Current Chemistry Letters 13 (2024) 277–286

Contents lists available at GrowingScience

Current Chemistry Letters

homepage: www.GrowingScience.com

Impact of organic amendments addition to sandy clay loam soil and sandy loam soil on leaching process of chlorantraniliprole insecticide and bispyribac-sodium herbicide

Mohamed R. Fouad[*], **Ahmed F. El-Aswad, Mohamed E. I. Badawy and Maher I. Aly**

Department of Pesticide Chemistry and Technology, Faculty of Agriculture, Alexandria University, Aflaton St., 21545, El-Shatby, Alexandria, Egypt

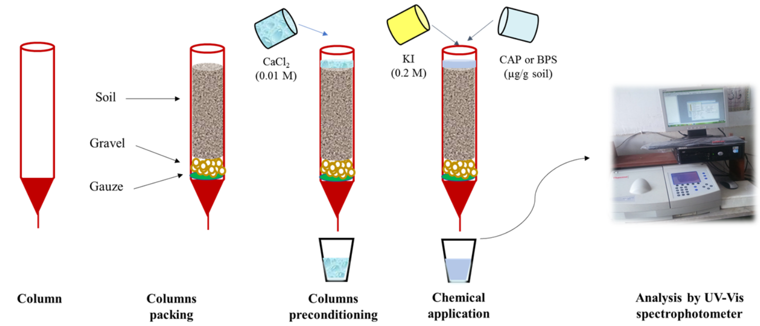
C H R O N I C L E

Article history:
Received March 25, 2023
Received in revised form
June 19, 2023
Accepted December 15, 2023
Available online
December 15, 2023

Keywords:
Organic amendments
Soil
Leaching
Chlorantraniliprole
Bispyribac-sodium

A B S T R A C T

The leaching of two pesticides, cholantraniliprole (CAP) and bispyribac-sodium (BPS) in sandy clay loam soil (soil A) and sandy loam soil (soil B) were examined, by soil columns under laboratory conditions. In addition, the effect of adding 5% biochar and wheat straw to the soils on the leaching of CAP and BPS was studied. It is clear from the results that BPS is more leachable than CAP in all soil columns, and more leached to soil B. It was found that the addition of biochar and wheat straw has a significant effect on the movements of these pesticides and can be used to reduce the environmental impact. For CAP, 71 to 97% and 84 to 97% were recovered from the soil A columns and soil B columns, respectively, while for BPS, 94 to 99% were recovered from columns of soil A and soil B.



Graphical abstract

1. Introduction

The environmental fate of pesticides depends essentially on their mobility in soils and their tendency to partition into other environmental compartments, such as air and water.[1] Transfer processes move pesticides in the environment. Concretely, leaching of pesticides through the soil profile from agricultural practices is receiving increasing attention. In the leaching process, the physico-chemical properties of the agrochemicals used as well as soil properties (texture, clay content, OM content and permeability) play a decisive role.[2] The displacement of pesticides from soil to water mostly depends on the extent to which they are retained in soils. The soil organic adsorption coefficient (K_{oc}) parameter plays a significant role in the fate of pesticides in aqueous/soil environment, like bioaccumulation and leaching ability, which is defined as: $K_{oc} = K_d/F_{oc}$, where F_{oc} is the OC fraction of the soil and K_d is the distribution coefficient. K_{oc} values are universally used as measures of the relative potential mobility of pesticides in soils and in fugacity models describing the partitioning of pesticides in soil/water/atmosphere systems. In general, compounds with higher log K_{oc} values will be less

---

[*] Corresponding author.
E-mail address mohammed.riad@alexu.edu.eg (M. R. Fouad)

doi: 10.5267/j.ccl.2023.12.004

mobile than those with lower values. Especially for the hydrophobic pesticides ($K_{ow} \geq 2$), their mobility, and therefore the risk of their leaching into groundwater, has been correlated with weak sorption on the soil, as quantified by K_{oc}. Generally, pesticides with log $K_{oc} \leq 3$ are potentially leacher compounds although pesticides with log $K_{oc} \geq 3$ have been find in groundwater and drainage water.[3, 4]

Groundwater pollution affects the health of humans not only by used for drinking purpose, but also can act as a source of contamination for food chain, when used for irrigation.[5] Pesticides are a main source of nonpoint-source pollutants to groundwater, and their discharge to the nation's surface water may be a contributing factor toward the decline of the living resources and the deterioration of the ecosystems. A survey by the US EPA found pesticide detection in 16,606 wells in 45 states, with concentrations in 10,000 of these exceeding health advisory limits. Cost-effective assessment tools are needed to regulate the use of agricultural chemicals, identify areas which are potentially vulnerable to nonpoint-source pollution, and support ecosystem restoration goals by improving the nation's water quality.[6, 7] Physically-based environmental simulation models can be cost-effective tools for resources managers as an alternative to costly and prolonged field monitoring strategies. The groundwater contamination has many sources, the agriculture's relative contribution may be significant as incidents of groundwater contamination from pesticides and fertilizers.[8] The major transport routes to aquatic ecosystems include surface runoff, soluble or insoluble fractions transported via snowmelt, leaching into groundwater, talc and graphite dust associated with seeding drills at the time of planting, decay of systemically treated plants in water bodies, and deposition of treated seeds, soil or spray drift into water bodies or depressions.[9, 10] The interest of regulation authorities in the possible contamination of groundwater by pesticides dates from the beginning of the 1970s.[11] The Council of the European established a maximum concentration of 0.1 μg/L for individual pesticide in drinking water and 0.5 μg/L for the sum of compounds.[12] The prevention of groundwater pollution is much cheaper than restoring polluted aquifers. For that very reason it is of maximum interest that the development of agricultural strategies be directed to the decrease in pesticide movement. Since soil OM is the main soil component contributing to the sorption of pesticides,[13, 14] and sorption is one of the main processes reducing the mobility of these chemicals in soils, the addition of exogenous OM to soil land has been suggested as a possible method to reduce pesticide leaching.[15, 16]

