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# Sorption of atrazine and trifluralin in relation to the physio-chemical characteristics of selected soils

O. Francioso, E. Bak, N. Rossi and P. Sequi*

*Institute of Agricultural Chemistry, University of Bologna, Viale Berti Pichat 10, 40127 Bologna, Italy*

## ABSTRACT

The sorption of two types of herbicide, atrazine (6-chloro-$N^2$-ethyl-$N^4$- isopropyl-1,3,5-triazine-2,4-diamine) and trifluralin (α,α,α-trifluoro-2,6-dinitro-*N*,*N*-dipropyl- *p*-toluidine), was studied in four different soils representative of the intensively cultivated soils of the Po Valley (northern Italy). To study the effect of the organic matter content, experiments were carried out with one of the soils after the organic matter had been removed by a sodium hypochlorite treatment. The sorption ability for atrazine and trifluralin was decreased considerably when the soil with high organic matter content was treated with sodium hypochlorite; moreover, the sorption of trifluralin also seems to be influenced by the inorganic components of the soil. In comparison to atrazine, the sorption of trifluralin by the different soils was in all cases very high. Using increasing concentrations of herbicide the sorption coefficient ($K_d$) for each of the four soils was calculated together with the relative sorption constant ($K_{oc}$) based on the organic carbon content of the soil. The values of $K_f$ and $1/n$ in the Freundlich equation for atrazine and trifluralin adsorbed by the four soils were related to the characteristics of the soils.

*Key words:* atrazine; trifluralin; soil sorption coefficient ($K_d$); soil sorption constant ($K_{oc}$)

## INTRODUCTION

The behavior of herbicides in the different soil phases is influenced by many factors. Of particular importance is the sorption process, a process that depends mainly on (i) the chemical and physical characteristics of the active ingredient (AI), (ii) the active surface of the soil and (iii) the amount of herbicide applied. The soil sorption coefficient ($K_d$) and the soil sorption constant ($K_{oc}$), based on the organic carbon content of the soil, are the parameters expressing the mobility of these organic molecules in the soil and their distribution between the solid and liquid phases of the system.

*Present address: Research Institute for Plant Nutrition, Via della Navicella 2, 00184 Rome, Italy.

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The active surface of the soil, represented mainly by clay minerals and organic matter, adsorbs molecules with different physico-chemical characteristics in very specific and selective ways. In particular, it has been observed that in soils with high organic matter content, herbicides can be 'fixed' to a considerable extent and thus the mobility of the active ingredient in the aqueous phase is reduced. Different behavior is found when herbicides are applied to mineral soils with low organic matter content or to sandy soils with low adsorbing surfaces (Grover, 1974). In these cases, the molecules do not remain at the site of application and their mobility increases in other parts of the system, which, in turn, increases the risk of a negative impact on the environment.

The potential for adverse environmental effects may be minimized or foreseen when the physical and chemical properties of the herbicide as well as those of the soil are sufficiently well defined. Although much information has been obtained concerning the fate and distribution of agrochemicals in soil, there are still relatively few references regarding the behavior of herbicides in the intensively cultivated soils of the Po Valley (northern Italy). The present research was directed towards evaluating the sorption of two active ingredients, atrazine and trifluralin, by selected soils with different physico-chemical characteristics.

## MATERIALS AND METHODS

Atrazine (6-chloro-$N^2$-ethyl-$N^4$-isopropyl-1,3,5-triazine-2,4-diamine) molecular weight 216.06, vapor pressure 0.04 mPa (20°C), solubility in water 30 mg $l^{-1}$ (20°C), and $K_{ow}$ 219, is a weakly basic molecule with a $pK_a$ value of 1.7 (21°C).

Trifluralin ($\alpha,\alpha,\alpha$-trifluoro-2,6-dinitro-*N*,*N*-dipropyl-*p*-toluidine) molecular weight 335.2, vapor pressure 13.7 mPa (25°C), solubility in water < 1 mg $l^{-1}$ (27°C), and $K_{ow}$ 118 000, is a non-ionic molecule, highly photolabile, very volatile and highly soluble in organic solvents. The reactive groups of the trifluralin molecule are the two $NO_2$ nitrogroups and the long *n*-propyl chain.

