



Reactivity of vadose-zone solids to *S*-metolachlor and its two main metabolites: case of a glaciofluvial aquifer

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Abstract

The vulnerability of groundwater to pesticides is governed in part by sorption mechanisms in the vadose zone, commonly studied in soil but less well-known in the geological solids. To alleviate this lack of knowledge, adsorption of the herbicide *S*-metolachlor (SMOC) and of two of its metabolites—metolachlor ethane sulfonic acid (MESA) and metolachlor oxanilic acid (MOXA)—was studied with batch equilibrium method on seventeen surface soils and three geological solids of the vadose zone overlying a glaciofluvial aquifer. In grainsize terms, the latter three were sand for the first two samples and gravel for the third. Adsorption is ordered as follows: SMOC >> MESA > MOXA, except for one of the geological solids for which MESA adsorption was slightly higher than that of SMOC ($K_d = 0.73$ vs. 0.44 L kg^{-1}). The low MOXA adsorption could only be quantified for the gravel sample ($K_d = 0.74 \text{ L kg}^{-1}$), which was also more reactive than all the other samples to MESA and SMOC ($K_d = 2.08$ and 28.8 L kg^{-1} , respectively). Statistical multivariate tests related the highest K_d values for SMOC with the soils and geological solids with the highest organic-carbon and clay-fraction contents. The highest K_d values for MESA were found in the samples containing high oxide concentrations. Our results shed a new light on the adsorption of SMOC, MESA and MOXA suggesting that during their transfer to groundwater, pesticides and metabolites can be adsorbed in the vadose zone on both soils and geological solids.

Keywords (6 à 8): Adsorption · Pesticide · Chloroacetanilide · Metolachlor ESA · Metolachlor OXA · Groundwater · Geological solids · Reactivity

Introduction

The contamination of groundwater by pesticides is a well-known problem affecting many aquifers in numerous countries (Kolpin et al. 1998a; Postigo and Barcelo 2015; Toccalino et al. 2014). The European Water Framework Directive (2000/60) and its sister Directive (2006/118/CE) set the objectives to be reached for the protection and conservation of groundwater

masses. More generally, the protection of water resources and the monitoring of groundwater quality are an issue to be treated at a worldwide scale, particularly where groundwater is used for drinking. Today, many questions remain concerning the velocity with which contaminants are transferred to groundwater, and its corollary of evaluating the risk of seeing contaminants reappear years after their application.

The mobility of pesticides in vadose (unsaturated) zone, and hence their transfer to groundwater compartment, depends on the degradation and sorption processes on solid particles, well-described for soils in the literature (Arias-Estevez et al. 2008; Dubus et al. 2003). Until now, it has been assumed that pesticides and/or their metabolites flushed from the soil will interact only little with geological solids in the underlying vadose zone because of their low organic matter content, meaning that their transfer to groundwater is essentially controlled by the hydrological conditions of aquifer recharge. Other work, though patchy, has shown that pesticides can react with geological solids in the vadose zone (Baran and Gourey 2013; Clausen et al. 2004; Coquet 2003; Coquet et al. 2004; Janniche et al. 2010; Madsen et al. 2000;

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Papiernik et al. 2006; Sidoli et al. 2016a). As an example among these previous studies, Sidoli et al. (2016a) showed that transfer of herbicide *S*-metolachlor in glaciofluvial solids is delayed compared with that of water tracer because of sorption processes. It is therefore essential to collect data on how pesticides are adsorbed on geological solids of the vadose zone, to understand if interactions in geological solids are negligible or contrary significant compared with the transfer through soil and thus if they are matters or not for risk analysis or even quantitative solute transport simulations.

The few data available on the adsorption of metabolites in the vadose zone is a major hindrance for understanding how such molecules are transferred. The differences in physicochemical properties between the metabolites and their parent molecule may cause a difference in reactivity to the solids in soil and the vadose zone. Such a change of physicochemical properties between mother molecule and metabolites is observed for several pesticides, including metolachlor. This pesticide is electrically neutral, whereas its two metabolites are negatively charged to the environmental pH. Metolachlor, applied as a mixture enriched in *S* isomer (*S*-metolachlor), is a selective herbicide used in particular on maize. Introduction of *S*-metolachlor (SMOC) in some countries in replacement of rac-metolachlor (racemic mixture of *R*- and *S*- isomers) was motivated by its higher herbicide efficiency (Blaser et al. 2007; Shaner et al. 2006). Metolachlor is massively used worldwide and is one of the most common organic compounds found in groundwaters in North America (Toccalino et al. 2014), in Europe (Loos et al. 2010) and in France (Lopez et al. 2015). The retention of SMOC in soil is moderate and mainly linked to organic matter content (Alletto et al. 2013; Baran and Gourcy 2013; Bedmar et al. 2011; Weber et al. 2003). SMOC can also be adsorbed on geological solids, as was shown by the batch equilibrium method on alluvial deposits (Baran and Gourcy 2013) and by column-percolation tests on glaciofluvial deposits (Sidoli et al. 2016a). Metolachlor ethane sulfonic acid (MESA) and metolachlor oxanilic acid (MOXA) are commonly quantified in groundwater at concentrations over that of metolachlor and which can reach 4.8 and 3.8 $\mu\text{g L}^{-1}$ respectively (Amalric et al. 2013; Baran and Gourcy 2013; Hancock et al. 2008; Hladik et al. 2008; Kolpin et al. 1998b, 2004; Postle et al. 2004; Steele et al. 2008). The metabolites MESA and MOXA have very low adsorption coefficients in soil (Krutz et al. 2004) and are more mobile in unsaturated media than their parent molecule (Baran and Gourcy 2013; Sidoli et al. 2016a). However, the key parameters involved in the adsorption of MESA and MOXA in soil are unknown. Few data exist for the adsorption of SMOC on geological solids in the vadose zone, and almost nothing is known about the adsorption of MESA and MOXA in the vadose zone. For those reasons, the role played by geological solids of the vadose zone in the transfer of pesticides and their metabolites is difficult to establish today without more data on adsorption values.

The purpose of this study was to improve our understanding of the role played by the vadose zone in retaining SMOC and its two metabolites MESA and MOXA. Our specific objectives are (i) to quantify and compare the adsorption of all three molecules on soils and on geological solids collected in the vadose zone of a glaciofluvial aquifer and (ii) to determine the factors governing molecular adsorption. Adsorption measurements (K_d values) were lead with batch laboratory experiments at equilibrium. We used multivariate analyses for linking the K_d values with soil and solid properties, to determine the factors governing molecular adsorption.

