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Adsorption onto granular activated carbons of a mixture of pesticides and their metabolites at trace concentrations in groundwater

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Abstract

The presence of pesticides (alachlor, metolachlor and atrazine) is a major concern for the production of drinking water. However, their main metabolites, namely oxanilic acid (OA) and ethanesulfonic acid (ESA) for alachlor and metolachlor, and desethyl- and deisopropyl-atrazine for atrazine, are also encountered in natural waters. The adsorption of these micropollutants onto two types of granular activated carbons under dynamic (fixed bed) conditions was studied. The performance of the adsorbers was evaluated under operating conditions comparable to those found for the production of drinkable water, *i.e.* inlet concentrations of $1.0 \mu\text{g L}^{-1}$ for each pesticide and metabolite added to groundwater containing $1.5 \text{mg}_C \text{L}^{-1}$ of natural organic matter. Regardless of the location in the column or the duration of the treatment, humic acids were preferentially removed compared to fulvic acids. As for micropollutants, a pseudo-steady state was reached after filtration of approximately 2.0m^3 of water (6000 equivalent bed volumes). The retention of micropollutants onto granular activated carbons is driven by their adsorption kinetics. Moreover, in the case of alachlor and metolachlor, but not atrazine, different adsorption profiles were observed between the parent pesticide and its metabolites. Desethyl- and deisopropyl-atrazine, were adsorbed quickly; the mass transfer zone was nar-

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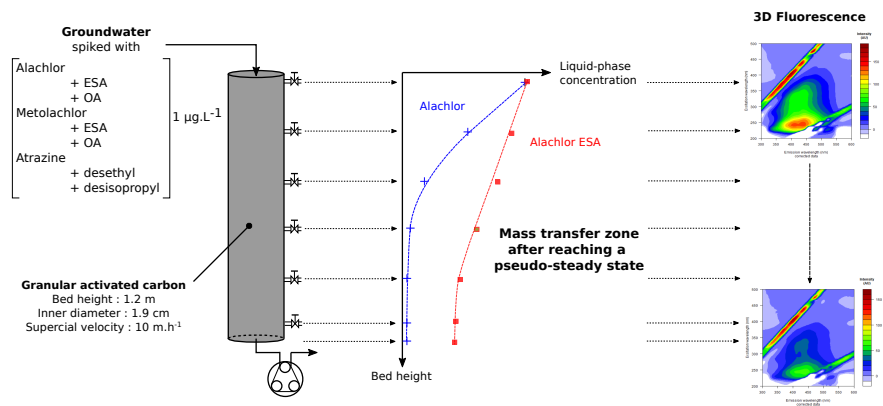
row (approximately 60 cm) with a superficial velocity of the liquid phase equal to 10 m h^{-1} . By contrast, the OA and ESA metabolites reached breakthrough when the mass transfer zones were larger than the height of the columns. The Amundson model was used to determine the adsorption rate and adsorption capacity each pollutant.

Keywords: dynamic adsorption, pesticides, metabolites, natural organic matters, 3D fluorimetry, granular activated carbon

Research Highlights

- Fate of the transformation by-products of pesticides in adsorbers
- Leakage of the ESA and OA metabolites of metolachlor and alachlor
- A pseudo-steady state reached after 6000 bed volumes
- Natural organic matters partially removed regardless of their nature
- Predominant impact of the kinetics of adsorption and of mass transfer limitations

Graphical Abstract



1. Introduction

For nearly 100 years, adsorption processes have been used for the production of drinking water and the treatment of domestic and industrial wastewaters [1, 2]. Activated carbons are the main adsorbents used for these purposes, either in powders form in slurry reactors or in granular form in fixed-bed adsorbers. Dynamic (fixed-bed) adsorption has two objectives: (*i*-) the removal of natural organic matter (NOM), since these compounds are precursors for disinfection by-products, and (*ii*-) the elimination of organic micropollutants, such as pesticides, pharmaceutical residues, personal care products, corrosion inhibitors, etc. Fixed-bed adsorption is a transient regime operation and its efficiency is characterized by the breakthrough curve of the targeted compounds. Because diffusion of these molecules from the bulk fluid to the inner pores of the activated carbons is slow, a mass transfer zone (or adsorption zone) is present inside the adsorber. The breakthrough curve (*i.e.* the plot of the outlet solute concentration as a function of time or throughput volume) represents the profile of this mass transfer zone. The shape of the breakthrough curve depends on several parameters including adsorption rate, temperature, flow rate, bed depth, inlet concentrations, presence of NOM, pH and the age of the adsorbent [1, 4, 5].

The presence of emerging organic micropollutants (EOMs) in natural waters has been largely reported [6, 7]. In particular, much attention has been paid to the removal of pesticides, personal care products and pharmaceutical residues [8]. The efficiency of available treatments is largely dependent on the physico-chemical properties of the compounds in question [9]. To comply with the European Union (EU) directive limiting pesticide concentration to less than $0.1 \mu\text{g L}^{-1}$ in drinking water, the adsorption process needs to be sufficiently efficient [10]. Moreover French regulation also limits the maximum concentration of these metabolites to $0.1 \mu\text{g L}^{-1}$. In natural waters, we find not only parent molecules such as pesticides but also chemical and bio-transformation products of these molecules [11, 12]. These study of these by-products and their removal for the production of drinking water is in its infancy however, it ap-

pears that these compounds are generally less adsorbed by activated carbons than their parent molecules [13]. In the environment, the chemical and/or biological transformations of pesticides produces protonated metabolites. As a consequence, electrostatic repulsion with the surface of activated carbons has
35 been observed and reduced the adsorption of these metabolites [14].

The production of drinking water from surface or groundwater also involves the elimination of natural organic matter (NOM) since NOM is a precursor for oxidation or disinfection by-products. Several processes can partially remove NOM (*e.g.* coagulation-flocculation, membrane filtration, adsorption, oxidation). Numerous techniques have been used to characterize NOM for drinking
40 water production [15]: total organic carbon (TOC), specific UV absorbance at 254 nm (SUVA), size exclusion chromatography, fluorimetry, fractionation, etc. These techniques provide quantitative and qualitative information that allow us to discriminate algonenic organic matter, bacterial organic matter and humic/fulvic acids [16, 17]. Furthermore, in fixed bed adsorbers, NOM type and
45 content [18], and the age of GAC [5] have a significant impact on the efficiency of organic micropollutant removal.

In most cases the presence of NOM decreases the adsorption capacity of activated carbon [19, 20, 21] as well as the rate of micropollutant adsorption
50 [22]. This decrease in the amounts adsorbed and molecules diffusivity in pores are the direct consequence of the competitions between NOM and organic micropollutants for adsorption sites, and reflects the differences in concentration of these compounds, ranging from several $\text{mg}_C \text{L}^{-1}$ for NOM to $\text{ng} - \mu\text{g} \text{L}^{-1}$ for trace contaminants. The complexity lies in the fact that this competition
55 is totally dependent on the nature of the organic molecule, the type/amount of NOM and the characteristics of the adsorbent [23]. Adsorption of the largest NOM molecules, onto the external surface of GAC can block the entrance to the pores and, thus, significantly decrease the number of accessible adsorption sites, while smaller fractions of NOM can compete with the target compounds for
60 the remaining adsorption sites. For example, the adsorption capacity activated carbon of atrazine in natural waters significantly is much lower than in ultra-

pure water; indeed, competition with NOM, which causes pore blockages, has been shown [24, 25]. However, complex bonds can also form between the target compounds and NOM such as humic substances, which increase the adsorption
65 of these compounds [26, 27]. It should also be kept in mind that adsorption processes are transient operating systems (fixed bed are run for 6 months to 2 years) and the types and content of organic species (micropollutants and NOM) will vary over time [28, 29]. In addition, bacterial growth may occur on the solid surface of the column [5], which, in turn, can modify the surface proper-
70 ties of the particles, change the nature/amount of NOM, etc. In conclusion, the performance of a fixed beds on an industrial scale is hard to predict if all these complex phenomena and their combination are taken into account.

Experimentally, several methods have been developed to address these issues, with different objectives: understand competition for adsorption sites, identify
75 the most relevant characteristics of the adsorbent to increase the efficiency of the process, predict the performance of a fixed bed on an industrial scale and adjust its operating conditions. One of these strategies is to use rapid small scale column tests (RSSCTs), the objectives of which are to miniaturize the industrial filters and obtain breakthrough curves over a short period of time
80 (*i.e.* within a few days). RSSCTs must be able to simulate industrial filters, and this is achieved by reducing GAC particle size (by grinding) and having a constant mass transfer rate (porous diffusivity and external mass transfer) [3]. RSSCTs present several advantages, such as the effect of the mass transfer zones inside the bed and the actual kinetic competitions between all the
85 components [30]. The impact of NOM from groundwater, surface water and wastewater effluents has been compared and the detrimental effects on adsorption of higher NOM contents has been demonstrated [31]. However, RSSCTs do not provide information regarding the fouling that occurs naturally inside the fixed beds (*e.g.* biofilms, deposition of solid particles and colloids). Another
90 option is to monitor the actual industrial filters (inlet and outlet compositions) and study all combined phenomena (adsorption, biodegradation) [32, 33]. But at this scale, the concentration of micropollutants varies over time, the behavior

of specific organic compounds is poorly understood and other processes such as biodegradation should be monitored.

