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THE ROLE OF HUMIC ACIDS FROM CARBONATIC SOILS IN THE SORPTION PROCESS OF AMETRYNE AND DIURON

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ABSTRACT: Pesticide sorption in soil involves many factors, such as pH, soil redox, the amount and type of humic acids (organic matter), clays and metallic species. Little work in carbonatic soils has been done to study the effect of the above mentioned factors on the sorption of pesticides. Studies were conducted to determine the interaction between these factors and the carbonatic soils. Twelve carbonatic soil series and nine non-carbonatic soil series showed that redox properties for carbonatic soils tended to be smaller and, contrary to the non-carbonatic soils, many of them with negative potentials. We observed a positive correlation between water extractable iron versus diluted acid extractable iron for the carbonatic soils ($R^2 = 0.88$) but not for the non-carbonatic soils. This finding suggests that the reductive environment of carbonatic soils favors the ferrous species (Fe^{+2}) rather than the ferric (Fe^{+3}). These factors apparently affect the solubility of the organic matter, thus decreasing the sorption of pesticides in carbonatic soils compared to that of non-carbonatic. We observed a positive correlation between the extinction coefficients (k) at 280 nm for the humic acids of carbonatic soils and the sorption coefficients of atrazine and diuron ($R^2 = 0.61$ and 0.56 , respectively). The k values at 300 nm did not show a significant correlation. The averaged pKa values for humic acids from the soils in this study were similar. However, the first derivative titration plots of humic acids showed that humic acids from soils in this study contained several kinds of functional groups with different pKa values, and also suggest that the properties of the functional groups are different. The data suggest that the aromatic rather than the aliphatic content of humic acids seems to have a predominant role in the soil sorption of pesticides. These findings indicate the importance of studying more in depth the sorption, mobility and degradation of pesticides in carbonatic soils in order to protect the water resources.

Keywords: Humic acids, carbonatic soils, sorption constant

INTRODUCTION

Water is a limited resource that must be preserved and protected. Surface and groundwater contamination as a result of the application of agricultural chemicals to soils is of national environmental concern. These valuable resources are being threatened by crop protection pesticides released into the soil. Pesticides that bind to the soil less tightly may leave the fields dissolved in runoff waters or may leach into the ground water. Pesticide interactions with soil depend on several extrinsic and intrinsic soil factors such as pH, soil redox, the amount and type of humic acids (organic matter), clays and metallic species. Sorption of neutral organic pesticides, such as atrazine and diuron, depends primarily on soil organic carbon (OC) content. A previous study demonstrated that retention of pesticides in the carbonatic soils is 1/3 weaker than in non-carbonatic soils (Nkedi-Kizza et al., 2006). This finding could be due to differences in organic matter (humic acids) properties between carbonatic and non-carbonatic soils (Figure 1).

The degradation and mobility of pesticides have been extensively studied in non-carbonatic soils. However, little work in carbonatic soils has been done to study the effect of the above mentioned factors on the sorption of pesticides. The aim of this study is to determine how the soil factors and the humic acid properties are interrelated in order to establish a correlation between the retention and movement of pesticides in the carbonatic soils.

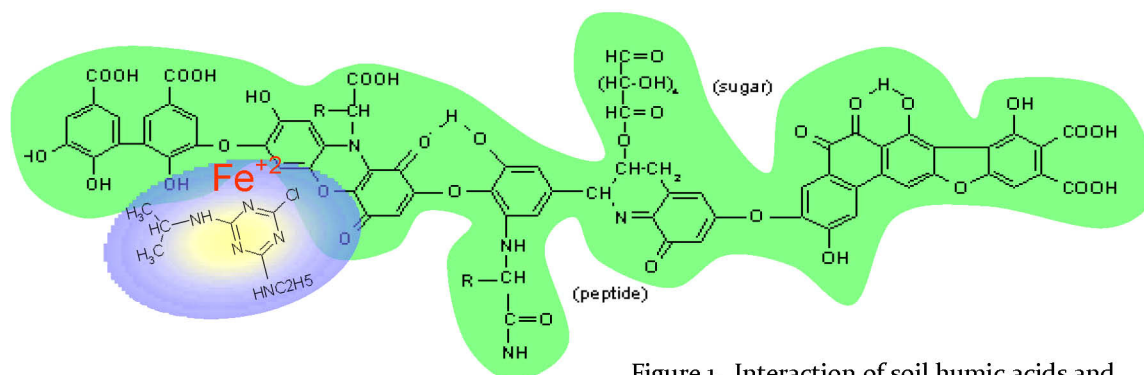


Figure 1. Interaction of soil humic acids and a pesticide molecule

MATERIALS AND METHODS

Soil Sampling: Six carbonatic soil series from Puerto Rico and seven from Florida, and eight non-carbonatic soil series from Puerto Rico were collected from 0 to 30 cm depth with a shovel. The soils were dried, mixed, and sieved.

Redox potential: Redox properties (Eh) were determined by mixing 5 g of soil with 10 ml of distilled water. The system was shaken thoroughly and the redox potential measured after 24 h of equilibration in closed and open systems.

Iron measurement: Five grams of soil were mixed with water and 0.1 N HCl for 1 h. The slurry was filtered, and iron was measured by atomic absorption.

Sorption Study: The sorption process of the herbicides ametryne and diuron was studied by the indirect batch method cited elsewhere.

Potentiometric titration: The humic acids were titrated by following the method of Takamatsu and Yoshida (1978). The acid constants of the humic acids were calculated from the Henderson-Hasselbalch Plots.

UV-Vis: The humic acid extinction coefficients were calculated from the Lamber-Beer equation.

