Assessment of Persistence and Presence of Alachlor Pesticide Residues in Surface Water

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The evaluation of the presence and persistence of alachlor was verified in surface waters, from a region with agricultural areas and agrochemical industry. Alachlor quantification was enabled by the development of an analytical method by High Performance Liquid Chromatography coupled to diode-array detector. Based on the land-use patterns, four sampling points were selected. The presence of alachlor was detected in only one of the points for the first campaign (9.65 ± 2.60 µg L⁻¹) and in three points for the samples from the second campaign (range from 3.33 ± 0.03 to 8.40 ± 0.44 µg L⁻¹). This higher incidence is due to the occurrence of rains in the period prior to sampling; this fact may have contributed to the runoff of the compound present in the soil to the water bodies. In addition, it was possible to identify the influence of time, in which the pesticide remains in contact with surface water, in the half-life of alachlor. Longer test times are responsible for the increased half-life of the compound. For the shortest test time, 15 days, the value obtained for the half-life was 43.1 days, however when the time is extended to 225 days, the half-life for the pesticide reaches 249.2 days. Therefore, it is clear, the importance of the monitoring time, when it is intended to evaluate the half-life of organic compounds.

Keywords: Pesticide; persistence of alachlor; surface water; liquid chromatography.

1. Introduction

Pesticides, also known as agricultural defensives, are used in different parts of the world for pest control, because of the maintenance of modern farming practices, since high productivity is required. In Brazil, in 2018, 310 active ingredients were formulated, and for 88 of these products the individualized sale was announced and represents 501.7 thousand tons, this number corresponds to 91% of the total value of sales of pesticides and the like.¹ The Paraná state consumes more than 90,000 tons of pesticides per year. In 2019 total sales amounted to 95,286.8 tons, with soy being the culture that consumes more pesticides, accounting for 53.21% of total use. The region of Arapongas marketed 296.5 tons of pesticides in 2019.²

Pesticides have in their composition chemicals that interfere with the biological activity of living beings that are targets of control. However, such substances, during their production, handling and or use, can reach different environmental compartments, such as water, soil and produce toxic effects on non-target organisms, including instant death.³,⁴

Surface water and groundwater may present pollution by pesticides when they are close to regions where there are intense agricultural practices. Thus, the evaluation of pesticides in water bodies is important so as to understand the contamination and to assess the impact of its risks on the ecosystem, as well as to highlight strategies and actions that enable changes in agricultural practices aiming to combine productivity with quality of water resources.⁵,⁷

Alachlor, 2-chloro-2’,6’-diethyl-N-methoxymethylacetanilide, is an herbicide used for pre-emergence control of annual grasses and weeds in crops, mainly corn, sorghum and soybeans. The compound acts by inhibition of protein synthesis in susceptible plants.⁸ Alachlor shows high persistence, high leaching potential and risk of runoff from farmlands to aquatic environments; therefore, it can contaminate surface and ground waters.⁹,¹⁰

Alachlor is listed as a canceled product on the website of the Agricultural Defense Agency of Paraná - ADAPAR.¹¹ Moreover, there are no data for trade of alachlor from 2013 in Brazil.¹ However, this compound is in the list of regularization of pesticides approved by National Health Surveillance Agency.¹²
Alachlor has been detected in various parts of the world in water samples, as Portugal, Greece, Spain, and other regions. Therefore, the present study aimed to assess persistence in water, under controlled conditions, and the presence of alachlor, in a region with suspected contamination of environmental matrices by pesticides.

2. Experimental

2.1. Materials and reagents

Alachlor pestanal (Sigma Aldrich, Saint Louis, USA), 99.8% purity, was used as standard. Acetonitrile (HPLC grade) (J.T. Baker and Sigma Aldrich) was filtered in 0.45 μm PTFE membrane (Sartorius). Ultrapure water was obtained from the Direct-Q 8UV Millipore system (Merck). The standard Alachlor was dissolved in acetonitrile and stock solutions at concentration of 400 mg L^{-1} were obtained. The working solutions were prepared in acetonitrile by using the stock solution. For the solid phase extraction (SPE) procedure, the C18 cartridges were used (500 mg/6 mL) (Agilent, Bond Elut).

