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ENVIRONMENTAL IMPACT OF AGROCHEMICAL USES ON THE ISLANDS AGRICULTURAL PRODUCTION AREA IN MARANHÃO BRAZIL

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Environmental Impact of Agrochemical uses on the Island's Agricultural Production Area in Maranhão, Brazil

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Abstract- Agriculture is the foundation of society, has provided humanity with its food needs for over ten thousand years. The use of pesticides in Brazil and the world has grown exponentially in recent decades. The objective of this study was assessment the use of agrochemicals and their environmental impact on agricultural production of the Island of Maranhão. The study area is located in Paço do Lumiar, Maranhão, Brazil. Soil samples were collected from agricultural land during the wet season (between the months of February and May) and dry season (between the months of September and October) seasons of 2018. We analyzed the soil Physico-Chemical characteristics, organic matter, organic carbon, moisture content, granulometry, pH, nutrient concentrations (nitrate and nitrite, total phosphorus), adsorption isotherms, and microorganisms in the Environmental Sciences Laboratory of the University Ceuma. The results of the physical and chemical analysis of the soil samples suggest the soils could be classified as sandy and silty to clay. There is a concern that the levels of nitrate, nitrite, and phosphorus, especially in rural areas, as well as runoff occurring during production increase due to the use of fertilizers. Microbiological examination showed the presence of gram-negative bacteria of the genus, *Pseudomonas* and *Escherichia coli*. Isotherm models show Kf values of <10 have a low adsorption capacity for the pesticide malathion, suggesting that the soil has the potential to increase contaminant availability to plants and contaminate the water table; however, other soil factors and climatic conditions should be evaluated when evaluating the behavior of pesticides in soil.

Keywords: agriculture, soil, pesticides, adsorption.

Resumo- A agricultura funciona como o alicerce da sociedade, pois há mais de dez mil anos fornece à humanidade o seu alimento. O uso de agrotóxicos no Brasil e no mundo cresceu de forma exponencial nas últimas décadas. O objetivo desse trabalho foi analisar a utilização de agroquímico e seu impacto ambiental na produção agrícola da ilha maranhense. A área de estudo localiza-se em Paço do Lumiar Maranhão, as amostras foram coletadas em três pontos do solo de produção agrícola, no período sazonal (chuvoso e seco) nos meses (fevereiro e maio) e (setembro e outubro) de 2018. Foram analisadas, as caracterizações

físico-químicas, matéria orgânica, carbono orgânico, umidade, granulometria, determinação do pH, concentrações dos nutrientes (nitrito e nitrito, fósforo total), isothermas de adsorção e isolamento de microorganismo no Laboratório de Ciências Ambientais da Universidade Ceuma. O resultado da classificação físico e química das amostras de solo variando entre os pontos, classificaram o solo como areia média à fina, e como siltoso à argiloso. Há uma preocupação com o aumento nos níveis dos íons nitrito, nitrito e fosforo, especialmente em áreas rurais, além do escoamento superficial que ocorre nas áreas de produção devido ao uso de fertilizantes. A análise microbiológica mostrou um aparecimento de bactérias Gram negativas do gênero *Pseudomonas spp* e *Escherichia coli*. Observando os modelos das isothermas mostram, pelos valores de Kf < 10, tem uma baixa capacidade de adsorção do pesticida Malathion. Portanto o solo mostrou ter potencial para disponibilizar contaminantes para as plantas e para o lençol freático, porém para uma melhor avaliação, devem ser considerados outros fatores como comportamento do agrotóxico no solo e condições climáticas.

Palavras-chave: agricultura, solo, pesticida, adsorção.

I. INTRODUCTION

Agriculture is the foundation of society, has provided humanity with its food needs for over ten thousand years. Over time, agriculture has undergone a series of changes resulting in the modernization of production processes, leading to the emergence of new methodologies and mechanization of systems (PEREIRA; JÉBUS; SILVA, 2015).

According to the National Sanitary Surveillance Agency (ANVISA, 2013), the Brazilian agrochemicals market has expanded rapidly in the last decade, with a growth rate (190%) that is twice that of the global market (93%). The Brazil is in first place in the world ranking, with a consumption of one million tons since 2008 (INCA, 2013).

The use of pesticides is considered one of the most important causes of environmental degradation owing to the contamination of natural resources. The

behavior of pesticides in nature is quite complex, with the potential to pollute many agricultural products. Ferreira and Santos (2018) emphasize that the Ministry of the Environment should evaluate the efficacy of agrochemicals intended for use in aquatic environments, native forests, and other ecosystems, and carry out environmental evaluations of pesticides, including their components, with the view to establishing their classification as potential ecological hazards when applied to plants or when water contamination occurs.

Soil pollution during crop cultivation occurs in two stages; when pesticides are applied to plants, or when water contamination occurs. Because soil is a great accumulator of microorganisms and minerals, it can also retain large amounts of chemical residues. Over time, fertility is reduced not only by the continuous use of pesticides but also by the practice of monoculture, which does not allow for the necessary rest for proper restoration of soil fertility, thereby diminishing biodiversity and increasing acidity. When this happens, agricultural productivity is reduced, the volume of water decreases, leading to desertification (PAREJO, 2013).

Significant advances in organophosphorus insecticides for agriculture use and the scientific knowledge of the structure-activity relationship have taken place owing to the discovery of the compound parathion by Schrader in 1944, the first product of a new group of revolutionary insecticides. Despite their relative toxicity, other less toxic insecticides such as Clorhion®, Fenthion®, and Fenitrothion® have been developed with few structural modifications.

Malathion, an organophosphate, is an acetylcholinesterase inhibitor that does not exist naturally. It is a colorless liquid in its pure state. It is used to control insects, diseases, or weeds that cause damage to crops. Technical grade malathion is more than 90% pure. It is a yellowish-brown liquid with a strong odor. This compound has a thioether group and exhibits high insecticidal activity (INCA, 2013).

In the study of soils in agro toxic application areas, the soil classification is determined the evaluation of the morphological, physical, chemical, and mineralogical data of the profile. Environmental aspects of the profile location, such as climate, vegetation, relief, raw material, water conditions, external characteristics, and soil-landscape relationships, are also used (SANTOS et al., 2007).

