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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 $1.0 \,\mu g \, L^{-1}$ for each pesticide and metabolite added to groundwater containing $1.5 \,\mathrm{mg}_{\rm C} \,\mathrm{L}^{-1}$ 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 2.0 m^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

- ⁵ 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.
- [1, 3]. 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 concen-
- ¹⁵ tration 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 nautral 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 µg 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 µg 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 been observed and reduced the adsorption of these metabolites [14].

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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 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

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 $mg_C L^{-1}$ for NOM to $ng - \mu g L^{-1}$ 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

- 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
- 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

- 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-
- 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 comptetion for adsorption sites, identify 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

- (*i.e.* within a few days). RSSCTs must be able to simulate indusctrial 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 fer 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, biodegration) [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.

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 and alachlor were among the 20 most frequently reported pesticides in ground-water 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 µg 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
- 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 µg L^{-1}), in groundwater, the NOM content of which was approximately of $1.5 \text{ mg}_{\text{C}} \text{ L}^{-1}$. 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 adosrption 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 de-

- termined using mercury porosimetry (Autopore IV 9500, Micromeritics). Total pore volum 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
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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 $(m^2 g^{-1})$ | 925 | 990 |
| Apparent density $(g cm^{-3})$ | 0.56 | 0.49 |
| Skeletal density $(g cm^{-3})$ | 0.90 | 0.83 |
| Total pore volume $(cm^3 g^{-1})$ | 0.68 | 0.83 |
| Mesoporous volume $(cm^3 g^{-1})$ | 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 $18.2 \,\mathrm{M\Omega}\,\mathrm{cm}^{-1}$, Millipore-Elga system). All chemicals were supplied by Sigma-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).

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|-------------------------------------------------------------------|------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------|---------------------------------------------------|----------------|----------------------------|
| Compound | CAS number | Formula | $\rm MW^{a}(gmol^{-1})$ | $s^{\rm b}~({ m mgL^{-1}}$ at $25^{\circ}{ m C})$ | log Kow | pK_{a} |
| Alachlor (ALA) | 15972-60-8 | CH ₃ , O N CH ₃ CH ₃ | 269.77 | 240 | 3.52 | 0.62 |
| Alachlor ESA (ALA ESA) | 140939-15-7 | CH3, ON CH3, O | ^{лм} 337.37 | 0.246 | 1.82 | NA |
| Alachlor OA (ALA OA) | 171262-17-2 | CH3, OH | 265.30 | NA | $2.31^{\rm c}$ | NA |
| Metolachlor (METO) | 512818-45-2 | CH3, CH3, CH3, CI | 238.79 | 530 | 3.13 | ND^{q} |
| Metolachlor ESA (METO ESA) | 947601-85-6 | CH3 CH3 CH3 CH3 CH3 CH3 CH3 CH3 CH3 CH3 | ыл. 351.39 | 212461 | -1.89 | NA |
| Metolachlor OA (METO OA) | 152019-73-3 | CH3 OH | 279.33 | 238 | $2.04^{\rm c}$ | NA |
| Atrazine (ATZ) | 1912-24-9 | $\begin{array}{ccc} & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & & \\ & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & \\$ | 1_3 215.68 | 35 | 2.61 | 1.7 |
| Desethyl-Atrazine (DEA) | 6190-65-4 | $CH_3 N \xrightarrow{N} N$ $CH_3 N \xrightarrow{N} N$ $CH_3 NH \xrightarrow{N} NH_C$ | 187.63 | 2700 | 1.51 | NA |
| Deisopropyl-Atrazine (DIA) | 1007-28-9 | CH ₃ ∧ NH ∧ N ⊂I | 173.60 | 980 | 1.15 | 1.3 |
| ^a Molecular Weight ^b Solubility in water | | H v | rom www.molinspir o Dissociation | ation.com version 2011.06 | | |

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

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).

