

Adsorption of Glyphosate on the Clay Mineral Montmorillonite: Effect of Cu(II) in Solution and Adsorbed on the Mineral

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Adsorption–desorption of the herbicide glyphosate (GPS) onto the clay mineral montmorillonite has been studied in presence of copper, in order to clarify the effects that this strongly complexing metal could have on the availability and mobility of GPS in soil environment. In contrast with previous findings, GPS adsorption on montmorillonite decreases in the presence of Cu, in solution or adsorbed on the mineral, due to the formation of Cu–GPS complexes that have a lower tendency to be adsorbed on montmorillonite than the free GPS. GPS adsorption is higher at pH 4.2 than at pH 6.8, both in the presence and in the absence of Cu, but the decrease in GPS adsorption in the presence of Cu is lower at pH 4.2 than at pH 6.8, since at this latter pH the concentration of Cu–GPS complexes in relation to free GPS in solution is high. It is commonly believed that GPS remains almost permanently adsorbed onto soils and has very limited mobility, but GPS desorption experiments show that the amount of GPS desorbed from montmorillonite is not negligible and increases in the presence of Cu. These experiments lead to the conclusion that, in relation to GPS release from soil, it is necessary to take into account not only the type of soil to which it is applied (e.g., whether it has high clay minerals content) but also whether there is any element in the soil solution or adsorbed on the soil capable of forming strong complexes with GPS.

Introduction

Glyphosate (GPS), *N*-(phosphonomethyl)glycine, is a non-selective, broad-spectrum, post-emergent herbicide extensively used in agriculture. It is inactivated relatively rapidly in soils, both by microorganisms to non-phytotoxic products and by binding to soil constituents.

GPS has three groups (amine, carboxylate, and phosphonate) that can form strong coordination bonds with metal ions, particularly with the hard transition metal ions (1–3). This ability places GPS in an almost unique class of strongly chelating herbicides. Although GPS is used as a phytotoxic agent, little is known about its affinities for the divalent and trivalent metal ions that occur in plants, soils, and water.

Phenomena of adsorption onto clay minerals appear to be one of the most important factors affecting the behavior and fate of pesticides and heavy metals in soil components. Sprankle *et al.* (4) found that Fe³⁺- and Al³⁺-saturated clays and organic matter adsorbed more GPS than when saturated

with Na⁺ and Ca²⁺. These authors postulated that GPS may bind to soils in a similar fashion to phosphate, possibly through the phosphonate group. This conclusion is corroborated by the fact that phosphate competes with GPS for the sites of adsorption in clay and soils in general. Binding does not seem to be related to the cation exchange capacity of clays but rather to the valence of the cation in the clay (5–7).

Another possible mechanism of adsorption is the formation of clay–cation–glyphosate bonds. Since GPS has a phosphonate group, the metal ions can play a major role in its adsorption, in a similar way to how organophosphates form stable complexes with metals through which they bind to soils (8). Some studies have been published on the adsorption onto clays of pesticides and heavy metals when both are present (9–14), but there is no information about GPS behavior when heavy metals are present.

The aim of this study is to clarify the effects of Cu, present in solution or adsorbed on the clay mineral montmorillonite, on the adsorption of GPS by this mineral. Cu has been selected due to its extensive use for agricultural purposes as a fungicide, being frequently added together with the pesticide GPS, and also due to its capacity for complex formation. At the same time, this element can increase its concentration in surface horizons of agricultural soils due to the addition of fertilizers, sewage sludge, and other wastes with significant copper content.

Materials and Methods

The clay mineral used was a standard montmorillonite from Arizona (designed SAZ-1) (15), supplied by the Clay Mineral Society (Source Clay Minerals Repository). Its cation exchange capacity (CEC) is 1.235 mol_c kg⁻¹, of which 100.78 × 10⁻² mol_c corresponds to Ca²⁺, 19.16 × 10⁻² mol_c corresponds to Mg²⁺, 2.6 × 10⁻² mol_c corresponds to Na⁺, and 9.6 × 10⁻³ mol_c corresponds to K⁺. It was used as received.

GPS is a non-residual herbicide, with solubility in water of 12 g L⁻¹ at 25 °C. GPS has a zwitterion structure depending on pH. The proposed dissociation diagram and protonation pK values (at 25 °C) have been given by Motekaitis and Martell (1) (Scheme 1).