95 In this study, we chose alachlor, metolachlor and atrazine as the pesticides of interest as they are frequently detected in natural waters [34, 35]. Moreover, we studied not only the parent molecule but also their metabolites: oxanilic acid (OA) and ethanesulfonic acid (ESA) for alachlor and metolachlor, and desethyl- and deisopropyl-atrazine for atrazine. Atrazine and its metabolites
100 and alachlor were among the 20 most frequently reported pesticides in groundwater quality monitoring sites in europe between 2007 and 2017 [36]. 3.49 % of 59,184 groundwater records had desethyl-atrazine concentrations that exceeded $0.1 \mu\text{g L}^{-1}$. We monitored their adsorption in different fixed bed adsorbers filled with two types of GAC obtained from different carbon precursors. The nature
105 of the precursor greatly influences the surface functional groups and the pore structure of activated carbon [37]. Kovalova *et al.* observed differences in the adsorption properties of activated carbons with different surface functions, impacting the removal of highly polar micropollutants from wastewater [38]. The fixed beds consisted of a 1.2 m deep column filled with 1.1 to 1.2 m of granular
110 activated carbon (GAC), which is comparable to an industrial configuration, with a superficial velocity of the liquid phase equal to 10 m h^{-1} . To reproduce what may be found in the environment, we diluted the micropollutants (inlet concentration equal to $1.0 \mu\text{g L}^{-1}$), in groundwater, the NOM content of which was approximately of $1.5 \text{ mg}_C \text{ L}^{-1}$. The objective of this study was to
115 understand the dynamics of adsorption of different micropollutants with different properties and the effect of NOM on their adsorption at different locations along the adsorber.

2. Materials and experimental methods

2.1. Activated carbons

120 Granular activated carbons from two different carbon precursors were supplied by DACARB (Asnières-sur-Seine, France). Boths GACs meet the require-

ments for the production of drinking water. Adsorbents were used as received after washing with ultrapure water (UPW) to remove fine particles. Activated carbons were characterized physically and chemically. Apparent density was determined using mercury porosimetry (Autopore IV 9500, Micromeritics). Total pore volume was estimated from the adsorption-desorption isotherms of nitrogen at 77 K (Autosorb AS-1 instrument, Quantachrome). Specific surface area was calculated using the BET model applied in the 0.03 to 0.015 range of relative pressures [39]. The content of functional surface groups on the surface of the GACs was evaluated using acid and base titrations (often referred to as Boehm’s method [40]). Acidic functional groups were titrated using NaOH whereas basic functional groups were quantified using HCl. Finally, after immersion of each GAC in UPW for 24 h, the residual pH was determined and confirmed the predominance of acidic functional groups in both adsorbents. The characteristics of two GACs are within the range of commercial GACs used for the production of drinking water (table 1).

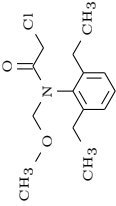
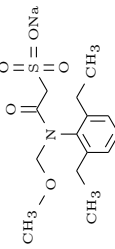
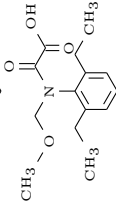
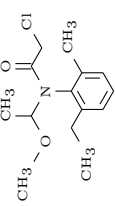
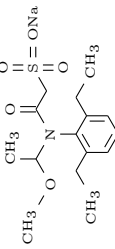
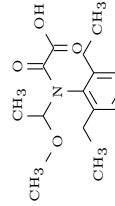
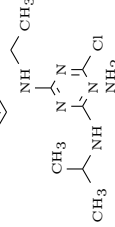
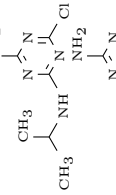
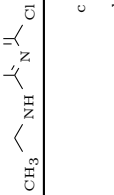
Table 1: Physico-chemical properties of granular activated carbons from different carbon precursors

Activated Carbon	GAC1	GAC2
Specific surface area ($\text{m}^2 \text{g}^{-1}$)	925	990
Apparent density (g cm^{-3})	0.56	0.49
Skeletal density (g cm^{-3})	0.90	0.83
Total pore volume ($\text{cm}^3 \text{g}^{-1}$)	0.68	0.83
Mesoporous volume ($\text{cm}^3 \text{g}^{-1}$)	0.47	0.67
Microporous volume ($\text{cm}^3 \text{g}^{-1}$)	0.21	0.16
Base surface functional groups (meq g^{-1})	0.20	0.20
Acid surface functional groups (meq g^{-1})	1.60	1.07
Residual pH	6.6	6.6

2.2. Stock solutions

Solutions containing micropollutants, were prepared in UPW (resistivity 18.2 M Ω cm⁻¹, Millipore-Elga system). All chemicals were supplied by Sigma-
140 Aldrich (analytical standard purity). The physico-chemical properties of the molecules of interest are summarized in table 2 [41]. Since values for these properties are not always available from experiments, some of the values reported here obtained with predictive models and tools for assessing chemicals under the toxic substances control act (www.epa.gov/tsca-screening-tools).

Table 2: Physico-chemical properties of the pesticides and their metabolites (NA: Not Available)

Compound	CAS number	Formula	MW ^a (g mol ⁻¹)	s ^b (mg L ⁻¹ at 25°C)	log Kow	pK _a
Alachlor (ALA)	15972-60-8		269.77	240	3.52	0.62
Alachlor ESA (ALA ESA)	140939-15-7		337.37	0.246	1.82	NA
Alachlor OA (ALA OA)	171262-17-2		265.30	NA	2.31 ^c	NA
Metolachlor (METO)	512818-45-2		238.79	530	3.13	ND ^d
Metolachlor ESA (METO ESA)	947601-85-6		351.39	212461	-1.89	NA
Metolachlor OA (METO OA)	152019-73-3		279.33	238	2.04 ^c	NA
Atrazine (ATZ)	1912-24-9		215.68	35	2.61	1.7
Desethyl-Atrazine (DEA)	6190-65-4		187.63	2700	1.51	NA
Deisopropyl-Atrazine (DIA)	1007-28-9		173.60	980	1.15	1.3

^a Molecular Weight

^b Solubility in water

^c From www.molinspiration.com version 2011.06

^d No Dissociation

145 *2.3. Analytical Methods*

The concentration of dissolved organic carbon (DOC) was measured after filtration through a 0.45 μm membrane (Chromafil®Xtra PET). Prior to analysis, samples were stored at 4 °C. DOC was determined by catalytic combustion (Shimadzu TOC-VCN).

150 The aromatic character of NOM is given by the specific UV absorbance (SUVA, $\text{L mg}_\text{C}^{-1} \text{cm}^{-1}$), *i.e.* the UV absorbance at 254 nm (cm^{-1}) divided by the DOC content ($\text{mg}_\text{C} \text{L}^{-1}$). Each sample was loaded in a quartz cell (QS Helma) with an optical path length of 50 mm and analyzed with a spectrophotometer (UVmini-1240 Shimadzu). First samples were filtered through a 0.45 μm 155 membrane. In addition, the spectral behavior of NOM was characterized using 3D fluorimetry, allowing us to identify the chromophores corresponding to the humic, fulvic and protein components of NOM (PerkinElmer Fluorescence Spectrometer LS45). Spectra were obtained by scanning within an excitation range of 200 to 500 nm and an emission range of 300 to 600 nm, with a pitch 160 of 5 nm and an acquisition rate of 1000 nm min^{-1} . Samples were loaded in a 4-sided quartz cell (PerkinElmer) with an optical path length of 10 mm. The fluorescence excitation–emission matrices (EEMs) data were processed using an R script following to the method described by Lapworth and Kinniburgh (2009) [42].

