

Assessment of the breakthrough of micropollutants in full-scale granular activated carbon adsorbers by rapid small-scale column tests and a novel pilot-scale sampling approach

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Abstract

This study aimed to compare three approaches for predicting the service life of full-scale GAC adsorbers for the removal of micropollutants. The approaches included (i) rapid small-scale column tests (RSSCT), (ii) two pilot-scale sampling approaches, and (iii) predictive correlations that consider micropollutant properties and background water matrix characteristics. The RSSCT could predict full-scale performance only if a micropollutant-specific fouling index was applied. At the pilot-scale, water samples were collected (1) over time at the top sampling point only (Empty Bed Contact Time (EBCT) of 1 minute) to minimize time to breakthrough (method 1) and (2) at different column depths at a single time point (method 2). Breakthrough curves obtained with method 2 more closely matched those obtained at the full-scale. In addition, method 2 is more convenient since it requires only one sampling campaign. Method 2 was used as a prognostic tool to predict breakthrough curves for micropollutants without full-scale data and a comparison with an existing prediction model gave satisfactory results for 6 out of 13 compounds.

Keywords: activated carbon, adsorption, full-scale breakthrough prediction, micropollutants.

1 Introduction

Drinking water safety is warranted by compliance with country-specific biological, physical and chemical standards (1). Apart from microbiological safety, control of anthropogenic micropollutants is of concern (2,3). The development of novel analytical tools that can measure a broader spectrum of compounds at lower concentrations has led to the detection of an increasing number of micropollutants in the aquatic environment and in drinking water (4,5). In terms of micropollutant abatement, a large number of non-destructive (e.g., adsorption, removal by membranes) (6,7) and destructive treatment processes (e.g., oxidation) (8) can be applied depending on raw water quality and micropollutant properties.

Granular activated carbon (GAC) and to a lesser extent powdered activated carbon (PAC) are commonly applied in drinking water treatment (9). This paper focuses on challenges associated with the prediction of GAC service life, which, for a given GAC, depends on the type and concentration of dissolved organic matter (DOM) and the physical chemical properties of the micropollutants (10). Rapid small-scale column tests (RSSCTs) offer a relatively simple and fast empirical method to estimate micropollutant breakthrough curves in a water matrix of interest (11,12). This approach has been intensively investigated over three decades to simulate full-scale adsorber performance (6,13–16). The main drawback of RSSCTs is that they overestimate the adsorption capacity of GAC for micropollutants that co-occur with DOM (17). GAC fouling by DOM is less pronounced in RSSCTs than in full-scale filters, because RSSCTs rely on GAC particles that are smaller than those applied in full-scale adsorbers (16). One explanation for the particle size-dependence of fouling is that micropollutants can penetrate into an adsorbent particle only up to a certain distance when DOM is present, and this penetration distance is independent of particle size (18). Thus, the inaccessible volume fraction at the core of an adsorbent particle increases with increasing grain size. Therefore, scale-up of RSSCT data requires the application of a fouling index to correct for the particle-size dependence of fouling (16), and this fouling index is compound-specific (17). Correlations to predict the fouling index were presented by Summers et al. (17).

Kennedy et al. (6) also developed an empirical model to predict the specific throughput for 10% micropollutant breakthrough. Model parameters include DOM concentration and micropollutant properties (e.g., pH-dependent octanol-water partition coefficient, log D_{ow} , and Abraham parameters) (6). The model was based on pilot-scale data obtained with a GAC grain size commonly used in full-scale treatment. The predictive model avoids the need for RSSCT experiments. However, when applied to a wastewater-impacted drinking water source, the specific throughput was overestimated, on average, by a factor of 4.2. Thus, it remains difficult to develop designs and cost estimate for GAC treatment systems without pilot tests. Therefore, in many cases pilot tests are still necessary to design a full-scale GAC adsorption system.

The goal of this study was to develop a reliable and efficient method to assess the breakthrough of a diverse selection of micropollutants in full-scale GAC adsorbers. To this end, we evaluated a RSSCT system and two methods for obtaining pilot-scale data: (1) tracking micropollutants in the GAC effluent as a function of time at a short empty bed contact time (EBCT) and (2) assessing micropollutant breakthrough at different bed depths in a GAC adsorber at a single time point. Finally, the benefits and drawbacks of the two pilot-scale sampling approaches relative to conventional predictive methods (i.e., RSSCT and model) were evaluated.

2 Materials and methods

2.1 Water samples

Pilot-scale tests were conducted with groundwater (water quality in Table S1, supporting information (SI)) at the Hardwald infiltration site near Basel (Switzerland) (19). The pilot plant was directly connected to the drinking water treatment plant influent in parallel to the full-scale GAC filters. For RSSCTs, Hardwald groundwater was collected and stored in 25 L containers at 4°C without pre-filtration prior to use (maximum storage time 3 weeks).

For RSSCTs, 20 synthetic organic micropollutants (Table S2, SI) were spiked into Hardwald groundwater with concentrations varying from about 30 to 3350 ng L⁻¹. These compounds, including X-ray contrast media, a sweetener, pesticides, pharmaceuticals, and anticorrosive compounds, were selected according to two criteria: (i) they were all present in Hardwald groundwater at different levels, and (ii) they represented a large range of hydrophobicity ($-3.1 < \log D_{ow} @ pH 8 < 3.4$), where $\log D_{ow}$ values were calculated online (<https://ilab.acdlabs.com/iLab2/>) for pH 8. Micropollutants were spiked at trace levels into the RSSCT feed water to permit the determination of contaminant breakthrough at low concentrations to avoid a preconcentration step, which would require larger sample volumes. Text S1, SI provides further information about the preparation of the RSSCT influent. No compounds were spiked into pilot- or full-scale systems.