Leaching studies of herbicide, bispyribac-sodium (BPS) in packed soil column indicated complete loss of soil applied herbicide under a simulated rainfall equivalent to 162 mm.[17] The herbicide, which is applied in paddy fields under flooded conditions, can contaminate groundwater through leaching or runoff.[18, 19] BPS is highly soluble in water and EPA classified it moderately to highly mobile in soils.[17] The groundwater ubiquity score (GUS) values of BPS were less than 2.9 in different soil types, and the residues were low to moderate to leacher (mobile) in the soil.[18] For cholantraniliprole (CAP), 33% and 22% were recovered from the upper and bottom layers by typical semiarid Mediterranean soil respectively. The calculated GUS index was higher than 5 for CAP, indicating they have the potential to leach.[20, 21]

2. Materials and methods

2. 1. Pesticides

Chlorantraniliprole

IUPAC name: 3-Bromo-N-[4-chloro-2-methyl-6-(methylcarbamoyl) phenyl]-1-(3-chloro-2-pyridine-2-yl)-1H-pyrazole-5-carboxamide. Solubility (20 ºC): Water 1.023 mg/L, methanol 1.714 g/L and dimethylformamide 124 g/L. Chemical class: Anthranilic diamide. Pesticide type: Insecticide.

Bispyribac-sodium

IUPAC name: Sodium 2,6-bis[(4,6-dimethoxypyrimidin-2-yl)oxy] benzoate. Solubility (20 ºC): Water 7330 mg/L. Chemical class: Pyrimidinyloxybenzoic acid. Pesticide type: Herbicide

2. 2. Soils

Two types of soils, sandy clay loam soil (soil A) and sandy loam soil (soil B) were tested in the present study. The physical and chemical properties were presented in **Table (1)**.[22]

Table 1. Physiochemical properties of soils

Properties	Soil A	Soil B
Texture class	Sandy clay loam	Sandy loam
EC (m mohs/cm) at 25˚C	1.32	2.33
Soil pH	8.25	8.20
Organic matter content (%)	3.31	1.32
Total carbonate (%)	7.87	40.09
Soluble cations conc. (meq/L)	19.01	33.50
Soluble anions conc. (meq/L)	13.50	23.31

2. 3. Tested soil amendments

Biochar and wheat straw were tested in the study,[23] obtained from Faculty of Agriculture, University of Alexandria, Egypt.

2.4. Leaching process

Leaching experiments were performed in PVC pipes columns of 10 cm (diameter) × 30 cm (length) packed with the natural soils (3 Kg) or with this soil amended with 5% biochar and wheat straw. Each column was oversaturated with $CaCl_2$ solution (0.01 molar) and the excess of water was allowed to drain freely for 3 days, so the soil moisture conditions approximated to field capacity. Pesticides and KI were applied to the top part of the columns following 4 days of free drainage. Each column received 10 mL KI solution (0.2 molar) as water tracer. The quantity of each tested pesticide dissolved in a methanol solvent was applied dropwise on the soil surface of each column, consistent with 10 µg/g soil. Next, the $CaCl_2$ solution was applied, and the leachates (25 mL leachate) were collected. The KI was determined in all leachate samples dependent on the iodimetric method.[24] Also, all leachates were analyzed to determine the tested pesticide by uv-vis spectrophotometer.[25]

