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Sorption and mobility of ^{14}C-fenamiphos in Brazilian soils

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Abstract Although fenamiphos is widely used as an insecticide and nematicide in bowling greens and agriculture, information on its sorption in tropical soils is limited. In this study, mobility, sorption, and desorption dynamics of ^{14}C-fenamiphos in three contrasting Brazilian soils were examined both in batch and column experiments. Fenamiphos sorption coefficients (K_d) were 2.33, 3.86, and 3.9 L kg^{-1} for the three soils tested. The insecticide exhibited linear adsorption isotherms in all the three soils, and desorption was in a range of 30–40% during a 72-h period. With its low mobility, fenamiphos did not percolate through the soil profile even after 48 h. However, there is a risk of leaching to water bodies due to runoff because of its high solubility in water. In view of the fact that fenamiphos and its oxidation products are highly toxic to aquatic invertebrates and could affect the soil microbial activities even at low concentrations, the present information is of great importance in risk assessment of fenamiphos in the environment.

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Introduction

Organophosphorus (OP) pesticides have been widely used in agriculture and public health for the past 50 years. Fenamiphos (*O*-ethyl-*O*-(3-methyl-4-methylthiophenyl)-isopropylamido-phosphate) is a systemic OP insecticide and nematicide registered for its use in more than 60 countries including several tropical regions. Fenamiphos is applied on a variety of plants such as tobacco, turf, bananas, pineapples, citrus and other fruit vines, some vegetables, and grains. In Brazil, this pesticide has been extensively used in tomato crop at planting and also in melon (Yamada 2006). Fenamiphos, as is typical of other OP pesticides, blocks the enzyme acetylcholinesterase in the target pests (Kidd and James 1991). Generally, under environmental conditions, fenamiphos can be oxidized primarily to fenamiphos sulfoxide (FSO) followed by further oxidation to fenamiphos sulfone (FSO_2) (Ou et al. 1994). Due to its high solubility in water (0.4 g L^{-1}) and moderate ability to adsorb onto soils (Kookana et al. 1997; Cáceres et al. 2002), it can be readily leached from sites of application to surface water bodies (Patrick et al. 2001). Leaching of fenamiphos to groundwater has also been reported (Franzmann et al. 2000). Similar to fenamiphos, its metabolites such as FSO, FSO_2, and their phenols have high aqueous solubilities, posing a potential concern on their fate and toxicity in water bodies. In fact, there is very limited information on the behavior of fenamiphos in tropical soils (Cáceres et al. 2002; Cáceres et al. 2010).

Only few studies are available on soil sorption of fenamiphos in the Latin America and Caribbean region, and majority of the reported data are concerned with soils from Ecuador (Cáceres et al. 2002; Cáceres et al. 2008b). There is a single report on soils from Costa Rica and Brazil (Simon 1990), and virtually, no data are available on leaching of fenamiphos in Brazilian soils. It is, therefore, important to increase the knowledge on sorption and leaching of fenamiphos in tropical soils from Latin America. The objectives of this study were to provide information on sorption of ^{14}C-labelled fenamiphos to selected Brazilian tropical soils, and to evaluate the mobility of this pesticide in tropical soils and its potential in contaminating surface water as well as groundwater. The new data presented here could be used for risk assessment and/or environmental modeling to measure the potential migration of fenamiphos into water bodies.

Materials and methods

Test chemical

^{14}C-Fenamiphos, ring-labelled, with specific activity of 62.62 μCi mg^{-1} was obtained from Mobay Company, USA. Aqueous solution of this radio-labelled compound was prepared in 0.01 M $CaCl_2$.

Soils

Three soils (designated as PV, LVd, and LVdf) were collected from a depth of 0–15 cm from sugarcane fields in São Paulo state, Brazil. The soils were air-dried at room temperature and passed through a 2-mm sieve. The physico-chemical properties (Table 1) were determined according to Van Raij and Quaggio (1983) and Camargo et al. (1986).

