



Selection of low cost materials for the sorption of copper and herbicides as single or mixed compounds in increasing complexity matrices

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ABSTRACT

Low cost materials (sugar beet pulp, corncob, corncob char, perlite, vermiculite, sand, sediment) have been tested for their ability to quickly sorb copper, glyphosate, diuron and 3,4-dichloroaniline (3,4-DCA) as single or mixed compounds. Tests have been performed in increasingly complex liquid matrices: ultra pure water (UPW), runoff water (RW) and sediment extract medium (SEM). Highest sorption levels in UPW are achieved with corncob char for Cu (93%), glyphosate (74%), diuron (98%) and 3,4-DCA (99%). Other ready-to-use adequate sorbents are sugar beet pulp for Cu and sand for glyphosate, diuron and 3,4-DCA. Sorption levels obtained in UPW are significantly altered in SEM as a result of its higher dissolved organic carbon concentration, tenuous changes being obtained with RW. Interactions between herbicides and Cu are pointed out: higher sorption level is observed for glyphosate in mixture with Cu, as it is observed with diuron and 3,4-DCA when mixed with all other pollutants. Langmuir model has been found to better fit the data for copper, whereas Freundlich one has been found more relevant for diuron and 3,4-DCA. Our results stress the need for studying adsorption in different matrices when searching for sorbents to be used in field conditions.

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1. Introduction

For many years, large amounts of mineral and organic pesticides have been used in agriculture. Herbicides, insecticides and fungicides used in vineyards account for 20% of the commercialized pesticides. Yet the surface dedicated to this production reaches only 1.6% of the total French farming surface [1]. Weeds are usually treated with diuron (3-(3,4-dichlorophenyl)-1,1-dimethylurea) and glyphosate (N-(phosphonomethyl)glycine), copper sulphate is used to constrict grape vine powdery mildew development. Due to vineyard topography, pesticide losses by surface runoff are often observed but represent less than 1% of the applied active substance, rarely exceeding 10% [2,3]. These losses contribute significantly, however, to surface water contamination—e.g. diuron was detected in 34.6% of superficial water samples from the French river basin in 2005 [4]—and to a lower extent to groundwater contamination. Resulting concentrations and masses are high enough for surface water to exhibit biologically relevant effects [5]. Mainly dissolved pesticides are encountered in runoff water but molecules adsorbed on the soil surface can also be convected by erosion phenomena [3].

Stormwater basins built at vineyard watershed outlets are specially designed for flood control by temporarily storing runoff

water. These constructed wetlands also encompass part of natural wetland ecological functions with the establishment of flora (macrophytes) and microflora taking advantage of sediment deposit in the basins. Pesticide mitigation has already been observed, but effectiveness still has to be demonstrated for weakly and moderately sorbing compounds [6]. As plant and micro-organism efficiency is inconsistent through the seasons, residence time is sometimes too short to achieve organic compounds breakdown by micro-organisms or metal uptake by plants. Hence pesticides are frequently detected at storm basins outlet.

Pesticide sorption on storm basin sediments was already demonstrated with atrazine [7]. Nonetheless, pesticides are most of the time not properly retained because pesticide sorption time on sediment usually exceeds hydraulic storage time. A potentially relevant method to alleviate this phenomenon lies in the addition of sorbing materials [8–12] to promote the pollutants transfer from the liquid to the solid phase, thus avoiding the discharge of polluted water. Increased pesticide residence time in the basin is then expected to be suitable for biological treatment. Low cost mineral and organic sorbents for metals [13,14] and organic compounds [12] are required for such rustic treatment plants. Recently, attention has been paid to agricultural waste materials [15,16]. Several studies have been carried out on copper [13], fewer on herbicides such as glyphosate [17] or diuron [18]. In addition, sorption performances have been mainly assessed with single compounds in ultrapure water, which cannot be compared to environmental conditions.

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Table 1

Main physical and chemical characteristics of the sediment sampled in the storm basin (0–10 cm depth) located at Rouffach (68, France). Analyses were performed according to French standard procedures.

Clay (<2 μm) (g kg ⁻¹)	436
Fine silt (2–20 μm) (g kg ⁻¹)	331
Coarse silt (20–50 μm) (g kg ⁻¹)	96
Fine sand (0.05–0.2 mm) (g kg ⁻¹)	49
Coarse sand (0.2–2 mm) (g kg ⁻¹)	82
OM (g kg ⁻¹)	11
pH	8.2
CaCO ₃ (g kg ⁻¹)	17
CEC (meq kg ⁻¹)	156
Cu (mg kg ⁻¹)	20
Glyphosate (μg kg ⁻¹)	<10*
Diuron (μg kg ⁻¹)	<300*
3,4-DCA (μg kg ⁻¹)	<200*

* These compounds were detected but were not quantifiable.

This work aims at (i) determining the maximum sorption capacity and time needed to reach it for copper, glyphosate, diuron and 3,4-DCA as single or mixed compounds in liquid matrices of increasing complexity, in order to choose relevant sorbing material(s) and (ii) estimating the compound affinity for the selected sorbent(s) by means of adsorption isotherms.