The objective of this study was assessment the impact of the use of pesticides on the agricultural production soil of Pindoba in the municipality of Paço do Lumiar, Maranhão, Brazil, as well as to determine the possible environmental changes due to the use of agrochemicals, and to evaluate existing data from the area. The data can support future studies and sustainable management with monitoring in the area studied.

II. MATERIALS AND METHODS

a) *Characterization of the study area*

The study area, Paço do Lumiar, is 38 meters above sea level, has the following geographical coordinates: Latitude: 2 ° 31 '50' 'South, Longitude: 44 ° 6' 19 " West. It is located in the western portion of the Island of Maranhão. It comprises the region between the municipalities of São Luís and São José de Ribamar (Figure1).

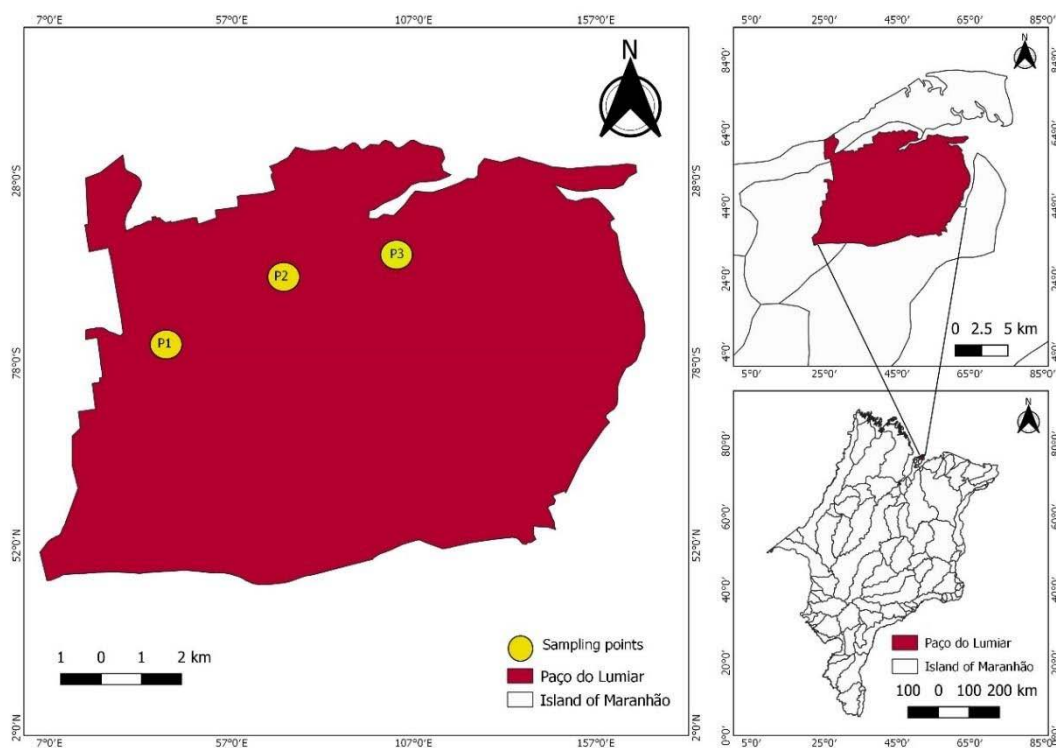


Figure 1: Study area and soil sampling points

Initially, the area of agricultural production was identified in a 4,500-ha private property where that grows vegetables like lettuce and cabbage and is located in the municipality of Paço do Lumiar, in the village of Pindoba. The soil sampling points were demarcated by the geographic coordinates using Garmin GPS Striker4 (Garmin, U.S.A.) The soil sampling coordinates are as follows: P1 (S02 29 '44.1 "and W440 07' 59.6"), P2 (S02 29 '44.4 "and W44 08 '01.3'), and P3 (S02° 29' 44.5 " and W 44° 07 '58.7'). Soil samples were collected during the wet (February and May) and dry (September and October) seasons of 2018. Soil samples were collected with a stainless-steel core, from up to 15 cm depth of soil. Materials from a couple of sampling were homogenized as a function of the size of the area, and a portion of approximately 500 g of each sample was placed separately in a plastic bag and stored at $4 \pm 2^\circ\text{C}$. The physical and chemical properties, organic matter, organic carbon, moisture, particle size, pH, and nutrient concentrations (nitrate and nitrite, total phosphorus) characteristics were determined by methods described by EMBRAPA (2017).

b) Isolation of microorganisms

Microorganisms were isolated from soil from three sample points where organophosphorus agrochemicals had been applied. Three soil samples were collected equidistantly from a single plot of the same garden. After collection, the samples were stored in hermetically sealed bags and stored under refrigeration for subsequent isolation of microorganisms.

Isolation: for the insulation of the microorganisms, composite soil samples were subjected to the serial dilution technique recommended by Costa et al. (2017). Composite soil samples (10 g) were weighed and diluted with 90 mL of sterilized water. From this solution, serial dilutions (1:10, 1:100, and 1:1000) were carried out in test tubes containing sterile water. Dilutions were plated on Muller Hinton (MH), Eosin Methylene Blue Agar (EMB), and Centremide Agar (CEN) selective culture media. All processing was performed in triplicate and incubated at 28°C for up to 72 hours. After incubation, colonies were quantified. Bacteria were selected for purification through the sowing methodology by exhaustion from their macromorphological characteristics. For the identification of the bacterial groups and micromorphological observation of the isolates, the Gram staining technique was performed to classify the bacteria into gram-positive and gram-negative based on the cell wall staining.

Adsorption: for the determination of adsorption isotherms. Langmuir and Freundlich's isotherms were used to determine the sorption process. To determine the adsorption of Malathion in soil, working solutions were prepared from the stock solution at concentrations of 0, 0.5, 1, 2, 3, 4, and 5.0 $\text{g}\cdot\text{mL}^{-1}$ of malathion in 0.01 mol L^{-1} CaCl_2 with pH 5.67. Aliquots of 20.0 ml were added to polypropylene tubes containing 2.0 g of soil. Absorption was then measured using the UV-vis spectrophotometry technique (Spectroquant prove 600), at wavelength $\lambda = 212 \text{ nm}$ (ALVES, 2013).

All statistical analysis was performed using the software Origin Pro 8.0. (OriginLab, MA, USA). Multivariate analysis techniques were also used as an additional tool, specifically Principal Component Analysis (PCA), using the Minitab 17 software (Minitab; USA) (HONGYU, 2015).