Materials and methods

S-metolachlor and its two main metabolites

The experiments were performed with *S*-metolachlor (purity $\geq 99.5\%$) purchased from Dr. Ehrenstorfer (Augsburg, Germany), and MESA (purity $\geq 96.2\%$) and MOXA (purity $\geq 97.9\%$) from Sigma-Aldrich (Steinheim, Germany) (Table 1). Individual standard stock solutions of SMOC, MESA and MOXA (500 mg L^{-1}) were prepared on a weight basis in methanol and stored at -20°C . Solutions used for spiking samples were prepared in a $\text{CaCl}_2 10^{-2} \text{ M}$ aqueous solution with ultrapure water (MilliQ® Merck Millipore) and stored at 4°C .

SMOC, MESA and MOXA concentrations were determined with an Acquity ultra-performance liquid chromatography system (UPLC™, Waters) interfaced to a triple quadrupole mass spectrometer (Quattro Premier XE/Q, Waters). Online extraction was done with an SPE cartridge (Oasis HLB-Column 25 μm). Chromatographic separation was done with a Waters Acquity UPLC BEH C18 column (2.1 mm \times 150 mm, particle size 1.7 μm). Mecoprop-d3 and simazine-d10 were used as internal standards for metabolite and metolachlor analyses, respectively. The quantification limit was $0.025 \mu\text{g L}^{-1}$ for metolachlor and $0.050 \mu\text{g L}^{-1}$ for both MESA and MOXA. The analytical method developed for offline extraction is described in detail in Amalric et al. (2013).

Sampling site

The sampling site is located in a quaternary glaciofluvial deposit (Würm age) of about 110 km^2 , east of Lyon, France. The regional aquifer is from 30 to 70 m thick and the water table is between 2 and 40 m below the soil surface. Seventeen surface soils were sampled in different agricultural plots at up to 30-cm depth. The soils are loamy to sandy-loamy characterized by large amounts of amorphous iron- and aluminium oxides (mean values 2.7 and 1.8 g kg^{-1} , respectively). They are chromic cambisols according to the WRB classification system (2006). Sampling strategy and physicochemical properties of the surface soils were described by Sidoli et al. (2016b) and in Table 2.

Table 1 Chemical structures of herbicide S-metolachlor (SMOC) and its anionic metabolites ESA-metolachlor (MESA) and OXA-metolachlor (MOXA)

Chemical structure			
	Name	S-metolachlor	Metolachlor ESA
Water solubility (mg/L)	430	212	238
pKa	-	1.8	4.8

The glaciofluvial solids (GFS) were collected in a quarry, several metres above the water table and 30 m below ground surface. Two main lithofacies were earlier identified and sampled on site based on grain size distribution (Goutaland et al. 2008, 2013; Lassabatere et al. 2010; Sidoli et al. 2016a).

Glaciofluvial solid analysis

The particle size distributions of the two main lithofacies are, for one, a bimodal mixture of gravel and sand with grain sizes up to 100 mm diameter (Gcm,b) and, for the other, sand with grain sizes between 0 and 2 mm (S-x) (Goutaland et al. 2008).

After air-drying, both samples (S-x and Gcm,b lithofacies) were sieved at 0 to 2 mm particle sizes (S-x and Gcm,b [0,2]). A coarser sieving diameter (2 to 10 mm particle size) was used on the bimodal gravel (Gcm,b [2,10]).

For S-x, Gcm,b [0,2] and Gcm,b [2,10], the following chemical properties were analysed: pH_{KCl}, pH_{water} (AFNOR 10390 (2005)), CEC Metson (AFNOR X 31.130 (1999)), total organic carbon content (AFNOR 10694 (1995a)), available phosphate (Olsen P) (AFNOR 11263, 1995b), crystallized oxy-hydroxides (Fe_{DCB} and Al_{DCB}) based on the Mehra-Jackson method (1960) and amorphous oxy-hydroxides (Fe_{Tamm} and Al_{Tamm}) based on the Tamm method (1922).

Table 2 Main physical and chemical properties of vadose zone solids

	pH CaCl ₂ ^a	pH water ^b	pH KCl ^c	CEC ^d (meq 100 g ⁻¹)	%			g kg ⁻¹						
					Clay	Silt	Sand	Organic C	Olsen P	Al _{DCB}	Fe _{DCB}	Al _{ox}	Fe _{ox}	CaCO ₃
Surface soils n = 17														
Min	5.1	6.1	4.9	4.4	8.9	29.5	40.8	7.2	0.04	1.5	2.1	1.2	2.1	< 1
Max	7.0	8.0	7.2	9.6	15.4	42.3	60.4	23.1	0.20	11.1	13.5	2.2	3.2	< 1
Mean	5.9	7.0	6.1	7.4	13.2	36.4	48.4	13.6	0.09	3.1	9.3	1.8	2.7	< 1
GFS														
S-x	7.2	9.2	8.8	1.2	2.1	2.2	95.7	2.5	< LQ	0.6	3.0	0.5	0.9	178
Gcm,b [0,2]	7.3	9.1	8.6	1.9	4.2	4.3	91.5	1.1	< LQ	0.7	4.0	0.7	1.2	233
Gcm,b [2,10]	7.3	9.2	8.9	1.1	-	-	-	1.2	< LQ	0.4	3.1	0.0	1.0	356

^a pH measured in 1:1 soil/0.01 M CaCl₂ solution (w/w) ratio

^b pH measured in 1:2 soil/water (w/w) ratio

^c pH measured in 1:2 soil/0.01 M KCl solution (w/w) ratio

^d Cationic exchange capacity

n.q. not quantifiable

The experimental pH, hereafter referred to as ‘pH_{CaCl₂}’, was measured in batch supernatants with a pH microelectrode (Inlab Flex-Micro).

Mineralogical compositions were determined by X-ray diffraction (XRD) measurements with a Bruker D8 Advance diffractometer, equipped with a CuK α source ($\lambda = 1.5418 \text{ \AA}$) operating at 40 kV and 40 mA, and a Lynx-Eye 1D detector. XRD patterns were collected from 5° to 90° 2 θ , with a step of 0.02°2 θ and a time step of 139.2 s. XRD diffraction patterns were interpreted with the DIFFRAC.Plus EVA software. The SIROQUANT™ quantitative X-ray diffraction analysis software processed the XRD spectra for quantifying the mineral phases. Quantification was done with the Rietveld method.

