Supplementary Information

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

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Abstract

Azocyclotin and cyhexatin are pesticides commonly used in mite control. However, these organotin (OT) 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 OT quantitation because of limitations on thermal stability and derivatization in gas chromatography. Hence, a new method was developed using high-performance liquid chromatography with photodiode-array detection (HPLC-PDA) for quality assurance and quality control (QA/QC) purposes and environmental behavior assessment. 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: hysteresis, HPLC-PDA, mobilization, soils, sorption, organometallic compounds

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Organotin pesticides

Although organotin compounds as azocyclotin and cyhexatin be extremely harmful to living beings, these type of compounds have been applied in agriculture. Besides no clear regulations in Brazil, studies on their mobility and behavior in the environment are lacking. Mobility and environmental risk assessment were determined in this study from surface interactions between the molecules and two types of soil (sandy and clayey soils). For this, a new HPLC-PDA method was developed in addition to the mathematical modeling.

Soil characterization

Clayey and sandy soil samples were characterized by XRD and FTIR. X-ray powder diffraction (XRD) patterns were collected on a XPert PROMPD (PANalytical, Almelo, The Netherlands) with CuKα radiation (λ= 1.5418 $\mathring{A}$), 40 kV and 30 mA, in 2θ scanning from 5° to 80° each 0.03° min^{-1}. Diffraction patterns were acquired from XPert HighScore software. Infrared spectra were recorded on a Prestige-21 spectrometer (Shimadzu, Kyoto, Japan), with resolution of 2 cm^{-1} and 20 accumulation scans ranging from 4000 to 400 cm^{-1}. Samples were analysed as KBr discs with 1.0% mass loading. Results are shown in Fig SI1 and SI2.

Calibration curves for azocyclotin and cyhexatin quantitation from the external standard method are shown in Fig SI3.

Statistical tests

ANOVA, Student's t, and F statistical tests were considered for the method validation with 95% confidence interval and 5% significance level. Two hypotheses were considered for azocyclotin, and cyhexatin sorbed concentration (C_{sorb}) and pH change (ΔpH) in both soil samples: (i) Null H_{0a} hypothesis: there is no significant difference between the two soil samples in the sorption process; (ii) Alternative H_{1a} hypothesis: there is a significant difference between the soil samples in the sorption process; (iii) Null H_{0b} hypothesis: there is no significant difference between the soil samples as for ΔpH; (iv) Alternative H_{1b} hypothesis: there is a significant difference between the soil samples as for ΔpH.

The Student's t-test was applied to sorption isotherms taking into account unknown standard deviation and normal distribution. The variances of the two soil samples were similar to $p>0.05$

