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Estimating the leaching of fenitrothion and thiobencarb in agricultural soils using laboratory lysimeters

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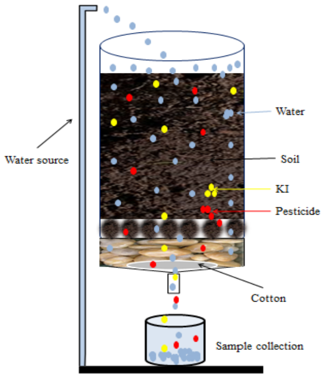
ABSTRACT

The total amount of iodide applied was recovered from all lysimeters in symmetrical curves. Fenitrothion-BTCs included two peaks, while thiobencarb-BTCs included one peak in the two tested soil types. The cumulative of fenitrothion (75.3%) and thiobencarb (75.8%) from sandy clay loam soil-lysimeter were significantly higher compared with that of fenitrothion (21.1%) and thiobencarb (60.9%) from clay soil-lysimeter. Also, in clay soil-lysimeters, thiobencarb was more leaching (60.9%) compared to fenitrothion (21.1%). Nevertheless, in the sandy-lysimeter, the cummulative amounts of both compounds were almost the same (75.5%). Thiobencarb was more leaching and more rapidly in clay soil than fenitrothion. Whereas the leaching of the two compounds was almost the same in sandy clay loam soil. However, the leaching of thiobencarb was the fastest one. Fenitrothion required more water (about twice) for leaching from the two tested soil types compared to thiobencarb. Leaching statistics are needed to manage environmental protection and keep pesticides from reaching groundwater, as well as to anticipate and comprehend the behavior of pesticides in various soil types.



Graphical Abstract

1. Introduction

A lysimeter is a methodical equipment to examine the fluxes of soil water and the chemicals dissolved in it.[1-3] The Greek word lysimeter links lyo, which means to loosen, with metron, which means to measure. It has been accepted as measuring device to study the behavior and fate of pesticides into soil/plant system, including sorption, degradation, and plant uptake of pesticide residues and transport of pesticide residues in leachate.[4-9] A lysimeter is a soil container intended to represent the field environment that is used to determine soil-water–plant interaction to study the movement and fate of gases, water, nutrients, pesticides, trace elements, heavy metals, metalloids, radionuclides, bacteria or viruses.[10-13] More than 300 years ago, the lysimeter was first used to assess crop water balance, evapotranspiration, and water percolation

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through the soil.[14-16] Recently, lysimeter techniques have been used in numerous investigations on the behavior and destiny of pesticides.[10, 17-18] Lysimeter experiments can offer data for risk assessment or database for modeling.[19-21]

Lysimeter experiments were used to study leaching models of pesticides according to Working the Group Modeling of the European Program. The dataset was obtained from a three-year lysimeter experiment conducted on a clay loam calcareous fluvisol near Rome, Italy, to evaluate the danger of herbicide use that is frequently employed in the Mediterranean region contaminating groundwater.[22] A methodical testing protocol has been devised to assess the possibility of pesticide contamination of soil and groundwater. This protocol comprises laboratory tests, field investigations, mathematical model calculations, and outdoor experiments like destiny studies utilizing undisturbed lysimeters. In 1990, the German authorities approved a test protocol for carrying out lysimeter studies. Thus, several recent experiences involved concentrating on the subjects of lysimeter experiments, mathematical model calculations, and comparative fate assessment based on laboratory tests. Indoor and outdoor lysimeter tests are carried out to compare the influence of water regime and climate on the pesticide leaching and the influence of soil characteristics on leaching process.[23-25]

The purpose of this study is to use a laboratory lysimeter to identify the leaching behavior of fenitrothion and thiobencarb in clay and sandy clay loam soils to reduce groundwater pollution and thus preserve the environment.