Sample porosity was measured by mercury-porosimetry analyses (Auropore IV 9500 Micromeritics). The S-x, Gcm,b [0,2] and Gcm,b [2,10] samples were quartered in order to obtain representative test samples of 5 to 7 g. The sample porosity was measured on six replicates for Gcm,b [2,10] and on two replicates for S-x and Gcm,b [0,2].

SEM analysis

Samples S-x, Gcm,b [0,2] and Gcm,b [2,10] were observed by scanning electron microscopy on a Tescan Mira3XMU SEM with an Edax Pegasus EDS (electron dispersive X-ray spectroscopy) microanalysis system using an Edax ApolloXPP silicon drift detector (SDD) (resolution 126 eV @ Mn Ka) and the EDS Edax TEAM software. The samples were observed at different high-tension values (15 or 25 kV) adapted to the analyses. A long acquisition time of 100 to 500 s, with a counting rate of several thousand cps, was used for acquiring EDS spectra in order to detect elements at several tenths of a percent. The Gcm,b [2,10] gravels were stuck on aluminium pin stubs with a conducting carbon lacquer (PELCO® water-based graphite paint from Ted Pella). The samples S-x and Gcm,b [0,2] were stuck by pressure on a conductive carbon adhesive (double-coated PELCO Tabs™ carbon conductive tabs, Ted Pella). The samples were then covered with a 10-nm carbon layer, using a carbon evaporator under a secondary vacuum (Cressington 208 Carbon) to ensure that the surface would be conductive.

Adsorption experiments

Adsorption experiments were run according to a normalized method (OECD guideline 106, 2000). The tests were run for a liquid/solid ratio of 1. Four grams of S-x and Gcm,b [0,2] solids were used. For Gcm,b [2,10], the experiments were done with 10 g in order to obtain repeatable replicates despite the high heterogeneity of this material. Dried solid samples were hydrated with a CaCl₂ background solution electrolyte. Dehydrated calcium chloride (CaCl₂), purity $\geq 98\%$, was

purchased from Merck. The hydration was done 16 h before spiking to reach near-equilibrium conditions. Spiking was done with a pesticide solution diluted in 0.01 M CaCl₂, shaken in a head-over-head agitator at 20 °C in a dark box. Based on a kinetic study (data not shown), the equilibrium adsorption experiments were conducted for 24 h for the seventeen surface soils, S-x and Gcm,b [0,2], and for 72 h in the case of Gcm,b [2,10]. Equilibrium adsorption was measured from a unique initial pesticide concentration of 1 mg L⁻¹. After centrifugation at 3000 rpm for 30 min and filtration through a 0.22- μm acetate cellulose filter, the supernatants were analysed for SMOC, MESA or MOXA concentrations.

The amount of pesticide adsorbed on the solid phase (Q_e , mg kg⁻¹) was calculated as the difference between initial concentration and equilibrium concentration (C_e , mg L⁻¹). The distribution between the amount adsorbed on solids and the supernatant concentration at equilibrium was expressed with the distribution coefficient K_d (L kg⁻¹), calculated with Eq. (1)

$$Q_e = K_d C_e \quad (1)$$

Solids blanks included in the experiments do not show any contamination of the samples before the experiments. No adsorption was measured on tubes and filters used for batch experiments. Molecule stability in solution was tested for the duration of the experiments, revealing any loss of molecules. Each experiment was carried out in triplicate.

Statistical analysis

Due to the nature of the dataset, usual statistical analyses such as multiple regression done to quantify relationship between sorption properties of pesticides and/or metabolites and physicochemical properties of soil could not be used in the present study. Indeed, these statistical analyses are not suitable for small dataset, which is the case notably for the GFS sub-dataset (Legendre and Legendre 1998). To overcome this limit, unsupervised and supervised ordination analyses were performed. Unsupervised analysis enables us to explain how soil and GFS samples could be distinguished according to their physicochemical properties and how these properties are linked between them. Supervised analysis was devoted to determine how the physicochemical properties of soils and GFS could explain their reactivity towards sorption of SMOC and MESA but not for MOXA as the amount of adsorbed MOXA could not be quantified. More details on these tools are given below.

First, a principal component analysis (PCA) was run to ordinate the 17 soils and the 3 GFS for each according to the following physicochemical variables: (1) pH measured in CaCl₂, water and KCl solutions (pH_{CaCl₂}, pH_{water}, pH_{KCl}); (2) cationic exchange capacity (CEC); (3) solid texture (clay, silt and sand contents); (4) total organic carbon (Organic C)

(5) phosphorus contents extracted by the Olsen method (Olsen P); (6) contents in poorly crystallized aluminium (Al_{ox}) and iron (Fe_{ox}) oxides, and contents in well-crystallized aluminium and iron oxides (Al_{DCB} and Fe_{DCB} , respectively). This unsupervised exploratory method allowed finding the best low-dimensional representation of the variance associated with physicochemical variables. Relationships between observations and physicochemical variables were investigated through the analysis of how such variables contribute to the calculated principal components. Before doing so, the variables were centred and scaled. The results were presented as a correlation circle for the physicochemical variables and a biplot build on the two principal axes to illustrate the ordination of the samples. The PCA was done on two distinct datasets, one gathering both soil and GFS and the other focusing only on soil materials, to determine whether the GFS with its specific physicochemical properties could be analysed together with the soil material.

Then, a partial least squares linear discriminant analysis (PLS-DA) was done. This supervised multivariate analysis computes the best discriminating functions based on the physicochemical properties of the samples to distinguish the K_d values measured on each of them. This statistical analysis was done for SMOC and MESA, respectively. This statistical test implies first to group soil and GFS samples based on the values of the K_d measured. For this purpose, we used a cumulative distribution function built from measured K_d values either for SMOC or MESA. Based on the cumulative distribution function, the first and third quantile values as well as the median values were calculated. These values were then used to separate measured K_d values into four groups, enabling us to transform the two quantitative variables—corresponding to K_d -value measurements for SMOC and MESA—into two categorical (discrete) variables. The first group, Kd_1 , combines the K_d values below the first quantile. The second group, Kd_2 , is for the K_d values above the first quantile and below the median, whereas the third group, Kd_3 , consists of the K_d values above those of the second rank and below the third quantile. The remaining K_d values were aggregated into a fourth group, Kd_4 .

The same physicochemical variables than those used in the PCA were integrated in the discriminant analysis. These variables were transformed into latent variables based on a partial least squares regression algorithm that searched for maximum covariance, representing the relevant sources of data variability with linear combinations of the original variables. The plots used to present the results are similar to those used for PCA. A confusion matrix comparing the a priori (real) and a posteriori (calculated) classification of the observations was calculated using the cross-validation technique.

