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PHOSPHATE AND GLYPHOSATE ADSORPTION BY HEMATITE AND FERRIHYDRITE AND COMPARISON WITH OTHER VARIABLE-CHARGE MINERALS

ANNE LOUISE GIMSING* AND OLE KRAGHOLM BORGGAARD

Department of Natural Sciences, The Royal Veterinary and Agricultural University, Thorvaldsensvej 40,
DK-1871 Frederiksberg C, Denmark

Abstract—Adsorption by synthetic 2-line ferrihydrite and hematite of glyphosate and phosphate, separately and together, was compared with adsorption results for goethite, gibbsite and two kaolinites in order to determine adsorption differences and similarities, in particular competition and phosphate preference, of these variable-charge minerals. Hematite rapidly adsorbed both compounds, while adsorption by ferrihydrite was slow, in particular of glyphosate, probably because of very slow diffusion of the bulky glyphosate molecules into interior sites in ferrihydrite particles. Accordingly, the Langmuir adsorption capacity of glyphosate (G_{AC}) was considerably smaller (1.85 μmol m^{-2}) than G_{AC} for hematite (2.61 μmol m^{-2}). The phosphate adsorption capacities (P_{AC}) for ferrihydrite and hematite were more alike, 2.91 μmol m^{-2} and 2.85 μmol m^{-2}, respectively. Differences between surface coordination (mono- or bidentate) may also contribute to the observed differences but conflicting information about the nature of the surface complexes makes this a difficult contributary factor to assess. The minerals were found to exhibit great variation in extent of competition and phosphate preference. Little competition and phosphate preference characterized hematite adsorption, while phosphate almost completely outcompeted glyphosate on goethite; ferrihydrite adsorption fell between these extremes. These differences may be attributed to different numbers of common (competitive) and specific (selective) adsorption sites on the three Fe oxides with a decreasing number of common sites in the order: goethite>>ferrihydrite>hematite, *i.e.* almost all goethite sites are common but with strong phosphate preference, while most hematite sites are specific for either glyphosate or phosphate. Alternatively, the result may be explained by adsorption in more planes, *e.g.* glyphosate adsorption onto the inner-Helmholtz-plane-adsorbed phosphate. For all six minerals compared, desorption of glyphosate following phosphate addition was found to be significantly correlated with the difference between the amounts of phosphate and glyphosate adsorbed indicating that this difference may be used as a competition index for predicting the influence of phosphate on glyphosate adsorption.

Key Words—Competitive Adsorption, Ferrihydrite, Glyphosate, Hematite, Phosphate, Variable-charge Minerals.

INTRODUCTION

The herbicide, glyphosate (*N*-phosphonomethylglycine), is adsorbed in a way similar to phosphate, by ligand exchange through its phosphonate moiety. This indicates that the two compounds may compete for adsorption sites (Barja and Afonso, 2000; Sheals *et al.*, 2002; Dideriksen and Stipp, 2003; Barja and dos Santos Afonso, 2005). Several studies have been performed on the competitive adsorption of glyphosate and phosphate both on pure minerals (such as oxides and clay silicates) and in soils with different characteristics (Sprankle *et al.*, 1975a, 1975b; McBride and Kung, 1989; de Jonge *et al.*, 2001; Dion *et al.*, 2001; Gimsing and Borggaard, 2001, 2002b; Dideriksen and Stipp, 2003; Kogan *et al.*, 2003; Gimsing *et al.*, 2004; Wang *et al.*, 2005). These studies show that the adsorption of glyphosate is affected by the presence of phosphate, and glyphosate adsorption in soils seems correlated with unoccupied phosphate adsorption capacity and it has also been found that phosphate can desorb significant amounts of glyphosate from both soils and pure minerals (Hance, 1976; Dion *et al.*, 2001; Kogan *et al.*, 2003; Gimsing *et al.*, 2004; Wang *et al.*, 2005). These studies indicate that there is competition between glyphosate and phosphate for adsorption sites and that phosphate is preferentially adsorbed but the extent of competition and phosphate preference is very mineral and soil-dependent. Regarding competition and phosphate preference, adsorption by goethite is extreme inasmuch as pre-adsorption of phosphate eliminated glyphosate adsorption and pre-adsorbed glyphosate was desorbed by phosphate addition (Gimsing and Borggaard, 2001). Whether the goethite behavior is unusual or common to Fe oxides is unknown as adsorption of glyphosate alone and together with phosphate has only been tested previously with one Fe oxide, goethite.

