SPECIAL ISSUE

Research Paper

Desorption rate of glyphosate from goethite as affected by different entering ligands: hints on the desorption mechanism

Jeison M. Arroyave,[A] *Carolina C. Waiman,*[A] *Graciela P. Zanini,*[A]
Wenfeng Tan[B,C] *and Marcelo J. Avena*[A,D]

[A]INQUISUR, Departamento de Química, Universidad Nacional del Sur (UNS)-CONICET,
  Avenida Alem 1253, 8000 Bahía Blanca, Argentina.
[B]College of Environment and Resources, Huazhong Agricultural University,
  Wuhan 430070, Hubei, China.
[C]Institute of Soil and Water Conservation, Chinese Academy of Sciences,
  Yangling 712100, Shananxi, China.
[D]Corresponding author. Email: mavena@uns.edu.ar

Environmental context. Glyphosate is a heavily used herbicide that is mobilised in soil and sediments through adsorption–desorption processes from the surface of mineral particles. We demonstrate that the desorption rate of glyphosate from goethite, a ubiquitous mineral, is nearly independent of the concentration and nature of the substance that is used to desorb it. The results elucidate the desorption mechanism and are relevant to understand and predict the environmental mobility of glyphosate.

Abstract. The desorption kinetics of glyphosate (Gly) from goethite was studied in a flow cell using attenuated total reflectance Fourier-transform infrared spectroscopy. Because Gly forms an inner-sphere surface complex by coordinating to Fe atoms at the goethite surface, the desorption process is actually a ligand-exchange reaction, where Gly is the leaving ligand and water molecules or dissolved substances are the entering ligands. A series of possible entering ligands that can be found in nature was tested to evaluate their effect on the desorption kinetics of Gly. Contrarily to expectations, the desorption rate was quite independent of the entering ligand concentration. Moreover, the identity of this ligand (phosphate, citrate, sulfate, oxalate, EDTA, thiocyanate, humic acid, water) had only a small effect on the value of the desorption rate constant. By analogy with the reactivity of transition metal complexes in solution, it is concluded that the rate is mainly controlled by the breaking of the Fe–Gly bond, through a dissociative or a dissociative interchange mechanism. The results are relevant in understanding and predicting the environmental mobility of Gly: irrespective of the identity of the entering ligand, Gly will always desorb from iron (hydr)oxides in nature at nearly the same rate, simplifying calculations and predictions enormously. The importance of studying desorption kinetics using mineral surfaces and environmentally relevant molecules is also highlighted.

Introduction

Many substances in soils, sediments and aquatic environments are adsorbed at the surface of mineral particles. Studying the desorption kinetics of these adsorbed substances is highly relevant to properly understand their mobility and fate in natural media. Desorption rate data, in addition, may give valuable information on the reaction mechanism.

Glyphosate (Gly) is a broad-spectrum herbicide used in agriculture for the control of many weeds. The World Health Organisation (WHO) has classified Gly as probably carcinogenic to humans (Group 2A),[1] and thus there is a substantial interest in studying this herbicide and its environmental behaviour. This article deals with the desorption kinetics of Gly from goethite, and explores the ligand-exchange mechanism that is involved in it. The basics of this mechanism could be then extended to understand the desorption kinetics of many other adsorbed substances.

Gly is strongly adsorbed to mineral surfaces by forming inner-sphere complexes. The most studied case is Gly adsorbed on goethite, where a Fe–O–P bond is formed between the phosphonate group of Gly and Fe^{III} ions on the goethite surface.[2] The desorption of Gly takes place by ligand exchange (ligand substitution) and can be written as.

$$\equiv Fe - Gly + L \rightleftarrows \equiv Fe - L + Gly \qquad (1)$$
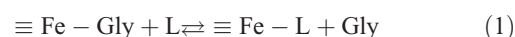
where $\equiv$Fe–Gly denotes the inner-sphere surface complex formed between Gly and Fe^{III} at the goethite surface, L is a ligand, and $\equiv$Fe–L is the surface complex formed between L and surface Fe^{III}. Eqn 1 represents a typical ligand-exchange reaction, where Gly is the leaving ligand and L is the entering ligand. There are many substances in natural media that can act as entering ligands, such as phosphate, arsenate, citrate, hydroxyl ions and water molecules. Polymeric or oligomeric substances

like humic acids (HA) or fulvic acids (FA) are also very good ligands for goethite groups. The simplest desorption process occurs when L = H_2O or L = OH^-, leaving a clean (bare) goethite surface.

Ligand exchange as represented by Eqn 1 has been studied with various ligands. The most investigated case is Gly–phosphate exchange; adsorption isotherms demonstrate that phosphate is effective in producing Gly desorption.[3–5] Similar effects are shown by HA, which can displace Gly from goethite.[6] The effects of other ligands have seldom been investigated.

The kinetics of the process represented by Eqn 1 have rarely been addressed in the literature. There is some information on the desorption rate of Gly in the presence of either phosphate[7] or HA.[6] However, a comparative study of desorption rates with different ligands that are present in nature has never been published. This is relevant to understand how fast Gly can become desorbed from minerals and how quickly the herbicide can become mobilised in water or become available to micro-organisms or higher plants.

