

Cosorption of zinc and glyphosate on two soils with different characteristics

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Abstract

Agricultural application of large amounts of glyphosate [*N*-(phosphonomethyl)-glycine] may affect soil metal behaviors to some extent, because glyphosate can react with many kinds of metals to form metal complexes. Cosorption of Zn and glyphosate on a Red soil (RS, Udic Ferrosols) and a Wushan soil (WS, Anthrosol) was studied. In comparison with the WS, the RS has less adsorption capacity for Zn and higher for glyphosate. The presence of glyphosate decreased Zn adsorption on the two soils, which are resulted from the decreased equilibrium solution pH caused by the added glyphosate, and also the formation of water-soluble complexes of glyphosate with solution Zn²⁺ that had lower affinity to soil surface in comparison with Zn²⁺ itself. Such effect is more significant on the RS than on the WS, mainly because of the less adsorption quantity of Zn on the former one. On the contrary, the presence of Zn increased the adsorption quantities of glyphosate on the RS and WS, which is resulted from the decreasing pH value of the equilibrium solution caused by Zn²⁺ exchange with H⁺ ions of soil surface. Such results suggest that glyphosate in field may increase the mobility and bioavailability of Zn and correspondingly increase its environmental risk.

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1. Introduction

Zinc is a key element in plant growth and human health. It has been used by human beings since immemorial time and is still widely applied in our industrialized society. Zinc is an essential element for the normal activity of DNA polymerase and protein synthesis. Its deficiency in human body can cause many diseases, such as liver disease, gastrointestinal disorders, renal diseases, neoplastic diseases, burns, skin disorders, etc. [1]. So, it plays a vital role in the healthy development of many life forms. Excessive amounts of Zn, however, may be toxic, especially to the aquatic biota.

Most agriculture soils contain Zn in the range of 10–300 mg kg⁻¹, depending on their parent materials [2]. The amounts, required by plant, are normally low. However, fast industrialization is associated with soil heavy metals pollution. Zinc, in particular, is a very common element in the contaminated areas.

Glyphosate (*N*-[phosphonomethyl]-glycine), a non-selective, postmergence herbicide, is widely used in agronomic and vegetable crops, and also in orchards. It contains functional groups of amine, carboxylate and phosphonate that can form strong coordination bonds with metal ions to give bidentate and tridentate complexes [3–6]. It suggests that the complexation of metal cations with glyphosate may affect plant metabolism and physiology of glyphosate depending on the presence of metal cations, and its degradation, distribution and bioavailability in soils [7–10]. Moreover, once glyphosate is applied to farmland, it will affect the behaviors of soil inherent and exogenous Zn more or less in field. Similar for the interaction between glyphosate and Cu or Cd has been studied [4,10–14]. Morillo et al. [15–17] investigated the cosorption of Cu(II) and glyphosate on soils of different characteristics and on the clay mineral montmorillonite. The presence of Cu in treatment solution enhanced glyphosate adsorption on the soils but it decreased glyphosate adsorption onto montmorillonite. In goethite, the adsorption of glyphosate in the presence of Cu increased about 9%, and Cu adsorption also increased in the presence of glyphosate [11].

Although the coadsorption of glyphosate and Cu or Cd on soils has been reported, it is not clear for the interaction of soil Zn

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and glyphosate. In fact, soil Zn normally has higher concentration than soil Cu or Cd. It means that soil Zn and glyphosate have a strong interaction in soil. This study investigated the adsorption and coadsorption of Zn and glyphosate on two soils with different characteristic, and discussed their interaction mechanisms through speciation simulation.