The aims of this study are therefore: (1) to present results on the adsorption of glyphosate and phosphate by hematite and ferrihydrite (which, to our knowledge, is

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* E-mail address of corresponding author:
angi@kvl.dk
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the first such report on glyphosate adsorption to ferrihydrite and one of the first on its adsorption to hematite); and (2) to compare these results with similar results obtained with other variable-charge minerals including goethite, gibbsite and kaolinite.

MATERIALS AND METHODS

So-called 2-line ferrihydrite (Schwertmann and Cornell, 1991) was synthesized by rapid hydrolysis of $Fe(NO_3)_3{\cdot}9H_2O$ at pH ~7 in the following way: 202 g of $Fe(NO_3)_3{\cdot}9H_2O$ were dissolved in 50 mL of 2 M HNO_3 and 200 mL of water by boiling for 10 min. After cooling to room temperature, ~800 mL of 2 M NaOH were added drop-wise under vigorous stirring and cooling until pH 7. Vigorous stirring was continued for a further 1 h. The Fe oxide precipitate was isolated by centrifugation and washed twice with water, twice with ethanol and once with acetone. Finally the precipitate was air dried.

Hematite was prepared by heating a portion of synthesized ferrihydrite to 350ºC for 16 h in an electric furnace.

The mineralogy of the products was assessed by X-ray diffraction (XRD) on a Siemens D5000 instrument using CoKα radiation. An XRD pattern (Figure 1, upper) is characteristic of 2-line ferrihydrite. The other XRD pattern (Figure 1, lower) shows the characteristic hematite peaks but also the occurrence of an impurity (possibly $NaHCO_3$). The specific surface area (SSA) was determined by applying the BET equation to N_2 adsorption. The ferrihydrite and hematite had surface areas of 343 $m^2\ g^{-1}$ and 33 $m^2\ g^{-1}$, respectively.

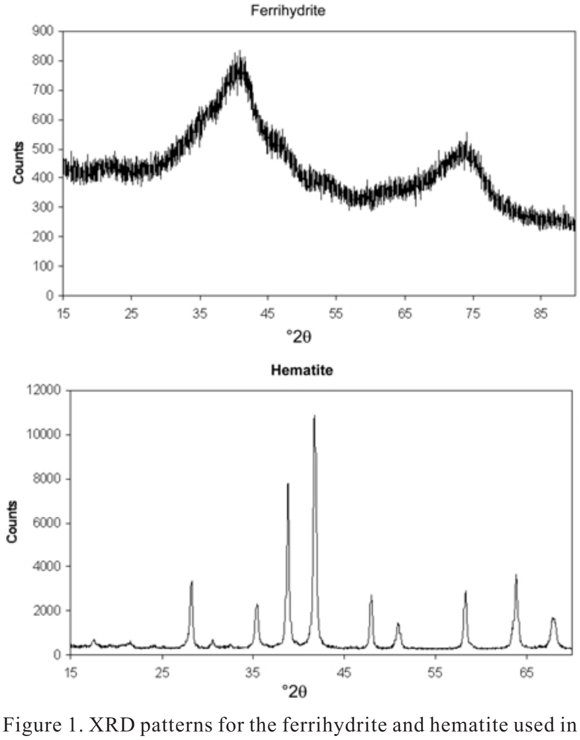

Figure 1. XRD patterns for the ferrihydrite and hematite used in this study. CoKα radiation.

