ± 5	27 ± 6	1 ± 4	18 ± 5	29 ± 11
	Gabapentin	35 ± 9	78 ± 5	3 ± 3	41 ± 5	72 ± 8
	Metoprolol	24 ± 5	86 ± 4	0 ± 6	9 ± 6	59 ± 12
	Sotalol	12 ± 10	59 ± 9	2 ± 6	6 ± 7	42 ± 11
	Sulfamethoxazole	14 ± 8	33 ± 5	0 ± 2	17 ± 4	31 ± 8
	Trimethoprim	72 ± 7	94 ± 2	1 ± 4	60 ± 8	81 ± 8
	Valsartan acid	6 ± 13	97 ± 3	0 ± 4	4 ± 7	91 ± 7
Percent removal (persistent;< 15 %)	*Carbamazepine*	-1 ± 6	-2 ± 5	1 ± 3	0 ± 4	-3 ± 3
	Tramadol	1 ± 3	3 ± 3	2 ± 3	2 ± 3	1 ± 3
	Venlafaxine	2 ± 3	3 ± 4	1 ± 3	2 ± 4	-1 ± 4

10.5 Supplementary information for Chapter 6

Following and describing the transformation of trace organic chemicals in sequential biofiltration systems using profile sampling and first-order biodegradation rate constants Supplementary information

Supplementary information

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Table SI-8: Limits of quantitation (LOQ); average concentrations with standard deviations in wastewater treatment plant effluent (c_0); number of detections above 3.5 x LOQ during the experimental campaign (5 samplings); Cumulative percent removal with standard deviation in columns A1 and A2 and in SBF systems A1+S1, A1+S2 and A1+S3.

Compound	**LOQ**	**c_0**	**Std. dev.**	**Occurr. above 3.5 x LOQ**	**A2**		**A1**		**A1+S1**		**A1+S2**		**A1+S3**	
	[ng/L]	**[ng/L]**	**[ng/L]**		**% Rem.**	**Std. dev.**	**% Rem.**	**Std. dev.**	**% Rem.**	**Std. dev.**	**% Rem.**	**Std. dev.**	**% Rem.**	**Std. dev.**
Degradable (removal > 25 % in at least one of the operated systems)														
Acesulfame	10	1990	480	5	87	4	90	3	91	3	90	3	91	3
Acridone	1	13	1	5	-39	12	-12	5	96	0	96	0	96	0
Acyclovir	20	50	60	1	92	-	92	-	92	-	92	-	92	-
Azithromycin	20	160	30	3	29	59	2	2	94	1	94	1	94	1
Benzotriazole	50	4330	540	5	28	3	26	5	83	1	86	2	86	3
Bezafibrate	1	65	17	5	91	9	75	10	99	0	99	0	99	0
Carbendazim	2	21	-	1	0	-	-10	-	0	-	5	-	48	-
Cetirizine	5	165	35	5	-10	9	-8	12	-3	14	15	13	37	10
Citalopram	5	140	25	5	45	8	21	5	76	4	49	6	48	5
Clarithromycin	1	28	13	5	98	1	72	14	95	5	91	9	85	14
Climbazole	2	68	10	5	37	4	23	6	50	5	75	5	71	5
N,N-Diethyl-meta-toluamide (DEET)	1	207	47	5	83	5	79	4	84	3	89	2	87	3
Diclofenac	5	505	75	5	26	8	19	4	22	6	30	3	46	7
Diphenhydramine	1	59	14	5	33	7	15	8	81	3	33	7	38	5
Furosemide	1	174	21	5	69	3	61	5	79	4	97	3	100	0
Gabapentin	10	1710	250	5	70	2	65	1	83	1	89	1	87	3
Gabapentin-Lactam	10	350	70	5	-15	6	-6	11	16	7	46	4	57	3
Mecoprop	1	50	21	5	41	11	21	6	79	13	95	9	99	1
Metoprolol	2	188	12	5	43	6	29	9	67	5	87	3	94	3
Naproxen	5	110	35	5	93	9	82	13	97	1	97	1	97	1
Saccharine	10	230	120	5	97	2	97	2	97	2	97	2	97	2
Sulfamethoxazole	2	120	32	5	39	6	27	7	38	5	54	7	50	17
Telmisartan	1	336	26	5	32	4	20	5	45	5	70	3	81	1
Terbutryn	0.5	32	7	5	9	5	7	6	9	3	29	6	38	9

Triclosan	1	34	26	5	98	2	61	23	84	19	98	2	98	2
Valsartan	1	886	289	5	99	0	98	1	100	0	100	0	100	0
Xipamide	1	7	2	4	24	46	24	46	1	8	-2	3	30	45
Persistent (removal < 25 % in all operated systems)														
4-amino-6-chloro-1,3-benzenedisulfonamide	5	285	40	5	3	6	6	6	5	4	0	5	-4	11
Aliskiren	2	175	90	5	-42	39	-53	80	-28	53	-11	26	13	46
Amisulprid	5	730	160	5	6	8	-3	5	-2	6	-6	5	2	8
Atenolol	5	n.d.	-	0	-	-	-	-	-	-	-	-	-	-
Bicalutamide	0.5	48	6	5	6	2	0	3	2	3	7	1	9	4
Candesartan	1	784	84	5	7	4	6	7	6	5	7	3	7	6
Carbamazepine	0.5	331	26	5	0	3	2	4	1	1	-2	3	-4	4
Chlorothiazide	0.5	100	8	5	-13	7	-4	2	-8	6	-20	4	-23	3
Denatonium	5	140	25	5	2	7	-7	7	0	7	-2	7	3	10
Diuron	0.5	16	5	5	11	7	5	3	7	4	11	4	10	9
Flecainide	2	102	12	5	3	5	3	5	7	8	8	5	11	7
Hydrochlorothiazide	2	2447	209	5	4	5	2	3	2	6	1	1	2	4
Irbesartan	0.5	567	51	5	12	3	9	5	11	4	18	4	24	4
Isoproturon	1	53	24	5	-1	4	2	5	1	6	1	7	7	6
Lamotrigine	50	780	40	5	-5	3	-3	3	-8	2	-12	5	-7	2
Lidocaine	1	87	6	5	3	6	3	4	4	4	3	6	4	14
Olmesartan	2	636	49	5	3	3	1	6	2	2	0	3	3	4
Saluamine	5	120	25	5	-26	5	-24	5	-33	8	-47	6	-81	16
Sitagliptin	10	1690	120	5	6	4	4	4	7	1	9	5	14	7
Sucralose	5	5505	300	5	2	3	2	4	4	2	3	3	8	4
Sulpirid	1	196	35	5	3	12	1	7	1	8	-6	8	1	5
Tetraglyme	2	50	5	5	3	2	-1	13	3	5	5	8	11	3
Torasemid	1	103	5	5	7	4	3	5	7	1	9	3	11	3
Tramadol	2	252	46	5	0	6	0	9	1	7	0	7	1	8
Venlafaxine	5	410	60	5	-1	4	-1	5	-2	4	-6	4	3	4

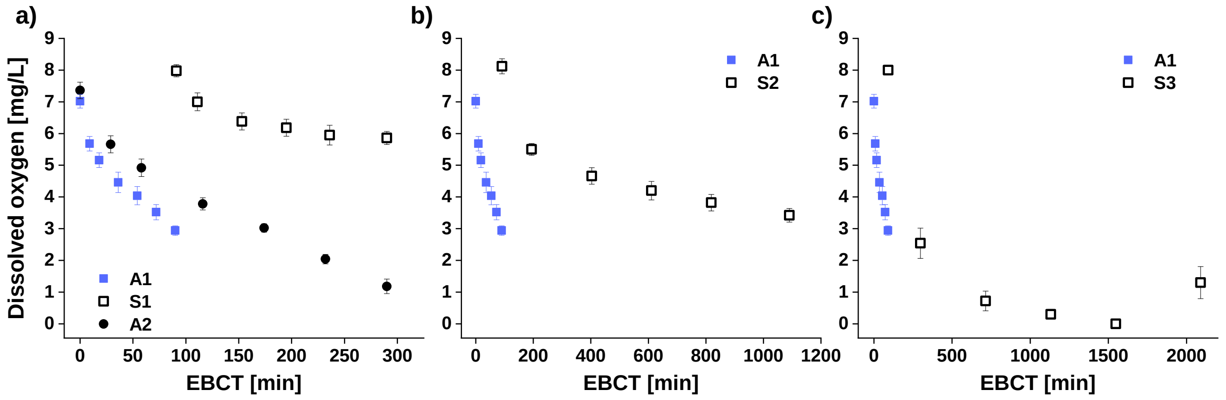

Figure SI-3: Dissolved oxygen profiles in column systems: a) A2 and A1+S1; b) A1+S2; c) A1+S3.

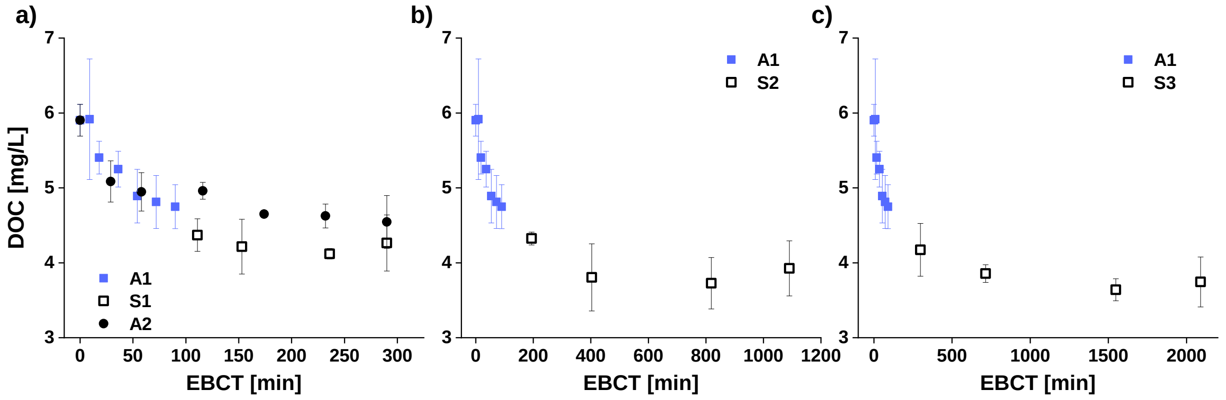

Figure SI-4: Concentrations of dissolved organic carbon (DOC) in column systems: a) A2 and A1+S1; b) A1+S2; c) A1+S3.

