Adsorption of glyphosate in Chilean soils and its relationship with unoccupied phosphate binding sites[1]

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Abstract – The objective of this work was to investigate glyphosate adsorption by soils and its relationship with unoccupied binding sites for phosphate adsorption. Soil samples of three Chilean soils series – Valdivia (Andisol), Clarillo (Inceptisol) and Chicureo (Vertisol) – were incubated with different herbicide concentrations. Glyphosate remaining in solution was determined by adjusting a HPLC method with a UV detector. Experimental maximum adsorption capacity were 15,000, 14,300 and 4,700 μg g^{-1} for Valdivia, Clarillo, and Chicureo soils, respectively. Linear, Freundlich, and Langmuir models were used to describe glyphosate adsorption. Isotherms describing glyphosate adsorption differed among soils. Maximum adjusted adsorption capacity with the Langmuir model was 231,884, 17,874 and 5,670 μg g^{-1} for Valdivia, Clarillo, and Chicureo soils, respectively. Glyphosate adsorption on the Valdivia soil showed a linear behavior at the range of concentrations used and none of the adjusted models became asymptotic. The high glyphosate adsorption capacity of the Valdivia soil was probably a result of its high exchangeable Al, extractable Fe, and alophan and imogolite clay type. Adsorption was very much related to phosphate dynamics in the Valdivia soil, which showed the larger unoccupied phosphate binding sites. However relationship between unoccupied phosphate binding sites and glyphosate adsorption in the other two soils (Clarillo and Chicureo) was not clear.

Index terms: herbicide, dosage effects, models.

Adsorção de glifosato em solos chilenos e sua relação com sítios de adsorção disponíveis para adsorção de fosfato

Resumo – O objetivo deste trabalho foi investigar a adsorção de glifosato em solos e sua relação com os sítios disponíveis para adsorção de fosfato. Amostras de três solos chilenos – Valdivia (Andisol), Clarillo (Inceptisol) e Chicureo (Vertisol) – foram incubadas com diferentes concentrações do herbicida. O glifosato remanescente na solução foi determinado pelo método de HPLC com detector de UV modificado. A capacidade de adsorção máxima experimental foi de 15.000, 14.300 e 4.700 μg g^{-1} para os solos de Valdivia, Clarillo e Chicureo, respectivamente. Os modelos Linear, Freundlich e Langmuir foram utilizados para descrever a adsorção de glifosato. As isotermas de adsorção variaram de acordo com o tipo de solo. A capacidade de adsorção máxima ajustada com o modelo Langmuir foi 231.884, 17.874 e 5.670 μg g^{-1} para os solos Valdivia, Clarillo e Chicureo, respectivamente. A adsorção do glifosato no solo Valdivia mostrou um comportamento linear na faixa de concentração usada e nenhum dos modelos ajustados chegou a ser assintótico. A alta capacidade de adsorção de glifosato no solo Valdivia pode ser explicada por seu alto teor de Al trocável, alta disponibilidade de Fe e presença de argilas de tipo alofana e imogolita. A adsorção esteve muito relacionada à dinâmica do fosfato no solo Valdivia, que mostrou grande número de sítios disponíveis para a adsorção de fosfato. Entretanto, a relação entre os sítios de adsorção de fosfato livre e a adsorção de glifosato nos solos Clarillo e Chicureo não ficou clara.

Termos para indexação: herbicida, efeito de dosagem, modelos.

Introduction

Glyphosate is an important herbicide in Chile. Because of its wide weed control spectrum, it is used mainly in forestry, orchards, vineyards and no-till cropping systems. Applications of herbicides in

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forestry, mainly in radiata pine afforestation, have been a public concern lately. Glyphosate is by far the most used herbicide. Following a post-emergence application, a large proportion of glyphosate could reach the soil. However, it shows little herbicidal activity when applied to the soil (Shoval & Yariv, 1979). This effect has been ascribed to its adsorption to soil particles, which is supported by several bench-mark studies such as those of Sprankle et al. (1975a), Rueppel et al. (1977) and Hensley et al. (1978).

Glyphosate primary adsorption to soil occurs through the phosphonic acid moiety in its phosphonate anion form as phosphate does in soil (Sprankle et al., 1975b), even though the carboxylic group can also participate in this process. Ion exchange and hydrogen bonding can explain glyphosate soil adsorption (Miles & Moye, 1988). However, glyphosate soil adsorption could be also variable and, in some cases, not as high as supposed. Hance (1976) showed that, in some soils, glyphosate was adsorbed as much as diuron, a typically soil-active herbicide.