Soils with different physico-chemical characteristics were used in these studies (Table 1). The four selected soils are typical of the intensively cultivated Po Valley region (northern Italy). Soil samples were air dried at room temperature and passed through a sieve (1-mm opening). To study the effect of the presence of the organic matter on the sorption of the two herbicides examined, further experiments were carried out with one of the soils after the organic matter had been removed by chemical treatments.

Treatment with sodium hypochlorite to destroy the organic matter of the soil was achieved using sodium hypochlorite following the procedure described by Lavkulich and Wiens (1970). With this procedure, the organic

matter is oxidized and the structure of the clay is not altered. Verification of the destruction of the organic matter was obtained via the determination of the total carbon content of the soil sample. In addition, X-ray diffraction analysis did not show any alteration of the primary structure of the clay. The soil samples were treated with hypochlorite at 90°C for 1 h (10 g of soil and 100 ml of 3 mol $l^{-1}$ sodium hypochlorite). The treatment with hypochlorite was repeated 5 times with removal of the liquid phase by centrifugation at 8000 × *g* for 30 min. Excess hypochlorite was removed by five washings with deionized water. At the end of the treatment, the soil was agitated overnight with a 1 $mol^{-1}$ l $CaCl_2$ solution to render it homoionic. The pH of the soil was measured and brought back to the original level with small additions of acetic acid.

Sorption tests for the two herbicides were carried out using the following procedure: 2 g of air dried soil were put into 10 ml centrifuge tubes and agitated for 24 h at 20 ± 2°C with 5 ml of 0.01 mol $l^{-1}$ $CaCl_2$ containing increasing amounts of active ingredient. The active ingredient was dissolved in EtOH and diluted with 0.01 mol $l^{-1}$ $CaCl_2$ solution in order to obtain the desired final concentrations. The concentrations of herbicide in the soil expressed as mg AI $kg^{-1}$ of soil were the following: 2.5, 12.5, 25, 50, 125, 200 and 250 for atrazine and 12.5, 25, 125, 250, 500, 750 and 1500 for trifluralin. After the 24-h equilibration period, the mixtures were centrifuged at 8000 × *g* for 15 min and the amount of herbicide adsorbed was determined by analyzing 2.5 ml of the supernatant obtained. The extent of adsorption was estimated as the difference between initial and final herbicide concentrations.

*Extraction and recovery of the active ingredients*

After the 24-h equilibration period and successive centrifugation, 2.5 ml of the supernatant liquid were transferred to 10-ml centrifuge tubes, 1.5 ml of 4% NaCl and 2 ml of *n*-hexane were added and the solution was agitated for 1 min until equilibrium was reached. The extraction was repeated 2-times with 2 ml of *n*-hexane. The organic phase was collected on anhydrous sodium sulfate, dried in a rotavapor at 35°C and the residue was collected with 1 ml of acetonitrile. Recovery tests of the active ingredients were carried out with solutions containing standards at various concentrations. The method of partition with *n*-hexane gave a recovery of 96% for atrazine and 99% for trifluralin. The tests were carried out in triplicate.

*Determination of the active ingredients*

The analytical determination of the active ingredients was carried out following the method proposed by Kanazawa (1989), using HPLC in the in-

verse phase with a UV detector. The instrumental conditions for the analysis of the active ingredients were as follows: (a) for atrazine, water-acetonitrile eluent (60:40 v/v), flow rate 1 ml $min^{-1}$, detection at 230 nm; (b) for trifluralin, water-acetonitrile eluent (20:80, v/v), flow rate 1 ml $min^{-1}$, detection at 274 nm. All samples were filtered with a 0.22 $\mu$m filter before analysis.

*Calculation of $K_d$ and $K_{oc}$*

The sorption coefficient ($K_d$) was calculated as the ratio between the amount of herbicide sorbed to the soil and the amount of herbicide in the water at equilibrium:

$K_d$ = (mg herbicide $kg^{-1}$ of soil)/ (mg herbicide $l^{-1}$ of water)

The sorption characteristics of a herbicide can be normalized to obtain a general soil sorption constant ($K_{oc}$) based on the organic carbon content (McCall et al., 1983):

$K_{oc}$ = ($K_d$ 100)/ (% of the organic carbon of the soil).

