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Article

Monitoring of the Harmful Concentrations of 2,4-Dichlorophenoxyacetic Acid (2,4-D) in Soils with and without Organic Matter

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Os pesticidas têm sido usados para eliminar formas indesejáveis de vida nocivas à agricultura ou em áreas urbanas. O êxodo rural e, conseqüentemente, o aumento de preço da mão-de-obra remanescente nas áreas agrícolas levaram a um aumento do uso de herbicidas nas lavouras, principalmente do 2,4-D. Através de processos de adsorção-dessorção a mobilidade do herbicida 2,4-D pode ser avaliada. A contribuição da matéria orgânica do solo foi avaliada no processo de sorção do referido herbicida, constatando-se que a mesma contribui para o aumento de sua adsorção. A concentração ideal de 2,4-D a ser aplicada em um solo tipo latossolo roxo foi determinada através de experimentos de adsorção-dessorção.

Agrochemicals have been used to eliminate different undesirable forms of life both in agriculture and in urban areas. The rural exodus and the increase of labor costs in the agricultural areas have induced a greater use of herbicides in crops, mainly of 2,4-D. Through adsorption-desorption processes the mobility of this herbicide can be evaluated. The effect of organic matter on sorption of 2,4-D in soil has been studied. Organic matter contributed to the increase of 2,4-D adsorption. The ideal concentrations of 2,4-D in yellow-red Latosol soils were determined based on adsorption-desorption experiments.

Keywords: sorption, soil, 2,4- dichlorophenoxyacetic acid , organic matter

Introduction

The herbicide 2,4-dichlorophenoxyacetic acid (2,4-D) is commonly used in Brazilian agriculture, mainly in sugar cane crops[1,2]. This herbicide is used for a control of wide range of broad leaf weeds and grasses in plantation crops, such as sugar cane, oil palm, cocoa and rubber[3].

Soil is the most important part of the geosphere. It provides most of foods, minerals and fuels[4]. On the other hand, soil can be considered as an open system, inside of which or on whose surface several physical, chemical and biological processes may occur[5]. The organic matter (OM) present in soils is a mixture of products in a wide range of decomposition stages, resulting from chemical and biological degradation of plant and animal residues and synthetic activity of microorganisms[5]. Among the soil OM constituents, humic substances are the most important, because of their widespread distribution in all terrestrial and aquatic environments[6].

Adsorption processes in the soil-water interface system depends directly on soil exchange properties. The OM plays an important role in forming aggregates which control the acidity, cycling the nutrient elements and degrading pollutants[7-9]. Nevertheless, various contaminants are firmly held onto the solid surface of the soil and are available to solid/liquid interface phenomena or are distributed among the arrays of silicates in bulk[7,10]. Adsorption is one of the key processes affecting the ultimate fate of pesticides in soils. In particular, the interactions at the interface between organic and inorganic soil colloids and pesticides through adsorption-desorption mechanisms may influence movement of pesticides, and thus availability for plant and contamination of rivers and underground waters[11]. The extent of adsorption is related to various soil properties, including OM content, type and clay content, exchange capacity, acidity, and to physical and chemical parameters of the adsorbed compound[11,12].

The objective of this work was to evaluate the harmful concentrations of 2,4-D added to the entire soil (with organic matter) (SPOM) and to the soil without organic matter (SAOM) for adsorption-desorption studies, and to understand the effect of OM on soil sorption.

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Materials and Methods

Reagents

All chemicals used such as methanol, sulfuric acid, Florisil (Merck), N-metil-N-nitro-p-toluenesulphamide (Aldrich), ethylic ether, $CaCl_2$ (QM) and 2,4-D (Sigma) were reagent grade. Florisil (ASTM), 60-100 mesh, was activated through heating at 923 K for 4 h.

Soil Samples

The soil collected was yellow-red Latosol, which covers around 60% of the São Paulo state, was obtained in Experimental Station of the Agronomic Institute of Campinas (IAC), in Pindorama Town, São Paulo state, Brazil.

The samples were collected from a depth of 5-10 cm, after removal of the top surface layer[13]. The samples were air dried for thirty days and homogenized by sieving, less than 2 mm[14].

The SPOM was obtained from yelow-red Latosol soil air dried and sieved, and SAOM was obtained from this soil combusted at 773 K for 24 h.

