

Adsorption and Degradation of Anilofos in Different Soils and its Environmental Impact in Soils

Maheswari, S.T.* and Ramesh, A.

International Institute of Biotechnology and Toxicology, Department of Analytical Chemistry,
Padappai, Chennai 601 301, Tamil Nadu, India

Received 19 May 2011;

Revised 14 Aug. 2011;

Accepted 26 Nov. 2011

ABSTRACT: Adsorption of anilofos was studied in four soils (topsoil from alfisol, inceptisol, oxisol and vertisol). The order of adsorption of anilofos was Vertisol > Oxisol > Alfisol > Inceptisol. The soil sorption coefficient K and the soil organic carbon sorption coefficient K_{oc} are the basic parameters used for describing the environmental fate of the herbicides. In top soil the calculated K values were 5.43, 3.35, 9.41, 11.73; K_{oc} values were 1086.00, 1288.46, 1191.14, 771.71 and K_c values were 9.05, 33.5, 20.02 and 36.66 from Alfisol, Inceptisol, Oxisol and Vertisol respectively. Field experimental plots with no previous history of anilofos were selected and studied the degradation of anilofos in top soil collected from Alfisol and Inceptisol. The half-life of anilofos in topsoil from Alfisol: T_1 - 3.17 days and T_2 3.67 days and in Inceptisol: T_1 - 3.91 days and T_2 - 4.55 days. The degradation of anilofos followed first order kinetics. Anilofos persisted for a longer duration in Inceptisol than in Alfisol. The combination of degradation data ($t_{1/2}$ - soil) and organic carbon based sorption (K_{oc}) data of herbicides have been used to assess the pesticide environmental impact in soils through Gustafson Ubiquity Score (GUS). The GUS values were found to be 0.48 in top soil from alfisol and 0.53 in inceptisol.

Key words: Anilofos, Adsorption, Desorption, Degradation, GUS

INTRODUCTION

Degradation is a fundamental attenuation process for pesticides and other organic contaminants on the environment and is affected by many factors like interaction with microorganisms, chemical and soil constituents (Rao *et al.*, 1983; Jury *et al.*, 1987; Ainsworth *et al.*, 1993; Alexander, 1994). It is generally accepted that sorption limits the degradation of pesticides by reducing their partition into soil liquid phase. Organophosphorus compounds are generally a concern in more localized situation than the organochlorines. These compounds are less persistent but more effective compared to the chlorinated compounds used for similar purpose (McEwen and Stephenson, 1979). They are readily degraded on the plant surface, inside plants, soil, water and pose less serious problems of environmental pollution. However, they are more acutely toxic than their chlorinated alternatives, but their persistence is much less. They are also much more soluble in water and as a consequence are less likely to accumulate in biological tissue. Degradation of anilofos under UV light was studied Gupta *et al.*, (1988 and 1993) and the photoproducts thus obtained were confirmed by GC-MS. Rai *et al.*, 1998 studied the adsorption and desorption pattern of anilofos in six diverse soils.

Degradation of anilofos in six different enrichment soil culture was studied by Rai *et al.*, 1999. In all the six different soil culture, anilofos showed 60 - 80% degradation. Data was compared with the persistence of anilofos with the pendimethalin and was reported that the fast degradation occurred when compared to pendimethalin. In another study conducted by them to study the persistence of pendimethalin and anilofos in six diverse soils reported that the dissipation of pendimethalin was less than anilofos and also the kinetics revealed that the degradation of two herbicides followed first-order reaction. Patnaik *et al.*, 1995 in their study reported that anilofos when applied singly had no effect on nitrogenase activity. Because sorption and degradation are the two most important processes governing fate and transport of chemical contaminants in the environment, a comprehensive understanding of their relationship would help in the management of pesticides in agricultural fields and in the assessment of their potential to contaminate ground water. This information is also essential for development of remedial techniques for chemical contaminants and for the optimization of remedial operations. The present study was conducted with an aim to know the adsorption and desorption of

*Corresponding author E-mail: maheswariraja@yahoo.com

anilofos in four different soils and degradation study in two soils. The data derived from both the studies were used to assess the environmental effect of anilofos by calculating the GUS.

MATERIALS & METHODS

Anilofos, analytical reference standard of purity 93% was procured from Gharda Chemicals Ltd., Mumbai, India. All other reagents, chemicals and solvents used for adsorption, desorption and degradation studies were procured from Merck, Germany.

