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Various causes behind the desorption hysteresis of carboxylic acids on mudstones

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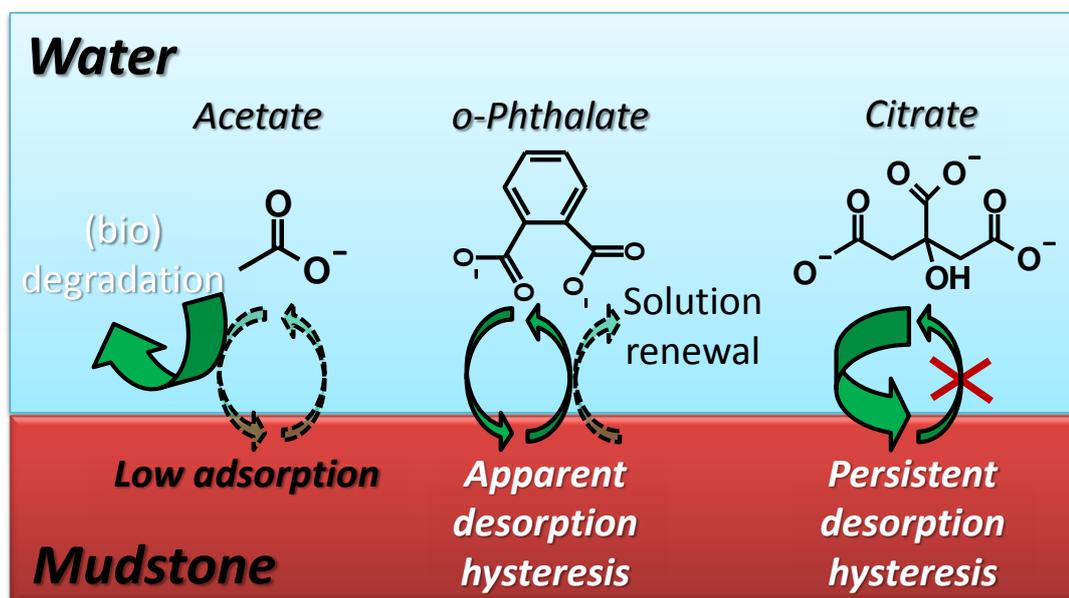
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Graphical Abstract



Highlights

- Desorption of acetate ortho-phthalate and citrate were studied on mudstone
- Soluble acetate was weakly adsorbed and degraded by bacterial activity
- Desorption hysteresis of phthalate vanished by porewater equilibration with mudstone
- Persistent hysteresis of citrate indicated a chemical reactivity with the solid
- Leaching protocol affects desorption hysteresis and thus environmental fate

Abstract

Adsorption-desorption is a key factor for leaching, migration and (bio)degradation of organic pollutants in soils and sediments. Desorption hysteresis of apolar organic compounds is known to be correlated with adsorption/diffusion into soil organic matter. This work focuses on the desorption hysteresis of polar organic compounds on a natural mudstone sample.

Acetic, citric and ortho-phthalic acids displayed adsorption-desorption hysteresis on Callovo-Oxfordian mudstone. The non-reversible behaviours resulted from three different mechanisms. Adsorption and desorption kinetics were evaluated using ^{14}C - and ^3H -labelled tracers and an isotopic exchange method. The solid-liquid distribution ratio of acetate decreased using a NaN_3 bactericide, indicating a rapid bacterial consumption compared with negligible adsorption. The desorption hysteresis of phthalate was apparent and suppressed by the equilibration of renewal pore water with mudstone. This confirms the significant and reversible adsorption of phthalate. Finally, persistent desorption hysteresis was evidenced for citrate. In this case, a third mechanism should be considered, such as the incorporation of citrate in the solid or a chemical perturbation, leading to strong desorption resilience.

The results highlighted the different pathways that polar organic pollutants might encounter in a similar environment. Data on phthalic acid is useful to predict the retarded transport of phthalate esters and amines degradation products in sediments. The behaviour of citric acid is representative of polydentate chelating agents used in ore and remediation industries. The impact of irreversible adsorption on solid/solution partitioning and transport deserves further investigation.

1. Introduction

The retention of organic compounds in soils and sediments is an important issue in many fields, such as decontamination processes, transport of landfill leachates, and nuclear and hazardous waste management (Luthy et al., 1997). Extensive studies illustrate that isotherm nonlinearity, adsorption-desorption hysteresis and slow-rate kinetics are characteristic of organic molecule transport in the environment (Hamaker and Thompson, 1972; Brusseau et al., 1989; Kan et al., 1994). Soil organic matter (SOM) and its meso/microporosity plays a key role in the adsorption and desorption of nonpolar, hydrophobic compounds (Oepen et al. 1991; Pignatello and Xing, 1996; Yang et al., 2013). Hindered diffusion through SOM contributes to the slow desorption of hydrophobic compounds (Brusseau et al., 1991; Weber et al., 1998); this mechanism was investigated with respect to the remediation of contaminated soils (Connaughton et al., 1993). The processes responsible for the adsorption of polar hydrophilic organic species differ from those for apolar compounds. The polar organic compounds and soluble fraction of SOM show strong affinity with (hydroxy)oxides (Gu et al., 1994; Hees and Lundström, 2000). These polar organic compounds also exhibit desorption hysteresis in soils and sediments (Gu et al., 1995). Unfortunately, most recent studies dealing with the adsorption of polar organic compounds tend to lack details on the quantification and origin of desorption hysteresis. Yet this information is crucial for predicting the solid-liquid partitioning of sorbates in a given physicochemical condition. In this work, we have studied the reversibility of desorption for three polar compounds, focusing on the role of the bio-geo-chemical conditions on desorption hysteresis and the implications for the environment.

The chosen mudstone is the Callovo-Oxfordian (COx) clay-rich rock. Adsorption of several polar organic compounds has already been studied on COx mudstone in the past: phthalate, oxalate, isosaccharinate and EDTA by Dagnelie et al. (2014), polymaleic acid by Durce et al. (2014), and Eu^{III}-EDTA by Descostes et al., (2016). In this study, desorption experiments were performed on this natural heterogeneous mudstone with three carboxylic acids. Acetate was chosen as reference for the carboxylate function. It is also known to enhance bacterial activity and used for bioremediation

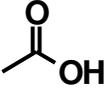
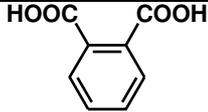
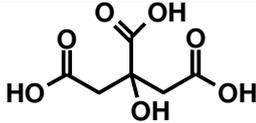
processes (Abromaitis et al., 2016). The ortho-phthalate was chosen as a major degradation product of phthalate esters and amides. The retarded migration of phthalate is relevant during the bioremediation of river sediments (Yang et al., 2013 and 2016). Finally, citrate was chosen as being representative of chelating agents. Citrate is especially used in the remediation processes of metals and PAHs from marine sediments and soils (Hahladakis et al., 2014; Ammami et al., 2015; Dias-Ferreira et al., 2015).