2.2 Activated carbon

All adsorption tests were performed with sub-bituminous coal-based Calgon Filtrasorb® 400 GAC (Chemviron Carbon Corporation). Its surface area is 1050 m²/g and the porosity includes substantial mesopore and micropore volumes (Table S3, SI). GAC was used without any modifications in pilot- and full-scale adsorbers. For the RSSCT, GAC was crushed with a mortar and pestle, and the fraction in the range of 63 - 100 µm was collected with sieves before use. Crushed GAC was washed with nanopure water to ensure an elimination of fine particles

and dried at 105°C. The particle size distribution was determined with a Mastersizer 2000 instrument and the average size was 94.3 µm (Figure S1, SI).

2.3 Adsorption experiments at various scales

2.3.1 Rapid small-scale column test (RSSCT)

The RSSCT was designed according to the proportional diffusivity design (12,17) since this approach has been shown to effectively describe the kinetics of micropollutant adsorption from water containing dissolved organic matter (DOM). It was run for about 2 years at 12°C (i.e., average temperature of the Hardwald groundwater) in the dark to avoid the photodegradation of micropollutants and the development of algae. The columns were not backwashed during the two years of operation. In addition, we monitored the dissolved oxygen concentration after the columns on-line for a year, but the variation was not significant to indicate biological activity. Biological activity is not expected in this set-up because DOC was very low and the groundwater already passed through a soil passage with significant biological activity. No material was extracted during the study to guarantee a consistent operation of the columns. The experimental conditions are summarized in Table 1.

Table 1. Operating parameters for RSSCT, pilot-scale GAC adsorbers and full-scale GAC adsorbers

Parameters	RSSCT (2 columns in series)	Pilot-scale (10 columns in series)	Full-scale (3 filters in parallel)
GAC mean particle diameter - d_p (µm)	94.3	1000	1000
Overall GAC mass (g)	3.31	210	80 x 10 ⁶
Adsorber dimensions (cm) ⁽¹⁾	25.8 x 0.6 (D x d)	100 x 2.4 (D x d)	1350 x 525 x 250 (L x W x D)
Empty Bed Contact Time - EBCT (min)	2.3±0.1	10±0.1	19.5±4.1
Hydraulic loading rate (m h ⁻¹)	6.6±0.2	6.0±0.1	7.7±1.6
Flow rate (mL min ⁻¹)	3.2±0.1	45.2±0.1	(32.7±6.8) x 10 ⁶
Duration of experiments (days)	700	220	800

⁽¹⁾ D: bed depth, d: inside diameter, L: length, W: width

The RSSCT system consists of two columns in series filled with GAC. The water was stored in a glass bottle and pumped through the columns with a HPLC pump (Figure 1). Further details of the RSSCT system set-up are provided in the caption of Figure 1.

Three sampling points were installed to quantify the micropollutant concentration before and after treatment: an inlet point (A) directly after the HPLC pump, an intermediate sampling point (B) between the two columns and a sampling point (C) after the second column. The intermediate point was useful to elucidate whether or not normalized micropollutant breakthrough was independent of the EBCT.

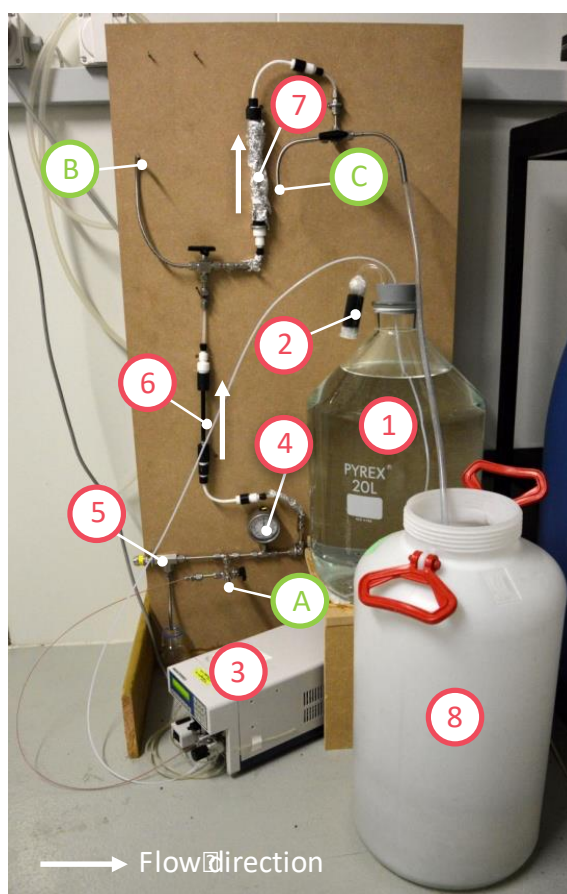


Figure 1. Experimental set-up for rapid small-scale column tests (RSSCTs). The feed solution was stored in a 20 L glass bottle (1) equipped on the top with a glass tube containing GAC (2) to avoid any pollution from the outside air. This solution was pumped with a HPLC pump (3) at a flow rate of 3.2 mL min^{-1} through two columns (6) and (7) in series. Each column was filled with 3 g of crushed GAC. A pressure gauge (4) was connected after the pump to guarantee a pressure of ≤ 3.5

bar, which is the maximum allowed pressure for the columns. Moreover, a relief valve (5) protected the columns against overpressure. The treated water was discharged into a waste tank (8). Three sampling points were added: before the column (A), between the two columns (B) and after the second column (C).

Twice a week, 50 g of water was sampled at the inlet, intermediate and outlet sampling points in glass beakers and immediately spiked with 50 µL of an internal standard solution (see Table S4, SI). These samples were frozen at -20°C prior to micropollutant analyses (see below).

In the analysis of RSSCT data, pore blockage induced by DOM was taken into account by introducing a fouling index calculated as follows (16), eq. 1:

$$\text{Fouling Index} = \text{SF}^Y \quad (1)$$

where SF is the scaling factor, the ratio between the GAC particle diameter in full-scale and in the RSSCT, and Y is an exponent equal to the ratio of Freundlich parameters determined for a breakthrough of 50% for RSSCT and full-scale adsorbers according to the method developed by Summers et al. (17).

