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Effect of peat, compost, and charcoal on transport of fipronil in clay loam soil and sandy clay loam soil

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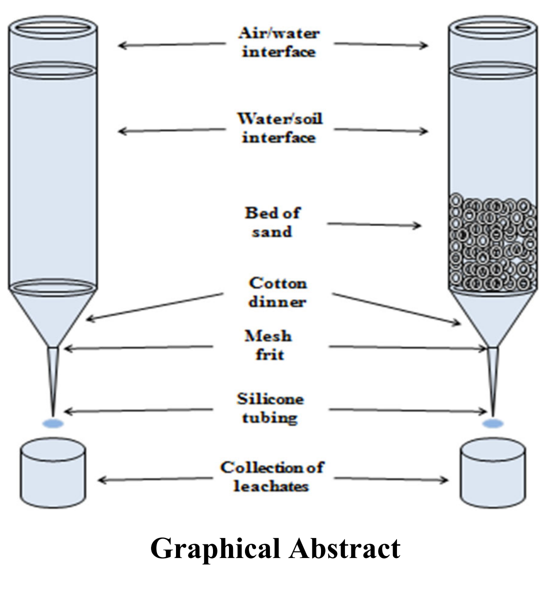
ABSTRACT

This study used 30 cm long packed by 3 kg soil columns to explore the effects of peat, compost, and charcoal at 5% on the movement of fipronil (99.9 % purity) in clay loam soil and sandy clay loam soil. The soil columns were preconditioned with calcium chloride solution (0.01 M) before applying the pesticide and potassium iodide. Potassium iodide solution (0.2 M) was added at a rate of 10 mL as a water tracer and a quantity of fipronil solution (10 µg g^{-1}soil) was applied on the soil surface of each column. Next, fipronil was leached from the soil columns with a calcium chloride solution (0.1 M) and the leachates were collected and analyzed. The results show that water tracer I^- leached fast in soil columns. The breakthrough curve of fipronil appeared from leachates of soil columns after iodide for a while, indicating that fipronil is a moderate or lower mobile compound depending on type of soil and type of soil amendments. In general, adding soil amendments (peat, compost, and charcoal) to clay loam soil and sandy clay loam soil resulted in improved fipronil adsorption and decreased the amount of fipronil that leached into groundwater. This study is very useful for preserving groundwater from pollution, especially in the Middle East due to the lack of water sources.



Graphical Abstract

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1. Introduction

Leaching is the term used to describe the downward transport of pesticides in groundwater. Leaching of pesticides is governed by mass transfer and molecular diffusion principles. Pesticide leaching through the soil profile is what contaminates groundwater. The degree of leaching is influenced by soil characteristics, pesticide physicochemical properties, formulation types, irrigation method, and hydrogeological processes.[1]The porosity and density of the soil both affect how much water flows through it. These soil features also influence the soil's ability to retain water. Because water flow through soil's macro-pores actually controls the transport of pesticides, soil density, and porosity indirectly control movement of pesticides from top layer to deeper soil layers. Low organic matter, loam, and sand-content soils are more likely to leach pesticides because macro-pore flow predominates in these soil types under conditions of high precipitation.[2,3]The leaching is significantly decreased if pesticides are administered in dry weather or/and during light wet seasons because macro-pore flow is not produced in these types of weather. Leaching of pesticides has been discovered to be dependent on the formulation and how soluble the pesticide is in water.[3]Pollution of groundwater and surface water has been found to grow over the past few years as a result of ineffective pesticide management. Increased overland flow and pesticide leaching into the soil have also been brought on by rising precipitation and irrigation. Pesticide pollution of water, particularly in agricultural areas throughout nations, is on the rise, and a wide variety of pesticide amounts have been discovered. Pesticides and their degradation products migrate from the land surface via the unsaturated zone and into the groundwater along a variety of transport paths, which are extremely changeable in both space and time.[3,4]