2. Experimental

2.1. Sorbents and matrices

The sorbents are perlite (0.6 mm up to 6 mm in diameter, *Etablissements Puteaux SA, Les Clayes sous Bois, 78, France*), vermiculite (diameter less than 5 mm, *Radis et Capucine, Trélazé, 49, France*), sediment (collected in a vineyard storm basin, *Rouffach, 68, France*) whose composition is given in Table 1, sand (0 to 4 mm diameter, rolled washed, *Holcim granulats, Herrlisheim, 68, France*), dried sugar beet pulp (from sugar refinery, *Erstein, 68, France*) and corncob (*Zea mays*) supplied by local farmers. Corncob char was obtained by burning corncob in the same conditions as Yang and Sheng [19]. All sorbents were used without pre-treatment.

Three matrices were used i.e. ultrapure water (UPW) from a Purelab UHQ distributor (Elga, France), runoff water (RW) collected at the stormwater basin inlet in *Rouffach* after a rainy period and sediment extract medium (SEM) prepared as described in Lebeau et al. [20]. RW and SEM compositions are given in Table 2.

2.2. Compounds

Two herbicides were tested, glyphosate (*Sigma-Aldrich, France, 95% purity*) and diuron (*Sigma-Aldrich, France, 99.5% purity*) as well as diuron main metabolite 3,4-dichloroaniline (3,4-DCA, *Sigma-Aldrich, France, 99.5% purity*) and a heavy metal, copper (CuSO₄·5H₂O, *Sigma-Aldrich, France*). Diuron and 3,4-DCA stock solutions were prepared in DMSO (*Carl Roth, Germany, 99.8% purity*). Glyphosate and copper stock solutions were prepared in UPW. Stock solutions were stored at 4 °C in polypropylene flasks (glyphosate, copper) or glass flasks (diuron, 3,4-DCA).

2.3. Sorption experiments

250-mL Erlenmeyers were filled with 150 mL of liquid matrix. Stock solutions with single compounds or all compounds-containing mixture were added to reach the following concentrations: 100 mg L⁻¹ of diuron and 3,4-DCA, 200 mg L⁻¹ of glyphosate and 500 mg L⁻¹ of Cu. 20 g L⁻¹ of sorbent were used. Prior to adding sorbents, pH was adjusted to 4.8 in the presence of pollutants with 0.1 M or 1 M of either HCl or NaOH. This pH value corresponded to the pH of SEM spiked with 500 mg Cu L⁻¹. Experiments were run

Table 2

Composition of runoff water (RW) sampled at the inlet of the storm basin and sediment extract medium (SEM) both used as liquid matrices.

	RW	SEM
Total nitrogen (mg N L ⁻¹)	<100*	46.5
NH ₄ ⁺ (mg N L ⁻¹)	0.34	8.03
NO ₃ ⁻ (mg N L ⁻¹)	<0.1*	0.11
H ₂ PO ₄ ⁻ (mg P L ⁻¹)	1.2	2.7
K (mg K L ⁻¹)	7	27.4
Ca (mg Ca L ⁻¹)	51	231
Mg (mg Mg L ⁻¹)	6.5	17.7
Na (mg Na L ⁻¹)	2.4	60.3
Fe (mg Fe L ⁻¹)	3.4	1.61
Mn (mg Mn L ⁻¹)	0.18	1.07
SO ₄ ²⁻ (mg SO ₄ L ⁻¹)	10	156
Cu (mg Cu L ⁻¹)	0.02	0.014
Zn (mg Zn L ⁻¹)	0.03	0.47
Total organic carbon (mg C L ⁻¹)	3.4	480

* This compound was detected but was not quantifiable.

at 20 °C and 200 rpm in triplicate. Samples were stored at 4 °C prior to analysis.

2.4. Sorption isotherms

Experimental conditions were the same as above. 20 g L⁻¹ sorbents were suspended in 150 mL liquid matrix containing single compound at various concentrations: 2 up to 20 mg L⁻¹ of diuron or 3,4-DCA, 4 up to 40 mg L⁻¹ of glyphosate and 50 up to 1000 mg L⁻¹ of copper. Sorption isotherm data were fitted to the Langmuir model:

$$q_e = \frac{q_{\max} b C_e}{1 + b C_e} \quad (1)$$

where q_e is the amount of pesticide sorbed at equilibrium (mg kg⁻¹), C_e is the equilibrium concentration (mg L⁻¹) and q_{\max} and b are the Langmuir constants.

Freundlich model was also used to fit data:

$$q_e = K C_e^n \quad (2)$$

where q_e is the amount of pesticide sorbed at equilibrium (mg kg⁻¹), C_e is the equilibrium concentration (mg L⁻¹) and K and n are the Freundlich constants. Sorption isotherm data are fitted using EasyPlot software (Spiral Software, Norwich, VT, USA).

2.5. Analysis

Copper was analysed by ICP-AES (*Ultima, Jobin Yvon Horiba Group, Kyoto, Japan*) at 324.7 nm. Diuron, 3,4-DCA and glyphosate were analysed by HPLC (Waters 2487 UV-vis detector and 1525 dual pump, UK) equipped with a reverse phase column (Lichrosorb RP18, 250 mm × 4 mm, Merck) at room temperature (20 °C). The mobile phase for diuron and 3,4-DCA analysis was acetonitrile/water (45/55 v/v) at 1 mL min⁻¹ and detection wavelength was 254 nm. Glyphosate was derivatised [21,22] by adding 50 μL of 0.4 M phosphate buffer (pH 11) and 20 μL of p-toluene sulphonyl chloride solution (10 g L⁻¹ in 99.9% purity acetonitrile (*Carl Roth, France*)) to a 100 μL sample. It was then heated in a water bath for 10 min at 50 °C before elution with acetonitrile/phosphate buffer (KH₂PO₄, *Sigma-Aldrich, France*) (30/70 v/v) at 1 mL min⁻¹ and detection at 240 nm.