The aim of the present article is to investigate for the first time the desorption rate of Gly from goethite in aqueous media using different substances of varying concentration as entering ligands. The desorption process was monitored by in situ attenuated total reflectance (ATR)-Fourier-transform infrared (FTIR) spectroscopy, which allows examination of the IR spectra of adsorbed Gly as the reaction proceeds. Intuitively, it was expected that the rate would strongly depend on the type and concentration of L, but this needed to be demonstrated and quantified.

Materials and methods

Goethite

The goethite sample used in the current work was the same as used in a previous publication.[6] It was synthesised according to the method proposed by Atkinson et al.[8] and kept as a stock suspension in water (9.63 g L^{-1}) at pH 4.5. It had a Brunauer–Emmett–Teller (BET) surface area of 89.7 m^2 g^{-1} and an iso-electric point (IEP) of 8.6.

Gly adsorption–desorption kinetics

Adsorption–desorption kinetics measurements were performed by ATR-FTIR, using a Thermo Fisher Scientific (Waltham, MA, USA) ARK flow cell containing a ZnSe crystal (area: 10×72 mm, incident angle: 45°, total reflections: 12) connected to a Nicolet iS50 470 spectrometer. A Gilson (Middleton, WI, USA) Minipuls 8 peristaltic pump was used to pump the solution of interest from a reservoir to the cell at a flow rate of 3.3 mL min^{-1}. An open flow system was used in all cases, meaning that fresh solution always flowed through the cell, being discarded by the outlet tubing. All experiments were performed in 0.1 M NaCl electrolyte and at pH 7.0 ± 0.2, which was continuously controlled with a glass electrode in the reservoir and corrected if necessary with the addition of small volumes (microlitres) of either NaOH or HCl solution. The working temperature was 24 ± 2°C. Each recorded spectrum was the average of 128 scans, with a spectral resolution of 16 cm^{-1}.

A goethite film was prepared by placing 210 μL of the stock goethite dispersion on the ZnSe crystal and evaporating to dryness at room temperature. The electrolyte was pumped through the cell and a blank spectrum was taken. A 2.95×10^{-4} M Gly solution (in 0.1 M NaCl, pH 7.0) was then pumped to produce Gly adsorption on goethite, and spectra were recorded as a function of time until the intensity of the signal levelled off (~60 min). Under these conditions, the adsorbed amount of Gly was 1.24 μmol m^{-2}, as dictated by the adsorption isotherm (adsorbed amount, Γ_{Gly}, v. equilibrium concentration, C_{Gly}), which was obtained with the same goethite sample for a previous publication[6] and can be seen in the Supplementary material (Fig. S1). Therefore, the IR absorbance at this point was assumed to correspond to Γ_{Gly} = 1.24 μmol m^{-2}, and all other Γ_{Gly} values were calculated assuming a linear relationship between absorbance and Γ_{Gly}.[6]

Gly desorption was induced by starting the flow of the desorbing solution, which could be pure electrolyte or a solution of a ligand different from Gly, always in 0.1 M NaCl and at pH 7.0. The spectra were then recorded as a function of time in order to evaluate the desorption kinetics. The ligands used were phosphate, citrate, oxalate, sulfate, thiocyanate and EDTA. Their concentrations were 10^{-4}, 3×10^{-4} and 10^{-3} M, except in the case of thiocyanate, where concentrations of 10^{-3}, 10^{-2} and 3×10^{-2} M were used, and phosphate, where concentrations 10^{-6}, 10^{-5}, 10^{-4}, 3×10^{-4}, 10^{-3} and 10^{-2} M were used. Phosphate,[9–11] citrate[12] and HA[13] are known to form inner-sphere surface complexes with goethite. Thiocyanate[14] and EDTA[15] are postulated to form outer-sphere surface complexes. Oxalate forms both inner- and outer-sphere complexes.[16] There are different opinions regarding sulfate adsorption.[17,18]

Results and discussion

Fig. 1 shows typical ATR-FTIR results for Gly adsorption–desorption. This is the case where desorption was induced under flowing phosphate solution. Spectra obtained during adsorption (Fig. 1a) showed main bands at 1400, 1120 and 980 cm^{-1} corresponding respectively to the v_s(C–O), v_a(P–O) and v_s(P–OFe) vibrations, which are characteristic of a monodentate mononuclear inner-sphere surface complex of Gly on goethite.[2] The concentration of this surface complex increased as a function of time, as can be deduced from the change in the IR absorbance as the adsorption reaction proceeded. Once the phosphate solution started to flow, the main bands at 1090 and 1044 cm^{-1} corresponding to an inner-sphere surface complex of phosphate[5] appeared (Fig. 1b). Phosphate bands intensity increased and Gly bands intensity decreased with time as a consequence of ligand exchange. The resulting Γ_{Gly} v. time t curves are shown in Fig. 1c and compared with those obtained by desorbing Gly with phosphate solutions of varying concentrations ranging from 10^{-6} to 10^{-2} M. Phosphate concentrations above 10^{-4} M are enough to completely saturate the goethite surface.[9,10] Except in the case of 10^{-6} M phosphate, which seemed to show a slightly lower desorption rate than the others, all desorption curves were very similar. In fact, instead of observing an increase in the desorption rate as phosphate concentration increased, as was expected, all desorption rates at phosphate concentrations higher than 10^{-6} M were the same within experimental error (see below). Even including data at 10^{-6} M, a 10 000-fold increase in phosphate concentration increased the desorption rate, at most, by a factor of 1.5.