Sorption test

Sorption of fenamiphos in the selected soils was measured following a standard protocol (OECD 2000) at room temperature by a batch equilibration method. Five grams of soil samples was taken in glass tubes, and 5 ml of aqueous solution of ^{14}C-fenamiphos was added. Five different concentrations of fenamiphos equivalent to 0.015, 0.036, 0.072, 0.149, and 0.288 mg L^{-1} with the corresponding activity of 2090, 5128, 10062, 20771, and 40081 dpm mL^{-1} were used. Blanks without soils indicated no significant sorption loss on tube walls. The soil solutions were equilibrated in a mechanical shaker for 24 h. The tubes were then centrifuged at 12100×*g* for 10 min, and aliquots (triplicates) of 1 mL of the supernatant were transferred to 10 mL of scintillation solution. The radioactivity in the samples was measured in a liquid scintillation counter (Packard, model Tri-carb 1600 TR).

Determination of sorption coefficient

The sorption coefficient (K_d) was determined using the ratio of pesticide sorbed by the soil samples (mg kg^{-1}) to the equilibrium solution concentration (mg L^{-1}), and was normalized on the basis of organic carbon content to obtain K_{oc} ($K_{oc} = K_d$/fraction of organic carbon).

Desorption test

The extent of desorption of fenamiphos was determined in soil samples used earlier for sorption. After 24 h equilibration, 2-ml portions of aqueous solution were removed from each tube, and 2 mL of fresh $CaCl_2$ (0.01 M) was added. Thus, the desorption of fenamiphos from soils was measured after 12, 24, 48, and 72 h of equilibration. One milliliter aliquots were taken at each sampling, placed in scintillation vials that contained 10 mL of scintillation solution, and the radioactivity was determined.

Table 1 Physico-chemical properties of the soils used

Soil designation	Soil classification	pH ($CaCl_2$)	OM (%)	Silt (%)	Sand (%)	Clay (%)
PV	Red eutrophic argisol	5.7	2.3	26	36	38
LVd	Dystrophic red latosol	3.8	2	12	22	66
LVdf	Red ferriferous latosol	4.4	4.2	10	49	41

Mobility of fenamiphos in soils

The mobility of fenamiphos in three different soils was determined using radio-TLC. Plates of soil were made using a mix of soil in water, and were dried at room temperature. Aliquots (10 μL) of ^{14}C-fenamiphos (equivalent to 3808 dpm μL^{-1}) were added to plates in duplicate, and the plates were developed using water as solvent. The plates were then dried at room temperature, and the mobility was determined using an automatic TLC linear analyzer (Berthold). The Rf value was calculated using the ratio between the distance of migration by the chemical and the distance of migration by the solvent.

Mobility of fenamiphos using columns

The mobility of fenamiphos in three different soils was also determined using glass columns (400-mm length and 50-mm diameter) with a conical end at the bottom. The bottom end of the column was sealed with glass wool. Sterilized sand (treated with HCl and air-dried) was added to cover the conical part of the column. Air-dried soil samples were evenly packed up to 300 mm in triplicates for each soil.

The packed soil columns were water-saturated by capillary forces using $CaCl_2$ solution (0.01 M). The excess solution was allowed to percolate for about 2 h.

