

COMPETITIVE SORPTION OF ATRAZINE AND METOLACHLOR IN SOIL

Key Words: herbicide, adsorption, desorption, commercial-formulation, analytical-grade

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ABSTRACT

Atrazine and metolachlor co-application to soil created competitive sorption between the two herbicides, producing smaller partitioning coefficients than for separate atrazine and metolachlor applications. The partitioning coefficients for both compounds were also less when applied in a commercial formulation, compared with separate analytical-grade applications. Since the Freundlich slope of the isotherms was less than unity (0.83 to 0.87), the sorption strength of the herbicides decreased with increasing solution concentrations. Based on the Freundlich adsorption values obtained, this study concludes that atrazine and metolachlor co-applications on agricultural fields have the potential to increase the mobility of these herbicides in soil, thereby also increasing the risk for groundwater contamination.

INTRODUCTION

The herbicides atrazine [2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine] and metolachlor [2-chloro-N-(2-ethyl-6-methylphenyl)-N-(2-methoxy-1-methylethyl)acetamide] are often used in combination on corn fields to provide for a greater control

of broadleaf weeds. Atrazine-metolachlor mixtures are more effective than either herbicide alone and require less total herbicide use (Solomon *et al.*, 1996).

Atrazine adsorbs on both inorganic and organic colloid surfaces, but preference is shown for organic matter over clay (Ma and Selim, 1996). Metolachlor sorption increases with increasing organic matter content (specifically humic matter), clay content, and cation exchange capacity in the soil (Kent *et al.*, 1991). For both atrazine and metolachlor, there are several mechanisms responsible for the retention by soil because of the heterogeneity of the soil components. For example, atrazine can be adsorbed by physical and chemical bonding such as van der Waals forces, hydrogen bonds, cation exchange, cation and water bridging, and hydrophobic bonds with varying degrees of strengths of interaction (Koskinen and Clay, 1997). Mechanisms of metolachlor sorption on soil include hydrogen-bonding, cation and water bridging, and charge transfer bonds (Kozak *et al.*, 1983; Chesters *et al.*, 1989; Peter and Weber, 1985).

Amongst the various methods used to characterize herbicide sorption onto soil, batch-type experiments and Freundlich isotherms are good measures for adsorption and desorption assessments (Green *et al.*, 1976). Freundlich adsorption and desorption values are important parameters in hydrological models that can be used to predict herbicide transport through the soil profile and by surface runoff (Leonard *et al.*, 1987; Tim and Mosraghimi, 1989).

Freundlich values are usually obtained using analytical grade single herbicide compounds but these chemicals may behave differently alone than when applied, in combination with others, or in commercial herbicide products. Various studies have been carried out on the effects of organic co-solvents on the sorption of organic chemicals by soils (Rao *et al.*, 1990; Wood *et al.*, 1990). However, apart from a recent paper by Businelli (1997), relatively little attention has been paid to the competition between co-applied herbicides for adsorption sites in soils. The objectives of the present study were: (1) to examine the influence of atrazine and metolachlor co-application on their individual adsorption-desorption behaviour in soil, and (2) to compare the application of commercial and analytical grade herbicide solutions on

atrazine and metolachlor retention in soil.

MATERIAL AND METHODS

Soil

A loamy Ap horizon (0-15cm) of a Gobles soil (Gleyed Brunisolic Gray Brown Luvisol) at a field moisture content of 13 % was collected from a no-till corn field near Belmont, Ontario. Neither atrazine nor metolachlor residues were detected in the sampled soil (HPLC detection limit 25 ng g⁻¹ soil). Key physical and chemical soil properties of the soil include the following: 29 % sand, 46 % silt, 24 % clay, 1.63 % organic carbon, pH 6.35, CEC 12.38 cmol kg⁻¹, and an exchangeable K, Ca, Mg and Na of 0.47, 5.62, 1.56 and 0.07 cmol kg⁻¹ respectively. Soil texture was determined by the hydrometer method (Gee and Bauder, 1986), organic C by the modified Walkley-Black volumetric oxidation method (Allison, 1965), pH in a 1:1 soil to 0.01 M CaCl₂ solution, CEC by the NH₄OAC method (Chapman, 1965), and exchangeable K, Ca, Mg and Na according to Jackson (1958).

Chemicals and Analytical Methods

A commercially available atrazine-metolachlor liquid formulation, Primextra[®] (label content: 153 g L⁻¹ atrazine, 364 g L⁻¹ metolachlor, and 10 g L⁻¹ unidentified other active triazines; Ciba-Geigy Co, Greensboro, NC) was used. Analytical standards (>97 % purity) of atrazine and metolachlor were obtained from Ciba-Geigy Co, Greensboro, NC.

