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Behavior of Insecticide Chlorpyrifos on Soils and Sediments with Different Organic Matter Content from Provincia de Buenos Aires, República Argentina

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Abstract Buenos Aires Province (República Argentina) has undergone, in the last years, a great increase in agricultural activities based on the incorporation of new technologies and reduction of diversity to meet the increasing food demand. The increase of intensive agricultural systems in Argentina involves the use of fertilizers and pesticides such as herbicides, insecticides, and fungicides. Chlorpyrifos is one of the insecticides most widely used in these crops and constitutes a risk for human health, birds, and aquatic biota such as macroinvertebrates and fishes. In order to assess the possible contamination that the use of this product may represent for the environment, it is necessary to study its interaction with the different types of soils because fate and transport of environmental pollutants may be influenced by their interactions with soil particles. The behavior of chlorpyrifos was analyzed through the study of the recoveries from spiked solid environmental matrices. A strong dependence with organic matter content was observed along with an important dependence with the initial concentrations employed. Here, we show that chlorpyrifos behavior on solid matrices not only depends on soil chemical composition. A significant dependence of recovery percentages with initial concentrations of the pesticide was evident in all cases. Recovery percentages decreased with an increase of the initial concentration employed, no matter the variations in matrices of chemical compositions.

Keywords Chlorpyrifos · Pesticides · Solid matrices · Agricultural intensification · Organic matter content · Pollution

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1 Introduction

Buenos Aires Province has undergone, in the last 30 years, a remarkable expansion in agricultural activities based on the incorporation of new technologies, an increase in specialization, and reduction of diversity to meet the increasing food demand. The increase of the cultivated area brought, as a consequence, an increase in the use of agrochemicals, as the agricultural intensification requires an even more aggressive fight against plagues, parasites, and other harmful factors.

In intensively cultivated regions, streams are severely affected by the input of agrochemicals such as pesticides and nutrients, which often enter streams associated with soil particles as a result of erosion caused by edge of field runoff and from agricultural land (Cooper et al. 1993). Together with the suspended soil, pesticides are transported to nontarget compartments such as aquatic ecosystems (Jergentz et al. 2005). The fate and transport of pollutants need to be studied in detail in order to assess if they represent a threat for the agricultural environments. Fate and transport of pesticides may be influenced by their interactions with solid environmental matrices as soil and sediments from water bodies. In some cases, soil organic matter content appears to be a predominant factor influencing their retention (Boivin et al. 2005; Stevenson 1972; Coquet 2002; Spark and Swift 2002). As a result, there are a wide variety of transport pathways for many different chemicals to enter and persist in the environment.

In 2010, the market for agrochemicals raised up to U$S 1,675,000,000 in respect to phytosanitary products. Soybean is the crop accounting for the highest proportional percentage of the pesticide market. The main products sold for soybean are, in order of importance, herbicides and insecticides. From 2008 to 2010, the amount of sales of herbicides used for soybean decreased to U$S 40,000,000 while the amount of insecticides sales increased in U$S 72,000,000 (CASAFE 2011). The principal insecticides in the market are, in order of importance, chlorpyrifos, endosulfan, and cypermethrin.

Chlorpyrifos (Fig. 1), common name for *O*,*O*-diethyl *O*-(3,5,5-trichloro-2-pyridyl) phosphorothioate is an organophosphate insecticide of foliar and edaphic application. It has been suggested that the ability of chlorpyrifos and other organophosphorus pesticides to accumulate in living tissues may create a potential risk to humans and other organisms (Serrano et al. 1997; Wang et al. 2005). For this reason, it constitutes a threat for aquatic species production systems if it reaches water bodies (Agency for Toxic Substances and Disease Registry (ATSDR) 2011).