2.2. Description of the sampling site

Surface water samples were collected in the region of Aricanduva, located in Arapongas, in northern Paraná, Brazil, in four distinct points identified as P1, P2, P3, and P4, as shown in Figure 1 (P1: 23º30'11,99'' S, 51º25'57,44'' W, P2: 23º30'00,34'' S, 51º25'59,84'' W, P3: 23º29'33,30'' S, 51º25'56,75'' W, P4: 23º30'20,49'' S, 51º25'03,88'' W). The samples were collected in two separate campaigns: in September 2015 (late winter) and in May 2016 (autumn). These four points were chosen because they present distinct characteristics. Point P1 is located near an unpaved road, and can receive residues from vehicular traffic and agricultural machinery. Point P2 is a well, which provided water for human consumption until the occurrence of reports that the water could be contaminated and unfit for consumption. Point P3 is located in an area used for growing tomatoes. Point P4 is located in a region used for raising cattle. Points P1 and P3 are water bodies tributaries to Pirapó river, and point P4 is a tributary to Ribeirão dos Apertados river. Rivers P1, P3, and P4 are shallow and stony. The main activities developed in the region are agriculture and the production of pesticides, in addition the location has little sanitation and drainage infrastructure.

2.3. Collection of samples

Sampling was based on the clean hands, dirty hands procedure. Surface water was collected at approximately 10 cm deep, with a polypropylene bucket sanitized with alcohol and ultrapure water and transferred to 4 L amber glass bottles, which had been previously washed. The bottles were placed in 3 L polypropylene bags, sealed, identified and stored in a cooler to be transported to the lab. In the laboratory, the samples were stored at 4 °C until the filtering procedure (no more than 48 h after sampling). Weather conditions for the day of sampling, and for a 5-day period prior to collection, were obtained at http://www.accuweather.com/en/br/brazil-weather.

2.4. Solid phase extraction procedure

The collected samples (4 L) were filtered, in 0.45 μm GF-3 glass-fiber filters (Macherey Nagel), to eliminate the particulate matter originated from the matrix. For the SPE procedure, C18 cartridges were conditioned, under vacuum, with 10 mL of acetonitrile and 10 mL of ultrapure water at a flow of 1 mL min^{-1}. During the conditioning, it is important to avoid the drying of the cartridge. Then, 250 mL of surface water sample was added to the cartridge, with a flow of 6 mL min^{-1} using a manifold (Agilent Technologies). Subsequently, the cartridge was washed with 5 mL of ultrapure water to remove the interferences from the matrix, and dried under vacuum for 30 minutes to remove the water.

Figure 1. Map of the study area, location of sampling points, identified by circles, in Arapongas, Paraná, Brazil (Google Earth, Jul 25, 2017)
Elution was performed with 10 mL of acetonitrile. After evaporation, until drying, under compressed air, the extract was reconstituted with 1 mL of acetonitrile and ultrapure water in the proportion of 70:30.

2.5. Instrumentation and chromatographic conditions

A high performance liquid chromatographer, model Shimadzu 920 LC, was used, equipped with a LC-20AT binary pump, DGU-20A5R degassing unit, SPD-M20A diode-array detector (DAD), CBM-20A controller, and SIL-10AF automatic sampler. The chromatographic column used was Poroshel 120 SB-C18 of 4.6 x 150 mm, 2.7 μm particle size (Agilent Technologies, USA), Poroshel 120 EC-C18, 4.6 x 5 mm guard column, 4.6 x 5 mm, 2.7 μm particle size (Agilent Technologies, USA). Chromatographic analyses were performed with injection of 20 μL of sample, and flow was maintained constant at 0.2 mL min⁻¹. Detection was evaluated at 203 nm wavelength. The proportions of the solvents were varied as follows: (i) an initial condition of H₂O:ACN of 60:40; (ii) the H₂O:ACN ratio was linearly altered to 34:66 during 88 min; (iii) reduction of the proportion of H₂O to zero during 10 min; (iv) only ACN was maintained for 10 min for cleaning of the column; (v) the H₂O:ACN relation was linearly altered to 60:40 during 10 min; and (vi) finally maintained at 60:40 for 27 min.

2.6 Validation of the method

The SPE-HPLC/DAD method for determination of alachlor was validated using the following figures of merit: linearity, sensitivity, selectivity, precision, accuracy and limits of detection and quantification. All figures of merit were evaluated in the surface water sample.