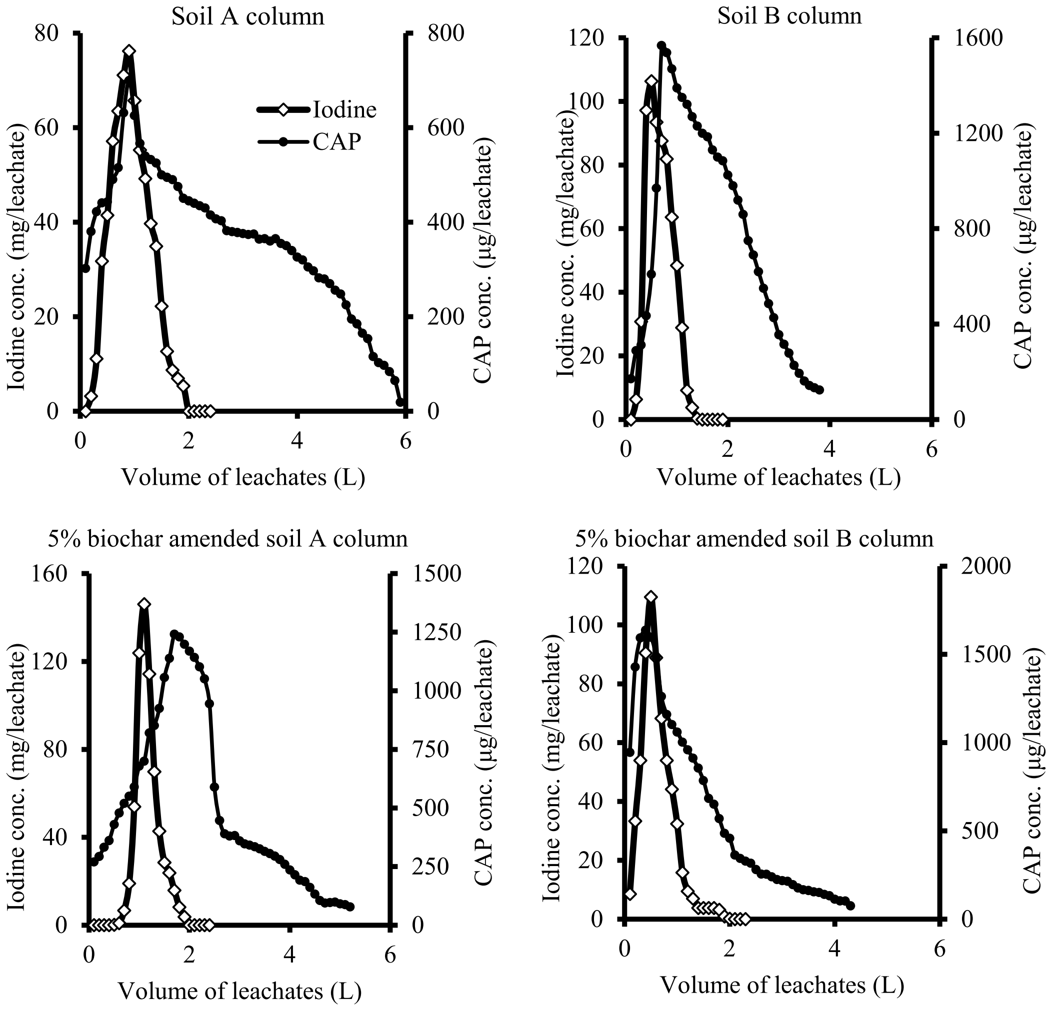
2. 5. Statistical analysis

Experimental data are presented as mean ± standard error was performed by Microsoft Excel 2019.

3. Results and discussion

The most definitive tests of organic chemicals mobility have occurred in tracer studies where a mobile, non-adsorbing tracer such as chloride or bromide has been added simultaneously with a sorbing organic tracer whose adsorption to soil has been charactarized independently through laboratory measurements.[3, 4, 25] In similar, iodide has been used as a water tracer at a rate of 10 ml KI (0.2 molar) 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 1000 ml of leachates from soil A columns, whereas in the first 500 mL of leachates from soil B columns. The breakthrough (BTC) curve of CAP appeared from leachates of soil A and soil B with that of iodide, indicating that CAP is highly mobile compound in both soil types, clay loam and sandy loam soil. However, the BTC of CAP is broad in the case of soil B and very broad in the case of soil A.



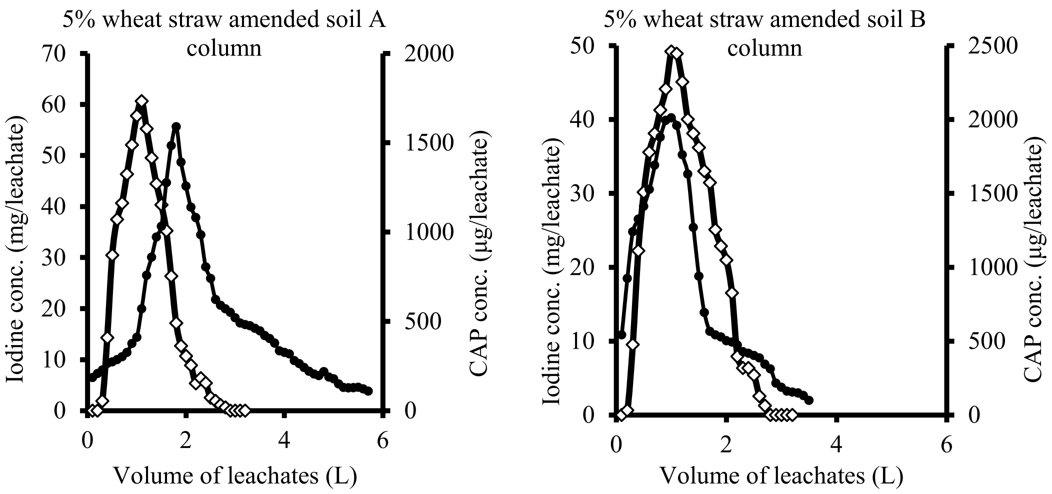
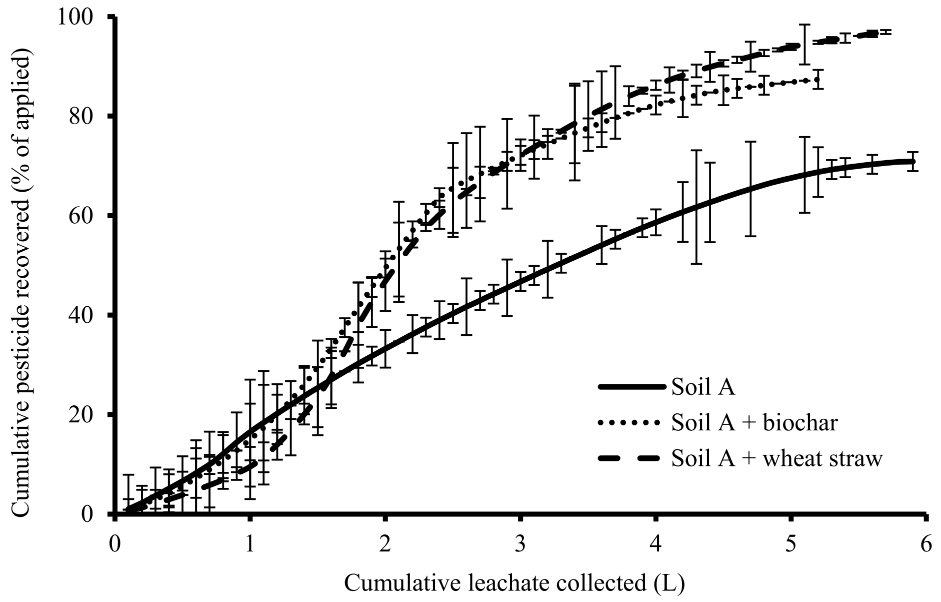


Fig. 1. Breakthrough curves of insecticide CAP and water tracer I^- in unamended and amended soil columns.

