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## Movement and adsorption of methamidophos in clay loam and sandy loam soils

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Laboratory batch and column experiments were performed to better understand the sorption and transport behaviour of commercial-grade methamidophos (Tamaron SL 600) in clay loam (CL) and sandy loam (SL) soils. The batch sorption experiments show that the soil texture and methamidophos concentration play a major role in the sorption and migration behaviour of methamidophos. At low surface coverage ( $q < 0.6 \text{ mg g}^{-1}$ ), methamidophos sorbs onto the CL soil more strongly than onto the SL soil. However, for  $q > 0.6 \text{ mg g}^{-1}$ , the SL soil exhibits a much higher sorption affinity for methamidophos than the CL soil. The equilibrium isotherms for the sorption of methamidophos onto the SL and CL soils were non-linear, and were best described by the Freundlich equation. The results of column experiments indicate that the recovery of methamidophos during desorption was incomplete due to either partially irreversible sorption to high-energy surface sites or strongly rate-limited desorption. Methamidophos was more readily leached out from the SL soil column as consistent with the batch isotherm data.

*Keywords:* Adsorption isotherm; Clay; Groundwater; Methamidophos; Pesticide; Soil

### 1. Introduction

During the last three decades, the contamination of soils, surface and groundwaters by pesticides has been recognized as an important environmental issue [1, 2]. Sorption onto immobile mineral surfaces is often the key process controlling the mobility in the subsurface environment [3, 4]. A number of factors contribute to the partitioning of pesticides between solutions and solid phases. Factors include general solution conditions (e.g. pH, concentration of pesticides), soil texture, and the characteristics of the mineral surfaces [2, 3, 5–9]. Recent studies also show that natural organic matter may act to either enhance or retard the migration of pesticides in subsurface environmental systems, depending on the system composition (e.g. quantity and characteristics of organic ligands) [2, 5, 8, 10, 11].

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Methamidophos is a potent acetylcholinesterase inhibitor [12], used to control chewing and sucking insects and spider mites on ornamental plants, citrus fruits, stone fruits, vegetables, cotton, tobacco, rice, and other intensive agricultural crops [13–15]. Methamidophos, classified as a Restricted-Use Pesticide by the US EPA, is highly toxic to mammals, birds, and bees [13, 16, 17].

Recent literature studies on methamidophos have mainly focused on the mechanisms of its toxicity, insect control, and residues in crops [18–22]. Relatively few studies deal with the fundamental processes affecting its sorption and movement in the subsurface environment [8, 15]. In a field study, Zhang *et al.* [23] detected methamidophos in natural soil, sediment, water and plant samples, indicating that methamidophos is persistent in the environment depending on environmental conditions (e.g. pH) [24]. The objective of this study was to investigate the sorption and transport behaviour of methamidophos in clay (CL) loam and sandy loam (SL) soils collected from agricultural soils in Mersin, Turkey. Methamidophos with different commercial names (e.g. Tamaron) has been widely used in agricultural areas in Turkey since about 1972.

## 2. Experimental

### 2.1 Materials

Soils used in this study were clay loam and sandy loam collected at predetermined locations in Mersin. These soils were selected on the basis of textural representation of major soils found in the region. Unpolluted surface samples (0–30 cm depth) of each soil were air-dried and sieved through a 2-mm screen prior to storage and use. Soil pH was measured by mixing 10 g of dry soil and 10 mL of deionized water. After 1 h of contact time, the pH of the slurry was measured using a pH meter [25]. The carbonate content was determined by a volumetric calcimeter method as described by Allison and Moodie [26]. A soil particle-size analysis was performed by inserting a Bouyoucouc hydrometer in a 1 L soil/water suspension containing 50 g of soil in a 1 L graduated cylinder [27]. The USDA particle size classes (clay: <2 µm, silt: 2–50 µm and sand: 50–2000 µm) were followed when assigning textural classes. The organic carbon percentage was determined by the Walkley–Black procedure [28], the result being multiplied by the Van Bemmelen factor of 1.724 to convert it to the total organic matter content [29]. Electrical conductivity (EC) was measured in 1:2 soil to water, and the total salt content was calculated from EC values [30]. Selected physical and chemical properties of these soils are presented in table 1. The soils used in the study are calcareous and contain very low amounts of organic matter. They are alkaline, with total soluble salt contents ranging from 0.018 to 0.024% (table 1).

