

Effects of Natural Attenuation, Organic Amendments and Metal Toxicants on 2, 4-Dichlorophenoxyacetic Acid Dissipation Dynamics in Soil

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Abstract: *The dissipation dynamics of the herbicide, 2,4-dichlorophenoxyacetic acid (2,4-D), in soil was studied under the influence of natural attenuation (NA), poultry manure (PM), swine manure (SM), urea (UR), and metal toxicants (Cd, Pb) in a laboratory microcosm. A sandy clay soil was characterized and used for the study. The effects of variables such as initial 2,4-D concentration (0 – 500 mg/kg), level of amendment (0 – 30 %w/w), amendment blends (binary and ternary), Cd/Pb loadings (0 – 200 mg/kg) and incubation time (0 – 30 days) on 2,4-D dissipation were investigated. In all the experiments, residual 2,4-D was recovered by solvent extraction, followed by reaction with chromotropic acid reagent for color development and assayed by UV-Vis spectrophotometry at λ_{max} 565 nm. 2,4-D naturally attenuated in soil, however, addition of PM, SM or UR did enhance the extent and rate of degradation. Relative to NA, the degrading efficiencies, DE (%) of the amendments increased with increase in incubation time and level of amendment, but did not necessarily depend on initial 2,4-D concentration. Pseudo-first-order degradation constants ($\times 10^{-2}$ /day) decreased with herbicide load and increased with amendment level; with corresponding half-lives (day) decreasing and increasing, respectively. DE values indicated that apart from the binary PM + SM amendment blend, the single amendments (especially PM and UR) were more effective at 2,4-D degradation in soil. The extent of 2,4-D degradation was reduced at increasing Cd and Pb loads, furnishing relatively low DE's (< 50%) for the amendments but more so in the presence of Cd.*

Keywords: Biodegradation, 2, 4-dichlorophenoxyacetic acid, Natural attenuation, Poultry manure, Swine manure, Urea

1. Introduction

To maximize crop yield, ensure food security and economic benefits for sustaining the ever increasing world population, modern agriculture depends greatly on herbicides [1]. Herbicides are a subset of pesticides that kill or control weeds and pathogens that compete with valuable crop plants for soil, water, air, and nutrients [2]. Currently, herbicides represent over 70% of agrochemical imports worldwide and there are indications that they would continue to be the most employed agrochemicals [3]. Extensive use of herbicides, however, poses some far-reaching consequences because of the potential runoff and leaching of particularly the poorly degradable ones through the soil leading to contamination of surface and groundwater [4, 5]. Herbicide residues may cause acute and genetic toxicity with attendant threat to the biota inhabiting the ecosystem. Literature suggests an array of possible toxicological implications of the persistent herbicides on the ecosystem [6].

The main chemical classes of herbicides include bipiridilium compounds, triazine derivatives such as atrazine, prometryn, propazin, etc), chlorophenoxy acid derivatives (2,4-D, 2,4,5-T), substituted chloro-acetanilides (alachlor, propachlor), derivatives of 2,6-dinitroaniline (benfluralin, trifluralin), substituted phenylcarbamates (carbetamide, chlorbufam), urea derivatives (chlorbromuron, chlorotoluron), substituted sulphonylureas (amidosulfuron, trifusulfuron), etc [7, 8].

2,4-dichlorophenoxyacetic acid (2,4-D) is a herbicide from the group of polychlorinated aromatic hydrocarbons and one of the most widely used for the control of broad leaf weeds

and grasses [9]. It is a synthetic auxin, and as such, often used in laboratories for plant research and as a supplement in plant cell culture media [10]. Although 2,4-D easily moves through the soil, its leaching into groundwater can be minimized due to degradation by microorganisms and also absorption by plants. Its primary route of degradation is by microorganisms, which increases with temperature, humidity, pH, and organic matter content [11 – 13].

The most important mechanism of microbial degradation involves the removal of the acetic acid side chain to yield 2,4-dichlorophenol, followed by ring cleavage and degradation to produce aliphatic acids such as succinic acid. The ability of micro-organisms to degrade herbicides has stimulated scientists to develop methods to assess the potential for the transformation of these anthropogenic chemicals via this route [14, 15]. Consequently, several approaches such as bioventing, biostimulation, bioaugmentation, composting, bioremediation, etc have been put in place to cleanup herbicide residues in soil. The biostimulation approach is the practice of using fertilizers, manures, compost and other limiting factors to stimulate indigenous microorganisms for accelerated herbicide degradation in soil [15 – 17].

