



Persistence of Oxyfluorfen at Different Temperature and Moisture Levels in Alfisol and Vertisol

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Persistence of oxyfluorfen in Alfisol and Vertisol was studied at three moisture levels (at saturation, FC and 50 % FC) and at two temperature levels ($10 \pm 2^\circ\text{C}$ and $27 \pm 2^\circ\text{C}$) for the period of 137 days in the laboratory. Degradation of oxyfluorfen was more rapid at high temperature and moisture levels. The disappearance curve / semi logarithmic plot followed first order kinetics with two distinct pathways, an initial faster rate followed by a slower and more gradual disappearance. The rate of degradation of oxyfluorfen increased with increase in temperature from 10°C to 27°C . In the present investigation for oxyfluorfen the rate of reentry into labile pool was considered negligible. The rate of entry into bound pool was higher for Vertisol than for Alfisol and was higher at higher temperature. It decreased with soil moisture in the order: saturation > field capacity > 50% field capacity. At high temperature and moisture level, the half values were lower compared to low temperature and moisture level. Persistence of oxyfluorfen was varied by more than 30 per cent between the field studies and laboratory studies.

Key words: Oxyfluorfen, persistence, Half life values, temperature and moisture levels, alfisol, vertisol.

Persistence is an important characteristic of an herbicide affecting efficacy, exposure to environmentally important transport, and carryover to subsequent crops. The period during which the pesticide remains intact and biologically active has great practical importance in determining how well it performs its intended task in soil. It is also called as time of residence of chemical in soil and is measured in terms of half life. The persistence of herbicide depends on number of factors like edaphic and climatic conditions as well as properties of chemical itself. The persistence of soil applied herbicide is of concern during the period in which weed control is required and also in regard to potential damage caused to succeeding susceptible crops. The effects of soil temperature and moisture on herbicide degradation are straight forward and the microbial and chemical degradation are enhanced with increased temperature and moisture. Degradation of many herbicides follows first order kinetics, meaning that the rate of degradation is proportional to the herbicide concentration (Brar *et al.*, 2006). The dissipation coefficients of oxyfluorfen in soils of different moisture contents (30 per cent, 60 per cent and 90 per cent of soil field capacity) and temperature (10°C , 25°C and 40°C) were studied by Yen *et al.* (2003). They reported that half life of oxyfluorfen ranged from 72 to 160 days and also revealed that the dissipation was rapid at high temperatures and almost there is no dissipation at 10°C . Scrano *et al.* (2004) reported that oxyfluorfen was moderately

persistent in most soil environments with a representative field half life of about 30 to 40 days. In laboratory studies, soil half life was six months indicating very low rates of microbial degradation. Oxyfluorfen is used extensively in vegetable crops in Andhra Pradesh, the information on persistence of oxyfluorfen was scanty, hence present experiment was carried out to study the persistence of oxyfluorfen in soil keeping in view Walker (1974) model of using lab incubated soil for predicting residues in soil under field conditions and to confirming these models under field conditions.

Materials and Methods

Soil samples were collected from different Agro climatic zones of Andhra Pradesh and at each selected location, the soil samples were collected from 15-20 different spots at a depth of 0 -22 cm, quartered and about 5 to 10 kg of each soil sample was brought to the laboratory, air dried under shade and processed by passing through a 2mm size sieve. These 2 mm sieved soils were properly labeled and stored in cloth bags for further studies. The physico-chemical properties of soils were given in Table 1.

A known quantity of 2 mm sieved soil samples were spread on paper and treated with oxyfluorfen. Oxyfluorfen was diluted in methanol in order to get a concentration of $10 \mu\text{g mL}^{-1}$. This was sprayed on the soil sample and then methanol was allowed to evaporate. Ten gram portions of herbicide treated soil samples were weighed in polythene bags and

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the polythene bags were sealed after adding predetermined quantities of water to bring the moisture levels to saturation, field capacity and 50 per cent field capacity. Duplicate soil blanks without the herbicide were maintained simultaneously.

