Sorption of pyrazosulfuron-ethyl by soils of different agro-climatic zones of Southern Karnataka

D.V. NAVEEN, R. C. GOWDA, T. H. HANUMANTHARAJU AND T. BHAGYALAKSHMI

Introduction

The fate of an herbicide applied to the soil is governed to a large extent by its adsorption on soil constituents, desorption of adsorbed herbicides, its persistence and degradation. Soil sorption study of a pesticide, can generate useful information regarding its fate in soil and provide a basis for its effective use in the field to reduce undesirable effects due to carry over, contamination and phytotoxicity. A survey literature (Calvet, 1980; Guenzi, 1974; Hamaker, 1972; Khan, 1980) show that much less attention has been paid to desorption compared to adsorption. Plant uptake, bio-efficacy and transport mainly depend on sorption equilibrium. pyrazosulfuron-ethyl is a highly active sulfonyleurea herbicide and is mainly registered for use in paddy fields. This chemical is available in commercial names of Sathi, Agreen, Sirius, Act, Spark, Star and Billy. This herbicide has become more popular due to its high activity at low application rates and low mammalian toxicity. Although pyrazosulfuron-ethyl would appear to be degraded rapidly in soils like other sulfonyleureas (Kim et al 2003a and 2003b; Mikada et al 1996). Pyrazosulfuron-ethyl herbicide application in soil leads to various reaction in

MEMBERS OF RESEARCH FORUM:

Corresponding author:
D.V. NAVEEN, Department of Soil Science and Agricultural Chemistry, College of Agriculture, University of Agricultural Science, G.K.V.K., BENGALURU (KARNATAKA) INDIA
Email: dvnaveena@gmail.com

Co-authors:
R.C. GOWDA,
T. H. HANUMANTHARAJU AND T. BHAGYALAKSHMI, Department of Soil Science and Agricultural Chemistry, College of Agriculture, University of Agricultural Science, G.K.V.K., BENGALURU (KARNATAKA) INDIA

Summary

Sorption studies were conducted with pyrazosulfuron-ethyl using batch equilibration technique and HPLC analysis. Four different paddy growing soils of Kathalagere, Mandya, Mudigere and Mangalore soil of Southern transitional zone, Southern dry zone, Hill zone and Coastal zone of Southern Karnataka were used in the study with a pH of 7.3, 6.9, 6.1 and 5.8 and organic matter (g kg⁻¹) of 12.9, 10.9, 6.4 and 10.4, respectively. The sorption isotherm (n) values were 0.104, 0.101, 0.085 and 0.165 for Kathalagere, Mandya, Mudigere and Mangalore soils, respectively. The sorption isotherm for pyrazosulfuron-ethyl was non-linear in all soils, as explained by the Freundlich equation (n < 1.0), indicating differential distribution of site energies for sorption. In general adsorption isotherms fitted well with Freundlich equation (r² > 0.96), and Freundlich constants ‘K’, ‘Koc’ and ‘Kc’ values were in the range from 5.45 to 9.52, 1099.46 to 1436.12 and 32.24 to 49.07 in different soils and described in the order of Kathalagere > Mandya > Mudigere > Mangalore, which is also in the order of decreasing organic matter content in the soils. The coefficient of determination showed an improvement up to 96 per cent using quadratic functions, suggesting a better goodness of fit in preceding pyrazosulfuron-ethyl sorption compared to the linearised form of the Freundlich equation. The cumulative desorption of five days of pyrazosulfuron-ethyl in these soils were determined and it ranged from 22.3 to 41.1 mg kg⁻¹ in Kathalagere soil, 25.6 to 49.4 mg kg⁻¹ in Mandya soil, 37.1 to 51.9 mg kg⁻¹ in Mudigere soil and 39.9 to 55.7 mg kg⁻¹ in Mangalore soil. The desorption was also in decreasing order of Mangalore > Mudigere > Mandya > Kathalagere soils. The sorption of pyrazosulfuron-ethyl increased with increasing organic matter content and was significantly correlated with organic matter content of the soils where as clay content did not greatly affect the sorption as indicated by low regression coefficient.

Key words: Pyrazosulfuron-ethyl, Sorption, Freundlich equation, HPLC

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soils and environment, which determine the toxicity and persistence in the soil and plants. The breakdown of pyrazosulfuron-ethyl is largely depends on soil temperature, moisture content, organic matter and pH. The chemical will degrade faster under acidic condition, and soil with higher moisture content at higher temperature. The objective of the present investigation was to examine the sportive behavior of pyrazosulfuron-ethyl in soils of different agro-climatic zones of Karnataka.