This study is aimed at assessing the dissipation dynamics of 2,4-D in soil under the influence of natural attenuation (NA) and/or poultry manure (PM), swine manure (SM), urea (UR), and two metal toxicants (Cd, Pb) in laboratory microcosms. The specific objectives were to check the effects of operating conditions such as initial 2,4-D concentration, amendment dosage, amendment blends (binary and ternary), metal

toxicant (Cd/Pb) loadings, and incubation time on 2,4-D dissipation in soil.

2. Materials and Methods

2.1 Sample Collection, Pre-treatment and Characterization

Ten top (0 – 20 cm) parent soil (PS) samples were randomly collected from the agricultural farm of the University of Agriculture, Makurdi (7.44°N, 8.33°E), north-central Nigeria using a hand trowel. Raw poultry (PM) and swine (SM) manures were collected from animal farms in Makurdi and allowed to age for 2 weeks. Urea (UR) was supplied by NAFCON, Nigeria. The samples were put in polythene bags and taken to the laboratory. The samples were air-dried, ground, sieved (< 2mm), and the PS composited. Standard operating procedures were used to test the PS, PM SM and UR for pH (1:25 soil/water ratio) [18], particle size distribution [19]; organic carbon/matter [20], total nitrogen [21], total phosphorus [22], and total Cd and Pb [23], as the case may be. Isolation and identification of bacteria and fungi were done according to the method described by Swift and Bignell [24].

2.2 Laboratory Microcosms to Monitor 2,4-D Dissipation in Soil

A concentrate of 2,4-D, Aminoforce (2,4-dimethylammonium salt, specific gravity = 0.72 g/mL, see Figure 1 for chemical structure) was supplied by Jubaili Agrotech Ltd. A 5000 mg/L 2,4-D stock was prepared by pipetting a 6.944 mL aliquot of the concentrate into a 1 L volumetric flask and the solution made up to the mark with distilled water. Thus 1.0 mL of this stock was equivalent to 5 mg of 2,4-D.

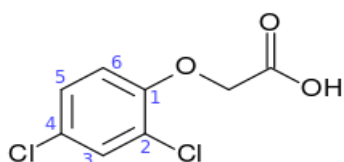


Figure 1: Chemical structure of 2,4-D (2,4-Dichlorophenoxyacetic acid)

In order to study the effect of initial 2,4-D concentration on its degradation in soil under natural attenuation (NA), PS was fortified with known concentrations of the herbicide, C_o (mg/kg), and its degradation was monitored as a function of time (day). Aliquots V (mL) of the 2,4-D stock, were used to spike fixed weights of PS, w (g) with 2,4-D to achieve $0 \leq C_o \text{ (mg/kg)} \leq 500$ levels with the aid of Equation (1):

$$C_o \text{ (mg/kg)} = \frac{5 \text{ (mg)}}{\text{(mL)}} \times \frac{V \text{ (mL)}}{10^3 \text{ (g)}} \times \frac{10^3 \text{ (g)}}{1 \text{ (kg)}} \times \frac{10^3 \text{ (g)}}{w \text{ (g)}} \quad (1)$$

More precisely, to separate fixed weights ($w = 25$ g) of the PS; 0, 0.5, 1.0, 1.5, 2.0 and 2.5 mL of the 5000-mg/L 2,4-D stock solution were added to achieve 0, 100, 200, 300, 400 and 500 mg/kg levels of artificial contamination with the herbicide. The set up was equilibrated for 5, 10, 20 and 30 days under NA.

The effect of 2,4-D concentration on its dissipation in amended soil was studied by adding aliquots of the 2,4-D stock (5000-mg/L) to separate fixed weights ($w = 25$ g) of the PS to furnish $0 \leq C_o \text{ (mg/kg)} \leq 500$ levels. The different set ups were treated with 2.78 g of PM, SM or UR to achieve 10 % w/w amendment. Each microcosm was incubated for 5, 10, 20 and 30 days.

In microcosms designed to check the effect of level of organic amendment on 2,4-D dissipation in soil, increasing levels of PM, SM or UR were added to the herbicide-fortified PS (500 mg/kg) at 5, 10, 15, 20 and 30% w/w and set up allowed to equilibrate for 5, 10, 20 and 30 days.

The effect of amendment blends on 2,4-D dissipation in soil was assessed by treating the herbicide-fortified (500 mg/kg) PS soil subsamples with different blends of the amendments (PM+SM, PM+UR, SM+UR or PM+SM+UR) at a fixed dose (10% w/w). Specifically, the binary blends were formulated at ratios of 1:1 (i.e., 1.39 g : 1.39 g); while the ternary blend was got by combining the amendments in the ratio 1:1:1 (i.e., 0.9259 g : 0.9259 g : 0.9259 g). The microcosms were left to stand under ambient conditions for 5, 10, 20 and 30 days.

