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The simultaneous presence of glyphosate and phosphate at the goethite surface as seen by XPS, ATR-FTIR and competitive adsorption isotherms

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HIGHLIGHTS

- Glyphosate and phosphate are simultaneously detected at the surface of goethite.
- Adsorption isotherms indirectly show that both substances coexist at the surface.
- XPS and ATR-FTIR directly detect both substances adsorbed together.
- The presence of one ligand at the surface does not alter the nature of the other adsorbed ligand.

GRAPHICAL ABSTRACT
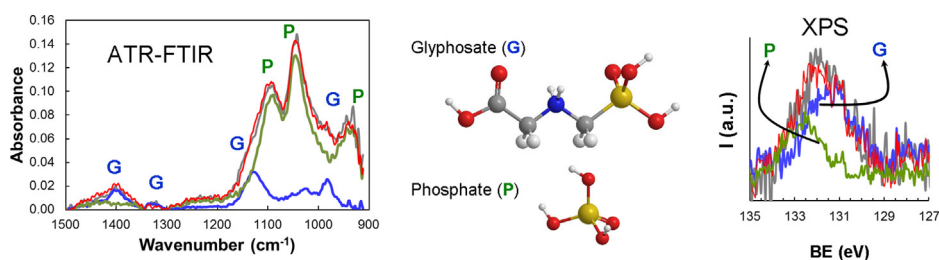
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ABSTRACT

The simultaneous adsorption of glyphosate and phosphate on goethite was studied by combining macroscopic (adsorption isotherms, electrophoresis) and spectroscopic (XPS, ATR-FTIR) techniques. Adsorption isotherms together with the Competitive Langmuir isotherm indirectly show that both substances coexist at the goethite surface. The adsorption maximum for phosphate was $2.50 \, \mu mol/m^2$ whereas for glyphosate it was $1.77 \, \mu mol/m^2$. The Langmuir adsorption constant was $0.15 \, \mu M^{-1}$ for phosphate and $0.01 \, \mu M^{-1}$ for glyphosate. The shape and position of the XPS signals of glyphosate did not change by the presence of phosphate at the surface and *vice versa*. Equivalent results were found with ATR-FTIR. Therefore, spectroscopic evidence indicates that the binding mode of glyphosate (type of inner-sphere complexes formed) to the goethite surface is not modified by adsorbing phosphate. This is valid for systems under equilibrium conditions and under dynamic conditions. The findings are important in environmental modeling, showing that surface complexation models can be used with confidence to predict speciation in double-ligand systems using adsorption parameters obtained with single-ligand systems.

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1. Introduction

Glyphosate (*N*-phosphonomethyl glycine) is a widely used organophosphorus anionic herbicide which has been the focus of many research articles. The mobility and availability of glyphosate in the environment are strongly influenced by adsorption-desorption processes on minerals, particularly on hydrous ferric

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oxides, which bear high affinity for it [1]. Glyphosate adsorbs on these solids mainly by a ligand exchange process, resulting in the formation of inner-sphere surface complexes, where the phosphonate group of the molecule binds iron(III) ions at the surface displacing coordinated water molecules and/or hydroxyl ions [2,3]. As in any ligand exchange reaction, the incoming ligand competes with other ligands for the binding to the metal ion, and thus glyphosate adsorption may be affected by the presence of other substances in the solution in contact with the surface. Ions such as phosphate, arsenate, bicarbonate, sulfate, etc., which are good ligands that can coordinate iron(III), are potentially good competitors of glyphosate for adsorption sites.

The competition between glyphosate and other ligand for binding sites on mineral surfaces has been actively investigated in the last decades for the case glyphosate-phosphate [4–14]. Since phosphate ions adsorb through the formation of inner-sphere surface complexes [15–18], they compete with different phosphonates [19] and therefore with glyphosate for adsorption sites. Evidences of this competition were given in several publications, including studies with soils, clay minerals and metal oxides [5–14]. Based on adsorption measurements using batch or column experiments, these studies show that both ligands can coexist at a mineral surface, and that the adsorption of one ligand decreases the adsorption of the other as a consequence of competition.

Surface spectroscopies such as XPS, ATR-FTIR and synchrotron-based spectroscopies are valuable techniques giving useful information that complements batch or column experiments. In batch experiments, for example, adsorption is indirectly deduced by measuring concentration changes in solution. Surface spectroscopies, instead, directly detect the adsorbed species. In a competition study these techniques could detect the simultaneous presence of the competing substances at the surface. In addition, several surface spectroscopies give also information on the structure of the surface complexes formed, and thus surface complexation can be assessed without the need of speculation from macroscopic adsorption measurements. This is very important for a mechanistic understanding of the reactions occurring at mineral surfaces and for a direct verification of the molecular assumptions made from adsorption data [20,21].

Direct spectroscopic studies of the simultaneous presence of glyphosate and phosphate at mineral surfaces are largely missing. Surface spectroscopies were always applied to single-ligand systems (either adsorbed glyphosate or adsorbed phosphate) [1–4,15,16,22], but not to double-ligand systems (both ligands adsorbed together). There is only one study in this respect, where glyphosate was desorbed by phosphate from the surface of goethite particles at pH 4.5, followed by ATR-FTIR spectroscopy [23]. The technique was able to detect and distinguish simultaneously both substances at the surface, but more information is still needed to understand the behavior of this system from a spectroscopic point of view. For instance, it is necessary to investigate the system at more environmentally relevant pH values and to evaluate spectroscopically if the presence of one adsorbed ligand alters the state of the other, either in dynamic or equilibrium situations. Such information is valuable for modeling the effects of mineral surfaces and phosphate on the speciation and mobility of glyphosate in the environment.

The aim of this work is to evaluate the adsorption of glyphosate and phosphate on goethite particles by using a combination of macroscopic (batch adsorption isotherms and electrophoretic mobility) and spectroscopic (XPS and ATR-FTIR) techniques. The existence of competition is first demonstrated, the simultaneous presence of both ligands at the surface is detected and the effects of one adsorbed ligand on the spectra of the other ligand are analyzed.