**Resources and Research Methods**

Experiments were conducted at the University of Agricultural Sciences Bengaluru, with 4 soils from different agro-climatic zones of Karnataka. Representative soils were collected from the Ap horizon (0-15 cm) with no history of pyrazosulfuron-ethyl application. Soils were air-dried and pass through 2 mm sieve. The physical and chemical properties of these soils were analyzed by using standard methods and the results are presented in Table A.

Technical grade pyrazosulfuron-ethyl (99.7% purity) obtained from M/s SIGMA-ALDRICH LABORCHEMI KALIEN GMBH was used for present study. Sorption to determine was conducted using batch equilibration technique (Raman et al., 1988).

Adsorption was studied by equilibrating 5 g 0.2 mm sieved soil with 20 ml of aqueous solution containing herbicide concentrations of 0 to 50 mg L\(^{-1}\) of pyrazosulfuron-ethyl in 0.01 M CaCl\(_2\) for 24 hrs at 28°C and centrifuged at 10,000 rpm for 15 minutes. Corresponding blanks without pyrazosulfuron-ethyl were also equilibrated. The equilibrium concentration of pyrazosulfuron-ethyl was determined by HPLC method.

For studying desorption, batch equilibration technique was followed by replacing 5 ml of the supernatant again with 0.01 M CaCl\(_2\) after removing 5 ml for the adsorption study, 5 ml of 0.01 M CaCl\(_2\) was added to the same centrifuge tubes to make volume 20 ml., the soils suspension was equilibrated again for 24 hrs as described above and centrifuged. The process of withdrawal of 5 ml of supernatant for measuring the herbicide concentration and replacing 5 ml of 0.01 M CaCl\(_2\) solutions for re-equilibration and was repeated for five times.

Adsorption isotherms were constructed using the best-fit regression equations. Freundlich constants \(K\) and \(1/n\) were calculated from the equation.

\[
\frac{X}{m} = K_c \frac{1}{n} \tag{1}
\]
\[
\log \frac{X}{m} = \log K + \frac{1}{n} \log C_e \tag{2}
\]

where,

- \(X/m\) = quantity of herbicide adsorbed per unit weight of soil
- \(C_e\) = Equilibrium concentration
- \(K\) = Freundlich constant
- \(1/n\) = Slope

\(K\) is an indicator of relative adsorption affinity among herbicides at unit concentration and \(1/n\) indicates relative linearity between adsorption and concentration of herbicides. The adsorption varies with a number of soil properties, with soil organic carbon content being apparently the single best predictor of the sorption co-efficient. The sorption co-efficient of pesticide when normalized with respect to soil organic carbon (OC) contents essentially independent of soil type and hence normalized sorption co-efficient (\(K_{oc}\)) was calculated as:

\[
K_{oc} = \frac{K}{\% OC} \times 100 \tag{3}
\]

\[
K_{clay} = \frac{K}{\% clay} \times 100 \tag{4}
\]

where,

- \(K\) is Freundlich constant and \(\% OC\) is the percent organic carbon content of soil.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Kathalagere</th>
<th>Mandya</th>
<th>Mudigere</th>
<th>Mangalore</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Particle size distribution</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sand (%)</td>
<td>70.3</td>
<td>65.3</td>
<td>75.4</td>
<td>70.6</td>
</tr>
<tr>
<td>Silt (%)</td>
<td>10.3</td>
<td>13.8</td>
<td>5.0</td>
<td>12.5</td>
</tr>
<tr>
<td>Clay (%)</td>
<td>19.4</td>
<td>20.9</td>
<td>19.6</td>
<td>16.9</td>
</tr>
<tr>
<td>Textural class</td>
<td>Sandy clay loam</td>
<td>Sandy clay loam</td>
<td>Sandy clay</td>
<td>Loamy sand</td>
</tr>
<tr>
<td>Taxonomic class</td>
<td>Chromic hplusterts</td>
<td>Typic utropepts</td>
<td>Ustic hplusterts</td>
<td>Chromic hplusterts</td>
</tr>
<tr>
<td><strong>pH (1:2.5 soil and water)</strong></td>
<td>7.3</td>
<td>6.9</td>
<td>6.1</td>
<td>5.8</td>
</tr>
<tr>
<td><strong>EC (dS m(^{-1})</strong></td>
<td>0.03</td>
<td>0.46</td>
<td>0.05</td>
<td>0.13</td>
</tr>
<tr>
<td><strong>Organic matter (g kg(^{-1})</strong></td>
<td>12.9</td>
<td>10.9</td>
<td>6.1</td>
<td>10.4</td>
</tr>
<tr>
<td><strong>CEC (c mol Kg(^{-1})</strong></td>
<td>24.7</td>
<td>18.3</td>
<td>12.1</td>
<td>10.6</td>
</tr>
</tbody>
</table>
Research Findings and Discussion