2. Materials and methods

2.1. Soils and chemicals

A surface (0–20 cm) Red soil (RS, Udic Ferrosols) and a surface (0–20 cm) Wushan soil (WS, Anthrosol) were sampled from Yingtan county, Jiangxi Province and Changshu county, Jiangsu Province, respectively. The soil samples were air-dried, passed through a 60-mesh screen, and stored in glass bottles for further use. The basic physico-chemical characteristics of the two soils are listed in Table 1. Soil organic matter (OM) was determined by the method of dichromate oxidation, the content of soil total Fe and Al oxides were determined by digestion of HF–HClO₄–HCl, and soil cation exchange capacity (CEC) was determined by the method of NH₄Ac exchange [18]. The RS, as a variable charge soil, has low pH value (4.95) and high contents of Fe oxides; while the WS, as a permanent charge soil, has high organic matter content, high CEC and pH value (7.20). Glyphosate was purchased from Sigma Co. All other chemicals are of analytical grade. Deionized water was used for all the experiments.

2.2. Zinc adsorption isotherms on the soils in the absence and presence of glyphosate

Zinc adsorption isotherms on the two soils with and without glyphosate were performed by batch experiments. Fifteen milliliters of 0.01 mol L⁻¹ NaNO₃ solution and 5.0 mL of 0.01 mol L⁻¹ NaNO₃ solution with different concentrations (0–25 mmol L⁻¹) of Zn(NO₃)₂ were added in 0.5 g soil. And 5.0 mL of 0.01 mol L⁻¹ NaNO₃ solution containing 0, 0.5, or 2.5 mmol L⁻¹ glyphosate was, respectively, added in every series of Zn concentrations. The final solution volume was 25 mL, and the final Zn concentration series were 0, 0.05, 0.10, 0.25, 0.50, 1.0, 2.5, and 5.0 mmol L⁻¹. When glyphosate was added in the equilibrium solution as a coexisting chemical of Zn, 0.10 or 0.50 mmol L⁻¹ glyphosate was contained in the final soil solutions.

The centrifuge tubes were continuously shaken for 2 h at 25 °C, and then centrifuged and filtrated through a filter paper. The Zn concentration in the centrifuged solution was determined by a Hitachi 180-80 Atomic Adsorption Spectrophotometer

(AAS). All solution pHs after the equilibrium were measured by a pH meter. All experiments were performed in two replicates.

2.3. Effect of pH on Zn adsorption on the soils in the absence and presence of glyphosate

0.50 g soil was weighed in every 50 mL centrifuge tube, and 5.0 mL of 0.01 mol L⁻¹ NaNO₃ solution containing 2.5 mmol L⁻¹ Zn was added. And then, different volume of 0.01 mol L⁻¹ NaOH or 0.01 mol L⁻¹ HNO₃ solution was added in each tube to adjust solution pH varying from 3 to 9. In following, 0.01 mol L⁻¹ NaNO₃ solution was supplied into each tube and the final solution volume was 25 mL. In the experiments in the presence of glyphosate, different concentrations of glyphosate (0.50, 2.5 or 5.0 mmol L⁻¹) were added in the respective pH series. The centrifuge tubes were continuously shaken for 2 h at 25 °C, and then centrifuged and filtrated through a filter paper. The Zn concentration in the centrifuged solution was determined by AAS. The amount of Zn adsorbed was calculated from the difference between its solution concentrations before and after equilibrium. All solution pHs after equilibrium were measured by a pH meter.

2.4. Glyphosate adsorption isotherm on the soils in the absence and presence of Zn

Glyphosate adsorption isotherms on the soils without Zn were carried out by adding 15 mL of 0.01 mol L⁻¹ NaNO₃ solution in 0.50 g soil, and then 5 mL of 0.01 mol L⁻¹ NaNO₃ solution with different concentrations of glyphosate (0–5.0 mmol L⁻¹) was added. The final solution volume was 25 mL, and the final glyphosate concentrations were 0, 0.1, 0.2, 0.4, 0.6, 0.8 and 1.0 mmol L⁻¹. When Zn is present, its concentrations in the final soil solution are 0.50, 2.0, or 4.0 mmol L⁻¹ for different adsorption isotherms of glyphosate. All experiments were performed in replicate. The centrifuge tubes were continuously shaken for 2 h at 25 °C, and then centrifuged and filtrated through a filter paper. The glyphosate concentration in the centrifuged solution was determined by an Agilent 1100 series HPLC, using a 4.6 mm × 150 mm Zorbax ODS column. At first, 0.50 mL supernatant content of glyphosate was derived with 130 mmol L⁻¹ *p*-toluenesulphonyl chloride in acetonitrile (1:1 (v/v)) for 5 min at 50 °C. The derivatized samples (20 μL) were then injected in the chromatography column equilibrated with 50 mmol L⁻¹ sodium phosphate (pH 2.3), containing 15% (v/v) acetonitrile. Elution proceeded at a flow rate of 1.0 mL min⁻¹, and was detected at 240 nm [10,19]. The amount of glyphosate adsorbed was calculated from the difference between its solution concentrations before and after equilibrium. All solution pHs after equilibrium were measured by a pH meter.