2. Experimental

2.1. Goethite synthesis and general characterization

Goethite particles were synthesized using a procedure similar to that proposed by Atkinson et al. [24]. Briefly, a 5 M NaOH solution was added dropwise to a 0.1 M $Fe(NO_3)_3$ aqueous solution. Carbon dioxide contamination was minimized during the synthesis by bubbling water-saturated N_2, and by using solutions prepared with bidistilled boiled water. The resulting ferrihydrite suspension was aged at 60 °C for 3 days in a capped Teflon container and then washed with bidistilled water until the conductivity was lower than 10 μS/cm. The so-prepared goethite was stored as a stock suspension at pH 5. Its goethite concentration was 15.5 g/L as measured in triplicate by drying 2 mL of the suspension at 30 °C until constant weight. An aliquot of this suspension was freeze-dried in order to perform X-ray diffraction (XRD) and surface area measurements. Teflon containers were used for the synthesis to avoid silicate contamination.

The XRD pattern (measured with a PHILIPS PW 1710 diffractometer) of the sample was typical of goethite (JCPDS-81-0464). Its N_2-BET surface area (measured with a Quantachrome Nova 1200e instrument) was 68.9 m^2/g. The IR spectrum (obtained with a Nexus 470 FTIR spectrometer equipped with a DTGS detector) was also typical of goethite [15]. The XRD pattern and IR spectrum are shown as Supplementary material.

2.2. Adsorption isotherms

Adsorption isotherms were performed at pH 6.0 and in 0.1 M KCl supporting electrolyte with a batch equilibration technique. Before starting the experiments, a 10 g/L suspension in 0.1 M KCl was prepared by mixing the adequate amounts of the stock suspension, water and KCl. Its pH was then raised to 6.0. Two types of isotherms were done: single-ligand adsorption isotherms and double-ligand adsorption isotherms. In the first case the adsorption behavior of glyphosate and phosphate was investigated separately; in the second case, both ligands were adsorbed simultaneously.

For the single-ligand adsorption isotherms, 0.3 mL of the 10 g/L suspension and 9.7 mL of an aqueous solution of either glyphosate or phosphate (concentration range 8.0×10^{-6} M to 2.9×10^{-4} M, in 0.1 M KCl, pH 6.0) were added to 15 mL polypropylene centrifuge tubes. The pH of the resulting dispersions was readjusted to 6.0 if necessary and kept constant by adding small volumes (a few microliters) of either KOH or HCl solutions, and the tubes were shaken overnight with an end-over-end rotator at 25.0 ± 2.0 °C. After equilibration, they were centrifuged at 3000 rpm (1558 g) for 10 min, and the supernatants were withdrawn for glyphosate or phosphate quantification. The amount of ligand adsorbed on goethite was calculated from the difference between the initial concentration and the concentration that remained in the supernatant solution.

For the double-ligand adsorption isotherms, the methodology was similar to that described above, except that both ligands were present in the system and they were both quantified in the supernatants to obtain their adsorbed amounts. Actually, these double-ligand experiments were glyphosate adsorption isotherms performed in the presence of a constant total phosphate concentration. Three isotherms were done, in each of them the total phosphate concentration was 8.0×10^{-6} M, 1.6×10^{-5} M and 3.2×10^{-5} M, respectively, whereas the glyphosate concentration was varied from 8.0×10^{-6} M to 2.9×10^{-4} M. The three total phosphate concentrations used explored a concentration range going from around 10% to around 62% of surface saturation with phosphate, and allowed to investigate conditions where the adsorbed

ligands on goethite varied from mainly adsorbed phosphate to mainly adsorbed glyphosate.

Glyphosate concentration in supernatants was measured by the UV–vis spectrophotometric method proposed in a previous work [25]. Phosphate concentration was measured by the molybdenum blue colorimetric method [26]. UV–vis spectra were recorded with an Agilent 8453 UV–vis diode array spectrophotometer equipped with a 1-cm Hellma quartz cell. The detection limit in both cases was around 1×10^{-6} M.

2.3. Electrophoretic mobility

Electrophoretic mobility of goethite in the absence and in the presence of ligand (either glyphosate, phosphate or a mix of both ligands) was measured with a Malvern NanoZS90 instrument. Dispersions of pure goethite (0.033 g/L, 0.01 M KCl) were prepared in 50 mL centrifuge tubes and their pH values were set between 4.0 and 10.0 by adding 0.1 M HCl and 0.1 M KOH. The dispersions were shaken overnight with an end-over-end rotator at $25.0 \pm 2.0\,^{\circ}$C. After equilibration, the pH was again measured and the electrophoretic measurement was conducted. The same procedure was applied to investigate the effects of glyphosate and phosphate on the electrophoretic mobility of goethite. Single-ligand experiments were performed with three different concentrations of glyphosate or phosphate (10^{-6} M, 10^{-5} M and 10^{-3} M). Double-ligand experiments were done with equimolar mixtures of both ligands (10^{-6} M, 10^{-5} M and 10^{-3} M). The supporting electrolyte was 0.01 M KCl.

Electrophoretic mobility data were converted to zeta potentials by using the Smoluchowsky equation [27]. Each data point is the average of two measurements. The standard deviation of the zeta potentials was 2 mV.

2.4. XPS

Solid samples from adsorption isotherms were analyzed by XPS. A pure goethite sample was analyzed also as a control. Once the supernatants were withdrawn from the centrifuge tubes, goethite particles were washed once with 0.1 M KCl at pH 6.0 to remove non-adsorbed ligands. According to a previous work, a gentle washing with electrolyte solution does not desorb significantly glyphosate or phosphate [23]. The solids were dried at $40\,^{\circ}$C for 3 days before analysis.