One approach is to incorporate organic wastes, such as crop residues, aquatic weeds, animal and human waste, urban solid waste, sewage sludge, etc., into the soil. The technique is commonly employed in agricultural practice to raise the organic matter content of the soil since it reduces the mobility of pesticides in soil modified with organic matter, increases the degradation, and so reduces run-off to surface water resources. Additionally, it aids in reducing pesticide-related soil and water contamination.[3,5]The fact that organic wastes are produced from wastes derived from industrial, agricultural, and animal activities is one of most significant advantages of employing them as amendments from an environmental point of view. Due to their high content of organic matter, these wastes can be employed directly as organic amendments in farmlands. Furthermore, numerous studies have shown that these organic residues can act as pesticide adsorbents. Pesticides adsorb, desorb, run-off, and leach in different ways depending on the kind and composition of the organic matter residue added as an amendment. By examining these processes of adsorption-desorption, transport, and degradation, among others, in an amended-soil environment, one may establish the effectiveness of the amendment and the behavior of pesticides.[3,6,7]The physical properties of soil are improved by addition of organic amendments. Organic matter immediately improves soil properties like porosity, aggregation and structural stability, and soil's ability to retain water. The biological characteristics of the soil are also impacted by the organic amendments.[3]Following leaching tests in soil columns, it was discovered that unmodified soil quickly leached alachlor versus synthetic soil. Through packed columns, the leaching capacity of clothianidin in farmyard manure-amended clay loam soil, and sandy loam soil was investigated. It was discovered that in soils with higher levels of clay and organic matter, pesticides have a minimal chance of leaching. Farmyard manure can be utilized as an organic residue amendment since it was found to significantly reduce the amount of clothianidin that leached when it was used as a soil amending agent.[3]In general, it was discovered that adding organic residues to soil resulted in improved pesticide adsorption and decreased the amount of pesticides that leached into groundwater.

Fipronil is a foliar insecticide that can be sprayed on crops and soil, and it works well against a range of foliar insects.[8,9]Fipronil is highly soluble in organic solvents and has modest water solubility (1.9 mg L^{-1}).[9,10,11]Fipronil can degrade through abiotic and biotic mechanisms in soil and water. Fipronilsulfone, amide, desulfinyl, and fipronilsulphide are breakdown products that are created through reduction, hydrolysis, photolysis, and oxidation, respectively when fipronil is present in soil or water. The biologically active insecticides fipronilsulphide, fipronilsulfone, and desulfinyl all work to control insect infestations.[10]Fipronil is transported and absorbed in soils in part by soil organic content, the soil/water ratio, and soil temperature.[8,9]Volatilization, leaching, surface runoff, biological degradation by microbes, photolysis, and adsorption are the main environmental decay mechanisms for fipronil.[8,9,12]As the amount of soil clay decreases, fipronil shows a considerable decrease in adsorption coefficient, increasing its bioavailability.[8,9,13]Fipronil's main route of entry into groundwater is through the soil profile, and its rate of movement through the soil matrix is influenced by both the physical and chemical properties of the soil and fipronil.[14]Fipronil's popularity has grown over the past few decades as a result of its broad spectrum and excellent efficacy.[8,9]However, because offipronil's high toxicity to some non-target creatures (earthworms), its environmental effects have long drawn significant attention.[7,15,16]Fipronil was said to have minimal mobility and little potential to move laterally or downward to contaminate surface and ground waters. However, according to certain accounts, fipronil is relatively mobile in soils.[8,9,17]

Higher levels of pesticide adsorption in soils can impact how they leach because adsorption reduces the amount of pesticides that are available in the soil solution. However, absolutely no information is available on the effect of soil amendments on the leaching behavior of fipronil in Egypt soils. Therefore, the present study reported the effect of peat, compost, and charcoal on the transport of fipronil in clay loam soil, and sandy clay loam soil of Northern Egypt.

2. Materials and Methods

2.1. Fipronil

Technical-grade fipronil (99.9 % purity), solubility in water: 1.9 mg L^{-1}, vapor pressure: 2.8 x 10^{-9} mmHg, P_{ow}: 4.0,molecular weight: 437.2 g mol^{-1}, was obtained from Egypt-Chem Pesticides and Chemicals Co., New Nubaria City, Beheira Governorate, Egypt.

