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Mobility of organotin pesticides: azocyclotin and cyhexatin in clayey and sandy soils from the Northern Paraná state - Brazil

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Abstract

Azocyclotin and cyhexatin are pesticides commonly used in mite control. However, these organotin compounds are highly harmful to the aquatic ecosystem and supposedly mobile in the soil. In addition to not existing defined rules of use, few studies have been carried out on organotins' behavior and environmental control. Liquid chromatography has been pointed out for the OTC quantitation because of gas chromatography's thermal stability and derivatization limitations. Hence, a new high-performance liquid chromatography method with photodiode array detection (HPLC-PDA) was developed for quality assurance and quality control (QA/QC) and environmental performance assessment purposes. Hysteresis index (*HI*) and mobilization factor were determined from sorption/desorption in sandy and clayey soils to assess mobility and environmental risk. Mobilization was observed for the two compounds by applying the dual-mode Freundlich-Langmuir model to the isotherms. Azocyclotin showed greater mobility, 23% and 19%, and *HI* of -0.15 and 7.8×10^{-4} for clayey and sandy soil samples, respectively. Although cyhexatin was practically immobile for both soil samples, it can be mobilized as an azocyclotin metabolite, increasing the environmental impact and risk for agricultural uses.

Keywords: organometallic compounds, soils, sorption, HPLC-PDA, hysteresis, mobilization

1 Introduction

World population growth requires a high demand for food and agricultural productivity, fueled by new technologies and increased use of pesticides. Although pesticides are an essential tool to control undesired living species, their toxicity may risk human beings and other non-target species (Fent and Mueller, 1991). Pests such as pathogenic fungi and mites in apple, citrus, eggplant, soybean, coffee, and cocoa have been efficiently controlled by organotin compounds (OTC) such as azocyclotin and cyhexatin (Godoi et al, 2003; Blunden and Evans, 1990). However, environmental risk is associated with its toxicity to the aquatic ecosystem and human health (Fent and Mueller, 1991; Kanimozhi et al, 2016). Adverse effects can be observed when the maximum residue limit for the total of azocyclotin and cyhexatin (expressed as cyhexatin) exceeds 2.0 mg kg⁻¹ for human consumption (Ning et al, 2015; EU, 2012). Cyhexatin, a metabolite of azocyclotin, is one the most toxic among triorganotin compounds. Health problems such as irreversible corneal opacity, high reproductive toxicity even at low concentrations, and animal teratogenicity make OTC a target for environmental behavior studies (Fent, 1996; PubChem, 2017a,b). OTC constitute Stockholm's persistent organic pollutants and share the same characteristics of being persistent, toxic, bioaccumulative, and capable of traveling long distances through different means (Ming et al, 2012). Concerning the matrix, OTC degradation in soils is considered to be longer, with a half-life of about several years to decades in soil compared to the water column (Furdek et al, 2016). Consequently, soils and sediments emerge as secondary and persistent OTC sources, becoming a potential threat in affected environments. Organotin compounds affect the ecosystem, and according to Ebdon et al (2001) should be listed as global pollutants.

The 1,2,4-triazole group characterizes the azocyclotin and the hydroxyl group the cyhexatin (Fig 1). These groups have different affinities for soil components, following mechanisms of sorption, complexation, dissolution, and diffusion, which can occur concurrently, and are highly dependent on factors such as organic matter, pH, and ionic strength (Godoi et al, 2003; Blunden and Evans, 1990). Cyhexatin is an azocyclotin metabolite obtained by simple hydrolysis. In soils, cyhexatin takes about 50 days to degrade to dicyclohexyltin oxide (C₁₂H₂₂SnO), cyclohexylstannoic acid (C₆H₁₁SnO₂H) and tin dioxide (SnO₂) (Muller and Markus, 1987), which also are important compounds on environmental risk assessment (Oliveira and Santelli, 2010).

