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Organic matter content in riparian areas of soil composed of woody vegetation and grass and its effects on pesticide adsorption

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Abstract

Purpose Riparian zones are identified as mitigation areas of agricultural pollutants to river ecosystems. However, the mitigation mechanisms of these pollutants remain unclear mainly on the effects of different types of riparian vegetation and its organic matter content in the pollutants removal process. This study aims to assess the content of organic matter in soils composed of woody vegetation and grass and its effects on four pesticides adsorption. Adsorption studies were conducted in soil collected in riparian vegetation areas composed of grass and trees under the influence of an agricultural area.

Methods The analyses were performed in 21 shakers containing 100 g soil and a L of water previously contaminated with pesticide that were stirred for 30, 60, 120, 240, 360, 720, and 1440 min. A study was made of maximum adsorption capacity using the time 360 min and the concentrations of 5, 20, 40, and 50 μg L^{-1}.

Results The soils of woody vegetation areas had a higher concentration of organic matter as compared with grass areas, and time 360 min achieved the highest adsorption capacity with minimum values of 84% adsorption for the area of land made up of trees and 67% for grass areas. The soils of woody vegetation areas had a higher concentration of organic matter as compared with grass areas, time 360 min.

Conclusion The best adsorption capacity was obtained with minimal adsorption amounts of 84% to the area of soil composed of 67% for trees and grass areas.

Keywords Riparian zones · Pesticides · Organic matter · Water contamination · Adsorption

Introduction

With the constant expansion of the world population, there is also an increase in demand for food and raw materials. An estimate of the United Nations (2008) stated that in 2050, the number of people on the planet will be approximately nine billion. This constant expansion of the population has driven the development of new technologies in the agribusiness segment, such as nanotechnology, biotechnology, natural resource management, and new pesticides.

Pesticides are substances with toxic action and include herbicides, insecticides, miticides, fungicides, and others (EXTOXNET 1996; Spark and Swift 2002); Illani et al.

2005). These chemical compounds have active ingredients formulated to prevent, combat, or destroy unwanted species or diseases that might interfere with agricultural production or in the storage and transport of planted crops (McBride 1994; Jakelaitis et al. 2006).

The interaction, presence, or removal of pesticides in the soil, as well as effective action for which the product is applied, are aspects influenced by different physical, chemical, and biological processes (McBride 1994; Freire et al. 2004; Coelho and Bernardo 2012). These processes often occur simultaneously, resulting in the complexity of this relationship pesticide–soil (Reemtsma et al. 1999; Lavorenti et al. 2003; Sarwar et al. 2018).

When applied to soil, pesticides can be degraded by chemical reactions, photolysis, or the action of microorganisms (McBride 1994; Zheng and Cooper 1996; Carmo et al. 2013; Correia and Langenbach 2006). However, molecules with high persistence can remain in the environment without undergoing any change. These molecules are subject to sorption and desorption of soil particles to leaching and

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may reach the saturated zone of the soils. Or they could be leached into rivers and lakes. In aquatic environments, pesticides may undergo sorption in dry sediment or water can be absorbed by plants, fish, and other aquatic fauna representatives (Mitchell and Simpson 2013).

The adsorption and desorption of organic compounds such as pesticides in the soil are the most important processes related to soil and water contamination by these compounds (Barriuso et al. 1992). In this context, the organic matter in the soil can have great influence on the evaluation of the soil mobility of the pesticides, which is important to the retention of these compounds in the agricultural area by preventing them to be leached into rivers, lakes, and underground water.

In tropical and subtropical soils, organic matter has a close relationship with the other physical, chemical, and biological properties of soil (Correia and Langenbach 2006). Thus, the sustainable management of soil organic matter is fundamental to maintaining the productive capacity of the soil in the long term. The management effect on stocks of organic matter depends on the type of soil (Aguiar et al. 2014).

The content of organic matter is an important factor in the soil, because strongly affects fertility by increasing the availability of nutrients for plants, the improvement of its structure and water-holding capacity, and also by the accumulation of toxic action phases and heavy metals. For McBride (1994), the organic matter in association with the clay has an extremely important influence on the physical and chemical properties of soil. This includes: maintenance of the pore structure accompanied by improved water retention, agricultural nutrient retention by the exchange cation, release nitrogen, phosphorus, sulfur and trace elements by mineralization, adsorption of potentially toxic organic and others (Celis et al. 1998; Ahmad et al. 2001; Carmo et al. 2013, Arne et al. 2019). Thus, the present study aims to assess the content of organic matter in riparian areas of soil composed of grass and trees with a view to its influence on pesticide adsorption capacity by these soils.