2.2. Soils

Two soils from Alexandria Governorate, Egypt; clay loam soil (obtained from Agricultural Research Station, Abis), sandy clay loam soil (from different locations in Elamria region) were used in the study. The physical properties and chemical properties of tested soils showed in Tables 1 and 2.[7,9,18]

Table 1. The soils' assessed for physical characteristics.

Soil code	Particle size distribution (%)			Texture class	Water holding capacity (mL/100g)
	Clay	Silt	Sand		
1	42	18	40	Clay loam	46
2	20	13	67	Sandy clay loam	38

Table 2. Chemical makeup of the examined soils.

Chemical properties	Clay loam soil	Sandy clay loam soil
EC (m mohs/cm) at 25˚C	1.32	5.03
Soil pH	8.25	8.15
Organic matter content (%)	3.31	1.54
Total carbonate (%)	7.87	44.64
Soluble cations conc. (meq/L):		
Ca^{++}	3.8	18.7
Mg^{++}	5.0	8.8
Na^{+}	9.4	22.5
K^{+}	0.5	0.3
Soluble anions conc. (meq/L):		
CO_3^{--}	1.6	0.8
HCO_3^{-}	2.6	4.6
Cl^{-}	8.5	21.0
SO_4^{--}	0.6	23.9

2.3 Soil amendments

Three amendment substances were tested in the study. Charcoal was obtained from Department of Soil and Water Sciences. Peat and compost were obtained from Agricultural Research Station. Air-dried substances were ground and passed through a 5-mm sieve. The data are shown in **Table 3** together with results of determination of organic carbon and organic matter contents.

Table 3. Tested amendment substances and their organic matter content.

Substance	Organic carbon (%)	Organic matter (%)
Peat	0.90	1.54
Compost	3.00	5.17
Charcoal	3.10	5.34

2.4. Transport study

The bench-scale soil columns were used to estimate transport potential of fipronil in soil and amended soil. The tested soil and amended soil with 5% of different amendments; peat, compost, and charcoal to obtain a rate of 1.25 kg m^{-2} were loaded into columns (about 30 cm high and 12 cm diameter PVC pipes). Each column was uniformly packed to a known bulk density by 3 kg soil.[19]A stainless steel plate with pores was supported by the bottom end cap. The columns were preconditioned before applying the pesticide and KI by saturation with 0.01 M $CaCl_2$.[9,20] Each column received 10 mL 0.2 M KI solution as a water tracer. The quantity of each tested pesticide dissolved in a solvent was applied dropwise on soil surface of each column, consistent with 10 µg g^{-1} soil. Next, the $CaCl_2$ solution was applied and the leachates (100 mL leachate) were collected (**Fig. 1**). The KI was determined in all leachate samples dependent on the Iodimetric method according to the reported methode.[21]Also, all leachates were analyzed to determine fipronil.

