

**Research Paper**

Electroanalytical Determination of ametryn using a Silver amalgam Electrode and a Sorption Study in Soils under Sugarcane Plantation or Native Area

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Abstract: In Brazil, the use of pesticides has been increasing and an important issue that should take care is the environmental risks. To assess the risk of water resources contamination by pesticides in field it is essential to study and understand the interactions between these chemicals and the soil material. The objective of this work was to study sorption of ametryn, a herbicide widely used in Brazil in sugarcane plantations, in two soils of contrasting textures (clay content), under sugarcane production and native forest. Generally it's used chromatographic techniques for pesticide sorption in soil, but these technique take long time to be done and could be expensive. The use of electroanalytical techniques is one way to solve these problem. An electroanalytical procedure was established and used to measure ametryn in the soil solutions with a solid silver amalgam as working electrode. Sorption coefficients obtained from the measured sorption isotherms for ametryn in four soil samples showed a moderate sorption behavior in the soil influenced principally by pH and organic matter (OM). In some cases, as pH soil higher than ametryn pKa or higher amount of humification OM, can present a considerable potential to be transported to the groundwater (lower Kf) as well as to surface waters (higher Kf). For this reason should use ametryn carefully in environment.

Keywords: Soil and groundwater contaminations, Electroanalytical pesticides determinations, Sugar cane, Sorption.

Introduction

Crop production in Brazil has been consistently increasing in the last years and also the demand for pesticides and fertilizers. Due to environmental concerns about the use of fossil fuel and its greenhouse gas emission, the production of sugarcane for ethanol in Brazil has been increasing in the São Paulo State (main producer) and also growing to new agriculture frontiers in the central and in the northeast States.

Among the herbicides used for controlling weeds in sugarcane plantations, ametryn (Figure 1), a s-triazine, is the mostly used. The fate of pesticides in soil and water depends on the medium characteristics as amount and quality of the organic matter (OM), pH, clay content and also the pesticides physicochemical properties (pKa, water solubility, vapor pressure, molecular size, and others). Additionally, the environmental conditions like temperature, precipitation and humidity play an important role on the pesticide behavior^[1].

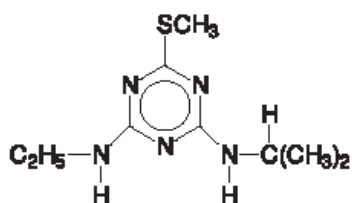


Figure 1: Ametryn structural formula

Sorption of a pesticide is a retention process in the natural sorbents of the soil (minerals and organic materials), involving the absorption and adsorption processes. Desorption is the reverse process, the pesticides molecules pull out in the sorbents. Determinations of ametryn in soil and water is usually obtained by HPLC^[2,3] or gaseous chromatography^[2]. Electroanalytical techniques have also been used for measuring ametryn in natural

matrices with working electrodes which contain mercury [4,5], gold [6] or copper [7] and the techniques mostly used for triazines herbicides determination are polarography and pulse techniques, adsorptive or not. The triazines present polarographic signals due to molecule protonated form and the dripping mercury electrode, as amalgams electrodes, are the most sensitive electrode for this purpose [4-8]. Square wave voltammetry was used for the ametryn determination in acidic solution with mercury electrode and the limit of detection was $0.1 \mu\text{g L}^{-1}$, with spiked samples which shows a good application of this methodology in this herbicides traces analyses [4]. Square wave voltammetry also has been used for the determination of atrazine, ametryn and simazine with mercury electrode. Atrazine and ametryn presented very well defined reductions peaks in potential values closed each other which may become difficult the individual determination in a solution. However, the deconvolution method enables the separation of two peaks. It was not possible the separation of simazine and atrazine voltammetric signals due the proximity of them [5].

For ametryn and atrazine determination in soils samples, the anodic stripping voltammetry with golden microelectrode has been used and it was possible the determination of the both herbicides at the same time, with different oxidation signals, which is not possible with mercury electrode [6]. Another electrode used for the ametryn and atrazine determination with square wave voltammetry was copper amalgam electrode in natural water samples where the ametryn reduction occurred at -1.1 V (Ag/AgCl) , with irreversible reactions characteristics controlled by diffusion process [7].