To complete the results from the PLS-DA, a non-parametric multivariate analysis of variance (MANOVA) based on permutation algorithm was run on the dataset to

statistically evaluate whether the whole physicochemical properties of the soil or GFS are statistically different according to the four groups derived from the K_d measurements done either on SMOC or on MESA, respectively. A Bray-Curtis similarity matrix was calculated on data that had been scaled and centred. A permutation matrix for calculating pseudo-F ratios was built using Markov Chain Monte Carlo methods (999 permutations). This multivariate approach was conducted with and without accounting for GFS in the dataset, to determine whether the results for soils and GFS could be interpreted simultaneously or not. In addition, a non-parametric Kruskal-Wallis test was used on each of the 13 physicochemical variables measured on samples by accounting also for the categorical variable derived from measurement on sorption of SMOC or MESA, respectively. In case of a significant difference, a Conover-Iman post hoc test was done to identify which groups differ from the others. This univariate approach was conducted in similar way that the non-parametric MANOVA (presence or not of GFS). Results are shown in supplementary Fig. 5. All statistical analyses were carried out with the R 3.4.2 software (R Core Team 2017). The FactoMineR, MASS and mixOmics libraries were used.

Results and discussion

Variability of the properties of vadose-zone solids

The first two PCA axes allow a correct description of much of the variance inherent in the soil and GFS observations as determined from their physicochemical properties (Fig. 1). The inertia associated with these first two axes is 81%. Analysis of the variance/covariance matrix shows that the first axis is constructed by the following physicochemical variables: pH_{KCl} , pH_{water} , $\text{pH}_{\text{CaCl}_2}$, CaCO_3 , Clay, Silt, CEC, Al_{ox} , Fe_{ox} and Organic C.

This first axis correctly separates the GFS points from soils, in particular those with a high calcium carbonate content ($\geq 178 \text{ g kg}^{-1}$ Table 2)—mainly calcite (Table 3)—, associated with high pH values. Compared with GFS, the surface soils are decarbonated with lower pH values (mean $\text{pH}_{\text{CaCl}_2}$ value of 5.9 vs. ≥ 7.2) and a higher Organic C (mean value of $13.6 \text{ vs. } \leq 2.5 \text{ g kg}^{-1}$), higher clay contents (mean value of $13.2\% \text{ vs. } \leq 4.2\%$) and higher Al_{ox} and Fe_{ox} contents (mean values of 1.8 and 2.7 vs. ≤ 0.7 and $\leq 1.2 \text{ g kg}^{-1}$, respectively) (Table 2). More details on the soils are given in (Sidoli et al. 2016a). The second axis has a lower inertia and is constructed by the Olsen P, Al_{DCB} and Fe_{DCB} variables, but does not provide a clear separation between the soils, except for soils 11, 13 and 2 that have different physicochemical properties. Compared with the other soils, 2 and 13 have the lowest P Olsen ($\leq 5.6 \text{ mg kg}^{-1}$) and highest Al_{DCB} contents (11.1 and 10.6 g kg^{-1} ,

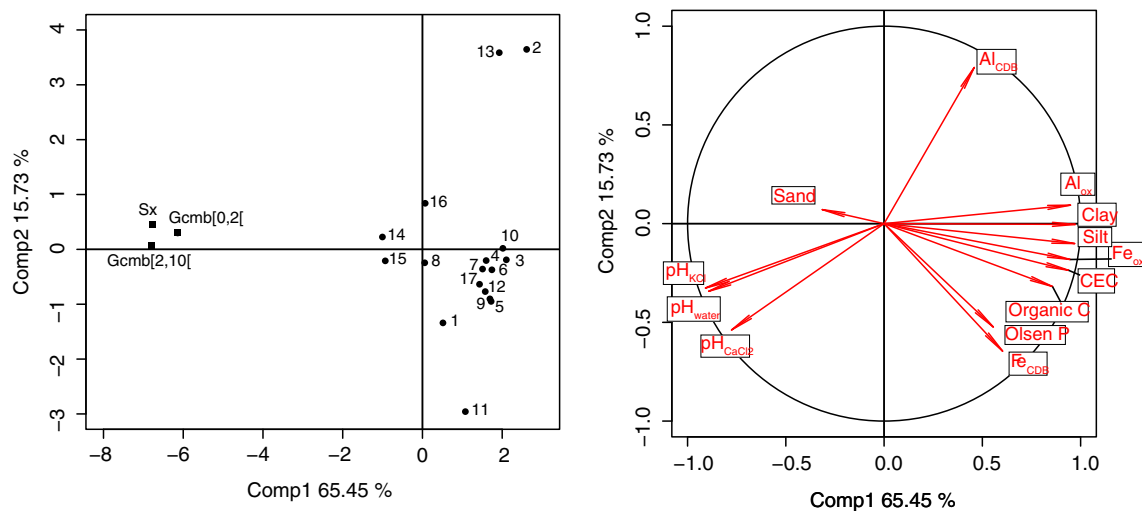


Fig. 1 Principal component analysis performed on physical and chemical properties measured for soils (samples 1 to 17) and glaciofluvial solids (S-x, Gcm,b [0,2] and Gcm,b [2,10])

respectively). Moreover, except for soil 18, soils 13 and 11 have the highest organic carbon contents ($\geq 16.1 \text{ g kg}^{-1}$).

The GFS mineralogy as determined by XRD analyses mostly consists of quartz ($> 32\%$) and calcite ($> 18\%$) (Table 3). To a lesser extent, feldspars, such as albite (sodic plagioclase) and microcline (potassic feldspar), and clay minerals (smectite, kaolinite and chlorite) are present as well, as are illite-type minerals, illite sensu stricto and/or micas. No trace of Fe or Al oxy-hydroxides were detected by DRX analyses, even though significant Fe and Al concentrations were measured with the Mehra-Jackson (Fe_{DCB} and Al_{DCB}) and Tamm (Fe_{ox} and Al_{ox}) extraction methods. These contrasting results indicate that Fe and Al oxy-hydroxides must be present, but that their abundances in the mineralogical assemblages of the three fractions are low. The abundance of the main mineral phases, quartz and calcite, is different between fraction S-x and the fractions Gcm,b [0,2] and Gcm,b [2,10].