2. Materials and methods

2.1. Pesticides

Fenitrothion

UPAC-name: O, O-dimethyl O-4-nitro-m-tolyl phosphorothioate, other names: fenthion and sumithion, chemical formula: $C_9H_{12}NO_5PS$, solubility in water: 0.038 g/L, P value: 0.57, pesticide type: insecticide and miticide, group: organophosphate, and product: EC 50%.[26-27]

Thiobencarb

UPAC-name: S-4-chlorobenzyl diethyl thiocarbamate, other names: bencarb and benthiocarb (it is approved by the Japanese Ministry of Agriculture, Forestry and Fisheries), chemical formula: $C_{12}H_{16}ClNOS$, solubility in water: 0.030 g/L, P value: 1.70×10^4, pesticide type: herbicide, group: thiocarbamate, and product: EC 50%.[26]

2.2. Soils

Clay soil (alluvial) and sandy clay loam soil (calcareous) are the two main types of soil found in Egypt. The physicochemical characteristics are presented in **Table 1**.[28-31]

Table 1. Physicochemical characteristics of tested soils

Soil type	Clay soil	Sandy clay loam soil
Water holding capacity (%)	46	38
EC	1.31	5.03
pH	8.24	8.15
Organic matter content (%)	3.30	1.54
Total carbonate (%)	7.86	44.64

2.3. Pesticide detection

For a 5 µg/mL pesticide solution, a spectral density curve (S-D curve) was created using a scanning range of 200–400 nm. The pesticide concentration was measured using the λ_{max} value throughout this investigation.

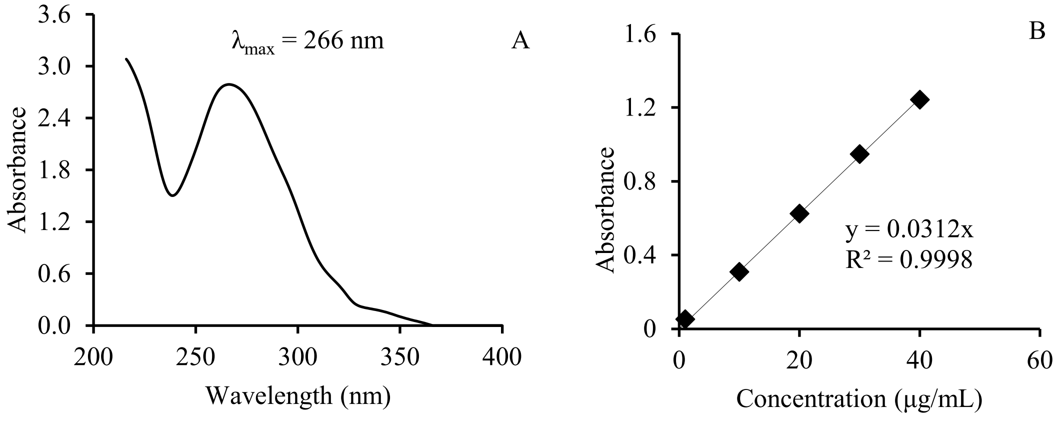


Fig. 1. Spectral density curve (A) and calibration density curve (B) of fenitrothion.

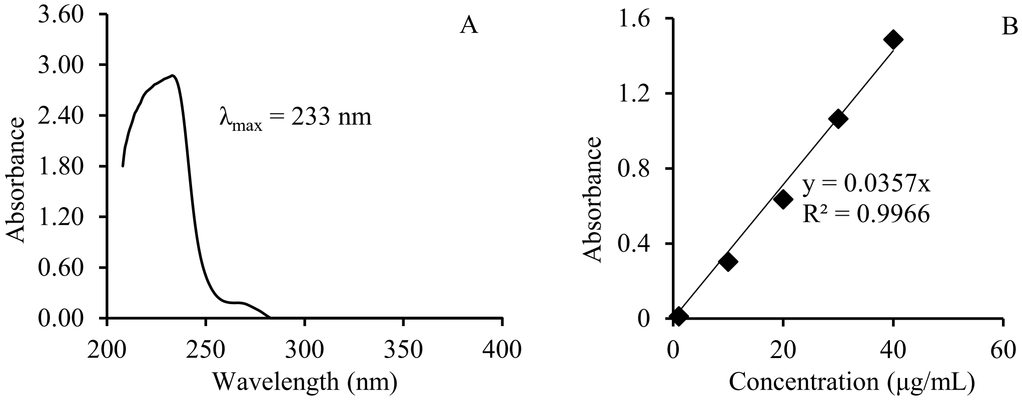


Fig. 2. Spectral density curve (A) and calibration density curve (B) of thiobencarb.

