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Article

# Adsorption of Aclonifen, Alachlor, Cd and Cu onto Natural River Suspended Matter in the Context of Multi-Pollutions: Influence of Contaminant Co-Presence and Order of Input into the Aqueous Solution

Desiree El Azzi <sup>1,2,\*</sup>, François Laurent <sup>1,3</sup>, Vincent Roussiez <sup>4</sup>, Lei Chou <sup>4</sup>, Maritxu Guiresse <sup>1</sup> and Jean-Luc Probst <sup>1</sup>

<sup>1</sup> EcoLab, Université de Toulouse, CNRS, UPS, INPT, Campus ENSAT, Avenue de l'Agrobiopole, 31326 Castanet Tolosan CEDEX, France; francois.laurent@toulouse.inra.fr (F.L.); Maritxu.Guioresse@ensat.fr (M.G.); jean-luc.probst@ensat.fr (J.-L.P.)

<sup>2</sup> Faculty of Agricultural and Food Sciences, Holy Spirit University, Kaslik, Jounieh B.P. 446, Lebanon

<sup>3</sup> INRA, UMR Xénobiotiques, B.P. 3, 180 Chemin de Tournefeuille, 31931 Toulouse CEDEX 9, France

<sup>4</sup> Service de Biogéochimie et Modélisation du Système Terre, Université Libre de Bruxelles, B-1050 Brussels, Belgium; roussiez@hotmail.com (V.R.); Lei.Chou@ulb.ac.be (L.C.)

\* Correspondence: desireeelazzi@usek.edu.lb; Tel.: +961-9-600-886

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**Abstract:** In the environment, a pollutant is rarely present alone, and other contaminants can influence its fate. To investigate the influence of the presence of other pollutants on the sorption of pesticides and trace metals (TM), the adsorption of Aclonifen, alachlor, Cd and Cu onto suspended particulate matter (SPM) was studied. SPM was isolated during the flood event of May 2010 in the Save agricultural watershed of SW France. Adsorption equilibrium was reached after 2 h of contact with SPM for pesticides and 24 h for TM. To simulate natural conditions, the SPM load allowing a maximum adsorption of pollutants was set at  $1 \text{ g L}^{-1}$  and the concentration of pollutants at  $10 \text{ } \mu\text{g L}^{-1}$ . These factors being established, the co-presence experiments showed that most contaminants were influenced by the presence of other pollutant(s) in the water, trace metals to a lesser extent than pesticides. The mutual influence can be either competition for the same adsorption sites or formation of new complexes between pollutants. These phenomena can modify the adsorption capacities of each pollutant. The order of introduction into the aqueous solution also influenced the amount of adsorption of pollutants onto SPM. These results open new perspectives on the fate of pollutants.

**Keywords:** pesticides; trace metals; suspended particulate matter; adsorption; co-presence

## 1. Introduction

Pesticides and trace metals (TM) are two important types of environmental pollutants which may be strongly sorbed onto particles after entering natural aquatic systems. Their sorption behavior governs their transport, bioavailability, ecotoxicity and finally their fate in the environment. The sorption mechanisms of organic and inorganic pollutants have been widely studied. However, the effect of coexisting contaminants is seldom reported.

Previous studies reported that the sorption of organic pollutants in the presence of trace metals and vice versa could decrease due to the formation of new pesticide-metal complexes. Trace metals can also act as a link between pesticides and other components of the soil (such as organic matter), facilitating their adsorption [1–4].

Besides complexation, the rate of adsorption of an ionic pesticide and a TM can be modified by a change in the physical-chemical characteristics of the solution closely related to the introduction of a new pollutant [1,3].

Furthermore, competitive adsorption to soil binding sites (clay minerals or organic matter for example) can sometimes explain the change in the adsorption rates of a pollutant in the presence of others [5–7]. Two cationic pollutants such as chlordimeform and Cu have been reported to compete for the exchange sites of montmorillonite [5]. Competition for adsorption sites also decreased p-nitrophenol's adsorption onto soils in the presence of Cu [6].

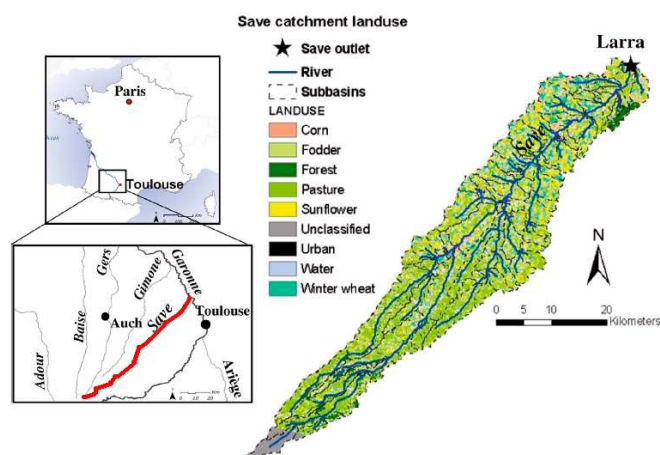
The order of presence of a pollutant in the aquatic environment has sometimes an impact on its influence on other contaminants. If, for example, Cu is present before glyphosate, it is adsorbed and thus influences less the adsorption of a subsequently arriving pesticide [8]. This remains true if Cu remains present at low concentrations and does not lead to competition for binding sites. If the pesticide is present before the TM, its influence on the adsorption of TM is also not the same [5]. In fact, when the pesticide is adsorbed first on specific sites, it can separate clay layers and facilitate the penetration of Cu in the network.

To our knowledge, few studies have focused on the mutual effects of the presence of TM and pesticides on their adsorption on natural suspended particulate matter (SPM). Hence, the overall objectives of this study were (1) to investigate, with respect to natural conditions, the adsorption characteristics of two pesticides and two TM in both mono and multi pollution scenarios and (2) to discuss the interaction mechanisms between TM, pesticides and SPM. Results of this work will provide an insight into the sorption of pollutants in natural environments frequently contaminated with various pollutants. Applications are various, from the assessment of contaminant removal capacities of naked mineral adsorbents to the understanding of mechanisms naturally occurring in natural environments [9,10].

## 2. Materials and Methods

### 2.1. Study Area

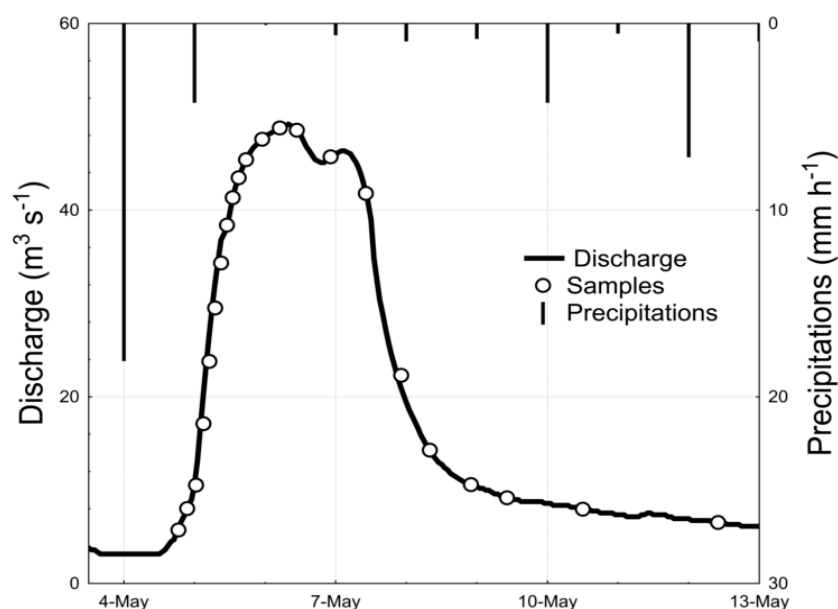
The source of the Save river, located in the “Côteaux de Gascogne” region (Gascony hills), is in the piedmont of the Pyrenees Mountains. Of about 140 km length, it drains an agricultural catchment of 1110 km<sup>2</sup>. Sampling was conducted at Larra station (01°14'40" E–43°43'4" N), ahead of the confluence of the Save river with the Garonne river (Figure 1). The upstream part of the catchment is a hilly agricultural area mainly covered with pasture and forest (56%), while the lower part is relatively flat along the Save main channel and hilly on both sides, mainly devoted to intensive agricultural activities (44%), mostly wheat, corn and sunflower which make the use of pesticides necessary.