Consequently, the specific throughput for full- and/or pilot-scale adsorbers can be calculated from the RSSCT as follows, eq. 2:

$$\text{Specific throughput}_{\text{Full-scale}} = \text{Specific throughput}_{\text{RSSCT}} / \text{SF}^Y \quad (2)$$

In this study, all RSSCT data were adjusted by the fouling index to represent the prediction of the specific throughput for full-scale GAC adsorbers.

2.3.2 Pilot-scale experiments

After the RSSCT experiments were completed, a pilot plant (SIMA-tec, Schwalmtal, Germany) was operated for 8 months at the drinking water treatment plant of the Hardwasser AG to follow the abatement of 20 micropollutants natively present in Hardwald groundwater and to investigate up-scaling of the RSSCT results. This pilot plant was built to test a novel sampling strategy with as-received GAC for an accelerated prediction of full-scale adsorber performance. The pilot-scale GAC set-up consisted of a series of 10 columns (Figure S2, SI, length: 10 cm,

inner diameter: 2.4 cm) and was operated at a flow rate of 45.2 mL min⁻¹. This set-up was built to mimic the first meter of bed depth of the full-scale GAC adsorbers at the Hardwald full-scale drinking water treatment plant.

Two sampling methods depicted in Figure 2 were tested to obtain breakthrough curves of micropollutants in the pilot-scale GAC columns. For method 1, time-resolved samples were collected after the first column (i.e., after 10 cm, EBCT = 1 min) during the entire testing period with the assumption that micropollutant adsorption is independent of the EBCT. This hypothesis was based on the RSSCT data described in section 3.1. With this approach, samples were collected over a relatively long time period (220 days). This approach requires either analysis of a small number of samples after each sampling event or storage of samples over a long time period. The main advantage of this method is that breakthrough is expected to occur 25 times faster than in a full-scale adsorber with a GAC bed depth of 250 cm. However, as shown by Hand et al. (20), if the column is too short, a constant adsorption pattern, i.e., a mass transfer zone of constant length and shape, will not develop and premature breakthrough might result.

For method 2, samples were collected only once (snapshot approach) after columns 1, 2, 3, 4, 5, 7, and 10 after 220 days of operation (i.e., about 8 months). The termination time was selected during the experiment based on the water quality after the first column of 10 cm. As shown in Figure 2, similar specific throughputs can be investigated using both methods because each column corresponds to one specific throughput at a given operation time. Method 2 requires only one sampling campaign, and micropollutant breakthrough curves were obtained after analyzing a single batch of samples. This main goal of these methods was to predict 20 months of full-scale operation in only 8 months of pilot testing with different ways. Considering sampling, handling, and analysis, method 2 is significantly more efficient than method 1.

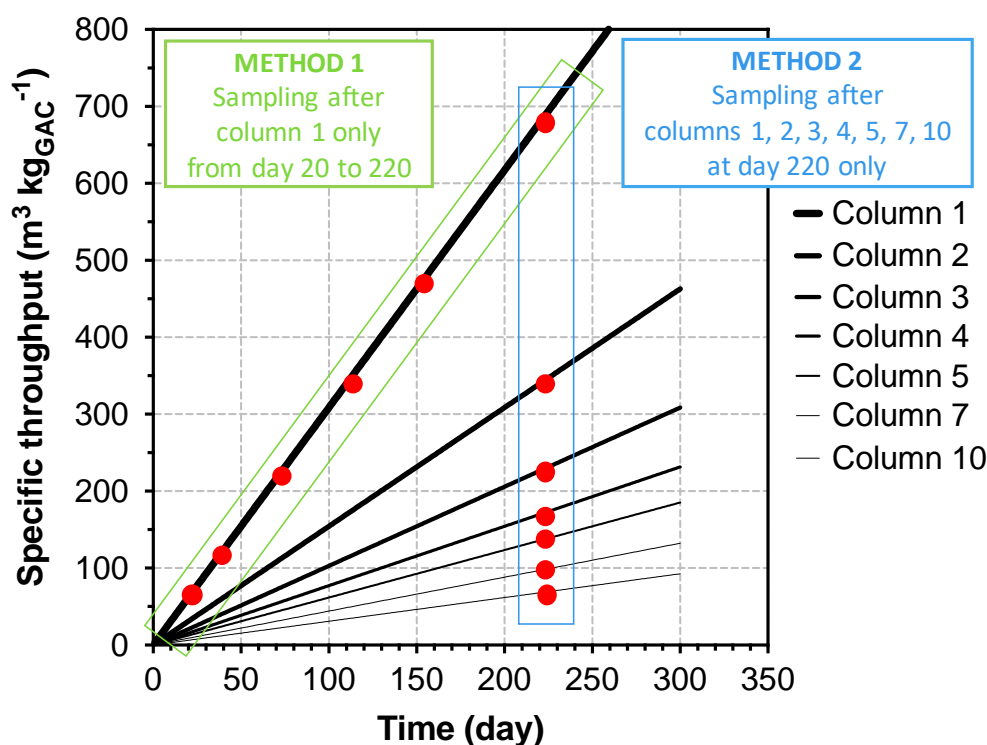


Figure 2. Two sampling strategies (method 1 and method 2, see text for discussion) were evaluated for the pilot-scale GAC adsorption system to assess micropollutant breakthrough as a function of specific throughput.

2.3.3 Full-scale facility

Full-scale GAC adsorbers at the Hardwasser drinking water treatment plant consisted of 3 rectangular contactors, operated in parallel, and filled with 177 m³ GAC each (Table 1; Gabriel and Meier, 2014). The adsorbers were backwashed every 2'000 hours. The activated carbon in the full-scale filters was fresh when RSSCT was started. Since the groundwater had a low turbidity, the adsorbers were run without pretreatment. Samples were collected after the effluents of the three adsorbers and were blended. The average hydraulic loading rate was 7.7±1.6 m h⁻¹ during the study period.