The maximum concentration of CAP in the soil A and soil B leachates was obtained after percolating about 1000 mL **(Fig. 1)**. Addition of 5% biochar or 5% wheat straw to soil A reduced the downward movement of CAP in the columns and affected the maximum concentration of CAP in the leachates. The maximum concentration of iodide in soil A columns were not affected by biochar or wheat straw, while the maximum concentration of CAP was obtained after 2000 mL of leachates cumulative volume. The amendment of soil A column with biochar or wheat straw decreased the bread of CAP BTC$_S$ compared to that of unamended soil. The BTC curve of CAP from column of biochar or wheat straw amended soil B is identical to the BTC curve of iodide as an internal water tracer, the BTC curves of CAP have some tailing. The maximum concentration of CAP was detected after percolating 500 mL and 1000 mL leachates cumulative volume of soil B column amended with biochar and wheat straw, respectively **(Fig. 1)**.

The results showed that iodide is a nonreactive water tracer. The water tracer I^- leached fast and the BTCs in unamended soil A and soil B and biochar and wheat straw amended soil columns are symmetrical. Also, obtained a symmetrical BTC for water tracer bromide.[26] The rapid release of CAP as well as I^- from soil B columns compared to soil A columns may be due to the soil type. Sandy soil containing more sand is more susceptible to leaching of agricultural chemicals.[27] The top of the BTC, corresponding to the maximum concentration of CAP was delayed in biochar and wheat straw amended soil A, whereas this observation did not record in the case of soil B. It may be due to soil B has macro and micro pores which influences the movement of chemicals.[28] **Fig. 2** shows the cumulative percentage of CAP collected in the leachates unamended and amended soil columns. Both organic amendments, biochar and wheat straw significantly increased the cumulative percentage of CAP throughout the percolation compared to that of unamended soil A.



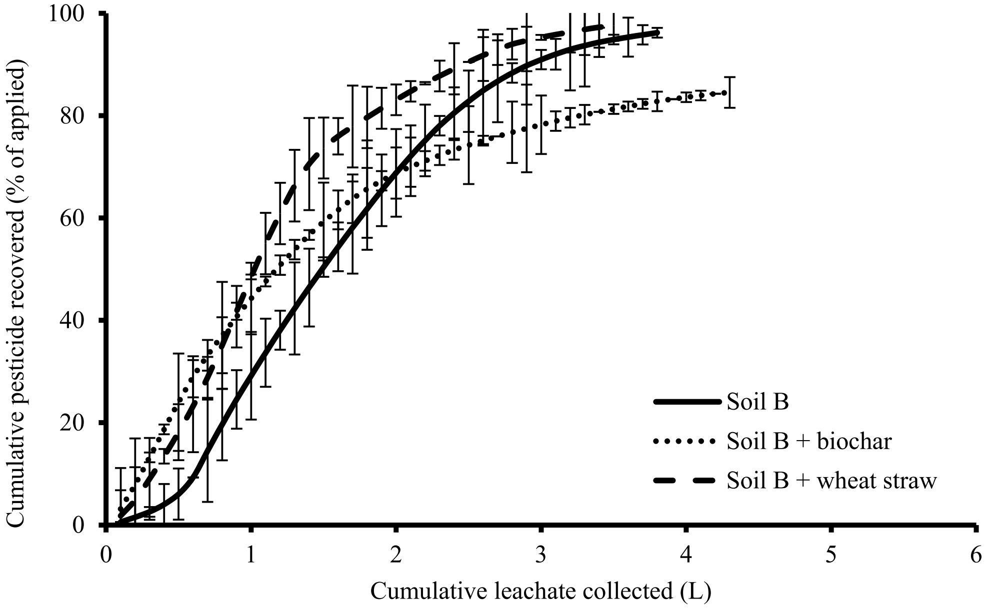
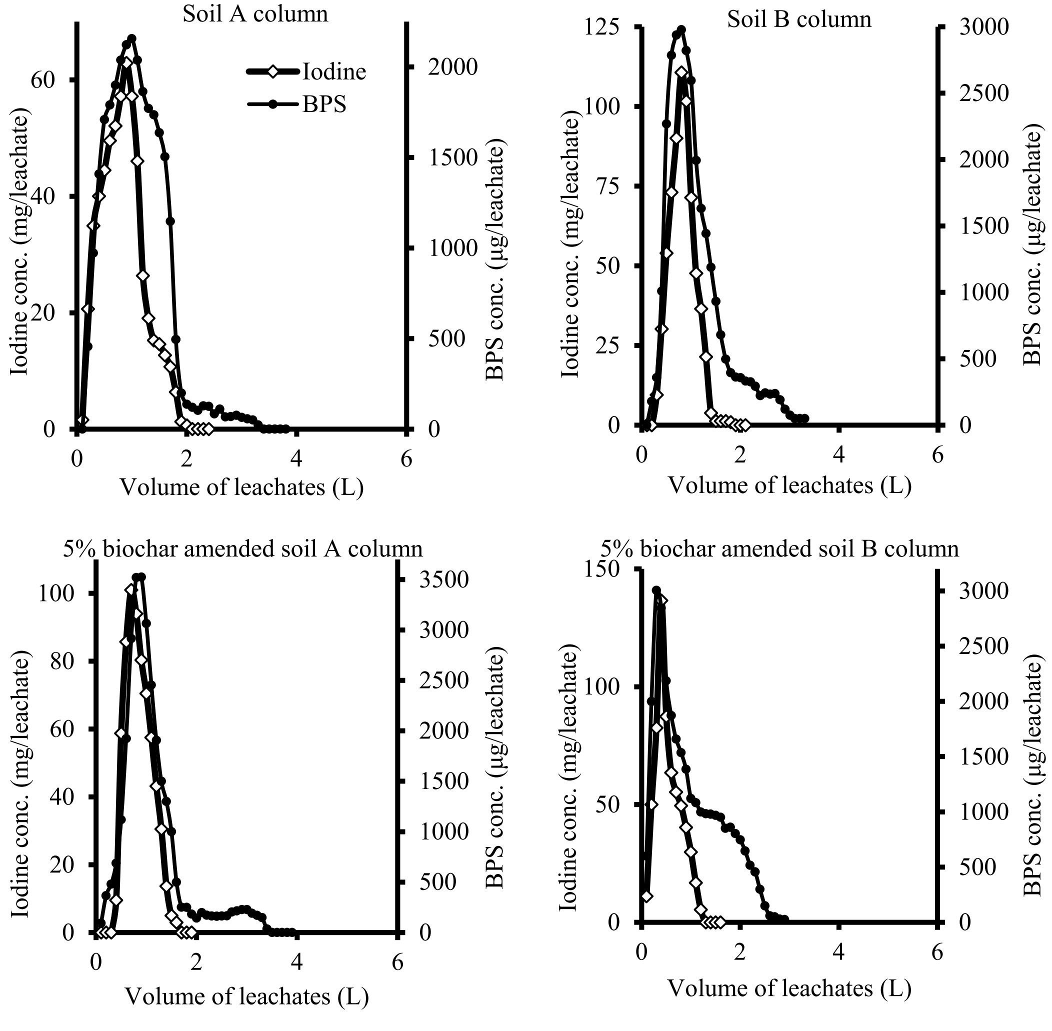


