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2,4-D mobility in clay soils: Impact of macrofauna abundance on soil porosity

B. Prado [a,*], A. Gastelum Strozzi [b], E. Huerta [c], C. Duwig [d], O. Zamora [a], P. Delmas [e], D. Casasola [a], J. Márquez [b]

[a] Instituto de Geología, Universidad Nacional Autónoma de México, México, D.F., Mexico
[b] Centro de Ciencias Aplicadas y Desarrollo Tecnológico, Universidad Nacional Autónoma de Mexico, Mexico, D.F., México
[c] El Colegio de la Frontera Sur. Unidad Villahermosa, Villahermosa, Tabasco, México, Mexico
[d] IRD/Université Grenoble1/CNRS/G-INP, LTHE UMR 5564, F-38000, Grenoble, France
[e] Department of Computer Science, The University of Auckland, Auckland, New Zealand

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ABSTRACT

Pesticides in agriculture are commonly used to meet the growing food demand; however they compromise the quality of water and soil. The pesticide 2,4-D is one of the most widely used herbicides in the world, it belongs to the group of synthetic herbicides that control broadleaf weeds. In this paper the risk of groundwater contamination by 24-D and its major metabolite, 2,4-DCP, is studied in a context of high density of soil worms. We compared the adsorption, desorption, degradation and displacement of 2,4-D in soils from Tabasco Region having different properties: clay, organic matter, iron and aluminum oxides contents. In addition to the classical soil physicochemical characterizations, a 3D analysis of the soil structure and porosity was performed by analyzing images acquired by Computed Tomography. The objective was to evaluate the effect of soil properties and macroporosity produced by the macrofauna activity on solute movement.

All the four soils studied sorbed the herbicides, more importantly 2,4-DCP, the metabolite, than 2,4-D itself. The distribution coefficients for 2,4-D sorption were linear and varied between 1 and 4 while those for 2,4-DCP were above 10. The contents of iron and aluminum have an important role in the adsorption of these two compounds. In aerobic conditions, the herbicides half-life was about 2 days. Water movement occurred in physical equilibrium in three of the four soils; soil dispersivity ranged from 1.2 to 7 cm, clay content being the main factor. After 20 to 60 days depending on the soil, no 2,4-D leaching was observed through the soil columns, except for one soil were there was preferential flow. Earthworms burrows were exhibited and quantified in the soils samples through the analysis of Computer Tomography (CT) images, they appeared as small, snail-shaped, rounded volume of 3 to 7 mm radius with a higher density with respect to the surrounding soil. They were extracted from the original data using a combination of image processing and mathematical morphology operators. Based on the results obtained, it can be concluded that preferential flow caused by both high clay content and the presence of macrofauna pores significantly reduces the buffering capacity of the soil, increasing the risk of contamination by herbicides of the underlying aquifer.

1. Introduction

Pesticide use is now commonly used in modern agriculture to achieve high production, however it compromises the quality of water and soil. The vulnerability of aquifers to contamination by pesticides is a complex process affected by soil physical properties, biochemical and hydrogeological properties, weather conditions and agricultural practices. The health risks posed by these pesticides to environment and human health has led to numerous studies about processes involved in the environmental fate of the herbicides.

2,4-dichlorophenoxyacetic acid (2,4-D) is the active ingredient of the most widely used herbicides in the world (Anon, 2002). It belongs to the group known as synthetic clorofenoxy herbicides; it is a systemic herbicide used to control many types of broadleaf weeds, grasses and other monocots. Due to low adsorption coefficients and high solubility in water, 2,4-D has often been detected in surface and ground water, which means an environmental problem and health hazard (Gaultier et al., 2008; Shareef and Shaw, 2008).

The processes of adsorption and degradation reduce mobility of a given pesticide once it has been applied to the soil. In the literature, studies have evaluated adsorption processes of 2,4-D (Khan, 1973; Hiradate et al., 2007), degradation processes (Fang et al., 2012; Girardi

* Corresponding author.
E-mail addresses: bprado@geologia.unam.mx (B. Prado), alfonso.gastelum@ccadet.unam.mx (A.G. Strozzi), ehuertaecosur@gmail.com (E. Huerta), celine.duwig@ird.fr (C. Duwig), oliviazm@geologia.unam.mx (O. Zamora), p.delmas@auckland.ac.nz (P. Delmas), jorge.marquez@ccadet.unam.mx (J. Márquez).

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Table 1
Experimental columns parameters: bulk density ρ, Darcy flow *q*, soil water content θ, and pore water velocity *v*.

Soil	ρ (g cm^{-3})	*q* (cm min^{-1})	θ (cm^{3}cm^{-3})	Pulse (pore volume)	*v* (cm min^{-1})
Soil 1	1.00	0.0008	0.57	0.47	0.0013
Soil 2	1.15	0.0009	0.47	0.39	0.0020
Soil 3	1.15	0.0030	0.54	0.34	0.0055
Soil 4	1.1.8	0.0017	0.506	0.88	0.0034

et al., 2013; Cycon et al., 2011) and desorption processes as an indicator of mobility; the latter process has also been evaluated in packed soil columns (Ismail et al., 2009; Candela et al., 2003). However, there are few studies evaluating all processes simultaneously (Estrella et al., 1993), which is indispensable to assess accurately the risk of contamination of soil and water resources. In addition, soil structure is critical to herbicide movement: Gerstl and Yaron (1983) showed that soil structure influences the distribution of agrochemicals applied at one point at soil surface. It is now well known that herbicide mobility through the soil towards aquifers is accelerated due to the existence of preferential flow, which can exist in either structured soils, or be produced by plants roots and/or soil mesofauna as worms. It is therefore important to characterize soil structure and porosity, and to consider them to evaluate herbicide mobility.