2.4 Micropollutant analyses

The 20 micropollutants spiked into Hardwald groundwater for the RSSCTs were quantified by a fully automated online solid phase extraction/liquid chromatography/mass spectrometry

system (online SPE-LC-MS/MS) (22). In a first step, 20 mL of a sample was loaded with a solution of acidic nanopure water (0.1% formic acid) on a 2-layer extraction cartridge made of 8 mg OASIS HLB (15 μ m, Waters) and 14 mg Isolute ENV+ (70 μ m, Biotage). The separation was performed at ambient temperature using an Atlantis T3 column (3.0 x 150 mm, 3 μ m particle size) with a HPLC gradient containing acidic nanopure water (0.1% formic acid) and methanol. The detection was performed with a Thermo TSQ-Vantage (Thermo Fisher Scientific) equipped with an electrospray ionization probe.

Calibration curves were established with standards prepared in nanopure water. The concentrations of the standards ranged from 1 to 1000 ng L⁻¹ for all compounds except the X-ray contrast agents, for which they were ten times higher, because of lower sensitivity of the analytical method for this class of compounds.

For the pilot- and full-scale experiments, the 20 native micropollutants listed in Table S5, SI were analyzed by liquid chromatography coupled with high-resolution mass spectrometry (QExactivePlus, Thermo Fisher Scientific). During sample preparation, 60 mL of sample was spiked with an internal standard mixture (see Table S6, SI) and concentrated under vacuum and reflux to 300 μ L using a Büchi Evaporator (Büchi Syncore Polyvap). The samples were reconstituted to 400 μ L using nanopure water and were centrifuged at 10,000 rpm for 2 min at room temperature to remove particles. Afterwards, 100 μ L of the concentrated sample was injected and separated on a reverse phase column (Atlantis T3C, 3 μ m, 3x150 mm). More information on the separation and detection of micropollutants is given by Munz et al. (23) and in the supporting information (Table S7, SI).

3 Results and discussion

3.1 Rapid small-scale column test (RSSCT)

The RSSCT was designed to simulate a full-scale filter with an expected EBCT of 27 min and was conducted over a period of 2 years, at which point only six of the selected compounds broke through at both the intermediate (i.e., after the first column) and the outlet sampling points: five X-ray contrast media (i.e., diatrizoate, iohexol, iomeprol, iopamidol and iopromide) and sucralose. These compounds were expected to break through early because they have log D_{OW} values < -0.8 at pH 8 (Table S2, SI) suggesting a low affinity for GAC (24).

Breakthrough curves for three compounds detected in the Hardwald groundwater during the test (i.e., diatrizoate, iopamidol and sucralose) are shown in Figure 2, and for the three X-ray contrast media absent in Hardwald groundwater at this period (iohexol, iomeprol, iopromide) in Figure S3, SI. Onset of breakthrough occurred at specific throughputs ranging from about 20 $m^3 kg_{GAC}^{-1}$ for diatrizoate to $> 60 m^3 kg_{GAC}^{-1}$ for sucralose (Figure 2). The specific throughput to 50% breakthrough, which is directly related to the adsorption capacity of the GAC (25), increased in the order diatrizoate $<$ iohexol $<$ iomeprol $<$ iopamidol $<$ iopromide $<$ sucralose. As shown previously (26), the elution order of these micropollutants is consistent with their log D_{OW} values except for diatrizoate (Table S2, SI). The poor removal of diatrizoate is most likely related to its low pK_a of 2.2, which means that it is negatively charged at pH 8. Neutral compounds are generally more adsorbable than their ionic counterparts (27,28). For the four other X-ray contrast agents, which are neutral at pH 8, removal efficiency decreased with an increasing number of hydroxyl groups on these structurally similar compounds in the order iopromide (4 OH groups) $>$ iopamidol (5 OH groups) $>$ iomeprol (5 OH groups) $>$ iohexol (6 OH groups) (Figures S3 b-e, SI) because their ability to strongly interact with water via H-bonding increased. As a result, the required energy to strip off the water shell to make an adsorption on activated carbon possible increased as the number of hydroxyl groups on the adsorbates increased (29).

Overall, there was a weak dependence of the EBCT on the breakthrough of micropollutants because the data at the intermediate and outlet points are closely overlaid (Figure 3 and S3, SI). For the tested water and micropollutants, this finding suggests that RSSCTs simulating shorter EBCTs, which can be completed more quickly, provide similar predications of carbon use rates to RSSCT's simulating long EBCTs.