Finally, the influence of two metal toxicants (Cd and Pb) on 2,4-D dissipation in amended soil was investigated by first, treating the herbicide-spiked (500 mg/kg) PS subsamples singly with PM, SM, or UR at a fixed dose (10% w/w). Next, Cd and Pb (in form of their nitrates dissolved in deionized water) were added at increasing doses (10, 50, 100, 150 and 200 mg/kg) and the set ups incubated for 2 weeks (14 days). This procedure was repeated under the NA scenario (i.e., without the amendments). In all microcosms, the residual 2,4-D was extracted at the elapse of a specified incubation time and assayed by UV-vis spectrophotometry.

2.3 Solvent Extraction 2,4-D Recovery in Soil and Formation of Calibration Curve for UV-vis Spectrophotometric Determination

Solvent extraction of 2,4-D in soil was done using the colorimetric procedure described by Durga Devi et al. [25]. Colorimetry is one of the earliest and instrumental techniques for the estimation of 2,4-D residues, and even today it continues to be a useful and facile method wherever costlier modern facilities like gas chromatograph are not readily available. Soil samples were shaken with solvents (acetonitrile: distilled water: glacial acetic acid (80:20:2.5) at soil:solvent ratios of 1:2 for a period of 30 min. That is, 10 mL of the mixed solvent were added to 5 g soil and then shaken for 30 min with the aid of a mechanical shaker (Milano, Italia). The filtrate was shaken with 50 mL 1.0 M NaOH, 7.5 mL concentrated HCl and 25 mL of diethyl ether in a 250 mL separating funnel. The ether portion was separated and the aqueous layer was again shaken with 25 mL diethyl ether. The ether portions were pooled and extracted twice with 12.5 mL of buffer solution (25 g $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ and 10 g $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ in 1 L of distilled water). The pooled buffer separate was shaken with 0.5 mL concentrated HCl and 5 mL carbon tetrachloride. The aqueous layer was separated and again shaken with 5 mL carbon tetrachloride. The combined carbon tetrachloride

layer was evaporated and the residue was treated with 1.5 mL chromatotropic acid reagent (0.4 g chromatotropic acid in 100 mL of concentrated H₂SO₄) and kept in an oven at 120 °C for 20 min. The wine purple colored complex obtained was cooled, diluted and made up to 25 mL with distilled water. It was transferred into another bottle and made up to 100 mL with distilled water. Absorbance of the colored complex was read on a UV-vis spectrophotometer (Jenway 6705) at λ_{max} 565 nm against a reagent blank.

A standard absorption curve for 2,4-D acid was prepared by diluting 0, 0.5, 1.0, 1.5, 2.0 and 2.5 mL of the 5000 mg/L 2,4-D stock in distilled water (equivalent to 0, 100, 200, 300, 400 and 500 mg 2,4-D per kg of soil) and the color was developed using the same procedure as for soil sample. The calibration curve (Figure 2) was constructed so that the absorbance (A) readings obtained from the experiments could be directly converted into residual 2,4-D concentration, C_{res} in soil (mg/kg) by extrapolating through the linearity range (slope = 1.20 x 10⁻³ kg/mg) with the aid of Equation (2):

$$C_{res} \text{ (mg/kg)} = \frac{A \text{ (mg)}}{\text{slope (kg)}} \times \frac{w \text{ (g)}}{y \text{ (g)}} \quad (2)$$

where w and y are the total weight of 2,4-D-spiked soil (25 g) and aliquot of the spiked soil taken for 2,4-D assay (5 g), respectively.

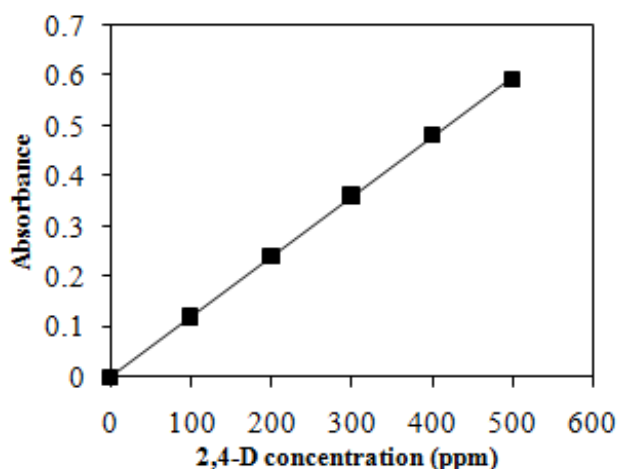


Figure 2: Calibration curve for UV-vis Spectrophotometric Determination of 2,4-D in Soil (λ_{max} 565 nm)