RESULTS AND DISCUSSION

Carbonatic soils are alkaline, and the pH of all carbonatic soils used in this study was above 7.6. The alkaline pH of carbonatic soils is mainly due to the great amount of calcium carbonate. The calcium carbonate content is related to soil properties such as the redox potential, iron speciation, and organic matter characteristics. The amount of water soluble organic matter for carbonatic soils was significantly higher than for non-carbonatic soils, except for the organic soils Tiburones and Isla Morada. Figure 2 shows the correlation between redox measurement for open soil-water and for closed systems. We observed lower redox values in closed systems for carbonatic soils but not for the non-carbonatic soils. This finding suggests faster oxygen

consumption and higher reductive conditions in the carbonatic soils. Figure 3 shows the correlation between acid extractable iron (Fe^{+3}) and water extractable iron (Fe^{+2}) in carbonatic soils. This correlation is in accord with the higher reductive conditions of carbonatic soils. Figure 4 shows the first derivative curves of the titration of humic acids. These data show the complex chemical nature of the humic acids that contain several kinds of functional groups, and also show differences in their acid properties. Figure 5 shows that there is a correlation between the sorption constant (K_{oc}) of ametryne and diuron and the iron index for carbonatic soils but not for non-carbonatic soils, all of which suggests that iron is involved in the retention of ametryne and diuron by the organic matter content in the carbonatic soils. Figure 6 shows the correlation between the humic acid extinction coefficients at 280 nm (ϵ_{280}) and the sorption coefficients of atrazine and diuron for carbonatic soils. No correlation between K_{oc} and ϵ_{280} was observed for non-carbonatic soils, which finding also indicated that humic acids from carbonatic and non-carbonatic soils are different.

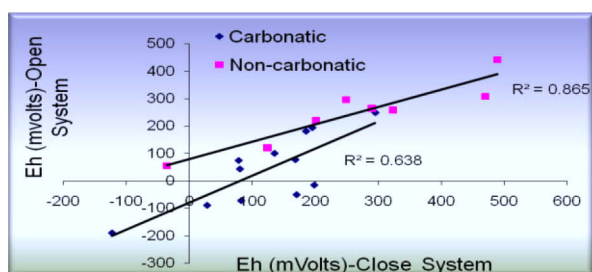


Figure 2. Correlation of Eh between open and closed systems

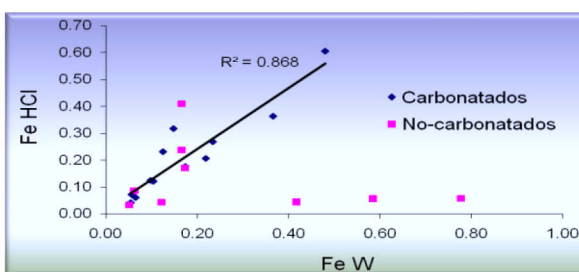


Figure 3. Correlation of acid extractable and water soluble iron.

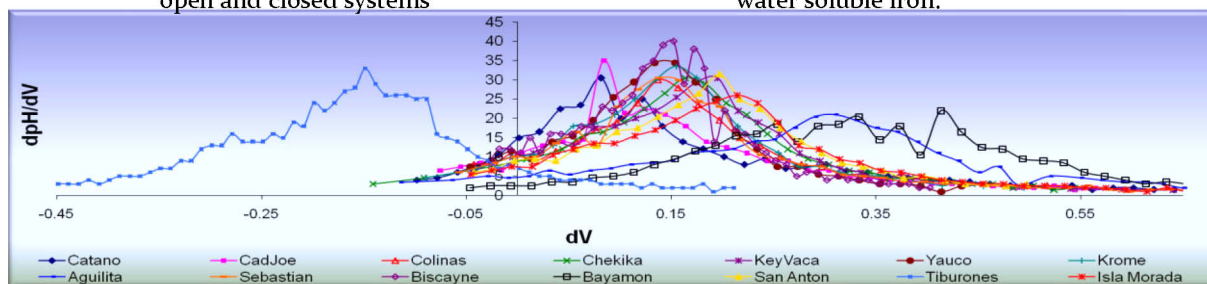


Figure 4. First derivative titration curves of humic acids

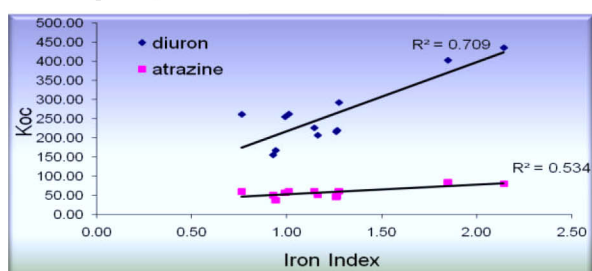


Figure 5. Correlation of K_{oc} and iron index

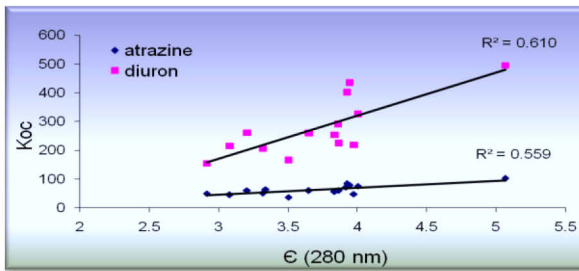


Figure 6. Correlation of K_{oc} and the Extinction coefficients of the humic acids

CONCLUSIONS

The organic matter pools in carbonatic soils showed different results as compared to those in non-carbonatic soils. Carbonatic soils had lower redox potentials than the non-carbonatic soils which affected the speciation of iron in the soils, the organic matter properties and the retention of pesticides by the soils.

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