The Tukey test and PCA were used to verify the association between the soil variables (sand, silt, clay, organic matter, moisture, organic carbon, pH, nitrite, nitrate, and total phosphorus), as well as the influences of the different seasonal periods.

c) *Determination of the adsorption isotherm*

The standard malathion solutions were analyzed directly, without any pretreatment, in the

spectrometer, to verify the analytical parameters. The concentrations were 0, 0.5 to 5.0 g.mL⁻¹. The standard malathion curve was 0.5 to 3.5 g.mL⁻¹ and was read in UV-vis spectrophotometer at a wavelength ($\lambda = 212$ nm). After obtaining the analytical curve, adsorption isotherms were calculated using the equation of a straight line with $a = 0.4719$, $b = 0.4008$, and $R^2 = 0.9945$.

III. RESULTS AND DISCUSSION

a) *Physical-chemical characteristics*

The physical-chemical properties of the three soil sample points during the two seasonal periods are shown in Table 1.

Table 1: Physical and chemical characteristics of sample points during rainy and dry seasons

| Sampling points | pH | NO ₃ ⁻ | NO ₂ ⁻ | PO ₄ ⁻ | Sand | Silt | Clay | O.M | Humidity | O.C |
|---------------------|------------------------|------------------------------|------------------------------|------------------------------|--------------------------|--------------------------|-------------------------|-------------------------|-------------------------|------------------------|
| | | | | | | | | | | |
| <i>Rainy season</i> | | | | | | | | | | |
| P1 | 6.35±0.49 ^a | 5.30±2.40 ^a | 3.03±4.20 ^a | 1.45±1.06 ^a | 62.32±3.08 ^a | 36.42±3.23 ^a | 1.26±0.15 ^a | 7.35±5.69 ^a | 5.85±2.33 ^a | 0.23±0.19 ^a |
| P2 | 6.20±0.28 ^a | 10.45±4.87 ^a | 1.53±2.07 ^a | 1.75±0.63 ^a | 73.32±0.70 ^a | 24.25±2.36 ^a | 2.42±1.66 ^a | 19.62±7.96 ^a | 9.10±0.42 ^a | 4.10±0.01 ^b |
| P3 | 6.50±0.14 ^a | 8.65±9.82 ^a | 0.28±0.30 ^a | 2.40±0.98 ^a | 67.12±20.71 ^a | 27.11±21.76 ^a | 3.31±0.41 ^a | 7.98±1.68 ^a | 10.25±4.73 ^a | 0.38±0.16 ^a |
| <i>Dry season</i> | | | | | | | | | | |
| P1 | 6.75±0.07 ^a | 7.40±0.14 ^a | 0.30±0.141 ^a | 3.60±0.14 ^a | 62.07±0.10 ^a | 35.63±0.72 ^a | 1.77±0.12 ^a | 12.76±2.35 ^a | 8.70±0.84 ^a | 0.22±0.03 ^a |
| P2 | 5.45±0.07 ^b | 12.00±1.41 ^b | 0.12±0.007 ^a | 5.95±0.77 ^b | 77.21±6.44 ^a | 12.23±0.72 ^b | 5.88±0.89 ^b | 11.59±0.71 ^a | 5.80±0.70 ^a | 4.18±0.11 ^b |
| P3 | 4.95±0.07 ^c | 2.05±0.07 ^c | 0.27±0.176 ^a | 1.40±0.28 ^c | 68.69±12.28 ^a | 14.30±2.82 ^b | 4.55±0.74 ^{ab} | 9.84±5.35 ^a | 12.87±0.88 ^b | 0.59±0.07 ^c |

*Values in mean (n = 3). Means followed by the same letter in the same column do not differ statistically from each other by the Tukey test (p < 0.05). NO₃⁻ (Nitrate), NO₂⁻ (Nitrite), PO₄⁻ (Phosphorus), O. M. (Organic Matter), O. C. (Organic Carbon).

The results of the particle size analysis of the soil samples in the rainy and dry period (points P1, P2, and P3) were observed, 62.32 to 73.32 % related to sand content in the rainy season. In the dry season, the values varied from 62.07 to 77.21% of sand content. It was clear the classification of the soil as being sandy, silty to clay because their rating influences environmental conditions. The sand fraction dominated all three samples. However, based on organic matter values, it can be considered that the soil is vulnerable to the percolation of contaminants, indicating losses to underground aquifers.

There was a variation in the maximum and minimum values for the particle size analysis in the dry period, probably as a function of the soil characteristics of the region. The soils could be classified as being medium to fine sand and silty to silty sand SILVA e SILVA (2014). Percentages of the sand fraction in the soil samples are typical of the characteristics of the region. The soil of the study area is quite porous, which reduces its potential to prevent agrochemical residues from getting through its profile. However, other characteristics of the soil environment need to be analyzed to determine the soils' ability to retain contaminants. Moreover, clay minerals have superior

activity due to the specific surface area of the particles and cation exchange capacity BARBOSA (2012).

Organic matter ranged from 7.35 ± 5.69 to 7.98% ± 1.68 in the rainy season and 9.84% ± 5.35 to 11.59% ± 2 in the dry season. Organic matter values above 10% suggest an anthropic intervention and below 10% are considered to indicate soils made up of predominantly silica and clay minerals combined with fertilizer compounds. Blainski et al. (2012) evaluated the influence of plant and residues on the density, porosity, and other physical attributes of a sandy-loam soil under no-tillage, and reported a considerable improvement in the physical quality, with a decrease in density, in contrast to the increase in density treatments without plant cover.

The organic matter in the soil determines the sorption index of the agrochemicals. Soils with higher organic matter content have a higher amount of pesticides. MURAKAMI et al. (2014). There were significant variations in moisture content among sampling points. It varied from 5.85to 10.25 % in the rainy season, while in the dry season, it ranged from 8.70to 12.87 %. The presence of water containing dissolved minerals and soluble organic materials is essential for agricultural soils. According to COSTA et al.