### 2.2 Methods

Methamidophos [*O,S*-dimethyl phosphoramidithiolate ( $C_2H_8NO_2PS$ ), m.p. 46.1°C, v.p. 4.7 mPa (25°C),  $\log K_{ow} -0.8$ ] is a colourless crystalline solid with a high water solubility (>2000 g L<sup>-1</sup> at 25°C). Commercial-grade methamidophos (Tamaron SL 600) was used in this study. The Tamaron SL 600 purchased from Bayer Chemical Co.

Table 1. Physical and chemical properties of the soils used in the study.

Soil characteristic	Sandy loam	Clay loam
<i>Particle size</i>		
% Sand	72	29.0
% Silt	5	27.5
% Clay	23	43.5
Total salinity (%)	0.018	0.024
pH (1:1)	7.8	7.9
Organic matter (%)	0.83	0.83
Organic C (%)	0.48	0.48
CaCO <sub>3</sub> (%)	26.5	29.0

(Turkey) contained 600 g L<sup>-1</sup> of methamidophos. A 2000 mg L<sup>-1</sup> stock solution of methamidophos was prepared in deionized water (D.I.), and stored below 4°C. Depending on the desired methamidophos concentration, an appropriate amount of stock solution was combined with 0.005 M CaCl<sub>2</sub> prior to the batch sorption experiments. The methamidophos content of commercial-grade Tamaron used in the experiments was checked with the calibration curves prepared from an analytical-grade methamidophos at 97% purity (Merck Co., Germany). All other chemicals used were of analytical grade.

**2.2.1 Adsorption of methamidophos in soils.** Pesticide solution (50 mL) containing 0, 20, 40, 60, and 100 mg of methamidophos per litre was added separately to the soil (5 g) in a glass centrifuge tube (a Pyrex tube equipped with a spiral lid). The samples contained 0.005 M CaCl<sub>2</sub> as the background electrolyte to maintain the ionic strength of samples at a constant level. The soil–water suspensions were continuously agitated for 24 h on a shaker (90 rpm) at room temperature (25°C). The pH of the supernatant was measured and centrifuged at 5000 rpm for 5 min and filtered. The methamidophos in supernatant was extracted twice with 50 mL of methanol and concentrated, then extracted twice with 15 mL of dichloromethane and concentrated to 2 mL using a similar method outlined by Yen *et al.* [15]. Following extraction, the methamidophos concentration of samples was determined using gas chromatography (GC) (Hewlett Packard 6890). The GC system was equipped with a nitrogen phosphorous detector (NPD), a split/splitless injector, a capillary column (HP-5 5% phenyl methyl siloxane, 30 m × 0.25 mm i.d., film thickness 0.25 μm), and a 7673A autosampler. Chemstation software was used from HP for instrument control and data analysis. Injector and detector temperatures were set at 220°C and 320°C, respectively. The temperature parameters of GC used were 70°C (2 min), 150°C (3 min), 200°C (8 min), and 260°C (post run) (5 min). The pressure of the carrier gas was 13.02 psi, and the flow rates of GC were H<sub>2</sub>: 3 mL min<sup>-1</sup>, N<sub>2</sub>: 100 mL min<sup>-1</sup>, air: 60 mL min<sup>-1</sup>. The total analysis time per sample was about 23 min. The injection volume was 1 μL for all samples. All experiments were conducted in triplicate. The amount of metamidophos sorbed to the soil was calculated from the difference between the aqueous methamidophos concentration (mg L<sup>-1</sup>) in samples with soil and the total methamidophos concentration in samples prepared with no soil.

