
Dissipation study of oxyfluorfen herbicide in sandy loam and clay loam soil

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Abstract

Oxyfluorfen is nitrodiphenyl ether herbicide utilized for managing weeds in food crops. The study was conducted for assessing persistence behavior of oxyfluorfen herbicide in sandy loam and clay loam soils having different physical composition. QuEChERS is an efficient and precise sample preparation approach which was enhanced for residual analysis of oxyfluorfen which offered 70.1-89.8 % recoveries with limit of detection (LOD) and quantification (LOQ) as 0.0001 and 0.0005 µg/g. A first order dissipation kinetics was confirmed by oxyfluorfen particles with half-life ranging from 10.4 to 14.1 days in alike variety of soils. The analysis study obtained the oxyfluorfen was detected in minimum concentration in soil samples of 45–60 days treatments at the application of 300 and 600 g a.i. ha⁻¹. In conclusion, oxyfluorfen has low run-off potential and it have no any phytotoxic symptoms on the succeeding crop.

Keywords: Oxyfluorfen, Persistence, QuEChERS, Half-life

1. Introduction

Weeds are the biotic constraint which emulate along crops for their basic support such as like water, nutriment, light and CO₂. Weeds emerge faster and reduce the crop space, photosynthesis capability and essential nutrient which was supplied to plants. The economic losses in crop yield by weeds in agriculture are significant and must be reduced. Yogita

Gharde et al. (2018) observed the total actual economic losses in 10 major crops of India (13.8%-35.8%) (Raghavendra KS et al. 2017) Chemical weed control is important factor for crop growth and enhances productivity. In chemical weed management, herbicides are the weed killer chemicals which inhibit the growth of weed plants. Oxyfluorfen is pre-emergence and topical herbicide used for regulating the broadleaved invasive plant in variety of field crops like maize, onion, rice, carrot, soyabean, groundnut and gram (P Janaki et al. 2017; Shobha Sondhia 2010; Sondhia, S., & Dixit, A. 2007, Laura Scranio et al. (2004). The use of oxyfluorfen herbicide in rice, onion, garlic, greengraam observed the effective weed control treatment (C.T. Abraham et al. 2010; Mahmood Dejam et al. 2014; Mahdi Aghabeigi et al. 2017; E. Sobhana et al. 2018). The use of oxyfluorfen in agriculture in the form of granular product and an emulsifiable liquid concentrate formation.

The chemical nature of oxyfluorfen belongs to the nitro diphenyl ether which act as photosynthetic inhibitor that induces necrosis in treated plants. Oxyfluorfen has high binding efficiency toward the most soils having large composition organic matter and clay content (N. Mantzos et al.2014). Thus, dissipation of oxyfluorfen is affected by the soil binding capacity. Herbicides are important for weed management but its residual impact is an important concern for environmental safety. When surface assimilation of oxyfluorfen with soil molecules then it is no easily carried out. Oxyfluorfen was dissipated steady and relatively immobile in soil-domain, having a half-life ranging amidst 30 to 40 days (Wauchope et al., 1992). The Perseverance of oxyfluorfen particles in soil has potential to contaminate the ground water from different routes. Oxyfluorfen is a poisonous and resistant herbicide, which accumulate land flora and underwater atmosphere by runoff (P Janaki et al. 2014). Therefore, it is important to look over the dissipation behaviour of oxyfluorfen herbicide in soil. Some field studies have investigated the continual of oxyfluorfen remnant in crops: Veeresh Hatti et al. 2014 investigated the effect of oxyfluorfen on crop amount, microbial biomass and phytotoxicity on maize. T. C. Poonia et al. (2017) and A Sireesha et al. (2012) analysed the residues of oxyfluorfen in groundnut and raddish crop were below the MRL values and their persistence in soil. Das et al. (2003) and Sondhia (2009) investigate the consequences of

oxyfluorfen in rice fields. In India, oxyfluorfen is a selective herbicide which was widely used in annual crops. R Sathya Priya et al. (2017) studied the carryover effect of Goal (23.5% EC) in paddy crop and their residual response on crop rotation. But no further details is accessible in literature regarding the persistence behaviour of oxyfluorfen under agro-climatic conditions of northern india. For better and effective treatment of chemicals there is need to awareness toward the effect of dissipated herbicides in soil. Thus, the research was executed to examine the residual effect of oxyfluorfen (23.5% EC) in two -textured soil.

