

# Contribution of organic matter to metolachlor adsorption on some soils\*

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**Abstract**—The adsorption of Metolachlor [2-chloro-N-(2-ethyl-6-methylphenyl)-N-(2-methoxy-1-methyl-1-ethyl) acetamide] on different soils of various physical and chemical properties was studied. Adsorption isotherms were conformed to the Freundlich equation. The  $K_f$  values increased in the order of increasing organic carbon content of the soils. The adsorption was found to be correlated to organic matter content better than to other soil properties, and decreased weakly with increasing pH. However, variations in  $K_{oc}$  values of about four orders of magnitude have been observed within three natural soils. Instead, for a given soil, the  $K_{oc}$  values remained essentially unchanged after lowering the carbon content by  $H_2O_2$  oxidation.

**Keywords:** adsorption; organic matter; metolachlor.

## 1 Introduction

The adsorption of herbicides by soil is important in governing their environmental fate, biological activity and persistence in soil. Metolachlor is a selective pre-emergence herbicide structurally related to the class of chloroacetanilides. Due to its extensive use, e. g. about 22 million kg are annually used only in the United States, many papers have been published on its behavior in soil. For instance, the metolachlor adsorption has been studied on whole soil and individual minerals by different analytical methods (Chesters, 1989). All these reports agree that soil adsorption of metolachlor is better described by Freundlich rather than Langmuir isotherms (Spillner, 1983) and the adsorption occurs in minor extent on clay and more importantly on organic matter. However, the  $K_d$  values of soil obtained by different studies are not correlated with the organic matter and clays contents very likely because of the different chemical and physical properties of samples examined. Analogously, the  $K_{oc}$  values vary in a large ranges, suggesting that this approach does not permit estimation of metolachlor adsorption based on a single soil property, i. e., the organic carbon (OC) content. The purpose of this study was to quantify the adsorption of metolachlor on three soils with varying physical and chemical properties. In addition, the correla-

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tions between the adsorption parameters and OC content, after removal of organic matter to a varying extent, have been investigated.

## 2 Experimental

### 2.1 Soil sample

A silt clay Entisol (soil I), a loamy sand Cambisol (soil II) and a sandy loam Andosol (soil III) were examined in this study. The soils were air-dried and passed through a 2 mm sieve. OC contents were determined by the Walkly - Black method. The cation exchange capacity (CEC) was determined according to the procedure of Hendershot and Duquette (Hendershot, 1986). The clay minerals present in the I soil were identified by X-ray Diffraction and showed mixed mineralogy consisting of illite, kaolinite and smectite. Some physico-chemical properties of the soils are given in Table 1.

Table 1 Some physical and chemical properties of soils

Property	I	II	III
O. M. %	1.70	2.40	16.00
Clay, %	46.58	9.10	14.60
Sand, %	16.44	70.10	32.90
Silt, %	29.92	16.80	26.20
Water, %	4.50	1.40	9.50
pH (soil:H <sub>2</sub> O-1:1)	7.20	5.12	5.44
CEC, meq/100g	23.73	4.03	17.62
Soil texture	silt clay	loamy sand	sandy loam

### 2.2 Chemicals

Metolachlor, mol. wt. 283.8, aqueous solubility 530 mg/L was supplied by Ciba - Geigy AG (USA) as an analytical grade sample (99.7% purity).

### 2.3 Metolachlor analysis

Metolachlor concentration were determined by high performance liquid chromatographic (HPLC) analyses. A Waters 501 liquid chromatography equipped with a 300×4 mm i. d. Waters 10 $\mu$  Boudapak C<sub>18</sub> analytical column, a multiwavelength Waters 490 programmable detector operating at 230 nm and a Waters Baseline 810 chromatographic workstation was used. The mobile phase (1 ml/min) was composed of acetonitrile + water (70 +30 by volume, pH 3).

### 2.4 Adsorption studies

Batch distribution isotherms in soils were determined at 25±2°C. In general, triplicate samples of 5 g of air-dried soil were equilibrated in centrifuge tube with 25 ml of metolachlor solution. The metolachlor concentrations before equilibration ranged from 12 to 650  $\mu$ m. The tubes were shaken (end-over-end) for 24 h. Generally, 95% of this adsorption was found to occur in the first 5 h. After equilibration, the suspension was centrifuged at 20000 r/min for 15 min. The supernatant was pipette off and analyzed immediately. The amount adsorbed by a soil was calculated from the difference between the initial and final concentrations of metolachlor in solution. The effect of varying pH was examined by the addition of HCl or NaOH and equilibrating

overnight. In order to evaluate the role of the different amounts of organic carbon on metolachlor adsorption, the isotherms were carried out on the same soils after lowering the carbon content. Variable amounts of organic carbon were obtained by consecutive addition of  $H_2O_2$  (10% by volume). In the III soil, the content of organic carbon was reduced from 9.28 to 2.49 and 1.51% after one and two oxidation treatments, respectively. In the II soil, a single treatment with hydrogen peroxide reduced the organic carbon to 0.48%. After removal of organic matter, the soils were centrifuged and air-dried.