The competition experiment between glyphosate and phosphate for adsorption sites was conducted as described by Gimsing and Borggaard (2002a). Briefly, 0.80 g of hematite or 0.20 g of ferrihydrite were transferred to a glass bottle and 381.5 mL of 0.1 M KCl were added as background electrolyte and 16 mL of 2.5 wt.% NaN_3 (sodium azide) solution were added to prevent glyphosate degradation. Before application of glyphosate or phosphate, the sample pH was adjusted to 7.0 by addition of KOH or HCl over the period of 1 week. Then, at time zero, 2.5 mL of 80 mM glyphosate (purified from a glyphosate concentrate from Cheminova (Lemvig, Denmark)) containing ^{14}C-labeled glyphosate (150 µL ^{14}C-labeled glyphosate solution in 100 mL of 80 mM glyphosate solution) or 80 mM phosphate solution (KH_2PO_4) were added to the suspensions that were kept under constant magnetic stirring. The ^{14}C-labeled glyphosate (200 µCi/mL, 55 mCi/mmol) was from Amersham Pharmacia Biotech (Hørsholm, Denmark). The initial glyphosate or phosphate concentration in the reaction bottle was 0.5 mM. To follow the reaction between the oxides and phosphate or glyphosate, eight 4 mL suspension aliquots were taken at appropriate time intervals from the reaction bottles and filtered through a 0.2 µm filter and the glyphosate and phosphate concentrations were measured as described below. After 6 days, 80 mM glyphosate was added to the reaction bottle with phosphate and 80 mM phosphate was added to the reaction bottle with glyphosate. The added volumes brought the concentration in the bottle to 0.5 mM. Again, eight 4 mL samples were taken during the following 6 days. After the last samples were taken, the pH in the reaction bottles was measured. In all experiments, the pH had only increased by 0.13−0.26 units.

The phosphate and glyphosate adsorption capacities were determined by applying the Langmuir equation to adsorption data obtained as follows: eight portions of 50 mg ferrihydrite or 200 mg hematite were suspended in 50 mL of 0.1 M KCl with 0.1 wt.% NaN_3 containing 0−2.0 mM glyphosate or 0−2.0 mM phosphate (KH_2PO_4) adjusted to pH 7.0 and shaken on a reciprocal shaker for a total of 4 days. The glyphosate was taken from the 80 mM glyphosate spiked with ^{14}C-labeled glyphosate described above. After shaking and centrifugation, the supernatant was filtered through a 0.2 µm Millipore filter and the glyphosate or phosphate concentrations were determined as described above. Adsorbed glyphosate or phosphate, which was taken as the difference between concentrations before and after shaking, was fitted by non-linear regression to the Langmuir equation by use of the procedure nlin in SAS V9. The calculated adsorption maxima were considered the glyphosate adsorption capacity (G_{AC}) and phosphate adsorption capacity (P_{AC}), respectively.

The glyphosate concentration in the clear filtrates was measured by liquid scintillation counting using an OptiPhase HiSafe-2 scintillation cocktail from Wallac (Turku, Finland) (5.00 mL scintillation cocktail to 0.50 mL sample). The measurements were made using a Wallac WinSpectral 1414 liquid scintillation counter. Phosphate was determined by flow injection analysis by the molybdenum blue/stannous chloride method using a Tecator FIAstar 5010 Analyzer with a 5027 sampler.

The experiments were done in triplicate. The amount adsorbed was determined by subtracting the solution concentration from the amount, which was added initially.

