

Dissipation patterns and characteristics of four pesticides in sandy and clay soil under controlled conditions

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Summary The dissipation of pesticides significantly influences their behaviour in soil, which is crucial for evaluating their stability and safety. This study investigated the dissipation patterns and half-lives of four pesticides—ametryn, bentazone, carbofuran, and oxamyl—in sandy and clay soils at two concentration levels (25 mg·kg⁻¹ and 100 mg·kg⁻¹). The experiment was conducted at 26°C with a 60% water-holding capacity. First-order kinetics effectively described the dissipation ($R^2 > 0.92$). After 60 days, pesticide dissipation exceeded 97% in sandy soil, while remaining residues were 80–86% for ametryn, 80–89% for bentazone, and 85–88% for carbofuran and oxamyl. In clay soil, dissipation was initially slower (<8% for all pesticides), but subsequently accelerated. The quantity of pesticides declined sharply in the first month, followed by a gradual decrease in the second month. Ametryn exhibited the longest half-life, whereas bentazone had the shortest. Overall, pesticide loss correlated with decreased concentrations and organic matter content.

Additional keywords: dissipation, half-life, pesticides, residue, soil

Introduction

A significant challenge confronting modern agriculture is the necessity to secure sufficient food supplies for the world's expanding population. As a result, pesticides are designed to enhance agricultural production (Marín-Benito *et al.*, 2019). Approximately 3.0 million tons (Mt) of active ingredients and 7.0 Mt of formulated products are utilised annually for crop protection (Silva *et al.*, 2019; FAO, 2022).

Herbicides play a crucial role in enhancing agricultural productivity by efficiently controlling the rivalry between crops and weeds for essential nutrients in the soil (FAO, 2018). Their application facilitates the optimisation of resource availability, thereby enhancing crop yields and ensuring effi-

cient nutrient utilization in diverse agricultural practices systems. The ideal herbicide should effectively target only the weed and stay active in the environment for a suitable period (Marín-Benito *et al.*, 2019). Ametryn and bentazone are two selective herbicides commonly used to control weeds in many crops in Egypt. These herbicides are typically applied either by pre-plant incorporated treatments or at pre-emergence stage. Their interactions and behaviour within the soil significantly affect their effectiveness in controlling weeds and their environmental impact persistence.

Carbofuran and oxamyl are pesticides frequently used to control insects and nematodes on several crops because they have a wide-range biological action (Subramanian and Muthulakshmi, 2016; Kuswandi *et al.*, 2017). As systemic insecticides, they enter the plant through its roots and are then distributed throughout its organs to reach insecticidal concentrations. These pesticides are applied directly to the soil surface or plants (Alvarez *et al.*, 2022). Despite their effectiveness, they are among the most dangerous pesticides (Kuswandi *et al.*, 2017).

Once pesticides reach the soil, they dissipate through various processes, includ-

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ing surface runoff, volatilization, chemical hydrolysis, leaching, and microbial degradation (Davie-Martin *et al.*, 2015). The contribution of each dissipation process varies depending on the pesticide, soil type, and environmental factors. Sorption and desorption, along with degradation, are the primary processes that influence the behavior of pesticides in soils (Vagi *et al.*, 2010; Marín-Benito *et al.*, 2019). Research on the environmental behavior of pesticides has indicated that certain pesticides remain in the soil for an extended period, while others degrade quickly and do not persist (Rahman *et al.*, 2020). There is a strong correlation between environmental pollution by pesticides and their persistence. Nonetheless, during breakdown processes, new chemicals that could be either more or less toxic than the original compound may be generated (El-Aswad *et al.*, 2024). The half-life of a pesticide is a crucial factor in determining whether it is likely to accumulate in the soil.

To effectively assess environmental safety, it is crucial to gather data on the rate of pesticide degradation. This information is needed to understand how the fate of applied pesticides changes, taking into account potential variations in degradation factors (Purnama *et al.*, 2014; Rani and Sud, 2015). At present, the nematicides carbofuran and oxamyl, along with the herbicides ametryn and bentazone, are being utilised across various agricultural crops in Egypt. Nonetheless, information regarding the dissipation rates of these pesticides in Egyptian clay and sandy soils remains insufficient. The half-lives of these pesticides can exhibit considerable variation influenced by soil properties and environmental conditions. Accordingly, it is essential to establish these parameters within controlled laboratory environments, which are both cost-efficient and labour-effective (Purnama *et al.*, 2014).

The present research focused on the dissipation trends and persistence of four commonly used pesticides—ametryn, bentazone, carbofuran, and oxamyl—within two prevalent soil types in Egypt: clay and sandy soil. Clay soil, renowned for its ex-

ceptional water retention and nutrient-rich properties, was contrasted with sandy soil, which offers improved drainage but has a lower nutrient content. Conducted under controlled conditions, the study aimed to closely monitor the degradation of these pesticides over time in each soil type. Understanding their environmental behavior is essential for promoting sustainable agricultural practices and assessing their potential impact on the ecosystem.