Plotting triplicates (n = 3) of known pesticide concentrations (1-50 µg/mL) against corresponding absorbance at the measured λ_{max} yielded the standard calibration curve (C-D curve) (**Figs. 1 & 2**). Three copies of the sample, one for control and one for quality assurance, were used.[32-35] Fenitrothion and thiobencarb residues were quantitively analyzed by UV-VIS Spectrophotometer (Thermo Corporation, Nicolet, evolution 100, Germany).

2.4. Laboratory lysimeter

The laboratory mini-lysimeter, stainless steel container (100 cm height × 30 cm diameter) was used to estimate the leaching potential of tested pesticides. The laboratory lysimeter is reliable to study the mobility of pesticides using their formulations, in homogeneous soil, with large scale, under laboratory conditions (**Fig. 3**). A homogeneous 25kg dirt was used to pack each mini-lysimeter to a given bulk density. The lysimeters were preconditioned before application of KI solution and pesticide solution. Each lysimeter received 100 mL 0.5M KI and 1.25 mL fenitrothion EC 50% or thiobencarb EC 50% to obtain 25 µg/g soil. The $CaCl_2$ solution was administered after 30 minutes, and the leachates were gathered. Iodide and pesticide residues were determined in all leachates.[36-38]

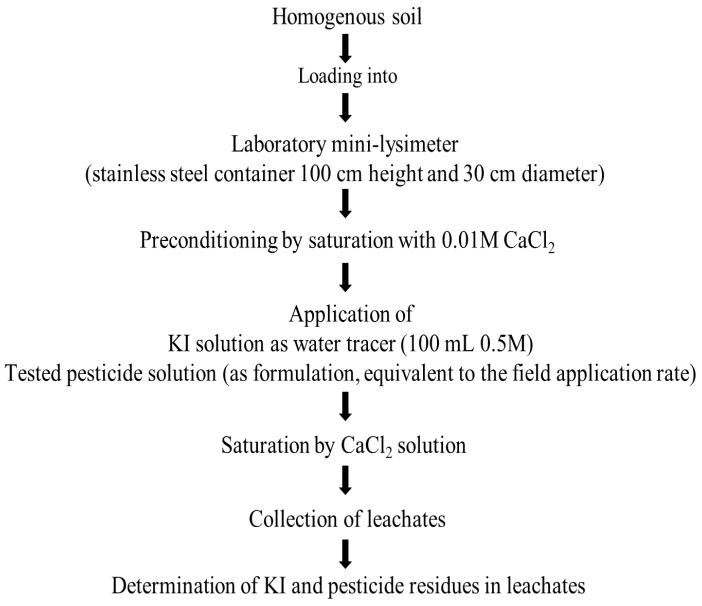


Fig. 3. Schematic diagram of tested pesticides leaching by laboratory mini-lysimeter.

3. Results and discussion

To estimate the pesticide leaching behavior in soil or to compare its mobility potential with other pesticides, it is required considerable data on behavior and fate of pesticides in the environment. Because conducting field experiments is expensive and long time consuming, it is useful to collect data of pesticide soil mobility by first using experimental laboratory approaches such as (soil column and laboratory lysimeter techniques). However, the results of such studies do not always represent what actually occurs in the field. Nevertheless, these studies usually provide valuable information on the potential pesticide mobility in soil if they are well-controlled.[39-45]