Some evidences of glyphosate soil activity have been reported. Rodriguez & Worsham (1980), cited by Torstensson (1985), found that ^{14}C-glyphosate applied to wheat (*Triticum aestivum* L.) foliage was exuded from the roots into the soil and caused root inhibition and foliage injury to corn (*Zea mays* L.) seedlings growing in the same soil. On the other hand, Salazar & Appleby (1982) showed that glyphosate can injure some plant species through uptake from soil, where the herbicide remained available for a sufficiently long period of time, one to five days. However, these experiments were done under a set of conditions which maximized soil activity. Cornish (1992) found injury in tomato plants (*Lycopersicon esculentum* Mill.), when they were transplanted into a soil previously treated with glyphosate and phosphorus.

Glyphosate degradation is brought about by soil microorganisms (Sprankle et al., 1975a; Rueppel et al., 1977). However, its half life values have been highly variable, from less than a week to one or two months (Roy et al., 1989). Considering these findings it looks like glyphosate can persist for certain period of time in the soil solution, being available for degradation and root absorption.

Although several studies on glyphosate adsorption in soils have been previously conducted in different parts of the world, there have not been reports for Chilean soils. Data generated on this regard is of major importance in determining environmental fate of this herbicide and understanding glyphosate soil dynamics.

The objective of this work was to investigate the adsorption capacity of glyphosate in soils and its relationship with unoccupied binding sites for phosphate adsorption.

Material and Methods

The names, soil taxonomy order and selected properties of the three soils used in the experiment are given in Table 1. Soils, collected from 0 to 10 cm depth, were ground and passed through a 1-mm sieve and then dried out at 40ºC, until they reached constant weight. Chemical analyses for characterization were performed using standard procedures (Sadzawka et al., 2000): soil pH was determined in a 1:2.5 soil: water suspension; organic carbon by colorimetry after a wet combustion using sulfuric acid and sodium dichromate; exchangeable calcium and aluminum by atomic absorption after an extraction with ammonium acetate at pH 7 and potassium chloride, respectively; extractable iron by atomic absorption using DTPA-TEA as extractant solution.

Soil samples (3 g) of each soil were mixed with 30 mL aliquots of increasing glyphosate (480 g isopropyl amine salt L^{-1}, equivalent to 360 g L^{-1} ae) concentrations (1,000, 1,500, 2,000, 2,500 mg L^{-1} ae) in plastic screw cap vials. Samples were placed on a reciprocal shaker at 20ºC, for

Table 1. Selected chemical and physical properties of studied soils.

Soil series	Soil order	pH	Organic C (g kg^{-1})	Exchangeable Al	Fe-DTPA (mg kg^{-1})	Exchangeable Ca	Sand	Silt (g kg^{-1})	Clay
Chicureo	Vertisol	7.38	9.8	0.51	8.3	5.29	66	354	580
Valdivia	Andisol	4.79	66.0	207.00	103.0	86.00	246	574	180
Clarillo	Inceptisol	7.76	15.2	0.53	32.2	4.17	174	486	340

four hours, to get the adsorption thermodynamic equilibrium (Sprankle et al., 1975a; Hance, 1976; Nomura & Hilton, 1977; Cheah et al., 1997). Samples were subsequently centrifuged for 20 min at 20,000 rpm at 1ºC (Ultracentrifuge Sorvall OTD-Combi) and the liquid phases were then passed through filter paper (MFS 5c, Whatman 42 equivalent). All soil samples were prepared in duplicate.

Blanks without herbicide were obtained following the same procedure to get a calibration curve for each soil, to avoid possible interference with the soil matrix.

Supernatants were passed through a membrane filter (cellulose acetate) 0.2 μm (Sartorius) to separate solid particles. Afterwards a 5 mL sample was collected from each filtered supernatant, and then dried out in a rotavapor with empty system (Bibby RE 200). The solid residue was reconstituted in 10 mL mobile phase used for HPLC analysis (4% methanol solution containing 0.08437 g KH_2PO_4 L^{-1}) and then sonicated for 10 minutes.

HPLC analysis were carried out using a Lachrom-Merck apparatus, equipped with a 20 μL fix loop, a UV detector at 195 nm, an anion exchange column (Partisil 10 SAX, 25 cm x 4,6 mm, Alltech) and a Varian software. The detection limit was determined at 30 mg L^{-1} and the quantification limit at 50 ppm.