Accurately weighed 10 mg of anilofos reference standard of purity 93% and made up the volume to 10 ml using mobile phase (acetonitrile:water, 70:30 v/v). Different concentrations of anilofos viz., 2.0, 1.0, 0.2, 0.1, 0.02 and 0.01 µg/mL were prepared by diluting the stock solution (930 µg/mL). Injected the standard solutions sequentially and measured the peak area resulting from the elution of the compound. A calibration curve was plotted for concentration of the standards injected versus area observed.

Alfisol and Inceptisol collected from the depth of 0-10 cm from the respective fields prior to herbicide application were used for adsorption study. The collected soil was air dried, sieved through a 2 mm sieve and stored. For determination of equilibration time, 5 g of soil was taken in a series of centrifuge tubes and 25 ml of known concentration of anilofos was added and kept shaking for different time intervals (2,4,8,12, 18 and 24 h). Weighed 10 mg of Anilofos 30% EC into a 10 ml standard flask and volume was made up using 0.01M CaCl₂. From this stock solution different concentrations of the test solution viz., 1, 2, 3, 4, 6 µg/mL which corresponded to 5, 10, 15, 20 and 30 mg/kg respectively. The experiment was conducted at temperature 22 ± 3°C. The equilibration time was found to be 6 h and was used in adsorption studies. Five grams of topsoil from each soil viz., alfisol and

inceptisol were transferred to two separate 50 ml centrifuge tubes and 25 ml each of the anilofos solutions of 6 µg/mL which corresponded to 30 mg/kg was transferred into it. A blank with 25 ml of 0.01M CaCl₂ alone was used for comparison. The contents were kept shaking for 6 h and at the end of the equilibration period the contents were centrifuged at 5000 rpm for 10 minutes. The supernatant was decanted without disturbing the soil, partitioning and column cleanup step was followed and and quantified for anilofos content.

Agricultural plots with no history of previous application of anilofos were selected for conducting the degradation studies. Field preparations were made by irrigating with water to a level of 5 cm above the surface. The field was ploughed once with mould board plough and leveled using a leveling board. Nine different trial plots each with a dimension of 5 x 4 m (20 m²) were prepared. Isolation distance of 1m was maintained between plots. All four sides of the plots were protected by soil boundaries (bunds) raised to a level of 30 cm height and 30 cm width. The seedlings (variety ASD19) were transplanted in the main field at the correct age and at optimum spacing of 20 x 10 cm. Spraying was done three days after transplanting. Anilofos (30% EC formulation) at recommended dose 450 g a.i./ha (T₁) and double the recommended dose 900 g a.i./ha (T₂) was applied. For T₁, 3 ml of anilofos 30% EC was dissolved in 1 l of water and sprayed in 20 m² using a knapsack sprayer. For T₂, 6 ml of anilofos 30% EC was dissolved in 1 l of water and sprayed in 20 m² using a knapsack sprayer. Three different plots (triplicates) were sprayed for each dose. A further three different triplicate plots were sprayed with water (T₀) without any herbicide and maintained as control. Degradation studies were carried in the topsoil of two soil alfisol and inceptisol. The physico chemical properties of soil are presented in Table 1. After spraying soil samples were collected at predetermined intervals (0,1,3,5,7,10,15,20,30,40,60 days).

Table 1. Physico- chemical properties of soil

Soil type	Alfisol	Inceptisol	Oxisol	Vertisol
pH (1 :5 H ₂ O)	4	7.2	6	5.2
Sand (%)	10	73	21	39
Silt (%)	30	17	32	29
Clay (%)	60	10	47	32
Organic Carbon (%)	0.5	0.26	0.79	1.52
CEC (meq/100g)	17.2	11.2	16.5	15.4

A composite surface soil sample was drawn from the experimental field for initial analysis. At each sampling occasion, soil samples were collected randomly from nine different spots from each plot. Likewise, soil samples were collected from all of the triplicate plots at two doses. Samples from the control plots were collected before samples were collected from the herbicide treated plots. The sample size was ~1 kg from each plot. Pebbles and stones were removed, the soil was mixed thoroughly, and 250 g was sub sampled for analysis. The sub samples were stored in refrigerator at -20°C until analysis.

A 10 g soil sample was weighed into an Erlenmeyer flask and extracted with 100 ml of distilled water / acetonitrile mixture (1:1 v/v) using an end-over-end mechanical shaker for 30 min. The sample was filtered into a 500 ml round-bottom flask and rinsed with 50 ml of the same solvent; the volume was reduced to 50 ml in rotary evaporator at 40°C.