2.4 Quality Control/Assurance and Data Handling

Analytical grade chemicals were used to prepare standard solutions and reagents. All glassware and plastics were washed with distilled water, rinsed with (1 + 1) HNO₃ and finally with distilled water. Procedural blank samples were subjected to similar treatments using the same amounts of reagents. In all cases, measurements were performed in triplicates. A Microsoft® Excel 2010 package was used to perform all algorithm plots and calculations. The percent degradation or degradation yield, DY (%), taken as a measure of the extent of degradation was calculated by:

$$DY(\%) = \left(\frac{C_o - C_{res}}{C_o} \right) \times 100 \quad (3)$$

where C_o is the initial herbicide concentration in soil (mg/kg) and C_{res} is the residual herbicide in soil (mg/kg) after a specified incubation time.

The biodegradation of modelled by pseudo-first order kinetics₉, a typical algorithm for which is given by:

$$C_{res} = C_o \exp^{-k_1 t} \quad (4)$$

where C_o and C_{res} are as defined in Eq. 3; t is the incubation time (day). k₁ is the biodegradation rate constant (day⁻¹). In practice, k₁ was obtained from the slope of the least-squares regression equation resulting from the plot of lnC_{res} versus t. The biodegradation half-life, τ_{1/2} (day), i.e., time taken for herbicide to degrade by one-half of its initial concentration in soil was calculated as:

$$\tau_{1/2} = \frac{0.693}{k_1} \quad (5)$$

The half life model is based on the assumption that the biodegradation rate of herbicides is positively correlated with the herbicide pool size in soil and may be applied during chemical screening, environmental fate modelling and description of the transformation of the herbicide in soil. The 2,4-D degrading efficiency, DE (%) of a particular amendment was calculated as:

$$DE(\%) = \left(\frac{C_{res(u)} - C_{res(a)}}{C_{res(u)}} \right) \times 100 \quad (6)$$

where C_{res(u)} is the residual 2,4-D concentration (mg/kg) in the unamended soil (i.e., under NA) and C_{res(a)} is the corresponding concentration in the amended soil (mg/kg).

3. Results and Discussion

3.1 Physicochemical Characteristics of Parent Soil and Organic Amendments

Some physicochemical properties of the parent soil and organic amendments used for the study are given in Table 1. The PS, PM, SM and UR had pH values of 5.98, 6.95, 6.99 and 7.80, respectively all in the range reported for typical agricultural soils and the amendments [26, 27]. Texturally, the sand, silt and clay fractions in the PS were 82.86, 3.28 and 13.85 %, respectively qualifying it as sandy clay. The particle size distribution of the soil suggests a low water-retention capacity and possible short- and long-term herbicide leachability. The respective organic matter content of the PS, PM, SM and UR were 1.36, 38.16, 38.53 and 0.25%, corresponding to organic C contents of 0.79, 22.07, 22.29 and 0.14. The organic matter content of the PS qualifies it as a mineral soil, a typical characteristic of most agricultural soils. The C:N ratio of 4.64 for the PS is rather low for effective herbicide mineralization, hence the need for supplementation with the organic amendments, especially

PM (C:N = 10.50) and SM (C:N = 7.69). The appreciable quantities of N and P in the amendments are necessary nutrients for bacterial biodegradative activities [28]. PM had the highest C content among the organic wastes and high N content, the most important limiting nutrient for effective biodegradation to take place [29].

The ranges of total Cd and Pb (mg/kg) in the PS and the amendments were: Cd (0.31 – 0.37) and Pb (0.31 – 0.35). These values are lower than their corresponding upper critical levels, defined as the range of values above which toxicity is considered to be possible [30], indicating that the PS and the amendments were relatively uncontaminated in terms of Cd and Pb. The bacteria identified in PS were *Bacillus* spp and *Nocardia* spp; while the fungal species were *A. fumigates*, *Penicillium* spp., and *Streptomyces* spp.

Table 1: Some physicochemical attributes of parent soil and organic amendments*

Parameter	PS	PM	SM	UR
pH	5.98	6.95	6.99	7.80
Sand (%)	82.86	-	-	-
Silt (%)	3.28	-	-	-
Clay (%)	13.85	-	-	-
Organic matter (%)	1.36	38.16	38.35	0.25
Organic carbon (%)	0.79	22.07	22.29	0.14
N (mg/kg)	0.17	2.10	2.90	45.58
P (mg/kg)	9.28	1.80	0.90	-
Total Cd (mg/kg)	0.39	0.37	0.31	-
Total Pb (mg/kg)	0.35	0.30	0.31	-