The objective of the present study was to establish an electroanalytical procedure to determine ametryn in soil solution samples and to apply such methodology to study ametryn sorption behavior on two Brazilian soils of contrasting texture (clay contents) in areas cultivated with sugarcane and under natural forest and finally, understand the relationships between ametryn sorption and the chemical/mineralogical soil characteristics.

Material and Methods

Reagents: Reagents used were of analytical grade. Ametryn was purchased from Sigma-Aldrich Riedel-deHäen with a purity of 98% and used without further purification. A stock solution of $4.39 \times 10^{-3} \text{ mol L}^{-1}$ ($1000 \mu\text{g mL}^{-1}$) was prepared in methanol/water (50/50% v/v) and used in all experiments. Samples with lower concentrations were obtained from the original stock solution by dilution.

The electrolyte was a sulfuric acid solution at pH 2. This electrolyte was obtained by adding sulfuric acid (a.g.) in ultrapure grade water until pH 2. All aqueous solutions were prepared with purified water from a Milli-Q system (Millipore®).

Soil samples: Soil (Oxisol) samples (0–20 cm depth) were taken from two different areas in São Carlos, Brazil, apart by around 10 km. Samples of sand and clay soils were collected in native forest (NF) and sugarcane cultivation (SC) conditions. These samples were air-dried and sieved through 2mm mesh. Some selected characteristics of the soils used for this study are presented in Soares et al. (2011) [9]. The samples had an organic matter (OM) content ranging between 23 to 54 g dm^{-3} and clay fraction content between 21 and 59%. Generally, soils with higher OM content present higher retention cation capacity and more resistance to pH variations, and consequently, it could present higher capacity to pesticides sorption. The pH of sugarcane soils were corrected for the agriculture use, presenting similar values. Clayey soils present both higher OM content and cation exchange capacity (CEC). The E_4/E_6 index is humification degree of soil humic material estimated with UV-visible spectra of soil solution and could be estimated by the relation of absorption intensities at 465 and 665 nm [10] and it presented in Table 1.

Apparatus and electrode: Voltammetric experiments were performed using a potentiostat/galvanostat AUTOLAB PGSTAT® 30 with a three-electrode cell (30 mL) and a saturated calomel electrode (SCE) as reference, a platinum wire as auxiliary and a silver solid amalgam (Ag-SAE) as working electrode.

Table 1
Some properties and information of two Brazilian oxisol soils (1 and 2) in native forest and sugarcane plantation conditions

soil*	soil	OM	pH in	clay	sand	CEC	E4/E6
	covering	g dm^{-3}	water	%		$\text{mmol}_c \text{ dm}^{-3}$	
NF1	forest	26	4.0	21	76	79	8.9
SC1	sugar cane	23	5.2	29	68	59	7.8
NF2	forest	54	6.0	59	38	200	7.8
SC2	sugar cane	44	5.3	58	38	157	7.9

*OM: organic soil matter, *NF: native forest, SC: sugarcane. 1: sandy soil and 2: clayey soil

The Ag-SAE was prepared by mixing silver and mercury at the same proportions (0.5 g). Five drops of

nitric acid (a.g.) was then added to the mixture to produce the amalgam that was introduced in a glass tube and

connected to an electric contact. Afterwards, the Ag-SAE was immersed into a small volume of liquid mercury for 2 days for the complete amalgamation of the electrode. Between each voltammetric measurement, the Ag-SAE electrode was cleaned on 1200-grit sandpaper.

Analytical procedures: The procedure for the determination of ametryn by differential pulse voltammetry (DPV) was established first in an electrolyte solution (sulfuric acid solution, pH 2). Afterwards, the quantification of the pesticide occurred in soil solutions at the optimized scanning conditions. The relationship between the reduction peak current and ametryn concentration (analytical curves) were obtained employing the standard addition procedure in the concentration range of $1.07 \times 10^{-6} \text{ mol L}^{-1}$ to $8.75 \times 10^{-5} \text{ mol L}^{-1}$ (0.10 to $20 \mu\text{g mL}^{-1}$).