Fig. 2 shows the case of Gly desorption under flowing citrate solution. After addition of citrate, the band at 1400 cm^{-1} due to carboxylate increased with time because of citrate adsorption, whereas the bands at 1120 and 980 cm^{-1} decreased because of Gly desorption. The comparison of the Γ_{Gly} v. t curves obtained with flowing citrate solutions of three different concentrations
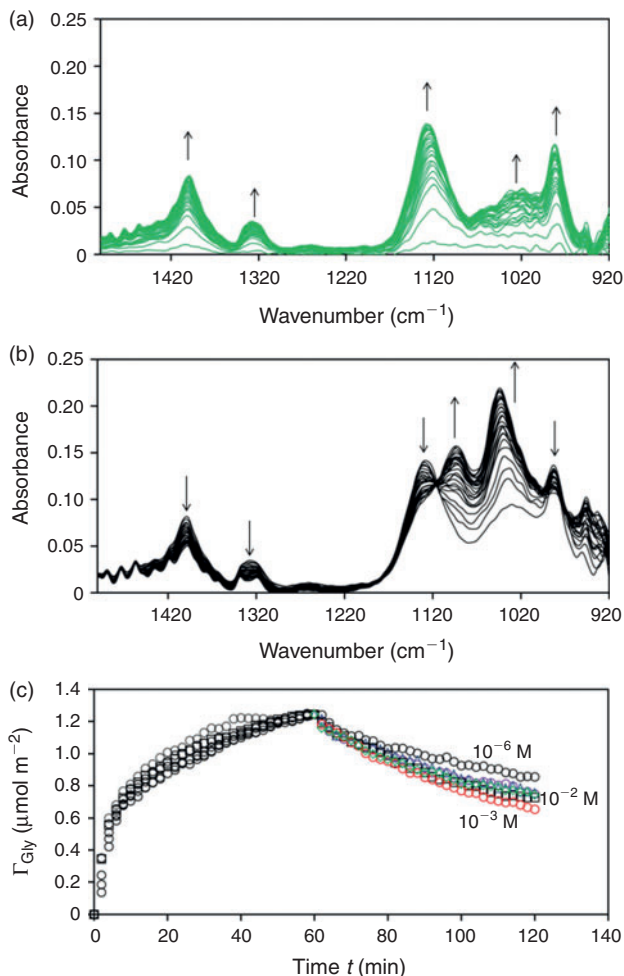
Fig. 1. Attenuated total reflectance Fourier-transform infrared (ATR-FTIR) spectra of (a) glyphosate (Gly) adsorption, and (b) Gly desorption after treatment with 1×10^{-4} M phosphate. Arrows indicate the evolution of spectra in time. (c) Gly adsorption–desorption curves after flow of (at $t = 60$ min) 1×10^{-6} M (circles), 1×10^{-5} M (stars), 1×10^{-4} M (triangles), 3×10^{-4} M (diamonds), 1×10^{-3} M (crosses) and 1×10^{-2} M (squares) phosphate solutions. Some phosphate concentrations are indicated on the figure for clarity. pH 7.0, 0.1 M NaCl.
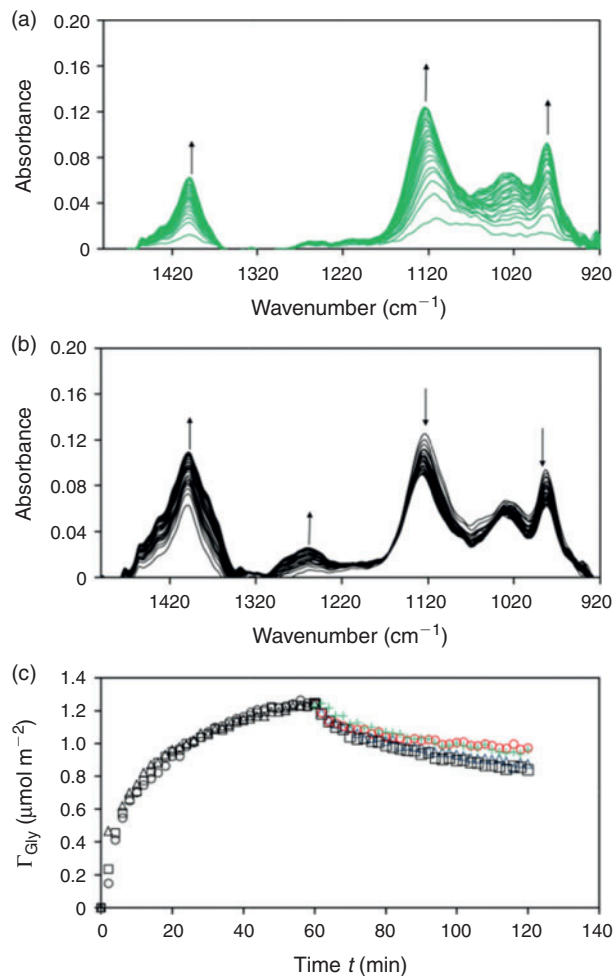
Fig. 2. Attenuated total reflectance Fourier-transform infrared (ATR-FTIR) spectra of (a) glyphosate (Gly) adsorption, and (b) Gly desorption after treatment with 3×10^{-4} M citrate. Arrows indicate the evolution of spectra in time. (c) Gly adsorption–desorption curves after flow of (at $t = 60$ min) 1×10^{-4} M (triangles), 3×10^{-4} M (squares) and 1×10^{-3} M (circles) citrate solutions. The desorption curve after washing with supporting electrolyte (crosses) is also shown. pH 7.0, 0.1 M NaCl.

