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Anne Louise Gimsing^a; Ole K. Borggaard^a

^a Department of Chemistry, Royal Veterinary and Agricultural University, Frederiksberg C., Denmark

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EFFECT OF PHOSPHATE ON THE ADSORPTION OF GLYPHOSATE ON SOILS, CLAY MINERALS AND OXIDES

ANNE LOUISE GIMSING* and OLE K. BORGGGAARD

*Department of Chemistry, Royal Veterinary and Agricultural University,
Thorvaldsensvej 40, DK-1871 Frederiksberg C., Denmark*

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The effect of phosphate (ortho-phosphate) on the adsorption of the widely used glyphosate herbicide was evaluated with three typical Danish agricultural soils as well as pure oxides (goethite, FeOOH and gibbsite, Al(OH)₃) and silicates (illite and montmorillonite), which are considered the most important glyphosate and phosphate adsorbents in soils. Batch experiments were made in order to find out how phosphate affects adsorption of glyphosate and how glyphosate affects adsorbed phosphate. Solution glyphosate was quantified by liquid scintillation counting of ¹⁴C-tagged herbicide and the concentration of phosphate by the molybdenum blue method. All experiments showed competition between phosphate and glyphosate for adsorption sites but the various adsorbents exhibited great variation in affinity for glyphosate and phosphate. Thus, gibbsite and, in particular goethite strongly prefer phosphate, whereas the competition on the silicates is more equal. The current studies showed that the competition in soils is almost equal, but still phosphate affects the sorption of glyphosate in soil.

The amount of glyphosate and phosphate adsorbed by the various kinds of adsorbents was found to decrease in the order: oxides > silicates > soils. For the soils tested aluminium oxides, and to a lesser extent iron oxides seem the most important components in determining a soil's ability to adsorb phosphate and glyphosate, whereas the clay content and clay type seem of minor or little importance for adsorption of these species.

Keywords: Competitive adsorption; Distribution coefficient; Glyphosate; Phosphate; Oxides; Clay silicates; Soils

INTRODUCTION

Glyphosate (*N*-phosphonomethylglycine) is among the most commonly used herbicides worldwide [1]. It has been found that the phosphate concentration is a very important factor in determining the amount of glyphosate, which can be sorbed. Phosphate is in some cases able to completely desorb glyphosate, probably because glyphosate and phosphate are adsorbed onto soil solids by similar mechanisms, due to the phosphonic acid moiety in the glyphosate molecule [2–7]. Phosphate may thus play an important role in determining the bioavailability and leaching potential of glyphosate in soil.

*Corresponding author. Fax: +45-35282398. E-mail: angi@kvl.dk

Studies of the competitive adsorption of glyphosate and phosphate, and hence greater knowledge of how phosphate affects the adsorption of glyphosate, are important because of increasing use of glyphosate [1]. It is also important because many agricultural soils, for example in Denmark and other parts of Western Europe, are considered saturated with phosphate because they have been fertilized for many years with phosphate in excess of uptake by plants [8].

The competitive adsorption of glyphosate and phosphate on clay minerals and oxides has previously been reported [7,9]. The aim of this study is to compare the adsorption of glyphosate and phosphate by pure clay silicates and oxides with the adsorption by three Danish soils of different origin and composition, in order to gain deeper insight into the factors that determine the adsorption of glyphosate and phosphate in soils. This may help to better understand the effect phosphate has on the adsorption of glyphosate in the soil environment.

EXPERIMENTAL

The glyphosate used in this study was purified from a glyphosate concentrate from Cheminova (Lemvig, Denmark). To 150 mL of glyphosate, 37% hydrochloric acid was added until pH was ~ 1 . The solution was maintained at $\sim 4^\circ\text{C}$ for approximately 15 h, which resulted in the precipitation of glyphosate crystals. The crystals were isolated and then dissolved in hot triple-distilled water and filtered into an Erlenmeyer flask. Ethanol was added to the glyphosate solution and the sample was stored at $\sim 4^\circ\text{C}$ for 2 d. The recrystallization process was repeated and the resulting crystals washed with ethanol and dried in a desiccator. The purity of the glyphosate crystals was tested by Fourier transform infrared (FT-IR) analysis (KBr technique on a Perkin Elmer system 2000 FT-IR) and by measuring C and N contents (in an integrated LECO apparatus). Both tests showed that the glyphosate was 99–100 % pure.