Soil solutions were obtained by adding 50 mL of $0.10 \text{ mol L}^{-1} \text{ CaCl}_2$ solutions in 5 g of each soil. The suspensions were shaken at $25 \text{ }^\circ\text{C}$ in a horizontal shaker for 24 hours to reach the equilibrium. Subsequently, the suspensions were centrifuged at 12000 rpm for 20 minutes and a 30 mL aliquot of supernatant solution was withdrawn from each sample to determine the ametryn concentration by DPV. Prior to the electroanalytical analysis, each suspension was adjusted to pH 2 using a concentrated H_2SO_4 solution.

The limit of detection (LD) was determined as $\text{LD} = 3\sigma/\text{tg } \alpha$, where σ is the current standard deviation of the voltammograms in the electrolyte solution (blank sample) and $\text{tg } \alpha$ is the slope of the analytical curve in the electrolyte solution. The limit of quantification (LQ) was determined as $\text{LQ} = 10\sigma/\text{tg } \alpha$. The precision of the electroanalytical procedure was checked in one day ($n = 10$, intraday) and several days ($n = 6$, interday) in $10 \mu\text{g mL}^{-1}$ ($4.38 \times 10^{-5} \text{ mol L}^{-1}$) ametryn solution, pH 2 (H_2SO_4 as electrolyte), calculated by the relative standard deviation. The accuracy of the electroanalytical method was evaluated from recovering experiments using spiked diuron solutions ($4.38 \times 10^{-5} \text{ mol L}^{-1}$) in each of the four soil solution samples.

Sorption Isotherms: Sorption isotherms of ametryn was determined at a room temperature ($25 \text{ }^\circ\text{C}$) employing the standard batch equilibration method. Sorption was measured using $0.01 \text{ Mol L}^{-1} \text{ CaCl}_2$ as a background electrolyte to minimize changes in ionic strength and promote flocculation. The same method used to obtain soil solution samples was used to determinate the sorption isotherm in each soil in duplicate samples.

The herbicide concentrations in solution were determined by the DPV and differences between initial and equilibrium concentrations were considered as the amount sorbed on the soil material. These values were used to calculate sorption isotherm. Blank suspensions, which included each soil sample with only 0.01 Mol L^{-1}

CaCl_2 solution were also performed to check some analytical interference due to soil extracts. The ametryn adsorption data was fitted to the form of the Freundlich adsorption equation, as follow:

$$X/M = K_f \times C_e^{1/n} \dots\dots\dots(1)$$

where X/M is the ametryn concentration sorbed by mass of sorbent ($\mu\text{g g}^{-1}$), C_e is the ametryn concentration in solution after equilibration ($\mu\text{g mL}^{-1}$), K_f and $1/n$ are the Freundlich affinity and non-linearity coefficients, respectively.

Results and Discussion

The ametryn analytical curve by DPV: The best scanning parameters for measuring ametryn with DPV using the Ag-SAE electrode was: pH = 2, pulse amplitude = 100 mV and potential increments = 5 mV. At those conditions the reduction current peak was linear up to around $10^{-4} \text{ mol L}^{-1}$, as can be observed in Figure 2.

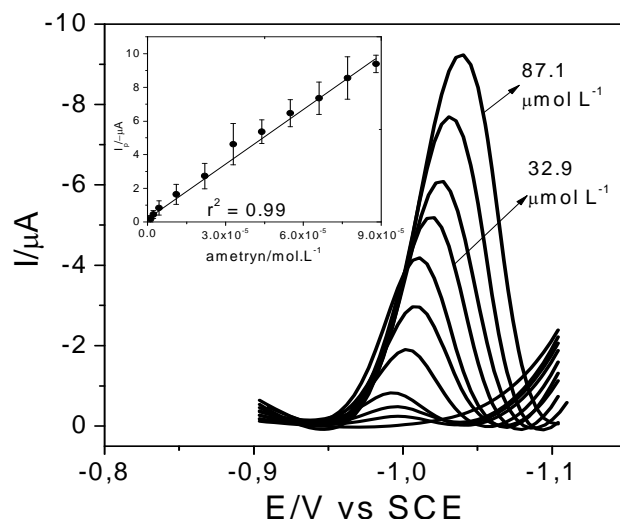


Figure 2: A) Ametryn differential pulse voltammograms in sulphuric acid solution, pH 2, $a = 100 \text{ mV}$, $\Delta E_s = 5 \text{ mV}$, $v = 2 \text{ mVs}^{-1}$. Insert shows the ametryn analytical curve in the electrolyte

