# Comparison of Dissipation Kinetics and Residual Behaviour for Fenitrothion Insecticide and Thiobencarb Herbicide in Clay Soil

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## ABSTRACT

Comparsion study of the residual behaviour and kinetics of insecticide fenitrothion and herbicide thiobencarb in clay soil were carried out under laboratory conditions. The residues of the tested pesticides were determined by GC-MS at different interval times (0, 2, 5, 13, 20, 27, 48, 55 and 84 day) after treatment. The recoveries were performed at level of 75 µg/g soil and the recovery percentages were found to be 85.69 and 90.89 for fenitrothion and thiobencarb in the tested soil, respectively. The residue of fenitrothion was 64.27 µg/soil, after 48 days of incubation and the dropped to 5.07 % of the initial residue remaining. Thiobencarb residues level recorded after treated soil with 75 µg a.i / g soil wes 68.17 µg/g soil. This concentration gradually decreased with the time and reached to 0.68 µg/g soil at 55 days after treatment. Both compounds fenitrothion and thiobencarb disappeared very rapidly in the soil following a bi-phasic pattern. Graphical and integral methods were used to select the fit kinetic model. The determination coefficient $R^2$ was the highest and the SD of K values were the lowest in 1st order model compared to other kinetic models. Therefor, the dissipation of fenitrothion and thiobencarb in soil fits with the 1st-order kinetic model. The estimated value of fenitrothion half-life was 11.21 days and that of thiobencarb was 10.61 days. In general, the dissipation of thiobencarb was slightly faster in the tested soil than fenitrothion.

**Key words: Dissipation, persistence, kinetics; half-life; fenitrothion; thiobencarb; soil.**

## INTRODUCTION

Once a pesticides enter the soil are subject to loss by two mechanisms, degradation and transport process. Among the many processes that rule the vital fate of pesticides in the environment, the degradation process plays an essential role (Khan and Manchur 2017). Degradation is the process of pesticide breakdown after application. The principal mechanisms of pesticide degradation in the soil are chemical degradation, photodegradation and microbial degradation. All these processes may participate in the breakdown of a single pesticide. The rate of degradation depends on physicochemical properties of the pesticide (e.g., water solubility, sportive affinity), characteristics of the soil (e.g., pH, organic content, biomass, redox status), environmental conditions (temperature, moisture), as well as management process (e.g., application rate, formulation type). Microbiological catabolism and metabolism are usually the major route of mineralization. Soil microbiota utilizes the pesticide as a source of carbon or other nutrients. The environmental fate and behavior studies of pesticides indicated that some pesticides are not persistent in soil that is due its rapid degradation. However, other pesticides are persistent in soil under different conditions (Rahman *et al.,* 2020).

Fenitrothion is one of most used organophosphorus pesticides to exterminate pest insects on wide range of agricultural products and also utilized as public health measures to control harmful insects such as mosquitoes and flies. In the last decades, production of fenitrothion in the world is estimated around 15,000-20,000 ton/year. Resulting of its widespread use, fenitrothion can extensively be detected in environment (Zayed and Mahdy, 2008; Wang *et al.,* 2012; Masia *et al.,* 2015; Oiwa *et al.*, 2020). The environmental studies of fenitrothion indicated that it is not persistent in soil because of its rapid degradation by physical, chemical or biological means. Although numerous reports on its environmental persistence are available. Fenitrothion residues were determined in environmental water and soil samples using developed method. In soil samples, the analytical procedure consisted of ultrasonic extraction of the compound with acetonitrile. The average recoveries from spiked water and soil samples at various concentration levels exceeded 86% with relative standard deviations of 1.8–5.1%. It was possible to determine concentrations of this pesticide in the range 0.1–2 ng/g in water and soil samples with a good level of reproducibility and accuracy (Sanchez *et al.*, 2003). Fenitrothion residue level was monitored after application. In sediment samples, the residue was varying from 1-3 µg/g in the first day to 0.5 µg/g two days after application. Half lives of fenitrothion in water and sediment samples under natural conditions were lower than 1 day and between 1-1.5 days, respectively (Barceló *et al.*, 1991). Fenitrothion and 3-methyl-4-nitrophenol, one of the major degradation products in soil, degraded with an initial half-life of less than 7 days. A main degradation route of fenitrothion was a cleavage of the P-O-aryl linkage, leading to the formation of 3-methyl-4-nitrophenol which underwent further metabolism to $CO_2$. In submerged soil, fenitrothion degraded mainly via reduction of the nitro group to the amino group with an initial half-life of less than 7 days. The resultant product was bound to the soil or metabolized further to the formylamino and acetylamino derivatives (Mikam *et al.*, 1985). The persistence of fenitrothion in five tropical soils of varying physicochemical characteristics was compared under flooded and non-flooded conditions. The degradation of the insecticide was more rapid under flooded conditions than under non-flooded conditions. Degradation of the compound proceeded by hydrolysis under no flooded conditions and essentially by nitro group reduction and to a minor extent by hydrolysis under flooded conditions. Kinetic analysis indicated that degradation of fenitrothion followed a first order reaction irrespective of the soil and water regime (Adhya *et al.*, 1987). Persistence of fenitrothion in a paddy soil was studied. The experiment was conducted on a sandy loam soil (pH 8.1) planted with rice during two consecutive cropping seasons. Concentrations of fenitrothion were monitored in paddy topsoil (5 cm). Dissipation of the pesticide from topsoil showed strong bi-phasic behavior. The half-life was less than one day, indicating strong influence of transport processes. Already 6 h after application fenitrothion was found at soil depths of 20 and 40 cm, suggesting preferential transport acting under submerged conditions (Anyusheva *et al.*, 2016).