(2017) coefficients of moisture variation can be classified as low ($CV < 4.04$), medium ($4.04 < CV < 17.50$), high ($17.50 < CV < 24.22$), and very high ($CV > 24.22$). The moisture content of the soils in this study could be classified as a medium for agricultural production. According to Ávila et al. (2011), soil moisture plays an important role in surface hydrologic processes and sediment transport due to the significant participation in the separation of precipitation into infiltration and surface runoff. Also, it exerts influence on the soil-atmosphere interaction, especially in evapotranspiration and in the interference of the processes related to water erosion. It is also useful for a wide range of applications aimed at soil and water conservation, for understanding alternative and rapid techniques of moisture determination, and may also help in decisions regarding agricultural operations, such as irrigation management.

Organic carbon from P1 and P3 were 0.23 to 4.10 % and 0.22 to 4.18 % in the rainy and dry seasons, respectively. The organic carbon content for P2 was the highest in the dry period indicating the stability of organic matter by the formation of organo-mineral complex, due to the presence of sandy-silty and clayey sediments. The organic carbon content may have been caused by high biomass production through the application of animal manure and leaves of pindoba and carnaúba palm.

The results of the carbon content in the humic fractions of the studied soils corroborate those of Campos et al. (2012), who showed that environments with the presence of vegetal residue (VR) had a higher organic carbon content in Q2 (0.49 g kg^{-1}) and the lowest in Q3 (0.16 g kg^{-1}). VR on the soil surface is source of carbon, nitrogen, and other elements that contribute to the maintenance of soil organic matter levels and nutrient cycling. Plant residues are initially colonized by microorganisms and at the same time, adsorb minerals. In the 0 cm to 20 cm layer the clayey P1 had a lower organic carbon content of 0.10 g, which can be explained by the intensity of the processes of the addition of vegetal residues with low decomposition rates at the soil surface, and increasing with depth Schenato, Eltz, and Rovedder (2007). The fact that P1 presents a minor organic carbon content is probably due to the difficulty of the formation of organo-mineral complexes that prevent organic acid formation from the decomposition of plant residues in the soil. Thus, clay soils have lower decomposition rates of organic matter and, consequently, excellent chemical stability.

pH values varied from 4.9 to 6.8 in the dry period (mean = 6.75 ± 0.07) and 6.4 to 6.7 in the rainy season with a mean value of 6.35 ± 0.07 . These values are within limits allowed by EMBRAPA (2017).

Nitrate in the dry period ranged from 0.13 mg L^{-1} to 0.4 mg L^{-1} (7.40 ± 0.14) and from 15.6 mg L^{-1} to 1.7 mg L^{-1} (5.30 ± 2.40) in the rainy period. The increase in

the levels of nitrate, nitrite, and phosphorus ions, especially in rural areas is of concern due to their high concentration in the applied chicken bed substrate, in addition to the surface runoff that occurs in the production areas due to the use of fertilizers.

Extensive soil cultivation, even with the application of fertilizers or manure, is currently believed to facilitate oxidation to reduce nitrogen nitrate in organic matter decomposed in the soil through the effect of aeration and moisture (BAIRD; CANN; GRASSI, 2011). According to Bastos, Bezerra, and Bevilacqua (2007), nitrite are unstable in the presence of oxygen, occurring as an intermediate form. The presence of the nitrite ion indicates the occurrence of active biological processes influenced by organic pollution.

Total phosphorus values ranged from 1.45 to 2.40 mg L^{-1} in the rainy season and from 1.40 to 5.95 mg L^{-1} in the dry season. The highest phosphorus content was found in P2, in the dry period, and P3, in the rainy season, what can be associated with the nutrients, organic matter content, and herbicides content of the substrates and fertilizers. These results are within the scope of the Embrapa (2017) resolution.

Berwanger (2006) and Klein and Agne (2012) evaluated the changes in soil P content saturation of adsorption sites with the continuous use of liquid swine manure and chicken litter. They observed increases in the levels of phosphorus, nitrate, and nitrite, and a decrease in pH. Applications of liquid waste can increase the transfer of total phosphorus, nitrate, and nitrite using flow and percolation, leading to concentrations higher than those established by legislation. The eutrophication contributing to the increase of biological processes and can be affect the planting of cabbage, lettuce, and other vegetables cultivated in the Pindoba region.

b) Statistical analysis

For the physical-chemical analysis, the results were expressed as mean and standard deviation (\pm SD). The comparative test between the averages of all parameters was performed using the Tukey test ($p < 0.05$). For the physical and chemical properties, a principal component analysis (PCA) was applied to the mean values of three replicates to identify correlations between the data and to group them according to the influence of seasonality.

Cluster and Principal Component Analysis to verify the association between soil variables and the influences of the different seasonal periods are shown in Figure 2. The first two dimensions of the PCA of all physicochemical parameters explained 60.04% of the variance. Five clusters can be identified: Cluster 1 includes sampling point P1 in rainy period), Cluster 2 include sampling point P1 in dry period), which showed correlation with high levels of silty, nitrite, and pH, but, low values of sand and clay. Cluster 4 include P3-dry

period with high levels of moisture and clay, but low levels of silt. Grouping 4 consists of sampling point P2 in the rainy season, Cluster 5 consist of sampling point P3 in the dry period.

The PCA technique was used to investigate possible correlations between all variables studied and to evaluate hypothetical models for the classification of samples. Initially, an evaluation of the relationships between the ten variables related to the two periods studied was performed by PCA based on a matrix of correlation data in which the variables were standardized and given equal weight. The graph of the score (Figure 2) revealed that the distribution of the

analyzed points was not significant. Based on axis 1 (PC1), P2, and P3 of the rainy and dry periods presented a positive correlation. P1 and P2 of the rainy and dry periods showed a negative correlation. The first component (PC1) was the most significant to describe the model, accounting for 38.80% of the total variance.

The first three principal components (PCs 1-3) are the most significant in the model description and together accounted for 75.60% of the total variance (Table 2). However, most of the system information (i.e., 60.04% of the cumulative variance) is attributed to PC1 (38.80%) and PC2 (21.60%).