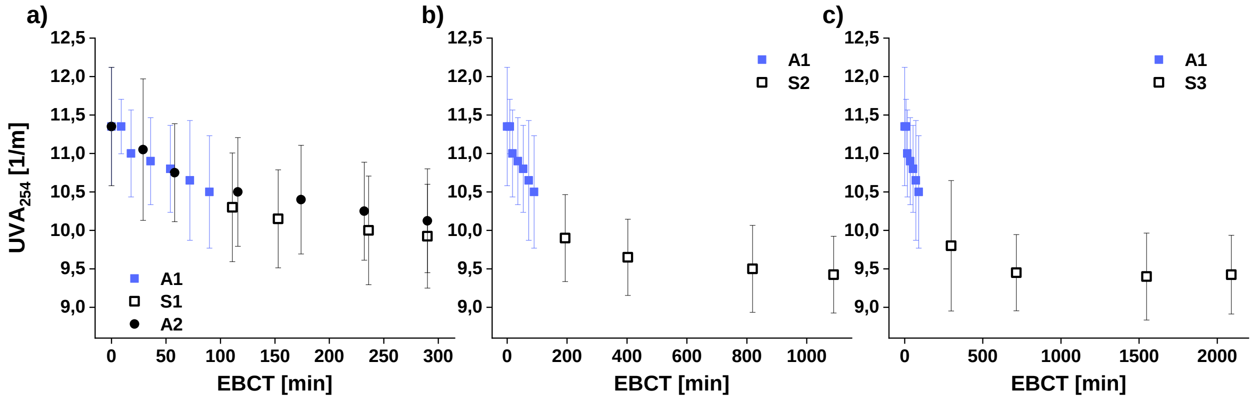

Figure SI-5: UV absorbance at 254 nm in column systems: a) A2 and A1+S1; b) A1+S2; c) A1+S3.

10.6 Supplementary information for Chapter 7

Capturing the oxic transformation of iopromide – A useful tool for an improved characterization of predominant redox conditions and the removal of trace organic compounds in biofiltration systems?

Supplementary information

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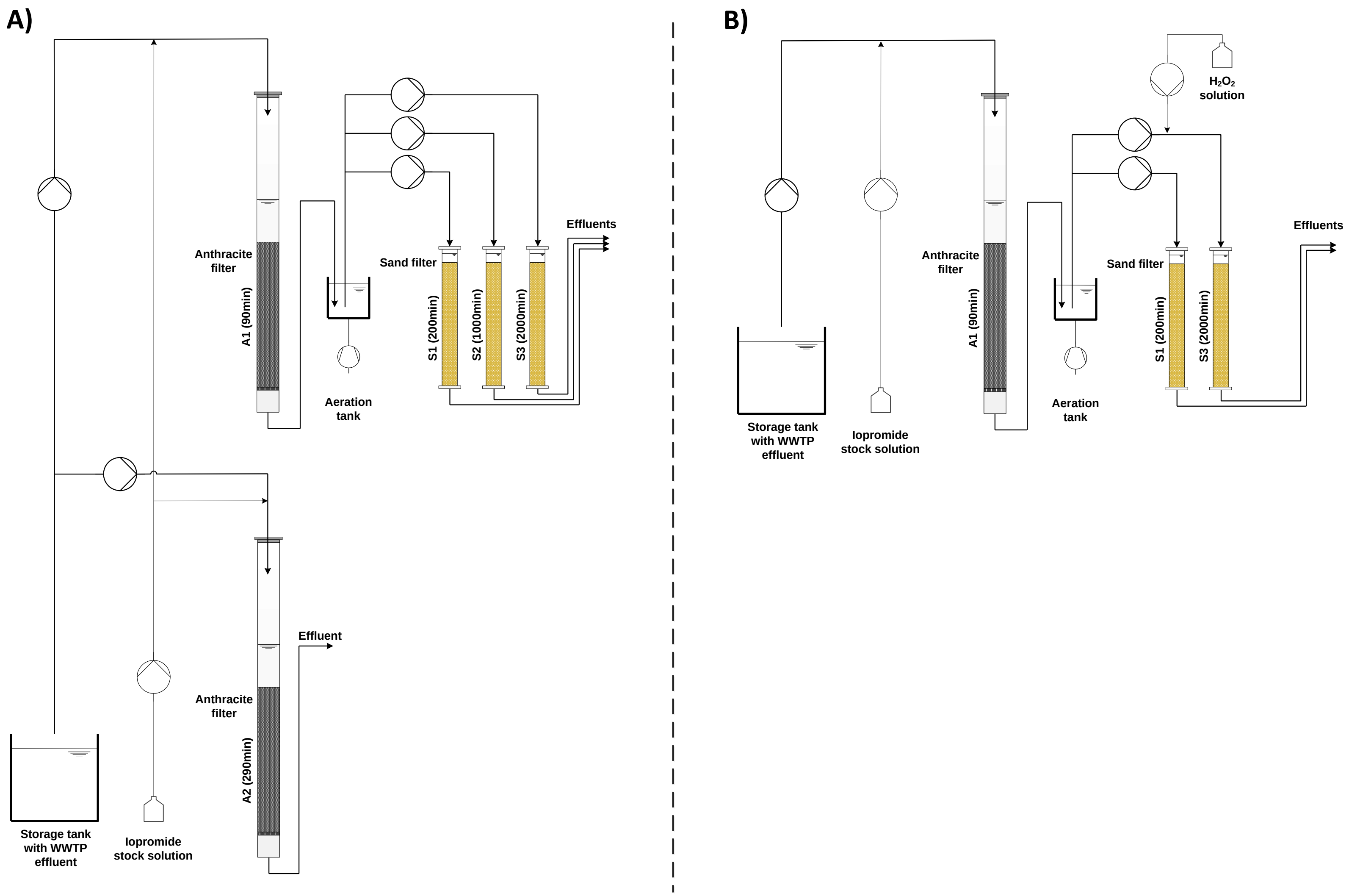

Figure SI-6: Experimental setup during first (A) and second experimental campaign (B).

Table SI-9: Limits of quantitation (LOQ), average concentrations with standard deviations in wastewater treatment plant effluent and number of detections above 3.5 x LOQ during the first experimental campaign (5 samplings).

Compound	*LOQ [ng/L]*	*c_0 [ng/L]*	*Std. dev. [ng/L]*	*Occurrence above 3.5 x LOQ*
Degradable (removal > 25 % in at least one of the operated systems)				
Acesulfame	*10*	*1990*	*480*	*5*
Acridone	*1*	*13*	*1*	*5*
Acyclovir	*20*	*50*	*60*	*1*
Azithromycin	*20*	*160*	*30*	*3*
Benzotriazole	*50*	*4330*	*540*	*5*
Bezafibrate	*1*	*65*	*17*	*5*
Carbendazim	*2*	*21*	*-*	*1*
Cetirizine	*5*	*165*	*35*	*5*
Citalopram	*5*	*140*	*25*	*5*
Clarithromycin	*1*	*28*	*13*	*5*
Climbazole	*2*	*68*	*10*	*5*
N,N-Diethyl-meta-toluamide (DEET)	*1*	*207*	*47*	*5*
Diclofenac	*5*	*505*	*75*	*5*
Diphenhydramine	*1*	*59*	*14*	*5*
Furosemide	*1*	*174*	*21*	*5*
Gabapentin	*10*	*1710*	*250*	*5*
Gabapentin-Lactam	*10*	*350*	*70*	*5*
Iopromide (after spiking)	*50*	*20,470*	*10,290*	*5*
Mecoprop	*1*	*50*	*21*	*5*
Metoprolol	*2*	*188*	*12*	*5*
Naproxen	*5*	*110*	*35*	*5*
Saccharine	*10*	*230*	*120*	*5*
Sulfamethoxazole	*2*	*120*	*32*	*5*
Telmisartan	*1*	*336*	*26*	*5*
Terbutryn	*0.5*	*32*	*7*	*5*
Triclosan	*1*	*34*	*26*	*5*
Valsartan	*1*	*886*	*289*	*5*
Xipamide	*1*	*7*	*2*	*5*
Persistent (removal < 25 % in all operated systems)				
4-amino-6-chloro-1,3-benzenedisulfonamide	*5*	*285*	*40*	*5*
Aliskiren	*2*	*175*	*90*	*5*
Amisulprid	*5*	*730*	*160*	*5*
Atenolol	*5*	*not detected*	*-*	*0*
Bicalutamide	*0.5*	*48*	*6*	*5*
Candesartan	*1*	*784*	*84*	*5*
Carbamazepine	*0.5*	*331*	*26*	*5*
Chlorothiazide	*0.5*	*100*	*8*	*5*
Denatonium	*5*	*140*	*25*	*5*
Diuron	*0.5*	*16*	*5*	*5*
Flecainide	*2*	*102*	*12*	*5*
Hydrochlorothiazide	*2*	*2447*	*209*	*5*
Irbesartan	*0.5*	*567*	*51*	*5*
Isoproturon	*1*	*53*	*24*	*5*
Lamotrigine	*50*	*780*	*40*	*5*
Lidocaine	*1*	*87*	*6*	*5*
Olmesartan	*2*	*636*	*49*	*5*
Saluamine	*5*	*120*	*25*	*5*
Sitagliptin	*10*	*1690*	*120*	*5*
Sucralose	*5*	*5505*	*300*	*5*
Sulpirid	*1*	*196*	*35*	*5*
Tetraglyme	*2*	*50*	*5*	*5*
Torasemid	*1*	*103*	*5*	*5*
Tramadol	*2*	*252*	*46*	*5*
Venlafaxine	*5*	*410*	*60*	*5*

Table SI-10: Limits of quantitation (LOQ), average concentrations with standard deviations in wastewater treatment plant effluent and number of detections above 3.5 x LOQ during the second experimental campaign (5 samplings).

Compound	***LOQ [ng/L]***	***c_0 [ng/L]***	***Std. dev. [ng/L]***	***Occurrence above 3.5 x LOQ***
Degradable (removal > 25 % in at least one of the operated systems)				
Benzotriazole	***50***	***5,930***	***910***	***5***
Citalopram	***10***	***210***	***50***	***5***
Climbazole	***10***	***150***	***70***	***5***
Diclofenac	***5***	***1,810***	***275***	***5***
Gabapentin	***5***	***2,720***	***295***	***5***
Iopromide (after spiking)	***50***	***28,910***	***5,650***	***5***
Metoprolol	***5***	***365***	***20***	***5***
Sulfamethoxazole	***5***	***120***	***60***	***5***
Persistent (removal < 25 % in all operated systems)				
Carbamazepine	***5***	***535***	***60***	***5***
Tramadol	***5***	***300***	***55***	***5***
Venlafaxine	***5***	***455***	***40***	***5***

Table SI-11: LC conditions during the analysis of iopromide and iopromide transformation products.

Analytical column	Agilent Eclipse Plus C18, 2.1x150mm, 3.5µm	
Column temperature	40°C	
Injection volume	80µL	
Flow rate	250 µL/min	
Eluent A	0.1 % formic acid in Milli-Q water	
Eluent B	Acetonitrile	
Eluent Gradient	Time (minutes)	Content Eluent B (%)
	0	0
	2	0
	8	50
	9	100
	13	100
	13.1	0
	18	0

Table SI-12: ESI source conditions during the analysis of iopromide and iopromide transformation products.

Curtain Gas	45 psi
Temperature	450°C
GS1	40 psi
GS2	45 psi
CAD (collision gas)	8
Ion Spray Voltage	5500 V
Entrance Potential	10 V

Table SI-13: MRM Transitions and compound dependent parameters, limits of quantitation (LOQ) and recoveries for iopromide and iopromide transformation products.