Materials and Methods

Chemicals and reagents

Ametryn, bentazone, carbofuran, and oxamyl (purity > 99%) reference standards were obtained from Dr Ehrenstorfer GmbH in Augsburg, Germany. The chemical structures of these pesticides are depicted in Figure 1. All reagents and chemicals used in the experiment were supplied by Supelco (Bellefonte USA). Stock solutions of ametryn, bentazone, carbofuran, and oxamyl were meticulously prepared at a concentration of 1000 $\mu\text{g}\cdot\text{mL}^{-1}$ using acetonitrile as solvent and stored at a temperature of -20°C . Subsequently, appropriate stock solutions were diluted in acetonitrile to generate working standard solutions for the studied pesticides. Calibration standards were then created by combining the working standards with acetonitrile and water in a 60:40 (v/v) ratio, covering a concentration range from 1 to 1000 $\text{ng}\cdot\text{mL}^{-1}$. The working standard solutions also underwent serial dilutions with blank soil extracts to establish a matrix-matched calibration standard.

Experimental soil

The clay soil utilised in this study was sourced from the experimental farm at Menofya University's Faculty of Agriculture. The sandy soil was acquired from the Sadat area in the Menofya Governorate of Egypt. Soil samples were collected from 0 to 15 cm depth, air-dried, and ground to pass through a 2 mm sieve to remove larger fragments and undecomposed plant material.

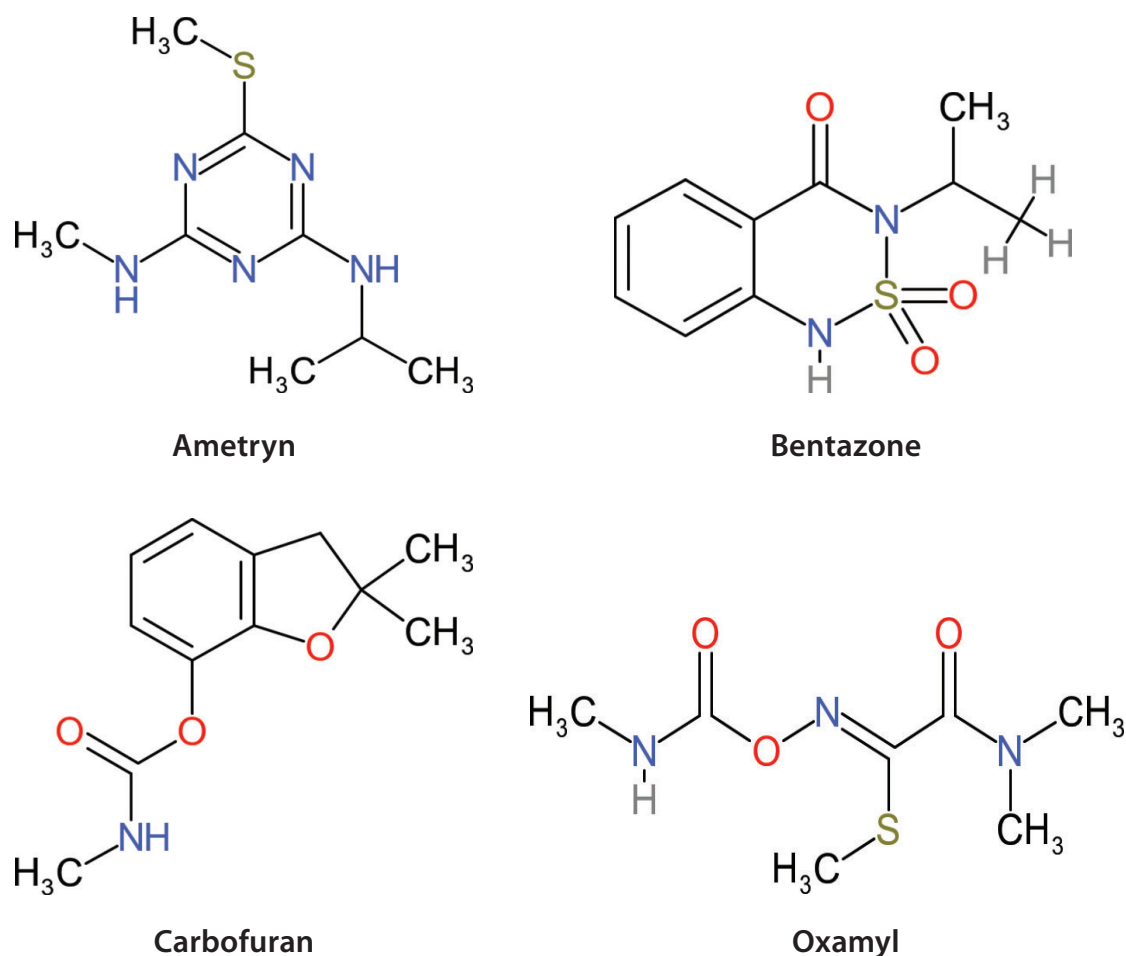


Figure 1. Chemical structure of the pesticides ametryn, bentazone, carbofuran, oxamyl.

The processed soil samples were carefully stored in plastic bags to prevent contamination and kept at room temperature throughout the study. To ensure accurate analysis, a representative subsample was meticulously extracted from each batch of soil samples for detailed physicochemical testing. The results of this analysis are presented in Table 1, which offers a comprehensive overview of several key characteristics, including the distribution of soil particle sizes, the concentration of total organic carbon, the pH level of the soil, and the cation exchange capacity, which indicates the soil's ability to hold and exchange essential nutrients. This information is essential in evaluating the soil's quality and potential agricultural productivity. The amount of water added to the soil was determined using a water retention curve established after one year of monitoring field soil moisture. The calculated gravimet-

ric water content (w) was determined using the following equation:

$$W = \frac{\text{wet soil weight} - \text{dry soil weight}}{\text{wet soil weight}} \quad (1)$$

The collected soil samples were oven-dried at 105°C for 24 h to obtain the dry weight.