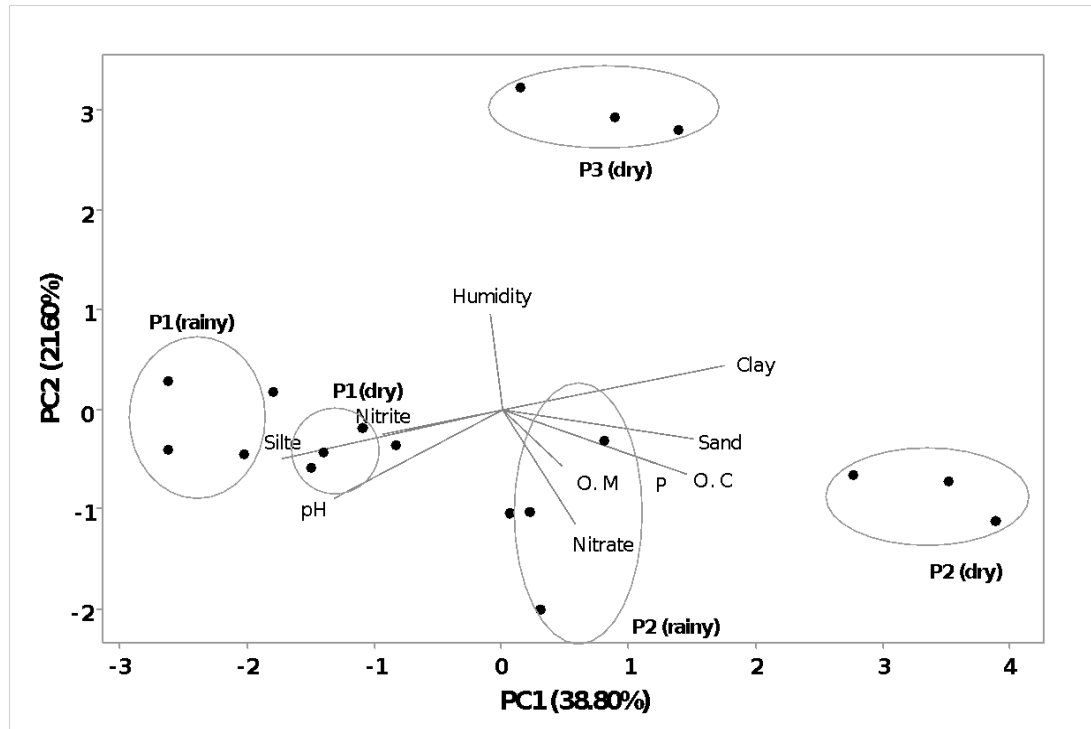


Figure 2: Principal component analysis (PCA) for dimensions 1 and 2. The vectors represent the physicochemical variables. (rainy): rainy season; (dry): dry season; Sampling points: (P1), (P2), and (P3). The ellipses represent the main groupings between sampling points in the dry and rainy seasons

Table 2: Correlation coefficients of the Principal components (Factors 1, 2, 3, and 4) for the physical-chemical parameters

| Variables | PC1 | PC2 | PC3 | PC4 |
|------------------------|-----------|-----------|-----------|-----------|
| pH | -0,341549 | -0,415674 | 0,246645 | -0,024025 |
| Nitrate | 0,147901 | -0,534413 | 0,219691 | -0,123296 |
| Nitrite | -0,240838 | -0,114391 | -0,668571 | 0,107265 |
| Phosphorus | 0,307993 | -0,248119 | 0,241546 | -0,412945 |
| Sand | 0,389760 | -0,138153 | -0,237190 | 0,090509 |
| Silt | -0,445924 | -0,230172 | 0,201121 | -0,104355 |
| Clay | 0,449893 | 0,201932 | 0,058884 | -0,241226 |
| O.M. | 0,122310 | -0,262082 | 0,171175 | 0,727492 |
| Moisture | -0,022381 | 0,443007 | 0,495836 | 0,334562 |
| O.C. | 0,374142 | -0,298639 | -0,101194 | 0,289384 |
| Eigenvalues | 3.88 | 2.15 | 1.44 | 1.28 |
| Total Variance (%) | 38.80 | 21.60 | 14.50 | 12.90 |
| Cumulative Variance(%) | 38.80 | 60.04 | 74.90 | 87.80 |

* Bold values indicate significant factors. O. M. (Organic Matter); O. C. (Organic Carbon).

According to the PCA, there were differences between the sampling points in February and September, what can be explained by the proximity to the sampling time. Axis 1, which accounts for 38.80% of cumulative variance explained the variations of silty, pH, nitrite in the rainy season at points P1 and P2. Axis 2 explains 60.04% of the sand, clay, organic matter, organic carbon, humidity, nitrite, and phosphorus variations during dry periods at P2 and P3. Thus, the temporal variation of the studied parameters can be confirmed through the separation of the months and grouping of the sampling points.

c) *Malathion adsorption in soil*

The results of the Langmuir (A) and Freundlich (B) isotherms are shown in Figure 3 and Table 3. There are several results of adsorption isotherms models describing the adsorption ratios for more media and substances. The partition coefficient (Kd) at the three sampling points ranged from 9.95 to 10.45 $\mu\text{g mL}^{-1}$, while correlation coefficients ranged from (0.99 to 1) for the Langmuir A isotherm and Freundlich isotherm B (Figure 3).

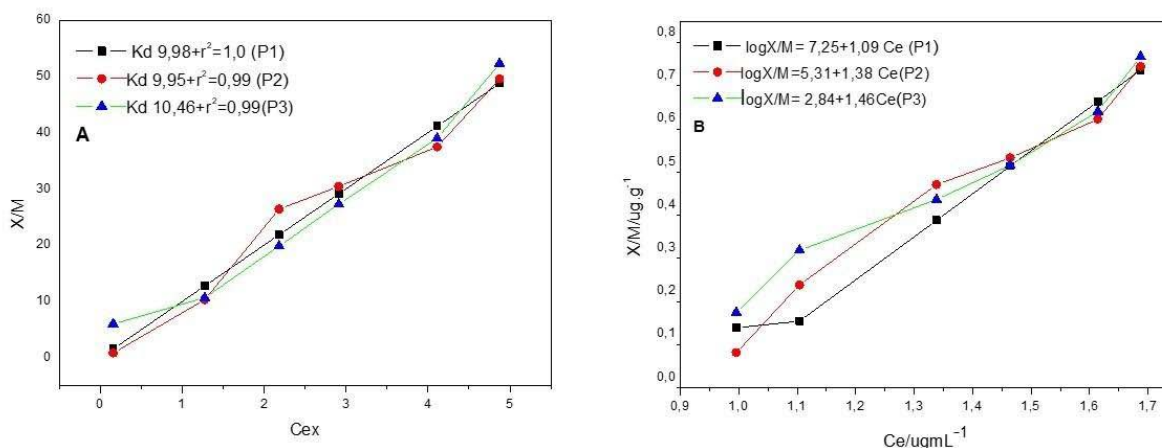


Figure 3: Langmuir (A) and Freundlich (B) Isotherms of Malathion absorption by three agricultural soil samples