2.5. Effect of pH on glyphosate adsorption on the soils in the absence and presence of Zn

0.50 g soil was weighed in every 50 mL centrifuge tube. Five milliliters of 0.01 mol L⁻¹ NaNO₃ solution containing

Table 1
Basic physico-chemical characteristics of the RS and WS

Soil	pH _{1:2.5(H₂O)}	CEC (cmol _c kg ⁻¹)	OM (%)	Fe ₂ O ₃ (%)	Al ₂ O ₃ (%)	Clay content (%)
RS	4.95	14.06	0.76	6.57	17.37	56.23
WS	7.20	23.63	4.57	5.55	15.40	34.30

2.5 mmol L⁻¹ glyphosate was added in the tube. And then, different volume of 0.01 mol L⁻¹ NaOH or 0.01 mol L⁻¹ HNO₃ solution was added in different tubes to adjust solution pH varying from 3 to 9. In following, 0.01 mol L⁻¹ NaNO₃ solution was supplied in each tube. The final solution volume was 25 mL, and the glyphosate concentration in the solution was 0.50 mmol L⁻¹. In the presence of Zn, Zn concentrations were 0, 0.25, 0.50 or 1.0 mmol L⁻¹ in a respective pH series. The centrifuge tubes were continuously shaken for 2 h at 25 °C, and then centrifuged and filtrated through a filter paper. The glyphosate concentration in the centrifuged solution was determined by HPLC. The amount of glyphosate adsorbed was calculated from the differences between its solution concentrations before and after equilibrium. All solution pHs after equilibrium were measured by a pH meter.

3. Results and discussion

3.1. Soil Zn adsorption in the absence and presence of glyphosate

Fig. 1 shows the adsorption isotherms of Zn on the RS and WS in the absence and presence of glyphosate. Zinc adsorption on both the soils increased with increasing solution Zn. It is lower on the RS than that on the WS, because the RS has lower CEC and soil pH than the WS, as shown in Table 1.

Previous results showed that the presence of glyphosate decreased Cu or Cd adsorption on soils [10,20]. In this paper, when glyphosate coexisted with Zn in the equilibrium solution, it decreased Zn adsorption on both soils. The higher the solution glyphosate concentration, the lesser the Zn adsorbed on the soils, especially for the RS.

The herbicide glyphosate is an acid with several functional groups. Its introduction into the soil solution decreased the equilibrium solution pH, as shown in Table 2. The equilibrium pHs after Zn adsorption on the RS in the presence of GPS are lower than those on the WS. With the increasing GPS concentrations, the equilibrium solution pH gradually decreased. At GPS concentration of 0.5 mmol L⁻¹, the equilibrium solution pH on the points of given isotherms of the RS and WS decreased 0.61–0.89 and 0.91–1.33 pH unit, respectively. The effect of pH change on