The samples after moisture treatment were incubated at $27 \pm 2^\circ\text{C}$ and $10 \pm 2^\circ\text{C}$ and the soil samples were analyzed at 0,3,7,15,30,45,60,90,105 and 135 days intervals for the amount of herbicide retained in the soil solution. For this soil sample collected at each interval was extracted with methanol to measure the quantity of herbicide extracted. The individual soil samples at each interval was transferred to 60 mL capacity screw capped test tubes and shaken with two 20 mL portions of methanol for 30 minutes on mechanical shaker and filtered through Whatman No 1 filter paper. The final volume of extract was made up to 50 ml and the absorbance was measured on UV Visible spectrophotometer (GS 5701) using matched silica cuvettes at wavelength of 213 nm for oxyfluorfen. The concentrations of oxyfluorfen and in methanol extract were determined with reference to the standard curves after correcting the soil blanks.

Table 1. Physico-chemical properties of soils under study

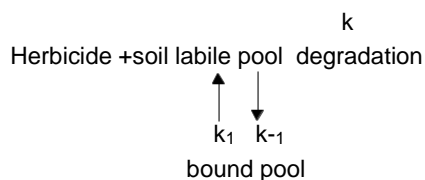
Physico-chemical character	Alfisol	Vertisol
P_H	7.71	7.82
E.C (dS m^{-1})	0.24	0.22
Organic carbon (g kg^{-1})	3.1	8.5
Sand	74.40	55.8
Silt	13.00	11.0
Clay	12.60	33.2
Texture	Sandy loam	Clay loam
Water Holding Capacity:		
At saturation	36%	28%
Field Capacity	20%	16%
50% Field Capacity	10%	8%

Models for persistence of herbicides in soils

The concentrations of methanol extractable herbicides at different moisture and temperature levels at various time interval were plotted against time. These were then plotted as logarithms of amount recovered vs time to determine the rates of disappearance. The disappearance curves consisted of two typical segments, one a steeper line followed by path of much smaller slope indicating two paths of disappearance. The disappearance in each case was interpreted in term of model suggested by Hamaker and Goring (1976). According to this model, a soil applied chemical distributes into two different compartments, which may be termed labile and bound. The labile pool consists of the fraction of chemical dissolved in soil solution and that adsorbed reversibly by soil. The herbicide in labile pool is easily degradable and extractable in suitable

organic solvents under mild conditions. The bound pool consists of the herbicide adsorbed strongly on more restricted sites on soil and unlike labile pool cannot be desorbed by solvents under mild conditions.

The scheme of events that take place during the interaction of chemical with soil can be pictured as



where, k is the rate constant for degradation of chemical

k^{-1} for reentry into labile pool

k_1 for entry into bound pool

As a valid approximation the slow rate of re entry into labile pool was considered negligible. The rate constants were obtained from semi log plots of herbicide extracted vs time.

The constants k, k_1 and k^{-1} were calculated as per the method of Hamaker and Goring (1976) as described below:

$$k_1 = -m - k - (1 + k/m)k^{-1}$$

$$k^{-1} = \frac{b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$\text{Where } a = \frac{(R_2 - 1) \times k_2}{m_2}$$

$$b = \frac{-4k_2 - 2(R_2 + 1)k}{m}$$

$$c = (R_2 - 1)m_2 - 4mk - 4k_2$$

$$R = \frac{2l}{C_0} - 1$$

$$C_0$$

Where k = Difference slope of semi log plot

m = Slope of the steady state line or smaller slope

l = Anti log of intercept of extrapolated line of steady state line or slope

C_0 = Initial conc. of the herbicide

These calculations involve a number of interdependent steps as they lead to large cumulative errors, since a clear two stage disappearance of herbicides was seen with time. The rate of re entry from bound pool to labile pool is considered negligible, as a valid approximation, the steeper slope (k) can be considered as rate of decomposition as the smaller slope (m) as the rate of re entry into bound pool. These were determined far from the slope of the curve and for the difference slope of the steep and flatter portion. This is explained in figure 1.

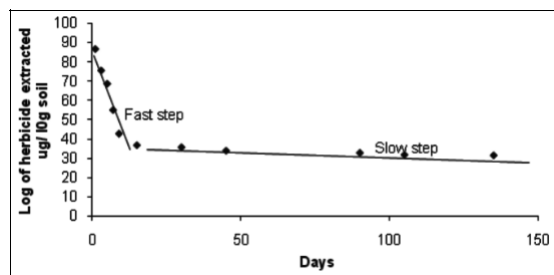


Fig.1 Disappearance curve

The activation energy was also calculated for all the rate constants from the

Arrhenius equation

$$E_a = R \times \ln \frac{k_2}{k_1} \times \frac{T_2 \times T_1}{T_2 - T_1}$$

where, k_1 and k_2 are the rate constants at temperatures T_1 and T_2 respectively and R is the gas constant. E is the energy of activation in K J mole^{-1} .