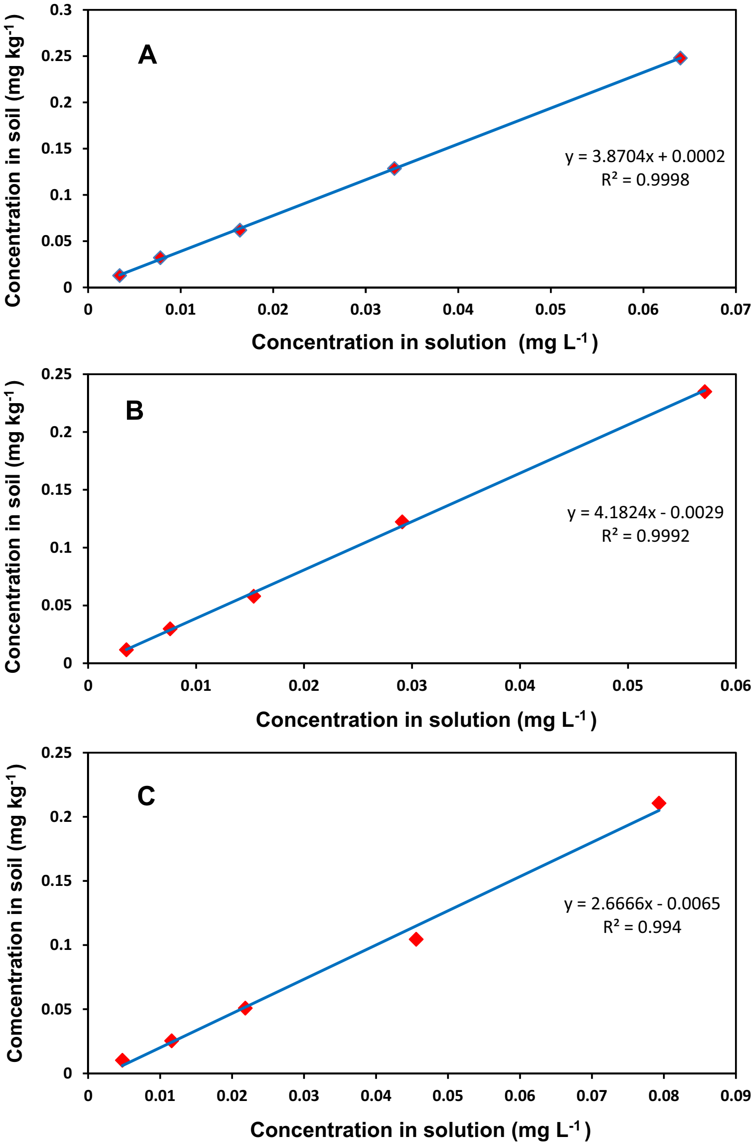

Fig. 1 ^{14}C-Fenamiphos sorption isotherms after 24 h for soils (**a**) LVd, (**b**) PV, and (**c**) LVdf

Aqueous solution of ^{14}C-fenamiphos was applied to soil in each column at a rate of 2 kg ha^{-1} and a radioactive concentration of 927,864 dpm/column. The column was covered with a disc of glass wool, and an inverted funnel was placed on the top of the column. The end of the funnel was connected to a Teflon tube that was attached to a peristaltic pump used to simulate a precipitation equivalent to 200 mm of rain in 48 h. The leachates were collected at regular intervals up to 48 h. The total volume in each leachate was determined. Aliquots (duplicates) of 10 mL were taken to measure the concentration of ^{14}C-fenamiphos by liquid scintillation spectrometry.

After leaching, the soil sample was removed from the columns using pressurized air, and the soil column was divided in sections of 5 cm. These soil cores were air-dried and weighed. Portions of 200 mg (in triplicates) were taken for combustion in a biological oxidizer (Harvey Instruments, model OX 500) to determine the bound residues of ^{14}C-fenamiphos in different soil sections.

Results and discussion

Fenamiphos sorption studies involving radio-labelled compound indicated that the sorption was moderate in all the soils tested, and the K_d values were 3.86, 3.91, and 2.33 L kg^{-1} in PV, LVd, and LVdf soils, respectively. The data presented in Fig. 1 clearly indicate linearity between sorption isotherms and the concentrations used in all the cases. The organic carbon sorption coefficients (K_{oc}) were 167, 93, and 111.5 L kg^{-1} for PV, LVd, and LVdf soils, respectively.