Analyses of variance were performed with a Least Significant Difference test (at $P < 0.05$) to identify significant differences between mean values (three replicates). The software used for statistical analyses was Statbox Pro software (*Grimmersoft, version 5, Paris, France*).

Table 3
Copper and herbicide sorption as single compounds in ultra pure water (UPW). Sorption is described by the maximum sorption percentage (%) and the time (t, in hours) to reach the maximum sorption level. Mean values with different letters within a line are significantly different (at $P < 0.05$).

		Sugar beet pulp	Corncob	Perlite	Vermiculite	Sediment	Sand	Corncob char
Copper	%	60 ± 1 c	21 ± 1 d	2 ± 1 e	52 ± 3 c	97 ± 3 a	75 ± 22 b	93 ± 1 a
	t	2	6	0.2	48	48	48	0.2
Glyphosate	%	49 ± 1 b	50 ± 2 b	47 ± 1 b	50 ± 8 b	27 ± 9 c	54 ± 9 b	74 ± 7 a
	t	1	5	1	1	0.2	4	24
Diuron	%	74 ± 4 bc	73 ± 16 bc	77 ± 1 abc	79 ± 13 abc	63 ± 3 c	94 ± 1 ab	98 ± 1 a
	t	1	5	5	0.5	0.5	6	6
3,4-DCA	%	80 ± 4 b	56 ± 2 c	54 ± 10 c	34 ± 3 d	54 ± 3 c	86 ± 2 b	99 ± 1 a
	t	2	6	4	1	4	0.5	2

3. Results and discussion

3.1. Sorption of copper and herbicides in ultrapure water

Maximum sorption percentage was reached with corncob char (93%) and sediment (97%) for copper (Table 3). Significant sorption of Cu was also observed with sugar beet pulp (60%), sand (75%) and vermiculite (52%), whereas little or no Cu sorption occurred onto corncob and perlite. There was no clear relationship between the sorption level of Cu and the CEC of the sorbents (Table 4), maybe because of the acidic pH of the solution (i.e., 4.8). Other processes than ion-exchange may have governed the sorption of Cu that would explain this absence of difference, too. The sorption kinetics of Cu varied strongly with the sorbents: the maximum sorption required 0.2 h for corncob char and perlite, 2 h for sugar beet pulp, 6 h for corncob and up to 48 h for vermiculite, sediment and sand. This sorption kinetics was consistent with reported ones for sugar beet pulp [23,24] and vermiculite [25].

Highest glyphosate sorption (74%) was achieved with corncob char (Table 3). Other sorbents were significantly less efficient, with sorption decreasing from 54% to 27%, in the following order: sand = vermiculite = corncob = sugar beet pulp = perlite > sediment. Maximum sorption levels were reached after 0.2 up to 24 h. The low glyphosate sorption on sediment was not expected since variable-charge sediment minerals, e.g. aluminium and iron oxides, usually promote glyphosate sorption [26]. Glyphosate sorption was not related to the CEC (Table 4), as already observed by Morillo et al. [27]. Conversely, it might be related to the SiO₂ content of mineral sorbents (sand, perlite and vermiculite), as a result of hydrogen bonding of the phosphonate moiety of the molecule, and to the specific area of organic sorbents (sugar beet pulp, corncob and corncob char).

Highest diuron and 3,4-DCA sorption (Table 3) were obtained with corncob char (98% and 99%, respectively) and surprisingly with sand (94% and 86%, respectively). Other materials showed high sorption capacities for diuron (63% up to 79%). For 3,4-DCA, sorption ranged from 34% to 80% in the following order: vermiculite < perlite = sediment = corncob < sugar beet pulp. Corresponding sorption times ranged from half an hour up to 6 h, for both compounds. The sorption of diuron and 3,4-DCA was expected to

Table 4
Cationic exchange capacity of the sorbents, from the literature.

	CEC (μeq g ⁻¹)	References
Sugar beet pulp	540	[51]
	860	[9]
Corncob	120	[52]
Perlite	60	[53]
Vermiculite	650	[54]
	400	[32]
Sediment	156	Table 1
Sand	30–80	[55]
	16	[56]
Corncob char	290	[57]

be positively related to the C content of sorbents [28]. This was not clearly observed, possibly in relation with differences in the specific area of the sorbents.

Although corncob was burnt under uncontrolled conditions, charcoal formation improved corncob sorption by 1.3 for diuron up to 4.4 for Cu (Table 3) thanks to extended surface area and microporous structure [29]. Chemically treated corncob was also shown to increase the sorption performances for copper. Indeed, corncob particles washed with 0.1 M NaOH and then treated with citric acid showed higher Cu sorption than untreated particles [30]. The increase of net negative charges on the surface of the sorbent was attributed to the solubilisation with NaOH of the surface lipids. Better sorption levels were reported by Khan and Wahab [31] with corncob char than with activated carbon sorbents prepared from other agricultural sources. Such performances have also been observed for diuron by Yang and Sheng [19] with wheat ashes being 400 times more efficient than unburned product. Though efficient, this material would not be picked up to implement a rustic depollution process, as an additional treatment step is required prior to its use.