Adsorption and desorption experiments

Sorption experiments were performed according to the following procedure: 1 g SAOM or 1 g SPOM samples were placed in erlenmeyer flasks and shaken for 24 h, at 25 ^oC, with 25.0 mL of a 1.0 mmol L^{-1} $CaCl_2$ solution. The herbicide was added to this solution in order to achieve the desired concentration from 0.01 mg to 1.5 mg of 2,4-D per gram of soil[2,6]. After an equilibration period of 24 h, each suspension was centrifuged at 3000 rpm, for 20 min. The liquid phase was carefully separated and acidified with sulfuric acid until pH 1[2]; it contains the herbicide concentration not adsorbed on soil. 2,4D was extracted from water by liquid-liquid extraction, using 10 mL of ethyl ether. Ether solution was evaporated to dryness, and suspended with 2 mL of methanol. Samples were estherified with diazomethane previously synthesized through experimental procedure recently described[2]. The amount of herbicide at equilibrium was determined by gas chromatography with electron capture detection (GC/ECD), using an Ultra II column (5% phenyl 95% dimethylpolysiloxane) with 25 m x 0.2 mm x 0.33 μm. The extent of adsorption was estimated as the difference between initial and equilibrium herbicide concentrations. To estimate desorption, all the supernatant was carefully removed and 25.0 mL of a 1.0 mmol L^{-1} $CaCl_2$ solution were added. The whole procedure was repeated. The extent of desorption was determined as herbicide concentration at equilibrium. All experiments were carried out in triplicate.

Results and Discussion

Soil characterization

Samples of yellow-red Latosol soil were selected for this study because this type of soil represents almost 60 % of the area of the São Paulo State[2].

Soil physical and chemical characteristics, such as pH, organic matter content, sand, silt, type and content of clay were important, because adsorption-desorption processes depend on them. The soil samples presented 0.70 % of organic matter, 69.0 % of sand, 12.0 % of silt, and 19.0 % of clay (kaolynite, gipsyte, mica and vermicoalynite), and pH = 6.90, according to previous measurements[15].

Quantitative analysis

The recovery of the total analytical procedure for 2,4-D was 83.32 ± 1.92 %. The experiments were performed, at least, in triplicates.

The herbicide equilibrium, adsorbed and desorbed concentrations were determined by GC/ECD. 2,4-D was determined as esther after reaction with diazomethane, whose excess was evaporated, not contaminating the samples[2].

The reaction mechanism of 2,4-D with diazomethane is shown in Figure 1. The chromatograms obtained had the profile shown in Figure 2.

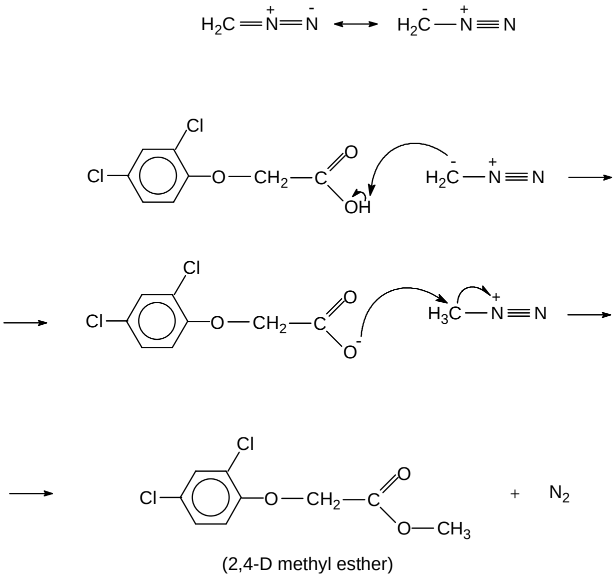


Figure 1. Reaction mechanism of 2,4-D with diazomethane.

The amount of the herbicide adsorbed, desorbed, bonded and free in SPOM and in SAOM samples for all applied concentrations are shown in Figures 3 and 4. Adsorption/desorption data were plotted through the chromatographic data obtained.

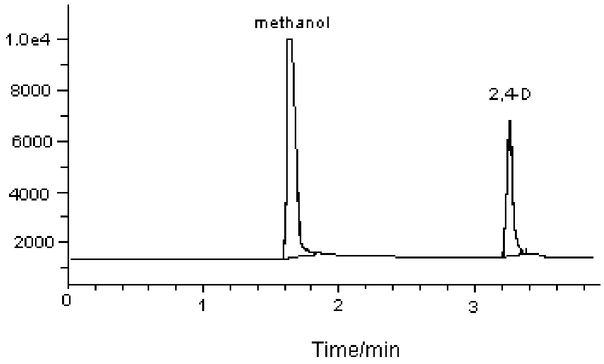


Figure 2. Gas chromatogram of 2,4-D methyl esther.