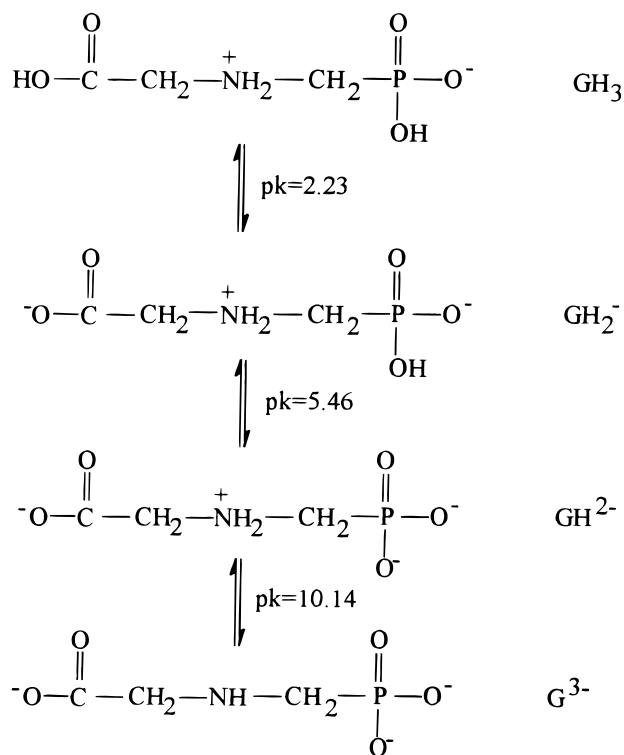
Triplicate adsorption experiments were done by mixing 1 g of clay mineral with 20 mL of 0.01 M NaCl solutions, containing various concentrations (0–50 mg L⁻¹) of GPS, with and without Cu (30 mg L⁻¹), in 50-mL polypropylene centrifuge tubes. The samples were shaken for 24 h at 20 ± 1 °C. As a result of the buffer effect of the sample, the pH in the solutions at equilibrium was 6.8 for all concentrations of GPS used. The amounts of pesticide GPS and Cu adsorbed were calculated from the differences between their concentrations before and after equilibrium.

Desorption experiments were performed after adsorption equilibrium was reached by removing half of the supernatant after centrifugation, replacing it by 10 mL of 0.01 M NaCl, allowing equilibration for an additional 24-h period, and after that operating as in the adsorption experiment. This process was repeated twice more.

The adsorption of GPS on montmorillonite previously treated with Cu (successive adsorption) was carried out by mixing 1 g of the standard clay with 0.01 M NaCl solutions containing Cu (30 mg L⁻¹). The samples were shaken for 24 h at 20 ± 1 °C. After reaching equilibrium, the suspensions were centrifuged, and the supernatant was separated. The solid samples were washed twice with 20 mL of distilled water and then treated with GPS solutions (0–50 mg L⁻¹) in 0.01 N NaCl medium for another 24 h at 20 ± 1 °C. GPS and Cu concentrations in equilibrium solutions were determined.

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SCHEME 1. Species of GPS Depending on pH and Protonation Constants



Adsorption of GPS on Cu-saturated montmorillonite [(SAZ-1)-Cu] was also performed in the same way as the adsorption on the SAZ-1 montmorillonite previously described. The standard montmorillonite was saturated with Cu^{2+} ions by washing several times with 0.5 M CuCl_2 solution. Excess salt was removed by washing with distilled water until free of excess chloride and freeze-dried.

Other experiments have been carried out at equilibrium pH 4.2 in order to study the influence of pH in GPS adsorption on this standard montmorillonite. To obtain pH 4.2 at equilibrium solutions, the initial solution pH was adjusted to 2.3. The adsorption experiments were carried out as done previously.

GPS was determined by high-performance liquid chromatography (HPLC), using a Waters ion exclusion column (Fast Fruit Juice, 7.8 mm \times 15 cm) and a postcolumn reaction specific for primary amines. GPS is oxidized in a postcolumn reactor coil with calcium hypochlorite (flow rate 0.5 mL/min) to form glycine. Glycine is treated with *o*-phthalaldehyde (OPA) in the presence of mercaptoethanol (flow rate 0.8 mL/min) in a second coil to form a fluorophor, which is detected fluorometrically (λ excitation 325 nm, λ emission 450 nm). The mobile phase used was 0.05% phosphoric acid, with an isocratic flow rate of 1 mL min^{-1} . The column temperature and that of both postcolumn reactors was 38 $^\circ\text{C}$.