Analyte	**MRM Transitions (m/z)**	**Retention time (min)**	**Declustering Potential (V)**	**Collision Energy (V)**	**Collision Cell Exit Potential (V)**	**LOQ [µg/L]**	**Recovery Spike 10 µg/L [%]**	**Recovery Spike 100 µg/L [%]**
Iopromide	**791.9 → 572.7**	**7.9**	101	33	20	0.1	91	98
	791.9 → 558.7		101	39	18			
TP819	**819.8 → 586.6**	**8.2**	101	35	18	0.1	97	104
	819.8 → 714.3		101	29	24			
TP817A*	**817.8 → 700.8**	**8.1**	91	27	24	0.3	-	-
	817.8 → 712.7		91	27	26			
TP805A*	**805.8 → 558.8**	**8.0**	91	39	14	0.1	-	-
	805.8 → 686.5		91	31	18			
TP805B*	**805.8 → 572.7**	**8.0**	101	33	20	0.1	-	-
	805.9 → 700.9		91	27	24			
TP787A*	**787.8 → 670.5**	**8.3**	81	27	22	0.3	-	-
	787.8 → 712.3		81	25	24			
TP759	**759.5 → 670.5**	**8.6**	66	23	18	0.3	109	102
	759.5 → 684.4		66	23	22			
TP731A*	**731.5 → 612.5**	**8.1**	91	27	18	0.1	-	-
	731.5 → 453.5		91	39	12			
TP731B	**731.9 → 626.4**	**8.3**	91	23	22	0.1	106	117
	731.9 → 467.6		91	41	14			
TP729A	**729.5 → 612.5**	**8.1**	76	27	18	0.3	91	86
	729.5 → 457.5		76	41	30			
TP701A	**701.5 → 612.7**	**8.4**	66	25	18	0.1	117	108
	701.5 → 453.7		66	43	26			
TP701B	**701.8 → 626.6**	**8.5**	81	17	14	0.1	106	102
	701.8 → 467.7		81	37	22			
TP643	**643.6 → 516.6**	**8.3**	61	19	16	0.1	102	114
	643.6 → 612.5		61	21	18			
Iopromide-d3 Surrogate Standard	**794.8 → 575.9**	**7.9**	81	33	14			

*no isolated standards available, concentrations are semi-quantified

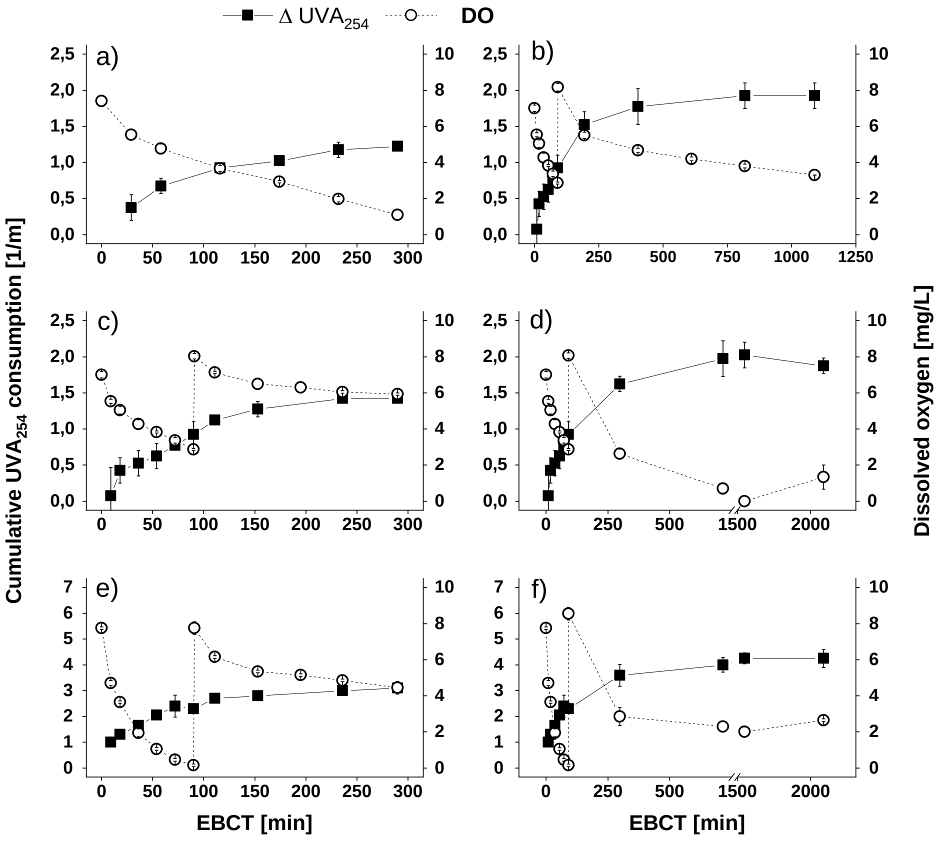

Figure SI-7: UVA$_{254}$ consumption and DO concentration profiles during first (a) A2; b) A1+S2; c) A1+S1; d) A1+S3) (UVA$_{254,0}$: 11.4 ± 0.7 1/m; n = 3; DO: n = 5)) and second experimental campaign (e) A1+S1; f) A1+S3) (UVA$_{254,0}$: 15.5 ± 0.1 1/m; n = 2; DO: n = 5).

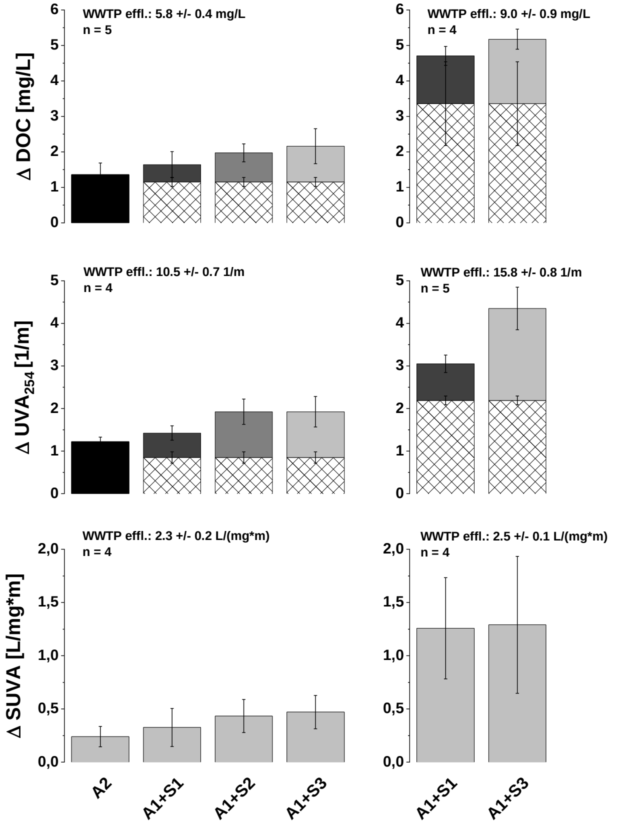

Figure SI-8: Consumption of DOC, UVA$_{254}$ and change in SUVA in filter systems during first (left side) and second experimental campaign (right side).

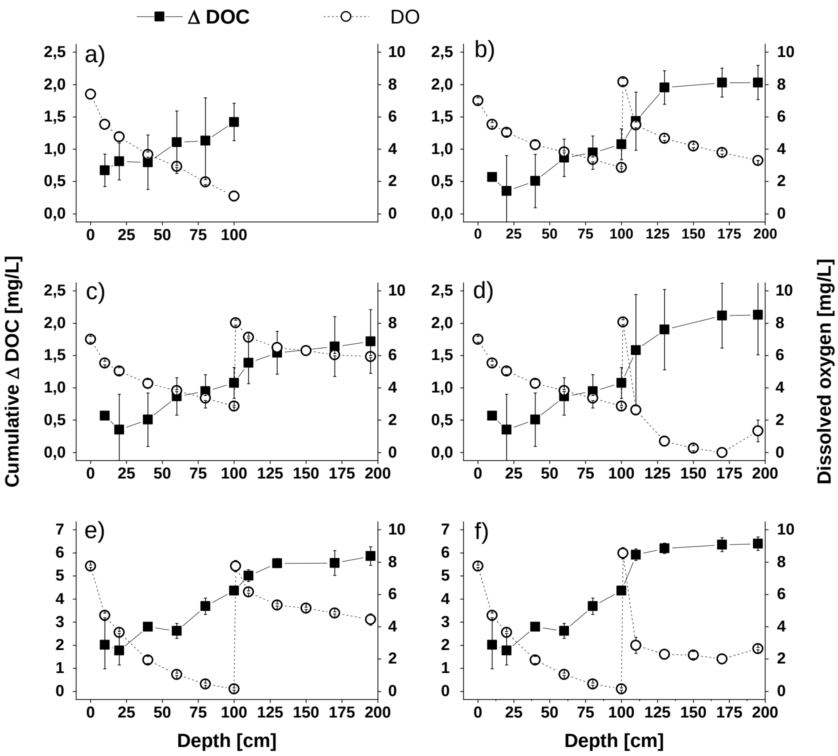

Figure SI-9: DOC consumption and DO concentration profiles as a function of column depths during first (a) A2; b) A1+S2; c) A1+S1; d) A1+S3) (DOC0: 5.3 ± 0.3 mg/L; n = 3) and second experimental campaign (e) A1+S1; f) A1+S3) (DOC0: 9.7 ± 0.2 mg/L; n = 2).

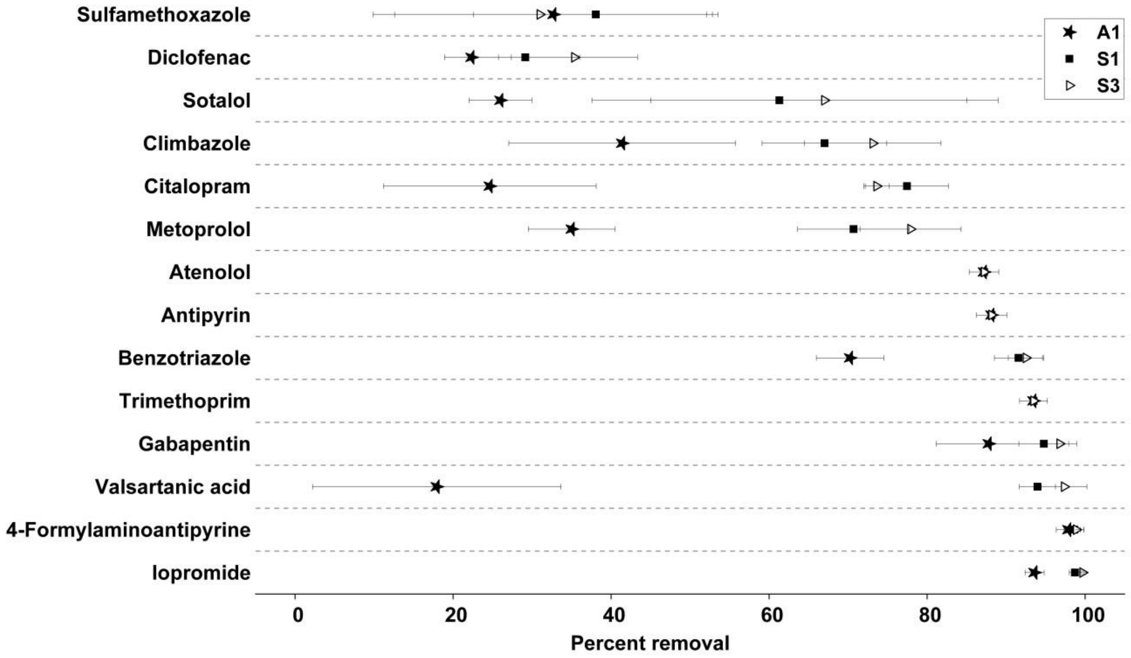

Figure SI-10: Cumulative removal of trace organic compounds in operated systems during second experimental campaign (n = 5); Detailed information in inlet concentrations can be found in Table SI-10.