The leaching of insecticide, fenitrothion and herbicide, thiobencarb was studied using laboratory lysimeter technique. There was small variability in leached iodide and tested pesticides loads from replicate lysimeters. This is because the soil (disturbed soil) is homogeneous; iodide is not soluble and the chemical and biological heterogeneities in the soil have less of an impact on its mobility. The total amount of iodide applied was recovered from all lysimeters in the first 20 L leachates, forming symmetrical curves (**Figs. 4 & 5**). Gaber *et al* obtained a systemical BTC for water tracer.[46]

As seen by **Fig. (4)** fenitrothion residues increased in leachates to a maximum of 2000 µg/leachate then decreased rapidly, after percolating of about 50 L, it increased again to a maximum of 3500 µg/leachate in alluvial clay soil. Also, the residues increased in leachates to a maximum of 8000 µg/leachate, then decreased, after that increased again to a maximum of 4500 µg/leachate in sandy clay loam soil then decreased. Two peaks in each soil type were formed. The second peak is much larger in clay soil-lysimeter but the second peak in sandy clay loam soil-lysimeter was the shortist one. The shape of the peaks was symmetrical in case of clay soil (**Fig. 4A**) whereas, that was flatter and asymmetrical in case of sandy soil (**Fig. 4B**). The BTC curve's particular shape depends on the chemical's physicochemical characteristics, the solids in the soil, and the soil's structure.[47-50] Tailing or increased dispersion is typical for BTCs obtained under nonequilibrium conditions. It appears that the sorption process is linked to the mechanism causing nonequilibrium because only the BTCs for the sorbing solute show enhanced dispersion or asymmetry.[51-54]

Fig. (5) showed that the high residues of thiobencarb were detected at the beginning with the leaching of iodide in the two soil types. The top of thiobencarb-BTCs was flat, corresponding to percolating of 4-12 L with the maximum value of 18800 µg/leachate in clay soil and corresponding to percolating of 2-15 L with the maximum value of 20400 µg/leachate in sandy soil. Then, there was a smooth decrease in thiobencarb residue in leachates. The BTCs in clay and sandy clay loam soils were obtained within 120 L for fenitrothion while, 60 L for thiobencarb however, the low concentrations of pesticides residues were continously released up to total percolating of about 135 L for fenitrothion and about 75 L for thiobencarb.