Chlorpyrifos is one of the most common pesticides frequently detected in surface water and groundwater in some regions of the world (USGS 2000; Domagalski and Munday 2003). A number of studies have been performed, tending to study the affinity of different pesticides with soil, but only a few refer to chlorpyrifos. In China (Shao-Nan et al. 2007), the mobility of the pesticide in soils has been studied using soil as stationary phase in thin layer chromatography. Correlation between Rfs and organic matter contents, pH, cationic interchange capacity, and clay contents was established. The adsorption of chlorpyrifos in soils from Almería (Spain) was also analyzed (Valverde García et al. 1992). Recently, Gebremariam et al. (2011) performed adsorption/desorption experiments with chlorpyrifos on eight soil and sediment samples collected from Washington and northern Idaho. Based on a review of the peer-reviewed literature, Gebremariam et al. (2012) proposed that pesticide partitioning cannot be fully accounted for by the fraction of soil or solid matrix organic matter or carbon content.

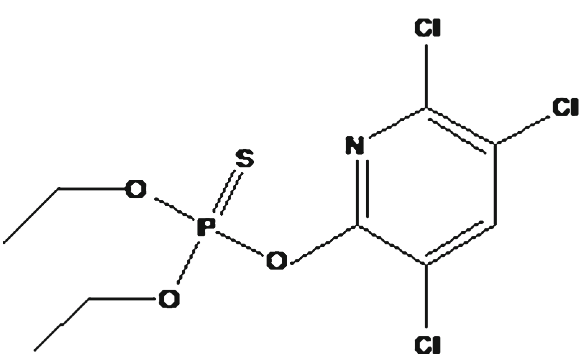

Fig. 1 Structure of chlorpyrifos

In Argentina, studies on the possible pollution caused by chlorpyrifos are scarce. There are several reports of the occurrence of chlorpyrifos in agricultural districts (Marino and Ronco 2005; Jergentz et al. 2004, 2005). As far as our knowledge, there are no studies on the affinity of chlorpyrifos with soils of the region. In order to prevent possible damages to the environment caused by the application of chlorpyrifos in crops, it is necessary to know the mechanisms that rule the transport of this pesticide.

Chlorpyrifos does no dissolve easily in water; it can stick to suspended particles and sediments and its reported half-life in soil varies from 10 to 120 days (Racke et al. 1988). This large variation in half-life has been attributed to variation in factors such as pH, temperature, moisture content, organic carbon content, and pesticide formulation (Getzin 1981). Due to the lack of systematic studies in this respect, it is essential to perform studies on the interaction of chlorpyrifos with Argentinean soils in order to assess the environmental impact caused by its application in crops. In this work, the behavior of chlorpyrifos in different solid matrices from Buenos Aires Province is analyzed and preliminary results are discussed, taking into account the influence of chemical composition and the initial concentrations of chlorpyrifos used in our experiments.

2 Materials and Methods

Three different solid matrices were chosen taking into account their difference in organic matter content.

Matrix A proceeded from an urban park soil (campus of the School of Veterinarian Medicine, University of Buenos Aires). Matrices B and C proceeded from Claromecó Stream, Tres Arroyos District, Buenos Aires, Argentina. Prior to their use, samples were air dried at room temperature, crushed, and passed through a 2-mm sieve. Solid matrices were analyzed for extractable phosphorous (Olsen), pH (1:2.5 soil/water ratio), organic carbon (Walkley–Black), nitrogen (micro-Kjeldahl), and clay content (Bouyoucos) by standardized methods (Sparks 1996; USDA 1993). The results of the soil analyses are shown in Table 1.

All reagents were analytical grade unless otherwise stated. Chlorpyrifos (*O*,*O*-diethyl-*O*-(3,5,5-trichloro-2-pyridyl phosphorothioate)) marked in the organophosphate insecticides group was used. Chlorpyrifos of 98 % purity was obtained from DuPont Argentina SA (Rosario, Argentina).

Before performing the experiments, blanks were carried out with the matrices to assure absence of chlorpyrifos. Samples (500 g) were spiked with chlorpyrifos to obtain a concentration of 1000 μg/g. The mixture was combined with uncontaminated soil to obtain concentrations of 2.5, 5, 10, 12.5, 14.7, 20, 25, and 50 μg/g. Spiked samples were allowed to rest for 3 days and extraction was performed.