Pesticides dissipation studies

The degradation rates of ametryn, bentazone, carbofuran, and oxamyl were studied in two different soil types (clay and sandy soils) following the OECD (Organization for Economic Co-operation and Development) Guideline for the Testing of Chemicals (OECD, 2025). Prior to the application of pesticides, 500 g of air-dried soil was positioned within a glass container, subsequently rehydrated to reestablish microbial activity, and

Table 1. Physical and chemical properties of the under study soils.

Parameters	Sandy soil	Clay soil
Depth (cm)	0-15	0-15
pH (H ₂ O)	7.93	7.82
Organic carbon content (%)	0.30	1.10
Organic matter content (%)	0.51	1.89
Electrical conductivity (ds/m)	29.53	1.91

incubated for a duration of two weeks at a temperature of 26°C in the absence of light to facilitate seed germination and removal. Both soil samples were contaminated with ametryn, bentazone, carbofuran, and oxamyl in glass bottles at 25 and 100 mg·kg⁻¹ concentrations. The contaminated soils were thoroughly mixed with pre-incubated samples before applying water treatments.

The soil specimens were kept in an incubator at a constant temperature of 26°C, maintaining the moisture level at 60% of the soil's water-holding capacity (WHC). Every 2 days, the samples were exposed to ensure adequate aeration and to regulate the moisture levels by replenishing the lost water. At the commencement of the experiment, soil samples were collected 0, 3, 7, 15, 30, and 60 days after treatment with the test pesticide.

Analytical procedures

Sample extraction

Five grams of soil samples (± 0.1 g) were procured from a glass container at regular intervals. These samples were subsequently processed in a 50-mL centrifuge tube by combining them with 10 mL of acetonitrile and 7 mL of distilled water; vigorous agitation followed for 15 minutes and sonication for 10 minutes (Asensio-Ramos *et al.*, 2010). Next, 1 g of sodium chloride, 4 g of anhydrous magnesium sulfate, 0.5 g of disodium hydrogen citrate sesquihydrate, and 1 g of trisodium citrate dehydrate were added to the extraction tube, and the mixture was once again vigorously shaken for 10 minutes

and centrifuged at 5000 rpm for 5 minutes. Then, 1 mL of the resulting supernatant was collected, filtered using a polytetrafluoroethylene (PTFE, 0.22 μ m) syringe filter, and transferred to a glass vial for analysis via LC-MS/MS.

Chromatographic conditions

The Exion liquid chromatography system, interfaced with a 6500 + AB SCIEX QTRAP mass spectrometer, was employed to analyze residues of ametryn, bentazone, carbofuran, and oxamyl in samples soil. The separation process was conducted on a Synergi C18 column (2.5 μ m Fusion-RP 100 Å, 3.0 \times 50 mm) from Phenomenex, with the column temperature maintained at 40°C. The mobile phase consisted of (a) 10 mM ammonium formate in water (pH=4) and (b) methanol. The total runtime was 15 minutes, following a gradient elution method: 0 min at 100% A; from 1 to 10 min, a transition from 100% to 0% A; from 10 to 12 min at 0% A; and from 12 to 15 min back to 100% A. Injection volume was 2 μ L, with a 15 min runtime. Ionization was achieved through electrospray (ESI) in the positive ion mode using multiple reaction monitoring (MRM). Details of the quantification and validation of critical parameters such as retention time, collision energy potentials (CE), collision cell exit potential (CXP), declustering potential (DP), and entrance potential (EP) for the tested compounds are provided in Table 2. Optimizations were made for gas sources and parameters: ion spray voltage set at 5500 v for ESI (+); ion source temperature at 400°C; curtain gas maintained at 20 psi; and adjustment of collision gas medium.

Method validation

The proposed method for analyzing residues was assessed following the EU SANTE/11312 guidelines for validating residue analytical methods (SANTE, 2021). Linearity was evaluated using linear regression analysis on calibration curves of standard solutions and matrix-matched samples. The complexity of the soil matrix may influence the analytical process by either suppressing

Table 2. LC-MS/MS parameters for determination of the pesticides ametryn, bentazone, carbofuran, oxamyl.

Compound	Retention Time (Min)	Precursor (m/z)	Product (m/z)	Declustering potential (Volts)	Entrance potential (Volts)	Collision energy (Volts)	Collision cell exit potential (Volts)
Ametryn	10.2	228.1	186.2	11.0	25.0	6.5	11.0
	10.2	228.2	96.1	4.5	33.0	4.0	4.5
Bentazone	5.9	241.0	199.0	10.0	19.0	10.0	10.0
	5.9	241.0	107.0	10.0	39.0	10.0	10.0
Carbofuran	7.9	222.1	165.2	9.5	17.0	6.5	9.5
	7.9	222.1	123.0	10.0	29.0	2.0	10.0
Oxamyl	2.7	237.1	90.1	4.0	11.0	3.0	4.0
	2.7	237.1	72.0	5.5	21.0	6.5	5.5

