Sorption and desorption of organophosphate pesticides, parathion and cadusafos, on tropical agricultural soils

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Abstract – Ecotoxicological impacts of organic pesticides on soil and aquatic ecosystems depend primarily on their behavior in soils. Actual pesticide knowledge is mostly restricted to soils from temperate climates, whereas knowledge of pesticide behavior in tropical soils is scarce. Here, the sorption behavior of two organophosphorous insecticides, parathion and cadusafos, was studied in three agricultural soil samples from central Mexico, Vertisols and Andosols. Using 14C-labeled substances, we assessed sorption and desorption properties in classical batch equilibrium and static soil incubation experiments. Our results show that cadusafos was less sorbed by the various soils (Kd values 7.6–12.7 L kg⁻¹) compared with parathion (Kd values 38.6–74.9 L kg⁻¹), despite similar log Kow values. Cadusafos exhibited a greater reversibility of sorption than parathion in both soil types. Time-dependent sorption was quantitatively significant, leading to a rapid decrease in the concentration of available insecticide. This finding is partly due to the formation of non-extractable, bound residues. The decrease in the available concentration of both insecticides was greater in the Andosol compared with the Vertisols. Soil organic matter clearly influenced the sorption behavior and availability of parathion. On the other hand, the sorption of cadusafos was more influenced by other soil properties such as clay content and cation exchange capacity. Calculation of residual insecticide levels in the soil solution suggests that both insecticides may have persistent toxic effects in the studied soils.

desorption / organophosphorous / insecticides / adsorption

1. INTRODUCTION

In Mexico, the agricultural use of pesticides has been generalized to many states and has considerably increased in the last few decades due to the development of intensive food production in some parts of the country (INEGI, 2004). Morelos State, with a large variety of crops cultivated in relatively intensive cropping systems (3 to 4 crop cycles per year), is representative of the agriculture of central Mexico. In this area, organophosphorous pesticides are still the main category of insecticides used (INEGI, 2004). Regarding the toxicity of these compounds and their degradation products, their widespread use has been reconsidered in several countries through limitations and interdictions. However, the persistent use of certain organophosphorous compounds necessitates evaluation of the risks to groundwater from movement through the soils and to soil organisms from uptake and transfer through the food chain (Pehkonen and Zhang, 2002). This is particularly needed in southern countries where available data on the effects of climatic and soil factors are less documented (Racket, 2003).

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Among the organophosphate compounds largely used, cadusafos [S,S-di-sec-butyl O-ethyl phosphorodithioate] is a nematicide and insecticide against a broad spectrum of nematodes and soil insects. It is employed on several important crops of Mexico, and other countries of central America, such as banana, tomato, sugar cane, coffee, citrus, maize and agave. This compound has a high toxicity and is also relatively mobile in the environment (Zheng et al., 1994; Agritox, 2005). Parathion [O,O-diethyl O-(4-nitrophenyl) phosphorothioate] is an insecticide formerly used on several crops. Due to its toxicity, its use has been restricted since 1991, but methylparathion is still used in Mexico (CICLOPLAFEST, 2004).

The behavior of pesticides in soils strongly depends on adsorption-desorption phenomena. As these processes influence the composition of the soil solution, knowledge and understanding of them is important to accurately predict the mobility and the bioavailability of these chemicals in soils, and therefore to limit their impact on non-targeted organisms and ecosystems. Pesticide availability in soil can be evaluated using indirect and direct methods. The most common indirect method to characterize pesticide availability is by using a
simplistic partition coefficient ($K_d$). Many pesticide fate models have traditionally used sorption $K_d$ values to predict the amount of pesticide that can be available in solution at a given time. However, sorption-desorption processes are complex and cannot be described by a single value assuming instantaneous totally reversible sorption (Koskinen and Harper, 1990; Pignatello, 2000).

Desorption processes control the release rates of pesticide into the soil solution and therefore have a major control of availability and bioavailability to soil organisms (Weber et al., 1993). Non-reversible sorption and hysteresis effects concern many pesticides (Koskinen and Harper, 1990; Pignatello, 2000). This implies that desorption cannot be predicted from their sorption isotherms. Increasing pesticide contact time or ageing affects sorption and desorption processes, and generally desorption decreases with the residence time in soil (Pignatello, 2000; Mamy and Barriuso, 2007). As a consequence, the availability of pesticide for transport or uptake by soil organisms decreases with time (Führemann et al., 1978; Weber et al., 1993; Gevao et al., 2001).

Several pedological factors are known to regulate sorption and desorption processes (Barriuso and Calvet, 1991; Weber et al., 2004). For ionized molecules, mineralogical composition and soil pH are key parameters, whereas sorption of neutral compounds is mostly governed by the soil organic matter (Hamaker and Thompson, 1972; Wauchope et al., 2002). These generally accepted rules have been obtained in studies considering large numbers of soil types and origins. Nevertheless, the role of soil characteristics is less documented for tropical soils compared with temperate soils (Barriuso et al., 1992; Zheng and Cooper, 1996; Oliver et al., 2005; Laabs and Amelung, 2005). Comparing the sorption properties of herbicides on various soil types including tropical soils such as Andosols, Vertisols and Ferralsols, Barriuso and Calvet (1991) have shown that relations between sorption and soil type characteristics strongly depend on molecular properties such as electrical state and polarity. The combination of the effects of soil organic matter and of mineral constituents such as smectite-type clays (Vertisols) and amorphous clays-allophanes (Andosols) usually increases the sorption of neutral molecules (Barriuso and Calvet, 1991).