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The aromatic character of NOM is given by the specific UV absorbance (SUVA, $L mg_C^{-1} cm^{-1}$), *i.e.* the UV absorbance at 254 nm (cm⁻¹) divided by the DOC content (mg_C 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
- 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].
- The selected micropolluants 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 μ m, 2.1 × 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 chro-
- $_{175}$ $\,$ matographic column oven and a $\rm C_{18}$ BEH Acquility UPLC column of Waters

 $(100 \text{ mm} \times 2.1 \text{ mm i.d.}, 1.7 \text{ µm})$. The mobile phase consisted of a mixture of UPW-ammonium acetate $(10 \text{ mmol } \text{L}^{-1}, \text{ pH} = 4)$ and methanol-ammonium acetate $(10 \text{ mmol } \text{L}^{-1}, \text{ pH} = 4)$. The flow rate was set at $0.4 \text{ mm } \text{min}^{-1}$ 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, collision energy and retention time (t_r) are reported in supporting information (Table A.1).

2.4. Dynamic adsorption

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Fixed bed adsorbers were designed and studied using realistic conditions that are comparable to industrial filters. Two columns, packed with GAC, 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 Superieure de Chimie de Rennes*, France) to which was added each organic pollutant separately $(1.0 \,\mu g \, L^{-1}$ 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 $2 \, m^3$ tank, which was treated with a biocide (sodium

azide, $[NaN_3] = 2.0 \text{ mg L}^{-1}$ to prevent bacterial growth and development. A centrifugal pump (~ 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 through the column was fixed at 10 m h^{-1} ($S = 2.84 \text{ cm}^2$, $Q = 47.3 \text{ mLmin}^{-1}$)

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).

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 = $1 \ \mu g \ L^{-1}$, flowrate through each adsorber 47.3 mL min⁻¹, superficial velocity = $10 \ m \ h^{-1}$, $D = 1.9 \ cm$, $S = 2.84 \ cm^2$)

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].

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

 $C \ (\mu g g^{-1})$ is the concentration of the adsorbate in the outlet, $C_{\text{input}} \ (\mu g g^{-1})$ is the concentration of the adsorbate in the inlet, $k_a \ (g \mu g^{-1} \min^{-1})$ is the Amundson rate constant, $N_a \ (\mu g g^{-1})$ is the maximum adsorption capacity of the adsorbent per mass of adsorbent, $t \ (\min)$ is the operating time, $u \ (\text{cm} \min^{-1})$ is the superficial velocity, $Z \ (\text{cm})$ 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.

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

²²⁰ N is the number of experimental data points, $C/C_{input, cal}$ is the theoretically calculated concentration ratio and $C/C_{input, exp}$ is the experimental concentration ratio.

3. Results and Discussion

3.1. Fixed bed adsorption and fate of the organic matters

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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 $1.6 \text{ mg}_{\text{C}} \text{ L}^{-1}$, but varied between $1.4 \text{ and } 1.9 \text{ mg}_{\text{C}} \text{ L}^{-1}$. Likewise, the nature of NOM changed during the experiment as seen from SUVA data which

varied from 2 to $5 \,\mathrm{L\,mg_C^{-1}\,cm^{-1}}$. 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).

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 $1.5 \text{ mg}_{\text{C}} \text{ L}^{-1}$, whereas DOC content in the output water is below $1.0 \text{ mg}_{\text{C}} \text{ L}^{-1}$ irrespective of the type of GAC. Over time and equivalent bed 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

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SUVA is a quantitative measure of the aromatic character of organic compounds. Generally, a SUVA lower than $2 \,\mathrm{L\,mg_C^{-1}\,cm^{-1}}$ indicates that NOM is mainly composed of non-humic substances, whereas a SUVA higher than $4 \,\mathrm{L\,mg_C^{-1}\,cm^{-1}}$ 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 $2.54 \,\mathrm{Lmg_C^{-1} \, cm^{-1}}$) 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)

²⁵⁵ [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 ²⁶⁰ surface with peaks (fig. 4). The spectrum of the blank, *i.e.* ultrapure water, was substracted 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]:

- □ 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

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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 µg 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

- time) of alachor 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 (approximatively 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
- 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 the first 60 cm of the bed. During dynamic adsorption, the adsorbers did not

- 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
- 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 of a lachor ESA using GAC1 and GAC2 at $35\,\mathrm{cm}$ and $31.5\,\mathrm{cm}$ respectively

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

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 µg L⁻¹ for GAC1 and GAC2, respectively. The main difference 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).