or enhancing the response, potentially compromising the accuracy, selectivity, and sensitivity of the method. To evaluate possible interferences in the chromatographic response, a matrix effect study was conducted in the range from 1 to 100 µg·L⁻¹. Calibration curves, prepared in triplicate either in the matrix extract or in the solvent for LC-MS/MS, were utilised. The matrix effect (ME) was assessed by comparing the response obtained for each analyte in the soil extract with that in the solvent at the same concentration in LC-MS/MS, after subtracting the background signal of the soil matrix. No significant matrix effects were deemed present when ME ranged between 80 and 120%. The predominant trend observed for ME in LC-MS/MS was a tendency towards signal suppression, although this effect was not statistically significant for the compounds tested. Nevertheless, to enhance the accuracy of quantification and to streamline the procedure, the decision was made to employ matrix-matched calibration LC-MS/MS.

Accuracy and precision were determined through recovery experiments conducted at three spiking levels (10, 30, and 60 µg·kg⁻¹) in the soil (Figure 2). These tests were performed over three consecutive days with six replicates each day. The limit of quantification (LOQ) was defined as the lowest concentration at which the recovery percentage falls between 80% and 120%

and the relative standard deviation (RSD) remains below 20% (SANTE/11312/2021, 2021).

Statistical analysis

The degradation of ametryn, bentazone, carbofuran, and oxamyl in the soil is presumed to follow the first-order kinetics model. A first-order rate equation determined the dissipation rate constant and half-life (DT₅₀).

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

The concentrations of ametryn, bentazone, carbofuran, and oxamyl residues (mg·kg⁻¹) at time *t* after treatment and the initial pesticide concentrations are denoted by *C_t* and *C₀*, respectively. The constant *k* represents the rate of dissipation. Furthermore, the half-lives (DT₅₀) of ametryn, bentazone, carbofuran, and oxamyl in the soil are calculated using the formula.

