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Adsorption of Atrazine by Soils Varying in Organic Carbon Content in the Presence of the Adjuvant Atpolan

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Adjuvants used as a component of pesticide formulations or spray adjuvants can change agronomic effects (effectiveness, phytotoxicity) of the product. An adjuvant may also affect the environmental impact, as dispersion patters may be altered, the functional activity period of the active ingredient may be lengthened, or its degradation delayed (Swarcewicz, 2002). The pesticides atrazine and coumaphos were degraded at a lower rate and to a lower extent in the presence of a nonionic surfactant (Mata-Sandoval et al., 2001). Addition of nonionic surfactants to soil decreases the mobility of the pesticides, which are probably adsorbed to the surfactants previously adsorbed to the soil. The mobility in soil of the pesticides diazinon, atrazine and acephate decreased in the presence of nonionic surfactants (Sánchez-Camazano et al., 1995; Iglesias-Jimenez et al., 1996). Soil organic matter is the primary soil constituent responsible for sorption of nonionic pesticides and surfactants in pesticides (Krogh et al., 2003). Atrazine is potentially toxic both to humans and to the ecosystem. It is a hydrophobic pesticide frequently found during monitoring of pesticides in aquifers in various countries (Carter, 2000). The aim of this study was to (i) determine contact times required for attainment of sorption equilibrium and (ii) explore the effect of Atpolan on the amount of atrazine sorbed by soil of varying organic carbon content.

Materials and Method

Three types of soil were used in laboratory experiments. Surface soils were taken from three locations, Korytowo, Ostoja and Lipnik, northwest Poland. Soil was collected from the surface 20 cm layer. A sandy loam with an organic matter content of 0.95% was selected from meadow soil in Korytowo. This soil contained 64% sand, 21% silt, and 15% clay. Soil pH was 5.5. A silt loam with an organic matter content of 1.5% was selected from field soil in Ostoja. This soil contained 40% sand, 34% silt, and 26% clay. Soil pH was 6.3. Third, muck soil from Lipnik with an organic matter content of 4.5% and contained 88% sand, 5% silt, and 7% clay, soil pH was 6.4. A suspension of a commercial formulation of atrazine (Azoprim 50 WP, 50% a.i., Jaworzno, Poland) was used in the study. An analytical standard for atrazine, of 99% purity, was obtained from Prochem Institute of Organic Industry, Warsaw. Stock solutions of atrazine were prepared in methanol at a concentration of 117 $\mu mol \cdot dm^{-3}$. Atpolan 80 EC containing 80% paraffin oil (Agromix, Poland) belongs to oil mineral adjuvants used as tank-mix. An adjuvant concentration of 0.5 % (v/v) was used. Three replicates of two sets of batch experiments were conducted in centrifuge tubes. In the first set, the equilibrium time for atrazine adsorption was determined with and without the adjuvant in the three soils. Four grams of air-dried soil was put into 50 cm^3 test tubes and 10 cm^3 0.01 M $CaCl_2$ was added. The tubes were treated with a solution of the atrazine alone (25.5 mg dm^{-3}) or atrazine with Atpolan (0.5% v/v). Then the tubes were shaken for various times: 5, 10, 15, 20, 30, 120, 480, 1440 and 2880 min at 20 ± 1°C to achieve equilibrium. At the same time, the degradation of atrazine in pure water was tested under the same conditions. In the second set of

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Table 1 Influence of Atpolan on equilibrium concentration of atrazine ($Q_{\max}$) in soil in kinetic study, the partition coefficient (K_d), and soil sorption constant (K_{oc})

Soil	Treatment	Q_{max} (mg·kg^{-1})	K_d (dm^3 kg^{-1})	K_{oc}	r^2
Sandy loam	Atrazine	27.84 (1.68)[a]	2.07 (0.15)	218	0.97
	Atrazine + Atpolan	28.85 (1.64)	2.15 (0.07)	226	0.97
Silt loam	Atrazine	27.67 (2.22)	2.06 (0.03)	137	0.94
	Atrazine + Atpolan	33.16 (1.82)	2.71 (0.13)	181	0.96
Muck soil	Atrazine	34.40 (1.820	2.87 (0.34)	64	0.97
	Atrazine + Atpolan	33.97 (2.69)	3.17 (0.41)	70	0.94