2. Material and Methods

2.1 Chemicals, reagents and standards

The chemical product oxyfluorfen (Goal 23.5% E.C.) was used in this experiment was acquired from Indofil India Limited. The chemicals and solvents used in the experiment were acquired from Merck India Ltd. The stock standard mixtures (100 µg/mL) of oxyfluorfen were formulated in acetone. The functional solutions were devised through stock utilize serial suspension with acetone and preserved at 4 ° C prior to use.

2.2 Soil Sampling

In this experimental study, soils were taken from two different places. Sandy loam soil was taken from cultivated research farm area, Hisar while the clay loam soil was taken from K.V.K. Fatehabad. These soil samples were dried completely and crushed into powdered form and pass through sieve. Both the collected soil was described for several rheological characteristics as per the procedure proposed by Sherrod et al. (2002), Rayment and Lyons (2011).

2.3 Dissipation study

The investigation was assisted in laboratory under regulate circumstances by using distinct container [25 × 25 (i.d.) cm] organized in a specific way along triad replications. The dried and sieved 1 kg of experimental soil filled in each pot separately. Soil moisture was maintained before the herbicide treatment. Oxyfluorfen formation was applied at suggested

field application dose (T1) of 300 g a.i./ha and dual dose (T2) of 600 g a.i./ha. After the herbicide application, the soils were assorted properly for appropriate distribution. One pot of both types of soils taken as control that was never treated with any herbicide application.

These containers were placed at normal temperature of $25\pm 2^{\circ}\text{C}$ with relative moisture of 90% and covered with tin foils. During the experiment water level in soils was preserved by spraying the measured quantity of water at 2–3 days interspace. Soil fragments were drawn from all the container at 0 (1 h), 1, 3, 7, 10, 15, 30, 45, and 60 days after application and analysed periodically. After each sampling, soil was mixed properly with a steel auger. The soil fragments were evaporated in shade and used the fine mesh strainer for uniformly distribution of soil particles. The aggregate 20 g soil sample was extract from container and further processed for residue analysis.

Table 1: Selected characteristics of oxyfluorfen herbicide and soil taken in the study

Molecular properties of oxyfluorfen		
Molecular Mass	361.7g/mol 84.0 °C 358.2 °C 2×10^{-6} bars	
Melting Point		
Boiling Point		
Vapour Pressure		
Solubility - In water	0.1mg/l at 25 °C	
Solubility - In organic solvents Acetone	72.5 g/100g	
Cyclohexanone	61.5 g/100g	
Chloroform	50-55 g/100g	
LD50	>500 mg/kg	

Koc	10000 ml/g	
Molecular properties of soils	Sandy loam	Clay loam
Texture	Sand 56%	Sand 48%
	Silt 29.2%	Silt 18%
	Clay 14.8%	Clay 34%
Ph	7.8	8.8
Electric Conductivity (dS/m)	0.19	0.18
Organic Carbon(%)	0.30	0.48

2.4 Optimization of sample preparation method

An appropriate sample preparation approach was required for analysis of oxyfluorfen molecules in loamy sand soil and loamy clay soil. For sample preparation, some conventional methods MSPD, LSE and QuEChERS (modern extraction approach in analytical chemistry) were used at two considered levels of 0.5 and 0.1 µg/g in both soils.

MSPD is a traditional sample preparation approach for extraction and clean soil samples simultaneous with minimise the analyte losses. Soil (20 g) was assorted with 10 g silica gel and 0.5 g charcoal and this mixture was closely packed in middle two surface of anhydrous Na₂SO₄ in a column. Different extraction columns pass through 100 ml Dimethyl ketone and Ethyl acetate. The eluate from separate columns was passing through anhydrous sodium sulfate (3 g) and collected in reagent bottles. The eluents were concentrated (5ml) for GC-MS/MS analysis.

LSE is residues extraction technique mostly applied for leachate fractions. A mixture of 20 g soil fragment with 50 mL of Dimethyl ketone and Methanol taken in flasks (250 mL) separately and extraction through shacking for 1hour. The extracts were vacuum filtered by using the 0.22 mm synthetic filter in different graduated bottles and purified to 10 mL through Buchi rotavapor. Sample purify was perform using solvent extraction thrice with Methanol. For complete removal of moisture, the primary layer was crossing from dehydrated Na₂SO₄

and get collected. The extracts were purified and re-dissolved with methanol for GC-MS/MS evaluation.