Spectra were recorded with a VG Multilab2000 X-ray photoelectron spectrometer with an Al Kα X-ray source (1486 eV) and a base pressure of 3×10^{-9} Torr in the analytical chamber. Survey scans were collected using a fixed pass energy of 100 eV and an energy step size of 1.0 eV, whereas for narrow scans a pass energy of 25 eV and an energy step size of 0.1 eV were used. The charge effect was corrected by adjusting the binding energy (BE) of C1s to 284.62 eV.

2.5. ATR-FTIR

ATR-FTIR spectra were obtained using a Nicolet Nexus 470 FTIR spectrometer equipped with a DTGS detector, a SMART-ARK ATR accessory and a ZnSe crystal (area: 10×72 mm; incident angle: $45°$; total reflections: 12), in its trough plate version. In all cases, each recorded spectrum was the average of 256 scans, with a spectral resolution of 4 cm^{-1}. The working temperature was $25.0 \pm 1.0\,^{\circ}$C.

Both single-ligand and double-ligand adsorption experiments were performed. For the single-ligand adsorption experiments of glyphosate, 200 μL of 10 g/L goethite dispersion at pH 6.0 were placed on the ZnSe crystal and evaporated to dryness at room temperature in order to obtain a dry goethite film. The film was then covered with 2 mL KCl solution (0.1 M, pH 6.0). After 1 min contact, this electrolyte solution was withdrawn and replaced by a fresh KCl solution (0.1 M, pH 6.0). This step was repeated 3–4 times
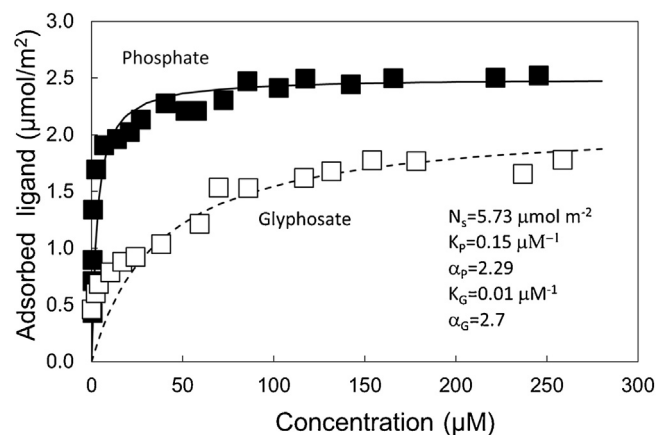

Fig. 1. Single-ligand adsorption isotherms at pH 6.0 (■) phosphate (□) glyphosate. Lines correspond to the fit with Langmuir Equations (1) and (2). Parameters used in calculations are given in the figure. $m = 0.003$ g, $S = 68.9$ m^2/g, V (0.01 L).

to ensure that experiment started at the desired pH 6.0. Then, a background spectrum was recorded and the electrolyte solution was withdrawn and replaced by a solution containing glyphosate (2.38×10^{-4} M, 0.1 M KCl, pH 6.0). Spectra were then recorded as a function of time in order to monitor glyphosate adsorption. Since some pH increase attributed to glyphosate/OH$^-$ exchange usually takes place during this step, after equilibration the supernatant was replaced by a fresh aliquot of the same glyphosate solution, and more spectra were collected. This step was repeated until no spectral variations were detected. This procedure ensures that the concentration of glyphosate in equilibrium with the goethite film is that of the starting solution and that the pH is 6.0.

The same procedure was employed to monitor phosphate adsorption by ATR-FTIR, but using a phosphate solution (2.38×10^{-4} M, 0.1 M KCl, pH 6.0) instead of the glyphosate solution.

In double-ligand adsorption experiments two cases were explored: glyphosate desorption induced by the adsorption of phosphate, and simultaneous adsorption of phosphate and glyphosate. In the first case, glyphosate was adsorbed as indicated above and, after collecting the spectra of adsorbed glyphosate, the solution was replaced by a phosphate solution (2.38×10^{-4} M, 0.1 M KCl, pH 6.0) to exchange some of the adsorbed glyphosate by phosphate. Spectra were then recorded until equilibration was attained. In the second case, after recording the background spectrum with the goethite film, a solution containing both glyphosate and phosphate (2.38×10^{-4} M for each ligand, 0.1 M KCl, pH 6.0) was added in order to produce the simultaneous adsorption of the ligands. After recording several spectra, the solution was replaced by a fresh glyphosate-phosphate solution and spectra were recorded again until no spectral variations were detected. This step was repeated several times in order to ensure that the final pH was 6.0.

Although bidistilled boiled water was used in all the experiments in order to minimize contamination with CO$_2$, and KOH solutions were prepared immediately before the experiments to avoid long contact of the alkaline media with air, the used ATR cell made not possible to perform ATR measurements under inert atmosphere.