$$DT_{50} = \frac{\ln(2)}{k} \quad (3)$$

Results and Discussion

Method validation

The conclusions of this examination were obtained from measuring peak areas

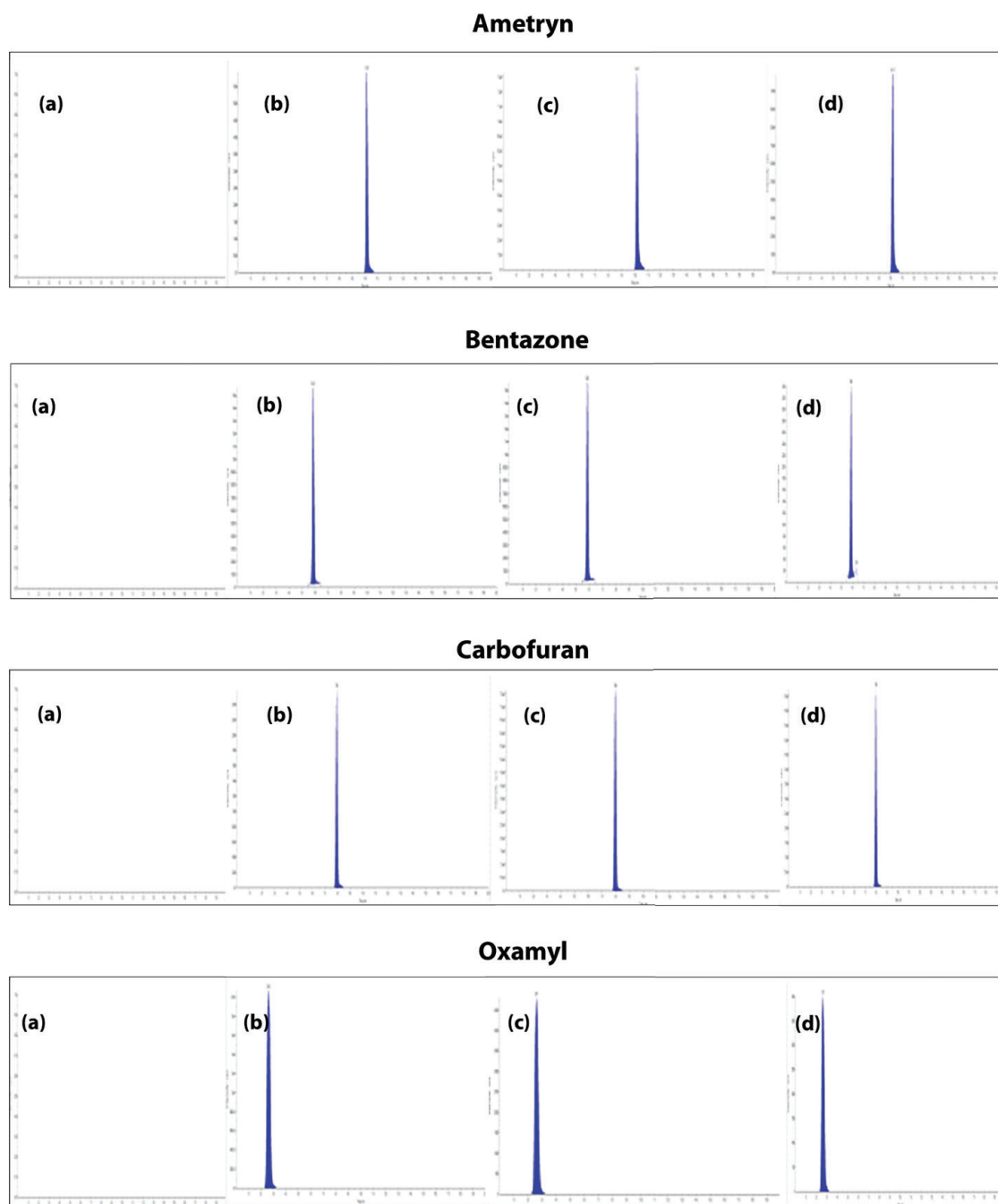


Figure 2. LC–MS/MS chromatograms of the pesticides ametryn, bentazone, carbofuran, oxamyl, in different media (a) blank soil, (b) standard in solvent ($10 \mu\text{g}\cdot\text{kg}^{-1}$) (c) standard in soil matrix ($10 \mu\text{g}\cdot\text{kg}^{-1}$), (d) spiked soil sample ($10 \mu\text{g}\cdot\text{kg}^{-1}$).

using a calibration curve. The correlation coefficient (R^2) for all pesticides analyzed was greater than 0.999, indicating a strong level of linearity in the findings. Additionally, the impact of the matrix was evaluated by comparing the pesticide standards in a solvent (acetonitrile) with standards specific to the matrix (soil) over six repetitions at a con-

centration of $30 \mu\text{g}\cdot\text{kg}^{-1}$. The results indicated no interference from natural peaks, and the retention time (RT) of the substances in the spiked soil sample matched that of the standard samples, as shown in Table 2. The average recovery values ranged from 91% to 98%, with a relative standard deviation (RSD) between 3.8% and 12.5% for all pes-

ticides tested. The study assessed measurement precision using two methods: repeatability and reproducibility. Repeatability (RSD_r) was established through three analyses conducted on the same day. In contrast, reproducibility (RSD_R) was evaluated via a single analysis performed over three days, focusing on a fortification level of $10 \mu\text{g}\cdot\text{kg}^{-1}$, as detailed in Table 3. The RSD_r and RSD_R values for all tested pesticides did not exceed 15% (Table 4). During the method validation process, the limit of quantification (LOQ) for ametryn, bentazone, carbofuran, and oxamyl in soil was established at $10 \mu\text{g}\cdot\text{kg}^{-1}$ based on validation and precision data obtained from recovery assessments. The satisfactory recovery and precision indicate that the analytical method is suitable for detecting ametryn, bentazone, carbofuran, and oxamyl in soil.

Dissipation of pesticides in soil

Pesticides are routinely employed to safeguard crop plants against weeds, diseases, insect damage, and nematodes. These chemicals typically interact with the soil, undergoing a series of transformations, resulting in a complex array of metabolites (Carpio *et al.*, 2021). Figure 3 presents the dissipation curves for ametryn, bentazone, carbofuran, and oxamyl at two varying con-

centrations in clay and sandy soils over a 60-day incubation period at 26°C . Overall, the dissipation graphs for the pesticides examined show a steady decline over time for all the soil treatments and concentration levels (Figure 3). The initial concentrations two h after pesticide treatments at low concentrations ranged from 22.52 ± 1.44 to $24.89\pm 1.90 \text{ mg}\cdot\text{kg}^{-1}$ for sandy soil and from 23.70 ± 1.71 to $25.56\pm 0.07 \text{ mg}\cdot\text{kg}^{-1}$ for clay soil. Also, high concentrations ranged between 81.70 ± 2.14 and 99.01 ± 1.92 for sandy soil and 97.60 ± 1.70 and 108.68 ± 2.92 for clay soil. After 30 days of incubation, ametryn residues at low concentrations in sandy and clay soil reduced to 10.20 ± 0.07 and $15.30\pm 0.04 \text{ mg}\cdot\text{kg}^{-1}$ (58% and 40% of the initial dose), while at high concentrations decreased to 40.20 ± 0.07 and $55.10\pm 0.01 \text{ mg}\cdot\text{kg}^{-1}$ (49%, and 51% of initial dose), respectively. Also, the residue of bentazone at low concentrations in sandy and clay soils decreased to 1.8 ± 0.90 and $9.1\pm 0.03 \text{ mg}\cdot\text{kg}^{-1}$ (92% and 62% of the initial dose), while at high concentrations decreased to 23.3 ± 0.05 and $62.1\pm 0.10 \text{ mg}\cdot\text{kg}^{-1}$ (76%, and 41% of initial dose), respectively. In addition, on the 30th day, the carbofuran residue in sandy and clay soil decreased to 5.4 ± 0.11 and $9.8\pm 0.06 \text{ mg}\cdot\text{kg}^{-1}$ (78% and 61% of the initial dose) at low concentration while decreased to 35.07 ± 0.091 and $46.3\pm$

Table 3. Recovery % and relative standard deviation (RSD%) of the pesticides ametryn, bentazone, carbofuran, oxamyl in soil (n = 6).

Compound	Spiked level ($\text{ng}\cdot\text{mL}^{-1}$)	Recovery (%)	RSD (%)
Ametryn	10	98	3.80
	30	92	5.23
	60	95	6.74
Bentazone	10	94	4.26
	30	91	8.43
	60	97	11.79
Carbofuran	10	96	6.54
	30	93	10.23
	60	91	12.50
Oxamyl	10	94	6.71
	30	92	9.44
	60	98	4.74

Table 4. Recovery%, RSD_r%, and RSD_R% values were acquired from the analysis of samples fortified with the pesticides ametryn, bentazone, carbofuran, oxamyl in soil at 60 ng·mL⁻¹ (n = 6).