*PS = Parent soil, PM = Poultry manure, SM = Swine manure, UR = Urea

3.2 Effect of Initial 2,4-D Concentration and Incubation Time on its Dissipation in Soil

At the (100 – 500 mg/kg) initial 2,4-D concentrations studied, the rate of disappearance of 2,4-D per unit time, $R(t)$ (mg/kg.day) between t_1 and t_2 (where $t_1 < t_2$), decreased with time, but increased at successively higher herbicide loads (Figure 3). A similar trend was found for the microbial degradation of 2,4-D by *Burkholderia cepacia*, *Pseudomonas* sp. and *Sphingomonas paucimobilis* [9]. Several transformation pathways such as hydrolysis, methylation and ring cleavage have been suggested for 2,4-D mineralization [10]. Seemingly, the extent of 2,4-D dissipation levelled up, after the 30 days of incubation. Conversely, the extent of herbicide degradation, DY increased with time, decreased with increasing herbicide load and ranged as: NA (29.18 – 87.38%), PM (39.04 – 94.87%); SM (32.97 – 90.93%); and UR (36.87 – 93.67). Under the single amendment scenarios, both $R(t)$ and DY increased in the order: NA > SM > UR > PM. The degrading efficiency of the amendments, DE (%) (calculated relative to the NA media) generally increased with increase in incubation time, but seemingly did not depend on C_0 .

Typical DE ranges for the single amendments were in the order: PM [13.50 ≤ DE(%) ≤ 61.97] > UR [7.73 ≤ DE(%) ≤ 49.84] > SM [4.67 ≤ DE(%) ≤ 34.99].

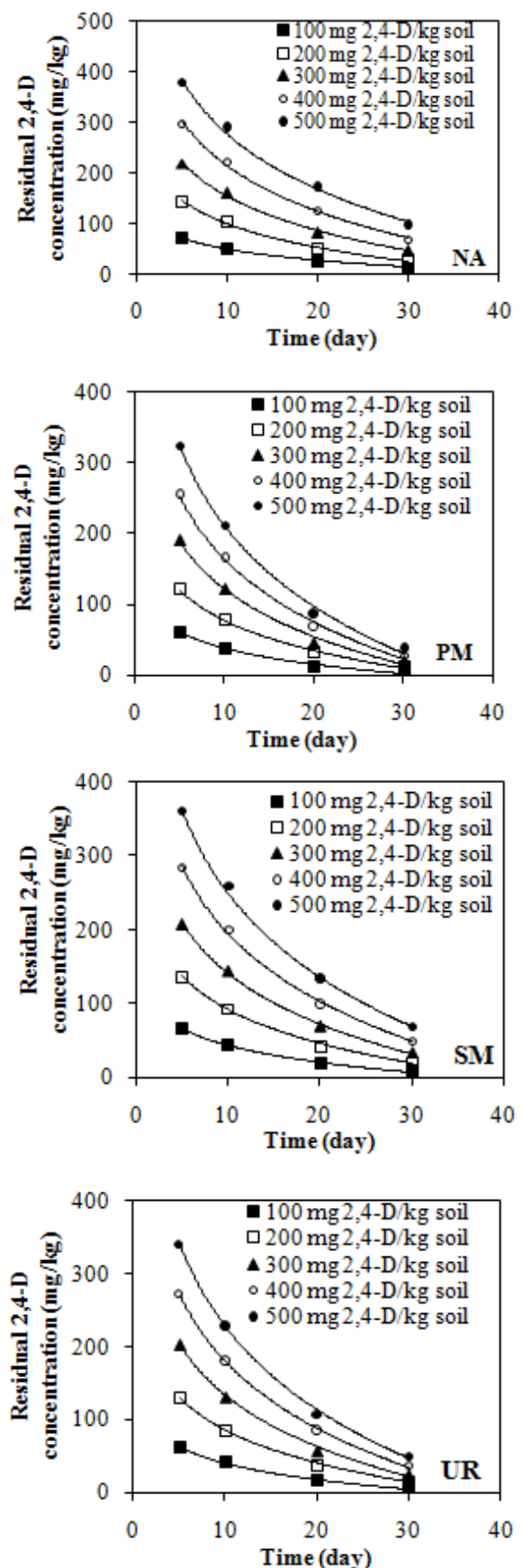


Figure 3: Dissipation of 2,4-D with time in soils with different herbicide loadings under natural attenuation (NA) or treatment with (10%w/w) poultry manure (PM), swine manure (SM) and urea (UR)

The values of k_1 ($\times 10^{-2}/\text{day}$) decreased with herbicide load;

while those of $\tau_{1/2}$ (day) increased correspondingly. Typical ranges of the kinetic parameters were: NA [$5.4 \leq k_1 \leq 0.68$; $10.2 \leq \tau_{1/2} \leq 12.8$], PM [$8.7 \leq k_1 \leq 10.0$; $6.9 \leq \tau_{1/2} \leq 8.0$]; SM [$6.4 \leq k_1 \leq 8.1$; $8.6 \leq \tau_{1/2} \leq 10.9$]; and UR [$7.6 \leq k_1 \leq 9.2$; $7.5 \leq \tau_{1/2} \leq 9.1$].

