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The effect of Atpolan 80 EC on atrazine residues in the soil

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The persistence of atrazine residues in soils may have an effect on the contamination of the ground water or surface water. Besides the active ingredients, pesticide formulations contain many other compounds called adjuvants. One of them is the Atpolan 80 EC which belongs to the group of oil mineral adjuvants used as tank-mix. The utilization of a fraction of paraffin oil 1113 is one of the examples of utilising waste as the component of Atpolan 80 EC in agriculture. When the Atpolan concentration comprised 1.25% (v/v), the atrazine degradation rate decreased in the sandy loam and muck soil. The half-life of atrazine increased over a period of 40 or 57 days, depending on the type of the soil. The least significant effect was caused by Atpolan concentration at 0.25 and 0.75%. This result points at the capability of limiting atrazine run-off and leaching down the soil profile. Each ingredient of the pesticide, besides having the overall ability to distribute between different phases, also demonstrates some single compound behaviour. This paper shows our current understanding of the factors that influence the adjuvant performance and their potentially complex interactions with the pesticide.

Keywords: atrazine, adjuvant, persistence, soil.

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INTRODUCTION

An adjuvant has been defined as „an ingredient in the pesticide prescription, designed to enhance the activity or other properties of a principal ingredient"[1]. With the growing use of surfactants and/or other adjuvants as additives capable of modifying the physicochemical properties, application technology, adsorption, action, and residual fate of agricultural chemicals, one must carefully consider their use in pesticides. Adjuvants used as postemergence sprays are of two general types: the formulation adjuvants which are part additives already present in the container when purchased by the dealer and the spray adjuvants are the substances added along with the formulated product to the water in the tank of the spray equipment before the application in the fields[2]. The liquid that is finally sprayed over the tops of weeds and crops often contains both the formulation and the spray adjuvants. Many papers concerning the efficacy studies of pesticides have compared the effectiveness of different adjuvants. Only very few papers discuss the environmental toxicity and the risk of adjuvants[2]. The Atpolan 80 EC belongs to oil mineral recommended for atrazine as a spray adjuvant. Atrazine, the 2-chloro-4-(ethylamine)-6-(isopropylamine)-s-triazine, has been used globally to stop pre- and post-emergence broadleaf and grassy weeds in major crops since 1959. This herbicide´s run-off and leaching down the soil profile has become a serious environmental problem and a primary source of surface- and groundwater pollution[3]. As of today, atrazine is supposed to be withdrawn from common use for crop protection by 2008 (Directive 2000/60/EC 2000). Recently, the EPA stated that individual re-registrations of atrazine products will be completed shortly. Nonetheless, research into atrazine residues has not been discontinued in different segments of the biosphere under various environmental conditions[4]. The papers published previously showed that the presence of Atpol influenced the persistence of atrazine in soils[5].

The purpose of the present experiment was to obtain the information on the persistence of atrazine in the presence of various concentration levels of Atpolan 80 EC in two soils over a period of 200 days under laboratory conditions. The experimental data have been used to develop either the empirical or process-driven estimation models for potential pesticide residues in the soil.