Currently, the primary technique used to quantify OTC is chromatography. Several methods have been developed annually to separate and quantify

Fig. 1 Azocyclotin and cyhexatin structures

pesticides by gas chromatography (GC) and high-performance liquid chromatography (HPLC). High-performance liquid chromatography (HPLC) has been the most applied technique. Due to some limitations on thermal stability and derivatization requirements in gas chromatography (Perez and Barasoain, 1983), studies have pointed to the use of photodiode array (PDA) and fluorescence detectors to quantify azocyclotin and cyhexatin pesticides (Joan et al, 1992). The main advantages of liquid chromatography for OTC analysis are broad applicability, high resolution, fast analysis, high sensitivity, high reproducibility, and separation of compounds, in addition to being a quantitative and easily automated technique. In this sense, HPLC-PDA proves to be a more straightforward technique for the analysis of organotin compounds.

Studies on environmental mobility for azocyclotin and cyhexatin have not been reported in the literature. Hence, the hypothesis that these pesticides mobilize in the environment, increasing the risk of biota contamination, motivated us to study the sorption and desorption processes and their mobility in two types of soil from Southern Brazil. Additionally, an HPLC-PDA method is herein developed and validated to quantify the target compounds in soil.

2 Material and Methods

2.1 Material

Clayey and sandy soil samples were collected in North Parana State, Southern Brazil (24°24'57.5"S 51°00'0.6"W and 23°00'57.4"S 51°11'28.3"W), at 20 cm depth. The samples were dried, sieved in a 2 mm stainless steel sieve, and preserved in properly decontaminated polyethylene flasks.

Solutions were prepared from CaCl₂·2H₂O (Synth, analytical grade), azocyclotin reference material (ACT, Sigma-Aldrich, 99,9%, CAS-No.[41083-1108]), cyhexatin reference material (CHT, Dr. Ehrenstorfer GmbH, 97,4%, CAS-No.[13121-70-5]), acetonitrile (ACN, PANREAC, HPLC grade), and dichloromethane (DM, Biotec, HPLC grade). Ultrapure water was obtained from Milli-Q[®] Simplicity 185 water purification system.

2.2 Characterization of the soil samples

The pH of the soil samples was measured in water and KCl at 1:2.5 soil:solution ratio to calculate ΔpH and determine the surface charge. The organic matter (OM) was quantified by oxidizing the samples with potassium dichromate in a sulphuric medium (Embrapa, 2011; Walkley and Black, 1934). The cation exchange capacity (CEC) was determined by the sum of bases (K^+ , Ca^{2+} , Mg^{2+}), and exchangeable aluminum ($\text{H}^+ + \text{Al}^{3+}$). The granulometry was determined by the hydrometer method based on the sample density change in water suspensions upon the particle settling (Cheng and Schachman, 1955; Embrapa, 2011). Infrared spectra were recorded on a Prestige-21 spectrometer (Shimadzu, Kyoto, Japan), with a resolution of 2 cm^{-1} and 20 accumulation scans ranging from 4000 to 400 cm^{-1} . The samples were analyzed in KBr discs with 1% mass loading.

X-ray powder diffraction (XRD) patterns were obtained in a Panalytical X'Pert Pro MPD diffractometer (Almelo, The Netherlands) with $\text{CuK}\alpha$ radiation ($\lambda = 1.5418\text{ \AA}$), 40 kV and 30 mA, in 2θ scanning from 5° to 80° each $0.03^\circ\text{ min}^{-1}$. The diffraction patterns were acquired by the XPert HighScore software. A Ray-Ny EDX 720 Shimadzu equipment was used for EDXRF analysis in quantitative mode with a 3 mm collimator, air atmosphere, 50 s analysis time, 50 kV X-ray and 30 mA current.

