Sorption and transport of imazamethabenz in agricultural soils

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Abstract

Sorption and transport characteristics of Imazamethabenz-methyl were investigated evaluating the validity of the transport ideality assumptions (i.e. isotherm linearity, sorption-desorption singularity, and instantaneous equilibrium). Laboratory batch equilibrium studies were conducted to evaluate the sorption-desorption behaviour and miscible displacement experiments on soil columns were performed at several pore water velocities. Experiments revealed a true hysteresis on desorption, with the adsorption isotherm being linear, and a transport-related nonequilibrium. Thus, this chemical will be detected at a given monitoring point earlier than when calculated by a local equilibrium assumption model and desorption will take longer than expected.

1 Introduction

The sorption-desorption processes are among the most important factors influencing mobility of pesticides in soil environment. Knowledge of the various physical, chemical and biological processes which affect groundwater contaminants is essential for research on contaminant transport. The sorption process is often simplified in modeling solute transport by assuming instantaneous equilibrium, isotherm linearity and sorption-desorption singularity (Brusseau & Rao'). These assumptions are adequate in certain situations, although their validity must be investigated for each specific soil-water-contaminant system.

Imazamethabenz (methyl6-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)-m-and-p-toluate) is an effective post-emergence herbicide with high soil persistence. Consequently, there is interest in developing a fundamental
understanding of the factors and processes influencing the mobility of this chemical in agricultural soils. Additionally, the relatively big size of this molecule can have a decisive effect on the transport of this chemical in porous media.

The aim of this paper is to discuss the factors which can affect the nonideal sorptive behaviour of Imazamethabenz (Imz) in soils evaluating the validity of the transport-ideality assumptions. The final goal is to investigate if simplifying transport analysis may be adequate under certain conditions or if these assumptions may yield erroneous results when modeling Imz transport in the subsurface.

2 Materials and Methods

The soil selected for this study is agricultural soil from Valladolid (Spain). It is a silty-clay collected from the top 20 cm (40% Sand, 30% Silt, 30% Clay, 1.3% O.M. and pH=7.84).

Chromatographically pure Imazamethabenz standards were obtained from Promochem (Wesel, Germany), and the commercial formulation Assert (30% w/v) was supplied by Cyanamid Ibérica (Spain).

Adsorption kinetics and isotherms: The mass soil-solution ratio used for the whole experiments was 1/2. In all cases, 0.01 N CaCl$_2$ was used as solvent in order to promote flocculation and to maintain a constant ionic strength on solution. For kinetic studies, several flasks containing suspensions with the same initial herbicide concentration were shaken at 25 °C (±0.1 °C) over different periods of time ranging from 10 min to 48 h. After each time, the suspensions were centrifugated at 3500 rpm for 10 min, and the supernatant were analyzed after filtering through 0.45 μm pore-size filters (Microfiltration Systems, Dublin, CA).

Adsorption isotherms were carried out using a shaking time of 24 h, at which the pseudoequilibrium was reached (Fig 1). Soils were equilibrated with Imz initial concentration ranging from 1 to 16 μg/g. At the end of the adsorption process, a fraction of the supernatant on each run was withdrawn and the volume of the remaining slurry was made up again to the original soil/solution ratio. The concentration of Imz present in solution was determined by HPLC (Atienza et al.) and the amount of herbicide adsorbed was estimated by a mass-balance.

Column experiments: A preparative chromatography column with an internal diameter of 2 cm and a length of 10 cm was packed in incremental steps to ensure constant bulk density. Two double piston HPLC pumps (LDC Analytical CM3200, Riviera Beach, FL) were connected to the column with a Rheodyne switching valve (model 7125 modified at 60° to avoid injection input). A UV detector (LDC Analytical SM 3200, Riviera Beach, FL) was used to monitor column effluent concentrations continuously. Data were collected in
a IBM-PC with an A/D card controlling column temperature and data acquisition system (Alvarez & Sobrón)³.

Soil column experiments were conducted under saturated flow conditions following the technique described by Brusseau et al⁴. Columns were saturated from bottom by capillarity and a electrolyte solution (0.01 N CaCl₂) was pumped through the soil until steady-state was established. Miscible displacement experiments were performed using various volumetric fluxes. The pulse input of solute was obtained by switching the valve between solutions that did or did not contain the tracers (in all cases with a constant concentration of electrolyte). Pentafluorobenzoic acid (PFB) was used as a nonsorbed tracer in order to determine the column hydrodynamic conditions.