The Freundlich model was used to describe the sorption of methamidophos to each soil. The equation used was:

$$q = K_f C^n, \quad (1)$$

where  $q$  is the amount of methamidophos taken up per unit mass of soil (mg methamidophos  $\text{g}^{-1}$  soil),  $C$  is the equilibrium concentration of methamidophos in solution ( $\text{mg L}^{-1}$ ),  $K_f$  is the Freundlich equilibrium coefficient relating to adsorption capacity, and  $n$  is the Freundlich exponent relating to adsorption intensity.

**2.2.2 Movement of methamidophos in soil columns.** Column leaching experiments were conducted to investigate the movement of methamidophos. The movement of methamidophos in the soil column was accomplished by leaching the surface-applied pesticide through a glass column (3 cm i.d. and 30 cm length) packed with either the CL or SL soil at room temperature (25°C). All column experiments were performed using a similar procedure given by Yen *et al.* [15]. A total of four columns were prepared for the experiments. In all of the column experiments, the background electrolyte was 0.005 M  $\text{CaCl}_2$ . Prior to performing methamidophos displacement experiments, each column was uniformly packed with about 375 g soil and continuously flushed with 0.005 M  $\text{CaCl}_2$  for 6 days to precondition the column. The flow was applied in the downward direction. The column was then drained, and a known volume of pesticide solution (20 mg of methamidophos in 2 mL 0.005 M  $\text{CaCl}_2$ ) was spiked instantaneously onto the upper layer of the column. The soil column was then leached with 0.005 M  $\text{CaCl}_2$  at a rate of 0.25  $\text{mL min}^{-1}$  for 7 days (50 mL of 0.005 M  $\text{CaCl}_2/\text{day}$ ). Effluent samples were collected in 50 mL aliquots. Samples collected were analysed for methamidophos concentration ( $\text{mg L}^{-1}$ ) in the same manner as the adsorption experiments. At the conclusion of a series of experiments, the column material was extruded and analysed for retained methamidophos concentration to determine mass loss during column displacement experiments using an extraction method outlined by Yen *et al.* [15]. The pore volumes and porosities were determined using the methods described by Kantar and Honeyman [31]. The values of pore volumes were estimated by the weight of pore water in the saturated packed column determined by weight differences. Table 2 shows experimental conditions for the column displacement experiments.

Table 2. Selected physical properties of column displacement experiments.

Variable	Units	Experiment			
		1	2	3	4
Soil		SL	SL	CL	CL
Linear velocity	$\text{cm min}^{-1}$	0.074	0.074	0.06	0.06
Column length	cm	30	30	30	30
Pore volume	mL	102	102	125	125
Soil/water ratio	$\text{kg L}^{-1}$	3.7	3.7	3	3
Porosity		0.48	0.48	0.59	0.59
pH		8.1	8.1	8.1	8.1
Methamidophos	% recovered	61.2	60.5	44.5	44.1

### 3. Results and discussion

#### 3.1 Batch adsorption experiments

Figure 1 shows the equilibrium isotherms determined for each soil–pesticide combination at a natural pH (about 8.1). The sorption isotherm for the CL soil is convex to the concentration axis. This means that the affinity of the CL soil for methamidophos sorption is higher at a low surface coverage and decreases with increasing methamidophos concentration as the available active surface sites are taken up. The isotherm for the sorption of methamidophos onto the SL soil, on the other hand, is concave to the concentration axis, suggesting that the affinity of the soil particles for methamidophos is less than that of water for the soil at low methamidophos concentration. The different sorption behaviours exhibited by methamidophos on SL and CL soils are probably caused by general physical/chemical soil and solution properties and temperature. For example, Yen *et al.* [15] found that the soil mineral content and temperature had a major role in sorption behaviour of methamidophos and acephate on clay loam and silt loam soils. Their results suggest that acephate produces a concave isotherm in a silt loam soil, whereas it exhibits a linear sorption behaviour in a silt clay loam soil at 30°C.