Fig. 2. Cumulative leachate curves of CAP in unamended and amended soil A (upper) and B (lower) columns



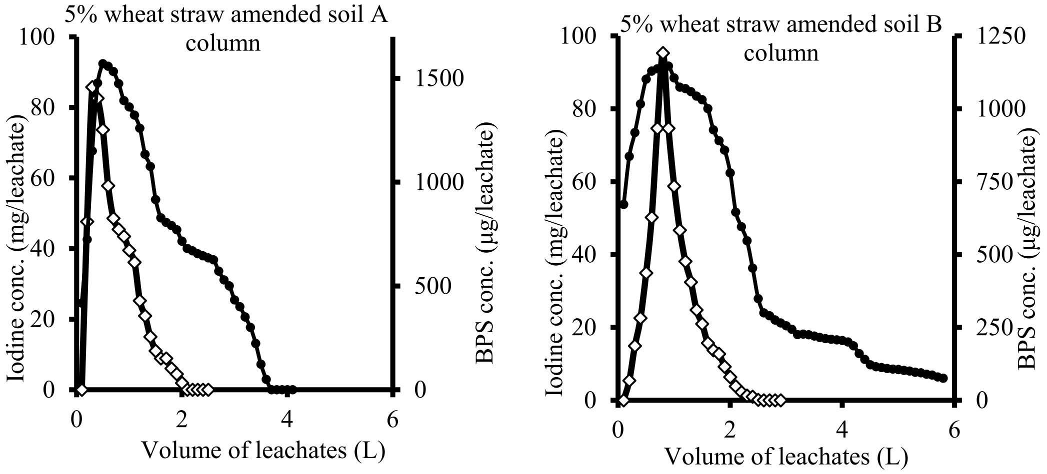
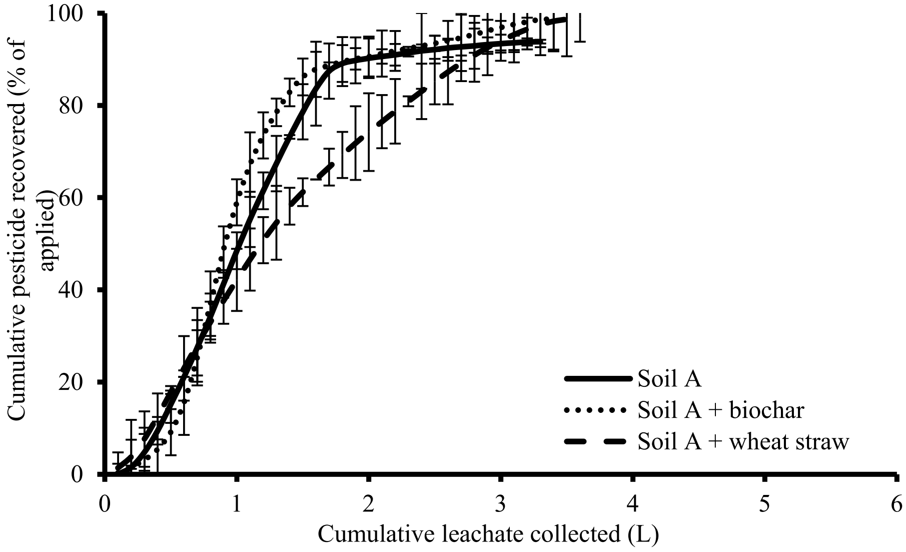


Fig. 3. Breakthrough curves of insecticide BPS and water tracer I^- in unamended and amended soil columns.

Also, biochar and wheat straw at a rate of 5% increased the cumulative percentage of CAP to about 2.5 L cumulative leachates, then 5% biochar amendment significantly reduced the cumulative percentage of CAP compared to those in unamended soil B. After application of 6 L percolating volume 71.0, 87.5 and 97.5%, of the applied CAP were recovered in the leachates of unamended soil A, biochar amended soil A and wheat straw amended soil A, respectively, whereas 96.2, 84.5 and 97.5 of the applied CAP were recovered in the leachates of unamended soil B, biochar amended soil B and wheat straw amended soil B, respectively. Leaching study of BPS suggested that the herbicide BPS was highly mobile in the unamended and amended soil A and B columns **(Fig. 3)**. Breakthrough curves of BPS in columns packed by unamended soil A and B and biochar and wheat straw amended soil at the rate of 5%, are identical to the breakthrough curves of iodide, but the BTC, of BPS in biochar and wheat straw exhibit flatter peaks and longer tailing. The BTCs, indicated that the release of BPS started with the first leachates. These results are supported by Beck et al, (1993) they showed BTCs for mobile chemicals having flatter peaks or some tailings.[29] The BTC curves of BPS indicated that the BTCs was obtained in the leachates of unamended soil A and B columns and biochar amended soil A column in cumulative percolation about 2 L and in the leachates of wheat straw amended soil A and B in cumulative volume nearly 5 L. Maximum concentration of BPS recovered in leachate fraction was 210, 350 and 150 µg/mL at cumulative percolation of 900 mL, 900 mL and 500 mL for unamended soil A, biochar amended soil A and wheat straw amended soil A, respectively. Also, the peaks top of the BTC curves for unamended soil B, biochar amended soil B and wheat straw amend soil B were obtained at cumulative percolation of 900 mL, 300 mL and 500 mL, corresponding the maximum concentrations of 300, 300 and 110 µg/mL, respectively. This result agrees with the results obtained by Singh and Singh,[17] they reported that the leaching study of BPS suggested that the herbicide was highly mobile in the soil column.