EPA Method 3540c was adapted for the extraction. The spiked samples (20 g) were extracted (Soxhlet) with 450 ml of acetone: hexane (50:50 *v*/*v*) mixture for 16 h. Extracts were passed through a drying column containing about 10 cm of anhydrous sodium sulfate. The extracts were concentrated in a rotatory evaporator to 2 ml final volume. All the experiments were conducted in duplicates. Matrices without the addition of the pesticide were used as blanks.

EPA method 8080 was adapted for quantification. The gas chromatographic analyses were performed on a Perkin-Elmer Autosystem XL instrument equipped with an electron capture detector and a capillary column Quadrex (phase, 007–5; large, 30 m; DI, 0.25; film, 0.25; program: initial temperature 100 °C hold for 2 min; 15 °C/min to 160 °C hold, 0 min; 5 °C/min to 270 °C hold, 10 min; injector, 225 °C; detector 300 °C). Standard solutions of 25, 50, 100, 125, 500, and 1,000 μg/l were used for calibration.

3 Results and Discussion

To perform our studies, experiments were designed employing three different solid matrices (A, B, and C) that, due to their origin, did not contain chlorpyrifos. Chemical characterization of matrices is shown in Table 1.

Samples A, B, and C were artificially contaminated with different concentrations of the pesticide, extracted (Soxhlet), and analyzed by capillary gas chromatography using electron capture detection to determine the amount of extracted chlorpyrifos in each case. Recovery was estimated as percentage of initial concentration. Control experiments with uncontaminated samples were run in all cases to rule out any previous contamination. High reproducibility was observed for the extractions. Recoveries (percent of initial concentration) are shown in Fig. 2. In the case of matrix A, with higher organic matter content, a maximum of about 60 % recovery was observed at the lowest initial concentration employed (2.5 ppm) while recovery percentages diminished up to about 12 % at the highest initial concentration (50 ppm) assayed. In the cases of matrices B and C, recoveries varied from about 75 % to about 25 % when initial concentrations varied from 2.5 to 20 ppm.

On matrix A, with the highest organic matter content and lowest pH, recoveries were lower than in the other two cases. On matrices B and C, with closer values of organic matter content and pH, recoveries were similar in spite of other differences in

Table 1 Chemical characterization of matrices A, B, and C

	% organic matter content	% carbon	% N	P (ppm)	pH	% clay	% loam	% sand
Matrix A	9.38	4.69	0.360	6.23	7.10	33	46	22
Matrix B	1.26	0.63	0.050	12	8.53	12.5	37.5	50
Matrix C	0.64	0.32	0.040	6.50	9.14	7.5	20.5	72