The limits of detection and quantification were $1.36 \times 10^{-6} \text{ mol L}^{-1}$ ($0.31 \mu\text{g mL}^{-1}$) and $4.52 \times 10^{-6} \text{ mol L}^{-1}$ ($1.03 \mu\text{g mL}^{-1}$), respectively. This result is adequate for the study purpose which is the determination of sorption isotherm, where samples are prepared and measured in the range of 0 (blank) to $20 \mu\text{g mL}^{-1}$. The intraday and interday precisions found were 3.8 % and 4.8 %, respectively, which are very reasonable, considering the electrode surface renewal between analyses.

To evaluate the influence of the soil matrix on the electroanalytical ametryn response, the relationship between the cathodic peak current with ametryn concentration in soil solutions (analytical curves) were presented in Figure 3. Similarly to the behavior on the electrolyte, the relationship in soil solutions was all linear

at the same range. Table 2 presents the regression equations and the determination coefficients (r^2) as well as the ametryn concentrations obtained in recovering experiments ($4,38 \times 10^{-5} \text{ mol L}^{-1}$) for each soil sample. The recovery was performed with the standard addition method to evaluate the accuracy of the method. It can be seen that the results were satisfactory with the recovery in the range of 74 – 104%, showing that the proposed electrode could be efficiently applied to ametryn detection in soils solutions. The angular coefficients of the analytical curves (b) are lower for the soil samples than for the electrolyte, decreasing therefore the sensitivity, due to the soil matrix interferences.

The influence of soil properties on the lower sensitivity was investigated by calculating the Pearson correlation coefficient (P) between the angular coefficients and the soil properties. The results showed a negative correlation between angular coefficients and pH (-0.74), OM (-0.99), CEC (-0.99) and clay content (-0.98). However, it is important to note that, in clayey soils, it's accelerated the sensitivity decrease than in the sandy ones. The soil properties that mostly influenced the sensitivity decrease were the OM, CEC and clay content.

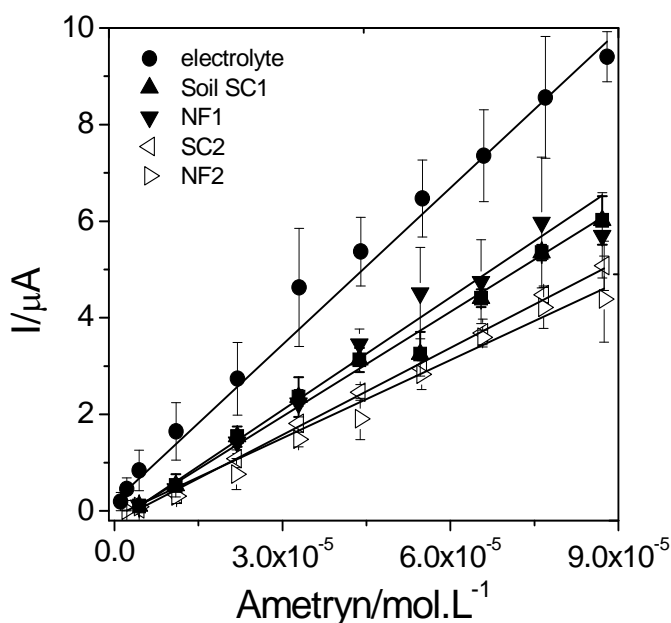


Figure 3: Ametryn analytical curves of in electrolyte and in two oxisol soils (sandy and clayey) in native forest (NF) and sugarcane plantation (SC) conditions, in pH 2 (H_2SO_4). 1: sandy soil and 2: clayey soil

Ametryn sorption isotherms: The sorption isotherms for ametryn were obtained for each soil, using the Ag-SAE and DPV. The peak current measured within the soil sample were converted in ametryn concentrations using the analytical curves presented in Figure 3. The isotherms

graphs are presented in Figure 4. The general shapes of the sorption isotherms were similar, suggesting that similar sorption mechanisms are involved. These isotherms are of the L type, indicating the high affinity of the adsorbent for the adsorbate^[11]. However, as the active sites of the adsorbent became saturated, adsorption of new molecules is not allowed to occur. The Freundlich constants (Kf) and $1/n$ obtained are presented in Table 3 and the linear correlation of these parameters with some soil characteristics are shown in Table 4.