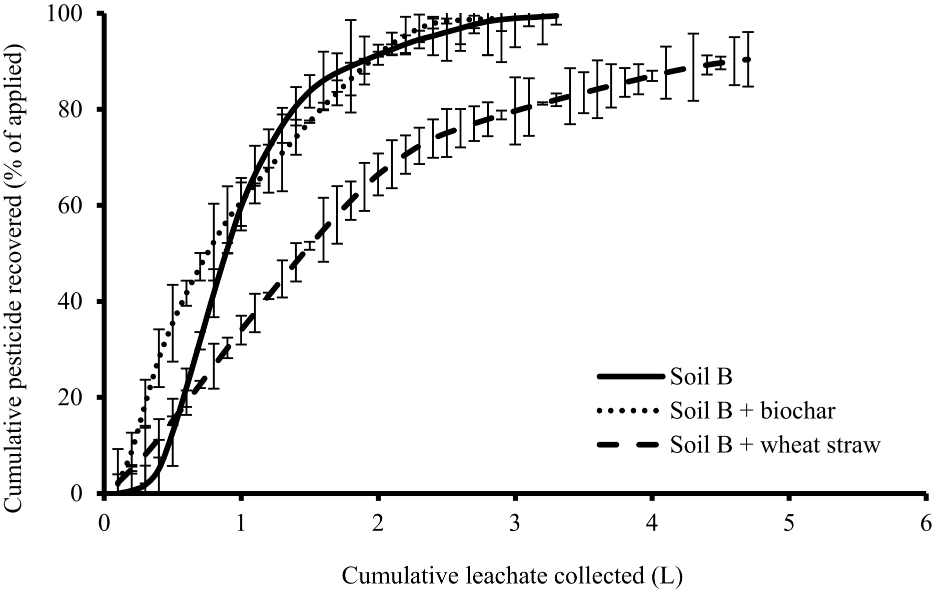
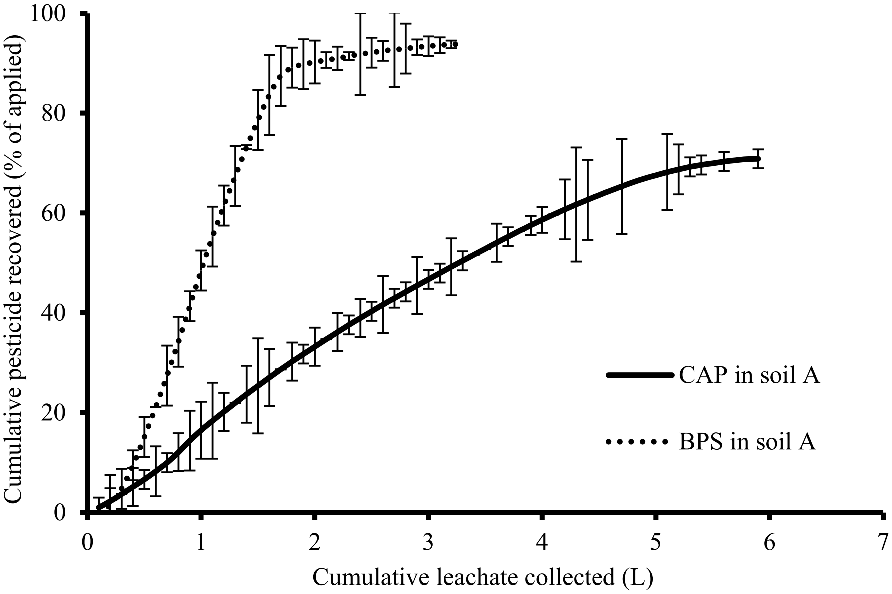


Fig. 4. Cumulative leachate curves of BPS in unamended and amended soil A (upper) and B (lower) columns.

Fig. 4 exhibited the cumulative percentage of BPS collected in different treatments leachate. The cumulative percentage of BPS collected in wheat straw amended soil was significantly reduced throughout percolation of 6 L in the case of soil B and within 1-3 L percolating in the case of soil A. Also, the results indicated that 93.8, 98.8 and 98.8% of the applied BPS were recovered in the leachates of unameded soil A, biochar and wheat straw amended soil A, respectively. The major amount (99.5%) of BPS was leached in unamended soil B, about 98.9 and 93.9% were recovered in the leachates of biochar and wheat straw amended soil B, respectively. Clearly, the wheat straw amendment significantly decreased the amount of BPS leached in sandy loam soil column. In addition, retardation of herbicide leachability has been extensively reported by various workers using different organic amendments and pesticides.[15, 30, 31]