MATERIALS AND METHODS

Two types of soil were used in laboratory experiments. The surface soils were taken from Lipnik, North-West Poland. The soils from the surface layer of 20 cm of soil were collected. First, the muck soil with an organic matter content of 4.5%, which contained 88% sand, 5% silt, and 7% clay, with the pH value of 6.4. The second soil, a sandy loam, with an organic matter content of 1.6% and containing 72% sand, 16% silt, and 12% clay, of the pH value 6.5. 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. Atrazine were prepared at a concentration level of 5.1 $mg \cdot kg^{-1}$. Atpolan 80 EC contained 80% paraffin oil (Agromix, Poland). An adjuvant concentration of 0.25; 0.75 and 1.25 % (v/v) was used. The experiment was conducted under control conditions and lasted 200 days. Portions of the soil (400 g) were treated with aqueous suspension of atrazine to produce a herbicide concentration of 5.058 mg kg^{-1} air-dried soil. Water was added to bring the water content to 60% field capacity (FC). After mixing the soil, the samples were transferred to jars and incubated at $20 \pm 2^{o}C$. All the treatments were replicated three times. The jars were opened once a week to allow aeration and the water content was adjusted at the same time. Subsamples (50 g) were taken for herbicide residue analysis 2 hours after the initial mixing, and 10, 50, 100, 150 and 200 days after treatment. Subsamples of soil were extracted in Soxhlet for 2 h with 100 cm^3 of acetone. After the final extraction, the soil was rinsed with several portions of acetone in a Buchner funnel. To the acetone extract 50 cm^3 distilled water and 100 cm^3 dichloromethane were added in a separatory funnel that was shaken to transfer the atrazine residue into the dichloromethane phase. The organic layer was collected, and stored over anhydrous Na_2SO_4. The extract was evaporated to obtain 2 cm^3 and cleaned on a Florisil column. Gas chromatography was done on a GLC instrument, Pye Unicam, with FID and ECD detectors and the capillary Carlo Erba-Vega 6180. The recovery rate of atrazine from soil fortified at the 5.1 mg kg^{-1} level was 98.1 ± 4.5%.

Data on soil degradation of atrazine were subjected to variance analysis (ANOVA). The assessment of homogeneous groups was performed by means of the calculated confidence interval at the 5% level of significance by means of Tukey's least significant difference test. The plots of linear model (Eqn 3) predicted curves were obtained from the STATISTICA v.6, available as part of „Statistics for Windows" package with the non-linear regression program. The values of the estimated parameters in equation 3 were found using the nonlinear least square Lavenberg-Marquardt method. The first-order reaction kinetic model was used for the description of degradation reaction of the atrazine in soils. So, it may be classified as a one-compartment, single-phase, model. The rate of degradation is proportional to the concentration in the soil, i.e.,

$$r = -\frac{dC_T}{dt} = kC_T \quad (1)$$

where C_T is the total concentration, t is the time (days) and k is the reaction rate constant ($days^{-1}$). The integrated form of Eq. (1) gives Eq. (2):

$$C_T(t) = C_0 e^{-kt} \quad (2)$$

where C_0 is the initial concentration at time t = 0. When Eqs. (1) and (2) are true, the logarithm of concentration is linear as a function of time:

$$\ln C_T(t) = \ln C_0 - kt \quad (3)$$

Thus the two parameters C_0 and k are commonly estimated using a simple linear regression of the natural logarithm of concentration onto time. The time at which the concentration reaches half of its initial value is referred to as the half-life ($T_{0.5}$, day). Substitution into Eq. (2) or (3) $C_T(T) = 0.5 \cdot C_0$ gives:

$$T_{0.5} = \frac{\ln 2}{k} \quad (4)$$

Under practical conditions, particularly in the field, degradation cannot always be separated from other processes leading to pesticide degradation[6].

RESULTS AND DISCUSSION

An analysis of variance for atrazine residues in the soil under controlled conditions showed a significant difference between the soil types (Table 1).

The influence of Atpolan 80 EC on atrazine residue was stronger in the muck soil than the sandy loam and this effect increased with the concentration of adjuvant. The simple first-order model was empirically fitting to data and obtained R^2 from 0.9499 to 0.9836 (Eq. 3). The linear regression analysis of atrazine alone as well as in the presence of various concentration levels of Atpolan 80 EC against time of incubation for each treatment was statistically significant ($P<0.05$), and the calculated half-lives are shown in Table 2 (Eq. 4) and Figures 1, 2. The results indicated the lack of difference between 0.25% and 0.75% of Atpolan 80 EC treatment on the degradation of atrazine in the sandy loam and the muck soil (Tab. 2).