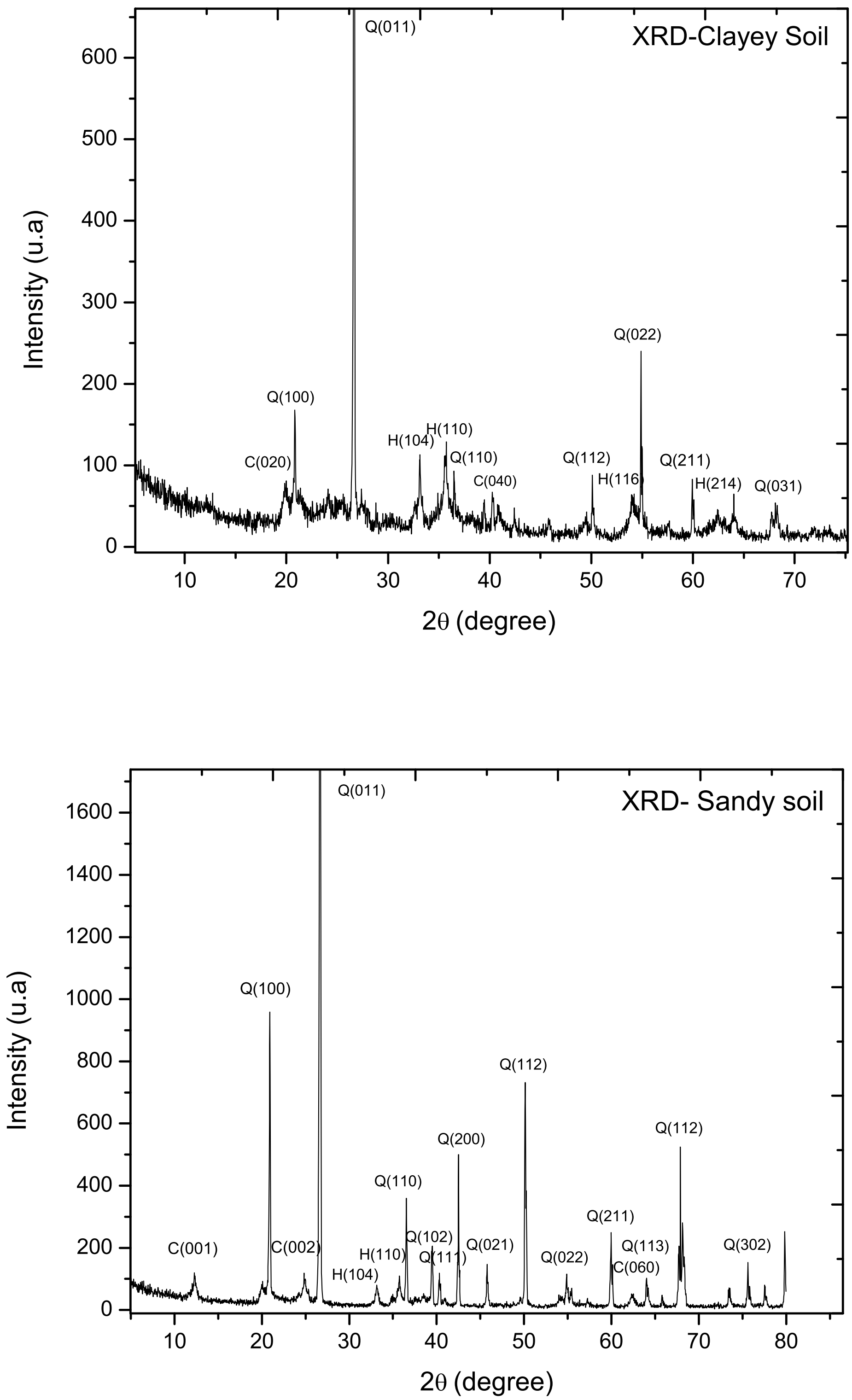


Figure SI1: X-ray diffractograms of clayey and sandy soil samples. Q:quartz, H:hematite, C:kaolinite