Freundlich sorption isotherms were determined as follows. Concentrations of herbicides in solutions were determined by HPLC with UV detector (Waters 486 Tunable Absorbance Detector, Waters Corporation, Milford, Massachusetts) and the following operating parameters: column - reversed-phase, 15.0 cm x 3.9 mm (5 μm spherical particle C18 packing); mobile phase - acetonitrile/water (40:60) at 0.9 mL min⁻¹ for atrazine, and acetonitrile/water (60:40) at 0.9 mL min⁻¹ for metolachlor; detector wavelength - 220 nm for atrazine, and 200 nm for metolachlor.

Herbicides were quantified by integrating the area of peaks in HPLC-UV analysis. Samples were appropriately diluted in volumetric flasks with 50: 50 MeOH-H₂O to obtain concentrations in the optimal working range of the UV detector (20 ng mL⁻¹ to 3 µg mL⁻¹). The minimum detectable concentrations for atrazine was in the 5 to 15 ng mL⁻¹ range, and for metolachlor, 20 to 30 ng mL⁻¹. The variation between repeat sample HPLC chromatograms was always less than 1 %.

Freundlich Isotherms

Atrazine and metolachlor adsorption isotherms on soil were determined using the batch equilibrium procedure and 15 mL volumes. The Gobles soil adsorbent was air-dried and sieved (2 mm). Adsorbates consisted of atrazine and metolachlor in four different solution composition treatments: Primextra[®], analytical-grade atrazine-metolachlor solutions, analytical grade atrazine, and analytical grade metolachlor. The analytical grade combined herbicide solutions were prepared by mixing the two analytical grade atrazine and metolachlor standards. All herbicide solutions were prepared in 0.01 M CaCl₂ and concentrations were for metolachlor approximately 0.9, 1.8, 4.8, 12, 30 and 60 mg L⁻¹ and for atrazine approximately 0.3, 0.6, 1.6, 4, 10 and 20 mg L⁻¹. Metolachlor concentrations were three times greater than that of atrazine as this was the composition of the commercially available product as determined by HPLC analysis. The ratio of atrazine:metolachlor in Primextra determined by HPLC was slightly different from that given on the product label (1 : 2.38).

Each herbicide solution (15 mL) was added to 5 g of air-dried soil in 30 mL glass COREX[®] centrifuge tubes in triplicate. Tubes were covered with parafilm and tumbled for 24 h at 21°C to reach equilibrium. Previous batch experiments have shown that atrazine and metolachlor sorption on soil occurred rapidly, with most of the herbicides being removed from solution within the first hour, and that a 24 h equilibrium period was sufficient to characterize the second phase of slow sorption (Seybold and Mersie, 1996). Preliminary testing revealed that neither atrazine nor metolachlor adsorbed onto glass or parafilm. Tubes were then centrifuged for 45 min at 7,000 RPM (5900 x g) and 13 mL of supernatant was removed and subsampled to determine the concentration of herbicides remaining in solution by HPLC analysis. Amount of herbicides adsorbed on soil was determined by the difference between the initial and

equilibrium herbicide concentration.

For the desorption procedure, supernatant was replaced by an equal amount of 0.01 M CaCl₂ solution (13 mL). Tubes were placed on a vortex shaker for 1 min to disperse soil pellets, and then tumbled and centrifuged as described for the adsorption isotherms. After centrifugation, the supernatant was subsampled to determine the herbicide concentration of the equilibrium solution after desorption by HPLC analysis. Desorption was calculated by the difference between the solutes adsorbed onto the soil at equilibrium after adsorption and that remaining at equilibrium after desorption.

Adsorption isotherms were fitted using the log transformation of the empirical Freundlich equation:

$$\text{Log } (X/M) = \text{Log } K_f + 1/n \text{ Log } C_e \quad (1)$$

where X/M = amount of herbicide adsorbed [mol] / amount of adsorbent [Kg⁻¹], K_f = Freundlich constant [mol^(1-1/n) L^{1/n} Kg⁻¹], $1/n$ = dimensionless Freundlich constant, and C_e = herbicide concentration of equilibrium solution [mol L⁻¹].

Statistical analysis included Analysis of Variance and Multiple Comparison (Student Newman-Keuls-Test, P 0.05) in SigmaStat[®] Windows Version 1.0 (Jandel Scientific) on K_f and n values, and on the amount of atrazine or metolachlor.