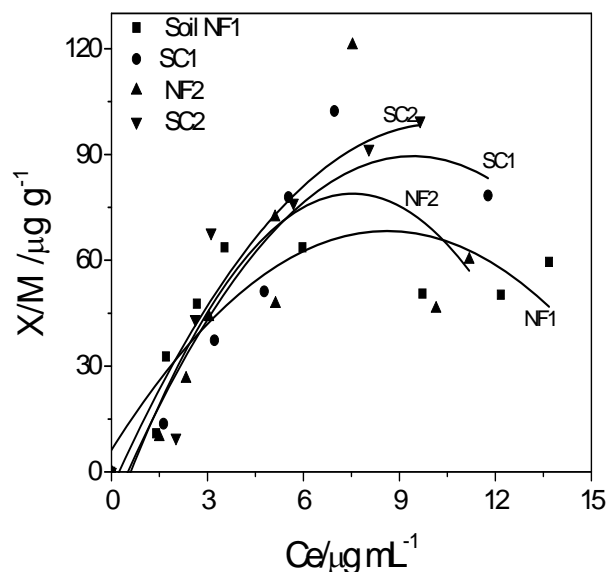


Figure 4: Ametryn sorption isotherm in two oxisol soils (sandy and clay) in native forest (NF) and sugarcane plantation (SC) conditions. 1: sandy soil and 2: clayey soil

The obtained ametryn Kf varied from 10.1 to 19.1 that represent a moderate sorption capacity. The soil with the highest sorption is the sandy soil under native forest (NF1), which presents one of the lower OM and clay content. This probably happens because the pH of this soil was very low (4.0). The soil with the lowest sorption is the one under sugar cane (SC2), which has the most humified organic matter.

Ametryn is a weak base molecule ($\text{pK}_a = 4.1$) and like others pesticides, could exist in protonated (cationic) or neutral (nonpolar) forms depending on the equilibrium reactions and soil pH. When the pH soil is lower than the ametryn pK_a , the protonated form is predominant. However, if the pH soil is higher than ametryn pK_a , the neutral form is predominant. The only soil that has the pH lower than the ametryn pK_a is NF1 soil.

Table 2
Ametryn analytical curves from Figures 3 and recovering experiments ($4.38 \times 10^{-5} \text{ mol L}^{-1}$) in the soil solution samples

Soils	Equation	r^2	Recovery
SC1	$y = -1.30 \times 10^{-7} + 0.054X$	0.99	74%
NF1	$y = -1.36 \times 10^{-7} + 0.047X$	0.98	107%
SC2	$y = -1.24 \times 10^{-7} + 0.083X$	0.99	87%
NF2	$y = -4.38 \times 10^{-8} + 0.081X$	0.99	78%

*NF: native forest, SC: sugarcane. 1: sandy soil and 2: clayey soil

Table 3
Ametryn Freundlich isotherm coefficient from Figure 4

Soils	K_F mL.g^{-1}	1/n
SC1	10.9 ± 1.5	0.98 ± 0.23
NF1	19.1 ± 1.6	0.50 ± 0.24
SC2	10.1 ± 1.9	1.10 ± 0.40
NF2	12.4 ± 1.6	0.81 ± 0.27

*NF: native forest, SC: sugarcane. 1: sandy soil and 2: clayed soil.