Fraction S-x is richer in quartz (54% vs. $\leq 36\%$), but calcite is less abundant (18% vs. 30 and 34%) compared with the two Gcm,b fractions. No difference was apparent between the minor mineral phases in the three fractions. Even though no mineralogical analysis was made of the soils, it is probable that they consist of an assemblage of goethite, inherited clays of the smectite and illite types, potassic feldspars, ferromagnesian micas and quartz, similar to the mineralogy of other, geographically close, fersiallitic soils, formed over glaciofluvial materials and in the same stage of pedological evolution (Bomand 1978).

K_d values in the vadose-zone profile

In soils, the K_d distribution coefficients of SMOC fall between 2.34 and 6.32 L kg^{-1} (Table 4), a normal range of K_d values as earlier measurements on different soil types provided a range

Table 3 Mineralogical composition (semi-quantitative XRD analysis) expressed as a percentage of the total of sand (S-x) and both [0,2] and [2,10] bimodal gravel fractions and intra-granular porosity (%)

	Mineralogical XRD composition										Intra-porosity (%)
	Quartz ($\pm 3\%$)	Calcite ($\pm 3\%$)	Albite ($\pm 3\%$)	Microcline ($\pm 3\%$)	Illite/micas ($\pm 5\%$)	Chlorite ($\pm 5\%$)	Smectite ($\pm 5\%$)	Kaolinite ($\pm 5\%$)	Antigorite ($\pm 5\%$)	Halite ($\pm 3\%$)	
S-x	54	18	7	8	5	3	3	2	-	-	n.q.
Gcm,b [0,2]	36	30	5	4	4	1	13	6	tr.	1	1.5–1.6**
Gcm,b [2,10]	32	34	4	5	8	2	7	8	tr.	tr.	1.8 \pm 0.2***

n.q. not quantifiable, tr. Traces

**Duplicate

***TriPLICATE

of 1.02 to 8.7 L kg⁻¹ (Alletto et al. 2013; Cassigneul et al. 2018; Krutz et al. 2004; Seybold and Mersie 1996; Vryzas et al. 2007; Weber et al. 2003). Regarding the metabolites, the K_d values are very low for MESA ($K_d < 0.75$ L kg⁻¹) and below the detection limit for MOXA (Table 4). The few available studies on these metabolites also showed very low adsorption on soils, for MESA K_d values below 0.19 L kg⁻¹ (Kupfersberger et al. 2018). The adsorption on the soils we studied follows the same decreasing order: SMOC >> MESA > MOXA, whereas Krutz et al. (2004) mentioned comparable K_d values for MESA and MOXA in a clayey soil (average K_d value of 0.75 and 0.77 L kg⁻¹ respectively). This adsorption difference might be due to the clayey nature of the soil, which may have favoured the MOXA adsorption process.

For the S-x and Gcm,b [0,2] samples, the K_d values for SMOC were lower than those for the soils, with 0.44 and 0.57 L kg⁻¹, respectively. The adsorption coefficients for MESA were 0.73 and 0.46 L kg⁻¹, respectively, within the 0.03 and 0.74 L kg⁻¹ range we measured for soils. MOXA does not seem to sorb with the solid phases in S-x and Gcm,b

[0,2]. These results are coherent with an earlier study on the fine [0,2] mm fraction of other sedimentary geological solids, that measured very low adsorption of MESA and no adsorption of MOXA (Baran and Gourcy 2013). Finally, the adsorption properties of the [2,10] mm fraction of Gcm,b are quite different from the two fine fractions of S-x and Gcm,b [0,2]), as the former fraction appears to be very reactive for SMOC, MESA and MOXA. The measured K_d values were 28.8, 2.08 and 0.74 L kg⁻¹, respectively. The coarse [2,10] mm fraction of the Gcm,b lithofacies thus has a much higher retention capacity for SMOC, MESA and MOXA than Gcm,b [0,2] and S-x, but also higher than those of the 17 soils studied. The adsorption order of the molecules is SMOC > MESA > MOXA for the solids of the vadose zone, except for facies S-x where MESA adsorption is slightly higher than that of SMOC. These results complete data obtained earlier during column-transfer experiments for the same solids (Sidoli et al. 2016a), with an identical adsorption order.

Key factors for adsorption on vadose-zone solids

Adsorption of SMOC

A discriminant analysis of the physicochemical properties of the solids (soil and GFS) for the SMOC adsorption values (K_d) identified four value groups Kd_1, Kd_2, Kd_3 and Kd_4. In a univariate analysis (ANOVA), the solids for which the K_d values are over the median (Kd_3 and Kd_4 groups) have significantly higher organic C contents than the solids of group Kd_1 (Supplementary Table 1). The solids of group Kd_4 also have a statistically higher CEC content than those of group Kd_1.

It should be noted that the sand fraction in the grainsize assemblage is significantly lower in the Kd_4 group solids than in those of group Kd_1. The latter, though, have lower crystallized aluminium oxide (Al extracted with the CDB method) as well as lower amorphous aluminium- and iron oxide contents (Al and Fe extracted with the ammonium oxalate method) than the other groups. Such differences in Al_{CDB} contents are, however, only significant in the solids of group Kd_3. Notwithstanding these correlations, this approach can only link the K_d values to the physicochemical properties of the solids on an individual basis. This consideration may be the simplest view of the relationship between sorption processes and solids properties, which probably interact with each other.

Therefore, the permANOVA aims at determining which collective physicochemical properties have a significant effect on the K_d values of SMOC; it shows that over 77% of the intra-group variance can be explained by the first two discriminant axes (Fig. 2). The physicochemical properties that contribute to these two axes suffice for determining a significant difference between the groups, as was seen from the

Table 4 Values of the K_d (L kg⁻¹) distribution constants at equilibrium of SMOC, MESA and MOXA measured on the ZNS solids. Average values of the experimental triplicates for an initial doping concentration of 1 mg/L

