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Displacement of Paraquat Solution Through a Saturated Soil Column with Contrasting Organic Matter Content

Y. Ouyang,[1] R. S. Mansell,[2] P. Nkedi-Kizza[2]

[1] Department of Water Resources, St. Johns River Water Management District, Post Office Box 1429, Palatka, FL 32178-1429, USA
[2] Soil and Water Science Department, University of Florida, Gainesville, FL 32611-0290, USA

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Herbicides provide indispensable tools for weed control in modern agricultural management. To be most effective, efficient, and environmentally favorable, however, the entire applied mass of a given herbicide should remain within the targeted surface soil. Unfortunately, numerous pesticides do not remain entirely in the root zone (USEPA, 1987). Non-point source leaching of toxic herbicidal compounds from agricultural fields and lawn yards presents serious problems for contamination of soil, surface water, and groundwater. Over the last two decades, many researchers have investigated the behavior and fate of herbicides and other pesticides in the root zone, and factors contributing to leaching in the soil environment, and potential for contamination of groundwater (Nofziger and Hornsby, 1986, Carsel et al. 1988, Kookana et al. 1992, Green et al. 1995, Ouyang and Mansell, 2000). These studies have improved the understanding of herbicide fate and transport in subsurface environments. However, a literature search reveals that little studies have been devoted to investigating the leaching of the herbicide paraquat in subsurface environments (WSSA, 1983).

Paraquat (1,1'-dimethyl-4,4'-dipyridinium dichloride) is a herbicide used for pre- and post-emergence weed control in agricultural crops and is highly toxic to human organs such as lungs, heart, liver, kidneys, cornea, adrenal glands, skin, and digestive system (US-EPA, 1987). When applied to soil, paraquat tends to be rapidly deactivated by strong multi-process sorption onto organic matter and clay minerals, but remains stable in the soil environment (Knight and Tomlinson, 1967, Weber et al. 1969, Burns et al. 1973). Adsorption of paraquat to various soils, clay minerals, and organic matter has been investigated by many investigators (Knight and Tomlinson 1967, Burns et al. 1973). Research results show that paraquat is strongly adsorbed by soil organic carbon (SOM) and clay minerals. The time required for the adsorption process to reach equilibrium is typically short, i.e., 1 to 3 h (Burns et al. 1973, Ouyang et al. 2004). Most studies have been focused on improved understanding of the relationship between the adsorption of paraquat and availability to uptake by plant roots. The fate and transport of paraquat in soils and potential adverse environmental impacts upon groundwater resources still remain incompletely understood. The purpose of this study was to investigate the fate and transport characteristics of paraquat during steady water flow through saturated soil columns using two soils with contrasting

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Correspondence to: Y. Ouyang

SOM content and to understand the associated potential environmental impacts.

MATERIALS AND METHODS

Wabasso fine sand (*Alfic Haplaquods, sandy, siliceous, hyperthermic*) soil from Ft. Pierce, Florida, was used for the experiments. Selected soil properties are shown in Table 1. Analytical grade paraquat (1,1'-dimethyl-4,4'-dipyridinium dichloride) was purchased as standard catalog items from commercial suppliers of radioisotopes. The methyl carbon atom of the paraquat chloride was labeled with ^{14}C and was supplied as a freeze-dried solid under a nitrogen atmosphere in glass ampoules. Specific activity of paraquat was 14.5 mCi /mM. Five grams of dried soil materials were placed into glass centrifuge tubes and appropriate volume of 10 mg L^{-1} 14C-paraquat aqueous solutions plus DI water to give 2, 4, 6, 8, and 10 mg L^{-1} paraquat initial soil solution concentration at a soil to solution ratio of 1:2. The tubes were placed on a mechanical shaker for 24 hours and centrifuged for 15 minutes. The concentration of paraquat in the supernatant was determined by placing one mL in 15 mL of Bray's counting solution (Bray, 1960) and counting the radioactivity with a liquid scintillation counter (LSC). The concentration C_0 of paraquat in the initial solution ranged from zero to 10 mg L^{-1}.

Table 1. Selected properties of Wabasso fine sand used in this study.

Property	Surface Layer	Subsurface Layer
Depth (cm)	0-10	33-76
pH (in water)	4.3	4.9
Organic Carbon-OC (%)	1.3	0.1
CEC (μmol g^{-1})	10.4	9.9
Sand (%)	92.6	92.4
Silt (%)	4.3	4.0
Clay (%)	3.1	3.2
Sorption coefficient K_d (ml g^{-1})	317.73 (measured)	24.44 (calculated)
*$K_{OC} = K_d/OC$	24441	

* Assuming sorption of paraquat in soil is predominantly due to organic carbon

A glass chromatography cylinder with a 2.54-cm inner diameter was used to contain a 30-cm long soil column. Air-dried soil, passed through a 2-mm sieve, was packed into the cylinder in 2-cm increments and stirred to prevent layering. The soil column was tapped to settle the soil to a desired bulk density of 1.32 g cm^{-3}. Two types of soil columns were packed, one with soil from 0-10 cm depths in the soil profile with a SOM content of 1.3% and the other from 33-76 cm depth with a SOM content of 0.1%. Distilled water was used to initially saturate the soil column using a variable-flow pump maintained at a fluid flow velocity of 6 cm h^{-1}. After one day of flow, the influent was changed from water to an aqueous solution of ^{14}C-labeled paraquat with specified