Methods

Characteristics of the study soil

The study of soil comes from two areas of riparian vegetation being one composed of trees and other soils (per gram) were collected at a depth of 0-20 cm, the soil samples were analyzed in the laboratory of the Brazilian Agricultural Research Corporation—Embrapa Forestry and soil laboratory of the Federal University of Parana (UFPR) to determine their chemical composition and organic matter

content. Adsorption studies were performed in Hydrogeological Research Laboratory of the Federal University of Parana. All soils collected were analyzed for presence of pesticides before the start of the tests.

Adsorption tests

The soils were collected from areas of forest preservation and free of pesticide application. For confirmation, pesticide analyses were performed to determine the presence of potential interferents in the sample. The soils were then dried in an oven at 80 °C for 24 h.

For the tests standards were used: atrazine, fluazifop-*p*-butyl, lactofen, and chlorpyrifos at the concentration of $10 \mu g \, L^{-1}$. The standards were added in 21 shakers containing 100 g soils with high organic matter content (from a riparian vegetation area composed of trees) and 21 shakers containing 100 g soil low in organic matter (from a riparian vegetation area comprising for grasses) in each shaker was added 1 L of purified water in a milli-Q water purification system (Millipore, Bedford, MA).

In shakers were then covered with aluminum paper to prevent photo-degradation of pesticides, and kept at room temperature with constant stirring for times 30, 60, 120, 240, 360, 720, and 1440 min, and at the end of each time, the samples were filtered using a cellulose acetate filter with porosity of 0.45 µm and analyses subsequently performed immediately in water.

Maximum adsorption capacity tests

For maximum adsorption capacity, assays were used concentrations of 5, 20, 40, and 50 µg L⁻¹ of atrazine, fluazifop-*p*-butyl, lactofen, and chlorpyrifos. For these tests, the temperature used was 25 °C (average temperature corresponding to the areas of study). Pesticides were added to 15 shakers and maintained with agitation, being withdrawn at each time a sample for analysis.

The calculations of linear isotherms were made by relationship between q CEQ. They are

$$q = a + b\left(c_{qe}\right).$$

This linear regression method can be used to find the slope (*b*) and the intercept (*a*) is an ideal model for studies with adsorbents that exhibit linear isotherms at low concentrations, as in the present study.

Sample extraction

The extraction protocol was optimized from studies developed by Lacorte et al. (2000) and Aguiar et al. 2015. In a sample of 1 L was added 0.1 µg of Atrazine-D5 (99% purity,

Bellefonte, PA, USA) as a standard replacement before extraction. The samples were first filtered using a cellulose membrane with a porosity of 0.45 mm and 47 mm diameter (Millipore Merck—Darmstadt, Germany).

1 L of water sample was extracted using extraction cartridges C18 SPE solid phase (Milford, MA, USA). The cartridges were cleaned first with 6 ml of ethyl acetate, 6 ml methanol, and 6 ml of purified water (Milli-Q, Millipore, Bedford, MA) and samples were then percolated through a vacuum system (JT Baker—Phillipsburg, NJ) at a flow rate of 6 ml/min.

After that, the cartridges were dried under vacuum for 15 min to remove excess water. Then, extraction was performed with 6 ml of ethyl acetate and 6 ml of methanol. The extract was dried with a gentle stream of nitrogen using a dry block (40 °C, Marconi, SP, BRA), and reconstituted in 100 ml of ethyl acetate. The samples were transferred to test tubes for analytical gas chromatography–mass spectrometry.