165 The selected micropollutants were analyzed using ultra-high-pressure liquid chromatography (UHPLC) coupled with tandem mass spectrometry (MS/MS) (Acquity, Waters, Quattro Premier, Micromass, USA) after online solid phase extraction (SPE) (Waters 2777). Filtered samples (0.2 μm Chromafil®Xtra PET) were passed through an Oasis HLB (Hydrophobic Lipophilic Balanced) 170 SPE cartridge (direct connect HP 20 μm , 2.1 \times 30 mm) for extraction and concentration of pesticides and their metabolites. UPW and methanol were used as eluents for loading and rinsing; the flow rate was set at 2.0 mL min^{-1} using a quaternary pump (Acquity QSM-Waters). SPE cartridges were connected to a chromatographic unit (Acquity BSM-Waters) equipped with a chromatographic column oven and a C₁₈ BEH Acquity UPLC column of Waters 175

(100 mm \times 2.1 mm i.d., 1.7 μ m). The mobile phase consisted of a mixture of UPW-ammonium acetate (10 mmol L⁻¹, pH = 4) and methanol-ammonium acetate (10 mmol L⁻¹, pH = 4). The flow rate was set at 0.4 mm min⁻¹ and the temperature of the column was maintained at 45 °C. The mass spectrometer
180 operated under the following conditions: cone gas (N₂, 50 L h⁻¹, 120 °C), desolvation gas (N₂, 750 L h⁻¹, 350 °C), collision gas (Ar, 0.1 mL min⁻¹), capillary voltage (3000 V). The ionization source of the mass spectrometer was an electrospray (ESI) used in the positive mode. Multiple reaction monitoring (MRM) transitions, limits of detection (LOD) and quantification (LOQ), cone voltage,
185 collision energy and retention time (t_r) are reported in supporting information (Table A.1).

2.4. Dynamic adsorption

Fixed bed adsorbers were designed and studied using realistic conditions that are comparable to industrial filters. Two columns, packed with GAC,
190 were run in parallel with the same inlet solution (fig. 1). The GAC particles were washed with UPW and packed randomly inside the adsorber. Both types of GACs were sieved; to retain only particles within 1.0 to 1.6 mm (> 75% *wt.*). These columns were fed groundwater (coming from run-off and infiltration in the well located at the *École Nationale Supérieure de Chimie de Rennes*,
195 France) to which was added each organic pollutant separately (1.0 μ g L⁻¹ for each molecule). Groundwater was used since it contains a similar NOM contents as clarified water during the process of drinking water production. The fed solution was stored in a 2 m³ tank, which was treated with a biocide (sodium azide, [NaN₃] = 2.0 mg L⁻¹) to prevent bacterial growth and development. A
200 centrifugal pump (\sim 50 L min⁻¹) ensured permanent recirculation at the top of the column.

The flow of the solution through the columns was ensured by a two-way peristaltic pump placed downstream of the column. Flow was maintained and checked multiple times daily. Inside each adsorber, the superficial velocity
205 through the column was fixed at 10 m h⁻¹ ($S = 2.84$ cm², $Q = 47.3$ mL min⁻¹)

as this corresponds to a value commonly encountered in water treatment systems [1]. The total height of the column was 1.2 m and its inner diameter was 1.9 cm. As the two GACs had different densities, each adsorber contained a different mass of adsorbent (column 1: $m_{GAC1} = 179.3$ g, column 2: $m_{GAC2} = 169.0$ g).
 210 Each column had 5 intermediate sampling ports so that the saturation and breakthrough curves could be determined at different locations along the fixed beds.

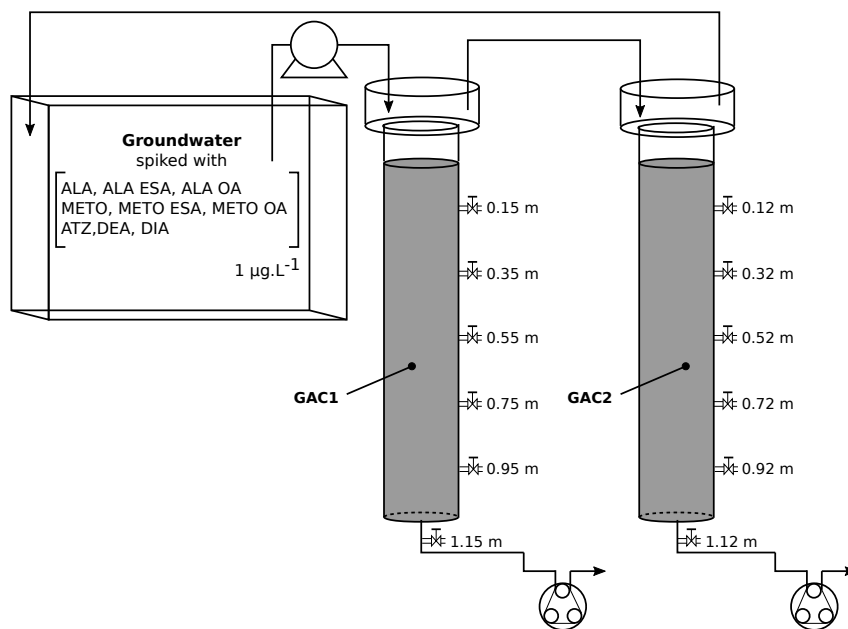


Figure 1: Experimental unit (inlet concentration of each micropollutant = $1 \mu\text{g L}^{-1}$, flowrate through each adsorber 47.3 mL min^{-1} , superficial velocity = 10 m h^{-1} , $D = 1.9 \text{ cm}$, $S = 2.84 \text{ cm}^2$)

The Bohart-Adams model has been an important tool for designing continuous flow adsorption systems. The Amundson model was derived from the original Bohart-Adams solution, and is a linear form best adapted to small exit concentrations at the column outlet [43]. Thus, to model fixed-bed adsorption,

we used a simplified form of the the Amundson model (eq. (1)) [44].

$$\frac{C}{C_{\text{input}}} = \frac{\exp(k_a \varepsilon C_0 t)}{\exp\left(\frac{k_a N_a Z}{u}\right) + \exp(k_a \varepsilon C_0 t) - 1} \quad (1)$$

C ($\mu\text{g g}^{-1}$) is the concentration of the adsorbate in the outlet, C_{input} ($\mu\text{g g}^{-1}$) is the concentration of the adsorbate in the inlet, k_a ($\text{g } \mu\text{g}^{-1} \text{ min}^{-1}$) is the Amundson rate constant, N_a ($\mu\text{g g}^{-1}$) is the maximum adsorption capacity of the adsorbent per mass of adsorbent, t (min) is the operating time, u (cm min^{-1}) is the superficial velocity, Z (cm) is the bed height and ε is the void fraction of the bed. The value of ε was obtained using mercury porosimetry (Autopore IV, Micromeritics).

The parameters of the Amundson model have to be adjusted to fit the experimental data. Assessment of the goodness-of-fit was obtained by the minimization of an error function. The error function used in this study was the average relative error (ARE) corresponding to eq. (2) [45]. Optimization was achieved using Microsoft Excel Solver.

$$ARE = \frac{1}{N} \sum \left| \frac{C/C_{\text{input, cal}} - C/C_{\text{input, exp}}}{C/C_{\text{input, exp}}} \right| \times 100 \quad (2)$$

N is the number of experimental data points, $C/C_{\text{input, cal}}$ is the theoretically calculated concentration ratio and $C/C_{\text{input, exp}}$ is the experimental concentration ratio.

3. Results and Discussion

3.1. Fixed bed adsorption and fate of the organic matters

Dynamic adsorption of micropollutants added to groundwater was carried out for 73 days. During this period, each fixed bed filtered almost 6 m^3 of water. The feeding reservoir had a storage capacity of 2 m^3 , and thus had to be refilled 6 times. As a consequence, the amount of NOM was variable: DOC content average was $1.6 \text{ mg}_C \text{ L}^{-1}$, but varied between 1.4 and $1.9 \text{ mg}_C \text{ L}^{-1}$. Likewise, the nature of NOM changed during the experiment as seen from SUVA data which varied from 2 to $5 \text{ L mg}_C^{-1} \text{ cm}^{-1}$. These temporal variations have to be taken

into account when discussing the results. NOM was characterized at different locations in each fixed bed by measuring the DOC, the SUVA as well as the fluorescence excitation-emission matrix (EEM).

235 Figure 2 shows the evolution of the DOC content (*i.e.* the bed volume, bv) at different times along the adsorbers. For each GAC, the first measurements show a partial removal of NOM along the column. At the start, the inlet water has a DOC content of $1.5 \text{ mg}_C \text{ L}^{-1}$, whereas DOC content in the output water is below $1.0 \text{ mg}_C \text{ L}^{-1}$ irrespective of the type of GAC. Over time and equivalent bed
 240 volume, DOC content increased and progressively reached saturation at a value greater than 15,000 bv. In conclusion, breakthrough of NOM was observed early on and led to the saturation of each fixed bed. These results are in agreement with previous observations of NOM adsorption onto activated carbons for a wide range of NOM fractions [46, 47].