	Mean K_d SMOC	Mean K_d MESA	Mean K_d MOXA
Surface soils			
1	4.23	0.23	n.q.
2	4.01	0.35	n.q.
3	4.01	0.40	n.q.
4	3.63	0.52	n.q.
5	3.90	0.70	n.q.
6	4.97	0.74	n.q.
7	4.74	0.17	n.q.
8	2.34	0.05	n.q.
9	4.21	0.27	n.q.
10	4.36	0.15	n.q.
11	6.32	0.10	n.q.
12	4.46	0.06	n.q.
13	3.50	0.03	n.q.
14	3.30	0.04	n.q.
15	2.84	n.q.	n.q.
16	2.90	0.04	n.q.
17	5.60	0.05	n.q.
GFS			
S-x	0.44	0.73	n.q.
Gcm,b [0–2] mm	0.57	0.46	n.q.
Gcm,b [2–10] mm	28.8	2.08	0.74

n.q. not quantifiable

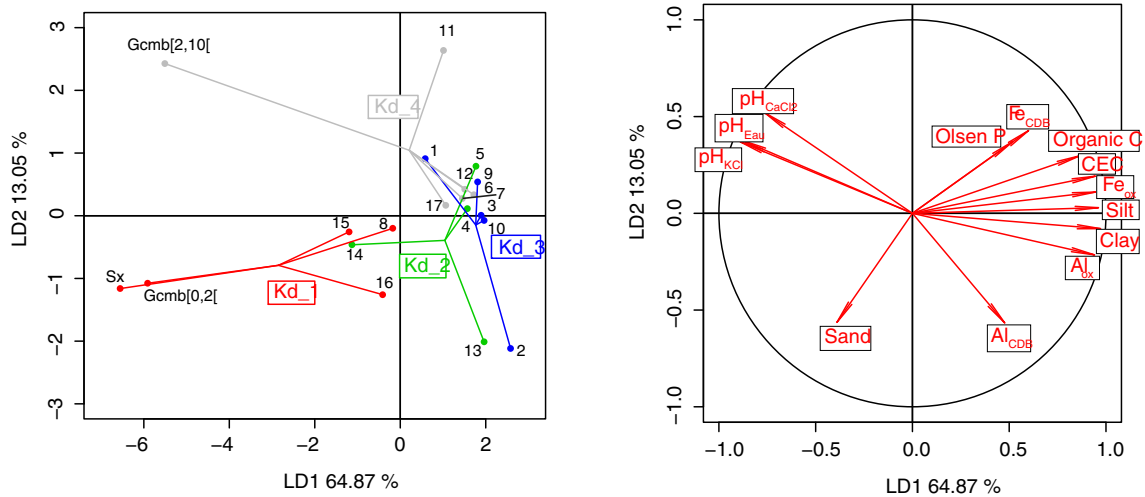


Fig. 2 Partial least square-discriminant analysis of physical and chemical properties for the K_d_1 group, K_d_2 group, K_d_3 group and K_d_4 group defined according to the sorption capacity of soils (samples 1 to 17), and

for glaciofluvial solids (S-x, Gcm,b [0,2] and Gcm,b [2,10]) towards metolachlor

perMANOVA results that indicated a significant difference between groups. Most of the variance is explained by the first discriminant axis constructed from the variables clay, Fe_{ox} , Al_{ox} organic C, CEC and silt, which correctly distinguishes three units (Kd_1 , Kd_4 and the $Kd_2 + Kd_3$ unit) (65%). The variance associated with the second axis is only 13%. Analysis of the correlation circle (Fig. 2) confirms the results from the univariate approach (Supplementary Table 1), showing that the solids in group Kd_1 stand out from the others by textures with less clay and silt, concentrations of weakly crystallized iron and aluminium oxides, less organic C and a lower CEC. The second discriminant axis distinguishes groups Kd_1 , Kd_2 and Kd_3 from group Kd_4 . The Olsen P, sand, Al_{DCB} and Fe_{DCB} variables are the main contributors to this axis. The solids with the highest affinity for SMOC (Kd_4 group solids) contain phosphorus concentrations and higher concentrations of well-crystallized iron oxides (Fe_{DCB}) than the other solids; they also contain less well-crystallized aluminium oxide and have a relatively depleted sand fraction.

The results obtained from a PLS-DA analysis, only considering data obtained from soil samples, are similar (Supplementary Fig. 1), indicating that the soil and GFS data can be processed in the same way. This implies that the mechanisms controlling the fate of SMOC are similar in soils and GFS.

The important role played by the organic carbon content in SMOC sorption, shown by this study, had already been mentioned in earlier work on soils (Alletto et al. 2013; Baran and Gourcy 2013; Bedmar et al. 2011; Kodesova et al. 2011; Patakious and Albanis 2002; Sanchezcamazano et al. 1995; Si et al. 2009; Vryzas et al. 2007; Weber et al. 2003; Wood et al. 1987), but no work on geological solids had been reported as far as we know. Cwielag-Piasecka et al. (2018)

showed that metolachlor is strongly adsorbed on humic acids extracted from soil. The earlier correlations between SMOC adsorption and clay content (Baran and Gourcy 2013; Si et al. 2009; Vryzas et al. 2007; Weber et al. 2003) and CEC (Si et al. 2009) were incorporated in our statistical work. In soil, organic matter and clays are arranged in a specific manner with oxides-hydroxides within organo-metallic complexes. This specific arrangement probably explains why iron- and aluminium oxides contribute to discriminating the K_d variance, even though no correlation between SMOC- and oxide adsorption is shown by classic univariate tests. The interactions between S-metolachlor and organic matter might be the result of hydrogen interaction (Liu et al. 2000, 2002) showed that the adsorption of chloroacetanilide herbicides (alachlor, acetochlor, propachlor, metolachlor) on the constituents of organic matter occurs through the formation of a hydrogen bond between the carbonyl ($-C=O$) and/or nitrogen ($C-N$) groups of the herbicides and the carboxyl and protonated hydroxyl groups of humic acids. The adsorption of chloroacetanilides on clays would be related to the formation of hydrogen bonds with water molecules directly present on the surface of clay platelets, or with water molecules that hydrate the exchangeable cations on platelet surfaces (Bosetto et al. 1993; Li et al. 2006; Liu et al. 2000; Pusino et al. 1992). As the three molecules we studied are part of this family, it is possible that the adsorption mechanisms are similar to those described in the abovementioned studies.

Adsorption of the anionic metabolites MESA (ESA-metolachlor) and MOXA (OXA-metolachlor)

A discriminant analysis shows that over 78% of the intra-group variance can be explained by the first two discriminant

axes (Fig. 3). Most (65%) of the variance is explained by the first discriminant axis, the variance associated with the second axis being only 13%. The first axis is mostly constructed by the variables clay, Fe_{ox}, Al_{ox}, organic C and silt. The parameters Fe_{DCB}, Al_{DCB} and pH_{CaCl2 - water} and KCl contribute to both the first and second axes. Even so, neither axis provides a significant distinction between the four groups, Kd_ESA_1, Kd_ESA_2, Kd_ESA_3 and Kd_ESA_4, as is outlined by the permANOVA results that show no significant difference between the groups. Analysis of the correlation circle confirms the univariate results, showing that the solids (soils or GFS) are not distinguished between the K_d groups when considering the physicochemical properties separately (Supplementary Fig. 1). The solids (soils or GFS) for which the K_d values are highest (group Kd_ESA_4) thus do not have significantly higher physicochemical properties than the solids of the three other groups Kd_ESA_1, Kd_ESA_2 and Kd_ESA_3. To summarize, the physicochemical properties governing the adsorption of MESA on GFS and soils cannot be identified in a significant manner.