Thiobencarb is a carbamate herbicide that has been widely used for weed control in rice crops. It is normally applied directly on the soil surface or by inundating the rice fields. After application, thiobencarb is distributed in the sediments and water of rice fields (Hartley and Graham-Bryce, 1980). Numerous methods exist for determining carbamate residues in both soil and water samples (Westcott and Worobey, 1985). The primary criteria for choosing the solvent have been extraction efficiency, selectivity (reducing the amount of unwanted co-extractives) and reproducibility of residue recovery. Partitioning with n-hexane for thiobencarb has been proposed (Crepeau *et al.*, 1991). Thiobencarb degradation was influenced by soil type, temperature, and soil water tension. When the soil was incubated at 25 $^{o}$C, the half-lives of thiobencarb were shorter on the muck (18.5 days) than on the sand (27 days). With the soil incubated at 35 $^{o}$C, the half-life of thiobencarb was shorter (14 days) on the muck than on the sand (21.5 days). Thiobencarb was degraded faster under moist conditions than dry conditions. Also, it was found extreme differences among different conditions of the soil, fast degradation of the herbicide occurring under upland condition in all soils followed by under oxidative flooded conditions then under reductive flooded condition. Submerged conditions, under which paddy rice is cropped, increase pesticide impact on the environment (Capri and Karpouzas, 2008). Thoan *et al.* (2013) and Hoai *et al.* (2011) reported chronic exposure of ecosystems to a number of pesticides used on rice of varying toxicity and at varying exposure levels. Therefore, further research expansion to assess pesticides fate in paddy fields. Degradation, sorption, and transport of pesticides in paddies are affected by the saturated conditions in paddy rice soil. Compared to aerobic soils, pesticides in flooded soils can be both more and less persistent (Roger *et al.*, 1994). The half-life period was calculated to be around 20, 50, and 200 days under upland, oxidative flooded, and reductive flooded conditions, respectively. In addition, thiobencarb dissipation was significantly affected by depth in the soil profile. The $DT_{50}$ value was 54 days at 2-cm depth and 94 days at the 60-cm depth where the soil was wettest (Johnson and Lavy, 1994). Half-lives of herbicides in soil and water were found to be 57-71 days for imidazoline, 13–60 days for phenylureas, 13-147 days for sulfonylureas, 12-58 days for triazines, 5-60 days for chloroacetinalides, 12-77 days for dinitroanilines, 19-29 days for diethyl-ethers, 19-24 days for thiocarbamates and 8–24 days for fop group of herbicides in the soil (Sondhia, 2019).

The present study was aimed to investigate and compare the residual behaviour, dissipation potential and kinetics of the fenitrothion insecticide and the thiobencarb herbicide in alluvial soil (clay soil) collected from Agricultural Research Station, Abis, Alexandria Governorate.

## MATERIALS AND METHODS

### Chemicals

Fenitrothion, O, O-dimethyl O-4-nitro-m-tolyl phosphorothioate and thiobencarb, S-4-Chlorobenzyl diethyl thiocarbamate, 97% purity were supplied by Shandong Chuangying Chemical Co. and Shandong SanYoung Industry Co., Ltd, respectively. Their chemical structures are shown in Figure (1) and their properties are given in Table (1). Anhydrous sodium sulfate ($Na_2SO_4$), sodium hydroxide (NaOH), also commercial solvents including acetonitrile and acetone were purchased from Algomhoria Chemical Co., Alexandria, Egypt. Solvents HPLC-grade methanol, dichloromethane, n-hexane and acetonitrile were purchased from Sigma Aldrich Co. (Spruce Street, Louis., MO, USA).