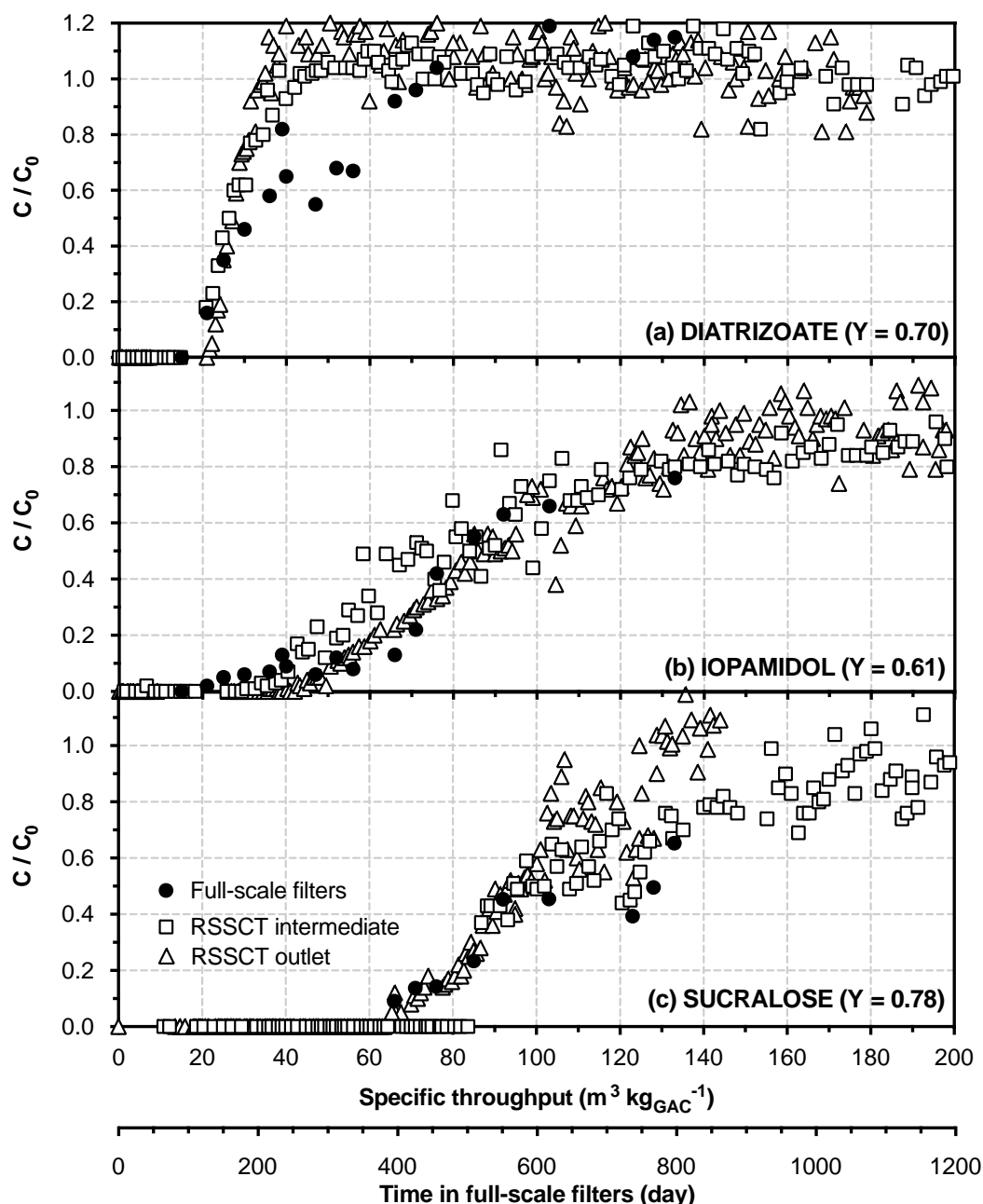


Figure 3. Breakthrough curves for (a) diatrizoate, (b) iomeprol and (c) sucralose (open squares for intermediate, open triangles for outlet sampling point). The full-scale data are shown in closed circles. RSSCT data were corrected with the fouling index calculated with compound-specific Y

exponents for comparison to the full-scale data set (see text). Note: The onset of sucralose breakthrough at the intermediate sampling point was not captured well because of a high limit of quantification (LOQ). For the outlet sampling point, the LOQ was improved, enabling measurements at lower concentrations. Hardwald groundwater: DOC = 0.49 ± 0.05 mgC L⁻¹; pH 8.05 ± 0.10 .

Full-scale GAC performance was effectively described by the RSSCT after scaling specific throughput values with a compound-specific fouling index [5.22 ($Y = 0.70$) for diatrizoate, 4.22 ($Y = 0.61$) for iopamidol and 6.31 ($Y = 0.78$) for sucralose] (Figure 3). Y may also vary with initial micropollutant concentrations (16). This criterion would be fulfilled here, since the initial concentrations of the X-ray contrast media were about an order of magnitude higher than for sucralose.

The GAC fouling was confirmed by DOC breakthrough, which occurs prior to breakthrough of all micropollutants (Figure S4, SI), suggesting that DOM preloading and associated GAC pore blockage affects micropollutant adsorption as shown by Corwin and Summers (16). Moreover, breakthrough curves for DOC and DOM constituents agreed well between the RSSCT and the full-scale plant, and there was little dependence on EBCT. In agreement with prior studies (16), the adsorption capacity of GAC for DOM does not depend on particle size when the proportional diffusivity design is used which is also consistent with previous findings showing that this design is appropriate for simulating DOM removal in field-scale adsorbers (14,30).

In addition, breakthrough of six pesticides was observed at the intermediate RSSCT sampling point (Figure 4) after a specific throughput of $> 1000 \text{ m}^3 \text{ kg}_{\text{GAC}}^{-1}$. These values are higher than for the compounds above and will allow GAC filter run times much longer until breakthrough. The data were not corrected since no full-scale data were available for these compounds which means that no comparison could be established between Figures 3 and 4. The specific throughput to breakthrough increased in the order 2,6-dichlorobenzamide (DCB) < desethylatrazine (DEA) < metolachlor (MET) < atrazine (ATZ) < deisopropylatrazine (DIA) < simazine (SIM) and is not clearly related to the log D_{ow} . Pilot-scale experiments with triazines

were performed by Kennedy et al. (31) with a surface water (Cahaba river, $\text{DOC} = 2.1 \text{ mgC L}^{-1}$), and their breakthrough occurred in a different order ($\text{ATZ} < \text{SIM} < \text{DIA} < \text{DEA}$). Jian and Adams (32) investigated these compounds with PAC (Calgon WPH) in deionized water with increasing adsorption in the order $\text{DEA} < \text{DIA} < \text{ATZ} < \text{SIM}$. A different trend (i.e., $\text{DEA} < \text{DIA} < \text{SIM} < \text{ATZ}$) was observed in Missouri river water ($\text{DOC} = 5\text{-}7 \text{ mgC L}^{-1}$). Thus, it is difficult to link the adsorbability of triazines and the other selected compounds to their $\log D_{\text{OW}}$ alone. Predictive models usually require incorporation of several molecular descriptions such as the initial micropollutant concentration (33). The background water matrix and characteristics of activated carbon play important roles as well.

RSSCT and pilot-scale data will be compared for DCB, DEA and ATZ in the following section.