Excluding corncob char from the sorbent selection the best compromise, i.e., high sorption level and short time contact to reach the maximal sorption, was sugar beet pulp for copper and sand for glyphosate, diuron and 3,4-DCA. Although the sorption levels on vermiculite were not the highest, this material shows a good resistance to mechanical abrasion [32]. Such a parameter should be considered in the sorbent choice.

3.2. Influence of liquid matrix on sorption

Most studies devoted to sorption use ultrapure water (UPW) whereas environmental liquid matrices are far more complex. Environmental liquid matrices contain several cations (Ca²⁺, Mg²⁺), anions (H₂PO₄⁻) and organic matter (OM) able to strongly modulate the sorption of contaminants. Thus potentially interesting sorbing materials when tested with UPW may then prove unsuitable in environmental matrices.

Runoff water (RW) and a sediment extract medium (SEM) have been tested as natural matrices whose compositions are supposed to be closer to that encountered in a storm basin. Surprisingly the sorption level of copper on most sorbents was close whether using RW or UPW (Fig. 1a). The sorption level was lower only for corncob and sand. In contrast, copper sorption strongly decreased by using SEM (up to 12-fold decrease) for vermiculite, sediment, sand and corncob char. Compared to RW, SEM analysis (Table 2) showed a much higher total organic carbon concentration, which probably explained most of the observed sorption differences between the two matrices. Indeed, dissolved organic carbon ability to complex copper strongly modifies sorption of the latter. Moreover, the dissolved organic matter in SEM was probably highly aromatic given that its specific UV-absorbance at 254 nm was high, i.e., 30.5 L g⁻¹ cm⁻¹. The ability of dissolved OM to complex Cu may thus have been stronger [33]. The concentration in exchangeable cations (e.g.,

