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Impacts of background organic matter on organic micro-pollutant adsorption onto activated carbon

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Abstract

Adsorption using powdered or granular activated carbon (PAC, GAC) is an advanced treatment for the removal of organic micro-pollutants (OMP) from waters like drinking waters (DW) or wastewater treatment plant (WWTP) effluents. Such waters contain background organic matter (BOM) which can adsorb at the same time as OMP. This competitive adsorption adversely affects OMP removals. The present study aims at advancing PAC and GAC laboratory tests for a more profound characterization of competitive adsorption in different waters, and its prediction using different mathematical and analytical tools.

The high and low molecular weight BOM of WWTP effluent were separated using membrane techniques. Then, the respective impacts on OMP adsorption onto PAC were investigated. The low molecular weight (LMW) organics are the most competitive BOM fraction. In miniaturized GAC filters, the concept of rapid small-scale column tests (RSSCT) was used on WWTP effluent. Among the BOM fractions, the LMW organics have the strongest retention and thus adsorption affinity, underlining their competitiveness. Using ozonation prior to PAC, the aromaticity and hydrophobicity of BOM were shown to crucially impact OMP adsorption. The results imply synergies of ozonation prior to activated carbon treatment.

The influence of the water origin on OMP-BOM adsorption competition was tested with PAC on five DW and seven WWTP effluents. High comparability was ensured by adjusting similar concentration ratios of OMP/BOM in all waters (BOM reflected by dissolved organic carbon — DOC). Within both groups of waters (DW or WWTP effluents), respectively, the relationships between the PAC loadings and the OMP liquid phase concentrations were similar (for a given OMP). Thus, BOM from different DW affects OMP adsorption similarly (the analogue applies to WWTP effluents). In the equivalent background compound (EBC) model, the EBC concentrations correlate with the DOC (DW/ WWTP effluents separately) and the LMW organics concentration (all waters together). OMP adsorption in waters excluded from the correlations could be modeled satisfyingly with the DOC or the LMW organics concentration. In further tests with GAC treating DW and WWTP effluent, the breakthrough curves could be superimposed by using the LMW organics throughput. In addition, the GAC capacity is proportional to the respective OMP influent concentration.

In a PAC performance test, the OMP removals from WWTP effluent by eight PAC correlated with the removals of the surrogate parameter UV_{254} absorption, mostly independent of the PAC. The UV_{254} removal also correlated with OMP removals in many other tests of this study. Additional tests were developed for lab-scale investigations of OMP adsorption in multi-stage PAC reuse. A single relationship between the PAC loadings and the liquid phase OMP concentrations appears valid for all stages. Based on this result, a simple modification of the EBC model was developed for assessing the efficiency of PAC reuse.

This study shows the transferability of PAC and GAC adsorption data in different waters. The developed approaches alleviate practical estimations of OMP adsorption in various waters, by using comparatively simple experimental, analytical, and mathematical tools.

Zusammenfassung

Die Adsorption an Pulver- oder granulierten Aktivkohle (PAK, GAK) dient der Entfernung organischer Spurenstoffe aus Wässern wie Trinkwasser (TW) oder Kläranlagenablauf (KAA). Solche Wässer enthalten Hintergrundorganik, die zeitgleich mit den Spurenstoffen adsorbiert. Diese Adsorptionskonkurrenz verschlechtert die Spurenstoff-Entfernung. In der vorliegenden Studie wurden PAK- und GAK-Labormethoden weiterentwickelt, um die Adsorptionskonkurrenz in verschiedenen Wässern zu charakterisieren und mittels mathematischer und analytischer Tools vorherzusagen.

Mittels Membrantechniken wurden höher- und niedermolekulare Hintergrundorganik getrennt. Anschließend wurde der jeweilige Einfluss auf die Spurenstoff-Adsorption an PAK in KAA untersucht. Die niedermolekulare Hintergrundorganik übt die stärkste Adsorptionskonkurrenz aus. In Miniatur-GAK-Filtern wurde das Konzept der *rapid small-scale column tests* (RSSCT) auf KAA angewendet. Rückhalt und somit Adsorptionsaffinität und Konkurrenzfähigkeit sind bei der niedermolekularen Hintergrundorganik am stärksten. Desweiteren wurde per Vor-Ozonung der Einfluss der Hintergrundorganik-Aromatizität und -Hydrophobizität auf die Spurenstoff-Adsorption an PAK gezeigt. Es ergeben sich synergetische Effekte bei einer Ozonung vor Aktivkohleadsorption.

Der Einfluss der Wasserherkunft auf die Adsorptionskonkurrenz zwischen Spurenstoffen und Hintergrundorganik wurde an fünf TW und sieben KAA mittels PAK getestet. Eine hohe Vergleichbarkeit wurde durch ähnliche Verhältnisse an Spurenstoff/Hintergrundorganik gewährleistet (letztere verkörpert per gelösten organischen Kohlenstoff, DOC). Die Zusammenhänge zwischen PAK-Beladung und wässriger Spurenstoff-Konzentration waren in der jeweiligen Wassergruppe (TW, KAA) ähnlich (für den jeweiligen Spurenstoff). Folglich ist die Beeinträchtigung der Spurenstoff-Adsorption durch die Hintergrundorganik verschiedener TW ähnlich (analoges gilt für KAA). Im *equivalent background compound* (EBC) Modell korrelieren die modellierten EBC-Konzentrationen mit dem DOC (separate Korrelationen für TW und KAA) und mit der Konzentration der niedermolekularen Hintergrundorganik (alle Wässer gemeinsam). Die Spurenstoff-Adsorption in von den Korrelationen ausgeschlossenen Wässern konnte mittels DOC oder der Konzentration der niedermolekularen Hintergrundorganik modelliert werden. Ferner konnten die GAK-Durchbruchskurven von Spurenstoffen in TW und KAA per Auftragung über den Durchsatz an niedermolekularer Hintergrundorganik überlagert werden. Außerdem ist die GAK-Kapazität proportional zur jeweiligen Spurenstoff-Zulaufkonzentration.

In einem Vergleich von acht PAK korrelieren die Spurenstoff-Entfernungen in KAA weitgehend unabhängig von der PAK mit der Entfernung des Surrogatparameters UV₂₅₄-Absorption. Auch in anderen Versuchen dieser Studie korreliert die Spurenstoff-Entfernung mit der UV₂₅₄-Entfernung. Desweiteren wurde ein Test für die Untersuchung der Spurenstoff-Adsorption bei mehrstufiger PAK-Wiederverwendung entwickelt. Zwischen der PAK-Beladung und der wässrigen Spurenstoff-Konzentration besteht in allen Stufen der gleiche

Zusammenhang. Das EBC Modell wurde modifiziert, um die Effizienz bei der PAK-Wiederverwendung abzuschätzen.

Diese Studie zeigt die Übertragbarkeit der Spurenstoff-Adsorption an PAK und GAK in verschiedenen Wässern. Die entwickelten Methoden ermöglichen praktische Vorhersagen der Spurenstoff-Adsorption mittels einfacher experimenteller, analytischer und mathematischer Tools.

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1 Introduction

This chapter gives an introduction to the aquatic occurrence of organic micro-pollutants (OMP) and the related problems (1.1). Furthermore, activated carbon adsorption as a potential advanced treatment strategy for OMP-impacted waters is introduced (1.2). The possible means for assessing the performance of activated carbon in OMP removal are discussed (1.3). The major research aims are defined and the structure of the study is presented (1.4).

1.1 Occurrence of organic micro-pollutants

Organic micro-pollutants (OMP) have been detected in aquatic environments with an increasing frequency during the last decades (e.g. Heberer 2002a, b, Luo et al. 2014, Reemtsma et al. 2006, Schwarzenbach et al. 2006). OMP comprise a variety of substances such as pharmaceuticals and industrial chemicals and many of them are biologically active. Thus, OMP have the potential to impact the aquatic environment or humans if drinking water sources are affected. Environmentally realistic OMP concentrations have been reported to harm aquatic organisms (e.g. Best et al. 2014, Melnyk-Lamont et al. 2014, Pomati et al. 2006). Little is known on the combinatory effects of several OMP acting simultaneously and the consequences of long-term exposure are difficult to assess (Dieter and Mückter 2007).

The most important sources of OMP are wastewater treatment plants (WWTP), where OMP are often only partially removed (Lindqvist et al. 2005). Increasing OMP consumption (demographic aging, rising living standards) and climate change (regional decline of precipitation, change of freshwater availability) may elevate environmental OMP concentrations in the future (van der Aa et al. 2011). Especially in cases where affected waters are directly or indirectly used for human drinking water production, potential negative impacts have raised concerns. Furthermore, the awareness of aquatic OMP has risen among legislators and environmental quality standards will come into force in the European Union within several years (EU 2013). Hence, even if the knowledge related to aquatic OMP and their effects is still scarce, water suppliers/ authorities are starting to address the issue (Gimbel et al. 2011, Jekel et al. 2013, Le-Minh et al. 2010, Zwickenpflug et al. 2010). In Berlin, Germany, the effluent of WWTP Schönerlinde is indirectly discharged into Lake Tegel which is used for drinking water production (Jekel et al. 2013). Low OMP concentrations in the range of ng/L– μ g/L can be found in the produced drinking water of the water works Tegel (Berliner Wasserbetriebe 2015). This partially closed urban water cycle demonstrates the potential of discharged OMP to affect humans.

Technological barriers for reducing the release of OMP into the environment include advanced treatments, e.g. with ozone or activated carbon. Ozone oxidizes compounds and inherently changes their structure (e.g. Hübner et al. 2015), partly leading to biologically active unknown substances (Magdeburg et al. 2014). Ozonation can also promote the formation of toxic/ mutagenic by-products such as bromate (Boorman 1999, Wert et al. 2007). In contrast, advanced water treatment with activated carbon typically decreases toxic effects (Guzzella et al. 2002, Magdeburg et al. 2014), as compounds are adsorbed onto the material and thus are removed from the water. Other factors affecting the feasibility of the potential techniques are the treatment targets, because the removal of specific OMP is differently effective with oxidative or adsorptive stages (Altmann et al. 2014, Margot et al. 2013).

Within the joint research project ASKURIS (Anthropogenic Organic Micro-Pollutants and Pathogens in the Urban Water Cycle: Assessment, Barriers and Risk Communication), extensive tests of activated carbon adsorption for the removal of emerging OMP were conducted at the Chair of Water Quality Control of Technische Universität Berlin. The feasibility of activated carbon adsorption was evaluated on drinking waters, WWTP effluents, and surface water. This study presents the gathered results on a variety of aspects regarding the adsorptive OMP removal from such waters.

1.2 Activated carbon adsorption

BASICS

In water treatment, adsorption describes the mass transfer process of a dissolved substance (adsorbate) being removed from a liquid phase and accumulated on a solid phase (adsorbent). In the process, the adsorbate must be transported from the liquid to the external surface of the adsorbent, enter the inner pore system and diffuse onto the typically very large internal surface of the adsorbent (e.g. activated carbon) to attach. The adsorptive attachment itself is very fast and the transport steps are usually rate controlling. The external mass transfer can be influenced via the hydrodynamic conditions whereas the internal mass transfer cannot be manipulated. Two mechanisms of attachment, namely chemisorption and physisorption, can be differentiated regarding the physico-chemical interactions between the adsorbate and the adsorbent. During chemisorption, a chemical binding is formed between the adsorbate and the adsorbent and the process is therefore normally irreversible (binding energies of >200 kJ/mol). Physisorption results from mostly reversible van-der-Waals forces (dipole interactions, induction, dispersive forces) between the adsorbent and the adsorbate (binding energies of $4\text{--}40$ kJ/mol). In activated carbon adsorption, physisorption is the predominant mechanism of attachment. However, a clear distinction between chemisorption and physisorption is not always possible (Crittenden et al. 2012, Sonthaimer et al. 1988, Worch 2012).

For the adsorptive removal of OMP, two process options can be applied, powdered activated carbon (PAC) and granular activated carbon (GAC). In PAC treatment, fine activated carbon particles (1–100 μm diameter) are suspended in the water and removed via flocculation and sedimentation/ filtration after a feasible period of time (e.g. 0.5 h). Due to the small particle size, the PAC capacity can be exploited relatively quickly, e.g. after several hours. Practically, a repeated reuse of PAC is often applied to increase the water-PAC contact time and better exploit the full PAC capacity. The reuse is achieved via sludge recirculation where used/ separated PAC is mixed to un-treated water. Typically, small doses of fresh PAC are added, and high PAC concentrations in the recirculation sludge are aimed at.

In GAC treatment, the water passes a fixed bed of coarse activated carbon particles (0.1–4 mm diameter). Accordingly, an excess mass of GAC is present compared to the treated water and the GAC capacity is exploited over a longer period of time (e.g. 1 a). At the beginning of a GAC filter run, the effluent concentration of the adsorbate is typically zero. Depending on the adsorbate-adsorbent affinity and the filter operation, the effluent adsorbate concentration starts to rise after a certain amount of time. The depiction of the relative effluent concentration (ratio of effluent to influent concentration) over time or over the volumetric throughput results in a breakthrough curve, which is normally S-shaped. When the capacity is exhausted or when the filter effluent OMP concentration exceeds a certain level, the filter bed has to be renewed.

The suitability of the two options depends on economic/ spatial/ operational considerations. PAC is well suited for intermittent application and the dosage can normally be adjusted to higher or lower demands. GAC is mostly used for continuous operation, e.g. where relatively constant volumetric flows are treated. A major advantage of GAC is that it can be reactivated and may be used for up to ten times. More information on the fundamentals of activated carbon adsorption can be found in the monographs of Worch, Crittenden, and Sontheimer (Crittenden et al. 2012, Sontheimer et al. 1988, Worch 2012).

CHEMISTRY

The overall feasibility of activated carbon adsorption as a treatment strategy for OMP-impacted waters depends on a variety of factors. From an economic/ ecologic perspective, the process design and dimensioning are the relevant factors. However, they themselves are primarily defined by the treatment goals and the physico-chemical properties of the adsorption system under consideration. The reason is that the OMP and water chemistry define the technological demands in terms of activated carbon type, contact time, and in particular carbon usage rate.

The basic structure of activated carbon consists of randomly ordered graphite-like microcrystallites built of sp^2 -hybridized carbon atoms, as shown in Fig. 1. The arrangement of the microcrystallites and the micro-, meso- and macro-pores define the internal pore system and internal surface of the activated carbon. Various possible chemical groups (like phenols, carboxylic acids, ketones ...) on the internal surface of the activated carbon result in

variable affinity towards specific adsorbates. The physico-chemical properties of the activated carbon internal surface are influenced by the source material (charcoal, wood, nutshells ...) and the manufacturing to some extent. Further information on the impacts of activated carbon properties on OMP adsorption can be found in the literature (e.g. de Ridder et al. 2012, Karanfil and Kilduff 1999, Knappe et al. 2003, Leng and Pinto 1997, Li et al. 2005, Quinlivan et al. 2005, Radovic et al. 1997).

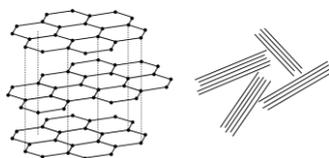


Fig. 1. *Left:* Graphite-like structure of activated carbon, *right:* Microcrystallites in random order; after Worch (Worch 2012).

Next to the chemistry of the activated carbon, the chemical properties of the adsorbate have a direct impact on the adsorption. Larger molecular sizes raise the number of possible interaction sites with the activated carbon surface, on the one hand. On the other hand, smaller molecular sizes increase the diffusivity of the molecule. The diffusive transport is further influenced by the spatial structure of a molecule (flat, spherical, flexible) which also impacts the interaction with the internal adsorbent surface (Cornelissen et al. 2004). The atomic composition of a molecule determines its aromaticity, hydrophilicity/ polarity (charged/ uncharged, dissociable depending on pH) which directly affect the adsorbability (Cornelissen et al. 2005, de Ridder et al. 2012, Radovic et al. 1997, Shih and Gschwend 2009). Interactions with activated carbons are typically stronger for aromatic, hydrophobic, non-polar substances. The influences of various physico-chemical adsorbate properties are discussed in detail in various studies (e.g. Godino-Salido et al. 2014, Karanfil and Kilduff 1999, Karanfil et al. 1996, Li et al. 2005, Quinlivan et al. 2005).

Besides the adsorbate/ adsorbent chemistry, the most crucial aspect when applying activated carbon on waters like drinking waters or wastewaters is the adsorption of background organic matter (BOM, normally expressed via the dissolved organic carbon – DOC) which adsorbs at the same time as the OMP (Corwin and Summers 2010, de Ridder et al. 2011, Ding et al. 2006, Ding et al. 2008, Graham et al. 2000, Hepplewhite et al. 2004, Karanfil et al. 1999, Li et al. 2003a, Li et al. 2003b, Matsui et al. 2003, Matsui et al. 2002a, Matsui et al. 2002b, Matsui et al. 2012, Najm et al. 1991, Newcombe and Cook 2002, Newcombe et al. 2002a, Newcombe et al. 2002b, c, Nowotny et al. 2007, Shimabuku et al. 2014, Zoschke et al. 2011). BOM is ubiquitous in such waters and its concentration (mg/L) is typically 10^3 – 10^6 times higher than that of most OMP (ng/L or $\mu\text{g/L}$). Even if the affinity of BOM to adsorb onto activated carbons may be variable and smaller than the affinity of most OMP, the sheer quantity of BOM can substantially reduce the activated carbon adsorption capacity for OMP.

The understanding, prediction and mitigation of BOM-induced competition against OMP adsorption are among the key research areas in the field of activated carbon adsorption.

1.3 Assessing OMP adsorption onto activated carbon

The above-discussed factors influencing the adsorption of OMP onto activated carbon necessitate assessing the feasibility of activated carbon adsorption stages prior to implementing them on a larger scale. From the practical perspective of engineers and water authorities, this is the most crucial aspect in planning and realizing full-scale plants. The common methods to estimate/ predict activated carbon adsorption are described in the following. A summarizing conclusion on the different possibilities to assess OMP adsorption onto activated carbon is given at the end of this section.

EXPERIMENTAL TESTS

The experimental testing of both, powdered and granular activated carbon (PAC, GAC) can be conducted on different scales. Full-scale plants are usually too large and thus too expensive and time consuming for being operated to investigate the feasibility of activated carbon in a specific setup. Therefore, pilot-scale plants can be realized which typically encompass smaller dimensions than full-scale plants but can depict the occurring processes realistically. However, the pilot-scale is still too large to conduct mechanistic/ systematical investigations because many process parameters such as the water quality cannot be kept constant for a longer period of time or during several tests.

Laboratory methods aim at representing larger-scale systems in a miniaturized form. They typically are time-saving, less laborious, and the related parameters are more controllable than on pilot-/ full-scales. If planned and conducted correctly, lab-tests can give mostly precise descriptions of larger systems. One shortcoming is that long-term effects (e.g. biologic) normally are not considered. In the present study, typical laboratory tests for PAC and GAC were implemented and different modifications/ advancements were developed for precise investigations of the occurring phenomena.

Powdered activated carbon (PAC)

Laboratory testing of PAC and the associated expectable feasibility is usually accomplished in batch tests. Variable concentrations of PAC can be adjusted in the water of interest; after the desired contact time, the PAC/ water suspension can be separated via filtration. During the adsorption, adsorbate molecules are removed from the free liquid and the liquid phase concentration decreases with time. At the same time, the adsorbate accumulates within the adsorbent and the solid phase concentration (loading) increases. The relationship between the loading and the liquid phase concentration is defined by a mass balance equation for the system, as given in Eq. 1.

$$q(t) = \frac{V}{m}(c_o - c(t)) \quad \text{Eq. 1}$$

where $q(t)$ and $c(t)$ are the loading and the concentration at time t , respectively, V is the volume, m is the adsorbent mass, and c_o is the initial concentration.

The temporal change of the loading and the concentration during adsorption results from kinetic mass transfer resistances. The end state of the system where the liquid phase concentration and the loading are not changing any more is called equilibrium. The equilibrium relationship between the loading and the liquid phase concentration is called isotherm. An exemplary isotherm is shown in Fig. 2 which also shows an operating line which describes the adsorption process from the initial state ($c(t=0)=c_o$, $q(t=0)=0$) to the equilibrium state ($c(t=t_{eq})=c_{eq}$, $q(t=t_{eq})=q_{eq}$). Different operating lines are practically obtained by changing the batch volume and/ or activated carbon mass in an experiment. The data points at the equilibrium give the experimentally determined isotherm. Such experiments can also be conducted for shorter times to reflect the loading-concentration relationships for non-equilibrium adsorption. Such non-equilibrium tests allow for the assessment of the kinetic mass transfer resistances without mathematically considering the precise transfer processes (cf. section 1.3, Kinetic models).

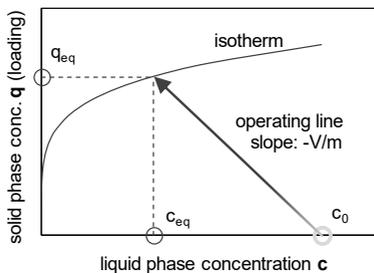


Fig. 2. Exemplary isotherm with initial concentration c_o , operating line with slope $-V/m$ as defined by batch volume and activated carbon mass, and equilibrium loading and concentration q_{eq} and c_{eq} .

Isotherms describe the affinity between adsorbates and adsorbents — the higher the loading at a given liquid phase concentration, the higher the affinity. Various models exist to mathematically describe the relationship between the loading and the concentration. The isotherm models used in this study are further described in section 1.3, p. 8.

In this study, typical PAC batch tests are used for the assessment of the adverse affects of background organic matter (BOM) on OMP adsorption, discussed in sections 2.1 – BOM size in powdered activated carbon adsorption (p.15), 2.2 – BOM aromaticity and hydrophilicity (p. 30), and 3.1 – Powdered activated carbon adsorption in different waters

(p. 55). Batch tests are further used for the assessment of PAC performance, as discussed in section 4.1 – UV absorption for activated carbon evaluation (p. 89).

Furthermore, the typical PAC batch procedure was modified in order to be able to investigate multi-stage PAC reuse. Most large-scale plants apply PAC reuse but so far, no satisfying laboratory procedure has been described in this respect. Hence, laboratory methods allowing for the easy assessment of multi-stage PAC reuse are strongly needed. The modifications to the batch test setup were necessary because normally, the PAC particles cannot be re-suspended after being removed from the liquid via filtration. The development and testing of such a multi-stage laboratory method is described in section 4.2 – Multi-stage powdered activated carbon adsorption (p. 101).

Granular activated carbon (GAC)

Lab-scale GAC tests are typically more laborious than tests for PAC because they require miniature GAC filters, involving grinding of the GAC material. Most commonly, rapid small-scale column tests (RSSCT) are used, aiming at directly representing large-scale GAC filters. An example of a miniature GAC filter with 1 cm bed length and a flow direction from bottom to top is shown in Fig. 3 a). The RSSCT dimensioning is obtained by scaling down the considered large-scale filter. The main process variables (empty bed contact time – EBCT, filter velocity/ hydraulic loading rate – HLR) are related to the particle sizes of the large-scale filter and the RSSCT (Crittenden et al. 1986, Crittenden et al. 1987, Crittenden et al. 1991). RSSCT are a powerful tool for quick and realistic representation of GAC filters but are only representative for the respective scaled-down dimensioning. Furthermore, the conduction and setup of RSSCT require precision and some experience, because the miniature filter bed easily causes high head losses or clogging, especially when treating turbid waters such as wastewater treatment plant (WWTP) effluents or surface waters. Many laboratory tests do not specifically aim at representing exactly defined large-scale GAC filters but rather at investigating particular conditions, e.g. the comparison of GAC products or different waters. In these cases, small-scale GAC filters (in the range of typical RSSCT dimensions) can be used for quick, systematic, and precise lab-scale comparisons.

The OMP adsorption onto GAC in fixed-bed filters results in breakthrough curves which depict the relative effluent concentration (effluent concentration / influent concentration) over time or the throughput. An exemplary breakthrough curve is shown in Fig. 3 b) together with the corresponding filter bed exploitations at different times. Also, a mass transfer zone (MTZ) is indicated which contains a concentration profile of the adsorbate in the liquid and solid phases. The MTZ is a result of the external and internal mass transfer resistances (and axial dispersion which is usually negligible) which forces some adsorbate molecules to travel faster along the filter bed than others, leading to a concentration gradient within the MTZ. Since high adsorbate concentrations normally travel faster than low concentrations, the MTZ does not necessarily continue to extend along the filter bed but can reach a constant pattern state where the blurring (mass transfer resistances) and sharpening (variable travel velocities) effects balance each other.

The aspects of using RSSCTs for GAC testing with WWTP effluents and the associated effects on OMP adsorption are discussed in section 2.3 – BOM size in granular activated carbon adsorption (p. 44). Means for transferring GAC breakthroughs of OMP at different locations (i.e. different source waters) would reduce the need for the demanding RSSCT testing and allow for quick GAC performance assessment at new locations. The adsorption of OMP onto GAC in different waters and at variable OMP concentrations, and the associated alignment of the breakthrough curves are discussed in section 3.2 – Unifying granular activated carbon breakthroughs (p. 75).

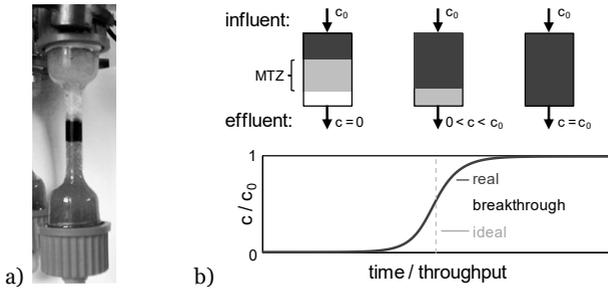


Fig. 3. *a)* Miniature GAC column used for rapid small-scale column tests (RSSCT) with 1 cm bed length, treating methylene blue solution, flow direction bottom-top. *b)* Filter exploitations (*top*) and corresponding breakthrough (*bottom*) over time, with influent and effluent concentrations, mass transfer zone (MTZ) indicated by light grey, and ideal breakthrough (dashed line).

MODELING

Mathematical models aim at describing activated carbon adsorption with theoretical or empirical formulas. Two modeling aspects have to be separated, namely the adsorption equilibrium which describes the driving force of the system, and the kinetics which describe the mass transfer within the system. A wide variety of more or less complex models exists. Typically, the models require initialization of the involved variables because activated carbon is a complex process with numerous influencing parameters. Initialization is a major drawback of mathematical models since it requires experimental testing which itself is a means for assessing activated carbon adsorption (as discussed above). For the modeling of both, PAC and GAC adsorption phenomena, equilibrium and kinetic models have to be used. However, several workarounds can be applied in PAC modeling to neglect the kinetic/time-related aspects. In GAC adsorption this would be an illegitimate simplification as the mass transfer processes have a major impact on OMP breakthrough curves.

Equilibrium models

Simple equilibrium models comprise the 2-parameter Langmuir (Langmuir 1918) and Freundlich (Freundlich 1906) isotherm equations. The first model is based on thermodynamic considerations whereas the second model is mostly empirical. In activated carbon adsorption, the Freundlich model, shown in Eq. 2, typically reaches better data fitting and is preferred over the Langmuir model. Their original purpose is the description of single-solute systems and using them on waters containing BOM (multi-solute systems) is a strong empirical simplification. However, such pseudo single-solute modeling can reach satisfying results. A further empirical simplification is the application of these isotherm equations on non-equilibrium systems.

$$q = K_F c^{\frac{1}{n}} \quad \text{Eq. 2}$$

where q is the loading, c is the (liquid phase) concentration, K_F is the Freundlich coefficient, and $1/n$ is the Freundlich exponent.

More complex models have to be applied if the multi-solute characteristics of waters containing BOM shall be considered. The ideal adsorbed solution theory (IAST) considers the simultaneous and competitive adsorption of several constituents in parallel (Radke and Prausnitz 1972). The individual components of the multi-solute system are characterized by single-solute models, e.g. the Freundlich model (Crittenden et al. 1985b). For the description of the adsorption of bulk water characteristics such as the BOM of a water, the concept of adsorption analysis (ADSA) was developed (Crittenden et al. 1985a, Johannsen and Worch 1994). The ADSA divides the bulk parameter DOC into several differently well adsorbable fractions, each characterized by individual Freundlich parameters. Different sets of Freundlich parameters have to be tested regarding the associated fitting of the measured DOC adsorption data.

The competitive adsorption of OMP and BOM can be modeled by modifications of the IAST, namely the Tracer model (TRM) or the Equivalent Background Compound Model (EBCM). The Tracer model uses the results from the ADSA, conducted on the water of interest, in combination with modified single-solute parameters of the OMP under consideration. The modification is necessary because several assumptions in the Tracer model are not realistic. The EBCM uses single-solute parameters of the respective OMP and assigns all of the observed adsorption competition to a fictive background compound. More information on approaches for modeling OMP adsorption in waters containing BOM is given in the literature (Worch 2010).

All of the mentioned strategies to model OMP/ BOM adsorption in waters containing BOM have the major shortcoming of being in need for experimental data in the multi-solute system under consideration. The reason is that BOM is a complex mixture of unknown composition. So far, no means for deriving the adsorptive properties of BOM without experimental adsorption data exists. In all cases, empirical adjustments of some model parameters are

required in order to obtain reliable modeling results. As empirical adjustments are always necessary, additional modifications can be incorporated. E.g. the EBCM was extended to non-equilibrium conditions by several studies (Shimabuku et al. 2014, Zoschke et al. 2011). The OMP single-solute input parameters should be determined for the considered adsorption time but this may not suffice to account for different OMP/ BOM adsorption kinetics as BOM show overall slower diffusion as compared to OMP. In the current study, the EBCM and several simplifications were used for modeling OMP adsorption in waters containing BOM, cf. sections 2.1 – BOM size in powdered activated carbon adsorption (p. 15), 2.2 – BOM aromaticity and hydrophilicity (p. 30), 3.1 – Powdered activated carbon adsorption in different waters (p. 55), 4.2 – Multi-stage powdered activated carbon adsorption (p. 101).

Kinetic models

Kinetic models for adsorption phenomena consist of a material balance equation for the description of the conservation of mass within the system, an isotherm equation for the description of the driving force, and mass transfer equations for the description of diffusion processes in the system. In doing so, several assumptions are made, e.g. a constant temperature and full mixture of the system, as well as spherically shaped and isotropic adsorbent particles. Two occurring diffusion processes are distinguished, external diffusion through the liquid film at the external surface of the adsorbent particles and internal diffusion within the adsorbent particles.

The mass transfer equation for the external (film) diffusion can be derived from Fick's first law of diffusion. By assuming a linear concentration gradient in the film around the adsorbent particles, a film diffusion coefficient k_F is defined as in Eq. 3. The external mass transfer equation for spherical particles is given in Eq. 4

$$k_F = \frac{D_L}{\delta} \quad \text{Eq. 3}$$

where k_F is the film diffusion coefficient, D_L is the liquid phase diffusion coefficient of the adsorbate and δ is the film thickness.

$$\frac{\partial \bar{q}}{\partial t} = \frac{3k_F}{r_P \rho_B} (1 - \varepsilon_B) (c - c_s) \quad \text{Eq. 4}$$

where $\partial \bar{q} / \partial t$ is the temporal change of the average loading, r_P is the particle radius, ρ_B is the bed density, ε_B is the bed porosity, c is the liquid phase concentration, and c_s is the liquid phase concentration at the surface of the particle.

The internal diffusion within the adsorbent particle can be described by surface diffusion along the internal adsorbent surface or by pore diffusion within the pore structure of the adsorbent, or by a combination of both. As an example, the internal mass transfer equation for surface diffusion is shown in Eq. 5 (Fick's second law of diffusion).

$$\frac{\partial q}{\partial t} = D_S \left(\frac{\partial^2 q}{\partial r^2} + \frac{2}{r} \frac{\partial q}{\partial r} \right) \quad \text{Eq. 5}$$

where $\partial q/\partial t$ is the temporal change of loading, D_S is the surface diffusion coefficient of the adsorbate, r is the particle radius, and $\partial q/\partial r$ is the radial change of loading.

The diffusive properties of the adsorbate are contained in D_S , or in D_P , the pore diffusion coefficient of the pore diffusion model. D_S can be determined by fitting calculated kinetic data to experimental data or by using more user-friendly empirical relationships (which have various practical limitations). D_P is related to the diffusion coefficient in the free liquid phase but cannot be derived directly from it because of additional transport hindrances in the adsorbent pore system. Typically, it is determined by fitting calculated data to experimental data. The intraparticle mass transfer can be described in a simplified form by assuming a linear concentration gradient (linear driving force, LDF model). The corresponding intraparticle mass transfer coefficient k_s^* is typically determined by fitting or from empirical formulas. For detailed descriptions of the external and internal diffusion models for kinetic modeling, the monographs of Worch and Sontheimer are recommended (Sontheimer et al. 1988, Worch 2012).

Breakthrough curve models

The model-based prediction of breakthrough curves in GAC fixed-bed filters typically consists of partial differential equations for the mass transport through the filter (Eq. 6) and for the mass transfer within the adsorbent grains (e.g. surface diffusion as in Eq. 5); also, the equilibrium relationship between the adsorbent loading and the liquid phase concentration at the external surface of the adsorbent particles applies. The material balance of Eq. 6 incorporates the advective adsorbate inputs and outputs of the differential filter element, the adsorbate within the voids, the sink due to adsorption of the adsorbate, and axial dispersion (the latter term is of minor importance and usually omitted). $\partial \bar{q}/\partial t$ can be substituted by the equation for the external mass transfer (Eq. 4).

$$v_F \frac{\partial c}{\partial z} + \varepsilon_B \frac{\partial c}{\partial t} + \rho_B \frac{\partial \bar{q}}{\partial t} - D_{ax} \varepsilon_B \frac{\partial^2 c}{\partial z^2} = 0 \quad \text{Eq. 6}$$

where v_F is the filter velocity, $\partial c/\partial z$ is the longitudinal change of concentration, ε_B is the bed porosity, $\partial c/\partial t$ is the temporal change of concentration, ρ_B is the bed density, $\partial \bar{q}/\partial t$ is the temporal change of the average loading, and D_{ax} is the axial dispersion coefficient.

The various breakthrough curve models differ in the respective degree of realism, e.g. considering or neglecting dispersion and/ or surface/ pore diffusion. E.g., in the homogeneous surface diffusion model (HSDM), dispersion is neglected and plug-flow conditions are assumed, and surface diffusion is considered as the only intraparticle mass transfer process. The equilibrium relationships are typically modeled by the Freundlich isotherm equation, in variable complexity (single-solute or multi-solute/ IAST). The mutual kinetic interactions of different components in multi-solute systems are normally not considered. The relatively

complex breakthrough models can be simplified, e.g. by assuming constant pattern flow conditions (the adsorbate concentration profile maintains its form whilst moving along the bed) or a linear adsorbate concentration gradient in the adsorbent particles (LDF model). The applicability of the simplifications depends on the respective case. Detailed descriptions of a variety of breakthrough curve models are contained in the monographs of Worch, Sontheimer, and Crittenden (Crittenden et al. 2012, Sontheimer et al. 1988, Worch 2012).

Empirical relationships

A wide variety of empirical relationships exists for the estimation of kinetic and equilibrium model parameters, OMP breakthroughs or OMP removals in PAC setups. Some of these empirical relationships are necessary because model parameters cannot always be experimentally determined or calculated from entirely theoretical equations. E.g., external mass transfer coefficients can be estimated (Gnielinski 1978) or Freundlich equilibrium parameters for breakthrough curve modeling have to be corrected in the presence of BOM (Jarvie et al. 2005, Sontheimer et al. 1988). Other empirical relationships aim at predicting threshold breakthroughs, e.g. 10% breakthrough of specific OMP (Kennedy et al. 2015, Summers et al. 2013), or equilibrium adsorption of specific OMP (e.g. de Ridder et al. 2011, Dickenson and Drewes 2010, Redding et al. 2009, Shih and Gschwend 2009, Zhang and Hofmann 2013). Empirical relationships are often based on quantitative structure activity relationships (QSAR) which relate activated carbon, adsorbate/ OMP, and BOM/ water characteristics to experimentally determined OMP adsorption data.

SURROGATE PARAMETERS AND MONITORING

Another possibility of empirically deriving the performance of activated carbon stages (regarding the adsorptive removal of OMP) is the application of surrogate parameters. Such parameters are typically very easily detectable, often in an online fashion, allowing for real-time monitoring. The direct measurement of OMP at low concentrations in aqueous matrices is normally relatively complex (e.g. via HPLC-MS/MS) and cannot be conducted online. Therefore, easily measurable surrogate parameters are being investigated which allow for deducing OMP removals. This can reduce the need for laborious direct determination of specific OMP. Once a large-scale plant is operating, the measurement of surrogate parameters allows for timely and effective online monitoring of the adsorptive removal of OMP. The surrogate parameter UV₂₅₄ has been successfully used in ozonation applications for inferring OMP removals. The feasibility of this surrogate parameter in activated carbon applications was initially tested as described in section 4.1 of this study. The applicability of UV₂₅₄ removal as an indicator for OMP removal was further tested in various other aspects of activated carbon adsorption, as shown in several other sections of this study.

SUMMARY

The prediction of activated carbon adsorption is the most crucial aspect for the feasibility assessment of this water treatment technique. The advantages and disadvantages of the different assessment possibilities are summarized in the following.

Laboratory methods can give mostly precise depictions of the adsorption phenomena occurring on larger scales. Some aspects such as biological degradation in GAC fixed-bed filters cannot be accounted for. A major drawback of laboratory methods is that they are based on the principle of a black box. The major importance lies in the experimental outcomes and not in the theoretical application of theoretical scientific principles.

On the contrary, theoretical models for the mathematical description of adsorption phenomena consider many of the mechanistic processes which occur during adsorption. Accordingly, they allow for a more profound understanding than laboratory tests. However, mathematical models are always based on more or less profound assumptions or simplifications. E.g., pseudo single-solute behavior may have to be assumed in multi-solute systems. Also, models cannot consider all of the theoretically occurring phenomena and therefore, depend on experimental data. E.g., the kinetic parameters (k_F , D_S , D_L , k_S^*) of kinetic models have to be determined from experimental data in most cases; empirical formulas for the a priori determination of the parameters exist but they may fail and thus have to be checked (against experimental data). Also, kinetic modeling requires knowledge on adsorption equilibria which is usually obtained from experiments.

Raising the laboratory effort only marginally (i.e. adding batches for kinetic experiments) allows for experimentally deriving the desired kinetic data — which questions the practical usefulness of the associated kinetic modeling. For the identification of the kinetic adsorption behavior in PAC setups, simple non-equilibrium batch tests for the desired contact time are practically sufficient in most cases. Competitive adsorption models (ADSA, EBCM, TRM) are very strong simplifications of the multi-solute system they reflect. So far, they cannot be initialized without experimental data which makes their usefulness for de facto predictions questionable. This problem is even more crucial for strictly empirical QSAR whose applicability must generally be checked for the specific setup (variability of water composition etc.).

Approaches for obtaining empirical model adjustments without prior experimental testing would be very useful for easy modeling. Such an approach is developed and tested in section 3.1 — Powdered activated carbon adsorption in different waters (p. 55) of the current study. Also, transferring PAC or GAC adsorption of OMP in different waters and waters from different regions would be very helpful for easily deriving the expectable adsorption phenomena at different locations. This is aimed at for PAC adsorption in section 3.1 — Powdered activated carbon adsorption in different waters and for GAC adsorption in section 3.2 — Unifying granular activated carbon breakthroughs. Furthermore, the practical prediction of activated carbon performance with the easily measureable surrogate parameter UV_{254} is demonstrated in several sections of this study.

1.4 Research aims and structure of the study

As discussed in section 1.2, the competitive adsorption of background organic matter (BOM) and organic micro-pollutants (OMP) onto activated carbon is the most crucial aspect affecting the adsorptive OMP removal in waters containing BOM — like drinking waters, WWTP effluents, and surface waters. This study gives detailed insights into the causes, effects and prediction of competitive adsorption of OMP and BOM in such waters, and further approaches several practical aspects of OMP adsorption onto activated carbon. An overview of the study structure and the related research aims is given in the following:

- Chapter 2 encompasses three publications investigating the main chemical properties leading to increased BOM competitiveness in the simultaneous adsorption of OMP and BOM onto activated carbon. The major BOM fractions responsible for a deterioration of OMP adsorption onto activated carbon are identified.
- Chapter 3 includes two publications on the comparison and prediction of OMP adsorption in the presence of BOM in various drinking waters, WWTP effluents, and surface water. The transferability of activated carbon adsorption phenomena between different waters is further explored, in PAC as well as in GAC setups.
- Chapter 4 comprises two publications addressing further practical applications of activated carbon. The first article aims at predicting activated carbon performance by surrogate parameters. The scope of the second article is the development of a new method for testing powdered activated carbon reuse on the lab scale. The related OMP-BOM competition is modeled and the efficiency of PAC reuse is investigated.
- Chapter 5 summarizes the main findings of this study and discusses the related theoretical and practical implications.

2

Properties of background organic matter (BOM) causing adsorption competition

This chapter contains the research that was conducted to investigate the chemical characteristics of background organic matter (BOM) competing with organic micro-pollutants (OMP) in adsorption onto activated carbon. On the one hand, different methodologies were used to influence and change molecular properties such as the molecular size (2.1, p. 15–29) or hydrophilicity (2.2, p. 30–43) of BOM. Subsequently, powdered activated carbon (PAC) adsorption experiments were conducted to evaluate the OMP adsorption in the presence of the differently altered BOM. On the other hand, the granular activated carbon (GAC) breakthrough behavior of OMP and BOM was simultaneously monitored in rapid small-scale column tests (RSSCT, section 2.3, p. 44–53). This allowed for investigating variable retention of different BOM fractions on GAC filters and the associated impacts on OMP adsorption. All experiments encompassed in this chapter were conducted with wastewater treatment plant (WWTP) effluent. Thus, a more precise denomination for the investigated BOM is effluent organic matter (EfOM). However, further laboratory tests shown in chapter 3 demonstrate that the key BOM characteristics affecting BOM competition against OMP adsorption are the same in different types of waters (drinking waters, WWTP effluents, ...). Accordingly, the more general term BOM and the more specific term EfOM are mostly interchangeable regarding BOM adsorption competition with OMP.

2.1 BOM size in powdered activated carbon adsorption

Impact of EfOM size on competition in activated carbon adsorption of organic micro-pollutants from treated wastewater

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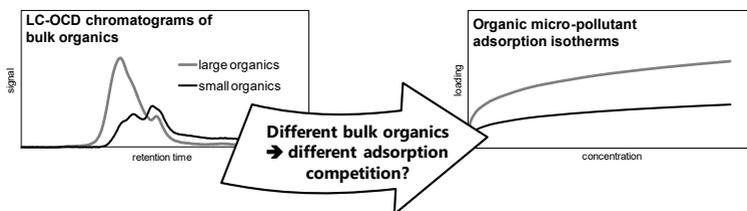
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GRAPHICAL ABSTRACT



ABSTRACT

The competitive impacts of different fractions of wastewater treatment plant effluent organic matter (EfOM) on organic micro-pollutant (OMP) adsorption were investigated. The fractionation was accomplished using separation by nanofiltration (NF). The waters resulting from NF were additionally treated to obtain the same dissolved organic carbon (DOC) concentrations as the initial water. Using size exclusion chromatography (LC-OCD) it could be shown that the NF treatment resulted in an EfOM separation by size. Adsorption tests showed different competitive effects of the EfOM fractions with the OMP. While large EfOM compounds that were retained in NF demonstrated a reduced competition as compared to the raw water, the NF-permeating EfOM compounds showed an increased competition with the majority of the measured OMP. The effects of small size EfOM are particularly negative for OMP which are weak/moderate adsorbates. Adsorption analysis was carried out for the differently fractionized waters. The small sized EfOM contain better adsorbable compounds than the raw water while the large EfOM are less adsorbable. This explains the observed differences in the EfOM competitiveness. The equivalent background compound (EBC) model was applied to model competitive adsorption between OMP and EfOM and showed that the negative impacts of EfOM on OMP adsorption increase with decreasing size of the EfOM fractions. The results suggest that direct competition for adsorption sites on the internal surface of the activated carbon is more substantial than indirect competition due to pore access restriction by blockage. Another explanation for reduced competition by large EfOM compounds could be the inability to enter and block the pores due to size exclusion.

INTRODUCTION

Organic micro pollutants (OMP) such as pharmaceuticals are increasingly found in all kinds of water sources such as wastewater, surface water, groundwater, and drinking water (Putschew et al. 2000, Reemtsma et al. 2006). OMP concentrations are rising in many cases because the consumption of drugs and other OMP is increasing and demographic aging will probably lead to an intensification of these trends (Dieter et al. 2010). The occurrence of OMP in our water sources is problematic because to this date, it is not fully understood which potentially harmful effects can be caused by OMP. Most OMP have very small concentrations and adverse impacts are not easily detectable (Dieter and Mückter 2007). Further-

more, the combinatory/ cumulative and chronic effects of exposition to OMP are not satisfactorily investigated (Bergmann et al. 2008). Due to the increasing concentrations of OMP in our water sources, the installation of additional water treatment steps in drinking water/ wastewater treatment plants will be necessary in the forthcoming years (Jekel et al. 2013, Snyder et al. 2003). Activated carbon is a promising treatment technology in this respect and has been applied successfully in drinking water and reservoir water treatment (Worch 2012). It is now also being tested with wastewater treatment plant (WWTP) effluent aiming at decreasing the pollution of receiving water bodies (Altmann et al. 2014, Boehler et al. 2012). In order to minimize activated carbon consumption and to attain high efficiencies, the activated carbon capacity should mainly be used for the target compounds, i.e. the OMP that are to be removed. This goal is not always achievable because several effects can impede OMP adsorption.

The affinity of OMP or adsorbing soluble organics (adsorbates) towards activated carbon depends on a variety of factors, e.g. properties of the applied activated carbon, such as internal surface area and chemistry (Newcombe et al. 2002a, Quinlivan et al. 2005). Stronger impacts on the activated carbon affinity of an adsorbate are due to the structural and chemical properties of the respective adsorbate itself, such as the hydrophilicity/ solubility and the molecular size (Knappe et al. 2003). In activated carbon adsorption from natural waters the most crucial factor impacting OMP adsorption is the competition caused by other soluble organic substances of the respective natural organic matter (NOM). (In WWTP effluents, the NOM is usually denominated effluent organic matter – EfOM). The general two interference mechanisms are direct competition for adsorption sites on the activated carbon surface and indirect competition due to pore blockage which can impede OMP transport within the activated carbon pore structure. Distinction between the two mechanisms is not easy but direct competition for adsorption sites at the activated carbon internal surface is considered to be more fundamental in WWTP effluent treatment (de Ridder et al. 2011). Differences between OMP and EfOM regarding concentration as well as the affinity towards activated carbon can have substantial impacts on adsorption (Matsui et al. 2003). If the concentration of the bulk EfOM compounds present in WWTP effluents is considered, it is obvious that OMP adsorption can be impeded substantially (Newcombe et al. 2002c). In the case of Berlin, Germany, which is in the focus of this study, the WWTP effluent DOC concentration is normally between 10 and 15 mg/L (~20–30 mg/L EfOM) which is about 10^3 – 10^5 times the concentration of most of the OMP considered. However, it has been noted that only a fraction of the EfOM present in natural waters is effectively competing in adsorption with OMP (Graham et al. 2000, Knappe et al. 1998). This is accounted for the different accessibilities of the pore structure areas within the activated carbon which cannot always be entered equally easily by all present EfOM molecules (Hepplewhite et al. 2004, Newcombe et al. 2002a).

Because of the potentially high amount of EfOM competing with OMP in activated carbon adsorption, it was the objective of the current study to better understand which compounds of the WWTP effluent EfOM are the major competitors in OMP adsorption. If the entire

EfOM of a WWTP effluent sample are evaluated in their competitiveness against OMP adsorption, the attribution to EfOM classes or fractions is not possible because of the vast variety of EfOM (measured via the bulk parameter DOC). Chromatographic techniques like liquid size exclusion chromatography with online carbon detection (LC-OCD) allow for some fragmentation but the chromatographic peaks overlap. Furthermore, EfOM adsorption onto activated carbon is nonspecific and this impedes concise statements as to the adsorbability of different EfOM fractions when all these fractions are present at the same time. Therefore, and since most OMP of interest have molecular masses between 100 and 1000 g/mol, the EfOM of a Berlin WWTP effluent sample was fractionized using nanofiltration which has a molecular weight cutoff in this range. This approach allowed for the separate investigation of the adsorption competition caused by differently sized WWTP effluent EfOM fractions.

MATERIALS AND METHODS

Study approach and pre-treatments

Prior to all other pre-treatments, particles/ microorganisms and macromolecules were removed with ultrafiltration (UF) from the initial WWTP effluent sample to obtain higher microbial/ chemical stability (for a comparison of the OMP adsorption in WWTP effluent and ultra-filtered WWTP effluent, see Supporting Information, Appendix B-1, p. 135). The resulting “raw water” was modified, using nanofiltration (NF), reverse osmosis (RO), and dilution with salt solution (ultra pure water with ionic composition like the raw water, cf. below), to produce three types of water. The applied treatment scheme is shown in Fig. 4. 20 L of the raw water were fractionated in NF, to produce 10 L NF retentate and 10 L NF permeate. After removing the 10 L NF permeate, the NF retentate was additionally depleted by continuously adding 30 L of ultra pure water during NF, to increase the removal of small organics. Hereafter, the NF retentate was diluted using salt solution to obtain a DOC concentration comparable to that of the raw water. The NF permeate was concentrated in RO to obtain a RO retentate with a DOC concentration comparable to that of the raw water.

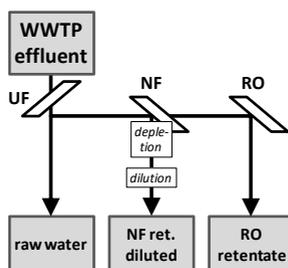


Fig. 4. Water treatment scheme prior to adsorption testing (UF – ultrafiltration, NF – Nanofiltration, RO – reverse osmosis, ret. – retentate).

Water samples

The wastewater sample was taken from WWTP Berlin Ruhleben, Germany, a WWTP with conventional mechanical/ biological treatment of domestic wastewater, and a capacity of ~247,500 m³/d (dry weather), on 28 October 2013. Ultra pure water (resistivity >17 MΩ*cm) was produced from fully de-ionized water, using an Ultra Maxima (*Elga Berkefeld Lab-Water*, Germany). Salt solution that was isotonic to the WWTP effluent was produced by adding salts to ultra pure water (KCl 50 mg/L, NaNO₃ 100 mg/L, Na₂SO₄ 220 mg/L, Ca₂(OH)₂ 180 mg/L, MgCl₂ 40 mg/L, pH adjusted to 7.5 with HCl, all salts at analytical grade, *Merck*, Germany, and *Sigma Aldrich*, Germany). Ultrafiltration (UF) was carried out with a bench-scale unit in dead-end mode with a *Dizzer* membrane module (*INGE*, Germany, molecular weight cut-off of 100 kDa). Nanofiltration (NF) and reverse osmosis (RO) were conducted with a *SIMAtec LSta80* bench-scale filtration unit, using cross-flow mode at 35 bar and a *NPO10* membrane (*Microdyn-Nadir*, Germany) for NF, and 50 bar and a *BW30* membrane (*Dow Chemicals*, USA) for RO. Prior to the adsorption tests with the three different water types, all the respective concentrations of the relevant organic micro-pollutants (OMP) were determined and all three waters were spiked to similar OMP concentrations using 20 mg/L OMP stock solutions (ultra pure water). The different water types are characterized in Tab. 1.