Compound	Analysis day	Recovery (%)	RSD _r (%)	RSD _R (%)
Ametryn	1	97	12.70	13.41
	2	100	11.80	
	3	95	9.80	
Bentazone	1	94	7.60	14.26
	2	92	3.14	
	3	96	4.56	
Carbofuran	1	98	12.21	9.40
	2	100	10.24	
	3	92	8.80	
Oxamyl	1	95	7.14	11.07
	2	93	6.36	
	3	99	8.79	

0.03 mg·kg⁻¹ (63%, and 53% of initial dose) at high concentration, respectively. Moreover, the residue of oxamyl at low concentrations decreased to 6.5±0.081 and 9.1±0.077 mg·kg⁻¹ (72% and 68% of the initial dose), while at high concentrations decreased to 32.07±0.03 and 25.1±0.05 mg·kg⁻¹ (72%, and 64% of initial dose), in sandy and clay soil, respectively.

The observed degradation of the tested pesticides exhibited a modest response to variations in concentration levels. Pesticides can undergo various processes in soil, including hydrolysis, photolysis, oxidation, or reduction (Singh *et al.*, 2021). Various factors, including microorganisms in the soil influence the breakdown rate of pesticides (Masutti and Mermut, 2007; Magalhães *et al.*, 2018). The elevated levels of pesticides can negatively impact soil microorganisms, which are essential for breaking down pollutants, potentially hindering their functions. After the incubation period, degradation levels in sandy soil reached an impressive percentage >97%, with pesticide residue percentages recorded as follows: 80–86% for ametryn, 89–80% for bentazone, 87–88% for carbofuran, and 87–85% for oxamyl after 60 days, for both low and high concentration levels. In contrast, the

initial dissipation of the tested pesticides in clay soil was slow (less than 8% for all pesticides) across both concentration treatment levels; however, the dissipation rate subsequently demonstrated a slight increase, as illustrated in Figure 3. These results indicate that pesticide dissipation occurred marginally faster in sandy soil than in clay soil. The significantly enhanced persistence of the tested pesticides in clay soil, as opposed to sandy soil, is likely attributable to the higher organic matter content and clay content, which result in a greater adsorption capacity for pesticides in clay soil (Badawy *et al.*, 2017; Fouad *et al.*, 2023; El-Aswad *et al.*, 2024). Besides, there is a higher activation energy threshold for degradation/volatilization (Carpio *et al.*, 2021). Therefore, pesticides are less bioavailable to be degraded (James *et al.*, 2019; Vischetti *et al.*, 2020). Within the first month of incubation, the pesticide quantities were strongly reduced, followed by a gradual decrease in the second month.

Half-lives of pesticides in soil

The dissipation rate constants for all examined pesticides in sandy soil, at both low and high concentration levels, ranged between 0.0485 and 0.0819 d⁻¹, corresponding