Table 2: 2,4-D degradation rate constants (k_1) and half-lives ($\tau_{1/2}$) in soils with different herbicide loadings under natural attenuation (NA) or treatment with (10%w/w) poultry manure (PM), swine manure (SM) and urea (UR)

Treatment	Initial 2,4-D load (mg/kg)	k_1 ($10^{-2}/\text{day}$)	$t_{1/2}$ (day)	R^2
NA	100	6.80	10.19	0.999
	200	6.60	10.50	0.998
	300	6.20	11.18	0.999
	400	5.80	11.95	0.999
	500	5.40	12.84	0.999
PM	100	10.00	6.93	0.995
	200	9.70	7.15	0.996
	300	9.10	7.62	0.999
	400	8.90	7.79	0.999
	500	8.70	7.97	0.999
SM	100	8.10	8.56	0.997
	200	7.60	9.12	0.998
	300	7.20	9.63	0.999
	400	6.70	10.35	0.993
	500	6.40	10.85	0.999
UR	100	9.20	7.53	0.997
	200	8.50	8.15	0.999
	300	8.30	8.35	0.998
	400	7.90	8.77	0.999
	500	7.60	9.12	0.999

3.3 Effect of Level of Organic Amendment on 2,4-D Dissipation in Soil

At the levels of amendments ($5 \leq \%w/w \leq 30$) under study, $R(t)$ decreased with increase in both incubation time and level of amendment (Figure 4). DY, on the other hand, increased with both incubation time and herbicide load such that, at the elapse of the 30-day incubation, minimum and maximum degradation yields were: PM (27.75 and 94.87%); SM (25.17 and 90.93%); and UR (29.18 and 93.67%). Both $R(t)$ and DY increased in the order: SM > UR > PM.

Under the single amendment scenario, DE generally increased with increase in incubation time and level of amendment. Typical DE ranges at the operating levels of amendments were: PM [$4.87 \leq DE(\%) \leq 98.71$]; UR [$6.76 \leq DE(\%) \leq 70.77$]; and SM [$1.49 \leq DE(\%) \leq 70.16$].

The values of k_1 increased with increase in level of amendment, but a converse trend was observed for corresponding values of $\tau_{1/2}$ (day), which decreased with increase in amendment level (Table 3). Depending on the type of amendment, the range of the kinetic parameters were: PM ($6.60 \leq k_1 \leq 20.10$; $3.45 \leq \tau_{1/2} \leq 10.50$); SM ($5.90 \leq k_1 \leq 9.50$; $7.30 \leq \tau_{1/2} \leq 11.75$); and UR ($6.90 \leq k_1 \leq 9.50$; $7.30 \leq \tau_{1/2} \leq 10.05$).

Overall, the magnitude of DY, DE and the kinetic parameters [$R(t)$, k_1 and $\tau_{1/2}$] indicated that among the amendments PM proved more efficient at 2,4-D dissipation in soil.