3. Results and discussion

Fig. 1 shows the single-ligand adsorption isotherms, which describe the equilibrium situation for the individual adsorption of glyphosate and phosphate. The results are in agreement with those reported in the literature [1,27]. Phosphate adsorption (P_{ads})
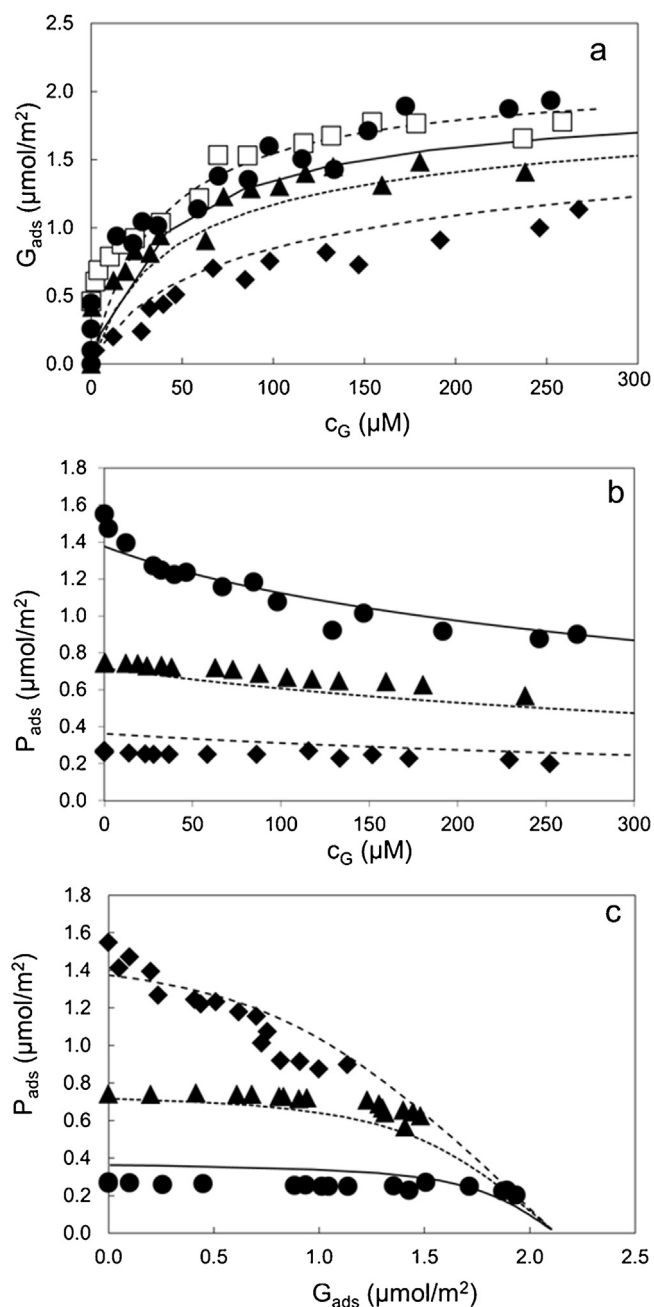
Fig. 2. Competitive adsorption isotherms. (a) Glyphosate adsorption isotherms at pH 6.0 at different total phosphate concentrations. (b) Effect of increasing glyphosate concentration on phosphate adsorption. (c) Adsorbed phosphate as a function of adsorbed glyphosate for the same experiments. Total phosphate concentrations: (□) 0 M, (●) 8.0 × 10⁻⁶ M, (▲) 1.6 × 10⁻⁵ M and (♦) 3.2 × 10⁻⁵ M. Solid lines correspond to the fit with Competitive Langmuir isotherms 1 and 2. Parameters used in calculations are given in Fig. 1. $m = 0.003$ g, $S = 68.9$ m^2/g, V (0.01 L).

was greater than glyphosate adsorption (G_{ads}) at all concentrations, reaching a maximum of 2.50 μmol/m^2 for phosphate compared to 1.77 μmol/m^2 for glyphosate at high concentrations. According to Gimsing and Borggaard [7] this effect may be caused by the difference in molecular sizes (steric hindrance).

Fig. 2 shows the results of double-ligand adsorption experiments. If glyphosate and phosphate compete for the adsorption sites, increasing the concentration of one of the ligands will increase its own adsorption and will also affect the adsorption of the other. Several types of plots may be presented in order to show these effects. Fig. 2a shows the glyphosate adsorption

isotherms obtained at different total phosphate concentrations. For each isotherm, glyphosate adsorption increased by increasing its concentration. In addition, by comparing different isotherms, the general effect of increasing total phosphate concentration was to decrease glyphosate adsorption. Results agree with reported data on soils and clay minerals by Dion et al. [5]. Fig. 2b, on the other hand, shows the effect of changing glyphosate concentration on the adsorption of phosphate. Since each isotherm was performed at a constant total phosphate concentration, increasing glyphosate concentration will decrease phosphate adsorption if competition takes place. This is what occurred in all cases of Fig. 2b. The effect was very small at low total phosphate concentration, but became more evident at intermediate and high total phosphate concentrations. An indirect way of analyzing the effects of increasing glyphosate concentration on the adsorption of phosphate is by plotting P_{ads} vs. G_{ads}. Even though G_{ads} is not an independent variable, it increased by increasing glyphosate concentration. Since P_{ads} and G_{ads} changed simultaneously as glyphosate concentration was changed, the advantage of such a plot is to depict the behavior of adsorbed phosphate as the surface became populated with glyphosate. These plots are shown in Fig. 2c. At low total phosphate concentration ($8.05 × 10^{-6}$ M, circles), P_{ads} was low and nearly constant, even though G_{ads} changed significantly. At intermediate total phosphate concentration ($1.61 × 10^{-5}$ M, triangles), P_{ads} was higher than in the previous case, and remained nearly constant as far as G_{ads} was lower than around 1 μmol/m^2; a slight decrease in P_{ads} was observed when G_{ads} was higher than 1 μmol/m^2. At high total phosphate concentration ($3.22 × 10^{-5}$ M, diamonds), there was a very significant decrease in P_{ads}, occurring together with an increase in G_{ads}.

Data in Figs. 1 and 2 were fitted using the Competitive Langmuir isotherms [28,29] for both ligands. The use of these equations does not intend to achieve a "perfect" fit of data, but to show that the full data set can be rather well explained using simple adsorption theories that consider continuous competition for surface sites. The Competitive Langmuir isotherms for phosphate and glyphosate adsorption can be written respectively as (see Supplementary material):

$$P_{ads} = \frac{N_s K_P c_P}{1 + \alpha_P K_P c_P + \alpha_G K_G c_G} \tag{1}$$

$$G_{ads} = \frac{N_s K_G c_G}{1 + \alpha_P K_P c_P + \alpha_G K_G c_G} \tag{2}$$

where K_P and K_G are the adsorption constants of phosphate and glyphosate, respectively, c_P and c_G are the respective equilibrium concentrations in solution and N_s is the surface sites density. Size effects that led to different adsorption maxima were introduced in the equations through the size factors α_P and α_G. They are assumed to result from steric hindrance and represent the average number of surface sites that are blocked by any adsorbed phosphate or glyphosate, respectively. These size factors do not need to be integers as in the case of stoichiometric factors.