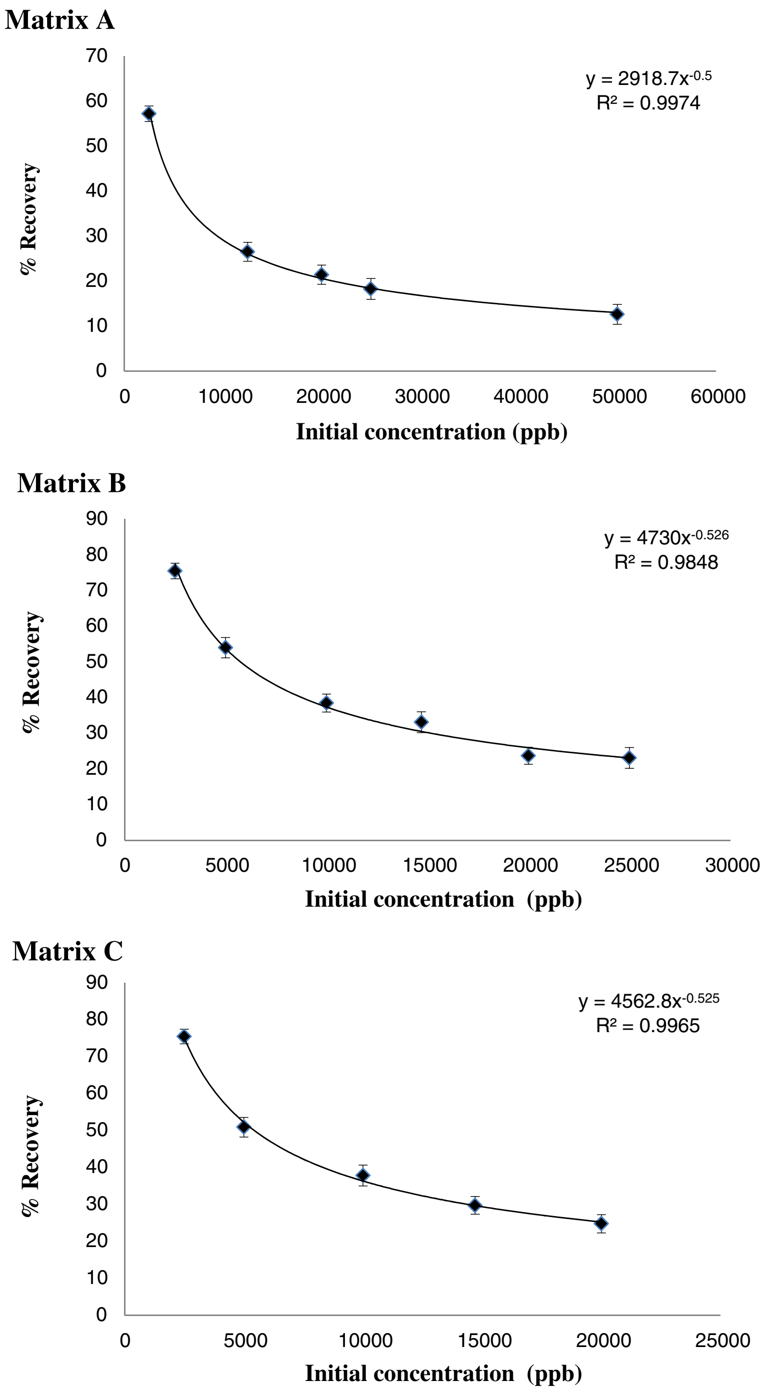

Fig. 2 Recoveries (percent of initial concentration) in matrices A, B, and C. Note the influence of the organic matter content and the dependence of recovery with initial concentration in all cases. *Error bars* are standard deviations

composition. These results are consistent with reports that indicate that soil organic matter content and pH appear to be the principal factors that rule the affinity of organic compounds with the matrix (Boivin et al. 2005; Stevenson 1972; Coquet 2002; Spark and Swift 2002; Ei Mon et al. 2009).

In all cases (Fig. 2), we observed that the recovery percentages decreased with an increase of the initial concentration employed. This observation indicates that the initial concentration of the pesticide has a strong influence on its interaction with the solid matrix.

4 Conclusions

Average recoveries were lower in the experiment performed using the matrix with the highest organic matter content and lower pH. These results are consistent with a previous work where it was reported that soil organic matter content appears to be a predominant factor influencing pesticide retention (Boivin et al. 2005; Stevenson 1972; Coquet 2002; Spark and Swift 2002). Besides, in all the experiments performed, it was observed that the recovery percentages of chlorpyrifos vary according to the initial concentrations employed. In all cases, in spite of the differences in the chemical composition of the solid matrices, an important decrease in recovery is observed with the increase of initial concentration. This behavior opposes to the behavior observed for the veterinary antibiotic monensin on soils from Buenos Aires Province (Yoshida et al. 2007) where recovery increased with the increase of initial concentration of the xenobiotic. This observation suggests that, besides organic matter content and pH, the amount of chlorpyrifos that reaches soils or sediments may be involved in the retention of this pesticide on those matrices and has to be taken into account when assessing site contamination produced by agricultural practices.

Chlorpyrifos behavior on solid matrices goes beyond soil chemical composition as the dependence with initial concentration persists in spite of the variations of chemical parameters. Cooperative effects in the interactions of chlorpyrifos with soils could cause this behavior and they should be taken into account in order to assess the environmental risks caused by this pesticide. As this substance is used in formulations together with surfactant compounds, the effect of different formulations must also be considered to perform those studies as the interactions with solid matrices may vary in the presence of surfactants.

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