Analytical-grade glyphosate (99% purity, Supelco certified) was used to calculate calibration curves for HPLC analysis.

The HPLC method used is described for 4,000 mg L^{-1} glyphosate concentration (AOAC 9831). Because glyphosate does not have a strong chromophore to impart UV absorbance, relatively high glyphosate concentrations were used to incubate the soils to allow adequate quantification. This method was then validated for lower glyphosate concentrations (50 to 400 ppm), evaluating the following parameters: selectivity, precision, linearity and sensitivity.

Each sample was injected twice to determine glyphosate content by integrating the obtained peak with the respective standard glyphosate calibration curve prepared at the same time than the sample. The glyphosate content was the average of two measurements, with no more than 5% deviation between samples.

Adsorption values, over the range of glyphosate concentrations used in this experiment, were utilized to fit Linear [1], Freundlich [2], and Langmuir [3] models:

$$C_s = K_d C_e , \quad [1]$$

$$C_s = K_f C_e^n , \quad [2]$$

$$C_s = C_m \frac{K_l C_e}{1 + K_l C_e} , \quad [3]$$

where C_s is the amount of glyphosate adsorbed (μg g^{-1}), C_m is the maximum amount of glyphosate adsorbed (μg g^{-1}), C_e is the equilibrium concentration of the herbicide in the solution (μg mL^{-1}), K_d, K_f, and K_l are the linear, Freundlich, and Langmuir absorption coefficients, respectively (mL g^{-1}), and n is a linearity factor (De Jonge et al., 2001; Zhu & Selim, 2002). The isotherm model parameters were obtained by a non-linear optimization routine in Microcal Origin (Microcal Software Inc., 2000).

Phosphate sorption at pH 2.6 was determined following the methodology described by Williams et al. (1958) by shaking 2.5 g of soil for 2 hours with 100 mL of 2.5% v/v acetic acid solution containing KH_2PO_4, equivalent to 150 mg of P_2O_5 per 100 g of soil. Samples were placed on a reciprocal shaker at 22ºC. Blank samples with no phosphorus addition were also included. The inorganic phosphate left in solution was determined by molecular absorption spectroscopy, according to Olsen & Sommers (1982). Phosphate sorbed was then calculated from (P_2O_5 added) + (ordinary acetic-soluble P_2O_5) – (P_2O_5 left in solution).

Results and Discussion

Fitted isotherm models were used to compare the studied soils in terms of their capacity of adsorbing glyphosate. Isotherm parameters for the different models are shown in Table 2. All models, except the linear one on the Clarillo soil, properly fitted the experimental data, however all of them were highly significant ($P<0.01$). Valdivia soil showed the highest capacity of glyphosate adsorption. At the maximum herbicide concentration tested (2,500 mg L^{-1}), sorbed

Table 2. Isotherm parameters for the Linear, Freundlich, and Langmuir models used to compare Chilean soils for glyphosate adsorbing capacity.

Soil	Linear model		Freundlich model			Langmuir model		
	K_d (mL g^{-1})	R^2	K_f (mL g^{-1})	n	R^2	K_l (mL g^{-1})	C_m (μg g^{-1})	R^2
Chicureo	3.71	0.76	839	4.20	0.99	0.00330	5,670	0.99
Valdivia	12.13	0.87	0.015	0.47	0.99	0.00005	231,884	0.86
Clarillo	16.67	0.40	1,667	3.20	0.98	0.00410	17,874	0.99

glyphosate reached approximately 15,000 μg g^{-1}. According to the Langmuir model, the maximum amount of glyphosate adsorbed by this soil was 231,884 μg g^{-1}. However, under these experimental conditions Valdivia soil did not reach saturation and none of the models became asymptotic (Figure 1). On the other side, maximum glyphosate adsorption for Clarillo and Chicureo soils were approximately 14,300 and 4,700 μg g^{-1}, respectively, while the maximum adsorption capacity estimated by the Langmuir model were 17,874 and 5,670 μg g^{-1}, respectively. The high adsorption capacity found on the Valdivia soil could be explained by its mineral composition, which consists on alophan and imogolite clay types (Besoain & Sadzawka, 1999). These amorphous clay structures and the high levels of extractable Fe (103 ppm) and Al (207 ppm) would be responsible for the high P fixation capacity that characterizes this volcanic Chilean soil and also would explain its high affinity for glyphosate.