Table 2 Adsorption constants (K_{oc}) for fenamiphos in soils of temperate and tropical regions

Location	Clay (%)	Silt (%)	Sand (%)	K_{oc} of fenamiphos
		Temperate region		
Canada	22.7	47.6	29.7	297.9
Sweden	8.5	9.0	82.5	279.7
Germany (Puch)	14.1	74.9	11.0	111.6
Netherlands	19.3	58.0	22.7	380.0
France	28.1	39.9	32.0	159.5
USA (Indiana)	12.0	25.6	62.4	234.7
Japan	9.8	48.1	42.1	76.2
Morocco	7.8	24.0	68.0	539.4
Morocco	5.7	11.0	83.0	132.4
Australia (M Lakes)	16.2	37.4	46.3	237.3
Australia (Kersbrook)	16.5	36.7	46.5	203.7
Australia (Kulpara)	9.4	12.8	77.8	189.4
		Tropical region		
Brazil (P Fundo)	44.4	41.6	28.8	140.5
Brazil (Parana)	53.5	30.9	15.6	264.1
Thailand	55.3	43.0	1.7	1432.0
Philippines	15.2	42.0	42.5	339.7
Costa Rica	29.6	41.6	28.8	363.4
India (Andhra)	27.4	10.4	62.3	336.2
Ecuador (N Colonia)	41.5	40.6	19.4	382.1
Ecuador (Quevedo)	23.3	25.0	52.2	298.0
Ecuador (Machala)	44.4	27.4	27.6	447.1
Ecuador (Riobamba)	30.9	7.2	61.8	2887.0
Ecuador (Salasaca)	8.0	31.9	60.1	96.0
Ecuador (Agoyan)	3.0	46.3	50.8	225.5

Adapted from Simon (1990), Cáceres et al. (2002), Cáceres et al. (2008a), Cáceres et al. (2008b) and El M'Rabet et al. (2000)

In the present study, LVd soil with the lowest organic matter content (2%) showed the highest sorption (K_d = 3.91 L kg^{-1}). However, this soil has a relatively high (66%) clay content. Previous studies on fenamiphos sorption in soils from Ecuador (Cáceres et al. 2002) and other reports with clays (Rodriguez et al. 1988; Sanchez-Martin 2000; Singh et al. 2003) indicated that fenamiphos is intercalated in the clay lattice and that high sorption coefficients are linked to clay content as well as its nature. PV soil exhibited a K_d of 3.86 L kg^{-1} followed by LVdf soil (K_d of 2.33 L kg^{-1}). However, the clay content in these two soils varied between 38 to 41%. On the other hand, PV soil has a higher percentage (26%) of silt as against 10% in LVdf soil. This could explain the differences in K_d values since silt and clay in combination could influence the sorption of xenobiotics to soil. Lvdf soil showed the lowest K_d value of 2.33 L kg^{-1} and the highest organic matter content (4.2%). From the data available on fenamiphos behavior in tropical soils, it is evident that not just organic matter is linked to fenamiphos sorption but that there is a complex interaction between other soil components including clays and silt.

It has been well established that soil properties such as the type and content of organic carbon, clay, and pH have influence on sorption of pesticides in soils