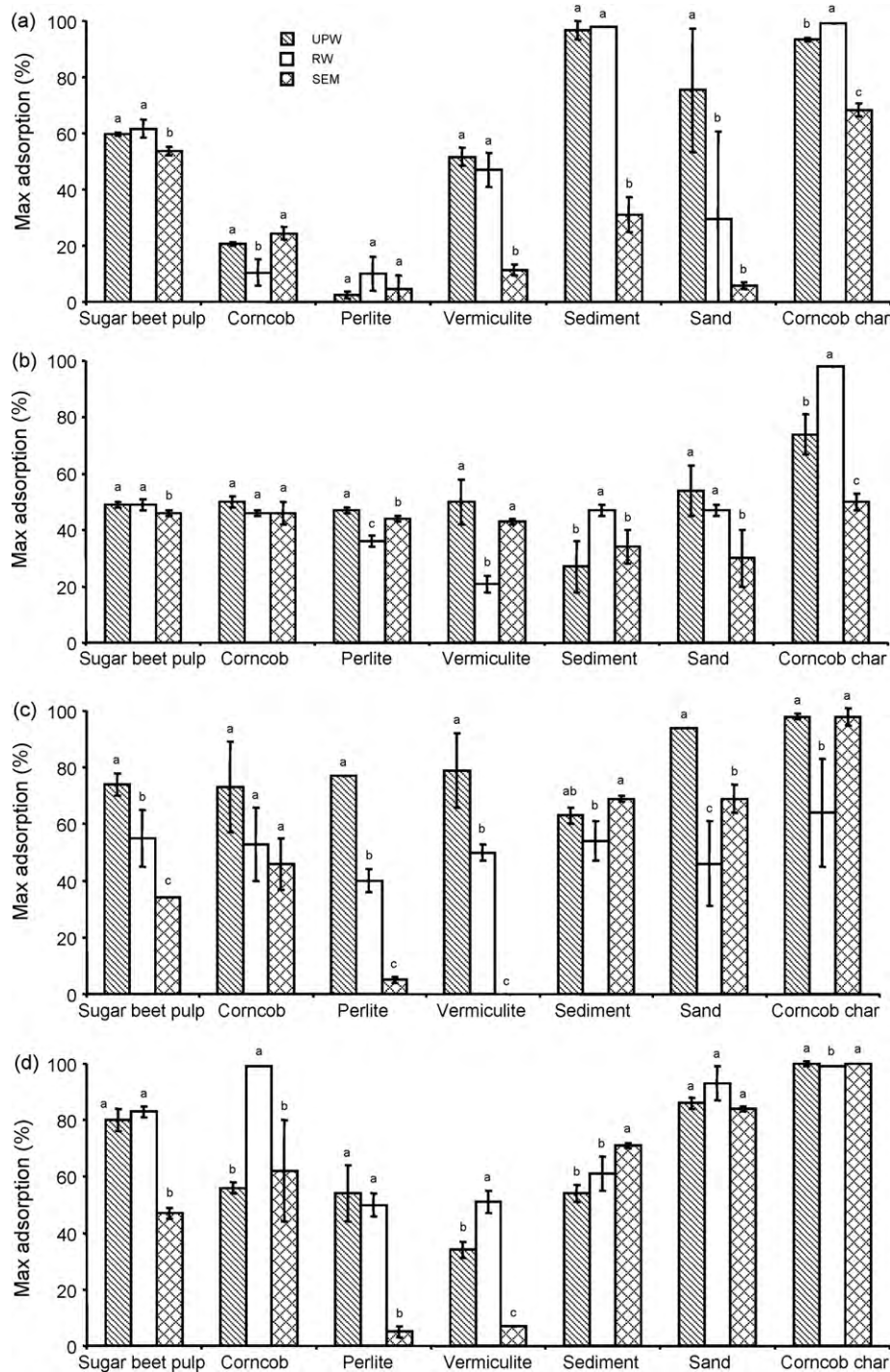


Fig. 1. Maximum sorption percentage of (a) copper, (b) glyphosate, (c) diuron and (d) 3,4-DCA on the selected sorbents in ultrapure water (UPW), runoff water (RW) and sediment extract medium (SEM). The error bars stand for mean standard errors. For each sorbent, mean values with different letters are significantly different (at $P < 0.05$).

Ca^{2+} ; Mg^{2+}) may also explain the differences in sorption observed between the two matrices, but to a lesser extent. Regarding sugar beet pulp, sorption differences amongst the three liquid matrices were low. This may suggest that specific processes govern the sorption of Cu on this sorbent. Sugar beet pulp and corncob char were eventually the best sorbing materials for copper since their sorption level remained high whatever the liquid matrix.

Glyphosate sorption slightly changed with sugar beet pulp and corncob (Fig. 1b). Yet contrasted effects were observed with other materials. Compared to UPW, glyphosate sorption was lower in RW for perlite and vermiculite but higher for sediment and corn-

cob char. As observed with copper, the average sorption level of glyphosate decreased with SEM for sugar beet pulp, and sediment, presumably caused by phosphate competition. Basically, glyphosate was already shown to compete with phosphate for sorption sites [26]. Controversies about the impact of phosphate on glyphosate sorption must nevertheless be underlined: while de Jonge et al. [34] found phosphate concentration to play an important role in glyphosate sorption, Barrett and McBride [35] concluded that the competition for sorption sites between the two species was limited. Among the best two sorbents in UPW, i.e., sand and corncob char, corncob char remained interesting with

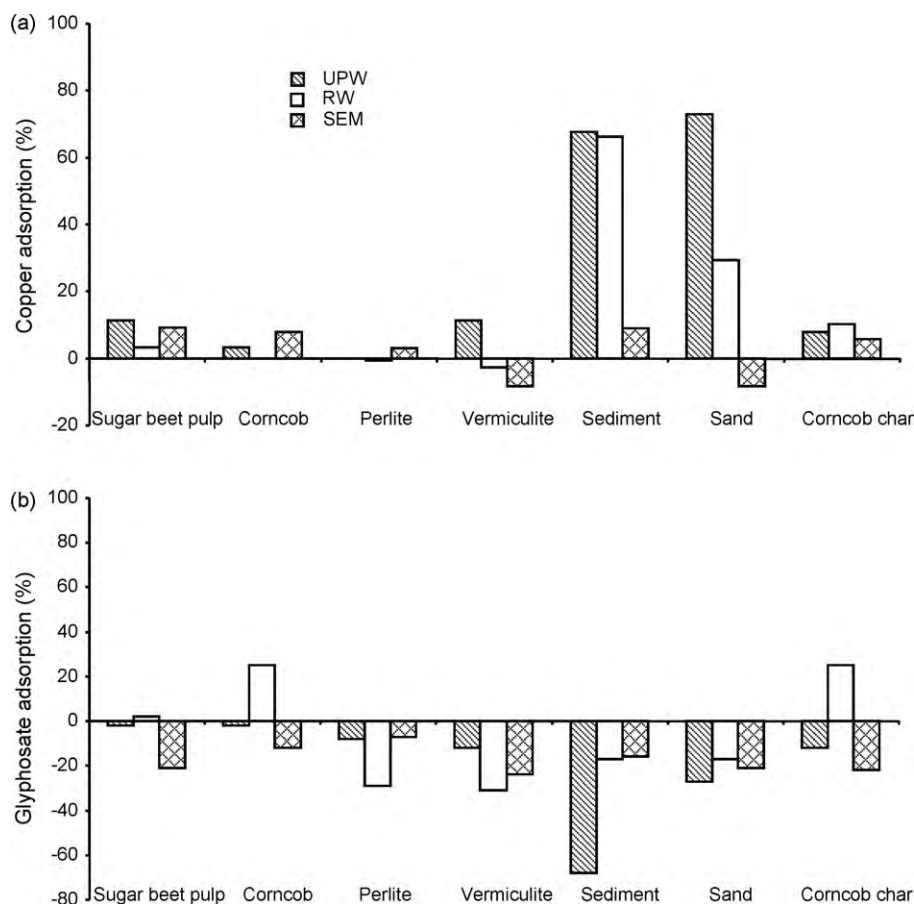


Fig. 2. Impact of (a) glyphosate and (b) copper on the sorption of (a) copper and (b) glyphosate on the selected sorbents in ultrapure water (UPW), runoff water (RW) and sediment extract medium (SEM). The data are presented by the difference in the maximum sorption percentage of (a) copper and (b) glyphosate between the single compound matrix and the mixture.

SEM whereas sand sorption level became lower than that of the other sorbents.