Tab. 1. Characterization of the different water types, UVA₂₅₄ – UV absorption at 254 nm, SUVA₂₅₄ – specific UV absorption at 254 nm.

	DOC [mg/L]	UVA ₂₅₄ [1/m]	SUVA ₂₅₄ [L/mg/m]	Benzotri- azole	Diclofenac	Gabapentin – [µg/L] –	Iopromide	Sulfame- thoxazole
raw water	11.2	27.2	2.4	16.9	22.1	26.0	15.0	15.4
NF reten. dil.	12.4	32.0	2.6	15.9	23.3	25.3	13.8	14.8
RO reten.	11.3	26.5	2.3	19.3	22.2	30.7	15.5	16.0

Powdered activated carbon adsorption tests

A stock suspension of the powdered activated carbon (PAC) *SAE Super* (*Norit*, Netherlands, B.E.T. surface 1150 m²/g, particle size d₅₀ 15 µm, data according to manufacturer) was prepared at 2 g/L in ultra pure water, and stored overnight for full wetting of the PAC. To obtain the desired PAC doses (5, 10, 15, 20, 30, 75, 150 mg/L), varying volumes of the PAC stock suspension (homogenized by stirring) were pipetted to 100 mL of the respective water sample in 300 mL flasks. A horizontal lab shaker was used for continuous and full mixture of the sample/ PAC suspensions. After the respective contact time (0.5 and 48 h), PAC was removed using *Chromafil Xtra* 0.45 µm membrane filters (regenerated cellulose, *Macherey-Nagel*, Germany, rinsed with ultra pure water).

Analytics

Organic micro-pollutants (OMP) were measured by high performance liquid chromatography with tandem mass spectrometry (HPLC-MS/MS) on an *XSelect HSS T3* HPLC column (2.5 μm particle size, 2.1*50 mm, *Waters*, USA) with a linear gradient (ultra pure water with 5 vol.-% Methanol (HPLC grade, *J.T. Baker*, USA) and 0.1 vol.-% formic acid (HPLC grade, *Sigma Aldrich*, Germany) versus 100% Methanol) running at 0.5 mL/min, and a *TSQ Vantage* (*Thermo Scientific*, USA) using $\text{ESI}\pm$. For each analyte, two mass fragments were chosen according to the *DAIOS* database (*Wasserchemische Gesellschaft* 2013). Deuterized isotopes (*TRC*, Canada, and *Dr. Ehrenstorfer*, Germany) were used for quantification. Data were evaluated with *Xcalibur 2.1* (*Thermo Scientific*).

Fractionized NOM/ EfOM was measured by liquid size exclusion chromatography with organic carbon detection (LC-OCD, *DOC-Labor Huber*, Germany) using a *HW50S* column (*Toyopearl*, Japan). The LC-OCD retention times were allocated according to the typical biopolymer, humics, building blocks, acids, and neutrals fractions (Huber et al. 2011). Due to the large overlapping of the LC-OCD peaks, especially in the range of high retention times, intensities of the signal responses at specific retention times were taken in order to obtain quantitative values, instead of integrating the chromatograms. The maximum signal responses between minutes 47 and 53 were taken for the acids fraction, and the signal responses at 56.5 min were taken for the intensity of the neutrals fraction. DOC was measured by catalytic combustion with a *varioTOC Cube* (*elementar Analysensysteme*, Germany). UV absorption at 254 nm was measured with a *Lambda 12 UV/ vis* spectrometer (*Perkin-Elmer*, USA) using quartz *Suprasil* 10 mm cuvettes (*Hellma GmbH & Co. KG*, Germany).

Calculations and modeling

The adsorption analysis was used to characterize the adsorptive properties of the effluent organic matter (EfOM). The EfOM is a mixture of unknown composition and is usually only measureable via the bulk parameter DOC. The adsorption analysis formally converts the EfOM into a finite number of fictive components, each of which accounts for a group of similarly adsorbing compounds within the EfOM. Practically, the respective DOC isotherm is determined; then the adsorption isotherm parameters of the fictive components are arbitrarily defined. A fitting procedure using a mixture adsorption model varies the initial concentrations of the fictive components to best fit the experimental DOC isotherm (Johannsen and Worch 1994, Sontheimer et al. 1988, Worch 2012). For the comparison of different waters, the fictive component adsorption isotherm parameters should be chosen so that the fitting procedure gives adequate results for all waters considered. In the current study, the adsorption analysis was carried out using the software *AdsAna* (Worch 2009). The software uses the Ideal Adsorbed Solution Theory (IAST) (Radke and Prausnitz 1972) in combination with the Freundlich adsorption isotherm equation. In the adsorption analysis, the Freundlich exponent $1/n$ was set to 0.25 and the Freundlich coefficients (K_F) for four fictive components were set to 0, 40, 80, and 160 (mg/g)*(L/mg)^(1/n), accounting for non-adsorbable, weakly, medium, and highly adsorbable EfOM compounds.

The Equivalent Background Compound (EBC) model (Knappe et al. 1998, Najm et al. 1991, Worch 2010, Zoschke et al. 2011) was used to model the competitive effect of the NOM/ EfOM compounds present in the respective water. The EBC model creates a fictive adsorption system, consisting of two adsorbing compounds of which one is the known OMP and the other one is the fictive competing EBC. Depending on the deterioration of the OMP adsorption in the multi-solute system (with competition) compared to the OMP adsorption in a single-solute system (without competition), a mathematical solver calculates the EBC characteristics that best fit the observed competition in the multi solute adsorption system. For the EBC model calculations, an automated spreadsheet procedure was developed using the Freundlich isotherm equation integrated into the equations of the IAST. For each experimental data point (i.e. PAC dose), two equations (Eq. 7 and Eq. 8) are obtained.

$$c_{o,1} - q_1 m - \frac{q_1}{q_1 + q_2} \left(\frac{n_1 q_1 + n_2 q_2}{n_1 K_{F,1}} \right)^{n_1} = 0 \quad \text{Eq. 7}$$

$$c_{o,2} - q_2 m - \frac{q_2}{q_2 + q_1} \left(\frac{n_2 q_2 + n_1 q_1}{n_2 K_{F,2}} \right)^{n_2} = 0 \quad \text{Eq. 8}$$

where the indices 1 and 2 refer to the OMP and the EBC, respectively, $c_{o,i}$ are the initial concentrations, q_i are the solid phase concentrations/ loadings, m is the PAC dose, $1/n_i$ and $K_{F,i}$ are the single solute Freundlich constants. The mathematical solver then solves all of the equations (number of experimental data points * 2) simultaneously for the three variables $c_{o,EBC}$, $1/n_{EBC}$, and $K_{F,EBC}$. The spreadsheet procedure optimized the calculations according to the minimization of the squared differences of the measured and calculated OMP concentrations and loadings (weighed by the respective measured value), and the guessed and calculated EBC loadings (weighed by the respective guessed value) (Graham et al. 2000). The single-solute isotherm parameters were obtained from PAC bottle point experiments in salt solution spiked with the respective OMP. Where possible, the Freundlich isotherm parameters of the EBC were set to those of the respective OMP, and only the initial concentration of the EBC ($c_{o,EBC}$) was allowed to vary (Zoschke et al. 2011), in order to obtain explicit results in the EBC modeling. Accordingly, the stronger NOM/ EfOM compete with the OMP in the water, the higher is the modeled value of $c_{o,EBC}$. This approach of equal OMP and EBC Freundlich parameters was not applicable to weakly adsorbing OMP and in these cases, only $1/n_{EBC}$ was kept fixed and $K_{F,EBC}$ was allowed to vary. All calculations were conducted with molar concentrations. The molar EBC concentrations can be converted into mass concentrations by choosing arbitrary molar masses (Graham et al., 2000). However, this is an extreme simplification because (i) the observed competition may be caused by substances of different molecular weights, (ii) the molecular carbon content of the EBC must be chosen arbitrarily if DOC-converted mass concentrations of the EBC shall be calculated, and (iii) the EBC represents a variety of natural substances which may have different properties regarding their competitiveness. Therefore, remaining with the initially calculated molar concentrations of the EBC is sufficient to empirically evaluate and compare the competition in different systems (Worch, 2010).

RESULTS AND DISCUSSION

Characterization of EfOM/ DOC

The LC-OCD chromatograms of the three different water types as well as the corresponding chromatograms of selected PAC-treated waters are shown in Fig. 5. Compared to the raw water sample, the bulk organics in the diluted NF retentate are larger (shorter retention times), whereas the bulk organics in the RO retentate are smaller (higher retention times) (Huber et al. 2011). Note that the differences appear throughout the entire chromatogram: The humics and building blocks peaks (40–47 min) are increased in the diluted NF retentate while being reduced in the RO retentate; the acids peak (~50 min) and neutral peak (>54 min) are reduced in the diluted NF retentate but increased in the RO retentate. We can therefore conclude that originating from the organic compounds of the initial raw water, the diluted NF retentate contains mainly large organic material such as humic substances and their fragments and the diluted NF retentate is reduced in small acids and neutrals. In contrast, the RO retentate contains mostly small organic acid and neutral compounds and the RO retentate contains fewer larger EfOM substances. (The raw water chromatogram and the fictional chromatogram that results from averaging the chromatograms of the two fractionized waters (RO-retentate and diluted NF retentate) are nearly the same, cf. Supporting Information (Appendix B-1, p. 135). Thus, the treatments did only result in physical separation of the raw water constituents but not in breakage/ formation of water constituent associations.)

The chromatograms of the PAC-treated waters show further that the adsorption in the diluted NF retentate is slower, while the adsorption in the RO retentate is faster, compared to the adsorption in the raw water: The difference between the 0.5 h and 48 h graphs for the diluted NF retentate is more pronounced than in the case of the RO retentate. This indicates that the large EfOM molecules of the diluted NF retentate have overall reduced adsorption kinetics as compared to the smaller RO retentate bulk organics which is in line with previous findings (Newcombe et al. 2002a).

Fig. 6 shows the results of the adsorption analysis conducted with *AdsAna* (Worch 2009). For both of the tested adsorption times (0.5 and 48 h), the adsorbability of the EfOM (expressed via the DOC) increases in the order NF retentate diluted < raw water < RO retentate (increase of the light and medium gray bars). Accordingly, EfOM fractions that are contained in the NF retentate are less adsorbable than the initial raw water EfOM fractions, and the EfOM fractions that passed the NF membrane are the most adsorbable. In combination with the results from the LC-OCD measurements shown in Fig. 5, it can be concluded that the large NF retentate (diluted) EfOM fractions are somewhat less adsorbable than the initial “normal” raw water EfOM fractions, and that the small RO retentate EfOM fractions are more adsorbable. Considering the values of specific UV absorption at 254 nm ($SUVA_{254}$) of the three waters (diluted NF retentate > raw water > RO retentate), shown in Tab. 1, it is furthermore notable that a high UV absorption potential of the EfOM does not necessarily imply good adsorption properties of the EfOM (Zietzschmann et al. 2014a).

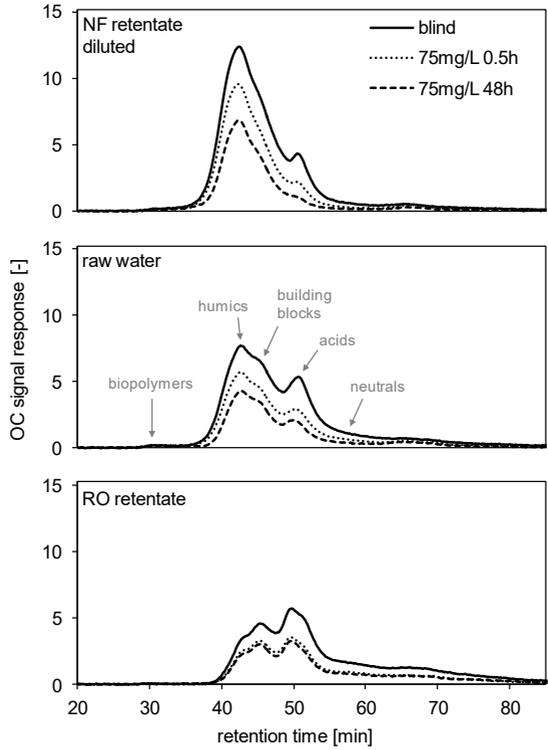


Fig. 5. LC-OCD chromatograms of diluted NF retentate, raw water, RO retentate, and 75 mg/L PAC-treated waters after 0.5 and 48 h contact time, with fraction indicators (Huber et al. 2011).

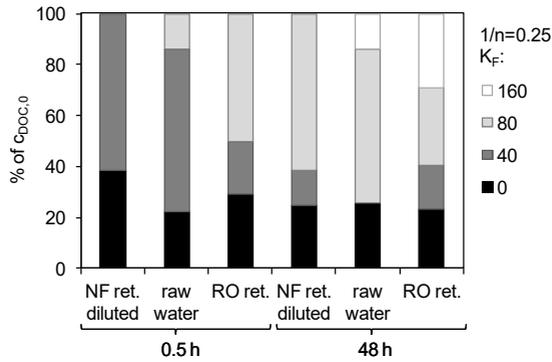


Fig. 6. Adsorption analysis DOC composition of diluted NF retentate, raw water, RO retentate, after 0.5 and 48 h.

Relative micro-pollutant removals

The relative OMP concentrations (residual concentration divided by initial concentration, c/c_0) that were achieved at a PAC dose of 20 mg/L in the three different water types are presented in Fig. 7 for selected OMP. The graphic gives a concise overview over the removabilities of the measured OMP in the presence of the different EfOM backgrounds. The relative OMP concentrations are the lowest in the diluted NF retentate, medium in the raw water, and high in the RO retentate. (e.g. after 0.5 h for benzotriazole: 0.15 in the NF retentate, 0.35 in the raw water, and 0.5 in the RO retentate, corresponding to a doubling and a tripling of the NF retentate relative concentration, respectively.) Accordingly, the competition evoked by the bulk EfOM increases from the diluted NF retentate over the raw water to the RO retentate. These findings are in line with the results from the adsorption analysis (Fig. 6) which show that the activated carbon affinity of the bulk EfOM increases in the same order. Considering the LC-OCD chromatograms shown in Fig. 5, it can be concluded that the small EfOM compounds of the RO retentate cause the strongest competitive effects while those of the raw water and the diluted NF retentate bear a reduced competitiveness.

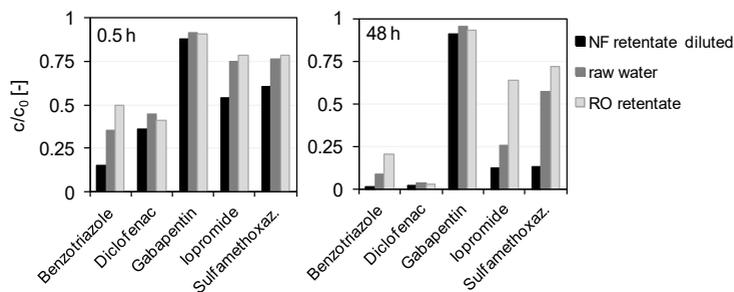


Fig. 7. Relative OMP concentrations at 20 mg/L PAC for the three different waters, after 0.5 h (left) and 48 h (right).

Fig. 7 also demonstrates that especially medium/ weakly adsorbable substances face strong differences in EfOM competition. For iopromide and sulfamethoxazole, longer adsorption times (comparison of 0.5 h and 48 h) come together with increasing differences of the relative removals in the three waters. In the case of the RO retentate, the relative concentrations of these OMP do barely decline between 0.5 h and 48 h, underlining the competitiveness of the RO retentate EfOM. Highly adsorbable compounds like benzotriazole and diclofenac are less impacted by the high competitiveness of the RO retentate EfOM and longer adsorption times do not increase the relative removal differences between the three waters. The hardly adsorbable OMP (like gabapentin) show little differences in the respective relative removals when comparing the three water types. Either, these OMP have generally very low affinity

towards the activated carbon (e.g. because they aim at specific scarce activated carbon surface sites, like polar substituted sites) or they are subject to competition by the majority of the EfOM compounds, mostly independent if these EfOM compounds are strong or weak adsorbates.

The results presented in Fig. 7 underline that even at a comparable initial DOC concentration ($c_{o,DOC}$) in the three water types, the relative OMP removals differ strongly. Thus, the concept to infer relative OMP removals at comparable bulk EfOM background concentrations (independent of the initial OMP concentration, given that $c_{o,OMP} \ll c_{o,DOC}$) simply from the carbon dosage (Cook et al. 2001, Knappe et al. 1998, Westerhoff et al. 2005) does not apply here. We can therefore conclude that the NF/ RO treatment does not only induce an EfOM fractionation by size but also by adsorption competitiveness with respect to OMP. In combination with the EfOM size fractionation shown in Fig. 5 these results demonstrate that the small fraction induces the strongest competitive effects while the large fraction is the least interfering. Accordingly, direct competition for adsorption sites is the major interference mechanism by WWTP effluent EfOM. Indirect competition or restriction of pore access due to blockage by larger EfOM molecules has a smaller impact on OMP adsorption. Another reason for reduced EfOM competitiveness could also be that the EfOM molecules are too large to enter and block the pores and remain un-adsorbed in the free solution.

PAC loadings with organic micro-pollutants and EBC modeling

The PAC loadings of selected OMP for the different waters after 48 h of adsorption are plotted against the respective OMP concentrations in Fig. 8. In all cases, the loadings decline in the order diluted NF retentate, raw water, RO retentate. As the initial concentrations of the competing bulk organics, expressed via $c_{o,DOC}$, are similar in the three water types, the differences in the OMP loadings must arise from different bulk EfOM compound properties influencing their adsorption competitiveness. Thus, the mainly large EfOM fractions of the diluted NF retentate evoke less interference with OMP adsorption whereas the small fractions of the RO retentate produce higher hindrance, compared to the raw water EfOM fractions.

Furthermore, the loading curves shown in Fig. 8 have differences at high OMP concentrations: In the case of the diluted NF retentate, the curves of the medium/ weak adsorbates show little to no bending towards negative slopes at high concentrations. In the case of the RO retentate, negative slopes do occur, demonstrating that especially in situations with high competition for few adsorption sites, the RO retentate bulk organics have a high negative impact on OMP adsorption. It is notable that a negative curve bending for OMP in the diluted NF retentate occurs only in the case of iopromide but not sulfamethoxazole. We assume that the comparatively large bulk organic molecules in the NF retentate compete stronger with larger substances like iopromide (molecular volume 445 \AA^3) than with smaller adsorbates such as sulfamethoxazole (205 \AA^3) (CAS 2014); but also other molecular properties such as polarity may play a role in the observed differences. During the water preparation, the NF retentate was depleted, meaning that small substances were mostly washed out.

This matches the high PAC loadings with sulfamethoxazole in the diluted NF retentate compared to the raw water and the RO retentate.

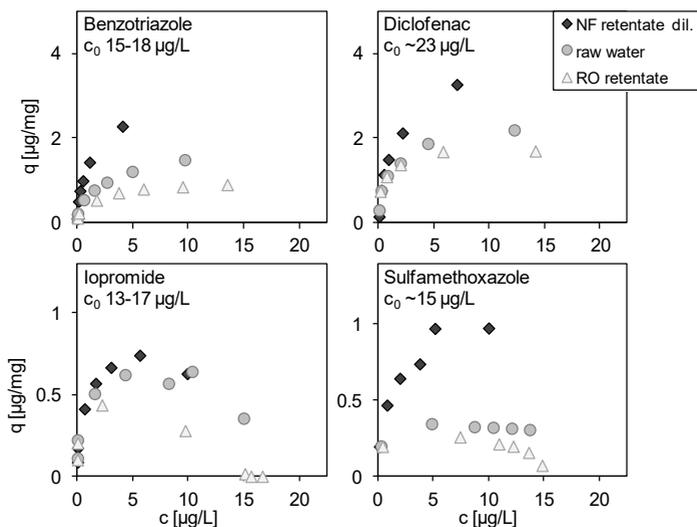


Fig. 8. PAC OMP loadings VS OMP concentrations in the three water types after 48 h of adsorption; note the different scales of the top/ bottom ordinates.

The equivalent background compound (EBC) model was used to model the competitive adsorption of OMP in the presence of EfOM. Where possible, the Freundlich $1/n$ and K_F parameters of the fictive EBC were set to the corresponding values of the respective OMP, in order to reduce the model complexity. This approach produces acceptable results for most good adsorbates but not for weak adsorbates. In the case of the latter, the K_F value of the EBC was therefore allowed to vary. (Keeping the Freundlich exponent $1/n$ constant for the waters that ought to be compared reduces complexity and facilitates the comparison). The experimentally determined data points as well as the EBC model results for selected OMP are shown in Fig. 9. Note that discrepancies between experimental and modeled data are mainly due to the fixation of the Freundlich exponent ($1/n_{OMP}$ is the same in the single solute pure water systems and in the multi solute WWTP effluent system) which fixes the slopes of the curves in the EBC model, especially at high PAC doses (left in the diagrams). The two diagrams at the top show the good adsorbates benzotriazole and diclofenac ($K_{F,EBC}$ equal to $K_{F,OMP}$). The two diagrams at the bottom show iopromide and sulfamethoxazole which are medium/ weak adsorbates. In all cases, the EBC model calculations produce initial values for the concentrations of the EBC in the order RO retentate > raw water > diluted NF retentate. Additionally, where $K_{F,EBC}$ was allowed to vary, $K_{F,EBC}$ are the highest in the RO

retentate, medium in the raw water and the lowest in the diluted NF retentate. Especially in the case of weak adsorbates and high concentrations/ low PAC doses, the negative impacts due to strong EfOM competitors are visible. However, also the OMP/ adsorbate size has an impact on the competitiveness of the different EfOM fractions. In the case of the comparatively large iopromide molecule, the loading-VS-concentration curves of the three waters are comparatively close to each other. The smaller OMPs sulfamethoxazole and benzotriazole are clearly more impacted by the raw water and RO retentate EfOM than by the diluted NF retentate EfOM. Therefore, the competition due to NF retentate EfOM is stronger in the case of iopromide and we assume this is due to size effects (large EfOM VS large OMP in the case of iopromide) and/ or variable molecular properties of the adsorbates. The removal of small-sized EfOM due to NF/ depletion in the diluted NF retentate has a high positive effect on the adsorption of benzotriazole and sulfamethoxazole.

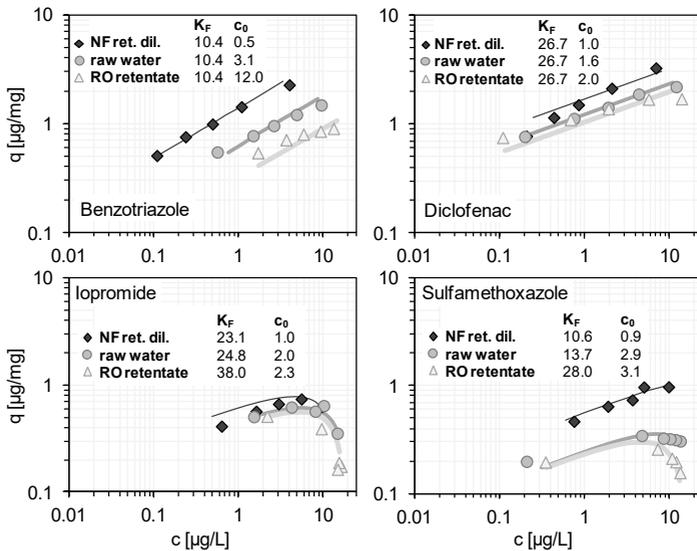


Fig. 9. EBC modeling of the adsorption in the three waters for selected OMP, 48 h; with EBC characteristics, K_F in $[(\text{mg/L}) \cdot (\text{L/nmol})^{1/n}]$, c_0 in $[\mu\text{mol/L}]$.

The initial concentrations of the EBC ($c_{0,EBC}$) for the respective OMP are plotted versus the organic carbon signal intensities of the LC-OCD acids and neutrals fractions of the three water types in Fig. 10. In all cases, the $c_{0,EBC}$ increase with increasing intensities of the small acids and neutrals LC-OCD fractions. Note that in the case of OMP where $K_{F,EBC}$ was allowed to vary, $K_{F,EBC}$ also increases along with $c_{0,EBC}$ (cf. Fig. 9), additionally underlining the increasing competition. The LC-OCD acids and neutrals intensities increase in the order diluted NF retentate, raw water, RO retentate. This again demonstrates the impact of the amount

of small bulk organics on the competition behavior of the EfOM compounds against OMP. We assume that these small substances measured by LC-OCD are in a similar molecular size range like most of the OMP and therefore target similar adsorption sites on the PAC surface. It has been suggested by several other authors that only specific fractions of the bulk NOM/EfOM do actually compete with OMP since a substantial amount of the bulk organics are too large to target the same micropore adsorption sites as the OMP (Graham et al. 2000, Knappe et al. 1998, Li et al. 2005). For the NOM competition on geosmin and 2-methylisoborneol in drinking water/ reservoir water, this effect was shown by removing large NOM fractions using flocculation (Zoschke et al. 2011).

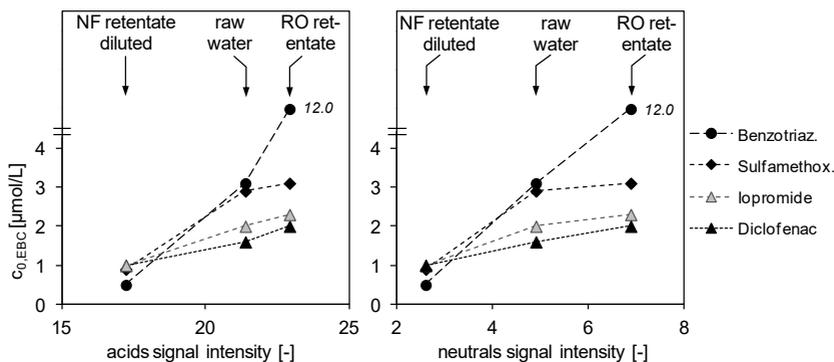


Fig. 10. Initial EBC concentrations for selected OMP VS acids and neutrals signal intensities (arbitrary units) of the respective initial water types.

CONCLUSIONS

In this study, the activated carbon adsorption of organic micro-pollutants (OMP) competing with differently sized but similarly concentrated fractions of wastewater treatment plant (WWTP) effluent organic matter (EfOM) was investigated. The different fractions of EfOM have variable adsorption behavior. Large EfOM molecules show slower and overall weaker adsorption than the raw water EfOM while smaller EfOM adsorb quickly and overall better. The EfOM fractions induce very variable competitive effects onto OMP adsorption. The small EfOM fraction is more competitive than the raw water EfOM and the large EfOM fraction provokes less competition compared to the raw water. With these results it is likely that direct competition for activated carbon adsorption sites is the main competition mechanism and indirect effects due to pore access restriction by large EfOM molecules is of less importance when considering OMP adsorption in WWTP effluent. The negative impacts of the small, highly competitive EfOM fraction are especially affecting medium and weakly adsorbing OMP such as iopromide and sulfamethoxazole. Modeling using the equivalent background compound (EBC) model confirms the analytical results. The study outcomes suggest

that waters with high amounts of small organics are likely to exhibit high adsorption competition. In these cases, techniques other than activated carbon adsorption such as oxidative treatments should be considered, too. Also, biologically active filters could be used prior to activated carbon stages in order to reduce the concentrations of adsorption competition-intense small organics. Furthermore, water pre-treatment with nanofiltration/ reverse osmosis is useful for detailed examination of adsorption competition mechanisms. With this laboratory procedure, the EfOM/ NOM competition can be enhanced for the comparison of different activated carbons under extreme conditions, for example.

ACKNOWLEDGMENTS

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SUPPORTING INFORMATION

Supplementary data related to this article can be found in the Supporting Information shown in Appendix B-1, p. 135.

REFERENCES

The cited references are contained in the general bibliography in Appendix A, p. 125.

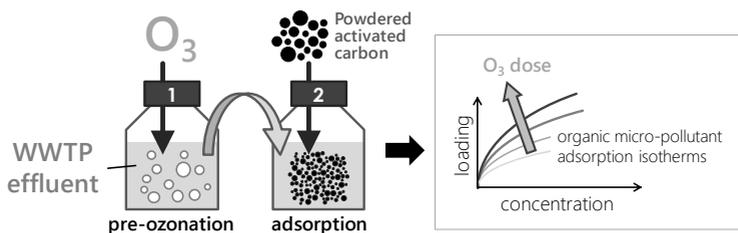
2.2 BOM aromaticity and hydrophilicity

Impacts of ozonation on the competition between organic micro-pollutants and effluent organic matter in powdered activated carbon adsorption

Water Research 84 (2015) 153–160

Frederik Zietzschmann¹, Raja-Louisa Mitchell¹ and Martin Jekel¹

GRAPHICAL ABSTRACT



ABSTRACT

This study investigates if ozonation of wastewater treatment plant (WWTP) effluent can reduce the negative impacts of effluent organic matter (EfOM) on the adsorption of organic micro-pollutants (OMP) onto powdered activated carbon (PAC). Pre-treatment of the water included membrane filtration for the removal of suspended/ colloidal organics, ozonation with various specific ozone consumptions, and subsequent OMP spiking to comparable initial concentrations in all of the ozonated waters. This approach allowed for comparative PAC adsorption tests. Adsorption analyses show that the adsorbability of EfOM decreases with increasing specific ozone consumptions. This is also reflected by liquid chromatography with online carbon and UV₂₅₄ detection (LC-OCD) which shows the ozone-induced disintegration of large EfOM into smaller fragments. Also, small organic neutrals are decreased while the small organic acids peak continuously increases with rising specific ozone consumptions. UV₂₅₄ demonstrates that the aromaticity of all LC-OCD fractions continuously declines together with increasing specific O₃ consumptions. This explains the varying EfOM adsorbabilities that occur due to ozonation. The ozone-induced decrease of EfOM adsorbability directly translates into reduced adsorption competition against the adsorption of OMP. With higher specific ozone consumptions, OMP removal and OMP loadings increase. The reduced adsorption competition is reflected in the outputs from equivalent background compound (EBC) modeling. In each of the ozonated waters, correlations between the OMP removals and the UV₂₅₄ removal were found.

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INTRODUCTION

Wastewater treatment plants (WWTP) which are a major contributor to the occurrence of organic micro-pollutants (OMP, e.g. pharmaceuticals) in aquatic environments, can additionally be equipped with advanced technologies like activated carbon adsorption or oxidation with ozone to reduce the release of OMP (e.g., Jekel et al. 2013). Also, these two techniques can be combined, usually by installing activated carbon treatment (e.g. via biological granular activated carbon filters) downstream of an ozonation stage. This approach can have beneficial effects on the toxicity/ mutagenicity and can reduce the concentrations of ozonation transformation products (Guzzella et al. 2002). Also, ozonation prior to an activated carbon treatment step may have advantageous effects on the activated carbon adsorption of OMP, which was elucidated in the current study.

The reasons for potential beneficial effects of ozonation prior to OMP adsorption are (i) OMP concentrations can be reduced by both techniques and (ii) ozone-induced transformation of effluent organic matter (EfOM) may enhance OMP adsorption onto activated carbon. The second aspect was in the focus of this study. Activated carbon adsorption of OMP can be strongly deteriorated by the adsorption of EfOM (Yu et al., 2012; Zietzschmann et al., 2014b, 2014c) or natural organic matter (de Ridder et al., 2011; Matsui et al., 2003; Ternes et al., 2002). The competition mechanisms are direct competition for adsorption sites on the activated carbon internal surface, and blockage of activated carbon pores with larger molecules of the EfOM bulk organics (Li et al., 2003). Some of the EfOM compounds may be too large to enter the activated carbon pore system and thus do not cause competition (Knappe et al. 2003). Ozonation of dissolved organic matter results in its disintegration leading to lower molecule sizes. As ozone preferably oxidizes electron-rich areas (aromatic π -delocalized systems) in target molecules, it can also reduce the aromaticity of the oxidized compounds (Treguer et al. 2010). It is also known that dissolved organics are less adsorbable onto activated carbon after ozonation (Matsui et al. 1999). The activated carbon adsorption of the herbicide atrazine was reported to increase after pre-ozonation of natural organic matter (NOM) in river water (Müller et al. 1996). The same study showed that NOM removal by pre-adsorption onto activated carbon improved subsequent atrazine adsorption.

It is the aim of the current study to investigate how the ozonation of WWTP effluent impacts the adsorptive behavior of EfOM in their competition against OMP adsorption. The experimental approach was to expose EfOM in a WWTP sample to varying amounts of ozone while keeping the concentrations of the dissolved organic carbon (DOC) and several OMP constant, followed by activated carbon adsorption. The approach was realized by WWTP effluent pre-treatment using ultrafiltration, followed by ozonation with different specific ozone consumptions, and subsequent spiking of OMP. Then, powdered activated carbon (PAC) adsorption batch tests were conducted.

MATERIALS AND METHODS

Water samples and pre-treatment

Wastewater treatment plant (WWTP) effluent was sampled on 10 March 2014 from WWTP Berlin Ruhleben (Germany), equipped with conventional mechanical and biological treatment for domestic wastewater (dry weather capacity of $\sim 250,000$ m³/day). To remove suspended solids and microorganisms, the WWTP effluent was ultra-filtered using a *dizzer*[®] *Multibore*[®] 1.5 membrane module (Polyethersulfone, molecular weight cutoff 100 kDa, INGE, Germany). Ultrafiltration also ensured that the subsequent ozonation did not lead to an increase of the dissolved organic matter/ carbon (DOC) which would have otherwise been the case due to the disintegration of large suspended/ colloidal organic substances/ microorganisms. The resulting water was then ozonated on a bench-scale ozonation plant equipped with an ozone generator (*Wedeco*, Germany). Ozone was bubbled into 3.6 L of the stirred ultra-filtered water in a glass jar. The specific ozone consumption was calculated by subtracting the ozone in the exhaust gas from the inflowing ozone, divided by the DOC of ozonated water. The organic micro-pollutant (OMP) concentrations of the resulting ozonated waters were then determined and all of the waters were spiked with OMP to comparable concentrations of ~ 20 mg/L, using OMP stock solutions at 20 mg/L. The stock solutions were prepared by dissolving 10 mg absolute weight of the respective OMP (*Sigma Aldrich*, Germany, and *Dr. Ehrenstorfer*, Germany) in 0.5 L ultra pure water (*ELGA Berkefeld*, *Veolia*, Germany) and adjusting the pH to ~ 7 with HCl or NaOH (both at analytical grade). An overview over the different waters is given in Tab. 2.

Tab. 2. Characterization of the differently ozonated waters with spiked organic micro-pollutants.

specific O ₃ consumption	DOC	UVA ₃₅₄	vis ₄₃₆	SUVA ₃₅₄	Acesulfame	Benzotriazole	Bezafibrate	Carbamazepine	Diclofenac	4-Formylaminoantipyrine	Gabapentin	Iomeprol	Iopromide	Methylbenzotriazole	Primidone	Sulfamethoxazole
[mg/mg]	[mg/L]	[1/m]	[1/m]	[L/mg/m]						– [µg/L]	–					
0	11.7	27.8	1.9	2.4	22	21	38	21	24	22	21	20	18	23	22	21
0.18	11.8	25.5	1.3	2.2	26	22	33	20	26	23	26	20	18	22	21	20
0.33	11.7	23.0	0.9	2.0	23	22	38	19	25	22	25	20	19	21	21	21
0.65	11.4	18.6	0.6	1.6	22	21	37	20	24	20	21	19	19	19	20	20
0.97	11.1	14.9	0.4	1.3	22	19	37	21	24	21	21	17	17	19	19	21
1.60	11.1	12.4	0.5	1.1	21	17	29	18	22	20	19	15	19	15	18	21
1.64	11.0	11.7	0.4	1.1	20	19	38	21	24	20	19	14	20	18	20	20

Powdered activated carbon batch tests

Powdered activated carbon (PAC) batch tests were conducted with all of the produced waters. PAC (*SAE Super*, *Norit*, Germany) was dried, cooled in a desiccator, suspended in ultra

pure water at 2 g/L, and stored overnight for full wetting. Different volumes of the thoroughly stirred 2 g/L PAC stock suspension were pipetted to 100 mL of the produced waters, to obtain PAC doses of 5, 10, 15, 20, 30, 75, and 150 mg/L. The potential dilution due to stock suspension addition can be neglected as shown in the Supporting Information (Appendix B-2). Upon PAC stock solution addition, the batches were put on a horizontal shaker for full mixture during 0.5 and 48 h. After these contact times, the batches were filtered through regenerated cellulose 0.45 μm -membrane filters (rinsed with ultra pure water, *Chromafil® RC-45/25, Macherey-Nagel, Germany*).

Analytics

OMP were measured with high performance liquid chromatography coupled with tandem mass spectrometry (HPLC-MS/MS). HPLC was carried out on a *XSelect HSS T3* column (2.1*50 mm, 2.5 μm particle size, *Waters, USA*) with a linear gradient at 0.5 mL/min from 98% aqueous phase (950 mL ultra pure water, 50 mL MeOH (HPLC grade, *J.T. Baker, USA*), 1 mL HCOOH (HPLC grade, *Sigma Aldrich, Germany*)) to 100% organic phase (MeOH). For MS/MS, a *TSQ Vantage* (*Thermo Scientific, USA*) was used in ESI^{+/−} modes, two mass fragments were used for identification (Wasserchemische Gesellschaft 2013) of which the more abundant one was used for quantification in combination with deuterized internal standards (*TRC, Canada* and *Dr. Ehrenstorfer, Germany*, cf. Supporting Information, Appendix B-2, p. 137), evaluated with *Xcalibur 2.1* software (*Thermo Scientific, USA*).

UV-vis absorption was measured on a *Lambda 12* (*Perkin-Elmer, USA*), with 10 mm *Suprasil* quartz cuvettes (*Hellma, Germany*). DOC was measured on a *varioTOC Cube* (*elementar Analysensysteme, Germany*). Fractionized DOC was measured using liquid size exclusion chromatography on a *HW50S* column (*Toyopearl, Japan*) coupled with online carbon and UV₂₅₄ detection (LC-OCD, *DOC-Labor Huber, Germany*). LC-OCD signal intensities at the respective peak maximum times were taken for quantitative values for the typical peaks (Huber et al. 2011).

Modeling

To analyze the adsorption properties of the DOC, the concept of adsorption analysis was used. The adsorption analysis classifies the organic compounds that are comprised within the bulk parameter DOC into several differently well adsorbable fractions, so-called fictive components which vary in their respective adsorptive properties. With the adsorption analysis, the DOC of the respective water is characterized, e.g., by listing the percentages of non/ slightly/ medium/ well adsorbable DOC fractions in the respective water. For the conduction of the adsorption analysis, a spreadsheet procedure was programmed whose data inputs were the measured DOC concentrations of a loading curve/ isotherm. The adsorptive properties of the fictive components are provided by the user by assigning different Freundlich constants $K_{F,i}$ to each fictive component, the Freundlich exponent $1/n_i$ is usually the same for all components (Johannsen and Worch 1994, Sontheimer et al. 1988). In a 1st

step, the procedure simultaneously minimizes the two main IAST-derived equations (cf. Eq. 9 and Eq. 10) for each point of the loading curve/ isotherm (Worch 2010). Then, an error term resulting from the differences between the measured and the modeled concentrations and loadings (cf. Eq. 11) is minimized by changing the initial concentrations of the fictive DOC components. With the new concentration values, the two-step procedure is repeated until a satisfying result is found (usually when the calculated error term is below 5% and cannot be minimized any further) (Johannsen and Worch 1994). The allocation of $K_{F,i}$ values by the user is arbitrary but constricted by the error of the adsorption analysis. When different waters are compared, a set of $K_{F,i}$ values that can adequately be used on all waters has to be found by trial and error. This can lead to higher individual error terms but is the only way to reach comparability between the individual adsorption analyses. If several sets of $K_{F,i}$ values reach adequate individual errors for all compared waters, the set with the lowest overall error should be chosen.

$$G_1 = 1 - \sum_{i=1}^k \frac{c_{o,i}}{\frac{mq_T}{V} + \left(\frac{\varphi}{n_i K_{F,i}}\right)^{n_i}} \quad \text{Eq. 9}$$

$$G_2 = \frac{\varphi}{q_T} - \sum_{i=1}^k \frac{n_i c_{o,i}}{\frac{mq_T}{V} + \left(\frac{\varphi}{n_i K_{F,i}}\right)^{n_i}} \quad \text{Eq. 10}$$

where G_1 and G_2 are the minimizations terms, k is the number of adsorbable components, $c_{o,i}$ is the initial concentration of component i , m/V is the ratio of adsorbent mass to volume, q_T is the total loading, $1/n_i$ is the Freundlich exponent, φ is the spreading pressure term (the calculated values are of no further importance, Johannsen and Worch 1994), and $K_{F,i}$ is the Freundlich coefficient of component i .

$$S = \frac{100}{2N} \sum_{j=1}^N \left(\left| \frac{c_{mod,j} - c_{meas,j}}{c_{meas,j}} \right| - \left| \frac{q_{mod,j} - q_{meas,j}}{q_{meas,j}} \right| \right) \quad \text{Eq. 11}$$

where S is the minimization term, N is the number of data points, and $c_{mod,j}$, $c_{meas,j}$, $q_{mod,j}$, and $q_{meas,j}$ are the modeled and measured concentrations and loadings at loading curve/ isotherm point j .

The organic micro-pollutant (OMP) adsorption isotherms were modeled according to the Equivalent Background Compound (EBC) model (Najm et al. 1991). The procedure combines the mass balance equations for the adsorbate in the liquid/ solid phase system of the solution/ adsorbent with equations from the Ideal Adsorbed Solution Theory (IAST) for two solutes of which one is the respective OMP under consideration and the other is a fictive component (the EBC) that accounts for the observed adsorption competition with the considered OMP (Shimabuku et al. 2014, Worch 2012). For more information on the mathematical modeling procedure we refer to a previous publication (Zietzschmann et al. 2014c). The EBC model normally results in three parameters that describe the competitive effect of

the EBC on the adsorption of the respective OMP, the EBC initial concentration $c_{0,EBC}$, and the EBC Freundlich parameters, $K_{F,EBC}$ and $1/n_{EBC}$. Since different combinations of these parameters may result in the same model outputs for the adsorption isotherms, simplifications of the EBC model can and should be applied where possible. The simplifications include an equalization of the EBC Freundlich exponent $1/n_{EBC}$ to that of the OMP $1/n_{OMP}$, as well as an equalization of the EBC Freundlich coefficient $K_{F,EBC}$ to that of the OMP $K_{F,OMP}$. The latter simplification only results in satisfying modeling for strong adsorbates whose isotherms have continuously positive slopes throughout the entire concentration range. In the case of weak adsorbates whose isotherms have negative slopes in the vicinity of the OMP initial concentration, $K_{F,EBC}$ should be allowed to vary in order to get adequate EBC modeling results (Worch 2010).

RESULTS AND DISCUSSION

Ozonation effects on effluent organic matter adsorption

The results from the adsorption analyses of the differently preozonated waters are shown in Fig. 11. The amount of the non-adsorbable fraction ($K_F = 0 \text{ mg/g} * (\text{L/mg})^{1/n}$, units of K_F omitted hereafter) increases with increasing specific ozone consumption, from ~30% in the non-ozonated initial water to ~60% in two waters whose specific O_3 consumptions were ~1.6 $\text{mg O}_3/\text{mg DOC}$. Similarly, the percentage of the medium/ well adsorbable fraction ($K_F = 70$) decreases with increasing specific O_3 consumptions, from ~50% to ~15%. The poorly/ medium adsorbable fraction ($K_F = 35$) increases slightly, while the percentage of the highly adsorbable fraction ($K_F = 140$) is widely similar in all waters. The assignment of K_F values to descriptions of adsorbability (“highly adsorbable” etc.) was made according to (Worch 2012).

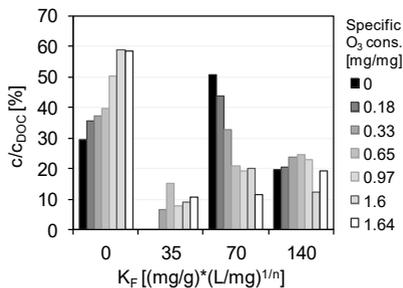


Fig. 11 Fictive component distribution of the DOC according to the adsorption analyses of the differently pre-ozonated waters.

The modeling results show that due to ozonation, medium/ well adsorbable effluent organic matter (EfOM) components are transformed to less adsorbable compounds. This finding is in line with previous studies (Matsui et al. 1999). Ozonation has been reported to reduce the size, hydrophobicity, and aromaticity of EfOM (Swietlik et al. 2004, Tang et al. 2014). Given that the adsorbability of organic compounds increases with their aromaticity, size, and hydrophobicity, EfOM that is transformed by ozonation is less adsorbable onto activated carbon. This, in turn, could imply reduced adsorption competition of these EfOM constituents against the adsorption of organic micropollutants (OMP). The fairly similar concentrations of the highly adsorbable fraction ($K_F = 140$) in all waters could indicate that the typical ozone-induced shift from aromatic to aliphatic structures (Westerhoff et al. 1999) may not necessarily alter the adsorbability of strongly adsorbing compounds. It could also indicate the existence of a highly adsorbable fraction of EfOM which is resistant to ozonation, e.g. saturated compounds such as paraffins or substituted alkanes like alcohols (Hoigne and Bader 1983a, b).

The LC-OCD liquid chromatography organic carbon (OC) and UV_{254} chromatograms of the waters with specific ozone consumptions of 0, 0.65, and 1.64 mg O_3 /mg DOC, without powdered activated carbon (PAC) treatment and after PAC treatment with 75 mg/L and adsorption times of 0.5 and 48 h, are shown in Fig. 12. (The chromatograms of Fig. 12 are also shown in the Supporting Information (Appendix B-2, p. 137) where they are differently grouped for easier comparison before/ after PAC adsorption.) The OC diagrams of the non-PAC-treated samples show that due to ozonation, the peaks of the large fractions (biopolymers (~31 min), humics (~43 min)) decrease, resulting in increasing peaks of the smaller fractions which confirms other studies (Altmann et al. 2014). Due to a possible O_3 -induced disintegration of biopolymers (non-ozonated sample compared to the sample with a specific O_3 consumption of 0.65 mg O_3 /mg DOC), the fragments of biopolymers appear later in the chromatogram, overlapping with the humics peak which results in a slight increase of the humics peak. With the higher specific ozone consumption of 1.64 mg O_3 /mg DOC, the humics peak decreases, likely due to breakage of humics into smaller constituents, because the building blocks (~45.5 min) and acids peaks (~50.5 min) further increase. The neutrals peak (~55 min and longer retention times) decreases due to ozonation, possibly due to the introduction of oxygen-containing functional groups (possibly leading to an increase of the acids peak), and/ or decomposition/ mineralization of the neutral compounds (Wert et al. 2007). In contrast to the OC signals, the UV_{254} signals of the non-PAC-treated ozonated samples show an overall trend of reduced UV_{254} absorption throughout the entire chromatogram. Accordingly, the aromaticities (Weishaar et al. 2003) of all fractions are reduced by ozonation, independent of the size of the fraction. The general decrease of the EfOM aromaticity is also underlined by the UV_{254} , vis_{436} , and SUVA values listed in Tab. 2. A highly preferential reaction of ozone with aromatic (sp^2 hybridized) organics has been reported while non-aromatic structures are little or not affected by ozone (Westerhoff et al. 1999) and ozone leads to selective cleavages of electron-rich structures such as aromatic ring systems due to electrophilic addition (Wenk et al. 2013). Given the comparatively high concentrations of the hydroxyl radical scavengers carbonate/ bicarbonate (Hoigne and Bader 1976) in

the tested wastewater treatment plant (WWTP) effluent with a typical total inorganic carbon (TIC) of >50 mg/L or 4.17 mmol/L (Sperlich et al. 2008b), oxidation by direct ozonation outweighs indirect hydroxyl radical oxidation (Chiang et al. 2006).

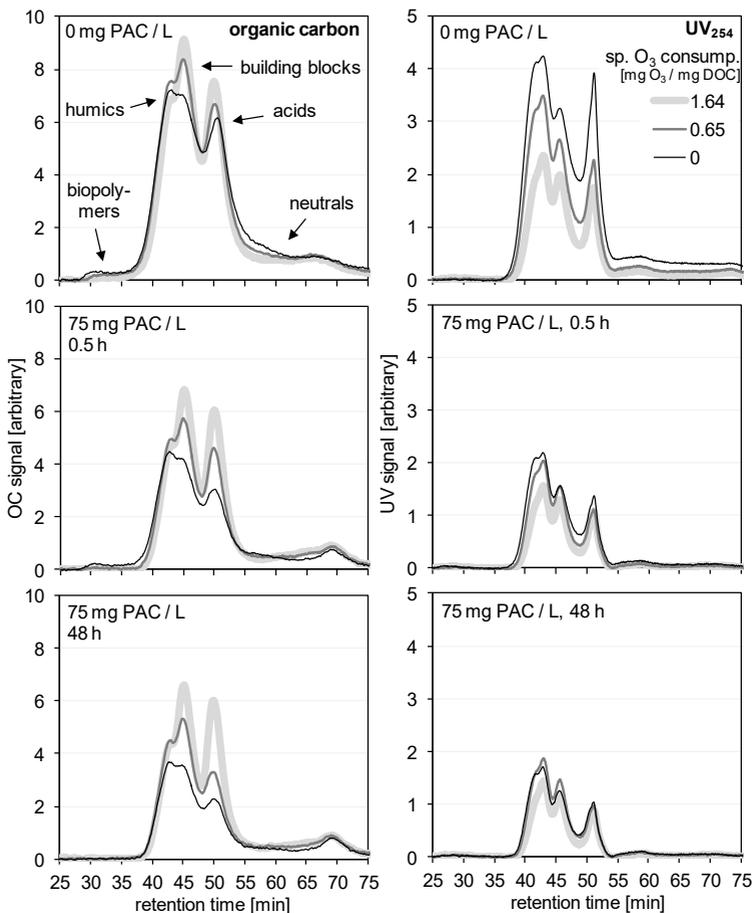


Fig. 12 LC-OCD organic carbon (*left*) and UV_{254} (*right*) chromatograms of differently ozonated blind samples (*top*), and PAC-treated samples at 75 mg/L after 0.5 h (*middle*) and 48 h (*bottom*) adsorption time.