A computer model of simulation of herbicide persistence described by Walker (1974) and revised by Walker and Barnes (1981) has been shown to predict the persistence of herbicides in the field.

Hence, the rate of degradation has been established in the same soil in the laboratory. However these studies were made in England, hence this model was evaluated in field conditions using the field persistence data for oxyfluorfen. For this a field experiment was conducted in College Farm, Agricultural college, Rajendranagar.

Results and Discussion

The disappearance curve consists of two distinct pathways, an initial faster rate followed by a slower and more gradual disappearance. The semi logerthemic plot of the data indicated that oxyfluorfen followed first order kinetics. The first order kinetic plot confirmed two distinct rates of disappearance. The faster mode of disappearance continued only till 45 to 60 days whereas slower rate of disappearance continued till the end of study. This pattern is similar to that was observed by Brar *et al.*, (2006). A complete analysis of the persistence data was carried out for resolving the constants k , k_1 , k_{-1} according to the method given by Hamaker and Goring (1976) and presented in Table 2. The rate of degradation of oxyfluorfen increased with increase in temperature from 10°C to 27°C and

Table 2. Specific reaction rates (day^{-1}) for different steps during dissipation of oxyfluorfen in Alfisol and Vertisol (V_2) at different temperatures and moisture levels

Soil	$27 \pm 2^\circ\text{C}$			$10 \pm 2^\circ\text{C}$		
	Saturation	FC	50% FC	Saturation	FC	50% FC
Alfisol						
k	0.0071	0.0063	0.0061	0.0046	0.0042	0.0036
k_1	0.0043	0.0038	0.0036	0.0028	0.0024	0.0021
k_{-1}	0.0022	0.0013	0.0008	0.0018	0.0011	0.0006
Vertisol						
	$27 \pm 2^\circ\text{C}$			$10 \pm 2^\circ\text{C}$		
k	0.0077	0.0073	0.0065	0.0056	0.0049	0.0047
k_1	0.0068	0.0064	0.0064	0.0051	0.0046	0.0041
k_{-1}	0.0056	0.0051	0.0046	0.0045	0.0038	0.0033

followed order $k_{-1} < k_1 < k$. The rate of entry into bound pool was higher for Vertisol than for Alfisol and was higher at higher temperature. It decreased with soil moisture in the order: saturation > field capacity > 50% field capacity. The constant for rate of entry in to bound pool was higher for Vertisol as compared to Alfisol. This can be attributed to the fact that the clay content and organic matter content of Vertisol was higher than Alfisol and there by herbicides may be adsorbed more strongly on these sites in soil and can not be desorbed by organic

solvents. From the rate constants, it can be seen that there was higher rate of degradation of herbicides at 27°C than at 10°C .

Half life values of oxyfluorfen at two temperatures and moisture levels were calculated from the corresponding rate constants. The half life of oxyfluorfen at different temperature and moisture levels in the present investigation was observed to be in the range of 90.05 to 192.50 days, which was similar to the findings of Yen *et al.*, (2003) and Scranio

Table 3. Half life values for oxyfluorfen in Vertisol and Alfisol at Different temperatures and moisture levels

Soil	$27 \pm 2^\circ\text{C}$			$10 \pm 2^\circ\text{C}$		
	Saturation	FC	50% FC	Saturation	FC	50% FC
Oxyfluorfen						
Alfisol	97.60	110.0	113.60	150.62	165.00	192.50
Vertisol	90.05	94.93	106.61	123.75	141.42	147.44

et al., (2004). Oxyfluorfen has a strong tendency to adsorb on to the soil particles and is nearly insoluble in water. This may be attributed to the herbicide availability in soils and once oxyfluorfen is adsorbed

to soil particles it is not readily removed.

The results indicated a decrease in half life values with increase in temperature. Brar *et al.* (2006) reported that the half life of sulfosulfuron

decreased with increase in temperature similarly Punea *et al.*(1996) and Amarjeet *et al.* (2004) also reported a decreased half life of chlorosulfuran with increase in temperature

Higher activation energy was obtained in Alfisol as compared to Vertisol.(Table.4) Similar trend was observed for atrazine by Shalali (1986), for metoxuron by Raman and Rao (1984) and atrazine and

isoproturon by Nagamadhuri (2003).However these values were lower than those reported by Walker and Zimdahl (1984). It may be pointed out here that they did not consider the existence of two rates of disappearance, but fitted the whole data to first order kinetics. This may be the reason for higher predicted levels of residues, in comparison with the field levels.