A decrease in diuron sorption was observed with RW compared to UPW for all sorbing materials (Fig. 1c). This may be the result of diuron sorption on the colloidal fraction of RW, as shown by Irace-Guigand and Aaron [36]. A larger decrease was observed with SEM for sugar beet pulp, corncob, perlite and vermiculite. Two hypotheses can be made: whether the competition for the sorption sites between diuron and dissolved OM, as shown for chlorotoluron by Song et al. [37], or the formation of stable mobile diuron-dissolved OM complexes [38] could explain the sorption decrease. In contrast, similar sorption levels were measured in UPW and SEM for sediment and corncob char. Corncob char thus remained interesting because of the maintenance of a high sorption level of diuron, even in SEM. Quite the same trend was observed for 3,4-DCA (Fig. 1d) when comparing SEM with UPW: the sorption percentage was found to be lower in SEM for sugar beet pulp, perlite and vermiculite. Opposite results were observed on sediment, in accordance with Flores-Céspedes et al. [39]: increased dissolved OM concentration promoted the sorption of 3,4-DCA. The fact that sorption of 3,4-DCA increases in the presence of dissolved organic carbon could be justified considering that the dissolved organic carbon is first sorbed on the sediment surface. Sorption of 3,4-DCA would be facilitated by the previously sorbed DOM, likely through hydrophobic (or physical) interactions [40]. Thus, corncob char and sand remained the best sorbing materials for 3,4-DCA in SEM. It differed from diuron as its sorption was similar most of the time in UPW and RW, but no explanation on the possible mechanisms involved could be found.

A global analysis of these results highlighted the similar sorption behaviour of copper and glyphosate with sugar beet pulp, corncob and perlite. Their sorption was weakly influenced by the liquid matrix, contrary to what was observed for the same sorbents with diuron and 3,4-DCA. The high ionisability of Cu and glyphosate on one hand and the electroneutrality of diuron and 3,4-DCA on the other hand most probably account for these differences. Using UPW as a reference, sorption levels were modified more by SEM than by RW. Potential competitors such as ions (Ca^{2+} and Mg^{2+} in the case of Cu, H_2PO_4^- in the case of glyphosate) and dissolved organic carbon are indeed present at higher levels in SEM (Table 2).

3.3. Interactions between copper and herbicides

3.3.1. Copper and glyphosate in mixture

Interaction between copper and glyphosate was clear when looking at the difference in the maximum sorption percentage between the single compound matrix and the mixture (Fig. 2). Copper was generally less sorbed in the presence of glyphosate (Fig. 2a) as already shown by Morillo et al. [41]. Indeed, glyphosate reacts with dissolved Cu to form a water-soluble complex with a lower affinity for most sorbents than Cu itself. This result may also mean that glyphosate exhibits a higher affinity for most sorbents than Cu, as previously observed for other ionisable pesticides on vineyard soils [42]. In contrast, glyphosate was generally much more sorbed in the presence of copper (Fig. 2b). On a natural sorbent such as soil, glyphosate-copper complexes were indeed shown to exhibit higher sorption levels than free glyphosate [27,43]. Copper is assumed to promote glyphosate sorption on Cu sites by acting as a bridge

Table 5

Copper and herbicide sorption as single compounds and in mixture with other pollutant(s) in sediment extract medium (SEM). Sorption is described by the maximal sorption percentage (%) and the time (*t*, in hours) to reach the maximal sorption level. For each pollutant (Cu, Glyphosate, Diuron and 3,4-DCA), mean values with different letters are significantly different (at $P < 0.05$).

		Sugar beet pulp	Corn cob	Perlite	Vermiculite	Sediment	Sand	Corn cob char
Cu	%	54 ± 2 b	24 ± 2 e	4 ± 5 ij	11 ± 2 hi	31 ± 6 d	6 ± 1 ij	68 ± 2 a
	<i>t</i>	6	6	1	4	72	48	32
+ glyphosate	%	44 ± 1 c	16 ± 2 fgh	1 ± 2 j	20 ± 1 efg	22 ± 8 ef	14 ± 4 gh	63 ± 4 a
	<i>t</i>	6	6	6	6	24	48	32
+ all other pollutants	%	44 ± 1 c	14 ± 6 gh	2 ± 1 j	10 ± 3 hi	20 ± 1 efg	10 ± 1 hi	67 ± 1 a
	<i>t</i>	6	32	0.2	72	72	32	32
Glyphosate	%	46 ± 1 b	46 ± 4 c	44 ± 1 b	43 ± 1 b	34 ± 6 c	30 ± 10 a	50 ± 3 b
	<i>t</i>	9	5	5	2	2	8	48
+ Cu	%	67 ± 8 a	58 ± 2 b	51 ± 7 b	55 ± 6 b	59 ± 2 b	51 ± 7 a	75 ± 1 a
	<i>t</i>	2	4	1	2	2	2	4
+ all other pollutants	%	65 ± 2 a	65 ± 3 a	65 ± 2 a	71 ± 3 a	76 ± 7 a	54 ± 14 a	79 ± 1 a
	<i>t</i>	6	6	24	48	24	48	48
Diuron	%	34 ± 1 b	46 ± 9 a	5 ± 1 a	0 b	69 ± 1 a	69 ± 5 a	98 ± 3 a
	<i>t</i>	5	24	8	–	6	1	24
+ all other pollutants	%	57 ± 1 a	57 ± 1 a	8 ± 6 a	47 ± 12 a	61 ± 4 b	76 ± 1 a	94 ± 2 a
	<i>t</i>	8	48	48	6	2	24	48
3,4-DCA	%	47 ± 2 b	62 ± 18 a	5 ± 2 a	7 ± 1 b	71 ± 1 a	84 ± 1 a	100 ± 1 a
	<i>t</i>	24	24	3	24	48	8	24
+ all other pollutants	%	86 ± 2 a	86 ± 1 a	30 ± 19 a	74 ± 9 a	49 ± 4 b	82 ± 3 a	97 ± 2 a
	<i>t</i>	8	8	2	8	2	1	48