The present study aimed to identify the main soil parameters affecting the sorption and desorption of cadusafos and parathion on agriculturally-representative tropical soils (Vertisols and Andosols from central Mexico). The relationships between the experimental parameters, soil properties and physico-chemical characteristics of the two compounds were examined to predict the availability of the pesticides. Laboratory incubations were also carried out to study the influence of time on the retention of the insecticides and to evaluate the availability of their residues.

2. MATERIALS AND METHODS

2.1. Soil samples

The soils originated from Morelos state, Mexico. They were selected on the basis of their relative extension on the regional scale, their texture and organic matter content (Tab. I). According to the FAO soil classification (WRB, 1998), soil types were classified as Andosol (Huitzilac site) and Vertisol (Ayala and Yautepec sites). In Morelos state, Andosols represent 12% of the land and are located in the northern temperate region of the state. Developed on slopes of the volcanic sierras, these soils naturally covered by forests have recently been converted for agriculture (INEGI, 2004).

Vertisols represent 21% of the total surface and are mainly distributed in the temperate subtropical area in the south of Morelos state. Historically, these soils have been used for agriculture for a very long period due to their fertility (INEGI, 2004).

Soils were taken from the surface layers (0–20 cm layer). Soil analyses were performed by the soil analysis laboratory (INRA Arras) according to ISO reference methods (AFNOR, 2005).

Table I. Physico-chemical characteristics and texture of the soils (0–20 cm layer). Soil analyses were performed by the soil analysis laboratory (INRA Arras) according to ISO reference methods (AFNOR, 2005).

<table>
<thead>
<tr>
<th>Parcel location</th>
<th>Ayala Vertisol 1</th>
<th>Yautepec Vertisol 2</th>
<th>Huitzilac Andosol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soil pH water</td>
<td>8.0</td>
<td>7.1</td>
<td>5.6</td>
</tr>
<tr>
<td>Sand g/kg</td>
<td>494</td>
<td>418</td>
<td>550</td>
</tr>
<tr>
<td>Silt g/kg</td>
<td>108</td>
<td>224</td>
<td>272</td>
</tr>
<tr>
<td>Clay g/kg</td>
<td>398</td>
<td>358</td>
<td>178</td>
</tr>
<tr>
<td>Organic carbon g/kg</td>
<td>10.8</td>
<td>17.8</td>
<td>54.3</td>
</tr>
<tr>
<td>Total N g/kg</td>
<td>0.804</td>
<td>1.44</td>
<td>3.67</td>
</tr>
<tr>
<td>C/N</td>
<td>13.5</td>
<td>12.4</td>
<td>14.8</td>
</tr>
<tr>
<td>C.E.C cmol/kg</td>
<td>44.6</td>
<td>23.9</td>
<td>21.9</td>
</tr>
<tr>
<td>Ca$^{2+}$ exch. cmol/kg</td>
<td>29.5</td>
<td>14.3</td>
<td>4.96</td>
</tr>
<tr>
<td>Mg$^{2+}$ exch. cmol/kg</td>
<td>16.4</td>
<td>7.38</td>
<td>0.464</td>
</tr>
<tr>
<td>K$^+$ exch. cmol/kg</td>
<td>0.404</td>
<td>1.57</td>
<td>0.447</td>
</tr>
<tr>
<td>Na$^+$ exch. cmol/kg</td>
<td>1.93</td>
<td>0.108</td>
<td>0.050</td>
</tr>
<tr>
<td>Al$^{3+}$ exch. cmol/kg</td>
<td>&lt; 0.05</td>
<td>&lt; 0.05</td>
<td>0.279</td>
</tr>
<tr>
<td>Al – total g/kg</td>
<td>8.39</td>
<td>9.16</td>
<td>8.84</td>
</tr>
<tr>
<td>Al – Tamm g/kg</td>
<td>0.177</td>
<td>0.134</td>
<td>3.03</td>
</tr>
<tr>
<td>Fe – total g/kg</td>
<td>3.51</td>
<td>3.4</td>
<td>4.47</td>
</tr>
<tr>
<td>Fe – Tamm g/kg</td>
<td>0.061</td>
<td>0.127</td>
<td>1.09</td>
</tr>
<tr>
<td>P – total g/kg</td>
<td>0.028</td>
<td>0.0548</td>
<td>0.0229</td>
</tr>
<tr>
<td>P – Olsen g/kg</td>
<td>0.013</td>
<td>0.0540</td>
<td>0.0010</td>
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</tbody>
</table>