The LC-OCD chromatograms of the PAC-treated samples show that with higher specific ozone consumptions, the effluent organic matter (EfOM) adsorbability onto PAC decreases. Also, the differences between the chromatograms of 0.5 and 48 h adsorption times decrease with increasing specific O_3 consumption, indicating increased kinetics, possibly due to

breakage of EfOM leading to smaller molecular sizes. Similar to the adsorption analysis results (cf. Fig. 11), these results show that ozonated EfOM are less adsorbable than the initial EfOM (higher specific O_3 consumptions go along with lower EfOM adsorbability). Furthermore, the adsorption of smaller EfOM fractions is not increased by a potentially better access to pores due to the breakage of large EfOM as a result of ozonation (Zietzschmann et al. 2014c). However, the effects of better access to pores on the one hand and weaker adsorbability of small EfOM fractions on the other hand may overlap and are not clearly distinguishable.

The chromatograms in Fig. 12 show that the ozonation of EfOM results mainly in an increase of the building blocks and low-molecular weight acids whereas the abundances of the other fractions are reduced. This does not only demonstrate the disintegration of the larger EfOM fractions into smaller components but also shows that the ozonation-induced integration of oxygen into EfOM constituents causes an increase in solubility, e.g. via formation of carboxylic acids or keto acids (Hammes et al. 2007, Swietlik et al. 2004, Westerhoff et al. 1999). The continuous increase of the low-molecular acids peak is likely to be enhanced by the abundance of carboxylic acid groups (-COOH) in these compounds. Carboxylic acids are reported to be electron withdrawing and to lower the ozone-related reactivities of associated compounds (Westerhoff et al. 1999). It has also been reported that ozonation can increase the amount of the overall DOC which is accessible by LC-OCD due to the oxidation of hydrophobic constituents (Altmann et al. 2014). This also explains why most of the low molecular weight EfOM in the ozonated water samples does not adsorb onto the PAC although these small organic components adsorb preferentially in non-ozonated WWTP effluent (Zietzschmann et al. 2014c).

Impacts on organic micro-pollutant adsorption

The PAC doses needed to remove 80% of the respective organic micro-pollutants (OMP) in the differently pre-ozonated waters (calculated by linear interpolation between the two PAC doses enclosing 80% removal) for adsorption times of 0.5 and 48 h, are depicted against the specific ozone consumptions of the pre-ozonated waters in Fig. 13. (The doses for gabapentin were calculated by linear extrapolation from the two highest PAC doses as the achieved removals were always <80%, since this compound is a very poor adsorbate.) Data for additional OMP that are not shown in Fig. 13 can be found in the Supporting Information (Appendix B-2, p. 137). In all cases, the PAC doses needed for 80% OMP removal decrease with increasing specific ozone consumptions. E.g., after 48 h of adsorption, less than 20 mg PAC/L are needed for 80% sulfamethoxazole removal in the water with a specific ozone consumption of ~ 1.6 mg O_3 /mg DOC. In contrast, more than 50 mg PAC/L are required in the non-ozonated water. Given that all of the waters had comparable DOC concentrations, the differences in the OMP removals are caused by different adsorbability of the EfOM compounds that result in variable adsorption competition against OMP. As the amount of very strong adsorbates of the EfOM ($K_F = 140$, cf. Fig. 11) appears mostly independent of the ozone consumption, the observed alleviation of adsorption competition due

to ozonation is likely due to the decrease of the medium/ well adsorbable compounds ($K_F = 70$). Furthermore, the results shown in Fig. 13 demonstrate that strong adsorbates which are also small in molecular size, such as benzotriazole (119 g/mol, 100 Å³) (molecular volumes according to ChemAxon 2014), are less affected by the ozone-induced decrease in adsorption competition than larger and weaker adsorbates like 4-formylaminoantipyrine (231 g/mol, 205 Å³) or iopromide (791 g/mol, 445 Å³), especially at short contact times (0.5 h): Between the waters with the lowest (0 mg O₃/mg DOC) and the highest (1.6 mg O₃/mg DOC) specific ozone consumptions in the pre-treatment, the PAC dose needed for 80% OMP removal decreases by ~50% for benzotriazole but by ~70% for 4-formylaminoantipyrine and ~75% for iopromide.

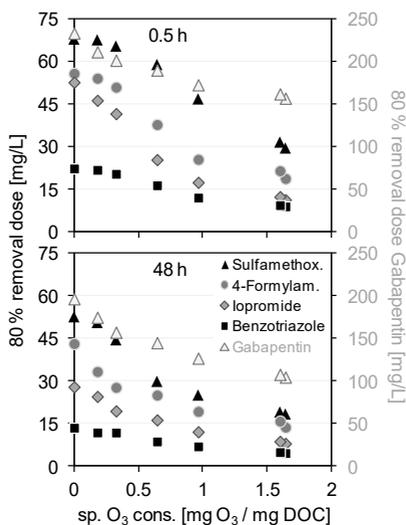


Fig. 13. Calculated PAC doses required for 80% OMP removal after 0.5 h (top) and 48 h (bottom) versus specific ozone consumptions; note the secondary y-axis for gabapentin.

We assume that strongly adsorbing OMP (as compared to weakly adsorbing OMP) are highly competitive against EfOM even in the non-ozonated sample. In the case of weakly adsorbing large adsorbates, the ozone-induced breakage of larger EfOM could also reduce the amount of EfOM aiming for similar adsorption sites as the OMP. According to the results, activated carbon consumption can be decreased by pre-ozonation of WWTP effluent when aiming at specific OMP removal targets. Also, combinations of ozonation and subsequent activated carbon adsorption would be beneficial for the overall removal of OMP. This is particularly interesting in constellations where the ozone dosage cannot be set arbitrarily high, e.g. due to the potential formation of bromate (Wert et al. 2007) and an additional activated carbon treatment step is needed to reach satisfactory concentration levels of OMP

that are only poorly/ medium affected by ozonation like benzotriazole, metoprolol, or some x-ray contrast agents (Margot et al. 2013). It should be noted that in practice, ozonation may transform some of the suspended organic matter into smaller fragments and increase the DOC concentrations accordingly; however, the DOC increase due to ozonation of WWTP effluent was shown to be <10% (Altmann et al. 2014).

The removals of benzotriazole, diclofenac, iopromide, and sulfamethoxazole are depicted versus the corresponding UV_{254} removals in two differently pre-ozonated waters and the non-ozonated water sample in Fig. 14. In all of the waters, a correlation exists between the removal of the OMP and UV_{254} (Altmann et al. 2014, Zietzschmann et al. 2014a). However, the observed correlations shift towards higher slopes and towards higher OMP removals as the specific ozone consumptions increase. This underlines that the preference of OMP adsorption as opposed to EfOM adsorption increases with rising specific ozone consumption. Due to the ozonation of UV_{254} -active EfOM, they are less favorably adsorbed. Apparently, those EfOM substances which still absorb UV_{254} after ozonation are less adsorbable onto PAC and thus cause less competition against OMP. Exemplary linear fits for the removals of diclofenac (w/o pre-ozonation), iopromide, and sulfamethoxazole in dependence of the UV_{254} removal indicate the predictability of OMP removal using UV_{254} removal (Altmann et al. 2014, Altmann et al. 2015, Zietzschmann et al. 2015a, Zietzschmann et al. 2014a). UV_{254} is thus a surrogate parameter representing EfOM compounds with similar adsorption properties like the investigated OMP. The similarity depends on the properties of the OMP and the composition of EfOM; the latter is affected by ozonation, as indicated by increasing linear slopes due to ozonation. Note that for strong adsorbates, the removal is very high even at low PAC doses and fitting may not be feasible due to very small data sets, e.g. for diclofenac in ozonated waters. (The overall small number of fittable data points is also the reason for comparatively high R^2 values.) The removal of UV_{254} can thus be used as an indicator for the removal of OMP by PAC even if ozonation was carried out previously. However, the correlations need to be adjusted if different or variable ozone consumptions are applied. The slopes of linear fits like the exemplary ones shown in Fig. 14 can indicate the competitiveness of EfOM in different constellations. High slopes demonstrate that OMP are strongly favored over the EfOM encompassed in UV_{254} . In the case of iopromide, the slope increases from 1.6 in the non-ozonated water sample to 2.5 and 4.2 in the ozonated samples, respectively. Thus, the preference of the adsorptive removal of iopromide against UV_{254} can increase by up to a factor of $4.2/1.6 \approx 2.5$ due to ozonation.

The adsorption isotherms (48 h adsorption time) of benzotriazole, diclofenac, and sulfamethoxazole in two pre-ozonated waters (specific ozone consumptions of 0.65, and 1.64 mg O_3 /mg DOC, resp.) and the non-ozonated water sample are shown in Fig. 15, together with isotherms resulting from equivalent background compound (EBC) modeling; the initial concentrations and Freundlich coefficients of the EBC are also given for all cases. For all three shown OMP, the isotherms of higher specific ozone consumptions are located above the isotherms of lower/ no specific ozone consumptions. This is also indicated by decreasing initial concentrations of the EBC (and decreasing Freundlich coefficients in the

case of sulfamethoxazole). Note that the EBC is a fictive compound (with the given Freundlich adsorption properties). Its initial concentration does not reflect actual quantities of EfOM but the theoretical initial concentration of a compound which would cause the observed competition (as caused by actual EfOM) against the considered OMP in a 2-component adsorption system. The EBC characteristics directly reflect the reduced adsorption competition due to the ozonation of EfOM.

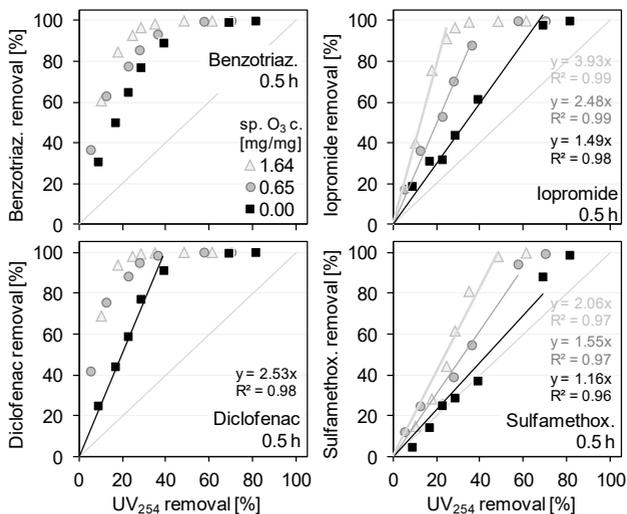


Fig. 14. PAC adsorptive removals of benzotriazole, diclofenac, lopromide, and sulfamethoxazole versus adsorptive UV_{254} removals in pre-ozonated waters and the non-ozonated water sample after 0.5 h of adsorption; with bisectrices indicating equal removal, and exemplary linear fits.

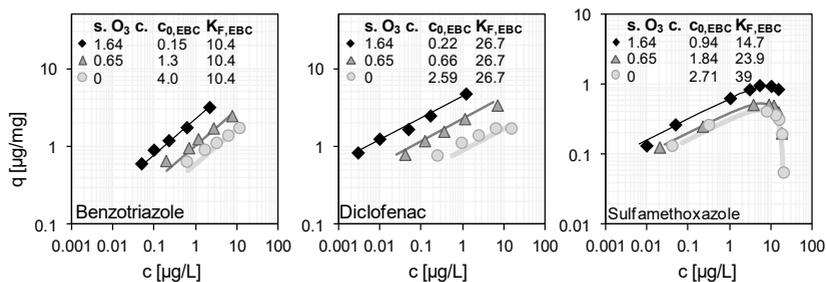


Fig. 15. Experimental (data points) and EBC-modeled (lines) isotherms for benzotriazole, diclofenac, and sulfamethoxazole in waters with previous ozone treatment of 1.64, 0.65 mg O_3 /mg DOC, and the non-ozonated water sample; with modeled initial concentrations and Freundlich coefficients of the EBC ($C_{0,EBC}$, $K_{F,EBC}$); note the different scaling of the y-axis.

The beneficial impacts of ozonation on the adsorption of OMP vary between the different OMP. For the strong adsorbates benzotriazole and diclofenac even the medium specific ozone consumption (0.65 mg O₃/mg DOC) has a strong positive effect: Over the entire concentration range, the OMP loadings on the PAC are at least twice as high as in the non-ozonated water. To achieve clear advantageous effects for the adsorption of sulfamethoxazole, the specific ozone consumption needs to be higher. When the specific ozone consumption is sufficiently high (1.64 mg O₃/mg DOC), the benefits are particularly high near the initial sulfamethoxazole concentration where the adsorption competition due to EfOM is very strong. This can also be seen from the EBC characteristics that were modeled for sulfamethoxazole, and from a less curved isotherm for sulfamethoxazole at 1.64 mg O₃/mg DOC compared to the isotherms modeled for medium or no ozonation. Accordingly, ozonation can abate the adsorption competition caused by EfOM against OMP and increase the exploitation of activated carbon capacity. The results from this study show that important factors influencing EfOM (or natural organic matter) adsorption competition are not only the concentration of the EfOM but, more importantly, their properties. Reduced EfOM adsorption competition can be expected with lower aromaticity, increased polarity, and to some extent smaller molecular size, all of which are typically caused by the ozonation of soluble organic matter.

CONCLUSIONS

- Ozonation of effluent organic matter (EfOM) reduces its aromaticity, molecular size, and hydrophobicity, leading to decreased adsorbability and in turn, to less adsorption competition against the adsorption of organic micro-pollutants (OMP).
- The reduced competition against OMP adsorption leads to reduced powdered activated carbon (PAC) usage because doses for specific OMP removals decrease.
- Similar to non-ozonated waters, UV₂₅₄ can be used as a handy indicator for adsorptive OMP removal in ozonated WWTP effluents. Higher specific ozone consumptions result in increased slopes of the linear correlations, since OMP adsorption is favored against UV₂₅₄ adsorption.
- For strong adsorbates (benzotriazole, diclofenac), the exploitation of the PAC capacity can be swiftly raised by ozonation, while for weaker adsorbates (sulfamethoxazole), higher specific ozone consumptions are needed to attain similar increases in additional PAC exploitation.
- Combinations of ozonation and activated carbon adsorption are clearly beneficial for the removal of OMP. On the one hand, both techniques can directly reduce OMP concentrations, and on the other, ozonation can alleviate adsorption competition caused by EfOM.

ACKNOWLEDGMENTS

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SUPPORTING INFORMATION

Supplementary data related to this article can be found in the Supporting Information shown in Appendix B-2, p. 137.

REFERENCES

The cited references are contained in the general bibliography in Appendix A, p. 125.

2.3 BOM size in granular activated carbon adsorption

Rapid small-scale column testing of granular activated carbon for organic micro-pollutant removal in treated domestic wastewater

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ABSTRACT

This study investigates the applicability of the rapid small-scale column test (RSSCT) concept for testing of granular activated carbon (GAC) for organic micro-pollutants (OMPs) removal from wastewater treatment plant (WWTP) effluent. The chosen experimental setup was checked using pure water, WWTP effluent, different GAC products, and variable hydro-dynamic conditions with different flow velocities and differently sized GAC, as well as different empty bed contact times (EBCTs). The setup results in satisfying reproducibility and robustness. RSSCTs in combination with WWTP effluent are effective when comparing the OMP removal potentials of different GAC products and are a useful tool for the estimation of larger filters. Due to the potentially high competition between OMPs and bulk organics, breakthrough curves are likely to have unfavorable shapes when treating WWTP effluent. This effect can be counteracted by extending the EBCT. With respect to the strong competition observed in GAC treatment of WWTP effluent, the small organic acid and neutral substances are retained longer in the RSSCT filters and are likely to cause the majority of the observed adsorption competition with OMPs.

INTRODUCTION

Organic micro-pollutants (OMPs) are nowadays found in wastewater treatment plant (WWTP) effluents, surface waters and, to some extent, also drinking waters (Heberer 2002a, Reemtsma et al. 2006). Since there is little knowledge on long-term or combinatory effects of trace-level amounts of OMPs in the different water bodies (Dieter and Mückter 2007), many water services plan additional water treatment steps for preventive OMP removal (Jekel et al. 2013). Among these additional steps are mainly oxidizing processes such as ozonation, and adsorptive processes like activated carbon adsorption (Altmann et al. 2014, Margot et al. 2013). With respect to WWTP effluent treatment, many studies focus on powdered activated carbon (Boehler et al. 2012, Zietzschmann et al. 2014a), but also granular activated carbon (GAC), which has been applied successfully in drinking and reservoir

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water treatment (Ridal et al. 2001), is discussed as a possible technique (Boehler et al. 2013, Gimbel et al. 2011).

Testing of powdered activated carbon products is comparatively simple (experiments with stirred or shaken batches containing the respective water and powdered activated carbon), whereas tests with GAC are more complex and therefore require more planning and time, usually involving bench- or pilot-scale filters. Simplification of this setup can be approached by a number of means. Equilibrium batch experiments with pulverized GAC can be used to assess the activated carbon capacity but this approach does not account for the relevant mass transfer processes in GAC filters. Therefore, mass transfer models were developed which simulate the transport of adsorbates in GAC filters. However, this approach requires somewhat numerous input parameters which cannot always be provided, especially when modeling multi-solute problems (Weber and Smith 1987). Most of these shortcomings can be avoided using rapid small-scale column tests (RSSCTs) which aim at reducing the experiment size, the water consumption, and the time effort that are generally encompassed in pilot/ large-scale filter experiments (Crittenden et al. 1986, Crittenden et al. 1991). RSSCTs are scaled-down from pilot/ large filters by using smaller sized GAC particles whilst keeping the hydrodynamic regime in a range that allows for direct comparability of the small and the large filters. RSSCTs account for many of the effects that cannot be accounted for by using equilibrium batch experiments and mass transfer modeling, and thus are a promising technique when needing estimation of GAC filter performance.

MATERIALS AND METHODS

Water samples and pre-treatment

All chemicals and reagents were of reagent grade or better. Ultra-pure water (resistivity $>17 \text{ M}\Omega \cdot \text{cm}$) was produced from fully de-ionized water using an *Ultra Maxima (Elga Berkefeld Lab Water, Germany)*. Effluent was sampled from the WWTP at Ruhleben, Berlin, Germany. In order to reduce the head loss that occurred due to filter blocking with suspended substances, the WWTP effluent was filtered with a *SIEMENS Memcor PVDF 200 kDa* membrane. The initial concentrations of the OMPs were left as in the WWTP effluent (which is the reason why they vary between some of the results shown).

Activated carbons

The used GAC product was *Jacobi Aquasorb 5000 G* (and, where indicated, *Norit 1240* and *CSC HC AZ 1050*). To obtain the desired reduced GAC grain sizes, the products were ground and sieved. Equilibrium experiments were conducted with pulverized GAC.

Equilibrium experiments

Equilibrium experiments were conducted using a typical bottle point method (Zietzschmann et al. 2014a). Single solute (OMPs spiked into ultra-pure water) and multi-solute (WWTP

effluent) data were fitted using the Freundlich isotherm equation. In multi-solute systems this results in pseudo single solute fitting. This approach gives satisfactory fitting results for adsorbates whose isotherm/ loading curves have continuous positive slopes (no bending to negative slopes at high adsorbate concentrations/ low activated carbon dosages).

RSSCT setup

Glass columns (inner diameter 8 mm) were used as filters, and glass pearls/ glass wool was used to hold the GAC in place. Depending on the dimensioning of the respective RSSCT filter, the bed volumes were 0.5 mL (1 cm bed height) and 1 mL (2 cm bed height). (With these bed volumes, throughputs of, for example, 100,000 bed volumes can be obtained with as little as 50 and 100 L of water, respectively.) To dimension the RSSCT filters, the constant diffusivity approach was used (Crittenden et al. 1986, Crittenden et al. 1991). The main equations necessary for the downscaling are given in Eq. 12 and Eq. 13. The empty bed contact time (EBCT) and the filter velocity/ hydraulic loading (v) of the small column (SC) and the large column (LC) are related through the ratios of the corresponding particle diameters (d_p). Since the GAC particle sizes of the SC can cause high head losses, the Reynolds number of the SC can be changed from that of the LC (Crittenden et al. 1991), as long as it is kept above 1 (referred to as $Re_{sc,min}$, cf. Eq. 13).

$$EBCT_{SC} = EBCT_{LC} \left(\frac{d_{p,SC}}{d_{p,LC}} \right)^2 \quad \text{Eq. 12}$$

$$v_{SC} = v_{LC} \left(\frac{d_{p,LC}}{d_{p,SC}} \right) \left(\frac{Re_{sc,min}}{Re_{LC}} \right) \quad \text{Eq. 13}$$

Note that the RSSCT results shown in the current study stem from *seemingly* short EBCTs. Using Eq. 12, the EBCTs of equivalent large-scale columns can be inferred, to obtain a more practical impression. Tab. 3 gives an exemplary overview on corresponding EBCTs on small-scale and large-scale columns for a particle diameter ratio of $d_{p,SC} \approx d_{p,LC}/10$, which results in an EBCT ratio of 1/100.

Tab. 3. Exemplary EBCTs for equivalent small-scale and large-scale columns, according to Eq. 12; $d_{p,SC} \approx d_{p,LC}/10$.

EBCT _{sc}	[s]	2	5	10
EBCT _{LC}	[s], [min]	200, 3.3	500, 8.3	1000, 16.7

Breakthrough modeling and calculations

The software *FAST 2.0* (Sperlich et al. 2008a) was used to model GAC filter breakthrough in a pseudo single solute approach.

Carbon usage rates (CURs) were calculated according to Eq. 14 where ρ_b is the apparent bed density and $BV_{10\%}$ is the number of bed volumes treated until a modeled breakthrough of 10% of the inlet concentration.

$$CUR = \frac{\rho_b}{BV_{10\%}} \quad \text{Eq. 14}$$

Analytics

Organic micro-pollutants – The OMP concentrations were measured using high performance liquid chromatography with tandem mass spectrometry (HPLC-MS/MS) using an *XSelect HSS T3* column (2.5 μm , 2.1 * 50 mm, *Waters*, USA) with a linear gradient (0.5 mL/min, ultra-pure water with 0.1% HCOOH and 5% methanol versus methanol) and a *TSQ Vantage* (*Thermo Scientific*, USA) using electrospray ionization. Two mass fragments were chosen for each analyte (*Wasserchemische Gesellschaft* 2013), and deuterated isotopes (*TRC*, Canada; *Dr. Ehrenstorfer*, Germany) were used for quantification.

Ultraviolet absorption at 254 nm and fractionized dissolved organic carbon – UV absorption was measured on a *Lambda 12* (*Perkin-Elmer*, USA). Fractionized dissolved organic carbon (DOC) was determined using liquid size-exclusion chromatography on an *HW50S* column (*Toyopearl*, Japan) with online carbon detection (LC-OCD, *DOC-Labor Huber*, Germany). The DOC fractions were allocated according to the literature (Huber et al. 2011). Data were evaluated using the software *ChromCalc* (*DOC-Labor Huber*, Germany).

RESULTS AND DISCUSSION

The single solute (ultra-pure water) and multi-solute (WWTP effluent) Freundlich parameters of selected OMPs are summarized in Tab. 4. From the data shown for the single solute systems, the order of the adsorbate affinity towards activated carbon is benzotriazole > diclofenac > carbamazepine. The multi-solute Freundlich coefficients are almost two orders of magnitude smaller than the single solute parameters. Also, carbamazepine and diclofenac, which have different single solute parameters, have similar multi-solute parameters. Benzotriazole has increased parameters compared to diclofenac in the single solute system but reduced parameters in the multi-solute system. The results indicate that the multi-solute system, which includes competition between the OMPs and the bulk organics, is too complex to be predictable from the single solute data (Tab. 4).

Tab. 4. Single solute and multi-solute (pseudo single solute) Freundlich parameters for selected OMPs; K_F in $(\mu\text{g}/\text{mg})^*(\text{L}/\mu\text{g})^{(1/n)}$.

Solute system	Benzotriazole		Carbamazepine		Diclofenac	
	single	multi	single	multi	single	multi
Freundlich coefficient (K_F)	251	2.3	159	3	251	3
Freundlich exponent ($1/n$)	0.45	0.27	0.31	0.3	0.36	0.28

The relative UV absorption and relative OMP concentrations are plotted against the throughput of four RSSCTs filled with two GAC products (each in duplicate) in Fig. 16. The breakthrough curves shown in Fig. 16 demonstrate that there is no full retention of either of the shown parameters. The UV absorption reaches 90% of the initial concentration earlier than 5000 bed volumes of throughput. Among the OMPs, benzotriazole has the strongest retention (50% of the initial concentration at $\sim 20,000$ bed volumes) while carbamazepine and diclofenac both reach 50% of the initial concentration earlier than 10,000 bed volumes. The duplicate RSSCTs of the respective GAC product yield nearly identical breakthrough curves. These results show that the chosen experimental setup is reproducible and yields a satisfying comparability.

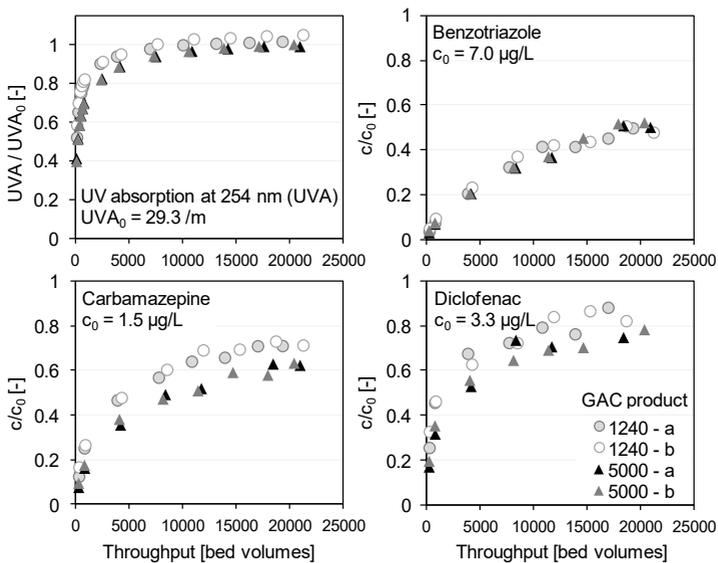


Fig. 16 UV absorption and benzotriazole, carbamazepine, and diclofenac concentrations (relative to the respective inlet WWTP effluent values) versus throughput, with two different GAC products in duplicate (*Norit 1240* and *Aquasorb 5000*), EBCT: 2.2 s, d_p : 125–200 μm .

The observed GAC filter breakthrough behaviors shown in Fig. 16 cannot be adequately predicted solely by using equilibrium data. The single-solute Freundlich parameters suggest a stronger retention for diclofenac than for carbamazepine whereas the RSSCT shows a different order of OMP adsorption. The multi-solute Freundlich parameters suggest that carbamazepine and diclofenac should have similar breakthrough behavior. These discrepancies between the information from equilibrium batch experiments and the information from RSSCTs underline the high relevance of mass transfer processes in GAC filters, which need to be considered in adequate breakthrough curve determination. Also, the potential for GAC

pore fouling cannot be determined from batch experiments with pulverized GAC (Corwin and Summers 2010).

With respect to the robustness of RSSCTs, the influences of the external and internal mass transfer must always be considered within the framework of the respective setup. Although the external mass transfer can be regulated by the filter velocity, the internal mass transfer cannot be influenced. Thus, high external mass transfer rates are generally desirable. Firstly, they result in good transport of adsorbates to adsorbent particles. Secondly, when the external mass transfer rate is high compared to the internal mass transfer rate, the breakthrough curve is only dependent on the internal mass transfer, resulting in robust experimental setups. In that case, variations of the filter velocity have no consequences on the breakthrough curve appearance. The relative filter effluent concentrations of benzotriazole and diclofenac, adsorbing from WWTP effluent, are plotted against the throughputs of two RSSCTs equipped with the same GAC product at two different bed lengths and different filter velocities, resulting in the same EBCTs, in Fig. 17. Both of the RSSCTs yield similar breakthrough curves which are not affected by the differences in the hydrodynamic regimes. Accordingly, the external mass transfer is of minor importance for the RSSCTs in the chosen configuration. These results show that using an approach with a reduced Reynolds number is applicable. Reducing the Reynolds number in order to minimize the head loss, the bed length, and the needed water volume does not affect the RSSCT results within the chosen setup.

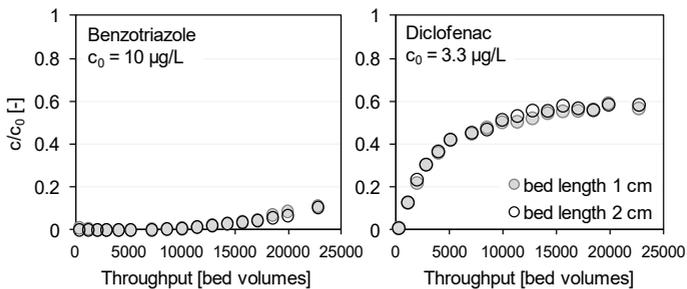


Fig. 17. Benzotriazole and diclofenac concentrations, relative to the respective inlet WWTP effluent values, versus throughput of two RSSCTs with different bed length and different filter velocities ($v_1 \approx 6$ m/h, $v_2 \approx 12$ m/h) and same EBCT (6 s), GAC *Norit 1240*, d_p : 90–140 μm .

A major aspect of the RSSCT concept is to transfer results produced with filters containing small-sized GAC (i.e. RSSCTs) to filters with larger sized GAC, for performance prediction. To check the transferability, the RSSCT equations (Eq. 12 and Eq. 13) can be used to relate GAC filters (containing differently sized GAC particles) to each other and evaluate the similarity of their breakthrough curves. The concentrations, relative to the influent WWTP effluent concentration, of benzotriazole and diclofenac at the filter outlets of two RSSCTs with differently sized GAC particles and different EBCTs (related via Eq. 12 and Eq. 13) are de-

pected versus the throughput in Fig. 18. The breakthrough curves of the two differently dimensioned RSSCTs show a high similarity. Accordingly, the downscaling from a larger GAC filter to a smaller GAC filter appears valid. The chosen setup can only demonstrate the feasibility of the downscaling to some extent since the particle diameter of the smaller GAC fraction is only ~ 0.5 times the size of the particle diameter of the large GAC fraction. Additional RSSCTs using GAC fractions with larger differences in their particle sizes are necessary to broaden the observed feasibility of the downscaling. However, the high similarity of the determined breakthrough curves underlines that small-scale filters which are scaled down from large filters using the RSSCT concept can produce results that allow for rough prediction of large-scale filters. Also, these results show that the chosen constant diffusivity approach (diffusivity of adsorbates is independent of the GAC particle size) appears feasible here (Crittenden et al. 1986).

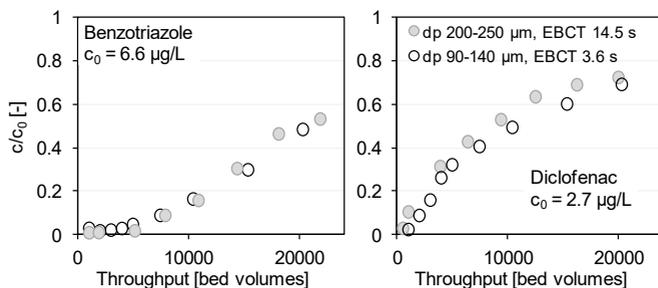


Fig. 18. Benzotriazole and diclofenac concentrations, relative to the respective inlet WWTP effluent values, versus throughput in two equivalent RSSCTs with differently sized GAC and different EBCTs.

The previous results showed adequate reproducibility and robustness, and the feasibility of reducing the SC Reynolds number in order to minimize experimental efforts. Furthermore, scaling between GAC filters/ RSSCTs with differently sized GAC particles is valid within the experimental conditions used here. However, most of the breakthrough curves obtained from treating WWTP effluent diverge from the typically preferred S-shaped form (Fig. 16, Fig. 17, Fig. 18). A comparison of these WWTP effluent breakthrough curves with breakthrough curves from the treatment of spiked ultra-pure water (cf. Supporting information, Appendix B-3, p. 141) confirms that the appearance of the WWTP effluent breakthrough curves does not originate from design errors or short-circuiting of the RSSCTs, but the reason is adsorption competition between the OMPs and the bulk organics contained in the WWTP effluent. The DOC concentration in the Berlin Ruhleben WWTP effluent is usually 10–12 mg/L, thus about 10^3 – 10^5 times the concentration of most OMPs, which explains the potentially high competition. The early OMP breakthrough and flat shapes of the breakthrough curves are highly unfavorable because they result in high CURs (mass of carbon used per volume of water treated) and low efficiency if specific OMP removals are targeted

(e.g. c/c_0 must be < 0.1 at any time). It is therefore highly relevant to delay the OMP breakthrough (and to minimize the CURs) and maximize the GAC filter efficiency.

The relative concentrations of benzotriazole and diclofenac from RSSCTs with different EBCTs are plotted against the throughput in Fig. 19; note that the scaling of the abscissae is relative and does not depict absolute volumes but the numbers of bed volumes. The graphs demonstrate that an increase of the water-GAC contact time yields longer retention of the OMPs and an improved shape of the breakthrough curves. This causes a reduction of the CUR (less GAC mass per volume of water/ more water treated per mass of GAC). Accordingly, the EBCT is a crucial parameter when dimensioning GAC filters for WWTP effluent treatment, and longer EBCTs cause improved retention of adsorbates and higher efficiency. Therefore, when treating WWTP with potentially strongly competing bulk organics, the EBCT should possibly be maximized to obtain efficient CURs. However, maximizing the EBCT means increasing filter beds in any application where a specific volumetric flow shall be treated, and accordingly the financial and technical efforts increase simultaneously. A balance between GAC filter efficiency and expenses must thus be found for any particular application/ problem.

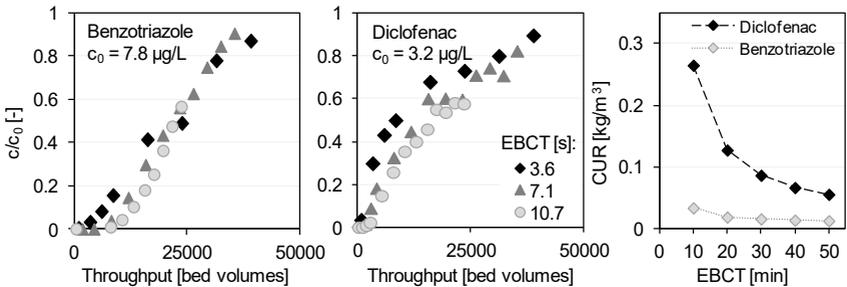


Fig. 19. *Left and middle:* Benzotriazole and diclofenac concentrations, relative to the inlet WWTP effluent values, versus throughput at varying EBCT, d_p : 90–140 μm ; *right:* Modeled CURs at 10% breakthrough for benzotriazole and diclofenac in relation to the EBCT.

Using the RSSCT results, scale-up modeling using the software *FAST 2.0* is possible. Fig. 19, right, shows the CURs at a breakthrough of 10% for benzotriazole and diclofenac in relation to the EBCT. For both OMPs, the CURs decline with increasing EBCT, especially in the EBCT range below 30 min. Accordingly, the maximization of the EBCT in constellations with high adsorption competition such as the treatment of WWTP effluent can improve CURs. Thus, reducing the volumetric flow or increasing the bed length in GAC treatment of WWTP effluent should be considered where possible. Pilot experiments with different WWTP effluents and EBCTs within the range of the EBCTs modeled in the current study showed CURs in a similar range as reported here (Boehler et al. 2012, Gimbel et al. 2011).

However, a direct comparison is not possible because of the strongly varying setups of the different studies (GAC products, WWTP effluents, backwashing).

The aforementioned strong competition between OMPs and bulk organics is unlikely to be caused equally by all of the bulk organics because the compounds comprising the bulk organics have different molecular composition, resulting in varying size, chemistry etc. (Zietzschmann et al. 2014c). Thus, different fractions of the bulk organics (the latter usually being encompassed in surrogate parameters such as DOC) cause different competition and accordingly have different affinities onto activated carbon. The relative concentrations of the bulk organic fractions as identified by LC-OCD are depicted versus the throughput of an exemplary RSSCT in Fig. 20, left, together with the chromatograms of the corresponding blind WWTP effluent sample and the RSSCT outlet after 10 min/ 200 bed volumes (Fig. 20, right). The biopolymers and humics fractions show nearly no retention and reach relative concentrations (c/c_0) of 0.9 at < 200 bed volumes and $\sim 1,200$ bed volumes, respectively. The smaller fractions of the acids and neutrals demonstrate stronger retention and reach $c/c_0 \approx 0.9$ at > 5,000 and 3,500–4,000 bed volumes, respectively. The retention of the bulk DOC (bypass-DOC) lies in-between the retention of the weakly and strongly adsorbable fractions. The breakthrough curves in Fig. 20 show that the small organic substances of the acid and neutral fractions have a comparatively strong affinity towards the GAC in the RSSCT filter. Accordingly, these substances are presumably causing the major competitive effects in the adsorption of OMPs from WWTP effluent, which confirms other studies (Zietzschmann et al. 2014c).

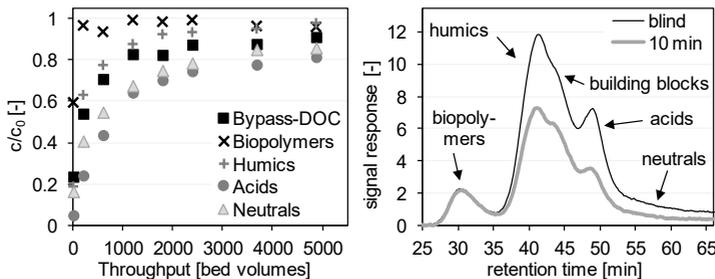


Fig. 20. *Left*: DOC ('bypass-DOC') and DOC fraction concentrations, relative to the inlet WWTP effluent values, versus throughput; GAC AZ 1050, d_p : 125–200 μm , EBCT (3 s); *right*: LC-OCD chromatograms of blind WWTP effluent sample and RSSCT outlet after 10 min, with fraction denominators (Huber et al. 2011).

CONCLUSIONS

The RSSCT concept for GAC testing in OMP removal from WWTP effluent was shown to be applicable. The reproducibility and robustness are satisfying within the chosen experimental setup. RSSCTs can be used to compare different performances of GAC products in OMP

removal from WWTP effluents. The performances of larger filters in WWTP effluent treatment can be estimated using RSSCTs. Due to potentially high concentrations of bulk organics in WWTP effluents, the competition for OMP adsorption can be substantial. This competition causes unfavorable OMP breakthrough curves (flat shape, early OMP appearance in the filter outlet) and high CURs. Extending the EBCT can improve the shape of the breakthrough curves and therefore can reduce CURs and increase the efficiency of GAC filters. It was shown that small organic acid and neutral substances are retained longer on the RSSCT filters than larger DOC compounds, and we conclude that these substances are responsible for the majority of the observed adsorption competition with OMPs. Future experiments should use GAC particles with larger differences in the large and small GAC filters in order to further verify the transferability of RSSCT results to large-scale filters in WWTP effluent treatment.

SUPPORTING INFORMATION

Supplementary data related to this article can be found in the Supporting Information shown in Appendix B-3, p. 141.

REFERENCES

The cited references are contained in the general bibliography in Appendix A, p. 125.

3

Adsorption competition in different waters

In chapter 2, the chemical properties of background organic matter (BOM) leading to increased competitive effects of the OMP/ BOM competitive adsorption system were investigated. In both, powdered activated carbon (PAC) and granular activated carbon (GAC) adsorption, the low molecular weight acid and neutral (LMW) organics of wastewater treatment plant (WWTP) effluent organic matter (EfOM) were identified as the most relevant fraction.

The current chapter further examines the impacts of BOM from different waters (drinking waters, WWTP effluents, surface water) with a focus on the LMW fraction. The first section (3.1, p. 55–74) shows an extensive comparison of OMP/ BOM competitive adsorption in various drinking waters and WWTP effluents from different regions in Germany, and describes a new approach for initializing the Equivalent Background Compound Model (EBCM) by using simple water characteristics. The second section of chapter 3 (3.2, p. 75–88) investigates possibilities of aligning OMP breakthrough curves on GAC filters fed with different waters and variable OMP concentrations, and discusses the corresponding effects on the GAC capacities.

3.1 Powdered activated carbon adsorption in different waters

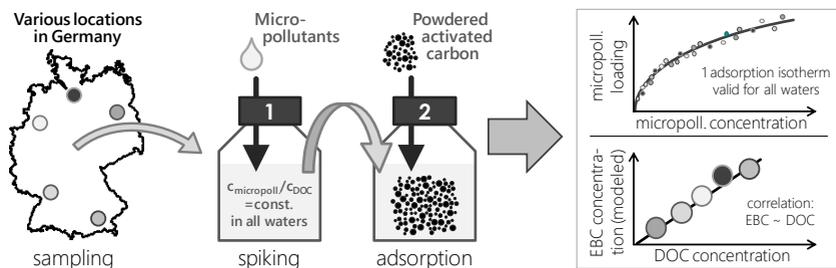
Comparing and modeling organic micro-pollutant adsorption onto powdered activated carbon in different drinking waters and WWTP effluents

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GRAPHICAL ABSTRACT



ABSTRACT

The adsorption of organic micro-pollutants (OMP) onto powdered activated carbon (PAC) was compared between regionally different waters within two groups, namely five drinking waters and seven wastewater treatment plant (WWTP) effluents. In all waters, OMP were spiked to adjust similar ratios of the initial OMP and DOC concentrations ($c_{o,OMP}/c_{o,DOC}$). PAC was dosed specific to the respective DOC (e.g. 2 mg PAC per mg DOC). Liquid chromatography with online carbon detection shows differences of the background organic matter (BOM) compositions. The OMP removals at given DOC-specific PAC doses vary by $\pm 15\%$ (drinking waters) and $\pm 10\%$ (WWTP effluents). Similar BOM-induced adsorption competition in the waters of the respective group results in overall relationships between the PAC loadings and the liquid phase concentrations of each OMP (in the case of strong adsorbates). Weaker adsorbates show no overall relationships because of the strong BOM-induced adsorption competition near the initial OMP concentration. Correlations between OMP removals and UV_{254} removals were independent of the water (within the respective group). The equivalent background compound (EBC) model was applied to the experimental data. Using global EBC Freundlich coefficients, the initial EBC concentration correlates with the DOC (both water groups separately) and the low molecular weight (LMW) organics concentrations (all waters combined). With these correlations, the EBC could be initialized by using the DOC or the LMW organics concentration of additional drinking water, WWTP effluent, and surface water samples.

INTRODUCTION

Powdered activated carbon (PAC) is widely used for the adsorptive removal of organic micro-pollutants (OMP) such as taste and odor compounds, pharmaceuticals, and industrial chemicals, in advanced treatment of drinking waters and wastewater treatment plant (WWTP) effluents (e.g., Boehler et al. 2012, Jekel et al. 2013, Westerhoff et al. 2005, Zoschke et al. 2011). In such waters, background organic matter (BOM, usually expressed via dissolved organic carbon, DOC) and OMP adsorb simultaneously. This adsorption competition can reduce the PAC capacity which is available for OMP adsorption by orders of

magnitude (Newcombe et al. 2002c, Yu et al. 2012). The adsorptive OMP removals by PAC in four wastewater treatment plant (WWTP) effluents from the same region in Germany were similar if the PAC was dosed relative to the DOC (Altmann et al. 2014). That study used similar initial OMP and DOC concentrations and due to the similar regional origin, the BOM compositions of the WWTP effluents were mostly comparable. Typically, the BOM concentrations and characteristics in waters from different studies/ origins are variable and the related competition against OMP adsorption may vary accordingly. Therefore, prior to establishing full-scale PAC adsorption treatment stages, lab-scale and/ or pilot-scale adsorption tests are carried out to estimate OMP removals in each particular case. The need for PAC adsorption tests may be reduced if methods for comparing and transferring OMP adsorption data between different waters would exist. Also, approaches to initialize adsorption models without prior batch testing but only by using water characteristics would be a major step towards a more practical assessment of PAC performance.

The current study compares OMP adsorption onto PAC in waters of variable regional origin. Five drinking waters of different regional origin are compared with each other. Also, seven wastewater treatment plant (WWTP) effluents of various regional origins are compared with each other. The sampling locations are given in the Supporting Information (Appendix B-4, p. 142). The partition into two groups (drinking waters and WWTP effluents) was made to maintain clarity. The different origins of the tested waters implied variable BOM composition and concentrations. Other studies showed that if a water is considered individually, the ratio of the initial OMP and BOM concentrations ($c_{o,OMP}/c_{o,DOC}$) marks the decisive parameter for PAC adsorption (Graham et al. 2000, Knappe et al. 1998, Qi et al. 2007). Accordingly, if this ratio is similar in different waters, the competitive impacts of the different BOM on OMP adsorption onto PAC could be directly compared. For the tests conducted in the current study, several OMP were spiked with respect to the DOC of the waters, resulting in similar ratios of the OMP and DOC initial concentrations ($c_{o,OMP}/c_{o,DOC} \approx const.$) in all examined waters. Additional tests with three WWTP effluents were also conducted at varied $c_{o,OMP}/c_{o,DOC}$. The overall approach allowed for exposing similarities and differences of the competitive effects of regionally different BOM on OMP adsorption onto PAC.

The experimental data were back-modeled using the Equivalent Background Compound (EBC) model (EBCM). The EBCM reflects an adsorption system with 2-components of which one is the respective OMP and the other is a fictive component (the EBC) which represents the competitive effects observed against the OMP in the water under consideration. Based on the Ideal Adsorbed Solution Theory (IAST), the EBCM is typically used for modeling equilibrium adsorption (Graham et al. 2000, Knappe et al. 1998, Matsui et al. 2003, Matsui et al. 2012, Najm et al. 1991, Newcombe et al. 2002c, Worch 2010, Zietzschmann et al. 2015b, Zietzschmann et al. 2014c). However, also non-equilibrium adsorption data (i.e. liquid and solid phase concentrations are still changing) can be modeled with the EBCM because of the fictive character of the EBC whose Freundlich parameters are usually fitted to experimental data during back-modeling (Shimabuku et al. 2014, Zietzschmann et al. 2015a, Zoschke et al. 2011).

According to the fictive nature of the EBC, adsorption batch tests have to be conducted in the water of interest because no other method exists to initialize the EBCM parameters. A method to derive the EBC characteristics without PAC batch testing, e.g. based on simple correlations, would clearly reduce the amount of time and work needed for PAC performance assessments. For the PAC adsorption of 2-methylisoborneol (MIB) and geosmin in three surface waters, higher modeled initial concentrations of the EBC coincided with higher measured total organic carbon (TOC) concentrations of the waters; a fourth surface water did not confirm this trend, possibly due to WWTP effluent impacts on that water (Graham et al. 2000). Similarly, the PAC doses for a defined removal of MIB and geosmin could not be related to the DOC, molecular weight distribution, UV absorbance, or color of four surface waters (Cook et al. 2001). A coefficient of determination of $R^2 = 0.61$ was found between the modeled initial EBC concentrations and the UV absorbance at 260 nm in four surface waters (Matsui et al. 2012).

Another approach was to relate the fitted initial EBC concentration $c_{o,EBC}$ (non-equilibrium conditions), divided by the DOC of several surface waters to the fluorescence index (FI, ratio of emission intensities at 520 nm–470 nm at an excitation at 370 nm) of these waters as higher FI indicated higher BOM competitiveness against OMP adsorption (Shimabuku et al. 2014). Other studies used the EBCM on waters whose BOM was artificially altered (membrane filtration, ozonation), and related increased BOM competitiveness to smaller molecular sizes (Zietzschmann et al. 2014c) or aromaticity and polarity (Zietzschmann et al. 2015b). Overall, there is still little knowledge on the comparability of EBCM results for different origins of real waters. Especially, an overall approach for initializing the EBCM using water characteristics of different waters (different regions as well as different types of waters, e.g. drinking waters and WWTP effluents) would be a powerful tool.

MATERIALS AND METHODS

Water samples

The water samples were frozen before shipping/ testing. Prior to the tests, the DOC and initial OMP concentrations (given in the Supporting Information, Appendix B-4, p. 142) of the waters were determined and a set of OMP (*Sigma Aldrich*, Germany, *Dr. Ehrenstorfer*, Germany, and *Toronto Research Chemicals*, Canada) was spiked from 20 mg/L stock solutions, prepared in ultra pure water (resistivity $>17 \text{ M}\Omega\cdot\text{cm}^{-1}$, *ELGA Berkefeld*, Germany), to obtain DOC-specific OMP concentrations of $\sim 5 \text{ }\mu\text{g OMP/mg DOC}$. In additional experiments with the WWTP effluents Kressbronn, Seevetal, and Schönerlinde, the specific OMP concentrations were $\sim 2.5 \text{ }\mu\text{g OMP/mg DOC}$ and $\sim 10 \text{ }\mu\text{g OMP/mg DOC}$.

To test the models developed in this study, results from additional batch tests are also included. The tested waters were sampled from the Berlin WWTP Waßmannsdorf, the effluent of the phosphorous elimination plant (PEP) Tegel in Berlin (cf. Jekel et al. 2013), and the Berlin drinking water; in these tests, the initial OMP concentrations were left unaltered.

Batch tests

Stock suspensions of the PAC *SAE Super* (Norit, Germany) were produced by drying (105 °C) the PAC over night, cooling it in a desiccator, and suspending it in ultra pure water while simultaneously degassing it in an ultrasonic bath with partial vacuum for 5 min. The batch volumes were 100 mL. During pipetting, the suspensions were magnetically stirred. The PAC was applied relative to the dissolved organic carbon (DOC) concentration of the respective water. Seven DOC-specific doses were applied: 0.25, 0.5, 1, 2, 4, 7, 15 mg PAC/mg DOC. These doses were adjusted by using two stock suspensions. Depending on the DOC of the respective raw water, the PAC concentrations of the stock suspensions were varied so that pipetting volumes always ranged between 0.1 and 1 mL, resulting in raw water dilutions of $\leq 1\%$. Upon PAC addition, the batches were put on a horizontal shaker for thorough mixing. After the respective contact time of 0.5 h or 48 h, the batches were filtered through regenerated cellulose membrane filters (0.45 μm , *Chromafil Xtra RC-45/25*, *Macherey-Nagel*, Germany) previously rinsed with ultra pure water.

To visualize possible errors of the OMP concentrations and the PAC loadings with OMP, as well as of the OMP removals in the conducted batch tests, an exemplary error calculation can be found in the Supporting Information (Appendix B-4, p. 142). The shown values result if maximally negative/ positive PAC dosing errors ($\pm 5\%$) are combined with maximally positive/ negative measurement errors of the initial OMP concentration ($\pm 10\%$) and maximally negative/ positive measurement errors of the OMP concentration after adsorption ($\pm 10\%$). Note that to reduce errors in the depiction of PAC loadings over OMP concentrations (loading curves and isotherms), only those OMP concentration values after PAC adsorption were considered that were $\leq 85\%$ of the initial OMP concentration. Also note that the initial OMP concentrations (after spiking) of all tested waters were measured in duplicate, further reducing the likeliness of erroneous data for the initial OMP concentrations.

