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Abamectin in soils: Analytical methods, kinetics, sorption and dissipation

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H I G H L I G H T S

- Sorption and dissipation of abamectin (ABM) were evaluated in Brazilian soils.
- K_F values indicate high sorption capacity of ABM in soils with limited mobility.
- Rapid dissipation of ABM was observed in non-sterile soils.
- No significant decrease in the concentration of ABM was verified in sterile soils.
- Aerobic microbial degradation is the main mechanism of dissipation of ABM.

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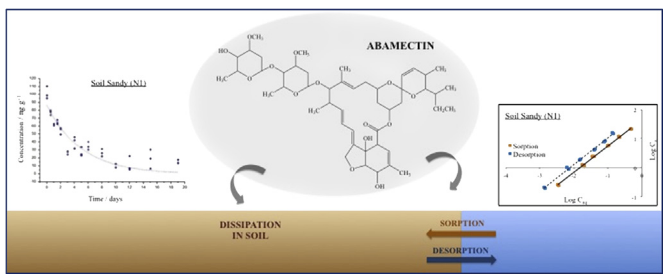

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A B S T R A C T

Abamectin is a broad-spectrum antiparasitic agent that has been widely employed in veterinary medicine and has also been used as a pesticide in agriculture. Veterinary drugs may reach the soil and may be transported to surface and ground waters, posing risks to terrestrial and aquatic organisms. Sorption, transformation and transport processes are primarily responsible for the fate of these substances in the environment. In this study, the sorption and the aerobic dissipation of abamectin in Brazilian soils (sand, clay and sandy–clay) were evaluated. For sorption studies, batch equilibrium experiments were performed. Sorption and desorption isotherms were fitted to the Freundlich model. Abamectin showed a high affinity to soil particles, with Freundlich sorption and desorption coefficients ranging from 44 to 138 $\mu g^{1-1/n}$ $(cm^3)^{1/n}$ g^{-1} and from 89 to 236 $\mu g^{1-1/n}$ $(cm^3)^{1/n}$ g^{-1}, respectively. Dissipation of abamectin was evaluated in sterile and non-sterile soils in an aerobic and dark environment under controlled temperature and humidity. The time required for a 50% reduction of the amount of abamectin present in non-sterile soils was up to 4 days, and the time period for 90% dissipation was up to 12 days. In sterilized soils, there was no reduction in the concentration of abamectin over 37 days of exposure, suggesting that aerobic microbial degradation must have been the primary mechanism responsible for the dissipation of abamectin in soils.

1. Introduction

Veterinary drugs have been widely used in livestock for the control of diseases, increasing the productivity and supply of foods of animal origin. In 2014, global sales of the animal health industry

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were estimated at 24 billion dollars. In Brazil, sales reached almost 2 billion dollars, with 22% corresponding to the commercialization of antiparasitic drugs (SINDAN, 2015), to which avermectin sales are an important contributor.

Avermectins are macrocyclic lactones produced by fermentation of the microorganism *Streptomyces avermitilis* in the soil, with a broad spectrum of activity against a variety of endoparasitic nematodes and ectoparasitic arthropods (Õmura, 2008; Campbell, 2012).

In Brazil, which is one of the largest producers and exporters of cattle, chicken and pig meat in the world, more than 180 formulations containing avermectins as active ingredients are commercially available for veterinary applications, including abamectin, ivermectin, doramectin, eprinomectin and selamectin (MAPA, 2015; SINDAN, 2015).

Among the most used avermectins, abamectin has also been used as a pesticide in agricultural crops against mites, plant parasitic nematodes, and insects pests. In Brazil, 15 formulations of abamectin are registered by the Ministry of Agriculture, Livestock and Supply, and they are suitable for foliar and seed applications in more than 20 kinds of crops, including cotton, potato, coffee, citrus, beans, apples, strawberries, tomatoes, and grapes, among others (MAPA, 2015).

The frequent use of avermectins in agriculture and livestock is an important input pathway for the dissemination of these compounds into the environment.

Many veterinary drugs are poorly metabolized in animals and are excreted in the feces and urine as the parent compound. High levels of avermectins have been detected in the feces of treated animals, indicating that most of the administered dose is excreted without transformation. Parent compounds and metabolites may then reach the soils directly through animal excrement or through the application of manure for fertilization purposes in agriculture. Resistance of avermectins to dissipation in animals manure has been observed, resulting in a high load of these compounds in soil (Alvinerie et al., 1999; Perez et al., 2001; Kolar et al., 2006; Litskas et al., 2013). Once in the soil, such compounds can be potentially transported to aquatic systems. Another important route of entrance of avermectins in the environment is their direct use in aquaculture (Luvizotto-Santos et al., 2009).