Adsorption–desorption isotherms for the soils are presented in Fig 1. Adsorption isotherms were generally S-shaped with a slight concavity in the initial stage of adsorption. This is a common feature for adsorption of organic chemicals in soils with low organic matter or clays (Weber et al., 1986; Raman and Rao, 1987; Raman and Rao, 1984). The reason seems to be the hydro-phylic nature of the surface of soils, for which water molecules compete with the pesticide, till a certain level of adsorbed pesticide build up. The biological efficacy of pesticides applied to soil is largely governed by the processes of adsorption which not only affect the movement of added compounds, but also regulate their availability to the weeds as there decomposition. Adsorption–desorption phenomena occupies central position in controlling the distribution of herbicides in soils, which controls the quantity of herbicides in soil solution and thus determine its biological activity, mobility in soil water and volatility. Inorganic and organic surfaces make up the soil adsorption complex (Calvet, 1980).

The adsorption of pyrazosulfuron-ethyl in different soils are in the decreasing order of Kathalagere > Mandya > Mudigere > Mangalore, which is also the order for organic carbon in these soils. Hence, higher adsorption of pyrazosulfuron-ethyl in Kathalagere soil was mainly due to higher organic carbon content than Mandya and Mangalore soils. Where as in Mudigere soil even though the organic carbon content is lower than Kathalagere soil, the adsorption of pyrazosulfuron-ethyl is low due to low pH value. This positive effect of organic matter on the adsorption of organic chemicals has been well established by Zhang and Wang (2007) and Mikata et al. (2000).

The values for 1/n (slope) were < 1.0 and indicate a non linear relationship between herbicide concentration and adsorption and can be characterized as L type of adsorption isotherm. The L shaped isotherms signifies that the soil has a high affinity for the applied herbicides. The adsorption occurred in a planar configuration and bonding was multifunctional (Schnitzer, 1978).

The Freundlich equation provided a good fit ($r^2 > 0.96$) to the adsorption data in all the four soils studied (Table 1). Adsorption of most of the sulfonylurea herbicides is better described by Freundlich equation than by Langmuir equation. The Freundlich equation is empirical and imposes no limits on adsorption and shows maximum adsorption when a monolayer covers all surfaces. The Freundlich equation relates adsorbed and solution phase concentration at equilibrium.

The Freundlich constant K values ranges from 5.45 to 9.52 and found an increase with the increase in the organic matter content. The K values followed the order of Kathalagere > Mandya > Mudigere > Mangalore soils and is in the decreasing order of organic carbon content of the soil. A significant positive correlation ($r^2 = 0.96$) between Freundlich constant K and organic carbon content of soil indicated and played a major role in pyrazosulfuron-ethyl adsorption. Hence, the absolute quantity of pyrazosulfuron-ethyl adsorbed by unit quantity of organic carbon content of soil was calculated. The sorption coefficient Koc is commonly a measure of pesticide sorption to soil organic carbon. Association with soil organic matter is commonly assumed to be a major mechanism of pesticide sorption in soils. Pyrazosulfuron-ethyl, a member of sulfonylurea group also exhibits high affinity towards the organic phase. The Koc values ranged from 1099.46 to 1436.12 for all the soils. Though the absolute quantity of pyrazosulfuron-ethyl adsorbed per unit of soil was the highest in Kathalagere soil, the contribution towards adsorption per unit of organic carbon is less as observed by the lowest Koc values among the soils. This may be due to higher organic matter–clay interaction and subsequent stabilization of organic matter, thereby, reducing the number of adsorption sites on the native organic fraction.