Recent spectroscopic investigations indicated that the adsorption of carboxylic acids on clay minerals is mostly dominated by outer-sphere complexes at neutral pH, with low energy bounds and fast reversible kinetics (Kang and Xing, 2007). However, natural samples display systematic desorption hysteresis, in contradiction with reversible adsorption. Kubicki et al. (1999) evidenced variable affinities of acetate, phthalate or citrate on illite kaolinite and montmorillonite. The authors suggested the irreversible chemisorption of carboxylic acids on clays is limited without the presence of Fe-hydroxides within the clay matrix. Similar assumptions were concluded by Li and Xu (2007) with respect to phthalate adsorption on various soils, as concluded by Yeasmin et al. (2014) for citrate on goethite and ferrihydrite. Ramos and Huertas (2014), however, observed the weak adsorption of lactate with a strong inner-sphere complex of citrate on montmorillonite. These contradictory results encouraged us to carry out further investigations focusing on desorption reversibility of carboxylates.

Several assumptions may explain hysteretic desorption. Among those, there is the distinction between “apparent” and “true” hysteresis (Brusseau and Rao, 1989). “Apparent” hysteresis is due to experimental artefacts such as slow kinetics, solid surface alteration by mixing, colloidal effects, or the dilution of competing adsorbate (Huang et al., 1998). Such artefacts can be eliminated using a suitable experimental protocol (Sander and Pignatello, 2005 and 2007). In such cases, the assumption of reversible adsorption is legitimate in predictive transport modelling. “True” hysteresis appears when an irreversible process occurs, thus modifying the system undergoing adsorption or desorption. For example, non-reversible retention can result from kinetically blocked exchange, i.e. covalent grafting such as described in Wu et al. (2013). A well-known mechanism is the modification of solid hydrophobic domains caused by the adsorption of large amounts of non-polar sorbent, as demonstrated

on soils (Xing and Pignatello, 1997) and other sediments (Huang et al., 2003). Another example on polar organic compounds is the effect of competitive adsorbents released from SOM discussed in the paper by Gu et al. (1995). Our work has focused on the desorption hysteresis of the chosen acids on a natural mudstone. Several adsorption and desorption protocols were compared and their effect is discussed herein. These various protocols may be representative of the conditions during transport in sediments or of waste (bio)remediation. The objective of our study was to improve understanding of solid/solution partitioning of the adsorbed carboxylic acids in sediments. We focused on desorption hysteresis under various physico-chemical conditions, i.e. undisturbed as in the environment or disturbed by leaching.

Table 1. Properties of the organic molecules used as adsorbates.

Acid	Formula	M (g mol ⁻¹)	pKa	Log K _{ow}
Acetic C ₂ H ₄ O ₂		60.1	4.76	-0.17
Ortho-phthalic C ₈ H ₆ O ₄		166.1	2.94 / 5.43	0.79
Citric C ₆ H ₈ O ₇		192.1	3.13 / 4.76 / 6.40	-1.6

2. Materials and Methods

2.1 Mudstone characterisation and preparation

Adsorption desorption experiments were carried out on a sample extracted from the Callovo-Oxfordian (COx) formation (East of Paris basin), which is currently studied as a potential host rock for the deep underground radioactive waste repository called Cigéo project. The sample was preserved from air (i.e. O₂) to prevent mineral oxidation (Fe being mostly in pyrite form, FeS). Neither the oxidative removal of SOM nor the reductive antibacterial treatment was performed in order to remain

similar to the environmental conditions. A core sample, referenced EST40471, was argon-drilled in CO_x at a depth between 497.7 and 498.1 m in the Andra underground research laboratory (Meuse/Haute-Marne, France). This clay-rich rock formation is mainly composed of illite (17-21%), interstratified illite-smectite (20-24%), kaolinite (3-5%), chlorite (2-3%), quartz (17-21%), calcite (20-23%), dolomite (3-6%) and accessory minerals (5%) (Gaucher et al. 2004). A bulk chemical analysis is provided in the supplementary material (table S1). A porosity of $18 \pm 2\%$ was measured by weighting before/after drying at 105°C. The content of carbonate contents were estimated by acidic dissolution to $30 \pm 0.5\%$ in mass. A total organic carbon content of 0.67% was measured by pyrolysis. The cation-exchange capacity (CEC) measured by the addition of CsCl on potassic samples gave values of 14.6 ± 0.4 meq/100 g. Specific surface areas were measured by nitrogen adsorption at 77K with an ASAP2010 device from micromeritics ($S^{\text{BET}}(\text{N}_2) = 39 \text{ m}^2 \text{ g}^{-1}$) and by the ethylene glycol monoethylether method, EGME, ($S^{\text{EGME}} = 150 \text{ m}^2 \text{ g}^{-1}$). The sample was crushed and sieved at less than 125 μm . The synthetic poral solution is described in Section 2.2.

Table 2. Composition of synthetic pore water used for this work. Theoretic data are reported in the literature ($10^{-3} \text{ mol L}^{-1}$) and measurements after desorption experiments.

	Measured in Vinsot et al. 2008	Calculated in Appelo et al. 2008	Synthetic pore water	After desorption protocol #1	After desorption protocol #2
pH	7.2	7.05	7.15	7.2±0.2	7.2±0.2
Na ⁺	52.3	54.0	46.0	51.1	54.3
K ⁺	0.6	0.65	1.0	1.4	2.1
Mg ²⁺	5.0	5.0	7.4	8.8	11.1
Ca ²⁺	6.3	6.5	6.7	9.1	13.4
Sr ²⁺	1.1	0.2	0.2	n.d.	n.d.
Fe ³⁺	n.d.	n.d.	0	0.006	0.032
Cl ⁻	41.0	46.8	41.0	51.4	53.7
SO ₄ ²⁻	15.6	13.5	15.6	19.4	26.9
Alk.	3.0	4.5	3.3	n.d.	n.d.
H ₄ SiO ₄	0.4	0.18	0.05	n.d.	n.d.
D.O.C. (mg/L)	6.5	0	0	0.6 - 1.1	1.4 - 2.2