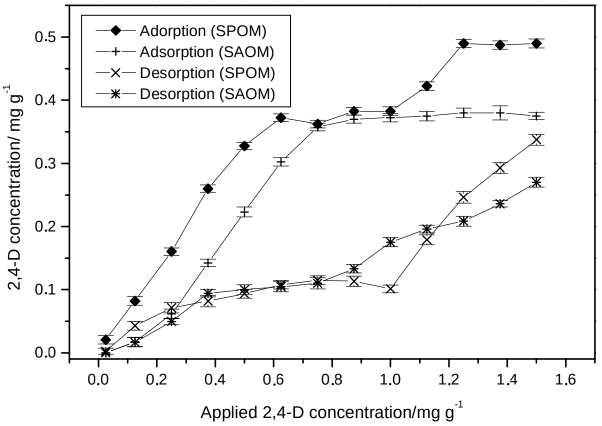
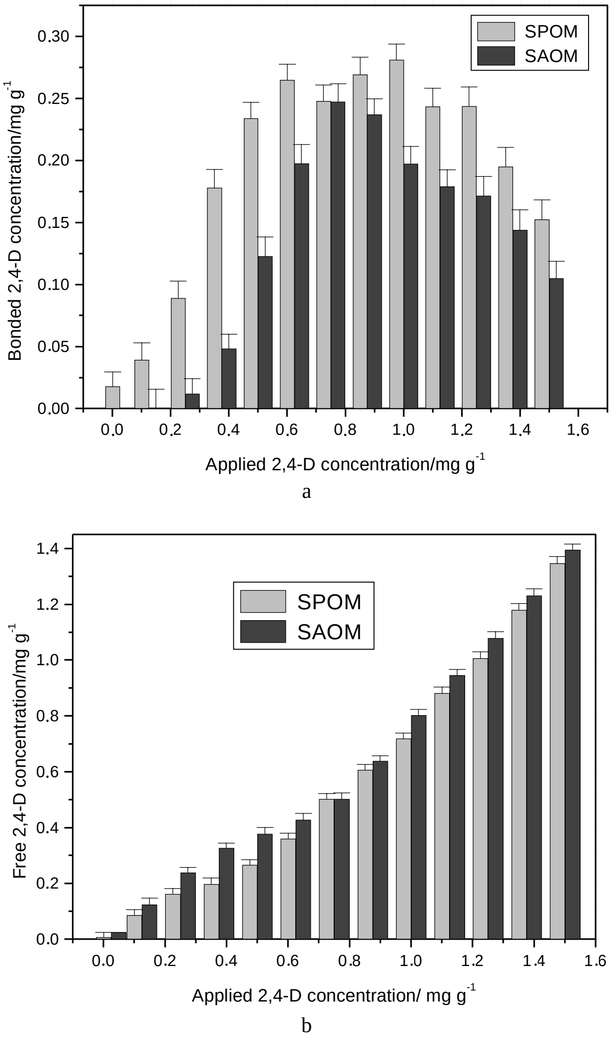


Figure 3. Adsorption and desorption curves of 2,4-D on SPOM and SAOM (in values of mg of 2,4-D per gram of soil, all experiments in triplicates).



a

b

Figure 4. (a) Bonded concentration of 2,4-D on SPOM and SAOM and (b) Free concentration of 2,4D on SPOM and SAOM (in values of mg of 2,4-D per gram of soil).

SAOM adsorbs 2,4-D less than SPOM, until a concentration of 0.6 mg g^{-1} (Figure 3). The adsorption becomes equivalent for both between 0.7 to 1 mg g^{-1}, considering the applied concentration values. Above this value, SAOM reaches the equilibrium, adsorbing 0.35 mg g^{-1} of 2,4-D. However, SPOM reaches the equilibrium at 0.5 mg g^{-1}. This difference occurs due to the presence of organic matter in this SPOM, equivalent to 0.7% of weight, which was eliminated by calcination in SAOM. This result shows that a small amount of organic matter influences directly the agrochemical adsorption in soil. Therefore, lability and inerteness of this pesticide is associated with organic matter present in soil.

The effect of the presence and absence of organic matter on desorption is presented in Figure 4.

The desorption of 2,4-D bound in SPOM and SAOM by using $CaCl_2$ solutions present similar behavior until 0.8 mg g^{-1} of applied 2,4-D concentration (Figure 4). Above this value up to 1.2 mg g^{-1}, SAOM desorbs more than SPOM. Above 1.2 mg g^{-1}, SPOM desorbs more than SAOM. The effect of the presence of organic matter in soil was not very intense for small concentrations of 2,4-D. However, above 1.2 mg g^{-1} the organic matter presented a direct effect on desorption. Even so, the SAOM desorbed more 2,4-D than SPOM, for higher applied quantities.