Cu was determined using atomic absorption spectrometry (AAS), with a nitrous oxide-acetylene flame, since the Cu measured concentrations with an air-acetylene flame in the presence of GPS were always lower than the real values because of the formation of Cu-GPS complexes. The inorganic cations (Ca and Mg) released during adsorption experiments were also determined by AAS (using an air-acetylene flame). The relative standard deviations were $\leq 6.04\%$ for GPS and $\leq 0.58\%$ for Cu.

Results and Discussion

Figure 1 shows the adsorption isotherms of GPS by montmorillonite (SAZ-1) at equilibrium pH 6.8, both in the absence of Cu and in the presence of 30 mg L^{-1} Cu in the initial

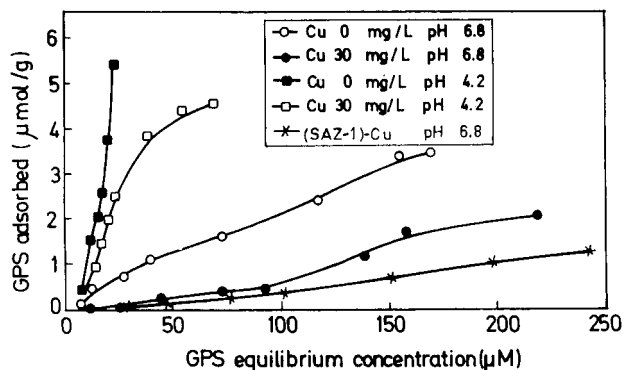


FIGURE 1. Adsorption isotherms of GPS on (SAZ-1)-Cu at pH 6.8 and on SAZ-1 in the absence and in the presence of Cu in solution, at pH values 6.8 and 4.2.

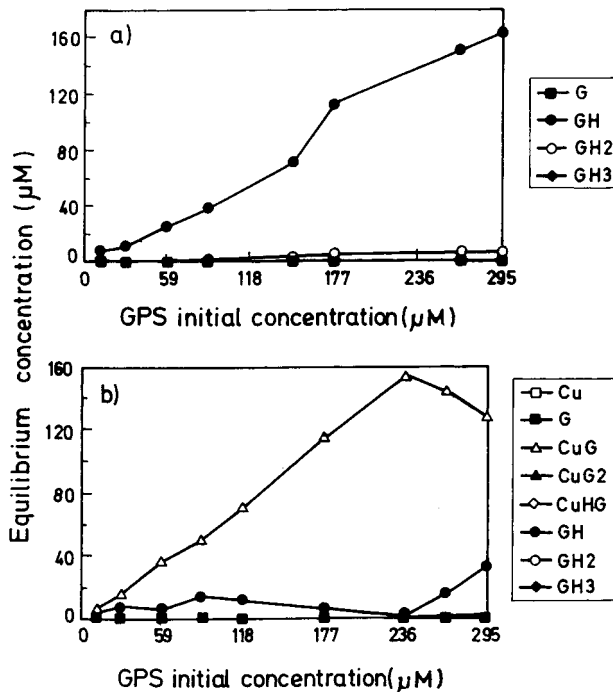


FIGURE 2. Calculated distribution curves of GPS species in equilibrium solutions at pH 6.8 (a) in the absence and (b) in the presence of Cu versus initial GPS concentration.

solutions. In the absence of Cu, the maximum adsorption of GPS by montmorillonite reached in our experiments was very low, corresponding to just 0.58% of the CEC of the sample, which suggests that adsorption takes place only on the external surface of the mineral and not in its interlayer space. According to Shoal and Yariv (5), no interlamellar adsorption of the GPS anion from aqueous solutions occurred on mono- and divalent cations montmorillonite. The adsorption of GPS by clay minerals seems to occur at the broken borders of these minerals via the hydroxyl groups. The phosphonate group of the pesticide binds to these in a similar way as phosphate groups bind to the clay minerals.