The soils used were from the A-horizon of three Danish soils (Fig. 1). All three soils are agricultural soils, and they are representative of the soils found in Denmark. In Table I basic properties of the soils are summarized. The soils were air-dried and sieved through a 2 mm sieve before use. Syntheses of the aluminium and iron oxides (gibbsite and goethite) as well as origin and purification of the clay silicates (illite and montmorillonite) are described elsewhere [9].

The adsorption experiments were conducted by transferring 40.0 g of soil, 0.80 g of oxide or 4.0 g of clay silicate to a glass bottle and adding 381.5 mL 0.1 M KCl as background electrolyte and 16 mL 2.5 wt% NaN_3 (sodium azide) solution. Consequently, the solid: solution ratios were 100 g/L (soils), 2 g/L (oxides) and 10 g/L (silicates), respectively. More details on the experiments with the minerals can be found elsewhere [9]. The azide was added to prevent glyphosate degradation. Sample pH was adjusted to 7.0 by addition of KOH or HCl. One week was used for the pH adjustment, and the soils were under stirring 1–2 h each day during this week. At time zero, 2.5 mL of 80 mM glyphosate 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) was added to the suspensions, which were kept under constant magnetic stirring. For these experiments, ^{14}C -labelled glyphosate (200 $\mu\text{Ci}/\text{mL}$, 55 mCi/mmol) from Amersham Pharmacia Biotech (Hørsholm, Denmark) was used. The glyphosate or phosphate concentration in the reaction

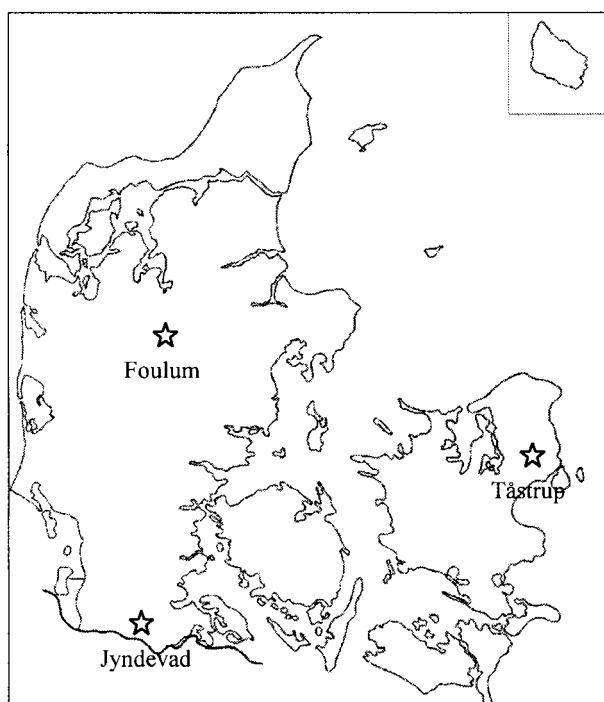


FIGURE 1 Map of Denmark with the three soil sampling sites.

TABLE I Characteristics of the three soils. Fe_{ox} and Al_{ox} is oxalate extractable Fe and Al. Fe_{cbd} and Al_{cbd} is citrate-bicarbonate-dithionite extractable Fe and Al. CEC is cation exchange capacity

Soil	pH_{CaCl_2}	% C	Olsen P [mg/kg]	Total P [mg/kg]	Max P sorption [μmol/g]	% Fe_{ox}	% Al_{ox}	% Fe_{cbd}	% Al_{cbd}	CEC [cmol(+)/kg]	% Clay < 2 μm	% Silt 2–20 μm	% Sand 20–2000 μm
Jyndevad	5.9	1.6	28.1	444.3	20.0	0.16	0.078	0.313	0.104	13.3	2.9	0.9	96.2
Foulum	5.7	1.2	24.9	915.8	28.5	0.23	0.156	0.343	0.137	14.4	9.7	7.6	82.7
Tåstrup	6.5	1.3	15.6	619.7	27.4	0.27	0.082	0.573	0.064	22.0	14.1	10.6	75.4

bottle was 0.5 mM. To follow the reaction between the soils and phosphate or glyphosate, 4.00 mL suspension aliquots were taken from the reaction bottles and filtered through a 0.45 μm filter. Within the first day after the application three samples were taken, and for the following days one sample was taken each day. After seven 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, samples were taken during the following seven days.

