

## ADSORPTION OF ATRAZINE ON SELECTED VERTISOLS AND ALFISOLS

K.V. Naga Madhuri<sup>1</sup>, P. Chandrasekhar Rao<sup>2</sup>, M. Subba Rao<sup>1</sup>, T. Prathima<sup>3</sup>,  
K. Vijay Krishna Kumar<sup>3</sup>, B. Ravindra Reddy<sup>3</sup> and V. Giridhar<sup>1</sup>

<sup>1</sup>Agricultural Research Station, Perumallapalle, <sup>2</sup> College of Agriculture, Rajendranagar, <sup>3</sup>Regional  
Agricultural Research Station, Tirupati.

Acharya N.G. Ranga Agricultural University, Rajendranagar, Hyderabad – 500 030, India

**ABSTRACT:** Adsorption of atrazine was studied on two Vertisols and two Alfisols varying in their physico-chemical properties. Soils were equilibrated with various concentrations of atrazine using batch techniques. Adsorption affinity for atrazine was approximated by Freundlich constant ( $K_f$ ), which is a measure of the strength or degree of adsorption.  $K_d$  values were calculated for atrazine despite some non-linearity in adsorption on both Vertisols and Alfisols. The  $K_d$  values are greater for Vertisols than Alfisols and increased with organic carbon content. Correlations were worked out between extent of adsorption and soil properties and were positively correlated with organic carbon ( $r = 0.688$ ), clay content ( $r = 0.712$ ) and clay + organic carbon ( $r = 0.708$ ).  $K_{oc}$  values were calculated taking into account the organic carbon content for both Vertisols and Alfisols.

**Keywords:** Atrazine, Vertisols, Alfisols

## INTRODUCTION

Pesticides and other organic chemicals in soils are subject to adsorption by soil constituents especially, the organic and mineral fractions. The extent of adsorption of organic chemicals determines its bioactivity and fate in the environment. Other dissipation modes such as microbial and chemical degradation, plant uptake and leaching are affected by the adsorption process. Atrazine is used for selective weed control in a variety of crops. Many factors influence the atrazine adsorption: soil pH (Kalouskova, 1989; Wang *et al.*, 1992; Weber, 1993); soil organic matter (Laird *et al.*, 1994); particle size (Huang *et al.*, 1984); clay minerals (Gilchrist *et al.*, 1993; Barriuso *et al.*, 1994); soil temperature (Hassett and Banwart, 1989); soil moisture content (Pignatello *et al.*, 1993). Clay minerals have a higher retention capacity for atrazine than sand (Huang *et al.*, 1980). Gilchrist *et al.* (1993) found that the adsorption capacity of clays for atrazine followed the order of Montmorillonite > Illite > Kaolinite. Brouwer *et al.* (1990) observed a logarithmic increase of atrazine distribution coefficient ( $K_d$ ) with organic matter content. They also found that pH was a better indicator of atrazine adsorption in soils with low organic matter content than organic carbon. Soil temperature effects the rate of diffusion and adsorption of chemicals in soils. Diffusion coefficients for many triazines decreased when temperature was lowered from 25°C to 5°C, resulting in decreased adsorption (Lavy, 1970).

The purpose of this research was to compare the adsorption characteristics of atrazine under laboratory conditions on two different types of soils i.e. Vertisols and Alfisols which vary in their properties.

## MATERIALS AND METHODS

Two soils from Vertisol and two soils from Alfisol with different physico-chemical and chemical properties were collected and utilized for the study. The physico-chemical properties were presented in the Table 1. Atrazine of analytical grade (> 95 % Purity) was obtained from M/S Rallis India Ltd. The soils were air dried, passed through 2 mm sieve and used for the study.

Adsorption studies were carried out for two Vertisols ( $V_1$  &  $V_2$ ) and two Alfisols ( $A_1$  &  $A_2$ ). Five grams of 2 mm sieved soils were equilibrated with 20 mL of atrazine solution of various concentrations ranging from 0 to 50  $\mu\text{g mL}^{-1}$  at  $27 \pm 2^\circ\text{C}$  for 24 hrs with intermittent shaking.