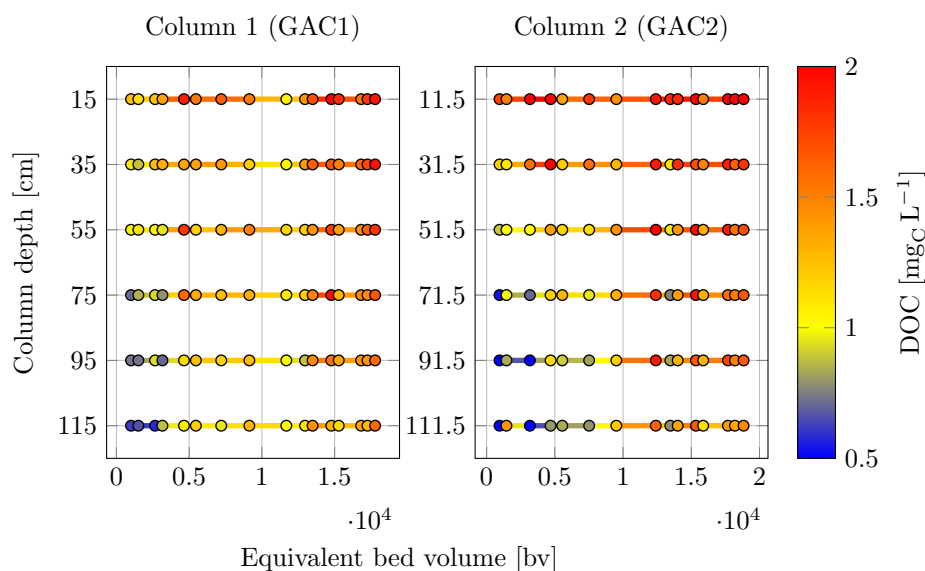


Figure 2: DOC content as a function of bed volume along the fixed bed for GAC1 and GAC2

245 SUVA is a quantitative measure of the aromatic character of organic compounds. Generally, a SUVA lower than $2 \text{ L mg}_C^{-1} \text{ cm}^{-1}$ indicates that NOM is mainly composed of non-humic substances, whereas a SUVA higher than

$4 \text{ L mg}_C^{-1} \text{ cm}^{-1}$ indicates that NOM consists of a mixture of humic substances with a strong terrestrial influence [48]. Figure 3 plots the mean values of SUVA (averaged over the entire duration of the adsorption) at different bed locations. For both adsorbents, the SUVA indicated that the NOM comprised mostly humic components (SUVA higher than $2.54 \text{ L mg}_C^{-1} \text{ cm}^{-1}$) and, overall, SUVA decreased along the fixed bed, thus showing the preferential adsorption of the most hydrophobic fractions of NOM by activated carbons. Velten *et al.* (2011) [49] observed the same behaviours of NOM with a preferential adsorption of larger aromatic structures over that of smaller molecules.

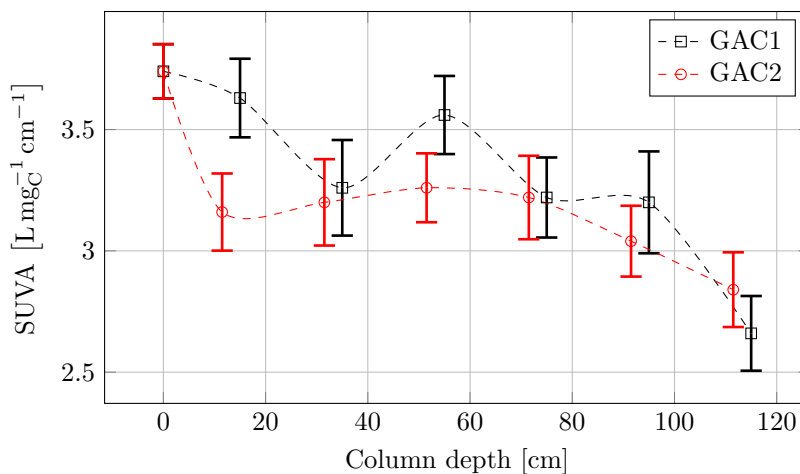


Figure 3: Mean SUVA (averaged over the entire duration of the breakthrough curve) as a function of column depth

3D fluorescence spectroscopy qualitatively describes the nature and composition of NOM. Its evolution was measured along the columns over time. A 3D emission-excitation matrix was measured and this 3D spectrum appeared as a surface with peaks (fig. 4). The spectrum of the blank, *i.e.* ultrapure water, was subtracted from the spectrum to better interpret the peaks [50]. Spectra should be analyzed carefully since the intensity of a peak is proportional to the concentration of fluorophores. Two main types of NOM were found in natural underground waters [51]:

265

- A humic type (zone A) at excitation/emission wavelengths (nm) at maximum fluorescence intensity: 237-260/400-500
- A fulvic acid type (zone C) at excitation/emission wavelengths (nm) at maximum fluorescence intensity: 300-370/400-500

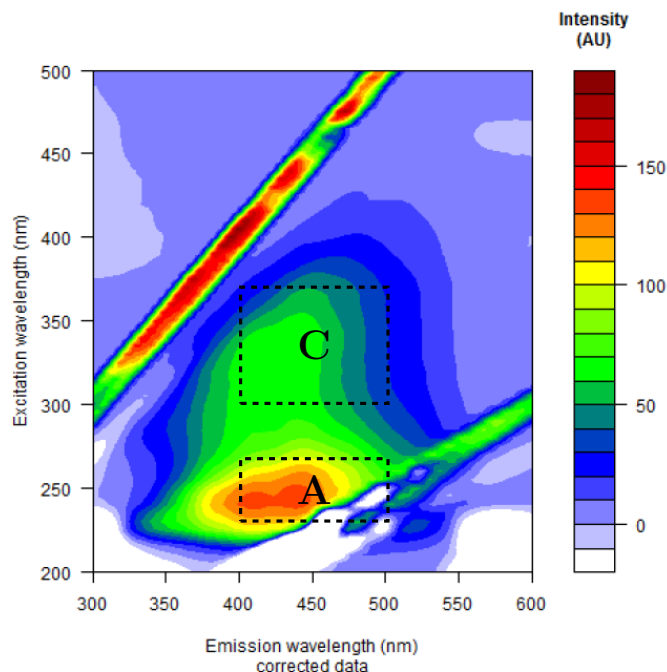


Figure 4: 3D Fluorescence spectrum of underground water (before adsorption)

Figure 4 shows that the water contains Type A and Type C fluorophores, corresponding to humic and fulvic acids, respectively. Moreover, the predominance of humic acids can easily be explained by the “terrestrial” origin of the organic matter present in the sampled groundwater (infiltration waters of the well). The maximum intensity of each zone was plotted at the different locations along the columns at the end of the adsorption, after 70 days and more than 17 500 bv (fig. 5). Regardless of the type of GAC, both fulvic and humic acids were adsorbed along the bed and their intensity decreased. Fulvic acids were poorly adsorbed and their intensity decreased only slightly between the

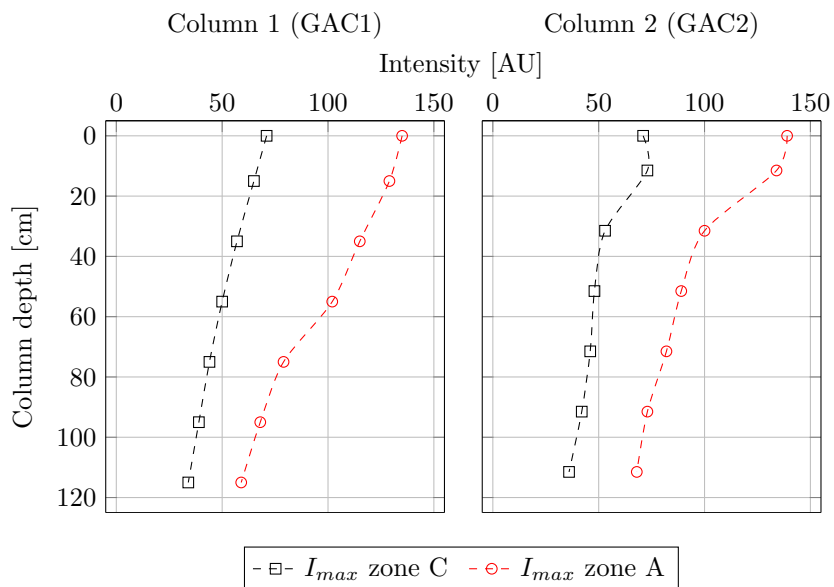


Figure 5: Evolution of the maximum intensity peak for zone A and zone C in columns containing GAC1 and GAC2 (respectively at 17 782 bv and 17 508 bv)

inlet and the outlet. By contrast, humic acid content decreased significantly along the bed and the maximum intensity was divided by two between the inlet and the outlet of each bed. Thus, we observed preferential adsorption of humic acids. A detailed analysis of this behavior over time (*i.e.* with different volumes of water treated) is shown in supporting information fig. B.1. Preferential adsorption of humic compounds was observed, independently of time and bed location, in agreement with previous work by Kilduff *et al.* (1996) [52].