between glyphosate and the sorbent. It depends however on sorbent characteristics (e.g., soil composition), solution pH and copper concentration, as already demonstrated by Dousset et al. [44].

Besides, the liquid matrix greatly acts upon the behaviour of Cu and glyphosate in mixture. The interaction observed between Cu and glyphosate in UPW was often restricted and even sometimes reversed in RW and SEM. For copper, this phenomenon was observed on vermiculite in RW and on vermiculite and sand in SEM (Fig. 2a). For glyphosate, lower glyphosate sorption in mixture with copper was noticed on corn cob and corn cob char in RW (Fig. 2b). These results undoubtedly show that copper and glyphosate interact not only together but also with other compounds of the matrix.

3.3.2. All compounds in mixture

This experiment was performed only with sediment extract medium (SEM). The non-significant differences (excepted for vermiculite) observed in the sorption of Cu between the Cu-Glyphosate-mixture and the four pollutant-mixture (Table 5) suggest that diuron and 3,4-DCA do not much impact on the sorption of Cu. This finding is in accordance with the results reported by Jacobson et al. [45] on diuron in vineyard soils. Similar conclusions can be drawn for glyphosate on sugar beet pulp, sand and corn cob char: the sorption of glyphosate seemed modified more by the addition of copper than by the addition of diuron and/or 3,4-DCA. In contrast, higher glyphosate levels were sorbed on all other sorbents when mixed with all pollutants. This reveals interactions

between diuron (or 3,4-DCA), glyphosate and Cu which impact on the sorption of glyphosate specifically on these materials.

Regarding diuron and 3,4-DCA, sorption levels did not differ very much when used as single compounds or with all other pollutants (sugar beet pulp and vermiculite excepted). This suggests, notably, that Cu does not much impact on the sorption of diuron on sediment, in accordance with Dousset et al. [44].

3.4. Equilibrium isotherm models

Sorption isotherms were obtained for each compound separately in UPW, RW and SEM. For isotherms in UPW and RW, sugar beet pulp was selected for copper, sand for glyphosate, and sediment for diuron and 3,4-DCA as these three sorbents were found the most relevant with these two liquid matrices. For isotherms in SEM, sugar beet pulp was selected for copper, sediment for glyphosate and sand for diuron and 3,4-DCA (Table 5).

As expected, the Langmuir model was found to better describe the data relative to copper (Fig. 3, Table 6), suggesting surface adsorption. In UPW, the sorption coefficient *b* of the sugar beet pulp was 0.021 L mg⁻¹. This is low compared to the values of *b* reported either for soils [46] or sediments [47]. This low affinity may be the result of the acidic pH since pH averages 4.0 at equilibrium. Surprisingly, *b* did not decrease with RW. It plummeted in SEM (3.5-fold decrease), as a result of a potential competition with ions in solution and/or complexation by dissolved OM. Another finding is that the maximum sorption (Q_{max}) capacity of the sugar beet pulp was

Table 6

Langmuir parameters applied to copper and Freundlich parameters applied to Diuron and 3,4-DCA in each matrix (ultrapure water, UPW; runoff water, RW; sediment extract medium, SEM) for the best adsorbent selected in SEM.

			Langmuir			Freundlich		
			Q_{max} mg kg ⁻¹	<i>b</i> L mg ⁻¹	r^2	K mg ¹⁻ⁿ L ⁿ kg ⁻¹	<i>n</i>	r^2
Cu	Sugar beet pulp	UPW	17100	0.021	0.988	–	–	–
		RW	15400	0.022	0.994	–	–	–
		SEM	21200	0.006	0.999	–	–	–
Diuron	Sediment	UPW	–	–	–	24.7	1.37	0.992
		RW	–	–	–	35.7	0.94	0.848
		SEM	–	–	–	–	–	–
3,4-DCA	Sediment	UPW	–	–	–	84.9	1.23	0.977
		RW	–	–	–	52.3	1.38	0.816
		Sand	–	–	–	–	–	–

