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R. S. Oliveira Jr.; W. C. Koskinen; N. R. Werdin; P. Y. Yen
Departamento de Agronomia, Universidade Estadual de Maringá, Maringá, PR, Brazil
Department of Agriculture, Agricultural Research Service, St. Paul, MN
Bayer Corporation, Stilwell, KS

To cite this Article Oliveira Jr., R. S., Koskinen, W. C., Werdin, N. R. and Yen, P. Y. (2000) 'Sorption of imidacloprid and its
metabolites on tropical soils', Journal of Environmental Science and Health, Part B, 35: 1, 39 — 49
To link to this Article: DOI: 10.1080/03601230009373252
URL: http://dx.doi.org/10.1080/03601230009373252
SORPTION OF IMIDACLOPRID AND ITS METABOLITES ON TROPICAL SOILS

Key Words: Sorption, imidacloprid, metabolites, tropical soils

R. S. Oliveira, Jr.¹, W. C. Koskinen², N. R. Werdin² and P. Y. Yen³

¹Departamento de Agronomia, Universidade Estadual de Maringá, Av. Colombo 5790, 87020-900, Maringá, PR, Brazil
³Bayer Corporation, 17745 South Metcalf, Stilwell, KS 66088

ABSTRACT

The sorption of imidacloprid (1-[(6-chloro-3-pyridinyl)-methyl]-N-nitro-2-imidazolid-inimine) (IMI) and its metabolites imidacloprid-urea (1-[(6-chloro-3-pyridinyl)-methyl]-2-imidazol-idinone) (IU), imidacloprid-guanidine (1-[(6-chloro-3-pyridinyl)-methyl]-4,5-dihydro-1H-imidazol-2-amine) (IG), and imidacloprid-guanidine-olefin (1-[(6-chloro-3-pyridinyl)methyl]-1H-imidazol-2-amine) (IGO) was determined on six typical Brazilian soils. Sorption of the chemicals on the soil was characterized using the batch equilibration method. The range and order of sorption (Kd) on the six soils was IG (4.75-134) ≥ IGO (2.87-72.3) > IMI (0.55 -16.9) > IU (0.31-9.50). For IMI and IU, Kd was correlated with soil organic carbon (OC) content and CEC, the latter due to the high correlation between OC and cation exchange capacity (CEC) (R²=0.98). For IG and IGO, there was no correlation of sorption to clay, pH, OC or CEC due to the high
sorption on all soils. Average $K_{oc}$ values were $IU = 170$, $IMI = 362$, $IGO = 2433$, and $IG = 3500$. Although $K_d$ and $K_{oc}$ values found were consistently lower than those found in soils developed in non-tropical climates, imidacloprid and its metabolites were still considered to be slightly mobile to immobile in Brazilian soils.

**INTRODUCTION**

Imidacloprid, a new chloronicotinyl insecticide, has activity on a broad range of economically important insects such as scales, many Coleopteran species, and selected species of Diptera and Lepidoptera (Mullins, 1993). Due to its novel mode of action, imidacloprid is also effective on many insects currently resistant to carbamates, organophosphates and pyrethroids. Also, due to its systemic characteristics and residual activity, the product is especially appropriate for seed treatment and soil application. Imidacloprid action takes place by ingestion, contact, or inhalation. Its excellent crop tolerance and broad spectrum activity allow for the potential use of imidacloprid on a wide range of economically important crops (Cabello et al., 1997).

Because of its insecticidal effectiveness and its safety for humans and the environment, it has been suggested that imidacloprid soil treatments may provide a more environmentally suitable and safe alternative to control different pests than is currently possible with foliar insecticide treatments (Palumbo et al., 1996). Although short-lived inhibitory effects on activities of microbes and enzymes can be caused by imidacloprid, the soil indigenous microbes are not affected by soil application of imidacloprid (Tu, 1995).

Contamination of surface water and ground water by pesticides has been a source of concern for the past several years. Vertical and lateral mobility of many soil-applied pesticides are inversely related to mineral and organic fractions of soil matrix. Recent laboratory studies have indicated that imidacloprid is strongly sorbed to both substrates, and does not readily desorb (Cox et al., 1997, 1998). However, there is no data available on the relative behaviour of imidacloprid or
its metabolites on tropical soils, which are chemically and physically distinct from soils developed in non-tropical climates.