Analytatics

The OMP were measured with high performance liquid chromatography (HPLC) coupled with tandem mass spectrometry (MS/MS) using a *XSelect HSS T3* column (2.5 μm particle radius, 2.1 mm diameter, 50 mm length, *Waters*, Germany) with a linear gradient at 0.5 mL/min (start conditions: 98% ultra pure water with 0.1% HCOOH (HPLC grade, *Sigma Aldrich*, Germany) and 2% MeOH (HPLC grade, *J.T. Baker*, USA), end conditions: 100% MeOH) and a *TSQ Vantage* (*Thermo Scientific*, Germany) in ESI^{\pm} modes. Two mass fragments of each analyte were chosen according to the DAIOS database (Wasserchemische Gesellschaft 2013) and the more intense fragment was used for quantification in combination with deuterated isotopes (*Toronto Research Chemicals*, Canada, and *Dr. Ehrenstorfer*, Germany); data were analyzed with *Xcalibur 2.1* (*Thermo Scientific*, Germany). The OMP quantification at very low concentration levels in the additional drinking water sample further included online solid phase extraction where 500 μL of the sample are loaded onto a *Hypersil Gold aQ* column (12 μm particle size, 20*2.1 mm) during 1 min at a flow of 1 mL/min with ultra pure water (0.1% HCOOH, *Sigma Aldrich*, HPLC grade). After

this extraction step, the column flow direction was reversed and the HPLC column (*XSelect HSS T3*, 2.1 * 50 mm, 2.5 mm particle size, *Waters*, USA) was automatically connected to the extraction column, running a gradient program at 0.35 mL/min, from 98% aqueous solvent (5% MeOH, HPLC gradient grade, *J.T. Baker*, 0.1% HCOOH) to 100% MeOH.

The measurement of fractionized BOM/ DOC was accomplished using liquid chromatography with online organic carbon and UV₂₅₄ detection (*LC-OCD, DOC-Labor Huber*, Germany) with a *HW50S* column (*Toyopearl*, Japan), and typical peak allocation (Huber et al. 2011); where sample dilution was necessary for measurements, data were correspondingly adjusted. LC-OCD data were evaluated with the software *Chromcalc (DOC-Labor Huber)* to obtain quantified amounts of the DOC assigned to the typical LC-OCD fractions. DOC was determined in triplicate with a *varioTOC cube (elementar Analysensysteme, Germany)*. UV₂₅₄ was measured on a *Lamda 12 UV/ vis spectrometer (Perkin-Elmer, USA)*.

Modeling

The EBCM is a 2-component competitive adsorption model, based on the IAST combined with the single-solute Freundlich isotherm equation. In the EBCM, one component is the OMP under consideration and the second component is a fictive EBC making up for all of the observed adsorption competition against the considered OMP in a real water (Najm et al. 1991). The equations of the EBCM are shown in Eq. 15 and Eq. 16. Note that each OMP has an individual EBC, as well as individual Eq. 15 and Eq. 16 for each PAC dose. Using (i) OMP Freundlich parameters from PAC tests with organic-free water (cf. Tab. 5) and (ii) the OMP liquid phase concentrations and solid phase loadings from PAC batch tests in the real water of interest, the EBC Freundlich parameters and initial concentration can be fitted.

$$c_{o,OMP} - d q_{OMP} - \frac{q_{OMP}}{q_{OMP} + q_{EBC}} \left(\frac{n_{OMP} q_{OMP} + n_{EBC} q_{EBC}}{n_{OMP} K_{F,OMP}} \right)^{n_{OMP}} = 0 \quad \text{Eq. 15}$$

$$c_{o,EBC} - d q_{EBC} - \frac{q_{EBC}}{q_{OMP} + q_{EBC}} \left(\frac{n_{OMP} q_{OMP} + n_{EBC} q_{EBC}}{n_{EBC} K_{F,EBC}} \right)^{n_{EBC}} = 0 \quad \text{Eq. 16}$$

where d is the activated carbon dose, and $c_{i,o}$ are the initial concentrations, q_i are the loadings, $1/n_i$ are the Freundlich exponents, and $K_{F,i}$ are the Freundlich coefficients of the OMP and the EBC, respectively; units are molar.

However, different sets of EBC characteristics may yield equally well fitted results (Najm et al. 1991). Therefore, the EBCM can be simplified by using global/ fixed EBC Freundlich parameters, e.g. by equalizing the single-solute Freundlich exponents $1/n_i$ of the EBC and the respective OMP and, for strong adsorbates, the Freundlich coefficients $K_{F,i}$ (Graham et al. 2000, Newcombe et al. 2002b, Schideman et al. 2006a, b, Worch 2010). This increases the significance and comparability as variable observed adsorption competition is described by less fitting parameters. In the current study, the initial EBC concentration $c_{o,EBC}$ and the EBC Freundlich coefficient $K_{F,EBC}$ were allowed to vary; the EBC Freundlich exponent $1/n_{EBC}$

was set to that of the respective OMP. A mathematical solver was used to minimize the sum of the absolute deviations of the measured and modeled liquid phase concentrations and PAC loadings, as shown in Eq. 17. (Minimization via relative deviations results in very strong weighting of low concentrations and loadings.) In the current case, the EBCM was applied on the adsorption data for benzotriazole, diclofenac, and sulfamethoxazole.

$$Min = \frac{1}{N} \sum_{j=1}^N \left(\left| (c_{OMP,meas} - c_{OMP,mod})_j \right| + \left| (q_{OMP,meas} - q_{OMP,mod})_j \right| \right) \quad \text{Eq. 17}$$

where Min is the minimization term, N is the number of data points (/ PAC doses), c and q are the liquid phase concentrations and PAC loadings, respectively, and indices $meas$ and mod refer to measured and modeled data, respectively.

Tab. 5. Organic micro-pollutant single-solute Freundlich coefficients K_F [(nmol/mg)*(L/nmol)^{1/n}] and exponents $1/n$.

	K_F		$1/n$	
	0.5 h	48 h	0.5 h	48 h
Benzotriazole	6.8	10.4	0.43	0.46
Diclofenac	20.2	26.7	0.3	0.28
Sulfamethoxazole	9.6	10.0	0.35	0.3

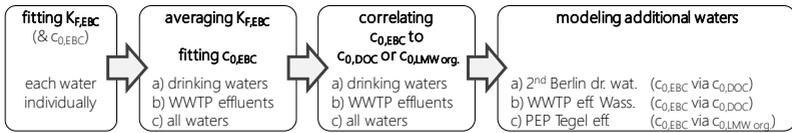


Fig. 21. Scheme of the approach to model waters using their DOC or LMW organics concentrations to derive the initial concentration of the EBC.

The overall approach to obtain EBCM initializations by using different water characteristics is shown in Fig. 21. Firstly, the EBC Freundlich coefficients $K_{F,EBC}$ and initial concentrations $C_{0,EBC}$ were fitted for benzotriazole, diclofenac, and sulfamethoxazole, for all tested waters individually and both adsorption times (0.5 h and 48 h), as indicated by the 1st box of Fig. 21 (the fitted $C_{0,EBC}$ were omitted). Using the fitted $K_{F,EBC}$ of the individual waters (for a specific pair of OMP and adsorption time), the $K_{F,EBC}$ of all drinking waters were averaged; analogously the $K_{F,EBC}$ of all WWTP effluents were averaged. Also, average $K_{F,EBC}$ for all waters (drinking waters and WWTP effluents) were calculated. With the average $K_{F,EBC}$ values, additional EBCM fittings were conducted with the initial EBC concentration $C_{0,EBC}$ being the only variable parameter (2nd box of Fig. 21). These fitted $C_{0,EBC}$ values could then be related to water characteristics such as the DOC or the concentrations of the low molecular weight (LMW) organic compounds of the tested waters (3rd box of Fig. 21). Using the developed

correlations, waters which were not used in the correlations were then EBC-modeled after using the water characteristics (DOC, LMW organics) to calculate the initial EBC concentrations (4th box of Fig. 21).

RESULTS AND DISCUSSION

Raw water characterization

The dissolved organic carbon (DOC) concentrations, ultraviolet absorbances at 254 nm (UV_{254}), specific ultraviolet absorbances (SUVA), low molecular weight (LMW) organics, and organic micro-pollutant (OMP) concentrations (after OMP spiking) of the examined drinking waters are shown in Tab. 6, those of the examined WWTP effluents are shown in Tab. 7, in descending order of the DOC values. Within the group of drinking waters, the DOC range from 1 mg/L in the Lake Constance drinking water to 4.7 mg/L in Berlin; the UV_{254} as well as the SUVA values increase with the DOC with the exception of the anonymous drinking water which has the highest UV_{254} and SUVA. The drinking water LMW organics concentrations are in the range of 0.2–1.3 mg/L, and account for 20–43% of the DOC. The absolute OMP concentrations are in the range of 4–29 $\mu\text{g/L}$ (ratios of the OMP and DOC concentrations ($c_{o,OMP}/c_{o,DOC}$) given in the Supporting Information, Appendix B-4, p. 142). Within the group of WWTP effluents, the DOC range from 4.2 mg/L in Kressbronn to 10.5 mg/L in Schönerlinde; the SUVA values of the WWTP effluents are in a relatively narrow range of 2.4–2.6 L/mg/m, except for Garching whose SUVA is lower. The LMW organics concentrations are in the range of 1.8–4.4 mg/L, and account for 36–47% of the DOC. The absolute OMP concentrations range from 19–64 $\mu\text{g/L}$ (ratios of the OMP and DOC concentrations ($c_{o,OMP}/c_{o,DOC}$) are given in the Supporting Information, Appendix B-4, p. 142).

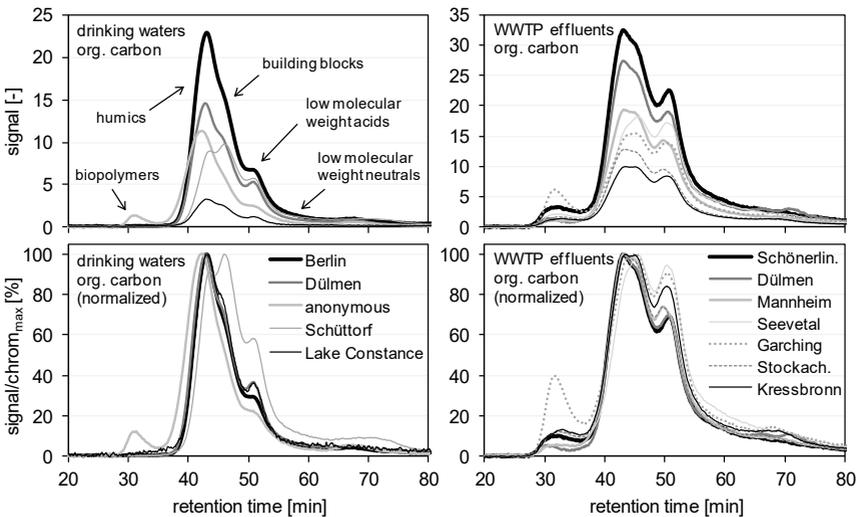
The liquid chromatography online organic carbon detection (LC-OCD) chromatograms of the tested drinking waters and WWTP effluents are shown in Fig. 22 which also presents normalized chromatograms resulting from dividing the signal intensities by the maximum measured intensity of the respective chromatogram. The normalized chromatograms are useful to compare qualitative differences between the waters irrespective of quantitative differences. The main fractions of all waters are humic substances (~42 min retention time), followed by building blocks (~45 min), low molecular weight (LMW) acids (~50 min), LMW neutrals (>55 min), and biopolymers (~32 min). Within the group of drinking waters, Schüttorf contains the highest percentage of building blocks and LMW acids. The humic substances of this water are comparatively small (as indicated by a relatively high retention time). The anonymous drinking water contains biopolymers and its humic substances are comparatively large (as indicated by a relatively small retention time). The corresponding UV_{254} and normalized UV_{254} chromatograms are shown in the Supporting Information (Appendix B-4, p. 142) and are similar to the organic carbon chromatograms. Due to its high UV_{254} and SUVA values, the anonymous drinking water has a UV_{254} chromatogram which is overall increased compared to the other drinking water chromatograms.

Tab. 6. Drinking water DOC, UV₂₅₄, SUVA, LMW organics, and organic micro-pollutant concentrations.

	DOC	UV ₂₅₄	SUVA	LMW org.	LMW org.	Benzotriazole	Carbamazepine	Diclofenac	Sulfamethoxaz.
	[mg/L]	[1/m]	[L/mg/m]	[mg C/L]	[% of DOC]		— [µg/L]	—	
Berlin	4.7	10.4	2.21	1.3	28	23	26	29	22
Dülmen	3.7	7.2	2.05	0.9	24	16	18	21	18
anonymous	2.9	12.2	4.16	0.8	28	14	17	21	14
Schüttorf	2.8	5.6	1.96	1.2	43	13	15	18	14
Lake Constance	1.0	0.9	0.90	0.2	20	4	5	7	4

Tab. 7. WWTP effluent DOC, UV₂₅₄, SUVA, LMW organics, and organic micro-pollutant concentrations.

	DOC	UV ₂₅₄	SUVA	LMW org.	LMW org.	Benzotriazole	Carbamazepine	Diclofenac	Sulfamethoxaz.
	[mg/L]	[1/m]	[L/mg/m]	[mg C/L]	[% of DOC]		— [µg/L]	—	
Schönerlinde	10.5	27.4	2.6	4.4	42	64	58	57	49
Dülmen	9.9	24.5	2.5	4.1	41	55	52	54	45
Seevetal	8.1	19.9	2.5	3.8	47	42	43	46	36
Mannheim	8.1	19.3	2.4	2.9	36	43	39	45	39
Garching	7.7	15.8	2.0	3.0	39	34	32	40	27
Stockacher Aach	4.9	12.6	2.6	2.0	41	24	23	28	25
Kressbronn	4.2	10.2	2.4	1.8	43	20	19	24	20

Fig. 22. LC-OCD absolute (*top*) and normalized (*bottom*) organic carbon chromatograms of the tested drinking waters (*left*) and WWTP effluents (*right*); with typical peak allocation; note the different y-axis scaling.

Within the group of WWTP effluents, Seevetal, Garching, and Kressbronn have higher percentages of LMW acids than the other WWTP effluents. Garching also contains a comparatively high percentage of biopolymers. The normalized chromatograms show that Seevetal contains a higher percentage of LMW neutrals than the other WWTP effluents. The UV₂₅₄ chromatograms (shown in the Supporting Information, Appendix B-4, p. 142) mostly reflect the organic carbon chromatograms. The WWTP effluent UV₂₅₄ signals of Garching and Seevetal show higher absorbance in the LMW acids fraction than the chromatograms of the other WWTP effluents (in the normalized chromatograms). The low SUVA of WWTP effluent Garching results from its high biopolymer content which increases the DOC but not the UV₂₅₄ (cf. Tab. 7). A comparison of the drinking water chromatograms with the WWTP effluent chromatograms of Fig. 22 reveals that the BOM of the drinking waters consists of a higher humic percentage than that of the WWTP effluents. The WWTP effluents contain overall more LMW acids and LMW neutrals as well as biopolymers than the drinking waters. These fractions were characterized as more biodegradable than other BOM/ NOM fractions; the relatively high humic content of the drinking water BOM indicates higher persistence (Huber et al. 2011). This is similarly reflected by the UV₂₅₄ chromatograms (cf. Supporting Information, Appendix B-4, p. 142) which show relatively higher UV₂₅₄ absorbance of WWTP effluent LMW compounds as compared to drinking water LMW compounds.

Experimental data on organic micro-pollutant adsorption

The PAC loadings of the OMP benzotriazole, carbamazepine, diclofenac, and sulfamethoxazole are depicted against the corresponding liquid phase concentrations in Fig. 23, for the tested drinking waters (left) and the tested WWTP effluents (right) and the adsorption times of 0.5 h and 48 h. Note that all graphs of each OMP have the same axis scaling for easier comparison. The loadings at given liquid phase concentrations are higher in the drinking waters than in the WWTP effluents for most OMP. This demonstrates that – given the similar DOC-relative OMP concentrations – WWTP-BOM induces stronger adsorption competition than drinking water-BOM. Within each of the two water groups, respectively, the data points of waters with higher initial $c_{o,OMP}$ and $c_{o,DOC}$ are located to the top right of the data points of waters with lower $c_{o,OMP}$ and $c_{o,DOC}$. E.g., the carbamazepine data of the WWTP effluent Schönerlinde are located to the top-right of the carbamazepine data of Kressbronn. However, the loadings of the well adsorbable OMP (carbamazepine, benzotriazole, diclofenac) are similar at given liquid phase concentrations, independent of the water origin. E.g., in all WWTP effluents, carbamazepine reaches a PAC loading of $\sim 2.5 \mu\text{g}/\text{mg}$ at liquid phase concentrations of $\sim 25 \mu\text{g}/\text{L}$ after 0.5 h of adsorption. (Benzotriazole and sulfamethoxazole in the drinking water Dülmen mark exceptions.) Accordingly, the PAC loading in dependence of the liquid phase concentration may be described by a single overall relationship within all waters of the respective group (drinking waters or WWTP effluents). Accordingly, the PAC loading in dependence of the liquid phase concentration may be described by a single overall relationship within all waters of the respective group (drinking waters or WWTP effluents). Thus, the BOM of different drinking waters mostly cause comparable adsorption competition against OMP. Analogously, the

BOM of different WWTP effluents cause similar adsorption competition. The results demonstrate that even in regionally different drinking waters (or, different WWTP effluents) and variable DOC/ BOM concentrations, strongly adsorbing OMP show similar relationships between the PAC loadings and the liquid phase concentrations, given that the ratios of the initial concentrations of the OMP and the BOM ($c_{0,OMP}/c_{0,DOC}$) are comparable. This demonstrates a practically useful transferability of adsorption data in different waters.

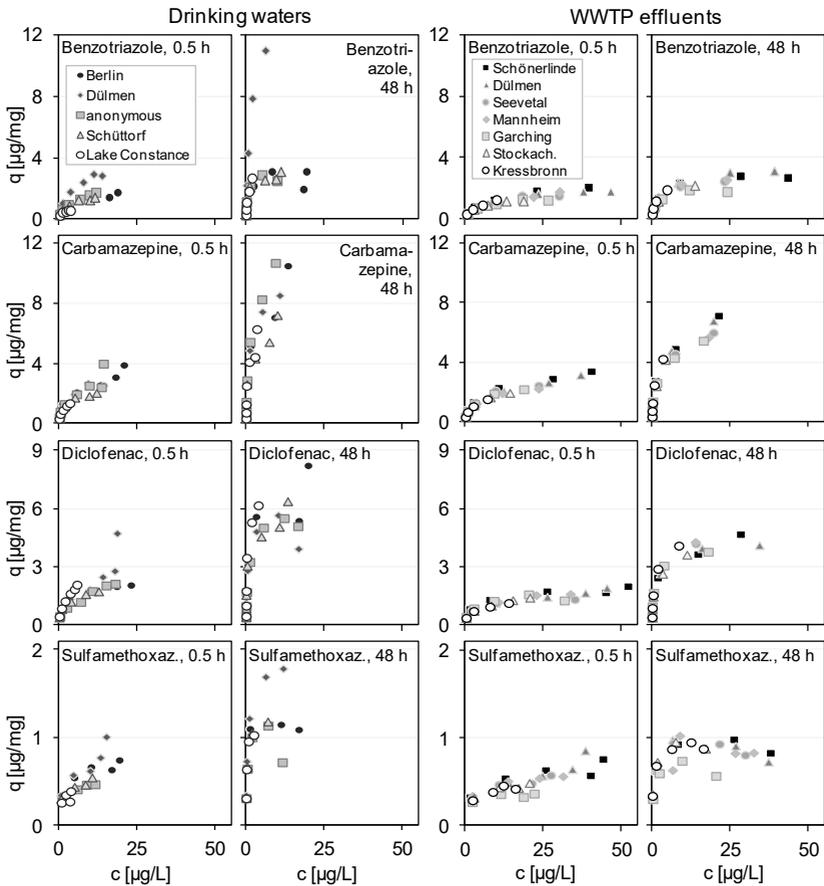


Fig. 23. Organic micro-pollutant loadings (q) versus concentrations (c) in the drinking waters (*left*) and the WWTP effluents (*right*) after 0.5 h and 48 h adsorption time.

Like for the well adsorbable compounds discussed above, the loadings of the weaker adsorbate sulfamethoxazole are in similar ranges within the waters of the respective group (except for the drinking water Dülmen). But in contrast to the well adsorbable compounds, the PAC loadings decrease near the initial concentration in most waters, particularly after 48 h of adsorption. The reason is strong BOM competition for adsorption sites at low PAC doses. As sulfamethoxazole is a rather weak adsorbate, it can be displaced from the PAC internal surface by better adsorbable compounds. Moreover, a trend can be seen that the sulfamethoxazole loadings are higher in waters with high $c_{o,OMP}$ and $c_{o,DOC}$ — e.g., the loadings in the WWTP effluent Schönerlinde are above those in the WWTP effluent Kressbronn. Likely, the PAC loadings depicted over the liquid phase concentrations of weak adsorbates such as sulfamethoxazole do not result in an overall curve for different drinking waters (or WWTP effluents) even if the ratios of $c_{o,OMP}/c_{o,DOC}$ are similar among the waters. This is also underlined by additional graphs in the Supporting Information (Appendix B-4, p. 142) for varied $c_{o,OMP}/c_{o,DOC}$.

As a consequence of the mass balance of an adsorptive system, OMP removals are directly linked to the relationships between the PAC loadings and liquid phase concentrations of the respective OMP. As an example for the OMP removals resulting from the relationships shown in Fig. 23, the removals of benzotriazole and diclofenac, obtained at the adjusted specific PAC doses in the tested WWTP effluents after 0.5 h of adsorption, are shown in Fig. 24 (left); the corresponding DOC removals are shown as well. (The removals after 48 h as well as UV_{254} removals and the removals of additional OMP, and the analogous data for the drinking waters as well as the three WWTP effluents whose $c_{o,OMP}/c_{o,DOC}$ were varied can be found in the Supporting information, Appendix B-4, p. 142.) About 40% DOC removal are attained at a specific PAC dose of 7 mg PAC/mg DOC after 0.5 h. Overall, the DOC removals obtained at a given specific PAC dose coincide widely and vary around $\pm 10\%$. The UV_{254} removals (cf. Supporting Information, Appendix B-4, p. 142) are similar in the tested waters, and are about 10–20% higher than the DOC removals. These results show that the partially different BOM compositions of the waters, as shown in Tab. 7, and Fig. 22 (right), do not lead to strongly varying behavior in the adsorption of the BOM. Particularly, the WWTP effluent Garching does not show different DOC/ UV_{254} adsorption behavior although the corresponding LC-OCD chromatogram differs from the other chromatograms.

With respect to the OMP, ~50% benzotriazole, and 40–60% diclofenac are removed at a specific PAC dose of 2 mg PAC/mg DOC and 0.5 h. After an adsorption time of 48 h (cf. Supporting Information, Appendix B-4, p. 142), these removals increase to ~70% (except for Stockacher Aach), and ~90%, respectively. The overall differences between the removals in the tested WWTP effluents are less than $\pm 10\%$ in most cases. Higher OMP removals are obtained in WWTP effluents with higher initial $c_{o,OMP}$ and $c_{o,DOC}$ (e.g. Schönerlinde) than in WWTP effluents with lower $c_{o,OMP}$ and $c_{o,DOC}$ (e.g. Kressbronn), which can analogously be observed for the tested drinking waters (cf. Supporting Information, Appendix B-4, p. 142). Theoretically, this observation is directly linked to the non-linearity of the loading/ concentration relationships (cf. Fig. 23). This phenomenon is highlighted with a fictive example in

the Supporting Information (Appendix B-4, p. 142) which also shows that higher initial OMP concentrations $c_{o,OMP}$ do not lead to accelerated OMP diffusion as a result of increased concentration gradients. Overall, it can be concluded that the removals of OMP at a given DOC-specific PAC dose do not diverge by more than $\pm 10\%$ between different WWTP effluents (or by more than $\pm 15\%$ between different drinking waters), neither at similar nor at different ratios of $c_{o,OMP}/c_{o,DOC}$.

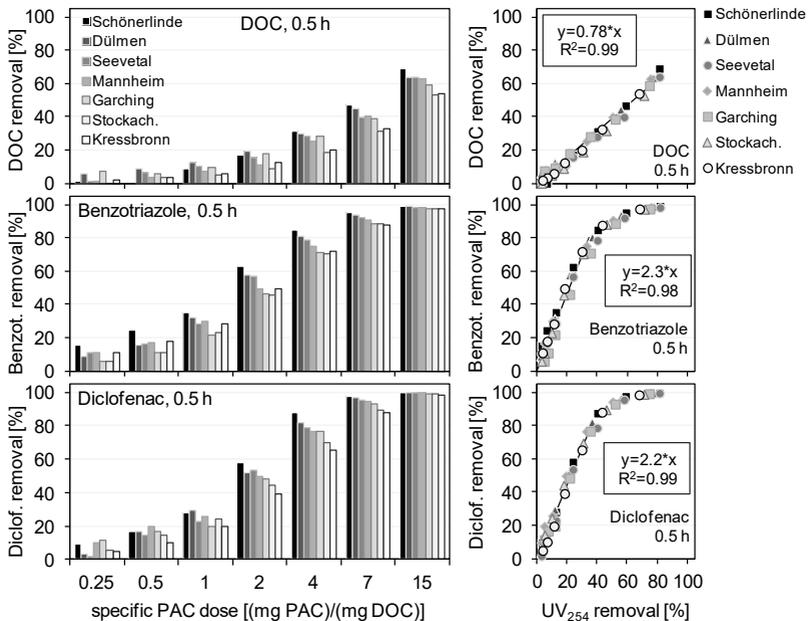


Fig. 24. Removals of the DOC, benzotriazole, and diclofenac at specific PAC doses (*left*) and DOC/ OMP removals versus UV₂₅₄ removals with corresponding linear correlations (*right*) in the tested WWTP effluents.

Regarding the practical prediction of adsorptive OMP removals, previous publications demonstrated the potential of the adsorptive UV₂₅₄ removal as a useful surrogate parameter in WWTP effluents (Altmann et al. 2014, Altmann et al. 2015, Anumol et al. 2015, Zietzschmann et al. 2015a, Zietzschmann et al. 2014a, Zietzschmann et al. 2015b). In different WWTP effluents of the same regional background, overall correlations were found for several OMP (Altmann et al. 2014). However, different regional origins have not yet been considered. The removals of the DOC, benzotriazole, and diclofenac are depicted against the corresponding UV₂₅₄ removals in Fig. 24 (right), for all tested WWTP effluents and an adsorption time of 0.5 h, with linear correlations for up to 65% DOC and up to 80% OMP removal. At 20% UV₂₅₄ removal, ~10–15% DOC, ~45% benzotriazole, and ~40% diclofenac are

removed, respectively. Within the range of the linear correlations, the DOC is less preferably removed as compared to the UV₂₅₄-active BOM compounds by a factor of 0.78. Benzotriazole and diclofenac are more preferably removed by factors of 2.3 and 2.2, respectively. The high coefficients of determination underline that the water origins have little to no influence. Accordingly, knowing the relationship between OMP removal and UV₂₅₄ removal in one WWTP effluent allows for the prediction in other WWTP effluents. Compared to the slopes of the correlations between the OMP and UV₂₅₄ removals in the tested drinking waters (cf. Supporting Information, Appendix B-4, p. 142), the slopes of the correlations in the tested WWTP effluents are smaller: 3.5 versus 2.3 for benzotriazole and 3.6 versus 2.2 for diclofenac. This is likely due to a higher adsorbability of UV₂₅₄-active BOM compounds in WWTP effluents than in drinking waters and less adsorption competition against OMP in drinking waters. Therefore, the adsorption of OMP against that of UV₂₅₄-active BOM compounds is more favored in drinking waters as compared to in WWTP effluents. The Supporting Information (Appendix B-4, p. 142) contains additional linear correlations for the three WWTP effluents whose $c_{o,OMP}/c_{o,DOC}$ were varied. The slopes are the same as in Fig. 24 (right), indicating that the UV₂₅₄ removal can be used in different WWTP effluents at variable initial OMP concentrations as a general indicator for OMP removal by PAC.

Initializing the EBCM using water characteristics

For each of the three tested OMP, the EBCM-fitted $K_{F,EBC}$ are shown in Tab. 8 (together with averages for the drinking waters, the WWTP effluents, and all waters). The EBCM-fitted $c_{o,EBC}$ using average $K_{F,EBC}$ are shown in Tab. 9 (different averages for the groups of drinking waters and WWTP effluents) and Tab. 10 (one average for the drinking waters and the WWTP effluents). Compared to the WWTP effluent $K_{F,EBC,av,WWTPeff.}$, the drinking water $K_{F,EBC,av,DRIN,WAT.}$ are 12.8% & -29% for benzotriazole (0.5 h & 48 h), -8.8% & 7.7% for diclofenac, and -8% & 3% for sulfamethoxazole, respectively (cf. Tab. 8, percentages not shown). Thus, neither of the two water groups shows overall higher or lower average values. This implies that the different competitive effects of the BOM in the waters can be reflected in the EBCM by varying the initial EBC concentrations $c_{o,EBC}$. Also, this underlines that it is feasible to average the $K_{F,EBC}$ of different waters for conducting a second fitting procedure with $c_{o,EBC}$ being the only fitted parameter, as also done in other studies (Graham et al. 2000, Shimabuku et al. 2014).

If all waters have the same $K_{F,EBC,av,ALL}$ (Tab. 10), $c_{o,EBC}$ is generally higher in the WWTP effluents than in the drinking waters, even at comparable BOM/ DOC concentrations: When comparing $c_{o,EBC}$ in the Berlin drinking water and in the WWTP effluent Stockacher Aach (similar DOC), the initial EBC concentration corresponding to sulfamethoxazole and 0.5 h of adsorption is 3.5 $\mu\text{mol/L}$ compared to 7.7 $\mu\text{mol/L}$. This demonstrates the increased BOM adsorption competition of WWTP effluent BOM as opposed to drinking water BOM.

Tab. 8. EBCM-fitted $K_{F,EBC}$ values for the tested waters (individually), and average $K_{F,EBC}$ values for the groups of the drinking waters, the WWTP effluents, and all waters.

[(nmol/mg)(L/nmol) ^{1/n}]	Drinking waters					WWTP effluents							AVERAGES			
	Berlin	Dülmen	anonymous	Schüttorf	Lake Constance	Schönerlinde	Dülmen	Seevetal	Mannheim	Garching	Stockacher Aach	Kressbronn	$K_{F,EBC,av,DRIN,WAT}$	$K_{F,EBC,av,WWTPeff}$	$K_{F,EBC,av,ALL}$	
Benzotriazole	0.5	11.4	7.4	6.8	8.4	9.9	6.8	8.7	7.4	6.8	9.5	8.7	6.8	8.8	7.8	8.2
	48	23.2	10.4	78.0	18.9	10.4	41.8	27.4	22.5	17.9	78.0	20.6	69.8	28.2	39.7	34.9
Diclofenac	0.5	22.1	20.2	20.2	20.9	20.2	31.0	20.9	24.6	20.2	20.2	20.2	21.5	20.7	22.7	21.9
	48	27.6	51.8	33.4	26.7	27.6	26.7	33.4	35.1	33.4	31.8	27.6	29.2	33.4	31.0	32.0
Sulfamethoxazole	0.5	11.1	10.5	11.7	12.9	11.1	11.7	9.9	12.0	12.0	16.8	13.2	12.0	11.5	12.5	12.1
	48	15.4	12.9	22.6	18.2	16.0	15.7	19.2	16.0	16.0	19.2	16.0	13.2	17.0	16.5	16.7

Tab. 9. EBCM-fitted $C_{0,EBC}$ values obtained when using different average $K_{F,EBC}$ for the groups of drinking waters and WWTP effluents – $K_{F,EBC,av,DRIN,WAT} \neq K_{F,EBC,av,WWTPeff}$.

[μmol/L]	Drinking waters					WWTP effluents							
	Berlin	Dülmen	anonymous	Schüttorf	Lake Constance	Schönerlinde	Dülmen	Seevetal	Mannheim	Garching	Stockacher Aach	Kressbronn	
Benzotriazole	0.5	1.5	0.24	0.72	0.73	0.41	5.0	6.3	4.9	5.0	4.5	3.0	1.6
	48	0.64	0.0073	0.32	0.38	0.04	4.8	3.9	3.8	3.5	4.3	1.7	1.2
Diclofenac	0.5	1.9	1.3	1.8	1.4	0.38	7.1	7.8	6.7	5.7	4.9	4.3	3.8
	48	0.32	0.20	0.28	0.31	0.056	1.6	1.8	1.4	1.2	1.4	0.88	0.56
Sulfamethoxazole	0.5	3.7	2.7	3.5	2.9	0.85	13.2	13.3	10.6	11.2	10.9	7.5	5.9
	48	0.61	0.29	0.38	0.35	0.085	2.7	2.8	1.9	2.0	2.1	1.2	0.91

Tab. 10. EBCM-fitted $C_{0,EBC}$ values obtained when using the same average $K_{F,EBC}$ for the groups of drinking waters and WWTP effluents – $K_{F,EBC,av,ALL}$.

[μmol/L]	Drinking waters					WWTP effluents							
	Berlin	Dülmen	anonymous	Schüttorf	Lake Constance	Schönerlinde	Dülmen	Seevetal	Mannheim	Garching	Stockacher Aach	Kressbronn	
Benzotriazole	0.5	1.5	0.26	0.75	0.77	0.44	5.0	5.9	4.8	4.8	4.4	2.9	1.6
	48	0.63	0.0073	0.31	0.35	0.04	5.0	3.9	3.8	3.5	4.3	1.8	1.2
Diclofenac	0.5	2.2	1.1	1.6	1.4	0.35	7.4	8.1	6.9	6.2	5.0	4.5	3.9
	48	0.30	0.28	0.30	0.28	0.051	1.6	1.8	1.3	1.2	1.3	0.85	0.53
Sulfamethoxazole	0.5	3.5	2.6	3.3	2.8	0.81	14	14	11	11	11	7.7	5.9
	48	0.63	0.29	0.38	0.36	0.085	2.7	2.7	1.9	2.0	2.1	1.2	0.91

Using Tab. 9, the modeled initial EBC concentrations ($c_{0,EBC}$) for benzotriazole, diclofenac, and sulfamethoxazole are depicted versus the measured initial DOC concentrations ($c_{0,DOC}$) of the tested drinking waters and WWTP effluents, for the adsorption times of 0.5 h and 48 h in Fig. 25 (left and middle), together with the corresponding linear correlations. Analogously and using Tab. 10, the modeled $c_{0,EBC}$ are depicted against the measured initial LMW organics concentrations of all waters in Fig. 25 (right).

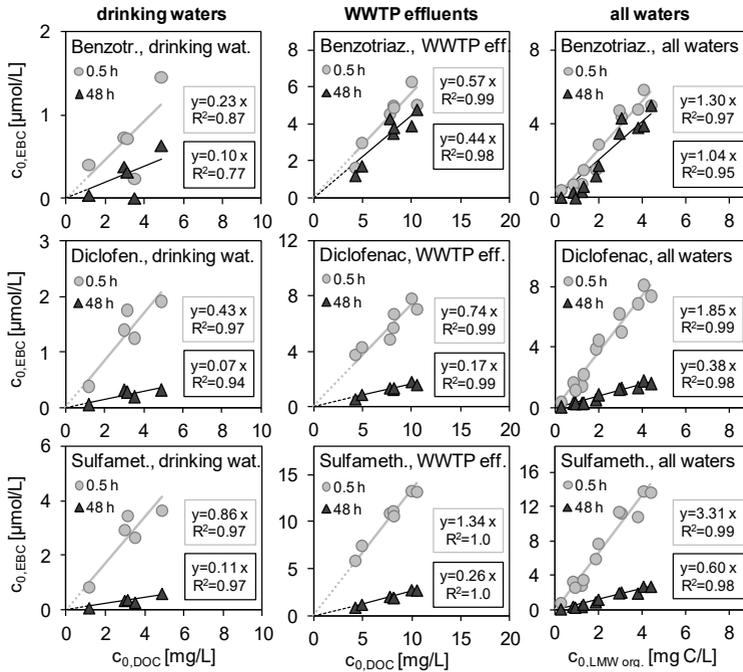


Fig. 25. Fitted initial EBC concentrations versus initial DOC in the tested drinking waters (left) and WWTP effluents (middle), and versus initial LMW organic concentration in all waters (right), for benzotriazole (top) diclofenac (middle) and sulfamethoxazole (bottom), for adsorption times of 0.5 h and 48 h, with linear correlations; note the different axis scaling.

In all cases, higher fitted $c_{0,EBC}$ coincide with higher $c_{0,DOC}$ or $c_{0,LMW\ org.}$. With the exception of benzotriazole in the group of drinking waters, the coefficients of determination R^2 are >0.9 which is partially caused by intentionally setting the y-axis intercept to 0. (DOC or LMW organics concentrations of 0 mg/L would imply water free of competing BOM.) Benzotriazole showed unexpectedly strong adsorption in the drinking water Dülmen which results in very low fitted initial EBC concentrations for this water. According to the correlations, the modeling parameter $c_{0,EBC}$ can be estimated from the DOC or LMW organics concentrations of the tested waters. Additionally, the initial concentration of the OMP, $c_{0,OMP}$, is

not contained in these relationships and accordingly, variable $c_{o,OMP}$ do not impact the initial concentration of the EBC $c_{o,EBC}$. The Supporting Information (Appendix B-4, p. 142) contains additional discussions on potential kinetic effects contained in the data shown in Tab. 8, Tab. 9, Tab. 10, and Fig. 25, and the fact that different $K_{F,EBC}$ were obtained for different adsorption times which contradicts another study (Shimabuku et al. 2014).

With the correlations shown in Fig. 25, the OMP adsorption can be modeled by measuring the initial OMP concentration in the water of interest and calculating the initial EBC concentration from the relationships to the DOC or LMW organics concentrations (for the tested PAC). This was conducted for additional water samples (Berlin drinking water, $c_{o,DOC} = 5.1$ mg/L, WWTP effluent Waßmannsdorf, $c_{o,DOC} = 12.9$ mg/L, and PEP Tegel effluent, $c_{o,LMW\ org.} = 2.8$ mg/L) which were not used to calibrate the linear correlations of Fig. 25, to check for the predictive capabilities of the shown correlations. In combination with the respective initial OMP concentrations $c_{o,OMP}$, EBC model runs were conducted. The experimental and EBCM-modeled relationships between the PAC loadings and liquid phase concentrations of benzotriazole, diclofenac, and sulfamethoxazole are shown in Fig. 26, together with the respective initial OMP concentrations, for non-equilibrium (0.5 h) and equilibrium (48 h) adsorption times.

Fig. 26 demonstrates that initializing the EBCM via the DOC or the LMW organics concentration can be used to directly model OMP adsorption onto PAC. However, in most cases, some under-predictions were obtained, particularly for an adsorption time of 48 h. For benzotriazole, the under-predictions were the highest in the drinking water sample at 48 h (60%) and the lowest in the WWTP sample at 48 h (34%). For diclofenac, the highest value was obtained for the PEP Tegel sample at 0.5 h (58%) and the lowest in the WWTP sample at 48 h (17%). For sulfamethoxazole, the highest under-prediction corresponds to the PEP Tegel sample at 0.5 h (69%) and the lowest to the drinking water sample at 0.5 h (-17% which is an over-prediction). The reason for the overall occurrence of under-predictions is that the initial OMP concentrations were substantially smaller than the initial OMP concentrations of the experiments used to calibrate the graphs shown in Fig. 25 (cf. Tab. 6 and Tab. 7). In the tested additional drinking water sample, the benzotriazole concentration was 74 times smaller than the lowest concentration used in the linear correlations of Fig. 25, for sulfamethoxazole, the factor is ~1923; in the additional WWTP effluent sample, the factors were 2.5 (benzotriazole), 10 (diclofenac), and 83 (sulfamethoxazole); in the PEP Tegel effluent sample, the factors were 9, 66, and 144, respectively. To compare the effects of variable initial OMP concentrations on the EBC model outcomes, additional EBCM fittings for PAC batch tests with the WWTP effluents Kressbronn, Seevetal, and Schönerlinde are shown in the Supporting Information (Appendix B-4, p. 142) for varied $c_{o,OMP}/c_{o,DOC}$. Overall higher $c_{o,EBC}$ were fitted for higher $c_{o,OMP}$ than for lower $c_{o,OMP}$, indicating that OMP-OMP competition can cause increased fitted $c_{o,EBC}$ at comparatively high $c_{o,OMP}$. Accordingly, the applicability of the correlations of Fig. 25 as demonstrated in Fig. 26 should be further refined using PAC adsorption tests with lower initial OMP concentrations to avoid biasing the fitting

of $c_{0,EBC}$. Moreover, the Supporting Information (Appendix B-4, p. 142) contains an example on the sensitivity of the EBCM if different $K_{F,EBC}$ values are used for the same water.

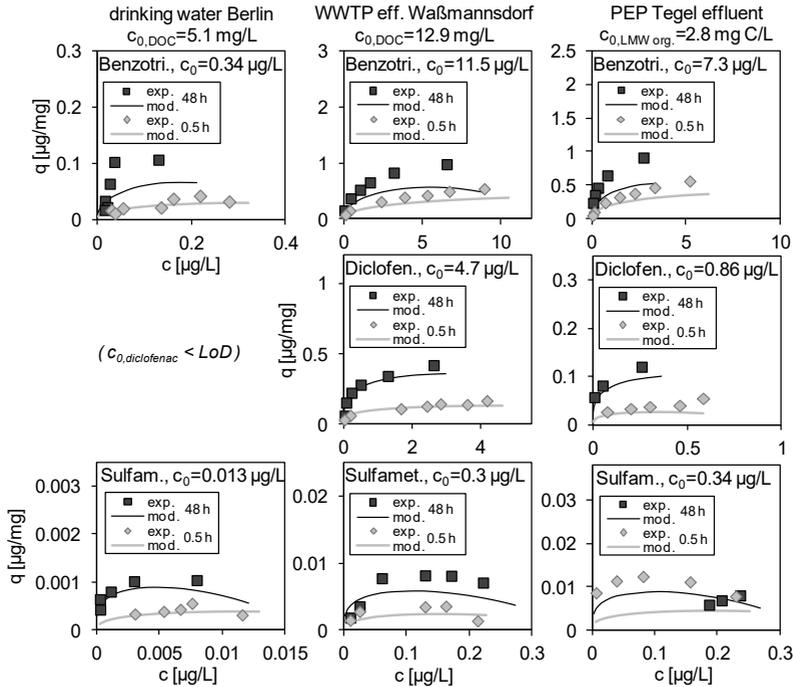


Fig. 26. EBC-modeled isotherms (48 h) and loading curves (0.5 h) in an additional Berlin drinking water sample (*left*), in WWTP effluent Waßmannsdorf (*middle*), and in PEP Tegel effluent (*right*), for benzotriazole (*top*), diclofenac (*middle*) and sulfamethoxazole (*bottom*), with initial EBC concentrations calculated from the correlations shown in Fig. 25; note the different axis scaling.

CONCLUSIONS

- The competitive impacts of background organic matter (BOM) on the adsorption of organic micro-pollutants (OMP) onto powdered activated carbon (PAC) in waters from different regional origins were evaluated. Five drinking waters were compared with each other (1st group) and seven wastewater treatment plant (WWTP) effluents were compared with each other (2nd group).
- High comparability between the tested waters was assured by adjusting similar DOC-relative OMP concentrations in all waters. PAC was applied proportional to the DOC (e.g. 2 mg PAC/mg DOC).

- Liquid chromatography with online organic carbon and UV₂₅₄ detection (LC-OCD) shows that within the respective group, most of the waters have a similar composition; however, some differences regarding the amount of large BOM (e.g., humics) and low molecular weight (LMW) BOM were also revealed.
- The variable BOM compositions of the different waters within the respective group appear to have little impact on the adsorption competition against OMP. In most cases, similar OMP removals are achieved at the same specific PAC doses (mg PAC/mg DOC) in the respective water group.
- However, slightly higher removals are obtained in waters with higher initial OMP and DOC concentrations at given DOC-specific PAC doses. The reason is that the PAC loadings in dependence of the liquid phase OMP concentrations are comparable between all waters of the respective group if the waters have similar ratios of the initial OMP/DOC concentrations (for strong adsorbates).
- For weak adsorbates, the PAC loadings at given liquid phase concentrations do not coincide between the different waters of the respective group. Here, the strong BOM-induced adsorption competition at high OMP liquid phase concentrations (i.e. low PAC doses) results in decreased PAC loadings which depend on the individual water.
- Varying $C_{o,OMP}/C_{o,DOC}$ results in shifted isotherms but the OMP removals at given DOC-specific PAC doses are not affected, neither for strong nor for weak adsorbates.
- The equivalent background compound (EBC) model (EBCM) was fitted to the experimental data for benzotriazole, diclofenac, and sulfamethoxazole. After averaging the Freundlich coefficients of the EBC, the initial EBC concentration was the only fitting parameter.
- Within each of the two tested water groups (drinking waters, WWTP effluents), the initial EBC concentration correlates with the DOC, for all tested OMP, respectively.
- If both water groups are considered together, the low molecular weight acid and neutral (LMW) organics can be used for an overall correlation.
- The developed correlations were used to EBC-model and predict the OMP isotherms (equilibrium adsorption) and loadings curves (non-equilibrium adsorption) in additional drinking water, surface water, and WWTP effluent samples. Some under-predictions were obtained because the additional samples had lower initial OMP concentrations than the waters used for developing the correlations (where OMP-OMP competition likely increased the fitted initial EBC concentrations).
- This study shows that the effective BOM-induced competition against OMP adsorption onto PAC is similar in drinking waters, or WWTP effluents, from different regional origin. These findings may increase the comparability of results from various studies. The approach to initialize the EBCM by using simple water characteristics may reduce the need for laborious pre-testing.

ACKNOWLEDGMENTS

This study was part of the project “Anthropogenic Organic Micro-Pollutants and Pathogens in the Urban Water Cycle: Assessment, Barriers and Risk Communication (ASKURIS)” funded by the German Federal Ministry for Education and Research (Bundesministerium für Bildung und Forschung, BMBF) under the sponsorship number 02WRS1278A. We gratefully thank Mr. Michael Petri and Dr. Roland Schick (Zweckverband Bodensee-Wasserversorgung), Dr. Steffen Metzger (Kompetenzzentrum Spurenstoffe Baden-Württemberg), Mr. Peter Jagemann (Emschergenossenschaft/ Lippeverband Dülmen), Dr. Jürgen Schönung (Eigenbetrieb Stadtentwässerung Mannheim), Mr. Martin Schulz (TU Hamburg-Harburg), and Mr. Johann Müller (TU München) for water samples and Ms Jutta Jacobs, Ms Ulrike Förster, Ms Katrin Noack, Mr. Daniel Mahringer, and Mr. Simon Mangold for laboratory assistance. The work of the reviewers is also gratefully acknowledged.

NOMENCLATURE

The nomenclature is given in Appendix C, p. 171.

SUPPORTING INFORMATION

Supplementary data related to this article can be found in the Supporting Information shown in Appendix B-4, p. 142.

REFERENCES

The cited references are contained in the general bibliography in Appendix A, p. 125.

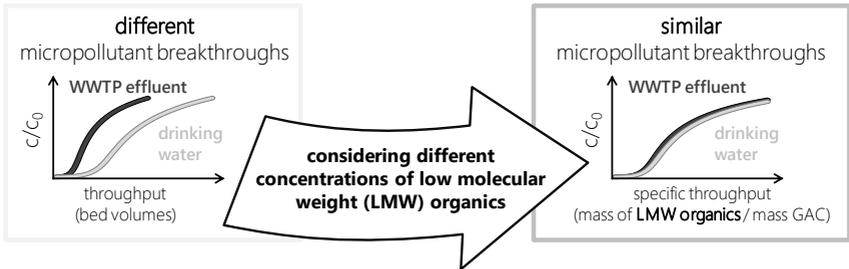
3.2 Unifying granular activated carbon breakthroughs

Granular activated carbon adsorption of organic micro-pollutants in drinking water and treated wastewater – aligning breakthrough curves and capacities

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GRAPHICAL ABSTRACT



ABSTRACT

Small-scale granular activated carbon (GAC) tests for the adsorption of organic micro-pollutants (OMP) were conducted with drinking water and wastewater treatment plant (WWTP) effluent. In both waters, three influent OMP concentration levels were tested. As long as the influent OMP concentrations are below certain thresholds, the relative breakthrough behavior is not impacted in the respective water. Accordingly, the GAC capacity for OMP is directly proportional to the influent OMP concentration in the corresponding water. The differences between the OMP breakthrough curves in drinking water and WWTP effluent can be attributed to the concentrations of the low molecular weight acid and neutral (LMW) organics of the waters. Presenting the relative OMP concentrations (c/c_0) over the specific throughput of the LMW organics (mg LMW organics/g GAC), the OMP breakthrough curves in drinking water and WWTP effluent superimpose each other. This superimposition can be further increased if the UV absorbance at 254 nm (UV_{254}) of the LMW organics is considered. In contrast, using the specific throughput of the dissolved organic carbon (DOC) did not suffice to obtain superimposed breakthrough curves. Thus, the LMW organics are the major water constituent impacting OMP adsorption onto GAC. The results demonstrate that knowing the influent OMP and LMW organics concentrations (and UV_{254}) of different waters, the OMP breakthroughs and GAC capacities corresponding to any water can be applied to all other waters.

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INTRODUCTION

The capability of granular activated carbon (GAC) to remove organic micro-pollutants (OMP), e.g. pharmaceuticals, taste/ odor compounds, or industrial chemicals, from various waters has been shown by numerous studies (e.g., Gimbel et al. 2011, Kennedy et al. 2015, Summers et al. 2013, Ternes et al. 2002). However, the results from different surveys are difficult to compare or to transfer, and usually, extensive testing is necessary to investigate the potential of GAC in each individual case. The lack of comparability/ transferability is caused by several factors like the filter dimensioning, the used GAC products, and the water composition (e.g., OMP concentrations and background organic matter (BOM) concentration and composition). Unlike the former two factors which are controllable via the process design, the water composition depends on the individual case and usually cannot be controlled. Complex waters contain BOM (usually expressed via the dissolved organic carbon – DOC) which induces adsorption competition and can substantially decrease the activated carbon capacity for OMP (e.g., Summers et al. 2013, Zietzschmann et al. 2014b).