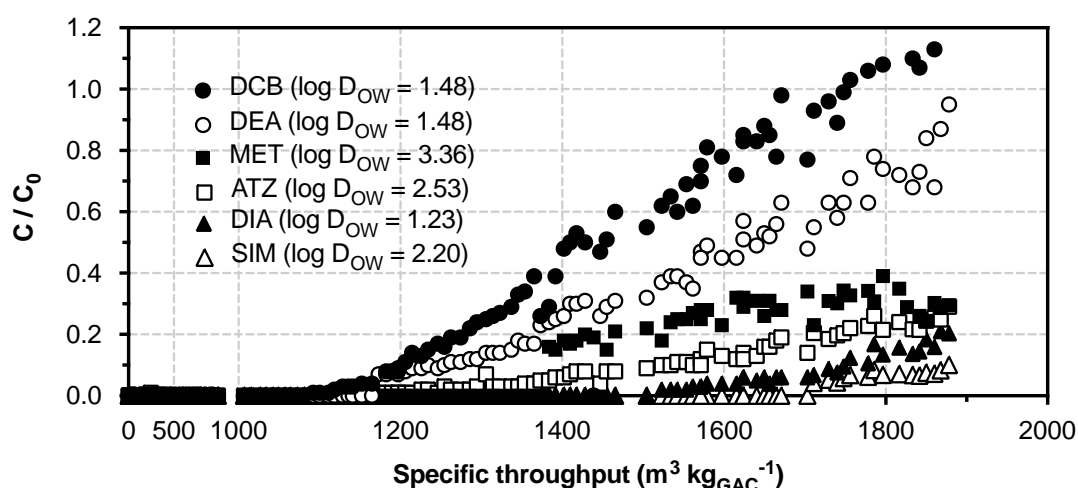


Figure 4. RSSCT breakthrough curves for the six selected pesticides at the intermediate sampling point (raw data, not corrected with the fouling index) (DCB: 2,6-dichlorobenzamide; DEA: desethylatrazine; MET: Metolachlor; ATZ: atrazine; DIA: Deisopropylatrazine; SIM: Simazine)

3.2 Pilot-scale adsorption tests

RSSCT results showed that the specific throughput to a given percentage of micropollutant breakthrough was independent of or only weakly dependent on EBCT. Moreover, it was shown that RSSCTs overestimate the adsorption capacity for micropollutants and scale-up of RSSCT data requires compound-specific fouling indices. Based on these findings, a pilot-scale test with

uncrushed GAC was developed to obtain direct predictions of breakthrough curves. In the two pilot test systems (see materials and methods), samples can be collected in 10 cm intervals for only 1 m instead of 2.5 m at full-scale to reduce the testing period.

In Figure 5, breakthrough curves for diatrizoate, iopamidol, and sucralose are compared directly for sampling methods 1 and 2 in the pilot plant and the full-scale GAC filter. Method 1 shows an earlier breakthrough at lower specific throughputs than method 2, which may be a result of the 1-min EBCT being too short to (1) completely capture the mass transfer and/or (2) establishing a constant breakthrough pattern. Hand et al. (20) demonstrated that a constant breakthrough pattern is not established at short EBCTs, which manifests itself in an earlier onset of the breakthrough. Both sampling methods yielded similar breakthrough curves at higher specific throughputs $> 110 \text{ m}^3 \text{ kg}_{\text{GAC}}^{-1}$. As expected, the pilot- and full-scale breakthrough curves matched reasonably well without the need for a fouling index because the same GAC grain size was used. The breakthrough curve of diatrizoate reached a $C/C_0 > 1$ in the full-scale and pilot-scale adsorbers (Figure 5a). The peaking phenomenon results when adsorbed diatrizoate is displaced by compounds with a higher adsorption affinity (34). Overall, the early portion of a breakthrough curve is more important to determine when GAC needs to be replaced than the full extent of breakthrough, when the GAC is exhausted.