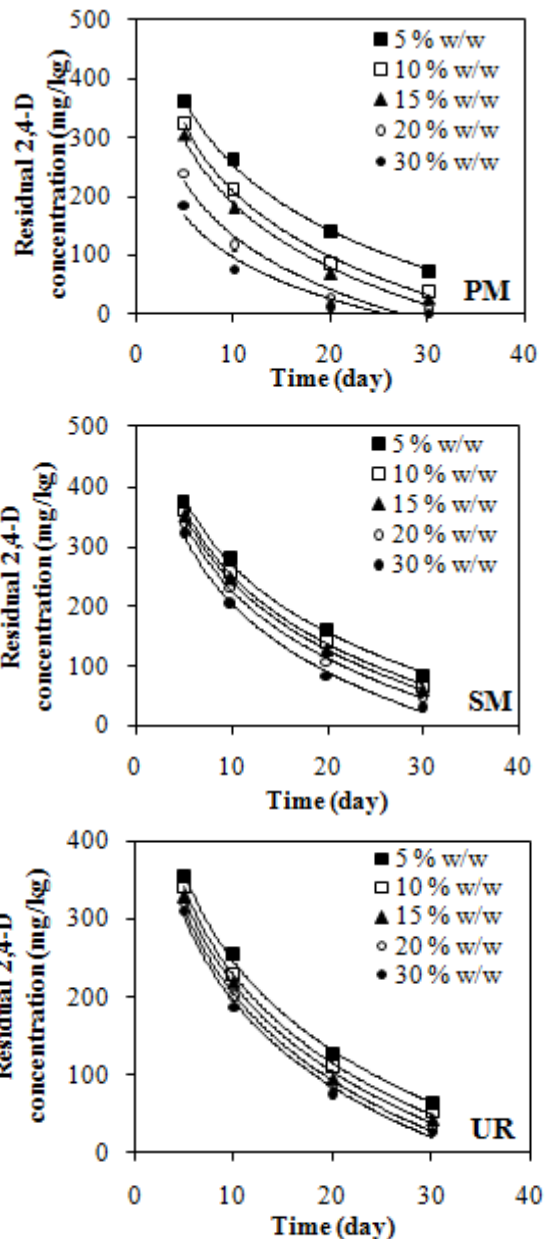


Figure 4: Dissipation of 2,4-D with time in soils loaded with herbicide (500 mg/kg) and different doses of poultry manure (PM), swine manure (SM) and urea (UR)

Table 3: 2,4-D degradation rate constants (k_1) and half-lives ($\tau_{1/2}$) in soils with herbicide (500 mg/kg) at different doses of poultry manure (PM), swine manure (SM) and urea (UR)

Treatment	Amendment dose (%w/w)	k_1 ($10^{-2}/\text{day}$)	$t_{1/2}$ (day)	R^2
PM	5	6.60	10.50	0.999
	10	8.70	7.97	0.999
	15	9.80	7.07	0.999
	20	14.90	4.65	0.998
	30	20.10	3.45	0.999
SM	5	5.90	11.75	0.998
	10	6.80	10.19	0.997
	15	7.00	9.90	0.999
	20	7.90	8.77	0.999
	30	9.50	7.39	0.997
UR	5	6.90	10.05	0.996
	10	7.50	9.24	0.992
	15	8.20	8.45	0.999
	20	9.00	7.70	0.994
	30	9.50	7.30	0.999

3.4 Effect of Amendment Blends on 2,4-D Dissipation in Soil

In the presence of the different amendment blends (binary and ternary), R(t) still decreased with increase in time (Figure 5); while DY followed the converse trend ranging as: PM + SM (39.92 – 95.00%); PM + UR (29.86 – 87.84%); SM + UR (24.75 – 82.36%); and PM + SM + UR (28.30 – 84.72%). DE increased with increase in incubation time and actual ranges were: PM + SM (20.90 – 73.90%); PM + UR (7.65 – 36.66%); SM + UR (0.92 – 8.18%); and PM + SM + UR (5.61 – 20.14%). Based on DE values, it can be inferred that, apart from the binary PM + SM amendment blend, the single amendments were superior at 2,4-D degradation in soil.

Accordingly (Table 4), the following kinetic parameters were furnished for the various amendment blends: PM + SM ($k_1 = 14.90$, $\tau_{1/2} = 4.65$); PM + UR ($k_1 = 9.8$, $\tau_{1/2} = 7.07$); PM + SM + UR ($k_1 = 8.7$, $\tau_{1/2} = 7.97$) and SM + UR ($k_1 = 6.60$, $\tau_{1/2} = 10.50$). Overall, it seemed that the single PM and binary PM + SM scenarios were most efficient at 2,4-D dissipation in the experimental soil.

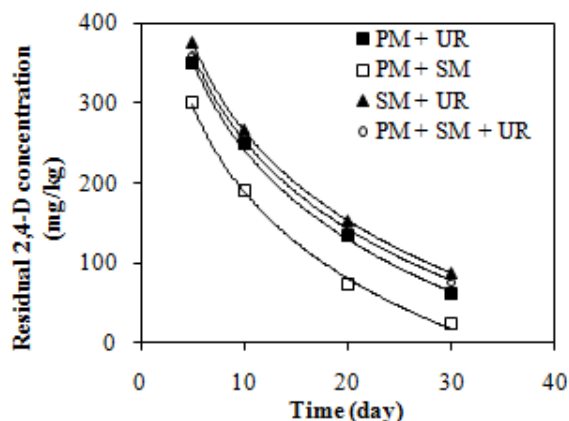


Figure 5: Dissipation of 2,4-D with time in soils with herbicide (500 mg/kg) and different blends of 10 %w/w poultry manure (PM), swine manure (SM) and urea (UR)

Table 4: 2,4-D degradation rate constants (k_1) and half-lives ($\tau_{1/2}$) in soils with herbicide (500 mg/kg) and different blends (10 %w/w) of poultry manure (PM), swine manure (SM) and urea (UR).