**Figure 1.** Localization of the Save catchment and the Larra sampling station (triangle) at the outlet. The land use map is extracted from [11].

## 2.2. Sampling Strategy

This study concerns the flood event of May 2010. This period coincides with a period of application of pesticides in the watershed. The mean instant discharge increased from  $3 \text{ m}^3 \text{ s}^{-1}$  to almost  $50 \text{ m}^3 \text{ s}^{-1}$  at the peak stormflow (Figure 2). This flood event was intensively sampled to study the transfer dynamics of organic and inorganic contaminants from the soils to the river in relation to the discharges of the different stormflow components [12].



**Figure 2.** Variations in the Save river discharge and precipitations during the storm flow event of May 2010. Sampling points are represented with the diamonds. Source CACG-France ([www.cacg.fr](http://www.cacg.fr)).

## 2.3. Sample Treatment and Analyses

The choice of the waters and the solid materials used for the mixing experiments correspond to the peak of the flow. Suspended Particulate Matter (SPM) was separated by Continuous-Flow ultracentrifugation at  $0.22 \mu\text{m}$ . Both water and solid materials used were meticulously characterized for major and trace elements as well as pesticides prior to the mixture experiments. Details of the physicochemical characterizations of water and sediments are presented in [12] and listed in the results tables.

## 2.4. Experimental Protocol

The experimental strategy consisted of putting SPM, collected in the field at the peak flow and separated by ultracentrifugation, into suspension again in the filtered water of the peak flow. This mixture was then shaken for 12 h before spiking with one or more pollutants.

### 2.4.1. Choice of Pollutants and Spiking Solutions

To be close to natural conditions, the most concentrated pollutants detected in the samples during the flood were chosen for the spiking experiment.

Two non-ionic pesticides were chosen, one more soluble and one less soluble: Alachlor (Ala; solubility:  $342 \text{ mg L}^{-1}$ ;  $K_{ow} = 3.03$ ) and Aclonifen (Acl; solubility:  $1.4 \text{ mg L}^{-1}$ ;  $K_{ow} = 4.67$ ) which had been already detected in the Save river [12]. Carbon-14 labeled pesticide solutions were used to detect low concentrations efficiently.

As trace elements, two highly anthropogenic and toxic elements detected were chosen: Cd and Cu, frequently present in fertilizers and in pesticides, which were found to be moderately (for Cu) to highly (for Cd) enriched in the river bottom sediments of this area [12]. Merck standard solutions CertiPUR<sup>®</sup>

(Merck, Kenilworth, NJ, USA) Cd ( $\text{Cd}(\text{NO}_3)_2$  in  $\text{HNO}_3$   $0.5 \text{ mol L}^{-1}$ ,  $1000 \text{ mg L}^{-1}$ ) and Cu ( $\text{Cu}(\text{NO}_3)_2$  in  $\text{HNO}_3$   $0.5 \text{ mol L}^{-1}$ ,  $1000 \text{ mg L}^{-1}$ ) were used to prepare  $1.0 \text{ mg L}^{-1}$  spikes. These standards have very acidic pH; therefore, after their addition to the mixtures, the pH was adjusted with Merck Suprapur<sup>®</sup> (Merck, Kenilworth, NJ, USA) sodium hydroxide (9.97 M) in order to maintain the pH at values between 8.0 and 8.5, close to the natural environmental conditions [12].

The stock solutions used in the adsorption experiments are:

Cd:  $0.996 \pm 0.04 \text{ mg L}^{-1}$

Cu:  $0.989 \pm 0.02 \text{ mg L}^{-1}$

Aclonifen (14C): 395 dpm/ng Aclonifen used to prepare solutions of 79,000 dpm in 20 mL equivalent to  $10.0 \mu\text{g L}^{-1}$

Alachlor (14C): 354 dpm/ng Alachlor used to prepare solutions of 70,800 dpm in 20 mL equivalent to  $10.0 \mu\text{g L}^{-1}$ .

#### 2.4.2. Analyses

Exchanges of pollutants between particulate and dissolved phases were followed by analyzing their respective concentrations in the dissolved and the particulate fractions as a function of time.

For each experimental sampling, 10 mL of the solution with the suspended matters was sub-sampled and filtered for the analysis of pesticides using Fischer glass syringes and for the analysis of metals using 1 N HCl pre-cleaned Nuclepore Whatman polycarbonate syringe filters (25 mm in diameter and  $0.22 \mu\text{m}$  in pore size).

Syringe filters served to remove the particulate phase from the dissolved phase. All experiments were conducted in duplicates.

##### - Pollutants in the dissolved phase:

Trace metal concentrations were determined by inductively coupled plasma quadrupole mass spectrometry (ICP-Q-MS Agilent 7500ce, Agilent Technologies, Santa Clara, CA, USA) on the acidified solution. Carbon-14 labelled pesticides were determined with a Tri-Carb<sup>®</sup> counter (Liquid Scintillation Analyzer, 1500 CA, Packard Instrument Company, Downers Grove, IL, USA) using Permafluor and Carborb as scintillation cocktails (PerkinElmer LAS, Boston, MA, USA).

##### - Pollutants in the particulate phase:

The recovered filters were first dried at  $40 \text{ }^\circ\text{C}$ . Once dry, they followed two different treatments depending on whether they were intended to be analyzed for TM or for pesticides. The filters analyzed for Cd and Cu underwent a total acidic digestion and the metal content was determined by ICP-MS. Total digestion was performed in a clean room on the fine fractions ( $<63 \mu\text{m}$  obtained after filtration) of SPM since metals are preferentially associated with the finest fractions of high specific surface areas [12]. Separation of the  $<63 \mu\text{m}$  fraction was done with the eventual purpose of correcting for the grain-size effect [12]. Taking the same fraction also allows for normalizing samples to one grain size distribution. The samples were put through the following total digestion procedure: 0.1 g dry weight was digested overnight with 0.6 mL of double-distilled  $\text{HNO}_3$  (68%) + 0.5 mL of concentrated HF (47% to 51%) at  $90 \text{ }^\circ\text{C}$ . Evaporation was then conducted at  $60 \text{ }^\circ\text{C}$  until the residue was dry. Next, the dry residue was attacked with 0.5 mL (four times) of  $\text{H}_2\text{O}_2$  35% to destroy the organic matter. Evaporation was then conducted another time at  $60 \text{ }^\circ\text{C}$  until the residue was dry. Finally, the dry sample was dissolved in 2 mL of double-distilled  $\text{HNO}_3$ . At this point, most solutions were clear. If not, the residue underwent the last step ( $\text{HNO}_3 + \text{H}_2\text{O}_2$ ) again. This procedure has been successfully tested for total digestion of fluvial sediments and soils [12]. During the digestion procedure, blanks and standards (Standard Reference Material SRM-1646a, estuarine sediment (National Institute of Standards and Technology (NIST), USA), SUD-1, lake sediment (National Laboratory for Environmental Testing at the National Water Research Institute, Environment Canada, Burlington, ON, Canada), WQB-1, stream sediment (National Water Resource Institute, Ontario, Canada) and STSD-3, stream sediment

(Natural Resources Canada, Ontario, Canada)) underwent the same treatment as the samples to evaluate potential external contamination and efficiency of the chemical procedure. Recovery rates of used standards were satisfactory: between 94% and 105% for SRM-1646a, SUD-1, WQB-1 and STSD-3. Thus, the total digestion can be considered reliable. Trace metal concentrations were determined by ICP-MS.

Filters destined for pesticides analyses were burned in an oxidizer (Sample Oxidizer model 307-Packard Instrument Company, Downers Grove, IL, USA) and radioactive molecules were then counted with a Tri-Carb<sup>®</sup> counter (Liquid Scintillation Analyzer, 1500 CA, Packard, Instrument Company, Downers Grove, IL, USA) using Permafluor and Carbosorb (PerkinElmer LAS, Boston, MA, USA).

#### 2.4.3. Preliminary Experiments

Previous laboratory experiments devoted to the description of the nature and extent of adsorption/desorption processes onto/from mineral surfaces proposed the dominant role of a combination of factors: pH, temperature [13], ionic strength, time of contact [14], adsorbent nature and content in solution [10] and initial concentration of pollutant of concern [14].