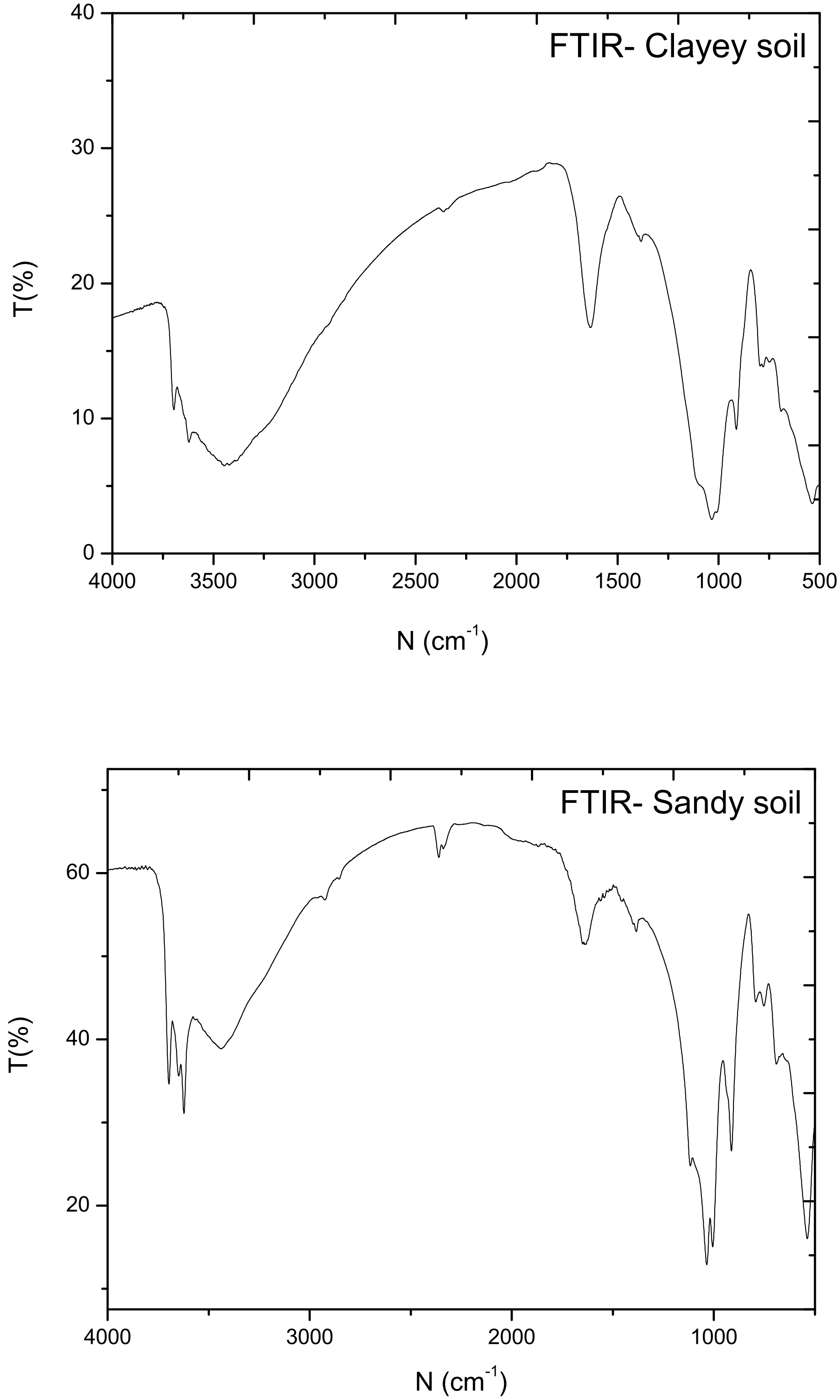
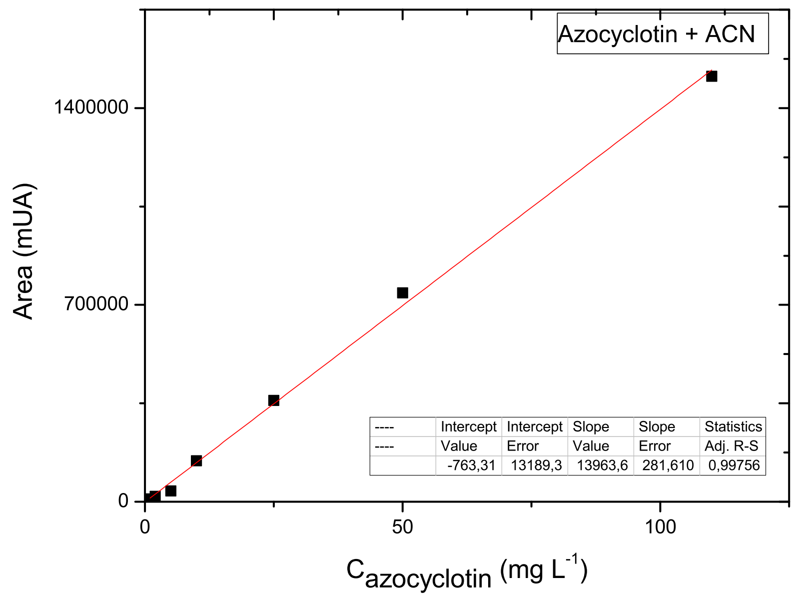