The glyphosate concentration in the 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 [10,11] 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 initially added.

RESULTS AND DISCUSSION

In Fig. 2 the adsorption of glyphosate followed by phosphate, and phosphate followed by glyphosate on the three Danish agricultural soils is shown.

The adsorption of glyphosate and phosphate on pure soil minerals (goethite, gibbsite, illite and montmorillonite) was studied by use of the same batch method as the one used in this study, except that the solid:solution ratio was different [9]. The main results relevant for the current investigation are summarised as K_d -values in Table II. The K_d -values for glyphosate and phosphate were calculated using the concentrations

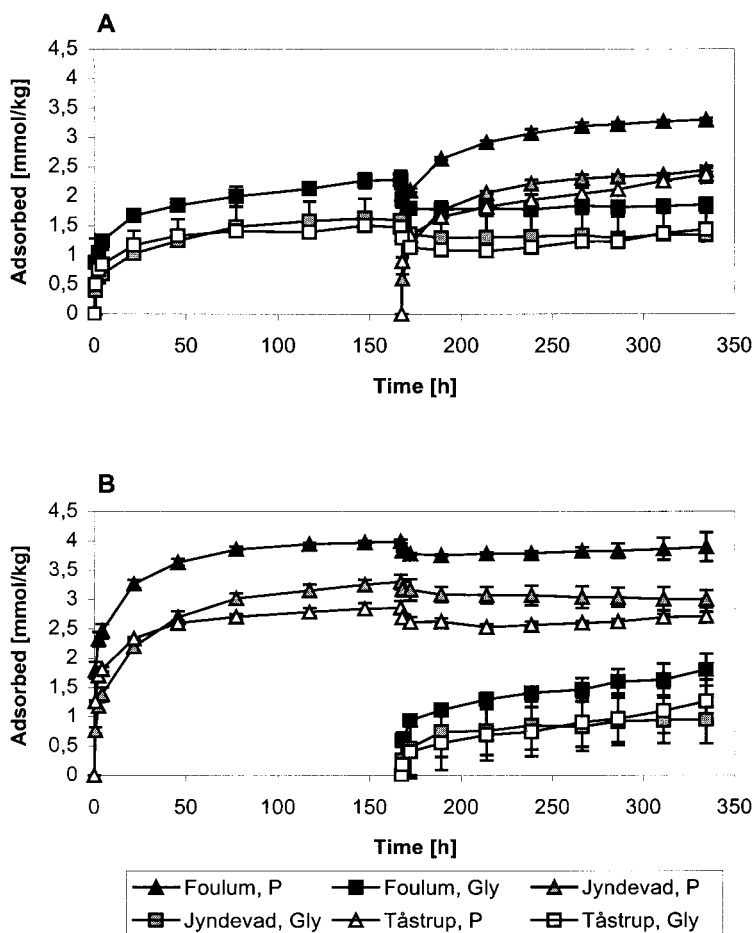


FIGURE 2 Adsorption of glyphosate followed by phosphate (A) and phosphate followed by glyphosate (B) on three typical Danish agricultural soils. In A glyphosate is applied at time 0h, and phosphate is applied after ~160h. In B phosphate is applied at time 0h, and glyphosate is applied after ~160h. Standard deviations are shown as error bars.