Ionic strength was maintained at 0.01M  $\text{CaCl}_2$ . After 24 hours, the slurry was centrifuged at 4000 rpm for 15 minutes. Identical soil blanks minus the herbicide were maintained. The absorbance for each treatment and the corresponding blank were measured at 221 nm. The difference was taken as the actual equilibrium for which the concentration was calculated with reference to the calibration curve. The amount of herbicide adsorbed per gram of soil was calculated from the difference in the initial and equilibrium concentration as follows:

$$q = \frac{(C_1 - C_2) V}{\text{soil mass}}$$

where, q is the amount adsorbed in  $\mu\text{g g}^{-1}$  soil,  $C_1$  = initial concentration in  $\mu\text{g mL}^{-1}$ ,  $C_2$  = equilibrium concentration in  $\mu\text{g mL}^{-1}$ , V = volume of solution added in mL, and soil mass is on an air dry basis in grams. Sorption isotherms for atrazine were described quantitatively by the Freundlich equation.

$$\frac{x}{m} = K_f C^{1/n}$$

Where, x/m is the amount of adsorbate per unit mass of adsorbent (soil),  $K_f$  is the Freundlich coefficient, 1/n is the Freundlich exponent and C is the equilibrium concentration. Values for  $K_f$  and 1/n were estimated by linear regression after log-log transformation. Atrazine adsorbed by soils after equilibration was plotted following the linearized form of Freundlich equation.

## RESULTS AND DISCUSSION

**Soil properties:** Soil properties of selected Vertisols and Alfisols relevant to adsorption processes are shown in the Table 1. For both Vertisols and Alfisols the pH was close to neutral. Organic carbon is high in Vertisols (V1 & V2) and whereas it is low in Alfisols (A1 & A2). Similarly the clay levels are low in Alfisols when compared to Vertisols.

### Adsorption of atrazine

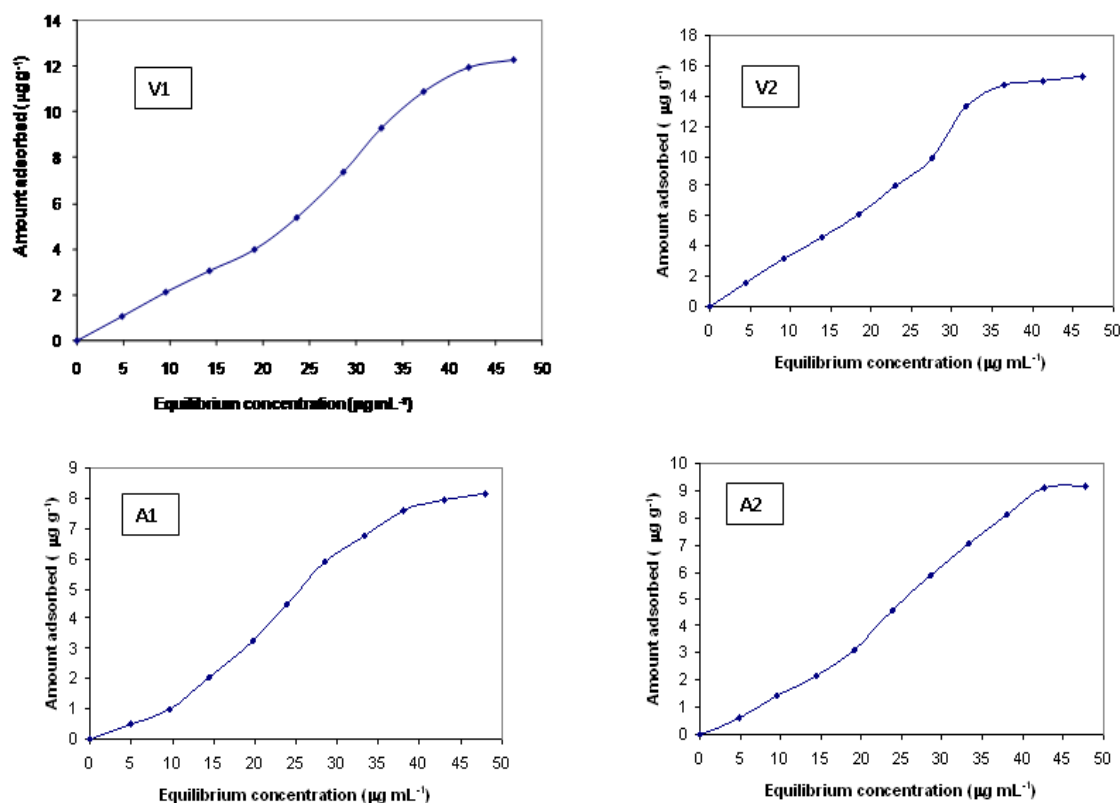
The atrazine adsorption data were evaluated quantitatively by the Freundlich equation and isotherms for Vertisols and Alfisols are presented in figures 1-4. The adsorption isotherms were mainly parabolic in nature with S-shaped character, a common feature of the adsorption of most neutral organic, chemicals on soil. The tendency for S-shaped character indicates a stronger initial competition of water molecules to the adsorbent as compared to the herbicide. The S-shaped isotherm, thus, reflect the initial resistance to the adsorption of herbicide to be overcome later by the cooperative effect of adsorbing molecules. The Freundlich parameters  $K_f$  obtained as an intercept and 1/n the slope of the isotherm were calculated as explained under materials and methods. The values of  $K_f$  and 1/n for adsorption of atrazine on Vertisols and Alfisols are presented in Table 2.