In order to perform calculations and fitting of adsorption results, the mass-balance equations for phosphate and glyphosate must be also considered for each data point:

$$c_{P,T} = c_P + \frac{P_{ads} mS}{V} \tag{3}$$

$$c_{G,T} = c_G + \frac{G_{ads} mS}{V} \tag{4}$$

where $c_{P,T}$ and $c_{G,T}$ are the total (in solution plus adsorbed) phosphate and glyphosate concentrations in the system respectively, m is the mass of goethite, S is its surface area and V is the volume of the system. Eqs. (1)–(4) conform a system of equations that can be solved for either single-ligand or double-ligand isotherms. For each data point in a system of known m (0.003 g), S (68.9 m^2/g),
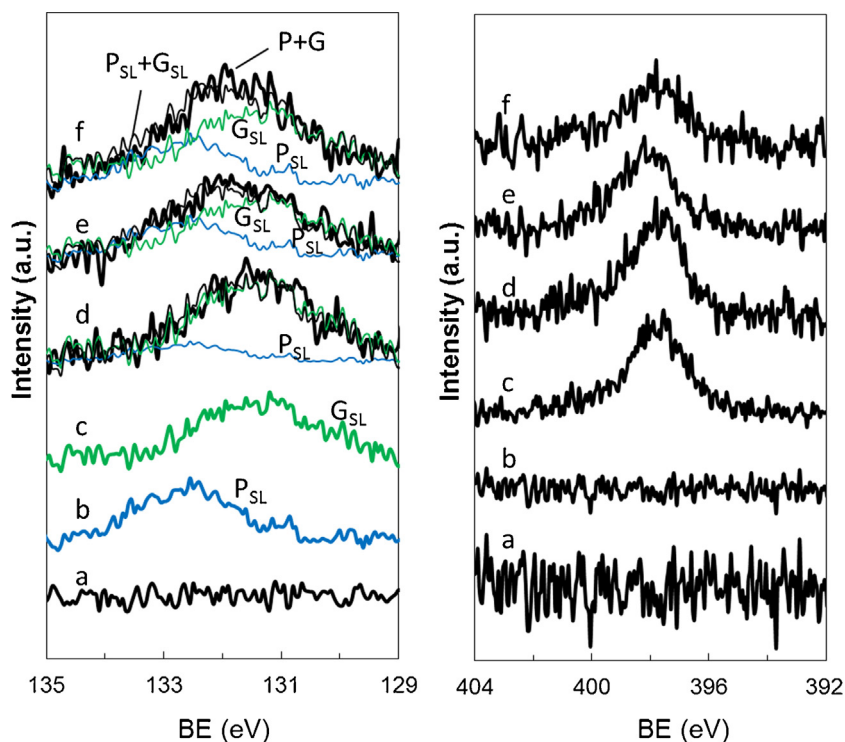
Fig. 3. P2p (left) and N1s (right) XPS spectra of goethite with (a) no adsorbed ligand, (b) adsorbed phosphate in single-ligand experiment (P_{SL}) with $P_{ads} \approx 1.5\,\mu\text{mol/m}^2$, (c) adsorbed glyphosate in single-ligand experiment (G_{SL}) with $G_{ads} \approx 1.2\,\mu\text{mol/m}^2$, and (d–f) adsorbed phosphate and glyphosate in double-ligand experiments with changing ligand concentrations. Thin lines in (d–f) show glyphosate and phosphate contributions and the sum of both contributions ($P_{SL} + G_{SL}$). (d) $P_{ads} \approx 0.25\,\mu\text{mol/m}^2$, $G_{ads} \approx 1.14\,\mu\text{mol/m}^2$; (e) $P_{ads} \approx 0.72\,\mu\text{mol/m}^2$, $G_{ads} \approx 0.90\,\mu\text{mol/m}^2$; (f) $P_{ads} \approx 0.63\,\mu\text{mol/m}^2$, $G_{ads} \approx 1.45\,\mu\text{mol/m}^2$.

N_S (5.73 μmol/m^2), V (0.01 L), $c_{P,T}$ and $c_{G,T}$, the values of P_{ads}, G_{ads}, c_P and c_G can be calculated if K_P, K_G, α_P and α_G are used as fitting parameters.

Predictions of Eqs. (1) and (2) for the single-ligand adsorption experiments are shown as lines in Fig. 1. The values of the parameters used in calculation are listed in the same figure. The value of N_S is the accepted value for goethite [30]. K_P and α_P were obtained by fitting the single-ligand phosphate isotherm with Eq. (1) using $c_G = 0$, whereas K_G and α_G were obtained by fitting the single-ligand glyphosate isotherm with Eq. (2) using $c_P = 0$. These parameters were then used to calculate the behavior of the system in double-ligand experiments (lines in Fig. 2a–c). Considering the simplicity of the Competitive Langmuir isotherm, the fact that the equations can reproduce well phosphate and glyphosate adsorption isotherms in single-ligand experiments, glyphosate adsorption isotherms at different total phosphate concentrations, the effects of increasing glyphosate concentration on the adsorption of phosphate, and the simultaneous adsorption of phosphate and glyphosate in double-ligand experiments strongly indicates that both substances compete for the same sites at the goethite surface. With the aid of Langmuir predictions it is easy to understand the behavior in double-ligand experiments, especially the P_{ads} vs. G_{ads} curves (Fig. 2c). At low total phosphate concentration P_{ads} was low and nearly constant (even though G_{ads} changed significantly) because there were sufficient sites for both substances at the surface. Contrarily, at high total phosphate concentration the surface was highly populated with either phosphate or glyphosate, the availability of surface sites was low, and thus there was a negative correlation between P_{ads} and G_{ads}, being the competition quite evident.