Gas chromatography–mass spectrometry (GC–MS)

The GC–MS was performed using a Varian gas chromatograph Varian 431. GC MS 220 coupled to an ion trap mass spectrometer equipped with a capillary column VF 5 ms (30×0.25 mm and 25 mm film thickness). The GC oven was programmed to 90°C, held for 0.5 min, then heated to 160 °C (for 4 min) at 15 °C min^{-1}, and heated again to 280 °C (hold for 10 min) 20 °C min^{-1}. The sources of ions and GC interface were 280 °C and 200 °C, respectively. The mass spectrometer ion trap was operated on impact ionization of electrons with an energy of 70 eV ionization and emission of 300 mA current. The helium at a constant flow rate of 1.0 ml min^{-1} was used as the carrier gas. The injection volume was 1 µL in a splitless mode (1 min) with the injector temperature at 250 °C. From the collision-induced dissociation (MS/MS), three mass fragment ions were selected for each compound atrazine (*m/z* 122*, 132, and 200), chlorpyrifos (*m/z* 258*, 286, and 314), fluazifop butyl-p (*m/z* 254, 238*, and 282), and lactofen (*m/z* 223*, 300, and 344), and the main fragment ions used as the precursor ion mass. The mass fragment ions labeled were used for quantification analysis and the other two were used for structural confirmation. The stock solutions were prepared for all agrochemicals (99% purity, Sigma-Aldrich, Missouri, USA) 10 mg ml^{-1} in ethyl acetate and were maintained at -4°C.

Atrazine-D5 was verified with the following ions m/z 127*, 139, and 205. The calibration curve was performed with diluted standards between 0.01 and 30 µg L^{-1}. Calibration curves resulted in correlation coefficients of 0.99 and relative standard deviation of less than 9% (*n* 4) for all compounds. The lower point of quantification was 0.01 µg L^{-1}, where all compounds showed significant signs. Recovery studies were performed with a mixture of five samples of agrochemical pesticides free groundwater at a concentration of 1 µg L^{-1} and recovery values ranged 83–97% with a standard deviation of less than 12% (*n* 5) for all analyses.

The protocols used in accordance with SANCO/10232/2006 EU (European Commission, 2006). The identification and confirmation of the target compounds were made based on the following criteria: (i) the retention time deviation from a standard of less than 2 s; (ii) three characteristics *m/z*; and (iii) features of intensities m/z compared with standard *m/z* (not more than 15% variation).

The significance of different samples was tested by analysis of variance (ANOVA). When significant probability was detected ($p < 0.05$), means were compared by Tukey's test, and multiple comparisons were performed testing to determine which buffer zone width. They were especially different based on the concept of Least Significant Difference (LSD) and were determined at 5%.

To calculate the percentage removal, the initial concentration in the solution, which was considered as 100% (A), was used. For the calculation of the removal of pesticides studied and the result found after stirring times (B), the percent removal was calculated by the difference between A and B.

Results and discussion

The physical characteristics of soils are presented in Table 1. The clay concentration was 15 g kg^{-1}, and the sand was of 12 g kg^{-1} and 13 g kg^{-1} silt. The average amount of organic matter present in soil consisting of woody vegetation was 370.9 g kg^{-1}; as for the land areas composed per gram, the amount of organic matter was observed 99.10 g kg^{-1}. The observed values of pH for the samples collected were between 5.27 and 5.8.

For comparative analysis of soils containing low and high organic matter content, significant differences were observed for all times used (Table 1). Analyzing the pesticide concentrations between the times of 30 min, 1 h,

Table 1 Characterization of samples analyzed for organic carbon concentration, organic matter, sand, silt, and clay

	Organic carbon (g kg^{-1})	Organic matter (g kg^{-1})	Sand (g kg^{-1})	Silte (g kg^{-1})	Clay (g kg^{-1})
ATMO	215.6 ($\pm$0.7)	370.9 ($\pm$1.3)	12	13	15
BTMO	57.5 ($\pm$0.7)	99.1 ($\pm$1.2)	11	12	13

ATMO high content of organic matter, *BTMO* low organic matter content

2 h, significant differences were observed between them, for all pesticides analyzed using both low concentration of organic matter when high concentrations of organic matter (Tukey, $p < 0.05$). There were no significant differences between 12 h and 24 h times for atrazine and chlorpyrifos both low organic matter and high organic matter content. (Tukey, $p > 0.05$) For fluazifop and lactofen pesticides, there were no significant differences between 6 h, 12 h, and 24 h. The pesticide fluazifop demonstrated no significant differences between 4 h times a 24 h.