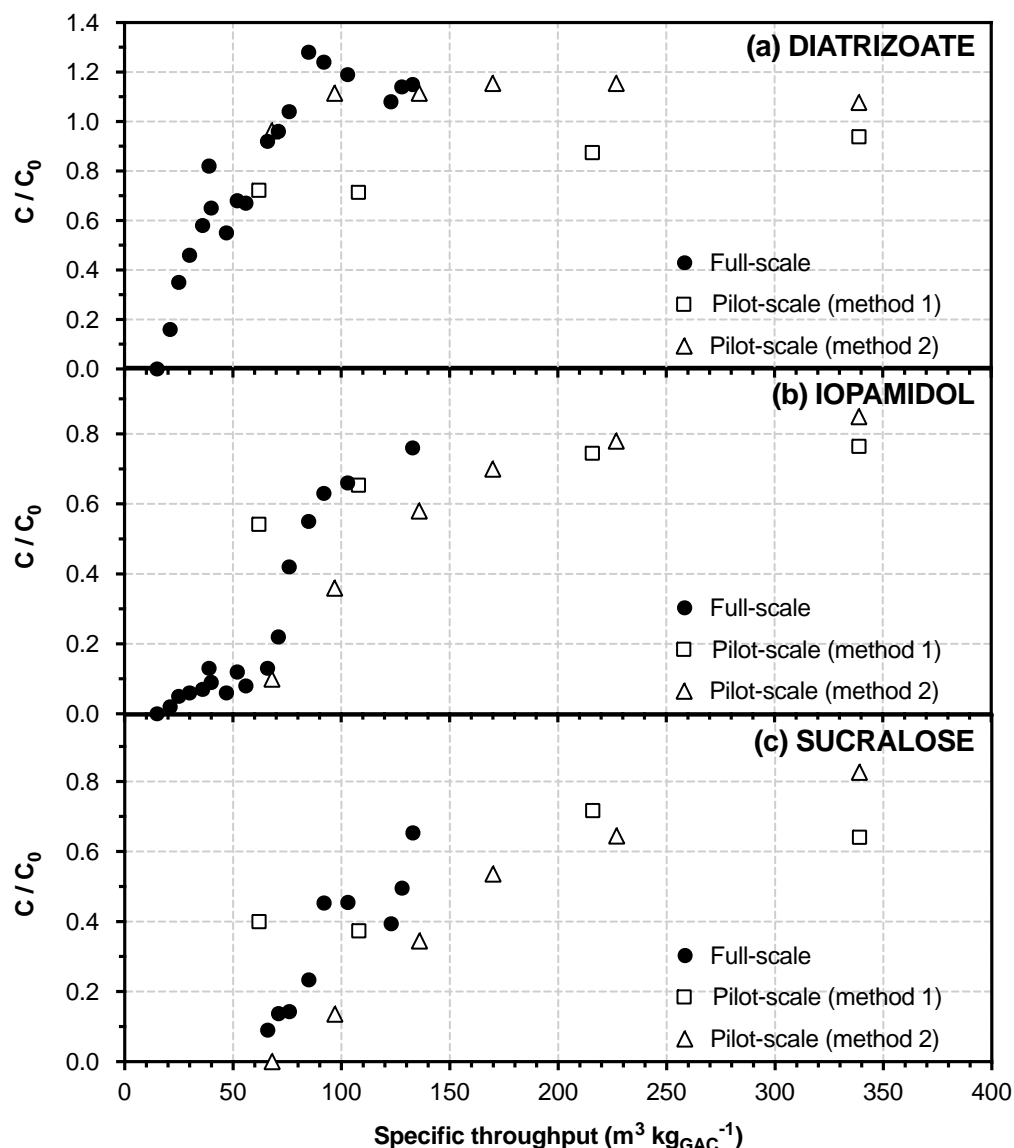


Figure 5. Breakthrough curves of (a) diatrizoate, (b) iopamidol and (c) sucralose in pilot-scale (open symbols) and full-scale GAC adsorbers (closed circles) as a function of specific throughput. In the pilot plant the two sampling methods 1 and 2 explained in the text and Figure 2 were used. Hardwald groundwater: DOC: $0.37 \pm 0.02 \text{ mgC L}^{-1}$ (pilot plant), $0.46 \pm 0.06 \text{ mgC L}^{-1}$ (full-scale plant), pH 7.65 ± 0.05 (pilot plant), 7.65 ± 0.20 (Table S1, SI).

A challenge for method 2 is the time point of sampling. As shown for diatrizoate, 220 days for the first sampling campaign was too long to capture the earliest portion of the breakthrough curve. Therefore, for method 2 at least two sampling campaigns should be carried out to capture breakthrough behavior of both weakly and strongly adsorbing compounds.

Data acquisition for the full-scale adsorber was only carried out up to a specific throughput of $136 \text{ m}^3 \text{ kg}_{\text{GAC}}^{-1}$ whereas it was up to $680 \text{ m}^3 \text{ kg}_{\text{GAC}}^{-1}$ for the pilot system. Consequently, we were able to obtain breakthrough curves using method 2 for eleven additional micropollutants for which full-scale data were not available (Figure S5, SI). In contrast to iopamidol (IOA) and sucralose (SUC), for which the breakthrough was observed in full-scale the specific throughput for 10% breakthrough for the 11 other pesticides and pharmaceuticals was $> 100 \text{ m}^3 \text{ kg}_{\text{GAC}}^{-1}$ (white bars in Figure 6). According to the data from the pilot-scale experiments, a breakthrough of candesartan (CDS) and metolachlor ESA (MTE) would have been expected in the full-scale adsorbers for the last sampling point (i.e., $136 \text{ m}^3 \text{ kg}_{\text{GAC}}^{-1}$). However, the very low concentrations for both compounds in the raw water (11 and 12 ng L^{-1} , respectively) close to the limit of quantification inhibited their detection. For seven micropollutants, a 10% breakthrough was observed in a narrow range between 150 and $200 \text{ m}^3 \text{ kg}_{\text{GAC}}^{-1}$. These compounds are expected to break through in the activated carbon filter soon after this study. The 10% breakthrough of atrazine (ATZ), desethylatrazine (DEA) and 2,6-dichlorobenzamide (DCB) occurred between 170 and $190 \text{ m}^3 \text{ kg}_{\text{GAC}}^{-1}$ while the non-corrected RSSCT data predicted values between 1200 and $1400 \text{ m}^3 \text{ kg}_{\text{GAC}}^{-1}$ (Figure 4). This demonstrates again, that RSSCT data for pesticides should not be used directly to predict full-scale performances without applying a fouling index. Lamotrigine (LMT) was the most retained compounds with a specific throughput of $280 \text{ m}^3 \text{ kg}_{\text{GAC}}^{-1}$.

To correlate the breakthrough data with the chemical properties of these compounds, the specific throughput for 10% breakthrough is compared to $\log D_{\text{OW}}$ values (Figure S6, SI). Based on this data set, a weak correlation between $\log D_{\text{OW}}$ values and the release order of the selected compounds can be observed.

3.3 Comparison of breakthrough prediction with an existing method

Specific throughputs at 10% breakthrough compared with a predictive model developed for surface water by Kennedy et al. (6) (Figure 6 and Text S2, SI) to assess the suitability of this model to make full-scale predictions for Hardwald groundwater. Predictions for specific

throughput matched the experimental results within 30% for 6 compounds out of 13 (iopamidol (-30%), sucralose (+4%), hydroxyatrazine (-24%), dihydroxycarbamazepine (-1%), 2,6-dichlorobenzamide (-24%), atrazine (+3%)). In general, the model under-predicted the specific throughput to 10% breakthrough, and the magnitude of the error tended to increase with increasing adsorbability of the micropollutants with a maximum for desphenylchloridazon (-66%). This observation suggests that DOM derived from surface water has a greater long-term fouling potential than DOM derived from groundwater.