### Tested soil

A common type of the Egyptian soil, alluvial was used. The soil samples were collected from the surface layer (0-20 cm) from different locations in Agricultural Research Station, Abis, Alexandria Governorate. The soil samples have no history with pesticides. The physical and chemical properties were determined at the Department of Soil and Water Sciences, Faculty of Agriculture, University of Alexandria and the data are presented in Tables (2). Soil was air-dried, ground and passed through a 2-mm sieve prior to use. The soil texture was determined by the hydrometer method (Gee *et al.*, 1986). Soil pH will be measured using 0.01 M calcium chloride ($CaCl_2$) in a 1:2 w/w soil: solution slurry. The organic matter content was determined by dichromate oxidation according to the Walkley-Black method (Nelson *et al.*, 1996).

**Instrumentation**

- GC-MS a thermo Scientific gas chromatograph GC Trace 1300 coupled with an EI Mass spectrometer ISQ 7000 model (Thermo Scientific USA) equipped with Thermo TR-50 MS capillary column (30 m in length × 250 µm in diameter × 0.25 µm in thickness of film).
- Sonicator, Mod: LBS 2 4, 5Lt; Cod: 616.1020.05; Ser.N°: B133276; Year: 2013.
- Rotary evaporator bibby scientific limited stone. Staffordshire. St15 0SA. UK.
- Centrifuge, Model 90-1 UK.
- Water distillatory, DESA 0035, Eu.
- Digital balance, ViBRA AJ-320E, 0.01-150 g, Japan.

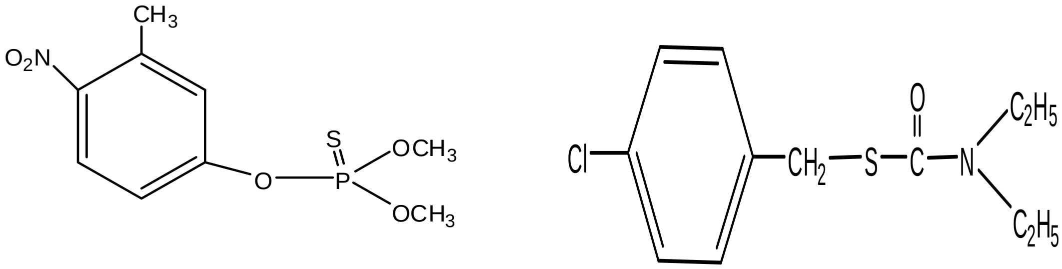
**Pesticide determination and recovery by GC-MS**

**GC standard solution**

Stock solutions of individual tested pesticides, fenitrothion and thiobencarb were prepared in methanol-HPLC grade (1000 mg/L), considering standard purity and stored at 4ºC in the dark. Working standard solution was freshly prepared by appropriately diluting the stock with dichloromethane-HPLC grade. The standard solution (100 µg/mL) was determined immediately before the samples.

**Determination by GC-MS**

Fenitrothion and thiobencarb residues in soil samples of persistence experiment were analyzed using GC-MS at the following conditions, spectroscopic detection by GC–MS involved an electron ionization system which utilized high energy electrons (70 eV); MS transfer line temperature 300 °C and ion source temperature 300 °C. Pure helium gas (99.995%) was used as the carrier gas with flow rate of 1 mL/min. The initial temperature was set at 60°C for 2 min, then increased to 100 °C at a rate of 10 °C/min kept for 5 min, then with 10 °C/min to 150 °C and kept for 5 min, then with 10 °C/min to 200 °C and kept for 5 min, then with 10 °C/min to 250 °C and kept for 20 min. One microliter of the prepared extracts was injected in a splitless mode.



Fenitrothion Thiobencarb

**Figure 1: Chemical structures of tested pesticides**

**Table 1: Properties of tested pesticides**

| Properties | Fenitrothion | Thiobencarb |
|---|---|---|
| CAS number | 122-14-5 | 28249-77-6 |
| Chemical formula | $C_9H_{12}NO_5PS$ | $C_{12}H_{16}ClNOS$ |
| Molecular weight | 277.2 $g \cdot mol^{-1}$ | 257.8 $g \cdot mol^{-1}$ |
| Solubility in water | 0.038 $g\ L^{-1}$ | 0.030 $g\ L^{-1}$ |
| In hexane (g/L) | 24 $g\ L^{-1}$ | 500 $g\ L^{-1}$ |
| P value | 0.57 | $1.70 \times 10^4$ |
| Usage | It is used for controlling chewing and sucking insects on rice, orchard fruits, vegetables, cereals, and cotton. Also fly, mosquito, and cockroach control in public health programs. | It is a pre-emergence and early post-emergence herbicide for weed control in rice paddy fields and other situations. |