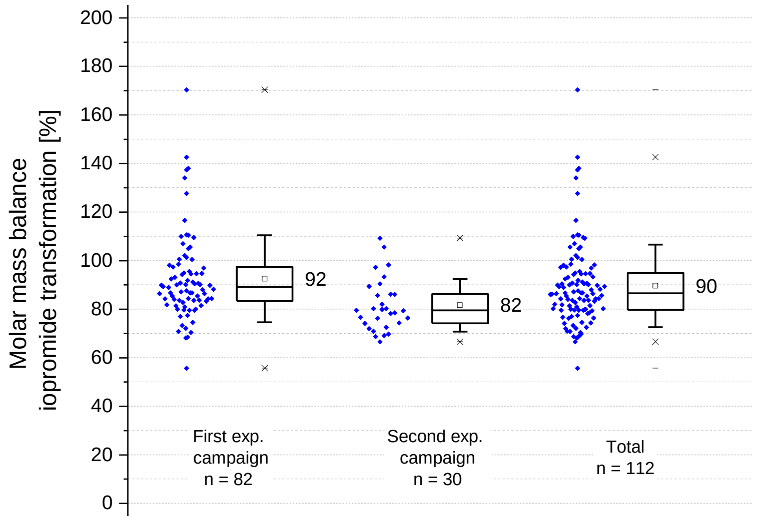

Figure SI-11: Molar mass balances for iopromide and transformation products. Percent recovery of molar influent concentrations in samples.

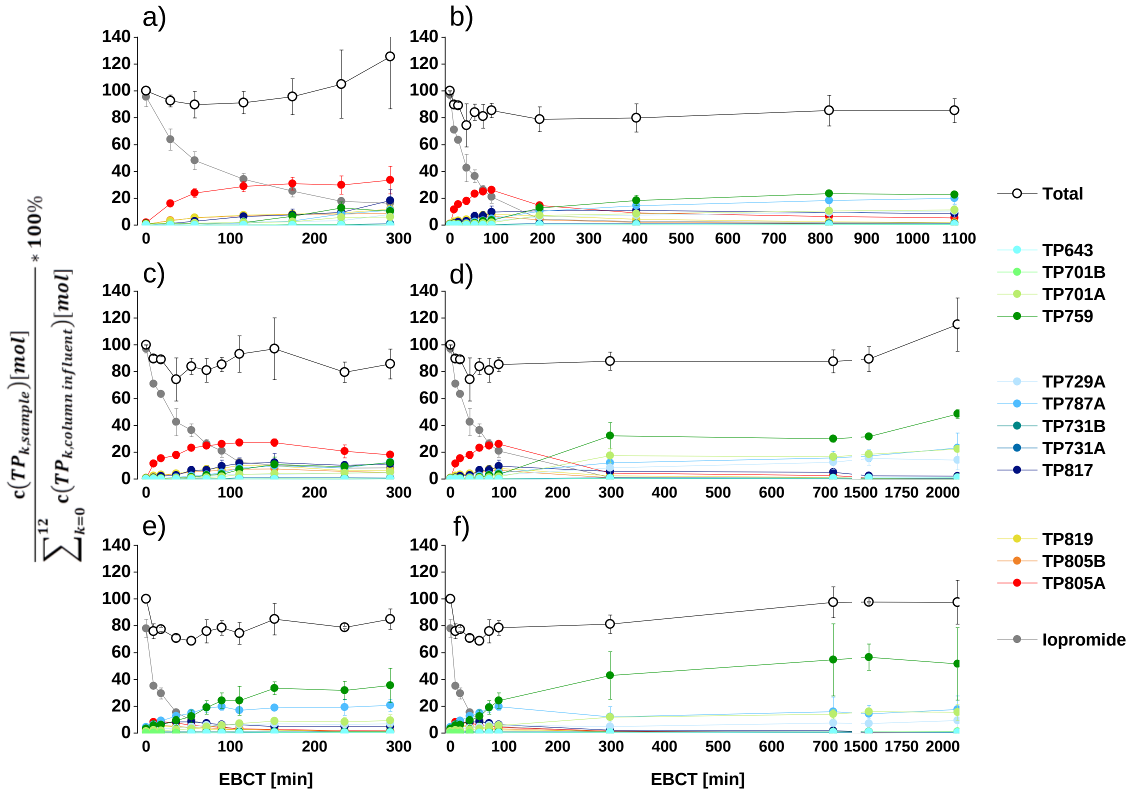

Figure SI-12: Molar concentrations of iopromide and iopromide transformation products in column systems normalized to the sum of molar concentrations found in the spiked WWTP effluent as a function of EBCT during first (a) A2; b) A1+S2; c) A1+S1; d) A1+S3) and second experimental campaign (e) A1+S1; f) A1+S3). See Table SI-14 for details on concentrations.

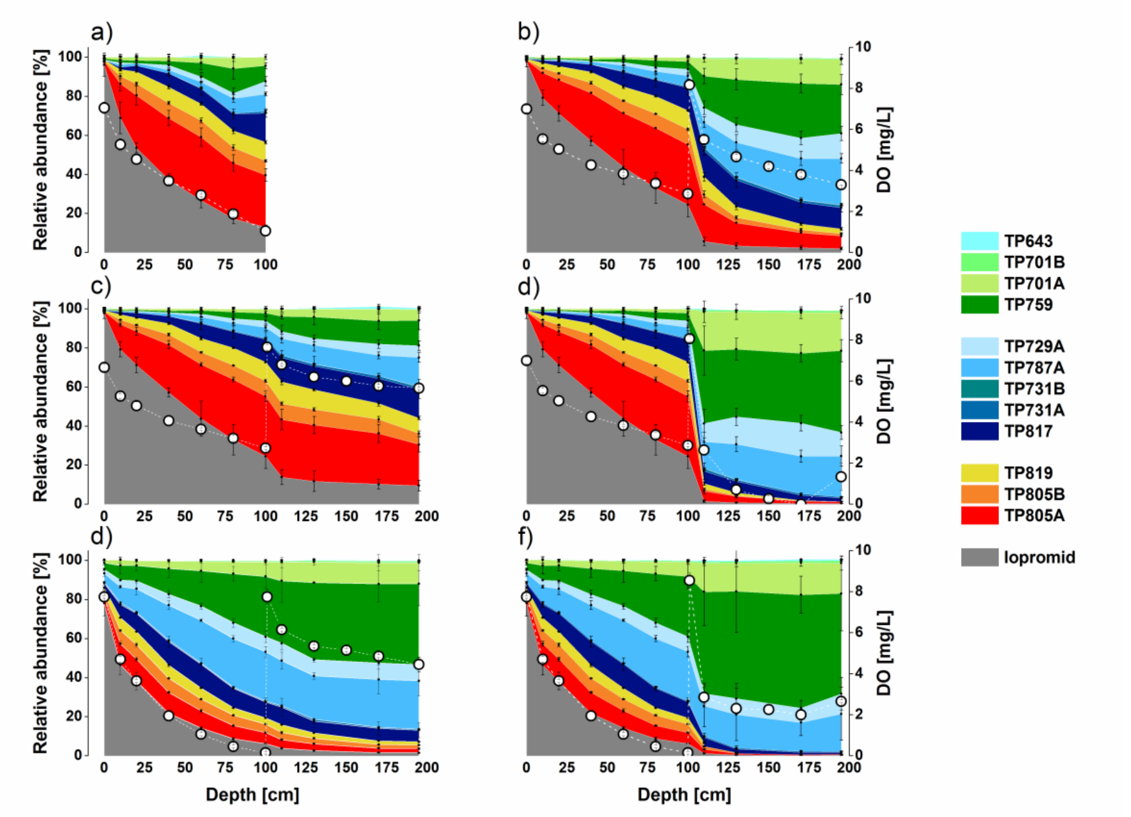

Figure SI-13: Relative abundances of iopromide, iopromide transformation products and DO concentration in column systems as a function of column depths during first (a) A2; b) A1+S2; c) A1+S1; d) A1+S3) and second experimental campaign (e) A1+S1; f) A1+S3).

Table SI-14: Detailed summary of mean iopromide and iopromide transformation product concentrations with standard deviations (SD) in nmol/L for all sampling ports during the first and second experimental campaign.