Xiaohu Wu et al.2013 proposed the QuEChERS is very simple, sensitive and effective method for the analysis of pesticide molecules in soil. Rani et al. 2020 approach ‘the QuEChERS is flexible and extremely accurate sample preparation technique in modern and sustainable chemistry’. QuEChERS is promising then MSPD and LSE as it has need of less dissolver and also providing a scope of modifications (kumari P et al. 2022). The fortified soil fragments were placed in 50 mL draw tubes and swirl with 20 mL Acetone and EA separately. The sample blends were swirled for 1h and extracted at 3500 rpm for 10 min and 5 ml the supernatants were collected into distinct tubes. For purify the supernatant two approaches were following as 4 g MgSO₄ + 0.5 g Primary Secondary Amine and using only 4 g MgSO₄. The contents were again vortexed for 5 min and extracted it. The supernatant was evaporated through rotary-evaporator and remnants were mixed again with methanol for further investigation.

2.5 Instrumentation for analysis

The Oxyfluorfen remnants were examined by using a MS System having an Agilent 7890 model with 7000 Triple- quarter Mass analyzer. The HP-5 column having proportions 30 m x 0.32 mm i.d. x 0.25 µm film concentration was utilised in the course of analysis. The injection port thermal energy placed at 280°C. By following the ramping process the oven thermal energy was maintained at 70°C. The mass detector was operated with parameters – source kelvin scale, 230°C; discharge current, 35 µA; chemical potential, – 70 eV; repeller potential, 11 V; ion strength, 12 V; extractor, –7.2 V; ion focus, –7.4 V. Both Quadrupole thermal energy was maintained at 150°C. Helium and nitrogen were worked as the mobile phase gas with flow density of 2.25 and 1.15 mL/min in collision cell. The Vacuum at high-constraint 2.23×10^{-5} torr and rough vacuum was 1.51×10^2 torr, Injection capacity was 2 µl pulsed in split-less mode.

2.6 Data analysis

The dissipation parameters of oxyfluorfen in soil was calculated by using the rate law $C_t = C_0 e^{-kt}$; where C_t be regarded as the weight percent of the oxyfluorfen residuum ($\mu\text{g/g}$) with respect to the time-days. C_0 is the initial weight concentration and k represents first-order uniform rate respectively. Period of time was calculated The Hoskins (1961) procedure enumerate the Half- life of oxyfluorfen. One-way analysis in Excel 2013 software was used to detect the inter-relationship and significant difference between different treatments in dissipation. In this experiment like method verification and dissipation study of oxyfluorfen, the figures were detected significant for sample distribution and homogeneity found ($p > 0.05$).

3. Results and discussion

3.1. Method validation

The LOD and LOQ for oxyfluorfen in soil was observed to be 0.0001 and 0.0005 $\mu\text{g g}^{-1}$. In MSPD, the average recoveries of oxyfluorfen by using solvents Acetone, ACN, Methanol, EA, EA: Hex (7:3 v/v) ranged from 25.7 to 72.1%. Recoveries obtained from LSE using solvents ACN, Acetone, Methanol 24.5 to 81.8%. In QuEChERS the average recoveries of oxyfluorfen by using solvents Acetone and EA ranged from 43.1 to 94.2% in soil. MSPD and LSE were not found beneficial for the present study by obtaining the unacceptable recoveries and requiring the expensive solvents, efforts and time consume in multistep process. Hence, the QuEChERS approach using acetone as separation solvent give better recoveries according to the instructions specified by EURL (2021) (Document No. SANTE/ 11312/2021). On that account, QuEChERS mechanism was preferred for sample formation in persistence study of oxyfluorfen herbicide in soil.

3.2 Persistence of Oxyfluorfen in soils

Oxyfluorfen applied in sandy loam soil at T_1 and T_2 application with gradient values as $T_1 =$

-0.019 and $T_2 = -0.016$ almost follow similar dissipation pattern. The initial residues of oxyfluorfen in soil immediately after herbicide application at T_1 and T_2 were found to be 0.032 and 0.065 $\mu\text{g/g}$ and there after significant reduction in residues with rise in days taken. In T_1 application ,95% residues were dispersed on 60 DAA Where in T_2 about 92 % dissipation of residues observed on 60 DAA. Residues in both T_1 and T_2 applied dose get to below detectable limit on 60 DAA with period of time 12.8 and 14.1 days and successive rate law dissipation kinetics with $R^2 = 0.9769$ and 0.9887, separately.