gave no particular trend, with the slowest desorption apparently obtained with 10^{-3} M citrate, intermediate desorption with 10^{-4} M citrate and the fastest desorption with 3×10^{-4} M citrate. Our experience with these systems indicates that, within experimental error, all desorption rates were the same. There is a fourth curve in the figure corresponding to desorption with pure electrolyte, showing a behaviour that is very similar to the others. The results are very conclusive: the presence of citrate did not affect the desorption rate of Gly.

Fig. 3 shows the adsorption–desorption behaviour of thiocyanate (SCN^-) on the system studied. These experiments were done in the absence of Gly, and were performed to evaluate how fast SCN^- goes in and out the goethite film. This anion is known to form outer-sphere complexes with goethite surface groups.[14] Indeed, the ATR-FTIR spectrum of adsorbed SCN^- is identical to the spectrum of 'free' SCN^- in solution. Knowing that the formation of outer-sphere complexes (ion pairs) should be very fast because no coordination bonds have to be broken or formed during the process,[19] the adsorption–desorption kinetics of SCN^- is controlled by diffusion, and therefore, it shows

the time needed by ions to diffuse through the goethite film. Total release of SCN^- took place in less than 10 min. By comparing this time with the longer times required to desorb Gly from goethite, it was possible to deduce that Gly desorption kinetics was not diffusion-controlled.

Experiments such as those shown in Figs 1 and 2 were performed with the other entering ligands, and desorption curves can be seen in Figs S2–S7 (available as Supplementary material to this paper). It must be noted that in all cases, waiting long enough during the desorption runs, the final situation must have been complete Gly desorption, as thermodynamics dictates, because no Gly was present in the desorbing solutions. Gly desorption rates (obtained at $t > 10$ min) for all studied ligands at different concentrations are listed in Table 1. As with phosphate and citrate, the desorption rates were quite independent of the ligand concentration. Changing the ligand concentration resulted in a random change in the desorption rate, with standard deviations that were similar to those obtained from six desorption runs with pure electrolyte. Because under the investigated conditions, the desorption rate practically did not depend on the
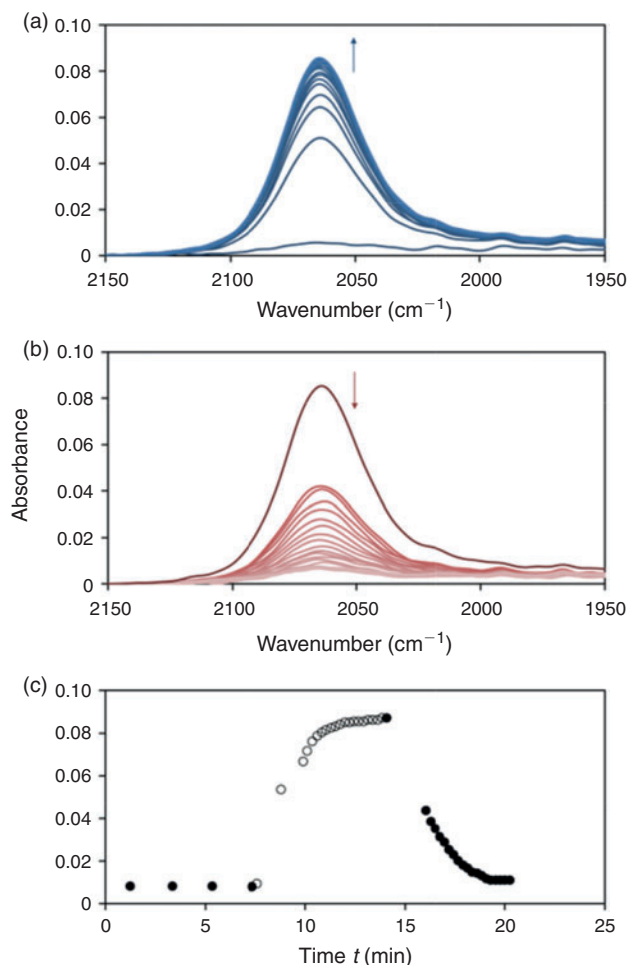
Fig. 3. Attenuated total reflectance Fourier-transform infrared (ATR-FTIR) spectra of (a) thiocyanate adsorption under flow of a 0.1 M thiocyanate solution; and (B) desorption after flow of supporting electrolyte. Arrows indicate the evolution of spectra in time. (c) Thiocyanate adsorption–desorption curves resulting from (a) and (b). pH 9.5.