RESULTS AND DISCUSSION

Adsorption by ferrihydrite and hematite

According to the X-ray results (Figure 1), the ferrihydrite is clearly 2-line ferrihydrite (*e.g.* Schwertmann *et al.*, 1999), while the hematite, even though the XRD pattern shows all the characteristic hematite peaks, may differ from hematite *sensu stricto* as described by Barrón and Torrent (1996). Conversion of ferrihydrite to hematite by heating is very dependent on experimental conditions such as water content (Schwertmann *et al.*, 1999). Therefore, the hematite used in this investigation, which is formed by heating ferrihydrite to 350ºC for 16 h, is probably still 'coated' with reactive OH groups and has retained the spherical morphology of ferrihydrite. However, in contrast to ferrihydrite, the OH groups on the hematite are readily available for adsorption of glyphosate and phosphate as shown by slow reaction with ferrihydrite but fast reaction with hematite in Figure 2.

By means of the Langmuir equation, the glyphosate adsorption capacity (G_{AC}) was found to be 635 mmol kg^{-1} for ferrihydrite and 86 mmol kg^{-1} for hematite, while the phosphate adsorption capacity (P_{AC}) was 998 mmol kg^{-1} for ferrihydrite and 94 mmol kg^{-1} for hematite, respectively. However, if the difference between the specific surface area (SSA) of ferrihydrite (343 m^2 g^{-1}) and hematite (33 m^2 g^{-1}) is accounted for, G_{AC} is 1.85 μmol m^{-2} for ferrihydrite and 2.61 μmol m^{-2} for hematite, while P_{AC} is 2.91 μmol m^{-2} for ferrihydrite and 2.85 μmol m^{-2} for hematite. For phosphate, these adsorption capacities are within the broad range of 1.1−4.7 μmol m^{-2} reported in the literature (Torrent, 1997; Arai and Sparks, 2001; Borggaard *et al.*, 2005). Unfortunately, there does not seem to be any information available about the adsorption of glyphosate by ferrihydrite, but for hematite, McConnell and Hossner (1985) found a glyphosate adsorption of 2.7−4.6 μmol m^{-2}, so our G_{AC} is in the lower end of the range reported by McConnell and Hossner (1985).

As shown in Figure 2, G_{AC} and P_{AC} are slightly larger but in good agreement with the amounts of glyphosate and phosphate adsorbed by the two Fe oxides during the first 6 days from an initially 0.5 mM glyphosate or phosphate solution. Adsorptions of both glyphosate and phosphate by hematite reached equilibrium within a few hours, while adsorption by ferrihydrite was rather slow and seemed to continue beyond 6 days. For phosphate, this behavior is in agreement with previous results showing fast adsorption by well crystallized Fe oxides with easily accessible outer adsorption sites but slow adsorption by poorly ordered ferrihydrite, probably because of time-consuming diffusion into less accessible interior sites or because of precipitation (Willett *et al.*, 1988; Torrent, 1997; Mikutta *et al.*, 2006). Different adsorption rates of glyphosate may, at least partly, explain why G_{AC} for ferrihydrite (1.85 μmol m^{-2}) is considerably less than G_{AC} for hematite (2.61 μmol m^{-2}). For ferrihydrite, slower adsorption of