2.2 Chemicals and radiolabelled compounds

The properties of the carboxylic acids are shown in Table 1. Stable solutions were prepared from high purity salts: sodium acetate (Merck, purity > 99%), phthalic acid (Merck, purity > 99.5%) and citric acid (Merck, purity > 99.7%). The pH was adjusted to 7.0 ± 0.2 with concentrated NaOH or HCl standard solutions. Experiments were performed with radiolabelled compounds: acetic acid [^3H] (ARC, 150 Ci/mol), acetic acid [^{14}C] (ARC, 58 Ci/mol), citric acid [$1,5\text{-}^{14}\text{C}$] (ARC, 112 Ci/mol), phthalic acid [$2,3,4,5\text{-}^3\text{H}$] (ARC, 60 Ci/mol) and phthalic acid [^{14}C] (homemade synthesis detailed in Dagnelie et al., 2014). The composition of the synthetic pore water is given in Table 2. It was prepared by the dissolution of salts before being mixed with mudstone powder with a solid/solution ratio $m/V \sim 50 \text{ g.L}^{-1}$, for the equilibration of trace elements (Si, Al, Fe). It was then filtrated and bubbled with a gaseous N_2/CO_2 mixture to reach $\text{pH} \sim 7.0 \pm 0.2$.

2.3 Adsorption and desorption protocols

Numerous methods exist to quantify adsorption and desorption. Typical methods are batch experiments, flow suspension or flow column, with the benefits and drawbacks discussed in Green et al. (1980). A standard adsorption method in batches was involved in this study using sealed polycarbonate tubes of 10 mL (Nalgene PC 3138-0010, Thermo scientific). All experiments were operated at ambient temperature ($21 \pm 1 \text{ }^\circ\text{C}$) in a sub-oxic glove box ($\text{P}_{\text{O}_2}/\text{P}_0 < 2 \text{ ppm}$). A carbon dioxide pressure was imposed ($\text{P}_{\text{CO}_2}/\text{P}_0 \sim 4000 \pm 1000 \text{ ppm}$) in order to maintain the $\text{pH} \sim 7.0 \pm 0.2$ by equilibrium with soluble carbonates. A mass of 1 g of dried clay was mixed with the synthetic pore water using a solution/solid ratio of $V/m = 4 \text{ L.kg}^{-1}$. A pre-equilibration of mudstone was achieved (Descostes et al. 2004) by twice performing three days of mixing, ultracentrifugation (50.000 g, 1h) and solution renewal there after. Then, radiolabelled and non-labelled compounds were simultaneously added respecting the same V/m ratio. Two triplicates and a blank without clay were performed for each molecule. One triplicate had an initial concentration of organic: $C(t=0) = 10^{-3} \text{ M}$ and the other: $C(t=0) = 10^{-6} \text{ M}$. The pH of the solution was controlled inside the glovebox at the beginning and the end of the experiments. Variations in the pH below 0.2 were measured during adsorption or desorption. Sorption and desorption experiments were investigated for about 6 weeks by successive

samplings. Desorption experiments started after the last adsorption sampling. It consisted in renewing supernatant by synthetic pore water using the same water/rock ratio as that used for the adsorption experiments. Before sampling, tubes were centrifuged at 15,000 rpm for 1 hour. An aliquot of 100 μL was taken, weighted and analysed by beta liquid scintillation counting (Perkin-Elmer Tricarb 2700). Blank experiments did not reveal any sorption on glassware. The distribution ratio, R_d (L kg^{-1}), defined by Eq. (1), was then calculated:

$$R_d(t) = \frac{[X]_{\text{adsorbed}}}{[X]_{\text{solution}}} = \left(\frac{n_0 - n(t)}{n(t)} \right) \times \frac{V}{m} \quad (1)$$

with n (moles), the quantity of the adsorbate X after a given period (t), V the solution volume (L) and m the dry mass of clay (kg). V was recalculated after each sample to take into account the change of V/m ratio in Eq. (1). The theoretical error bars on R_d values were calculated by propagating the uncertainties (2σ) of masses, volumes and concentrations. It is important to note that batch experiments only provide a distribution ratio, R_d . The notion of K_d assumes the reversibility of the adsorption processes. The notation of R_d was thus preferred in this manuscript.

Determining R_d from the batch method is usually considered as reliable, as soon as the pH (7.0 ± 0.2) and ionic strength ($0.10 \pm 0.01 \text{ M}$) are constant during the experiment. However, the addition of adsorbates may induce other perturbations. Chemical perturbation for example implies surface dissolution or surface grafting. Such conditioning effects modify the affinity for a sorbate in a second sorption cycle (Lu and Pignatello, 2002). In order to assess such phenomena, an isotopic exchange method was also used in this study.

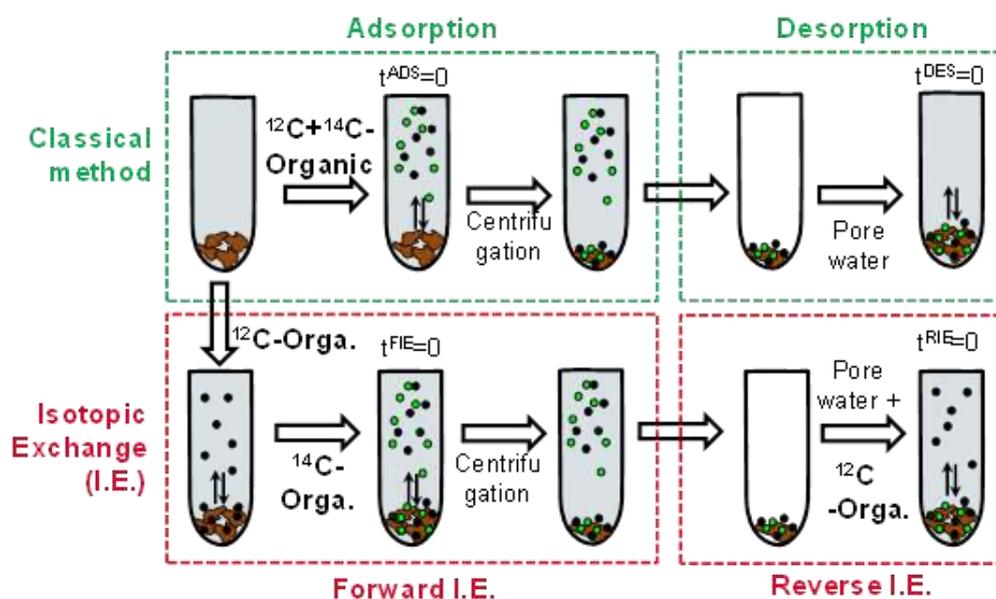


Figure 1. Scheme of adsorption and desorption experimental setup. Comparison of classical batch method (top) and isotopic exchange (bottom). ^{12}C - and ^{14}C -organics are represented by black and green dots respectively.