3 Results and discussion

Figure 1 shows the evolution of Imz concentration in solution versus time in a kinetic experiment starting at 12 μg/g. This figure suggests that Imz adsorbs in two steps during the 48 h of the run: an initial fast adsorption followed by a slower one. Similar results were reported by Hermosin et al⁵ and Jardine & Sparks⁶ among others. These two steps could correspond to two different adsorption mechanisms. In fact, Imz can be found in several forms depending on pH. As found with other pesticides, soil pH often plays an important role on the mobility and presence of Imz in the soil.

![Figure 1. Evolution of the concentration of Imz in solution with time.](image-url)
Many authors have reported this slower second stage. It has also been found that this stage is not quickly reversible enough to recover the herbicide by the usual extraction methods. An alternative explanation of the two-steps phenomena lies in the existence of diffusion in the interior of soil intra-aggregates (pore diffusion, surface diffusion or both) as described by Ruthven. Several physical mechanisms were suggested to be as rate limiting when applying the parabolic diffusion law. This was done by means of a representation of the Imz concentration in solution versus the square root of time (Fig 1.a).

Sorption of Imz was adequately described by the linear equations ($r^2>0.99$) as shown by Table 1 and Fig 2. The magnitude of the estimated $K_d(0.4)$ is indicative of the overall weak binding of this compound to the soil matrix. Desorption isotherms conformed fairly well to the Freundlich and Langmuir equations. Desorption of Imz presented hysteresis (Fig 2). This behaviour may be partially apparent as a consequence of failure to reach equilibrium in the adsorption processes (Brusseau & Rao). No other contribution to apparent hysteresis can be found in this case because several tests proved that degradative losses did not occur during experiments. Nevertheless, the main contribution to this phenomenon must be a true hysteresis due to a slowly reversibly sorption or binding. Support for the existence of true desorption hysteresis was provided in studies showing that some fraction of Imz was unrecoverable (Atienza et al).

![Figure 2. Sorption-Desorption Isotherms of Imazamethabenz.](image-url)
Table 1. Sorption-Desorption Isotherm parameters.

<table>
<thead>
<tr>
<th></th>
<th>Linear $S=K_d C$</th>
<th>Freundlich $S=K_f C^n$</th>
<th>Langmuir $S=q_s K_f C/(1+K_f C)$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$K_d$</td>
<td>$r^2$</td>
<td>$K_f$</td>
</tr>
<tr>
<td>Ads.</td>
<td>0.402</td>
<td>0.996</td>
<td>0.821</td>
</tr>
<tr>
<td>Des.</td>
<td>0.947</td>
<td>0.302</td>
<td>0.997</td>
</tr>
<tr>
<td></td>
<td>2.273</td>
<td>0.122</td>
<td>0.887</td>
</tr>
<tr>
<td></td>
<td>4.582</td>
<td>0.122</td>
<td>0.943</td>
</tr>
</tbody>
</table>

A bicontinuum model based on first-order mass transfer was used to analyze the results of the column experiments. The various models available for simulating nonequilibrium sorption are reviewed elsewhere (Brusseau & Rao; Brusseau). The following equations were used to describe the transport of solutes during steady water flow in soil (Van Genuchten & Wierenga, Nkedi-Kizza et al.):

\[
\beta R \frac{\partial C_I}{\partial T} + (1-\beta)R \frac{\partial C_{II}}{\partial T} = \frac{1}{P} \frac{\partial^2 C_I}{\partial Z^2} - \frac{\partial C_I}{\partial Z}
\]

(1)

\[
(1-\beta)R \frac{\partial C_{II}}{\partial T} = w(C_I - C_{II})
\]

(2)

Where: $C_I=C_m/C_o$, $C_{II}=C_{im}/C_o$, $R=1+(\rho K_d/\theta_m)$, $P=V_m/L/D_m$, $w=\alpha L/q$, $q=\theta_m V_m$, $\beta=(\theta_m+\rho K_d)/(\theta+\rho K_d)$, $Z=x/L$, $T=V_m/Lt$. $C_m$ and $C_{im}$ are the solute average concentration in mobile and immobile liquid regions (ML⁻³), $C_o$ is the concentration of the influent solution (ML⁻³), $x$ is the distance (L), $t$ is the time (t), $L$ is the column length (L), $D_m$ is the apparent dispersion coefficient of mobile region (L²t⁻¹), $V_m$ is the pore-water velocity (averaged in mobile region) (Lt⁻¹), $\alpha$ is a first order mass transfer coefficient (t⁻¹), $K_d$ is the linear equation sorption constant, $f$ is the fraction of sorption sites in the mobile region, $\theta_m$ is the volumetric water content in mobile region, $\theta$ is the volumetric water content, and $\rho$ is the soil bulk density (ML⁻³).