2.3 Sorption and desorption experiments

Standard stock solutions of ACT in ACN and CHT in 1.0% (v/v) DM in ACN (eluent) 110.0 mg L^{-1} were prepared for the sorption experiments. Blanks were prepared by adding 10.0 mL of $0.010\text{ mol L}^{-1}\text{ CaCl}_2\cdot 2\text{H}_2\text{O}$ to 2.0 g of soil sample. Isotherms were built ranging ACT or CHT initial concentration from 2.0 to 50.0 mg L^{-1} . The OTC solutions were added to $0.010\text{ mol L}^{-1}\text{ CaCl}_2\cdot 2\text{H}_2\text{O}$ and 2.0 g of soil sample up to 10 mL to keep ionic strength and achieve adequate peak resolution (Gui et al, 2016). The suspensions were equilibrated at 30 rpm for 24 h at $22\pm 2^\circ\text{C}$ and centrifuged at 3048 rpm ($1350\times g$) for 5 min (EV025 Evilab). A 5.0 mL aliquot of the supernatant was then liquid-liquid extracted with ACN in an ultrasonic bath. The sample was filtered (Filtril 0.22 μm nylon) and analyzed by HPLC-PDA, described in Section 2.4. The assays were carried out in triplicate and the pre- and post-sorption pH was measured.

Desorption experiments started from the higher sorption concentration (50.0 mg L^{-1}) in a fractional way by exchanging 5.0 mL of the supernatant per 5.0 mL of $0.010\text{ mol L}^{-1}\text{ CaCl}_2\cdot 2\text{H}_2\text{O}$ to increase ionic strength gradually. The suspension was equilibrated at 30 rpm for 24 h. Desorption procedure was repeated sequentially until the OTC were no longer detected. The pH was determined at the start and end of each fraction. Samples were taken at each step, ACN extracted and analyzed by HPLC-PDA using the same procedure as the sorption samples.

ANOVA, Student's *t*, and *F* statistical tests were applied at 95% confidence interval and 5% significance level for testing two hypotheses on the sorbed

concentration (C_{sorb}) of azocyclotin or cyhexatin in both soil samples: H_{0a} - no significant difference between the two soil samples in the sorption process, and H_{1a} - a significant difference between the soil samples in the sorption process. Hypotheses on the sorption and desorption ΔpH , called H_{0b} and H_{1b} , were also statistically evaluated (see results in SI, Statistical tests).

2.4 Chromatographic method for quantitation of azocyclotin and cyhexatin

A chromatographic method was developed for azocyclotin and cyhexatin quantitation from sorption and desorption procedures. Analysis of ACT and CHT was carried out on a Shimadzu Prominence[®] HPLC using a Hypersil GOLD PFP column (150×4.6 mm i.d.; 3 μ m particle size, Thermo Scientific, USA) and PDA detector (SPD-20A) at 205 nm. The mobile phase was ACN and ultrapure water acidified with H_3PO_4 , pH = 2.5 (Synth, analytical grade) in the 70:30 ratio. The injection volume was adjusted to 20 μ L and the temperature to 40°C. Chromatograms were obtained from sorption and desorption extracts at 205 nm (Ning et al, 2015; Gui et al, 2016). Data acquisition and integration of chromatographic peaks were carried out with LC Solutions software (Shimadzu corp., Japan).

2.5 Chromatographic method validation

The chromatographic method developed for azocyclotin and cyhexatin quantitation from sorption and desorption procedures was validated. Stock solutions of 110.0 mg L⁻¹ ACT in ACN and 110.0 mg L⁻¹ CHT in ACN and 1.0% DM were prepared, and the analytical curve constructed (1.0 to 110.0 mg L⁻¹) from the external standard method for QC/QA purposes. It is worth noting the use of DM with ACN for better solubilization of cyhexatin. The method was validated in terms of linearity, precision, repeatability, detection limit, quantitation limit, and accuracy, as described in ICH Guidelines (2005).

Linearity was assessed by standard seven-point calibration curves constructed over a range of 1.0 to 110.0 mg L⁻¹. All standards and samples were injected in triplicate. The mean peak area of azocyclotin and cyhexatin was plotted *versus* concentration, and a linear least square regression analysis was carried out.