**Table 2: Physical and chemical properties of the tested soil**

| Particle size distribution (%) | | | Texture class | WHC (mL) | EC (m mohs/cm) at 25°C | pH | OM (%) | Total carbonate (%) | Total soluble cations (meq/L) | Total soluble anions (meq/L) |
|---|---|---|---|---|---|---|---|---|---|---|
| Clay | Silt | Sand | | | | | | | | |
| 42 | 18 | 40 | Clay | 46 | 1.32 | 8.25 | 3.31 | 7.87 | 18.7 | 13.3 |

### Persistence study

### Soil treatment

The persistence of fenitrothion and thiobencarb in clay soil was studied under laboratory conditions. A weight of 150 g soil was placed in 500-mL glass bottle and treated with each tested pesticide (75 µg a.i. /g soil). Three replicates were made for each treatment. The tested pesticides were dissolved in an amount of distilled water equals to 60 % of water holding capacity (WHC) of the tested soil. The solution was added to the soil to reach the adequate concentration of 75 µg/g. All bottels were incubated at 25 °C up to 84 days. Through the incubation period, the appropriate amount of water was added to replace lost soil moisture (Fouad, 2017; Badawy *et al.*, 2017).

### Extraction, clean upand determination of pesticides

The soil was sampled at different times (0, 2, 5, 13, 20, 27, 48, 55 and 84 day). The tested pesticides were extracted from air dried soil samples by dichloromethane-HPLC grade with sonication. The extraction and clean-up of pesticide residues from soil samples were processed as follow: Soil sample (10 g) was mixed with sodium sulfate unhydrous (5 g), 30 mL dichloromethane-HPLC and methanol-HPLC (1:1) was added, then the samples were extracted using sonication for 15 min twice, after that the samples were filitered through Glass fiber filter. The samples were concentrated using Rotary evaporator, and the residue was redissolved in 1 mL n-hexane-HPLC. The extract was analyzed by GC-MS (Redondo *et al.*, 1994).

### Recovery experiment

Untreated soil samples were homogenized and spiked with standard solutions of fenitrothion and thiobencarb (75 µg/g). The samples were processed similar to the procedure of treated samples. Results of the pesticides in persistence experiments were corrected according to the recovery rate. Blank analyses were performed in order to check interference from the matrix (Redondo *et al.*, 1994; Camara et al., 2020).

### Assessment of half-life values

Dissipation kinetics of fenitrothion and thiobencarb were investigated, different kinetic models were tested to select the fit model with the data. The dissipation rate was obtained from the streight line plot of the 1st-order kinetic model, $\ln[C_t] = \ln[C_o] - Kt$ . The half-life values of tested pesticides were assessed by the following equations (Moye *et al.*, 1987; Badawy *et al.*, 2017; Yuan *et al.*, 2020).

$$\mathrm{DT}_{50} = \frac{0.6932}{\mathrm{k}}$$

Where, k is the dissipation rate, $DT_{50}$ (Half-life) is a time it takes for an amount of a compound to be reduced by half through degradation (Badawy *et al.*, 2017; Fardillah *et al.*, 2020).

## RESULTS AND DISCUSSION

### Recovery of tested pesticides

Recovery experiments were carried out to validate the extraction and clean up method and chromatographic analysis for determination of fenitrothion and thiobencarb in soil. The recoveries were performed at level of 75 µg/g soil with extraction by dichloromethane-HPLC, clean up and residue determination as followed in the applied methods. The recovery values were calculated according to the formula of; Recovery % = ((µg pesticide determined/g soil)/(µg pesticide add/g soil)) x 100. The recovery percentages were 85.69 for fenitrothion and 90.89 for thiobencarb in clay soil. These results confirmed by Likas and Tsiropoulos (2007) who found recovery of fenitrothion was 94±10% in soil by GC and Redondo *et al.* (1994) who found the recovery of thibencarb in soil 63%. Similar carbamate recoveries were obtained from soil samples using liquid-liquid extraction with methylene chloride (Redondo *et al.*, 1994).

### Dissipation of fenitrothion and thiobencarb in soil

The dissipation of fenitrothion and thiobencarb in clay soil treated individually with 75 µg/g soil was studied under laboratory conditions. The incubated soil at 25 °C was sampled at different times (0, 2, 5, 13, 20, 27, 48, 55 and 84 day) and analyzed by GC-MS.