	Iopromide			**TP805A**			**TP805B**			**TP819**		
	Mean	**SD**	**n**	**Mean**	**SD**	**n**	**Mean**	**SD**	**n**	**Mean**	**SD**	**n**
First experimental campaign												
A2_influent	10.5	4.5	5	0.3	0.2	4	0.2	0.0	2	0.2	0.0	2
A2_1	7.9	0.7	3	2.0	0.6	3	0.5	0.2	3	0.4	0.1	3
A2_2	5.9	0.5	3	3.0	0.6	3	0.7	0.1	3	0.7	0.1	3
A2_3	4.2	0.4	3	3.6	0.5	3	0.9	0.1	3	0.9	0.2	3
A2_4	3.1	0.3	3	3.8	0.4	3	1.0	0.1	3	1.0	0.1	3
A2_5	2.2	0.2	3	3.6	0.3	3	1.0	0.1	3	1.1	0.1	3
A2_effluent	1.7	0.7	5	3.5	1.4	5	1.0	0.3	5	1.2	0.5	5
A1_influent	36.5	4.1	5	0.3	0.3	5	0.2	0.0	2	0.5	0.1	3
A1_1	27.8	3.7	3	4.4	0.1	3	0.8	0.1	3	0.9	0.1	3
A1_2	24.8	3.4	3	6.0	0.1	3	1.2	0.1	3	1.3	0.1	3
A1_3	16.9	5.7	3	7.1	1.9	3	1.5	0.4	3	1.6	0.4	3
A1_4	14.3	3.4	3	9.0	0.2	3	2.1	0.1	3	2.3	0.2	3
A1_5	10.3	2.4	3	9.7	0.4	3	2.3	0.1	3	2.8	0.1	3
A1_effluent	7.8	2.1	5	9.8	1.2	5	2.5	0.3	5	3.1	0.2	5
S1_1	4.9	1.2	3	10.7	2.1	3	2.9	0.5	3	4.0	0.4	3
S1_2	4.2	1.1	3	10.6	0.8	3	2.9	0.2	3	3.8	0.6	3
S1_3	3.2	1.3	3	8.2	2.7	3	2.3	0.8	3	2.6	0.8	3
S1_effluent	3.2	0.7	5	7.0	1.0	5	1.9	0.3	5	2.6	0.5	5
S2_1	1.7	0.6	3	5.8	1.5	3	1.5	0.5	3	2.8	0.6	3
S2_2	1.1	0.4	3	3.6	1.0	3	0.8	0.3	3	1.7	0.4	3
S2_3	0.8	0.3	3	2.5	0.8	3	0.5	0.2	3	1.0	0.2	3
S2_effluent	0.6	0.2	5	2.0	0.6	5	0.4	0.1	5	0.8	0.2	5
S3_1	0.5	0.2	3	1.7	0.5	3	0.4	0.1	3	0.9	0.3	3
S3_2	0.3	0.0	3	1.1	0.3	3	0.2	0.1	3	0.5	0.1	3
S3_3	0.1	0.0	3	0.4	0.1	3	< BG	-	0	0.1	0.0	3
S3_effluent	0.2	0.2	5	0.4	0.1	5	< BG	-	0	< BG		0
Second experimental campaign												
A1_influent	46.5	1.1	2	1.9	0.4	2	1.3	0.6	2	1.5	0.4	2
A1_1	21.0	0.5	2	4.9	0.1	2	3.1	0.5	2	3.0	0.4	2
A1_2	17.6	1.3	2	5.2	0.3	2	3.4	0.3	2	3.1	0.1	2
A1_3	9.2	0.3	2	4.5	0.3	2	3.0	0.3	2	2.9	0.1	2
A1_4	5.8	0.4	2	3.6	0.0	2	2.5	0.4	2	2.3	0.2	2
A1_5	3.9	0.4	2	3.0	0.4	2	2.4	0.3	2	1.7	0.3	2
A1_effluent	2.9	0.2	4	2.6	0.2	4	2.0	0.1	4	1.5	0.1	4
S1_1	1.7	0.1	2	1.9	0.1	2	1.6	0.0	2	1.8	0.3	2
S1_2	1.3	0.1	2	1.7	0.2	2	1.4	0.1	2	1.4	0.3	2
S1_3	0.8	0.0	2	1.1	0.1	2	0.9	0.0	2	0.9	0.1	2
S1_effluent	0.8	0.0	2	1.1	0.1	2	0.9	0.1	2	0.9	0.0	2
S3_1	0.6	0.1	2	1.0	0.0	2	0.7	0.0	2	0.9	0.0	2
S3_2	0.3	0.0	2	0.4	0.0	2	0.2	0.0	2	< BG	-	0
S3_3	0.1	0.0	2	0.2	0.0	2	< BG	-	0	< BG	-	0
S3_effluent	0.2	0.1	2	0.2	0.1	2	< BG	-	0	< BG	-	0

	TP817			**TP787A**			**TP731A**			**TP731B**			**TP729A**		
	Mean	**SD**	**n**	**Mean**	**SD**	**n**	**Mean**	**SD**	**n**	**Mean**	**SD**	**n**	**Mean**	**SD**	**n**
First experimental campaign															
A2_influent	< BG	-	0	< BG	-	0	< BG	-	0	< BG	-	0	< BG	-	0
A2_1	0.5		1	0.5	-	1	< BG	-	0	< BG	-	0	0.4	-	1
A2_2	0.5	0.0	2	0.5	-	1	< BG	-	0	< BG	-	0	< BG	-	0
A2_3	0.8	0.1	3	0.6	-	1	< BG	-	0	< BG	-	0	0.4	0.0	2
A2_4	0.9	0.3	3	0.6	0.3	2	0.1	-	1	< BG	-	0	0.5	0.1	2
A2_5	1.1	0.3	3	1.0	0.3	3	0.1	-	1	< BG	-	0	0.5	0.2	2
A2_effluent	2.0	0.9	5	1.2	0.4	5	0.2	0.1	3	< BG	-	0	0.9	0.5	5
A1_influent	< BG	-	0	0.4	-	1	< BG	-	0	< BG	-	0	< BG	-	0
A1_1	0.6	0.0	2	0.5	-	1	< BG	-	0	< BG	-	0	< BG	-	0
A1_2	0.9	0.1	3	0.6	-	1	< BG	-	0	< BG	-	0	0.4	-	1
A1_3	1.1	0.3	3	0.7	0.3	2	< BG	-	0	< BG	-	0	0.4	-	1
A1_4	2.4	1.0	3	1.0	0.5	3	0.2	0.1	2	< BG	-	0	0.8	0.1	2
A1_5	2.6	1.0	3	1.3	0.5	3	0.2	0.1	2	< BG	-	0	1.0	0.5	2
A1_effluent	3.5	1.0	5	1.9	0.5	5	0.2	0.1	4	< BG	-	0	1.2	0.5	4
S1_1	4.4	1.2	3	3.1	1.0	3	0.4	0.2	3	0.1	-	1	2.1	0.6	2
S1_2	4.6	2.1	3	3.7	1.6	3	0.4	0.1	3	0.1	-	1	1.3	0.8	3
S1_3	4.0	0.9	3	3.3	0.3	3	0.4	0.1	3	< BG	-	0	1.7	0.5	3
S1_effluent	4.6	2.0	5	5.0	0.9	5	0.3	0.1	5	0.1	0.0	5	1.9	0.9	5
S2_1	4.1	0.6	3	3.9	1.0	3	0.5	0.2	3	0.1	0.0	2	2.3	1.0	3
S2_2	4.2	1.1	3	5.5	1.3	3	0.4	0.0	3	0.1	0.0	2	2.8	1.1	3
S2_3	3.6	0.8	3	7.0	1.3	3	0.4	0.1	3	0.1	0.0	2	3.5	1.2	3
S2_effluent	3.2	0.9	5	7.3	1.2	5	0.4	0.1	5	0.1	0.0	5	3.9	1.1	5
S3_1	2.1	1.2	3	4.6	1.3	3	0.4	0.1	3	0.1	0.0	3	3.1	2.2	3
S3_2	2.0	0.4	3	6.1	1.2	3	0.3	0.1	3	0.1	-	1	4.8	1.4	3
S3_3	0.9	0.1	3	6.6	0.9	3	0.3	0.1	3	< BG	-	0	5.9	1.3	3
S3_effluent	0.8	0.3	5	9.3	2.3	5	0.2	0.1	5	0.1	-	1	5.2	1.6	5
Second experimental campaign															
A1_influent	1.4	0.6	2	2.8	1.1	2	0.3	-	1	< BG	-	0	1.2	0.4	2
A1_1	3.0	0.3	2	3.8	0.9	2	0.4	-	1	< BG	-	0	1.5	0.2	2
A1_2	4.3	0.0	2	5.6	1.6	2	0.3	0.0	2	< BG	-	0	1.9	0.1	2
A1_3	5.0	0.7	2	7.7	1.7	2	0.3	0.0	2	< BG	-	0	2.3	0.6	2
A1_4	5.0	0.8	2	9.0	0.7	2	0.2	0.1	2	< BG	-	0	2.9	0.3	2
A1_5	4.5	0.3	2	11.4	2.7	2	0.3	0.0	2	< BG	-	0	3.6	0.4	2
A1_effluent	3.7	0.7	4	11.8	1.9	4	0.3	0.1	4	< BG	-	0	3.6	1.1	4
S1_1	3.8	1.4	2	10.2	0.2	2	0.3	0.1	2	< BG	-	0	3.8	0.8	2
S1_2	3.0	0.1	2	11.3	1.4	2	0.5	-	1	< BG	-	0	4.3	1.4	2
S1_3	2.9	1.4	2	11.4	2.9	2	0.3	0.2	2	< BG	-	0	3.9	1.3	2
S1_effluent	2.9	1.5	2	12.3	2.0	2	0.3	0.2	2	< BG	-	0	4.1	1.2	2
S3_1	1.3	0.8	2	7.1	4.1	2	0.3	0.1	2	< BG	-	0	2.9	2.1	2
S3_2	1.0	0.8	2	9.3	6.0	2	0.3	0.2	2	< BG	-	0	4.4	3.7	2
S3_3	0.6	-	1	8.4	3.3	2	0.3	0.1	2	< BG	-	0	4.3	1.9	2
S3_effluent	0.5	-	1	10.4	5.4	2	0.3	0.2	2	< BG	-	0	5.5	3.5	2

	TP759			**TP701A**			**TP701B**			**TP643**		
	Mean	**SD**	**n**	**Mean**	**SD**	**n**	**Mean**	**SD**	**n**	**Mean**	**SD**	**n**
First experimental campaign												
A2_influent	0.4	0.0	2	0.2	0.1	3	< BG	-	0	< BG	-	0
A2_1	0.5	-	1	0.3	0.2	2	< BG	-	0	< BG	-	0
A2_2	0.5	-	1	0.3	0.2	2	< BG	-	0	< BG	-	0
A2_3	0.8	-	1	0.2	0.2	3	< BG	-	0	< BG	-	0
A2_4	0.9	0.5	3	0.3	0.3	3	0.1	-	1	< BG	-	0
A2_5	1.6	0.8	3	0.7	0.3	3	0.1	-	1	< BG	-	0
A2_effluent	1.2	0.2	5	0.7	0.2	5	< BG	-	0	< BG	-	0
A1_influent	0.5	0.1	2	0.3	0.1	3	< BG	-	0	< BG	-	0
A1_1	0.7	-	1	0.4	0.3	2	< BG	-	0	< BG	-	0
A1_2	0.7	-	1	0.3	0.2	2	< BG	-	0	< BG	-	0
A1_3	0.9	-	1	0.3	0.1	3	< BG	-	0	< BG	-	0
A1_4	0.6	0.3	3	0.4	0.2	2	< BG	-	0	< BG	-	0
A1_5	1.1	0.8	3	0.5	0.3	3	0.1	-	1	< BG	-	0
A1_effluent	1.6	0.9	5	0.7	0.4	5	0.1	0.0	2	< BG	-	0
S1_1	2.9	1.0	3	1.4	0.8	3	0.1	-	1	0.2	-	1
S1_2	4.3	2.2	3	1.6	0.8	3	0.1	0.0	2	< BG	-	0
S1_3	3.6	1.0	3	1.8	0.6	3	0.1	0.0	2	< BG	0.0	0
S1_effluent	5.3	2.4	5	2.2	0.9	5	0.1	0.0	4	0.2	0.0	2
S2_1	5.0	1.5	3	2.8	0.7	3	0.1	0.0	2	0.2	0.0	2
S2_2	7.2	1.9	3	3.3	1.0	3	0.2	0.1	3	0.2	0.0	2
S2_3	9.2	1.5	3	4.1	0.8	3	0.2	0.1	3	0.2	0.1	3
S2_effluent	9.1	2.5	5	4.6	1.1	5	0.2	0.1	5	0.2	0.1	5
S3_1	12.9	4.9	3	6.8	2.3	3	0.3	0.1	3	0.3	0.1	3
S3_2	11.8	2.1	3	6.5	1.4	3	0.3	0.0	3	0.3	0.1	3
S3_3	12.4	1.7	3	7.2	1.2	3	0.3	0.1	3	0.4	0.1	3
S3_effluent	19.4	2.8	5	9.1	1.5	5	0.5	0.1	5	0.4		5
Second experimental campaign												
A1_influent	2.0	0.7	2	0.9	0.2	2	0.1	-	1	< BG	-	0
A1_1	3.6	2.4	2	1.4	0.9	2	0.1	-	1	< BG	-	0
A1_2	3.7	1.5	2	1.1	0.4	2	0.1	-	1	< BG	-	0
A1_3	5.7	2.4	2	1.6	0.5	2	0.1	0.0	2	< BG	-	0
A1_4	7.6	3.3	2	2.0	0.6	2	0.1	0.0	2	0.2	-	1
A1_5	11.6	3.7	2	2.8	0.3	2	0.2	0.1	2	0.2	-	1
A1_effluent	14.7	4.1	4	3.5	1.0	4	0.2	0.1	4	0.2	0.0	4
S1_1	14.7	7.4	2	4.4	1.9	2	0.3	0.2	2	0.2	0.0	2
S1_2	20.2	4.1	2	5.5	1.9	2	0.4	0.2	2	0.2	0.1	2
S1_3	19.2	5.3	2	5.1	2.2	2	0.4	0.1	2	0.2	0.1	2
S1_effluent	21.5	8.9	2	5.7	3.0	2	0.4	0.1	2	0.2	0.1	2
S3_1	26.0	12.2	2	7.2	1.7	2	0.4	0.1	2	0.3	0.0	2
S3_2	33.2	18.1	2	8.6	2.6	2	0.5	0.1	2	0.3	0.0	2
S3_3	34.1	7.9	2	9.6	1.7	2	0.6	0.0	2	0.5	0.0	2
S3_effluent	31.4	18.1	2	9.4	4.2	2	0.7	0.2	2	0.4	0.1	2