In the research reported here, because of the exclusive use of materials collected in the field, pH and ionic strength reflect in-situ conditions. The temperature is maintained constant at room temperature. To determine the appropriate time of contact, adsorbent content and initial concentration of pollutant, preliminary experiments were conducted.

##### - Influence of the time of contact-adsorption kinetics

To determine the contact time required to reach equilibrium for each pollutant, sorption experiments were performed at specific pH, SPM load and pollutant concentrations. The only variable factor was the elapsed time after the addition of the pollutant. The principle of the experiments is described in the literature [15]. The SPM load selected is  $1 \text{ g L}^{-1}$ , average at the peak of the studied Save flood also corresponding to the world average SPM load in surface waters [16]. Spikes of pollutants had concentrations fixed to  $10 \text{ } \mu\text{g L}^{-1}$  that could be observed in field-contaminated samples. Sub-samples were extracted with syringes, as described in the Section 2.4.2, at different times  $t$  (1, 5, 10, 15, 30, 45 min and 1, 2, 4, 8, 10, 24, 48 and 120 h).

Recovery rates of pollutants spiked were as follows:  $108 \pm 31\%$  for Cd;  $106 \pm 33\%$  for Cu;  $60 \pm 10\%$  for Aclonifen and  $102 \pm 4\%$  for Alachlor.

##### - Influence of the suspended sediment load

Series of suspensions with various loads of SPM were prepared (0.01, 0.1, 0.5, 1, 2 and  $10 \text{ g L}^{-1}$ ). These large spectrums cover the SPM loads regularly observed in the Save river [12]. Spikes of pollutants had concentrations fixed to  $10 \text{ } \mu\text{g L}^{-1}$ . Adsorption processes of solutes onto/off adsorbents are governed by equilibriums between dissolved and particulate contents. These equilibriums can be characterized by empirical equations called isotherms. Graphically, the latter are curves relating the mass-normalized contents of a solute on the adsorbent surface to the contents of the solute in the dissolved phase at the equilibrium state and constant temperature.

Recovery rates of pollutants spiked were as follows:  $110 \pm 20\%$  for Cd;  $65 \pm 9\%$  for Cu;  $103 \pm 15\%$  for Aclonifen and  $100 \pm 6\%$  for Alachlor.

##### - Influence of the initial concentration of pollutant-sorption isotherms

The sorption experiments were carried out with a SPM load of  $1 \text{ g L}^{-1}$ . Series of suspensions were prepared with different spiked freshwaters, to obtain the following initial pollutant contents in the dissolved phase: 1, 5, 10, 50 and  $100 \text{ } \mu\text{g L}^{-1}$ . The curve representing the percentage of pollutant adsorbed at equilibrium versus the initial spiked concentration allowed determining the appropriate initial concentration of pollutants to be used in the adsorption experiments.

Recovery rates were as follows:  $84 \pm 13\%$  for Cd;  $82 \pm 25\%$  for Cu;  $80 \pm 15\%$  for Aclonifen and  $91 \pm 5\%$  for Alachlor.

#### 2.4.4. Co-Presence Experiments

In the following experiments, the time of contact, the SPM load and the initial concentration of pollutants spiked were kept constant. In fact, the studied factor here was the mutual influence of a contaminant on another. Following the same experimental protocol described above, the adsorption of a pollutant alone in the solution was compared to its adsorption when present with one or more additional pollutants. This aims to simulate the fate of pollutants in a natural environment.

The order of the presence of pollutants in the environment may have a role in their mutual influence [8], so we varied the order of spikes. When one pollutant was added, the second one was introduced after the equilibrium time determined for each. A summary of the studied mixtures is shown in Table 1.

**Table 1.** Summary of the studied mixtures. Each line corresponds to a case study. The numbers represent the order of introduction in the mixture. Two pollutants with the same number were introduced simultaneously.

Aclonifen	Alachlor	Cd	Cu
1	2	-	-
1	2	3	-
1	2	-	3
1	-	2	-
1	-	-	2
2	1	-	-
-	1	2	-
-	1	-	2
2	1	3	-
2	1	-	3
1	1	-	-
1	1	2	-
1	1	-	2
2	-	1	-
-	2	1	-
-	-	1	2
3	-	1	2
-	3	1	2
2	-	-	1
-	2	-	1
-	-	2	1
3	-	2	1
-	3	2	1
-	-	1	1
2	-	1	1
-	2	1	1
1	1	1	1

#### 2.5. Statistical Analysis

STATISTICA 8.0 data analysis software (StatSoft Inc., Tulsa, OK, USA) and GraphPad Prism software, version 7.04 (GraphPad Software Inc., La Jolla, CA, USA) were used to carry out graphical fitting and statistical analysis of the data set.

To study the influence of the SPM load on pollutants' adsorption, data was fitted to a Michaelis-Menten-like model:

$$A = A_{\max} \times \frac{S}{K_m + S} \quad (1)$$

where  $A$  is the adsorption percentage of the pollutant of concern initially added,  $S$  the SPM load,  $A_{\max}$  the saturation percentage and  $K_m$  the SPM load at which the adsorption is half of  $A_{\max}$ .

To study the influence of the initial pollutant's concentration on its adsorption, adsorption isotherms were used. Adsorption equilibrium is usually described by an isotherm equation whose parameters express the surface properties and affinity of the adsorbent. Adsorption isotherms can be generated based on theoretical models such as Langmuir and Freundlich isotherms. The Langmuir model assumes that uptake of metal ions occurs on a homogenous surface monolayer adsorption without any interaction between adsorbed ions whereas the Freundlich equation is an empirical equation based on adsorption on a heterogeneous surface. Because SPM has a heterogeneous surface, the Freundlich equation was more applicable to our results. The Freundlich equation is commonly represented as:

$$\ln Q_e = \ln K_F + \frac{1}{n} \times \ln C_e \quad (2)$$

where  $Q_e$  = the amount adsorbed ( $\text{mol g}^{-1}$ ) at equilibrium,  $C_e$  = equilibrium concentration ( $\text{mol L}^{-1}$ ),  $K_F$  and  $n$  are Freundlich constants characteristics of the system, indicating the adsorption capacity and the adsorption intensity, respectively.

### 3. Results and Discussion

#### 3.1. Water and SPM Characterization

The water of the studied peak flow from the Save river was filtered and used for all the adsorption experiments. Table 2 shows its main characteristics.

Due to the carbonates present in the basin, the pH of water is basic despite the input of precipitations [17]. Electrical conductivity and alkalinity are within normal ranges for flood episodes in this catchment [12]. Dissolved Organic Carbon (DOC) presents a value of  $7.61 \text{ mg L}^{-1}$ , higher than the values usually found in lower discharges. The increase in DOC concentration with the flow is related to raindrops percolating through the soils of the basin and transporting organic matter to the watercourse [18].

SPM value is high,  $726 \text{ mg L}^{-1}$ , more than 20 times higher than its average level in low water ( $30 \pm 20.5 \text{ mg L}^{-1}$ ) [12]. This increase is due to the erosion related to the heavy rainfall [19] but also to the nature of the soils, agricultural practices, etc. [20].

Major cations and anions were also tested, and results show that some are more concentrated during the storm ( $\text{NO}_3$  and  $\text{K}$ ) whereas others are diluted ( $\text{Ca}$ ,  $\text{Cl}$ ,  $\text{Mg}$ ,  $\text{Na}$ ,  $\text{PO}_4$  and  $\text{SO}_4$ ).

More details about the variation of all these characteristics during the studied storm event can be found in [12].

$\text{Cu}$ ,  $\text{Cd}$ , Aclonifen and Alachlor increased during the peak of the storm. Aclonifen was found to be linked to SPM whereas Alachlor seems to be linked to the dissolved organic carbon [12]. Organic matter plays a significant role in the transfer of both  $\text{Cu}$  and  $\text{Cd}$  [12].

It is commonly reported that the nature of the adsorbent especially the clay fraction and its coating formations (e.g., organic matter, iron and manganese oxides), play an important role in the pollutant binding capacity of particles. The specific compositions—and hence the adsorptive properties—of the used SPM, were studied by analysis of many parameters of interest: specific surface area, organic carbon contents, and redox-sensitive element contents (i.e., total  $\text{Fe}$  and  $\text{Mn}$ ), etc. The results of these analyses are summarized in Table 3.



**Table 2.** Physico-chemical characteristics of the filtered peak water used in the adsorption experiments. Details of the methods used can be found in [12].