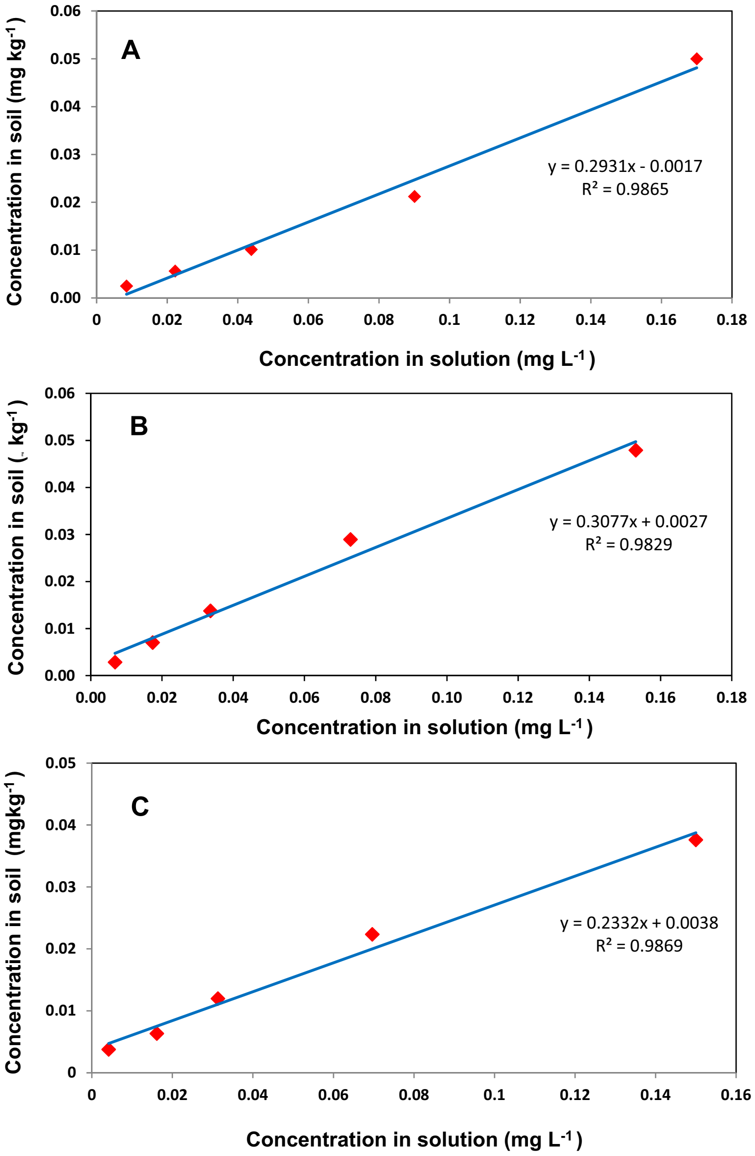

Fig. 2 ^{14}C-Fenamiphos soil desorption isotherms (72 h) for soils (**a**) LVd, (**b**) PV, and (**c**) LVdf

(Graham-Bryce 1981; Loch 1991; Kookana et al. 1998), but the best correlation is usually observed with soil organic matter (Brouwer et al. 1990). The K_{oc} values of fenamiphos for soils of temperate regions around the world ranged from 76.2 to 539 (Table 2). The correlation between soil sorption and organic matter in these soils was high (95% confidence) with an R^2 value of 0.79. On the other hand, the adsorption constants (K_{oc}) of fenamiphos in soils from tropical countries were within a range of 96–2887 (Table 2). However, the correlation between fenamiphos soil sorption and organic matter for these soils was very low ($R^2 = 0.23$). These data indicate that organic matter has a considerable influence on fenamiphos sorption in temperate soils but not in those of tropical regions. The composition and structure of organic matter vary due to its origin, geological history, and land use (Oliver et al. 2003). In addition, the chemistry of organic matter influences pesticide sorption (Ahmad and Kookana 2002). These observations could explain the difference in K_{oc} values reported from tropical and temperate regions.

Fenamiphos presented a medium desorption behavior during a 72-h period. Thus, the desorption percentages were 40.18, 34.03, and 30.78 for PV, LVd, and LVdf soils, respectively. The desorption isotherms also showed linearity over the concentrations used as well as the different sampling times with R^2 values of 0.98–0.99, 0.97–0.99, and 0.98–0.99 for PV, LVd, and LVdf soils, respectively (Fig. 2). Fenamiphos showed very low mobility as determined by the movement of