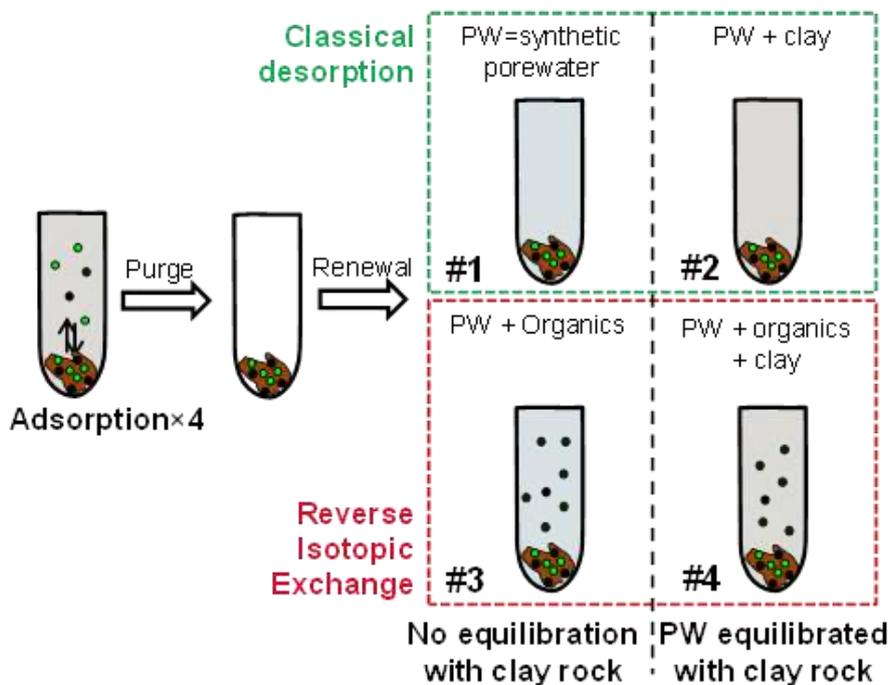


Figure 2. Scheme of the desorption protocols #1 to #4, with various renewal solutions. ^{12}C - and ^{14}C -organics are represented in black/green points respectively. Synthetic and clay-equilibrated pore waters are represented in blue and brown respectively.

Forward isotopic exchange

Radiolabelled molecules can be used to distinguish chemical perturbation from adsorption (Sander and Pignatello, 2005 and 2007). The Fig. 1 details the experimental protocol performed for adsorption and forward isotopic exchange (FIE). Forward isotopic exchange consisted in a first step to add organic ($C(t=0) = 10^{-3}$ M or $C(t=0) = 10^{-6}$ M) to the tubes after the equilibration phase. Then the mixture was stirred for 6 weeks to reach macroscopic equilibrium. A small amount of ^{14}C - or ^3H -labelled organic molecules ($C(t=0) = 10^{-8}$ to 10^{-11} M) were only added in a second step. The isotopic ratio $^{14}\text{C}/^{12}\text{C}$ was then modified in the liquid phase and equalled to zero in solid. Monitoring started from this second step and was investigated for about 6 weeks by successive samplings. Reverse isotopic exchange (REI) experiments consisted in renewing supernatant by organic solution at the concentration measured after the FIE step. Adsorption-desorption equilibrates the $^{14}\text{C}/^{12}\text{C}$ ratio between solid and liquid at constant macroscopic concentrations in both phases. Both methods, classical and isotopic give different information. The classical method quantifies simultaneous effects of adsorption and chemical perturbation by adsorbates. Forward isotopic exchange isolates adsorption at a constant macroscopic concentration on the system which is already perturbed by the first step of adsorption/equilibration. A “conditioning effect” during this first step would be evidenced by different distribution ratios measured by classical adsorption, R_d^{ADS} , and forward isotopic exchange R_d^{FIE} .

Desorption protocols and hysteresis index

The Fig. 2 represents the experimental protocols evaluated for desorption. Adsorption experiments were investigated during 6 weeks ($C(t=0) \sim 10^{-6}$ M; $V/m \sim 4$ L.kg $^{-1}$; $\text{pH} = 7.0 \pm 0.2$). Then tubes were centrifuged at 15,000 rpm for 1 hour to renew supernatants by different solutions. Therefore, protocols #1 to #4 differed by the renewal solution. Protocol #1 used synthetic pore water. Protocol #2 used pore water equilibrated with mudstone respecting the same V/m ratio than adsorption step. Protocol #3 used organic solution at the concentration measured after adsorption step. Protocol #4 used organic solution equilibrated with mudstone at the same concentration and V/m ratio as that used for the adsorption step. Classical desorption, DES (protocols #1 and #2) and REI (protocols #3 and #4) were investigated during 6 weeks. The sampling and analysis methods used were the same as

those described above. Hereafter, the results will be noted R_d^{DES} and R_d^{RIE} . The reversibility of the process was evidenced if $R_d^{ADS} = R_d^{DES} = R_d^{RIE}$. Protocol #4 minimised the chemical perturbation during solution renewal. It assesses the reversibility of adsorption with low sorbate concentrations, close to far-field environmental conditions. Protocols #1 and #2 were more standard desorption protocols. They were representative of leaching or decontamination processes using synthetic solutions.

A desorption hysteresis index will be defined by equation (3):

$$H.I. = \frac{q_e^{DES} - q_e^{ADS}}{q_e^{ADS}} \Bigg|_{T, C_e} \quad (3)$$

where q_e (mol kg⁻¹) represents the quantity adsorbed by the solid, with the superscripts DES and ADS representing desorption and adsorption steps respectively, at constant temperature and equilibrium concentration (T, C_e). This index is equal to zero when adsorption becomes completely reversible. H.I. increases with the degree of irreversibility.

3. Results and Discussion

3.1 Adsorption isotherm and hysteresis kinetics

The adsorption isotherms of the carboxylic acids are shown in Fig. 3 (top). The data $R_d = f$ [phthalate]_{eq.}, is taken from Dagnelie et al. (2014) on similar COx samples. The adsorption isotherms of acetate and citrate were determined for the present study. The R_d values for acetate were below detection limit, $R_d(\text{acetate}) < 2\sigma \sim 0.2 \text{ L kg}^{-1}$ (discussed in section 3.3.1). In the case of phthalate and citrate, the isotherms displayed Langmuir shapes, which can be described using the following equation (2)

$$C_{ads} = Q \times \frac{K \times C_{eq}}{1 + K \times C_{eq}} \quad (2)$$

where C_{ads} is the concentration of the adsorbed molecule on the solid (mol kg^{-1}); C_{eq} , the equilibrium concentration in solution (M); K , the adsorption constant (L mol^{-1}); and Q , the maximum amount adsorbed by the material (mol kg^{-1}).