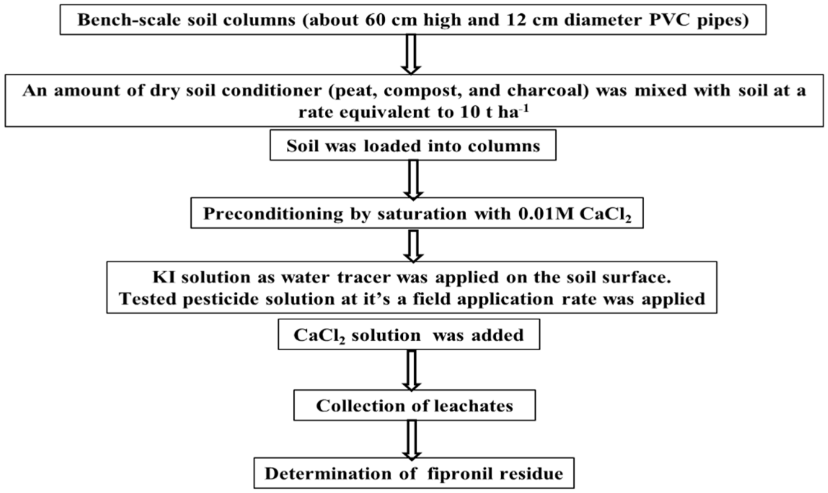
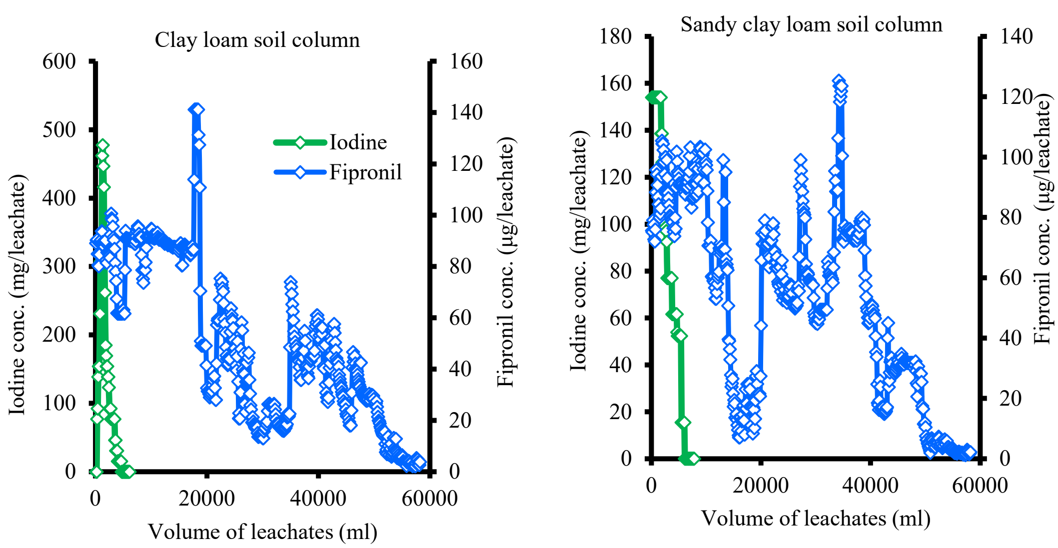


Fig. 1. Schematic diagram of transport of fipronil in soils

3. Results

The effect of peat, compost, and charcoal on the transport behavior of fipronil in clay loam soil, and sandy clay loam soil was investigated using 30 cm long packed columns as the water percolation rate was slow in clay loam soil compared to sandy clay loam soil (**Fig. 2**).The most thorough examinations of the mobility of organic chemicals have taken place in tracer experiments, in which a mobile, non-adsorbing tracer, like chloride or bromide, has been added alongside a sorbing organic tracer whose adsorption to soil has been independently characterized by laboratory measurements. In similar, iodide has been used as a water tracer at a rate of 10 ml KI 0.1 M for each soil column. The results show that the water tracer I^- leached fast in soil columns. The highest concentration of iodide could be detected in the first 1300, 2900, 1600, 1400, 100, 3100, 1300, and 500 mL of leachates from clay loam soil, 5% pet amended clay loam soil, 5% compost amended clay loam soil,5% charcoal amended clay loam soil, Sandy clay loam soil, 5% pet amended sandy clay loam soil, 5% compost amended sandy clay loam soil and 5% charcoal amended sandy clay loam soil columns, respectively. Breakthrough curve of fipronil appeared from leachates of soil columns after iodide, indicating that fipronil is moderate or lower mobile compound depending on type of soil and type of soil amendments. Addition of 5% peat, 5% compost, and 5% charcoal to soil A reduced the downward movement of fipronil in the columns and affected the maximum concentration of fipronil in the leachates. The maximum concentration of iodide in soil columns did not affect by peat, compost, and charcoal, while the maximum concentration of fipronil was obtained after 17.8 and 34.2 L for clay loam soil, and sandy clay loam soil, 24.5 and 10.5 L for 5% pet amended clay loam soil and 5% pet amended sandy clay loam soil, 10.7 and 2.1 L for 5% compost amended clay loam soil and 5% compost amended sandy clay loam soil, 2.3 and 12.7 L for 5% charcoal amended clay loam soil and 5% charcoal amended sandy clay loam soil of leachates cumulative volume (**Fig. 2**). **Fig. 3** and **Table 4** shows the cumulative percentage and volume of cumulative percolates of fipronil collected in the leachates unamended and amended soil columns. Both organic amendments (peat, compost, and charcoal) significantly increased the cumulative percentage of fipronil throughout the percolation compared to that of unamended soil.