The sorption isotherms of methamidophos for both soils (figure 1) are non-linear and can be accurately described by a Freundlich isotherm over a wide range of methamidophos concentrations. This suggests that the adsorption sites were not saturated at any concentration studied [3]. This kind of behaviour has been commonly observed for the adsorption of pesticides on soil surfaces [2–4, 15, 32]. The Freundlich isotherm parameters for each soil are given in table 3. The Freundlich isotherm parameters are empirical values, and are highly dependent on subsurface chemical conditions (e.g. soil properties). In many systems involving pesticides, the Freundlich

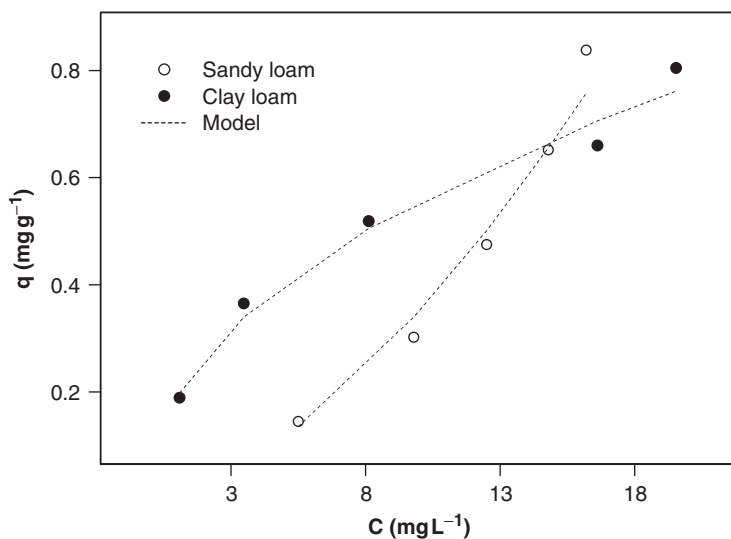


Figure 1. Freundlich sorption isotherms of methamidophos in sandy loam and clay loam soils at pH 8.1 and a  $\text{CaCl}_2$  concentration of 0.005 M.

Table 3. Freundlich isotherm parameters obtained from batch experiments.

Soil	$R^{2a}$	$\ln K_f$	$n$
Clay loam	0.982	$-1.66 \pm 0.077$	$0.467 \pm 0.04$
Sandy loam	0.982	$-4.71 \pm 0.295$	$1.590 \pm 0.12$

<sup>a</sup>In this article,  $R^2$  refers to the coefficient of determination.

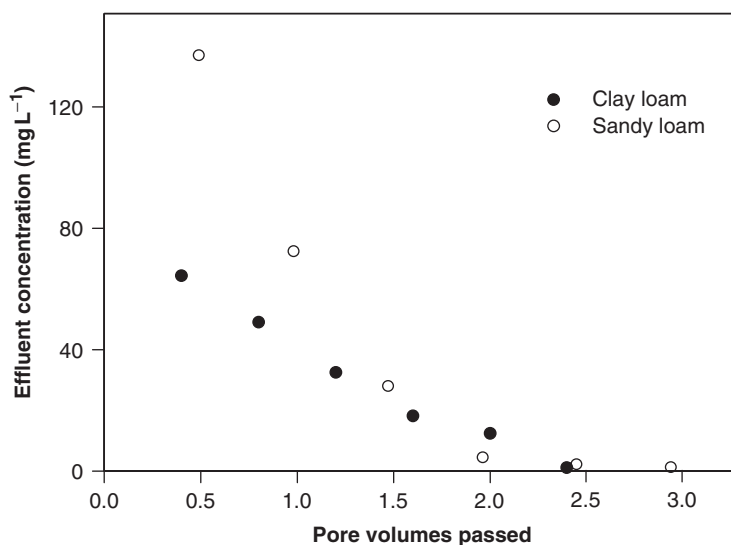


Figure 2. Desorption breakthrough curves of methamidophos in columns packed with either sandy loam or clay loam soil at pH 8.1 and a  $\text{CaCl}_2$  concentration of 0.005 M.

isotherm slope,  $n$ , is typically less than 1, and the sorption data have been interpreted as evidence of contaminant sorption to multiple-site types, with sorption occurring first on high energy sites of soils, followed by sorption onto low-energy sites [4, 33].