The adsorption of GPS decreased by half with Cu (Figure 1). To explain the behavior observed, it is necessary to calculate the GPS species present in the equilibrium solutions, taking into account the pK values of protonation of GPS (Scheme 1) and the pK values of formation of GPS-Cu complexes (1). The calculation was carried out by a computer program based upon the Newton method for solving polynomial n -degree equations. Figure 2 shows the calculated distribution curves of the different GPS species in the equilibrium solutions in the absence and in the presence of 30 mg L^{-1} Cu. The distribution of GPS species in the absence

TABLE 1. Ca and Mg Desorbed from Montmorillonite ($\mu\text{mol/g}$) after Treatment with GPS and GPS + Cu Solutions

GPS initial concn (mg/L)	GPS		GPS + Cu	
	Ca	Mg	Ca	Mg
2	22.7	4.8	29.3	6.5
5	23.0	4.8	29.5	6.3
10	23.4	4.9	27.9	6.1
15	23.6	5.1	26.5	6.0
20	23.6	5.1	27.4	5.8
25	23.9	5.2	27.4	6.3
30	24.3	5.7	28.1	6.5
40	25.8	5.9	28.4	6.4
45	27.4	6.8	28.0	6.6
50	28.0	8.6	29.0	6.6

of Cu (Figure 2a) indicates that most of the pesticide is in the GH form, i.e., the major species has two net negative charges (Scheme 1).

In the equilibrium solutions in the presence of Cu (Figure 2b), the predominant species is CuG, which has just a single net negative charge. Its proportion increases as the concentration of GPS increases up to 40 mg L^{-1} , ranging from 61.5% for a GPS concentration of 2 mg L^{-1} (at which the GH species represents 37.6%) to 98.3% for the maximum concentration of GPS (50 mg L^{-1}). According to Motekaitis and Martell (1), in 1:1 complex systems, the formation of the CuG complex is favored over the CuHG complex at pH values close to neutrality. In the latter complex, the proton resides in the amine N and the phosphonate group donates electrons in the formation of the copper chelate. As the complex is polarized, the proton is easily removed from the amine group as the GPS coordinates with the metal ion.

The most significant feature to be observed in Figure 2 is the drastic reduction in the concentration of free GPS in the solution due to the formation of Cu-GPS complexes, which suggests that the reduction in the adsorption of GPS by montmorillonite in the presence of Cu is due to the fact that the Cu-GPS complexes formed tend not to be adsorbed by the clay to the same extent as the free GPS. According to Sprankle *et al.* (4), if the phosphonate group does not act as a complexing agent, the GPS binds to the soil in a similar way as to phosphate. Thus, the fact that the formation of the complex with Cu takes place via the phosphonate group may explain the decrease in the adsorption of GPS in the presence of Cu.

The amounts of Ca and Mg desorbed from the montmorillonite after treatment with GPS solutions in the presence of Cu (Table 1) were independent of the concentration of GPS, since the desorption was due principally to the cationic exchange with Na cations of the background electrolyte and with the Cu cations present in the solution, both of which remained practically constant in all cases. However, when Cu was absent from the solution, the amounts of Ca and Mg desorbed increased as the concentration of GPS increased, especially Mg. The desorption of Mg was almost double that observed with the lower GPS concentration. This suggests that GPS is able to remove interlayer Ca and Mg since it tends to form complexes with them (1, 2), although the chelates formed with these cations are far less stable than those formed with Cu. Thus, when Cu is present in the solution, no release of interlayer cations by GPS can be detected. In these conditions, GPS tends to form strong complexes with Cu. According to Motekaitis and Martell (1), the divalent cation with which GPS forms the strongest complexes is Cu and the weakest is Ca.

To test if Cu adsorbed on montmorillonite (in the same concentration as that used previously in solution) could influence GPS adsorption, an experiment was performed in which montmorillonite was previously treated with a solution of 30 mg L^{-1} Cu. After reaching equilibrium, the solution

was removed, and the sample was washed twice with distilled water prior to its subsequent treatment with GPS (successive adsorption). All of the Cu in the solution was adsorbed onto the montmorillonite, and none was desorbed during the washes. This successive adsorption of GPS onto montmorillonite after Cu adsorption gave an isotherm (not shown) similar to GPS adsorption on SAZ-1 at pH 6.8. It was, therefore, different from the adsorption of GPS when Cu is in solution. This stresses the importance of the presence of metals in solution, as opposed to the presence of the same amount of metal adsorbed onto the clay, on the amount of GPS that can be adsorbed. There is some slight decrease, but in no case has an increase been observed as has been reported in the literature (4, 6, 7) when heavy metals are present in the interlayer space of clays. The metal that is already adsorbed has little influence on the adsorption of GPS, since the amount of Cu adsorbed represents only 1.58% of the CEC of the sample (SAZ-1). It is for this reason that the behavior is similar to that of the original sample. However, the small decrease in GPS adsorption observed for the successive experience may have been due to the presence of GPS in solution, which tends to desorb Cu from the montmorillonite, giving rise to the formation of Cu-GPS complexes in solution. This in turn leads to a slight decrease in the adsorption of GPS.