**Table 1 : Physico-chemical properties of selected soils**

| S.No.                                  | pH   | EC<br>(dS m <sup>-1</sup> ) | organic<br>carbon<br>(g Kg <sup>-1</sup> ) | Mechanical composition |             |          | Texture            |
|----------------------------------------|------|-----------------------------|--------------------------------------------|------------------------|-------------|----------|--------------------|
|                                        |      |                             |                                            | Sand (%)               | Silt<br>(%) | Clay (%) |                    |
| V1 (College form<br>ANGRAU, Hyderabad) | 7.32 | 0.61                        | 0.53                                       | 30.0                   | 41.8        | 28.2     | Silty clay<br>loam |
| V2(ICRISAT,<br>Hyderabad)              | 6.99 | 1.44                        | 1.17                                       | 18.8                   | 46.2        | 35.0     | Silty clay<br>loam |
| A1 (College form<br>ANGRAU, Hyderabad) | 7.03 | 0.19                        | 0.09                                       | 69.4                   | 18.6        | 12.3     | Loamy sand         |
| A2 (ICRISAT,<br>Hyderabad)             | 6.67 | 0.53                        | 0.37                                       | 75.6                   | 6.2         | 18.2     | Loamy sand         |

**Table 2 :  $K_f$ , 1/n,  $K_d$  and  $K_{oc}$  values for Vertisols and Alfisols**

| Soil | Organic carbon<br>(g kg <sup>-1</sup> ) | $K_f$ | $\frac{1}{n}$ | $K_d$ | $K_{oc}$ |
|------|-----------------------------------------|-------|---------------|-------|----------|
| V1   | 0.53                                    | 0.14  | 0.75          | 0.21  | 39.62    |
| V2   | 1.17                                    | 0.51  | 0.83          | 0.33  | 28.21    |
| A1   | 0.09                                    | 0.03  | 0.62          | 0.16  | 177.1    |
| A2   | 0.37                                    | 0.22  | 0.65          | 0.23  | 62.16    |



**Fig. 1-4 : Adsorption isotherms of atrazine on selected Vertisols and Alfisols**

The Freundlich constant  $K_f$  is a measure of the strength or degree of adsorption.  $K_f$  values for Vertisols are 0.14 (V1), 0.51 (V2) and for Alfisols are 0.03 (A1) and 0.22 (A2). The Freundlich parameter,  $1/n$  is a measure of the non-linearity of the adsorption isotherm. If  $1/n$  is not different from 1, then the relationship between  $q$  and  $c$  is linear and  $K_d$  would be a more appropriate means of representing the data. The values for  $1/n$  (Table 2) are similar to those reported by Shalali (1986), Sonon and Schwab (1995) and suggest that the atrazine adsorption in both Vertisols and Alfisols is truly non-linear. Because  $1/n$  was less than 1 in these soils, the fraction of atrazine adsorbed decreased with increasing equilibrium concentration.