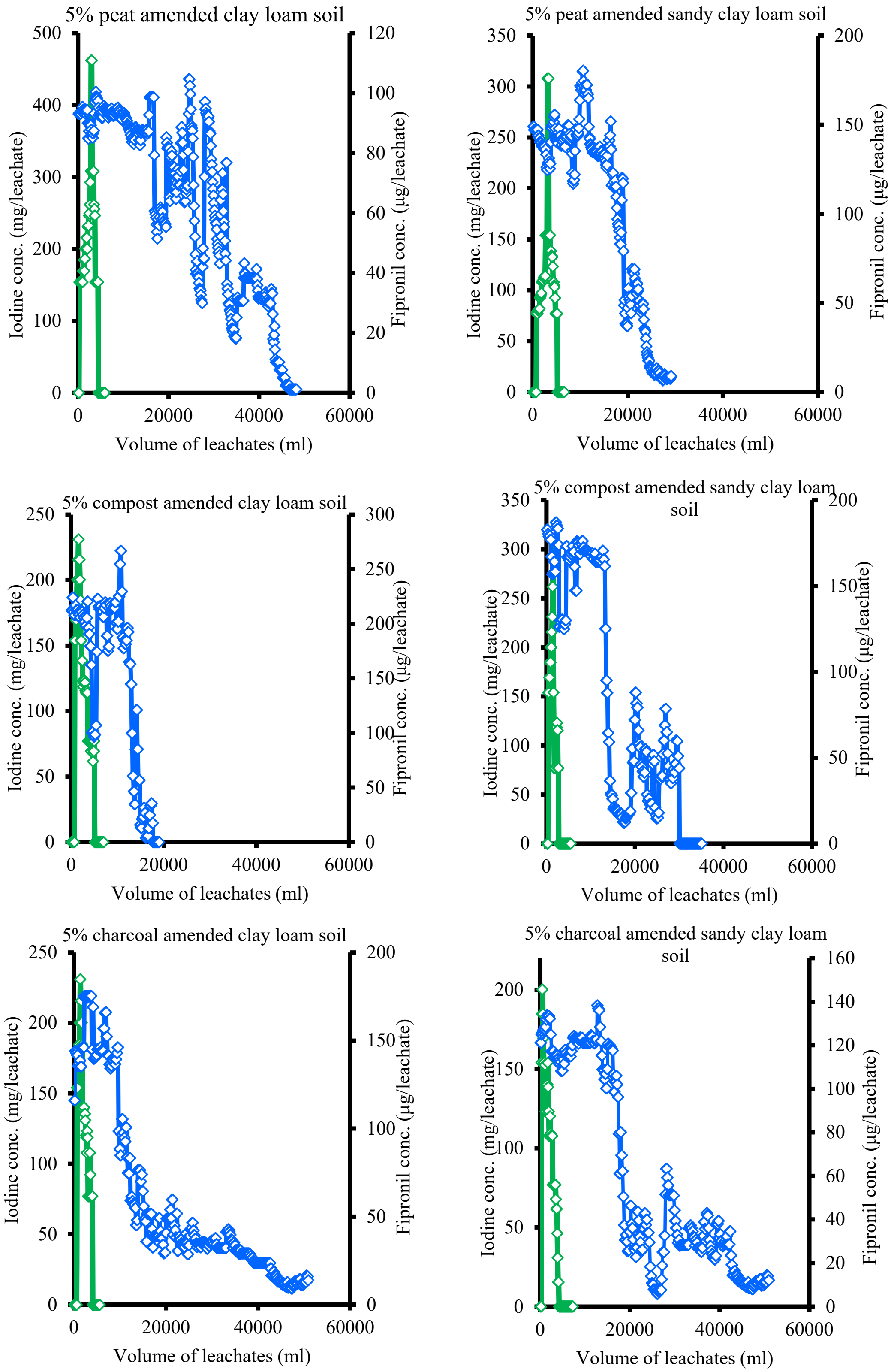