Table 4. Rate constants (day⁻¹) and activation energy (KJ mole⁻¹ day⁻¹) at different temperature and moisture levels for oxyfluorfen

Soil	Oxyfluorfen						Activation energy (KJ mole ⁻¹ day ⁻¹)		
	27±2°C			10±2°C			Sat	FC	50% FC
	Sat	FC	50% FC	Sat	FC	50% FC			
Alfisol	0.0071	0.0063	0.0061	0.0046	0.0042	0.0036	24.88	23.24	30.23
Vertisol	0.0077	0.0073	0.0065	0.0056	0.0049	0.0047	18.26	22.85	18.59

The rate of loss of oxyfluorfen was affected by both the temperature and moisture content of the soil. An increase in temperature and moisture increased the loss of herbicide from soil. The order of disappearance of oxyfluorfen at three moisture levels was saturation> field capacity> 50% field capacity.

The rate of disappearance in two soils was compared and it indicated the rate of disappearance was inversely related to organic carbon content of the soil. Lower persistence of oxyfluorfen was observed in Alfisol, having low organic matter and low clay content in comparison to Vertisol, which showed maximum persistence indicating that the

Table 5. Persistence of oxyfluorfen in field conditions and lab incubated samples

Treatments	0 DAA		15 DAA		30 DAA		45 DAA	
	Lab conditions	Field conditions	Lab conditions	Field conditions	Lab conditions	Field conditions	Lab conditions	Field conditions
Oxyfluorfen @ 0.1 kg a.i.ha ⁻¹	0.037	0.021 (43.0 %)	0.019	0.011 (42.1%)	0.017	0.009 (47.0%)	0.015	0.007 (53.3%)
Oxyfluorfen @ 0.15 kg a.i.ha ⁻¹	0.056	0.034 (39.28 %)	0.048	0.022 (54.4)	0.036	0.015 (58.0 %)	0.028	0.011 (60.7 %)

Values in parenthesis indicate percentage variation between Lab and Field persistence

soil O M and clay content are the most important factors in determining the persistence of soil applied herbicides. These observations corroborate the findings of Arvind *et al.* (2000) and Eleftheronihos (1989).

The results of this study are significant as they clearly brought qualitatively and quantitatively, the content of herbicides being partitioned into bound pool and labile pool. Although the concentration in

labile pool has been considered more important in bioactivity of chemical, certain investigations have focused on the importance of bound pool as well. Kearney (1976) opined that the bound residues may be considered both as hidden residues capable of subsequent release and long term bioactivity and also as a process of deactivation helping to avoid long term effects. Barriuso *et al.* (1991) observed 15-40 per cent in bound form after 6 months of incubation in three French soils and showed that

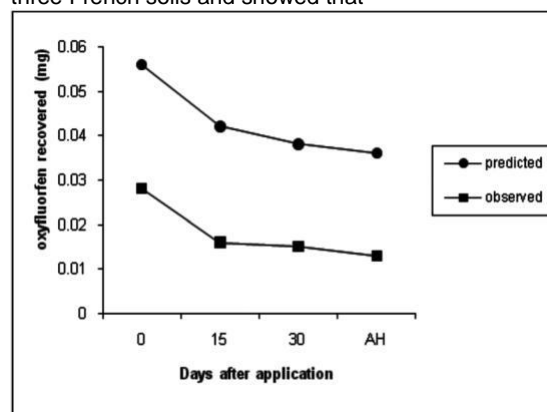
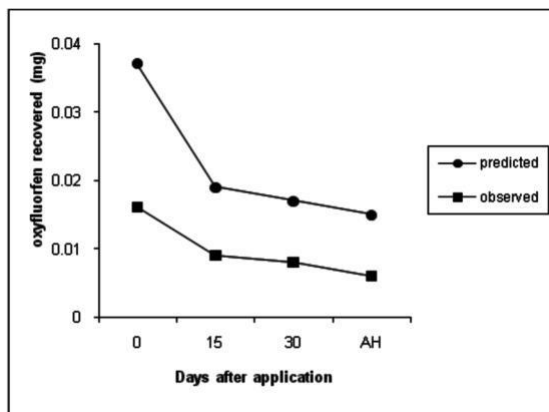