Typical Brazilian soils are classified as Quartzipsamment (AQ), Hapludult (PV) and Haplororthox (LR). They are usually deep mineral soils, with a composition based on 1:1 clays such as kaolinite, goethite, gibbsite and hematite, with low organic matter contents and low pH. The soils are subject to relatively high year round temperatures and occasional high rainfalls. Previous reports evaluating the mobility of herbicides in Brazilian soils have used mainly bioassay techniques (Silva et al., 1998; Souza, 1988), but have indicated the necessity of the need for studies of pesticides under tropical conditions, including a more thorough evaluation of the factors controlling sorption of these chemicals by tropical soils.

The objective of the present study was to characterize the sorption of imidacloprid and three of its metabolites on typical Brazilian soils. An understanding of the sorption phenomena would help in the safe and effective use of imidacloprid in Brazil.

MATERIALS AND METHODS

Pure analytical standards (chemical purity > 99%) and radiochemical materials (radiochemical purity > 97%) were supplied by Bayer Corp. Specific activities of the radiolabeled standards were 32.1, 26.8, 49 and 23.18 mCi mmol⁻¹, respectively for IMI, IU, IGO and IG. Figure 1 shows the chemical structures of imidacloprid and its metabolites. The imidacloprid data are from Tomlin (1994) and Chamberlain et al. (1996). Unlabeled 3.91, 4.72, 4.79 and 4.75 μmol L⁻¹ solutions of IMI, IU, IGO, and IG, respectively, were mixed with ¹⁴C-chemicals to give a final solution concentration of ~4000 dpm mL⁻¹.

¹ Mention of a company or product name is for information only and does not imply an endorsement by Universidade Estadual de Maringá, USDA-Agricultural Research Service, or Universidade Federal de Viçosa.
Surface soil samples (0 to 20 cm depth) were taken from six locations in Brazil, air-dried and passed through a 2-mm diameter sieve. Soil texture was determined by the hydrometer method (Gee and Bauder, 1986). Soil pH was measured in a 1:1 (w:w) soil:CaCl$_2$ 0.01 M solution mixture. Organic carbon content was determined using a modified Walkley Black method (Nelson and Sommers, 1982). Selected properties of soils are given in Table 1.

Sorption was characterized using the batch equilibration method, details of which have been previously published (Oliveira et al., 1999). In brief, quadruplicate 10-mL aliquots of imidacloprid and its metabolites solution were added to 10 g of soil in 50-mL centrifuge tubes, sealed, agitated and shaken for a 24-h period of equilibration. After equilibration, soil slurries were centrifuged (30 min/2000 rpm) and 1-mL aliquots of supernatant were analyzed by LSC (Packard 1500 Tri-Carb liquid scintillation analyzer, Packard Instruments, Pittsburgh, PA, 51225, USA). Imidacloprid and metabolite concentrations in
### TABLE 1
Soil Classes, Origins, and Physical and Chemical Characteristics

<table>
<thead>
<tr>
<th>Class (code in text)</th>
<th>Origin</th>
<th>Clay</th>
<th>Silt</th>
<th>Sand</th>
<th>Texture</th>
<th>pH</th>
<th>OC</th>
<th>CEC cmolc dm⁻³</th>
<th>Base sat'n.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Latossolo Roxo (Haplorthox)</td>
<td>Capinópolis, MG (LR-CP)</td>
<td>42</td>
<td>17</td>
<td>41</td>
<td>Clay</td>
<td>4.8</td>
<td>1.45</td>
<td>14.5</td>
<td>38.5</td>
</tr>
<tr>
<td>Latossolo Roxo (Haplorthox)</td>
<td>Londrina, PR (LR-LN)</td>
<td>75</td>
<td>21</td>
<td>4</td>
<td>Clay</td>
<td>6.3</td>
<td>2.78</td>
<td>26.1</td>
<td>71.4</td>
</tr>
<tr>
<td>Areia Quartzoza (Quartzipsamment)</td>
<td>Mocambinho, MG (AQ-MC)</td>
<td>10</td>
<td>3</td>
<td>87</td>
<td>loamy sand</td>
<td>4.3</td>
<td>0.35</td>
<td>3.0</td>
<td>33.3</td>
</tr>
<tr>
<td>Areia Quartzoza (Quartzipsamment)</td>
<td>Três Marias, MG (AQ-TM)</td>
<td>6</td>
<td>10</td>
<td>84</td>
<td>Sand</td>
<td>4.5</td>
<td>0.58</td>
<td>4.4</td>
<td>18.9</td>
</tr>
<tr>
<td>Areia Quartzoza (Quartzipsamment)</td>
<td>Venda Nova, ES (AQ-VN)</td>
<td>14</td>
<td>15</td>
<td>71</td>
<td>sandy loam</td>
<td>4.6</td>
<td>7.45</td>
<td>46.8</td>
<td>22.9</td>
</tr>
<tr>
<td>Podzólico Vermelho-Amarelo (Hapludult)</td>
<td>Viçosa, MG (PV-VÇ)</td>
<td>34</td>
<td>7</td>
<td>59</td>
<td>sandy clay loam</td>
<td>4.5</td>
<td>1.74</td>
<td>14.4</td>
<td>39.2</td>
</tr>
</tbody>
</table>