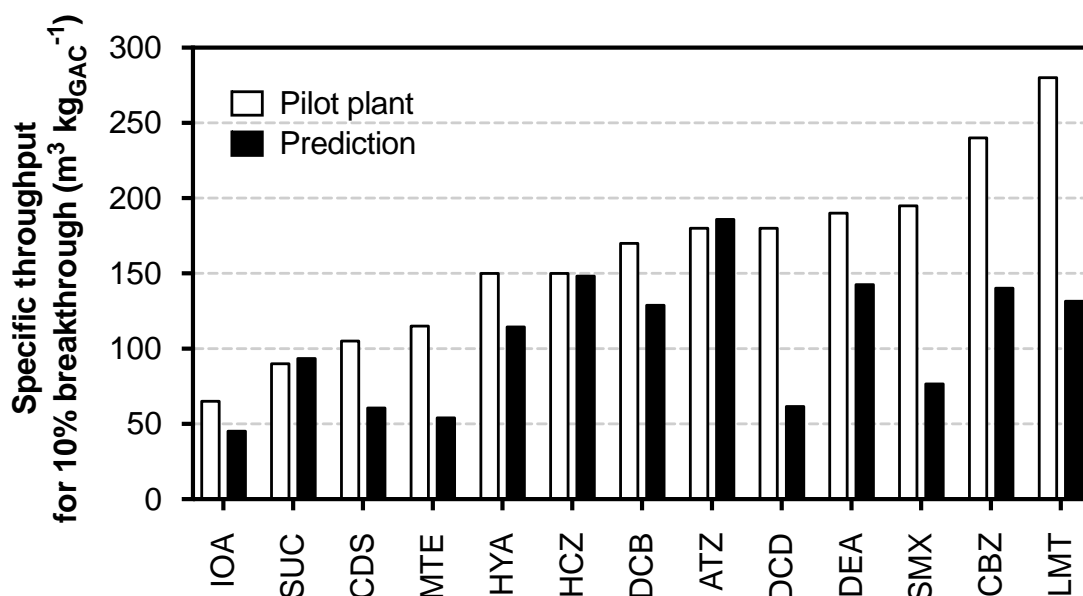


Figure 6. Comparison of specific throughput at 10% breakthrough obtained with pilot-scale GAC columns (method 2, white bars) and predicted values from model calculations (black bars, Kennedy et al. (6)). Note: 10% breakthrough for diatrizoate (DTZ) was not determined since the first point of the breakthrough curve started at $C/C_0 = 0.7$. The compounds are arranged according to an increasing specific throughput for the pilot plant experiments. Compound abbreviations; IOA: iopamidol; SUC: sucralose; CDS: candesartan; MTE: metolachlor ESA; HYA: hydroxyatrazine; HCZ: dihydroxycarbamazepine; DCB: 2,6-Dichlorobenzamide; ATZ: atrazine; DCD: desphenylchloridazon; DEA: desethylatrazine; SMX: sulfamethoxazole; CBZ: carbamazepine; LMT: lamotrigine)

3.4 Practical implications

RSSCT is always operated with small particle size (ca. 100 μm) yielding a pressure drop of a few bars. Thus, pumps for this set-up should be able to deliver a constant flow with pressures in the range of 3 to 3.5 bars (e.g., HPLC pumps). In contrast to the RSSCT, pilot GAC columns are filled with unaltered GAC. The pressure drop in the pilot-scale filters was below 0.8 bar and this can be supported by a normal gear pump. HPLC pumps typically require more maintenance than gear pumps (i.e., plunger washing, replacement of plunger seals due to possible scaling, addition of a restrictor pipe to add a back pressure at the pump outlet and cleaning).

In terms of data acquisition, method 2 in the pilot-scale tests is overall cheaper than RSSCT since it requires only one sampling campaign and therefore, a limited amount of analyses while water must be sampled continuously for RSSCT over a longer period. The number of sampling campaigns would need to be increased to 2 or 3 if one would like to study compounds with a wide range of adsorbabilities. For a given micropollutant, a breakthrough curve with 10 points requires 10 sampling campaigns for the RSSCT, whereas only one sampling campaign will be required for method 2 type sampling at the pilot plant. Furthermore, the extrapolation of breakthrough curves to full-scale GAC adsorbers obtained from RSSCT is more difficult because fouling indexes have to be considered. They may depend on water quality and sometimes of compound properties.

However, it is important to point out that method 2 type sampling at pilot-scale was only developed for groundwater with a limited number of polar compounds. To further validate this method, other water qualities and a broader range of compounds would have to be tested. In comparison, RSSCT has been studied for decades and a large body of data is available in the literature for different water qualities and different groups of micropollutants.

Conclusions

Methods for determining the breakthrough of 20 micropollutants in a GAC adsorber of a full-scale drinking water treatment plant were assessed in bench- and pilot-scale GAC columns tests:

- The Rapid Small-Scale Column Test (RSSCT) was only a good predictor of full-scale GAC adsorber performance if a compound-specific fouling index was applied. In addition, the fouling factor may depend on the initial micropollutant concentration and the character and concentration of the background dissolved organic matter. When the GAC grain size was crushed from an average of 1000 μm to 94.3 μm for the RSSCT, the fouling index exponent (Y) was about 0.7. The gain in time compared to full-scale data collection was in the range of a factor of 4.2 to 6.3.
- Pilot-scale GAC column experiments were performed with 10 columns in series and two sampling methods. Method 1 consisted of sampling after the first column (i.e., EBCT = 1 min) while method 2 required only one sampling campaign after several columns to get the same breakthrough curves.
- Compared to the full-scale data, method 1 provided inconsistent results for the early portion of the breakthrough curve. An EBCT of 1 min was too short to establish a constant adsorption pattern that develops in GAC columns with longer EBCTs.
- Method 2 showed an overall better agreement with full-scale micropollutant breakthrough. Method 2 is promising for simulating full-scale performance and effective from a sample collection and analysis perspective. In addition, this method is up to 25 times faster and can be used to predict breakthrough curves of micropollutants for full-scale adsorbers without applying a compound-specific fouling index.
- A mathematical model for predicting 10% breakthrough of micropollutants was tested for 11 compounds that broke through during pilot-scale testing. Overall, the

427 comparison showed reasonable agreement for several weakly adsorbable compounds,
428 but discrepancies were more pronounced for strongly sorbing micropollutants.

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