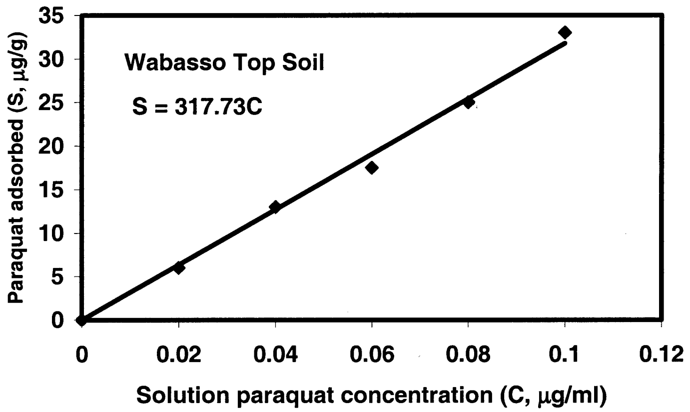

Figure 1. Equilibrium sorption isotherm of paraquat at 24 h in Wabasso top soil.

concentration of 10 mg L^{-1}. After 100 mL of paraquat solution entered the column, the influent was switched back to water. Water was used to miscibly displace the paraquat from the column until 5 pore volumes of column effluent had been collected. At that time the influent was switched to a 10N KCl aqueous solution. Effluent samples were collected in test tubes using an automatic fraction collector and were analyzed with LSC for ^{14}C-paraquat.

RESULTS AND DISCUSSION

Sorption of paraquat by Wabasso fine sand with initial concentrations ranging from 0-10 mg L^{-1} at 24 h is shown in Fig. 1. A linear Freundlich type equilibrium sorption isotherm was found in this soil, indicating soil maximum sorption capacity was not yet attained under these experimental conditions. Figure 1 further reveals the sorption coefficient (K_d) of paraquat in the top-soil was 317.73 ml g^{-1}. This implies that the transport velocity of paraquat in the soil was about 318 times less than the flow velocity of water. Assuming that the major difference in paraquat sorption for the two soil materials is due to OC content since other properties of the two materials are very similar (Table 1), the organic carbon partition coefficient (K_{OC}) in the top-soil can then be calculated by normalizing Kd to OC (i.e., $K_{OC} = K_d/OC = 24441$ ml g^{-1}). Using the K_{OC} concept, the sorption coefficient of paraquat in the sub-soil was then estimated to be 24.44 ml g^{-1} (Table 1). Therefore, the adsorption of paraquat in the sub-soil was 13 times (i.e., 317.73/24.44 = 13) less than in the top-soil. In other words, a decrease in SOM content from 1.3% in the top-soil to 0.1 % in the sub-soil decreased the adsorption of paraquat by 13 times. It has been reported that

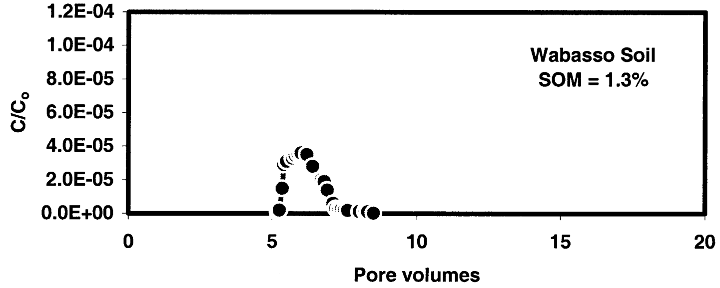

Figure 2. Paraquat BTC representing displacement with DI water (before 5 pore volumes) and 10N KCl solution (5-15 pore volumes) from surface layer (0-10 cm) of Wabasso soil.

adsorption of paraquat onto various soil materials was mostly completed in about 1 h and the primary mechanism for rapid adsorption of paraquat by soil was cation exchange under conditions of electroneutrality. Secondary sorption mechanisms were presumed to include rupture of weak cross-linkages within organic matter molecules in the presence of large paraquat cations and steric rearrangement of weakly cross-linked organic matter molecules (Burns et al. 1973). Paraquat can react with more than one negative site on soil humic colloids and is readily adsorbed on clay minerals, whereas on organic matter, it is loosely bound and can be leached by a saturated salt solution (Kahn, 1980). Calderbank and Tomlinson (1968) reported that paraquat is more strongly adsorbed by montmorillonite (an expanding clay) than by kaolinite (a non-expanding clay).