## RESULTS AND DISCUSSION

The physico-chemical characteristics of the soils used in these studies are reported in Table 1. For soils 1–3, the atrazine sorption patterns were very

TABLE 1

Physico-chemical characteristics of the soils examined

| Soil No.<br>Locality | Soil 1<br>Settefonti | Soil 2<br>Tolara | Soil 3<br>Zena | Soil 4<br>Brasimone | Soil 4′[a]<br>Brasimone |
|---|---|---|---|---|---|
| Clay (%) | 26 | 54 | 11 | 6 | 6 |
| Organic C (%) | 0.8 | 1.2 | 0.4 | 7.6 | tr |
| CEC [cmol(+)$kg^{-1}$] | 31 | 24 | 11 | 27 | 16 |
| pH | 7.4 | 7.8 | 8.0 | 4.4 | 4.6 |
| Total $CaCO_3$ (%) | 0.3 | 3.0 | 17 | N.D. | N.D. |
| Clay min. | *S, I, C* | *K, C, I, I/S* | *I, S* | *I, C* | *I, C* |
| Soil taxonomy | Typic | Typic | Calcixerollic | Typic | |
| Classification | Xerochrept | Pelloxerert | Xerochrept | Rendoll | |

[a]Soil 4′ is soil 4 after treatment with hypochlorite to remove the organic matter.
[b]*C* = chlorite, *I* = illite, *K* = kaolinite, *S* = smectite, *I/S* = intergrade.

similar and the amount of herbicides sorbed by these three soils was about 40% of the amount applied, while for soil 4 it was approximately 75%. When the organic matter was removed from the soil by the treatment with hypochlorite the sorption of the soil for atrazine decreased significantly: the quantity sorbed decreased from 75% to approximately 20% (soil 4 and soil 4′ in Fig. 1).

In comparison to atrazine, the sorption of trifluralin on the different soils in all cases was very high. The amount of trifluralin applied to the soils was almost completely sorbed and the concentration of the herbicides that remained in the solution after the equilibration period was very low (Lafleur, 1979). The removal of soil organic matter using hypochlorite did not cause a significant decrease in the sorption capacity of the soil for trifluralin (soil 4 and soil 4′ in Fig. 1). At the same time, the trifluralin sorption patterns were very similar for all the four soils (Fig. 1).

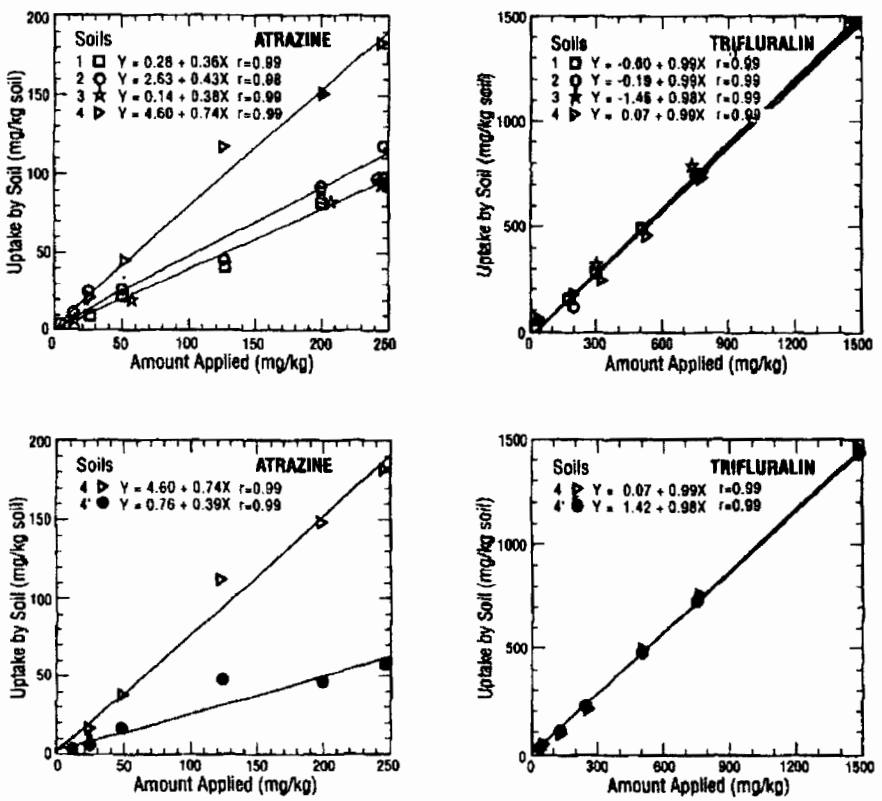


Fig. 1. Soil uptake of atrazine and trifluralin in relation to the amount applied (soil 4′ = soil 4 after treatment with sodium hypochlorite to remove the organic matter).