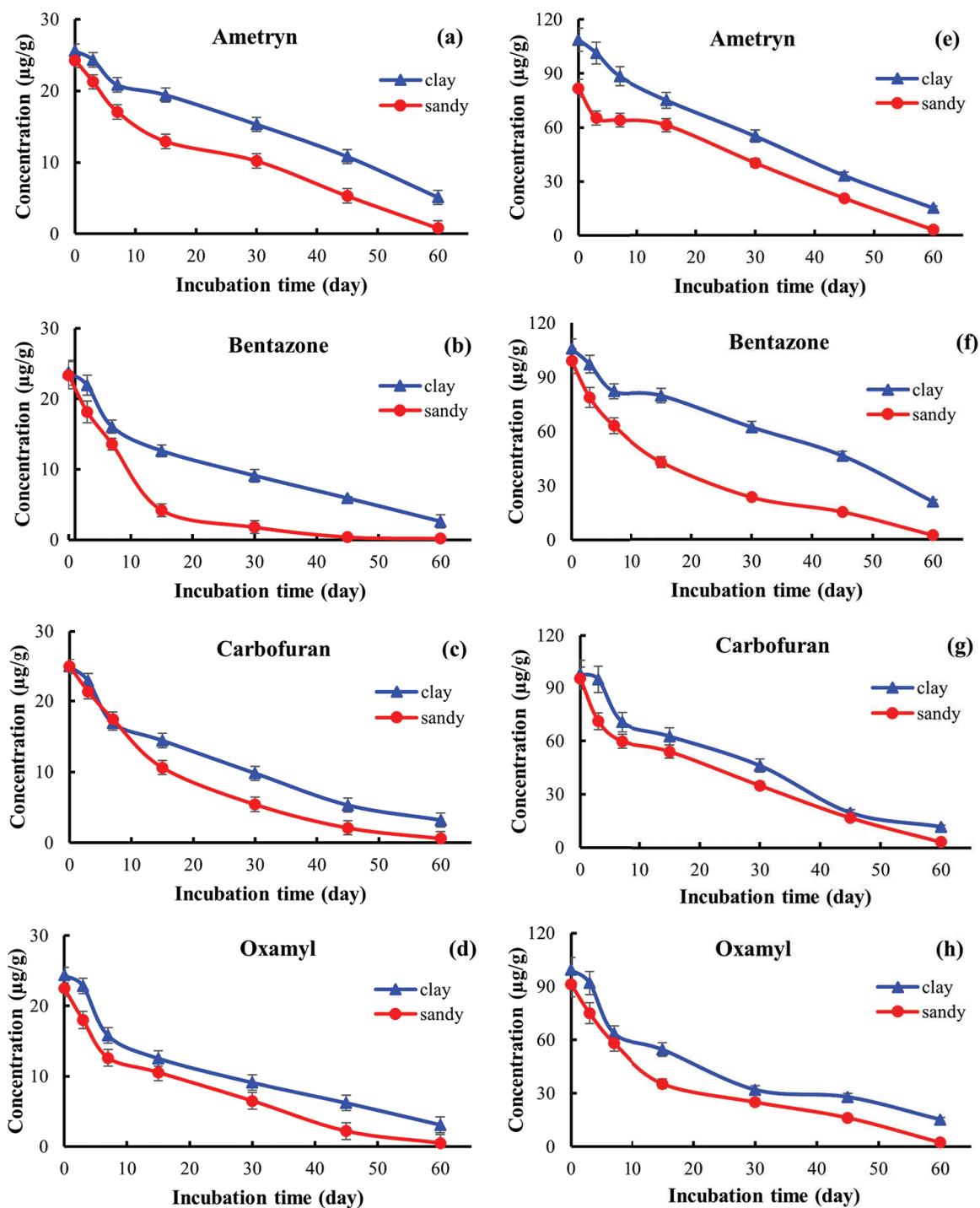


Figure 3. Dissipation pattern of the pesticides ametryn, bentazone, carbofuran, oxamyl, in sandy and clay soils spiked with low concentrations (a, b, c, d) and high concentrations level (e, f, g, h).

to half-lives spanning 14.3 to 8.5 days. In addition, the rates for low and high concentration levels were measured between 0.0466 and 0.0550 d^{-1} , translating to half-lives ranging from 14.8 to 12.6 days, respectively (see Table 5). Conversely, in clay soil, the dissipa-

tion rate constants for all tested pesticides at low and high concentration levels varied between 0.0242 and 0.0340 d^{-1} , with corresponding half-lives from 28.6 to 20.4 days and between 0.0237 and 0.0348 d^{-1} , correlating to half-lives between 29.2 and 19.9

Table 5. Regression equation, correlation coefficient and half-life (DT₅₀) of the pesticides ametryn, bentazone, carbofuran, oxamyl in soil.

Low concentration						
Compound	Regression equation		Correlation coefficient (R ²)		DT ₅₀ (days)	
	Sandy	Clay	Sandy	Clay	Sandy	Clay
Ametryn	-0.0485x + 3.3124	-0.0242x + 3.2913	0.8889	0.9417	14.3	28.6
Bentazone	-0.0819x + 3.0370	-0.0340x + 3.1336	0.9848	0.9775	8.5	20.4
Carbofuran	-0.0599x + 3.2837	-0.0333x + 3.1831	0.9903	0.9919	11.6	20.8
Oxamyl	-0.0578x + 3.1591	-0.0319x + 3.1261	0.9579	0.9772	11.9	21.7

High concentration						
Compound	Regression equation		Correlation coefficient (R ²)		DT ₅₀ (days)	
	Sandy	Clay	Sandy	Clay	Sandy	Clay
Ametryn	-0.0466x + 4.5931	-0.0307x + 4.749	0.8551	0.9691	14.8	22.6
Bentazone	-0.0550x + 4.6242	-0.0237x + 4.6874	0.9391	0.9270	12.6	29.2
Carbofuran	-0.0485x + 4.6052	-0.0348x + 4.6271	0.9175	0.9761	14.3	19.9
Oxamyl	-0.0523x + 4.5278	-0.0293x + 4.4977	0.9169	0.9670	13.3	23.6

days, respectively (see Table 5). Variations in rate constants and half-lives were noted based on the soil type.

A strong linear relationship was established between the logarithmic concentrations of ametryn, bentazone, carbofuran, and oxamyl residues over time, indicating first-order kinetic rates of pesticide dissipation, as evidenced by a correlation coefficient R² values were generally greater than 0.92, except for ametryn in sandy soil. Several studies addressing pesticide dissipation have described the dissipation process utilizing first-order kinetics (Huan *et al.*, 2013; Wang *et al.*, 2014; Hou *et al.*, 2016; Badawy *et al.*, 2017; Ge *et al.*, 2017; Fouad *et al.*, 2023; El-Aswad *et al.*, 2024). The half-lives of all tested pesticides were longer in the case of clay soil than in sandy soil. This result agrees with those obtained for different pesticides (Badawy *et al.*, 2017; Fouad *et al.*, 2023; El-Aswad *et al.*, 2024). It can be observed that among the pesticides studied, ametryn possesses the longest half-life. In comparison, bentazone exhibits the shortest half-life in sandy soil, recorded as 14.3 and 8.5 days, and in clay soil, measured at 28.6 and 20.4 days, at the lower concentration levels of 14.8 and 12.6 days in sandy soil, and at the higher concentration (Table 5).