The zeta potential curves of pure goethite and goethite in the presence of either glyphosate, phosphate or a mix of both ligands are shown as supplementary material. The isoelectric point (IEP) of pure goethite was 8.3, and shifted towards lower values in the presence of ligands. Electrokinetic results are typical of spe-

cific adsorbing anions that form inner-sphere surface complexes [27,30,31]. Although they show that phosphate and glyphosate adsorb at the goethite surface, they are unable to reveal competitive adsorption.

Fig. 3 shows the XPS spectra of pure goethite, and goethite subject to adsorption of phosphate and glyphosate. The P2p BE of adsorbed phosphate occurs at 132.6 eV and that of glyphosate occurs at 131.2 eV. The difference in BE corresponds to the typical chemical shift that arises from the slightly different atomic environments that surround the emitting atom [32], P in this case: whereas P in phosphate is surrounded by four oxygens, P in glyphosate is surrounded by three oxygens and a carbon atom. The slightly more electronegative environment of P in phosphate results in a higher BE [32]. This ability of XPS is a desirable feature that allows distinguishing adsorbed phosphate from adsorbed glyphosate. Using appropriate weighting factors, the sum of the spectrum of phosphate and the spectrum of glyphosate obtained in single-ligand systems reproduces the spectra obtained in double-ligand systems, showing that the overall P2p signals result from the contribution of the individual signals of phosphate and glyphosate.

Fig. 3 also shows the N1s signal that appears on XPS spectra of samples containing glyphosate. The N1s BE of adsorbed glyphosate is the same (it only changes randomly by around 0.2 eV) regardless of whether phosphate is present or absent at the surface. It is known, for example, that changing the protonation state of nitrogen in the adsorbed glyphosate molecule changes the N1s BE by around 2 eV [2]. This implies that the BE could change somewhat if there is some lateral interaction, such as hydrogen bonds, between an adsorbed glyphosate and an adjacent phosphate. There is no indication of such an interaction.

Fig. 4a shows the ATR-FTIR spectra of glyphosate and phosphate adsorbed on goethite in single-ligand experiments. Spectral signals are observed in the 900–1500 cm^{-1} region, where bands assigned to P—O bonds of glyphosate and phosphate occur at
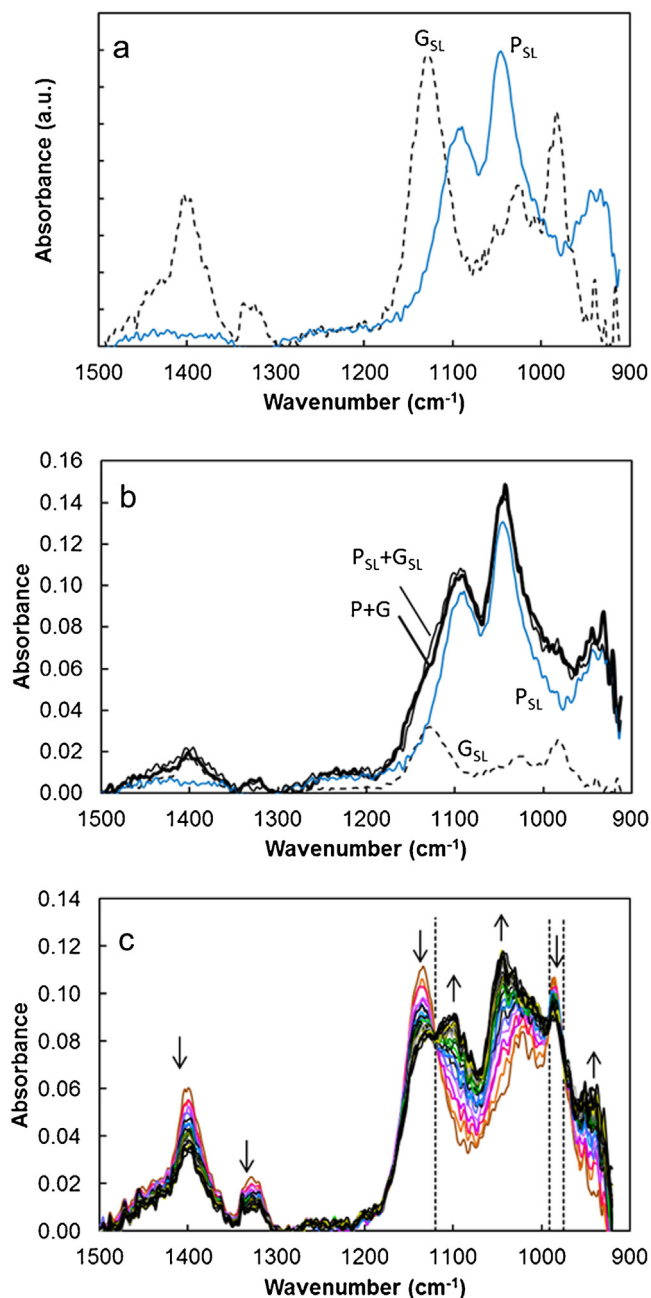
Fig. 4. (a) ATR-FTIR spectra of adsorbed glyphosate and adsorbed phosphate on goethite in single-ligand experiments (G_{SL} and P_{SL}, respectively). (b) Spectrum of adsorbed glyphosate and phosphate in a double-ligand experiment (thick line, P + G) compared to the sum spectrum obtained by adding the individual spectra of glyphosate and phosphate (thin line, P_{SL} + G_{SL}). (c) Spectra in double-ligand experiments obtained by adding phosphate to goethite with previously adsorbed phosphate. Arrows indicate the direction of changing spectra with time as reaction takes place. Dashed lines indicate the position of the isosbestic points.

900–1200 cm^{-1}, and bands assigned to the carboxylate group of glyphosate occur at 1300–1500 cm^{-1}. Based on previous works, the spectra correspond to inner-sphere surface complexes. In the case of phosphate, there is still some uncertainty about the surface complexation, either monodentate, bidentate or a mix of mono- and bidentate complexes [16–18,22,33]. In the case of glyphosate, the complex is mainly monodentate, with the phosphonate group coordinating surface iron [2,3,34]. A tentative band assignment for both adsorbed ligands is given in Supplementary material.