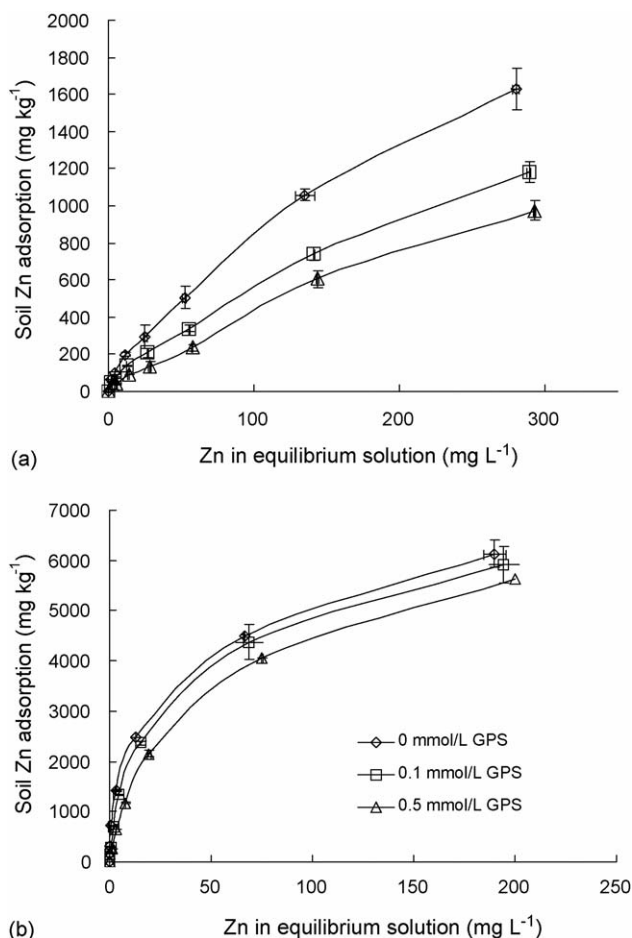


Fig. 1. Adsorption isotherms of Zn on the RS (a) and WS (b) affected by glyphosate.

Zn adsorption on the WS was lower than that on the R because Zn adsorption was much higher on the former one.

In order to know if pH was the only variable controlling Zn adsorption when coexisting with glyphosate, Zn adsorption on the soils in the absence and presence of glyphosate at different equilibrium solution pHs was carried out. Fig. 2 shows the experimental results with glyphosate in comparison with Zn adsorption without glyphosate on the RS and WS. Zinc adsorption alone on the soils increased with the increasing equilibrium

Table 2
Soil solution pHs after different concentrations of Zn were equilibrated with the RS and WS in the absence and presence of glyphosate

Soil solution pH						
Zn (mmol L ⁻¹)	RS			WS		
	0 mmol L ⁻¹ GPS	0.10 mmol L ⁻¹ GPS	0.50 mmol L ⁻¹ GPS	0 mmol L ⁻¹ GPS	0.10 mmol L ⁻¹ GPS	0.50 mmol L ⁻¹ GPS
0	4.50	4.24	3.61	6.81	6.46	5.48
0.05	4.38	4.21	3.60	6.78	6.47	5.53
0.10	4.34	4.18	3.60	6.66	6.39	5.45
0.25	4.27	4.14	3.55	6.50	6.24	5.30
0.50	4.19	4.10	3.52	6.31	6.02	5.18
1.0	4.17	4.05	3.51	6.04	5.81	5.02
2.5	4.08	3.98	3.46	5.74	5.51	4.76
5.0	4.04	3.94	3.43	5.50	5.34	4.59