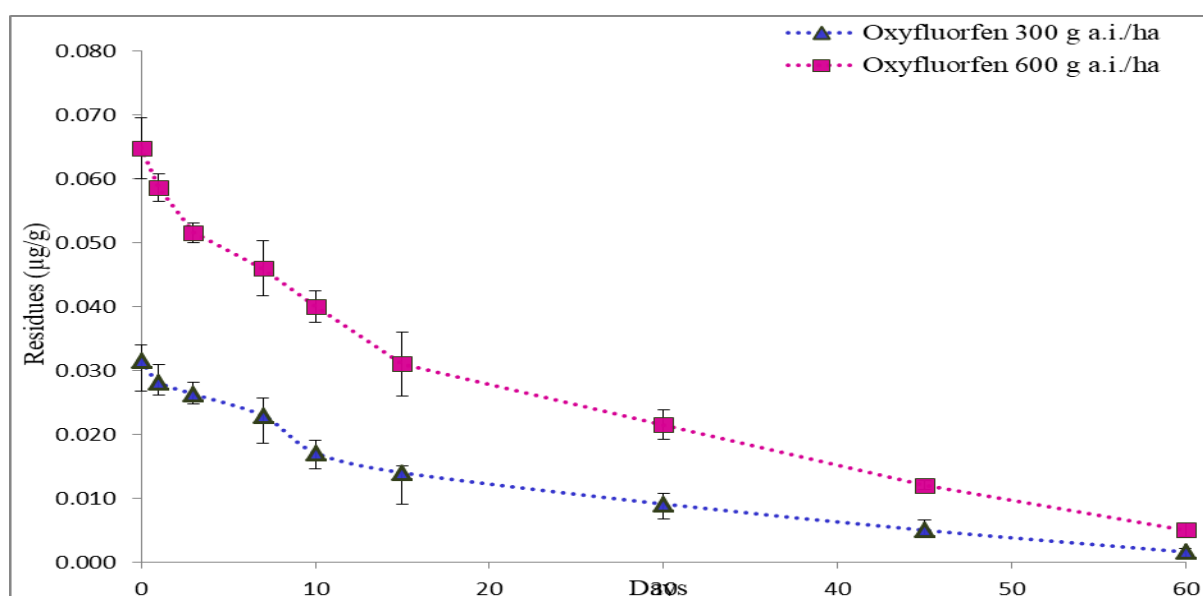


Fig 1: Dissipation behaviour and kinetics of Oxyfluorfen in sandy loam soil. Dissipation curve and semilogarithm plot showing first order kinetics of Oxyfluorfen applied at 300 and 600 g a.i. ha⁻¹.