The limitations on fulvic acid adsorption could be explained by the fact that most fulvic acid molecules may not access the micropores of activated carbon, as shown by Islam *et al.* (2020) [53]. We observed only the adsorption of small fulvic acid molecules in micropores of activated carbon [54].

3.2. Adsorption of micropollutants

290 3.2.1. Pseudo-steady state

The inlet concentration, C_{input} , of each micropollutant (atrazine, metolachlor, alachlor and their metabolites) was maintained at $1 \mu\text{g L}^{-1}$ at all times. The breakthrough curves were thus obtained along the adsorbers. Figure 6 illustrates the breakthrough curve (the relative concentration (C/C_{input}) against
295 time) of alachlor ESA obtained with GAC1 and GAC2, respectively, at 31.5 and 35 cm. Interestingly, a C/C_{input} plateau was reached between 0.757 to 0.820 after 6000 bv (approximately 2.0 m^3 of treated water). Thus, a pseudo-steady state was established. This specific behavior indicates that the mass transfer of molecules from the bulk of the fluid to the inner porosity of the adsorbent was
300 limited and that the adsorption rate was equilibrated by the contact time of the molecule in liquid-phase. Indeed, the relative concentration was constant with relative variations within the range of 2.91 to 21.03%. This pseudo-steady state was found for all molecules and all bed locations. In the following sections, *i.e.* the mean relative concentration, when the plateau is reached, are compared.

305 3.2.2. Pesticides and metabolites

Figure 7 shows the pseudo-steady state reached for all pesticides and metabolites with GAC1 and GAC2. No significant difference was observed for ATZ, DEA and DIA between the two activated carbons and both adsorbers completely removed these compounds. The mass transfer zone only represented
310 the first 60 cm of the bed. During dynamic adsorption, the adsorbers did not reach saturation and the adsorption capacities at equilibrium were not reached. Transfer from the bulk of the liquid phase to the adsorption sites inside the pores of the GACs implies various mechanisms, including external mass transfer, transportation to larger pores and surface diffusion to reach the adsorption
315 sites. Although atrazine and its metabolites have different physical and chemical properties, mass transfers were equivalent for these molecules and were, most probably, the consequence of simultaneous adsorption with NOM. At low concentrations, similar observations have been made for the adsorption of a binary

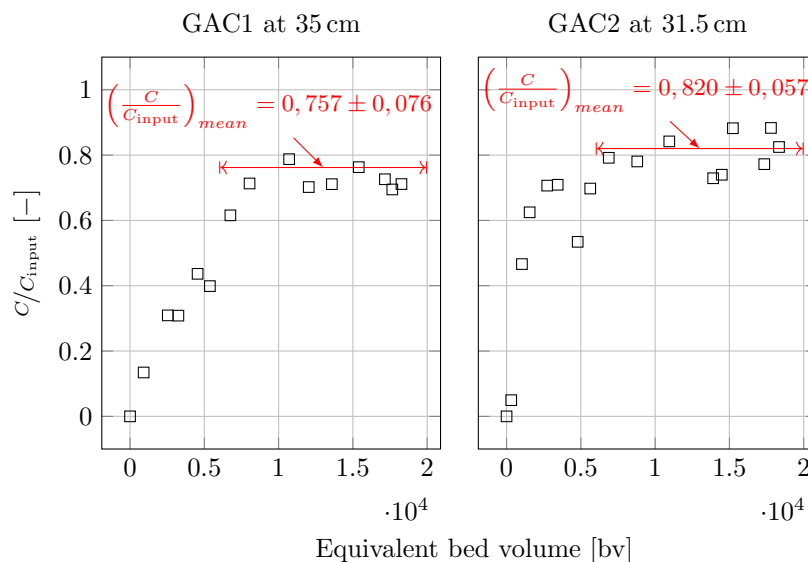


Figure 6: Breakthrough curves ofalachor ESA using GAC1 and GAC2 at 35 cm and 31.5 cm respectively

mixture of DEA and DIA onto activated carbon [55].

320 The parent molecules ALA and METO had similar adsorption behaviors. However, the metabolites ALA ESA, ALA OA, METO ESA and METO OA, were found to reach breakthrough when the mass transfer zone was larger than the height of the columns. As a consequence, the outlet contained ALA OA at 0.26 and 0.14 $\mu\text{g L}^{-1}$ for GAC1 and GAC2, respectively. The main differ-

325 ence between the parent molecules and their metabolites is the chemical functionalization (oxanilic acid or ethanesulfonic acid) of the latter, which greatly decreases their hydrophobicity. Consequently, adsorption under real conditions (trace concentrations and presence of NOM) was slow and the mass transfer zone was larger than the actual size of the adsorbers (1.2 m).

330 The narrow mass transfer zones of ALA and METO could be explained by the presence of NOM, particularly humic acids. Indeed, the adsorption of ALA has been shown to be enhanced by humic acids [56]. By contrast, NOM is likely to interact with the metabolites and thus decrease their transfer to the

external surface of GAC and/or impact their adsorption in the porous materials
335 due to competition [57]. Dynamic adsorption of hydrophilic metabolites (OA
and ESA) was slower despite their fast adsorption in UPW. Two phenomena
could be hypothesized: (i) interaction with NOM in the liquid phase limiting
the external mass transfer, (ii) detrimental adsorption competitions with NOM
with restricted inner adsorption rates [58, 59].

340 3.3. Modeling dynamic adsorption

The Amundson model was used to describe the breakthrough curves along
the fixed beds. As described in section 2.4, in this model, two parameters need
to be adjusted by fitting the experimental data: the adsorption rate k_a and the
adsorption capacity N_a . The experimental breakthrough curves were used at
345 the top three locations (15, 35 and 55 cm depth for GAC1 and 11.5, 31.5 and
51.5 cm for GAC2) to adjust the model. Below these locations, the aqueous
concentrations of the pesticides and their metabolites could not be quantified
for most compounds.

The breakthrough curves of atrazine onto GAC1 and GAC2 are shown in
350 fig. 8. The Amundson model provided a relevant description of the breakthrough
curves in the top layers of each fixed bed.

The adjusted parameters of the Amundson model were determined to min-
imize the average relative error (ARE) for all depths and are given in table 3.
However, the ARE was high (up to 91.8 %) for certain molecules, and this
355 should be taken into consideration. Indeed, dispersion of the experimental con-
centrations along the breakthrough curves led to significant discrepancies be-
tween the experimental data and the model. Nevertheless, several conclusions
can be drawn from the model. The adsorption rates (k_a) were adjusted at
two different orders of magnitudes. Adsorption rates between 1.1×10^{-4} and
360 $1.4 \times 10^{-4} \text{ L } \mu\text{g}^{-1} \text{ min}^{-1}$ were found for atrazine and its metabolites, alachlor
and metolachlor regardless of the GAC used. These compounds were completely
removed by the fixed bed since the rate of adsorption was sufficiently high com-
pared to the residence time in the adsorber. In addition, GAC1 and GAC2