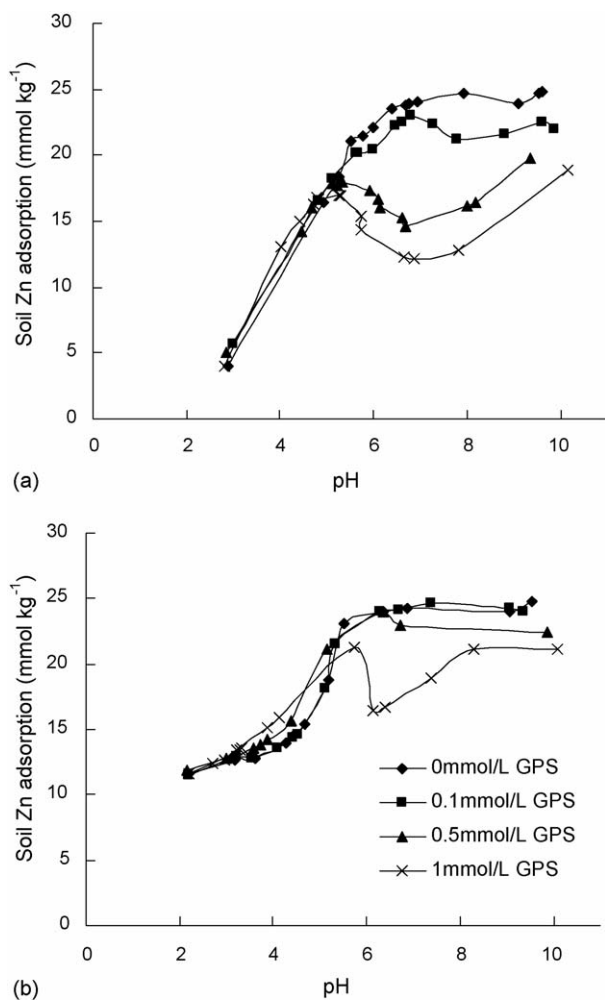


Fig. 2. Adsorption of Zn on the RS (a) and WS (b) as affected by soil solution pH and glyphosate.

solution pH. When the solution pH arrived at about 6.6, Zn adsorption on the soils reached a plateau. The increasing solution pH increased the negative charges density of soil surface, and correspondingly increased adsorption sites for Zn on these soils.

When the equilibrium solution pH was below 5.0, glyphosate hardly affected Zn adsorption; when the solution pH was above 5.0, glyphosate decreased Zn adsorption on these two soils drastically in comparison with Zn adsorption alone at a same pH. It suggests that the formation of Zn–glyphosate complexes, besides pH, affected Zn adsorption on these soils.

Glyphosate exists in solution as H_3L , H_2L^- , HL^{2-} and L^{3-} (L being the ligand GPS), depending on the solution pH, and can react with Zn^{2+} to form complexes as: $ZnHL$, ZnL^- , ZnL_2^{4-} and $Zn(OH)L^{2-}$ [5,21], as shown in Fig. 3. When the solution pH was above 4.5, the complexes of Zn and glyphosate, mainly existed as the negatively charged complexes ZnL^- and $Zn(OH)L$, which would have a lower affinity to the soil surface rather than free Zn^{2+} . An increase in GPS concentration further decreased the concentration of Zn^{2+} in the equilibrium solution, and this could be the reason of the lower Zn adsorption on these soils at $pH > 4.5$. Similarly, the concentration of free Cu^{2+}

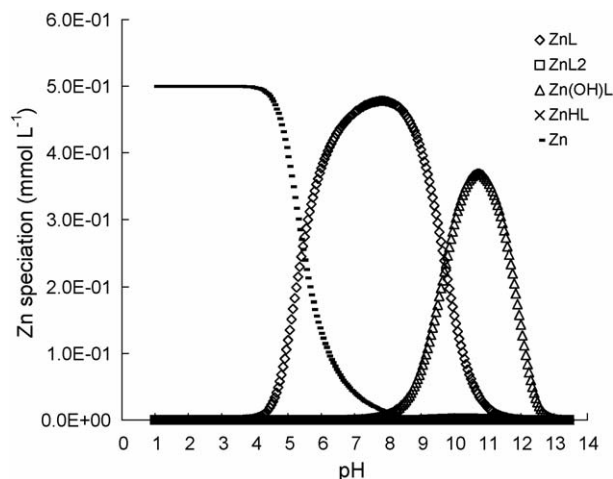


Fig. 3. Solution Zn speciation ($C_0 = 0.5 \text{ mmol L}^{-1}$) in the presence of 0.5 mmol L^{-1} glyphosate, calculated using WinSGW. Available from http://www.chem.umu.se/dep/inorgchem/samarbeta/WinSGW_eng.stm. The constants used in the calculation are defined according to the general equation: $pH + q(H_3L) + r(M^{2+}) = H_p(H_3L)_qM_r^{(p+2r)}$. The deprotonation of H_3L is given by Motekaitis and Martell [21]: $\log \beta_{-1,1,0} = -2.23$; $\log \beta_{-2,1,0} = -7.69$; $\log \beta_{-3,1,0} = -17.83$.

or Cd^{2+} in equilibrium solution was reported to be drastically reduced in the presence of glyphosate [10,14,16].