[a] Standard errors of means are in parentheses

experiments, the effect of Atpolan on the various amount of atrazine sorbed by soils of various content of organic carbon was determined. Equilibrium adsorption isotherms for all soil-atrazine-adjuvant combinations were measured by the batch equilibrium method at 25°C, with five sorbate concentrations. An equilibrium was achieved by shaking samples of 4 ± 0.001 g air-dried soil with 10 cm^3 atrazine solution, at concentrations of 10, 15, 20, 25 and 30 mg dm^{-3}, and Atpolan 0.5% v/v, for 24 h. After centrifugation, 4 cm^3 aliquots were collected in 10 cm^3 tubes. The herbicide in the supernatants was extracted by dichloromethane and purified by a Florisil column. The eluates were analyzed by gas chromatography (GC). GC analyses were performed using Carlo Erba-Vega 6180 gas chromatograph, equipped with a flame-ionization detector (FID). The column used in this study was a capillary column DB-17 (column length 30 m, column ID 0.54 mm, film thickness 1 μm). Nitrogen was used as both the carrier and make-up gas at the flow rate of 30 ml/min. Hydrogen was used at a flow rate of 3.5 cm^3/min and air at 110 cm^3/min. The oven temperature was programmed from 60°C (1 min) to 200°C (10 min) at a rate of 25°C/min, and from 200°C to 260°C (5 min) at a rate 31°C/min and detector temperature at 280°C. Retention time for atrazine was 10.43 min. Recovery of atrazine from water sample was 94 ± 4.5% for 25 mg dm^{-3} atrazine.

Results and Discussion

The contact times required to attain sorption equilibrium for atrazine in the presence of the adjuvant and the influence of this adjuvant on the soil-water distribution of the herbicide (K_d) and general soil sorption constant (K_{oc}) was studied in this experiment. The experiment with atrazine alone and the adjuvant and atrazine at a single concentration was conducted to investigate the equilibrium time and the sorption behaviour of atrazine over a 48 h period. The results indicated that atrazine sorption occurred in the same period of time (less than 8 h sandy loam and 24 h in silt loam) both in the presence or absence of the adjuvant. Equilibrium sorption is usually achieved and measured within 24 h (Carter, 2000). The sorption data fit a hyperbolic (Bernhard-Bitaud et al., 1994) model well, as reflected by the high determination coefficients (r^2) of 0.9401 to 0.9713 (Table 1). In the presence of Atpolan, the percentage of the sorbed atrazine increased to an average value of 25% only in silt loam soil. In other soils there was no significant difference. Abu-Zreig et al. (1999) noticed that surfactants had little effect on the equilibrium time for atrazine sorption.

The study of adjuvant influence on soil-water distribution (K_d) of atrazine from a hyperbolic model showed an increased value of K_d after addition of Atpolan to the three soils. The greatest difference of K_d after addition of Atpolan was found in the silt loam (Table 1). In our study, soil rich in organic matter caused an increase of the K_d value of atrazine alone by about 87%, but in the presence of Atpolan this effect was minor. The relationship between organic matter content in soil and the value of K_d was studied by Payá-Pérez et al. (1992).

They reported that not only the concentration, but also the composition of the organic matter plays important roles in soil sorption of atrazine. They obtained values of K_d ranging from 0.01 dm^3 kg^{-1} to 64 dm^3 kg^{-1}of atrazine with a mean value of 2.4 dm^3 kg^{-1}. Similar results were reported by Barriuso et al. (1992) and Dousset et al. (1994). The sorption characteristics of atrazine can be normalized to obtain a general soil sorption constant (K_{oc}) based on the soil organic carbon (SOC) content. In our study, we noticed that addition of Atpolan caused an increase of the K_{oc} values (Table 1), thus an increase in retention of atrazine residues in soil. The organic carbon soil sorption (K_{oc}) of atrazine in sandy loam was similar to that obtained by Payá-Pérez et al. (1992). In our study, addition of adjuvant Atpolan to atrazine formulation as a tank mix caused a slight increase of the K_d and K_{oc} values, but the type of soil had a much greater influence on both these factors.

The second experiment was concerned with the influence of adjuvant on the sorption isotherm of atrazine. The results (Table 2) indicated that the sorption data fit the Freundlich model well, as reflected by the high determination coefficients (r^2). The K_f value decreased both in sandy loam and silt loam for atrazine in the presence of Atpolan, but in muck soil this difference was less. The

Table 2 Freundlich adsorption coefficient (K_f), slope (n) and r^2 for atrazine in soils with and without of adjuvant

Soil	Treatment	K_f [a]	n	r^2
Sandy loam	Atrazine	2.69 (0.42)[a]	0.81 (0.07)	0.96
	Atrazine + Atpolan	2.03 (0.55)	1.01 (0.06)	0.97
Silt loam	Atrazine	3.41 (0.80)	0.81 (0.09)	0.95
	Atrazine + Atpolan	2.41 (0.75)	1.08 (0.13)	0.95
Muck soil	Atrazine	2.60 (0.47)	1.04 (0.07)	0.98
	Atrazine + Atpolan	3.89 (0.83)	0.94 (0.09)	0.95