TABLE 2

Soil sorption coefficients ($K_d$) and soil sorption constants ($K_{oc}$) for atrazine and trifluralin

| Soil | Atrazine | | Trifluralin | |
|---|---|---|---|---|
| | $K_d \pm$ S.E. | $K_{oc}$ | $K_d \pm$ S.E. | $K_{oc}$ |
| 1 | 1.5 ± 0.6 | 186 | 410 ± 72 | 51250 |
| 2 | 3.1 ± 0.4 | 260 | 620 ± 113 | 51670 |
| 3 | 1.6 ± 0.1 | 390 | 109 ± 18 | 27250 |
| 4 | 10.9 ± 1.3 | 145 | 2990 ± 940 | 39340 |
| 4' | 1.4 ± 0.2 | n.d. | 172 ± 28 | n.d. |

In general the $K_d$ values depend on the properties of the soil tested. Since it has been shown that the primary active surface that interacts with the non-ionic molecules in the sorption process is the organic fraction of the soil (Lindstrom et al., 1967), the sorption characteristics of a soil for a herbicide can be normalized to obtain a more general soil sorption constant ($K_{oc}$) based on the soil organic content.

The $K_d$ values for the four soils with the herbicides at 7 concentrations are reported in Table 2 together with the values for $K_{oc}$. For atrazine the average $K_d$ values obtained for the 7 different concentrations varied largely in accordance with the characteristics of the soil used. For the soil with high organic matter content (soil 4) the average $K_d$ value (10.9) was higher than that for the low organic matter soils. Just as for atrazine, the $K_d$ values for trifluralin were influenced by the soil characteristics. In particular the removal of organic matter caused a decrease in the values from almost 3000 to about 200. When the sorption of the two herbicides by the soils examined was expressed by the sorption constant ($K_{oc}$) based on the organic carbon content of the soils, the differences between soils, although still marked, became less. For atrazine the highest $K_{oc}$ value was almost 400 for soil 3, while the lowest was around 150 for soil 4. For trifluralin the highest value for $K_{oc}$ was around 50 000 for soil 1 and soil 2, while the lowest value was 27 000 for soil 3.

The sorption isotherms for atrazine and trifluralin are reported in Fig. 2 while the relative fittings of the experimental data are reported in Table 3. The different $b$ values for the soils examined are an indication that the sorption process is specific for each type of soil. For atrazine the $b$ values are higher for soil 2 and especially for soil 4 where organic matter is higher than for the other samples. The sorption of trifluralin by soil 1, soil 2 and soil 4 was very similar and very high in comparison to that of soil 3 (the soil with