3.2. Adsorption of glyphosate on the soils in the absence and presence of Zn

Fig. 4 indicates glyphosate adsorption isotherms on the RS and WS in the absence and presence of different concentrations of Zn. The adsorbed amounts of glyphosate alone on the two soils increased with the increasing solution glyphosate concentration. Glyphosate adsorption on the RS was significantly higher than that on the WS, which can be ascribed to the higher content of iron oxides and lower pH value for the RS. Morillo et al. [17] studied the adsorption of glyphosate on some soils with different characteristics, and found that the adsorption of glyphosate is highly related to the content of the amorphous Fe and Al oxides. This conclusion was consistent with our experimental results. Recently, we examined the adsorption behavior of glyphosate on several soils with different characteristics. Our results indicated that GPS adsorption on the soils was related to the physico-chemical soil properties, which increased with increasing clay and iron oxides content and with decreasing soil pH [22].

Equilibrium solution pH is one of the factors responsible for GPS adsorption on soils. In the absence of Zn, the equilibrium solution pHs after GPS adsorption on the RS were lower than those on the WS (Table 3). Zinc increased the adsorption of glyphosate on the two soils. The more Zn added, the more glyphosate adsorbed. A possible explanation for these results could be that when Zn was present in the solutions, the equilibrium solution pHs decreased compared with that without Zn, which can be clearly observed in Table 3. There was a great decrease in equilibrium pH when solution Zn concentration increased, and they are 0.11–0.48 and 0.7–1.33 pH units lower

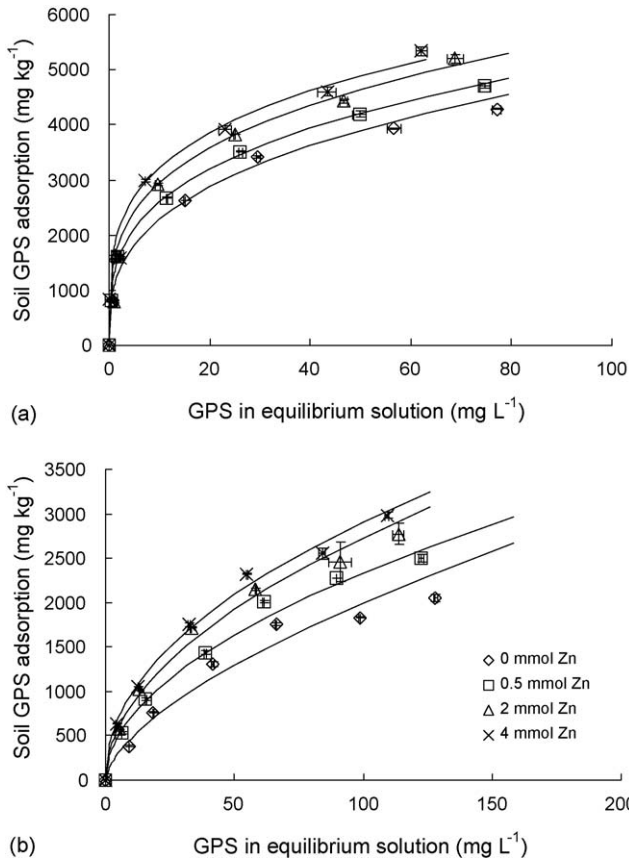


Fig. 4. Adsorption isotherms of glyphosate in the absence and presence of Zn on the RS (a) and WS (b).