### 3.2 Column displacement experiments

Column leaching experiments were performed to study the transport of methamidophos under advective and dispersive conditions similar to those observed in the field. For example, columns were packed to solid/liquid ratios approximating the field conditions. Our main goal was to better understand the fundamental processes affecting the movement of methamidophos. Figure 2 shows the desorption breakthrough curves of methamidophos in soil columns artificially contaminated with methamidophos plotted as a function of effluent methamidophos concentration ( $\text{mg L}^{-1}$ ) versus pore volumes. The results of a mass-balance analysis of curves given in figure 2 show that a portion of the methamidophos bound to soil particles is not readily recoverable, although the effluent methamidophos concentration in breakthrough curves almost approaches zero. This is likely due to the strong binding of methamidophos with high-energy surface sites on each soil (partially irreversible sorption) or rate-limited desorption. After about

three pore volumes of flushing with 0.005 M  $\text{CaCl}_2$ , the total methamidophos recoveries were 44 and 62% for columns packed with the CL and SL soils, respectively (table 2). The analysis of extruded column material for methamidophos after the displacement experiments indicates that little or no degradation of methamidophos was observed in the columns under the experimental conditions studied. Several authors have reported methamidophos degradation half-lives ranging from a couple of days to 309 days in different soils and water, depending on factors such as soil moisture content and pH [15, 34, 35].

Compared with the SL soil, the CL soil exhibits a higher sorptive capacity for methamidophos, especially at a low surface coverage, consistent with the sorption experiments (figure 1). Previous studies show that the clay and silt content of soil play a major role on pesticide sorption, especially in soils with less than 2% organic matter [2, 36]. The organic matter content was about 0.83% for both soils (table 1). The protonation of  $-\text{NH}_2$  groups in methamidophos may be responsible for the sorption onto clay minerals under the experimental conditions studied (e.g. pH 8.1) [37, 38].

As shown in table 3, the convex isotherm observed for the CL soil has a slope ( $n$ ) of less than 1, indicating that the fractional adsorption decreases with increasing concentration. This decrease in fractional adsorption at high methamidophos concentrations results in a greater mobility in the subsurface environment [39]. The desorption front for convex isotherms is usually characterized by a broad, diffuse front (long tailing). A similar behaviour was also observed in the desorption breakthrough curve of methamidophos in columns packed with the CL soil (figure 2). In contrast to the CL soil, column displacement experiments with the SL soil resulted in a self-sharpening desorption front. This kind of behaviour is usually exhibited by organic molecules which obey a concave adsorption isotherm.

#### 4. Conclusion

Pesticide contamination of soil and groundwater is a common problem in the environment. In this study, we have examined the movement and sorption behaviour of methamidophos in SL and CL soils. The results show that the soil texture and pesticide concentration are important factors in the sorption and migration behaviour of methamidophos in the subsurface environment. The sorption isotherm for the SL soil was concave to the concentration axis, whereas that for the CL followed a convex sorption isotherm. The sorption isotherms for both soils were non-linear and could be accurately described by a Freundlich isotherm over a wide range of methamidophos concentration. Column experiments show that a portion of methamidophos bound to soil particles was not readily recoverable due to partially irreversible sorption and/or rate-limited desorption processes.

The mobility of methamidophos in the SL was faster than that in the CL under the experimental conditions studied. This is consistent with the results from the batch experiments with  $q < 0.6 \text{ mg g}^{-1}$ , since the overall solid/liquid ratio (375 g/352 mL) and methamidophos concentration (20 mg/352 mL) in the column are comparable with those of batch experiments considering the volume of liquid passed through the column (about 352 mL in 7 days).



Finally, overall results suggest a possibility of contamination of groundwater sources in the light-textured agricultural soils such as sandy loam soils with overuse of methamidophos and accumulation of its residues over time.

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