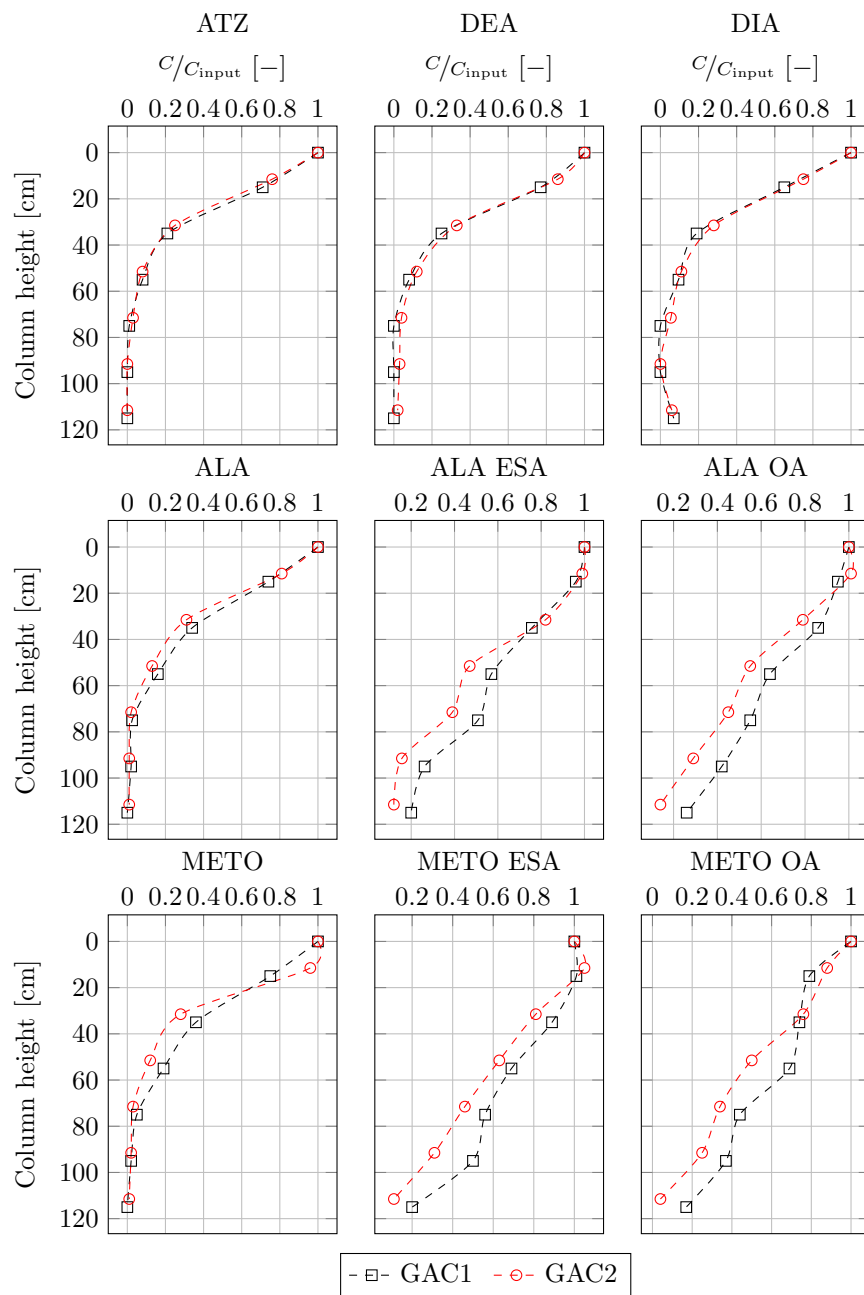


Figure 7: Dynamic adsorption of pesticides and their metabolites onto GAC1 and GAC2 at a pseudo-steady state

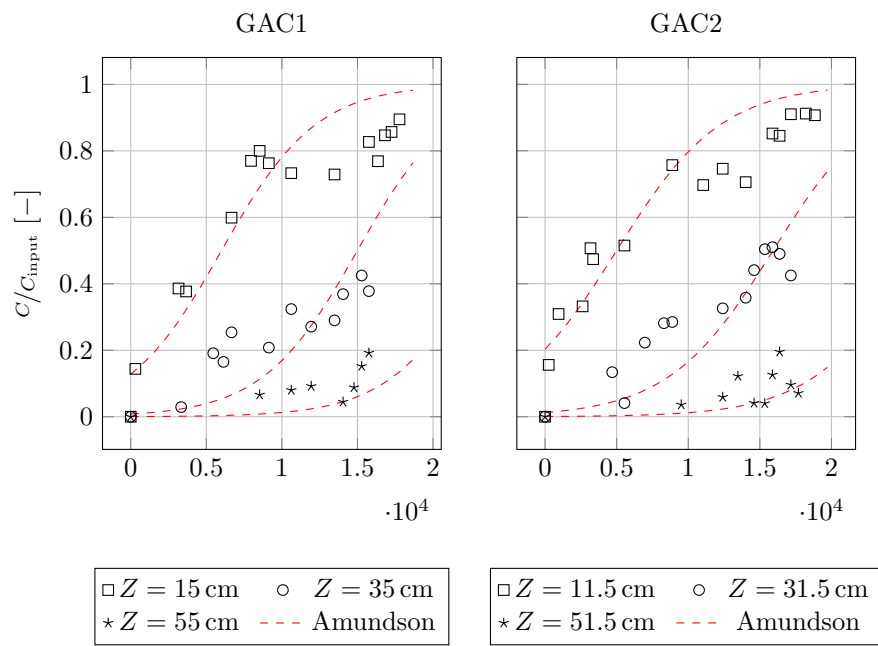


Figure 8: Breakthrough curves of the adsorption of atrazine onto GAC1 and GAC2 at different locations along the fixed beds – application of the Amundson model

displayed similar adsorption behaviors. By contrast,alachlor ESA,alachlor
365 OA,metolachlor ESA and metolachlor OA had lower adsorption rates with k_a
ranged from 4.5×10^{-5} to $8.5 \times 10^{-5} \text{ L } \mu\text{g}^{-1} \text{ min}^{-1}$. These molecules were leak-
ing out of the adsorbers, showing that the residence time was not sufficient for
their entire removal by either fixed beds. The kinetics of the adsorption pro-
cess is thus the key parameter. Adsorption capacities (N_a) ranged from 10.7 to
370 $41.8 \mu\text{g g}^{-1}$ for metolachlor OA andalachlor, respectively. This narrow range
indicates that adsorption was not driven by the capacity of the adsorbent and
this observation confirms the predominance of kinetic effects.

Under dynamic conditions, only two groups of molecules could be distin-
guished: fast adsorbing compounds (ATZ, DIA, DEA, ALA and METO) and
375 slow adsorbing compounds (ALA ESA and OA, METO ESA and OA) with
similar amounts adsorbed in each category. In conclusion, mass transfer in the
presence of NOM was shown to be critical and enhancement of the adsorption
efficiency can be achieved if the mass transfer is enhanced (by adjusting particle
size, liquid velocity, etc.).

Table 3: Adjusted parameters of the Amundson model

Compound	GAC	k_a ($\text{L} \mu\text{g}^{-1} \text{min}^{-1}$)	N_a ($\mu\text{g g}^{-1}$)	ARE (%)
Alachlor	1	1.1×10^{-4}	34.7	54.1
	2	1.4×10^{-4}	41.8	64.0
Alachlor ESA	1	4.5×10^{-5}	22.8	53.8
	2	6.2×10^{-5}	22.6	35.0
Alachlor OA	1	7.5×10^{-5}	21.6	43.9
	2	8.5×10^{-5}	17.6	27.3
Metolachlor	1	1.2×10^{-4}	33.5	55.8
	2	1.3×10^{-4}	35.0	51.4
Metolachlor ESA	1	5.1×10^{-5}	41.0	84.5
	2	5.8×10^{-5}	28.6	41.5
Metolachlor OA	1	6.7×10^{-5}	10.7	24.3
	2	4.9×10^{-5}	33.9	46.6
Atrazine	1	1.4×10^{-4}	33.3	34.3
	2	1.4×10^{-4}	34.6	39.2
Desethyl-Atrazine	1	1.3×10^{-4}	36.2	70.8
	2	1.3×10^{-4}	31.0	30.9
Deisopropyl-Atrazine	1	1.1×10^{-4}	37.7	54.9
	2	1.4×10^{-4}	35.7	91.8

380 **4. Conclusion**

Under dynamic and realistic conditions (trace concentrations of organic pollutants, presence of NOM in underground water) over more than 70 days, no saturation of the adsorbers was observed and a pseudo-steady state was even reached after the treatment of 2.0 m³ of water (approximately 6000 equivalent
385 bed volume) with constant liquid-phase concentrations of the trace compounds. This observation emphasizes that micropollutant adsorption is mainly dependent on kinetic factors and that the adsorption rate for each molecule is the key parameter in this process. Both GACs exhibited similar efficiencies for hydrophobic molecules (ATZ, ALA, METO, DEA, DIA), which were adsorbed
390 within the first 60 cm of the adsorber. Differences were found for the OA and ESA metabolites of ALA and METO. These molecules have different chemical functions, with hydrophilic properties and slower adsorption kinetics onto activated carbon.

The fate of NOM was also studied over time at different bed locations. Unlike organic micropollutants, NOM progressively saturated the adsorbers and
395 the DOC content at the outlet gradually equaled the inlet content. 3D fluorescence showed the predominance of humic acids in underground water, the concentration of which decreased along the column. Fulvic acids were also present but their adsorption was lower. The impact of NOM on the elimination of micropollutants is crucial since it impacted the adsorption kinetics by interacting
400 with the trace molecules and competing for adsorption sites.