Partitioning step was followed by transferring the sample into a clean 250 ml separatory funnel and extracted with 100 ml of methylene chloride. The contents were shaken vigorously to partition the entire test chemical into methylene chloride. The pressure built in the separatory funnel was released often. The funnel was kept undisturbed for the layers to separate and the organic layer was collected in an evaporation flask. The aqueous layer was again partitioned with 100 ml of methylene chloride, shaken and the funnel kept undisturbed and collected the organic layer. Combined the collected organic layers and concentrated to near dryness in a vacuum rotary evaporator at 40°C.

Column cleanup step was performed using a glass column packed with 2 g of florisil (60-100 mesh), and washed with two 5 ml portions of 2% methanol in methylene chloride followed by two 5 ml portions of iso-octane. After the column had been conditioned, the sample was redissolved in 2 ml methylene chloride and diluted with 8 ml iso-octane. The entire sample was then transferred into the column; sample was eluted with 40 ml of 2% methanol in methylene chloride at a rate of 1 ml /min. The collected eluate was evaporated to dryness by rotary evaporator. The residue was dissolved in 3 ml of 10% acetonitrile in water, filtered and analyzed by HPLC.

The method adopted in the study was published by Ramesh and Maheswari, 2003.

All samples were separated and quantified by Shimadzu High Performance Liquid Chromatographic system (Shimadzu, Kyoto, Japan) equipped with LC-10ATvp pump and SPD-10 AVvp UV-VIS detector. A CBM-101 communication module

supported by CLASS LC-10 software was used. A Phenomenex C₁₈ column 25cm length x 4.6mm i.d was attached to the system. The mobile phase (acetonitrile:water (70:30 v/v)) flow rate was fixed at 1.5 ml/min. The λ_{max} was set at 220 nm for detection purposes. The approximate retention time for anilofos was 7.8 minutes. At the limit of detection 0.01µg/ml the signal to noise ratio maintained was 3:1.

Different known concentrations of anilofos (2.0, 1.0, 0.2, 0.1, 0.02 and 0.01 µg/ml) were prepared in acetonitrile by diluting the stock solution. Injected 20 µl of standard solution and measured the peak area. Validation of the method was performed in terms of recovery studies before the analysis of unknown sample. The recovery study was conducted in the soil and 0.01M CaCl₂. 10 g of control soil sample was taken. Using pipette, 1ml of standard solution of anilofos of known concentration was added uniformly on the surface of the matrix and mixed well before extraction. The extraction was performed as described in the methodology. Recovery study was conducted for adsorption study with 10ml of 0.01M CaCl₂.

The recovery and detection limits of anilofos are shown in Table 2. The recovery ranges from 85 to 94% in soil and the limit of quantification is 0.001 µg/g and the signal to noise ratio is 3:1. No substrate interference was observed at this quantification level as evidenced by the control sample analysis.

From the data on the quantities of anilofos adsorbed the corresponding equilibrium concentration, adsorption isotherms were constructed. They were plotted as per Freundlich adsorption equation since this could be applied to such heterogenous systems like soil herbicide and water suspension as

$$x/m = KC^{1/n}$$

where

x/m=quantity of herbicide adsorbed per unit weight of soil (mg/g),

C= equilibrium concentration, K=adsorption coefficient and 1/n = slope.

The constants K and n were obtained respectively from the intercept and reciprocal of the slope of straight line obtained by plotting the data on a log-log scale as $\log(x/m) = \log K + 1/n \log C$. Data is presented in Table 3.

The normalized sorption coefficient (K_{oc}) was calculated as

$$K_{oc} = (K/OC) \times 100,$$

Table 2. Recovery and limits of detection of Anilofos from top soil of Alfisol, Inceptisol, Oxisol and Vertisol

	Soil				0.01M CaCl ₂
	Alfisol	Inceptisol	Oxisol	Vertisol	
Recovery (%)	87.17±1.47	91.67 ±1.97	89.83±2.64	89.00±3.85	87.83±1.47
RSD (%)	1.69	2.15	2.94	4.32	1.68

Limit of detection: 0.001 µg/g ; Fortification level : 1.0 – 0.005µg/g

Limit of quantification : 0.005 µg/g

No. of analysis: Six replications

Table 3. Anilofos adsorption isotherms, coefficients of determination (r²), adsorption coefficient (K), distribution coefficient based on clay content (K_c) and organic carbon normalized distribution coefficients(K_{oc}) in top soil from alfisol, inceptisol, oxisol and vertisol

Soil	pH	Organic carbon (%)	K	K _c	K _{oc}
Alfisol	4	0.5	5.43	9.05	1086.00
Inceptisol	7.2	0.26	3.35	33.5	1288.46
Oxisol	6	0.79	9.41	20.02	1191.14
Vertisol	5.2	1.52	11.73	36.66	771.71

where

K is the Freundlich constant and OC is the percent organic carbon content of soil.