Table 4
Correlation coefficient between the ametryn Freundlich isotherm coefficient and some properties and information regarding two Brazilian oxisol soils

	r K_F	r 1/n
OM (g dm^{-3})	-0.368	+ 0.289
pH	-0.786	+ 0.665
CTC ($\text{mmol} \cdot \text{dm}^{-3}$)	-0.336	+ 0.267
Clay (%)	-0.322	+ 0.295
E4/E6	0.953	-0.800

Therefore, since soil NF1 presented the lowest pH (pH = 4.0), close to the ametryn pKa, it was the soil material with the highest capacity for the ametryn sorption and it can be speculated that ametryn binds in this acidic soils mainly by electrostatics forces, since soil particles presents generally negative charges^[12]. The soil pH was the soil property that mostly influenced the ametryn sorption

Matallo *et al.*^[13] obtained for clayey soils from Ubatuba (SP, Brazil) region, a K_f value of 33.50 mL g^{-1} and 1/n of to 0.19. The high sorption was associated to the high amount of soil organic carbon (OC) (10.2%) and the low pH value (4.1) in this soil. Yamane and Green^[14] reported that s-triazine herbicides bind on soils at pH from 1 to 10, but the highest sorption occurs at pH close to the pKa of the molecule. As the soil pH increased, the ametryn sorption intensity also increased, since a positive correlation between 1/n and pH was observed. Laird *et al.*^[15] presented similar results, showing a negative correlation

between K_f and pH and a positive correlation between the pH and 1/n.

It can also be noticed that NF1 is the soil with the less humified organic matter or, on the others hands, there are less complex organic matter particles and could facilitate the chemical bonds, mainly by electrostatics forces. For this reason and especially for the soil pH, NF1 presented the higher ametryn sorption coefficient.

For the others soils, the prevalent form of ametryn are the neutral (nonpolar) and, therefore sorption by electrostatics forces practically does not occur. The results obtained here suggest that a hydrophobic interaction between the ametryn and humic substances^[16] is present, especially because ametryn has low solubility in water. In soils with the same mineralogy (SC2 and NF2), the differences in the sorption could be assigned to the amount of soil organic matter (OM) since generally soils under

natural forest present higher organic matter contents than cultivated soils.

The soil with lower sorption is under sugarcane (SC2), which is one that presents most humified organic matter. These results show that both soil pH and characteristics of OM are important in the ametryn sorption on the soils and the Pearson correlation coefficient between the Kf and soils characteristics confirms this hypothesis (Table 4). Significant correlations were found among pH and E₄/E₆ index, with the coefficient sorption (Kf) values, with a negative correlation in case of soil pH and positive correlation in case of E₄/E₆ index. On the other words, the ametryn sorption is higher as the soil pH increases and the organic matter humification decreases. The others Pearson's coefficients for other soils parameters were very low and statistically insignificant.

No significant correlation was found between the Freundlich sorption coefficient and the clay and organic matter contents for the four soils samples analyzed. Ahmad *et al.*^[17] evaluated the ametryn sorption in thirty-five soils of Pakistan and Australia and did not show correlations between soil clay percentage and ametryn sorption.

Environmental implications: Ametryn is one of the most commonly used herbicides in the Brazilian sugarcane production. The ametryn degradation half-life time in soils is about 54 days^[3] and some metabolites have been found in ground and surface water after a long period of its application^[6]. According to data presented, ametryn has a moderate sorption behavior in the Brazilian soils and in some cases, as pH soil higher than ametryn pK_a or higher amount of humification OM, can present a considerable potential to be transported to the groundwater (lower Kf) as well as to surface waters (higher Kf).

Conclusion

The herbicide ametryn was determined in soil solution by an electroanalytical procedure using a Ag-SAE electrode. Limits of detection and quantification obtained were 1.36 x 10⁻⁶ mol L⁻¹ (0.31 µg mL⁻¹) and 4.52 x 10⁻⁶ mol L⁻¹ (1.03 µg mL⁻¹), respectively and the intraday and interday precisions 3.8% and 4.8%, respectively. Such limits are appropriate to the objective of this study, considering the reproducibility due to the electrode surface renewal.

Measured ametryn Kf in two soils under sugarcane and forest varied from 10.1 to 19.1, which can be considered a moderate sorption capacity. The highest sorption occurred on the sandy soil under forest (NF1) and the smallest sorption capacity on the soils under sugarcane plantation (SC1 and SC2). Ametryn sorption was mainly influenced mainly by the soil pH. Other soil parameters as clay content, organic matter and cation exchange capacity practically did not influence sorption of ametryn in these soils. In agricultural soils, where pH is around neutral due

to lime application, ametryn has relatively low sorption capacity and, in this case, can be transported to groundwater, needing a continuous monitoring.

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