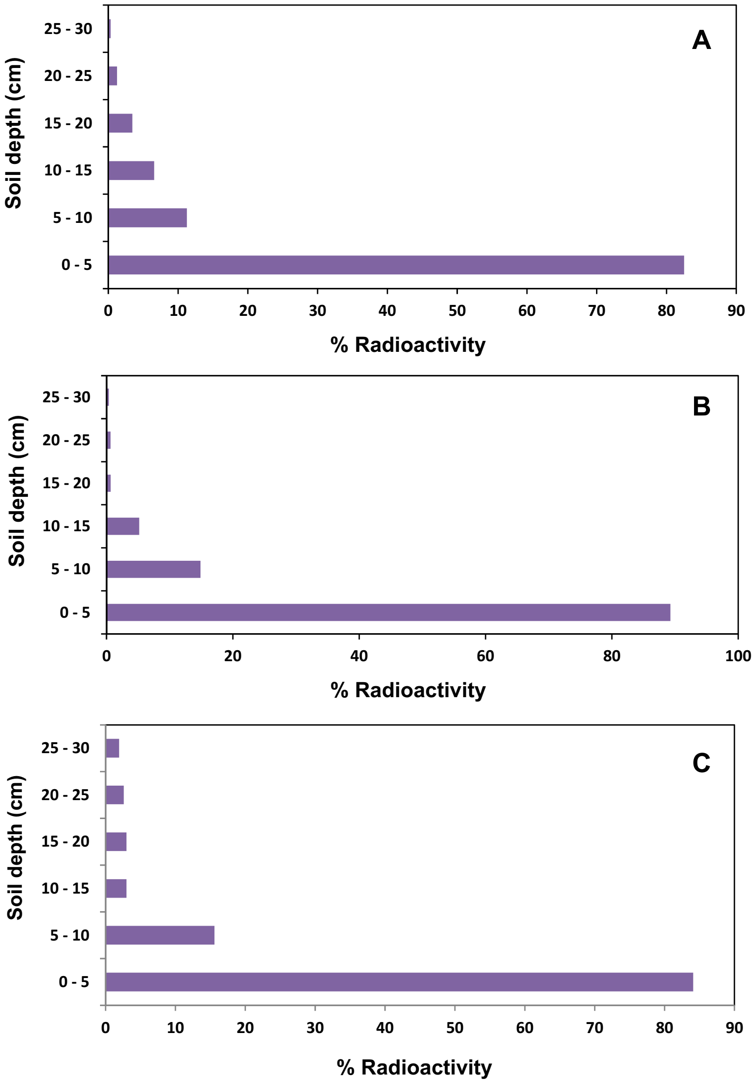

Fig. 3 Movement of ^{14}C-fenamiphos in profiles of soils (**a**) LVd, (**b**) PV, and (**c**) LVdf

^{14}C-labelled compound on soil TLC plates. The Rf determined for the three soils were as follows: PV = 0.29; LVd = 0.31, and LVdf = 0.50. Thus, the mobility of fenamiphos in the soils tested followed the order: LVdf > LVD > PV. The column studies revealed that the pesticide did not percolate through the soil profile after a 48-h period. The radioactivity detected in the leachates was < 0.01% of the total activity applied to the soil. Most of the radioactivity remained in the first 10-cm column of the soils (Fig. 3).

The data on mobility from the column studies showed that a major portion of the pesticide remained in the top 5 cm. Thus, 89.26, 82.45, and 84.10% of ^{14}C-fenamiphos was detected at the top in PV, LVd, and LVdf soils, respectively. The pesticide migrated up to the final section of soil profile (25–30 cm), but in a very small amount. About 1.94% of the pesticide moved down in LVdf while the corresponding percentages were 0.34 and 0.36 in LVd and PV soils, respectively. These findings are of particular importance as there is a tendency for fenamiphos to migrate to the lower profiles in soil such as LVdf and could contaminate groundwater. Moreover, due to the moderate sorption of fenamiphos in all the three soils and desorption over time, as has been demonstrated in this study, there is a high probability that the pesticide contaminates water through surface runoff. This could be a serious concern in aquatic ecosystems since fenamiphos and its main metabolites are toxic to freshwater organisms like *Daphnia* and algae (Cáceres et al. 2007; Cáceres et al. 2008b, c, d). Previous studies carried out in other regions have reported contamination of surface and groundwater with fenamiphos (Franzmann et al. 2000; Patrick et al. 2001). As fenamiphos could become bioavailable due to desorption processes, it may also affect the soil microbial activity. Cáceres et al. (2009) reported that fenamiphos even at low concentrations inhibits soil nitrification process. The pesticide also could affect the survival of terrestrial invertebrates such as earthworms (Cáceres et al. 2011). The results of this study would help in better understanding of the behavior and fate of fenamiphos in tropical soils while minimizing the risk of its contamination. It also contributes to generate input data on local soils to perform risk assessment evaluations.