concentration of the entering ligand, the rate law for the ligand exchange reaction (Eqn 2) can be simply formulated as:

$$r_{des} = k_{des}\Gamma_{Gly} \qquad (2)$$

where r_{des} is the desorption rate and k_{des} is the pseudo-first-order rate constant of the reaction. k_{des} values for each entering ligand are also listed in Table 1, including data with water as entering ligand (washing with electrolyte) and data from a previous publication where Gly was desorbed with HA using the same goethite sample.[6] It is noteworthy to see that all rate constants are quite similar, differing at most by a factor of 3 for the eight ligands considered. It does not matter if the ligand forms inner-sphere or outer-sphere complexes, or if the ligand is negatively charged (one, two or more charges) or uncharged (water). Even HA, a polyelectrolyte with several binding groups, displaces Gly at similar rates. It is also noteworthy that decreasing the ionic strength from 10^{-1} to 10^{-3} M did not change the desorption rate. In order to have an estimation of the times needed for near-complete desorption, the average k_{des} value of 3×10^{-3} min^{-1} indicates that 95 % desorption should take place in ~16–17 h and 99 % desorption in 25–26 h.

The mechanisms of ligand-exchange reactions of transition metal complexes in solution have been intensively investigated over several decades. Langford and Gray[20] classified these reactions as dissociative or associative processes. These are actually two extreme and ideal cases,[19,21] which are shown in schematic form in Fig. 4. At one extreme, in a first step, the leaving ligand breaks its bond with the metal centre, and in a second step, the entering ligand binds to the metal. This is the D (dissociative) mechanism. At the other extreme, first the entering ligand binds to the metal centre, and then the leaving ligand goes out. This is the A (associative) mechanism. Between these two extremes is interchange, I, which can be of the I_d type (dissociative interchange) or the I_a type (associative interchange).[19,21] In D or I_d mechanisms, the reaction rate depends weakly on the nature of the entering ligand because bond-breaking between the ligand and the metal centre controls the rate.[22] In A or I_a mechanisms, the reaction rate depends strongly on the nature of the entering ligand because bond-making between the ligand and the metal takes control of the rate. For example, for the substitution of one water molecule by different L$^-$ entering ligands in $[Ni(H_2O)_6]^{2+}$, the rate constants are all within the same order of magnitude, which is typical of D or I_d mechanisms.[22] In contrast, the rate constants for the analogous reactions in $[Cr(H_2O)_6]^{3+}$ differ by more than three orders of magnitude,[23] which is typical of A or I_a mechanisms.

The full data set shown in Figs 1, 2 and Table 1 tends to support a D or I_d mechanism for Gly desorption from goethite. Bond-breaking takes precedence over bond-making and thus a weak effect of the entering ligand is observed. The reactivity of the surface $\equiv$Fe–Gly complex is then in line with the general reactivity of octahedral complexes in solution, which are normally dissociative in character.[22]

It is clear from Table 1 that there are some differences in reaction rate constants among different ligands. Actually, a pure D mechanism only exists ideally. In transition metal complexes in solution, there is always a fairly small effect of the entering ligand, which results in rate variations that remain all within the same order of magnitude.[19–22] This seems to be the situation for the ligands investigated here. In the case of ligands that form mainly outer-sphere complexes, the entering moiety must be water, and thus rate constants for Gly desorption should be similar. The cases of citrate, HA and phosphate, which form inner-sphere complexes, support the D or I_d mechanism, because rate constants keep within a fairly small range instead of spanning several orders of magnitude. It is interesting that even a polyelectrolyte, like HA, with several binding groups that could act simultaneously on the surface, cannot displace Gly at a much higher rate. However, if the controlling step is the breaking of the Gly–Fe bond, each HA group has to 'wait' for Gly to leave the surface before binding to it and thus the Gly desorption rate is not significantly modified.