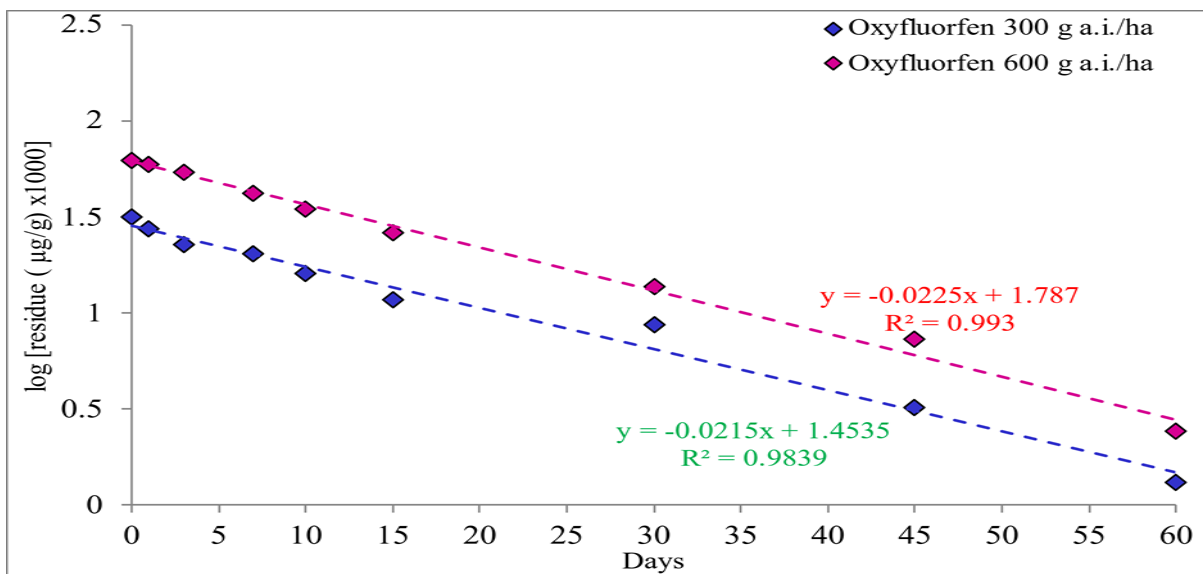
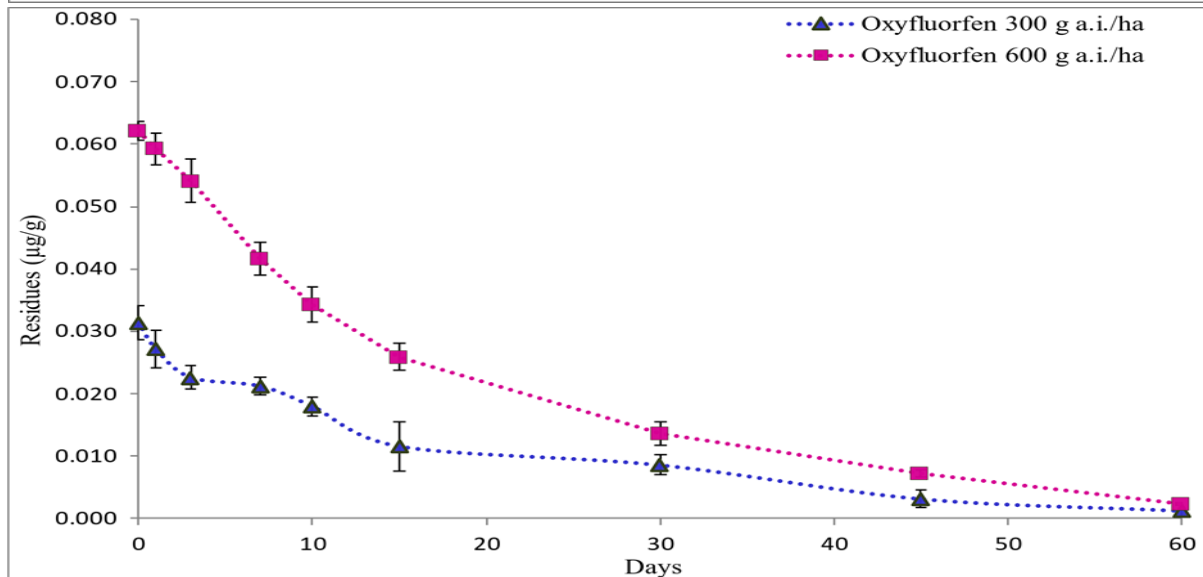
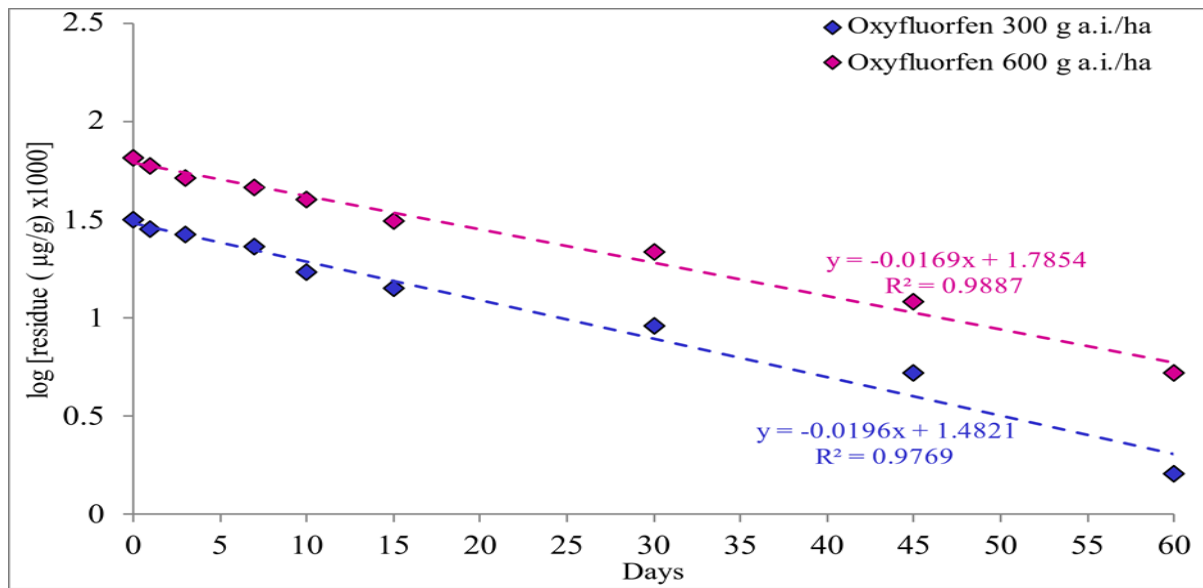