Fig.2. (i& ii) Oxyfluorfen persistence (observed and predicted) at 0.1 kg a.i./ha and 0.15 kg ai /ha

bound residues were clearly related to the organic fraction of the soil. Greater quantities of bound residues in soil with high organic matter could be expected as pesticide can be retained by adsorption and entrapped in the organic matter (Khan, 1980). The amount of residue, in the form of atrazine or its degradates increases with atrazine soil reaction time (Sorenson *et al.*, 1993; Topp *et al.*, 1994).

In the end, it is relevant to point out that Walker's model for predicting the persistence of pesticides did not take into consideration, the possibility of the pesticide applied to soil being retained in the bound fraction. The model suggested by him assumed a straight forward one phase kinetics for disappearance of pesticides involving first order kinetics. This is certainly a lacuna and a correction for partitioning into bound pool is necessary, as there is overwhelming evidence now that this happens in a large number of cases. The possible reasons for obtained higher values of pesticide residues through predictive modeling equations by Walker and his coworkers was actually due to this factor. Thus, a two phase kinetic pattern of disappearance of soil applied chemicals was observed by Katan *et al.* (1976) for the disappearance of ¹⁴C-parathion, Liechtenstein *et al.* (1977) for ¹⁴C-parathion, fonofos, and Raman (1987) for degradation of atrazine.

Comparison between field and lab persistence of herbicides

The herbicide oxyfluorfen applied as a pre-emergence to predict their persistence under field conditions based on the studies carried out on the laboratory under controlled conditions of temperature and moisture. The values of persistence of oxyfluorfen ranged from 0.037 to 0.015 $\mu\text{g g}^{-1}$ and 0.056 to 0.028 $\mu\text{g g}^{-1}$ at 0.1 and 0.15 kg ha^{-1} at 0 to 45 days respectively. Persistence decreased progressively from 0 Days After Application to 45 Days After Application and under field conditions. The values for oxyfluorfen ranged from 0.021 to 0.007 $\mu\text{g g}^{-1}$ and 0.034 to 0.011 $\mu\text{g g}^{-1}$ at 0.1 and 0.15 kg ha^{-1} at 0 to 45 days respectively. The variation of oxyfluorfen persistence was more than 30 per cent between the laboratory and field studies. It has been suggested that if the model could predict the residues within 30 percent of the difference between the field and lab studies, this could be sufficiently accurate for the practical purpose of forecasting aspects under field conditions. (Walker and Bond 1978). Although in some circumstances the model may provide accurate prediction of residues in the field in present case, it underestimates rates of loss leading to over prediction of residues. These over predictions might occur because the loss processes such as photochemical degradation, volatilization and movement in soil layers below the sampling depths are not allowed in this simulation model. Further

the variable soil conditions such as alternate wetting and drying (as a result of irrigating the field) and their effect on temperature and moisture variations have stimulating effects on microbial activity that are not apparent under laboratory incubated conditions. These reasons suggest that this model may not accurately describe the rate of oxyfluorfen dissipation from soil. However a large number of field experiments at different sites will have to be carried out on soils varying in soil properties to arrive at meaningful conclusions for predicting the fate of herbicides in soil. The observed values were much lower as compared to the predicted values; the reasons could be that there could be losses during application while spraying and the second loss immediately after application at the time when herbicide remain on the soil surface is the interaction between the herbicide and soil colloids. Hamaker (1975) observed that the losses during the spray drift and adsorption phases could be difficult to model quantitatively because of their complex and dynamic nature whereas the final degradation phase would be simpler to describe in quantitative terms.

The results from the present investigation are consistent with the suggestions of Hamaker (1975), Walker and Zimdahl (1984), Walker and Barnes (1981) and Nagamadhuri (2003). The model over estimated the oxyfluorfen residue by large amounts and discrepancies between the predicted and organic matter data was apparent specially during the initial 45 days period. This suggested that this model could be inaccurate during the initial short period under field conditions, when the compound is likely to remain at the soil surface. Therefore the model described by Walker (1974) and revised by Walker and Barnes (1981) could be inaccurate in predicting the oxyfluorfen residues in field conditions.

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