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

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 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 minimize 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, add this should be taken into consideration. Indeed, dispersion of the experimental concentrations anlong the breakthrough curves led to significant discrepancies between 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 $1.4 \times 10^{-4} \,\mathrm{L\,\mu g^{-1}\,min^{-1}}$ 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 compared 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 a trazine 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

- OA, metolachlor ESA and metolachlor OA had lower adsorption rates with k_a ranged from 4.5×10^{-5} to 8.5×10^{-5} L µg⁻¹ min⁻¹. These molecules were leaking 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 process is thus the key parameter. Adsorption capacities (N_a) ranged from 10.7 to
- $_{370}$ 41.8 µg g⁻¹ for metolachlor OA and alachlor, 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 distinguished: 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.).

| Compound | GAC | $k_a \ (\mathrm{L}\mathrm{\mu}\mathrm{g}^{-1}\mathrm{min}^{-1})$ | $N_a \ (\mathrm{\mu g}\mathrm{g}^{-1})$ | ARE (%) |
|------------------------|-----|------------------------------------------------------------------|-----------------------------------------|---------|
| | 1 | $1.1	imes 10^{-4}$ | 34.7 | 54.1 |
| Alachlor | 2 | $1.4 	imes 10^{-4}$ | 41.8 | 64.0 |
| | 1 | $4.5 	imes 10^{-5}$ | 22.8 | 53.8 |
| Alachlor ESA | 2 | $6.2	imes 10^{-5}$ | 22.6 | 35.0 |
| | 1 | $7.5 	imes 10^{-5}$ | 21.6 | 43.9 |
| Alachlor UA | 2 | $8.5	imes 10^{-5}$ | 17.6 | 27.3 |
| | 1 | $1.2	imes 10^{-4}$ | 33.5 | 55.8 |
| Mevolacinor | 2 | $1.3	imes 10^{-4}$ | 35.0 | 51.4 |
|) (- 4 - 1 Tr C A | 1 | $5.1	imes10^{-5}$ | 41.0 | 84.5 |
| Merolaciilor E.S.A. | 2 | $5.8	imes10^{-5}$ | 28.6 | 41.5 |
| | 1 | $6.7	imes 10^{-5}$ | 10.7 | 24.3 |
| Merolacinor OA | 2 | $4.9 	imes 10^{-5}$ | 33.9 | 46.6 |
| A traveiro | 1 | $1.4 	imes 10^{-4}$ | 33.3 | 34.3 |
| Autazine | 2 | $1.4 	imes 10^{-4}$ | 34.6 | 39.2 |
| Docethed Atmosta | 1 | $1.3	imes10^{-4}$ | 36.2 | 70.8 |
| Desertify F-Aut azarte | 2 | $1.3 	imes 10^{-4}$ | 31.0 | 30.9 |
| Doissessed Attention | 1 | $1.1 	imes 10^{-4}$ | 37.7 | 54.9 |
| Deisopropyr-Autazine | 2 | $1.4 	imes 10^{-4}$ | 35.7 | 91.8 |

Table 3: Adjusted parameters of the Amundson model

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 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 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. Un-³⁹⁵ like organic micropollutants, NOM progressively saturated the adsorbers and 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 mi-

400 cropollutants is crucial since it impacted the adsorption kinetics by interacting with the trace molecules and competing for adsorption sites.

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Supporting Information

A. Materials and experimental methods

| Molecule | MRM transition | Cone Voltage (V) | Collision Energy (eV) | LOD ^a | ^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 |

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

^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)