Table 3: Partition coefficients (Kd), organic carbon constant (Koc), organic matter constant (Km), Freundlich coefficient of linearity of the isotherm (1/n), and the correlation coefficient (R²) for the pesticide Malathion, at the three soil sampling points

| Sampling Point | Kd | Koc % | Km % | K _f | 1/N | R ² |
|----------------|-------|--------|--------|----------------|------|----------------|
| P1 | 9.98 | 171.10 | 99.25 | 7.25 | 1.09 | 1.0 |
| P2 | 9.95 | 110.38 | 64.03 | 5.31 | 1.38 | 0.99 |
| P3 | 10.45 | 202.22 | 117.38 | 2.83 | 1.46 | 0.99 |

The degree of linearity (1/n) varies between 1.09 and 1.46, that in this concentration range, the isotherms are type C, amenable to linearization. We can assume that the low values of K_f in P2 and P3 varied from 2.83 kg L⁻¹ to 5.31 kg L⁻¹. The P1 value was 7.25 kg L⁻¹, showing its low affinity for the solid phase of the soils and a high availability of this insecticide in the soil solution and great potential for leaching and or biodegradation.

Isotherms with K_f < 10, suggests low adsorption capacity of malathion, following the criterion of IBAMA (1990) and IBAMA (2017). This behavior is in agreement with the influence of the soil on the degradation of malathion.

The slope of an isotherm from Souza et al. (2007) is given by the adsorption coefficient, Kd. This coefficient is an index of the adsorption energy, which allows for a comparison of the performance of different soils concerning to the adsorption of solute. The linearized form of the Freundlich isotherms proved to be

satisfactory for most of the combinations versus the herbicide. Therefore, according to the adsorption intensity, identified in the curve, (n) is close to 1. The significant similarity between the coefficients obtained by the Freundlich isotherms, and their linearized form can be used to describe the sorptive behavior of the compounds. The degradation rate of Malathion varies depending on the type of soil and is closely linked to sorption phenomena.

In studies such as Luchini et al. (1984), the pesticide carbendazim and parathion had intermediate R_f (0.10 to 0.31), whereas malathion and lindane showed the good mobility in the soils studied, according to their R_f (0.57 to 0.96), therefore, there is an inverse relationship between the movement of pesticides in the 0 cm to 5 cm layers of soil and their partitioning behavior. These values reported are smaller than what we have presented in this study.

The organic carbon coefficient for the soils varied between 110.38% and 202.22%, and from

64.03% to 117.38% to Km. These values suggest that the nature of the organic matter and other attributes of the soils can influence the sorption of malathion in soil.

After leaving samples in dark bottles wrapped with aluminum foil. Malathion under laboratory conditions is degraded by light at a constant and slower rate. Therefore, this pesticide in the environment undergoes soil degradation, indicating an ongoing degradation half-life over time.

When studying the sorption of thiamethoxam in soils with different organic matter contents, Schmidt, Salton, and Scorza, Júnior (2015) observed a high correlation between organic matter content and its sorption. Thus, it is possible that the lower values of K_f are due to the organic matter content found in this soil.

Isolations of the microorganisms in the three selective culture media are presented in Figure 4.