1 According to Brazilian Soil Science Society and Soil Taxonomy
solution were determined by difference between initial and final solution radioactivities. Sorption coefficient, \( Kd \), was determined for each soil-chemical combination, by means of the following relationship:

\[
K_d = \frac{C_s}{C_w}
\]

where \( Kd \) is the sorption coefficient (L kg\(^{-1}\)), \( C_s \) is the concentration of herbicide sorbed to soil (\( \mu \)mol kg\(^{-1}\)), and \( C_w \) is the concentration of herbicide remaining in solution (\( \mu \)mol L\(^{-1}\)), after equilibration. \( Koc \) coefficients were calculated by normalizing the corresponding \( Kd \) values to the total OC of the soils.

**RESULTS AND DISCUSSION**

In general, the order and range of sorption (as indicated by \( Kd \) values) of imidacloprid and the three metabolites for all soils were IG (4.75-134) \( \geq \) IGO (2.87-72.3) \( \geq \) IMI (0.55-16.9) \( \geq \) IU (0.31-9.50) (Table 2). Sorption of imidacloprid and these metabolites has previously been shown to be concentration dependent in a number of soils (Cox et al., 1997; 1998), whereby sorption would be better characterized by Freundlich coefficients, \( Kf \) and \( 1/n \). However, to determine the effect of different soil properties on sorption, comparison of \( Kd \) values is acceptable. For IMI and IU, the main soil properties influencing sorption, i.e. \( Kd \), were OC content and CEC (Table 3). The most important single factor affecting \( Kd \) for IMI and IU was OC. OC and CEC were strongly correlated (\( R^2 = 0.98 \)) since a great part of CEC in soils with a predominant 1:1 clay type is due to OC.

While \( Kd \) and OC are highly correlated for IMI and IU, other interactions are occurring, particularly for soils LR-CP and PV-VÇ, although no significant correlations (\( P < 0.05 \)) were found between \( Kd \) or \( Koc \) and mineral fraction components. For soils LR-CP and PV-VÇ, more sorption (average IMI \( Koc = 700 \), IU \( Koc = 303 \)) was observed than would be predicted from the OC content of the four other soils (average IMI \( Koc = 193 \), IU \( Koc = 103 \)). Deleting LR-CP and PV-VÇ soils from the regression analyses of \( Kd \) vs. OC, \( R^2 \) increased from 0.62 to 0.99 for IMI and from 0.75 to 0.97 for IU (Figure 2).
## TABLE 2
Sorption Coefficients ($Kd \pm s.d.$ and $Koc$) for Imidacloprid and its Metabolites on Six Brazilian Soils

<table>
<thead>
<tr>
<th>Soil</th>
<th>Imidacloprid (IMI)</th>
<th>Imidacloprid-urea (IU)</th>
<th>Imidacloprid-guanidine (IG)</th>
<th>Imidacloprid-guanidine-olefin (IGO)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$Kd$  $\pm$ s.d.</td>
<td>$Koc$</td>
<td>$Kd$  $\pm$ s.d.</td>
<td>$Koc$</td>
</tr>
<tr>
<td>LR-CP</td>
<td>11.3  $\pm$ 1.4</td>
<td>779</td>
<td>4.33  $\pm$ 0.40</td>
<td>297</td>
</tr>
<tr>
<td>AQ-MC</td>
<td>0.55  $\pm$ 0.01</td>
<td>158</td>
<td>0.31  $\pm$ 0.01</td>
<td>89</td>
</tr>
<tr>
<td>LR-LN</td>
<td>5.18  $\pm$ 0.21</td>
<td>186</td>
<td>2.00  $\pm$ 0.29</td>
<td>72</td>
</tr>
<tr>
<td>AQ-TM</td>
<td>1.18  $\pm$ 0.12</td>
<td>203</td>
<td>0.72  $\pm$ 0.02</td>
<td>124</td>
</tr>
<tr>
<td>AQ-VN</td>
<td>16.9  $\pm$ 0.6</td>
<td>227</td>
<td>9.50  $\pm$ 0.33</td>
<td>128</td>
</tr>
<tr>
<td>PV-VÇ</td>
<td>10.8  $\pm$ 0.4</td>
<td>620</td>
<td>5.37  $\pm$ 0.41</td>
<td>309</td>
</tr>
</tbody>
</table>
### TABLE 3
Pearson Correlation Coefficients Between Imidacloprid and Metabolites Sorption Coefficients and Soil Characteristics