RESULTS AND DISCUSSION

The Freundlich nonlinear adsorption isotherms showed an excellent fit to the measured data for all herbicide solutions, $r^2 > 0.99$ (Table 1). Slopes of isotherms were not significantly different amongst herbicide solution treatments, indicating that K_f values amongst treatments could be compared. Slopes of isotherms ranged between 0.83 and 0.87 for atrazine and between 0.85 and 0.87 for metolachlor suggesting that herbicide sorption on soil was nonlinearly proportional to the equilibrium solution concentration.

TABLE 1: Best-fit Parameters (K_f , $1/n$) and Goodness of Fit (r^2) of the Freundlich Model to Describe Atrazine and Metolachlor Adsorption by Gobles Soil.

Herbicides	K_f [mol ^(1-1/n) L ^{1/n} Kg ⁻¹]		$1/n$		r^2
Atrazine:					
Analytical alone	1.397 ± 0.033 ¹	a ²	0.853 ± 0.008	a	1.000 ± 0.000
Analytical mixture ³	1.211 ± 0.027	b	0.834 ± 0.007	a	0.997 ± 0.001
Primextra	1.096 ± 0.011	c	0.870 ± 0.015	a	0.994 ± 0.001
Metolachlor:					
Analytical alone	2.622 ± 0.015	d	0.850 ± 0.002	a	0.999 ± 0.000
Analytical mixture ³	2.372 ± 0.031	e	0.856 ± 0.002	a	0.999 ± 0.000
Primextra	2.315 ± 0.020	e	0.867 ± 0.004	a	0.997 ± 0.002

¹ Mean of three replicates followed by standard error.

² Means followed by same letters are not significantly different.

³ Mixture refers to both herbicides in the same solution

The affinity between herbicides and soil was greatest at initial low herbicide concentrations and decreased with increasing initial herbicide concentrations, as might be expected. Thus, the Freundlich fitting of atrazine and metolachlor isotherms was L-type (Giles *et al.*, 1960), reflecting the saturation of the adsorption sites as the herbicide concentration increased.

The K_f value for metolachlor was significantly greater ($P < 0.05$) than those for atrazine in the same soil-solution system (Table 1). Since metolachlor was more strongly sorbed on soils than atrazine, it may have a lower mobility in soils (Bowman, 1989; Bowman *et al.*, 1994). This sorption behaviour was in accordance with the K_{ow} values for the two compounds (metolachlor, 2.9; atrazine, 2.5). Generally, pesticide sorption on soil is quite well correlated with the K_{ow} , much better than with water solubility (Gawlik *et al.*, 1997).

The correlation between K_{ow} and sorption seems to suggest that the mechanism of pesticide sorption by soil is a partitioning process, but which would not necessarily exclude hydrogen-bonding, or some other "weak force" mechanisms. In fact, it is likely that there was a range of adsorption mechanisms and sorption intensities responsible

for the retention of atrazine and metolachlor by soil, as the various soil constituents (e.g. humic substances, clays) offered different types of adsorption sites. Given the pH of the soil (6.35), hydrogen-bonding was probably the most important adsorption mechanism of atrazine by soil (Hayes 1970). Metolachlor may also have formed complexes with functional groups of soil organic matter through hydrogen-bonds (Kozak *et al.* 1983).

K_f values for atrazine and metolachlor decreased when both herbicides were present in the same soil-water system, either in analytical-grade form, or in the commercial product, Primextra (Table 1). This behaviour is indicative of competitive sorption between the two herbicides. This "competition" indicated that the sorption process of the herbicides was adsorption rather than partitioning (Businelli, 1997). Unlike atrazine, metolachlor sorption by the soil was not measurably different when it was in the commercial formulation, Primextra[®] compared with it in the analytical-grade combination with atrazine.

Atrazine in the commercial mixture showed significantly less adsorption on soil than atrazine in the analytical grade mixture. Other compounds in Primextra[®] (label indicated 2 % unidentified other active triazines) may have competed with atrazine for adsorption sites. For example, Businelli (1997) reported that the soil adsorption capability for atrazine was reduced when it was applied with prometryn and terbuthylazine. Unlike atrazine, metolachlor sorption by soil did not measurably change in the commercial formulation, Primextra, compared with analytical-grade metolachlor.