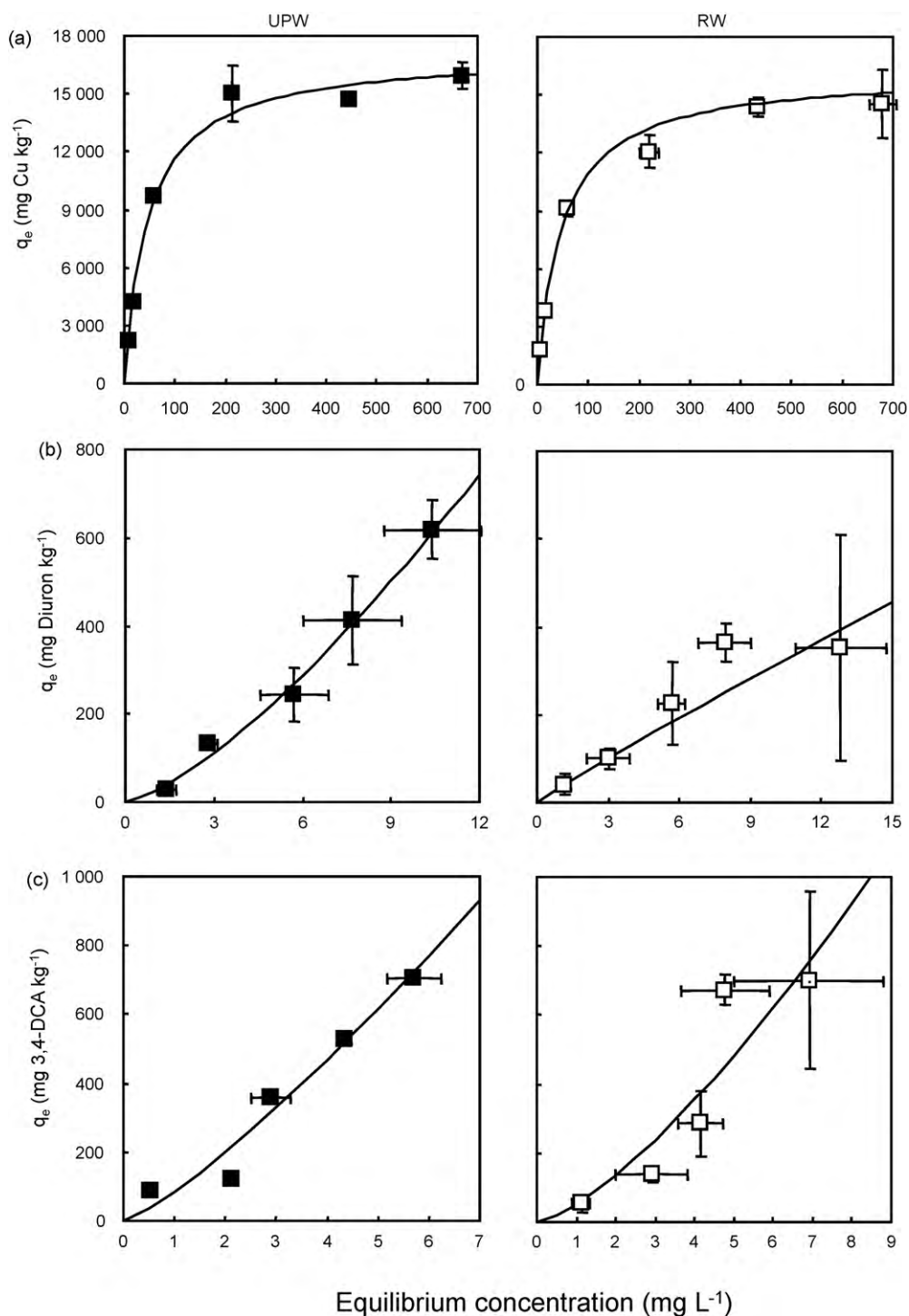


Fig. 3. Equilibrium sorption isotherms of (a) copper on sugar beet pulp, (b) diuron and (c) 3,4-DCA both on sediment, obtained in ultrapure water (UPW, ■) and runoff water (RW, □). The solid line represents the fit of sorption data to the Langmuir expression for copper and to the Freundlich expression for diuron and 3,4-DCA. The error bars stand for mean standard errors.

high. Q_{\max} varied between 15400 and 21200 mg Cu kg⁻¹ according to the matrix. This is up to 20-fold higher than the common values reported for acidic soils [46]. This highlights the relevance of adding sugar beet pulp in contaminated areas in order to increase the sorption capacities of soils or sediments for Cu.

For diuron and 3,4-DCA, the Freundlich model was found to better describe the data (Fig. 3, Table 6). The non-curvilinear Langmuir type of the isotherms was attributed to intra organic matter diffusion. In UPW, the sorption coefficient K of the sediment was 24.7 mg¹⁻ⁿ Lⁿ kg⁻¹ for diuron and 84.9 mg¹⁻ⁿ Lⁿ kg⁻¹ for 3,4-DCA.

These are high values compared to those reported for soils [48–50]. It shows a fairly high affinity of sediment for diuron and 3,4-DCA, which needs however to be validated in more complex matrices like SEM. No model was found to describe adequately the data regarding glyphosate.

4. Conclusions

Low cost sorbents were tested experimentally in this study for their ability to sorb copper and herbicides in matrices of increas-

ing complexity. The discrepancies found between the results in the different matrices highlight the need for caution when interpreting UPW performed sorption experiments. The major result of this study is that several sorbents requiring no preliminary treatment, i.e., sugar beet pulp for Cu and sand for diuron and 3,4-DCA, were able to sorb more than 50% of the corresponding pollutant at the studied concentration, even in SEM. Another finding is that the interactions between herbicides and Cu led to significant differences in their sorption when tested in mixtures. Further investigations are required on a larger scale to test the accuracy of these low cost sorbents in field conditions.

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