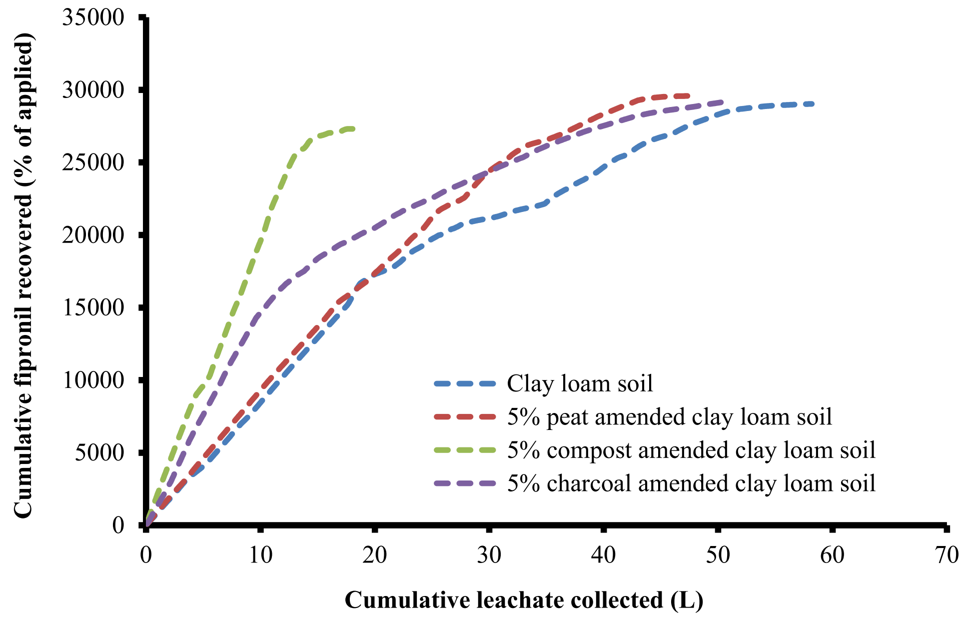