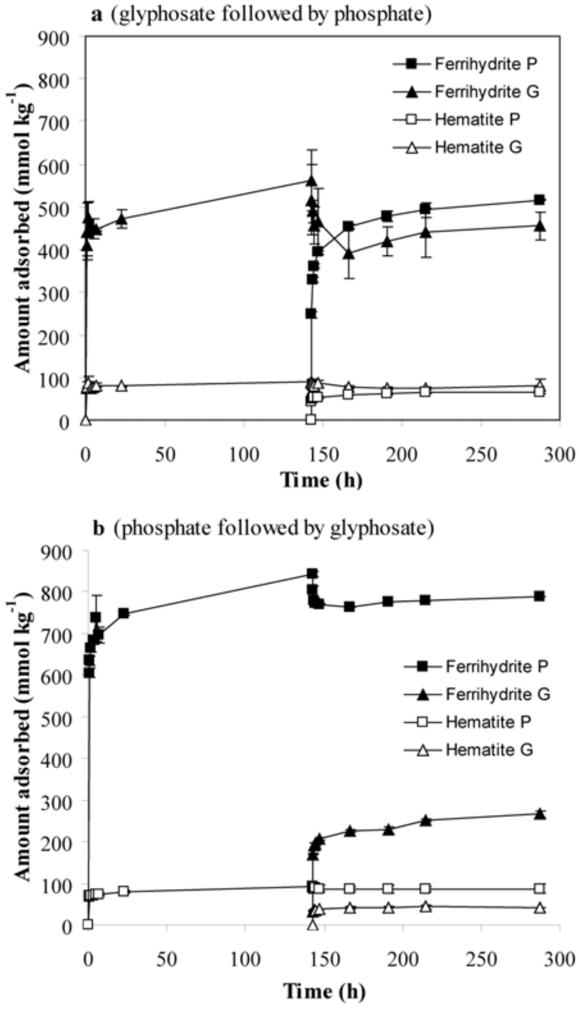

Figure 2. Adsorption of glyphosate (G) and phosphate (P) by hematite and ferrihydrite. (a) Glyphosate applied at time zero and phosphate added after 143 h; (b) phosphate added at time zero and glyphosate after 143 h. Error bars show the standard deviation.

glyphosate than phosphate may be the reason for the different amounts adsorbed, namely 1.85 μmol m^{-2} for glyphosate but 2.91 μmol m^{-2} for phosphate. The larger and bulkier glyphosate ions compared to phosphate ions (Gimsing and Borggaard, 2001; Dideriksen and Stipp, 2003) may be anticipated to have a lower diffusion rate into ferrihydrite particles than phosphate resulting in less glyphosate being adsorbed during 4 days, *i.e.* before establishment of equilibrium (Figure 2), or it may be that some sites are inaccessible to glyphosate.

Alternatively, formation of different surface complexes between the two compounds and ferrihydrite may explain why less glyphosate than phosphate is adsorbed. Studies of the surface complexes mainly of goethite by spectroscopic, atomic force microscopic and other surface techniques indicated that phosphate is adsorbed by Fe oxides under the formation of mainly bidentate, binuclear complexes (Martin and Smart, 1987; Tejedor-Tejedor and Anderson, 1990; Arai and Sparks, 2001), while monodentate coordination seems to dominate glyphosate adsorption (Sheals *et al.*, 2002; Dideriksen and Stipp, 2003; Barja and dos Santos Afonso, 2005). Studies of glyphosate complexes with Fe show that both the phosphonate and the carboxylate moiety will coordinate with Fe in the solid state (but not in solution) (Barja *et al.*, 2001) which may also explain why less glyphosate than phosphate can be adsorbed. However, the precise nature of the surface complexes is still a matter of dispute because the coordination number depends on pH and concentrations as well as interpretation of the results of the surface techniques (Tejedor-Tejedor and Anderson, 1990; Persson *et al.*, 1996; Arai and Sparks, 2001; Sheals *et al.*, 2002; Dideriksen and Stipp, 2003). Consequently, although monodentate and bidentate coordination seems to dominate glyphosate and phosphate adsorption, respectively, the information available is too uncertain to draw safe conclusions. Therefore, it is still unresolved whether or not the formation of different surface complexes contributes to the observation that ferrihydrite adsorbs considerably less glyphosate (1.85 μmol m^{-2}) than phosphate (2.91 μmol m^{-2}).

Comparison with other variable-charge minerals

In contrast to ferrihydrite and hematite, glyphosate adsorption by goethite has been the subject of several studies (Gimsing and Borggaard, 2001; Sheals *et al.*, 2002; Dideriksen and Stipp, 2003; Barja and dos Santos Afonso, 2005), which indicate that although monodentate surface complexes probably dominate, bidentate complexation cannot be ruled out. The comparable amounts of glyphosate adsorbed by ferrihydrite, goethite and hematite (Figure 3) indicate the formation of similarly coordinated surface complexes for all three Fe oxides, probably dominated by monodentate coordination but as already noticed, the precise nature of the surface complexes is still unresolved.