The residues and remaining percentages of fenitrothion and thiobencarb detected during 12 weeks after application are shown in Table (3). Initial residue of fenitrothion in soil was 64.27 µg/g soil, while after 48 days of incubation, fenitrothion residue dropped to 3.26 µg/g soil (5.07 % of the initial residue remaining). Thiobencarb residues were detected in all samples up to 8 weeks of incubation and their concentrations were decreased with the time from 68.17 µg/g soil at zero time to 0.68 µg/g soil after 55 days (0.99 % of the initial residues remaining) in clay soil.

**Table 3: Residues of tested pesticides (µg/g soil) in clay soil during 12 weeks determined by GC-MS**

| Time (day) | Fenitrothion | | Thiobencarb | |
|---|---|---|---|---|
| | Residue (µg/g soil) | Remaining (%)* | Residue (µg/g soil) | Remaining (%)* |
| 0 | 64.27 | 100.00 | 68.17 | 100.00 |
| 2 | 54.48 | 84.77 | 56.62 | 83.05 |
| 5 | 42.75 | 66.53 | 26.05 | 38.22 |
| 13 | 36.76 | 57.20 | 18.15 | 26.63 |
| 20 | 16.00 | 24.89 | 11.02 | 16.17 |
| 27 | 12.25 | 19.07 | 5.91 | 8.67 |
| 48 | 3.26 | 5.07 | 4.35 | 6.39 |
| 55 | ND | - | 0.68 | 0.99 |
| 84 | ND | - | 0.243 | 0.36 |

ND: None-detectable
-: no data
* : data calculated according to the recovery percentages.

In addition, the lowest residue level of thiobencarb was detected at 84th day (0.24 µg/g soil, 0.36% of the initial residue remaining). It was found that the pesticide degraded linearly with incubation time (Roy *et al.,* 1996). Our results indicated that the dissipation rate of thiobencarb from the tested soil was greater than fenitrothion at the intial 5 day after treatment. As volatilization and microbial degradation are considered the main aspects that explain dissipation of fenitrothion in soil (Durand and Barcelo, 1992). Nitro group reduction was the major pathway of degradation for fenitrothion in soil (Adhya *et al.,* 1987). It was observed that the unextractable concentrations of tested pesticides at 0 time after soil treatment might be attributed to the formation of the soil-bound residue that non-extractable residue (Scheunert, 1992). It was reported that the bound residues of different pesticides in different soils expressed as % of applied pesticide ranged from 7 to 90% (Khan and Dupont, 1987).

Figure (2) exhibited the disappearance curves of fenitrothion and thiobencarb in soil during 12 weeks. Immediately after treatment, both tested pesticides were determined in the samples as a zero time. Both pesticides fenitrothion and thiobencarb disappeared very rapidly from the soil following a bi-phasic pattern. Just two weeks after treatment the maximum concentrations of fenitrothion were reduced to about a half in clay soil. This sharp drop was followed by a period of a slow incremental decrease for five weeks. At 55th day fenitrothion residues were non detectable in tested soil. Also, just two weeks after treatment the maximum concentration of thiobencarb was reduced to about one fourth in soil. This sharp drop was followed by a period of a slow incremental decrease for six weeks. At 84th day thiobencarb residue was still detected in soil sample.