The intraday and interday precision was determined by analyzing three blank samples spiked with OT standard solutions at 2.0, 25.0, and 50.0 mg L⁻¹, with three replicates each. Accuracy was evaluated by analyzing three replicates of three independently prepared samples at 2.0, 25.0, and 50.0 mg L⁻¹ of OT standard solutions. The sensibility of the HPLC-PDA method was characterized by the limit of detection (LOD) and limit of quantification (LOQ), defined as the lowest concentration that could be detected or quantified for the signal-to-noise ratio of 3.3 and 10, respectively.

2.6 Modeling the sorption-desorption isotherms

Dual-mode Freundlich-Langmuir model and Langmuir model were fitted to the sorption and desorption isotherms using MatLab[®] R2010. The sorbed concentration (C_{sorb} , mg kg⁻¹) was calculated by the difference between the initial concentration (C_{in} , mg L⁻¹) and the equilibrium concentration (C_{eq} , mg L⁻¹), considering the mass (m , kg) and the volume (V , L), in Eq (1).

$$C_{sorb} = \frac{(C_{in} - C_{eq})V}{m} \quad (1)$$

In the fractional desorption experiment, serial dilutions were prepared from the maximum sorption concentration after equilibrium. From the first dilution, step by step, C_{in} becomes half of the C_{in} from the previous step. Thereby, $C_{eq(s)}$ was obtained after each desorption step from the mass balance in Eq (2), with step s varying from 0 to 7 (Constantino et al, 2018; Galunin et al, 2014). The 0 (zero) step is the maximum concentration from the sorption isotherm.

$$C_{sorb(s)} = \frac{(C_{in(s-1)} - \frac{C_{eq(s-1)}}{2} - C_{eq(s)})V}{m} \quad (2)$$

Isotherms were obtained from the sorbed concentration and the concentration in solution after equilibrium. The experiments were carried out in triplicate. Langmuir model and Langmuir-Freundlich dual-mode model were applied to the isotherms. The Langmuir model is described by the Eq (3) (Langmuir, 1916; Blahovec and Yanniotis, 2009).

$$C_{sorb} = \frac{bKC_{eq}}{1 + bC_{eq}} \quad (3)$$

where C_{sorb} (mg kg⁻¹) is the sorbed concentration at equilibrium, b the maximum sorption amount for the formation of a complete monolayer, K (L kg⁻¹) the Langmuir constant related to sorbate-sorbent affinity, and C_{eq} (mg L⁻¹) the concentration of the sorbate in solution at equilibrium.

In some cases, the best fit is from the dual-mode Langmuir-Freundlich model, which extrapolates the Langmuir model limitations to more than one type of interaction site, in Eq (4) (Galunin et al, 2010; Constantino et al, 2018).

$$C_{sorb} = \sum_{j=1}^J \frac{b_j (K_j C_{eq})^{n_j}}{1 + (K_j C_{eq})^{n_j}} \quad (4)$$

where j represents different types of sorption sites, b_j (mg kg⁻¹) the maximum sorption capacity or the number of available sites, K_j (L kg⁻¹) the sorbate-sorbent affinity parameter and n_j the heterogeneity of sorption sites. The lower n_j , the more irreversible the sorption (Do, 1998).