While more metolachlor was sorbed onto soil than atrazine, its sorption process was less reversible than for atrazine. This might be explained by the different types or strength of bonding involved in atrazine and metolachlor sorption on soil. Percentage of desorption (averaged across formulation and initial solution concentration treatments) was 45 % for atrazine and 36 % for metolachlor, suggesting that a relatively larger proportion of metolachlor was retained by high-energy bonding mechanisms. It should be noted that the desorption process in this study involved one desorption step. Additional desorption steps may approach a complete desorption of atrazine from soil (Moreau and Mouvet, 1997), but hysteresis has been observed for

TABLE 2: Least Square Means for Metolachlor Desorption from Gobles Soil Treated with Primextra[®], Analytical-grade Metolachlor Solutions, and Analytical-grade Atrazine-metolachlor Mixtures.

Herbicide solution	Metolachlor desorbed As % of adsorbed
Primextra [®]	37.4 a ¹
Analytical alone	36.4 a
Analytical mixture	32.7 b

¹ Means followed by same letters are not significantly different.

TABLE 3: Least Square Means for Atrazine Desorption from Gobles Soil Treated with Primextra[®], Analytical-grade Atrazine Solutions, and Analytical-grade Atrazine-metolachlor Mixtures.

Herbicide solution	Atrazine desorbed As % of adsorbed
Primextra [®]	49.8 a ¹
Analytical alone	44.1 b
Analytical mixture	41.3 c

¹ Means followed by same letters are not significantly different.

both atrazine and metolachlor (Seybold and Mersie, 1996).

Desorption of atrazine and metolachlor from soil was significantly greater (P 0.05) for herbicides in Primextra[®] than for herbicides in analytical grade mixtures (Tables 2 and 3). This indicated that both atrazine and metolachlor were more weakly adsorbed on soil with Primextra[®] solutions than with analytical grade mixtures, perhaps due to a competition between the herbicide and other materials in Primextra[®] for adsorption sites.

Metolachlor desorption generally increased with increasing initial solution concentrations (Table 4). Obrigawitch *et al.* (1981) suggested that monolayer adsorption of metolachlor on soil is predominant at low equilibrium solution concentrations (< 12 mg L⁻¹), while multilayer adsorption occurs at higher equilibrium concentrations. Multilayer bonding energies are lower than that of monolayer bonds,

TABLE 4: Least Square Means for Metolachlor Desorption from Gobles Soil for an Initial Metolachlor Concentration of 60, 30, 12, 4.8, 1.8, and 0.9 Mg L⁻¹.

Concentration [mg L ⁻¹]	Metolachlor desorbed as % of adsorbed
30	39.2a ¹
60	38.4a
12	35.8b
4.8	34.7b
1.8	33.5bc
0.9	31.4c

¹ Means followed by same letters are not significantly different.

TABLE 5: Least Square Means for Atrazine Desorption from Gobles Soil for an Initial Atrazine Concentration of 20, 10, 4, 1.6, 0.6 and 0.3 Mg L⁻¹.

Concentration [mg L ⁻¹]	Atrazine desorbed as % of adsorbed
10	47.5 a ¹
4.0	46.3 a
1.6	46.3 a
0.6	45.9 a
0.3	42.5 b
20	41.9 b

¹ Means followed by same letters are not significantly different.

thus desorption occurred most readily from multilayer sites. At the metolachlor concentrations that were used in the present study, it is likely that only fractional monolayer coverage occurred, but localized domains of soil surfaces may have had more than one layer. The desorption differences among initial solution concentrations may also have reflected variable sorption energies on the heterogeneous soil surfaces. Metolachlor desorption was also dependent on initial solution concentration in other studies (Seybold and Mersie, 1996).

The percentage of atrazine desorption was less influenced by the initial solution concentration (Table 5). Other studies have found that desorption was dependent on the sorbed atrazine concentration, with high concentrations being retained to a lesser extent and more easily to desorb than lower concentrations (Barriuso *et al.*, 1992). In the present study, atrazine was probably predominantly adsorbed by weak binding

mechanisms (independent of the sorbed atrazine concentration) and readily desorbed from the Gobles soil.

CONCLUSION

Freundlich K_f values were significantly greater ($P < 0.05$) for metolachlor than for atrazine with loamy soil, indicating that metolachlor is more strongly sorbed by soil than atrazine. Atrazine and metolachlor co-application resulted in a competition between the two herbicides for adsorption sites leading to less-energetically-sorbed atrazine and metolachlor, compared with individual atrazine and metolachlor applications. Other materials or related compounds in commercial available mixtures also influenced herbicide retention by soil. Desorption from soil was significantly greater ($P < 0.05$) for atrazine and metolachlor in Primextra (containing 2 % unidentified triazines) than for atrazine and metolachlor in analytical grade atrazine-metolachlor mixtures. These results indicate that co-applications of herbicides on agricultural fields has the potential to increase the mobility of these chemicals in soil profiles.

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