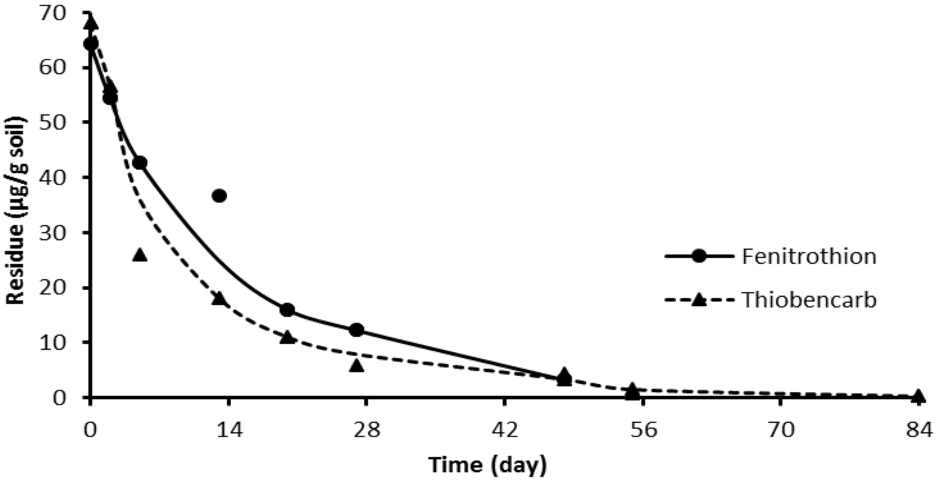


**Fig. 2: Disappearance curves of fenitrothion and thiobencarb in clay soil**

### Dissipation kinetics of tested pesticides in soil

To evaluate the decline of fenitrothion and thiobencarb residues in soil, residue data should be subjected to statistical analysis to determine the statistical parameters that describe these processes, as proposed by Likas and Tsiropoulos (2007). Two methods were used to determine the best kinetic model for the dissipation data, graphical and integral methods. A linear regression can be obtained after an appropriate transformation of the residue using different formal models described in Table (4). To select the best fit model, the values of determination coefficient $R^2$ were calculated for each model. As is well known, $R^2 \leq 1$, and the larger this coefficient, the better the decline curve fits the data. If $R^2$ becomes negative or zero for any model, then the fit is automatically rejected (Lopez-Lopez *et al.*, 2003). The determination coefficient $R^2$ was higher in 1st order model, having the highest $R^2$ value ($\geq 0.95$), whereas $R^2$ values were 0.86 and 0.56 in zero-order, 0.86 and 0.75 in 2nd-order, and 0.73 and 0.62 in 3rd-order for fenitrothion and thiobencarb, respectively. Moreover, according to the integral method, the correlation is confirmed when the values of calculated K are equal in other words, when SD of calculated K values is zero or low value. For comparing among the different models, SD of the K values were calculated as K 100%. The SD values were the lowest in the 1st-order, 22.18 for fenitrothion and 76.12 for thiobencarb. Accordingly, it can be stated that the dissipation of fenitrothion and thiobencarb in soil fits with the 1st-order kinetic model. A number of studies have been carried out fitting decline curves in a first-order model for many pesticides (Adhya *et al.,* 1987). However, that interpretation is not always applicable, because the residues frequently diminish quicker at first and much more slowly at a later stage in comparison with the 1st-order model (Aguilera-del *et al.,* 1999; Martinez-Galera *et al.,* 2003).

Therefore, the dissipated residues of fenitrothion and thiobencarb were estimated by first-order exponential decay model $C_t = C_o\, e^{(-kt)}$ , where $C_t$ is the concentration of insecticide remaining in the soil after time t, $C_o$ is the initial concentration and K is the first-order kinetic constant (Fouad, 2017; Badawy *et al.,* 2017). It can be seen from Figure (3) the streight line plot of the 1st-order kinetic model, $\ln[C_t] = \ln[C_o] - Kt$ . The rate constant (k) values for dissipation of the two pesticides were 0.062 for fenitrothion and 0.065 for thiobencarb. The data of linear equation, rate constant (K) and half-life ($DT_{50}$) of fenitrothion and thiobencarb in soil are shown in Figure (3) and Table (5).

The half-live ($DT_{50}$) has been calculated (Table 5) from the 1st-order model using equation ($DT_{50} = 0.6932/K$). It can be seen that the estimated value of fenitrothion half-life was 11.21 days. Also, the half-life of thiobencarb was 10.61 days. These values are in agreement with the half-life fenitrothion values in the literature, which from 10.5, 10.9 and 20 days in three soils different organic matter (Adhya *et al.*, 1987). Fenitrothion degraded in upland and submerged soils with the half-life of less than 7 days and was of shorter persistence as compared with its half-life of 12-28 days under upland conditions and less than 14 days under submerged conditions found by Takimoto *et al.* (1976). Fenitrothion half-lives in soil of about 17-21 days (Likas and Tsiropoulos, 2007). Studies carried out by Sundaram *et al.* (1987) and Sundaram *et al.* (1989) showed that the amount of fenitrothion deposited on soil dissipated quickly. Also, the half-life of thiobencarb is in agreement with previous studies which found that the half-life was 12 days in soil (Redondo *et al.*, 1994) and this result was not supported by the earlier studies carried out by Wauchope *et al.* (1992) which cited that the half life of thiobencarb ranged from 14 to 21 days. The dissipation of the pesticide residues in soil depending on the environmental conditions, type of application, dosage, temperature, pH, and interval between applications (Khay *et al.,* 2008; Scholz-Starke *et al.*, 2017). Recently, the degradation of fenitrothion under different conditions was studied (Pergal *et al.*, 2020; Potireddy *et al.*, 2019) and that of thiobencarb (Mwevura *et al.*, 2021; Wang *et al.*, 2019).