The difference between the isotherms that describe glyphosate adsorption on Chicureo and Clarillo soils is reflected on the K_i (where i = d, f, and l) values obtained for both soil types (Table 2). The greatest K_i estimated for the Clarillo soil could be explained by its higher DTPA extractable Fe content which is about four times the amount found in Chicureo soil (Table 1). It has been reported that this cation is one of the most important in inactivating glyphosate in soil solution (Sprankle et al., 1975a; Hensley et al., 1978; McConnell & Hossner, 1985; Glass, 1987; Gerritse et al., 1996). As clay content is also a factor that has been reported affecting glyphosate adsorption, it can be thought that adsorption should be higher in the case of Chicureo soil that has a higher clay content than Clarillo soil. However, it seems like clay type is more important than its percent content (Sprankle et al., 1975a; McConnell & Hossner, 1985; Glass, 1987; Miles & Moye, 1988). The predominant clay type found in Chicureo soil is montmorillonite (2:1 form) while in the Clarillo soil, due to its more recent formation, there is a mixture of 2:1 and 1:1 (kaolinite) clays and probably, some alophan. These results agree with those of Glass (1987), who considered that adsorption capacity of kaolinite was higher than montmorillonite, although this can vary depending on experimental conditions, such as pH, clay minerals origin and others.

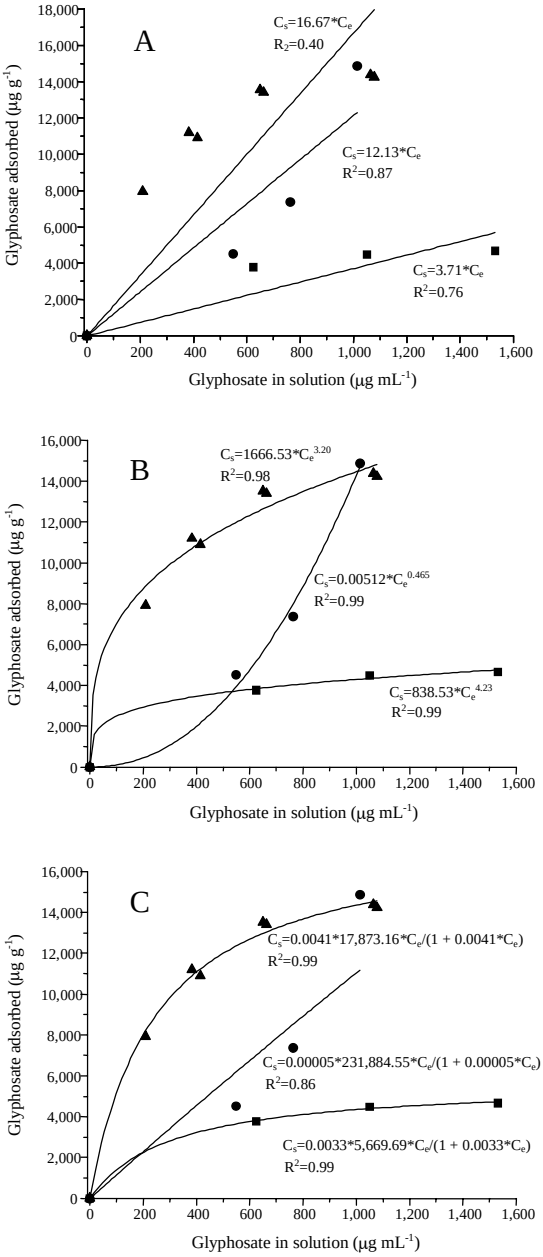

Figure 1. Adsorption isotherms for glyphosate on Clarillo (▲), Chicureo (■), and Valdivia (●) soils, using Linear (A), Freundlich (B), and Langmuir models (C), to compare their ghyphosate adsorbing capacity.

Values obtained for K_i constants seem to be high but they can be explained by the high glyphosate concentrations used to incubate the soils, in order to determine this compound with the available HPLC equipment. Gerritse et al. (1996) pointed out that K_f values obtained using Freundlich linear adsorption model could vary according to the herbicide concentration used to incubate the soil.

Valdivia soil showed a linear behavior in terms of glyphosate adsorption in the range of concentrations used. Thus none of the fitted models became asymptotic, although only the Langmuir one allowed to estimate a maximum adsorption capacity. According to Green (1974), Freundlich model is not able to describe soils with high adsorption rates. A similar situation was described by Nomura & Hilton (1977), working with high sorption capacity Hawaiian soils. These findings were probably referred to the linearization process needed to adjust the model in absence of proper software at that time. Besoain & Sadzawka (1999) mentioned Freundlich model as the best adapted to describe phosphorus sorption in Chilean Andisols. More recently, De Jonge et al. (2001) found that glyphosate sorption isotherms were best fitted with an extended Freundlich model, which had been shown earlier to properly describe phosphate sorption. For future experiments, the selected isotherm model would depend on the studied range of glyphosate concentrations and the objectives pursued, with simpler linear models being probably more appropriate for glyphosate concentrations near to commercial rates.