The adequacy of the adjustment was evaluated using the coefficient of determination (R^2), and the root mean square error in Eq (5) at 95% confidence limit.

$$RMSE = \sqrt{\frac{1}{N-p} \sum_{i=1}^N (C_{sorb_i} - \hat{C}_{sorb_i})^2} \quad (5)$$

where C_{sorb_i} and $\hat{C}_{sorb_i}$ are the i th experimental sorbed OTC concentration and the i th predicted point in the model of Eq (4), respectively, N is the number of data points, and p is the number of the fitted coefficients estimated from the model, *i.e.*, $p = S = 3J$ is the cardinality of

$$S = \{b_1, b_2, \dots, b_J, K_1, K_2, \dots, K_J, n_1, n_2, \dots, n_J\}$$

The hysteresis index is defined by the area of sorption and desorption ratio from isotherms (Galunin et al, 2014), according to Eq (6).

$$HI = \frac{(A_{des} - A_{sor})}{A_{des}} \quad (6)$$

The mobilization factor in Eq (7) is normalized and B , absolute value in Eq (8), gives the difference between the area of the desorption isotherm and the ideal desorption area (Galunin et al, 2014).¹

$$MF = (1 - HI) * B \quad (7)$$

$$B = \frac{1 - A_{des}}{A_{des.ideal}} \quad (8)$$

3 Results and Discussion

3.1 Soil sample characterization

Azocyclotin and cyhexatin sorption and desorption phenomena can be better understood from the physical and chemical properties of the soil samples, described in Table 1.

The negative ΔpH , calculated by the difference between pH_W and pH_{KCl} , is related to negative charges on the soil surface and indicates a preference for positive ion sorption. In the case of OTC, the Sn, as a positive center in the molecules, can be involved. Besides, the clayey soil presented a higher CEC and OM amount than sandy soil, which can be related to the sorption

¹The main numerical results in this section can be generated from the MatLab script available at <https://data.mendeley.com/datasets/2xz2w7w2jd/1>. Ferreira Lima, Andre; Onishi, Bruno S. D.; Watanabe, Lycio S.; Santos, Maria Josefa; Abrao, Taufik (2021), "Mobility of organotin pesticides: azocyclotin and cyhexatin in clayey and sandy soils from the Northern Parana state - Brazil", Mendeley Data, V1, doi: 10.17632/2xz2w7w2jd.1

Table 1 Physical and chemical characterization of the soil samples. Average $\pm$ standard deviation (sd). CEC- cation-exchange capacity in $\text{cmol}_c \text{ dm}^{-3}$; $\Delta\text{pH} = \text{pH}_{KCl} - \text{pH}_W$; OM- organic matter in %; Major elements in g kg^{-1} ; Texture in %

Soil sample	pH_W	pH_{KCl}	ΔpH	CEC	OM	Major elements			Clayey	Texture	
						Fe	Si	Al		Sandy	Silt
Clayey	6.04	4.77	-1.27	22.5	2.37	52.2	22.8	11.3	37.1	32.7	30.1
$\pm sd$	0.01	0.01	0.02	0.10	0.06	0.61	0.54	0.30	-	-	-
Sandy	6.16	4.63	-1.53	9.65	0.76	21.7	51.3	20.8	25.4	69.6	5.07
$\pm sd$	0.02	0.01	0.03	0.08	0.15	2.06	0.93	0.78	-	-	-

- sd not available

capacity. The higher CEC and OM, the higher sorption capacity is expected. The potential interaction of OTC with carbonyl and phenol groups in humic substances can also influence their mobility in the soil (Giacalone et al, 2006).

The mineralogical characterization by XRD (see in Supplementary Information, Fig SI1) showed the presence of hematite, quartz, and kaolinite minerals in both soils, with the predominance of hematite in the clayey soil and quartz in the sandy soil. These results agree with the EDXRF data since Fe is the major component of the clayey soil and Si of the sandy soil. In Fig SI2, the 3453, 1624, and 1000 cm^{-1} bands in the infrared spectrum are characterized by structural OH^- stretching, CO stretching of carbonyl groups from humic and fulvic acids in soils, and Si-O, respectively (Silva and Guerra, 2013).