For pesticides studied the soil with higher content of organic matter from riparian areas composed of woody vegetation, they showed the best results, being that the balance in the adsorption process occurred only after 360 min of agitation (6 h). Thus, the time 360 min was used for maximum adsorption capacity test (Fig. 1).

For the time 360 min, atrazine had a 84% adsorption percentage in riparian area of soil composed of woody vegetation and 67% for grass areas. Chlorpyrifos had already obtained 91% adsorption in areas with woody vegetation and 77% for areas with grasses. For fluazifop areas with woody vegetation removal achieved 94% and 71% in areas with vegetation composed per grasses. The lactofen achieved 86% removal in areas with woody vegetation and 61% for areas with vegetation consists of grasses (Fig. 1).

In studies of maximum adsorption capacity (Fig. 2) was identified isotherms a linear model, fluazifop pesticide had a higher adsorption coefficient Kd (L/kg) of 259.29, followed by chlorpyrifos with 140.70, since the pesticide atrazine and lactofen obtain one low value being 54.50 and 49.31, respectively.

The soil riparian areas composed of woody vegetation obtained the best results in the composition of organic matter in relation with the area of the compound per grasses soil. This difference can be explained by observing the larger amount of promoted vegetable waste deposition on the trees. Otherwise, the density of planted trees reduces the impact of raindrops on the soil promoting greater stability and reducing the transport of sediment and organic matter itself.

The riparian soil region composed of trees, which had a higher amount of organic matter obtained a better retention of pesticides studied compared with the areas with vegetation soil composed per grasses with a reduction of more than 84% for the pesticides against 67% for grass areas on time 360 min.

In isotherms, studies found a linear model of adsorption due to the low concentration of the compounds studied, the pesticide fluazifop showed the most adsorption capacity followed by chlorpyrifos, atrazine and lactofen. Other studies have found similar results, Oliver et al. (2005) and Ling et al. (2006) studied the kinetics of pesticides in different soil types and found a positive correlation between the pesticides and adsorption to organic carbon. This data also are consistent with studies in the field made by Katsoyiannis and Samara (2007) and Aguiar et al. (2015) in which the pesticide was fluazifop with a higher rate of removal, followed by chlorpyrifos, lactofen and atrazine, and in environmental factors other than influence of organic matter degradation of these compounds.