It can be concluded that both compounds fenitrothion and thiobencarb disappeared very rapidly in the soil following a bi-phasic pattern. Just two weeks after treatment the maximum concentrations of fenitrothion and thiobencarb were reduced to about a half and about one fourth in soil, respectively. This sharp drop was followed by a period of a slow incremental decrease for about five weeks. At 55th day fenitrothion residue was non detectable whereas thiobencarb residue was still detected at 84th day in soil sample. The graphical and integral methods illustrated that the dissipation of fenitrothion and thiobencarb in soil fits with the 1st-order kinetic model. The values of the dissipation rate constant (K) were 0.062 for fenitrothion and 0.065 for thiobencarb. The half-life ($DT_{50}$) calculated from the 1st-order model was 11.21 and 10.61 days for fenitrothion and thiobencarb, respectively. In general, the dissipation of thiobencarb was slightly faster in the tested soil than fenitrothion.

**Table 4: Determination coefficient ($R^2$) obtained from graphical method and standard division (SD) of calculated k values obtained from integral method for fenitrothion and thiobencarb residues in soil using different kinetic models**

| Model | Empirical equation | Pesticide | $R^2$ | SD of calculated k (as k 100%) |
|---|---|---|---|---|
| Zero order | $C_t = C_o - kt$ | Fenitrothion | 0.86 | 51.04 |
| | | Thiobencarb | 0.56 | 79.03 |
| 1st order | $C_t = C_o\ e^{-kt}$ | Fenitrothion | 0.99 | 22.18 |
| | | Thiobencarb | 0.95 | 76.12 |
| 2nd order | $1/C_t = (1/C_o) + kt$ | Fenitrothion | 0.86 | 76.01 |
| | | Thiobencarb | 0.75 | 135.84 |
| 3rd order | $1/C_t^2 = (1/C_o^2) + 2kt$ | Fenitrothion | 0.73 | 179.83 |
| | | Thiobencarb | 0.62 | 230.36 |