To determine whether the presence of a greater amount of interlayer Cu would increase or decrease the adsorption of GPS by montmorillonite, this adsorption was carried out on montmorillonite saturated with Cu [(SAZ-1)-Cu]. Adsorption of GPS was found to decrease when the montmorillonite was saturated with Cu as compared to the adsorption achieved with the original sample (Figure 1). This finding does not agree with that of Glass (7), who found that adsorption of GPS by montmorillonite saturated with Cu was greater than that saturated with Ca, using experimental conditions similar to those used in the present paper. The latter author reasoned that the relative ease with which some cations form coordination compounds or complexes is the main factor responsible for the differences in adsorption observed. However, no explanation is given as to how this relative ease of complex formation influences adsorption. The author proposes that a superficial interaction between GPS and the metal in the solid/liquid interface must play an important role in the process. But, at the same time, the increase in the adsorption of GPS is also attributed to the formation of GPS-Cu complexes in solution. Sprankle *et al.* (4) have postulated that cations help in the formation of new sites for adsorption to clay minerals.

The results obtained in these experiments indicate that the Cu cations leave the interlayer space of the montmorillonite not only by cation exchange with Na ions of the background electrolyte but also by the formation of complexes with GPS in the external solution while the protons in the solution occupy the interlayer positions (in fact the pH of the final solutions is higher than that of the initial solutions). McBride (3) concluded that GPS was able to mobilize exchangeable Cu^{2+} from clays, forming uncharged or anionic complexes that released into solution. No Cu-GPS complex remained adsorbed on the clay. At the same time, the amount of Cu desorbed increased as the amount of GPS in solution increased, this being probably due to the formation of strong complexes of Cu with GPS. As a result, there is less pesticide with free phosphonate groups available for adsorption in a similar fashion to the phosphate ion, its adsorption therefore decreasing since the tendency of Cu-GPS for adsorption is lower. The results reported here, therefore, disagree with those reported in the literature, which indicate that as Cu-GPS complexes form there is an increased adsorption of pesticide.

Since the experiments on GPS adsorption on montmorillonite saturated with Cu were performed in a 0.01 N NaCl medium, the possibility exists that a considerable amount of

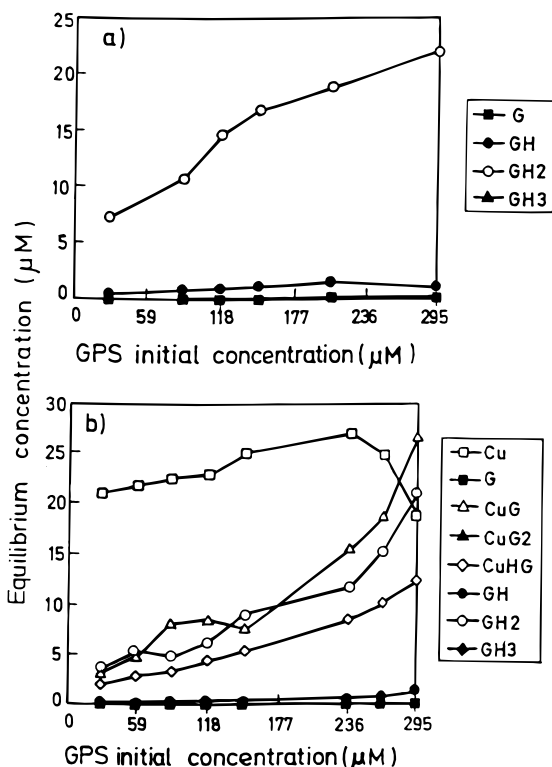


FIGURE 3. Calculated distribution curves of GPS species in equilibrium solutions at pH 4.2 (a) in the absence and (b) in the presence of Cu versus initial GPS concentration.