The per cent cumulative desorption was found to increase with increase in the initial concentration in all the soils given in Table 2, however, the desorption of pyrazosulfuron-ethyl in soils decreased in the order of Mudigere > Mangalore > Mandya > Kathalagere which is also in the increasing order for organic carbon content of the soils.

![Fig. 1: Adsorption of pyrazosulfuron-ethyl on Kathalagere, Mandya, Mudigere and Mangalore soils](image_url)

**Table 1:** Freundlich constants (K and 1/n), determination coefficients ($r^2$) and sorption for pyrazosulfuron-ethyl adsorption in different agro-climatic soils of Southern Karnataka

<table>
<thead>
<tr>
<th>Soils</th>
<th>K</th>
<th>1/n</th>
<th>$r^2$</th>
<th>$K_{oc}$</th>
<th>$K_e$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mudigere</td>
<td>8.05</td>
<td>0.085</td>
<td>0.968</td>
<td>1238.46</td>
<td>43.31</td>
</tr>
<tr>
<td>Kathalagere</td>
<td>9.52</td>
<td>0.101</td>
<td>0.981</td>
<td>1436.12</td>
<td>49.07</td>
</tr>
<tr>
<td>Mandya</td>
<td>8.79</td>
<td>0.101</td>
<td>0.981</td>
<td>1389.41</td>
<td>42.05</td>
</tr>
<tr>
<td>Mangalore</td>
<td>5.45</td>
<td>0.165</td>
<td>0.969</td>
<td>1099.46</td>
<td>32.24</td>
</tr>
</tbody>
</table>
soil. This shows that there is an increase in adsorption with lesser per cent desorption when related to the organic matter content of the soils.

Decrease in the amount of herbicide desorbed from the soil in comparison to that adsorbed, and with successive desorption steps, are referred to as the hysteresis effect (Braverman et al., 1990). The desorption process exhibited pronounced hysteresis in all the soils and for every level of initially adsorbed pyrazosulfuron-ethyl which was subjected to desorption. This is evident from the desorption isotherms corresponding to each initial pyrazosulfuron-ethyl concentration. The hysteresis was more pronounced when the desorption was carried out from higher levels of adsorbed pyrazosulfuron-ethyl. Thus, when the adsorption was carried out from soils where in only 5 to 11 mg kg\(^{-1}\) of pyrazosulfuron ethyl was present, the desorption isotherms were very close to the adsorption isotherms. This shows that the degree of irreversibility in the adsorption process increases with increase in sorbed pyrazosulfuron-ethyl. Similar features were also observed by Mikata et al. (2000).

The main cause of hysteresis during desorption is the presence of a number of heterogeneous adsorbing sites of varying energy levels on soils. In addition to this, modifications will take place in the soil itself during the adsorption-desorption process (Calvet, 1980). Thus, the desorption methodology itself imposes an inbuilt lacuna and the adsorption-desorption data are obtained under continuously changing conditions like surface area, aggregate size and texture of the soil. Also, as pointed out by Sabadie and Alcoholysis (2008) and Youbin et al. (2004) sometimes, biochemical or chemical degradation can also destroy adsorption-desorption isotherms and result in effects apparently but not truly due to hysteresis. However, the exact causes of this effect are still under dispute (Braverman et al., 1990).

### Table 2: Cumulative per cent desorption of pyrazosulfuron-ethyl (mg kg\(^{-1}\)) in soils of different agro-climatic soils of Southern Karnataka

<table>
<thead>
<tr>
<th>Initial concentration (mg kg(^{-1}))</th>
<th>Mandya</th>
<th>Mudigere</th>
<th>Mangalore</th>
<th>Kathalagere</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>49.4</td>
<td>51.9</td>
<td>55.7</td>
<td>41.1</td>
</tr>
<tr>
<td>20</td>
<td>43.9</td>
<td>42.9</td>
<td>38.1</td>
<td>40.4</td>
</tr>
<tr>
<td>30</td>
<td>40.6</td>
<td>36.9</td>
<td>39.3</td>
<td>38.6</td>
</tr>
<tr>
<td>40</td>
<td>37.6</td>
<td>38.6</td>
<td>38.1</td>
<td>35.6</td>
</tr>
<tr>
<td>50</td>
<td>25.6</td>
<td>37.1</td>
<td>39.9</td>
<td>22.3</td>
</tr>
</tbody>
</table>

### Literature Cited


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