References

- [1] Worch, Eckhard, Adsorption Technology in Water Treatment, De Gruyter, Berlin, Boston, 2012. URL: <https://www.degruyter.com/view/title/37581>. doi:10.1515/9783110240238.
- [2] A. Katsigiannis, C. Noutsopoulos, J. Mantziaras, M. Gioldasi, Removal of emerging pollutants through Granular Activated Carbon, *Chemical Engineering Journal* 280 (2015) 49–57.
- [3] A. A. d. A. Alves, G. L. d. O. Ruiz, T. C. M. Nonato, L. C. Müller, M. L. Sens, Performance of the fixed-bed of granular activated carbon for the removal of pesticides from water supply, *Environmental Technology* 40 (2019) 1977–1987. Publisher: Taylor & Francis.
- [4] M. Ahmed, B. Hameed, Removal of emerging pharmaceutical contaminants by adsorption in a fixed-bed column: A review, *Ecotoxicology and Environmental Safety* 149 (2018) 257–266.
- [5] N. Ye, N. Cimetiere, V. Heim, N. Fauchon, C. Feliens, D. Wolbert, Upscaling fixed bed adsorption behaviors towards emerging micropollutants in treated natural waters with aging activated carbon: Model development and validation, *Water Research* 148 (2019) 30–40.
- [6] N. H. Tran, M. Reinhard, E. Khan, H. Chen, V. T. Nguyen, Y. Li, S. G. Goh, Q. Nguyen, N. Saeidi, K. Y.-H. Gin, Emerging contaminants in wastewater, stormwater runoff, and surface water: Application as chemical markers for diffuse sources, *Science of The Total Environment* 676 (2019) 252–267.
- [7] M. Stuart, D. Lapworth, E. Crane, A. Hart, Review of risk from potential emerging contaminants in UK groundwater, *Science of The Total Environment* 416 (2012) 1–21.
- [8] Y. Yang, Y. S. Ok, K.-H. Kim, E. E. Kwon, Y. F. Tsang, Occurrences and removal of pharmaceuticals and personal care products (PPCPs) in

- drinking water and water/sewage treatment plants: A review, *Science of The Total Environment* 596-597 (2017) 303–320.
- [9] C. Teodosiu, A.-F. Gilca, G. Barjoveanu, S. Fiore, Emerging pollutants removal through advanced drinking water treatment: A review on processes and environmental performances assessment, *Journal of Cleaner Production* 197 (2018) 1210–1221.
- [10] S. Cosgrove, B. Jefferson, P. Jarvis, Pesticide removal from drinking water sources by adsorption: a review, *Environmental Technology Reviews* 8 (2019) 1–24. Publisher: Taylor & Francis.
- [11] J. P. Vink, S. E. Van der Zee, Pesticide biotransformation in surface waters: Multivariate analyses of environmental factors at field sites, *Water Research* 31 (1997) 2858–2868.
- [12] K. Kiefer, A. Müller, H. Singer, J. Hollender, New relevant pesticide transformation products in groundwater detected using target and suspect screening for agricultural and urban micropollutants with LC-HRMS, *Water Research* 165 (2019) 114972.
- [13] T. Matsushita, A. Morimoto, T. Kuriyama, E. Matsumoto, Y. Matsui, N. Shirasaki, T. Kondo, H. Takanashi, T. Kameya, Removals of pesticides and pesticide transformation products during drinking water treatment processes and their impact on mutagen formation potential after chlorination, *Water Research* 138 (2018) 67–76.
- [14] R. M. Abdelhameed, H. Abdel-Gawad, B. Hegazi, Effective adsorption of prothiofos (o-2, 4-dichlorophenyl o-ethyl s-propyl phosphorodithioate) from water using activated agricultural waste microstructure, *Journal of Environmental Chemical Engineering* 8 (2020) 103768.
- [15] Q. Zheng, X. Yang, W. Deng, X. C. Le, X.-F. Li, Characterization of natural organic matter in water for optimizing water treatment and minimizing

- disinfection by-product formation, *Journal of Environmental Sciences* 42 (2016) 1–5.
- [16] K. Chon, J. Cho, H. K. Shon, Advanced characterization of algogenic organic matter, bacterial organic matter, humic acids and fulvic acids, *Water Science and Technology* 67 (2013) 2228–2235.
- [17] A. Bhatnagar, M. Sillanpää, Removal of natural organic matter (NOM) and its constituents from water by adsorption – A review, *Chemosphere* 166 (2017) 497–510.
- [18] H. Fallou, S. Giraudet, N. Cimetière, D. Wolbert, P. Le Cloirec, Adsorption onto acfc of mixture of pharmaceutical residues in water–experimental studies and modelling, *Environmental Technology* (2020) 1–11.
- [19] G. Baldauf, Removal of Pesticides in Drinking Water Treatment Entfernung von Pestiziden bei der Trinkwasseraufbereitung, *Acta hydrochimica et hydrobiologica* 21 (1993) 203–208. Publisher: John Wiley & Sons, Ltd.
- [20] R. J. Miltner, D. B. Baker, T. F. Speth, C. A. Fronk, Treatment of Seasonal Pesticides in Surface Waters, *Journal - AWWA* 81 (1989) 43–52. Publisher: John Wiley & Sons, Ltd.
- [21] I. N. Najm, V. L. Snoeyink, Y. Richard, Effect of Initial Concentration of a SOC in Natural Water on Its Adsorption by Activated Carbon, *Journal - AWWA* 83 (1991) 57–63. Publisher: John Wiley & Sons, Ltd.
- [22] E. H. Smith, S.-K. Tseng, W. J. Weber Jr., Modeling the adsorption of target compounds by GAC in the presence of background dissolved organic matter, *Environmental Progress* 6 (1987) 18–25. Publisher: John Wiley & Sons, Ltd.
- [23] W. Bunmahotama, W.-N. Hung, T.-F. Lin, Prediction of the adsorption capacities for four typical organic pollutants on activated carbons in natural waters, *Water Research* 111 (2017) 28–40.

- [24] L. Gicquel, D. Wolbert, A. Laplanche, Adsorption of Atrazine by Powdered Activated Carbon: Influence of Dissolved Organic and Mineral Matter of Natural Waters Adsorption de L'atrazine Par Charbon Actif en Poudre: Influence des Matieres Organiques et Minerales Dissoutes des Eaux Naturelles, *Environmental Technology* 18 (1997) 467–478. Publisher: Taylor & Francis.
- [25] E. H. Smith, Evaluation of multicomponent adsorption equilibria for organic mixtures onto activated carbon, *Water Research* 25 (1991) 125–134.
- [26] S. U. Khan, Adsorption of Pesticide by Humic Substances. A Review, *Environmental Letters* 3 (1972) 1–12. Publisher: Taylor & Francis.
- [27] R. L. Wershaw, P. J. Burcar, M. C. Goldberg, Interaction of pesticides with natural organic material, *Environmental Science & Technology* 3 (1969) 271–273. Publisher: American Chemical Society.
- [28] J. G. Jacangelo, J. DeMarco, D. M. Owen, S. J. Randtke, Selected processes for removing nom: an overview, *Journal-American Water Works Association* 87 (1995) 64–77.
- [29] J.-P. Croue, G. V. Korshin, M. M. Benjamin, Characterization of natural organic matter in drinking water, *American Water Works Association*, 2000.
- [30] Jaman Sanaa, Rodriguez Regina, Mazyck David W., Evaluation of Common Granular Activated Carbon Parameters for Trace Contaminant Removal, *Journal of Environmental Engineering* 145 (2019) 04019035. Publisher: American Society of Civil Engineers.
- [31] Y. Ling, D. M. Alzate-Sánchez, M. J. Klemes, W. R. Dichtel, D. E. Helbling, Evaluating the effects of water matrix constituents on micropollutant removal by activated carbon and β -cyclodextrin polymer adsorbents, *Water Research* 173 (2020) 115551.

- [32] A. Sperlich, M. Harder, F. Zietzschmann, R. Gnirss, Fate of trace organic compounds in granular activated carbon (GAC) adsorbers for drinking water treatment, *Water* 9 (2017) 479.
- [33] O. Gibert, B. Lefèvre, M. Fernández, X. Bernat, M. Paraira, M. Calderer, X. Martínez-Lladó, Characterising biofilm development on granular activated carbon used for drinking water production, *Water Research* 47 (2013) 1101–1110.
- [34] R. M. De Souza, D. Seibert, H. B. Quesada, F. de Jesus Bassetti, M. R. Fagundes-Klen, R. Bergamasco, Occurrence, impacts and general aspects of pesticides in surface water: A review, *Process Safety and Environmental Protection* 135 (2020) 22–37.
- [35] T. Reemtsma, L. Alder, U. Banasiak, Emerging pesticide metabolites in groundwater and surface water as determined by the application of a multi-method for 150 pesticide metabolites, *Water research* 47 (2013) 5535–5545.
- [36] V. Mohaupt, J. Völker, R. Altenburger, S. Birk, I. Kirst, D. Kühnel, E. Küster, S. Semerádová, G. Šubelj, C. Whalley, Pesticides in european rivers, lakes and groundwaters—data assessment (2020).
- [37] V. Jiménez, P. Sánchez, J. L. Valverde, A. Romero, Effect of the nature the carbon precursor on the physico-chemical characteristics of the resulting activated carbon materials, *Materials Chemistry and Physics* 124 (2010) 223–233.
- [38] L. Kovalova, D. R. Knappe, K. Lehnberg, C. Kazner, J. Hollender, Removal of highly polar micropollutants from wastewater by powdered activated carbon, *Environmental Science and Pollution Research* 20 (2013) 3607–3615.
- [39] K. Sing, The use of nitrogen adsorption for the characterisation of porous materials, *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 187-188 (2001) 3–9.