The case of phosphate needs some extra attention. Its average k_{des} value is twice the value obtained with supporting electrolyte. Although this variation is considered in the literature as a small variation that correctly allows selecting a D (or I_d) mechanism, it seems that phosphate does have an accelerating effect on Gly desorption. In order to confirm this effect, extra experiments were performed, adsorbing Gly as before, then desorbing it with electrolyte for 1 h, and finishing in the same run with desorption with phosphate for an extra hour. This enabled comparison of desorption rates with electrolyte and phosphate in the same run and under exactly the same experimental conditions, avoiding changes caused by small uncontrolled variations in, for example, temperature, mass of goethite in the film, and film roughness or thickness. The results, using

Table 1. Desorption rates and rate constants obtained with different entering ligands

r_{des}, desorption rate; k_{des}, desorption rate constant

Ligand	Ligand concentration	r_{des} (μmol m^{-2} min^{-1})	Average $\pm$ s.d. (μmol m^{-2} min^{-1})	k_{des} (min^{-1})
Phosphate (1− and 2−)[A]	1×10^{-2} M	6.0×10^{-3}	$(6.5 \pm 0.9) \times 10^{-3}$	$(5.2 \pm 0.8) \times 10^{-3}$
	1×10^{-3} M	7.8×10^{-3}		
	3×10^{-4} M	7.2×10^{-3}		
	1×10^{-4} M	6.7×10^{-3}		
	1×10^{-5} M	6.2×10^{-3}		
	1×10^{-6} M	5.1×10^{-3}		
	1×10^{-3} M[B]	5.6×10^{-3}		
Citrate (2− and 3−)	1×10^{-3} M	2.2×10^{-3}	$(3.4 \pm 1.0) \times 10^{-3}$	$(2.7 \pm 0.8) \times 10^{-3}$
	3×10^{-4} M	4.1×10^{-3}		
	1×10^{-4} M	3.9×10^{-3}		
Sulfate (2−)	1×10^{-3} M	2.9×10^{-3}	$(2.1 \pm 1.1) \times 10^{-3}$	$(1.7 \pm 0.9) \times 10^{-3}$
	3×10^{-4} M	1.3×10^{-3}		
Oxalate (2−)	1×10^{-3} M	3.0×10^{-3}	$(3.0 \pm 0.2) \times 10^{-3}$	$(2.4 \pm 0.2) \times 10^{-3}$
	3×10^{-4} M	2.8×10^{-3}		
	1×10^{-4} M	3.2×10^{-3}		
EDTA (2− and 3−)	1×10^{-3} M	4.3×10^{-3}	$(4.0 \pm 0.6) \times 10^{-3}$	$(3.2 \pm 0.5) \times 10^{-3}$
	3×10^{-4} M	4.3×10^{-3}		
	1×10^{-4} M	3.3×10^{-3}		
Thiocyanate (1−)	3×10^{-2} M	4.4×10^{-3}	$(4.5 \pm 1.1) \times 10^{-3}$	$(3.6 \pm 0.9) \times 10^{-3}$
	1×10^{-2} M	3.4×10^{-3}		
	1×10^{-3} M	5.6×10^{-3}		
HA[C] ($\Gamma_{Gly} = 0.75$ μmol m^{-2})	466 ppm	2.8×10^{-3}	$(2.2 \pm 0.5) \times 10^{-3}$	$(2.9 \pm 0.7) \times 10^{-3}$
	233 ppm	2.4×10^{-3}		
	116 ppm	2.2×10^{-3}		
	50 ppm	1.4×10^{-3}		
Water	0.1 M NaCl	2.8×10^{-3}	$(3.2 \pm 0.4) \times 10^{-3}$	$(2.6 \pm 0.3) \times 10^{-3}$
	0.1 M NaCl	3.7×10^{-3}		
	0.1 M NaCl	3.1×10^{-3}		
	0.1 M NaCl	3.6×10^{-3}		
	0.1 M NaCl	3.1×10^{-3}		
	0.1 M NaCl	2.9×10^{-3}		

[A]The charges of the main ionic species at pH 7 are given.
[B]10^{-3} M phosphate in 10^{-3} M NaCl.
[C]Data for HA are from ref. 6.
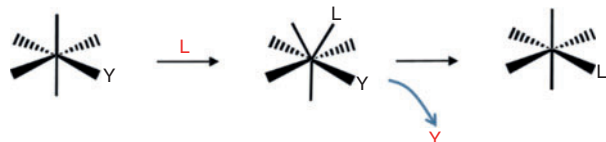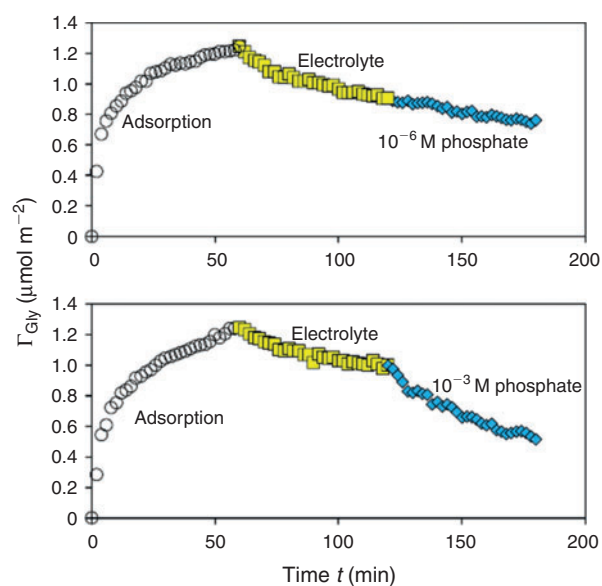

Fig. 4. The two extreme cases for ligand substitution in an octahedral transition metal complex in solution. Y is the leaving ligand and L is the entering ligand. Ligands that are not coordinated to the metal centre are shown in red.