When compared with results obtained in similar experiments as in Figure 2 with other variable-charge minerals (Figure 3), oxides and clay silicates generally adsorb more phosphate than glyphosate, except hematite, where equal amounts are adsorbed. Figure 3 also shows that the ability to adsorb glyphosate and phosphate differs among the minerals with goethite adsorbing most phosphate, while most glyphosate was adsorbed by hematite. Kaolinite adsorbed much less of both glyphosate and phosphate when compared to the oxides, a tendency which is also seen for other clay silicates such as illite and montmorillonite (Gimsing and Borggaard, 2002a). The smaller amounts adsorbed by the kaolinites compared to the oxides agree with previous results for phosphate adsorption by kaolinites (Sei *et al.*, 2002). For gibbsite, goethite and kaolinites, where the adsorption equilibrium was achieved within a few hours (Gimsing and Borggaard, 2002) as for hematite (Figure 2), the observed difference between the amounts of glyphosate and phosphate adsorbed may be ascribed to steric reasons because of the larger size of glyphosate compared to phosphate (Gimsing and Borggaard, 2001; Dideriksen and Stipp, 2003), although differences in the surface complexes cannot be ruled out as a possible additional explanation.

Differences between the Fe oxides in adsorption behavior may very well also be due to differences in the structure of the surface groups participating in the specific adsorption of glyphosate and phosphate. Unfortunately, studies on the structure of the surface groups were not performed as a part of this project, but it may be expected that the different oxides will have different surface properties, which may influence adsorption (Barrón and Torrent, 1996; Schwertmann *et al.*, 1999).

Competitive adsorption

Glyphosate and phosphate compete to some extent for adsorption sites on ferrihydrite as phosphate addition leads to desorption of glyphosate (Figure 2a) and glyphosate addition is followed by desorption of some

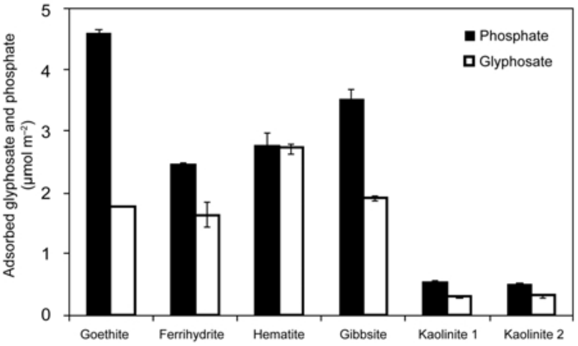

Figure 3. Glyphosate and phosphate adsorbed by the various minerals in μmol m^{-2} (initial concentration of both glyphosate and phosphate was 0.5 mM). Error bars show the standard deviation.

phosphate (Figure 2b). On hematite, the ability of the adsorbates to desorb each other is less pronounced (Figure 2). The competition can, however, also be seen from the ability of the two compounds to suppress the adsorption of each other. Thus, from Figure 2a it can be seen that the adsorption of glyphosate on ferrihydrite without phosphate present is 561 mmol kg^{-1} but when phosphate is already adsorbed, only 265 mmol kg^{-1} glyphosate can be adsorbed (Figure 2b). This suppression is also observed for hematite indicating competition between the two anions for at least some adsorption sites. Judged from the ability to desorb each other and from adsorption depression, phosphate is the strongest competitor in accordance with previous results for other adsorbents (Gimsing and Borggaard, 2002).