Cu might have desorbed by cation exchange with the sodium cation, giving rise to the formation of Cu-GPS complexes. In studies reported in the literature (7), no background electrolyte was used in the adsorption experiments. To test the possibility that the Na^+ accounted for the difference between our results and other studies, further experiments were conducted, in the same conditions as those previously exposed, except that NaCl was excluded from the treatment solutions. Even in this case a lower adsorption of GPS was obtained when the montmorillonite was saturated with Cu than when the predominant interlayer cation was Ca.

Influence of pH. Since the pesticide GPS presents different species depending on the pH of the solution, experiments were performed on GPS adsorption alone and in the presence of 30 mg L^{-1} Cu in solution at equilibrium pH 4.2 to determine whether adsorption under these conditions differs from that observed above. Figure 1 shows the adsorption isotherms obtained at pH 4.2. The adsorption of GPS was much greater at pH 4.2, both in the absence and in the presence of 30 mg L^{-1} Cu.

The results obtained agree with those reported in the literature that the adsorption of GPS varied inversely with the pH of clay suspensions. McConnell and Hossner (8) related the higher adsorption of GPS at low values of pH with the decrease in the negative charge of the pesticide (at pH 4.5 the net charge was -1 , while at pH 7 the net charge was -2). According to these authors, the pesticide can react more strongly with the surface of the mineral at lower charge. Figure 3 shows the species distribution in the equilibrium solution in the presence and in the absence of Cu at pH 4.2. At this lower pH, the predominant species was GH_2 , while at pH 6.8 the predominant species was GH (Figure 2).

There was also a difference between the GPS species distribution at equilibrium in the presence of Cu at pH 4.2 (Figure 3) and that at pH 6.8 (Figure 2). Most of the GPS present at pH 6.8 was in the form of a CuG complex. However, at pH 4.2 the concentrations of CuG and GH_2 were practically equal. Thus, the increase in CuG concentration when the

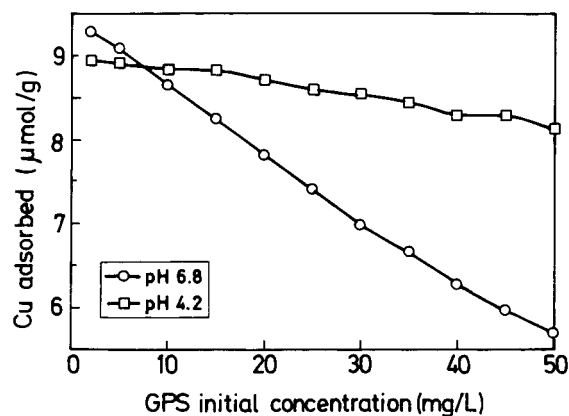


FIGURE 4. Cu adsorbed on SAZ-1 for various GPS initial concentrations at pH values 4.2 and 6.8.

TABLE 2. Total Cu and Free Cu^{2+} in Equilibrium Solutions after Treatment of Montmorillonite with GPS + Cu Solutions at pH Values 4.2 and 6.8

GPS initial concn (mg/L)	pH 4.2		pH 6.8	
	total Cu (μM)	free Cu (μM)	total Cu (μM)	free Cu (μM)
5	26.2	21.0	17.8	0.55×10^{-2}
10	29.8	21.7	38.9	2.19×10^{-2}
20	36.3	22.9	81.5	1.82×10^{-2}
30	44.7	21.4	123.0	7.96×10^{-2}
45	57.4	20.4	173.4	4.34×10^{-2}
50	65.3	18.0	187.6	1.96×10^{-2}

GPS concentration in solution increased, was accompanied by a parallel increase in the concentration of GH_2 . The GH_2 species has the greatest tendency for adsorption. This also explains why the adsorption of GPS is less affected by the presence of Cu at pH 4.2 than at pH 6.8, since the concentration of GH_2 in solution remains high in all cases. This is more evident when the percentage decrease in adsorption of GPS in the presence of Cu is calculated, both at pH 4.2 and at pH 6.8. A maximum decrease of 16.8% was observed at pH 4.2, while at pH 6.8 the maximum decrease observed was 87.5%.