- [40] S. L. Goertzen, K. D. Thériault, A. M. Oickle, A. C. Tarasuk, H. A. Andreas, Standardization of the Boehm titration. Part I. CO₂ expulsion and endpoint determination, *Carbon* 48 (2010) 1252–1261.
- [41] D. W. Rankin, *CRC handbook of chemistry and physics*, 89th edition, edited by David R. Lide, *Crystallography Reviews* 15 (2009) 223–224. Publisher: Taylor & Francis.
- [42] D. J. Lapworth, D. Kinniburgh, An r script for visualising and analysing fluorescence excitation–emission matrices (eems), *Computers and Geosciences* 35 (2009) 2160–2163.
- [43] K. H. Chu, Breakthrough curve analysis by simplistic models of fixed bed adsorption: In defense of the century-old bohart-adams model, *Chemical Engineering Journal* 380 (2020) 122513.
- [44] N. R. Amundson, A note on the mathematics of adsorption in beds, *The Journal of Physical Chemistry* 52 (1948) 1153–1157.
- [45] M. C. Ncibi, Applicability of some statistical tools to predict optimum adsorption isotherm after linear and non-linear regression analysis, *Journal of Hazardous Materials* 153 (2008) 207–212.
- [46] R. S. Summers, P. V. Roberts, Rate of humic substance uptake during activated carbon adsorption, *Journal of Environmental Engineering* 113 (1987) 1333–1349.
- [47] O. Gibert, B. Lefèvre, M. Fernández, X. Bernat, M. Paraira, M. Pons, Fractionation and removal of dissolved organic carbon in a full-scale granular activated carbon filter used for drinking water production, *Water research* 47 (2013) 2821–2829.
- [48] S. A. Parsons, B. Jefferson, E. H. Goslan, P. R. Jarvis, D. A. Fearing, Natural organic matter—the relationship between character and treatability, *Water science and technology: water supply* 4 (2004) 43–48.

- [49] S. Velten, D. R. Knappe, J. Traber, H.-P. Kaiser, U. Von Gunten, M. Boller, S. Meylan, Characterization of natural organic matter adsorption in granular activated carbon adsorbents, *Water research* 45 (2011) 3951–3959.
- [50] E. C. Holahan, Mathematical decomposition and multivariate analysis applied to Raman imaging, Ph.D. thesis, University of Delaware, 2019.
- [51] N. Hudson, A. Baker, D. Reynolds, Fluorescence analysis of dissolved organic matter in natural, waste and polluted waters—a review, *River Research and Applications* 23 (2007) 631–649. Publisher: John Wiley & Sons, Ltd.
- [52] J. E. Kilduff, T. Karanfil, W. J. Weber, Competitive interactions among components of humic acids in granular activated carbon adsorption systems: effects of solution chemistry, *Environmental science & technology* 30 (1996) 1344–1351.
- [53] M. A. Islam, D. W. Morton, B. B. Johnson, M. J. Angove, Adsorption of humic and fulvic acids onto a range of adsorbents in aqueous systems, and their effect on the adsorption of other species: A review, *Separation and Purification Technology* 247 (2020) 116949.
- [54] T. Karanfil, J. E. Kilduff, Role of granular activated carbon surface chemistry on the adsorption of organic compounds. 1. priority pollutants, *Environmental science & technology* 33 (1999) 3217–3224.
- [55] C. Faur, H. Métivier-Pignon, P. Le Cloirec, Multicomponent adsorption of pesticides onto activated carbon fibers, *Adsorption* 11 (2005) 479–490.
- [56] M. Ghani, H. Asghar, H. Nadeem, M. Shahid, M. Zeshan, A. Niaz, S. Husain, Processes governing the environmental fates of alachlor in soil and aqueous media: a critical review, *International Journal of Environmental Science and Technology* (2021) 1–18.
- [57] Y. Matsui, D. R. Knappe, K. Iwaki, H. Ohira, Pesticide adsorption by granular activated carbon adsorbents. 2. effects of pesticide and natural organic

matter characteristics on pesticide breakthrough curves, *Environmental science & technology* 36 (2002) 3432–3438.

- [58] P. A. Quinlivan, L. Li, D. R. Knappe, Effects of activated carbon characteristics on the simultaneous adsorption of aqueous organic micropollutants and natural organic matter, *Water research* 39 (2005) 1663–1673.
- [59] J. Hu, A. Martin, R. Shang, W. Siegers, E. Cornelissen, B. Heijman, L. Ritveld, Anionic exchange for nom removal and the effects on micropollutant adsorption competition on activated carbon, *Separation and Purification Technology* 129 (2014) 25–31.
- [60] M. Ribani, C. H. Collins, C. B. Bottoli, Validation of chromatographic methods: Evaluation of detection and quantification limits in the determination of impurities in omeprazole, *Journal of Chromatography A* 1156 (2007) 201–205.

Supporting Information

A. Materials and experimental methods

Table A.1: SPE-UHPLC-MSMS analysis information

Molecule	MRM transition	Cone Voltage (V)	Collision Energy (eV)	LOD ^a	LOQ ^a	t_r (min)
ALA	271 > 238	19	12	4.2	12.8	6.23
ALA ESA	334 > 162	25	15	5.7	17.2	3.88
ALA OA	284 > 234	20	10	3.0	9.1	3.75
METO	285 > 252	21	26	8.9	27.0	4.04
METO ESA	331 > 202	45	30	9.6	29.1	3.05
METO OA	281 > 248	25	25	4.8	14.5	3.37
ATZ	217 > 174	32	20	3.8	11.6	6.25
DEA	188 > 146	35	20	4.1	12.4	4.57
DIA	174 > 132	31	22	4.4	13.3	3.95

^a $LOD = \frac{3.3 \times s_b}{a}$ and $LOQ = \frac{10 \times s_b}{a}$ in ng L^{-1} determination by standard deviation of the response with s_b the standard deviation of the y intercept of the regression line and b the slope of the analytical curve [60]

B. Fixed bed adsorption and fate of the organic matters

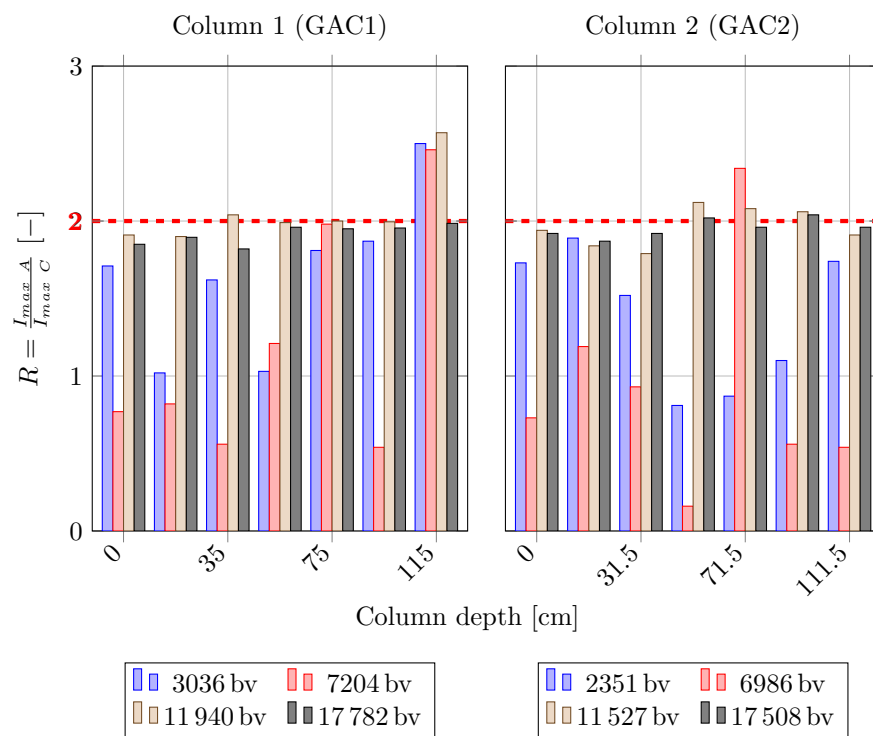


Figure B.1: Determination of the ratio $R = \frac{I_{max,A}}{I_{max,C}}$ as a function of column depth (cm) for GAC1 and GAC2 at different equivalent bed volumes (bv)