The sum of glyphosate and phosphate adsorbed during the entire adsorption period, *i.e.* after 12 days (286 h) depends on the order of application (Figure 2). If glyphosate is adsorbed first (Figure 2a) then the total amounts adsorbed are 971 mmol kg^{-1} and 147 mmol kg^{-1} for ferrihydrite and hematite, respectively, while 1054 mmol kg^{-1} (ferrihydrite) and 128 mmol kg^{-1} (hematite) in total are adsorbed if phosphate is added first (Figure 2b). The influence of the order in which glyphosate and phosphate are added has previously been reported for other adsorbents (Gimsing and Borggaard, 2002) as well as for competitive adsorption of phosphate with other adsorbates (Borggaard *et al.*, 2005; Mikutta *et al.*, 2006).

The sums of glyphosate and phosphate adsorbed correspond to 2.83 μmol m^{-2} and 3.07 μmol m^{-2} for ferrihydrite but for hematite they correspond to 4.45 μmol m^{-2} and 3.88 μmol m^{-2}, respectively. For ferrihydrite, the average sum of glyphosate and phosphate adsorbed (2.95 μmol m^{-2}) equals the phosphate adsorption capacity, P_{AC} = 2.91 μmol m^{-2}, while the adsorption by hematite nearly doubles in the presence of both compounds (average 4.17 μmol m^{-2}) compared to P_{AC} (2.85 μmol m^{-2}). The different 'adsorbabilities' of ferrihydrite and hematite may be interpreted as different numbers of common (competitive) and specific (selective) adsorption sites on the two adsorbents. Common sites can adsorb both glyphosate and phosphate, while specific sites either accept glyphosate or phosphate, *i.e.* glyphosate and phosphate compete for common sites but not for specific sites. On ferrihydrite, most sites are common, while specific sites dominate on hematite. Accordingly, competition is more pronounced for ferrihydrite than for hematite (Figure 2) and relatively more glyphosate or phosphate is desorbed from ferrihydrite than from hematite by addition of the other adsorbate (Figure 4). Stronger competition is seen for gibbsite and, in particular, for goethite (Figure 4). In fact, almost all adsorption sites on goethite are common sites with a strong preference for phosphate as shown by nearly complete desorption of glyphosate following phosphate addition and negligible glyphosate adsorption by phosphate-saturated goethite (Figure 4; Gimsing and Borggaard, 2001). The observed large adsorption capacity in the presence of both compounds may also be caused by adsorption in different planes, *e.g.* glyphosate adsorption onto phosphate groups bound at the inner-Helmholtz plane as suggested by Nowack and Stone (2006) for the competitive adsorption of various phosphonates and phosphate. This would give an increase in the observed adsorption capacity, but surface techniques have to be employed to determine the precise adsorption mechanism(s).

A comparison of the results in Figures 3 and 4 indicates that the extent of competition and phosphate preference can be related to the difference in the amounts of phosphate and glyphosate adsorbed, *i.e.* the greater the difference between adsorbed glyphosate and phosphate, the more glyphosate is desorbed and the greater the preference for phosphate. This is most obvious when comparing the results for goethite and hematite, but it is shown more generally in Figure 5, where the percentage of glyphosate desorbed by phosphate is seen to be significantly correlated with the difference between adsorbed phosphate and adsorbed

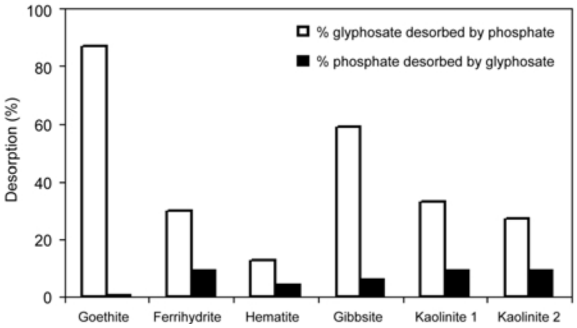

Figure 4. Ability of phosphate to desorb glyphosate and the ability of glyphosate to desorb phosphate measured as the % of previously adsorbed glyphosate or phosphate which is desorbed by phosphate or glyphosate, respectively.