To understand the influence of OM in the interaction of 2,4-D with soil, a curve of bonded concentration of 2,4-D in SPOM and SAOM was plotted (Figure 4). Bonded concentration corresponds to the adsorbed concentration less desorbed concentration. Bonded concentration shows the real quantities of 2,4-D linked to the soil. The free concentration, which is represented by the sum of desorbed and equilibrium concentrations, was plotted in reference to applied concentration to better show the quantities of 2,4-D lost in the environment.

Figure 4a shows that 2,4D is more bonded in SPOM than SAOM for all range of applied concentrations. The loss to the environment is smaller in SPOM than in SAOM for any applied concentration of 2,4D (Figure 4b). These results confirm that OM is a key factor in the interaction process of agrochemicals on soil.

To analyze the behavior of mobility of 2,4-D on yellow-red Latosol soil, the curves showing adsorbed and desorbed concentrations of 2,4-D for applied concentrations of this herbicide were plotted (Figure 3), which show the characteristics of mobility of this pesticide on yellow-red Latosol soils.

Figure 3 shows that values above 1 mg g^{-1} of applied concentration of 2,4-D on yellow-red Latosol soil is harmful to the environment, because above this value, the desorption increases quickly, while the adsorption increases gradually. This result shows that 2,4-D can be applied in a concentration up to 1 mg g^{-1} to be effective without causing much damage to the environment.

Conclusions

The OM is shown to be a key factor for the sorption of 2,4-D in soil. Even small amounts of OM contribute to the increase of 2,4-D sorption. The reduced content of OM in yellow-red Latosol soil is fundamental for the properties of this soil type, due to the increase of the inertness of 2,4-D in presence of OM that results in a decrease of the amount lost to the environment. The small amount of 0.7% of OM present in yellow-red Latosol soil was significant to increase considerably the sorption of this herbicide. It was also shown that applications of 2,4-D in concentrations above 1 mg g^{-1} are harmful to the environment; this is a result of the fact that desorption from this value increases quickly while adsorption increases gradually above this applied concentration.

Acknowledgements

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References

1. Vieira, E. M.; Prado, A. G. S.; Landgraf, M. D.; Rezende, M. O. O. *Quim. Nova* **1999**, *22*, 305.
2. Prado, A. G. S.; Vieira, E. M.; Rezende , M. O. O. *An. Ass. Bras. Quim*. **1998**, *47*, 239.
3. Cheah, U. B.; Kirkwood, R. C.; Lum, K. Y. *Pestic. Sci.* **1997**, *50*, 53.
4. Landgraf, M. D.; Rezende, M. O. O. *Cien. Cult. J. Braz. Ass. Adv. Sci.* **1997**, *49*, 117.
5. Silva, W. T. L.; Silva, S. C.; Rezende, M. O. O. *J. Radioanal. Nucl. Chem.* **1997**, *222*, 29.
6. Landgraf, M. D.; Silva, S. C.; Rezende, M. O. O. *Anal. Chim. Acta* **1998**, *368*, 155.
7. Airoldi, C.; Critter; S. A. M. *Clay Clays Minerals,* **1997**, *45*, 125.
8. Lobartini, J. C.; Tan, K. H.; Rema, J. A.; Gingle, A. R.; Pape, C.; Himmelsbach, D. S. *Sci. Total Environ.* **1992,** *113*, 1.
9. Barriuso, E.; Houot, S. Serra-Wittling, C. *Pestic. Sci.* **1997**, *49*, 65.
10. Patzko, A.; Dekany, I. *Colloid. Surface A* **1993**, *71*, 299.
11. Sannino, F.; Violante, A.; Gianfreda, L. *Pestic. Sci.* **1997**, *51*, 429.
12. Gennari, M.; Negre, M.; Raimondo, E. *J. Agr. Food Chem.* **1994**, *42*, 2329.
13. Barros, N.; Feijoó, S., Simoni, J. A.; Prado, A. G. S.; Barboza, F. D.; Airoldi, C. *Thermochim. Acta* **1999**, *328*, 99.
14. Prado, A. G. S.; Airoldi, C. *Thermochim. Acta* **1999**, *332*, 71.
15. Tavares, M. C. H.; Landgraf, M. D.; Vieira, E. M.; Rezende, M. O. O. *Quim. Nova* **1996**, *19*, 605.

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