10.7 Supplementary information for Chapter 8

Investigating synergies in sequential biofiltration-based hybrid systems for the enhanced removal of trace organic chemicals from wastewater treatment plant effluents

Supplementary information

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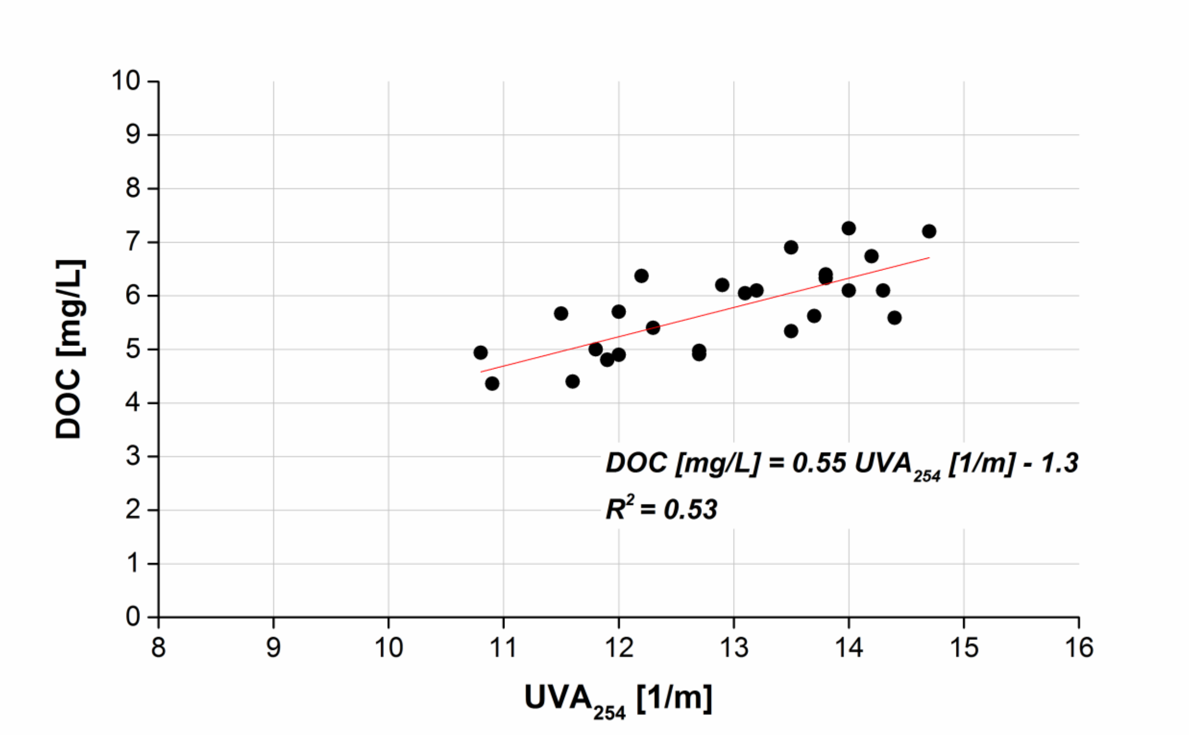

Figure SI-14: DOC/UVA$_{254}$ correlation for samples taken from column A effluent (n = 25). Correlation was used to estimate DOC values in column A effluent prior to pilot-scale ozonation.

Table SI-15: Limits of quantitation (LOQ), average concentrations with standard deviations in wastewater treatment plant effluent and number of detections above LOQ and 3.5 x LOQ during 10 sampling campaigns. Second-order rate constants for the reaction with ozone (k_{O3}) and hydroxyl radicals (k_{OH}).

Compound	LOQ [ng/L]	c_0 [ng/L]	Std. dev. [ng/L]	Occurrence above LOQ	Occurrence above 3.5 x LOQ	k_{O3} [M^{-1} s^{-1}]	k_{OH} [M^{-1} s^{-1}]
4-Formylaminoantipyrine (4-FAA)	10	670	260	10	10	n/a	n/a
Atenolol	10	30	10	10	2	1.7 x 10^{3} [a]	6.3 x 10^{5} [c]
Antipyrine	10	30	10	10	2	6.2 x 10^{5} [j]	8.9 x 10^{9} [k]
Benzotriazole	50	5,880	1,190	10	10	2.4 x 10^{2} [g]	7.6 x 10^{9} [i]
Caffeine	50	170	90	4	2	2.5 x10^{4} [j]	6.4 x 10^{9} [l]
Carbamazepine	5	410	40	10	10	3.0 x 10^{5} [a]	8.8 x 10^{9} [b]
Citalopram	5	160	60	10	10	n/a	n/a
Climbazole	5	90	20	10	10	n/a	n/a
Diclofenac	5	1,440	450	10	10	10^{6} [a]	7.5 x 10^{9} [b]
Gabapentin	2.5	1,530	420	10	10	2.2 x 10^{2} [g]	9.1 x 10^{9} [g]
Iopromide	50	90	40	4	1	< 1 [b]	3.3 x 10^{9} [b]
Metoprolol	2.5	280	60	10	10	2.0 x 10^{3} [g]	7.3 x 10^{9} [c]
Phenytoin	5	6	1	4	0	< 10 [a]	6.3 x 10^{9} [d]
Primidone	10	50	10	10	10	< 10 [a]	6.7 x 10^{9} [e]
Sotalol	5	60	20	10	10	1.9 x 10^{4} [g]	10^{10} [g]
Sulfamethoxazole	5	180	70	10	10	5.7 x 10^{5} [a]	5.5 x 10^{9} [b]
Tris(2-chloroethyl) phosphate (TCEP)	50	118	40	8	2	< 1 [a]	5.6 x 10^{8} [g]
Tramadol	5	210	70	10	10	4.0 x 10^{3} [g]	6.3 x 10^{9} [h]
Venlafaxine	2.5	370	60	10	10	8.5 x 10^{3} [g]	10^{10} [g]
Trimethoprim	5	40	30	10	8	2.7 x 10^{5}	6.9 x 10^{9} [f]
Valsartanic acid	5	3,440	1,330	10	10	n/a	7.9 x 10^{9} [k]

[a] Lee et al. (2013); [b] Huber et al. (2003); [c] Benner et al. (2008); [d] Yuan et al. (2009); [e] Real et al. (2009); [f] Watts and Linden (2009); [g] Lee et al. (2014); [h] Zimmermann et al. (2012); [i] Naik and Moorthy (1995); [j] Javier Rivas et al. (2011); [k] Wols et al. (2014); [l] Wols and Hofman-Caris (2012)

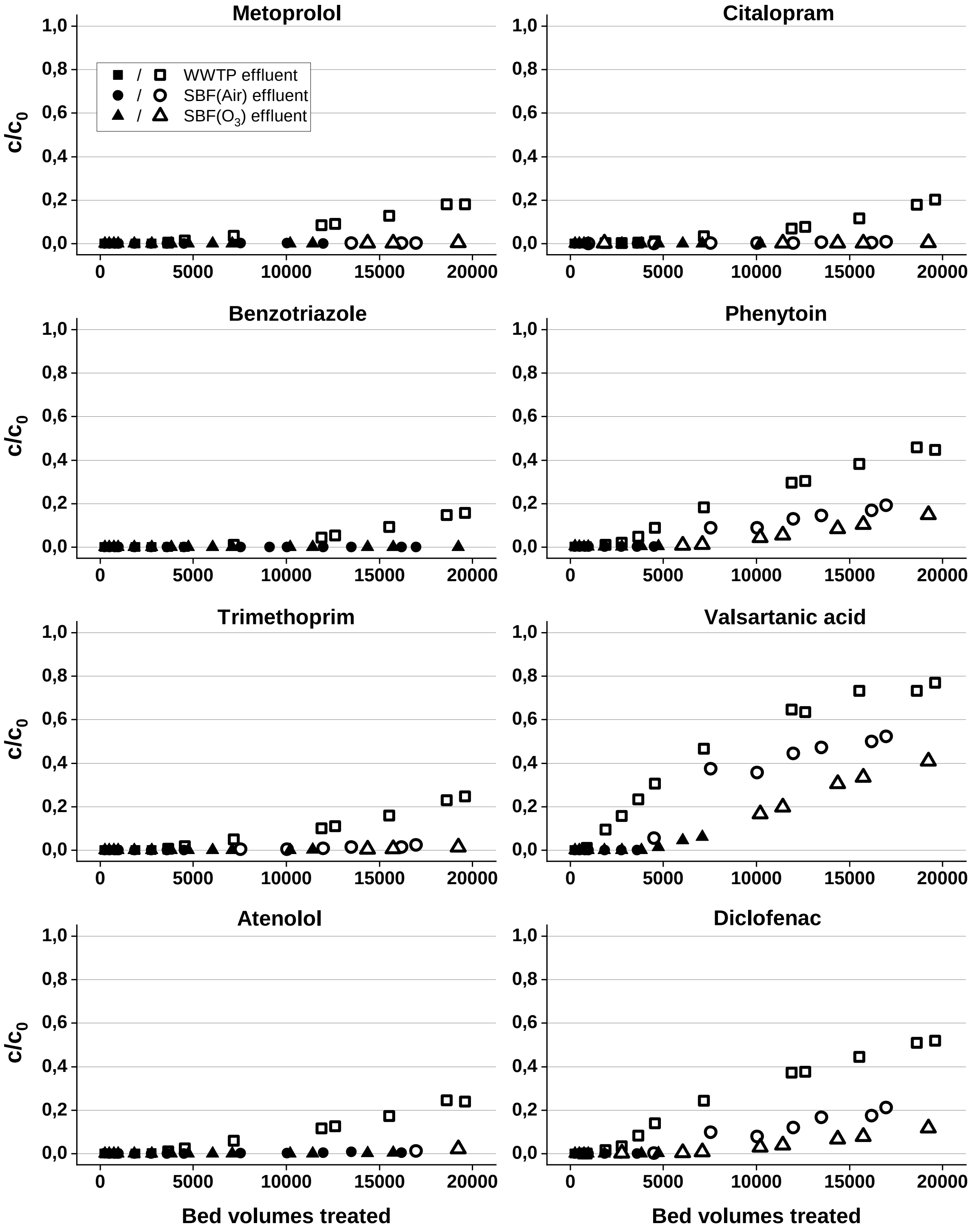

Figure SI-15: Breakthrough curves for indicator compounds from RSSCTs fed with WWTP effluent and effluent of systems SBF(Air) and SBF(O$_3$). Full symbols indicate values < LOQ, empty values indicate values > LOQ.