The results obtained from a PLS-DA analysis when considering only the data from soil samples are similar (Supplementary Fig. 5), indicating that GFS and soil data can be processed in the same way. This result also implies that the mechanisms controlling MESA adsorption are similar in soil and GFS. Only few data were published on MESA adsorption coefficients in soil (Baran and Gourcy 2013; Krutz et al. 2004), and no adsorption mechanisms were described for this metabolite.

Nevertheless, we can question the potential role of iron- and aluminium oxides, and of clays, on MESA adsorption in soils and GFS. With a pKa of 1.8 (Table 1), MESA effectively is an anionic molecule with respect to the surrounding pH values. And, the adsorption of anionic molecules in soil is known to occur on protonated hydroxyl groups on oxide

surfaces and clay-platelet edges (MacKay and Vasudevan 2012). As the gradients in contents of iron- and aluminium oxides are very slight between the different groups of soil or GFS solids (Kd_ESA_1, Kd_ESA_2, Kd_ESA_3 and Kd_ESA_4, supplementary Table 1), their role in the adsorption of MESA is probably masked in the PLS-DA statistical analysis, the results appearing to be non-significantly different.

pH contributes to the correlation circle (Fig. 3). Its impact is on the oxide charges, but it has no effect on the MESA charge as the negative charge of the molecule conferred by the sulfonate group is constant under the environmental pH (Table 1).

Concerning MOXA, no adsorption value could be determined for either surface soils or the fine fractions [0,2] mm of GFS (S-x and Gcm,b [0,2]), adsorption appearing to be extremely limited. No statistical analysis could be carried out on the single K_d value obtained for Gcm,b [2,10]. No description was found in the literature concerning the parameters governing its adsorption. Even though both MOXA and MESA are anionic molecules at environmental pH (pKa of 1.8 and 4.8, respectively, Table 1), their adsorption is different in the solids of the vadose zone. As is suspected for MESA, iron oxy-hydroxides might play a role in adsorbing the anionic MOXA molecule, even though this is very slight, or even unmeasurable, in our study. The nature of the functional grouping of the negatively charged molecule might be at the origin of the difference in adsorption between the two molecules. MESA has an anionic sulfonate group that may be more reactive to the protonated hydroxyl groups of oxides and clays than the anionic carboxyl group of MOXA. This hypothesis is supported by work that showed that, on the surface of goethite, the affinity constant of the carboxylic group (log K = 1.26; Filius et al. 1997) is much weaker than the affinity constant of a sulphate (log K = 19.5; Geelhoed et al. 1997). Such affinity constants are coherent with the adsorption order

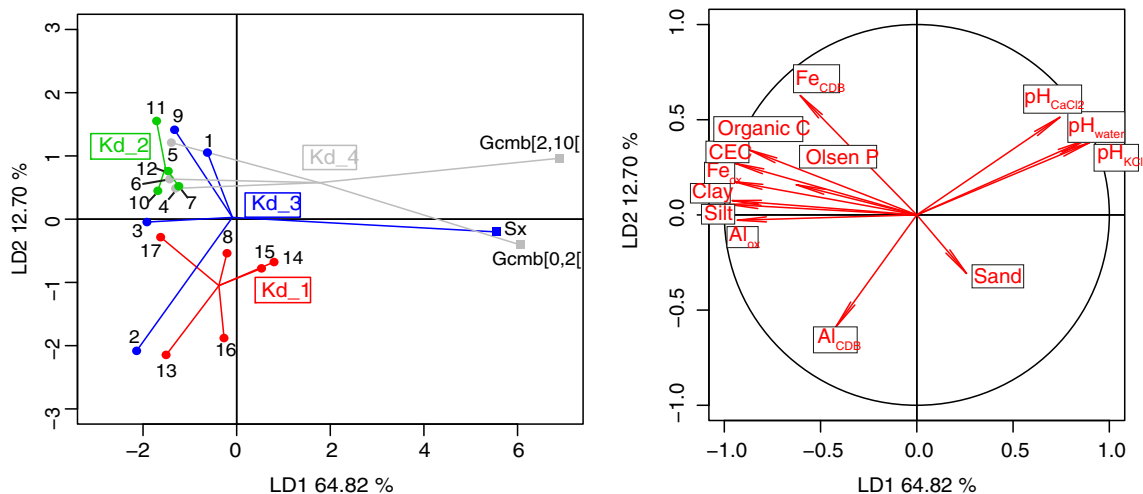
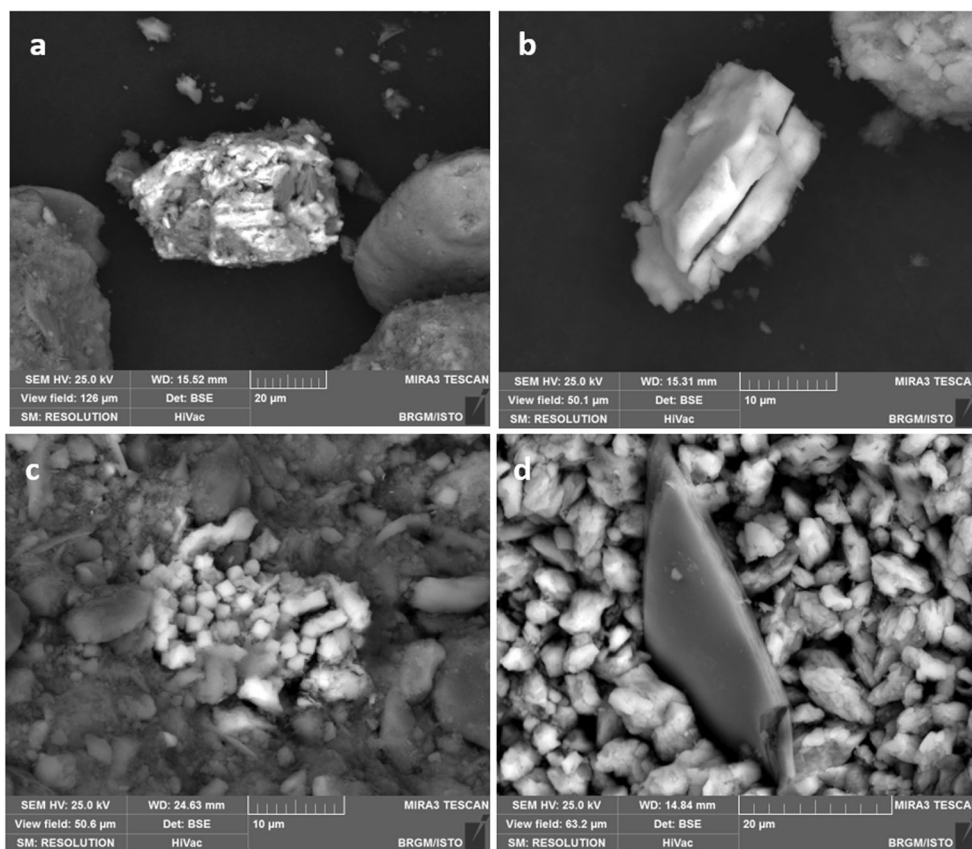