The affinity of anilofos towards the clay content of soils was also evaluated by calculating K_c by the formula

$K_c = (K/C) \times 100$, where K is the Freundlich constant and C is the percent of clay content in soil.

Groundwater ubiquity score (GUS) is an indicator of pesticide environmental impact. It is a function of field half-life (DT₅₀) and organic sorption constant (K_{oc}).

$$GUS = \log_{10}(DT_{50}) \times (4 - \log_{10}(K_{oc}))$$

Based on the adsorption and degradation results, herbicides have been classified as “leachers” or “non-leachers”.

RESULTS & DISCUSSION

Adsorption was greater in the topsoil collected from vertisol followed by oxisol, alfisol and inceptisol which is due to the organic carbon content in respective soils (Table 3 and 4). The higher value of Freundlich K in topsoil from Vertisol may be due to its high soil organic carbon content. Topsoil from vertisol adsorbed greater amount of anilofos per unit organic carbon as noticed by higher K_{oc} than top soil from oxisol, alfisol and inceptisol. The ratio of clay content to organic carbon content is useful parameter to predict adsorption of herbicides in soil (Liu *et al.*, 2008). Hysteresis effect was observed viz, the amount of herbicides desorbed from the soil in comparison to that adsorbed decreased with successive desorption steps (Braverman *et al.*, 1980).

Table 4. Comparison of anilofos adsorbed and desorbed in topsoil of alfisol, inceptisol, oxisol and vertisol

Soil	Amount adsorbed (%)	Amount Desorbed (%)
Alfisol	52.07	45.54
Inceptisol	40.17	50.31
Oxisol	65.30	23.14
Vertisol	70.10	20.31

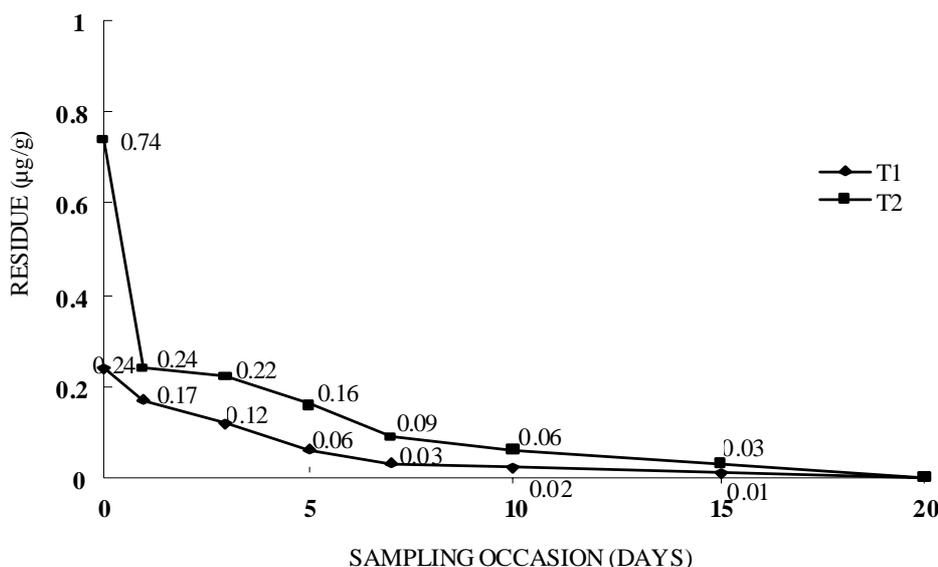


Fig. 1. Initial concentration of anilofos (topsoil from Alfisol)