Because glyphosate and P adsorption dynamics are believed to be highly related (Sprankle et al., 1975a ; Hance, 1976; Nomura & Hilton, 1977), the differences found between soils for glyphosate adsorption could be partially explained by the unoccupied phosphate binding sites in each soil more than by the total phosphate sorption capacity.

Glyphosate adsorption was very much related to phosphate dynamics in the Valdivia soil, which showed both the highest glyphosate (Figure 1, Table 2) and phosphate adsorption (Table 3). This is in agreement with the large number of unoccupied phosphate binding sites found for that soil. In contrast Clarillo soil showed higher glyphosate adsorption than Chicureo soil, but unoccupied phosphate binding sites were very much similar (Table 3). A good relationship between glyphosate adsorption and unoccupied phosphate sites for these two soils was expected. However, it must be mentioned that Clarillo soil had a higher organic carbon content than Chicureo soil (Table 1). Although there are research results showing less glyphosate adsorption as the soil carbon increases (Gerritse et al., 1996), there are also other experiments that attribute an important role to the organic matter on glyphosate soil adsorption, through hydrogen bonds (Nomura & Hilton, 1977; Piccolo et al., 1996). It must be considered that the large glyphosate concentration used in this experiment, to incubate the soil, could have displaced the equilibrium between adsorbed and solution fractions.

Glyphosate binding can also be influenced by the presence of specific cations. Hensley et al. (1978) demonstrated that Fe^{2+}, Fe^{3+} and Al^{3+} inactivated glyphosate much more than other cations. Glass (1987) suggested that glyphosate can be complexed by cations released from cation-saturated clays via cation exchange with solution protons. Indeed, Clarillo soil has about four times more available iron than Chicureo soil, which could explain in part its larger glyphosate adsorption.

Table 3. Phosphorus sorptive capacity and unoccupied binding sites (average values from three replications) of Chilean soils.

Soil serie	P in solution (µg in 100 mL)	Occupied sites (µg g^{-1})	Fixed P (mg)	Unoccupied sites (µg g^{-1})	Total sorptive capacity (µg g^{-1})
Chicureo	2,130	274.8	0.198	79.2	354.0
Valdivia	140	1.6	1.502	600.8	602.4[(1)]
Clarillo	2,650	478.0	0.186	74.5	552.5

[(1)]Corresponds to the maximum P fixed, because this soil was not saturated with the amount of P used for the experiment.

Conclusions

1. Glyphosate adsorption capacity by Chilean soils is high and it is related to unoccupied phosphate binding sites for the Andisol soil type.
2. The use of different adsorption models allows a better understanding of the variability in adsorption capacity among studied soils.

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References

BESOAIN, E.; SADZAWKA, M. A. Fenómenos de retención de fósforo en los suelos volcánicos y sus consecuencias. In: BESOAIN, E.; ROJAS, C.; MONTENEGRO, A. (Ed.). **Las rocas fosfóricas y sus posibilidades de uso agrícola en Chile**. Santiago: Instituto Nacional de Investigaciones Agropecuarias/Ministerio de Agricultura, 1999. p. 23-40.

CHEAH, U.; KIRKWOOD, R.; LUM, K. Adsorption, desorption and mobility of four commonly used pesticides in Malaysia agriculture soils. **Pesticide Science**, Chichester, v. 50, p. 53-63, 1997.

CORNISH, P. Glyphosate residues in a sandy soil affect tomato transplants. **Australian Journal of Experimental Agriculture**, Collingwood, v. 32, p. 395-399, 1992.

DE JONGE, H.; DE JONGE, L. W.; JACOBSEN, O. H.; YAMAGUCHI, T.; HOLDRUP, P. Glyphosate sorption in soils on different pH and phosphorus content. **Soil Science**, Baltimore, v. 166, p. 230-238, 2001.

GERRITSE, R.; BELTRAN, J.; HERNANDEZ, F. Adsorption of atrazine, simazine and glyphosate in soils of the Gnangara mount, Western Australia. **Australian Journal of Soil Research**, Collingwood, v. 34, p. 599-607, 1996.