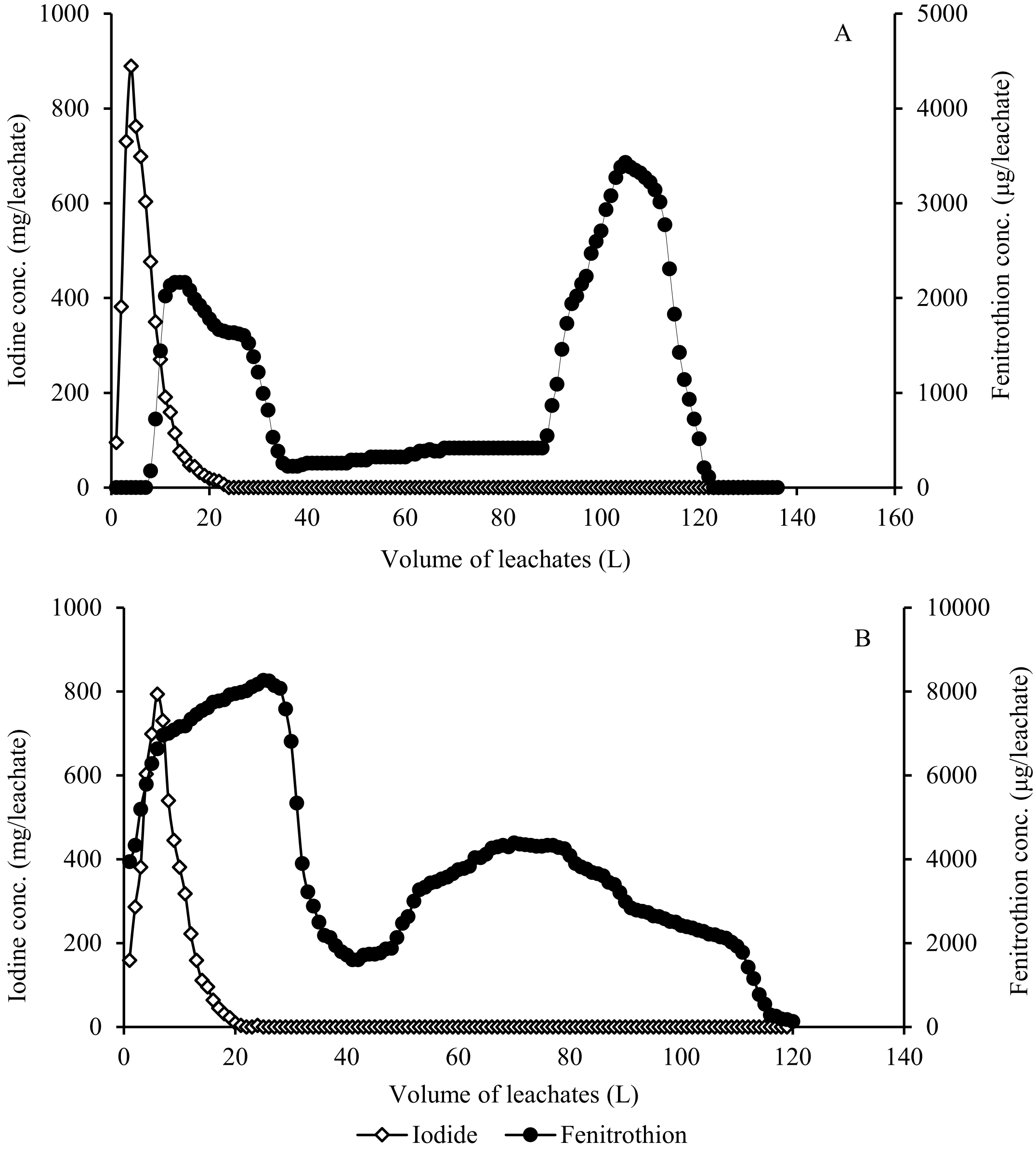


Fig. 4. Breakthrough curves of fenitrothion and water tracer I^- in clay soil (A) and sandy clay loam soil (B) using laboratory lysimeters.