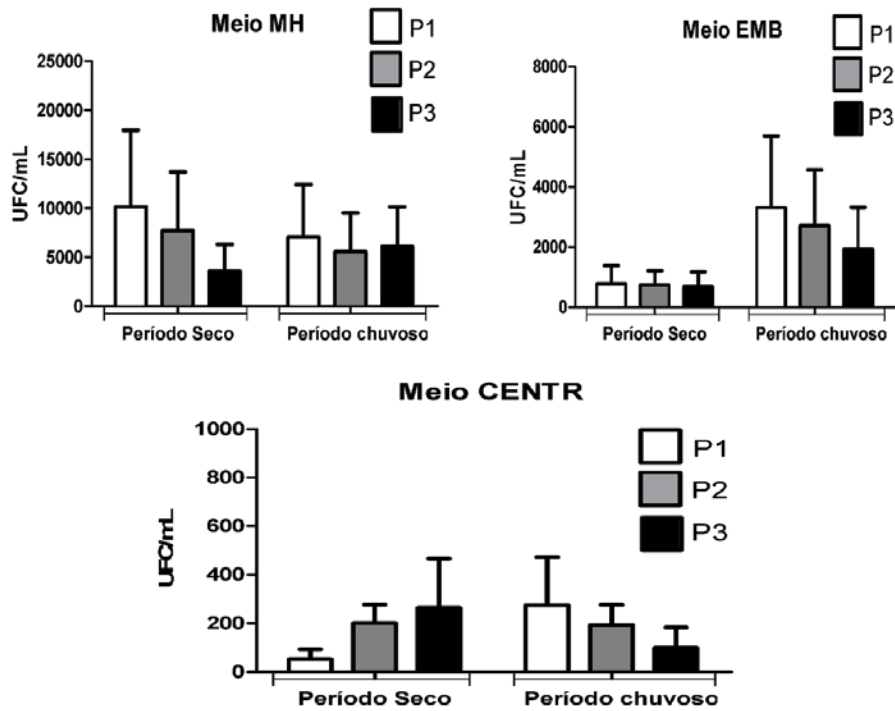


Figure 4: Isolation of microorganisms in the three-culture media in soil samples

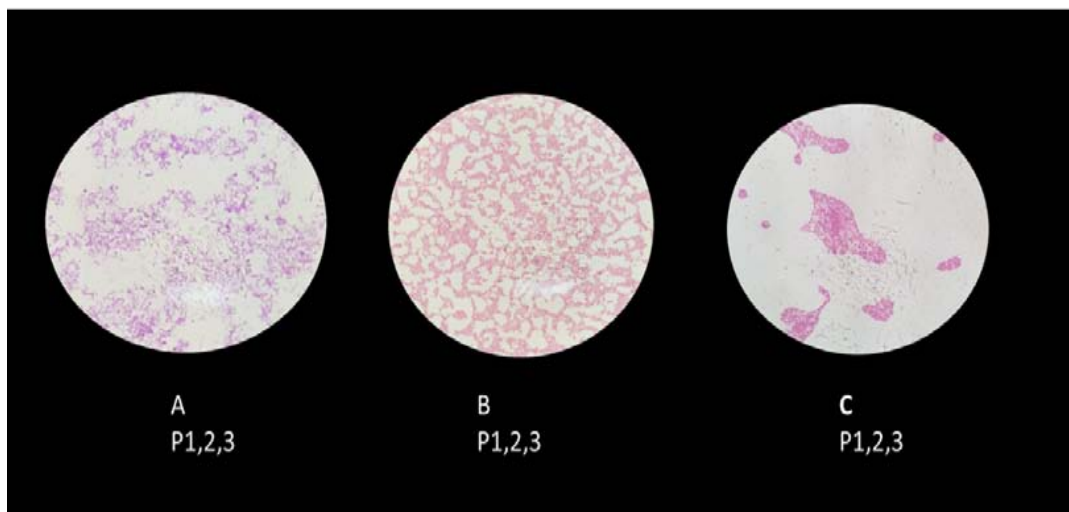


Figure 5: Morphological characterization of Gram-negative bacteria from the sampling points

A variation in the microbial quantities among soil samples can be observed depending on the culture medium used. The Muller Hinton culture medium presented the highest number of bacteria in the two seasonal periods studied. P1 had 10,000 CFU/mL in the dry period, while in the rainy period, 800 CFU/mL was observed. P2 had almost the same microbial quantity in both periods when the isolation was done in MH medium, whereas P3 was the only one that presented the highest number of bacteria in the rainy period with 700 CFU/mL, and 300 UFC/mL in the dry period. The MH medium is complex, and therefore perfect for the isolation of all types of bacteria, which explains the high number of colonies in this medium. The highest microbial quantity in the dry period can be explained by a higher pH than in the rainy season. This pH range favors the growth of bacteria, while acidic pH favors the growth of fungi. The EMB culture medium showed larger counts of bacteria in the rainy season in all three samples. P1 presented the highest bacterial quantification with 3,800 CFU/mL in the rainy season, while in the dry period, it was 1,000 CFU/mL. P2 and P3 presented similar bacterial quantification in the dry period, while in the rainy season, P2 showed 3,000 CFU/mL and P3 2,000 CFU/mL.

The Methylene Blue Eosin medium is a differential selective medium, which may indicate that Gram-negative bacteria prevail in soils contaminated with pesticides in the rainy season, proven by the higher soil moisture in this period, and by the ability of most bacteria to form a colony and hence biofilm, thereby protecting their cells from stress caused by environmental changes. The Cetrimide agar medium presented the smallest amount of bacteria since it is a selective culture medium for *Pseudomonas pyocyanea* bacteria. These bacteria have adaptive capacity to environmental changes by forming a biofilm, and are known to be producers of bioactive substances such as rhamnolipids. Semedo-Lemsaddek et al. (2018) *Pseudomonas* bacteria have nutritional characteristics of oligotrophy; that is, they need only little nutrient to survive. This fact can be observed by the inverse relationship between growth and the nitrogen and phosphorus contents during both dry and rainy periods.

Based on the characterization of the soils analyzed, it was possible to determine that agricultural of the region is very vulnerable to impacts from the excessive use of pesticides. The occurrence of pesticide residues is a potentially problem, based on the micromorphology of the isolated microorganisms. The presence of Gram-negative, rod-shaped bacteria reinforces the adaptive capacity of this microbial group. Some authors have reported the isolation of microorganisms from soils contaminated with agrochemicals. Costa et al. (2018) isolated microorganisms from soil with the organochlorine pesticide DMA 806 BR, obtaining large quantities using

Muller Hinton culture medium. However, in the same study, the authors reported the isolation of a few Gram-negative rod-shaped bacteria. Costa et al. (2017) isolated microorganisms from soil contaminated with Chlorpyrifos, an organophosphate, and reported the presence of Gram-Negative bacteria. Their results showed a higher bacterial count in the dry period than in the rainy season.

IV. CONCLUSIONS

Based on the characterization of the soils, it was possible to determine that the agricultural region is very vulnerable to the effects of the excessive use of pesticides. Pesticide residues are a potentially problem impacting the preservation of the environment. The use of pesticides for prolonged periods can cause radical changes in soil structure. Sorption is the mechanism for the interaction between pesticides and the soil or sediments. It occurs commonly when solute (adsorbate) passes from the aqueous phase to the surface of an adsorbent solid. Understanding the physical and chemical properties of a pesticide often allows for an estimation of its adsorption behavior.

The increases in the levels of nitrate, nitrite, and phosphorus ions is due to the high concentration of these ions in chicken litter substrate applied to these soils, in addition to surface runoff that occurs in the production areas due to the use of fertilizers. Soil characteristics interfere with the selection of bacteria.

The application of pesticides should be carried out in appropriate way, with the view to maximizing the protection of the environment. Agricultural strategies for the reduction of contamination and pollution of natural resources, soil, and water should seek to reduce runoff and the use of agrochemicals on crops. Reducing environmental pollution will only be possible by raising farmers' awareness of the importance of preserving these finite natural resources.

REFERENCES RÉFÉRENCES REFERENCIAS

1. Alves, M. S. Soil microbiological diversity of soil and its potential for soil quality assessment. Monograph (Completion of course). Biological Sciences. Federal University of Pelotas. Institute of Biology. Pelotas. 2013.
2. Ávila, L. F.; Mello, C. R.; Mello, J. M.; Silva, A. M. Spatial-temporal pattern of soil volumetric moisture in a basin with a predominance of latosols. Brazilian Journal of Soil Science, v. 35, p. 1801-1810, 2011.
3. Baird, C.; Cann, M.; Grassi, M. T. Química Ambiental. 4. ed. Porto Alegre: Bookman, 2011. 844 p.
4. Barbosa, S. C. B. Determination of pesticide residues in products of plant origin. Master's Dissertation in Human Biology and Environment.