Fig. 4b shows the ATR-FTIR spectrum (thick line) obtained in a double-ligand experiment that resulted in the simultaneous adsorption of phosphate and glyphosate. The spectrum corresponds to an equilibrium situation. Using appropriate weighting factors, the sum of spectra obtained in single-ligand experiments reproduces very well the experimental spectrum. The results show that ATR-FTIR can detect both ligands adsorbed together in goethite, and that the overall IR signal results from the contribution of the individual signals of phosphate and glyphosate.

The above conclusion can also be drawn from kinetic data. Fig. 4c shows the evolution on time of spectra obtained in double-ligand experiments in the case where a phosphate solution was added to produce the partial desorption of a previously adsorbed glyphosate. There is a decrease in the intensity of glyphosate bands and a concomitant increase in phosphate bands as reaction proceeds, with the appearing of three isosbestic points at 1120, 991 and 975 cm^{-1}. These isosbestic points could be better observed if a smoothing spline is applied to the spectra (see Supplementary material). This kind of behavior was already informed for kinetic measurements at pH 4.5 [23], and it is now shown that it also occurs at pH 6.0. The existence of isosbestic points indicates that the shape of the individual glyphosate and phosphate bands did not change during the ligand-exchange reaction. The bands only change in intensity responding to changes in the respective concentrations of adsorbed glyphosate and phosphate.

Besides distinguishing adsorbed phosphate from adsorbed glyphosate, XPS and ATR-FTIR data can give useful information on the effects of one adsorbed ligand on the binding mode of the other. By binding mode we mean the type of surface complex or complexes that each ligand forms in its adsorbed state. In the case of phosphate in single-ligand systems, for example, it has been proposed that bidentate inner-sphere complexes are predominantly formed at low coverages in goethite, and that they change to a monodentate mode as surface coverage increases [17,22]. The rationale for why a monodentate complex should prevail at high surface coverages is that this mode should be favored as the surface P/Fe ratio increases [22]. In double-ligand systems such as glyphosate-phosphate on goethite, increasing the surface population with one ligand increases the P/Fe ratio and thus may affect the binding mode of the other ligand, either because of lack of site availability or because of lateral interactions. The results obtained in this work all converge towards the same conclusion, namely the presence of phosphate at the goethite surface does not alter the binding mode of glyphosate and *vice versa*. The conclusion is supported by the following evidences coming from the modelling of the adsorption isotherms and from XPS and IR spectra:

- In the case of adsorption isotherms, the Competitive Langmuir equations allowed a good fitting in double-ligand systems using the adsorbed species and adsorption parameters of single-ligand experiments. It seems then that the same phosphate and glyphosate species are present at the goethite surface in single-ligand and double-ligand systems.
- In the case of XPS, the overall P2p signal in double-ligand systems resulted from the contribution of the signals of phosphate and glyphosate in single-ligand systems. This indicates that the shape and position of the P2p signal of adsorbed phosphate were not modified by the presence of glyphosate at the surface and *vice versa*, showing that surface complexes in double-ligand systems were the same as in single-ligand systems. In addition, the N1s signal of adsorbed glyphosate only changed randomly its shape and position when phosphate was also present at the surface, suggesting that lateral interactions such as hydrogen bonds between adjacent species were not present, at least as seen from XPS. This

indicates that adsorbed phosphate did not change appreciably the structure and conformation of glyphosate at the surface.

- In the case of ATR-FTIR, since spectra of adsorbed phosphate and glyphosate are rather sensitive to their binding mode, it would be expected that the IR signals would change if one adsorbed ligand affects the binding mode of the other. This was not observed in any condition.

The findings are important in environmental modeling. They show that surface complexation models can be used with confidence to predict speciation of glyphosate and phosphate using adsorption parameters obtained in single-ligand experiments. If the same kind of behavior can be demonstrated for mixtures of other environmentally relevant anions, the use of surface complexation models in environmental modelling will become very reliable.

4. Conclusions

Goethite is an important adsorbent of both, the herbicide glyphosate and the fertilizer phosphate. Since both have similar coordinative properties, they adsorb on goethite forming inner-sphere surface complexes and compete for surface sites. Adsorption isotherms indirectly show that both substances coexist at the goethite surface. XPS and ATR-FTIR directly detect the simultaneous presence of adsorbed glyphosate and phosphate. Both surface spectroscopies indicate that the binding mode of one substance to the surface is not affected by the presence of the other substance, finding that is important in the modelling of double-ligand and perhaps in multiple-ligand systems.

Acknowledgments

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.colsurfa.2016.03.049.