Our results revealed that ametryn was more persistent than bentazone in sandy and clay soils, whereas carbofuran was less persistent in these soils. This result can be attributed to the adsorption process, which is correlated with water solubility. The water solubility of ametryn (200 mg/L) is lower, while that of bentazone (7112 mg/L) is higher than that of carbofuran (351 mg/L). Other studies supported this result (El-Aswad *et al.*, 2024).

Furthermore, the molecular structure of the pesticides determined the breakdown mechanism; a significant and minor mechanism could occur, or some mechanisms could occur together or consequently (Kah *et al.*, 2007; Juretic *et al.*, 2014; Ruomeng *et al.*, 2023). The chemical structure of bentazone, which had a shorter half-life than carbofuran, includes S=O and C=O bonds that can chemically break down quickly. Additionally, the molecule contains a few methyl groups that may be easily demethylated. Meanwhile, ametryn, which has a longer half-life than carbofuran, only has methyl groups that can be demethylated. Both bonds of C=O and methyl groups are included in the chemical structure of carbofuran. The breakdown of these compounds could be attributed to the chemical breakdown

of these bonds and the demethylation process.

Moreover, the persistence of pesticides in soil could be due to the amino groups that bind with soil components (El-Aswad *et al.*, 2023). The ametryn molecule has two amino groups, the carbofuran molecule has one amino group, and the bentazone molecule lacks any amino groups. The soil's combination of moisture and temperature fluctuations encourages the growth of different microorganisms (Broznić and Milin, 2012). Consequently, microbial breakdown is among the initial possible routes for the loss of pesticides, as bacteria have adapted to use pesticides as energy sources (Bending *et al.*, 2003). It was observed that adding clay to the soil increased adsorption processes, resulting in increased pesticide persistence in the soil (Copaja and Gatica-Jeria, 2021). High concentration increased persistence in a laboratory trial using thiobencarb and butachlor for 90 days (Jitender *et al.*, 1993). In this study, the degradation rate of the examined pesticides at elevated concentration levels exceeded 96% of the initial concentration. However, the residual concentration of the tested pesticide in both soil samples was 9% higher than at the lower concentration level. This finding indicates the persistence of pesticides at higher concentration levels.

Conclusion

The dissipation patterns of ametryn, bentazone, carbofuran, and oxamyl in clay and sandy soils were evaluated over a 60-day incubation period at 26°C, using two distinct concentration levels. The dissipation process adhered to first-order kinetics and demonstrated a notable increase in the dissipation rate in sandy soil relative to clay soil. Among the pesticides examined, ametryn exhibited the most extended half-life. In contrast, bentazone exhibited the shortest half-life in sandy soil at both low and high concentration levels, and in clay soil at lower concentrations.

Author contribution

Sara Heikal: conceptualization, methodology, formal analysis, software, data curation, investigation, writing—review and editing. Farag Malhat: conceptualization, investigation, visualization, writing—original draft, writing—review and editing. Anwar El-Sheikh: investigation. Mahmoud Rashwan: investigation. Ahmed F. El-Aswad: conceptualization, supervision, writing—reviewing and editing, project administration.

Data availability

All of the data analyzed and used during the current study will be available from the corresponding author on reasonable request.

Competing interests

The authors declare no competing interests.

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Μοτίβα αποδόμησης και χαρακτηριστικά τεσσάρων φυτοφαρμάκων σε αμμώδες και αργιλώδες έδαφος υπό ελεγχόμενες συνθήκες

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Περίληψη Η αποδόμηση των φυτοφαρμάκων επηρεάζει σημαντικά τη συμπεριφορά τους στο έδαφος, γεγονός κρίσιμο για την αξιολόγηση της σταθερότητας και ασφάλειάς τους. Η παρούσα μελέτη εξέτασε τα μοτίβα αποδόμησης και το χρόνο ημίσειας ζωής τεσσάρων φυτοφαρμάκων—ametryn, bentazone, carbofuran και oxamyl—σε αμμώδη και αργιλώδη εδάφη, σε δύο επίπεδα συγκέντρωσης (25 mg/kg και 100 mg/kg). Το πείραμα πραγματοποιήθηκε στους 26°C με 60% ικανότητα κατακράτησης ύδατος, με την κινητική πρώτης τάξης ($R^2 > 0.92$) να περιγράφει αποτελεσματικά την εν λόγω αποδόμηση. Μετά από 60 ημέρες, η αποδόμηση των φυτοφαρμάκων ξεπέρασε το 97% στο αμμώδες έδαφος, ενώ τα εναπομείναντα υπολείμματα ήταν 80–86% για το ametryn, 80–89% για το bentazone και 85–88% για τα carbofuran και oxamyl. Στο αργιλώδες έδαφος, η αποδόμηση ήταν αρχικά πιο αργή (<8% για όλα τα φυτοφάρμακα), αλλά επιταχύνθηκε στη συνέχεια. Η ποσότητα των φυτοφαρμάκων μειώθηκε απότομα τον πρώτο μήνα και ακολούθησε σταδιακή μείωση τον δεύτερο μήνα. Το ametryn παρουσίασε τον μεγαλύτερο χρόνο ημίσειας ζωής, ενώ το bentazone τον μικρότερο. Συνολικά, η μείωση των φυτοφαρμάκων συσχετίστηκε με τη μείωση της συγκέντρωσης και της περιεκτικότητας σε οργανική ουσία.

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