### 3 Results and discussions

A kinetic study indicated that a period of 24 h was enough to permit all three soils to reach equilibrium. In fact, no detectable change in adsorption occurred between 5 and 24 h. The adsorption isotherms were generally of the L-type according to the Giles classification, with indicates that the soils have a medium affinity for the pesticide. Although these isotherms appear to be Langmuirian, the Freundlich equation has been preferred because it is more realistic for systems as heterogeneous as these of soils (Polyzopoulos, 1985). On the other hand, the more general Langmuir equation proposed by Giles *et al.* (Giles, 1960) when applied to dilute solution (as is in our case), reverts to the Freundlich equation (Calvet, 1985). In the linear form the relation can be expressed as:

$$\log C_s = \log K_f + n \log C_e,$$

where  $C_s$  ( $\mu\text{mol/kg}$ ) is the amount of herbicide adsorbed by soil,  $C_e$  ( $\mu\text{M}$ ) is the equilibrium concentration in solution, and  $K_f$  and  $n$  are empirical constants representing the intercept and the slope of the isotherm, respectively. The Freundlich constants  $K_f$  and  $n$  determined on our system, together with the correlation coefficients ( $r^2$ ) for the linear fit, are given in Table 2. All the  $r^2$  values are higher than 0.990, indicating a good correlation of data, as interpreted by the Freundlich equation over such a wide concentration range.

**Table 2 Parameters of the Freundlich equation and  $K_{oc}$  values for Metolachlor at different OC% values**

Soil	OC%	$K_f$	$n$	$r^2$	$K_{oc}$
I	0.98	0.98	0.86	0.998	100
II	1.39	5.28	1.07	0.997	380
II*	0.48	1.93	0.95	0.996	402
III	9.28	16.73	1.09	0.996	181
III*	2.49	4.20	0.86	0.998	169
III**	1.51	2.77	0.84	0.997	183

\* After one treatment with  $H_2O_2$ ; \*\* After two treatments with  $H_2O_2$ .

In most studies concerning the pesticide transport, the Freundlich coefficient ( $n$ ) has often been assumed as equal to 1. In the present work, it range from 0.86 to 1.09. Similar deviations from the linearly have been noticed in other studies observed that low values of  $n$  are often associated with a high soil organic matter content, but such a trend is not supported by our results.

More likely, the very wide range of solution concentrations examined here is responsible for the lack of linearity in the pattern. Inspection of the data listed in Table 2 shows that  $Kf$  decreased in the order  $\text{III} > \text{II} > \text{I}$ , which is also the order of decreasing organic matter content in the soil. This confirms the positive effect of soil organic matter on the metolachlor adsorption, as well established by many other investigations (Weber, 1980; Peter, 1985).

The adsorption of metolachlor occurs primarily at the organic matter and to a less extent on clay colloid. In particular, Kozak *et al.* (Kozak, 1983) studied the adsorption of metolachlor by different fractions of soil organic matter and found that humic substances, except humins, exhibit high affinity for metolachlor. These findings are consistent with our results, in spite of the wide range of the composition and chemical properties of the soil examined (clays: 9%–46%; organic matter: 1.7%–16.0%; pH: 5.12–7.21). For the analysis of the adsorption constants, the relationship based on the soil OC content. In particular, by assuming that all the soil organic matter has the same adsorptive characteristics, whereas the mineral components are not significantly active in the adsorption process, they considered the ratio between the sorption constant  $Kf$  and the OC constant of soil in the place of the total mass:

$$K_{oc} = (Kf \times 100) / \text{OC}\%$$

Many investigations have found that, for a given herbicide, the  $K_{oc}$  values obtained from different soils are less scattered than the corresponding  $Kf$  values calculated from the total soil-weight basis. In our case, as it can be seen in Table 2, by relating the sorption to OC, a 17-fold variation of  $Kf$  is reduced to less than a fourfold variation of  $K_{oc}$ . These findings confirm that organic carbon is the most important factor in determining the adsorption of metolachlor. However, the correlation between the adsorption parameter and the OC content is scarce. In this case, the soils used had quite comparable physical and chemical properties.

To evaluate the dependence of  $K_{oc}$  values on the soil properties, the adsorption of metolachlor on II and III soils before and after  $\text{H}_2\text{O}_2$  oxidation was compared. As it is apparent from the data reported in Table 2, this soil treatment caused a sequential loss of adsorptive capacity.

These findings are in agreement with the known role of organic matter in the adsorption of the herbicide. In principle, if the nature of soil does not affect the adsorption capacity of the organic matter, it may be expected that the extent of adsorption of a given herbicide, referred to the unit weight of organic carbon ( $K_{oc}$ ), should be similar for different soils. Instead, even at comparable OC% contents, different  $K_{oc}$  values are found for metolachlor adsorption on the soils examined (Table 2). This discrepancy has been generally attributed to the different composition of the soil organic matter. However, it is interesting to observe that, for a given soil, e. g. III soil, the  $K_{oc}$  value remains essentially constant over a wide range of OC content. Since it is expected that peroxidation alters the organic matter composition (e. g. humic acids are more oxidizable than humins), the finding suggests that other factors, rather than the nature of organic matter itself, are important in determining the adsorption properties. In particular, the association mechanisms between organic and inorganic constituents could be relevant.

The results of adsorption of metolachlor at different pH values of the three soils suspensions showed that the adsorption decreases with increasing pH of soil suspension, but this effect ap-

pears only slightly pronounced. It may be observed that since the molecule of metolachlor is a weakly basic, the herbicide is in the molecule form over the range of pH tested.

Weber and Peter (Weber, 1980) suggested that metolachlor is adsorbed by organic matter by H-bonds between the carbonyl oxygen of the herbicide and H atoms of carboxyl and hydroxyl groups of the organic suffices and through charge transfer ( $\pi$ ) bonds between the aromatic nucleus of the herbicide molecule and aromatic rings in the organic matter surfaces. To some extent, these adsorption mechanisms are also affected by pH. In conclusion, the study confirms that organic carbon is responsible for metolachlor adsorption in soil. However, it is apparent that the nature of the organic component does not affect significantly the extent of adsorption.

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