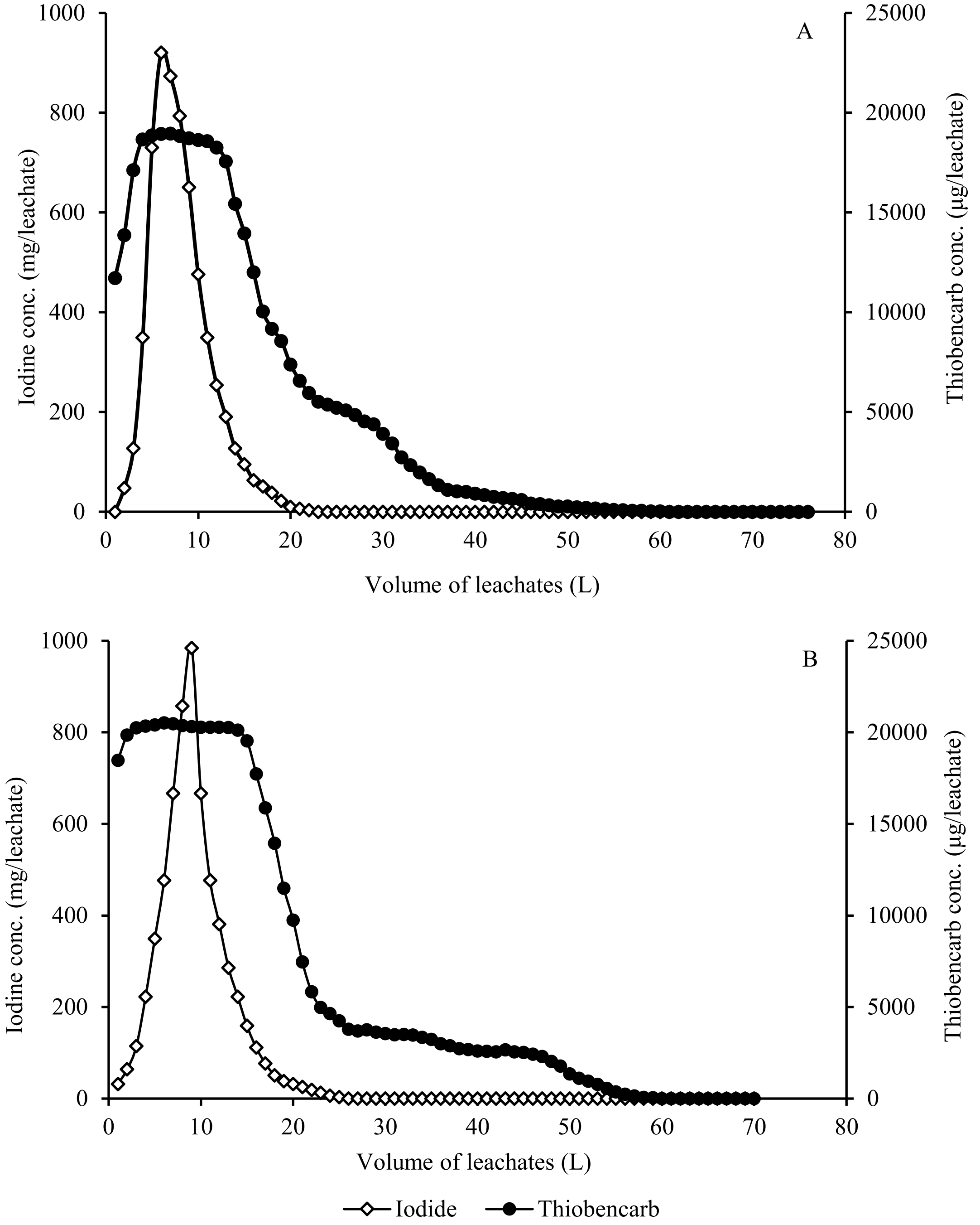


Fig. 5. Breakthrough curves of thiobencarb and water tracer I$^-$ in clay soil (A) and sandy clay loam soil (B) using laboratory lysimeters.

The cumulative amounts collected in the leachates of clay soil and sandy clay loam soil-laboratory lysimeters were exhibited in **Fig. (6A)** for fenitrothion and **Fig. (6B)** for thiobencarb. The cumulative amounts of fenitrothion (470 mg, equivalent to 75.3%) and thiobencarb (470 mg, equivalent to 75.8%) from sandy clay loam soil-lysimeter were significantly higher compared with that of fenitrothion (130 mg, equivalent to 21.1%) and thiobencarb (380 mg, equivalent to 60.9%) from clay soil-lysimeter. In addition, in the case of clay soil-lysimeters, thiobencarb was more leaching (its cumulative amount was 380 mg, 60.9% in 75 L) compared to fenitrothion (its cumulative amount was 130 mg, 21.1% in 135 L). Nevertheless, in the case of sandy-lysimeter, the cumulative amounts of both compounds fenitrothion and thiobencarb were almost the same (470 mg, about 75.5%) in percolate of 120 L and 70 L, respectively (**Table 2 and Fig. 7**).

According to the results of laboratory lysimeters, it was very interesting to observe that thiobencarb was leaching more rapidly in clay soil than fenitrothion. Whereas the leaching of the two compounds were almost the same in sandy clay loam soil. However, the leaching of thiobencarb was the fastest one. In addition, fenitrothion required more water (about twice) for leaching from both soil types; clay and sandy clay loam soils compared to thiobencarb. The leaching statistics are helpful in forecasting and comprehending how pesticides would behave in various soil types.[55-57] Moreover, these data are required to manage the environmental protection and to prevent the pesticides to groundwater. In addition to harming human health when it is used for drinking, groundwater contamination can also contribute to food chain contamination when it is used for irrigation.[58-61] The Drinking Water Directive (98/83/EC) states that the maximum concentration of pesticides in drinking water is 0.1 µg/L for a single pesticide and 0.5 µg/L for all pesticides combined. It has been claimed that adding organic amendments to the soil can gradually lower the danger of pesticide-related groundwater contamination, especially in calcareous and sandy soils.[62-66]