Fig. 5. Glyphosate (Gly) desorption curves after flow of supporting electrolyte (squares) first, followed by either 10^{-6} M or 10^{-3} M phosphate (diamonds). pH 7.0, 0.1 M NaCl.

10^{-6} M phosphate in one desorption run and 10^{-3} M phosphate in another run, are shown in Fig. 5. The 10^{-6} M phosphate did not change the rate; however, 10^{-3} M phosphate increased the rate from 2.9×10^{-3} μmol m^{-2} min^{-1} (electrolyte) to

6.3×10^{-3} µmol m^{-2} min^{-1}, confirming the accelerating effect by a factor of ~2. There is so far no clear explanation on how phosphate increases the Gly desorption rate. More studies should be done specifically with the phosphate–Gly–goethite system by changing pH, ionic strength, temperature, Gly and phosphate concentration, performing binary adsorption isotherms, etc., in order to achieve a full understanding of the process. Although this is outside of the scope of the present manuscript, it is possible to speculate and propose two possible explanations. In a ligand-exchange process that is dissociative in character, the rate-controlling step is the breaking of the Fe–Gly bond. Therefore, in order to increase the desorption rate, the adsorbing ligand should be able to somehow weaken that bond. One possibility is that phosphate binds surface sites in the neighbourhood of an adsorbed Gly, affecting the Fe–Gly bond and facilitating desorption. Because phosphate attaches to a neighbouring Fe centre (not the target Fe centre bonded to Gly), the change in the rate should not be very large. Carboxylate groups belonging to citrate and HA are weaker ligands than phosphate, and this may be the reason why the effects of citrate and HA are smaller. Another possibility is that the process is not purely dissociative, but more of the I$_d$ type. In this case, even though bond-breaking is still the main rate-controlling process, the entering ligand has a small but significant effect on the rate.[19] Again, the differences between carboxylate groups and phosphate explain the weaker effects of citrate and HA.

It must be stated that in the two possible cases mentioned above, phosphate or other ligands affecting the rate should be located very close to the adsorbed Gly species in order to affect the rate. Changing the ionic strength, for example, would change the potential drop in the double layer, but this should not change the strength of the Fe–Gly bond. In a dissociative process, the electrostatics of the double layer will act mainly after the Fe–Gly bond is broken, thus having a very low effect on the rate if the controlling step is the breaking of that bond. The fact that decreasing the ionic strength 100 times did not produce a significant change in the desorption rate supports the explanations given above.

Conclusions

The findings in the present work were quite counterintuitive. The desorption rate of Gly from goethite practically did not change when changing the entering ligand concentration and, also surprisingly, the identity of this ligand had only a fairly small effect on the value of the desorption rate constant. It is thus concluded that the reaction rate is mainly controlled by the breaking of the Fe–Gly bond at the surface, in a kind of dissociative mechanism, as usually occurs with transition metal complexes in solution.

The results shown here are relevant in understanding and predicting the environmental mobility of Gly. Even though Gly desorbs by a ligand-exchange process in which an entering ligand participates, the nature of the entering ligand is not very important. In practice, in a field study, for example, it is not necessary to measure the desorption rate of Gly with different possible ligands, because they will be quite similar, within a factor of 3, as compared with changes of several order of magnitude occurring with associative mechanisms. In theoretical studies, the relevance of the results may be even higher; the assumption of a D or I$_d$ mechanism simplifies calculations enormously because the same k_{des} value could be used as a good approximation in fairly different situations, with different ligands and at different concentrations.

The results obtained with Gly and goethite as an example highlight the importance of studying desorption kinetics using other mineral than goethite and other environmentally relevant desorbing ligands. Because the metal–ligand bond controls the rate, it is expected that reaction rates are significantly different for different metal oxides and for different leaving ligands. We envision that desorption studies that move in this direction will allow an understanding and correct prediction of the environmental fate of many different molecules and ions.

Supplementary material

Gly adsorption isotherm on goethite and Gly desorption curves with different entering ligands are available from the Journal's website.

References

[1] K. Z. Guyton, D. Loomis, Y. Grosse, F. El Ghissassi, L. Benbrahim-Tallaa, N. Guha, C. Scoccianti, H. Mattock, K. Straif, Carcinogenicity of tetrachlorvinphos, parathion, malathion, diazinon, and glyphosate. *Lancet* **2015**, *16*, 490. doi:10.1016/S1470-2045(15)70134-8

[2] J. Sheals, S. Sjöberg, P. Persson, Adsorption of glyphosate on goethite: molecular characterization of surface complexes. *Environ. Sci. Technol.* **2002**, *36*, 3090. doi:10.1021/ES010295W

[3] A. L. Gimsing, O. K. Borggaard, Competitive adsorption and desorption of glyphosate and phosphate on clay silicates and oxides. *Clay Miner.* **2002**, *37*, 509. doi:10.1180/0009855023730049