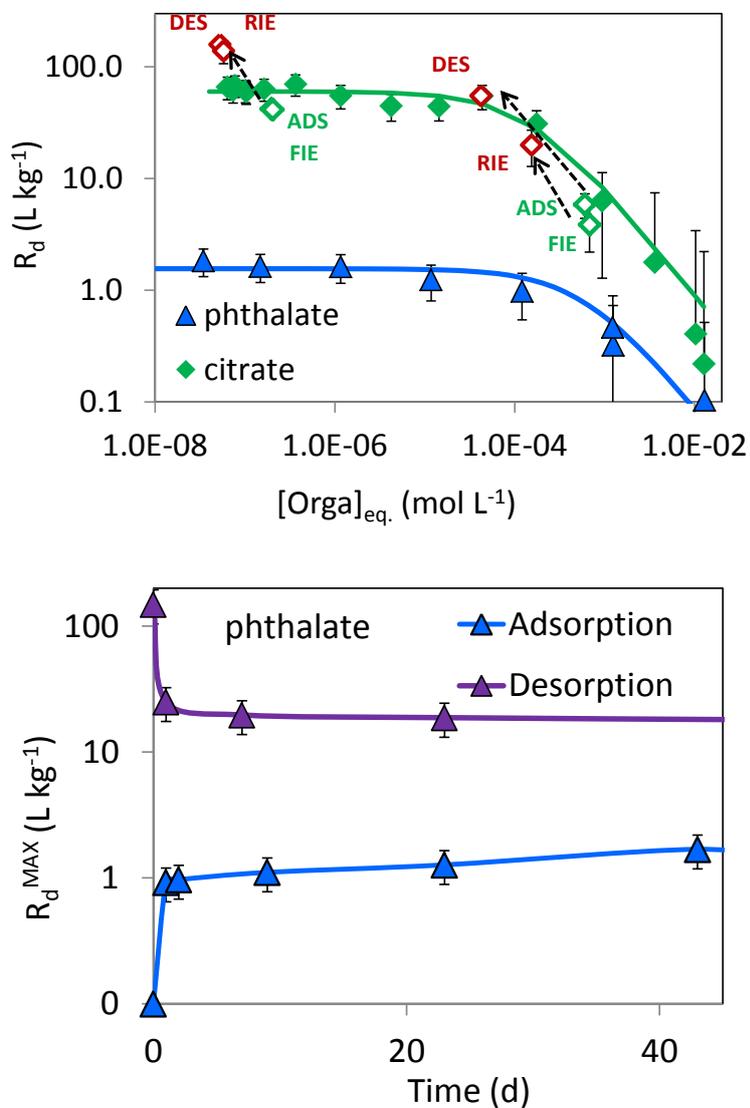


Figure 3. (Top) Adsorption isotherm for ^{14}C -phthalate (triangles, taken from Dagnelie et al., 2014) and of citrate (squares). Solid lines are best fit with Langmuir model. Empty squares represent adsorption/desorption (ADS, DES), forward/reverse isotopic exchange (FIE, RIE). (Bottom) Adsorption and desorption kinetics for phthalate.

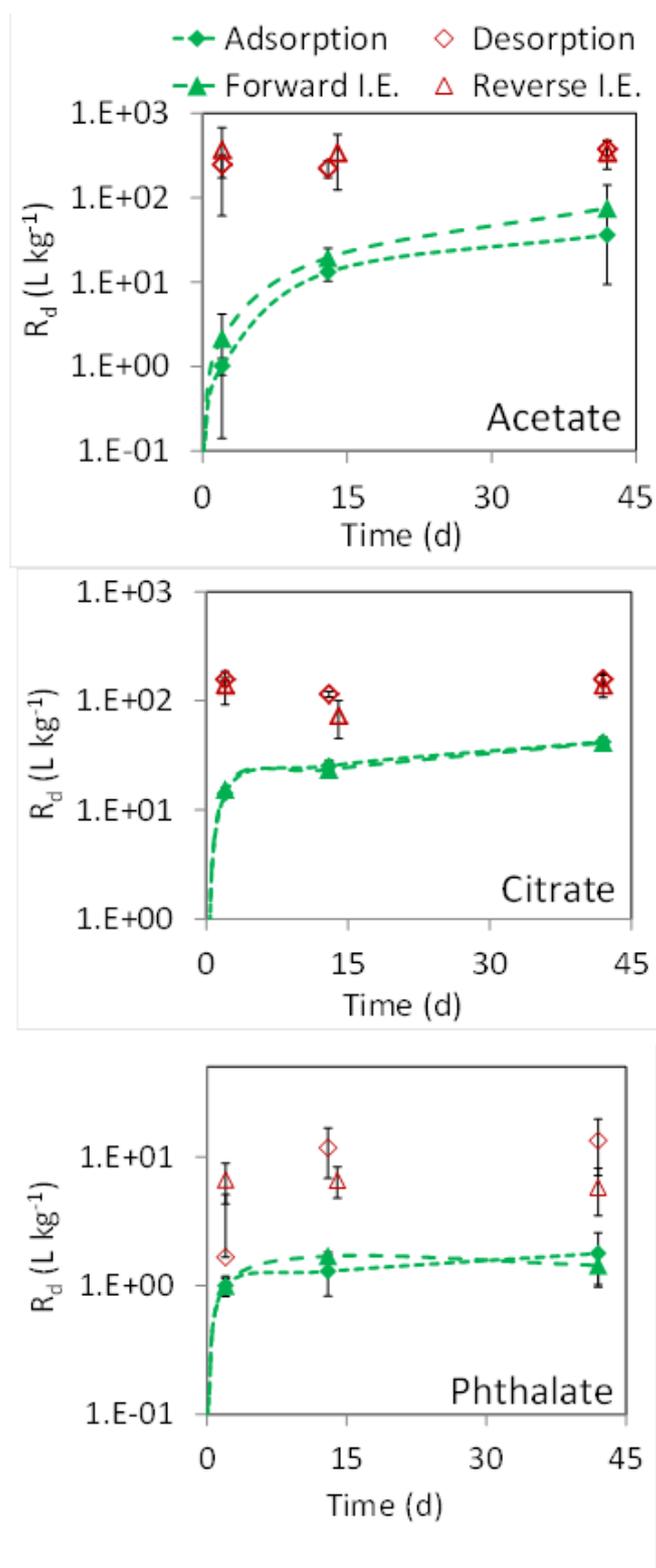


Figure 4. Kinetic of retention and release of acetate (top), citrate (middle) and phthalate (bottom).