GLASS, R. Adsorption of glyphosate in soil and clay minerals. **Journal of Agricultural and Food Chemistry**, Washington, v. 35, p. 497-500, 1987.

GREEN, R. Pesticide-clay-water interaction. In: GUENZI, W. D. (Ed.). **Pesticides in soil and water**. 3rd ed. Madison: Soil Science Society of America, 1974. p. 2-37.

HANCE, R. J. Adsorption of glyphosate by soils. **Pesticide Science**, Chichester, v. 7, p. 363-366, 1976.

HENSLEY, D.; BEUERMAN, D.; CARPENTER, P. The inactivation of glyphosate by various soils and metal salts. **Weed Research**, Oxford, v. 8, p. 287-291, 1978.

McCONNELL, J.; HOSSNER, L. X-ray diffraction and infrared spectroscopic studies of adsorbed glyphosate. **Journal of Agricultural and Food Chemistry**, Washington, v. 37, p. 550-560, 1985.

MICROCAL SOFTWARE INC (Northampton, United States). **Microcal help**: curve fitting. Northampton, 2000. p. 509-594.

MILES, C.; MOYE, H. Extraction of glyphosate herbicide from soil and clay minerals and determination of residues in soils. **Journal of Agricultural and Food Chemistry**, Washington, v. 36, p. 486-491, 1988.

NOMURA, N.; HILTON, H. The adsorption and degradation of glyphosate in five Hawaiian sugarcane soils. **Weed Research**, Oxford, v. 17, p. 113-121, 1977.

OLSEN, S.; SOMMERS, L. Phosphorus. In: PAGE, A. (Ed.). **Methods of soil analysis**. 2nd ed. Madison: American Society of Agronomy/Soil Science Society of America, 1982. v. 2, p. 403-427.

PICCOLO, A. G.; CELANO, G.; CONTE, P. Adsorption of glyphosate by humic substances. **Journal of Agricultural and Food Chemistry**, Washington, v. 44, p. 2242-2246, 1996.

ROY, D.; KONER, S.; BANERJEE, S.; CHARLES, D.; THOMPSON, D.; PRASSAD, R. Persistence, movement and degradation of glyphosate in selected Canadian boreal forest soils. **Journal of Agricultural and Food Chemistry**, Washington, v. 37, p. 551-559, 1989.

RUEPPEL, M.; BRIGHTWELL, B.; SCHAEFER, J.; MARCEL, J. Metabolism and degradation of glyphosate in soil and water. **Journal of Agricultural and Food Chemistry**, Washington, v. 25, p. 517-528, 1977.

SADZAWKA, A.; GREZ, M.; MORA, M.; SAAVEDRA, N.; CARRASCO, M.; ROJAS, C. **Métodos de análisis de suelo recomendados para suelos Chilenos**. Santiago: Comisión de Normalización y Acreditación de la Sociedad Chilena de la Ciencia del Suelo, 2000. p. 1-63.

SALAZAR, L.; APPLEBY, Z. Herbicidal activity of glyphosate in soil. **Weed Science**, Lawrence, v. 30, p. 463-466, 1982.

SHOVAL, S.; YARIV, S. The interaction between Roundup (glyphosate) and montmorillonite - part I: infrared study of the sorption of glyphosate by montmorillonite. **Clays and Clay Minerals**, Boulder, v. 27, p. 19-28, 1979.

SPRANKLE, P.; MEGGIT, W.; PENNER, D. Adsorption, mobility and microbial degradation of glyphosate in soil. **Weed Science**, Lawrence, v. 23, p. 229-234, 1975a.

SPRANKLE, P.; MEGGIT, W.; PENNER, D. Rapid inactivation of glyphosate in the soil. **Weed Science**, Lawrence, v. 23, p. 224-228, 1975b.

TORSTENSSON, L. Behaviour of glyphosate in soils and its degradation. In: GROSSBARD, E.; ATKINSON, D. (Ed.). **The herbicide glyphosate**. London: Butterworths, 1985. p. 137-150.

WILLIAMS, E. G.; SCOTT, N. M.; McDONALD, M. Soil properties and phosphate sorption. **Journal of the Science of Food and Agriculture**, Barking, v. 9, p. 551-559, 1958.

ZHU, H.; SELIM, M. H. Retention and mobility of deltamethrin in soils – 1: absorption-desorption. **Soil Science**, Baltimore, v. 167, p. 513-523, 2002.