References

[1] B. Barja, M. dos Santos Afonso, Aminomethylphosphonic acid and glyphosate adsorption onto goethite: a comparative study, Environ. Sci. Technol. 39 (2005) 585–592.
[2] J. Sheals, S. Sjöberg, P. Persson, Adsorption of glyphosate on goethite: molecular characterization of surface complexes, Environ. Sci. Technol. 36 (2002) 3090–3095.
[3] C.M. Jonsson, P. Persson, S. Sjöberg, J. Loring, Adsorption of glyphosate on goethite (α-FeOOH): surface complexation modeling combining spectroscopic and adsorption data, Environ. Sci. Technol. 42 (2008) 2464–2469.
[4] P. Sprankle, W.F. Meggitt, D. Penner, Adsorption, mobility, and microbial degradation of glyphosate in the soil, Weed Sci. 23 (3) (1975) 229–234.
[5] H.M. Dion, J.B. Harsh, H.H. Hill, Competitive sorption between glyphosate and inorganic phosphate on clay minerals and low organic matter soils, J. Radioanal. Nucl. Chem. 249 (2001) 385–390.
[6] H. de Jonge, L.W. de Jonge, Influence of pH and solution composition on the sorption of glyphosate and prochloraz to a sandy loam soil, Chemosphere 39 (5) (1999) 753–763.
[7] A.L. Gimsing, O.K. Borggaard, Effect of KCl and CaCl$_2$ as background electrolytes on the competitive adsorption of glyphosate and phosphate on goethite, Clays Clay Miner. 49 (2001) 270–275.
[8] A.L. Gimsing, O.K. Borggaard, Competitive adsorption and desorption of glyphosate and phosphate on clay silicates and oxides, Clay Miner. 37 (2002) 509–515.
[9] 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. 82 (2002) 545–552.
[10] A.L. Gimsing, O.K. Borggaard, M. Bang, Influence of soil composition on adsorption of glyphosate and phosphate by contrasting Danish surface soils, Eur. J. Soil Sci. 55 (2004) 183–191.
[11] A.L. Gimsing, C. Szilas, O.K. Borggaard, Sorption of glyphosate and phosphate by variable-charge tropical soils from Tanzania, Geoderma 138 (2007) 127–132.
[12] O.K. Borggaard, A.L. Gimsing, Fate of glyphosate in soil and the possibility of leaching to ground and surface waters: a review, Pest. Manag. Sci. 64 (2008) 441–456.
[13] Y.J. Wang, D.M. Zhou, R.J. Sun, Effects of phosphate on the adsorption of glyphosate on three different types of Chinese soils, J. Environ. Sci. 17 (2005) 711–715.
[14] B. Zhao, J. Zhang, J. Gong, H. Zhang, C. Zhang, Glyphosate mobility in soils by phosphate application: laboratory column experiment, Geoderma 149 (2009) 290–297.
[15] M.I. Tejedor-Tejedor, M.A. Anderson, The protonation of phosphate on the surface of goethite as studied by CIR-FTIR and electrophoretic mobility, Langmuir 6 (1990) 602–611.
[16] P. Persson, N. Nilsson, S. Sjoberg, Structure and bonding of orthophosphate ions at the iron oxide-aqueous interface, J. Colloid Interface Sci. 177 (1996) 263–275.
[17] R. Rahnemaie, T. Hiemstra, W.H. Van Riemsdijk, Geometry, charge distribution, and surface speciation of phosphate on goethite, Langmuir 23 (2007) 3680–3689.
[18] J.D. Kubicki, K.W. Paul, L. Kabalan, Q. Zhu, M.K. Mrozik, M. Aryanpour, A.-M. Pierre-Louis, D.R. Strongin, ATR-FTIR and density functional theory study of the structures, energetics, and vibrational spectra of phosphate adsorbed onto goethite, Langmuir 28 (2012) 14573–14587.
[19] B. Nowack, A.T. Stone, Competitive adsorption of phosphate and phosphonates onto goethite, Water Res. 40 (2006) 2201–2209.
[20] S. Goldberg, C.T. Johnston, Mechanisms of arsenic adsorption on amorphous oxides evaluated using macroscopic measurements, vibrational spectroscopy, and surface complexation modeling, J. Colloid Interface Sci. 234 (2001) 204–216.
[21] G. Sposito, The Surface Chemistry of Natural Particles, Oxford University Press, Oxford, U.K, 2004.
[22] D.B. Abdala, P.A. Northrup, Y. Arai, D.L. Sparks, Surface loading effects on orthophosphate surface complexation at the goethite/water interface as examined by extended X-ray Absorption Fine Structure (EXAFS) spectroscopy, J. Colloid Interface Sci. 437 (2015) 297–303.
[23] C.V. Waiman, M.J. Avena, A.E. Regazzoni, G.P. Zanini, A real time in situ ATR-FTIR spectroscopic study of glyphosate desorption from goethite as induced by phosphate adsorption: effect of surface coverage, J. Colloid Interface Sci. 394 (2013) 485–489.
[24] R.J. Atkinson, A.M. Posner, J.P. Quirk, Adsorption of potential-determining ions at the ferric oxide-aqueous electrolyte interface, J. Phys. Chem. 71 (1967) 550–559.
[25] C.V. Waiman, M.J. Avena, M. Garrido, B. Fernández Band, G.P. Zanini, A simple and rapid spectrophotometric method to quantify the herbicide glyphosate in aqueous media. Application to adsorption isotherms on soils and geothite, Geoderma 170 (2012) 154–158.
[26] J. Murphy, J.P. Riley, A modified single solution method for the determination of phosphate in natural waters, Anal. Chim. Acta 27 (1962) 31–36.
[27] 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. 285 (2005) 476–486.
[28] W. Stumm, Chemistry of the Solid-water Interface: Processes at the Mineral-Water and Particle-Water Interface in Natural Systems, John Wiley and Sons, Inc., New York, 1992.
[29] F. Molina, Soil Colloids: Properties and Ion Binding, CRC Press Taylor & Francis Group, 2013.
[30] T. Hiemstra, W.H. van Riemsdijk, A surface structural approach to ion adsorption: the charge distribution (CD) model, J. Colloid Interface Sci. 179 (1996) 488–508.
[31] M. Kosmulski, pH-dependent surface charging and points of zero charge. III Update, J. Colloid Interface Sci. 298 (2006) 730–741.
[32] J.F. Watts, X-ray photoelectron spectroscopy, in: J.M. Walls, R. Smith (Eds.), Surface Science Techniques, Pergamon, Elsevier, Oxford, 1994, pp. 5–23.
[33] J. Antelo, F. Arce, M. Avena, S. Fiol, R. López, F. Macías, Adsorption of a soil humic acid at the surface of goethite and its competitive interaction with phosphate, Geoderma 138 (2007) 12–19.
[34] L. Tribe, K.D. Kwon, C.C. Trout, J.D. Kubicki, Molecular orbital theory study on surface complex structures of glyphosate on goethite: calculation of vibrational frequencies, Environ. Sci. Technol. 40 (2006) 3836–3841.