Comparison between data from classical adsorption method and forward isotopic exchange. Initial

concentration, $C(t=0) = 10^{-6} \text{ mol L}^{-1}$.

The parameters were obtained by the least square fitting of $1/C_{ads}$ as a function of $1/C_{eq}$. We obtained $Q(\text{phthalate}/\text{COx}) = 9.1 \cdot 10^{-4} \text{ mol kg}^{-1}$ and $K(\text{phthalate}/\text{COx}) = 1.7 \cdot 10^3 \text{ L mol}^{-1}$ with a coefficient of determination $R^2 = 0.9992$. At low concentrations, the ratio R_d rose to a plateau of $R_d^{MAX}(\text{phthalate}) = Q \times K = 1.6 \text{ L kg}^{-1}$. The Langmuir adsorption parameters for citrate were $Q(\text{citrate}/\text{COx}) = 9.1 \cdot 10^{-3} \text{ mol kg}^{-1}$ and $K(\text{citrate}/\text{COx}) = 6.6 \cdot 10^3 \text{ L mol}^{-1}$ with a coefficient of determination $R^2 = 0.9964$ and $R_d^{MAX}(\text{citrate}) = 60 \text{ L kg}^{-1}$. This result indicated that more adsorption sites are available for citrate than for phthalate and a stronger affinity of citrate.

A typical variation of R_d^{MAX} over time is shown for phthalate adsorption and desorption in Fig. 3 (bottom). In both cases, the system reached apparent equilibrium within a few hours. The corresponding R_d values were $1.6 \pm 0.5 \text{ L.kg}^{-1}$ and $18 \pm 7 \text{ L.kg}^{-1}$ for the adsorption and desorption experiments respectively. These results are representative of the typical hysteretic behaviour of organic compounds in sediments (Gu et al., 1995; Chen et al., 2004). We applied isotopic methods in order to assess the origin of such hysteretic behaviour in COx mudstone.

3.2 Desorption hysteresis confirmed by isotopic exchange

To better understand these non-reversible aspects, four experiments were performed for each molecule, namely adsorption, desorption, forward isotopic exchange (FIE) and reverse isotopic exchange (RIE). Data obtained at low concentrations ($C(t=0) = 10^{-6} \text{ M}$) to avoid saturation effects is discussed herein. Results at higher concentrations ($C(t=0) = 10^{-3} \text{ M}$) are available in the supplementary material and discussed in section 4. The distribution ratios, R_d , are presented in Fig. 4. The average of the triplicate results is represented as a function of time with (2σ) theoretical error bars. The results obtained by adsorption were consistent with results obtained by FIE for all three molecules (error bars overlapping). This indicated that there was no major modification in the solid during the first adsorption step. The results obtained by desorption were also consistent with results obtained by RIE for all three molecules (error bars overlapping). However, a significant difference was obtained between the adsorption and desorption results even after 42 days for all three molecules (error bars not overlapping).

Despite the systematic desorption hysteresis, some major differences appeared between the three acids. Firstly, the affinity of carboxylic acids for the mudstone strongly varied from $1.6 \pm 0.2 \text{ L kg}^{-1}$ for phthalate, up to $42 \pm 5 \text{ L kg}^{-1}$ for acetate, and $56 \pm 12 \text{ L kg}^{-1}$ for citrate respectively. The retention kinetics of phthalate and citrate were rapid and equilibrium was reached within 48 h (Fig. 4). On the contrary, R_d values for acetate increased between 2 and 42 days. The differences in the R_d values between phthalate and citrate, and the slow kinetics for acetate indicated a specific retention mechanism for each molecule. Nevertheless, significant hysteresis was quantified for each species. The corresponding indexes obtained with classical desorption (protocol #1) were H.I. = 3.9 ± 0.4 , 3.3 ± 0.6 , 3.3 ± 0.8 for acetate, citrate and phthalate respectively (Table 3). These values decreased to H.I. = 2.4 ± 0.6 , 2.3 ± 0.6 , 1.0 ± 1.5 using another desorption protocol (#4) discussed in the following section.

3.3 Effect of desorption protocol

The variation in hysteresis was investigated using various desorption protocols starting from the same adsorption state (Fig. 2). The desorption data was compared with the adsorption data in Fig. 5.

Table 3. Experimental results from adsorption and desorption of acetate, citrate and phthalate on COx mudstone. The different renewal pore waters used in protocols #1 to #4 are detailed in Fig. 2.

	Acetate	Phthalate	Citrate
$R_d^{\text{ADSORPTION}}$ (L kg^{-1})	< 0.2 (with NaN_3)	1.6 ± 0.2 (with or without NaN_3)	60 ± 12
	42 ± 5 (without NaN_3)	$1.4 [1.2 - 2.0]$ (Dagnelie et al., 2014)	$[10-40] \text{ C} > 10^{-3} \text{ mol L}^{-1}$ (Durce, 2011)
$R_d^{\text{DESORPTION}}$ (L kg^{-1})	143 ± 6	2.0 ± 0.3 (protocol #2 & 4)	183 ± 8 (protocol #4)
H.I.	Protocol #1	3.9 ± 0.4	3.3 ± 0.6
	Protocol #4	2.4 ± 0.6	2.3 ± 0.6
		on ferrihydrite (Yeasmin et al., 2014)	3.3 ± 0.4
		on goethite (Yeasmin et al., 2014)	5.0 ± 3.4