than those for the GPS adsorption isotherm without 4 mmol L⁻¹ Zn in the RS and WS solution, respectively. Similar results were reported by Morrilo et al. [17] and Zhou et al. [10]. When metal cations were present in the soil solution, they can be adsorbed on the soil surface to exchange with H⁺. The more metal cations added, the more H⁺ ions released from soil. The decreased solution pH would reduce the negative charge of glyphosate molecules and therefore they would be in a larger extension adsorbed on the soils, mainly by an exchange-ligand mechanism between the phosphonate moiety of the herbicide molecule and the Fe- and Al-oxides [11–13]. Reduction of the negative charge

Table 3
Soil solution pHs after different concentrations of glyphosate were equilibrated with the RS and WS in the absence and presence of Zn

GPS (mmol L ⁻¹)	Soil solution pH				Soil solution pH			
	RS		WS		RS		WS	
	0 mmol L ⁻¹ Zn	0.5 mmol L ⁻¹ Zn	2.0 mmol L ⁻¹ Zn	4.0 mmol L ⁻¹ Zn	0 mmol L ⁻¹ Zn	0.5 mmol L ⁻¹ Zn	2.0 mmol L ⁻¹ Zn	4.0 mmol L ⁻¹ Zn
0	4.32	4.04	3.89	3.84	6.80	6.24	5.56	5.47
0.10	4.06	3.91	3.81	3.76	6.52	5.94	5.46	5.25
0.20	3.84	3.74	3.65	3.61	6.17	5.67	5.21	5.00
0.40	3.42	3.42	3.35	3.31	5.63	5.24	4.84	4.63
0.60	3.25	3.19	3.13	3.10	5.28	4.95	4.56	4.38
0.80	3.08	3.04	2.98	2.96	4.99	4.71	4.36	4.17
1.0	2.95	2.92	2.87	2.84	4.72	4.47	4.17	4.02

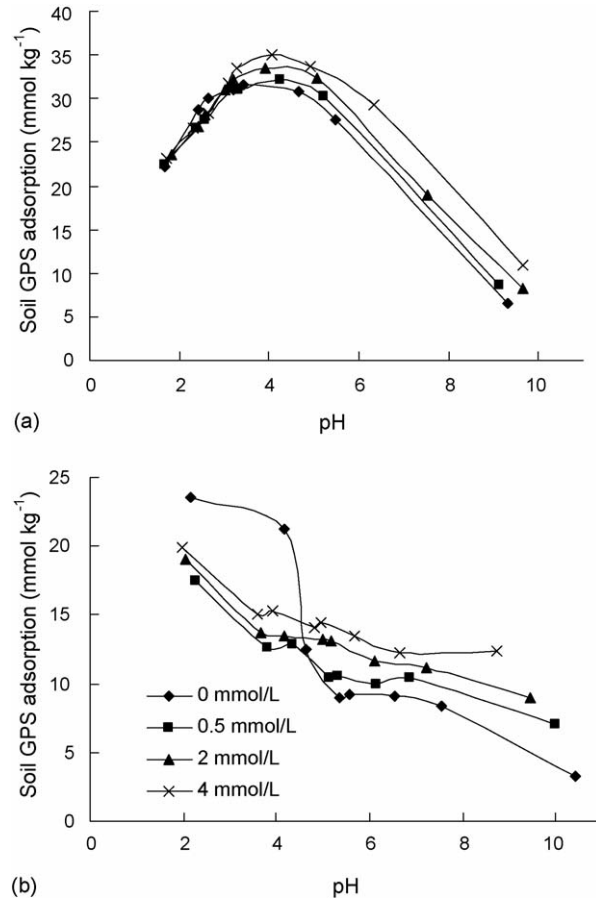


Fig. 5. Adsorption of glyphosate on the RS (a) and WS (b) as affected by soil solution pH and Zn.

of GPS molecules was found to promote its adsorption on soils and minerals [10,17].