TABLE II Glyphosate and phosphate distribution coefficients (K_d [L/kg]) for adsorption on goethite, gibbsite, illite, montmorillonite and three soil samples (Jyndevad, Foulum, Tåstrup). Glyphosate K_d -values in absence and presence of phosphate and phosphate K_d -values in absence and presence of glyphosate are shown

	<i>Goethite</i>	<i>Gibbsite</i>	<i>Illite</i>	<i>Montmorillonite</i>	<i>Foulum soil</i>	<i>Jyndevad soil</i>	<i>Tåstrup soil</i>
Glyphosate	197.45 ± 0.40	261.05 ± 8.84	12.97 ± 0.40	17.41 ± 9.41	8.16 ± 0.83	4.09 ± 0.24	4.19 ± 0.48
Glyphosate with phosphate	16.05 ± 20.42	44.64 ± 17.59	5.29 ± 2.93	5.75 ± 1.27	5.91 ± 1.28	2.34 ± 0.24	3.37 ± 0.29
Phosphate	1378.19 ± 67.61	886.07 ± 78.83	20.00 ± 2.00	12.13 ± 1.84	32.82 ± 0.46	17.52 ± 1.90	13.40 ± 1.27
Phosphate with glyphosate	1159.72 ± 7.55	382.40 ± 10.67	16.03 ± 1.59	11.34 ± 0.04	19.36 ± 0.50	9.55 ± 0.83	9.01 ± 1.03

right before the second application of glyphosate or phosphate. The K_d -value for phosphate with glyphosate was calculated using the concentrations in the last point in the graph where glyphosate was added first and phosphate added in the second application (Fig. 2A). Similar for glyphosate with phosphate.

The pure minerals behave very differently regarding both the amounts of glyphosate and phosphate they adsorb and the effect phosphate had on glyphosate adsorption. The oxides are capable of adsorbing much more glyphosate and phosphate than the clay minerals (Table II). The clay silicates illite and montmorillonite adsorb similar amounts of glyphosate and phosphate, indicating that the type of clay does not affect the adsorption capacity. Adsorption on pure minerals also showed that there is a competition between glyphosate and phosphate for adsorption sites. On goethite, phosphate can almost completely desorb glyphosate and when phosphate is adsorbed the adsorption of glyphosate is negligible. On gibbsite, phosphate also influences the adsorption of glyphosate, but the influence is not as strong as on goethite, and glyphosate also affects phosphate adsorption. On the clay silicates the effect of phosphate on glyphosate adsorption is weaker than on the oxides, and glyphosate has a greater effect on phosphate adsorption.

The very different behaviour of aluminium and iron oxides and of clay silicates as adsorbents of glyphosate and phosphate indicates that soils with different mineralogical composition (type and amount of oxides and silicates) will behave differently with regard to glyphosate and phosphate adsorption.

The amounts of glyphosate and phosphate adsorbed by the soils are smaller than the amounts adsorbed by the pure minerals (Table II). This is probably due to a relatively large amount of sand in all three soils (Table I). The sand fraction mainly consists of quartz, which does not adsorb phosphate and glyphosate (data not shown).

Of the three soils, the Foulum soil is the one, which adsorbs most glyphosate and phosphate. The Tåstrup and Jyndevad soils adsorb similar amounts of glyphosate, but the Jyndevad soil adsorb a little more phosphate than the Tåstrup soil. All three soils adsorb more phosphate than glyphosate, indicating that more sorption sites are available to phosphate than to glyphosate. This is also seen for the pure minerals (Table II).

The reason why the Foulum soil adsorbs more glyphosate and phosphate than the two other soils may be that this soil contains the largest amounts of aluminium oxides, both oxalate and citrate-bicarbonate-dithionite (CBD) extractable (Table I). Aluminium oxides have a great sorption capacity for both glyphosate and phosphate [9], and therefore it is not surprising that the soil with the greatest amount of aluminium

oxides adsorb most glyphosate and phosphate. The Foulum soil contains the second highest amounts of iron oxides, both oxalate and CBD extractable, and this undoubtedly also influence the soils ability to adsorb phosphate and glyphosate. Thus several soil studies have shown glyphosate and phosphate adsorption capacities to be correlated with the content of iron and aluminium oxides [12–16].

The Foulum soil is also the soil, which has the highest maximum phosphate sorption capacity (see “max P sorption” in Table I), even though it is the soil with the highest content of total phosphate and a relatively high amount of available phosphate (Olsen P). This shows that it is not the amounts of phosphate found in soils, which affects the ability to adsorb glyphosate, but the capacity to adsorb additional phosphate. This was also found by Hance [4]. However, it should be noted that only three soils have been used in this study, and more experiments with more soils are needed before conclusions about phosphorus content and glyphosate sorption can be made.