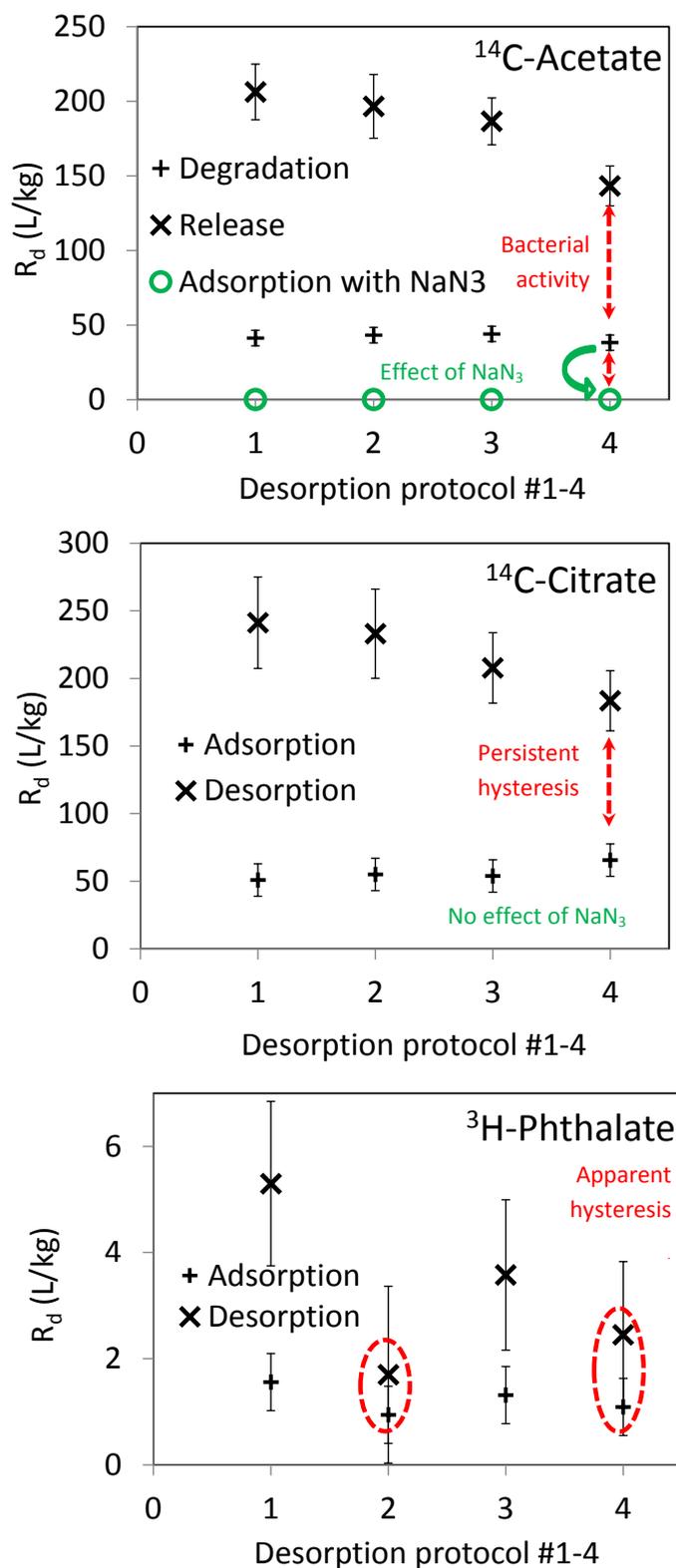


Figure 5. Effect of desorption protocol on the release of acetate (top), citrate (middle) and phthalate (bottom) from mudstone after 42 days.

3.3.1 Case of acetate

We first discriminated adsorption on the solid from degradation due to bacterial activity. For this reason, adsorption experiments were performed in presence of sodium azide (10^{-3} M) which is an inhibitor of bacterial activity. The values obtained were below uncertainties, $0 < R_d(\text{acetate}) < 0.2 \text{ L kg}^{-1}$. Similar results were also reported on COx mudstone with the low affinity of monocarboxylic acids ($R_d(\text{sorbate}) \sim 0.7 \text{ L kg}^{-1}$, $R_d(\text{tiglate}) \sim 0.4 \text{ L kg}^{-1}$; Vu-Do, 2013). This result evidenced low affinity between the sole carboxylic groups and the COx mudstone. The process driving acetate disappearance from the solution was bacterial activity, leading either to methane, carbon dioxide, carbonates or biomass (Weber et al., 1984; Abromaitis et al., 2016) and apparent desorption hysteresis. This sole biodegradation phenomenon was in agreement with the observations made of a slow kinetics (Fig. 4). The R_d value of phthalate and citrate stabilised within 48 hours without effect from NaN_3 , in consistency with fast adsorption processes.

3.3.2 Case of phthalate

In the case of phthalate, desorption hysteresis that was observed with protocols #1 and #3 vanished when using protocols #2 and #4. These protocols, #2 and #4, included an equilibration of the renewal solution with a sacrificial sample of mudstone. This equilibration step lowered the chemical perturbation during supernatant renewal. The observations on phthalate suggested that trace elements contained in mudstone strongly affected the desorption step. Synthetic pore water is typically used to perform adsorption and desorption experiments. This protocol was efficient with most cations, but was found to be inadequate here despite an equilibration step of the synthetic pore water with the mudstone based on a solid/solution ratio of 50 g L^{-1} . The fact that protocol #2, without phthalate in renewal pore water, also suppressed the hysteresis phenomenon, indicated that chemical perturbation induced by phthalate does not influence the retention capacity of mudstone. The key fact remains that adsorption reversibility was demonstrated for phthalate with desorption protocols #2 and #4. This is in agreement with results of Conkle et al. (2010) on the reversible adsorption of fluoroquinolones (aromatic acids) in a wastewater treatment wetland soil.

3.3.3 Case of citrate

A specific behavioural pattern was observed for citrate. The use of protocols #2, #3 and #4 only partially reduced the desorption hysteresis phenomenon. Hysteresis indexes decreased from 3.3 ± 0.6 (protocol #1) to 3.1 ± 0.5 (protocol #2), 2.7 ± 0.6 (protocol #3), and 2.3 ± 0.6 (protocol #4). The most efficient protocol was #4, which minimised chemical perturbation by using a renewal solution equilibrated with both clay and organic molecules. Nonetheless, such protocols could not fully suppress desorption hysteresis. This result suggested the existence of “true” hysteresis, meaning that the adsorption process modifies the sorbing phase or incorporates sorbate in a solid phase. Similar hysteresis was reported for citrate on several model phases by Yeasmin et al. (2014). Based on this data, the adsorption of citrate rather tends to occur on minor iron-rich phases such as ferrihydrite or goethite with R_d values above 10^4 L kg^{-1} . Assuming a percentage $P = 99.9 \%$ of citrate retained during desorption ($99 < P < 100 \%$ detailed in the study), the hysteresis indexes $\text{H.I.}(\text{citrate}) = 3.3 \pm 0.4$ and 5.0 ± 3.4 were calculated on ferrihydrite and goethite respectively at equilibrium concentrations ranging from $2 \cdot 10^{-8}$ and $2 \cdot 10^{-6} \text{ M}$ (Table 3). Similar values were also reported for another dicarboxylic acid, namely oxalate, with a better level of confidence on the retained percentage: $\text{H.I.}(\text{oxalate}) = 3.2 \pm 0.2$ and 3.6 ± 1.3 on ferrihydrite and goethite respectively.