Fig. 1 Pesticide removal efficiency atrazine (**a**), chlorpyrifos (**b**), fluazifop (**c**), and lactofen (**d**) in soils containing high concentrations of organic matter (filled circle) and low concentrations of organic matter (filled square)
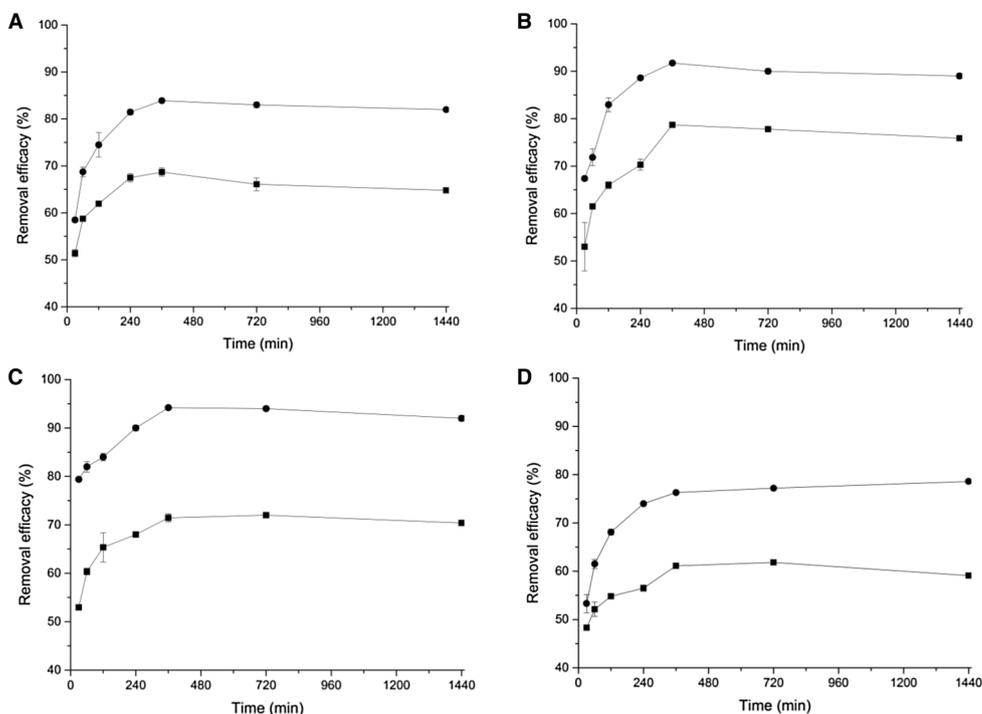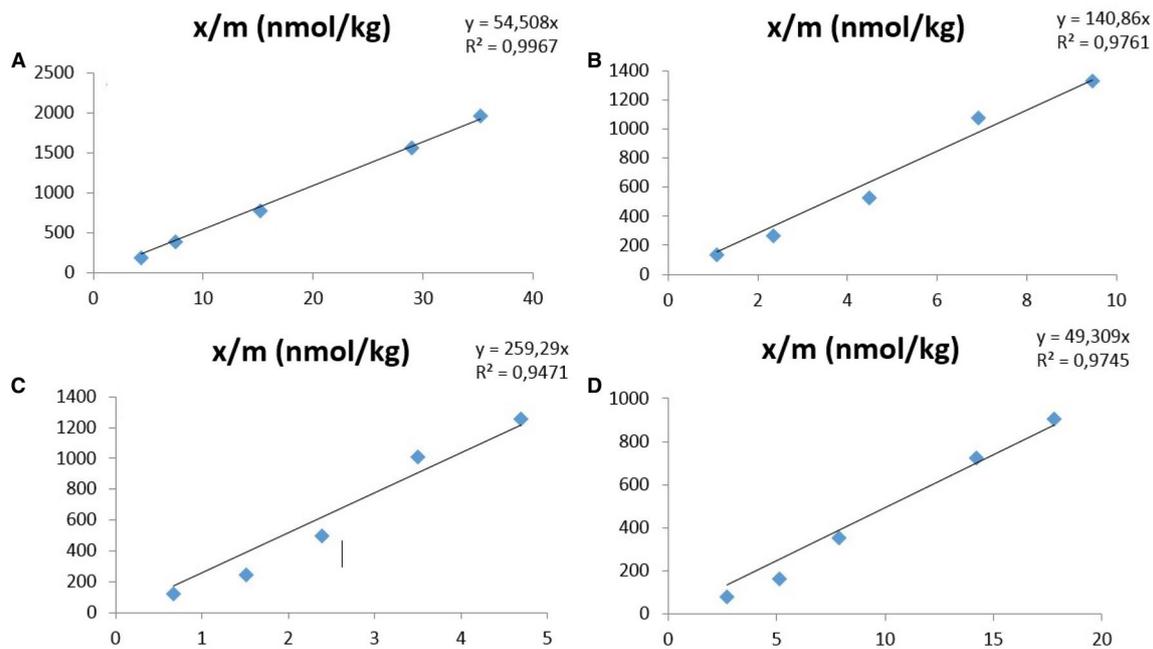
Fig. 2 Adsorption isotherms for atrazine (**a**), chlorpyrifos (**b**), fluazifop (**c**), and lactofen (**d**) riparian area of soil composed of trees containing high concentrations of organic matter

Due to the low pH of the soil studied, there was an increase in the protonation of pesticides molecules, causing most of them would meet in the neutral form and, consequently, to increase its sorptive organic matter. In neutral form, the sorption becomes more dependent on the organic matter to the soil mineral fraction.

Soils with low organic matter content have a high negative charge making it less able to accommodate the neutral species of pesticides studied with the solid phase. Furthermore, the release of organic matter into the solutions (soil, water, pesticides, etc.) makes it more efficient for soils to accommodate molecules of pesticides, causing the sorption of the compound increases and decreases of leaching.

Conclusion

In the present study, soil materials with a high content of organic matter presented a higher adsorption index of pesticides studied with 84% reduction, as the soils with lower content presented a reduction of 67%. In tropical and subtropical soils, organic matter has a close relationship with the other physical, chemical and biological soil properties.

Therefore, sustainable management of soil organic matter is essential to maintaining the productive capacity of

the soil and reducing leaching of agricultural pollutants such as pesticides.

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