[a] Standard errors of means are in parentheses

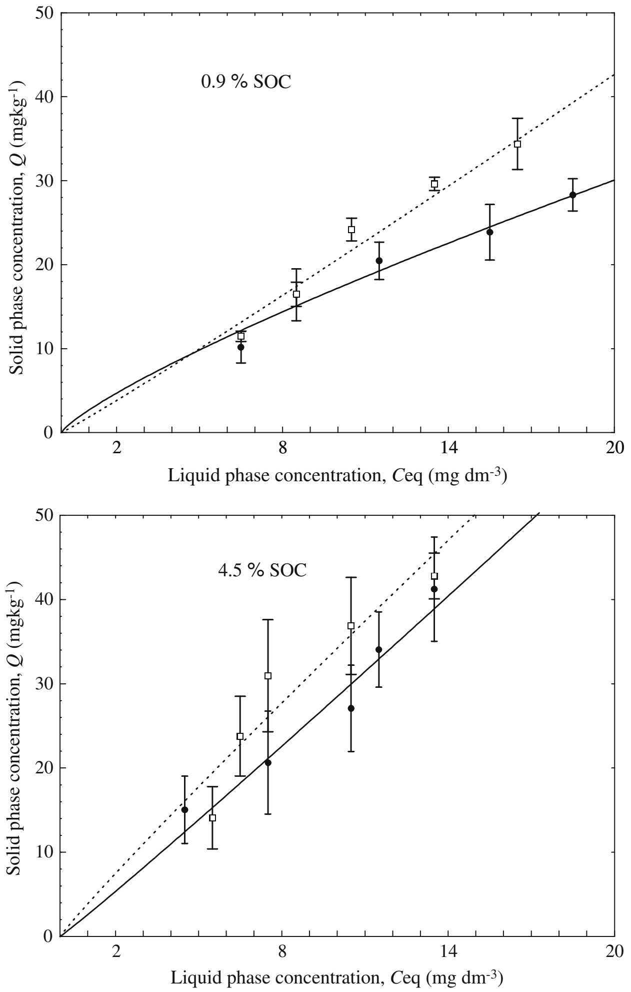

Fig. 1 Adsorption isotherms of atrazine alone and atrazine in the presence of Atpolan by soils with various organic carbon (SOC) contents; Atrazine alone -●-; Atrazine plus Atpolan - -☐ - -; data points are means and the error bars represent 95% confidence intervals

sorption isotherm was nonlinear in nature as depicted by the n values ($n < 1.0$) (Xing et al., 1996). These observations are consistent with our sorption results. The n value was of a higher value in the presence of Atpolan in sandy loam and silt loam but it increased in muck soil. Using the Langmuir or the Freundlich - Langmuir models, we obtained worse fitting of the data. Sorption isotherms of atrazine by soils with the various organic carbon contents are shown in Fig. 1. Curves are adjusted to the Freundlich equation. In muck soil, (4.5% SOC) which has a higher organic content, atrazine showed stronger sorption by solid phase than in soil with 0.9% SOC. Competition for the sorption sites was observed when atrazine was mixed with Atpolan. We observed that Atpolan caused an increase in atrazine sorption. Atrazine sorption isotherms were nearly linear in sandy loam and silt loam, but were non linear in muck soil; sorption coefficients were strongly correlated to soil organic content, as shown by earlier studies (Payá-Pérez et al., 1992; Bernhard-Bitaud et al., 1994; Moreau and Mouvet, 1997). In soil, clay and organic components are usually strongly associated so their individual effects on sorption are difficult to distinguish. In our studies, sorption of atrazine in soil was found to be influenced primarily by the organic matter, while the adjuvant did not greatly affect this process. In this study, atrazine was in formulation, and Atpolan was a mixture of a mineral oil and a surfactant. Such mixtures of various components may complicate the process of sorption. The sorption of herbicide has usually been studied using only standard herbicides. This slight effect of the adjuvant on atrazine sorption by soil may be due to a stronger persistence of the herbicide in soil (Swarcewicz, 2002). Addition of a mixture of paraffin oil and the surfactant Atplus 300F, as Atpol, to atrazine in soil caused a slight change of herbicide sorption in a soil-water system (Muliński et al., 1996). Unfortunately, very little information on the effects and fate of adjuvant are available in the literature (Sánchez-Camazano et al., 1995; Iglesias-Jiménez et al., 1996; Mata-Sandoval et al., 2001; Krogh et al., 2003). It is expected that the requirements for registration will be extended to also include the adjuvants used in pesticide formulations or tank-mix, and to the behaviour of surfactants in the environment.

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