<table>
<thead>
<tr>
<th></th>
<th>clay</th>
<th>pH</th>
<th>OC&lt;sup&gt;a&lt;/sup&gt;</th>
<th>CEC&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>%</td>
<td></td>
<td>%</td>
<td>cmol&lt;sub&gt;e&lt;/sub&gt; dm&lt;sup&gt;3&lt;/sup&gt;</td>
</tr>
<tr>
<td>IMI</td>
<td>0.112</td>
<td>-0.042</td>
<td>0.788*</td>
<td>0.794*</td>
</tr>
<tr>
<td></td>
<td>0.234</td>
<td>-0.167</td>
<td>-0.173</td>
<td>-0.112</td>
</tr>
<tr>
<td>IU</td>
<td>-0.035</td>
<td>-0.127</td>
<td>0.864*</td>
<td>0.835*</td>
</tr>
<tr>
<td></td>
<td>0.079</td>
<td>-0.323</td>
<td>-0.154</td>
<td>-0.128</td>
</tr>
<tr>
<td>IG</td>
<td>0.337</td>
<td>0.071</td>
<td>0.242</td>
<td>0.319</td>
</tr>
<tr>
<td></td>
<td>0.114</td>
<td>-0.139</td>
<td>-0.401</td>
<td>-0.352</td>
</tr>
<tr>
<td>IGO</td>
<td>-0.058</td>
<td>-0.256</td>
<td>0.564</td>
<td>0.545</td>
</tr>
<tr>
<td></td>
<td>-0.201</td>
<td>-0.377</td>
<td>-0.444</td>
<td>-0.460</td>
</tr>
</tbody>
</table>

<sup>a</sup> Soil organic carbon content  
<sup>b</sup> Cation Exchange Capacity.  
* Significant at (P<0.05).

It is not known what mineralogical property is responsible for the additional sorption. As occurs with representative soils from tropical areas, the mineral fractions of Brazilian soils are mainly composed by clays like kaolinite, gibbsite, and Fe and Al-hydroxides, all of which have limited specific surfaces. A more detailed mineralogical characterization of these soils is needed to determine sorption mechanisms.

For IG and IGO, there was no significant correlation between sorption and measured soil properties, indicating that these two metabolites are highly sorbed, regardless of soil type and properties (Tables 2 and 3). It appears that mineralogical properties significantly affected 3 of the 6 soils, LR-CP, PV-VC, and AQ-TM. The average Koc for IG sorption on LR-CP, PV-VC, and AQ-TM was 5718 as compared to 1283 for the other three soils. Similarly, for IGO, the
average $Koc$ was 4105 for LR-CP, PV-VÇ, and AQ-TM as compared to 761 for the other three soils.

The magnitude of the sorption coefficients and the fact that sorption increases with decreasing concentration, suggests that imidacloprid residues would be relatively immobile in soil. In studies on the movement of imidacloprid applied at the highest proposed label rate to field soils, including coarse-textured soils with a high sand content, no imidacloprid residues were found below the 30.5 cm soil level, regardless of soil type (Mullins, 1993). Efficacy studies with soil applications have demonstrated that, unlike other more soil mobile insecticides, imidacloprid performs best when the product is placed precisely...
where root uptake can occur (Palumbo et al., 1996), which is also an indicative of its low mobility on soil.

CONCLUSIONS

The order of sorption of imidacloprid and metabolites for all soils, IG ≥ IGO > IMI > IU, are supportive of previous results obtained for other soils, in relation to main individual soil properties affecting sorption. Although $K_d$ and $K_{oc}$ values found were somewhat lower than those found in soils developed in non-tropical climates, presumably due to their lower OC contents and their characteristic clay mineralogy, imidacloprid and its metabolites would still be considered to be slightly mobile to immobile in Brazilian soils.

ACKNOWLEDGEMENTS

The authors would like to thank CAPES (Brazil) for the partial financial support and Bayer Corp. for providing $^{14}$C-chemicals.

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Received: June 15, 1999