In Tabasco State, the natural vegetation has been modified to become agricultural areas, affecting approximately 60% of the stat. In this region, the effect of soil macroinvertebrates on soil fertility was evaluated, especially in terms of ecosystem services provided by earthworms such as organic matter decomposition of organic matter and water infiltration (Huerta et al., 2011). Earthworms can influence organic matter quality: each earthworm group according to their ecological category can produce a given footprint on organic matter (Huerta et al., 2013). When they move underground, earthworms form tunnels and galleries, which can be horizontal or vertical, and this affects soil structure. In the Mexican tropics, endogeic worms are the most abundant specie (Fragoso and Lavelle, 1992) and their tunnels are mostly horizontal. However, there are some anecic exotic worms: these form vertical burrows to go to soil surface to search for litter and bury it into the soil. Earthworms play an important role in water infiltration and mobility of dissolved contaminants (Ehlers, 1975; Bouma et al., 1982; Bouché and Al, 1997; Capowiez et al., 2009). In tunnels formed by worms, water as well as chemical compounds such as nitrate are transported (Edwards et al., 1988, and 1989; Shipitalo et al., 2004), especially when high fertilization rates are applied (Tomlin et al., 1995).

The aim of this study was to evaluate the risk of soil and groundwater contamination by the herbicide 2,4-D and one of its main metabolites, 2,4-dichlorophenol (2,4-DCP). Processes of adsorption, desorption, degradation and transport of 2,4-D were evaluated in soils of Tabasco in Teapa and Central regions, characterized with high density of earthworms.

2. Materials and methods

2.1. Studied sites and soil sampling

We studied two soils from the Center Region (soil 1 and soil 2, 17° 54′ 32.52″N 93° 2′20.54″O), and two soils from the Teapa Region (soil 3 and soil 4, 17° 54′ 32.52″N 93° 2′20.54″O) at Tabasco, southeastern of Mexico. The soils from the Center Region correspond to Fluvisols (FAO-ISRIC, ISSS, 1998 or Fluvent (Soil Survey Staff, 1999), while the soils from the Teapa Region correspond to Vertisols in both the FAO-ISRIC and ISSS (2014) and Soil Survey Staff (1999). Both sites were under grassland planted with banana trees, without mechanical tillage, and with agrochemical application. Climate is warm and humid, with annual rainfall around 2000–2500 mm, and average annual temperature around 26 °C. In these sites, we previously studied the abundance and the contribution of endogeic earthworms (*Methaphire houlleti*) and shrimps (*Procambarus llamasi*) to soil ecosystem services (Huerta et al., 2011).

At each of the four sites, six monoliths of 25 × 25 × 25 cm were manually excavated at the soil surface, and then they were transported to the laboratory in plastic containers. At each site, five monoliths were used for macrofauna determination and one for CT images acquisition and displacement experiments.

2.2. Macrofauna characterization

Macroinvertebrates were taken out of five monoliths manually and were collocated in formol at 4% (earthworms) and alcohol 70% (arthropods) to be identified in the soil laboratory of Colegio de la Frontera Sur (Villahermosa, Tabasco).

2.3. Soil characterization

The soil left from each monolith was sieved (<2 mm) at field capacity and stored at 4 °C before soil analysis and sorption experiments. Soil texture was determined with the Pipette method. The pH was measured in water and KCl 1 M using a 1:2.5 soil/solution ratio. To extract "free" Fe and Al compounds (Fed, Ald), a citrate dithionite solution was used (Mehra and Jackson, 1960). Concentrations of Fe and Al in supernatants were analyzed with ICP-OES (Perkin Elmer 8300). C and N contents were determined with a Total Analyzer (TOC, Perkin Elmer 2400) heating the sample at 980 °C with He as a carrier gas. Soil surface charge was determined through the measurement of potential zeta of soil suspension (Prado, 2006): for each monolith, 8 mg of soil (dry soil weight) was sampled in triplicate and mixed with 100 mL of $CaCl_2$ 8 mM, and the ultrasounds were applied to the suspension to obtain particles size around 2 μm. The pH was adjusted using NaOH 1 M and HCl acid 1 M.

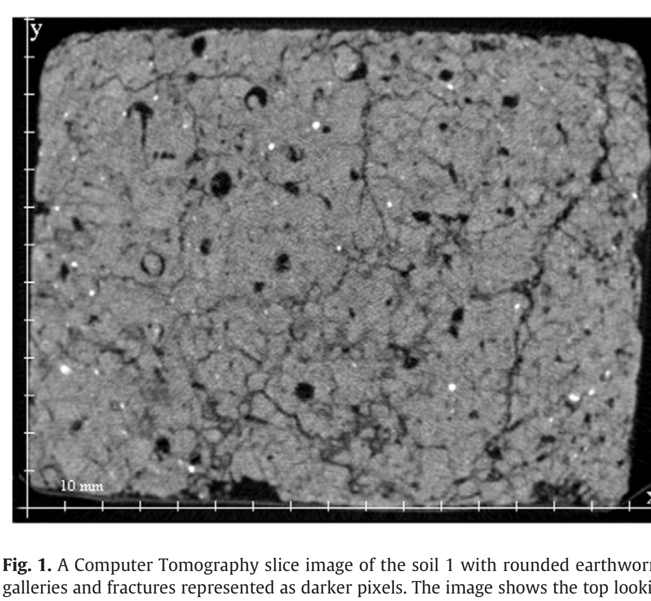

Fig. 1. A Computer Tomography slice image of the soil 1 with rounded earthworms galleries and fractures represented as darker pixels. The image shows the top looking downward.