In the same drinking source water, the relative breakthrough of 2-methylisoborneol (MIB) was shown to be mostly independent of the influent concentration (50–200 ng/L) of this OMP (Summers et al. 2013). Accordingly, more OMP can be adsorbed at higher influent OMP concentrations, implying that the GAC capacities for OMP in waters containing BOM are variable and depend on the influent OMP concentration. This behavior is different from single-solute systems where variable influent concentrations result in shifts of the breakthrough curve (because the GAC capacity for OMP is not variable). Dilution of a natural water led to quantitatively varied BOM concentrations and the OMP breakthrough behavior was directly impacted (Matsui et al. 2002a). Similarly, empirical models were used to relate the breakthrough of MIB and geosmin to the influent total organic carbon (TOC) of different drinking source waters (Summers et al. 2013). When treating different WWTP effluents on GAC filters, the relative effluent concentrations of several OMP could be aligned using fluorescence (Anumol et al. 2015). Quantitative structure-activity relationships (QSAR) have been used to derive empirical models for OMP breakthrough in GAC filters; these models are based on chemical/ molecular properties of the OMP (Magnuson and Speth 2005, Redding et al. 2009). One shortcoming of the above-cited studies is that all approaches investigated qualitatively similar BOM, respectively (e.g. drinking water *or* WWTP effluent). However, the BOM characteristics affecting adsorption competition can vary strongly between different types of waters (de Ridder et al. 2011, Zietzschmann et al. 2015b, Zietzschmann et al. 2014c). For different water types and, accordingly, different BOM characteristics, WWTP effluent had a substantially stronger negative impact on OMP breakthrough than was expected from previously known surface water data (Kennedy et al. 2015). This discrepancy between different waters is likely caused by the variable BOM competitiveness against OMP adsorption. Empirical relationships which consider the potential impact of different BOM are practically difficult to use because of their complexity requiring various experimentally-determined parameters in several waters (Jarvie et al. 2005). However, extensive laboratory testing and/ or model calibration is typically not feasible in practice. A

method for direct comparisons of OMP breakthrough curves on GAC filters treating different waters, without laborious pre-testing or calibration, would be a powerful tool in transferring results from different studies and reducing the need for testing each water individually.

The low molecular weight (LMW) acid and neutral organic fractions (LMW organics) of WWTP effluent organic matter (EfOM) were identified as the major competitors in powdered activated carbon (PAC) adsorption (Zietzschmann et al. 2014c). On GAC filters, these fractions show the strongest retention among surface water BOM (Velten et al. 2011) as well as among EfOM (Zietzschmann et al. 2014b). Accordingly, the LMW organics are the strongest adsorption competitors against OMP in GAC filters. The current study investigates how the LMW organics of drinking water and WWTP effluent impact the GAC breakthrough behavior of OMP in combination with variable OMP concentrations. It was furthermore tested if the GAC capacity could be predicted by taking into account variable OMP and LMW organics concentrations (and LMW organics UV_{254} absorbances).

MATERIALS AND METHODS

Water samples and pretreatments

Berlin (Germany) tap water was used as drinking water. Wastewater treatment plant (WWTP) effluent was obtained from WWTP *Berlin Schönerlinde* which is equipped with conventional mechanical/ biological treatment (dry weather capacity of 105,000 m³/d). The WWTP effluent samples were pre-filtered by ultrafiltration with a polyethersulfone membrane (molecular weight cutoff 100 kDa, *Dizzer, INGE*, Germany) in order to remove suspended solids and to increase the microbial stability. It was shown in a previous study that this kind of pre-filtration does not affect organic micro-pollutant (OMP) adsorption (Zietzschmann et al. 2014c). To obtain three OMP concentration levels in each water (“low”, “medium”, “high”), the OMP (*Sigma Aldrich*, Germany and *Dr. Ehrenstorfer*, Germany) were spiked from stock solutions (20 mg/L) in ultra pure water (*ELGA Berkefeld, Veolia*, Germany). The resulting drinking water and WWTP effluent are characterized in Tab. 11.

Experimental setup

Granular activated carbon (GAC) *Aquasorb 5000* (*Jacobi*, Germany) was ground on a *Pulverisette* mill (*Fritsch*, Germany) and sieved (*Retsch*, Germany) to obtain GAC grains between 90 and 140 μm . Particle measurement using dynamic image analysis on a *Camsizer* (*Retsch*, Germany) determined 120 μm as the average particle size in this fraction. The particle diameter from the shortest particle axis as determined from the maximum of the volume-related density distribution was taken as the average particle diameter. Results from the dynamic image analysis are given in the Supporting Information (Appendix B-5, p. 155). The ground/ sieved GAC was then wetted in ultra pure water and degassed in a partial vacuum and subsequently fixed with glass wool and glass pearls in 7 mm glass columns (ratio of

column to GAC diameters ~ 58) to obtain 2 cm filter bed lengths for the desired rapid small-scale column test (RSSCT) setup. The hydraulic loading rate (HLR) was set to 8 m/h, resulting in an empty bed contact time (EBCT) of 0.15 min. The filter flow direction was set from bottom to top and peristaltic pumps (*Ecoline*, *Ismatec*, Germany) were used for feeding. The filter outlets were furnished with T-fittings to connect a part of the outlet to an autosampler fed by a peristaltic pump (*Reglo*, *Ismatec*, Germany). The autosampler was a modified fraction collector (*SuperFrac*, *LKB Bromma*, Sweden) and allowed for highly resolved sampling of several RSSCTs in parallel.

Tab. 11. Characterization of differently spiked drinking waters and WWTP effluents.

	spiking level	DOC	UV ₂₅₄	SUVA	LMW org. conc.	LMW org. UV ₂₅₄	Benzotriazole	Carbamazepine	4-Formylaminoantip.	Primidone	Sulfamethoxazole
		[mg C/L]	[1/m]	[L/mg/m]	[mg C/L]	[1/m]	– [µg/L] –		–		
drinking water	low	4.9	10.6	2.2	1.1	1.9	0.9	1.1	1.0	0.9	0.9
	med.	4.9	11.0	2.2	-	-	9.0	10.2	9.5	8.8	9.5
	high	5.0	11.8	2.4	-	-	41.3	47.1	41.4	39.3	41.2
WWTP effluent	low	10.7	25.9	2.4	4.5	9.2	9.5	2.3	6.0	0.4	0.4
	med.	10.8	26.5	2.5	-	-	16.3	18.3	17.8	17.5	16.0
	high	10.7	27.5	2.6	-	-	38.2	49.5	42.6	47.0	38.0

Analytics

High performance liquid chromatography with tandem mass spectrometry (HPLC-MS/MS) was used for OMP quantification. An *XSelect HSS T3* column (2.5 µm particle size, 50*2.1 mm, *Waters*, USA) was used for HPLC, with a linear gradient from 98% aqueous phase (ultra pure water, 5 vol.-% MeOH, 0.1 vol.-% HCOOH) to 100% organic phase (MeOH). A *TSQ Vantage* (*Thermo Scientific*, USA) in ESI[±] modes was used for mass spectrometry. Two fragments, according to the *DAIOS* database (*Wasserchemische Gesellschaft* 2013), were chosen for the identification of each OMP. The more intense fragment was used for quantification in combination with deuterated internal standards.

Dissolved organic carbon (DOC) was quantified on a *varioTOC cube* (*elementar Analysensysteme*, Germany). A *Lambda 12* (*Perkin-Elmer*, USA) with 1 cm quartz cuvettes (*Suprasil*, *Hellma*, Germany) was used for the quantification of UV absorption at 254 nm (UV₂₅₄). Fractionated dissolved organic carbon was measured using liquid chromatography with online organic carbon and UV₂₅₄ detection (*LC-OCD*, *DOC-Labor Huber*, Germany). The LC-OCD peaks were allocated according to the literature (Huber et al. 2011). The software *Chromcalc* (*DOC-Labor Huber*, Germany) was used for chromatogram integration and the local minimum between the fractions of the building blocks and the low molecular weight acids was used as the left integration limit; as the right integration limit, the baseline at the end of the chromatogram was used. A previous study showed that the substances left

of the integration limit (humics and building blocks) exhibit less adsorption competition against OMP than the substances right of the integration limit (Zietzschmann et al. 2014c). Analogous observations were made regarding the GAC breakthrough behavior of these LC-OCD fractions (Zietzschmann et al. 2014b). Accordingly, the chosen integration limit encompasses the BOM compounds with the highest negative impacts on OMP adsorption. The Supporting Information (Appendix B-5, p. 155) contains retention times of several polyethylene glycols, illustrating the molecular weight ranges of the different LC-OCD fractions.

Capacity calculations

The GAC capacities for OMP which exhibited a full breakthrough during the experimental runtime (i.e. weakly adsorbing OMP) were calculated by adding up the GAC loadings with the respective OMP. The GAC loading with an OMP during a sampling period is the influent OMP concentration minus the respective outlet concentration, multiplied with the volume fed to the filter during the corresponding sampling period, divided by the GAC mass of the filter. The GAC loading with the respective OMP at 60,000 bed volumes (BV) of throughput was taken as the capacity.

RESULTS AND DISCUSSION

Water characterization

The dissolved organic carbon (DOC), UV absorbance at 254 nm (UV_{254}), specific UV absorbance (SUVA), and organic micro-pollutant (OMP) concentrations of the respective three different spiking levels (indicated by “low”, “med.”, “high”) in the tested drinking water and wastewater treatment plant (WWTP) effluent are given in Tab. 11. The concentrations and UV_{254} of the low molecular weight acids and neutrals (LMW organics), as determined via liquid chromatography with online organic carbon and UV_{254} detection (LC-OCD), are given for the “low” spiking level only. The DOC of the drinking water is ~5 mg/L for all spiking levels but the UV_{254} and SUVA increase from 10.6 to 11.8 1/m and 2.2 to 2.4 L/mg/m, respectively, due to the spiking of OMP which contain double and aromatic bonds absorbing UV_{254} (Weishaar et al. 2003). Similar to the drinking water values, the DOC of the WWTP effluent at the different spiking levels are fairly constant (~10.7 mg/L) while the UV_{254} increases from 25.9 to 27.5 1/m and the SUVA from 2.4 to 2.6 1/m. The concentrations of the LMW organics are 1.1 mg C/L in the drinking water and 4.5 mg C/L in the WWTP effluent; the respective UV_{254} are 1.9 and 9.2 1/m (corresponding to SUVA values of 1.7 and 2 L/mg/m, respectively). The corresponding LC-OCD organic carbon chromatograms of the drinking water and WWTP effluent are shown in Fig. 27, together with indicators for the LMW acids and neutrals fractions as well as the integration limit that was used to obtain the quantitative LMW organic concentrations of Tab. 11. As shown in Tab. 11 and Fig. 27, the WWTP effluent contains not only a higher absolute value of LMW organics than the drinking water; also, the proportion of LMW organics as part of the respective DOC is higher in the WWTP effluent (~42% of the DOC) compared to the drinking water (~23% of the DOC).

Also, the LMW organics of the WWTP effluent show a higher UV₂₅₄ than those of the drinking water. Between the spiking levels of the tested drinking water, the OMP concentrations vary from ~ 1 $\mu\text{g/L}$ at the low spiking level to ~ 10 $\mu\text{g/L}$ (medium) and 39 – 50 $\mu\text{g/L}$ at the high level. As the OMP concentrations in the low spiking level of the WWTP effluent were left unaltered, the variation between the OMP is higher (e.g., 0.4 $\mu\text{g/L}$ primidone compared to 9.5 $\mu\text{g/L}$ benzotriazole). In the WWTP effluent, the medium levels range from 16.3 $\mu\text{g/L}$ (benzotriazole) to 18.3 $\mu\text{g/L}$ (carbamazepine), and the high levels from 38 $\mu\text{g/L}$ (sulfamethoxazole) to 49.5 $\mu\text{g/L}$ (carbamazepine).

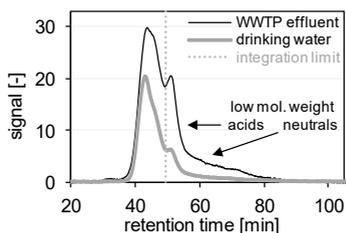


Fig. 27. LC-OCD chromatograms of the WWTP effluent and the drinking water with low molecular weight acids and neutrals indicators and corresponding integration limit.

Variation of organic micro-pollutant concentrations

The relative GAC filter effluent concentrations of benzotriazole, carbamazepine, and primidone are depicted against the corresponding throughputs (in bed volumes — BV) in drinking water and WWTP effluent at different OMP influent concentrations in Fig. 28. At low and medium concentrations of benzotriazole in drinking water, nearly no breakthrough occurs. At the highest concentration, $\sim 20\%$ breakthrough is reached at $\sim 55,000$ BV of throughput. For carbamazepine in drinking water, 20% breakthrough is obtained at $20,000$ BV, independent of the influent concentration. However, the breakthrough curves of the different influent concentrations diverge at higher throughputs. The breakthrough of primidone in drinking water at $20,000$ BV of throughput is $\sim 50\%$ for the low and medium concentrations and $\sim 60\%$ for the high concentration. The results show that the breakthrough curves in the drinking water filter runs with the low and medium OMP concentrations superimpose each other. The test with the highest influent concentration shows an earlier breakthrough. Accordingly, below concentrations of ~ 10 $\mu\text{g/L}$ in drinking water, the influent OMP concentration does not impact the relative breakthrough behavior and the breakthrough curve appearance at any OMP influent concentration can be estimated from breakthrough curve data at other influent OMP concentrations. Similar observations were made for comparatively low concentrations (50 – 200 ng/L) of 2-methylisoborneol in drinking water (Summers et al. 2013). In the tested WWTP effluent, benzotriazole shows $\sim 25\%$ breakthrough at $20,000$ BV of throughput, mostly independent of the respective influent

concentration. The carbamazepine breakthrough is $\sim 50\%$ at 20,000 BV in all cases. Primidone occurs to $\sim 50\%$ at 10,000 BV of throughput, independent of the influent concentrations. The lowest influent concentration of this OMP is very low which causes higher scattering of the measured relative effluent concentrations compared to the two tests with higher influent concentrations. The tests with WWTP effluent show that the OMP concentrations can be as high as $\sim 50 \mu\text{g/L}$ without having an impact on the overall breakthrough curve appearance. The tests with both waters show that the GAC capacity is related to the influent OMP concentrations. At higher OMP concentrations, OMP adsorption is more competitive against the adsorption of background organic matter (BOM) and thus, a higher amount of OMP can be adsorbed.

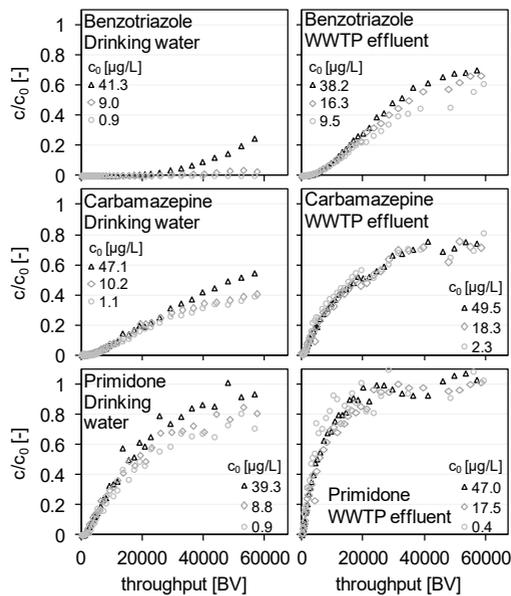


Fig. 28. Relative GAC filter effluent concentrations of benzotriazole, carbamazepine, and primidone (c/c_0) versus throughput at different influent concentrations in drinking water (*left*) and WWTP effluent (*right*).

The similarity of the breakthrough curves (at variable concentrations in the respective water) shown in Fig. 28 can be directly transferred into a proportional relationship between the GAC capacity and the influent OMP concentrations. I.e., if the relative breakthrough curve is comparable at different influent OMP concentrations $c_{0,i}$, the relative effluent concentration at a given throughput x is constant, $c_{x,i}/c_{0,i} = \text{const.} = u$, with $c_{x,i}$ being the effluent OMP concentration. For a filtered water volume V , the adsorbed OMP amount onto the GAC mass (m_{GAC}), q_i , at an influent OMP concentration $c_{0,i}$ is given by Eq. 18. Accordingly, q_i is

linearly linked to the influent OMP concentration $c_{o,i}$; e.g. doubling the influent concentration causes a doubling of the capacity. This phenomenon also occurs in powdered activated carbon adsorption (Knappe et al. 1998, Qi et al. 2007, Zietzschmann et al. 2016). Only at very high OMP concentrations, the GAC capacity cannot be proportionally increased, as shown by the drinking water test with the highest influent OMP concentrations which shows earlier breakthrough behavior than the tests with lower concentrations. The threshold influent OMP concentration above which the breakthrough curve similarity is no longer given appears to be higher in WWTP effluent (40–50 $\mu\text{g/L}$ or even higher) than in drinking water ($<50 \mu\text{g/L}$). This is likely a result of the different BOM concentrations/ compositions in both waters. The DOC of the WWTP effluent (10.7 mg/L) is more than twice as high as the DOC in the tested drinking water (4.9 mg/L). Therefore, the impact of the OMP concentration as compared to the BOM concentration is of less consequence in WWTP effluent as compared to in drinking water. The findings underline that the capacity of GAC filters can be more efficiently exploited by OMP at increasing OMP concentrations relative to the concentrations of BOM. Practically, this manifests the potential of GAC filters in series as strongly adsorbing OMP and BOM can be removed in early GAC filters while weakly adsorbing OMP or OMP with small concentrations face less adsorption competition in late GAC filters. The tested OMP concentrations in both waters were comparatively high and it is unlikely that these concentrations are exceeded in most advanced treatment stages for drinking waters or WWTP effluents. Thus, from a practical perspective, OMP breakthrough curves are presumably constant for any specific water.

$$q_i = \frac{V(c_{o,i} - c_{x,i})}{m_{GAC}} = \frac{V c_{o,i} (1 - u)}{m_{GAC}} \quad \text{Eq. 18}$$

Normalization of breakthrough curves in different waters

The relative concentrations of the OMP benzotriazole, carbamazepine, primidone and sulfamethoxazole, in the tested drinking water and WWTP effluent (“low” concentration levels, cf. Tab. 11), are depicted against several possible alternatives of throughput presentation in Fig. 29: Throughput in bed volumes (left), specific throughput of DOC (DOC per mass of GAC, middle-left), specific throughput of LMW organics (middle-right), and specific throughput of LMW organic UV₂₅₄ (right). The depiction over bed volumes (Fig. 29, left) shows that the breakthrough of all OMP occurs later in drinking water than in WWTP effluent, e.g. $<60\%$ primidone breakthrough at 25,000 BV in drinking water compared to 80–100% in WWTP effluent. The strong water-dependent differences in OMP breakthrough behavior are likely a reason of the competitiveness of the BOM of the respective water. The concentrations of (potentially competing) BOM is greater in the WWTP effluent than in the drinking water (cf. DOC shown in Tab. 11), leading to increased adsorption competition in the former case as compared to in the latter case. To consider the different BOM concentrations of the drinking water and the WWTP effluent, a DOC-proportional graph is shown in

Fig. 29, middle-left. (Note that the x-axis shows the specific throughput of DOC — fed masses of DOC per mass of GAC, and not adsorbed masses.) Using this kind of presentation, the different organic compositions of the waters can be accounted for. At the same volumetric throughput, less than half the mass of BOM/ DOC is fed to the GAC filter treating drinking water as opposed to the GAC filter treating WWTP effluent. E.g., at a throughput of 1000 BV, the specific throughputs of DOC per GAC are: $4.9 \text{ mg DOC/L} * 0.77 \text{ L} / 0.25 \text{ mg GAC} = 15.1 \text{ mg DOC/mg GAC}$ (drinking water) and $10.7 \text{ mg DOC/L} * 0.77 \text{ L} / 0.25 \text{ mg GAC} = 32.96 \text{ mg DOC/mg GAC}$ (WWTP effluent). Accordingly, the specific throughput of BOM/ DOC mass per GAC mass incorporates the different BOM/ DOC concentrations.

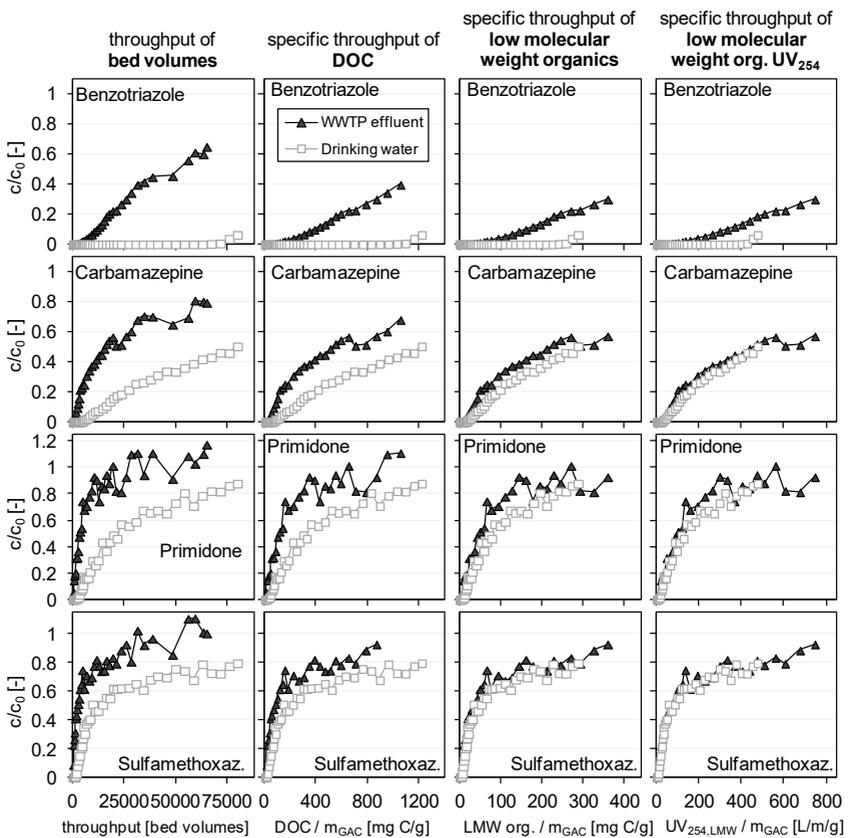


Fig. 29. Relative effluent concentrations of benzotriazole, carbamazepine, primidone and sulfamethoxazole in drinking water and WWTP effluent depicted against: *left* — throughput in bed volumes, *middle-left* — specific throughput as mass of DOC per mass of GAC, *middle-right* — specific throughput as mass of low molecular weight (LMW) organic carbon per mass of GAC, and *right* — specific throughput of LMW organic UV₂₅₄ per mass of GAC.

Compared to the presentation using bed volumes of throughput in Fig. 29, left, the respective OMP breakthrough curves in both of the waters appear closer to one another in Fig. 29, middle-left. At ~ 400 mg DOC fed per g of GAC, $\sim 60\%$ primidone breakthrough can be observed in the drinking water and $\sim 90\%$ in the WWTP effluent. Thus, considering the amount of BOM fed to a GAC filter increases the comparability between filter runs in different waters as opposed to only considering the throughput of influent water volumes. This appears logical, as waters with high BOM concentrations will cause a quicker exhaustion of the GAC capacity than waters with low BOM concentrations. However, the curves shown in Fig. 29, middle-left, are not superimposing each other. This indicates that the overall BOM/DOC concentration is not sufficient to explain the differences between OMP breakthrough behaviors in the different waters. Similarly, when using a breakthrough curve prediction calibrated with surface water data, the OMP retention in a GAC filter fed with WWTP effluent-impacted surface water was over predicted (Kennedy et al. 2015). The predictive relationship was based on DOC concentrations only and did not consider potentially variable composition of the BOM from different water sources.

Given the competitiveness of the LMW organics against OMP adsorption, an OMP breakthrough curve normalization using the influent concentrations of the LMW organics, as shown in Fig. 29, middle-right, appears reasonable. (Note that the x-axis shows the specific throughput of LMW organics — fed masses of LMW organics per mass of GAC, and not adsorbed masses.) For carbamazepine, primidone, and sulfamethoxazole, the depiction of the relative effluent concentrations over the fed masses of LMW organics per mass of GAC results in very similar breakthrough curves in the two tested waters. At ~ 100 mg LMW organics fed per g of GAC, the breakthrough of carbamazepine is $\sim 25\%$ in the drinking water and $\sim 30\%$ in the WWTP effluent, and $\sim 70\%$ and $\sim 80\%$ for primidone, and $\sim 65\%$ for sulfamethoxazole, respectively. These results underline the impact of the LMW organics on the adsorption of OMP. A further alignment of the OMP breakthrough curves in the tested WWTP effluent and drinking water is given in Fig. 29, right. Here, the x-axis shows the specific throughput of the LMW organic UV_{254} of the respective water. UV_{254} reflects the aromaticity of organic compounds (Weishaar et al. 2003); as the internal surface characteristic of activated carbons is aromatic, interactions with aromatic compounds are favored (Zietzschmann et al. 2015b). Accordingly, higher UV_{254} goes along with higher aromaticity and adsorbability of the associated BOM compounds. Therefore, it is likely that the BOM competitiveness against OMP adsorption is related to the UV_{254} of the BOM. As shown in Fig. 29, right, incorporating the LMW organic UV_{254} of the respective influent water into the specific throughput further increases the similarity of the OMP breakthrough curves.

The relative OMP breakthrough is mostly independent of the respective OMP influent concentration (cf. Fig. 28) and thus, the major factor impacting the relative OMP breakthrough behavior in complex waters is the concentration (and UV_{254}) of the LMW organics. Accordingly, the breakthrough curves of these OMP in different waters, like drinking waters or WWTP effluents, can be aligned using the respective specific LMW organics throughput

(and UV_{254}). Also, if the OMP breakthrough curves are known in one water, the corresponding breakthrough curves in other waters can be estimated by using the specific LMW organics throughput (or LMW organic UV_{254}) on the x-axis. This observation improves the comparability of the performances of GAC filters treating waters from different origins and with different BOM/ DOC concentrations and compositions, as well as with different influent OMP concentrations. Also, this finding may be a step towards a reduced need for performing GAC pilot studies: The breakthrough curves of an OMP on identically scaled GAC filters treating different waters can be satisfactorily transferred to one another using the presented LMW-related plotting. In the case of benzotriazole, the normalization via the LMW organics does not result in similar breakthrough curves in drinking water and WWTP effluent (even if the curves approach each other). Apparently, the adsorption of this OMP is not only affected by LMW organics acting as competitors. The reason could be specific compounds of the BOM which compete for adsorption sites with benzotriazole but which are not comprised within the LMW organics as determined via LC-OCD. Also, benzotriazole may only be impacted by a sub-fraction of the LMW organics, possibly due to its relatively small molecular size (119 g/mol).

GAC capacity prediction

The GAC capacities for the weakly adsorbing OMP (i.e., OMP with full breakthroughs during the experimental runtimes) 4-formylaminoantipyrine, primidone, and sulfamethoxazole are depicted against the respective OMP influent concentrations in the tested waters in Fig. 30, left. The GAC capacity for the OMP increases with increasing influent OMP concentrations but the slopes of the increase depend on the respective water. In drinking water, the increase is more pronounced than in WWTP effluent, likely because of more intensely competing BOM in the WWTP effluent than in the drinking water. Thus, the GAC capacity for OMP increases stronger for a given increase of the influent OMP concentration in drinking water than in WWTP effluent. With these results, the GAC capacity for an OMP adsorbing from a specific water at a given concentration can be estimated if the capacity at a different concentration of that OMP is known in the respective water. (Note that no linear correlations are shown due to the low amount of data points for each water.) The GAC capacities for the OMP shown in Fig. 30, left, are plotted against the corresponding ratios of the influent OMP concentrations and the influent concentrations of the LMW organics in Fig. 30, right, together with the corresponding linear correlations. In each case, two correlations are shown: Grey lines and grey formulas include all data points, whereas black lines and black formulas do not include the highest data point which corresponds to the drinking water test with comparatively high OMP concentrations. Both, the grey and the black lines demonstrate that the GAC capacity for OMP rises proportionally with increasing ratios of the influent OMP to LMW organics concentrations. According to the correlations shown in Fig. 30, right, the ratios of the influent OMP and LMW organics concentrations can be used as the independent variables (on the x-axis) to predict the GAC capacities for the shown OMP, independent of the water. Therefore, the GAC capacities for these OMP can be estimated simply by knowing the respective influent OMP and LMW organics concentrations. The UV_{254} of

the LMW organics can also be included into the shown correlations but this does not increase the coefficients of determination noticeably (data not shown).

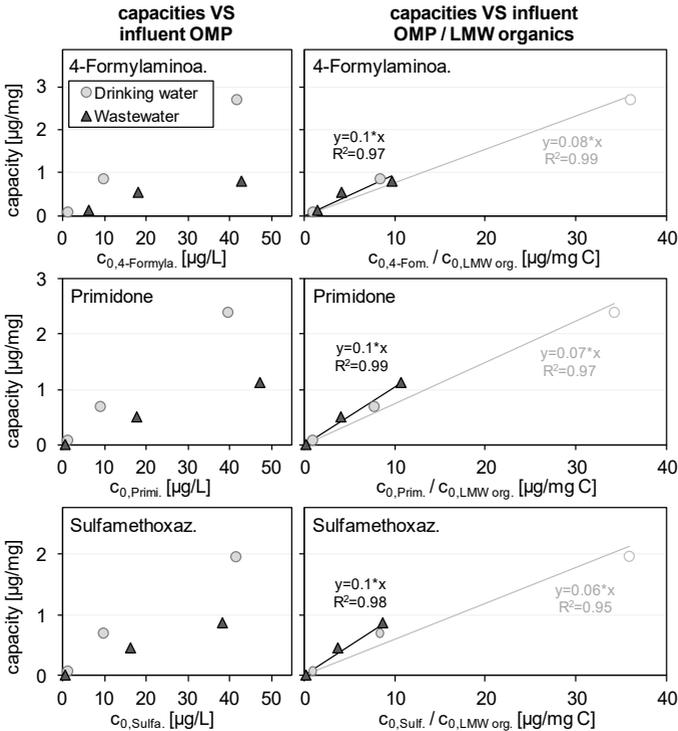


Fig. 30. *Left* – GAC capacities for 4-formylaminoantipyrine, primidone, and sulfamethoxazole against influent OMP concentrations, *right* – GAC capacities against ratio of OMP/LMW organics in influent concentrations, with linear correlations with/ without highest data point.

The highest data points (which are excluded in the correlations which are labeled black) correspond to the drinking water test with the highest influent OMP concentrations. In this test, slightly divergent breakthrough behavior was observed as compared to the drinking water tests with lower influent OMP concentrations (cf. Fig. 28, left). As discussed above, the GAC capacities increase proportionally with the influent OMP concentrations but threshold influent concentrations exist above which the proportionalities are no longer valid. As the respective highest data points of the correlations in Fig. 30, right, are above that threshold, decreased slopes of the grey lines as compared to the black lines are obtained. It is furthermore noticeable that the slopes of the correlations which are labeled black are similar for all of the three tested OMP. Accordingly, the GAC capacities of any of the OMP

can be estimated from the relationships of the other tested OMP. E.g., at an influent concentration ratio of 10 μg OMP/mg LMW organics, the GAC capacities are 1 μg /mg in all cases.

The results demonstrate that GAC capacities are predictable in different waters if the initial OMP and LMW organics concentrations of these waters are known. Furthermore, the breakthrough curves of a given OMP in different waters can be transferred by using the concentrations of the LMW organics of the respective waters, provided that the same filter design was used. We encourage additional experiments with other drinking waters and WWTP effluents as well as with other OMP and further GAC products. Also, filter dimensions other than the one tested in the current study should be examined for feasible relationships of the GAC capacities with the influent OMP and LMW organics concentrations, as well as for the breakthrough curve alignment using the LMW organics concentrations and UV_{254} . Precise monitoring of the LMW organics breakthrough would allow for the calculation of the corresponding GAC loadings. This would further elucidate the competitive mechanisms between OMP and BOM adsorbing from different waters onto GAC fixed-bed adsorbers.

CONCLUSIONS

- Organic micro-pollutant (OMP) breakthrough in small-scale granular activated carbon (GAC) filters treating drinking water and wastewater treatment plant (WWTP) effluent was investigated at variable influent OMP concentrations. Below certain thresholds, the influent OMP concentration does not impact the relative breakthrough curve appearance in the respective water.
- The similarity of the OMP breakthrough curves is directly linked to a proportionality between the GAC capacity and the influent OMP concentration in the respective water (drinking water or WWTP effluent). At increased OMP concentrations, the OMP competitiveness against BOM adsorption appears higher.
- The GAC breakthrough behavior of OMP in complex waters is mainly impacted by the concentration of low molecular weight acid and neutral (LMW) organics. Using the specific throughput of the LMW organics on the x-axis of the breakthrough curves, a superimposition of curves obtained in drinking water and WWTP effluent is reached. An integration of the LMW organic UV_{254} can further increase the superimposition of the breakthrough curves.
- The GAC capacities for OMP are linearly proportional to the ratio of the influent OMP/LMW organics concentrations, independent of the water. Accordingly, knowing the OMP and LMW concentrations in different waters, GAC capacities can be empirically transferred between the waters. Also, the slopes of the correlations for different OMP (all weakly adsorbing) are very similar, allowing for transferability between these OMP, too.
- The transferability of capacities and breakthrough curves in different waters such as drinking waters and WWTP effluents may reduce the need for laborious and expensive lab-/ pilot-/ full-scale studies.

ACKNOWLEDGMENTS

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REFERENCES

The cited references are contained in the general bibliography in Appendix A, p. 125.

4 Additional experimental methods

This chapter gathers experimental data on further methods for activated carbon testing. The first part (4.1, p. 89–100) examines the usefulness of commonly used activated carbon characteristics, such as the B.E.T. surface, for the prediction of activated carbon performance in organic micro-pollutant (OMP) adsorption. Also, the applicability of the widely used water quality parameter UV absorption at 254 nm for the assessment of activated carbon performance in adsorptive OMP removal is tested. The second part of chapter 4 (4.2, p. 101–115) shows the development of a new method for testing powdered activated carbon (PAC) reuse on the laboratory scale. The benefits from PAC reuse and potential advancements of the developed lab method are discussed. Furthermore, this work investigates the relationship between OMP solid phase loadings and liquid phase concentrations in multi-stage reuse setups, as well as predicting the related OMP removals using UV_{254} . Also, an extension of the equivalent background compound model (EBCM) for multi-stage PAC reuse modeling is presented. The developed laboratory test was further explored for investigating the effects of continuously increasing the PAC concentrations in each consecutive stage in another study which is not included here (Meinel et al. 2015).

4.1 UV absorption for activated carbon evaluation

Estimating organic micro-pollutant removal potential of activated carbons using UV absorption and carbon characteristics

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GRAPHICAL ABSTRACT



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ABSTRACT

Eight commercially available powdered activated carbons (PAC) were examined regarding organic micro-pollutant (OMP) removal efficiencies in wastewater treatment plant (WWTP) effluent. PAC characteristic numbers such as B.E.T. surface, iodine number and nitrobenzene number were checked for their potential to predict the OMP removal of the PAC products. Furthermore, the PAC-induced removal of UV_{254 nm} absorption (UVA₂₅₄) in WWTP effluent was determined and also correlated with OMP removal. None of the PAC characteristic numbers can satisfactorily describe OMP removal and accordingly, these characteristics have little informative value on the reduction of OMP concentrations in WWTP effluent. In contrast, UVA₂₅₄ removal and OMP removal correlate well for carbamazepine, diclofenac, and several iodinated x-ray contrast media. Also, UVA₂₅₄ removal can roughly describe the average OMP removal of all measured OMP, and can accordingly predict PAC performance in OMP removal. We therefore suggest UVA₂₅₄ as a handy indicator for the approximation of OMP removal in practical applications where direct OMP concentration quantification is not always available. In continuous operation of large-scale plants, this approach allows for the efficient adjustment of PAC dosing to UVA₂₅₄, in order to ensure reliable OMP removal whilst minimizing PAC consumption.

INTRODUCTION

Anthropogenic organic micro-pollutants (OMP) can pass existing conventional barriers in wastewater treatment plants (Putschew et al. 2000, Reemtsma et al. 2006) and therefore may reach surface waters often used as bathing waters and/ or drinking water sources (Bergmann et al. 2008). Concern has risen whether the concentrations of some OMP could jeopardize our drinking water quality. Climate change is predicted to lead to declining precipitation and reduced river runoff in many areas (Trenberth et al. 2007) and decreasing dilution of OMP in water cycles. The consumption of OMP such as pharmaceuticals will rise in the future due to demographic aging (Dieter et al. 2010).

In order to control the levels of OMP in surface waters that are under the influence of wastewater discharge, additional treatment steps in wastewater treatment plants (WWTPs) will be necessary in the future (Jekel et al. 2013, Snyder et al. 2003). These advanced purification stages can encompass oxidizing techniques or activated carbon adsorption. Oxidation processes may also produce unknown and potentially harmful by-products, because target compounds may only be altered but not removed out of the water (Huber et al. 2003, Wert et al. 2007). Adsorption can offer a higher level of safety in this respect (Liu et al. 2009). Activated carbon adsorption can generally be applied successfully if the target OMP contain aromatic groups and are medium polar to nonpolar. Depending on the source material of the activated carbon and its processing during the activation steps, adsorption characteristics can be altered to some extent and the range of adsorbable substances may be widened (Crittenden et al. 2012, Sontheimer et al. 1988). Different powdered activated carbon (PAC) characteristics influence the efficiency of target compound removal: The surface chemistry,

pore size distribution and internal surface, among others (Worch 2012). However, the determination of these characteristics can be laborious and costly. Also, PAC characteristics may not suffice to predict OMP removal from WWTP effluent (Quinlivan et al. 2005).

In the current study, eight commercially available PAC products are tested regarding their potential to reduce the concentrations of the fairly common OMP benzotriazole (deicing and anti-corrosion agent), carbamazepine (anticonvulsant), diclofenac (anti-inflammatory, analgesic), iomeprol, iopamidol, iopromide (radiocontrast agents), and sulfamethoxazole (antibiotic) from WWTP effluent. Subsequently, we investigated if the determined OMP removal rates correlate with conventional PAC characteristic numbers and/ or with UV_{254 nm} absorption (UVA₂₅₄) removal. To our knowledge, a correlation between the PAC-induced removals of UVA₂₅₄ and OMP has not been considered in the scientific literature yet. In studies focusing on ozonation, correlations were found between the removals of UVA₂₅₄ and specific OMP (Bahr et al. 2007). In order to periodically select the best available PAC and to control the quality of different PAC shipments, simple and quick but reliable testing methods or indicators are necessary. Furthermore, adjustment of PAC dosing to parameters that are online-measurable (such as UVA₂₅₄) would optimize PAC usage which, at a constant dose of 20 mg/L, would be as high as 770 Mg/a for the WWTP considered in this study (Schönerlinde, Germany, capacity of 105,000 m³/d).

MATERIALS AND METHODS

Activated carbons

PAC samples were obtained from the respective manufacturers. The selection of the PAC was made according to manufacturer suggestions for WWTP effluent treatment, choices from other studies (see below) and to obtain PAC from different source materials. Tab. 12 shows an overview of the manufacturers, products and the product properties as specified by the manufacturers. The PAC *Norit SAE Super* (Boehler et al. 2012, Margot et al. 2013, Nowotny et al. 2007), *CSC PHC HKP 1050* (Boehler et al. 2012), and *Carbopal MB4* (Haberkamp et al. 2007) have been tested in published studies.

Tab. 12. Activated carbon manufacturers, products, and product properties as given by manufacturers (n/a – not available).

Manufacturer Product	CSC (PHC) HK 950	CSC (PHC) HKP 1050	CSC (PHC) AZ 1050	Norit SAE Super	Jacobi 5000 P	Carbopal AP	Carbopal CCP 90D	Carbopal MB4
Source material	Wood charcoal	Wood charcoal	Hard coal	Mixture	Brown coal	Brown coal	Coconut husk	Wood charcoal
Humidity [% weight]	<10	<10	<5	<6	<5	<5	<8	<10
Ash [% weight]	<8	<10	<10	n/a	<18	n/a	<5	<9

Water samples

Treated domestic wastewater was sampled from the effluent of the WWTP Schönerlinde, Brandenburg, Germany. The characteristics of the WWTP effluent sample are shown in Tab. 13. Ultra pure water was supplied by an *ELGA Maxima Ultra Pure Water* system (*ELGA Berkefeld LabWater*, resistivity >17 MΩ*cm).

Tab. 13. Characteristics of the WWTP Schönerlinde effluent sample.

DOC	UVA ₂₅₄	Benzotriazole	Carbamazepine	Diclofenac	Iomeprol	Iopamidol	Iopromide	Sulfamethoxazole
[mg/L]	[1/m]	[µg/L]	[µg/L]	[µg/L]	[µg/L]	[µg/L]	[µg/L]	[µg/L]
12.0	28.1	34	2.5	6.1	3.4	2.6	1.1	0.4

Nitrobenzene number

The nitrobenzene numbers of the PAC products tested in this study were determined according to the DVGW W 239 (A) technical regulation of the DVGW German Technical and Scientific Association for Gas and Water (DVGW 2011). The nitrobenzene number is the theoretical powdered activated carbon dose that is necessary to remove 90% of the nitrobenzene contained in a 2 mg/L solution in ultra pure water. Freundlich isotherms for nitrobenzene and the respective PAC product are determined and the nitrobenzene number is obtained by back calculation using the Freundlich isotherm fitting.

Activated carbon experiments with WWTP effluent

Stock suspensions of the tested powdered activated carbon (PAC) products were prepared at 2 g/L in ultra pure water, and stored overnight for full wetting of the PAC. To obtain the desired PAC doses (5, 10, 20, 30, 50, 100 mg/L), varying volumes of the PAC stock suspensions (homogenized by stirring) were pipetted to 100 mL of the Schönerlinde WWTP effluent contained in 300 mL flasks; the resulting maximum dilution of the WWTP effluent was 5%. Upon dosage, the flasks were closed and put on a horizontal lab shaker allowing for continuous and full mixture of the WWTP effluent/ PAC suspensions for 48 h, whereupon PAC was removed using 0.45 µm membrane filters (regenerated cellulose, *Macherey-Nagel*, Germany, rinsed with ultra pure water).

Quantification of organic micro-pollutants

Organic micro-pollutants (OMP) were quantified by high performance liquid chromatography tandem mass spectrometry (HPLC-MS/MS). HPLC-MS/MS measurement of carbamazepine, diclofenac, and sulfamethoxazole was done with online solid-phase extraction (1 mL sample volume, *Hypersil Gold aQ* column, 12 µm particle size, 20*2.1 mm) preceding HPLC with a *Hypersil Gold* HPLC column (particle size 0.19 µm, 50*2.1 mm, *Thermo Scientific*), using ultra pure water with 0.5% formic acid (p.a., *Sigma Aldrich*) and methanol

(HPLC gradient grade, *J.T. Baker*) as mobile phases in a linear gradient running at 250 mL/min, and a *TSQ Vantage (Thermo Scientific)* using positive electro-spray ionization. Mass fragments were chosen according to the DAIOS MS/MS database (Wasserchemische Gesellschaft 2013). Deuterized internal standards (*Toronto Research Chemicals*, Canada) were used for quantification. Data were evaluated using *Xcalibur 2.1 (Thermo Scientific)*. Benzotriazole, iomeprol, iopamidol, and iopromide were quantified by the Berliner Wasserbetriebe using a *Waters Xevo TQS*, with a *Waters Acquity UPLC HSS T3* column (particle size 1.8 μm , 100*2.1 mm), running a linear gradient with water (0.1% formic acid) and methanol.

UV absorption at 254 nm

UV absorption was measured at 254 nm wavelength with a *Smartline UV Detector 200 (Knauer, Germany)*.

Correlation

In order to obtain comparable data points for the tested carbons, theoretical PAC doses for 80% OMP removal were determined. This was accomplished by linear interpolation using the two data points which were closest to the theoretical value of 80% OMP removal. Similarly, PAC doses for the removal of 50% of the WWTP effluent UV_{254 nm} absorption (UVA₂₅₄) were identified. The doses for 80% OMP removal were then correlated with PAC characteristic numbers such as B.E.T. surface and nitrobenzene number as well as with the doses for 50% UVA₂₅₄ removal.

RESULTS AND DISCUSSION

Estimation of OMP removal using PAC characteristics

The B.E.T. surfaces and iodine numbers as given by the manufacturers as well as the nitrobenzene numbers that were determined in this study are listed in Tab. 14 for the tested PAC products. Also, the percentages of these characteristic numbers in relation to the PAC product with the highest capacity for the respective adsorbate are given. Note that the B.E.T. surface and the iodine number both are positively proportional to the adsorption capacity of a PAC for nitrogen/ iodine, respectively (high values of these characteristic numbers indicate high capacities). In contrast, the nitrobenzene number is negatively proportional to the adsorption capacity of a PAC for nitrobenzene (high values indicate low capacities). For calculations, the lowest indicated values of the manufacturers' data were used (except for the B.E.T. surface of CCP 90D, where 1050 was taken).

Tab. 14. Carbon characteristics of tested PAC products (*manufacturer data, †this study)

Product		HK 950	HKP 1050	AZ 1050	SAE Super	5000 P	AP	CCP 90 D	MB 4
B.E.T. surface*	[m ² /g]	>950	>1050	>1050	1150	1150	1300	1000–1100	900
% of max. B.E.T. surface		73	81	81	89	89	100	77–85	69
Iodine number*	[mg/g]	>950	>1050	>1050	1050	>1100	1250	>1000	~900
% of max. iodine number		76	84	84	84	88	100	80	72
Nitrobenzene number†	[mg/L]	203.4	92.9	20.7	21.9	21.4	21.0	14.1	18.8
% of min. nitrobenzene num.		1443	659	147	155	152	149	100	133

Tab. 14 shows that the differences of both, the B.E.T. surfaces and the iodine numbers, between all tested PAC products are maximum 31%/ 28%, respectively: E.g., the B.E.T. surface of PAC “MB 4” (min.) is 69% of that of PAC “AP” (max.). On the other hand, the nitrobenzene numbers of the tested PAC products diverge more distinctively: The nitrobenzene number of PAC “HK 950” is 1443% of that of PAC “CCP 90 D”. However, the nitrobenzene numbers of six of the PAC are in a similar range (14–22 mg/L).

The relationships between the iodine number (a)/ nitrobenzene number (b) and the B.E.T. surface of the tested PAC products are shown in Fig. 31. The iodine number and the B.E.T. surface correlate linearly and are also in a similar absolute range (for example, a B.E.T. surface ~1000 m²/g is equivalent to an iodine number ~1000 mg/g). Thus, there is no additional information contained in either of these two characteristic numbers if the other one is known and the conversion factor between these characteristics is ~1, which confirms information from the literature (Worch 2012). In contrast, the nitrobenzene number cannot be represented by the B.E.T. surface since there is no correlation between these two PAC characteristic numbers (Fig. 31 b). Accordingly, the capacity for nitrobenzene by the tested PAC products cannot be inferred by their individual B.E.T. surfaces.

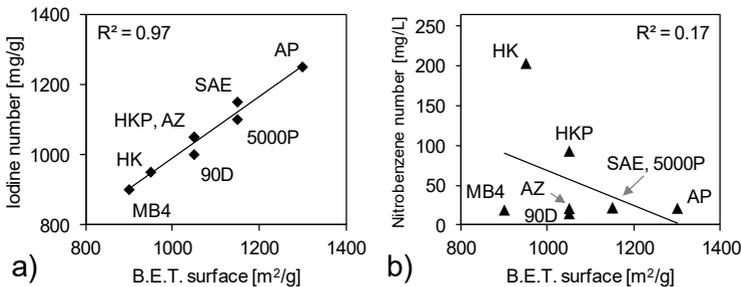


Fig. 31. Iodine numbers VS B.E.T. surfaces (a) and nitrobenzene numbers VS B.E.T. surfaces (b) of the tested PAC products, with the coefficients of determination of the linear correlations, and PAC designators.

The PAC doses required to remove 80% of the OMP iopamidol, benzotriazole, sulfamethoxazole, and diclofenac are plotted against the B.E.T. surfaces of the PAC products tested (one data point per OMP and PAC product) in Fig. 32, with the corresponding coefficients of determination (R^2) of the linear correlations. The B.E.T. surface of the tested PAC does not correlate with the PAC dose for 80% OMP removal of any OMP. A PAC product with a high B.E.T. surface compared to the B.E.T. surfaces of other PAC products does not necessarily have higher adsorption capacities for OMP contained in WWTP effluent. For the OMP carbamazepine, iomeprol, iopromide, no correlations were found either (data not shown).

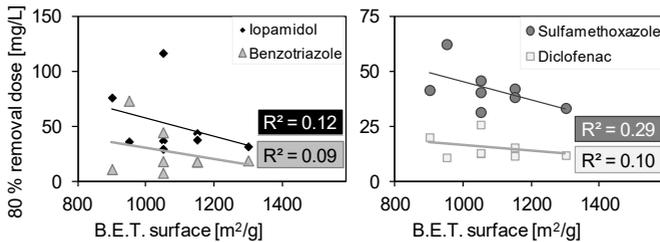


Fig. 32. PAC doses for 80% OMP removal VS B.E.T. surfaces of the PAC products tested, with linear correlations (max. data point of 80% removal dose for iopamidol by extrapolation since highest applied PAC dose was 100 mg/L).

The PAC doses required to achieve an OMP removal of 80% are plotted against the nitrobenzene numbers of the corresponding PAC products in Fig. 33. Fig. 33 a) shows the correlations that result if all eight tested PAC products are included. The nitrobenzene numbers of the PAC products “CSC HK” and “CSC HKP” are comparatively high and thus, they have a strong influence on the coefficients of determination (R^2) of the correlations. Therefore, Fig. 33 b) is also presented which gives the correlations that result if “CSC HK” and “CSC HKP” are excluded from the linear regression (NIST/SEMATECH 2012).

For diclofenac and iopamidol, the R^2 are poor for the fittings resulting if all PAC products are included in the linear regression (Fig. 33 a). Therefore, the nitrobenzene number cannot predict the efficiency of the tested PACs in the removal of these two OMP. Within the subset of six data points (Fig. 33 b), the R^2 for these two OMP are above 0.8 and the slopes of the linear regressions are negative. Accordingly, the subset of data leads to the interpretation that lower nitrobenzene numbers (high efficiency in nitrobenzene removal) indicate poor efficiency in diclofenac and iopamidol removal.

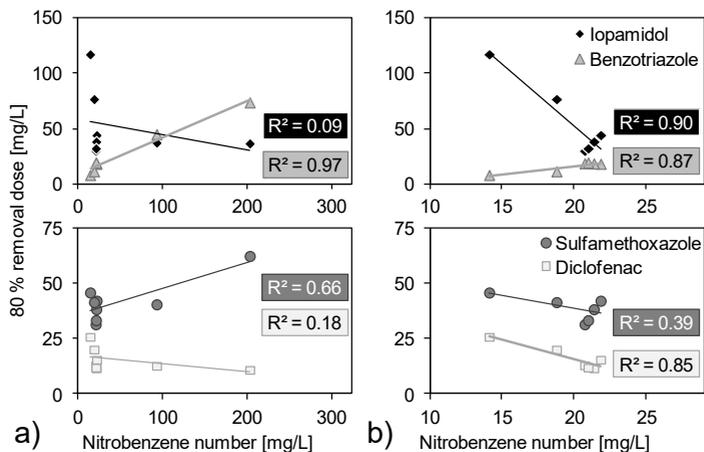


Fig. 33. PAC doses for 80% OMP removal VS nitrobenzene numbers of the PAC products tested, with linear correlations for 8 PACs (a, left) and a subset of 6 PACs (b, right) (max. data point of 80% removal dose for iopamidol by extrapolation since highest applied PAC dose was 100 mg/L).