Water Characteristics	Value	Method Used
pH	8.1	On-site Measurement, WTW multi parameter tool (pH/Cond 340i/SET, Weilheim, Germany).
Conductivity (dS m <sup>-1</sup> )	0.247	
Alkalinity (mgHCO <sub>3</sub> <sup>-</sup> L <sup>-1</sup> )	157.60	Acid Titration to a final pH of 3.0.
DOC (mg L <sup>-1</sup> )	7.61	Shimadzu TOC 5000 Analyzer (Shimadzu Corporation, Tokyo, Japan; limit of quantification 0.14 mg L <sup>-1</sup> and uncertainty of 2%).
SPM (mg L <sup>-1</sup> )	726	Continuous-flow ultracentrifugation (Beckman Coulter, Indianapolis, IN, USA; 700 mL/min; 17,000 RPM) at 0.22 µm.
Ca (mg L <sup>-1</sup> )	51.20	Inductively coupled plasmaoptical emission spectrometry (ICP-OES Thermo IRIS INTREPID II XDL, Thermo Fischer Scientific Inc., Waltham, MA, USA). Typical limits of quantification were between 0.5 and 0.3 mg L <sup>-1</sup> for Na <sup>+</sup> and K <sup>+</sup> and between 0.07 and 0.03 mg L <sup>-1</sup> for Ca <sup>2+</sup> and Mg <sup>2+</sup> .
K (mg L <sup>-1</sup> )	4.18	
Mg (mg L <sup>-1</sup> )	6.49	
Na (mg L <sup>-1</sup> )	6.60	
Cl (mg L <sup>-1</sup> )	15.81	
NO <sub>3</sub> (mg L <sup>-1</sup> )	8.53	Dionex 4000I series Ion chromatography System (Dionex Corporation, Sunnyvale, CA, USA). Typical limit of quantification was 0.1 mg L <sup>-1</sup> .
PO <sub>4</sub> (mg L <sup>-1</sup> )	0.03	
SO <sub>4</sub> (mg L <sup>-1</sup> )	5.20	
Cd (µg L <sup>-1</sup> )	0.01 ± 0.00	Inductively coupled plasma quadrupole mass spectrometry (ICP-Q-MS Agilent 7500ce, Agilent Technologies, Santa Clara, CA, USA) equipped with a collision cell He. Typical detection limits are between 1 and 100 ng L <sup>-1</sup> and the external precision is ±5%.
Cu (µg L <sup>-1</sup> )	3.06 ± 0.09	
Alclonifen (µg L <sup>-1</sup> )	0.081	GC-MS: Gas chromatography column from Zebra ZB-5MS 30 m, 0.25 mm i.d., and 0.25 µm film from Phenomenex® (Torrance, CA, USA) with Thermo Fisher Scientific (Waltham, MA, USA) Trace GC 2000 coupled with a DSQ II mass detector. The detection limit, based on a signal-to-noise ratio of 3, was estimated to 1 to 3 ng L <sup>-1</sup> depending on the molecule.
Alachlor (µg L <sup>-1</sup> )	0.002	

**Table 3.** Physico-chemical characteristics of the particles used in the adsorption experiments. Details of the methods used can be found in [12].

Suspended Matter Characteristics	Value	Method Used
Particulate Organic Carbon (mg g <sup>-1</sup> )	22.127	CarloErba NA2100 protein CHN analyzer (Carlo Erba Instruments, Milan, Italy; limit of quantification < 0.02%).
C/N	5.630	-
Grain Size	Clay 14% Silt 83% Sand 3%	MasterSizer laser diffraction particle size analyzer (Malvern Panalytical, Malvern, UK).
Clay mineralogy	Smectite 13% Illite 62% Kaolinite 25%	G3000 diffractometer coupled with CuKα radiation (INEL, Artenay, France; 0.15418 nm at 30 kV and 40 mA with a step interval of 0.032° 2θ and counting times of 3 s).
SiO <sub>2</sub> (%)	56.75	Total elemental composition was analyzed at the Service d'Analyse des Roches et des Minéraux (SARM-CRPG, Nancy, France) using ICP-OES after alkaline fusion and dissolution by acid attack ( <a href="http://crpg.cnrs-nancy.fr/SARM">http://crpg.cnrs-nancy.fr/SARM</a> ).
Al <sub>2</sub> O <sub>3</sub> (%)	16.45	
Fe <sub>2</sub> O <sub>3</sub> (%)	6.46	
MnO (%)	0.15	
MgO (%)	1.33	
CaO (%)	1.28	
Na <sub>2</sub> O (%)	0.30	
K <sub>2</sub> O (%)	2.57	
TiO <sub>2</sub> (%)	0.88	
P <sub>2</sub> O <sub>5</sub> (%)	0.25	
Specific Surface Area (m <sup>2</sup> g <sup>-1</sup> )	26.06 ± 0.08	Nitrogen gas adsorption at liquid nitrogen temperature using a Micromeritics Flowsorb II 2300 (Micromeritics, GA, USA). The sediments were outgassed during 30 min in flowing nitrogen at 250 °C. The accuracy of the obtained values is ±3%.
Alclonifen (µg g <sup>-1</sup> )	0.059	GC-MS: Gas chromatography column from Zebra ZB-5MS 30 m, 0.25 mm i.d., and 0.25 µm film from Phenomenex® (Torrance, CA, USA) with Thermo Fisher Scientific (Waltham, MA, USA) Trace GC 2000 coupled with a DSQ II mass detector. The detection limit, based on a signal-to-noise ratio of 3, was estimated to 1 to 3 ng L <sup>-1</sup> depending on the molecule.
Alachlor (µg g <sup>-1</sup> )	0.001	
Cd (µg g <sup>-1</sup> )	0.415 ± 0.01	Total digestion was performed in a clean room on the fine suspended matter fraction (>0.22 µm) then analysis was done by ICP-Q-MS Agilent 7500ce (Agilent Technologies, Santa Clara, CA, USA).
Cu (µg g <sup>-1</sup> )	39.5 ± 0.29	

The chemical and mineralogical compositions of sediments transported by a river reflect those of the soils of the watershed from which they were eroded. Smectites, kaolinites and illites are commonly found in the SPM of the Garonne river basin to which the studied river is connected [21–23]. Illite is the dominant mineral. Kaolinite is only present in the SPM during high water periods. Smectites are always present and increase during flood events of molassic origin. Specific surface area is strongly correlated with cation exchange capacity [24] controlling the importance and type of adsorption/desorption

reactions between dissolved and particulate fractions. As shown in Table 3, values for our samples ( $26.06 \pm 0.08 \text{ m}^2 \text{ g}^{-1}$ ) are close to pure clays (i.e., pure kaolinite  $7\text{--}30 \text{ m}^2 \text{ g}^{-1}$ ). This high value is mainly due to the presence of illites and smectites which have high specific surface areas [25]. This high specific area combined with the high cationic exchange capacity of smectite ( $80\text{--}150 \text{ meq } 100 \text{ g}^{-1}$ ), illite ( $10\text{--}40 \text{ meq } 100 \text{ g}^{-1}$ ) and to a lesser extent kaolinite ( $5\text{--}15 \text{ meq } 100 \text{ g}^{-1}$ ) [26] suggest that particles used for the adsorption experiments have an important quantity of surface binding sites, thus a significant adsorption capacity.

Al, K and Na are more concentrated in Pyrenean origin floods. The silica content of the suspensions shows a weight ratio  $\text{SiO}_2/(\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3)$  close to 2 often found in this river [22]. Organic matter also increases the pollutant loading capacity of sediments. Organic carbon content of the used particles is  $22.13 \text{ mg g}^{-1}$  falling in the range of values observed for many rivers [27]. At first inspection, river suspended particles exhibit significant aptitudes for adsorbing and carrying dissolved pollutants.