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Introducing sequential biofiltration hybrid systems for enhanced removal of chemicals of emerging concern and pathogens during water reclamation

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Abstract

Sequential biofiltration (SBF) aims to establish oxic and oligotrophic conditions which were reported to be favourable for improved biotransformation of moderately biodegradable chemicals of emerging concern (CECs), disregarding highly persistent compounds (Regnery et al., 2015, Müller et al., 2017). The efficacy of granular activated carbon (GAC) in fixed-bed adsorbers for the removal of a wide range of CECs has been demonstrated in many studies. However, poor adsorbability of polar compounds and competitive adsorption of effluent organic matter (EfOM) are considered drawbacks (Summers et al., 2013). To overcome these limitations of the two individual treatment options, hybrid systems combining SBF with subsequent GAC filtration are proposed as an advanced above-ground treatment process suitable for water reclamation schemes. Findings revealed that biodegradation during SBF achieved EfOM reduction and a partial removal of polar, moderately degradable CECs. Results from GAC rapid small scale column tests (RSSCTs) underlined the efficacy of GAC adsorbers for the attenuation of a wide range of CECs. Substantially later breakthrough of various CECs was observed in RSSCTs fed with SBF treated secondary effluent suggesting that extended bed volumes could be achieved. Isotherms indicate increased adsorption capacity for some CECs in the secondary effluent after SBF treatment. Results of an adsorption analysis indicate that SBF treatment does not substantially change the adsorbability of the EfOM present but reduces the total amount, resulting in reduced competitive adsorption during adsorptive treatment. Results of this study indicate that making use of synergies in sequential treatment steps is a viable option to increase performance and cost-effectivity of advanced water treatment systems in water reclamation schemes.

Introduction

The wide-spread occurrence of contaminants of emerging concern (CECs), such as pharmaceutical residues, industrial chemicals and personal care products at low concentrations in water bodies, has been subject of extensive studies in the field of water research (Benotti et al., 2009; Ternes, 2007; Dong et al., 2015). While ecotoxicological effects were reported by different authors, acute toxic effects on human health seem unlikely (Schriks et al., 2010; National Research Council, 2012). However, little is known about the potential risk arising from long-term exposures to trace amounts of many different substances (Cuklev et al., 2011; Stuart et al., 2012; Brodin et al., 2013; Wilkinson et al., 2016). With respect to indirect potable reuse (IPR) scenarios in which recycled water is used for drinking water augmentation, this potential threat to public health is gaining importance (National Research Council, 2012).

Wastewater treatment plants (WWTPs) are known to be major point sources for the discharge of CECs into the aquatic environment (Dong et al., 2015; Ternes, 2007). Conventional wastewater treatment commonly employs activated sludge processes to achieve biological removal of bulk organic parameters and nutrients. However, these processes often fall short in efficiently mitigating CECs which often exhibit a high degree of persistence (Joss et al., 2006; Vieno et al., 2007; Falås et al., 2016). To allow for an enhanced CEC removal various treatment options are being considered, such as adsorptive, oxidative or separation processes. However, increasing costs of operation, residual generation, reduced efficiencies due to the high amount of organic matter present, or the formation of undesired by-products must be considered substantial drawbacks of these technologies (von Gunten, 2003; Zietzschmann et al., 2014b).

In the light of often unsatisfactory CEC removal during conventional biological wastewater treatment, additional biological systems as advanced treatment steps have drawn less attention. Recent studies, however, identified different key parameters which were found suitable to foster the establishment of a microbial community capable of increased CEC degradation. Many authors described oxic conditions to be favourable for an improved biological removal of CECs (Massmann et al., 2008; Baumgarten et al., 2011; Regnery et al., 2015b) while other studies depicted oligotrophic conditions as beneficial (Li et al., 2012, 2013, 2014; Alidina et al., 2014). The groundwater recharge concept of sequential managed aquifer recharge technology (SMART) aims to put these findings into practice by using a sequential infiltration approach to establish oxic and oligotrophic conditions (Regnery et al., 2016). Regnery et al. (2016) reported a significantly improved and accelerated removal of various moderately degradable CECs during SMART compared to conventional managed aquifer recharge (MAR) processes. The successful optimization of natural treatment systems motivated the attempt to establish a biological above-ground treatment system which efficiently exploits the biological potential for CEC mitigation while drastically reducing required hydraulic retention times. The concept of above-ground sequential biofiltration (SBF) represents a promising option for an enhanced biological removal of moderately biodegradable CECs (Müller et al., 2017).

While SBF is a promising approach for the improved removal of moderately biodegradable CECs, it is certainly not sufficient for the high hygienic requirements a treatment train needs to fulfil in IPR applications. To achieve highly reliable and robust treatment processes, multi-barrier approaches need to be applied to generate a water quality that is protective to public health (National Research Council, 2012; Gerrity et al., 2013). Water reclamation with the purpose of IPR demands highly effective above-ground treatment of secondary effluent prior to MAR by surface spreading or direct injection. As infectious diseases caused by waterborne pathogens pose the highest risk for human health, efficient and reliable removal of pathogens is paramount (National Research Council, 2012).

The need for multi-barrier approaches in IPR schemes due to the stringent hygienic requirements, allows for a further development of the SBF system. By combining SBF with other advanced treatment technologies, process efficiency is expected to be increased substantially also for the removal of CECs. The combination of different treatment technologies in a hybrid process unit aims for maximized additive and synergistic effects between the individual technologies. By optimizing the sequence and operational settings of selected technologies, hybrid systems present a viable alternative to single technology-based advanced treatment by profiting from increased process efficiency, sustainability, and lower costs of operation (Gerrity et al., 2013; Sudhakaran et al., 2013; Zhang et al., 2016).

Materials and methods

The SBF system consisted of a two-stage biofiltration train with filter columns operated in series under saturated top-down flow conditions. A backwashable first filter stage (FS1; filter bed length (l) = 1 m, inner diameter (ID) = 0.15 m) used anthracite as filter material with grain sizes ranging from 1.4 to 2.5 mm (Everzit N type II, Evers GmbH, Germany). Second stage filter columns (FS2; l = 0.95 m, ID = 0.10 m) used technical sand with grain sizes ranging from 0.2 to 1.0 mm (Euroquarz GmbH, Germany). An intermediate aeration basin resupplied oxygen to the water treated in FS1 using compressed air. EBCTs of 90 and 200 min were used in FS1 and FS2, respectively. The system was fed with fully nitrified secondary effluent from a wastewater treatment plant located in Garching, Germany. Peristaltic pumps delivered the water to the column systems.

RSSCTs were conducted to investigate potential changes in the breakthrough behavior of indicator CECs due to changes in EfOM concentration during SBF. For design and operation of the RSSCT columns the constant diffusivity (CD) approach was used (Crittenden et al., 1991). GAC (Chemviron CycleCarb 401) was grinded and sieved to obtain an average particle diameter of 250 µm. RSSCT columns were built using glass columns (height 30 cm, inner diameter 1 cm) with a GAC bed height of 18 cm and operated at an EBCT of 0.5 min. Assuming validity of the CD-RSSCT approach, the constructed RSSCT should mimic the performance of a full-scale adsorber using GAC with a particle diameter of 1,500 µm, a bed height of about 1 m, and an EBCT of 16.5 min. To compare CEC breakthrough behaviour in the different water matrices, two RSSCT columns were operated in parallel with collected secondary effluent and the corresponding effluent of the SBF setup.

Batch tests with powdered activated carbon (PAC) and secondary effluent with and without pre-treatment by SBF were performed to determine dissolved organic carbon (DOC) and CEC isotherms for the different water matrices. Secondary effluent and corresponding SBF effluent were collected for the experiments. CEC concentrations in the samples were fortified between 0.5 and 2 µg/L by spiking aqueous CEC stock solutions into the collected raw waters. For the batch tests, GAC (Chemviron CycleCarb 401) was grinded and sieved to achieve PAC with particle diameters of less than 25 µm. Batch samples with varying PAC concentrations (2, 4, 6, 8, 10, 25, 50, 100, 150 mg/L) were prepared. After terminating the experiment, samples were filtered using 0.45 µm syringe filters to remove PAC.

Samples were analysed for the organic bulk parameters DOC, UV absorbance at 254 nm (UVA_{254}), and for a set of indicator CECs. To determine the effect of SBF on the EfOM adsorbability, an adsorption analysis was carried out using the modelling software AdsANA 1.5 (Worch, 2016).

Results and discussion

Results of the study revealed that SBF can achieve substantial reduction of EfOM due to microbial activity in the filter system which is indicated by the mean reduction of DOC and UVA_{254} (32 ± 11 % (n = 3) and 13 ± 4 % (n = 6), respectively). Different DOC and UVA_{254} feed values and removal efficiencies during the experiment indicate the presence of varying amounts of biologically degradable EfOM in the secondary effluent batches fed to the system (data not shown). The breakthrough curves for DOC and UVA_{254} of both columns show very similar patterns (Figure 1), only the very beginning of the operation is characterized by slightly higher removal of DOC and UVA_{254} in the RSSCT fed with SBF effluent. A difference between the breakthrough curves of DOC and UVA_{254} in both systems could be observed in the immediate breakthrough of a non-adsorbable DOC fraction at the beginning of the operation whereas UVA_{254} removal is close to 100 %. This can be explained by higher adsorption affinities of compounds with aromatic moieties which are detected by UVA_{254}. Differences between the two DOC breakthrough curves of the compared RSSCTs indicate that the portion of non-adsorbable DOC constituents decreased during SBF resulting in a lower DOC amount that immediately breaks through the filter. This assumption is supported by the DOC isotherms acquired in secondary effluent and SBF effluent and the results of adsorption analyses conducted using the software AdsAna 1.5 (Figure 2). For modelling DOC isotherms, four DOC fractions with different adsorbabilities were defined. The fractions are characterized by different adsorbabilities with adsorption coefficients ranging from not (K: 0), weakly (K: 30), moderately (K: 60) to strongly adsorbing (K: 180). The DOC isotherm indicates an improved adsorbability of the remaining DOC in the SBF effluent which is indicated by higher loadings at comparable equilibrium concentrations. The shift in adsorbability seems to have mainly been caused by the removal of non-adsorbable DOC constituents. This is also indicated by the similar shape of both isotherms, only shifted along the x-axis. An explanation for this observation might be that non-adsorbable DOC is made up of rather polar organic substances such as organic acids which are easily biodegradable and removed during biofiltration. The adsorption analysis reveals that SBF does not result in a substantial change in the composition of adsorbable DOC fractions but mainly achieves a reduction of organic background constituents across different fractions of adsorbability. According to the adsorption analysis, the sum of the concentration of adsorbable DOC-fractions (K: 30, 60, 180) decreased by more than 30 %.