For sulfamethoxazole, the full data set indicates a trend-wise positive correlation of the nitrobenzene number and the dose for 80% OMP removal (Fig. 33 a). However, Fig. 33 b shows that the exclusion of the two PAC products with very high nitrobenzene numbers leads to a poor R^2 and a negative slope. The correlation found in Fig. 33 a is based on only two data points and therefore is not reliable. Hence, the nitrobenzene number cannot reliably predict the efficiency of the tested PAC products in reducing the sulfamethoxazole concentration in WWTP effluent.

Other than for diclofenac, iopamidol, and sulfamethoxazole, both the full data set of eight PAC products (Fig. 33 a) and the subset of six PAC products (Fig. 33 b) yield positive linear correlations with high R^2 for benzotriazole. These findings show that the nitrobenzene number can indicate the efficiency in benzotriazole removal in WWTP effluent when using the tested PAC products. In the cases of carbamazepine, iomeprol, and iopromide, no correlations were found (data not shown).

The molecular weights of sulfamethoxazole (253.3 g/mol), diclofenac (296.2 g/mol), and iopamidol (777.1 g/mol) exceed the molecular weight of nitrobenzene (123.1 g/mol) by at least 100%, while benzotriazole (119.1 g/mol, ~97%) and nitrobenzene weigh about the same. These two substances are also structurally similar, due to their benzene-based molecules. We suggest that the similarity of benzotriazole and nitrobenzene regarding their size and structure is the reason for the above discussed correlation between the dose for 80% benzotriazole removal in WWTP effluent and the nitrobenzene number. Therefore, we suppose that the usefulness of the nitrobenzene number in predicting PAC efficiency under

practical conditions, such as OMP removal in WWTP effluent, may be restricted to OMP that are structurally similar to nitrobenzene; this assumption should be further tested.

Estimation of OMP removal using $UV_{254\text{ nm}}$ absorption removal

Fig. 34 depicts the removals of the OMP iopamidol, diclofenac, sulfamethoxazole, and benzotriazole plotted against the respective $UV_{254\text{ nm}}$ absorption (UVA_{254}) removals that were measured at different doses of the tested PAC products. For iopamidol (Fig. 34 a) and diclofenac (Fig. 34 b), the data points of all PAC products follow a similar S-shaped curve and scatter only little, indicating that UVA_{254} removal can be used to predict the concentration removal of these OMP, independent of the PAC product, and thus, also independent of the PAC raw material. For example, 20% UVA_{254} removal indicate about 20% iopamidol removal and about 70% diclofenac removal. These relationships can be useful for the assessment of the iopamidol and diclofenac removal potential of unknown PAC products simply by determining the UVA_{254} removal obtained with these unknown products.

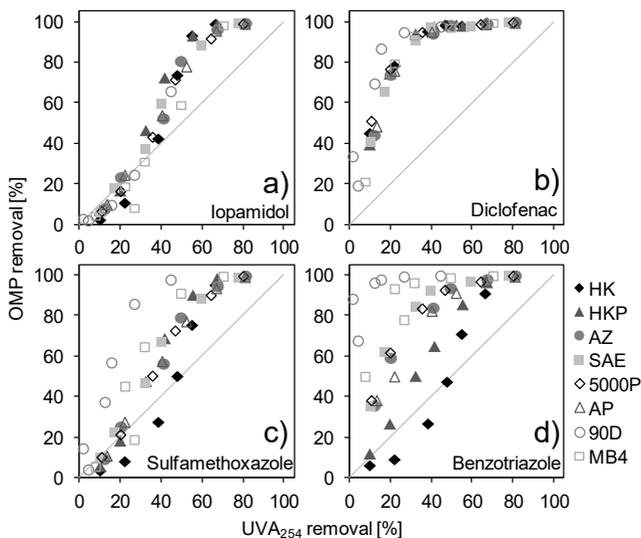


Fig. 34. OMP removals VS UVA_{254} removals at varying doses of different PAC products, and bisectrices indicating equal OMP and UVA_{254} removals; a) iopamidol, b) diclofenac, c) sulfamethoxazole, d) benzotriazole.

Furthermore, UVA_{254} removal can be applied in practical applications to indirectly estimate OMP removals. This is helpful where OMP measurements are not available and/ or where UVA_{254} is measured online. The data for carbamazepine, iomeprol and iopromide are not shown, since the graph for carbamazepine is fairly similar to that of diclofenac and for

iomeprol/ iopromide, the graphs are similar to that of iopamidol. It is notable however, that the competition for PAC adsorption sites between OMP and UVA₂₅₄ (the latter reflecting the bulk organics of the WWTP effluent) is presumably strongly depending on the WWTP effluent itself. Therefore, we encourage additional tests with other WWTP effluents in order to obtain a broader view on the relationships found in this study.

In contrast, Fig. 34 c and Fig. 34 d show that in the cases of sulfamethoxazole and especially of benzotriazole, there is no overall correlation between UVA₂₅₄ removal and the OMP removal. At 20% UVA₂₅₄ removal, the PAC product “HK” yields a sulfamethoxazole removal of about 10% whereas the PAC product “90 D” yields about 70% removal. This discrepancy is even more pronounced in the case of benzotriazole: The PAC product “HK” yields <10% removal of this OMP at 20% UVA₂₅₄ removal while the product “90 D” yields >90%. However, each PAC product has an individual curve indicating that sulfamethoxazole/ benzotriazole removal can still be inferred from UVA₂₅₄ removal if the individual PAC correlation is known. Thus, the relation of UVA₂₅₄ and sulfamethoxazole/ benzotriazole removal for a PAC product or PAC charge only needs to be established once and UVA₂₅₄ can serve as a sulfamethoxazole/ benzotriazole removal indicator thereafter. Furthermore, the diagrams in Fig. 34 c and Fig. 34 d can be used to obtain thresholds of UVA₂₅₄ removal. Above these thresholds of UVA₂₅₄ removal, specific OMP removal rates can be expected which may be useful for practical application. (For example, a 50% removal of UVA₂₅₄ indicates that the benzotriazole removal is $\geq 50\%$, independent of the PAC product applied.)

Fig. 34 also shows bisectrices (depicted as grey lines) that separate the regions where the PACs have higher affinity towards the OMP than to UVA₂₅₄ (area above bisectrices) and where the affinity towards UVA₂₅₄ is higher (area below bisectrices). The graphs in Fig. 34 are not located on the bisectrices but are mostly S-shaped, showing that most of the OMP adsorb better than UVA₂₅₄ is reduced in the range of high removals (upper-right corners of the graphs) while in the low removal ranges UVA₂₅₄ may show higher adsorption than the OMP elimination by adsorption. This underlines the heterogeneous adsorbability of compounds gathered within the bulk parameter of UVA₂₅₄. Accordingly, graphs like those in Fig. 34 can be used to assess the selectivity of an activated carbon towards a specific OMP compared to the bulk compounds contained in UVA₂₅₄. Note that the graphics are hardly useful to compare the efficiency of different PAC products. This is because the diagrams do not designate equal PAC doses of different PAC products; the same PAC dose of different PAC products can lead to different positions in the diagrams.

The average PAC doses required for 80% OMP removal are plotted against the PAC doses for 50% UVA₂₅₄ removal in Fig. 35. The average PAC dose for 80% OMP removal was calculated for each PAC: For all seven OMP included in the study, an individual 80% removal dose was determined; these individual doses were summed up, the sum was divided by the number of OMP (7). Accordingly, the resulting value weighs all OMP equally, independent of the respective initial concentration. Note that the calculated value is an average and thus reflects a PAC dose that would yield reduction of some OMP to >80% and of other OMP to <80%. There is a linear correlation between the average PAC doses for OMP removal and

UVA₂₅₄ removal. (If the data point with the highest values, 90 D, is excluded from the correlation, R^2 is reduced to 0.76.) Accordingly, the PAC dose for 50% UVA₂₅₄ removal in WWTP effluent can be applied to estimate the average relative OMP removal. Even if it was shown above that individual OMP removal may not be inferred from UVA₂₅₄ for some OMP, the removal of the majority of OMP measured in this study can be deduced from UVA₂₅₄. The efficiency of a PAC in removing OMP from WWTP effluent is thus swiftly inferable from the efficiency of the PAC in removing UVA₂₅₄. For quick and easy comparison of products or commercial charges, and to estimate overall OMP removal potential of a PAC, UVA₂₅₄ removal can serve as a very handy tool reducing the frequency of direct OMP measurements e.g. via HPLC-MS/MS. Also, UVA₂₅₄ can serve as an online tool for indirectly controlling OMP removal. Accordingly, PAC dosing can be adjusted to UVA₂₅₄ measurements, in order to reduce PAC consumption. The relationships found should be additionally tested with other WWTP effluents. This is relevant since the competition for adsorption sites between OMP and bulk organics depends on the composition and adsorbability of the bulk organics which can vary between different waters (Müller et al. 1996). Also, the relevance of these findings with respect to treatment schemes including PAC/ sludge return should be further checked. Presumably, additional counter current PAC usage may reduce adsorption competition for medium/ weak adsorbates and the relations between UVA₂₅₄ and OMP removals found in this work should be additionally verified in this constellation.

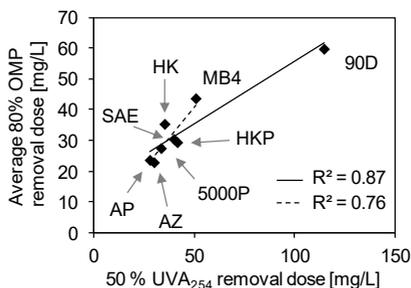


Fig. 35. Average PAC doses for 80% OMP removal VS doses for 50% UVA₂₅₄ removal, linear correlations (all PAC products/ without 90 D), and PAC designators (50% UVA₂₅₄ removal dose for PAC “90 D” from extrapolation since highest applied PAC dose was 100 mg/L).

CONCLUSIONS

The aim of this study was to assess whether organic micropollutant (OMP) removal in wastewater treatment plant (WWTP) effluents by powdered activated carbon (PAC) is inferable using other parameters, such as PAC characteristic numbers (like the B.E.T. surface or the nitrobenzene number), or WWTP effluent UV_{254 nm} absorption (UVA₂₅₄) removal. Eight PAC products were included in the survey and the examined OMP were benzotriazole, carbamazepine, diclofenac, iomeprol, iopamidol, iopromide, and sulfamethoxazole. The B.E.T.

surface and the iodine number are interchangeable and both cannot predict WWTP effluent OMP removal. The nitrobenzene number could only predict the removal of benzotriazole which is structurally similar to nitrobenzene. Therefore, we conclude that PAC characteristic numbers are generally poor indicators for OMP concentration removal in WWTP effluent. In contrast, UVA_{254} removal could be applied to predict the removal of OMP. For most OMP (carbamazepine, diclofenac, iomeprol, iopamidol, iopromide), we found overall correlations, mostly independent of the PAC product, while for benzotriazole and sulfamethoxazole, each PAC product had an individual relation between UVA_{254} and OMP removal. The average carbon doses that were necessary to remove all measured OMP by 80% correlates with the carbon doses needed to reduce UVA_{254} by 50%: High UVA_{254} removal efficiency of a PAC product implies high average OMP removal efficiency. Accordingly, UVA_{254} removal can be used as a simple tool to predict the average removal of OMP. Furthermore, UVA_{254} removal can be used to identify PAC products which perform poorly in removing OMP from WWTP effluent. For the operation of large-scale plants, the PAC dosing could be adjusted to online UVA_{254} measurements. The relationship of UVA_{254} removal and OMP removal should be verified for additional OMP other than those in the current study, as well as for other WWTP effluents and treatment schemes including PAC recycling/ counter current usage of PAC.

ACKNOWLEDGMENTS

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SUPPORTING INFORMATION

Supplementary data related to this article can be found in the Supporting Information shown in Appendix B-6, p. 157.

REFERENCES

The cited references are contained in the general bibliography in Appendix A, p. 125.

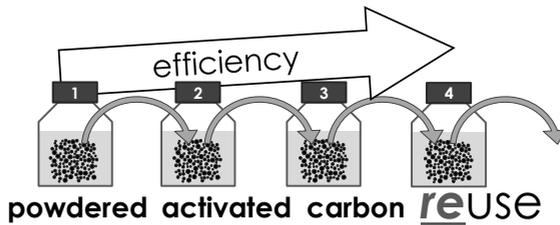
4.2 Multi-stage powdered activated carbon adsorption

Lab-testing, predicting, and modeling multi-stage activated carbon adsorption of organic micro-pollutants from treated wastewater

Water Research 83 (2015) 52–60

Frederik Zietzschmann¹, Johannes Altmann¹, Christin Hannemann¹ and Martin Jekel¹

GRAPHICAL ABSTRACT



ABSTRACT

Multi-stage reuse of powdered activated carbon (PAC) is often applied in practice for a more efficient exploitation of the PAC capacity to remove organic micro-pollutants (OMP). However, the adsorption mechanisms in multi-stage PAC reuse are rarely investigated, as large-scale experiments do not allow for systematic tests. In this study, a laboratory method for the separation of PAC/ water suspensions and the subsequent reuse of the PAC and the water was developed. The method was tested on wastewater treatment plant (WWTP) effluent in a setup with up to 7 PAC reuse stages. The tests show that the overall OMP removal from WWTP effluent can be increased when reusing PAC. The reason is that a repeated adsorption in multi-stage PAC reuse results in similar equilibrium concentrations as a single-stage adsorption. Thus, a single relationship between solid and liquid phase OMP concentrations appears valid throughout all stages. This also means that the adsorption efficiency of multi-stage PAC reuse setups can be estimated from the data of a single-stage setup. Furthermore, the overall OMP removals in multi-stage setups coincide with the overall UV_{254} removals, and for each respective OMP one relationship to UV_{254} removal is valid throughout all stages. The results were modeled by a simple modification of the equivalent background compound model (EBCM) which was also used to simulate the additional OMP removals in multi-stage setups with up to 50 reuse stages.

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INTRODUCTION

To reduce the potential adverse effects of organic micropollutants (OMP) on the environment or human health, the removal of OMP from wastewater treatment plant (WWTP) effluents is nowadays considered by many water suppliers, by using advanced technologies such as powdered activated carbon (PAC) adsorption (Dieter and Mückter 2007, Jekel et al. 2013). When treating water with PAC, the contact time between the water and the PAC is usually not long enough to fully exploit the entire PAC capacity. For a better exploitation, used PAC can be separated from the treated water and be reused on untreated water. This PAC separation/ reuse technique within the WWTP effluent treatment process is integrated into many treatment plants (Boehler et al. 2012, Margot et al. 2013) and PAC reuse was shown to decrease the overall PAC consumption (Metzger 2010, Nicolet and Rott 1999).

However, besides many practical applications of PAC reuse, the theoretical knowledge on the beneficial effects of PAC reuse for higher PAC capacity exploitation is scarce. In order to investigate the occurring adsorption mechanisms during PAC reuse (e.g. calculation of PAC loadings, displaying loading curves/ isotherms), large- or full-scale experiments are not feasible. This is because they are laborious, time consuming, and it is difficult to precisely adjust PAC dosages, separation, and recycling; furthermore adsorptive and potential biological OMP removals may overlap and the water quality may change over time. Therefore, systematic lab-scale tests would help in investigating and understanding the mechanisms involved in PAC reuse. For instance, knowing the relationships between solid phase (PAC) and liquid phase (water) concentrations in additional adsorption stages would enable the prediction of multi-stage processes. It would also broaden the knowledge on the adsorption competition between OMP and effluent organic matter (EfOM) when reusing PAC.

However, the separation of the water/ PAC suspension and the subsequent PAC reuse are difficult to realize on the lab-scale. Membrane filtration for PAC/ water separation has been tried but it remains questionable and unclear whether the PAC could be fully removed from the membrane and be re-suspended to guarantee full mixture (Zhao et al. 2012). It was one of the objectives of the current study to establish an easy and reliable laboratory procedure for multi-stage reuse of PAC with separation and subsequent full re-suspension of the PAC. The test should then be used for multi-stage PAC reuse on WWTP effluent, in order to understand the occurring adsorption phenomena. Short and equilibrium contact times were applied, to know practical and maximally achievable OMP removals. Also, it should be investigated if the OMP removal in PAC reuse processes is predictable using the removal of the easily measurable surrogate parameter UV_{254} , a concept which was successfully applied in other studies (Altmann et al. 2014, Altmann et al. 2015, Zietzschmann et al. 2014a). Additionally, it was tested if the observed adsorption phenomena could be modeled, in order to estimate OMP removals in multi-stage PAC reuse as well as the occurring adsorption competition between OMP and effluent organic matter (EfOM).

MATERIALS AND METHODS

Water samples and pretreatments

Wastewater treatment plant (WWTP) effluent was obtained from WWTP Berlin Ruhleben which is equipped with conventional mechanical/ biological steps and has a dry weather capacity of $\sim 250,000 \text{ m}^3/\text{d}$. The WWTP effluent samples were pre-filtered with cellulose nitrate membrane filters (pore size $0.45 \mu\text{m}$, *Sartorius Stedim Biotech*, Germany), in order to increase the microbial stability of the samples. Pre-filtration with this pore size does not alter the impacts of the effluent organic matter (EfOM) on organic micropollutant (OMP) adsorption (Zietzschmann et al. 2014c). In order to obtain clearly measureable concentrations, OMP (*Sigma-Aldrich*, Germany) were spiked to $\sim 20 \mu\text{g/L}$ from stock solutions in ultra pure water (*ELGA Berkefeld*, *Veolia*, Germany).

Experimental setup

Powdered activated carbon (PAC, *SAE Super*, *Norit*, Germany) was dried at $105 \text{ }^\circ\text{C}$, cooled to room temperature in a desiccator, suspended at concentrations between 0.5 g/L and 4 g/L in ultra pure water and degassed using vacuum and an ultrasonic bath, and homogenized with a magnetic stirrer until dosing with lab pipettes (*Eppendorf*, Germany). The batch tests were conducted directly inside centrifuge flasks (175 mL , *Falcon*, USA) which were filled with 100 mL of the pre-treated WWTP effluent. Upon PAC addition, the flasks were put on a horizontal shaker for thorough mixing. After the respective contact time (0.5 or 24 h), the flasks were centrifuged at $\sim 3000 \text{ g}$ for 10 min (*Hettich Rotanda*, Germany). Then, $>95\%$ of the supernatant were removed using a modified bulb pipette with an electric pipetting aid (*Easy Pet*, *Eppendorf*, Germany). To the remaining PAC, fresh WWTP effluent was added and the adsorption procedure was repeated for additional adsorption stages. The removed supernatant itself could be reused by pouring it into a new centrifuge flask and adding fresh PAC. For analysis, supernatant samples were filtered with $0.45 \mu\text{m}$ regenerated cellulose membrane filters (*Chromafil Xtra*, *Macherey-Nagel*, Germany). The PAC reuse procedure was repeated up to 7 times for a contact time of 0.5 h and up to 3 times for a contact time of 24 h . An equilibrium contact time of 24 h as also applied in other studies was chosen to keep the experimental procedure manageable (Altmann et al. 2014, Nowotny et al. 2007). A scheme showing the PAC and water fluxes in an exemplary 3-stage PAC reuse setup compared to a typical single-stage setup is given in the Supporting Information (Appendix B-7, p. 158). The corresponding operating lines with respect to an isotherm that is valid for all adsorption stages are shown, too. The aspect of the validity of the isotherm is further considered in the results and discussion section.

Analytics

Organic micro-pollutants (OMP) were measured with high performance liquid chromatography with tandem mass spectrometry (HPLC-MS/MS). HPLC used an *XSelect HSS T3* column ($2.5 \mu\text{m}$ particle size, $50 \times 2.1 \text{ mm}$, *Waters*, USA) with a linear gradient from 98%

aqueous phase (ultra pure water with 5 vol.-% MeOH and 0.1 vol.-% HCOOH) to 100% organic phase (MeOH). MS/MS was conducted on a *Thermo Scientific TSQ Vantage* in ESI^{+/}- modes, using two fragments, chosen according to the *DAIOS* database (Wasserchemische Gesellschaft 2013), of each OMP for identification, and using the more intense fragment for quantification in combination with deuterated internal standards.

Dissolved organic carbon (DOC) was measured on a *varioTOC cube (elementar Analysensysteme, Germany)*, UV absorption at 254 nm (UV₂₅₄) was measured on a *Lambda 12 (Perkin-Elmer, USA)* using 1 cm quartz cuvettes (*Suprasil, Hellma, Germany*). Liquid chromatography with online UV₂₅₄ and organic carbon detectors (LC-OCD) was used for fractionated organic carbon measurement (Huber et al. 2011).

Modeling of multi-stage PAC reuse

Modeling was achieved using the Equivalent Background Compound (EBC) model (EBCM) (Crittenden et al. 1985a, Najm et al. 1991, Zietzschmann et al. 2014c) and mass balance equations for 1, 2, 3, n stage setups, under non-equilibrium (30 min) and equilibrium (24 h) conditions. The EBCM takes into account adsorption competition caused by background organic matter (e.g. effluent organic matter, EfOM, in the current case) by creating a fictive two-component adsorption system of which one is the OMP under consideration and the other is the EBC that accounts for all of the observed adsorption competition. Single-solute Freundlich parameters for the organic micro-pollutants (OMP) benzotriazole, diclofenac, and sulfamethoxazole were determined in ultra pure water salt solution (isotonic to the applied WWTP effluent) for 30 min and 24 h adsorption times. The mass balance equations for all PAC doses in any additional stages i (2, 3, n) were extended by the loadings of the corresponding PAC doses from the previous stages $i-1$. (This is because the PAC contains the loading of stage $i-1$ and is transferred to stage i .) Accordingly, the modeling must be carried out stage by stage since the equations for any stage are correct only if the equations of all previous stages are correct. (Note that due to the necessity of calculating stage after stage, a substantial amount of calculation time may be required.) The integration of the EBCM and the multi-stage mass balances is given in the equations Eq. 19 and Eq. 20. The only difference from the typical EBCM (e.g., Knappe et al. 1998, Najm et al. 1991) are the terms $d^*q_{i-1,OMP}$ and $d^*q_{i-1,EBC}$ which account for the PAC loadings with the OMP and the EBC, respectively, that are transferred from any previous stage $i-1$ to any stage i because of the reuse of the PAC. A numerical solver simultaneously minimizes Eq. 19 and Eq. 20 for the OMP and the EBC in stage i , by varying $q_{i,OMP}$ and $q_{i,EBC}$:

$$c_{o,OMP} + d q_{i-1,OMP} - d q_{i,OMP} - \frac{q_{i,OMP}}{q_{i,OMP} + q_{i,EBC}} \left(\frac{n_{OMP} q_{i,OMP} + n_{EBC} q_{i,EBC}}{n_{OMP} K_{F,OMP}} \right)^{n_{OMP}} = 0 \quad \text{Eq. 19}$$

$$c_{o,EBC} + d q_{i-1,EBC} - d q_{i,EBC} - \frac{q_{i,EBC}}{q_{i,OMP} + q_{i,EBC}} \left(\frac{n_{OMP} q_{i,OMP} + n_{EBC} q_{i,EBC}}{n_{EBC} K_{F,EBC}} \right)^{n_{EBC}} = 0 \quad \text{Eq. 20}$$

where indices *OMP* and *EBC* refer to the organic micro-pollutant and the equivalent background compound, respectively, c_o is the initial concentration, d is the PAC dose, q is the loading, $i-1$ indexes the previous stage, i indexes the current stage, $1/n$ are the single-solute Freundlich exponents, and K_F are the single-solute Freundlich coefficients. The single-solute Freundlich parameters of the EBC were set equal to those of the OMP in order to reduce the model complexity (Worch 2010) and because multi-stage EBC modeling requires it (see the Supporting Information for details, Appendix B-7, p. 158).

In order to evaluate the additional benefits from multi-stage setups compared to single-stage setups, the OMP removals from the multi-stage modeling were compared with the OMP removals from single-stage modeling with equivalent PAC doses. The latter aspect is important since a reuse of PAC increases the amount of water treated while keeping constant the amount of PAC used. E.g. a 1st stage PAC dose of 10 mg/L reduces to an effective 2nd stage PAC dose of 5 mg/L because the same PAC is used on twice the amount of water. This implies that the equivalent single-stage PAC dose to be compared with the respective multi-stage PAC dose must be divided by the number of PAC reuse stages under consideration. E.g. a PAC dose of 100 mg/L that is reused 10 times must be compared with a single-stage PAC dose of 10 mg/L.

In the Supporting Information (Appendix B-7, p. 158) we also present a method for multi-stage PAC reuse modeling based on pseudo single-solute Freundlich equations. This method is less realistic but more simple and produces similar results compared to the EBCM-based method presented above.

RESULTS AND DISCUSSION

Adsorption of dissolved organic carbon (DOC)

The liquid chromatography online carbon detection (LC-OCD) chromatograms of selected samples from 0.5 and 24 h multi-stage tests with different PAC reuse stages are shown in Fig. 36. The graphs show that with increasing PAC dose, all fractions of the DOC are better removed; e.g. in Fig. 36 c) and d) higher PAC doses go along with overall lower chromatogram intensities. However, the large fractions of the biopolymers can only be removed to some extent when the PAC doses are sufficiently high. Especially the low molecular weight fractions (acids and neutrals, retention times >48 min) are effectively removed. With each PAC reuse stage, the removal of all fractions decreases and this effect is stronger for lower PAC doses; e.g., after 0.5 h of adsorption per stage and 5 PAC reuse stages, 500 mg PAC/L can still remove DOC from nearly all fractions (Fig. 36 b) while 100 mg PAC/L can barely remove additional DOC from any fraction, even in the 3rd stage (Fig. 36 a). The better adsorbable low molecular weight fractions (acids and neutrals) can still be removed even at high stage numbers; e.g., Fig. 36 b) shows that in the 7th PAC reuse stage, the low molecular weight acids and neutrals can be removed by ~40% while the humics/ building blocks decrease by only ~20%. Accordingly, these low molecular weight fractions are highly

adsorbable and are likely to cause major competition against the adsorption of organic micro-pollutants (OMP) in all PAC reuse stages (Zietzschmann et al. 2014b, Zietzschmann et al. 2014c). Furthermore, a comparison of Fig. 36 d) with the other graphs shows that 24 h adsorption time can increase the adsorption of all LC-OCD fractions but the additional effect compared to the chromatograms of 0.5 h adsorption time is relatively small.

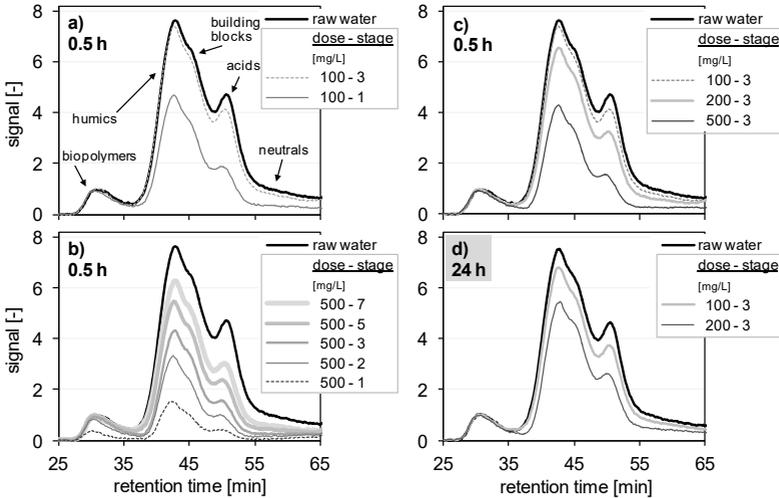


Fig. 36. LC-OCD chromatograms of selected samples from multi-stage tests with different numbers of PAC reuse stages; a)–c) 0.5 h, d) 24 h; with fraction designators (*top-left*); note that the symbol order in the legends corresponds to the chromatogram order in each graphic.

Effective removals of organic micro-pollutants

For means of comparability, effective removals and effective powdered activated carbon (PAC) doses for multi-stage setups were calculated as follows. Effective removals are the average removals from all stages in a multi-stage setup. E.g. if the 1st, 2nd, and 3rd stage removals are 75, 50, 25%, respectively, the effective 3-stage removal is 50%. Effective PAC doses are obtained via dividing the applied PAC mass by the total volume of the treated water in a multi-stage setup. E.g. if 30 mg PAC are used in a 3-stage setup on 1 L water in each stage (3*1 L), the effective PAC dose is 10 mg/L (30 mg/3 L). As resulting from the conducted lab-tests, the effective removals are depicted versus the corresponding effective PAC doses for 1, 3, 5, and 7-stage PAC reuse setups with 0.5 h contact time per stage (left), and 1, 2, and 3-stage setups with 24 h contact time (right), in Fig. 37, for benzotriazole, diclofenac, sulfamethoxazole, and the DOC.

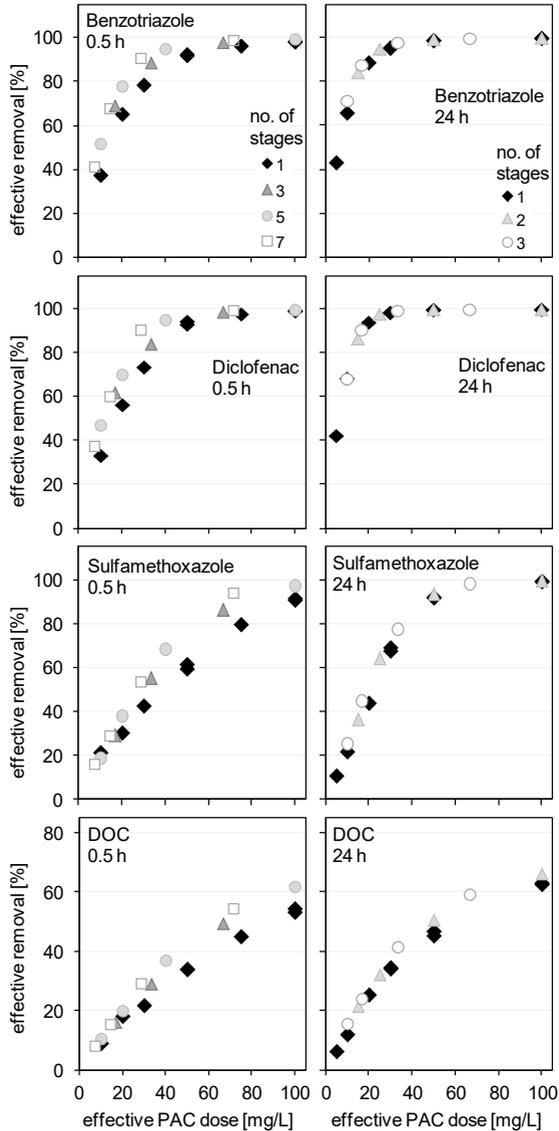


Fig. 37. Effective removals versus effective PAC doses for selected organic micro-pollutants and the DOC, for 1, 3, 5, 7-stage setups with 0.5 h contact time (left), and 1, 2, 3-stage setups with 24 h contact time (right); note the different symbol allocations on the left and right sides.

The effective removals of all organic micro-pollutants (OMP) and the DOC increase with an increasing number of PAC reuse stages, e.g. from ~75% diclofenac removal in the 1st stage to ~90% in the 7th stage at an effective PAC dosage of ~30 mg/L and 0.5 h contact time per stage. The beneficial effects on the overall efficiency are clearer for 0.5 h than for 24 h contact time because in the former case, 7 stages were conducted whereas in the latter case only 3 stages could be conducted. The results show that PAC reuse can increase the exploitation of the PAC capacity for OMP and the DOC. Containing the used PAC in the system increases the hydraulic residence time of the PAC. Together with the periodical restoration of the concentration gradient (due to the addition of fresh water) the overall efficiency is increased. It is also demonstrated that weak adsorbates such as sulfamethoxazole are not displaced by the periodical introduction of strongly competing effluent organic matter (EfOM) that results from the addition of fresh WWTP effluent in each PAC reuse stage. We assume that this is because the EfOM and OMP concentrations are simultaneously renewed in each stage, resulting in a balanced re-establishment of (i) the EfOM-induced adsorption competition and (ii) the OMP adsorption driving force.

The additional removal of OMP and the DOC that can be achieved by reusing PAC could practically translate into a saving of PAC when aiming at specific OMP/ DOC removal targets. This is particularly beneficial in the case of sulfamethoxazole which is a moderate/ weak adsorbate. For this OMP, the graphs shown in Fig. 37 have a comparatively small slope, implying that an increase of the effective removal goes along with a comparatively strong decrease of the needed effective PAC dosage. E.g., at 0.5 h contact time, for 90% sulfamethoxazole removal, 100 mg PAC/L are needed in a single-stage setup whereas only ~70 mg PAC/L are needed if the PAC is reused in 7 stages. This corresponds to a PAC saving of >20%. Practically, the PAC reuse could be realized by a discontinuous PAC dosage into a mixing reactor with continuous water flow and subsequent PAC separation and recirculation into the mixing reactor. Additional experimental data from lab-tests with lower carbon doses can be found in the Supporting Information (Appendix B-7, p. 158), which also includes the comparison of a 3-stage/ 0.5 h PAC reuse setup to a single-stage/ 1.5 h setup. Both of these setups reach comparable results, underlining the benefits from PAC reuse, considering that a 3-stage 0.5 h PAC reuse setup theoretically requires only 1/3 of the contactor space of a single-stage 1.5 h setup.

Furthermore, the Supporting Information (Appendix B-7, p. 158) also includes the effective removals that result from scenarios which include (A) the addition of fresh PAC to previously PAC-treated water, and (B) a combination of using pre-loaded PAC on fresh water, followed by reuse of that water with fresh PAC in the 3rd stage. Setup (A) reflects the addition of fresh PAC in three subsequent stages treating the same water. This setup yields overall poorer results than the PAC reuse setups. Setup (B) simulates a typical practical PAC reuse constellation for the removal of strong adsorbates with pre-loaded PAC and the removal of poorer adsorbates from pre-treated water with fresh PAC. This is usually realized in a two-stage process with addition of fresh PAC in the 2nd stage and recirculation of used PAC to the 1st stage (Jekel et al. 2013). Scenario (B) reaches similar effective removals as the PAC reuse

setups for the good adsorbates benzotriazole and diclofenac but poorer results for sulfamethoxazole and the DOC.

Prediction of organic micro-pollutant removals using UV_{254}

The effective removals of the organic micro-pollutants (OMP) and the DOC are depicted versus the effective removals of the UV absorption at 254 nm (UV_{254}) that were achieved at the effective PAC doses in the examined single- and multi-stage setups, in Fig. 38, after 0.5 h adsorption time. In all cases, the removals of the target parameters (OMP, DOC) and the removals of the surrogate parameter (UV_{254}) lie on distinct lines. Accordingly, the removals of the OMP and the DOC are predictable using the removal of UV_{254} , as indicated by other studies (Altmann et al. 2014, Altmann et al. 2015, Zietzschmann et al. 2014a). Similar correlations were found for 24 h adsorption time and are shown in the Supporting Information (Appendix B-7, p. 158).

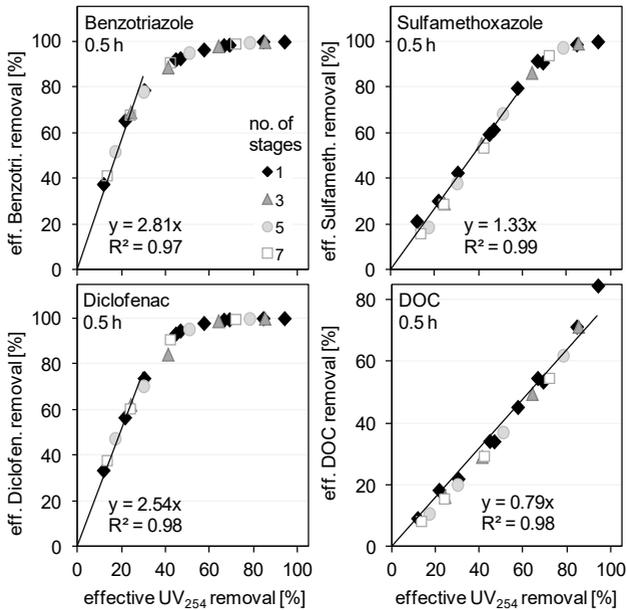


Fig. 38. Effective organic micro-pollutant and DOC removals versus effective UV_{254} removals in single- and multi-stage setups, after 0.5 h adsorption per stage, with linear trend lines ($\leq 80\%$ OMP removal).

UV_{254} is a surrogate parameter and does not measure the concerned OMP directly; but the compounds encompassed within UV_{254} and the individual OMP coincide in their adsorption behavior (Altmann et al. 2015). The reason is that the investigated OMP have one or several

aromatic ring systems in their respective molecular structure which is a property which they share with the entity of primarily aromatic substances comprised in the parameter UV_{254} (Wert et al. 2009). The affinity of activated carbons towards the adsorption of aromatic organics is caused by the overall graphite-like structure of the activated carbon microcrystallites (Worch 2012). Fig. 38 also shows that the graphs from subsequent stages follow the graph of the 1st stage. Thus, the expectable OMP and DOC removals in multi-stage setups can be estimated easily from the UV_{254} removals of the 1st stage. This could be particularly useful in applications where OMP measurement is not available or where online monitoring of the process efficiency is needed, such as in full-scale plants. Given the correlations between the OMP/ DOC and UV_{254} removals and their nearly linear shapes, linear trend lines were fitted (the removal range for the OMP was limited to 80% because above that, the curves bend and lose their linearity; note that the R^2 values are overall very high due to the inclusion of the origin and the small size of the data sets; the data sets in the cases of benzotriazole/ 24 h and diclofenac/ 24 h are particularly small). These fits demonstrate that OMP/ DOC removals are easily and precisely predictable using UV_{254} removal.

Adsorption loading curves/ isotherms of organic micro-pollutants

The adsorption loading curves (after a non-equilibrium contact time of 0.5 h) of benzotriazole, diclofenac, sulfamethoxazole, and the DOC in single- and multi-stage setups are shown in Fig. 39. The graph of benzotriazole also includes exemplary operating lines for the reuse of a PAC dose of 100 mg/L. Loaded PAC from previous stages is further exploited in additional stages and the loading increases as can be seen from the exemplary operating lines. The graphs also show that in most cases, the loading curves/ isotherms of the 2nd, 3rd, ... stages are located on or close to the curves of the 1st stage. Accordingly, the 1st stage loading curves/ isotherms can be applied to estimate the adsorption in subsequent stages. The effects are similar for equilibrium contact times of 24 h, for which the data are shown in the Supporting Information (Appendix B-7, p. 158). In some cases, the multistage setups reach slightly higher (diclofenac, 24 h) or lower (benzotriazole) loadings than the single-stage setups. (Data from additional experiments shown in the Supporting Information, Appendix B-7, p. 158, show that the slight over- or underestimations are not systematical.)

We assume that the overall validity of the 1st stage loading curves/ isotherms results from the simultaneous re-creation of higher organic micro-pollutant (OMP) concentrations and higher effluent organic matter (EfOM) concentrations in every additional stage when fresh WWTP effluent is added to the batches. This implies that the relative concentrations (C_{OMP}/C_{EfOM}) are similar in all stages and the adsorption competition between OMP and EfOM is not altered. These findings imply that the position of the loading curves can be attributed on the one hand, to the initial concentration of the respective OMP (Knappe et al. 1998, Najm et al. 1991), and on the other hand, to the concentration of the EfOM or background organic matter (BOM). Thus, the ratio of the OMP to EfOM concentrations is a major factor determining the adsorption competition between the OMP and the EfOM/ BOM and hence, the position of the OMP loadings. Furthermore, since the loading curves/ iso-

therms of the 1st stage are continuously reached in subsequent stages, the OMP mass transfer to the PAC internal surface appears to be unaffected by the periodical introduction of potentially pore-blocking EfOM. However, this may also be a result of pore-blocking large EfOM hindering smaller EfOM components from direct competition with the OMP; also, pore-blockage could hinder previously adsorbed OMP from being removed from the PAC internal surface/ pore system to the liquid phase (To et al. 2008a).

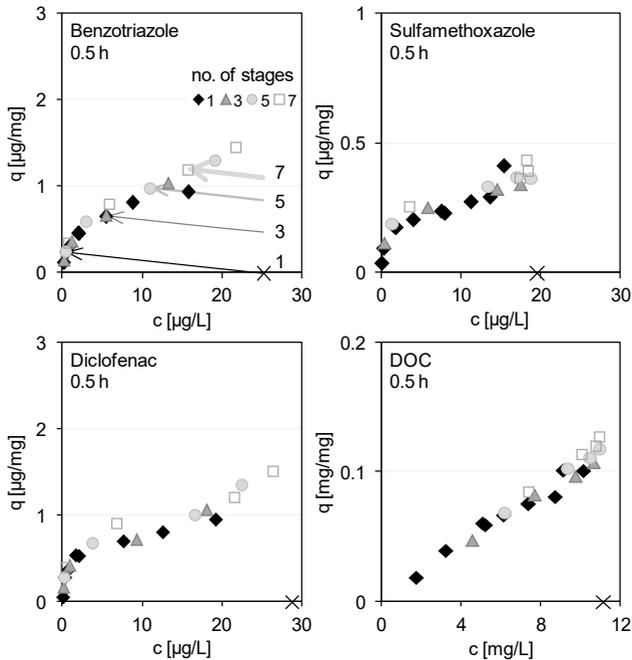


Fig. 39. Loading curves (0.5 h) for organic micro-pollutants and the DOC, after single- and multi-stage PAC adsorption; with initial concentrations (× signs) and exemplary operating lines for a PAC dose of 100 mg/L (benzotriazole).

Multi-stage adsorption modeling

The additional removals, calculated from the effective multi-stage removals subtracted by the corresponding single-stage removals with equivalent PAC doses were chosen as a meaningful output parameter from the results of the Equivalent Background Compound Model (EBCM). In doing so, the additional effect of multi-stage PAC reuse compared to single-stage PAC application can be evaluated. The modeled additional removals for multistage PAC reuse for benzotriazole, diclofenac, and sulfamethoxazole are shown in Fig. 40 (0.5 h). Each line represents a fictive multi-stage setup with a fixed number of stages. All curves

increase to a respective maximum which is the PAC dosage that produces the highest additional removals. If the PAC dosage is further increased, the additional effect decreases. The modeling produces similar additional removals as the experiments shown in the previous sections (cf. differences between removals in 1-stage and multi-stage setups in Fig. 37). 7 PAC reuse stages with a respective contact time of 0.5 h result in ~11% modeled additional removal. With an increasing number of stages, the initial PAC dosage must be raised in order to obtain the best results. The results are similar for equilibrium contact times of 24 h and the corresponding data are given in the Supporting Information (Appendix B-7, p. 158).

The graphs in Fig. 40 and the Supporting Information (Appendix B-7, p. 158) show that additional removals of up to ~14% can be expected at both of the modeled contact times. The graphs also show that the initial PAC dosage cannot be set arbitrarily high since the beneficial additional removals decrease for very high dosages. This is due to the fact that very high equivalent single-stage PAC dosages reach 100% OMP removal which can be met by multi-stage treatment but cannot be outperformed. (E.g., for diclofenac at 24 h contact time, a 10-stage PAC reuse setup with 1000 mg PAC/L and the equivalent single-stage setup with 100 mg PAC/L both reach an overall 100% removal.)

The graphs in Fig. 40 also demonstrate that the optimum PAC dosage for maximal additional removal increases with the number of stages. The reason is that with increasing stage number, the intersections between the operating lines and the loading curves/ isotherms (cf. Fig. 39) move up and right, towards decreased removals (decreased $c_o - c_i$). Thus, when increasing the stage number, the PAC dose must be raised in order to optimize the average concentration difference of all stages which is given by $1/i * \sum(c_o - c_i)$. Accordingly, if the number of stages is to be increased, the PAC dose should be increased and vice versa. For low stage numbers, the maximally achievable additional removal increases quickly with the number of stages. (E.g., 6% for 2 stages against >10% for 5 stages) However, the beneficial effect flattens towards very high stage numbers. (E.g., for diclofenac and 10, 20, 30, 40, 50 stages, the maxima are at about 12, 13, 13.25, 13.5, 13.5%, respectively.) We give an overview over a variety of graphs for the additional removal in dependence of the PAC dose at several sets of K_F , $1/n$, and $c_{o,EBC}$ values in the Supporting Information (Appendix B-7, p. 158). These graphs show that with increasing K_F values, the benefits from adding additional stages decrease. This is logical, given that higher K_F values mean a higher position of the overall isotherm and thus, high removals are achievable at lower PAC doses (steeper operating lines) even at low stage numbers. Also, increasing the Freundlich exponent $1/n$ to ~0.5 increases the maximally achievable additional removal.

As demonstrated in Fig. 40, a maximally achievable additional removal exists for each number of stages. A spreadsheet procedure was programmed to approximate that maximum for up to 50 stages. The modeled maxima together with the respective needed PAC doses are depicted versus the corresponding stage number in Fig. 41 for several Freundlich exponents $1/n$, and two initial EBC concentrations $c_{o,EBC}$.

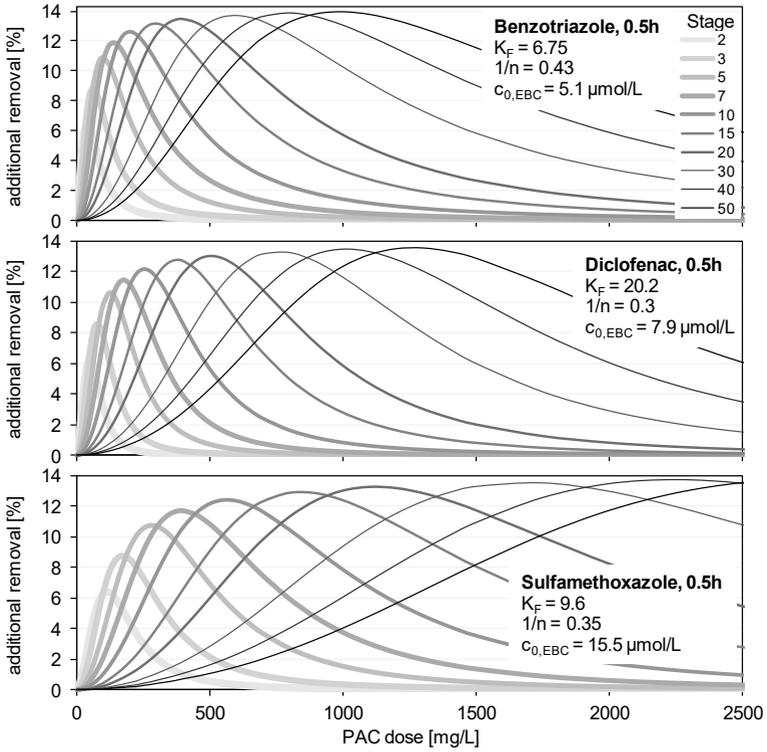


Fig. 40. Modeled additional OMP removals in multi-stage PAC reuse setups compared to single-stage setups with the same effective PAC dose for 0.5 h adsorption time.

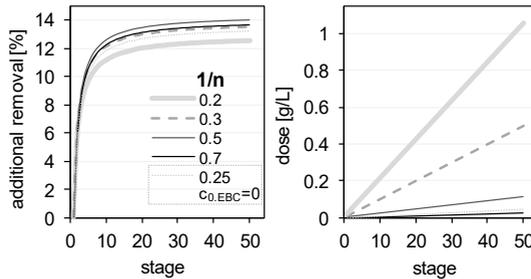


Fig. 41. Modeled maximally achievable additional removals (*left*) and corresponding PAC doses (*right*) in dependence of the PAC reuse stage number; $K_F = 20 \text{ (nmol/mg)} \cdot (\text{L/nmol})^{1/n}$, $c_{0,OMP} = 50 \text{ nmol/L}$, $c_{0,EBC} = 2,000 \text{ nmol/L}$ (unless indicated otherwise).

The maximally achievable additional removal is highest for Freundlich exponents $1/n \sim 0.5$; below or above that value, the maximally achievable additional removals are slightly lower. The Freundlich coefficient K_F has no impact (cf. Supporting Information, Appendix B-7, p. 158). Similarly, if the initial concentration of the EBC is set to zero ($C_{0,EBC} = 0$), the maximally achievable additional removal does not increase. However, the PAC dose needed to achieve the maximally achievable additional removals decreases with decreasing $C_{0,EBC}$. Overall, the maximally achievable additional removal does not pass a value of $\sim 14\%$. Accordingly, besides underlining the beneficial effects on the overall OMP/ DOC removals and PAC consumption, this research demonstrates the boundaries that must be considered when planning PAC reuse. However, it must be noted that the examined and modeled multi-stage setups represent a recirculation of PAC without the addition of fresh PAC. Pilot- or full-scale PAC recirculation typically aims at increasing the amount of PAC in the system over time (Metzger 2010). As shown in the Supporting Information (Appendix B-7, p. 158) of the current study, data on a combination of PAC reuse and subsequent addition of fresh PAC to the treated water indicate that this is a promising approach. This practical setup should be examined in more detail with the lab test developed in the current study.

CONCLUSIONS

- An easy laboratory procedure was developed allowing for detailed investigation of organic micro-pollutant (OMP) adsorption in multi-stage powdered activated carbon (PAC) setups, such as PAC or water reuse.
- PAC reuse in several subsequent stages can increase the OMP removal efficiency. Higher initial PAC doses increase the efficiency if the number of reuse stages is also increased. The low molecular weight organic acid and neutral compounds are better removed than larger effluent organic matter (EfOM) fractions and thus are likely to cause the majority of adsorption competition against OMP.
- The effective removals of OMP and the DOC in all stages correlate with the effective UV_{254} removal and can be predicted using the 1st stage removal of UV_{254} . This allows for swift practical surveillance of processes where OMP measurements are not available or where online monitoring is needed.
- The OMP isotherms (24 h) and loading curves (0.5 h) of 2nd, 3rd, nth stages follow the corresponding curves of the 1st (single) stage. Accordingly, knowing the 1st stage relationship between the OMP concentration and loading, the adsorption in subsequent stages can be estimated. Also, modeling of subsequent stages can be achieved using the 1st stage data. We assume that the overall validity of the 1st stage isotherm is due to a balanced adsorption competition between the OMP and the EfOM in all stages: The addition of fresh water in every additional adsorption stage results in a simultaneous restoration of the OMP and EfOM initial concentrations. This causes a simultaneous and balanced restoration of the antagonistic forces of the OMP adsorption drive on the one hand and the EfOM competition on the other hand.

- The developed lab test would also be suitable for OMP desorption testing. Also, we encourage further practical applications like PAC reuse in combination with fresh PAC dosage for studying the run-in period of plants with PAC recycling which aim at increasing the PAC concentrations in the recirculation sludge.

ACKNOWLEDGMENTS

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SUPPORTING INFORMATION

Supplementary data related to this article can be found in the Supporting Information shown in Appendix B-7, p. 158.

REFERENCES

The cited references are contained in the general bibliography in Appendix A, p. 125.