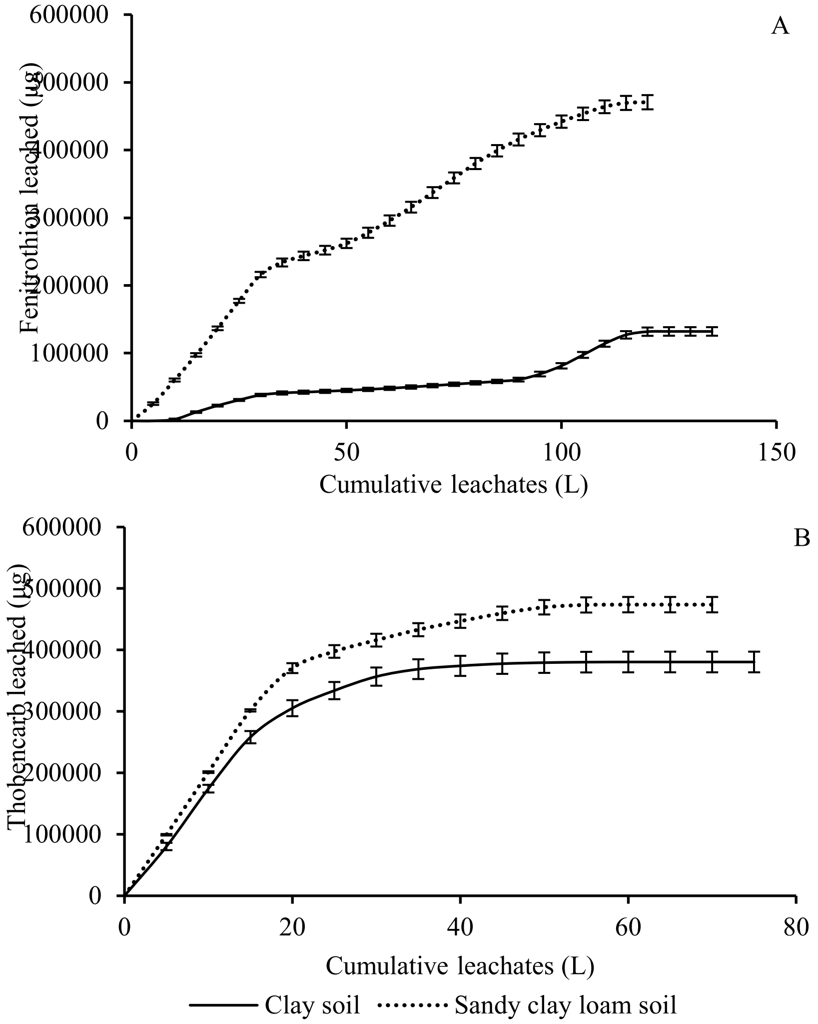
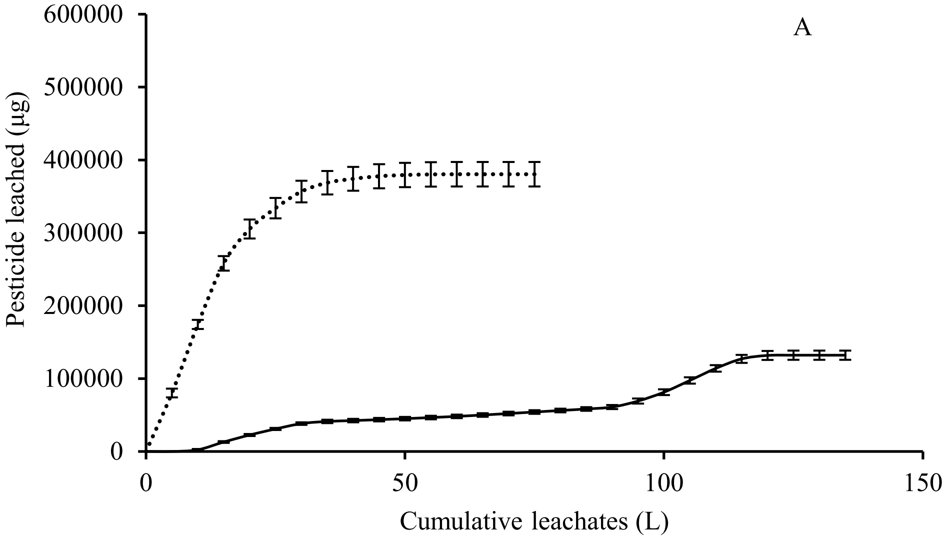