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References

Ahmad, R., Kookana, R. (2002). Role of the chemistry of soil organic carbon in pesticide sorption in soils. In: Proceedings of the 17th world soils congress, Thailand.

Brouwer, W. W. M., Boesten, J. J. T. I., & Siegers, W. G. (1990). Adsorption of transformation products of atrazine by soil. *Weed Research, 30*(2), 123–128. https://doi.org/10.1111/j.1365-3180.1990.tb01695.x

Cáceres, T., Ying, G. G., & Kookana, R. (2002). Sorption of pesticides in banana production on soils of Ecuador. *Australian Journal of Soil Research, 40*(7), 1085–1094. https://doi.org/10.1071/SR02015

Cáceres, T., Megharaj, M., & Naidu, R. (2007). Toxicity of fenamiphos and its metabolites to the Cladoceran *Daphnia carinata*: the influence of microbial degradation in natural waters. *Chemosphere, 66*(7), 1264–1269. https://doi.org/10.1016/j.chemosphere.2006.07.027

Cáceres, T., Megharaj, M., & Naidu, R. (2008a). Degradation of fenamiphos in soils collected from different geographical regions: the influence of soil properties and climatic conditions. *Journal of Environmental Science and Health, B43*, 314–322.

Cáceres, T., Megharaj, M., & Naidu, R. (2008b). Sorption of fenamiphos to different soils: the influence of soil properties. *Journal of Environmental Science and Health, B43*, 605–610.

Cáceres, T., Megharaj, M., & Naidu, R. (2008c). Toxicity and transformation of fenamiphos and its metabolites by two microalgae *Pseudokircheriella subcapitata* and *Chlorococcum* sp. *Science of the Total Environment, 398*(1-3), 53–59. https://doi.org/10.1016/j.scitotenv.2008.03.022

Cáceres T, Megharaj M, Naidu R. (2008d) Biodegradation of the pesticide fenamiphos by ten different species of green algae and cyanobacteria. Current Microbiology, 57, 643–646. https://doi.org/10.1007/s00284-008-9293-7.

Cáceres, T., Megharaj, M., & Naidu, R. (2009). Effect of the insecticide fenamiphos on soil microbial activities in Australian and Ecuadorean soils. *Journal of Environmental Science and Health, B44*(1), 13–17.

Cáceres, T., Megharaj, M., Venkateswarlu, K., Sethunathan, N., & Naidu, R. (2010). Fenamiphos and related organophosphorus pesticides: environmental fate and toxicology. *Reviews of Environmental Contamination and Toxicology, 205*, 117–162. https://doi.org/10.1007/978-1-4419-5623-1_3

Cáceres, T., Megharaj, M., & Naidu, R. (2011). Toxicity and transformation of the insecticide fenamiphos to the earthworm *Eisenia fetida*. *Ecotoxicology, 20*(1), 20–28. https://doi.org/10.1007/s10646-010-0552-6.

Camargo, O.A., Moninz, A.C., Jorge, J.A, Valadares, J.M.A.S. (1986). Métodos de análise química, mineralógica e física de solos do Instituto Agronômico de Campinas. Campinas: Instituto Agronômico. *Boletim Técnico,* 106. 94 pp.

El M'Rabet, M., Dahchour A., Massoui M., Badraoui, M., Sanchez Martin M.J. (2000). Adsorption of carbofuran and fenamiphos by Moroccan soils. Agrochimica, Vol XLVI, 10–17.