3.2 The Chromatographic Method

The LOD and LOQ determined for the two matrices enriched with the reference materials (standards) were: LOD for ACT(0.1) and CHT(0.2) mg L^{-1} and LOQ for ACT(0.3) and CHT(0.9) mg L^{-1} after injecting a series of dilute standard solutions with known concentrations. Calibration curves for ACT and CHT are shown in Fig SI3. Seven-point calibration curves showed linearity, with $R^2 > 0.9995$ for the standards between 1.0 and 110.0 mg L^{-1} . All standards and samples were injected in triplicate. The mean peak area of ACT and CHT was plotted *versus* concentration, and the linear least square regression analysis was carried out. Multiple injections showed results highly reproducible and low standard error.

The intraday precision RSD for the blank spiked samples ($n=3$) ranged from 6 to 10% for ACT and CHT. The interday RSD ($n=3$) was 8 and 13% for ACT and CHT, respectively. Spiked samples with the standards in three concentrations showed recovery of 71% and 105% for ACT and CHT, respectively. The results indicate an accurate, reliable, and reproducible method.

Both ACT and CHT absorb in the UV region, 205 nm approximately. Thus, ACN was chosen as the best mobile phase by not absorbing in the same region. Studies show that the UV-vis detector here used works very well to quantify organotin compounds and other pesticides, using ACN as mobile phase and reversed-phase HPLC columns (Xiupin et al, 2006; Tomasz and Jan, 2009).

According to Figs 2 and 3, azocyclotin standard in ACN was detected at 3.6 min retention time, while cyhexatin standard was at 3.4 min. The peaks for both ACT and CHT post-sorption in the two soil samples showed a good shape and complete separation from the other soil components. Furthermore,

Fig. 2 HPLC-PDA chromatograms for azocyclotin: PFP column, 205 nm, ACN and ultra pure water (Mili-Q[®]) acidified with H₃PO₄ (pH 2.5) 70:30 as mobile phase and 20.00 μ L injection volume.

no interfering peak from CaCl₂ electrolyte was detected. A peak from the PFP selectivity column could be seen in both chromatograms, ACT-ACN standard and CHT-ACN-DM standard, due to the pentafluorophenyl stationary phase. The π orbitals of the PFP column interact with the π orbitals of the 1,2,4-triazole ring in azocyclotin. The ring acts as an electron donor group (Lewis base) and promotes the bond between the F of the column and the N of azocyclotin. Thus, the column becomes much more selective, performing better separation of the compounds (Gobbo et al, 2015).

3.3 Sorption and desorption

Sorption and desorption isotherms for ACT in the clayey and sandy soil are shown in Fig 4 and for CHT in Fig 5. The adjusted parameters are in Table 2, and the confidence intervals are presented in Figs 4 and 5. The mobilization of the OTC can be observed from the desorption isotherm below the sorption isotherm, with a negative hysteresis index – hysteretic behavior (Galunin et al, 2014). A non-hysteretic behavior would show the desorption isotherm superimposed on the sorption isotherm. Although the observed hysteresis index (*HI*), directly related to the OT mobilization factor (*MF*) in the soil, can be considered low, mobility is observed. The dual model was applied to adjust

Fig. 3 HPLC-PDA chromatograms for cyhexatin: PFP column, 205 nm, ACN and ultra pure water (Mili-Q®) acidified with H₃PO₄ (pH 2.5) 70:30 as mobile phase and 20.00 μ L injection volume.

the sorption isotherm, while the Langmuir model adjusted the desorption isotherm. Azocyclotin presents practically non-hysteretic behavior in sandy soil, although it has a lower maximum sorption capacity than in clayey soil. This behavior can be interpreted considering the OT's interaction with soil organic matter and the composition of each type of soil (Huang and Matzner, 2004; Gui et al, 2016). The higher organic matter amount in the clayey soil is related to the stronger interaction with the metallic center and its organic moiety. These results on OT-soil interaction are described as sorption mechanisms and supported by literature (Sparks, 1995; Essington, 2015).