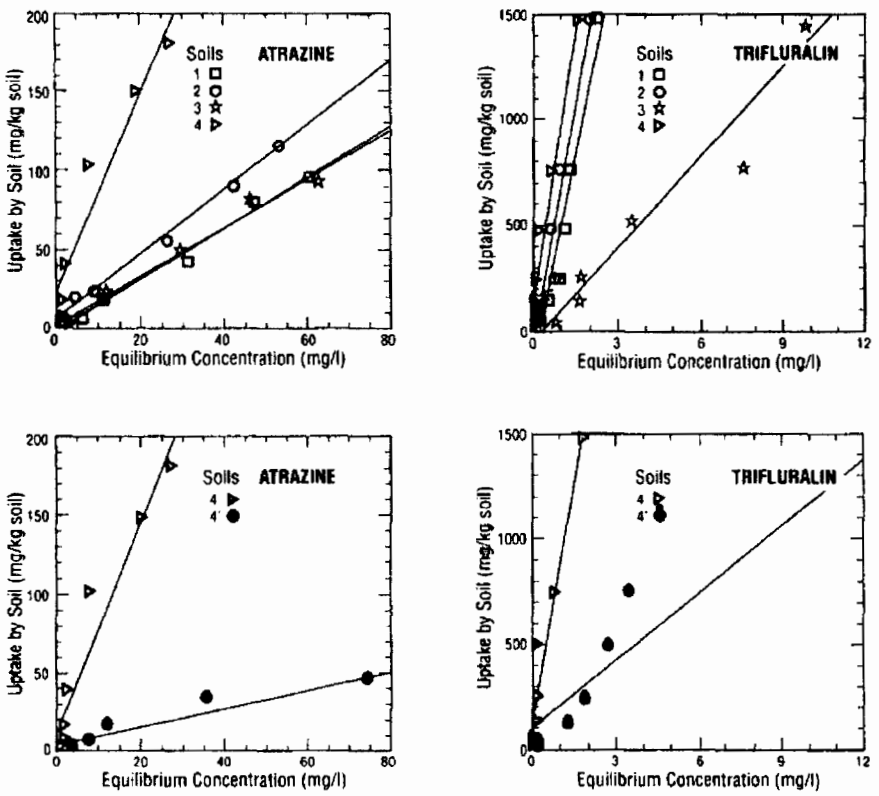


Fig. 2. Soil sorption isotherms of the two herbicides examined (soil 4′ is soil 4 after treatment with sodium hypochlorite to remove the organic matter).

TABLE 3

Regression analysis linear model ($Y = a + bX$) for sorption of atrazine and trifluralin by the soils examined. [$Y$ = uptake by soil (mg kg$^{-1}$), $X$ = equilibrium concentration (mg l$^{-1}$)]

| Soil | Atrazine | | | Trifluralin | | |
|---|---|---|---|---|---|---|
| | $a \pm$ S.E. | $b \pm$ S.E. | $r$ | $a \pm$ S.E. | $b \pm$ S.E. | $r$ |
| 1 | 0.9 ± 4.1 | 1.5 ± 0.1** | 0.98** | -130 ± 93 | 670 ± 82** | 0.97** |
| 2 | 3.2 ± 6.2 | 1.9 ± 0.2** | 0.97** | -11 ± 100 | 715 ± 110** | 0.94** |
| 3 | 0.6 ± 3.4 | 1.5 ± 0.1** | 0.98** | -43 ± 76 | 141 ± 26** | 0.97** |
| 4 | 8.7 ± 5.7 | 6.5 ± 0.4** | 0.99** | 167 ± 47* | 764 ± 106** | 0.98** |
| 4' | 10.8 ± 6.2 | 0.5 ± 0.1** | 0.88* | 94 ± 60 | 108 ± 13** | 0.96** |

*$P \leq 0.05$.
**$P \leq 0.01$.

a low clay mineral content as well as low organic matter content). The behavior of soil 4 after removal of the organic matter (soil 4') is similar to that of soil 3 (Fig. 2). The removal of organic matter from soil 4 decreases the sorption for the two herbicides used: the sorption of atrazine was less than that of the sorption of trifluralin. According to Chen (1976) the –Si–O–Si– bonds of the clay minerals are hydrophobic in nature and thus potential sites for the sorption of non-polar compounds. In the case of soil 4′ the hydrophobic sites associated with mineral surfaces are not covered by natural humus materials and hence fully contribute to the sorption of non-polar compounds (Walker and Crawford, 1968; Stevenson, 1976).

The sorption of herbicides by soil can also be expressed in terms of the Freundlich isotherm equation, which in the logarithmic form is as follows:

$$\ln X/M = \ln K_f + 1/n \ln C$$

where $X/M$ is the ratio of herbicide mass to the adsorbent mass, $C$ is the herbicide concentration in the solution at equilibrium and $K_f$ and $1/n$ are constants. The linear fitting of the experimental data according to the Freundlich equation is reported in Table 4. The parameters $K_f$ and $1/n$ of the regression lines in the Freundlich plots are thought to provide estimates of the adsorption capacity and intensity of adsorption respectively (Adamson, 1967). For atrazine $K_f$ and $1/n$ increase with increasing organic matter content. For trifluralin the value of $K_f$ seems to be in relation to both the clay content and the organic matter content of the soil. Moreover, according to our experimental data, the $K_d$ values differ significantly from the $K_f$ values of the Freundlich equation; particularly for soil 4 the discrepancies