The soil may also be exposed through agricultural pesticide applications, including direct application in the soil by seed treatment. Pesticides may reach soils and the surface and ground waters, primarily due to the winds and the rainwater, which promote drift, wash of the treated leaves, leaching and erosion.

Studies reported in the literature show that avermectins have potential for neurotoxicity and can affect the survival, growth and reproduction of non-target species, posing risks to terrestrial and aquatic organisms even at very low concentrations (Katharios et al., 2004; Garric et al., 2007; Kolar et al., 2008). The presence of avermectins in the environment may also contribute to the development of parasitic resistance induced by the wide variety of products used in the control of parasites, which are often administered without epidemiological criteria and with incorrect dosages and failures in the handling procedures (Molento, 2005; Rangel et al., 2005).

Knowledge of the processes that determine the fate of veterinary drugs in the environment is essential for the evaluation of the environmental impact of their application. Transportation, transformation and bioavailability of these compounds in soils and sediments, surface and ground waters depend on the sorption, degradation and leaching process, which in turn are governed by the local climate and physicochemical properties of the substances, such as structure, solubility, hydrophobicity and speciation, and also of the soil, such as pH, organic matter content, texture and cation exchange capacity (Boxall et al., 2003; Horvat et al., 2012).

Sorption studies may be useful for estimating the mobility of a chemical in soil, water and air, and its availability for degradation, volatility, and uptake by terrestrial and aquatic organisms, leaching and runoff to natural waters. Sorption studies reported in the literature suggest that avermectins bind tightly to soil and are therefore highly immobile in the environment (Gruber et al., 1990; Krogh et al., 2008; Litskas et al., 2011).

The risks arising from the presence of veterinary drugs in the environment also depend on their dissipation in soil and water. Degradation processes may be responsible for minimizing problems associated with the persistence and accumulation of these compounds in the environment. Studies reported in the literature suggest that avermectins are generally characterized as moderately to highly susceptible to dissipation in soil, which depends on soil characteristics, oxygen content and the microbial activity (Mougin et al., 2003; Krogh et al., 2009; Litskas et al., 2013).

Information about sorption and the dissipation of abamectin in soils are limited, and environmental impact studies of avermectins in Brazil are practically absent. Research has been conducted primarily in countries with climate and soil types that are significantly different from those found in Brazil, contributing to different behaviors of these substances. The objective of this study was to evaluate the sorption and aerobic dissipation of abamectin in four types of Brazilian soils.

2. Material and methods

2.1. Soil samples

Sorption and aerobic dissipation studies were conducted on sandy, sandy–clay and clay soils from São Paulo, Brazil. The origins of the soils were as follows:

N1 – Sandy, city of Santa Rita de Passa Quatro, SP, Brazil (21°42′18.12″S and 47°28′04.82″W, altitude 773 m; pasture);
N2 – Clay, city of Sertãozinho, SP, Brazil (21°05′20.44″S and 47°48′10.73″W, altitude 538 m; sugar cane plantation);
S1 – Sandy–clay, city of Jaguariúna, SP, Brazil (22°43′14.92″S and 47°01′14.20″W, altitude 617 m; citrus plantation);
S2 – Clay, city of Jaguariúna, SP, Brazil (21°42′59.50″S and 47°01′00.05″W, altitude 609 m; covered with *Brachiaria*).

For sorption experiments, soil samples (N1, N2, S1 and S2) were collected, air-dried, sieved to a particle size ≤ 2 mm, and stored in plastic bags at room temperature until use. For dissipation experiments, soil samples (N1 and S2) were sieved immediately after collection and stored at 4 °C for no more than 3 months before the beginning of the tests, to ensure the maintenance of microbial activity of the soils. The physicochemical and textural characteristics

Table 1
Physicochemical and textural characteristics of the selected soils.

Property		Soil			
		N1	N2	S1	S2
pH (in 0.01 mol L^{-1} $CaCl_2$)		5.0	4.9	4.1	4.4
Organic matter (%, w/w)		1.53	2.88	2.48	3.23
Texture (%)	Sand (>0.053 mm)	91.1	14.9	52.9	43.5
	Silt (0.053–0.002 mm)	1.8	30.2	10.5	7.0
	Clay (<0.002 mm)	6.2	54.6	36.2	49.2
Cation exchange capacity ($mmol_c$ kg^{-1})		19.3	52.7	51.9	66.0
Water holding capacity[a] (g g^{-1})		0.05	–	–	0.21

[a] Water holding capacity determined at pF = 2.