Glyphosate adsorption on the soils in the absence and presence of Zn at different equilibrium solution pHs was carried out to know whether pH was the only variable affecting glyphosate adsorption in the presence of Zn (Fig. 5). The results showed that glyphosate adsorption alone on the WS decreased with increasing the equilibrium solution pH. However, the adsorption of the herbicide on the RS was different when the solution pH is below

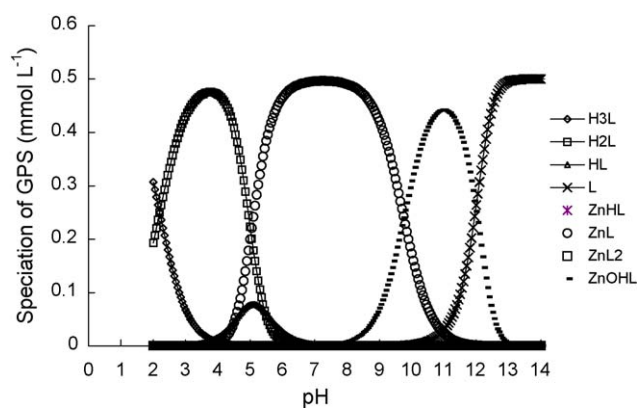


Fig. 6. Speciation of glyphosate ($C_0 = 0.5 \text{ mmol L}^{-1}$) affected by 1.0 mmol L^{-1} Zn, calculated using WinSGW.

4.0, since glyphosate adsorption increased with increasing the solution pH.

Fig. 6 shows the modeled species of glyphosate (0.5 mmol L^{-1}) in the absence and presence of 1.0 mmol L^{-1} Zn^{2+} , respectively. Glyphosate existed in the solution as H_3L , H_2L^- , HL^{2-} , L^{3-} , ZnHL , ZnL^- , ZnL_2^{4-} and $\text{Zn}(\text{OH})\text{L}^{2-}$. When solution pH is below 4, the main species of glyphosate are H_3L and H_2L^- ; but when pH is between 4 and 10, the main species of glyphosate are HL^{2-} and ZnL^- , and the presence of Zn^{2+} decreased the concentration of glyphosate species as H_2L^- and HL^{2-} . The complexes of Zn and glyphosate have more positive charges than H_2L^- and HL^{2-} , which resulted in their higher affinities to be adsorbed on the soils.

When Zn is present, the adsorption of glyphosate on the soils was affected. For the RS, Zn increased GPS adsorption in the examined pH range. For the WS, the effect is different. When the solution pH was below 4.7, Zn slightly decreased the adsorption of glyphosate; but when it was above 4.7, the presence of Zn increased its adsorption. Solution Zn reacted with glyphosate to form water-soluble complexes, which had less negative surface charge and were easily to be adsorbed on soil surface rather than HL^{2-} . In addition to that, glyphosate adsorption can take place on sites where Zn was specifically adsorbed at high pH, and acted as a bridge between the soil and glyphosate. Morillo et al. [16] also studied the effect of Cu on the adsorption of glyphosate on montmorillonite. They postulated that glyphosate adsorption on montmorillonite decreased in the presence of Cu due to the formation of Cu–glyphosate complexes that have a lower tendency to be adsorbed on montmorillonite than the free. Zhou et al. [10] studied the effect of Cd on the adsorption of glyphosate on two soils, and found that the presence of Cd increased adsorption quantity of glyphosate on soils by decreasing solution pH and forming Cd–glyphosate complexes with different solubilities depending on solution pH.

4. Conclusions

Glyphosate decreased the adsorption of Zn on the RS and WS by changing solution pH and complexing with soil Zn^{2+} to form water-soluble complexes of lower affinity for the soil surface than free Zn^{2+} , which suggests that the mobility of Zn^{2+}

from soil to the surface and underground water in field will increase when large amounts of glyphosate are applied. Application of Zn to both soils increased glyphosate adsorption, which was resulted from the decrease of equilibrium solution pH and triple-complexes formed among soil, Zn and glyphosate. It also suggests that the activity of glyphosate may be decreased by the presence of soil metals.

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