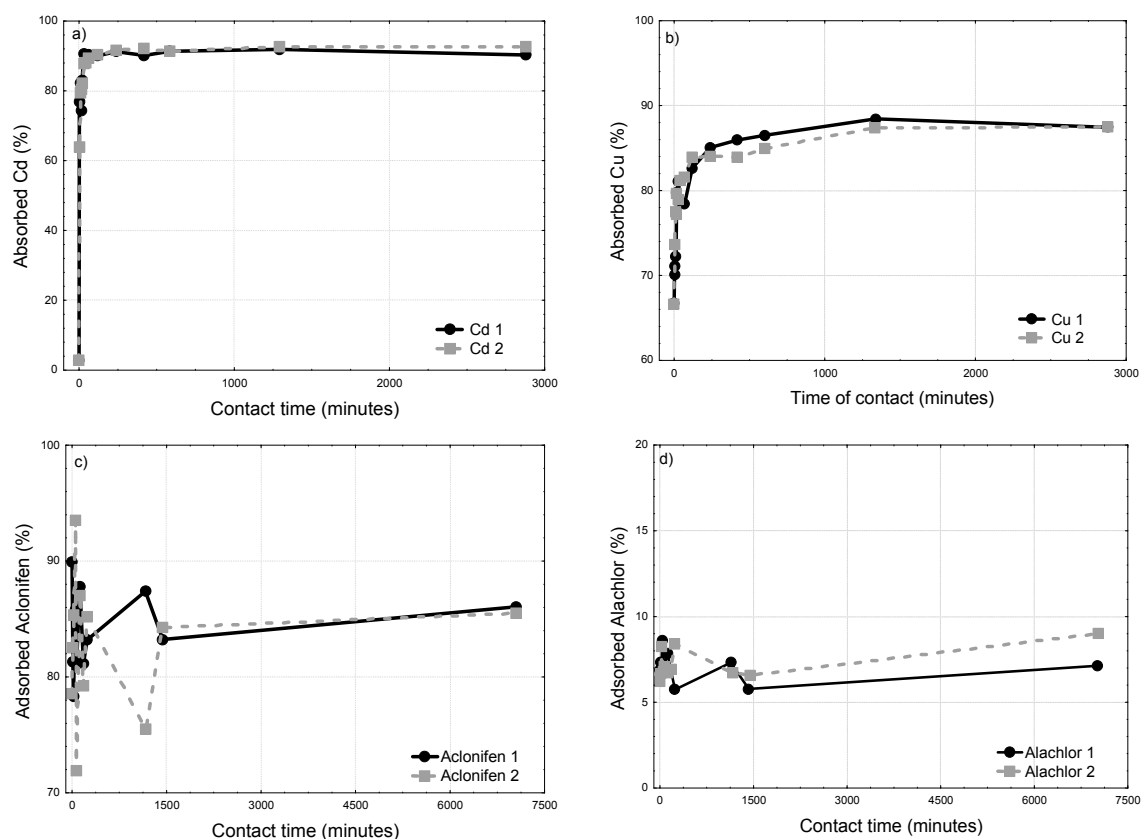
### 3.2. Adsorption Kinetics

According to Figure 3, the kinetics of pollutants removal by SPM presents two main features. On the one hand, TM presented a shape characterized by a fast removal from the aqueous solution during the first hours of contact between the solution and SPM followed by a slow removal until a state of equilibrium was reached, attaining a plateau. Mechanisms involved in particle/water exchanges of metals are often observed by these two-steps, a reversible process, combining an initial fast sorption and a second slower sorption [28]. The former stage corresponds to the achievement of an equilibrium between dissolved metals and weak binding sites, while the second refers to the movement of sediment-bounded metals towards higher-energy binding sites. The time necessary to reach this equilibrium was about 24 h and an increase to 48 h did not show notable effects. These observations are in agreement with previous works with other metal ion–biomaterial systems [10,14].

The difference in the sorption efficiency of heavy metal ions may be attributed to the different electronegativity of the metallic elements, the hydrated ionic radii in the solutions, the electric charge, the hydrolysis constant, etc. [29]. In our study, a comparison of the relative adsorption values of Cd and Cu shows similar total adsorption, the only difference being the rapidity of the adsorption of Cd as compared to Cu. This difference can be explained by differences in metal electronegativity and hydrolysis constants [29]. In fact, electronegativity values for  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  are 2.00 and 1.7, respectively [29,30], and the hydrolysis equilibrium pK values are  $6.8 \pm 1.5$  for  $\text{CuOH}^+$  and  $10.2 \pm 1.6$  for  $\text{CdOH}^+$  [31].

On the other hand, the maximum adsorption of both pesticides occurred in the first few minutes, the equilibrium being reached after 2 h. The total adsorption of 7 different pesticides was estimated to be reached in the first 7 h of contact with river bed sediments [32]. The same time was assessed for the adsorption of 4 different herbicides on soils [33]. Alachlor's adsorption reached a maximum of approximately 10% whereas 75% of Aclonifen was adsorbed. This difference is due to the different physicochemical characteristics of the pesticides studied. Aclonifen is a non-ionising pesticide with a water solubility of  $1.4\text{--}2.5 \text{ mg L}^{-1}$  whereas Alachlor has a water solubility of  $240 \text{ mg L}^{-1}$ , therefore, its adsorption will be less important than Aclonifen [34].

Based on the results of this experiment, we fixed the necessary contact time to reach equilibrium of adsorption to 2 h for pesticides and 24 h for heavy metals. These values were used for further experiments conducted at constant contact time.



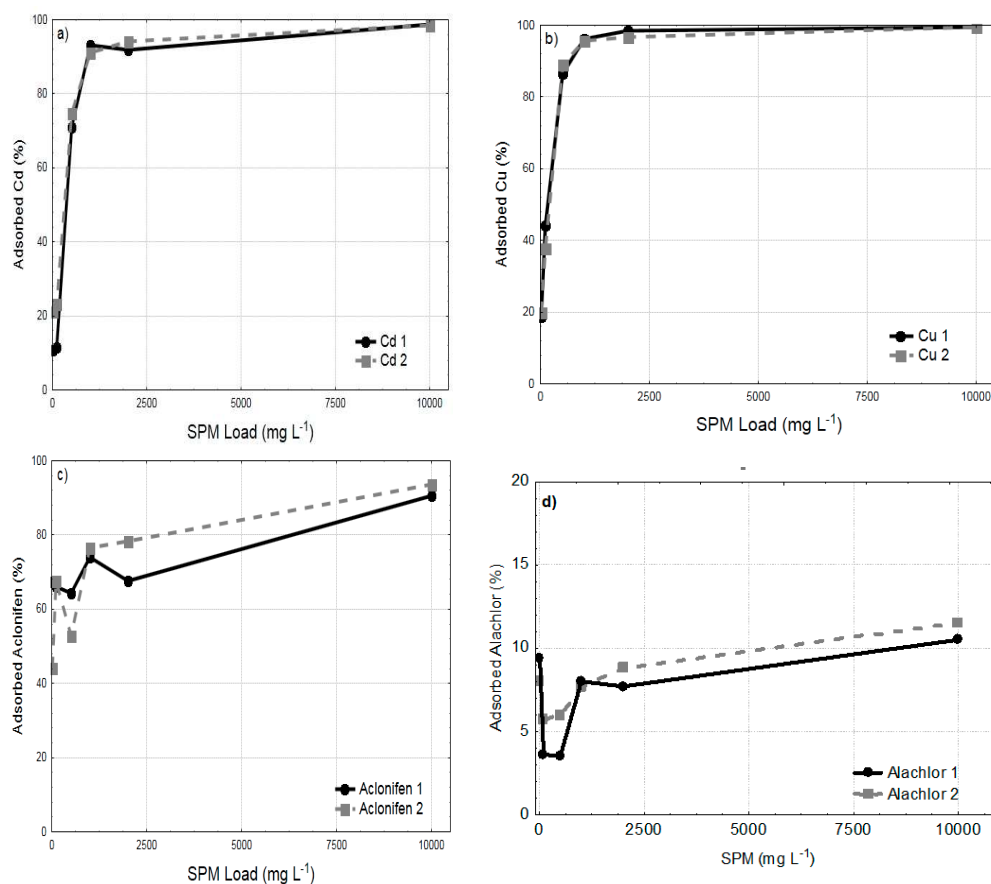
**Figure 3.** Sorption kinetics of Cd (a), Cu (b), Aclonifen (c) and Alachlor (d) onto river suspended particulate matter. 1 and 2 are duplicates. SPM Load is  $1 \text{ g L}^{-1}$ .