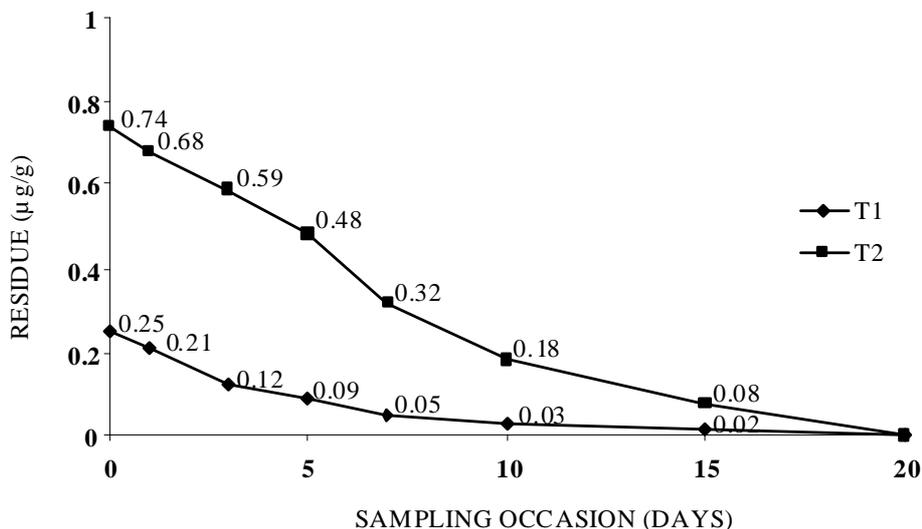


Fig. 2. Initial concentration of anilofos (topsoil from Inceptisol)

K_{oc} , sorption coefficient is a measure of pesticide sorption, which in association with soil organic matter is commonly assumed to be a major mechanism of pesticide sorption in soils. Desorption was high in Inceptisol followed by Alfisol, oxisol and vertisol. This may be due to the lower organic carbon content in the soil (organic carbon content in soil Vertisol > Oxisol > Alfisol > Inceptisol). Thus it is presumed that the molecules are strongly bound at adsorption site. Hence at normal equilibrium the molecules cannot be easily desorbed. It may be concluded that the contribution of organic matter content towards adsorption may mask other factors if the soil contain high amount of organic matter. However, the use of K_{oc} to predict herbicide adsorption fails if the ratio of clay to organic carbon exceeds 30 to 40 (Pionke and De Angelis, 1980).

Soil samples (topsoil from Alfisol) collected from field had the initial concentration of anilofos as 0.24 µg/g and 0.74 µg/g at the tested dosages 450 g a.i./ha (T_1) and 900 g a.i./ha (T_2) respectively (Fig. 1). The residues rapidly dissipated to 0.17 µg/g (T_1) and 0.24 µg/g (T_2) on 1st day. Steady decrease in residues were observed in later on 3rd, 5th and 7th day, with 10th day residues as 0.02 µg/g and 0.06 µg/g in T_1 and T_2 respectively. The residue levels on 15th day were 0.01 µg/g (T_1) and 0.03 µg/g (T_2). By 20th day the residues of anilofos were below minimum detectable level (0.01 µg/g) in both the tested dosages.

Soil samples (topsoil from Inceptisol) collected from field had the initial concentration of anilofos as 0.25 µg/g and 0.74 µg/g at the tested dosages 450 g a.i./ha (T_1) and 900 g a.i./ha (T_2) respectively (Fig. 2).

Herbicide showed continuous dissipation on 3rd, 5th and 7th day. Samples showed continuous dissipation and by 10th day the residues went to 0.03 µg/g (T₁) and 0.18 µg/g (T₂) level. The values observed on 15th day showed the residues of anilofos as 0.02 µg/g and 0.08 µg/g at the tested dosages T₁ and T₂ respectively. By 20th day the residues of anilofos dissipated to below the minimum detectable level in both the tested dosages.

Anilofos had a half-life of 3.17 days in Alfisol in 450 g a.i./ha (T₁) and 3.67 days in 900 g a.i./ha (T₂) whereas in Inceptisol the half-lives were 3.91 and 4.55 days in T1 and T2 respectively.

Degradation pattern can also be correlated with organic carbon content. The organic carbon content in alfisol is high than in inceptisol. In alfisol the molecules are strongly adsorbed to soil and the herbicide molecules available for degradation is less. This plausible mechanism supports the difference in half life between alfisol and inceptisol.