Several mechanisms can be responsible for non – linear adsorption. One is a decrease in available sites as adsorption increases. This is especially true in soils low in effective surface area and organic matter content. Another factor that affects the fraction of herbicide adsorbed in the type of adsorption sites (Sonon and Schwab, 1995).

To compare  $K_f$  values, the  $1/n$  values or slopes need to be statistically equivalent (other wise comparison will be meaning less). This fact, combined with the generally linear adsorption isotherms, suggests that the proper comparison for atrazine adsorption is through the  $K_d$ .

Therefore,  $K_d$  values were calculated for atrazine despite some non – linearity in adsorption on both Vertisols and Alfisols. The adsorption distribution coefficient ( $K_d$ ) defined as  $(x/m) / C$ , where  $x$  is the amount of chemical adsorbed,  $m$  is the amount of adsorbent and  $C$  is the chemical concentration at equilibrium.

The linear adsorption distribution coefficient ( $K_d$ ) values (Table 2) are similar to other reported values (Clay and Koskinen, 1990 a, b; Ma *et al.*, 1993) and indicated that  $K_d$  values are greater for Vertisols than Alfisols.  $K_d$  values increase with organic carbon. Low adsorption in Alfisols could be a result of either low organic carbon or low clay content. Correlations were worked out between extent of adsorption and soil properties and were positively and significantly correlated with organic carbon ( $r = 0.688$ ), clay content ( $r = 0.712$ ) and clay + organic carbon ( $r = 0.708$ ). Similar results were reported by Graham and Conn (1992), Ma *et al.* (1993), Raman and Reddy (1993) and Rocha and Walker (1995).

Organic carbon content has been shown to be the first critical parameter positively and significantly correlated with adsorption of atrazine in soils (Moreau and Mouvet, 1997). Clay content of soils is said to be another critical parameter in the adsorption of atrazine soils and its role is often masked by that of organic matter and this can become a significant factor when organic carbon content decreases (Grundle and Small, 1993). In the present study, both the clay and organic carbon could contribute in adsorption of atrazine so the values were more for Vertisols than Alfisols.

Rao and Davidson (1980) suggested that the variability of  $K_d$  with soil properties can be normalized by taking into account the organic carbon fraction;  $K_{OC} = K_d/f_{oc}$ , where  $f_{oc}$  is the fraction of organic carbon in the soil. This relationship indicates that soil adsorption is linearly related to the amount of organic carbon in the soil. While  $K_d$  may vary greatly in different soils,  $K_{OC}$  often differs by less than a factor of 2-3. When organic carbon is low, however the variability in  $K_{OC}$  can be very high. The  $K_{OC}$  values are widely used to predict herbicide adsorption because for many non-ionic compounds including herbicides, organic carbon is the main soil component responsible for adsorption (Shea, 1989). The values are presented in Table 2. The Vertisol (V2) has relatively high organic carbon content and the atrazine would mostly be adsorbed to this fraction than the other soils. The  $K_{OC}$  values are similar to those reported by Mersie and Seybold (1996).

In summary, the magnitude of atrazine adsorption in this study was well described by both non-linear Freundlich model and linear  $K_d$  models. Results showed that the atrazine was more strongly and extensively adsorbed to the Vertisol which has more organic carbon and clay content. The Vertisol has higher adsorptive and retention capacity than Alfisol and  $K_d$  values are highly and significantly correlated with organic carbon and clay content in the both the soils.