Numerical solution of the transport equations was obtained using the Crank-Nicolson scheme (Press et al.). The following boundary conditions were used:

\[
-D_m \left( \frac{\partial C_I}{\partial Z} \right) + V_m C_I \bigg|_{Z=0} = V_m C_0(t)
\]

(3)

\[
\frac{\partial C_I}{\partial Z} \bigg|_{Z=1} = 0
\]

(4)

A more detailed description of the boundary conditions can be found in De...
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Smedt & Wierenga and Kreft & Zuber. Figure 3 shows the breakthrough curves (BTCs) for the non sorbed tracer and Imz at 1 ml/min. Table 2 shows the complete set of values of main parameters after fitting BTCs using a Levenberg-Marquardt algorithm (Press et al.).

The parameter R was fixed to a value of 1, neglecting possible effects of anion exclusion when fitting the BTCs of PFB. If the hydrodynamic dispersion is the major component of the apparent dispersion, P must be the same value for two different solutes (under the same hydrodynamic conditions). Thus, the value of P obtained for PFB was used in the experiments for the Imz BTCs. Finally, the value of β was estimated using the fourth approach of Nkedi-Kizza et al. Thus, only w was fitted. Additionally, the value for R obtained from Imz batch experiments (initially kept constant) must be taken as a fitting parameter. These discrepancies between batch and column experiments are probably due to a different soil/solution ratio. Further experiments using a soil/solution ratio 2/1 presented a value for K_d=0.2, which implies an estimated R= 1.4, close to those shown in Table 2. The same effect was reported by Koskinen & Cheng among others.

Table 2. Results after fitting for the main model parameters. PFB: 12 μg/g. Imz: 5 μg/g. (ρ=1.1 g/cm³, θ=0.62).

<table>
<thead>
<tr>
<th>Solute</th>
<th>l/min.</th>
<th>R</th>
<th>P</th>
<th>β</th>
<th>w</th>
<th>SSQ.</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFB</td>
<td>1.0</td>
<td>1.00</td>
<td>25.8</td>
<td>0.84</td>
<td>0.50</td>
<td>1.9·10⁻⁵</td>
</tr>
<tr>
<td>Imz</td>
<td>1.0</td>
<td>1.31</td>
<td>25.8</td>
<td>0.84</td>
<td>0.33</td>
<td>1.4·10⁻⁴</td>
</tr>
<tr>
<td>PFB</td>
<td>2.0</td>
<td>1.00</td>
<td>34.0</td>
<td>0.83</td>
<td>0.41</td>
<td>1.3·10⁻⁵</td>
</tr>
<tr>
<td>Imz</td>
<td>2.0</td>
<td>1.28</td>
<td>34.0</td>
<td>0.83</td>
<td>0.35</td>
<td>8.0·10⁻⁵</td>
</tr>
<tr>
<td>PFB</td>
<td>3.0</td>
<td>1.00</td>
<td>36.2</td>
<td>0.84</td>
<td>0.47</td>
<td>6.4·10⁻⁶</td>
</tr>
<tr>
<td>Imz</td>
<td>3.0</td>
<td>1.30</td>
<td>36.2</td>
<td>0.84</td>
<td>0.30</td>
<td>4.9·10⁻⁵</td>
</tr>
</tbody>
</table>

Nonequilibrium was present in the experiments performed with Imz and also with PFB, which supports the hypothesis of a transport-related nonequilibrium represented with a two-region model. Nevertheless, the sum of squared residuals (SSQ) values were higher for Imz, probably due to the existence of other nonequilibrium mechanisms. In fact, a major constraint associated with bicontinuum models is the assumption that a single process is responsible for the observed nonequilibrium. Based on the data on Table 2, it appears that the range of pore water velocity is not greater enough to observe variations of β with V_m.
4 Conclusions

Kinetic experiments carried out in this work suggest either the existence of two sorption mechanisms or different resistances. Besides, it might be concluded that a time of 24 h is needed to reach pseudo-equilibrium. The data presented in Figure 2 show that adsorption conforms well with the isotherm linearity. Nevertheless, a marked hysteresis effect is present in the desorption studies. The desorption isotherms are highly nonlinear. Real hysteresis effect can be important in predicting Imazamethabenz behaviour in soil-water environment in contrast to predictions based only on the $K_d$ parameters of adsorption isotherms, which would yield important overestimations. More detailed descriptions about the importance of using both adsorption and desorption parameters are shown in Van Genuchten & Cleary.

Miscible displacement experiments suggest a transport-related nonequilibrium, even when the hypothesis of a minor contribution of sorption-related nonequilibrium is supported by the differences in SSQ of the sorbed and non-sorbed chemicals. A practical consequence of nonequilibrium during solute transport is a compound mobility higher than that predicted by local equilibrium models. Hence, an early contaminant arrival at the monitoring points will be observed. On the other hand, desorption processes will take longer than that predicted using approximations based on $K_d$ adsorption values.

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References