3.4 Discussion

This section focuses on the origin of desorption hysteresis for small soluble carboxylic acids and the environmental implications.

Concerning acetate, the low affinity of the carboxylic group with the solid surfaces of minerals was confirmed. This is in agreement with adsorption data of acetate on alfisol and sediments reported by Oepen et al., 1991. After 24 hours, the increase in R_d is representative of the disappearance of molecules from the solution. The apparent hysteresis of acetate was due to bacterial degradation. Several bacteria in these media are able to degrade molecules like acetate, ethanol or carbohydrates (Abromaitis et al., 2016). Complementary experiments would be useful in order to quantify the

fractions of carbon from acetate which is metabolised in “living” organic matter, incorporated in calcite or released as soluble carbonates or into the gas phase.

Ortho-phthalate displayed a higher affinity with mudstone than expected. Oepen et al. (1991) reported lower values, $R_d < 0.5 \text{ L.kg}^{-1}$, for benzoate, phthalate and phenylacetate in alfisol and sediment with similar pH levels and amounts of natural organic matter and clay minerals. The adsorption of ortho-phthalate seems related to the presence of two carboxylic groups (Gu et al., 1995). Outer-sphere complexes with low-energy bonds were also evidenced on oxides by Hwang et al. (2007) and on clay minerals by Kang and Xing (2007). These low-energy interactions are consistent with the reversible adsorption of phthalate on COx mudstone. A striking result was that desorption hysteresis occurred because of pore water renewal. One assumption is that the leaching of a fraction of natural organic leads to the releases of adsorption sites. Unfortunately, the ATR-FTIR signal of adsorbed phthalate was too low on COx mudstone to confirm or deny such an assumption. Regardless of this mechanism, significant differences in R_d^{DES} values were expected for phthalates, depending on the desorption protocol. Some soil science guidelines recommend desorption protocol in CaCl_2 , NaClO_4 or NaCl to impose the pH and ionic strength. This could lead to the overestimation of desorption in natural samples. The use of a synthetic solution may also be inadequate for phthalate removal from sediments. Nonetheless, the reversible adsorption of phthalate consolidates the estimations of solid liquid partitioning and retarded transport in soils and sediments.

Citrate displayed persistent desorption hysteresis on COx mudstone. Yeasmin et al. (2014) quantified citrate and oxalate adsorption on several pure phases. Based on this data, an additive model would predict the adsorption of dicarboxylic acids driven by iron-rich phases. Hees and Lundström (2000) also suggested that Fe and Al oxyhydroxides drive the adsorption of citrate in natural systems. However, in both papers, hysteresis is reported without further interpretation on solid solution partitioning. Yang et al. (2001) demonstrated that complexing agents, such as citrate, EDTA or oxalate, mobilise cations (Fe, Al) in the aqueous phase, leading to the dissolution of natural organic matter. However, the authors suggested that this mechanism would rather enhance the desorption of

apolar compounds. Another assumption studied by Lee and Reeder (2006) is the incorporation of citrate in solid phases. The authors suggested that citrate co-precipitates with calcite whereas phthalate does not. Our mudstone samples contained 30% of carbonates which are a potential trap for citrate. We thus performed adsorption experiments on decarbonated samples (Fig. S2 in the supplementary material). The adsorption of citrate on decarbonated sample was similar to adsorption on raw samples. This invalidates the assumption of co-precipitation in carbonate phases. This result is supported by the shape of citrate's adsorption isotherm which differs from typical adsorption/precipitation shapes (case of oxalate illustrated in Fig. S2). Citrate is also known to be sensitive to reduction processes and ferric citrate is used as an oxidant to measure the reducing capacity of organic matter in mudstones (Bleyen et al., 2016). It would be worth studying the immobilisation of citrate in COx mudstone, which is a reductive medium, to see if it is affected by oxydo-reduction processes.

The case of citrate remains the most puzzling. The desorption hysteresis indicated a chemical perturbation of the solid. This is contradictory to the similar values obtained by adsorption and forward isotopic exchange at low concentrations, $C(t=0) \sim 10^{-6}$ M (Fig. 3). The pre-equilibration of mudstone with higher concentrations ($C(t=0) \sim 10^{-3}$ M), led to a very slight decrease in adsorption, i.e. $R_d^{\text{FIE}} < R_d^{\text{ADS}}$, and in desorption hysteresis, i.e. R_d^{DES} and R_d^{REI} values almost on adsorption isotherm (Fig. 3). These effects were not significant in comparison with uncertainties and concentration dependency. Nevertheless, such behaviour would be in agreement with the capping of non-reversible adsorption sites leading to a lowered but reversible second step of adsorption/desorption (RIE). A similar effect is expected during the transport of chelating agents in sediments. It would be worth performing transport experiments before/after equilibration with citrate in order to assess if the irreversible capping of sorbing phases does indeed lead to a reduction in the retardation factor. Similar systems, chelating agents/sediments, warrant such studies in order to improve the prediction of solid/solution partitioning with focus on desorption modelling.

4. Conclusions

The adsorption and desorption of acetate, ortho-phthalate and citrate was studied on a Callovo-Oxfordian mudstone. The mudstone displayed equal parts of carbonates, clay minerals, quartz and may be considered as being similar to many sedimentary rocks. The three species displayed similar desorption hysteresis evidenced by a classical method and reverse isotopic exchange. Yet, this behaviour was shown to result from three different mechanisms.

Acetate was mainly removed from the liquid phase by bacterial activity. Adsorption and desorption of acetate were isolated by adding sodium azide and found to be negligible compared with other carboxylic acids. In the case of phthalic acid, the equilibration of the renewal pore water with mudstone suppressed desorption hysteresis. This result confirmed the significant and reversible adsorption of phthalate in the mudstone. It also highlighted the impact of trace elements on desorption. The use of a synthetic solution may prove to be inadequate for phthalate removal from sediments. Finally, a high level of adsorption and persistent desorption hysteresis was evidenced for citrate. This result suggested the existence of a third adsorption mechanism. Citrate may involve chemical perturbation such as surface capping, dissolution or oxydo-reduction processes. At low concentrations, adsorption is constant before/after equilibration with citrate and desorption remaining hysteretic in both cases. At high concentrations, adsorption and desorption hysteresis were slightly reduced by pre-equilibration with citrate but in proportions lower than saturation effects. Such systems (chelating agents/sediments) warrant further studies in order to improve the prediction of solid/solution partitioning. It would be worth performing transport experiments before/after equilibration with citrate in order to evidence the irreversible capping of sorbing phases and a decrease in the retardation factor.

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