The value of half-life of atrazine in the presence of 0.75% Atpolan in the sandy loam increased over 17 days. After increasing Atpolan concentration to 1.25% , this value enhanced over 40 days. Figure 1 shows the degradation of atrazine in the presence of 0.75% and 1.25% of Atpolan 80 EC. In all the cases the degradation follows the first-order kinetics (r significant at $P \leq 0.001$). The kinetics of atrazine uptake by the muck soil as affected by the presence of adjuvant listed in Table 2 is given in Figure 2, respectively. The results indicated that in the presence of Atpolan 80 EC the persistence of atrazine in the muck soil was significantly affected.

The half-life of atrazine in the muck soil increased over 27, 39, and 57 days in the presence of 0.25, 0.75, and 1,25% Atpolan 80 EC, respectively. The first-order model however, commonly underestimates the initial rate and over-estimates the final rate[7]. This failure has been accounted for by assuming two first-order processes which appear to fit the data but have no theoretical basis[8, 9]. Several hypotheses to explain these phenomena have been offered and included: reaction kinetics of an order higher than one; processes in addition to decomposition affecting the catabolism of the pesticide; sorption processes influencing the availability of the substrate for decomposition; the heterogeneity or spatial variability of the soils; the multiphase solution of herbicide formulation. In this case, the term $DT_{0.5}$ value is more appropriate and reflects

Table 1. An analysis of variance (ANOVA) of atrazine in the soil under laboratory conditions

Experimental factor	Variability of experimental factor	Concentration of herbicide in soil ($mg \cdot kg^{-1}$)		
		100 DAT	150 DAT	200 DAT
Soil type	Sandy loam	2.26 a	1.56 a	1.39 a
	Muck soil	3.30 b	2.70 b	2.62 b
Concentration of adjuvant	Atrazine alone	2.58 a	1.92 a	1.77 a
	+ 0.25% Atpolan	2.69 ab	2.06 ab	1.92 b
	+ 0.75% Atpolan	2.87 ab	2.16 b	2.05 b
	+ 1.25 % Atpolan	3.00 b	2.39 c	2.30 c

a, b, c – means in the column marked by the same letters do not differ significantly at the level of 0.05 (Tukey test)

Table 2. A summary of the parameters obtained while fitting the first order kinetic model of atrazine degradation in the presence of Atpolan 80 EC in the soil

Treatment	Soil					
	Sandy loam			Muck soil		
	$k \pm$ SE (10^{-3} day^{-1})	r^2	$T_{0.5}$ (days)	$k \pm$ SE (10^{-3} day^{-1})	r^2	$T_{0.5}$ (days)
Atrazine alone	7.26 ± 0.33	0.98	95	3.83 ± 0.27	0.96	180
Atrazine + 0.25 % Atpolan	6.90 ±0.42	0.97	100	3.35 ± 0.28	0.95	207
Atrazine + 0.75 % Atpolan	6.16 ± 0.30	0.98	112	3.16 ± 0.26	0.95	219
Atrazine + 1.25 % Atpolan	5.13 ± 0.32	0.97	135	2.93 ± 0.23	0.96	237

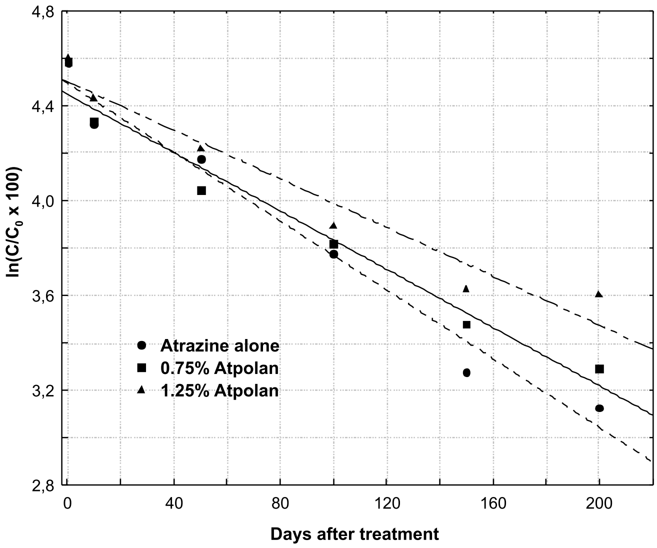

Figure 1. The effect of Atpolan 80 EC on the degradation rate of atrazine in the sandy loam under controlling conditions