Franzmann, P., Zappia, L., Tilbury, A., Patterson, B., Davis, G., & Mandelbaum, T. (2000). Bioaugmentation of atrazine and fenamiphos impacted groundwater: laboratory evaluation. *Bioremediation Journal, 4*(3), 237–248. https://doi.org/10.1080/10588330008951112

Graham-Bryce, I. J. (1981). The behaviour of pesticides in soil. In D. J. Greenland & M. H. B. Hayes (Eds.), *The chemistry of soil processes* (pp. 621–670). NY: John Wiley and sons.

Kidd, H., & James, D. R. (1991). *The agrochemicals handbook* (3rd ed.pp. 6–10). Cambridge: Royal Society of Chemistry Information Services.

Kookana, R., Phang, C., & Aylmore, A. G. (1997). Transformation and degradation of fenamiphos nematicide and its metabolites in soils. *Australian Journal of Soil Research, 35*(4), 753–762. https://doi.org/10.1071/S96105

Kookana, R. S., Baskaran, S., & Naidu, R. (1998). Pesticide fate and behaviour in Australian soils in relation to contamination and management of soil and water: a review. *Australian Journal of Soil Research, 36*(5), 715–764. https://doi.org/10.1071/S97109

Loch, J. P. (1991). Effect of soil type on pesticide threat to the soil/ground water environment. In M. L. Richardson (Ed.), *Chemistry, agriculture and the environment* (pp. 291–307). UK: The Royal Society of Chemistry.

Oliver, D., Kookana, R. S., & Salama, R. B. (2003). Land use effects on sorption of pesticides and their metabolites in sandy soil. I Fenamiphos and two metabolites, fenamiphos sulfoxide and fenamiphos sulfoxide and fenarimol and azinphos methyl. *Australian Journal of Soil Research, 41*(5), 847–860. https://doi.org/10.1071/SR02094

Organisation for Economic Co-operation and Development (OECD). (2000). *Adsorption-desorption using a batch equilibrium method* (45 pp). Guideline for testing chemicals: OECD.

Ou, L. T., Thomas, J. E., & Dickson, D. W. (1994). Degradation of fenamiphos in soil with a history of continuous fenamiphos applications. *Soil Science Society of America Journal, 58*(4), 1139–1147. https://doi.org/10.2136/sssaj1994.03615995005800040019x

Patrick, G., Chiri, A., Randall, D., Libelo, L, Jones, J. (2001). Fenamiphos environmental risk assessment. US Environmental Protection Agency. Provided for SRRD by EFED's Fenamiphos RED Team. www.epa.gov/oppsrrd1/op/fenamiphos/env_risk.pdf. Accessed 14 October 2008.

Rodriguez, J. M., Lopez, A. J., & Bruque, S. (1988). Interaction of fenamiphos with montmorillonite. *Clays and Clay Minerals, 36*(3), 284–288. https://doi.org/10.1346/CCMN.1988.0360311

Sanchez-Martin, M. (2000). Adsorption of carbofuran and fenamiphos by montmorillonite. *Fresenius Environment bulletin, 9*, 582–589.

Simon, L. (1990). Metabolism of fenamiphos (Nemacur) in soil types of different geographic origin. Dissertation Technical University Munich. Report N M5680.

Singh, N., Megharaj, M., Gates, W. P., Churchman, J., Anderson, J., Kookana, R. S., Naidu, R., Chen, Z., Slade, P. G., & Sethunathan, N. (2003). Bioavailability of an organophosphate pesticide fenamiphos sorbed on an organo-clay. *Journal of Agricultural and Food Chemistry, 51*(9), 2653–2658. https://doi.org/10.1021/jf025978p

Van Raij, B., Quaggio, J. A. (1983). Métodos de análise de solo para fins de fertilidade. Campinas: Instituto Agronômico. *Boletim Técnico* 81. 31 pp.

Yamada, Y. (2006). *Fenamiphos evaluation*. Japan: National Food Research Institute www.fao.org/ag/AGPP/Pesticid/JMPR/Download/2006_eva/Fenamiphos%20206%20Evaluation.pdf. Accessed 10 September 2016