Cyhexatin has a hydroxyl directly attached to the Sn, different from the azocyclotin having the triazole ring. Therefore, OH groups–organic matter and other interactions with soil components can interfere directly with the cyhexatin sorption and desorption processes (Jones et al, 2005; Sithole and Guy, 1987). Although the triazole ring has sp^2 carbon that allows π - π interaction with PFP column, cyhexatin has no sp^2 carbon, and the interactions are van der Waals type. The asymptote is visible in both the adjusted sorption and desorption isotherms, and the main difference is in desorption. Cyhexatin has a hysteretic desorption profile, and there is virtually no desorption after sorption. The explanation for this profile is related to OT OH⁻ groups interacting

Fig. 4 Sorption and desorption isotherms for azocyclotin on (a) clayey soil and (b) sandy soil. Sorption carried out in batch, shaking 24 h at 22°C, C_{in} from 2.0 to 50.0 mg L⁻¹ in 2:10 solid:liquid ratio. Fractional desorption (7 points; each point is the mean $\pm$ sd of three experiments) from the highest sorption initial concentration, taking aliquots of half the volume for analysis, filling with the electrolyte solution in the same volumetric ratio every 24 h. R^2 is determination coefficient and RMSE root mean square error, with s or d associated with sorption and desorption, respectively. 95% confidence intervals are shown for seven data point triplicate

Fig. 5 Sorption and desorption isotherms for cyhexatin on (a) clayey soil and (b) sandy soil. The experimental conditions are the same as in Fig. 4. 95% confidence intervals are shown for ten data point; each point is the mean $\pm$ sd of three experiments

with the soil, in addition to the ΔpH for both OT and soils (Jones et al, 2005; Sithole and Guy, 1987). The ACT ΔpH was prior in the positive region of the curve considering that $\text{pH}_{\text{final}} > \text{pH}_{\text{initial}}$, and with the OT initial concentration increasing, the curve gone to a $\Delta\text{pH} < 0$ (Fig 6). The curve for CHT always shows $\Delta\text{pH} < 0$ and, therefore $\text{pH}_{\text{final}} < \text{pH}_{\text{initial}}$. When OH^- directly bound to the metal center is released, Sn becomes more electronically deficient and binds more strongly to the soil surface (Dhananjay et al, 2016).

The sorption isotherm has an H-type profile (*High Affinity*), which is a particular case of the Langmuir isotherm whose sorbate has a high affinity for the sorbent, considering a very pronounced increase in sorption up to 150 mg kg^{-1} (Essington, 2015). Some sorbent materials show a very pronounced increase in sorption by increasing sorbate concentration without any initial slope, which is a characteristic of the H-type isotherm (Dhananjay et al, 2016).

The cyhexatin sorption and desorption isotherms for sandy soil were well adjusted by the Langmuir model, obtaining a very characteristic profile. Sandy soil isotherms were similar to clayey soil.

Table 2 depicts the adjusted parameters from the isotherm mathematical modeling for azocyclotin and cyhexatin for both soils. The results indicate

Table 2 Adjusted parameters of sorption and desorption isotherms for azocyclotin and cyhexatin in clayey and sandy soil samples. K_j, b_j, n_j are from the dual-mode F-L model; K_{sorb} and b_{sorb} are from the Langmuir model; desorption parameters are from both models

Azocyclotin	K_1	K_2	b_1	b_2	n_1	n_2	K_{sorb}	b_{sorb}	K_{des}	b_{des}
Clayey Soil	0.242	5.20	4×10^{-5}	171	9.37	7.06	-	-	0.719	229
Sandy Soil	0.002	0.62	3×10^{-4}	120	3.30	0.96	-	-	0.336	137
Cyhexatin	K_1	K_2	b_1	b_2	n_1	n_2	K_{sorb}	b_{sorb}	K_{des}	b_{des}
Clayey Soil	0.583	20.7	11.5	148	2.23	2.98	-	-	2631	188
Sandy Soil	-	-	-	-	-	-	2.36	249	781	218