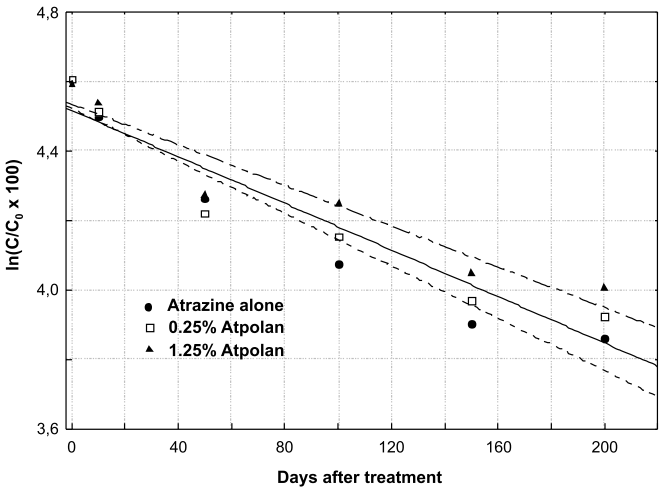

Figure 2. The effect of Atpolan 80 EC on the degradation rate of atrazine in the muck soil under controlling conditions

the time for the degradation of half of the initial concentration better than $T_{0.5}$. The experimental data have been used to develop either the empirical or the process-driven models for estimating the potential pesticide residues in the soil[6].

Soil is a complex biological and chemical medium in which factors such as texture, nutrient status, organic matter, and pH are important variables[7]. Atrazine is known to be poorly adsorbed by soil and to have high solubility, resulting in an increase in mobility and detection of this compound in the surface and ground water[10]. The organic matter content of soil may be also important in determining herbicide persistence. The half-life of atrazine alone increased in the sandy loam from 95 days to 180 days in the muck soil (Table 2). The degradation rates of atrazine in soil in the presence of Atpolan decreased as the concentration of adjuvant increased, presumably because of the increased adsorption and, hence, decreased the availability for degradation in soil with a higher content organic matter content. The influence of the soil type and adjuvant on the rate of atrazine degradation is shown in Figures 1 and 2.

For pesticides the important factors influencing the mobility at landfill sites are the presence of the co-solvent, surfactant and dissolved organic carbon in the landfill leachate[10]. Surfactants have been used to increase the mobility or the solubilization of hydrophobic organic compounds, such as polycyclic aromatic hydrocarbons, herbicides in soils in the remediation or the soil washing process. The addition of surfactants increases the concentration of hydrophobic compounds in water by the solubilization or emulsification. In addition, surfactants have strong adsorption capacities onto organic matter and clay minerals. The previous study showed that addition of four nonionic surfactants increased the aqueous solubility of the triazines by 3 to 4-folds[10].

When the Atpolan concentration was 1.25% (v/v), the atrazine degradation rate decreased in the sandy loam and the muck soil. The half-life of atrazine increased over the period of 40 or 57 days, depending on the type of the soil. The smallest effect was caused by Atpolan concentration at 0.25 and 0.75%. This result indicates the capability of limiting the run-off and leaching down the soil profile of atrazine in the presence of Atpolan 80 EC adjuvant. Each ingredient of the pesticide, besides having the overall ability to distribute between different phases, also exhibits some single compound behaviour. Also, further, studies are needed concerning the influence of adjuvants on the mobility of xenobiotics in the soil, particularly the sorption processes. The utilization of a fraction of paraffin oil 1113 is one of the examples of utilising waste as the component of Atpolan 80 EC in agriculture.

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