### 3.3. Influence of the Suspended Matter Load

For a given volume of unfiltered river water, a greater abundance of SPM implies a greater quantity of available binding sites. A batch of experiments was therefore carried out to study the extent to which the suspended sediment load could influence the removal of the studied pollutants from the aqueous phase. The aim is to focus on the conditions that are likely to occur in the Save river. Results obtained are plotted in Figure 4. Adsorption percentages of dissolved Cd and Cu, Aclonifen and Alachlor as a function of SPM load, showed the same nonlinear patterns. One can note the considerable variability of adsorption extent within the range of low SPM loads ( $0\text{--}1000 \text{ mg L}^{-1}$ ), before its rapid stabilization.

When fitting our data sets to the commonly used Michaelis-Menten-like distribution model (Equation (1)), we generate  $A_{\text{max}}$  and  $K_m$  constants presented in Table 4. It is noteworthy that the maximum adsorption capacity of the investigated SPM is high, e.g., about 100% for Cd and Cu, and 75% for Aclonifen. Only Alachlor presented 10% of maximum adsorption which agrees with the fact that it is a soluble pesticide.

Based on the results of this experiment, we fixed the concentration of SPM to  $1000 \text{ mg L}^{-1}$  for further experiments conducted. It is a good compromise with respect to the pollutant uptake ability of the particles at the contaminant concentration and to the world average SPM load in surface waters.



**Figure 4.** Adsorption percentage of Cd (a), Cu (b), Aclonifen (c) and Alachlor (d) as a function of the suspended particulate matter load. 1 and 2 are duplicates. Pollutant spikes are  $10 \mu\text{g L}^{-1}$ .

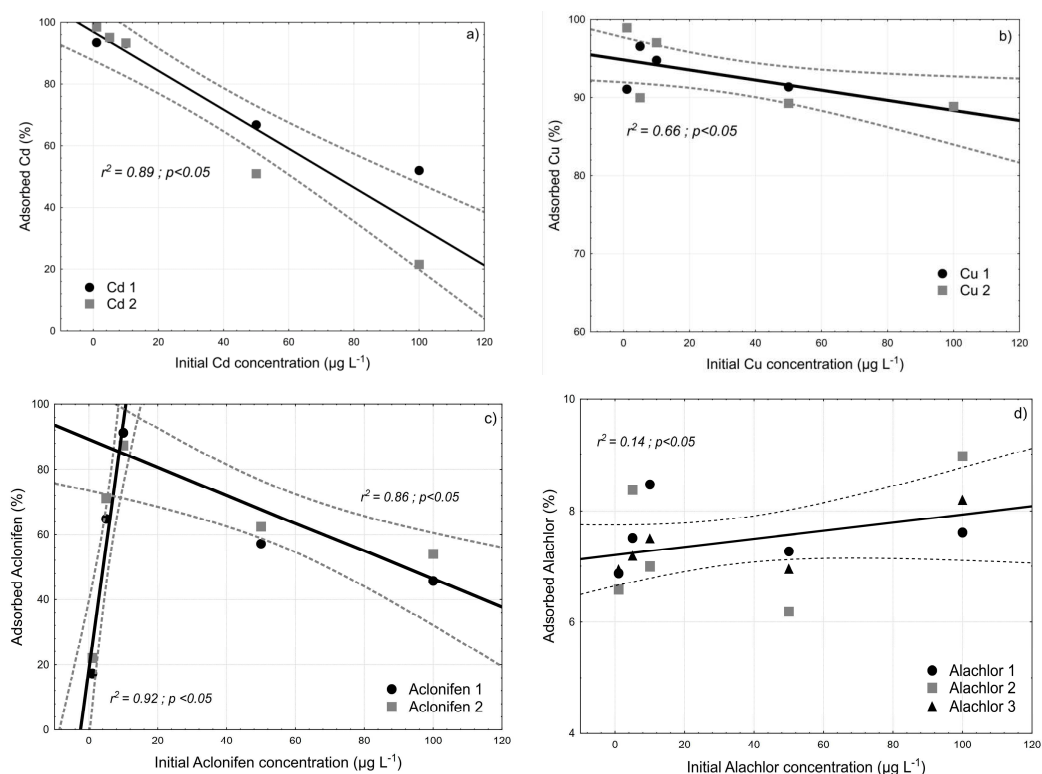
**Table 4.** Am and Km constants determined by the fitting of the experimental values for Cd, Cu, Aclonifen and Alachlor following the Michaelis-Menten relationships.

Constants	Cd	Cu	Aclonifen	Alachlor
Amax (%)	106.6	104.0	74.1	10.4
K <sub>m</sub> ( $\mu\text{g L}^{-1}$ )	267.4	118.8	3.6	306.7
Confidence Interval 95%				
Amax	93.3–119.8	96.7–111.2	64.9–83.3	6.9–13.9
K <sub>m</sub>	112.5–422.4	70.2–167.3	0.0–8.9	0.0–847.5
r <sup>2</sup>	0.9	1.0	0.3	0.1

### 3.4. Influence of the Initial Pollutant Concentration

The effect of initial pollutant concentration on the adsorption of the pollutants on SPM was examined. Results showed that increasing initial pollutant concentration from  $10$  to  $100 \mu\text{g L}^{-1}$  led to different removal extent for TM and pesticides. With the increase in initial pollutant concentrations, all studied TM and pesticides presented increased adsorbed quantities ( $\mu\text{g g}^{-1}$  SPM). Figure 5 shows the percentage of adsorbed pollutants as a function of the initial pollutant concentration. TM presented a decrease of the adsorbed percentage with the increase of the initial pollutant concentration spiked. This could be explained by a rising competition for the adsorption sites [35,36] indicating a decrease in the active sites on the sorbents as more metal ions were adsorbed [14]. In fact, as metal concentrations increased, the adsorption efficiencies of TM decreased (Figure 5). That can be explained by the constant SPM load that has a finite number of adsorption sites becoming more saturated as the TM concentration increased [37].

Pesticides presented another pattern with the increase of the initial pollutant concentration. In fact, the percentage of adsorbed pesticides increased with the increase of the initial pollutant concentration until a level where it started decreasing for Aclo and stabilizing for Ala (Figure 5). These non-linear sorption isotherms are due to a modification of the affinity between pesticides and SPM when concentrations increase [38]. The accessibility of a pesticide to the sorption sites in the soil decreases with increasing pollutant concentration [38,39]. The difference between Aclo and Ala could be due to the nature and strength of the bonding between the pesticide and SPM [39].



**Figure 5.** Adsorption percentage of Cd (a), Cu (b), Aclonifen (c) and Alachlor (d) as a function of the initial pollutant's concentration. Linear regressions are presented with corresponding correlation coefficients. 1, 2 and 3 are duplicates. SPM Load is  $1 \text{ g L}^{-1}$ .

For all pollutants, there is a concentration that produces the maximum adsorption for the given SPM load, and thereafter, adding more pollutant cannot increase adsorption because all adsorption sites are already occupied.

Based on the results of this experiment, we fixed the initial concentration of pollutants spiked at  $10 \mu\text{g L}^{-1}$  for further experiments conducted at constant pollutant spikes. This SPM load presented good adsorption rates for all pollutants (Figure 5).