Fig. 3 Partial least square-discriminant analysis of physical and chemical properties for the K_d_1 group, K_d_2 group, K_d_3 group and K_d_4 group defined according to the sorption capacity of soils (samples 1 to 17), and for glaciofluvial solids (S-x, Gcm,b [0,2] and Gcm,b2,10] towards MESA

Fig. 4 Scanning electron microscope (SEM) observations of iron oxides and/or hydroxides (white) on grain surfaces **a** in S-x, **b** in Gcm,b [0,2] mm, **c** in Gcm,b [2,10] mm and **d** of clay leaflets on grain surfaces in Gcm,b [2,10]mm



of MESA and MOXA observed on the soil or GFS solids of our study.

Influence of the GFS adsorption interface on herbicide adsorption

In the perMANOVA analysis, the K_d variance between the different groups of solids was studied using physicochemical property contents, in order to identify the mechanisms involved in SMOC and MESA adsorption. As is standard when identifying the adsorption of pesticides in soil, the next step would be to draw up the pedotransfer rules that lead to predictive values for adsorption (Wauchope et al. 2002; Weber et al. 2004). The fact of considering the total sample mass in pedotransfer rules can be criticized when dealing with a soil rich in aggregates, where pesticide molecules would not have access to the central part of the aggregate (Wauchope et al. 2002); in fact, such an approach would not be representative of the real composition of the soil/pesticide interface available for adsorption. For such fluvioglacial solids with low porosity (< 2%, Table 3), the adsorption interface is smaller. Therefore, it is impossible to draw up predictive adsorption values for SMOC, MESA and MOXA when using only physicochemical mass properties measured via general analyses of a solid. For a quantitative prediction of the adsorption of these molecules, one should consider the adsorption interface on the

surface of the solids rather than their overall composition, which, by itself, is insufficient for a precise understanding of their reactivity.

For this reason, we carried out MEB-EDS analyses to complete the mineralogical and other data, in order to understand if potentially reactive mineral phases might be present on the surfaces of fluvioglacial solids. We identified iron oxides on the surface of S-x, Gcm,b [0,2] and Gcm,b [2,10] grains (Fig. 4). The morphology of these iron oxides and/or hydroxides on the surface of the S-x and Gcm,b [0,2] samples seems relatively similar, with dimensions of about a dozen microns, whereas those on the surface of Gcm,b [2,10] are much smaller—around one micron—and assembled in clusters.

However, without more mineralogical information on the nature of these oxides, we can draw no conclusions on differences in reactivity. The clay platelets on the surface of Gcm,b [2,10] grains could also adsorb SMOC. Concerning S-x and Gcm,b[0,2], no clays were observed, but the MEB-EDS analyses were not exhaustive. The higher adsorption of SMOC, MESA and MOXA on Gcm,b [2,10] could be explained by either a different chemistry or a different structural arrangement of the clay minerals, iron oxides and reactive organic matter, more favourable for the adsorption of molecules than that of the adsorption interfaces of Gcm,b [0,2] and S-x.

Thus, rather than the content in overall mineral and organic phases of the solid, it may be the difference in chemistry and reactivity at the adsorption interface that should be looked for and defined. This new approach should lead to a more precise explanation of the adsorption differences between solids and, more generally, to the construction of future predictive models of the adsorption of pesticides and their metabolites for both soils and geological solids.

Conclusions

The adsorption properties in the vadose zone of the herbicide *S*-metolachlor (SMOC) and its ethane sulfonic (MESA) and oxanilic acid (MOXA) metabolites were measured on surface soils as well as on heterogeneous geological solids. The latter are glaciofluvial (GFS) deposits with grain sizes ranging from sand (samples S-x and Gcm,b [0,2]) to gravel (Gcm,b [2,10]).

The adsorption coefficients K_d are variable, from low values (0.03 to 2.08 L kg⁻¹) to values below the detection limits for the metabolites, and from low to high values for SMOC (0.44 to 28.8 L kg⁻¹). For all three molecules, gravel is the most reactive solid matrix of the vadose zone. These variations of adsorption in soils and GFS seem to be mainly related to the presence and reactivity of iron oxides for the negatively charged molecules MESA and MOXA. For the neutral molecule SMOC, the highest K_d values were measured on solids with higher organic matter contents and reactivity values than the others, even in the case of GFS. Clay minerals also contribute to increasing the reactivity of solids in the vadose zone for SMOC adsorption.

In view of our results showing the importance of the solid/liquid interface in characterizing the reactivity of GFS for SMOC and its metabolites, it is probable that—even when increasing the number of samples—it would not be possible to apply pedotransfer rules. In fact, as the geological solids have a very low to nil porosity, the physicochemical parameters taken as a whole do not reflect the physicochemical composition of the SMOC adsorption interface and of that of its metabolites. It is thus essential to define the spatial distribution and reactivity of the mineral and organic phases located at the reactive adsorption interface, in order to arrive at a precise definition of the sorption capacity of complex solid matrices, such as GFS.

We provide new data on the adsorption of SMOC, MESA and MOXA on geological solids of the vadose zone. In addition, we have added to the few available data on soils for both MESA and MOXA. Geological solids are often hardly considered when studying pollutant transfer to groundwater, but our work shows that such relatively deep solids can be more reactive than the surface horizons of soils. Integrating the sorption parameters of pesticides and their metabolites on geological solids in predictive transfer models will lead to a more

precise estimate of the transfer time of molecules to groundwater, leading in turn to a more reliable long-term monitoring of the changes in groundwater quality.

In short, refining the temporal predictions of groundwater quality will improve the suitability and quality of management measures.

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