The adsorption of Cu in the presence of GPS at pH 4.2 and pH 6.8 was also studied (Figure 4). In both cases the adsorption of Cu decreases as the initial GPS concentration increases, as reported elsewhere (11); however, the decrease was much greater at pH 6.8. On the other hand, the amount of Cu adsorbed is in general greater at pH 4.2 than at pH 6.8, whereas the adsorption of heavy metals onto clays is always greater at higher pH values. In the system used in this study, the cause is the formation of Cu-GPS complexes. Table 2 shows the calculated amounts of total and free Cu in the equilibrium solutions of treatments at pH 4.2 and pH 6.8. At pH 4.2, the concentration of free Cu decreased in relation to the total Cu as GPS concentration increased. The concentration of free Cu in solution lies between 18 and $23 \mu\text{mol/L}$. In contrast, at pH 6.8, the concentration of free Cu as compared with the total Cu concentration is extremely low in all cases, being 1000 times lower than at pH 4.2. Due to this low concentration of free Cu at this pH, the possibility that some amount of metal adsorbs onto the montmorillonite as a Cu-GPS complex cannot be discarded.

Desorption Processes. Experiments of GPS adsorption-desorption on montmorillonite in the presence and in the absence of 30 mg L^{-1} Cu in the initial solutions were performed. The desorption curves (Figure 5) showed hysteresis. In the absence of Cu, almost 40% of the GPS previously adsorbed desorbed after three successive desorptions. This represents a high amount if one takes into account that GPS is strongly retained in soils (4, 16, 17). The fact that the

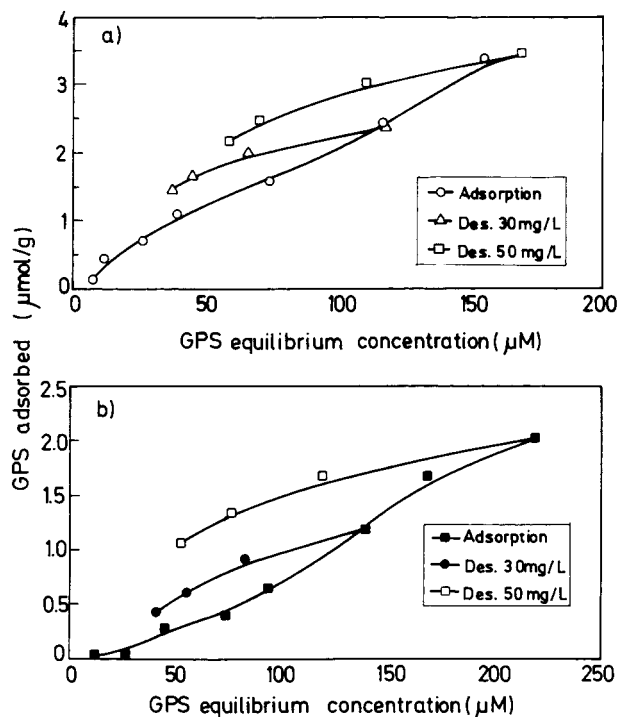


FIGURE 5. Adsorption-desorption isotherms of GPS in SAZ-1 in the absence (a) and in the presence of Cu (b).

desorption of GPS from the montmorillonite was high may corroborate further the suggestion that GPS adsorbs onto the broken borders of the clay mineral (positions with variable charge). When desorption processes take place, GPS can be replaced by hydroxyl groups or by water on the surface of the mineral, as McConnell and Hossner (18) suggested to occur in the case of GPS adsorption by minerals with pH-dependent charge, such as hematite and goethite. Piccolo *et al.* (19) also studied the desorption of GPS from four different soils and found that the soil with the greatest percentage of desorption (up to 80%) was that which had the highest content in expandable clay minerals (smectites) and the highest capacity for cation exchange, but a very low organic matter content and very low soluble and amorphous Fe and Al contents. This supports the suggestion that soil components other than the clay minerals are the principal factors responsible for adsorption and for the low mobility of this pesticide in soils.

It is also worth pointing out that the percentage desorption of GPS increased in the presence of Cu. It is possible that, as part of the interlayer Cu desorbs by cation exchange with the Na ions from the background electrolyte, the increase in the Cu concentration of the solutions changes the equilibrium of formation of Cu-GPS complexes. The GPS tends to desorb to a greater extent due to the formation of complexes with Cu in solution.

These GPS desorption experiments show that, despite the fact that GPS is commonly believed to remain almost permanently adsorbed onto soils, it is necessary to take into account not only the type of soil to which it is applied (e.g., whether it contains high contents of organic matter, iron, and aluminum oxides or of smectitic clays) but also whether there is any element in the soil solution or adsorbed onto the soil capable of forming strong complexes with GPS. The presence of heavy metals, for example, can facilitate desorption of the pesticide.

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