TABLE 4

Values of $K_f$ and $1/n$ for atrazine and trifluralin tested with the Freundlich adsorption equation

| Soil | Atrazine | | | Trifluralin | | |
|---|---|---|---|---|---|---|
| | $\ln K_f$ | $1/n$ | $R^2$ | $\ln K_f$ | $1/n$ | $R^2$ |
| 1 | 2.2 ± 0.8* | 1.1 ± 0.2** | 0.90 | 5.2 ± 0.6** | 0.9 ± 0.1** | 0.93 |
| 2 | 4.4 ± 0.7** | 1.3 ± 0.1** | 0.97 | 5.8 ± 0.6** | 0.9 ± 0.1** | 0.93 |
| 3 | 1.7 ± 0.3** | 1.0 ± 0.1** | 0.98 | 3.9 ± 0.6** | 0.9 ± 0.1** | 0.92 |
| 4 | 13.0 ± 3.2** | 1.1 ± 0.1** | 0.91 | 8.8 ± 1.5* | 1.2 ± 0.2** | 0.90 |
| 4' | 0.9 ± 0.5** | 1.2 ± 0.1** | 0.94 | 5.7 ± 0.5** | 1.1 ± 0.09* | 0.96 |

*$P \leq 0.05$.
**$P \leq 0.01$.

observed between the $K_d$ and $K_f$ values can be attributed to the low concentration of the active ingredient in the solution after the equilibration period (Kanazawa, 1989).

In conclusion, the experimental results obtained in this research confirm that the sorption of atrazine and trifluralin by soil depends on the chemical properties of the herbicides as well as the characteristics of the soils. The sorption of atrazine by the soils examined was much lower than that of trifluralin. The sorption of both atrazine and trifluralin decreased considerably when the soil with high organic matter content was treated with hypochlorite. Even so, substantial sorption remained after removal of the organic matter, such that the values measured are similar to those of soil 3 (the soil with the lowest clay content as well as a low organic matter content). The evaluation of the sorption pattern for atrazine and trifluralin in the different types of cultivated soil where herbicides are frequently used should be extended to a larger number of soil samples in order to collect useful information for the preparation of suitable models to be used in the projection of the likely behaviour of these compounds in our specific soils.

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## REFERENCES

Adamson, A.W., 1967. Physical Chemistry of Surfaces. Academic Press, New York, p. 747.

Chen, N.Y., 1976. Hydrophobic properties of zeolites. J. Phys. Chem., 80: 60–64.

Grover, R., 1974. Adsorption and desorption of trifluralin, triallate and diallate by various adsorbents. Weed Sci., 22: 405–407.

Kanazawa, J., 1989. Relationship between the soil sorption constants for pesticides and their physicochemical properties. Environ. Tox. Chem., 8: 477–484.

LaFleur, K.S., 1979. Sorption of pesticides by model soils and agronomic soils: rates and equilibria. Soil Sci., 127: 94–101.

Lavkulich, L.M., 1970. Comparison of organic matter destruction by hydrogen peroxide and sodium hypochlorite and its effects on selected mineral constituents. Soil Sci. Soc. Am. Proc., 34: 755–758.

Lindstrom, F.T., R.G. Haque, V.H. Freed and L. Boersma, 1967. Theory on the movement of some herbicides in soils — linear diffusion and convection of chemicals in soil. Environ. Sci. Technol., 8: 561–565.

McCall, P.J., R.L. Swann, D.A. Laskowski, S.M. Ingor, S.A. Vrona and H.J. Dishburger, 1980. Estimation of chemical mobility in soil from liquid chromatography retention times. Bull. Environ. Contam. Toxicol., 24: 190–195.

Stevenson, F.J., 1976. Organic matter reactions involving pesticides in soil. ACS Symp. Ser., 29: 180–207.

Walker, A. and D.V. Crawford, 1968. The role of organic matter in adsorption of the triazine herbicides by soil. In: Isotopes and Radiation in Soil Organic Matter Studies. IAEA, Vienna, pp. 91–108.