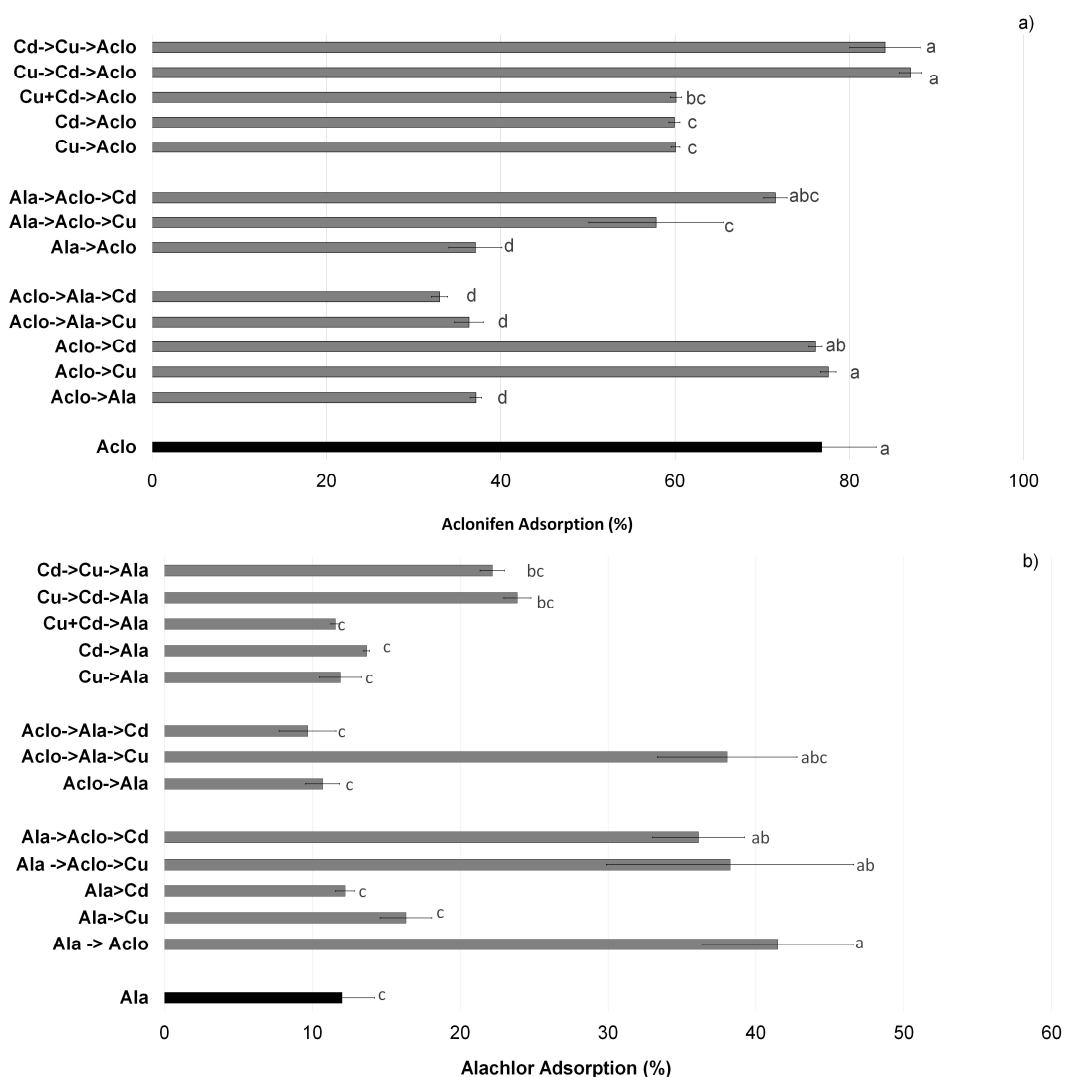
The coefficients obtained with the Freundlich model (Equation (2)) are summarized in Table 5. It is noteworthy that the correlation coefficients were satisfactory, the lowest being for Aclo with 0.54. This corresponds with the fact that the adsorption sites on SPM are non-uniform and nonspecific in nature with different types of possible adsorption sites with considerable difference in energy [14]. Freundlich constants  $n$  and  $KF$ , fundamentally differ but their values present a possible sequence of selectivity for the studied SPM as follows:  $\text{Cd} > \text{Cu} > \text{Aclo} > \text{Ala}$ . The value of  $n$  was greater than one for Cd, Cu and Aclo indicating that adsorption was favorable to SPM [14]. These coefficients allow predicting the amount of pollutant adsorbed when the dissolved amount is known and vice versa. This result can help in the future environmental monitoring of the Save river. Data fitting to the Freundlich isotherm can help estimate the sorption capacity and affinity of the sorbents to the sorbates and predict the fate of pollutants once in the environment [40,41].

**Table 5.** Freundlich Coefficient for Cd, Cu, Aclonifen and Alachlor in the studied system.

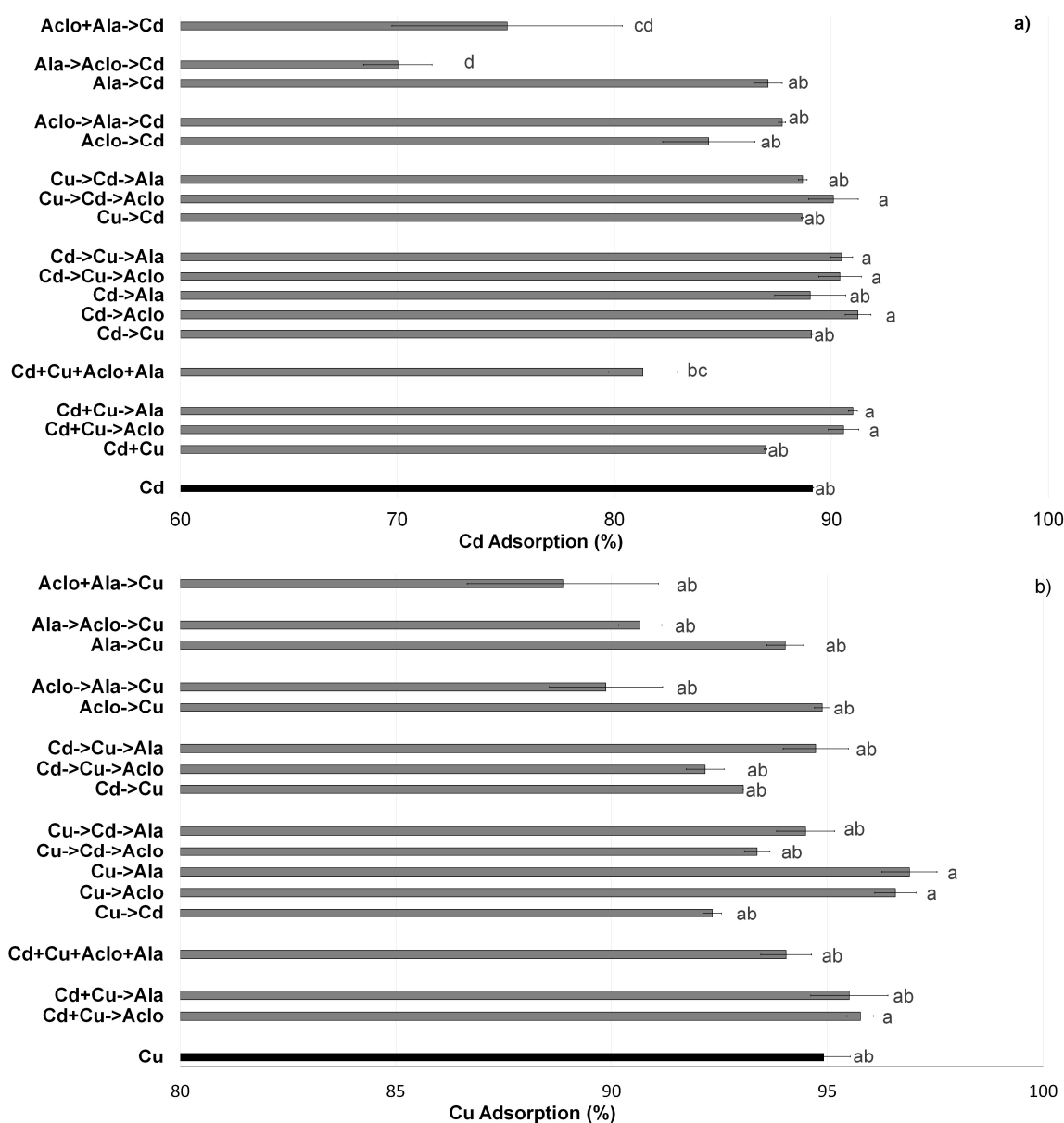
		Cd	Cu	Aclonifen	Alachlor
Freundlich	n	1.17	1.14	1.13	1.00
	$K_F$	7.76	7.54	1.47	0.08
	$r^2$	0.91	0.85	0.54	0.97

3.5. Co-Adsorption of Pollutants on Suspended Particulate Matter

In this section, the adsorption of a pollutant onto SPM was studied in the absence or presence of other pollutant(s). The influence of the pollutants' order of presence in the experimental solution was also considered. Results are shown in Figures 6 and 7, respectively for pesticides (Aclonifen and Alachlor) and trace metals (Cd and Cu).



**Figure 6.** Average percentage of Aclonifen (a) and Alachlor (b) adsorbed on Suspended Matter in different multipollution scenarios. Means with the same letter (a, b, c, d) are not significantly different (ANOVA,  $p < 0.05$ ).



**Figure 7.** Average percentage of Cd (a) and Cu (b) adsorbed on Suspended Matter in different multipollution scenarios. Means with the same letter (a, b, c, d) are not significantly different (ANOVA,  $p < 0.05$ ). In the lower graph, all means are not significantly different.