[4] A. L. Gimsing, O. K. Borggaard, Effect of phosphate on the adsorption of glyphosate on soils, clay minerals and oxides. *Int. J. Environ. Anal. Chem.* **2002**, *82*, 545. doi:10.1080/0306731021000062964

[5] C. V. Waiman, J. M. Arroyave, H. Chen, W. Tan, M. J. Avena, G. P. Zanini, The simultaneous presence of glyphosate and phosphate at the goethite surface as seen by XPS, ATR-FTIR and competitive adsorption isotherms. *Colloids Surf. A Physicochem. Eng. Asp.* **2016**, *498*, 121. doi:10.1016/J.COLSURFA.2016.03.049

[6] J. M. Arroyave, C. V. Waiman, G. P. Zanini, M. J. Avena, Effect of humic acid on the adsorption/desorption behavior of glyphosate on goethite. Isotherms and kinetics. *Chemosphere* **2016**, *145*, 34. doi:10.1016/J.CHEMOSPHERE.2015.11.082

[7] A. L. Gimsing, O. K. Borggaard, P. Sestoft, Modeling the kinetics of the competitive adsorption and desorption of glyphosate and phosphate on goethite and gibbsite and in soils. *Environ. Sci. Technol.* **2004**, *38*, 1718. doi:10.1021/ES030572U

[8] R. J. Atkinson, A. M. Posner, J. P. Quirk, Adsorption of potential-determining ions at the ferric oxide–aqueous electrolyte interface. *J. Phys. Chem.* **1967**, *71*, 550. doi:10.1021/J100862A014

[9] J. Antelo, M. Avena, S. Fiol, R. López, F. Arce, Effects of pH and ionic strength on the adsorption of phosphate and arsenate at the goethite–water interface. *J. Colloid Interface Sci.* **2005**, *285*, 476. doi:10.1016/J.JCIS.2004.12.032

[10] T. Hiemstra, W. H. Van Riemsdijk, A surface structural approach to ion adsorption: the charge distribution (CD) model. *J. Colloid Interface Sci.* **1996**, *179*, 488. doi:10.1006/JCIS.1996.0242

[11] M. I. Tejedor-Tejedor, M. A. Anderson, Protonation of phosphate on the surface of goethite as studied by CIR-FTIR and electrophoretic mobility. *Langmuir* **1990**, *6*, 602. doi:10.1021/LA00093A015

[12] K. Lackovic, B. B. Johnson, M. J. Angove, J. D. Wells, Modeling the adsorption of citric acid onto Muloorina illite and related clay

minerals. *J. Colloid Interface Sci.* **2003**, *267*, 49. doi:10.1016/S0021-9797(03)00693-3

[13] L. Weng, W. H. Van Riemsdijk, T. Hiemstra, Humic nanoparticles at the oxide–water interface: interactions with phosphate ion adsorption. *Environ. Sci. Technol.* **2008**, *42*, 8747. doi:10.1021/ES801631D

[14] H. P. Vu, J. W. Moreau, Thiocyanate adsorption on ferrihydrite and its fate during ferrihydrite transformation to hematite and goethite. *Chemosphere* **2015**, *119*, 987. doi:10.1016/J.CHEMOSPHERE.2014.09.019

[15] K. Norén, J. S. Loring, J. R. Bargar, P. Persson, Adsorption mechanisms of EDTA at the water–iron oxide interface: implications for dissolution. *J. Phys. Chem. C* **2009**, *113*, 7762. doi:10.1021/JP809190M

[16] K. Axe, M. Vejgården, P. Persson, An ATR-FTIR spectroscopic study of the competitive adsorption between oxalate and malonate at the water–goethite interface. *J. Colloid Interface Sci.* **2006**, *294*, 31. doi:10.1016/J.JCIS.2005.07.013

[17] D. Peak, R. G. Ford, D. L. Sparks, An in situ ATR-FTIR investigation of sulfate bonding mechanisms on goethite. *J. Colloid Interface Sci.* **1999**, *218*, 289. doi:10.1006/JCIS.1999.6405

[18] R. P. J. J. Rietra, T. Hiemstra, W. H. van Riemsdijk, Sulfate adsorption on goethite. *J. Colloid Interface Sci.* **1999**, *218*, 511. doi:10.1006/JCIS.1999.6408

[19] R. B. Jordan, *Reaction Mechanisms of Inorganic and Organometallic Systems, 3rd edn* **2007** (Oxford University Press: Oxford, UK).

[20] C. H. Langford, H. B. Gray, *Ligand Substitution Processes* **1966** (Benjamin, Inc.: New York).

[21] S. Ašperger, *Chemical Kinetics and Inorganic Reaction Mechanisms, 2nd edn* **2003** (Springer Science + Business Media, LLC: New York).

[22] R. G. Wilkins, Mechanisms of ligand replacement in octahedral nickel (II) complexes. *Acc. Chem. Res.* **1970**, *3*, 408. doi:10.1021/AR50036A003

[23] D. Thusius, Rate constants and activation parameters for the formation of monosubstituted chromium(III) complexes. *Inorg. Chem.* **1971**, *10*, 1106. doi:10.1021/IC50099A061

Handling editor: Kevin Wilkinson