Treatment	k_1 ($10^{-2}/\text{day}$)	$t_{1/2}$ (day)	R^2
PM + SM	14.90	4.65	0.998
PM + UR	9.80	7.07	0.997
SM + UR	6.60	10.50	0.998
PM + SM + UR	8.70	7.97	0.999

3.5 Effect of Metal Toxicants (Cd and Pb) on 2,4-D Dissipation in Soil

Figure 6 illustrates the effect of different doses (C_M) of Cd or Pb [$10 \leq C_M(\text{mg/kg}) \leq 200$] on the dissipation of 2,4-D ($C_0 = 500 \text{ mg/kg}$) in soil studied under NA and treatment with (10%w/w) PM, SM, and UR after 2 weeks of incubation.

Under NA and in the absence of Cd or Pb, 54.82% of 2,4-D was degraded after 2 weeks (Figure 2). DY was, however, suppressed in the presence of metal toxicants and decreased with increasing Cd and Pb doses. Typical DY ranges were: 30.52 – 47.46% for the NA-Cd and 37.88 – 53.48% for the NA-Pb scenario. In the presence of PM and metal toxicants, DY was 57.94 – 68.18% and 64.42 – 68.18% for the PM-Cd and PM-Pb microcosms, respectively. For SM, 55.88 – 58.88% and 57.46 – 60.00% of 2,4-D were degraded in the presence of SM-Cd and SM-Pb, respectively. Addition of UR achieved 60.88 – 64.00% and 62.82 – 64.72% of 2,4-D dissipation for the UR-Cd and UR-Pb media, respectively.

Relative to the NA-metal toxicant media, the ranges of DE were: PM-Cd (32.51 – 42.55%), PM-Pb (32.09 – 42.72%); SM-Cd (21.74 – 36.50%), SM-Pb (13.83 – 31.52%); and UR-Cd (27.31 – 43.70%), UR-Pb (20.00 – 40.15%). Overall, the decrease in DY for 2,4-D degradation with increasing Cd and Pb doses and the relatively low DE (< 50%) of the amendments indicates the suppression and vitiation of the biodegradation process in presence of the metal toxicants.

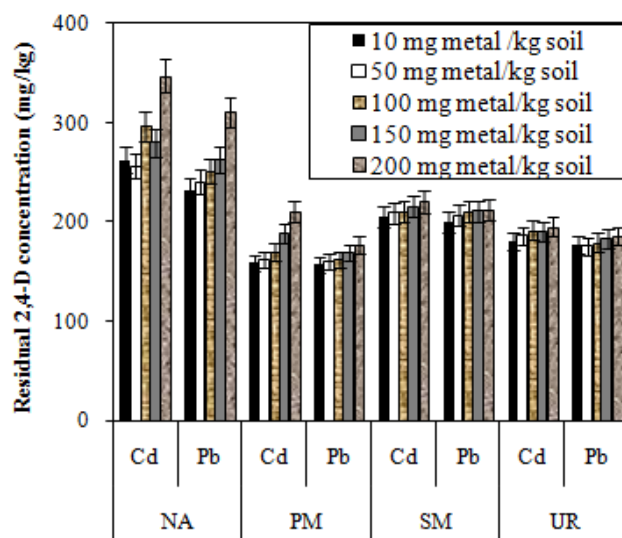


Figure 6: Effect of different doses of Cd/Pb (mg/kg) on 2,4-D (initial concentration = 500 mg/kg) dissipation in soil under natural attenuation (NA) or treatment with (10%w/w) poultry manure (PM), swine manure (SM) and urea (UR) after 2 weeks of equilibration.

4. Conclusion

This study has demonstrated that even though 2,4-D concentration naturally is attenuated in soil under the conditions investigated, organic amendments did enhance the extent and rate of degradation. Relative to NA, the efficiencies of the amendments generally increased with increase in incubation time and level of amendment, but did not necessarily depend on initial 2,4-D load. Pseudo-first-order degradation constants ($\times 10^{-2}/\text{day}$) decreased with herbicide load and increased with adsorbent dosage; with corresponding half-lives (day) decreasing and increasing, respectively. The efficiencies of the single amendments were in the order: SM < UR < PM; while those for the binary and ternary blends followed the sequence: (SM + UR) < (PM + SM + UR) < (PM + UR) < (PM + SM). The extent of 2,4-D degradation decreased with increasing Cd and Pb doses and

the amendment efficiencies were relatively low (< 50%) (but more so in the presence of Cd than Pb). This indicates that the biodegradation process was suppressed or vitiated in the presence of metal toxicants.

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