Fig 2: Dissipation behaviour and kinetics of Oxyfluorfen in clay loam soil. Dissipation curve and semilogarithm plot showing first order kinetics of Oxyfluorfen applied at 300 and 600 g a.i. ha⁻¹.

In clay loam soil, there was also significant decrease of oxyfluorfen residues at T₁ applied dose with the standard initial residues of 0.031 µg/g and T₂ having the average initial residues 0.062 µg/g. However, oxyfluorfen residues reduced significantly from 0 to 60 DAA and in both application around 95% of herbicide residues dissipated within 60 days of herbicide application. Residues reached on below the limit value in both application rates. The half-lives of oxyfluorfen 10.4 days in T₁ and 11.9 days in T₂ showed identical dissipation figure with gradient values (T₁= -0.021 and T₂ = -0.022) following the specific rate constant dissipation kinetics with R² = 0.9839 and 0.993, respectively. The standard amount of dispersed oxyfluorfen in soil be based on several factors like thermal energy, photodegradation and soil moisture content (Yen J. H. et al. 2003). Sondhia S. (2009) reported that high humidity increase the rate of degradation of oxyfluorfen. But this study was executed under research environment where temperature (25 ± 2 °C) and moisture were preserved stable for the duration of the experiment. Janaki P et al. (2013) reported that the dissipation of oxyfluorfen herbicide in soil was also influenced by the molecular properties of soil and climate characteristics. The molecular properties like alkalinity, organic components and ion exchange magnitude were accountable for regulate the consequence of the herbicide in soil. Priya R. S. et al. (2017) observed the oxyfluorfen herbicide has highly binding capacity to soil organic carbon and low ability to move in loamy red sandy clay soil. Khumbar M B et al. (2017) reported that the oxyfluorfen herbicide has highly persisted in clay soil then sandy and sandy loam soil. Soil organic carbon was also contributing effect for persistence of weed killers. The molecular properties of soil explained clay loam soil possess OC 0.48% confirmed the almost more dissipation than sandy loam soil with 0.30% OC. Along with organic matter, the clay can take part a significant role in degradation rate of toxicant Sondhia, S. (2008). The soil was rich in clay content favoured the faster dissipation of oxyfluorfen. The soil alkalinity also take part a significant role in the degradation of agro-chemicals (Morrica et

al. 2001; Sondhia 2007). Therefore, soil OC , clay content and pH is the major factor for dissipation of herbicide. Alister A. et al. (2009) observed the smaller half-life values of oxyfluorfen which indicated that herbicide residues remain in upper 2.5 cm soil layer and there is very low risk of herbicide to contaminate groundwater. In like manner, based on the small half lives values of oxyfluorfen for both type of soils and residues reached at below detectable limit indicated that oxyfluorfen has small persistence. On the basis of this experiment, oxyfluorfen particles were found within safe limits (0.003 µg/g) in sandy loam and clay loam soil at the application of 300 and 600 g a.i. ha⁻¹.

4. Conclusion

In the current analysis, the oxyfluorfen residue dissipated rapidly in clay loam soil with half-lives of 10.4 and 11.9 days. Oxyfluorfen could bound to the soil organic carbon and has low ability to move in sandy loam soil with a pH of 7.8 and organic carbon content of 0.30%. The results showed that oxyfluorfen residues did not persist for more than 60 days in soil even herbicide is applied at double dose. Thus, oxyfluorfen herbicide might not be phytotoxic when applied at recommended rates.

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