Environmental effect of anilofos was studied using the Gustafson equation (Gustafson, 1989). GUS values were calculated and were found to be low: 0.48 in topsoil from alfisol and 0.53 in topsoil from inceptisol and hence classified as “ non-leachers”

CONCLUSION

The key factor for predicting the environmental fate of herbicides is the sorption mechanism which in turn is dependent mainly on the organic carbon content. The extrapolation of analytical data indicated that the adsorption of anilofos was positively related with organic carbon content. The sorption coefficient (K) values were 5.43, 3.35, 9.41, 11.73; K_{oc} values were 1086.00, 1288.46, 1191.14, 771.71 and K_c values were 9.05, 33.5, 20.02 and 36.66 from Alfisol, Inceptisol, Oxisol and Vertisol respectively. The data clearly indicated that anilofos is bound to organic carbon, subsequently the degradation of anilofos is found to be longer in persistence. The data is supported by low indicative value of GUS.

ACKNOWLEDGEMENT

We are grateful to Indian Council of Agricultural Research, Government of India for their financial support and Director, IIBAT, Dr. P. Balakrishna Murthy for providing necessary facility to conduct the work.

REFERENCES

Ainsworth, C. C., Frederickson, J. K. and Smith, S. C. (1993). Effect of sorption on the degradation of aromatic acids and bases. (In: Linn, D.M. (Ed.), Sorption and Degradation of Pesticides and Organic Chemicals in Soil. SSSA Special

Publication Vol. 32 Soil Science Society of America and American Society of Agronomy, pp. 125-144. Madison, WI. Alexander, M. (1994). Chapter 8, Sorption. In Biodegradation and Bioremediation. Academic Press, San Diego, CA, pp. 114-130.

Braverman, M. P., Dusky, J. A., Locascio, S. J. and Hornsby, A. G. (1990). Sorption and degradation of thiobencarb in three Florida soils. Weed Sci., 38, 583-588.

Gupta, N., Dureja, P. and Sharma, B. K. (1993). Photodegradation of organophosphorous herbicides anilofos. Toxicol. Environ. Chem., 37, 191-194.

Gupta, N., Dureja, P. and Sharma, B. K. (1998). Degradation of organophosphorous herbicides anilofos under UV light. Pesticide Res. J. 10, 123-126.

Gustafson, D. I. (1989). Groundwater ubiquity score: A simple method for assessing pesticide leachability. Environmental Toxicology and Chemistry, 8, 339-357.

Jury, W. A., Focht, D. D. and Farmer, W. J. (1987). Evaluation of pesticide groundwater pollution from standard indices of soil chemical adsorption and biodegradation. J. Environ. Qual. 16, 422-428.

Liu, Z., He, Y., Xu, J., Huang, P. and Jilani, G. (2008). The ratio of clay content to organic carbon content is a useful parameter to predict adsorption of the herbicide butachlor in soils. Environ Pollut., 152 (1), 163-71.

McEwen, F. L. and Stephenson, G. R. (1979). The use and significance of pesticides in the environment. Inc, John Wiley and Sons, 112-115.

Patnaik, G. K., Kanungo, P. K., Moorthy, B. T., Mahana, P. K., Adhya, T. K. and Rao, V. R. (1995). Effect of herbicides on nitrogen fixation (C₂H₂ reduction) associated with rice rhizosphere. Chemosphere, 30 (2), 339-43.

Pionke, H. B. and De Angelis, R. J. (1980). Method for distributing pesticide loss in field runoff between the solution and adsorbed phase. In: CREAMS. A field scale model for chemicals runoff and erosion from Agricultural Management systems. USDA Conservation Research Report. 26. USDA. SEA, Washington DC, pp. 607 - 643.

Rai, A. K., Chhonkar, P. K. and Agnihotri, N. P. (1998). Adsorption-desorption of anilofos on six diverse soils. Pestic. Res. J. 10, 172-177.

Rai, A. K., Chhonkar, P. K. and Agnihotri, N. P. (1999). Persistence of pendimethalin and anilofos in six diverse soils. Pestic. Res. J. 11 (2), 132-137.

Ramesh, A. and Maheswari, S. T. (2003). Dissipation of Sulfosulfuron in Soil and Wheat Plant under Predominant Cropping Conditions and in a Simulated Model Ecosystem. J. Agric. Food Chem., 51, 3396 - 3400.

Rao, P. S. C., Bellin, C. A. and Brusseau, M. L. (1993). Coupling biodegradation of organic chemicals to sorption and transport in soils and aquifers: paradigms and paradoxes. In: Linn, D.M. (Ed.), Sorption and Degradation of Pesticides and Organic Chemicals in Soil. SSSA Special Publication Vol. 32 Soil Science Society of America and American Society of Agronomy, Madison, WI, pp. 1-26.