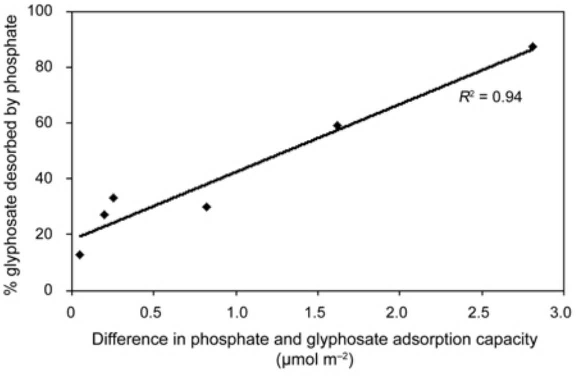

Figure 5. The percentage of glyphosate desorbed by phosphate addition as a function of the difference in the amounts of adsorbed phosphate and adsorbed glyphosate.

glyphosate. The relationship in Figure 5 indicates that the difference between adsorbed phosphate and glyphosate may serve as an index of competition, which may be used to predict the influence of phosphate on glyphosate adsorption.

From an environmental point of view, Figure 5 indicates that phosphate fertilization may seriously increase the risk of water pollution with glyphosate that may be desorbed and leached in soils dominated by minerals behaving like goethite. In contrast, soils that possess mainly specific adsorption sites may behave like hematite, *i.e.* phosphate addition will have limited effect on glyphosate desorption and leaching. Accordingly, studies have shown substantial desorption of glyphosate after phosphate addition for some soils, while on other soils phosphate application has a limited effect on release or adsorption of glyphosate (Hance, 1976; de Jonge *et al.* 2001; Dion *et al.*, 2001; Kogan *et al.*, 2003; Gimsing *et al.*, 2004; Vereecken, 2005; Wang *et al.*, 2005).

Another important result of this investigation is the indicated risk of serious mistakes, which may result from simple extrapolation from one mineral to another even with minerals belonging to the same group such as Fe oxides. This is clearly demonstrated by the very different behavior of ferrihydrite, goethite and hematite.

CONCLUSIONS

Similar Langmuir phosphate adsorption capacities (P_{AC}), in good agreement with the literature, were found for ferrihydrite (2.91 μmol m^{-2}) and hematite (2.85 μmol m^{-2}), while the Langmuir glyphosate adsorption capacity (G_{AC}) was slightly less for hematite (2.61 μmol m^{-2}) but substantially less for ferrihydrite (1.85 μmol m^{-2}). The relatively small G_{AC} for ferrihydrite was mainly attributed to slow diffusion of glyphosate into ferrihydrite particles in contrast to fast adsorption by hematite. In addition, different coordination of the surface complexes, *i.e.* bidentate coordination dominating phosphate adsorption but the larger glyphosate molecule forming mainly monodentate complexes, may also contribute to the observed differences, although the precise nature of the surface complexes is still uncertain. When present together, glyphosate and phosphate compete for adsorption sites on ferrihydrite and hematite as well as on other variable-charge minerals. However, the extent of competition and phosphate preference depend on the mineral type even within the same mineral group, in the case of Fe oxides. Strong competition and phosphate preference characterize adsorption by goethite, while adsorption by hematite exhibits limited competition and phosphate preference and with ferrihydrite adsorption falling in between. These differences are attributed to different contents of common (competitive) and specific (selective) adsorption sites, where goethite almost exclusively has common sites with high phosphate preference whereas most hematite sites are specific for either glyphosate or phosphate. Alternatively, adsorption in more planes may explain the behavior of the two adsorbates when added together. For all variable-charge minerals tested, desorption of glyphosate following phosphate addition was found to be significantly correlated with the difference between the amounts of phosphate and glyphosate adsorbed indicating that this difference may be used as a competition index for predicting the influence of phosphate on glyphosate adsorption.

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