5 Conclusion

Dissolved background organic matter (BOM) of drinking waters, surface waters and wastewater treatment plant (WWTP) effluents causes a substantial deterioration of the adsorption of organic micro-pollutants (OMP) onto activated carbon. This study investigates the causes, effects and prediction of this adsorption competition between OMP and BOM in various waters, in powdered as well as in granular activated carbon (PAC, GAC) setups. Additional tests were conducted to derive surrogate parameters for activated carbon performance indication and monitoring, and new methods for lab-scale testing and modeling PAC reuse were developed. The main findings of the research are summarized and discussed in the following.

5.1 Summary and discussion

Different techniques were used as pre-treatments prior to activated carbon adsorption to elucidate the properties of WWTP effluent organic matter (EfOM, representing BOM) regarding the adsorption competition with OMP. Using ultrafiltration, nanofiltration, and reverse osmosis, a size separation of EfOM was achieved whilst keeping the overall BOM concentrations comparable (EfOM inferred from the dissolved organic carbon – DOC). The EfOM separation was demonstrated with liquid chromatography with online carbon detection (LC-OCD). In subsequent PAC tests, it could be shown that the low-molecular weight (LMW) EfOM are stronger competitors than larger EfOM. Weakly adsorbing OMP like sulfamethoxazole are particularly affected by these LMW organics.

In GAC adsorption tests on miniature fixed-bed filters, the concept of rapid small-scale column tests (RSSCT) was applied to WWTP effluent. Because of suspended particles/ colloids, ultrafiltration treatment prior to GAC filtration was necessary to obtain acceptable head losses/ flux declines during the tests. Auxiliary tests showed no impact on OMP adsorption due to the removal of large dissolved and colloidal/ particulate substances by ultrafiltration. The EfOM breakthrough was monitored with LC-OCD, and large EfOM fractions show less retention on the GAC filter while the LMW organics show comparatively strong retention and accordingly, adsorption affinity. This observation underlines the relevance of the LMW competitors and confirms other studies.

PAC adsorption tests after ultrafiltration and ozonation of WWTP effluent were conducted to investigate the impacts of different ozone consumptions on BOM competitiveness. Due to pre-ultrafiltration, similar DOC concentrations could be obtained even after ozonation, implying high comparability. Furthermore, the investigated OMP were spiked to comparable

initial concentrations after ozonation. With increasing ozone consumption prior to PAC adsorption, the BOM-induced adsorption competition decreases. This underlines the relevance of aromaticity and hydrophobicity to BOM competitiveness against OMP adsorption. Also, this demonstrates the feasibility of combinations of ozonation and activated carbon adsorption: Both techniques can reduce OMP concentrations and the ozone-induced change of BOM results in a decrease of the BOM adsorption competitiveness. Summing up, the lowest BOM adsorption competition can be expected for high molecular weight, hydrophilic, little aromatic BOM.

In an extensive comparison of waters from various origins, five drinking waters and seven WWTP effluents were compared regarding the respective adsorption competition between OMP and BOM. A high comparability between the adsorption tests in the waters was ensured by artificially adjusting the OMP concentrations relative to the respective DOC, to OMP/DOC ratios of $\sim 5 \mu\text{g OMP/mg DOC}$. LC-OCD analyses showed mostly similar BOM compositions in the waters of the respective group (drinking waters, WWTP effluents). Also, the OMP removals were similar in the different waters of the respective group. Slightly higher removals were observed in waters with higher absolute initial OMP and DOC concentrations. The reason is that the relationships between the PAC loadings and the liquid phase OMP concentrations are similar in the waters of the respective group. Thus, the OMP adsorption was similarly affected by the BOM from the different waters of each group, respectively. These results demonstrate the general similarity of the adsorption phenomena in drinking waters or WWTP effluents, respectively, from different sources. Thus, if the type of water (drinking water or WWTP effluent) is the same at different locations, the activated carbon adsorption behavior of OMP is mostly transferrable.

The comparison of a drinking water and a WWTP effluent with similar DOC reveals that the BOM-induced adsorption competition is overall higher in WWTP effluents than in drinking waters. Relating to previous results on the variable competitiveness of different BOM fractions, these differences were attributed to generally higher concentrations of the LMW organics in WWTP effluents than in drinking waters. The microbiological degradation in WWTP typically leads to extensive decreases of the BOM concentrations but the BOM in WWTP effluents is still relatively fresh. This BOM can be further degraded along the natural pathways in surface and ground waters. This ongoing natural degradation is shown by the fact that compared to WWTP effluents, drinking waters contain lower percentages of LMW substances but higher percentages of humic-like compounds. These different compositions affect the corresponding BOM-induced adsorption competition.

The results from the comparison of adsorption competition in waters of different origins were further explored by back-modeling the OMP adsorption in the different waters with the equivalent background compound (EBC) model (EBCM) for the OMP benzotriazole, diclofenac, and sulfamethoxazole. Using average Freundlich parameters for the EBC of the respective OMP in the different drinking waters and/or WWTP effluents, the initial concentration of the EBC was the only variable back-modeling parameter. The back-modeled initial EBC concentrations could then be related to the DOC of the waters or the concentrations of

the LMW organics. Correlations were found between the initial EBC concentration and the DOC in both groups of waters, respectively. If all waters (drinking waters and WWTP effluents) are considered simultaneously, the initial EBC concentration correlates with the LMW organics concentration. The gained correlations were tested on additional samples of drinking water, WWTP effluent, and surface water which were not included for deriving the correlations. The EBCM results inferred from the DOC or LMW organics concentrations of these waters could predict the experimentally determined OMP adsorption satisfyingly well. Thus, the EBCM can be initialized using the DOC or the LMW organics of a water and a more cumbersome initialization by experimental batch testing is not necessary. However, different relationships between the initial EBC concentration and the DOC/ LMW organics concentration can be expected for different PAC products.

In concordance with the overall relevance of the LMW organics, OMP breakthrough curves in GAC filters treating drinking water and WWTP effluent could be aligned with a simple normalization of the throughput using the fed masses (or UV_{254} absorbance) of the LMW organics. These GAC tests furthermore showed that OMP breakthrough curves are independent of the OMP influent concentration (below certain thresholds). As a result of this finding, the capacity of the GAC for an OMP in a given water is directly proportional to the influent OMP concentration. This proportionality was further extended by the LMW organics concentrations of the tested waters. The resulting correlations show that the GAC capacity for the three moderately adsorbing OMP 4-formylaminoantipyrine, primidone, and sulfamethoxazole can be predicted irrespective of the water type. Also, the obtained correlations for these OMP have similar coefficients, implying that the GAC capacities of any of the three OMP can be estimated from the capacities of the other OMP. With these results, OMP breakthrough curves in GAC filters and the related capacities are now transferrable between different types of waters (for the same GAC filter design). Accordingly, the breakthrough curve of an OMP can be defined irrespective of the water. This may allow for the specification of breakthrough curves which are overall valid for a given combination of OMP/ GAC/ filter design. The effects of different GAC filter designs on these normalized breakthrough curves should be further examined.

Additional tests for the comparison of different PAC show that common parameters such as B.E.T. surface, iodine number, and nitrobenzene number are of little use for the performance evaluation of different activated carbons regarding OMP removal. However, the activated carbon-induced removal of the bulk parameter UV_{254} correlates linearly with the removal of the measured OMP (until ~80% OMP removal). Activated carbons which reach high UV_{254} removals reach overall high OMP removals. Furthermore, the revealed correlations are independent of the PAC for most OMP. Thus, the relationships between OMP and UV_{254} removals can be transferred between different PAC. The usefulness of the surrogate parameter UV_{254} removal was also shown in various other test setups of this study (after different pre-treatments, in PAC multi-stage reuse etc.). Accordingly, OMP removals can be inferred from the UV_{254} removal, and UV_{254} is likely to be effective for the online monitoring of OMP removals, e.g. in pilot or full-scale activated carbon stages.

Another aspect of the study was the development of a laboratory test for the investigation of the adsorption mechanisms in multi-stage PAC reuse. This technique is often applied in practice but the mechanisms regarding OMP-BOM adsorption competition have not been examined in detail so far. In the PAC reuse variant tested in this study, the same PAC was used repeatedly for a defined adsorption time on fresh WWTP effluent. Thus, the OMP and EfOM concentrations, respectively, were restored to the same levels in each stage. The tests show that the relationships between the PAC loadings and the liquid phase OMP concentrations of the first (single) stage are valid for the subsequent (multi) stages, too. Accordingly, the repeated restoration of the initial OMP and EfOM concentrations results in similar adsorption competition in each additional stage. Overall, the PAC capacity can be exploited more efficiently due to PAC reuse and up to ~14% additional removals can be obtained when reusing PAC in multiple stages. In typical practical applications, fresh PAC is usually added to the reused PAC, leading to continuously increasing PAC concentrations in the recirculation sludge. This technique is likely to further raise the additional OMP removals and was further investigated with the developed lab-test in another study.

5.2 Final remarks

The various laboratory tests conducted in this study underline the relevancy of the LMW organics regarding the competitive adsorption between OMP and BOM in WWTP effluents, drinking waters, and surface waters. The identification of this BOM fraction containing the major competitors allowed for increasing the transferability of adsorption data between different waters, in PAC as well as in GAC adsorption.

The PAC adsorption of OMP in the competitive system of OMP and BOM can be modeled more easily based on the results of the present study. It was shown that the EBCM can be initialized by using average Freundlich coefficients for different waters and modeling the initial EBC concentration using linear relationships with the DOC or the LMW organics concentration. This makes the laborious experimental testing and subsequent back-modeling — normally used to initialize the EBCM — unnecessary.

In GAC adsorption, the developed method to plot over the LMW organics throughput allows for obtaining overall valid OMP breakthrough curves for given GAC filter designs, mostly independent of the respective water. This means that OMP breakthrough curves can be estimated if the LMW organics concentration (or the LMW UV₂₅₄) of a water is known and the GAC filter design has been tested elsewhere on another water. This transferability may also reduce the need for the relatively complex modeling of breakthrough curves which typically requires extensive data from laboratory tests.

The derivation of OMP removals using the easily measureable removal of UV₂₅₄ in a variety of tested setups facilitates quick performance assessments in the laboratory and online monitoring on pilot- or full-scales. This can decrease the need for laborious direct meas-

urements of OMP by high performance liquid chromatography with tandem mass spectrometry.

The development of a laboratory test realizing the separation of PAC-water suspensions with the possibility of subsequent re-suspension of the PAC allows for the investigation of various new aspects in activated carbon adsorption/ desorption research. Different combinations of PAC/ water reuse were already tested in the present study. In addition, the effects of consecutively increasing PAC concentrations in subsequent stages as well as different setups for desorption testing can now easily be realized on the laboratory scale for systematic investigation of the involved mechanisms.

Most PAC adsorption tests of this study were conducted for equilibrium (48 h) and non-equilibrium (0.5 h) adsorption times. In nearly all investigations, analogous outcomes were found for both tested times, e.g. in most of the EBCM applications. This shows that the practical aspects of non-equilibrium adsorption can be inferred by using shorter timescales in tests that are typically designed for equilibrium-like contact times.

The findings of this study are mostly based on advancements of experimental and analytical tools and their combinations for the characterization of adsorption phenomena under different conditions. The results show that relatively simple methods like using the LMW organics concentration can have substantial impacts on the prediction and transferability of adsorption data in various setups. Sole mathematical adsorption modeling is impeded by its need for experimental data in many cases. To a considerable extent, this crucial practical limitation can be avoided with the approaches developed in this study.

Appendix

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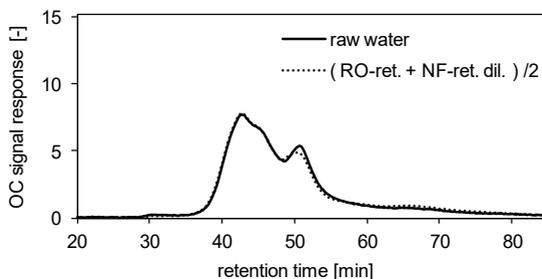
B Supporting Information

B-1 BOM size in powdered activated carbon adsorption

Impact of EfOM size on competition in activated carbon adsorption of organic micro-pollutants from treated wastewater

Water research 65 (2014), 297–306

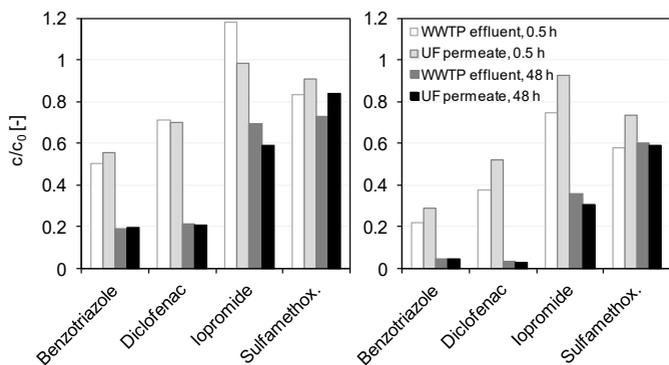
The LC-OCD chromatogram of the raw water and the fictional chromatogram that results from averaging the chromatograms of the RO retentate and the diluted NF retentate (added and then divided by 2) are presented in Supp. Fig. 1. The averaging of the LC-OCD signals of the two fractionized waters results in nearly the same chromatogram as the raw water. There is a slight decrease of the small organic acids peak compared to the raw water but within typical fluctuations of LC-OCD measurements, the difference is small. We suggest that any noticeable alteration due to breaking/ creation of associations between the raw water constituents would have resulted in shifts of the LC-OCD chromatogram peaks in the average of the fractionized waters. Therefore, we assume that the NF treatment mainly resulted in a physical fractionation of the raw water compounds but did not create or break associations between raw water compounds.



Supp. Fig. 1. LC-OCD chromatograms of the raw water (continuous line) and the average of the two fractionized waters (dotted line).

The relative concentrations of the organic micro-pollutants (OMP) benzotriazole, diclofenac, iopromide, and sulfamethoxazole in an exemplary wastewater treatment plant (WWTP) effluent sample and the UF permeate of the corresponding WWTP effluent sample, after

10 mg/L (left) and 20 mg/L (right) powdered activated carbon (PAC) treatment and contact times of 0.5 h and 48 h are shown in Supp. Fig. 2. The concentrations in the WWTP effluent and the UF permeate are either similar or in the range of the typical deviations of the applied HPLC-MS/MS procedure. (E.g. for benzotriazole, the relative concentration is ~ 0.5 after 0.5 h and a PAC dose of 10 mg/L, and ~ 0.2 after 48 h.) Therefore, we can conclude that the UF treatment of the WWTP effluent does not remove compounds of the effluent organic matter (EfOM) that are relevant in the adsorption competition between EfOM and OMP. Accordingly, WWTP effluent pre-treatment with UF is feasible in order to remove suspended material to attain higher stability of the WWTP effluent sample whilst maintaining the EfOM adsorption competitiveness against OMP.



Supp. Fig. 2. Relative concentrations of OMP after treatment with 10 mg/L (left) and 20 mg/L (right) PAC of WWTP effluent and WWTP effluent after ultrafiltration (UF), after 0.5 h and 48 h.

B-2 BOM aromaticity and hydrophilicity

Impacts of ozonation on the competition between organic micro-pollutants and effluent organic matter in powdered activated carbon adsorption

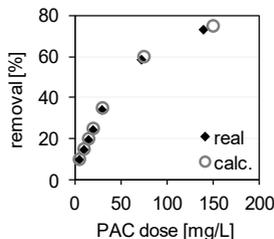
Water research 84 (2015), 153–160

Errors due to dilution by the addition of PAC stock suspension

An exemplary series of 7 batches with the PAC doses and the PAC stock concentration (2 g/L) used in the study and fictive (but typical) dissolved organic carbon (DOC) values is shown in Supp. Tab. 1. Columns 3–8 give the corrected values (batch volume increase considered), columns 9–10 give the uncorrected values (batch volume increase *not* considered), and columns 11–12 give the resulting %-errors of the removals and the loadings. The table shows that the error resulting from neglecting the dilution due to stock suspension addition remains $\leq 3.1\%$. The effects of considering/ neglecting the dilution due to stock suspension addition on the real/ calculated removals are shown in Supp. Fig. 3. The calculated removals are slightly higher than the real removals; however, this is also the case for the calculated/ real PAC doses and accordingly, the curves of real/ calculated removals versus real/ calculated PAC doses are very close to one another.

Supp. Tab. 1. Exemplary series of batches with 7 different PAC doses, corresponding batch volume increases, PAC concentration decreases, DOC concentration decreases, as well as resulting effects on real and calculated DOC removals and loadings and corresponding errors.

PAC _{aim} [mg/L]	V _{stock} [mL]	V _{batch} [mL]	real values					calculated values		errors	
			PAC _{real} [mg/L]	DOC _{start} [mg/L]	DOC _{end} [mg/L]	removal [%]	loading [mg/mg]	removal [%]	loading [mg/mg]	removal [%]	loading [%]
0	0	100	0.00	10.00	10.00	0.0		0.0			
5	0.25	100.25	4.99	9.98	9.00	9.8	0.196	10.0	0.200	2.3	2.3
10	0.5	100.5	9.95	9.95	8.50	14.6	0.146	15.0	0.150	2.9	2.9
15	0.75	100.75	14.89	9.93	8.00	19.4	0.129	20.0	0.133	3.1	3.1
20	1	101	19.80	9.90	7.50	24.3	0.121	25.0	0.125	3.1	3.1
30	1.5	101.5	29.56	9.85	6.50	34.0	0.113	35.0	0.117	2.9	2.9
75	3.75	103.75	72.29	9.64	4.00	58.5	0.078	60.0	0.080	2.6	2.6
150	7.5	107.5	139.53	9.30	2.50	73.1	0.049	75.0	0.050	2.6	2.6



Supp. Fig. 3. Real and calculated removals VS real and calculated PAC doses.

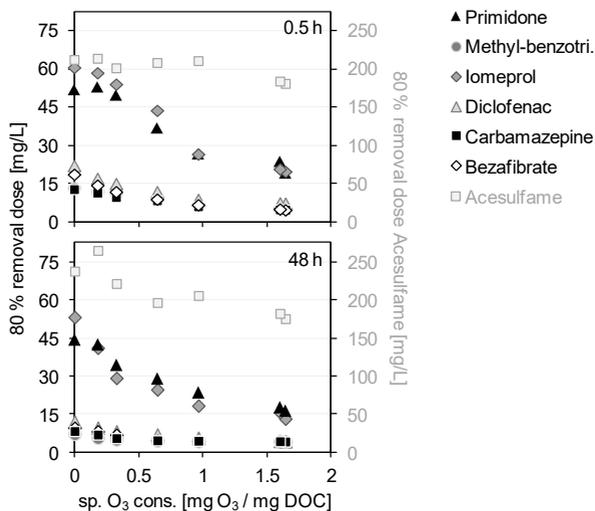
Deuterized internal standards for HPLC-MS/MS quantification

The following list shows the deuterized internal standards that were applied for the quantification of the measured organic micro-pollutants (OMP). For 4-formylaminoantipyrine and gabapentin, no substance-specific deuterized internal standards were available, and the deuterized internal standard of sulfamethoxazole which has a similar retention time was used. In all cases, the method was validated by standard addition of variable amounts of the OMP and testing of the corresponding recovery.

• Acesulfame	Acesulfame-d4
• Benzotriazole	Benzotriazole-d4
• Bezafibrate	Bezafibrate-d4
• Carbamazepine	Carbamazepine-d8
• Diclofenac	Diclofenac-d4
• 4-Formylaminoantipyrine	Sulfamethoxazole-d4
• Gabapentin	Sulfamethoxazole-d4
• Iomeprol	Iomeprol-d3
• Iopromide	Iopromide-d3
• Methylbenzotriazole	5-Methylbenzotriazole-d6
• Primidone	Primidone-d5
• Sulfamethoxazole	Sulfamethoxazole-d4

Powdered activated carbon doses for 80% removal of organic micro-pollutants

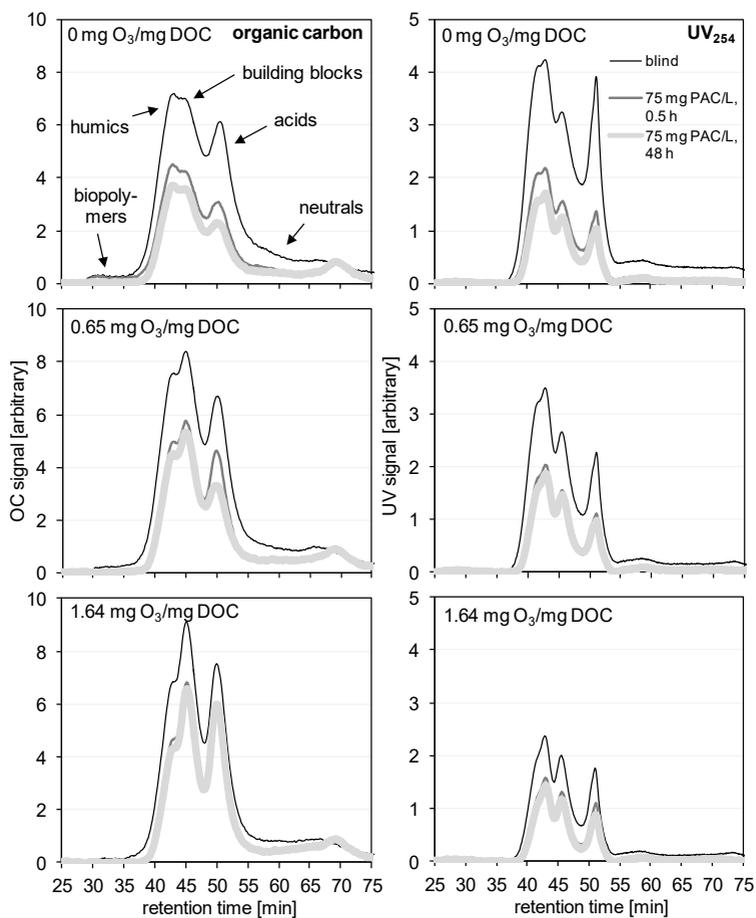
The powdered activated carbon doses for 80% removal of organic micro-pollutants that are not shown in the main document are given in Supp. Fig. 4. Due to the very poor adsorbability of acesulfame, the corresponding doses could not be calculated from interpolation and were obtained by extrapolation.



Supp. Fig. 4. Powdered activated carbon doses for 80% removal of selected organic micro-pollutants after 0.5 h (*top*) and 48 h (*bottom*) versus specific ozone consumptions.

Additional LC-OCD chromatograms

The LC-OCD chromatograms of the main document are differently grouped in Supp. Fig. 5. The top row shows the non-ozonated samples before and after PAC adsorption (0.5, and 48 h), the middle row shows the corresponding samples of the water with an ozone consumption of 0.65 mg O₃/mg DOC, and the bottom row shows the corresponding samples of the water with an ozone consumption of 1.64 mg O₃/mg DOC.



Supp. Fig. 5. LC-OCD organic carbon (*left*) and UV₂₅₄ (*right*) chromatograms of differently ozonated samples (*top, middle, bottom*), without and with PAC addition (0.5 and 48 h).

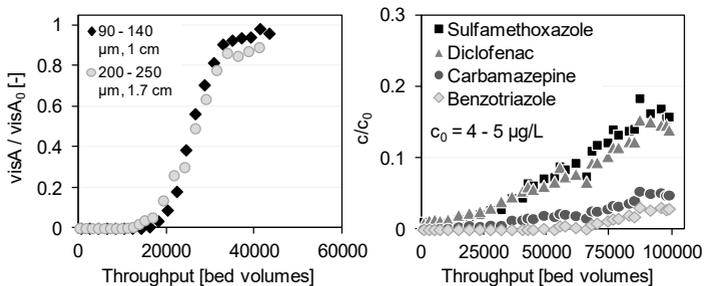
B-3 BOM size in granular activated carbon adsorption

Rapid small-scale column testing of granular activated carbon for organic micro-pollutant removal in treated domestic wastewater

Water Science & Technology 70.7 (2014), 1271–1278

The relative visual light absorption (measured at 667 nm) by a methylene blue pure water solution is depicted versus the throughput of two correspondingly dimensioned RSSCTs with differently sized GAC grains Supp. Fig. 6, left. Both breakthrough curves demonstrate a similar S-form shape and the same point of breakthrough. We can conclude therefore that the RSSCT setup of the current study is able to produce typical S-form breakthrough curves under ideal single-solute conditions.

The relative concentrations of four OMP mixed in pure water versus the corresponding throughput are shown in Supp. Fig. 6, right. The breakthroughs are strongly belayed as compared to those of the WWTP effluent breakthrough curves for these OMP shown in the study. Therefore, the bulk organic background matrix of the WWTP effluent must be the reason for the observed early OMP breakthroughs and the unfavorable shapes of the breakthrough curves.



Supp. Fig. 6. *Left:* Relative visual light absorption (visA) at 667 nm (methylene blue) versus throughput from two correspondingly dimensioned RSSCT filters with different GAC grain sizes; *right:* relative organic micro pollutant concentrations versus throughput of a RSSCT with spiked pure water.

B-4 Powdered activated carbon adsorption in different waters

Comparing and modeling organic micro-pollutant adsorption onto powdered activated carbon in different drinking waters and WWTP effluents

Water Research 102 (2016), 190–201

Water origins



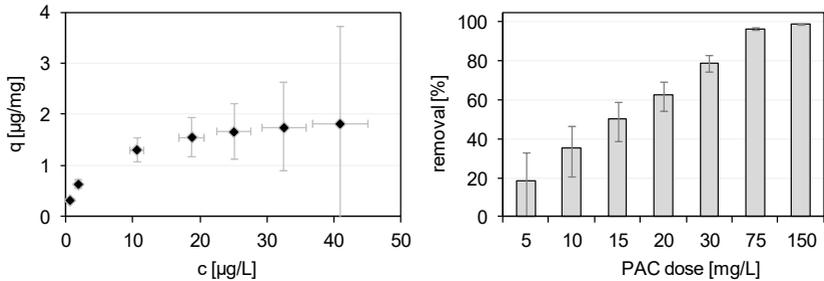
Supp. Fig. 7. Drinking water (*left*) and WWTP effluent (*right*) sampling sites in Germany (note that the origin of the anonymous drinking water is not shown).

Error calculation

An exemplary isotherm with typical organic micro-pollutant (OMP) concentrations and powdered activated carbon (PAC) doses is given in Supp. Fig. 8, together with error bars which result if PAC dosing errors of $\pm 5\%$ and OMP measurement errors of $\pm 10\%$ are stipulated. Corresponding to the isotherm shown in Supp. Fig. 8 (left), the resulting removals and related errors are shown in Supp. Fig. 8 (right). The horizontal error bars in Supp. Fig. 8 result from assuming measurement errors of the OMP concentrations after adsorption of $\pm 10\%$. The vertical minimum values of the error bars result from assuming that the dosing error was maximally positive ($+5\%$), the measurement error of the initial OMP concentration was maximally negative (-10%), and the measurement error of the OMP concentration after adsorption was maximally positive ($+10\%$), as shown in Supp. Eq. 1. The vertical maximum values of the error bars result from assuming that the dosing error was maximally negative (-5%), the measurement error of the initial OMP concentration was maximally positive ($+10\%$), and the measurement error of the OMP concentration after adsorption was maximally negative (-10%), as shown in Supp. Eq. 2. The vertical minimum error values shown in Supp. Fig. 8 (right) were calculated by assuming maximally negative measurement errors of the initial OMP concentration (-10%), and maximally positive measurement errors of the OMP concentration after adsorption ($+10\%$). The maximum error values were calculated analogously.

$$q_{\min} = \frac{c_{o,\min} - c_{i,\max}}{m_{i,\max}} = \frac{c_o \times 0.9 - c_i \times 1.1}{m_i \times 1.05} \quad \text{Supp. Eq. 1}$$

$$q_{\max} = \frac{c_{o,\max} - c_{i,\min}}{m_{i,\min}} = \frac{c_o \times 1.1 - c_i \times 0.9}{m_i \times 0.95} \quad \text{Supp. Eq. 2}$$



Supp. Fig. 8. Fictive OMP isotherm (*left*) and OMP removals (*right*) with maximum possible errors for PAC dosing $\pm 5\%$ and OMP measurement $\pm 10\%$.

Water characteristics

The initial raw water OMP concentrations before OMP spiking are given in Supp. Tab. 2 and Supp. Tab. 3. Note that the OMP concentrations of these waters were determined without online solid-phase extraction (SPE) before HPLC-MS/MS; the OMP concentrations of the additional Berlin drinking water sample shown in the main document were determined with online SPE.

The absolute and DOC-relative OMP concentration (after OMP spiking) values of the examined drinking waters are shown in Supp. Tab. 4. The absolute and DOC-relative OMP concentrations of the tested WWTP effluents are shown in Supp. Tab. 5. The DOC-specific OMP concentrations deviate by about $\pm 20\%$ from the targeted value of 5 µg OMP/mg DOC in most cases. In the cases of benzotriazole and carbamazepine, a slight trend can be observed that the OMP/DOC ratio increases with the raw water DOC.

The raw water LC-OCD UV_{254} absolute (top) and normalized (bottom) chromatograms are shown in Supp. Fig. 9, for the tested drinking waters (left) and the wastewaters (right). The unattributed drinking water shows early and strong UV_{254} absorption, indicating a substantial percentage of humics with aromatic structures (Weishaar et al. 2003). The UV_{254} signal of the Lake Konstanz drinking water shows overall high noise due to the very low BOM concentrations (cf. DOC in main document). The SUVA differences shown in the main document can be explained with the information from the LC-OCD measurements. The high SUVA of the anonymous drinking water mainly results from its high percentage of UV_{254} -absorbing humics despite the biopolymers contained in that water. Large average molecular sizes of humic substances have been shown to increase the UV_{254} absorbance

(Huber et al. 2011). The comparatively low SUVA of the Lake Constance drinking water may likely stem from measurement imprecision, due to very low DOC and UV₂₅₄ values.

Supp. Tab. 2. Initial OMP concentrations of the tested drinking waters (before spiking).

	Benzotriazole [µg/L]	Carbamazepine [µg/L]	Diclofenac [µg/L]	Sulfamethoxazole [µg/L]
Berlin	0	0	0	0
Dülmen	0	0	0	0
anonymous	0	0	0	0
Schüttorf	0	0	0	0
Lake Constance	0	0	0	0

Supp. Tab. 3. Initial OMP concentrations of the tested WWTP effluents (before spiking).

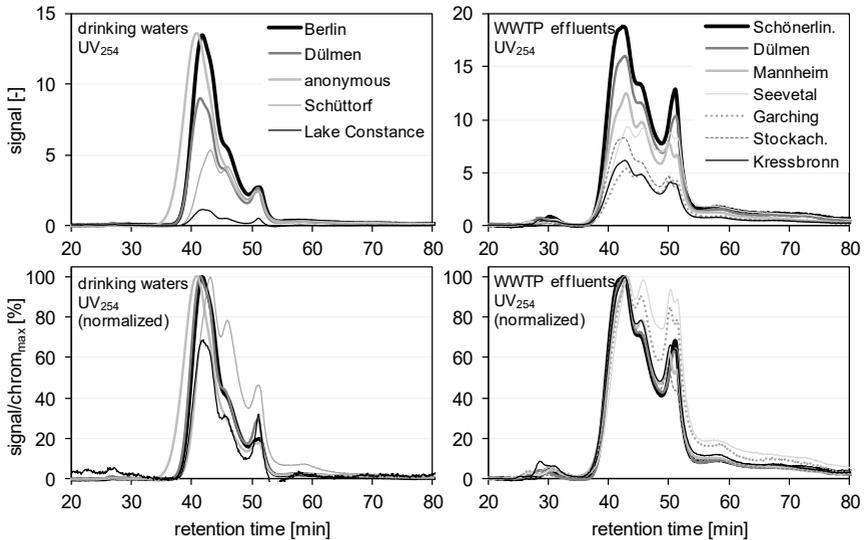
	Benzotriazole [µg/L]	Carbamazepine [µg/L]	Diclofenac [µg/L]	Sulfamethoxazole [µg/L]
Schönerlinde	15	2.9	4.8	0.3
Dülmen	9.2	0.7	3.6	0.4
Seevetal	7.6	3.8	4.8	0.3
Mannheim	8.1	1.1	2.6	0.3
Garching	4.4	0.5	1.8	0.1
Stockacher Aach	2.2	0.3	1.5	0.2
Kressbronn	1.7	0.2	1.0	0.1

Supp. Tab. 4. Absolute and DOC-relative OMP concentrations of the tested drinking waters.

	Benzotriazole		Carbamazepine		Diclofenac		Sulfamethoxazole	
	c [µg/L]	c/DOC [µg/mg]	c [µg/L]	c/DOC [µg/mg]	c [µg/L]	c/DOC [µg/mg]	c [µg/L]	c/DOC [µg/mg]
Berlin	23	4.7	26	5.3	29	5.9	22	3.9
Dülmen	16	4.6	18	5.3	21	6.2	18	4.6
anonymous	14	4.5	17	5.5	21	6.7	14	4.5
Schüttorf	13	4.5	15	5.1	18	6.0	14	5.3
Lake Konstanz	4	3.8	5	4.3	7	6.0	4	3.9

Supp. Tab. 5. Absolute and DOC-relative OMP concentrations of the tested WWTP effluents.

	Benzotriazole		Carbamazepine		Diclofenac		Sulfamethoxazole	
	c [µg/L]	c/DOC [µg/mg]	c [µg/L]	c/DOC [µg/mg]	c [µg/L]	c/DOC [µg/mg]	c [µg/L]	c/DOC [µg/mg]
Schönerlinde	64	6.1	58	5.5	57	5.5	49	4.7
Dülmen	55	5.5	52	5.2	54	5.5	45	4.6
Seevetal	42	5.2	43	5.3	46	5.7	36	4.5
Mannheim	43	5.3	39	4.8	45	5.6	39	4.8
Garching	34	4.4	32	4.2	40	5.2	27	3.5
Stockacher Aach	24	4.9	23	4.8	28	5.7	25	5.2
Kressbronn	20	4.7	19	4.6	24	5.6	20	4.7

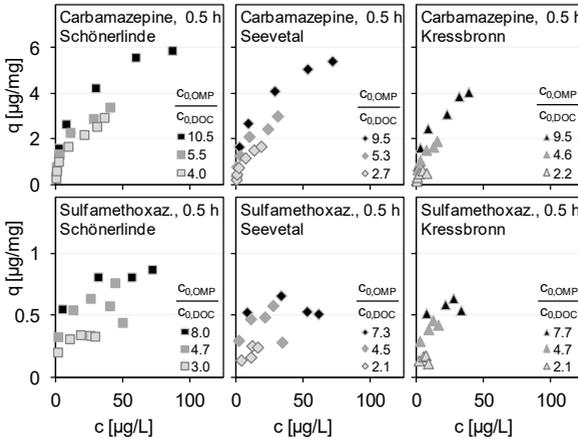


Supp. Fig. 9. Raw water LC-OCD UV₂₅₄ absolute (top) and normalized (bottom) chromatograms of the tested drinking waters (left) and wastewaters (right).

PAC loadings with OMP at variable OMP/DOC concentrations

The PAC loadings of the OMP carbamazepine and sulfamethoxazole are depicted against the corresponding liquid phase concentrations after 0.5 h of adsorption in the WWTP effluents Schönerlinde, Seevetal, and Kressbronn in which variable ratios of the OMP and the DOC initial concentrations ($c_{o,OMP}/c_{o,DOC}$) were tested, in Supp. Fig. 10. For carbamazepine, the $c_{o,OMP}/c_{o,DOC}$ ratios range from 2.2 $\mu\text{g}/\text{mg}$ (units omitted hereafter) in Kressbronn to 10.5 in Schönerlinde, and for sulfamethoxazole from 2.1 in Kressbronn and Seevetal to 8 in Schönerlinde. In the case of the strong adsorbate carbamazepine, typical curves are obtained with continuously increasing loadings at higher concentrations. For the weaker adsorbate sulfamethoxazole, the loadings increase until a certain concentration, and remain similar above that concentration or even decrease at higher concentrations. This diminishing loading at higher concentrations is typical for weak adsorbates as a result of BOM-induced adsorption competition. The effects of variable ratios of $c_{o,OMP}/c_{o,DOC}$ are similar for both shown adsorbates: In all cases, higher loadings are obtained at higher ratios of $c_{o,OMP}/c_{o,DOC}$. This confirms other studies (Knapp et al. 1998, Najm et al. 1991) and is a reason of the higher relative presence of OMP compared to BOM at higher initial OMP concentrations. The graphs also show that for strong adsorbates such as carbamazepine, similar loadings are obtained in different WWTP effluents if the ratios of $c_{o,OMP}/c_{o,DOC}$ are similar in the considered WWTP effluents. This underlines that the competition between OMP and BOM is similar in different WWTP effluents. In the case of sulfamethoxazole, the relation-

ships between the PAC loadings and the liquid phase concentrations at similar ratios of $c_{0,OMP}/c_{0,DOC}$ in the three WWTP effluents cannot be described by a single graph: The typical bending towards lower PAC loadings at high concentrations appears farer to the right in Schönerlinde than in Seevetal and Kressbronn.

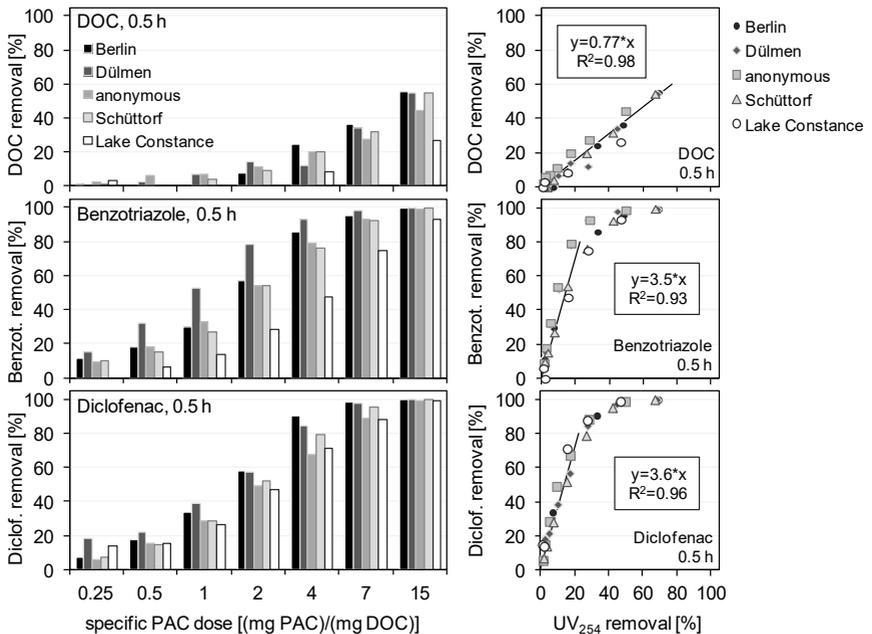


Supp. Fig. 10. Loadings (q) versus concentrations (c) of carbamazepine (*top*) and sulfamethoxazole (*bottom*) in the WWTP effluents Schönerlinde (*left*), Seevetal (*middle*), and Kressbronn (*right*) at different ratios of $c_{0,OMP}/c_{0,DOC}$ (in µg/mg) after 0.5 h of adsorption.

Additional removal data

The removals of the DOC, benzotriazole, and diclofenac, obtained at the adjusted specific PAC doses in the tested drinking waters after 0.5 h of adsorption, are shown in Supp. Fig. 11 (left). The corresponding removal data after 48 h of adsorption, as well as UV_{254} and additional OMP removals, are given in Supp. Fig. 12. Note that the DOC removals in the drinking water of Lake Constance are subject to high error because this water has a particularly low initial DOC of 1 mg/L. This results in DOC values which are close to the limit of quantification (0.5 mg/L) after PAC adsorption. About 30% DOC removal are reached with a specific PAC dose of 7 mg PAC/mg DOC. The overall variation of the DOC removals at a given specific PAC dose is $\pm 10\%$ (with the exception of the Lake Constance water). Similar to the DOC removals, the UV_{254} removals in the different drinking waters coincide mostly and are about 10–20% higher than the DOC removals. The anonymous drinking water is an exception as it shows lower DOC and UV_{254} removals compared to the other drinking waters. Overall, the results show that the partially different BOM compositions of the waters, as shown in the main document, do not lead to strongly varying behavior in the adsorption of the BOM. This is particularly the case after 48 h of adsorption.

Considering the removals of OMP, 50–90% benzotriazole and 70–90% diclofenac are removed at 4 mg PAC/mg DOC after 0.5 h of adsorption. These removals increase to >95% after 48 h of adsorption. The overall variation of OMP removals at given specific PAC doses is $\pm 15\%$, with the exception of benzotriazole in the drinking water Dülmen, where removals are higher. This could indicate the existence of specific BOM components which compete directly with benzotriazole. Apart from this exception, the differences of the BOM compositions of the tested drinking waters as shown in the main document do not lead to strong variations of the OMP removals. The drinking water Schüttorf contains comparatively large amounts of LMW compounds (cf. main document) which typically have stronger negative impacts on OMP adsorption than other BOM fractions (e.g., Zietzschmann et al. 2014c). However, no considerable effects on the OMP removals in this water can be observed. Also, the anonymous drinking water contains more relatively large BOM (biopolymers, humics) which normally have less negative impacts than smaller fractions. In this water, no particularly improved OMP removals as compared to the other drinking waters are discernible. Accordingly, the competitive impacts of BOM from different drinking water origins are comparable even if the BOM composition varies to some extent.

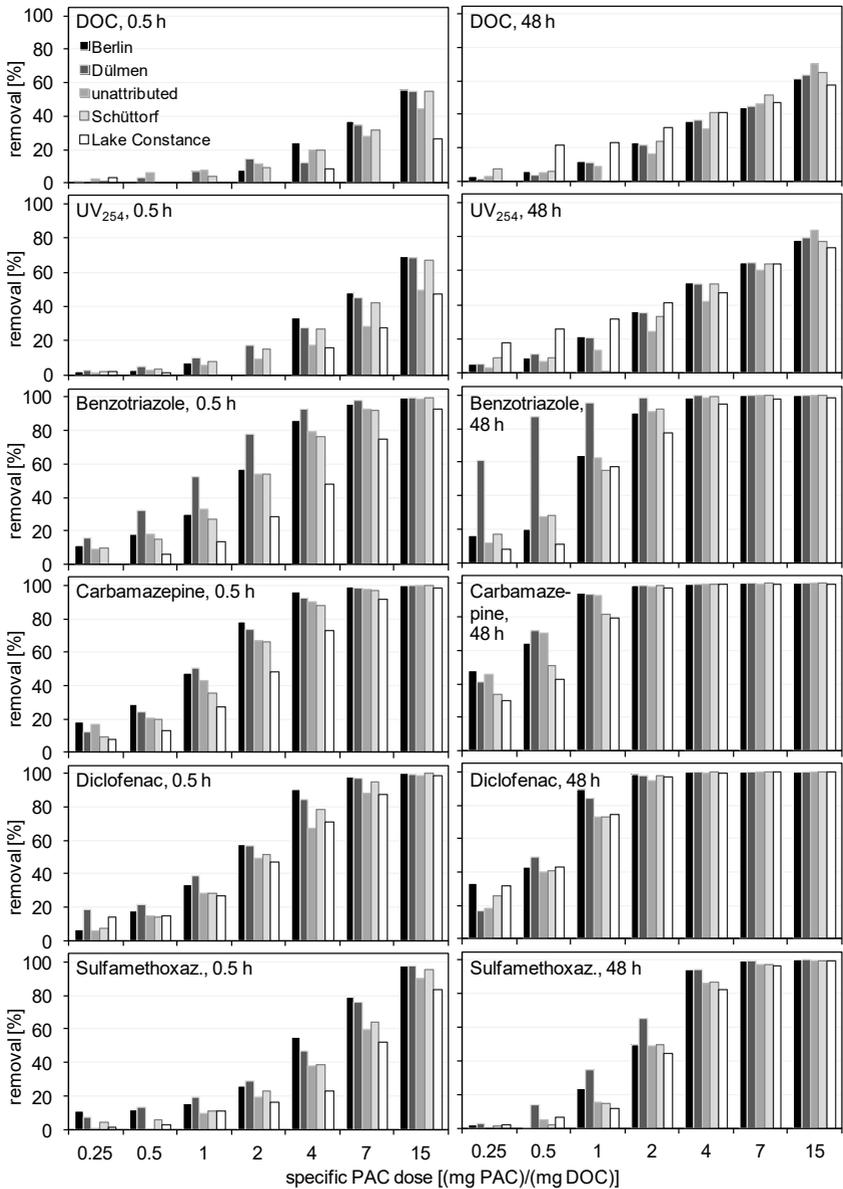


Supp. Fig. 11. Removals of the DOC, benzotriazole, and diclofenac at specific PAC doses (*left*) and DOC/ OMP removals versus UV₂₅₄ removals with corresponding linear correlations (*right*) in the tested drinking waters.

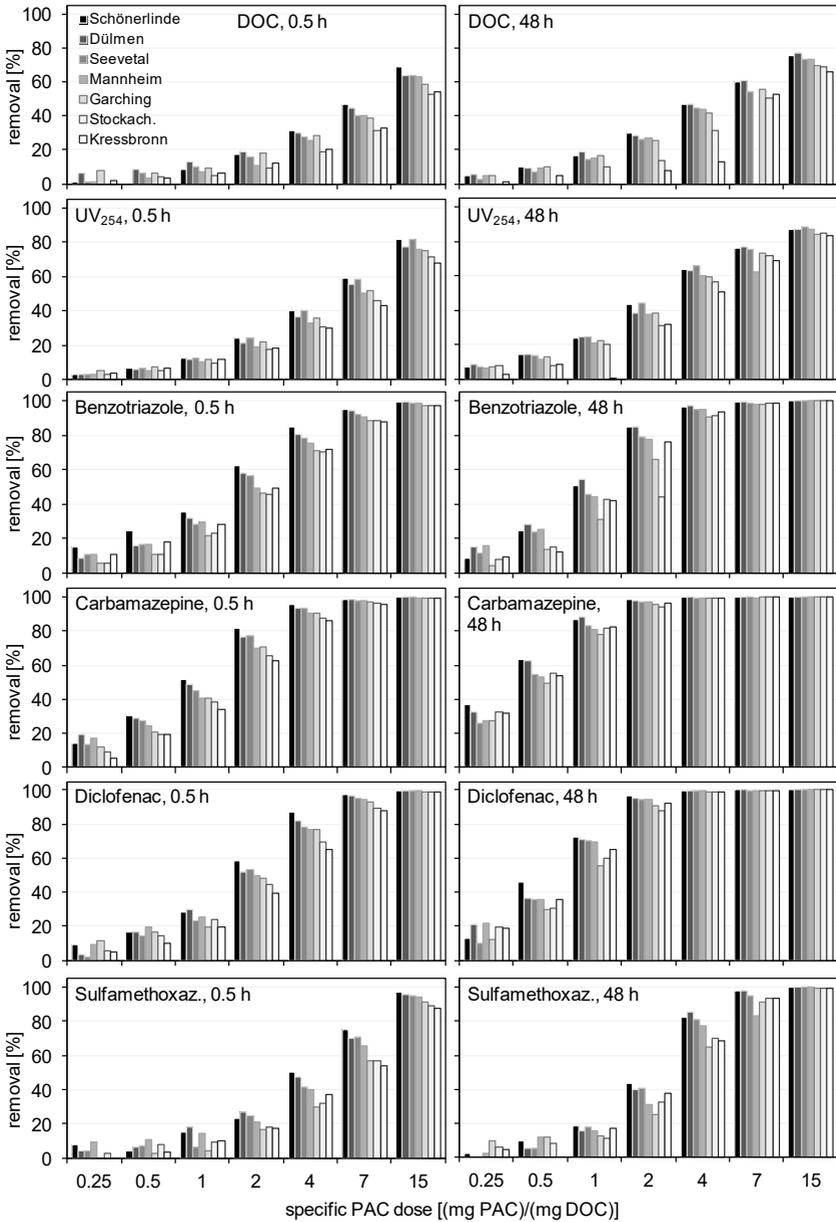
The removals of the DOC, benzotriazole, and diclofenac after 0.5 h adsorption are depicted versus the corresponding UV_{254} removals in all tested drinking waters in Supp. Fig. 11 (right), together with linear correlations for up to 60% DOC removal and 80% OMP removal. (Note that the diagrams contain all applied PAC doses for all drinking waters.) About 30% DOC removal are obtained at 40% UV_{254} removal, ~60% benzotriazole and diclofenac removal are reached at ~20% UV_{254} removal. The slopes of the linear correlations show if the target parameters are less or more preferentially adsorbed than the UV_{254} -active BOM compounds. DOC is less favorably adsorbed than the UV_{254} -active BOM compound by a factor of 0.77 while Benzotriazole and Diclofenac are favored by factors of 3.5 and 3.6, respectively. Due to the overall lower adsorbability of UV_{254} in the anonymous drinking water, the corresponding data points are located slightly above those of the other drinking waters. However, the overall high coefficients of determination (R^2) of the linear correlations demonstrate that the adsorptive UV_{254} removal can be used as a surrogate parameter for DOC and OMP removal, mostly independent of the drinking water origin.

Additional removal data for the WWTP effluents is given in Supp. Fig. 13.

As shown in the main document, overall higher OMP removals are obtained in water with higher initial OMP and DOC concentrations compared to waters with lower initial concentrations. A possible explanation for the observed trend could be an increased OMP diffusion resulting from higher $c_{o,DOC}$, as postulated in another study (To et al. 2008b), or because of an increased driving force at higher $c_{o,OMP}$. However, the proportions between BOM/ DOC, OMP, and PAC were the same in all tested waters in the current study (DOC-proportional OMP spiking and PAC dosing). This implies that similar relative amounts of free adsorption sites on the PAC were available for OMP and DOC adsorption in all tested waters (at a given specific PAC dose). The removals of the OMP benzotriazole, carbamazepine, and sulfamethoxazole at the tested specific PAC doses after 0.5 h of adsorption in the three WWTP effluents, each with three different ratios of $c_{o,OMP}/c_{o,DOC}$, are shown in Supp. Fig. 14 (left). (Note that diclofenac is not shown as the concentrations of some of the “high” spiking levels were outside the linear range of the HPLC-MS/MS method.) The OMP removals at different $c_{o,OMP}/c_{o,DOC}$ in the same WWTP effluent vary by about $\pm 10\%$. E.g., at a specific PAC dose of 4 mg PAC/mg DOC, ~80% benzotriazole are removed in the WWTP effluent Schönerlinde, irrespective of the ratio of $c_{o,OMP}/c_{o,DOC}$. Similarly, ~85% carbamazepine are removed in the three Seevetal waters and ~30% sulfamethoxazole in the three Kressbronn waters. No trend can be observed that higher/ lower $c_{o,OMP}/c_{o,DOC}$ leads to increased/ decreased OMP removals. Accordingly, the initial OMP concentration $c_{o,OMP}$ (or the initial ratio of $c_{o,OMP}/c_{o,DOC}$) appears to have little to no influence on the removal of the respective OMP at a given PAC dose in the corresponding water. This confirms other studies where the relative OMP concentration after adsorption was constant in a water at a given PAC dose for variable $c_{o,OMP}$ (Graham et al. 2000, Knappe et al. 1998, Qi et al. 2007).