Figure SI2: FTIR spectra of clayey and sandy soil samples



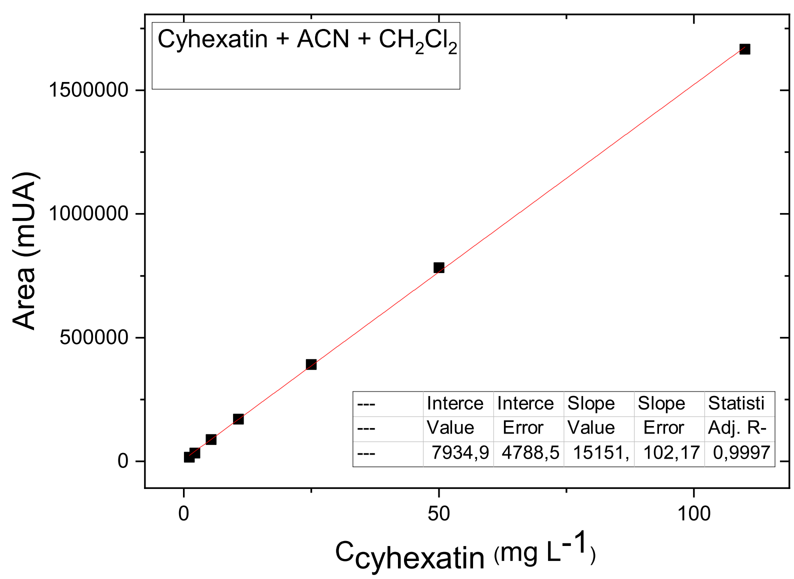


Figure SI3: Calibration curves for azocyclotin and cyhexatin quantitation by the external standard method; HPLC-PDA, PFP column, 205 nm, 70:30 ACN and ultra pure water (Mili-Q®) acidified with H_3PO_4 (pH 2.5) as mobile phase and 20.00 μL injection volume from the F test. From Tables SI1 and SI2, the p values indicated a significant difference in the sorption for the two soil samples. ANOVA was applied for ΔpH. The p values were usually lower than 0.05 (Table SI3), indicating significant difference for the [H^+] leaching between the two soil samples. Thus, the null hypothesis was rejected. However, the H_{0b} is accepted for cyhexatin ΔpH, with no significant difference between the soils, probably due to their shallow mobilization factor, which reflects very low [H^+] movement into the solution.

Table SI1: Statistical tests for sorbed azocyclotin concentration (C_{sorb}) in clayey and sandy soil samples with their respective p values from the F test and the two-tailed (TT) Student's t-test with 5.0% significance level, 95% confidence interval, and 6 degrees of freedom; C_{in} in (mg L^{-1}); C_{sorb} in (mg kg^{-1})

C_{in}	Clayey C_{sorb}	Sandy C_{sorb}	p (F distribution)	p (t distribution, TT)
2.0	9.43	25.3	0.124	4.92E-11
5.0	24.3	69.1	0.017	1.20E-05
20	48.7	91.0	0.988	5.87E-07
25	98.6	101	0.050	1.10E-05
30	123	128	0.010	1.82E-01
40	147	113	0.780	9.59E-07
45	171	123	0.477	7.26E-07

Table SI2: Statistical tests for sorbed cyhexatin concentration (C_{sorb}) in clayey and sandy soil samples with their respective p values from the F test and the two-tailed (TT) Student's t-test with 5.0% significance level, 95% confidence interval, and 6 degrees of freedom; C_{in} in (mg L^{-1}); C_{sorb} in (mg kg^{-1})

C_{in}	Clayey C_{sorb}	Sandy C_{sorb}	p (F distribution)	p (t distribution, TT)
2.0	9.88	9.16	0.021	2.60E-02
5.0	25.1	24.3	0.990	8.37E-03
20	49.4	48.1	0.088	1.81E-03
25	99.5	94.4	0.212	8.00E-04
30	124	121	0.843	3.63E-06
40	155	137	0.325	6.66E-01
45	164	158	0.048	1.24E-01

Table SI3: ΔpH ANOVA test for azocyclotin in the clayey and sandy soil samples and the respective total sum of squares (TSS), F and p values with 5.0% significance level, 95% confidence interval, and 1 degree of freedom; C_{in} in (mg L^{-1})

C_{in}	Clayey ΔpH	Sandy ΔpH	TSS	F	p
2.0	0.15	0.60	0.001	1.00	4.23E-01
5.0	0.16	0.30	0.189	261	3.81E-03
20	0.14	−0.31	0.152	608	1.64E-03
25	0.11	−0.28	0.164	77.2	1.27E-02
30	0.05	−0.35	0.226	694	1.44E-03
40	−0.03	−0.44	0.148	49.0	1.98E-02
45	−0.13	−0.63	0.106	845	1.18E-03

Table SI4: ΔpH ANOVA test for cyhexatin in the clayey and sandy soil samples and the respective total sum of squares (TSS), F and p values with 5.0% significance level, 95% confidence interval, and 1 degree of freedom

C_{in}	Clayey ΔpH	Sandy ΔpH	TSS	F	p
2.0	−0.75	−0.60	0	0	1.000
5.0	−0.52	−0.52	1.32E-02	1.02	0.420
20	−0.46	−0.35	4.90E-03	0.84	0.457
25	−0.20	−0.40	9.00E-04	0.56	0.531
30	−0.51	−0.44	1.00E-02	4.00	0.184
40	−0.52	−0.55	3.60E-03	0.64	0.508
45	−0.68	−0.78	1.44E-02	4.96	0.156