Fig. 6. Cumulative leachate curves of fenitrothion (A) and thiobencarb (B) using laboratory lysimeters.



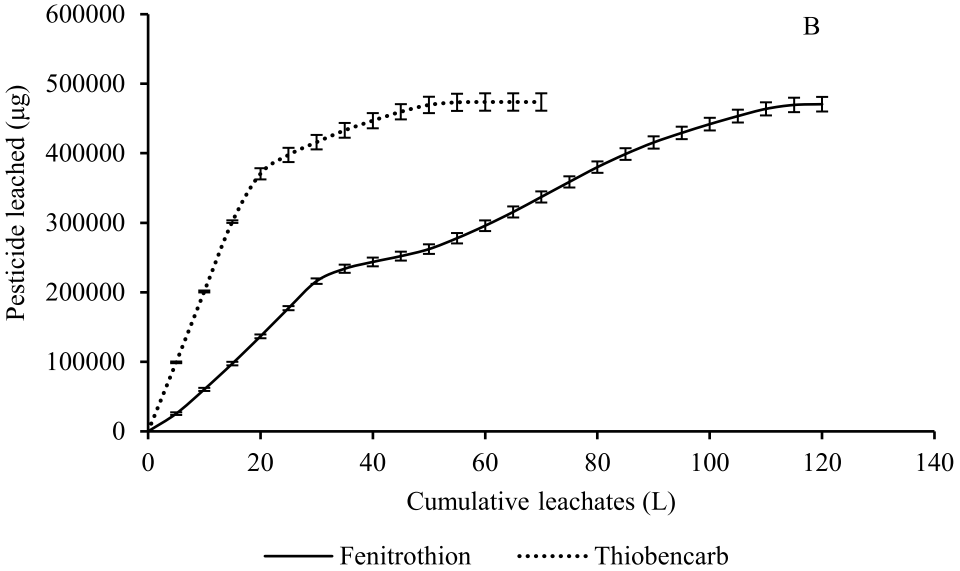


Fig. 7. Cumulative leachate curves of tested pesticides in clay soil (A) and sandy clay loam soil (B) using laboratory lysimeters.

Table 2. Percentage of cumulative leachates and volume of cumulative percolates from laboratory lysimeters

Parameters	Fenitrothion		Thiobencarb	
	Clay soil	Sandy clay loam soil	Clay soil	Sandy clay loam soil
Cumulative leachates (%)	21.1	75.3	60.9	75.8
Cumulative percolates (L)	135.0	120.0	75.0	70.0

4. Conclusion

The conclusion highlights that laboratory lysimeter studies provide valuable insights into the soil mobility and leaching behavior of pesticides like fenitrothion and thiobencarb, serving as practical preliminary tools before field investigations. The findings demonstrate that soil type significantly influences pesticide leaching. The data underline the importance of understanding pesticide-soil interactions to assess environmental risks, particularly groundwater contamination. Such information is crucial for developing strategies to mitigate pesticide leaching, comply with water quality standards such as the EU Drinking Water Directive, and adopt soil management practices (like organic amendments) that can reduce groundwater pollution risks. Overall, laboratory studies are essential for predicting pesticide behavior and guiding environmental protection measures, although they should be complemented by field data for comprehensive risk assessment.

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