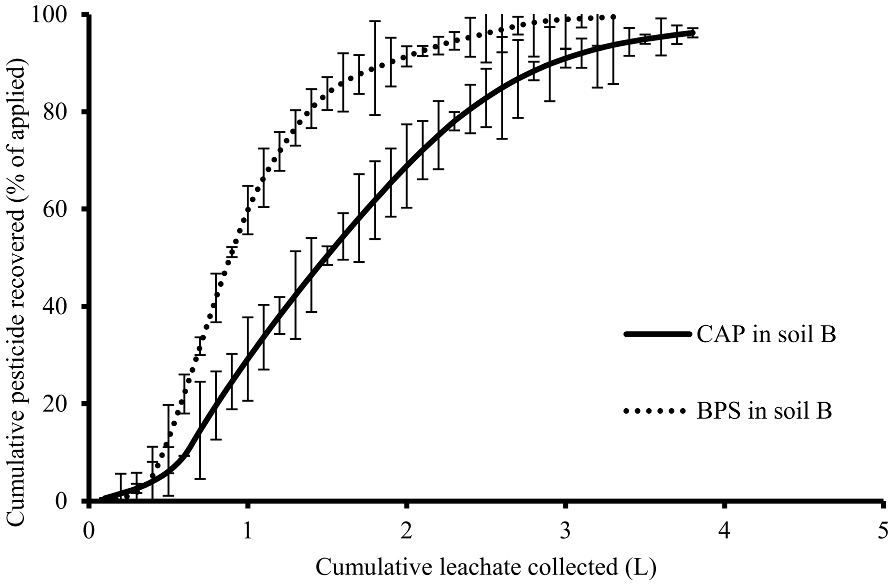


Fig. 5. Comparison of tested pesticides cumulative leachate curves in unamended and amended soil A (upper) and B (lower) columns.

Regarding the comparison of tested pesticides leachability in soil A and soil B columns. The amounts recovered were adjusted to 100% of that applied to allow for direct comparison of CAP and BPS **(Fig. 5)**. The leaching rate and cumulative amount of BPS more than CAP in soil A and B columns. The significant differences detected among the tested pesticides leaching were more in soil A columns than in soil B columns. Significant differences were detected among the cumulative percentages of pesticides. Harris (1966) and Rodgers (1968) studied the leaching of several herbicides and found water solubility played a role in leaching, but that adsorption data provided a better indicator of mobility.[32, 33] Moreover, the information available in registration date suggested that the BPS is highly mobile, indicated that the BPS was highly mobile in the soil columns.[17, 34, 35]

After calculation of Kd values for the tested pesticides, the results indicated that the Kd value of CAP = 0.805 and 0.238 mL/g, BPS = 0.072 and 0.105 mL/g in soil A and soil B, respectively. These results illustrated that CAP required more water to leach from soil A than that from soil B. In contrast more water was needed to leach BPS from soil B compared to soil A.

4. Conclusion

The water tracer I- leached fast and their BTCs into all soil columns are symmetrical. CAP was rapidly released from soil B columns compared to soil A columns. Therefore, its BTC is broad in the case of soil B and very broad in the case of soil A. Addition of 5% biochar or wheat straw to soil A reduced the downward movement of CAP in the columns and reduced the maximum concentration in the leachates. The BTCs of BPS in columns packed by unamended soil A and B and biochar and wheat straw amended soil at the rate of 5%, are identical to the BTCs of iodide, but the BTC of BPS in biochar and wheat straw amended soil columns exhibit flatter peaks and longer tailing. The wheat straw amendment significantly decreased the amount of BPS leached in soil B column. Regarding the comparison of tested pesticides leachability as 100% of applied pesticide, the leaching rate in soil A and B columns can be arranged in the order; BPS > CAP. The log K_{oc} values of tested pesticides were equal or lower than 3. Therefore, CAP and BPS in soil A and soil B are potentially leacher compounds. According to the Kd values for the tested pesticides in soil columns, both pesticides, CAP required more water to leach it from soil A than that from soil B. In contrast more water was needed to leach BPS from soil B compared to soil A.

References

1. Shamsan A. Q. S., Fouad M. R., Yacoob W. A. R. M., Abdul-Malik M. A., and Abdel-Raheem Sh. A. A. (**2023**) Performance of a variety of treatment processes to purify wastewater in the food industry. *Curr. Chem. Lett.*, 12 (2) 431–438.