a higher number of sorption sites (b_2) with a higher azocyclotin-soil affinity (K_2) for both soils and a low number of sorption sites (b_1) with low affinity for azocyclotin (K_1). For cyhexatin on clayey soil sorption, there was also a higher number of sites (b_2) of more significant energy (K_2), characterizing a higher sorption affinity and low mobility (Galunin et al, 2014). For sandy soil, it was not possible to distinguish between types of sorption sites. However, the affinity between cyhexatin and sandy soil, although low concerning the clayey soil, results in a low mobilization to the environment. In desorption, K_{des} and b_{des} were higher for clayey soil, indicating higher azocyclotin affinity post-desorption in addition to the higher number of occupied sites compared to sandy soil. Cyhexatin-soil affinity appeared to be much higher compared to azocyclotin-soil affinity. It is worth noting a higher cyhexatin-soil post-desorption affinity compared to post-sorption. Cyhexatin sorbed to the lower affinity sites comes out first, remaining only at the high-affinity sites. Azocyclotin presents a higher mobilization factor in the clayey soil, shown in Table 3. Although AZO has greater sorption capacity in clayey soil, its mobility

Fig. 6 pH variation before and after sorption for azocyclotin (a) and cyhexatin (b), ($\text{pH}_i - \text{pH}_f$) on clayey and sandy soil samples

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is increased by desorption. A shallow hysteresis index (HI) shows a practically non-hysteretic behavior in the sandy soil, with azocyclotin sorption and desorption occurring in the same proportion.

Table 3 Hysteresis Index and Mobilization Factor for azocyclotin and cyhexatin in both soil samples

Azocyclotin	HI	MF	Cyhexatin	HI	MF
Clayey Soil	-0.146	0.235	Clayey Soil	0.003	0.001
Sandy Soil	7.8×10^{-4}	0.186	Sandy Soil	0.186	0.001

The desorption steps determine the mobility of OTC in soils. The negative HI in the clayey soil means mobilization. The MF indicated low mobility of cyhexatin in clayey soil and higher mobility for azocyclotin in both soil types. The mobilization of azocyclotin determined in this study demonstrates the feasibility of traveling over long distances and establishes, to the best of our knowledge, both azocyclotin and cyhexatin as potentially toxic substances (PTS). Although of a different concept, the soil sorption constant (K_{oc}) can be used to interpret mobility. Swann et al (1983), using the reversed-phase HPLC technique with refractive index detector and mobile phase 85:15 methanol:water, established K_{oc} values from 2,000 to 5,000 as slight mobility. Thus, cyhexatin has been considered slightly mobile (K_{oc} : 4,365) based on some mobility studies (RS.Agricultural, 2017). Even though cyhexatin has shown slight mobilization in both types of soil, its mobility stands out as a secondary source of azocyclotin degradation.

4 Conclusions

The study of sorption and desorption processes of azocyclotin and cyhexatin was associated with the characterization and the structural soil composition and mobility of the OT compounds. The chromatographic method was validated and proved helpful for quantifying both OT species in soils by applying a simple sample preparation with ACN liquid-liquid extraction. Azocyclotin presented mobility in both clayey and sandy soils with MF of 23.5% and 18.6% respectively, while cyhexatin was poorly mobile in both soils with MF 0.1%. As much as the results show, cyhexatin is still a metabolite of azocyclotin. One can, therefore, infer about the mobility of cyhexatin in the water table. Azocyclotin degrades to cyhexatin in the short term, implying an environmental risk associated with using azocyclotin and cyhexatin as pesticides.

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355 (i) made substantial contributions to the conception or design of the work;
356 the acquisition, analysis, and interpretation of data, (ii) drafted the work
357 or revised it critically for important intellectual content, (iii) approved the
358 version to be published, and (iv) agree to be accountable for all aspects of the
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Figure SM1a

Figure SM1b curvecih

Figure SM2a

Figure SM2b

Figure SM3a

Figure SM3b

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