



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



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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 ($c_{0,OMP}/c_{0,DOC}$). 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.

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1. 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., 2002b; 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

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compared with each other. The sampling locations are given in the [Supporting Information](#). 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 ($c_{0,OMP}/c_{0,DOC}$) 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 ($c_{0,OMP}/c_{0,DOC} \approx const.$) in all examined waters. Additional tests with three WWTP effluents were also conducted at varied $c_{0,OMP}/c_{0,DOC}$. 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, 2012; Najm et al., 1991; Newcombe et al., 2002b; Worch, 2010; Zietzschmann et al. 2014b, 2015b). 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 $c_{0,EBC}$ (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., 2014b) 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.

2. Materials & methods

2.1. 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](#)) 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 $\sim 5 \mu\text{g OMP/mg DOC}$. In additional experiments with the WWTP effluents Kressbronn, Seewetal, and Schönerlinde, the specific OMP concentrations were $\sim 2.5 \mu\text{g OMP/mg DOC}$ and $\sim 10 \mu\text{g OMP/mg DOC}$.

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.

2.2. Batch tests

Stock suspensions of the PAC *SAE Super* (*Norit*, Germany) were produced by drying ($105 \text{ }^\circ\text{C}$) 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 ($0.45 \mu\text{m}$, *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](#). 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 the PAC loadings over the 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.

2.3. Analytics

The OMP were measured with high performance liquid chromatography (HPLC) coupled with tandem mass spectrometry (MS/

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