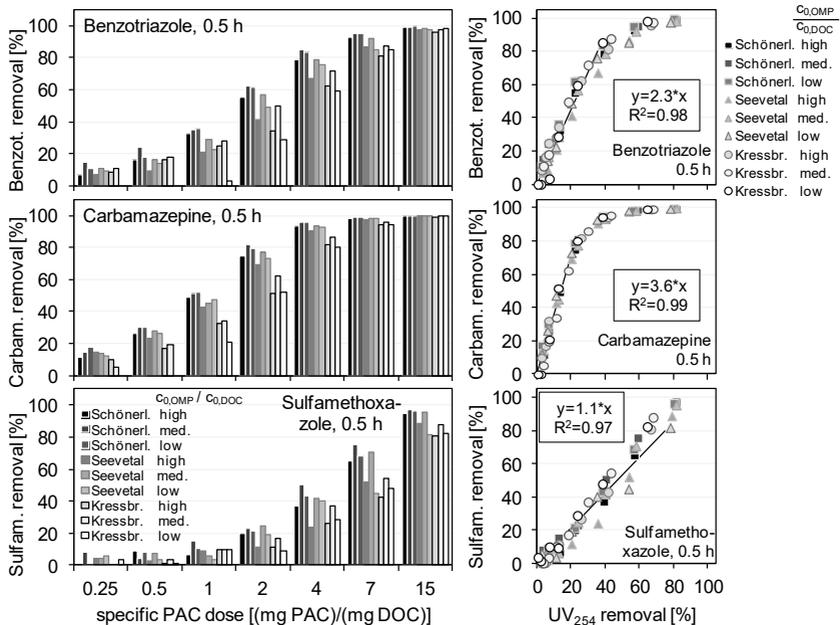


Supp. Fig. 12. Removals of the DOC, UV₂₅₄, benzotriazole, carbamazepine, diclofenac, and sulfamethoxazole versus specific PAC doses in the tested drinking waters, for 0.5 h (left) and 48 h (right) of adsorption.



Supp. Fig. 13. Removals of the DOC, UV₂₅₄, benzotriazole, carbamazepine, diclofenac, and sulfamethoxazole versus specific PAC doses in the tested WWTP effluents, for 0.5 h (*left*) and 48 h (*right*) of adsorption (note that the 0.5 h data for the DOC, benzotriazole, and diclofenac are also shown in the main document).

The OMP removals after 0.5 h of adsorption are depicted against the corresponding UV_{254} removals in the three WWTP effluents which were each spiked to three $C_{O,OMP}/C_{O,DOC}$ levels, in Supp. Fig. 14 (right), together with linear correlations for up to 80% OMP removal. At 20% UV_{254} removal, ~40% benzotriazole, ~60% carbamazepine, and 15–20% sulfamethoxazole removal are obtained, irrespective of the concentration level that was adjusted prior to the PAC adsorption tests. Accordingly, the different spiking levels in the three WWTP effluents have no impact on the correlations between the OMP and UV_{254} removals.

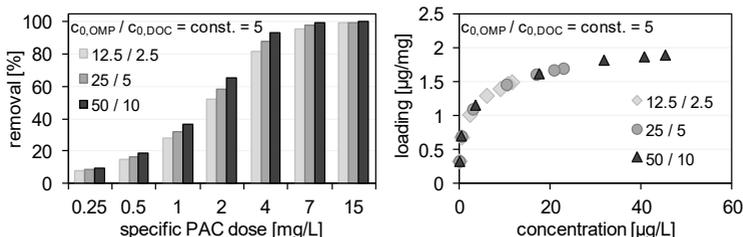


Supp. Fig. 14. *Left*: Benzotriazole (top), carbamazepine (middle), and sulfamethoxazole (bottom) removals at given specific PAC doses after 0.5 h of adsorption in the WWTP effluents Schönerlinde, Seevetal, and Kressbronn, at three different $C_{O,OMP}/C_{O,DOC}$ ratios, respectively, and *right*: Corresponding relationships to UV_{254} removal, with linear correlations.

Fictive exemplary calculations for loading and removal considerations

As calculated in a fictive example for a strong adsorbate with constant ratios of $C_{O,OMP}/C_{O,DOC}$ but varying absolute $C_{O,OMP}$ and $C_{O,DOC}$, the removals at given specific PAC doses are shown in Supp. Fig. 15 (left). The corresponding relationships between the PAC loadings with the OMP and the OMP liquid phase concentrations as resulting from the fictive example are given in Supp. Fig. 15 (right). The relationships between the loadings and the liquid phase concentrations overlap similar to the experimental data shown in the main document. Correspondingly, the removals increase with increasing $C_{O,OMP}/C_{O,DOC}$, as was observed in the

experiments. Accordingly, the experimentally observed increase of the OMP removals with increasing absolute $c_{o,OMP}$ and $c_{o,DOC}$ are a consequence of the relationships between the loadings and liquid phase concentrations.



Supp. Fig. 15. Exemplary removals and corresponding relationships between loadings and concentrations in three fictive waters with varying absolute OMP concentrations but constant DOC-relative OMP concentrations ($c_{o,OMP}/c_{o,DOC} = \text{const.}$).

Equivalent background compound model (EBCM) fits at variable initial OMP concentrations

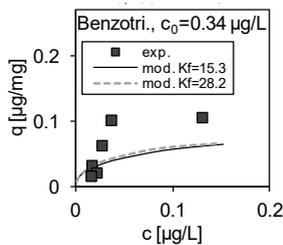
With the WWTP effluents Kressbronn, Seewetal, and Schönerlinde, additional PAC batch tests were conducted at lower and increased ratios of the initial OMP/ DOC concentration ratio, namely at ~ 2.5 µg/mg DOC (“low”) and ~ 10 µg/mg DOC (“high”), compared to ~ 5 µg/mg DOC (“medium”) in the main experiments conducted with all tested waters. The EBCM-based fits values for $c_{o,EBC}$ are shown in Supp. Tab. 6. In most cases, the fitted $c_{o,EBC}$ for the high concentration level are above the fitted $c_{o,EBC}$ for the medium and low concentration levels. Accordingly, the observed adsorption competition against the OMP is higher at the “high” concentration level, indicating additional adsorption competition, potentially caused by OMP competing against each other. This is relatively likely, as a spiked concentration level of ~ 10 µg/mg DOC corresponds to ~ 100 µg/L in a WWTP effluent with a DOC of 10 mg/L which is typical for e.g. Schönerlinde. The fitted $c_{o,EBC}$ for the “low” and “medium” concentration levels are more similar to each other in most cases, which indicates less additional OMP-induced mutual adsorption competition.

Supp. Tab. 6. Fitted initial EBC concentrations ($c_{o,EBC}$) for three WWTP effluents with varied ratios of the initial OMP/DOC concentrations (“low”, “medium”, “high”) at the two tested adsorption times.

	t [h]	Schönerlinde			Seevetal			Kressbronn		
		low	medium	high	low	medium	high	low	medium	high
Benzotriazole	0.5	5.5	5.0	6.8	6.1	4.9	8.5	3.7	1.6	3.1
	48	4.3	4.8	7.5	5.3	3.8	6.5	1.0	1.2	1.6
Diclofenac	0.5	7.7	7.1	8.5	5.3	6.7	7.9	4.8	3.8	4.3
	48	1.7	1.6	2.0	1.4	1.4	1.9	0.6	0.6	0.7
Sulfamethoxazole	0.5	17.3	13.2	19.4	23.0	10.6	19.4	7.7	5.9	8.1
	48	2.9	2.7	3.7	3.9	1.9	4.1	1.2	0.9	1.5

Sensitivity of the EBC initialization to $K_{F,EBC}$

Depending on the average EBC Freundlich coefficient $K_{F,EBC}$ used for fitting the initial EBC concentration $c_{o,EBC}$, different linear correlations between $c_{o,EBC}$ and $c_{o,DOC}$ will result. I.e., if $K_{F,EBC}$ is arbitrarily set to a lower value than in the main document, the fitted $c_{o,EBC}$ will generally be higher because the lower $K_{F,EBC}$ will characterize the EBC less competitive and thus, a higher $c_{o,EBC}$ is needed to model the observed adsorption competition against an OMP. The water-individual $K_{F,EBC}$ showed the highest variation for benzotriazole in the tested drinking waters, particularly because the value for the anonymous drinking water was comparatively high ($78 \text{ nmol/mg}^*(\text{L/nmol})^{1/n}$, units omitted hereafter). The sensitivity of the presented modeling procedure was checked by arbitrarily excluding this water from calculating the average $K_{F,EBC}$ and then conducting the fitting of $c_{o,EBC}$ again. The averaged $K_{F,EBC}$ were 28.2 (all drinking waters) versus 15.3 (without the anonymous drinking water). The new $c_{o,EBC}$ were again linearly correlated to the drinking water DOC values and the $c_{o,EBC}$ of the additional Berlin drinking water sample was determined using that correlation. Using the new $K_{F,EBC}$ (15.3) and $c_{o,EBC}$, the EBCM was conducted for the additional Berlin drinking water. The results, as well as the original EBCM run (all drinking waters included), are shown in Supp. Fig. 16. The two EBCM runs produce very similar results. Accordingly, the averaging of $K_{F,EBC}$ has overall little impact on the final outcomes of the presented procedure.



Supp. Fig. 16. EBCM runs of the additional Berlin drinking water sample at different average $K_{F,EBC}$ used for the fitting of $c_{o,EBC}$.

Considerations on OMP and BOM adsorption kinetics (based on the EBCM results)

Regarding the data shown in the main document, in almost all cases the fitted $K_{F,EBC}$ for 48 h of adsorption are higher than those fitted for 0.5 h of adsorption. This demonstrates that the BOM-induced adsorption competition increases during continuing OMP adsorption, even if more OMP are adsorbed after 48 h than after 0.5 h (as shown by decreased $c_{o,EBC}$ after 48 h compared to after 0.5 h). This observation indicates that OMP adsorb overall faster than most of the competing BOM.

The fact that the fitted EBC Freundlich properties vary for different adsorption times contradicts another study where globally constant EBC Freundlich parameters were used for variable adsorption times (Shimabuku et al. 2014). Different single-solute Freundlich parameters were used for modeling the two tested adsorption times of each OMP. Accordingly, similar $c_{o,EBC}$ should be fitted for both times if kinetic effects could be neglected. However, the relationships for 0.5 h of adsorption are located above those for 48 h. This demonstrates the BOM-induced kinetic hindrance of OMP in drinking waters/ WWTP effluents as compared to single-solute systems.

For benzotriazole, the linear correlations for the two tested adsorption times are located closer to each other than for diclofenac or sulfamethoxazole. In contrast, the differences of the $K_{F,EBC}$ for the two tested adsorption times are higher for benzotriazole. These differences between the tested OMP may be caused by the different molecular sizes of the OMP, 119 g/mol (benzotriazole), 253 g/mol (sulfamethoxazole), and 295 g/mol (diclofenac). The potential effect may be that benzotriazole is subject to very little BOM competition at the beginning and reaches its equilibrium loadings faster than the other OMP. Due to the ongoing adsorption of BOM, the increase of the BOM competition increases with time more than for the other OMP.

References

The cited references are contained in the general bibliography in Appendix A, p. 125.

B-5 Unifying granular activated carbon breakthroughs

Granular activated carbon adsorption of organic micro-pollutants in drinking water and treated wastewater – aligning breakthrough curves and capacities

Water Research 92 (2016), 180–187

Determination of average particle diameter

The particle fraction distribution, with a fraction width of 0.005 mm (5 μm), resulting from the dynamic image analysis is given in Supp. Fig. 17. As indicated by the framed box, the density distribution reaches its maximum around 0.12 mm. Accordingly, taking 120 μm as the average particle diameter for subsequent calculations of the rapid small-scale column tests appears feasible.

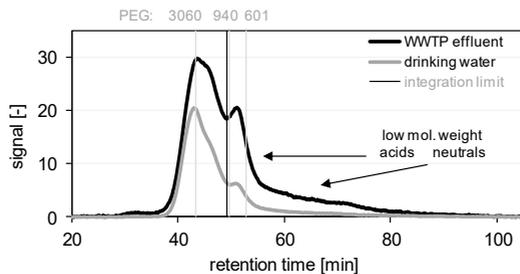
Particle fraction distribution				Particle fraction distribution (continued)			
from [mm]	to [mm]	density distribution [%]	cumulative distribution [%]	from [mm]	to [mm]	density distribution [%]	cumulative distribution [%]
	< 0.045	0.0	0.0	0.190 -	0.195	0.8	96.4
0.045 -	0.050	0.0	0.0	0.195 -	0.200	0.6	97.0
0.050 -	0.055	0.0	0.0	0.200 -	0.205	0.5	97.5
0.055 -	0.060	0.1	0.1	0.205 -	0.210	0.5	98.0
0.060 -	0.065	0.4	0.5	0.210 -	0.215	0.3	98.3
0.065 -	0.070	0.6	1.1	0.215 -	0.220	0.3	98.6
0.070 -	0.075	1.0	2.1	0.220 -	0.225	0.2	98.8
0.075 -	0.080	1.5	3.6	0.225 -	0.230	0.2	99.0
0.080 -	0.085	2.2	5.8	0.230 -	0.235	0.2	99.2
0.085 -	0.090	3.2	9.0	0.235 -	0.240	0.1	99.3
0.090 -	0.095	4.0	13.0	0.240 -	0.245	0.1	99.4
0.095 -	0.100	5.0	18.0	0.245 -	0.250	0.1	99.5
0.100 -	0.105	5.9	23.9	0.250 -	0.255	0.1	99.6
0.105 -	0.110	6.6	30.5	0.255 -	0.260	0.0	99.6
0.110 -	0.115	6.9	37.4	0.260 -	0.265	0.1	99.7
0.115 -	0.120	7.2	44.6	0.265 -	0.270	0.0	99.7
0.120 -	0.125	7.1	51.7	0.270 -	0.275	0.1	99.8
0.125 -	0.130	6.8	58.5	0.275 -	0.280	0.0	99.8
0.130 -	0.135	6.2	64.7	0.280 -	0.285	0.0	99.8
0.135 -	0.140	5.6	70.3	0.285 -	0.290	0.1	99.9
0.140 -	0.145	5.0	75.3	0.290 -	0.295	0.0	99.9
0.145 -	0.150	4.2	79.5	0.295 -	0.300	0.0	99.9
0.150 -	0.155	3.6	83.1	0.300 -	0.305	0.0	99.9
0.155 -	0.160	3.0	86.1	0.305 -	0.310	0.0	99.9
0.160 -	0.165	2.4	88.5	0.310 -	0.315	0.0	99.9
0.165 -	0.170	2.0	90.5	0.315 -	0.320	0.0	99.9
0.170 -	0.175	1.7	92.2	0.320 -	0.325	0.0	99.9
0.175 -	0.180	1.3	93.5	0.325 -	0.330	0.1	100.0
0.180 -	0.185	1.2	94.7	0.330 -	0.335	0.0	100.0
0.185 -	0.190	0.9	95.6	0.335 -	0.340	0.0	100.0

Supp. Fig. 17. Fraction distribution of the ground and sieved granular activated carbon used in the rapid small-scale column tests.

Molecular weight ranges of LC-OCD fractions

The retention times of several polyethylene glycols (PEG) are shown in Supp. Fig. 18, together with the WWTP effluent and drinking water chromatograms, and the chosen integration limit. The numbers right to “PEG” refer to different nominal molecular weights of the PEG, with the corresponding retention times indicated as vertical grey lines below. As

demonstrated, the chosen integration limit is $\sim 1,000$ g/mol. Most OMP have smaller molecular weights and accordingly, the fractions of the low molecular weight acids and neutrals contain background organic matter (BOM) of a similar size range.



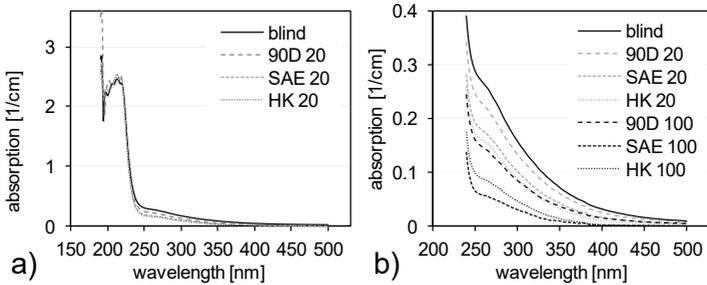
Supp. Fig. 18. LC-OCD chromatograms of the tested WWTP effluent and drinking water, with low molecular weight acid and neutral indicators and low molecular weight organics integration limit (thin black vertical line) and retention times for three polyethylene glycols (PEG, grey vertical lines).

B-6 UV absorption for activated carbon evaluation

Estimating organic micro-pollutant removal potential of activated carbons using UV absorption and carbon characteristics

Water Research 56 (2015), 48–55

UV/ vis scans in the wavelength range 190–500 nm of the blind wastewater treatment plant (WWTP) effluent sample and selected PAC-treated samples are shown in Supp. Fig. 19. Below a wavelength of 250 nm, the differences between the untreated blind WWTP effluent sample and the treated water samples are very low and vary without apparent relationship to the applied PAC dose. Above 250 nm, the absorption intensity declines continuously, in the untreated blind WWTP effluent sample as well as in the PAC-treated water samples. Therefore, choosing a wavelength of 254 nm for UV absorption measurements guarantees a high sensitivity and appears feasible to assess overall UV/ vis absorption in these water samples.



Supp. Fig. 19. UV/ vis absorption scans from 190–500 nm wavelengths (*a*, left) and 245–500 nm (*b*, right) for the blind WWTP effluent sample and selected PAC-treated samples; 20: 20 mg/L PAC, 100: 100 mg/L PAC.

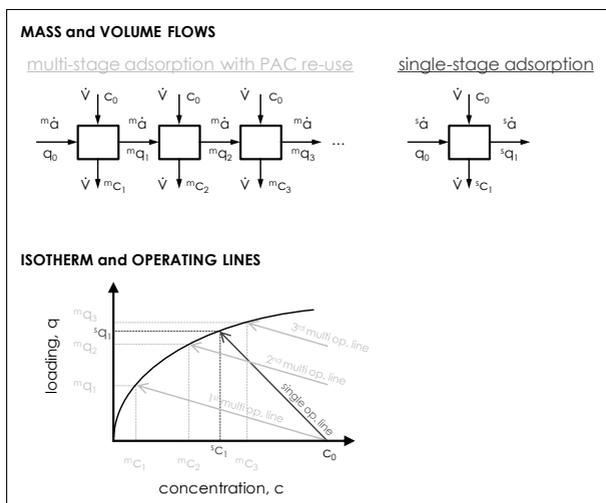
B-7 Multi-stage powdered activated carbon adsorption

Lab-testing, predicting, and modeling multi-stage activated carbon adsorption of organic micro-pollutants from treated wastewater

Water Research 83 (2015), 52–60

Schematic overview of mass and volume flows, isotherm & operating lines

A scheme of the occurring mass and volume flows in multi-stage and single-stage setups is given in Supp. Fig. 20 (top), with \dot{V} , \dot{a} , c_i , q_i being the water volumetric flow, the powdered activated carbon (PAC) mass flow, the concentration, and the loading, and the indices m and s corresponding to multi- and single-stage setups, respectively. The corresponding operating lines of the multi- and single-stage setups are given in Supp. Fig. 20 (bottom). The 2nd and 3rd stage operating lines of the multi-stage setup begin at $q \neq 0$, because loaded PAC from the previous stages is used. The operating line of the single-stage setup is steeper than the operating lines of the multi-stage setup, because in the shown scheme $m\dot{a} = 3 * s\dot{a}$. This is because the total volume of water treated in the multi-stage setup is $3 * V$. Altogether, the PAC/ water ratio in the multi-stage setup is $(3 * s\dot{a}) / (3 * \dot{V}) = s\dot{a} / \dot{V}$ which is the PAC/ water ratio in the single-stage setup and which is the only feasible ratio for comparison.



Supp. Fig. 20. *Top*: Scheme for mass and volume fluxes in multi-stage (*left*) and single-stage (*right*) setups; *bottom*: Isotherms and multi- & single-stage operating lines with corresponding concentrations and loadings.

Separation of powdered activated carbon-water suspensions

Photos of the laboratory equipment used to separate the suspension of the powdered activated carbon (PAC) and the water and to remove the supernatant from the centrifuge beakers are shown in Supp. Fig. 21, together with an image of the centrifuge beaker interior after the centrifugation and the removing of the supernatant. The modified bulb pipette was equipped with a fixed rubber ring so that it was not possible to insert the pipette too deeply into the centrifuge beaker (which could otherwise have caused removal of settled PAC from the bottom of the beaker).



Supp. Fig. 21. Modified bulb pipette (*left*), the removal of supernatant from a centrifuge beaker (*middle*), and the inside of a centrifuge beaker after the removal of the supernatant (*right*).

Simplified multi-stage modeling with pseudo single-solute Freundlich equations replacing the more complex Equivalent Background Compound Model equations

The typical Freundlich isotherm equation is given in Supp. Eq. 3, with the loading q , the concentration c , and the Freundlich parameters K_F and $1/n$. Supp. Eq. 4 shows the mass balance for stage i , with d , c_o , c_i , q_i , and q_{i-1} being the PAC dose in [mg/L], the initial concentration in [$\mu\text{g/L}$] or [nmol/L], the concentration in stage i , and the loadings in stage i , and stage $i-1$, respectively. While the PAC is reused from stage $i-1$ to stage i , the loading q_{i-1} is transferred to stage i . Accordingly, with each additional stage i , the loading increases, following the operating line defined by m , c_o , and q_{i-1} . The mass balances for various PAC doses d and variable stages i can be equated with the Freundlich isotherm equation of the respective OMP (Supp. Eq. 5), using a mathematical solver program, in order to find c_i . With the c_i values, removals can be calculated from which the corresponding removals of a single stage process with a comparable PAC dose can be subtracted. Comparable multi/ single stage PAC doses can be calculated using Supp. Eq. 6.

$$q = K_F c^n \quad \text{Supp. Eq. 3}$$

$$Q_i = \frac{c_o - c_i}{d} + Q_{i-1} \quad \text{Supp. Eq. 4}$$

$$\frac{c_o - c_i}{d} - K_F c_i^n = 0 \quad \text{Supp. Eq. 5}$$

$$d_{single} = \frac{d_{multi}}{i} \quad \text{Supp. Eq. 6}$$

Additional graphics

In addition to Fig. 38 of the main document, Supp. Fig. 22 shows the corresponding 24 h correlations of effective organic micro-pollutant and UV_{254} removals (for means of comparability, the 0.5 h data are included, too). In addition to Fig. 39 of the main document, Supp. Fig. 23 shows the corresponding 24 h isotherms of the 3-stage tests that were conducted. In addition to Fig. 40 of the main document, Supp. Fig. 24 shows the modeled additional removals for a contact time of 24 h.

Additional experiments

Data of a multi-stage experiment with lower PAC doses than shown in the main document are presented in the following. The effective removals of different organic micro-pollutants (OMP) and the DOC are depicted versus the effective PAC doses in several single and multi-stage setups after 0.5 h and 24 h adsorption time in Supp. Fig. 25. Note that the graphics for 0.5 h also include curves from a single-stage test with 1.5 h adsorption time. The results from that setup can be compared with the 3-stage test with 0.5 h adsorption time.

Similar to the experiments shown in the main document, the data presented here demonstrate that the multi-stage reuse of PAC can increase the removal of OMP and the DOC. Also, a 3-stage PAC reuse setup with 0.5 h contact time per stage can reach comparable effective removals as a 1-setup with 1.5 h contact time. Practically, the 3-stage 0.5 h setup would require only 1/3 of the contactor space of the 1-stage 1.5 h setup. This underlines the practical benefits from multi-stage PAC reuse.

Furthermore, two other possible experimental setups are shown in Supp. Fig. 25 (right): A water-only reuse configuration (addition of fresh PAC to the same water in three stages), as well as a configuration which combines PAC and water reuse (1st stage: fresh water + fresh PAC, 2nd stage: fresh water + PAC after 1st stage, 3rd stage: water after 2nd stage + fresh PAC). For benzotriazole and diclofenac, the combination setup reaches similar results as the PAC-only reuse setups, for sulfamethoxazole and the DOC the effective removals are lower. The water-only setup reaches overall poorer results than the other configurations.

Analogous to the loading curves/ isotherms shown in the main document, additional data from experiments with lower PAC dosages are shown in Supp. Fig. 26. In contrast to the data shown in the main document, the data shown here suggest that in the case of weak adsorbates like sulfamethoxazole, additional PAC reuse stages are barely useful because the weak adsorbates appear to not adsorb onto the PAC after the first stage. This demonstrates that PAC doses must be set high enough to reach additional adsorption in subsequent stages and to test for reliable loading data for the estimation of additional adsorption.

Modeling weak adsorbate multi-stage adsorption with the Equivalent Background Compound Model (EBCM)

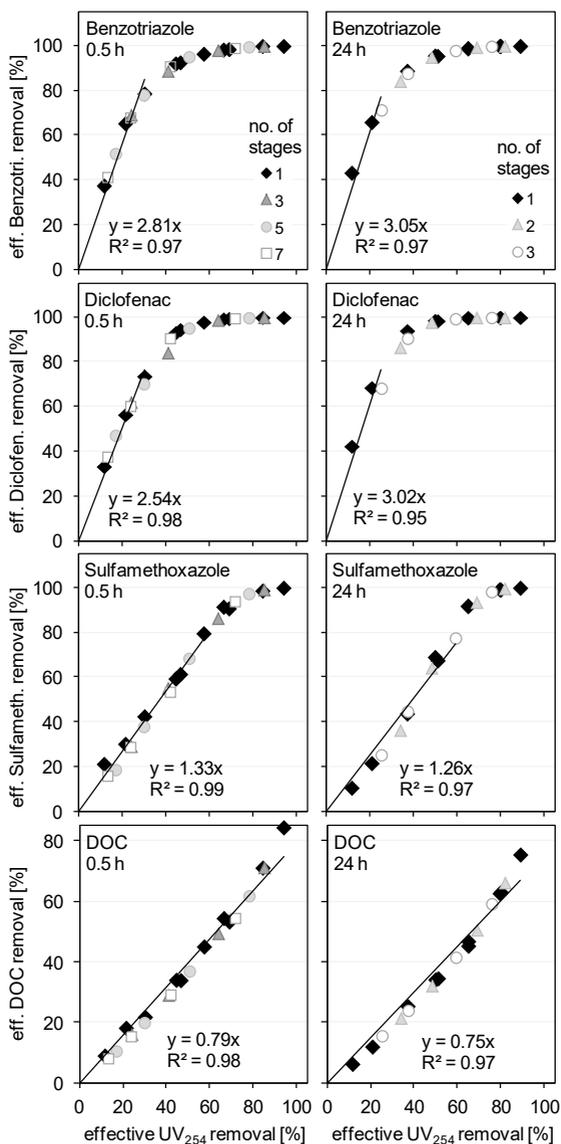
In typical single-stage scenarios, the EBCM can adequately predict loading curves/ isotherms which have negative slopes close to the initial concentration, which is usually the case for weak adsorbates. This feature of the EBCM cannot be successfully applied for the prediction of multi-stage adsorption phenomena. Given that the 1st stage loading curve/ isotherm is valid for subsequent stages, the loadings of weak adsorbates near the initial concentration would decline from stage to stage: $q_{i,OMP} < q_{i-1,OMP}$. However, this was only observed to a very little extent, for sulfamethoxazole and very low PAC dosages and short contact times (0.5 h), cf. Supp. Fig. 26.

Furthermore, for weak adsorbates, the Freundlich coefficient of the OMP is usually smaller than the Freundlich coefficient of the EBC: $K_{F,OMP} < K_{F,EBC}$. However, this leads to modeled multi-stage OMP loadings $q_{i,OMP}$ that lie above the 1st stage loading curve/ isotherm. This does not go in line with the experimental observations (loadings of subsequent stages near/ on 1st stage loading curve/ isotherm).

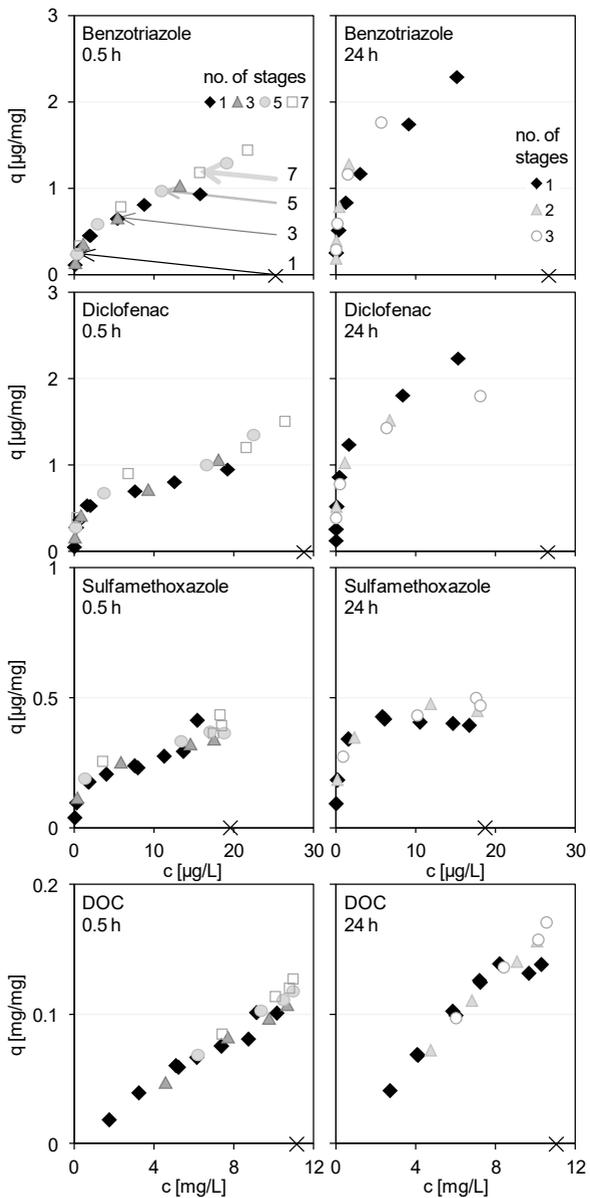
Accordingly, weak adsorbates such as sulfamethoxazole should be modeled by setting $K_{F,EBC} = K_{F,OMP}$ and omitting data points close to the initial concentration so that the negative slopes of the 1st stage loading curves/ isotherms remain unconsidered in the EBCM. This constraint appears acceptable, given that PAC reuse can only be successful if PAC doses are chosen high enough.

Equivalent Background Compound Model (EBCM) results for fictive parameter combinations

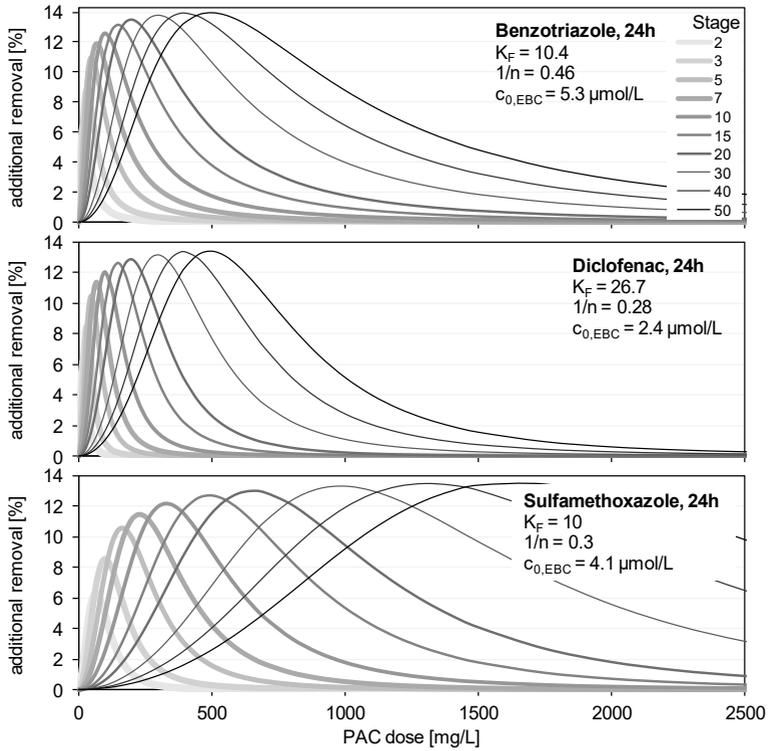
A collection of graphs for several fictive input parameter sets to the EBCM multi-stage modeling is shown in Supp. Fig. 27, Supp. Fig. 28, and Supp. Fig. 29. These graphs demonstrate the different impacts of the input parameters to the model results. Higher Freundlich parameter values lead to curves of the additional removal that are shifted to the left. Decreasing initial concentrations of the EBC result in a similar effect. As shown in the main document, the Freundlich coefficient $1/n$ has an impact on the maximum possible achievable additional removal.



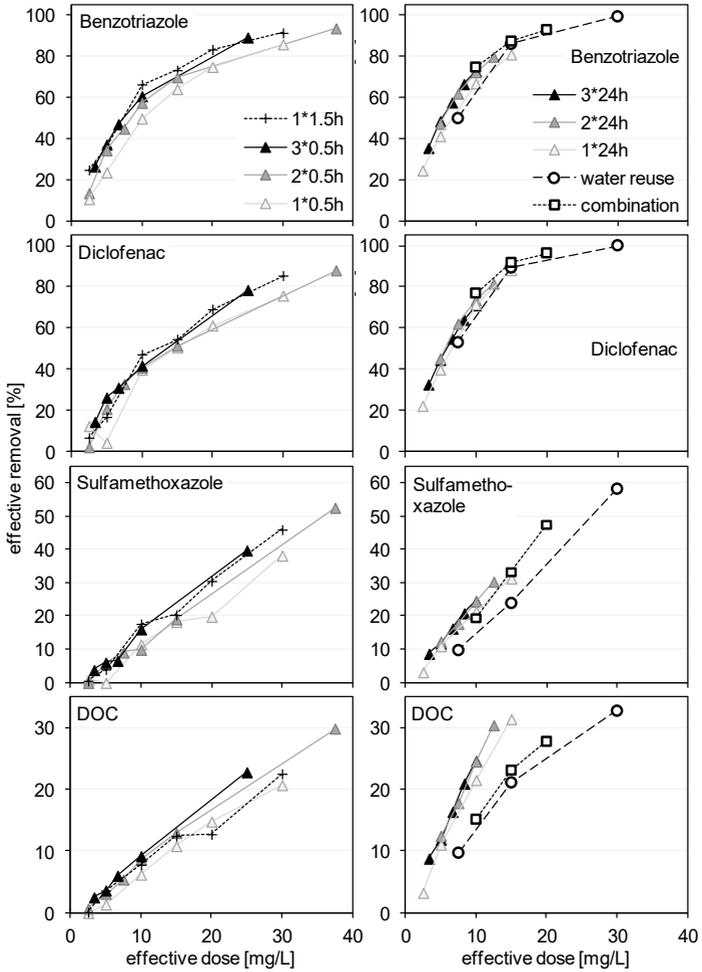
Supp. Fig. 22. Effective organic micro-pollutant and DOC removals versus effective UV₂₅₄ removals in single and multi-stage setups, after 0.5 h (*left*) and 24 h (*right*) adsorption per stage, with linear trend lines ($\leq 80\%$ OMP removal); note the different symbol allocation on the left and right sides.



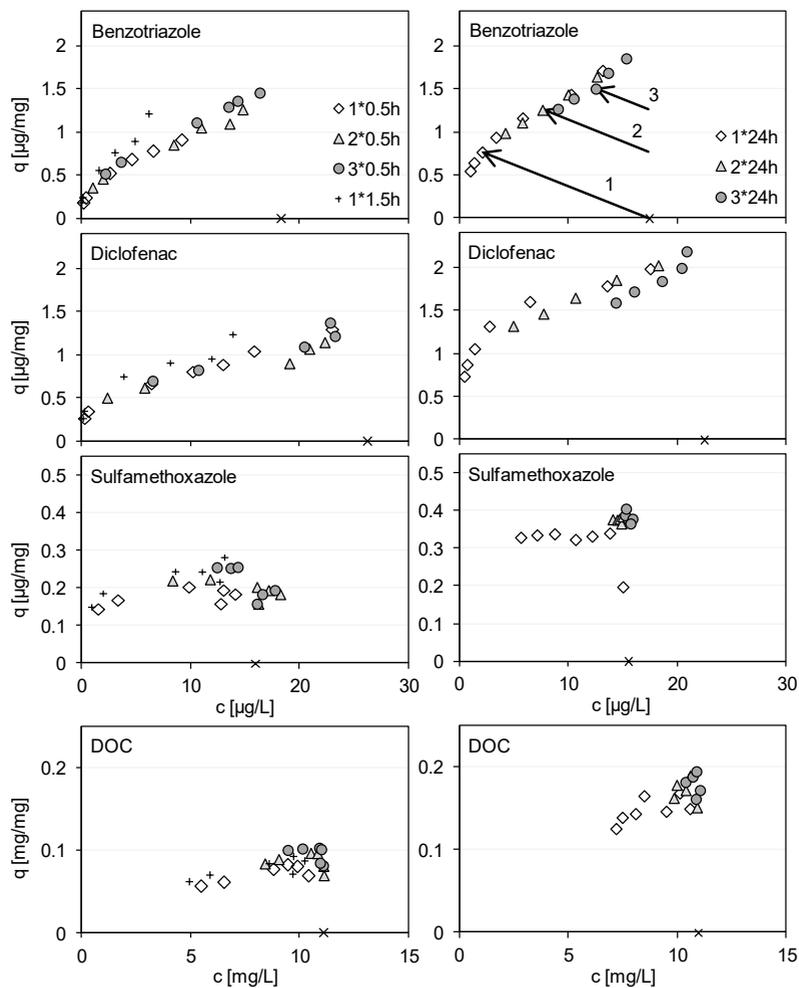
Supp. Fig. 23. Loading curves (0.5 h, left) and isotherms (24 h, right) for organic micro-pollutants and the DOC, after single and multi-stage PAC adsorption; with initial concentrations (\times signs) and exemplary 0.5 h operating lines for a PAC dose of 100 mg/L (benzotriazole); note the different symbol allocation on the left and right sides and the different x- and y-axes scaling.



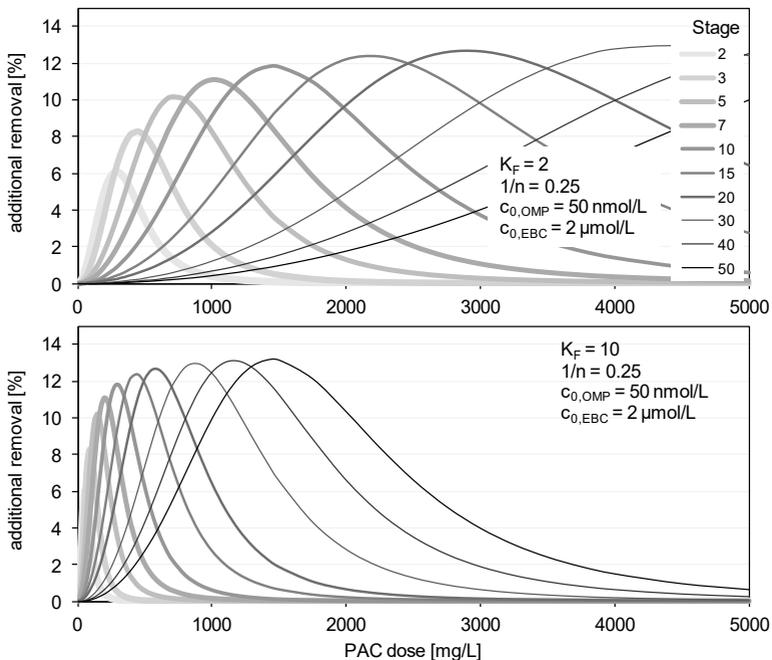
Supp. Fig. 24. Modeled additional OMP removals in multi-stage PAC reuse setups compared to single-stage setups with the same effective PAC dose for 24 h adsorption time.



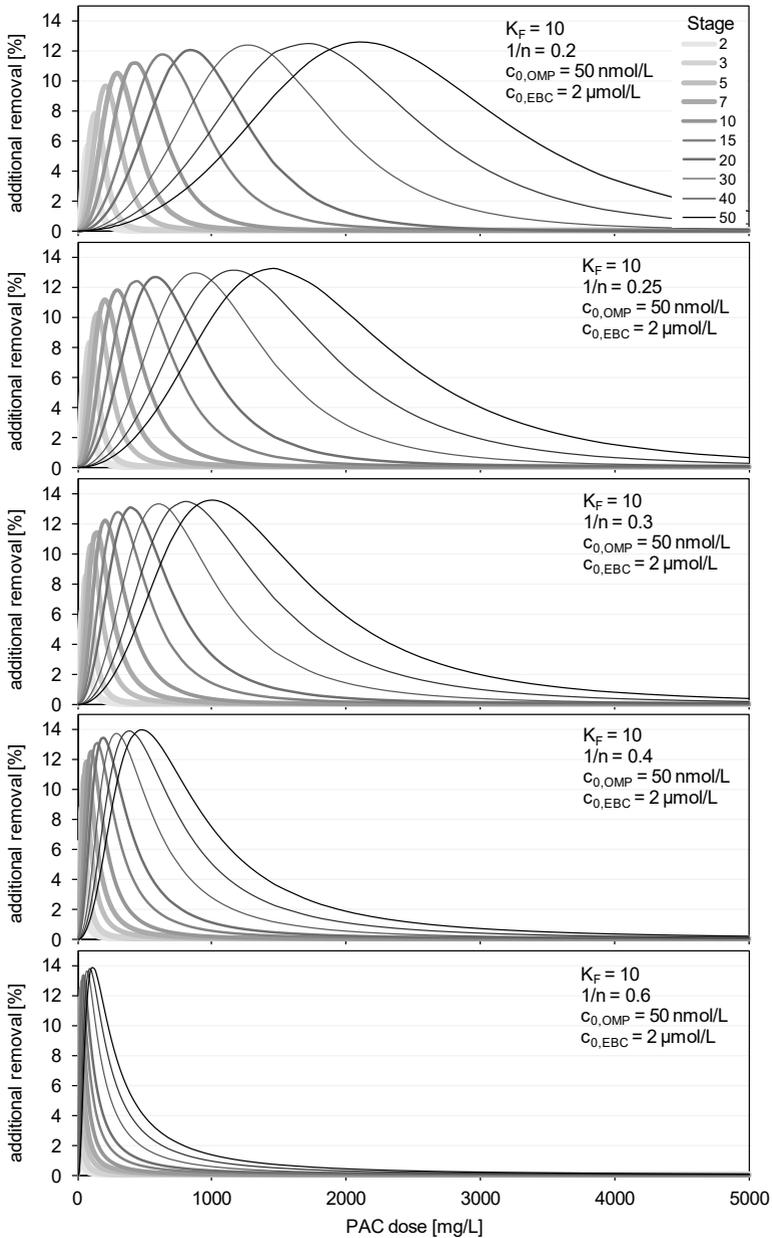
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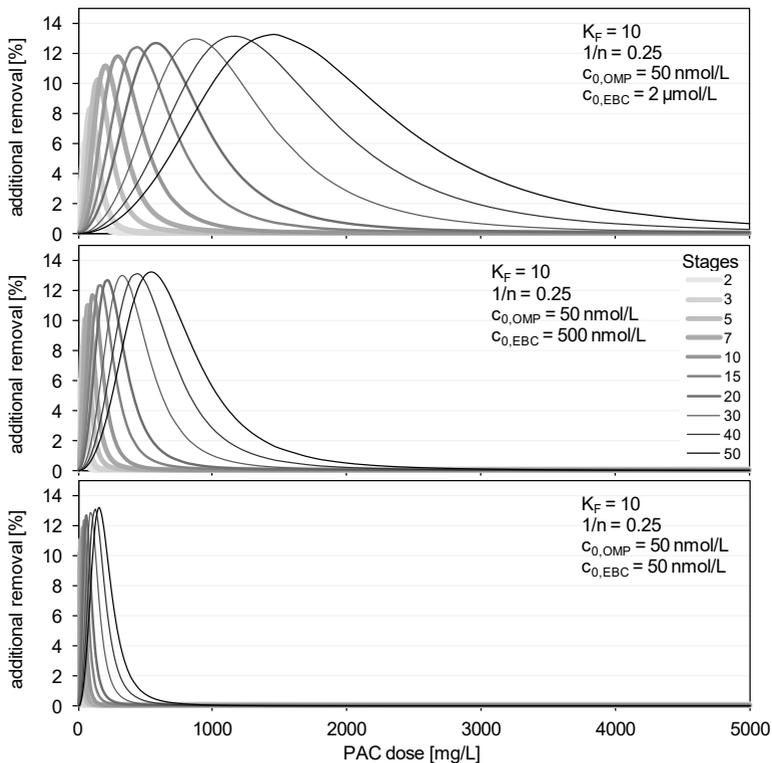
Supp. Fig. 26. Loading curves (0.5 h and 1.5 h adsorption time, *left*) and isotherms (24 h adsorption time, *right*) for selected organic micro-pollutants and the DOC, after 1, 2, 3 adsorption stages, with exemplary 24 h operating lines for a PAC dose of 20 mg/L (benzotriazole); note the different x- and y-axes scaling.



Supp. Fig. 27. Multi-stage EBCM additional removals (compared to single-stage setups with equivalent PAC dosages) for Freundlich coefficient K_F values of 2 and 10.



Supp. Fig. 28. Multi-stage EBCM additional removals (compared to single-stage setups with equivalent PAC dosages) for Freundlich exponent $1/n$ values of 0.2, 0.25, 0.3, 0.4, and 0.6.



Supp. Fig. 29. Multi-stage EBCM additional removals (compared to single-stage setups with equivalent PAC dosages) for initial EBC concentrations of 2,000, 500, and 50 nmol/L.

C Acronyms & notation

ACRONYMS

AC	activated carbon
ADSA	adsorption analysis
B.E.T.	Brunauer-Emmett-Teller (surface)
BOM	background organic matter
BTC	breakthrough curve
BV	bed volume
BV _{x%}	bed volumes at x% breakthrough
CUR	carbon usage rate
CUR _{x%}	carbon usage rate at x% breakthrough
DOC	dissolved organic carbon
DW	drinking water
eff.	effluent
EBC	equivalent background compound
EBCM	equivalent background compound model
sEBCM	simplified equivalent background compound model
EBCT	empty bed contact time
EBCT _{LC} , EBCT _{SC}	empty bed contact time of large/ small column
EfOM	effluent organic matter
ESI	electrospray ionization
FI	fluorescence index
GAC	granular activated carbon
HCOOH	formic acid
HLR	hydraulic loading rate
HPLC	high performance liquid chromatography
HPLC-MS/MS	high performance liquid chromatography with tandem mass spectrometry
HSDM	homogeneous surface diffusion model
IAST	ideal adsorbed solution theory
LC	large column
LC-OCD	liquid chromatography with online carbon detection
LDF	linear driving force
LMW	low molecular weight
MeOH	methanol
MIB	2-methylisoborneol
MS	mass spectrometry
MS/MS	tandem mass spectrometry
MTZ	mass transfer zone
NF	nanofiltration

NOM	natural organic matter
O ₃	ozone
OC	organic carbon
OMP	organic micro-pollutant
PAC	powdered activated carbon
PEP	phosphorous elimination plant
PVDF	polyvinylidene fluoride
QSAR	quantitative structure activity relationship
Re	Reynolds number
Re _{LC} , Resc	Reynolds number of large/ small column
Re _{SC,min}	minimum Reynolds number of small column
RO	reverse osmosis
RSSCT	rapid small-scale column test
SC	small column
SUVA	specific ultraviolet absorption
TIC	total inorganic carbon
TOC	total organic carbon
TP	throughput
TRC	tracer (model)
UF	ultrafiltration
UPLC	ultra high performance liquid chromatography
UV ₂₅₄ , UVA ₂₅₄	ultraviolet absorption/ absorbance at 254 nm
UV/ vis	ultraviolet/ visual light
VS	versus
visA	visual light absorption
WWTP	wastewater treatment plant

NOTATION

$1/n$	Freundlich exponent
$1/n_i$	Freundlich exponent of component i
c	concentration (liquid phase concentration)
c/c_o	relative concentration
c_{eq}	equilibrium concentration
c_i	concentration of component i
$c_{i,meas}$	measured concentration of component i
$c_{i,mod}$	modeled concentration of component i
$c_{mod,j}$	modeled concentration at isotherm/ loading curve point j
$c_{meas,j}$	measured concentration at isotherm/ loading curve point j
c_o	initial concentration
$c_{o,i}$	initial concentration of component i
c_s	concentration at external particle surface
$c_{x,i}$	concentration of component i at throughput x
δ	film thickness
D_{ax}	axial dispersion coefficient
D_L	liquid diffusion coefficient

D_P	pore diffusion coefficient
D_S	surface diffusion coefficient
d	activated carbon dose
d_P	particle diameter
$d_{P,LC}, d_{P,SC}$	particle diameter of large/ small column
ε_B	bed porosity
G_i	minimization term
i	component i
k_F	film diffusion coefficient
k_S^*	intraparticle mass transfer coefficient of linear driving force model
K_F	Freundlich coefficient
$\widehat{K}_{F,EBC,av,ALL}$	average equivalent background compound Freundlich coefficient
$\widehat{K}_{F,EBC,av,DRIN.WAT.}$	average drinking water equivalent background compound Freundlich coefficient
$\widehat{K}_{F,EBC,av,WWTPeff.}$	average wastewater treatment plant effluent equivalent background compound Freundlich coefficient
$\widehat{K}_{F,i}$	Freundlich coefficient of component i
m	mass (or activated carbon dose if indicated)
m_{GAC}	mass of granular activated carbon
$\widehat{M}in$	minimization term
N	number of data points
q	loading (solid phase concentration)
\bar{q}	average particle loading
q_{eq}	equilibrium loading
q_i	loading of component i
$q_{i,OMP}, q_{i,EBC}$	loading of organic micro-pollutant/ equivalent background compound in stage i
$q_{i-1,OMP}, q_{i-1,EBC}$	loading of organic micro-pollutant/ equivalent background compound in stage i-1
$q_{i,meas}$	measured loading of component i
$q_{i,mod}$	modeled loading of component i
$q_{mod,j}$	modeled loading at isotherm/ loading curve point j
$q_{meas,j}$	measured loading at isotherm/ loading curve point j
q_o	loading at initial concentration
$q_{o,i}$	loading at initial concentration of component i
q_T	total loading
ρ_B	bed density
ρ_P	particle density
R^2	coefficient of determination
r_P	particle radius
S	minimization term
t	time
V	volume
v	velocity
v_F	filter velocity
v_{LC}, v_{SC}	filter velocity in large/ small column
φ	spreading pressure term

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