Changes in paraquat concentrations in effluent from soil columns with increasing number of effluent pore volumes for the miscible displacement experiments for the soil with a high SOM (1.3 %) are shown on Fig. 2. No paraquat was observed in the effluent when paraquat contaminated soil column was initially flushed with 5 pore volumes of DI water. Paraquat cations were thus assumed to be completely adsorbed in the soil columns. This assumption was further confirmed by the equilibrium adsorption isotherm of paraquat obtained from the same soil materials (Fig. 1). A linear adsorption isotherm of paraquat strongly indicated that the maximum adsorption capacity of paraquat had not been attained in this soil material partly due to the high SOM and partly due to the low maximum initial paraquat concentration (10 mg L^{-1}) used in this study. However, when the soil columns were flushed with KCl solution the paraquat was displaced from the soil although paraquat recovered in the effluent was extremely small or only 0.001% (Fig. 2). Paraquat removal apparently occurred primarily due to cation exchange between paraquat(++) and K^+.

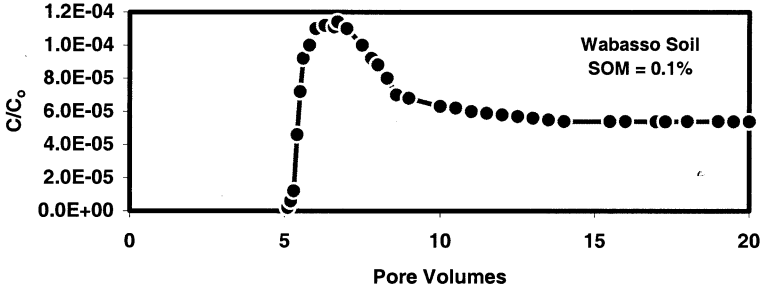

Figure 3. Paraquat BTC representing displacement with DI water (before 5 pore volumes) and 10N KCl solution (5-15 pore volumes) from subsurface layer (33-76 cm) of Wabasso soil.

The breakthrough curve (BTC) for paraquat from soil columns in the miscible displacement experiments for the soil with a lower SOM (0.1 %) is shown in Fig. 3. The experimental data are identical to the soil with a higher SOM. As with the experiments for the soil with a higher SOM, no paraquat was found in the effluent when paraquat in the soil columns was flushed with 5 pore volumes of DI water. These data imply that sorption of paraquat in the Wabasso soil was strong regardless of soil organic matter content and that cation-exchange is an important process in displacing paraquat from the soil. Unlike the case for the soil with a higher SOM, a relatively sharp paraquat BTC was obtained when the soil column with lower SOM was flushed with 10 N KCl solution (Fig. 3). Low SOM generally tends to provide a unfavorable condition (less binding sites or less sorption) considering the 10N KCl used for paraquat desorption. Note that the sorption coefficient of paraquat in the sub-soil was about 13 times less than in the top-soil. As a result, more paraquat was flashed out by KCl solution. Although a sharp BTC was observed paraquat concentrations in the effluent was five orders of magnitude lower than that of the initial concentration. For example, the maximum paraquat concentration at the peak (Fig. 3) was only 5 x 10^{-4} mg L^{-1} while the initial paraquat concentration C_0 was 10 mg L^{-1}. Obviously paraquat was desorbed extremely slowly from the soil columns.

Comparison of the BTCs shows that the maximum paraquat concentrations in the effluent were 5 x 10^{-4} for the soil with a higher SOM (Fig. 2) and 3.5 x 10^{-5} mg L^{-1} for the soil with a lower SOM (Fig. 3). The former concentration was about 14 times greater than the latter although this is only a fraction of the original influent paraquat concentration used in the experiment. Nonetheless, this study showed that soil organic matter content played an important role in release of herbicide paraquat from the soil since all other soil properties (Table 1) are very similar for both soils used in the column experiments.

Paraquat is sold in about 130 countries for use on large and small farms, plantations and estates and in non-agricultural weed control. It is a quick acting, non-selective herbicide, which destroys green plant tissue on contact and by translocation within the plant. Paraquat is often considered to be strongly and rapidly adsorbed by soils such that potential leaching into water sources is not generally considered. In the past, major concern has focused upon accidental and deliberate ingestion of the active ingredient, where even small quantities are fatal. Exposure to the concentrated active ingredient is a problem during mixing and loading sprayers. In developing countries the conditions of safe use are very difficult. Although not fatal at normal spray strength, regular use such as required on plantations can often lead to health problems. What is most interesting from this study, however, is that small concentrations of paraquat remained in the effluent from contaminated soil columns even after 15 pore volumes of 10N KCl solution was used during flushing. Small magnitude of paraquat leaching was thus observed for soil low in organic matter. Under field conditions such slow desorption and leaching of paraquat herbicide from agricultural soils low in organic matter content could lead to contamination of groundwater and thereby pose a health threat to the subsurface environments. Unfortunately, such a phenomenon has not yet received great attention. Further research is therefore warranted to understand multi-process sorption/desorption for paraquat applied to soils low in organic matter content. At present, paraquat is considered to be instantaneously and strongly adsorbed by soil and leaching into water sources is not generally a problem. Our findings imply that frequent application of paraquat to soils with low organic matter content could lead to potential contamination of local groundwater and thereby pose a health hazard to the subsurface environment.

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