2. El-Aswad A. F., Aly M. I., Fouad M. R., and Badawy M. E. I (**2019**) Adsorption and thermodynamic parameters of chlorantraniliprole and dinotefuran on clay loam soil with difference in particle size and pH. *J. Environ. Sci. Health B,* 54 (6) 475-488.
3. Fouad M. R. (**2023**) Effect of peat, compost, and charcoal on transport of fipronil in clay loam soil and sandy clay loam soil. *Curr. Chem. Lett.*, 12 (2) 281-288.
4. Fouad M. R. (**2023**) Effect of Soil Amendments on Leaching of Thiamethoxam in Alluvial and Calcareous Soil. *Basrah J. Agric. Sci.,* 36 (1) 164-172.
5. Navarro S., Fenoll J., Vela N., Ruiz E., and Navarro G. (**2009**) Photocatalytic degradation of eight pesticides in leaching water by use of ZnO under natural sunlight. *J. Hazard. Mater.* 172 (2-3) 1303-1310.
6. Hantush M. M., Marino M. A., and Islam M. R. (**2000**) Models for leaching of pesticides in soils and groundwater. *J. Hydrol,* 227(1-4) 66-83.
7. Fouad M. R. (**2023**) Validation of adsorption-desorption kinetic models for fipronil and thiamethoxam agrichemicals on three types of Egyptian soils. *Egypt. J. Chem.*, 66 (4) 219-222.
8. Milburn P., O'Neill H., Gartley C., Pollock T., Richards J., and Bailey H. (**1991**) Leaching of dinoseb and metribuzin from potato fields in New Brunswick. *Can. Agric. Eng.,* 33 (2) 197-204.
9. Morrissey C. A., Mineau P., Devries J. H., Sanchez-Bayo F., Liess M., Cavallaro M. C., and Liber K. (**2015**) Neonicotinoid contamination of global surface waters and associated risk to aquatic invertebrates: A review. *Environ. Int.,* 74: 291-303.
10. Fouad M. R., Aly M. I., El-Aswad A. F and Badawy M. E. I. (**2024**) Effect of particles size on adsorption isotherm of chlorantraniliprole, dinotefuran, bispyribacsodium, and metribuzin into sandy loam soil. *Curr. Chem. Lett.,* 13 (1) 61-72.
11. Leistra M., Van der Linden A., Boesten J., Tiktak A., and Van den Berg F. (**2001**) PEARL model for pesticide behaviour and emissions in soil-plant systems: description of the processes in FOCUS PEARL v 1.1. 1. Alterra.
12. Van der Linden A. M. A. (**1994**) Monitoring ground and surface waters: sampling strategy and implementation in legislation. *Environmental Behaviour of Pesticides and Regulatory Aspects. Copin A. y col (eds) European Study Service, Rinonhart, Belgium. pp*, 299-305.
13. El-Aswad A. F., Fouad M. R., Badawy M. E., and Aly M. I. (**2023**) Effect of Calcium Carbonate Content on Potential Pesticide Adsorption and Desorption in Calcareous Soil. *Commun. Soil Sci. Plant Anal.,* 54 (10) 1379-1387.
14. Fouad M. R. (**2023**) Effect of temperature and soil type on the adsorption and desorption isotherms of thiamethoxam using the Freundlich equation. *Egypt J. Chem.,* 66 (7) 197-207.
15. Cox L., Celis R., Hermosin M., Becker A., and Cornejo J. (**1997**) Porosity and herbicide leaching in soils amended with olive-mill wastewater. *Agric. Ecosyst. Environ.,* 65 (2) 151-161.
16. El-Aswad A. F., Aly M. I., Fouad M. R., and Badawy M. E. I (**2019**) Adsorption and thermodynamic parameters of chlorantraniliprole and dinotefuran on clay loam soil with difference in particle size and pH. *J. Environ. Sci. Health B,* 54 (6) 475-488.
17. Singh N., and Singh S. (**2015**) Adsorption and Leaching Behaviour of Bispyribac-Sodium in Soils. *Bull. Environ. Contam. Toxicol.,* 94: 125-128.
18. Chirukuri R., and Atmakuru R. (**2015**) Sorption characteristics and persistence of herbicide bispyribac sodium in different global soils. *Chemospher,* 138: 932-939.
19. Fouad M. R., El-Aswad A. F., Aly M. I., and Badawy M. I. (**2023**) Sorption characteristics and thermodynamic parameters of bispyribac-sodium and metribuzin on alluvial soil with difference in particle size and pH value. *Curr. Chem. Lett.,* 12 (3) 545-556.
20. Vela N., Pérez-Lucas G., Navarro M. J., Garrido I., Fenoll J., and Navarro S. (**2017**) Evaluation of the leaching potential of anthranilamide insecticides through the soil. *Bull. Environ. Contam. Toxicol.,* 99: 465-469.
21. Fouad M. R. (**2023**) Physical characteristics and Freundlich model of adsorption and desorption isotherm for fipronil in six types of Egyptian soil. *Curr. Chem. Lett.,* 12 (1) 207-216.
22. Abdel-Raheem S. A., Fouad M. R., Gad M. A., El-Dean A. M. K., and Tolba M. S. (**2023**) Environmentally green synthesis and characterization of some novel bioactive pyrimidines with excellent bioefficacy and safety profile towards soil organisms. *J. Environ. Chem. Eng.,* 11 (5) 110839.
23. Fouad M. R., El-Aswad A. F., Badawy M. E. I., and Aly M. I. (**2024**) Effect of soil organic amendments on sorption behavior of two insecticides and two herbicides. *Curr. Chem. Lett.,* 13 (doi: 10.5267/j.ccl.2023.10.007).
24. Mendham J., Denney R., Barnes J., Thomas M., Denney R., and Thomas M. (**2000**) Vogel's Quantitative Chemical Analysis. Prentice Hall, New York. 71: 65-70.
25. El-Aswad A. F., Fouad M. R., and Aly M. I. (**2023**) Experimental and modeling study of the fate and behavior of thiobencarb in clay and sandy clay loam soils. *Int J. Environ. Sci. Technol.*, 1-14.
26. Gaber H., Inskeep W., Comfort S., and El-Attar H. (**1992**) A test of the local equilibrium assumption for adsorption and transport of picloram. *Soil Sci. Soc. Am. J.*, 56 (5) 1392-1400.
27. Perry D. G., Kusel S. J., and Perry L. C. (**1988**) Victims of peer aggression. *Dev. Psychol.,* 24 (6) 807-814.
28. Shipitalo M., Edwards W., Owens L., and Dick W. (**1990**) Initial storm effects on macropore transport of surface-applied chemicals in no-till soil. *Soil Sci. Soc. Am. J.*, 54 (6) 1530-1536.
29. Beck A. J., Johnston A. J., and Jones K. C. (**1993**) Movement of nonionic organic chemicals in agricultural soils. *Crit. Rev. Environ. Sci. Technol.,* 23 (3) 219-248.

30. Fouad M. R., Badawy M. E. I., El-Aswad A. F., and Aly M. I. (**2023**) Experimental modeling design to study the effect of different soil treatments on the dissipation of metribuzin herbicide with effect on dehydrogenase activity. *Curr. Chem. Lett.*, 12 (2) 383-396.
31. Fouad M. R., Shamsan A., and Abdel-Raheem S. (**2023**) Toxicity of atrazine and metribuzin herbicides on earthworms (*Aporrectodea caliginosa*) by filter paper contact and soil mixing techniques. *Curr. Chem. Lett.*, 12 (1) 185-192.
32. Harris C. (**1966**) Adsorption, movement, and phytotoxicity of monuron and s-triazine herbicides in soil. *Weeds,* 14 (1) 6-10.
33. Rodgers E. (**1968**) Leaching of seven s-triazines. *Weed Sci.,* 16 (2) 117-120.
34. Skogsdata S. L. U. (**2017**) Aktuella uppgifter om de svenska skogarna från Riksskogstaxeringen. *Sveriges lantbuksuniversitet, Umeå*.
35. Fouad M. R., El-Aswad A. F., Badawy M. E. I., and Aly M. I. (**2024**) Effect of pH variation and temperature on pesticides sorption characteristics in calcareous soil. *Curr. Chem. Lett.,* 13 (1) 141-150.