It is surprising that the Tåstrup and Jyndevad soils adsorb almost similar amounts of glyphosate and phosphate, since the Tåstrup soil contains more clay, oxalate- and CBD-extractable iron oxides and has a higher maximum phosphate sorption capacity than the Jyndevad soil. However, Jyndevad contains more CBD-extractable aluminium oxides than Tåstrup, and this may account for some of the adsorption capacity of the Jyndevad soil. Jyndevad is the soil with the highest amount of organic matter. It has previously been found that glyphosate sorption is correlated with the content of organic matter [15,17] and this may thus explain the sorption capacity of the Jyndevad soil. On the other hand it has also been found that glyphosate sorption is not correlated, or is sometimes even negatively correlated, with the content of organic matter [16]. A more likely explanation is that the aluminium oxides in the Jyndevad soil possess an extraordinary high adsorption capacity as was found in an earlier study of the phosphate adsorption by sandy soils similar to the Jyndevad soil [18]. Maybe the high sorption capacity of the aluminium oxides in the Jyndevad soil is due to the low clay content, so that the aluminium oxides are little affected by interactions with clay silicates.

The glyphosate sorption capacity of soils has previously been found to correlate with the clay content and the cation exchange capacity (CEC) [19]. This could not be confirmed by the findings in this and a previous study [9]. According to these studies clay silicates only adsorb small amounts of glyphosate (and phosphate), irrespective of the clay type and CEC; montmorillonite has a very high CEC while the illite CEC is in-between. Moreover, sorption of glyphosate by the soils did not correlate with the clay content or the CEC.

From Fig. 2 it is seen that glyphosate and phosphate compete for adsorption sites in the three soils. Phosphate can desorb glyphosate (Fig. 2A), and adsorbed phosphate decreases the amount of glyphosate, which can be adsorbed (Fig. 2B and Table II). This shows that phosphate affects the glyphosate adsorption in soil, and therefore phosphate will affect the bioavailability and leaching potential of glyphosate. Previous studies have also shown that phosphate affects the glyphosate sorption in soils [2,3,20]. Pure soil minerals behave quite differently regarding the competitive adsorption of glyphosate and phosphate [9], so it might be expected that there would be differences between the three soils with respect to the competitive adsorption. However, this is not the case. The reason for the absence of different competition behaviour may be that the soils are not different enough with respect to constituents, such as oxides, that affect sorption.

If soils with more extreme mineralogical composition such as soils very rich and poor in iron and/or aluminium oxides, had been included in the study then differences would undoubtedly have been seen.

Figure 2 and Table II shows that glyphosate also affects the adsorption of phosphate, so the competition between glyphosate and phosphate in soil is much more equal than the competition on the oxides, especially goethite [9].

The kinetics of adsorption on the pure minerals is different from the adsorption kinetics of the soils. On the pure minerals adsorption is fast, and equilibrium is reached [9], although when an exchange of glyphosate for phosphate takes place, the process is a bit slower. On the soils the adsorption of both glyphosate and phosphate is time dependent, and it does not look like equilibrium is reached within the adsorption time used in this study. This difference in kinetics is almost certainly due to differences in crystallinity. The pure minerals used in this study are all well crystallized, whereas the minerals in the soils are less well developed or amorphous. Diffusion into poorly developed and amorphous solids to inner, less accessible sorption sites means that the reaction will be much slower than when adsorption occurs onto outer surface sites, which dominates on well developed crystals [21,22]. Figure 2 shows that the three soils have different kinetics of adsorption, which may be due to different crystallinity of the adsorbing minerals in the soils. Diffusion into minerals may also affect the competition between phosphate and glyphosate, because it is more difficult to desorb a molecule or ion, which is adsorbed at an interior, less accessible site inside the mineral than to displace a readily accessible species held at an outer surface.

The observed non-equilibrium in the adsorption of glyphosate and phosphate may, at least to some extent, also be due to the constant magnetic stirring used in the experiments because magnetic stirring can lead to disintegration of aggregates, and thus to the exposure of new surfaces. It should be noted that the soils had been stirred before glyphosate or phosphate was added, so that dispersion of the soil could take place before addition of glyphosate or phosphate. Also, the background electrolyte used had a relatively high concentration (0.1 M KCl), which promotes flocculation.

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