- University of Lisbon, Faculty of Science. Lisbon. 2012.
5. Bastos, R. K.; Bezerra, N. R.; Bevilacqua, P. D. Water Safety Plans: New Paradigms in Water Quality Control for Human Consumption in Consistency with Brazilian Legislation. In: Brazilian Congress of Sanitary and Environmental Engineering, Belo Horizonte, 2007.
 6. Berwarger, A. L. Changes and transfers of phosphorus from the soil to the aquatic environment with the use of swine net waste. Master's Dissertation, Federal University of Santa Maria, 2006.
 7. Blainski, E.; Tormena, C. A.; Guimarães, R. M. L.; Nanni, M. R. Physical quality of a latosol under no-tillage influenced by soil cover. *Brazilian Journal of Soil Science*, v. 36, p. 79-87, 2012.
 8. Campos, M. C. C.; Ribeiro, M. R.; Souza Júnior, V. S.; Ribeiro Filho, M. R.; Almeida, M. C. Toposequence of soils in the transition Natural Fields-Forest in the region of Humaitá, Amazonas. *Acta Amazônica*, v. 42, n. 3, p. 387-398, 2012.
 9. Costa, M. S.; Araújo, T. R. R.; Martins, A. J.; Silva, Q. H. S.; Costa, C. H.; Miranda, R. C. M. Isolation of microorganisms of biotechnological interest originated from areas contaminated with agrochemical. *Revista de Investigação Biomédica*, v. 9, n.1, p. 17-23, 2017.
 10. Costa, C. H. J.; Ramos Filho, A. J.; Sousa, J. S. S.; Castro, E. J. M.; Pereira, C. D. S.; Miranda, R. C. M. Bioprospecting for microorganisms of biotechnological importance in soils contaminated with agrochemicals. *Ciência e Natura*, v.40, p.02-18, 2018.
 11. EMBRAPA. Empresa Brasileira de Pesquisa Agropecuária. National Center for Soil Research (Rio de Janeiro, RJ). Manual of soil analysis methods. 2. ed. Rio de Janeiro: EMBRAPA, 2017.
 12. Ferreira, R. A.; Santos, M. B. The right to environmental protection of port work. Available. Disponível em: <http://www.tractorfinder.com.br/artigos/seguranca%20e%20medicina/artigo_05.pdf>. Acesso em: 10 out 2018.
 13. Hongyu, K. Comparison of weighted GGE-biplot and MIA-weighted with other genotype × environment interaction models. Thesis (Ph.D. in Statistics and Agronomic Experimentation) - Luiz de Queiroz College of Agriculture, University of São Paulo, Piracicaba, 2015.
 14. IBAMA. Instituto Brasileiro do Meio Ambiente e dos Recursos Renováveis. Manual de Pesticidas para Avaliação da Ecotoxicidade de Agentes Químicos. Brasília: IBAMA, 1990, v.1, 351p.
 15. IBAMA. Instituto Brasileiro do Meio Ambiente e dos Recursos Renováveis. Manual de Pesticidas para Avaliação da Ecotoxicidade de Agentes Químicos. Brasília: IBAMA. 2017. Disponível em: <ibama.gov.br/phocadownload/agrotoxicos/reavaliacao-ambiental/2017-07-25-Manual-IBAMA.> Acesso em: 25 jun 2018.
 16. INCA. Instituto Nacional de Câncer. Brasil lidera o ranking de consumo de agrotóxicos. Rio de Janeiro, 2013.
 17. Klein, C.; Agne, S. A. A Phosphorus: from nutrient to pollutant! *Rev. Elet. in Environmental Management, Education and Technology*, v. 8, n. 10, p. 1713-1721, 2012.
 18. Luchini, C. L.; Hirata R.; Rüegg, E. F. Sorption and mobility of pesticides associated with physico-chemical properties of cerrado soils of the State of São Paulo. *Pesq. agropec. bras.*, v. 19, n. 2, p. 157-162, 1984.
 19. Murakami, L. Y.; Ferreira, R. C. B.; Souza, G. S.; Luchini, L. C. Mineralization and sorption of the fungicide fluopicolide of samples of neosol and latosol soils in preserved areas and treated areas. *Pesticides: r. ecotoxicol. and environment*, v. 24, p. 33-42, 2014.
 20. PAREJO, L. C. Desertification: Causes and consequences of land misuse. 2013 .
 21. Pereira, J. A.; Jesus, J. F. V.; Silva, N. C. The use of pesticides by farmers in the community of Baixa do Juá, Santana de Mangueira-PB. *Revista Verde*, v.10, n. 2, p. 126-131, 2015.
 22. Santos, V. M. R.; Donnici, C. L.; Costa, J. B. N.; Caixeiro, J. M. R. Pentavalent organophosphorus compounds: history, synthetic methods of preparation and applications as insecticides and antitumor agents. *Química Nova*, v. 30, n. 1, p.159-179, 2007.
 23. Schenato, R. B.; Eitz, F. L. F.; Rovedder, A. P. Teor de carbono em solos arenosos: comparativa entre área de revegetação, campo nativo e solo arenizado. In: Periódico XXXVI (Congresso Brasileiro de Ciência do Solo). Gramado –RS. 2007.
 24. Schmidt, T. D.; Salton, J. C.; Scorza Júnior, R. P. Sorption and desorption of thiamethoxam and atrazine in soil under different management systems. *Brazilian Journal of Agricultural and Environmental Engineering*, v. 19, n. 6, p. 613-618, 2015.
 25. Smedo-Lemsaddek, T.; Pedroso, N. M.; Freire, D.; Nunes, T.; Tavares, L.; Verdade, L. M.; Oliveira, M. Otter fecal enterococci as general indicators of antimicrobial resistance dissemination in aquatic environments. *Ecological Indicators*, v. 85, p. 1113–1120, 2018.
 26. SILVA, V. L.; SILVA, M. R. C. Caracterização físico-química da água e sedimento do rio Pindaré, nos trechos correspondentes aos municípios de Pindaré-Mirim, Tufilândia e Alto Alegre). Monografia (Graduação em Química). São Luís. Universidade Federal do Maranhão. 2014.

27. Souza, D.; Toledo, R. A.; Galli, A.; Banda, G. R. S. Determination of triazine herbicides: development of an electroanalytical method utilizing a solid amalgam electrode that minimizes toxic waste residues, and a comparative study between voltammetric and chromatographic techniques. *Analytical and Bioanalytical Chemistry*, v.187, n.6, p.2245-2253, 2007.