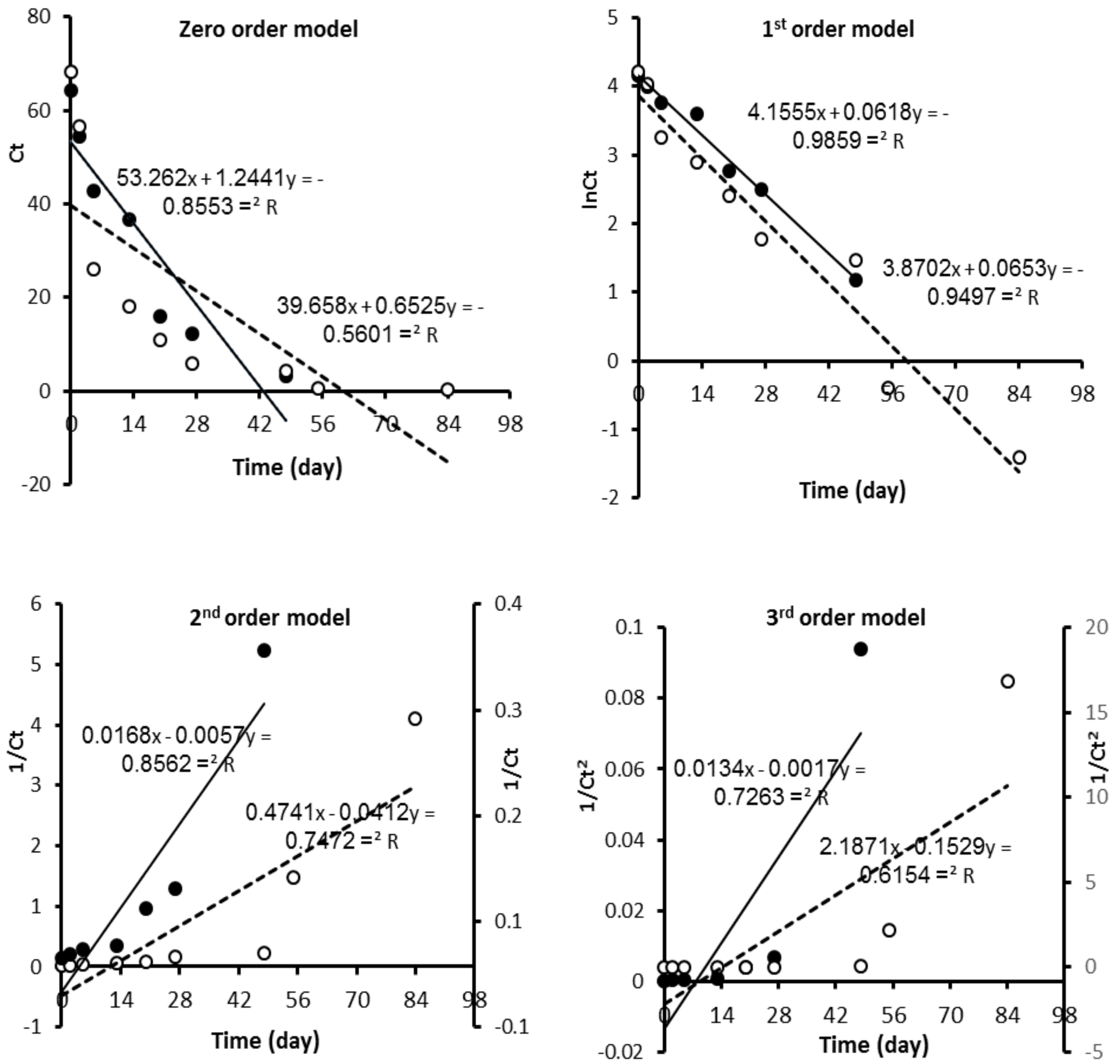


**Fig. 3: Plots of different orders rate for dissipation of fenitrothion and thiobencarb in soil.**

Fenitrothion ● Thiobencarb ○

**Table 5: Dissipation kinetics of fenitrothion and thiobencarb in soil fitted in first-order kinetic model**

| Pesticide | Linear equation | K | $DT_{50}$ (day) |
|---|---|---|---|
| Fenitrothion | y = -0.062x + 4.156 | 0.062 | 11.21 |
| Thiobencarb | y = -0.065x + 3.870 | 0.065 | 10.61 |

K is a dissipation rate

$DT_{50}$ is the time required for a quantity to reduce to half of its initial value

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## الملخص العربى

# مقارنة حركية الاختفاء ومستوى متبقيات المبيد الحشرى فنترثيون ومبيد الحشائش ثيوبينكارب فى التربة الطينية

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تم دراسة مقارنة حركية الاختفاء وسلوك متبقيات المبيد الحشرى فنتروثيون ومبيد الحشائش ثيوبينكارب فى التربة الطنية المتحصل عليها من محطة البحوث الزراعية بأبيس. تم تقدير المتبقيات بواسطة جهاز الكروماتوجرافى الغازى– مطياف الكتلة على فترات زمنية صفر، ٢، ٥، ١٣، ٢٠، ٢٧، ٤٨، ٥٥، ٨٤ يوم من المعاملة. درست تجربة استرجاع المبيد بتركيز ٧٥ ميكروجرام/ جرام تربة وكانت النسبة المئوية للاسترجاع لمبيد الفنترثيون ٨٥,٦٩ % ولمبيد الثيوبنكارب ٩٠,٨٩% مما يشير الى كفاءة عملية الاستخلاص والتقدير. متبقيات الفنترثيون انخفضت من ٦٤,٢٧ ميكروجرام/ جرام تربة عند الزمن صفر الى ٥,٠٧ % بعد ٤٨ يوم وكانت متبقيات الثيوبينكارب ٦٨,١٧ ميكروجرام/ جرام تربة عند الزمن صفر وانخفضت الى ٠,٩٩ % بعد ٨ أسابيع. كلا المبيدين اختفيا من التربة بسرعة وكان منحنى الاختفاء لكل مركب يشمل جزئين الجزئ الأول سريع جدا والجزء الثانى بمعدل بطيئ. للتعرف على النموذج الأنسب لوصف حركية التحطم تم اختبار نماذج الرتبة صفر، الأولى، الثانية، الثالثة وذلك بطريقتين الطريقة البيانية والتى يعتمد فيها على قيمة $R^2$ (القيمة الأعلى هى الأفضل) والطريقة التكاملية وقد تم حساب SD لقيم K (القيمة المنخفضة هى الأفضل) واتضح أن حركية تحطم المركبين تتبع الرتبة الأولى. أعلى قيمة $R^2$ وأقل قيمة SD لقيم K كانت هى الناتجة من تطبيق نموذج الدرجة الأولى وعليه فان اختفاء الفنتروثيون والثيوبينكارب من التربة الطينية يتبع نموذج الرتبة الأولى. واتضح أن فترة نصف العمر للفينتروثيون ١١,٢١ يوم وللثيوبينكارب ١٠,٦١ يوم. وعموما يمكن القول أن تحطم الثيوبينكارب فى التربة الطينية كان أسرع قليلا عن تحطم الفينتروثيون.