Fig. 2. Breakthrough curves of fipronil and water tracer I^- in unamended and amended soil columns

Also, 5% peat, 5% compost, and 5% charcoal amendment significantly reduced the cumulative percentage of fipronil compared to those in unamended soil in clay loam soil and sandy clay loam soil. After application of percolating volume, 96.78, 98.62, 93.00 and 97.45%, of the applied fipronil were recovered in the leachates of clay loam soil, 5% peat amended clay loam soil, 5% compost amended clay loam soil and 5% charcoal amended clay loam soil, respectively, whereas 97.93, 97.44, 94.84 and 99.32% of the applied fipronil were recovered in the leachates of sandy clay loam soil, 5% peat amended sandy clay loam soil, 5% compost amended sandy clay loam soil and 5% charcoal amended sandy clay loam soil, respectively.



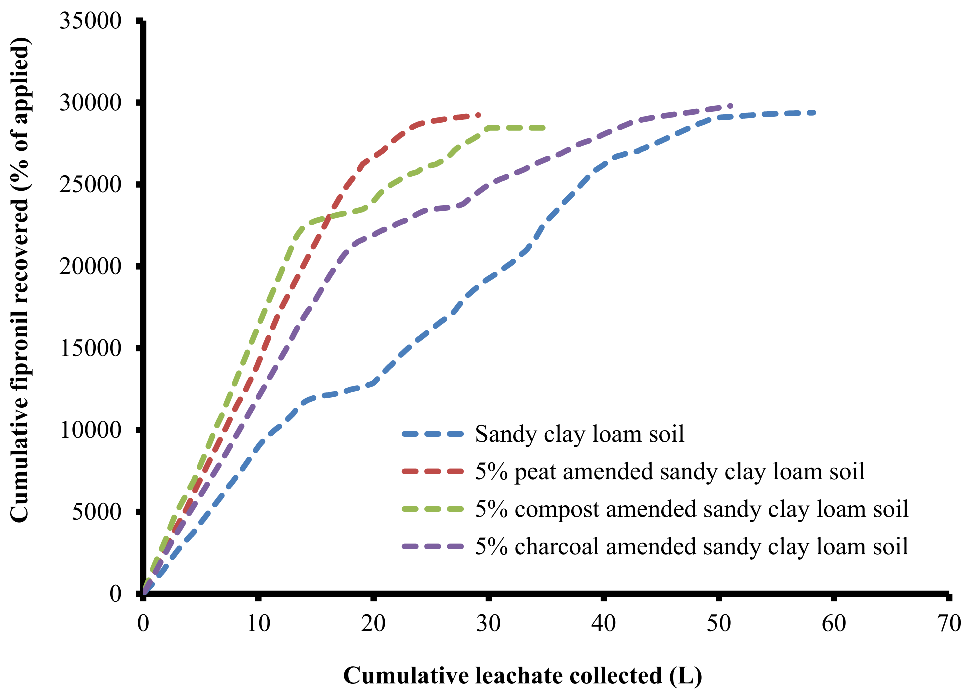


Fig. 3. Cumulative leachate curves of fipronil in unamended and amended soil columns

Table 4. Percentage of cumulative leachates and volume of cumulative percolates from soil columns

Columns	Cumulative leachates (%)	Cumulative percolates (L)
Clayloam soil	96.78	58.2
5% peat amended clayloam soil	98.62	48.2
5% compost amended clayloam soil	93.00	28.9
5% charcoal amended clayloam soil	97.45	50.9
Sandy clay loam soil	97.93	58.2
5% peat amended sandy clay loam soil	97.44	29.1
5% compost amended sandy clay loam soil	94.84	35.1
5% charcoal amended sandy clay loam soil	99.32	51.0

4. Discussion

The results showed that iodide is a nonreactive water tracer. The water tracer I^- was leached fast and the breakthrough curves in unamended soil and 5% peat, 5% compost, and 5% charcoal amended soil columns are symmetrical. Also, Gaber et al, (1992) obtained a symmetrical breakthrough for water tracer bromide.[22]The rapid release of fipronil as well as I- from sandy clay loam soil columns compared to clay loam soil columns may be due to the soil type. Sandy soil containing more sand is more susceptible to the leaching of agricultural chemicals.[23]Generally, fipronil has a moderate Koc value.[8,9,13,24,25]After artificial rain was applied to the soil column for this study, fipronil demonstrated a good ability to hold onto soil particles. Prior research has shown that rising soil organic matter promotes pesticide sorption.[1,2,13,18]Clay loam soil showed a higher percentage of organic matter than sandy clay loam soil with 3.31% and 1.54%. Fipronil was able to retain its higher concentration in clay loam compared to sandy clay loam. The exchange capacity increases with content of organic matter. Soil with a higher cation exchange capacity and organic content may be able to bind to fipronil more readily while also lowering the likelihood of leaching. Moreover, fipronil has moderate water solubility.[13,26,27]Fipronil may therefore mildly leach from the treated soil. According to a study by Shuai et al. (2012), fipronil was desorbed from the treated soil by a leaching process or runoff caused by the simulation of artificial rain.[10]Fipronil lost 96% of its levels during the experiment, according to another study.[13,28,29] This work confirms that chemical and biotechnological fields are very important in nature, and the applications of bioactive compounds are very useful as reported before.[30-39]

5. Conclusions

Fipronil has a higher K_{oc} value and lower water solubility. There was a significant difference for soils tested (clay loam and sandy clay loam) modified and unmodified. Thus, soil type and soil amendments (peat, compost, and charcoal) used in this study did affect transport process in soil columns.

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