## REFERENCES

- Barriuso, E., Laird, D. A., Koskinen, W. C. and Dowdy, R. H. (1994). Atrazine desorption from smectites. Soil Science Society of America Journal 58 : 1632-1638.
- Brouwer, W. W. M., Boesten, J. J. T. and Siegers, W. G. (1990). Adsorption of transformation products of atrazine by soil. Weed Research 30 : 123-128.
- Clay, S. A. and Koskinen, W. C. (1990a). Characterization of alachlor and atrazine desorption from soils. Weed Science 38 : 74-80.
- Gilchrist, G. F., Gamble, D. S., Kodama, H. and Khan, S. U. (1993). Atrazine interactions with clay minerals : Kinetics and equilibria of sorption. Journal of Agricultural Food Chemistry 41 : 1748-1755.
- Graham, J. S. and Conn, J. S. (1992). Sorption of metribuzin and metolachlor in Alaskan Subarctic agricultural soils. Weed Science 40 : 155-160.
- Grundle, T. and Small, G. (1993). Mineral contribution to atrazine and alachlor sorption in soil mixtures of variable organic carbon and clay contents. Journal of Contamination Hydrology 14 : 117-128.
- Hassett, J. J. and Banwart, W. L. (1989). The sorption of non polar organics by soils and sediments. In B.L. Sawhney and K. Brown (ed.) Reactions and movement of organic chemicals in soils. SSSA Srec. Publication 22. SSSA and ASA, Madison, WI, pp. 31-44.
- Huang, D. M., Grover, R. and Mckercher, R. B. (1984). Components and particle size fractions involved in atrazine adsorption by soils. Soil Science 138 : 20-24.
- Huang, D. M., Grover, R. and Mckercher, R. B. (1984). Components and particle size fractions involved in atrazine adsorption by soils. Soil Science 138 : 20-24.
- Kalouskova, N. (1989). Adsorption of atrazine on humic acids. Environmental Science Health 24 : 549-617.
- Laird, D. A., Yen, P. Y., Koskinen, W. C., Steinheimer, T. R. and Dowdy, R. H. (1994). Sorption of atrazine on soil clay components. Environmental Science Technology 28: 1054-1061.
- Lavy, T. (1970). Diffusion of three Chloro S-triazines in soil Weed Science 18 : 53-56.
- Ma, L., Southwick, L. M, Willis, G. H. and Selim, H. M. (1993). Hysteretic characteristics of atrazine adsorption - desorption by a Sharkey soil. Weed Science 41 : 627-633.

- Mersie, W. and Seybold, C. (1996). Adsorption and desorption of atrazine, deethylatrazine, deisopropylatrazine and hydroxyatrazine on levy wetland soil. *Journal of Agricultural Food Chemistry* 44 : 1925-1929.
- Moreau, C. and Mouvet, C. (1997). Sorption and desorption of atrazine, deethylatrazine, and hydroxyatrazine by soil and aquifer solids. *Journal of Environmental Quality* 26 : 416-424.
- Pignatello, J. J., Ferrandino, F. J. and Huang, L. Q. (1993). Elusion of aged and freshly added herbicides from a soil. *Environmental Science Technology* 27 : 1563-1571.
- Raman, S. and Reddy, D. S. (1993). The effect of soil solution ratio, pH, cations and organic matter on the adsorption of isoproturon. *Indian Journal of Agricultural Research* 27 : 131-136.
- Rao, P. S. C. and Davidson, J. M. (1980). Estimation of pesticides retention and transformation parameters required in non point source pollution models. In : M R overcosts and Davidson J M (ed) environmental import of non-point source pollution. Ann. Arbor. Science. Publ. Ann. Arbor, MI, pp. 23-67
- Rocha, F. and Walker, A. (1995). Simulation of the persistence of atrazine in soil at different sites in Portugal. *Weed Research* 35: 179-186.
- Shalali, M. K. (1986). Adsorption and persistence of atrazine on four soils of Hyderabad. M.Sc.(Ag.) thesis submitted to A.P. Agricultural University, Hyderabad.
- Sonon, S. L. and Schwab, P. A. (1995). Adsorption characteristics of atrazine and Alachlor in Kansas soils. *Weed Science* 43 : 461-466.
- Wang, Z., Gamble, D. S. and Langford, C. H. (1992). Interaction of atrazine with Laurentian soil. *Environmental Science Technology* 26 : 560-565.
- Weber, J. B. (1993). Ionization and sorption of fomesafen and atrazine by soils and soil constituents. *Pesticide Science* 39 : 31-38.