### 3.5.1. Aclonifen (Aclo)

When Ala and Aclo are alone in the solution, Ala being present either before or after Aclo, Aclo's adsorption onto SPM was decreased (−50%) (Figure 6). An interaction between these two pesticides of different hydrophobicities could occur.

When Aclo is the only pesticide in the solution, Cu and Cd have similar behaviors on its adsorption. When they followed Aclo in the solution, they had no effect on its adsorption. However, when they were present before Aclo, they decreased its adsorption from 77% to approximately 60%. Aclo being slightly soluble, its adsorption is less when TM were previously present in the solution probably because they compete for adsorption sites, directly or indirectly, making stronger bonds with SPM [6,42]. There may also be formation of complexes between the active sites of Aclo and TM present in the medium. These complexes often decrease the ability of the pesticide's adsorption [8]. On the

contrary, according to literature, these complexes can sometimes be more likely adsorbed onto SPM, soils, silicates, etc. [4,43].

### 3.5.2. Alachlor (Ala)

Alachlor is more soluble than Aclonifen and is therefore adsorbed to a lesser extent when found alone in the solution (approximately 12%). Trace metals did not significantly modify Ala's adsorption. On the contrary, previous studies concluded that Cd and Cu could act as a link between SPM components and highly soluble pesticides thus facilitating their adsorption [1,2,44]. They may also become complexed with dissolved organic matter leading to its aggregation and flocculation thereby increasing the percentage of adsorption of pesticides [44,45].

Our results showed that the only significant improvement of Ala's adsorption was when Aclonifen followed in the solution (Figure 6), either in the presence or in the absence of TM. The positive effect of Aclonifen was not visible when it preceded Ala in the solution. It can be concluded that Aclonifen facilitates the sorption of Ala once adsorbed on SPM but more investigation should be done to understand the mechanisms involved in this interaction.

### 3.5.3. Cd and Cu

The main result is that other contaminants present in the medium seemed to have little influence on the percentage of adsorption of TM. In fact, TM did not show significant changes in their adsorption when in presence of other pollutants, regardless of the order of presence (Figure 7). This allows hypothesizing that metals have a greater affinity for SPM sites than pesticides and can form stronger bonds.

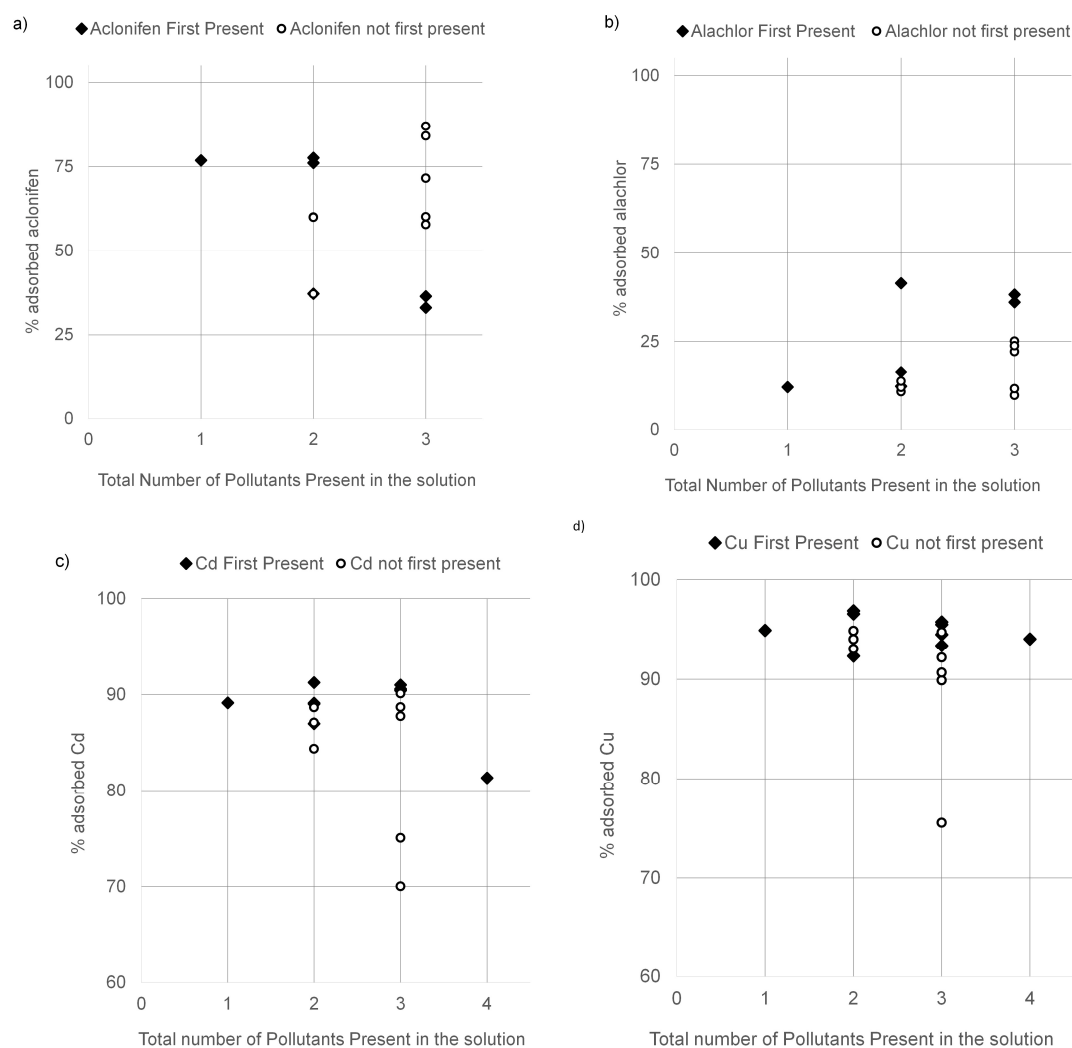
The presence of the other TM did not influence the adsorption of Cu nor Cd. Serpaud et al. [46] showed that there was no competition for adsorption on river sediments between metals present in the same medium. However, [47] revealed that Pb and Cd competed for organic matter's binding sites in the soil. At pH 5, in other soils, these two elements were not found to be in competition [48].

However, TM was the least adsorbed when introduced in a solution where Ala and Aclonifen were already present. This can be due to a saturation of available adsorption sites on the SPM. For example, the present study showed that when Aclonifen followed in the solution, Ala tended to be more adsorbed, resulting in a greater occupation of potential sites for Cd and Cu or simply an obstruction of space preventing metals from being adsorbed. Maqueda et al. [5] revealed that the adsorption of Cu on pure montmorillonite increased in the presence of chlordimeform. The pesticide was found to occupy specific sites separating montmorillonite's layers and thereby facilitating the penetration of Cu.

In the case of less reactive pesticides, other effects can be observed. For example, Cu was not influenced by the presence of a pesticide (diuron) in the solution [49].

The influence of the presence of other pollutants in the solution is summarized in Figure 8. However, more investigation is needed to characterize complexes formed between SPM and pollutants and determine the stability of the existing interactions.





**Figure 8.** Percentage of adsorption of Aclonifen (a), Alachlor (b), Cd (c) and Cu (d) as a function of the total number of pollutants present in the solution. Present first: the studied pollutant was the first added to a solution; Not present first: the studied pollutant was added to a solution where one or more other pollutants were already present.

#### 4. Conclusions

The approach presented in this study provided new insights into the fate of pollutants in the environment while approaching as close as possible the natural conditions. Co-presence experiments showed that when pollutants were present alone, they had different adsorption behaviors than when they were in the presence of other pollutants.

The adsorption of the less soluble Aclo was decreased by the presence of Ala in the solution while the more soluble Ala showed significant improvement of its adsorption on SPM when Aclo was introduced after it. There is therefore a possible interaction between the studied pesticides with different physicochemical properties.

Trace metals were less influenced than pesticides by the presence of other pollutants. They did not modify the adsorption of highly soluble pesticide (Ala) and competed with the slightly soluble pesticide (Aclo) for binding sites.

Pollutants can interact with each other in direct or indirect ways. They can form complexes with each other, modifying their solubility. They can also compete for the same binding sites. Although further work is needed to have a more fundamental understanding of the adsorption of pollutants onto

natural material, the results presented here showed possible interaction between pesticides and trace metals and may have practical significance for the elimination of contaminants from the environment.

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