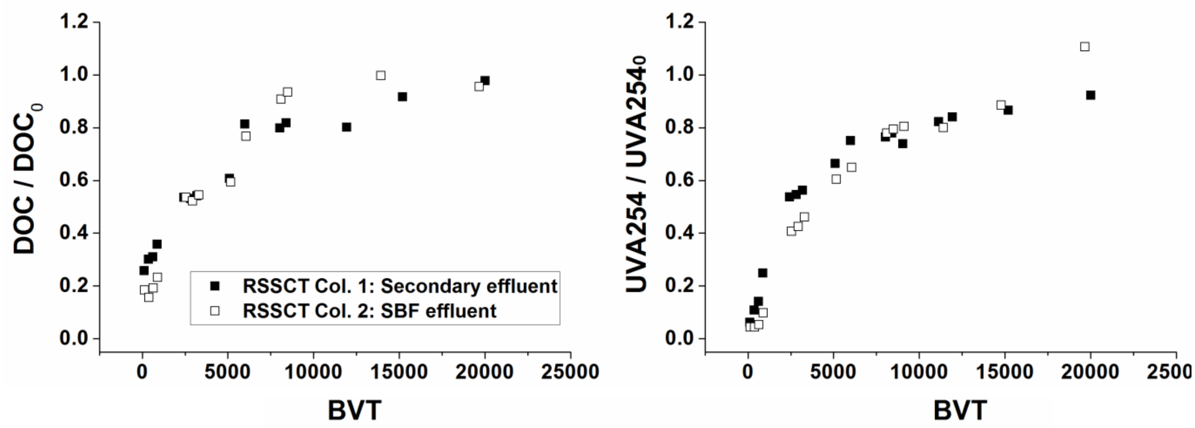

Figure 1: RSSCT breakthrough curves normalized to influent values for DOC (DOC_0: RSSCT fed with secondary effluent: 11.3 ± 2.1 mg/L and SBF efluent: 7.7 ± 1.9 mg/L (n = 3)) and UVA_{254} (UVA_{2540}: RSSCT fed with secondary effluent: 20.9 ± 7.8 1/m and SBF effluent: 18.0 ± 6.5 1/m (n = 6)) displayed as a function of number of bed volumes treated (BVT).

Regarding biological CEC removal during SBF, compound specific differences were found. While the treatment proved to be effective for the removal of some compounds, others exhibit high persistence in the operated systems. The compounds acesulfame and gabapentin were identified as well biodegradable and were removed by 91 ± 5 % and 71 ± 16 %, respectively. Other compounds showed only limited (benzotriazole 23 ± 23 %) or even no removal (carbamazepine and venlafaxine, -3 ± 10 % and -2 ± 14 %) during SBF.

Findings from GAC-RSSCT experiments underline the efficacy of GAC adsorbers for the attenuation of many different CECs in secondary effluent, both, untreated and pre-treated by SBF, especially at the beginning of the operation. Figure 3 exemplarily shows CEC breakthrough curves for the compounds carbamazepine, benzotriazole and venlafaxine. Unlike a typical sigmoidal shape, the curves shown exhibit a decreasing slope without reaching 100 % of the inlet concentration. This can most likely be attributed to changes in the feed water matrix due to the fact that three different batches of secondary effluent had to be used to feed the SBF system during the experiment. By changing the water matrix composition, adsorption and desorption dynamics might have been influenced resulting in the untypical shape of the determined breakthrough curves. The comparison of breakthrough curves in both RSSCT columns indicated beneficial effects of a SBF pre-treatment on the breakthrough behaviour of all compounds under investigation. Compared to the RSSCT fed with untreated secondary effluent, SBF pre-treatment resulted in an estimated increase of more than 50 % of bed volumes treated (BVT) until a breakthrough of 5 % was found in the column effluent.

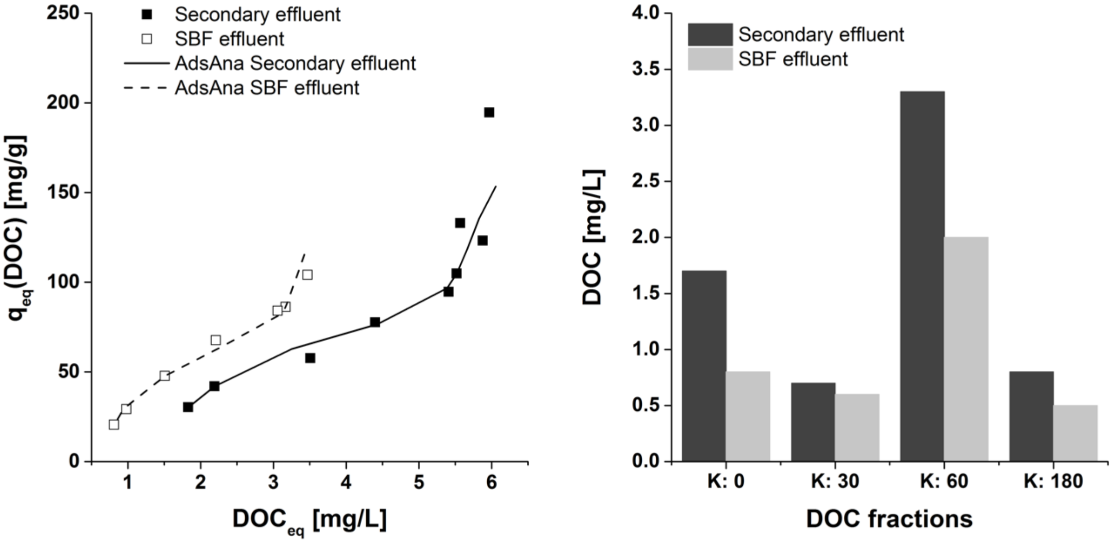

Figure 2: DOC isotherms in secondary effluent and SBF effluent determined experimentally and modelled with AdsAna 1.5 (left side); DOC fractions in secondary effluent and SBF effluent determined by adsorption analysis with AdsAna 1.5 (c_0 (Sec. effl.): 6.4 mg/L DOC, c_0(SBF): 3.9 mg/L DOC; adsorption analysis with four DOC-fractions (K: 0, 30, 60, 180, n constant at 0.22)).

The removal of easily degradable EfOM during biofiltration is most likely responsible for the prolonged GAC filter bedlifes. The determination of CEC isotherms in secondary effluent and SBF effluent supports this assumption by revealing higher equilibrium adsorption capacities for several CECs in SBF effluent compared to isotherms acquired in secondary effluent. This is exemplarily shown for carbamazepine and venlafaxine and is confirmed by the calculation of the Freundlich coefficients for both cases (Figure 3). The improved adsorption capacity in equilibrium due to decreased direct competitive adsorption is believed to be one reason for the observed prolonged GAC filter bedlifes. However, the example of benzotriazole shows that also other mechanisms might be responsible for the observed improvements. Although the comparison of breakthrough curves in the RSSCT experiments indicates improved removal in the RSSCT fed with SBF effluent, this is not reflected in a higher adsorption capacity in equilibrium (Figure 3).

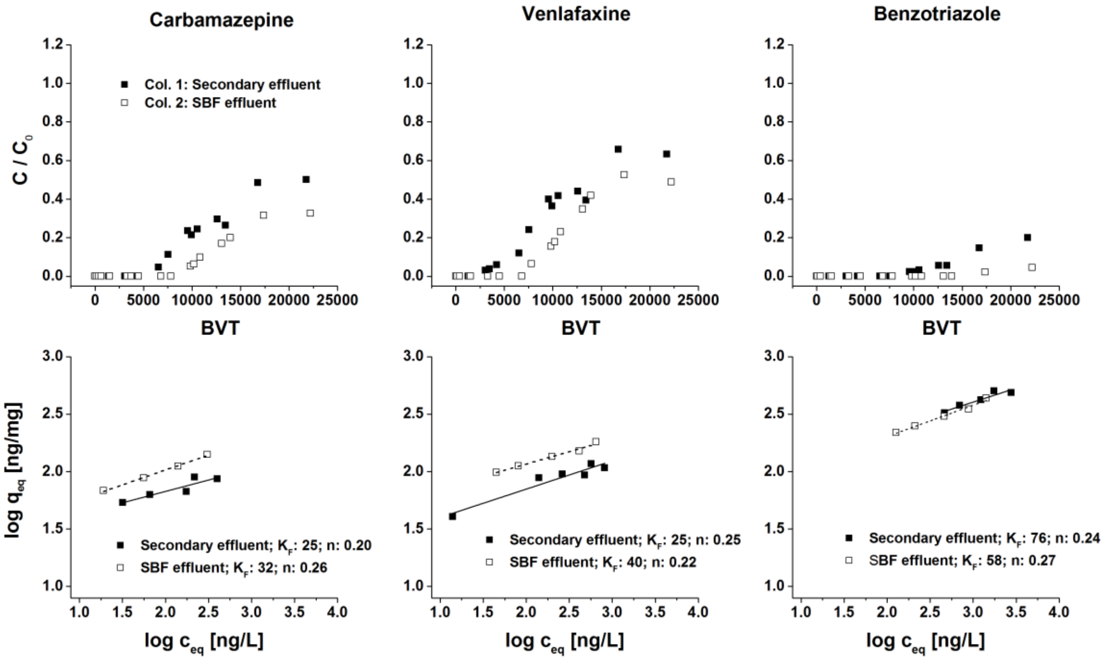

Figure 3: Breakthrough curves from CD-RSSCT experiments (upper row) and isotherms (lower row) for carbamazepine, venlafaxine and benzotriazole in secondary effluent and secondary effluent pre-treated by SBF.

Conclusions

For the combination of SBF with subsequent GAC filtration, promising effects were observed. Compounds that exhibited a high degree of persistence during SBF, such as carbamazepine and venlafaxine, were effectively removed during GAC filtration. Rather polar compounds such as acesulfame or gabapentin, known to exhibit only very limited or even no removal during GAC filtration, might be susceptible to biodegradation during SBF, as shown in this study. The removal of weakly adsorbing compounds during SBF and of persistent but adsorbing compounds in a subsequent GAC filter proves the expected additive effects when combining different treatment technologies. Regarding potential synergies which could lead to an increase in process efficiency, SBF was observed to have a positive effect on the performance of the subsequent GAC filter. Comparing the retention of CECs in the RSSCT fed directly with untreated secondary effluent with the one receiving secondary effluent pre-treated by SBF, prolonged GAC filter bedlifes were observed until breakthrough occurred.

Further studies will focus on additional options for SBF based hybrid systems. Hybrid systems combining SBF with an intermediate ozonation are currently under investigation.

Besides the advanced removal of CECs in these systems, also the mitigation of microbial contaminants such as fecal indicating bacteria and antibiotic resistances will be examined.

Acknowledgments

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