Sensitivity was evaluated at three wavelengths (203, 205, and 220 nm) using an analytical curve varying the concentration from 0.5 to 5 mg L⁻¹ (0.5; 1.0; 1.5; 2.0; 2.5; 3.0; 3.5; 4.0; 4.5; and 5.0 mg L⁻¹), built in ACN:H₂O (70:30). The concentration range was used for the development, validation and application of the analytical method. To investigate linearity, the samples were fortified with the alachlor solution, to obtain the concentrations of: 2; 4; 8; 12; 16; and 20 μg L⁻¹, and submitted to the SPE-HPLC/DAD procedure, the concentration was obtained by the linear regression method through the alachlor peak area. This process enables the pre-concentration of the analyte in 250 times, so the reading provided by the equipment will be the value of each concentration added to the sample, multiplied by 250, which will be equivalent to the range from 0.5 to 5 mg L⁻¹. The procedure was analyzed in triplicate. Selectivity was evaluated by comparing the analytical curves in ultrapure water and in the surface water sample, being parallel, the method is selective. The limits of detection (LOD) and limits of quantification (LOQ) were calculated by 3.3 and 10 times the estimate of the standard deviation of the linear coefficient divided by the angular coefficient of the analytical curves, respectively. Precision and accuracy were determined by SPE-HPLC/DAD at three concentration levels (3; 10; and 18 μg L⁻¹), after fortification with a standard solution of alachlor and pre-concentration of 250 times. The quantification of alachlor concentration in actual samples of surface water was calculated by external calibration.

2.7 Evaluation of alachlor persistence

Alachlor persistence in the environment was evaluated after fortification of ultrapure water and surface water samples with 20 μg L⁻¹ of standard solution of alachlor in acetonitrile, without the addition of preservatives. After fortification the samples were stored at room temperature and in the absence of light for 0; 15; 30; 44; and 225 days. After each period the samples were filtered in 0.45 μm pore size GF-3 glass-fiber filters (Macherey Nagel) and submitted to the SPE-HPLC/DAD procedure.

The decay coefficient and half-life of alachlor were estimated using the first order model, since the degradation of alachlor is exponential, according to equations 1 and 2 respectively.

\[ C_t = C_0 e^{-kt} \]  
\[ t_{1/2} = \frac{\ln \ln 2}{k} \]

Where \( C_t \) and \( C_0 \) are the total (dissolved + particulate) alachlor concentration at time \( t \) and \( t = 0 \), respectively, (μg L⁻¹), \( k \) is the decay coefficient (day⁻¹) and \( t_{1/2} \) is the half-life (day).

3. Results and Discussion

3.1. Method validation

Chromatographic runs were held at three different wavelengths, 203; 205; and 220 nm, in order to select that of greater sensitivity, in the concentration range from 0.5 to 5 mg L⁻¹, the typical correlation coefficients presented values around 0.999 for all wavelengths evaluated. The angular coefficients were 679829; 560378, and 252878 at 203; 205; and 220 nm, respectively; therefore, the best sensitivity was obtained at the wavelength of 203 nm. According to Lacorte et al., it is possible to analyze alachlor and metolachlor by LC-DAD in the range from 190 to 251 nm, and for the analysis of chromatograms at lower wavelengths, a certain amount of background absorption is detected.

Linearity was observed within the range from 2 to 2 μg L⁻¹ (concentration factor of 250 times, so this range corresponds to the range from 0.5 to 5 mg L⁻¹), with correlation coefficient of 0.9989 for surface water sample. The result shows that, in this concentration range corresponds to the range from 0.5 to 5 mg L⁻¹, the typical correlation coefficients presented values around 0.999 for all wavelengths evaluated. The angular coefficients were 679829; 560378, and 252878 at 203; 205; and 220 nm, respectively; therefore, the best sensitivity was obtained at the wavelength of 203 nm. According to Lacorte et al., it is possible to analyze alachlor and metolachlor by LC-DAD in the range from 190 to 251 nm, and for the analysis of chromatograms at lower wavelengths, a certain amount of background absorption is detected.

Linearity was observed within the range from 2 to 2 μg L⁻¹ (concentration factor of 250 times, so this range corresponds to the range from 0.5 to 5 mg L⁻¹), with correlation coefficient of 0.9989 for surface water sample. The result shows that, in this concentration.
range, the method is linear. The angular coefficients of the analytical curves, in both water samples, were used to evaluate selectivity. Values of 177344 and 176141 were observed, respectively. The curves were parallel, so the method is considered selective. The relationship of slope between the curves was 0.99; according to Peček et al., a 1.0 relationship indicates absence of effects of the matrix, and proportions of up to 10% different from 1.0 were considered by the authors as being responsible for a negligible matrix effect on the results. Thus, it is concluded that the surface water sample evaluated in this study did not promote matrix effect on the determination of alachlor.

LOD and LOQ for alachlor, in surface water were 0.68 μg L⁻¹ and 2.05 μg L⁻¹, respectively. In the literature, there are studies that determined alachlor concentration by high performance liquid chromatography and gas chromatography, coupled with different detectors. The significant variation in the LOD and LOQ values, obtained by different authors, is caused by several factors, such as extraction methodology, sample volume, number of analytes of interest, type of detector, separation technique.

The precision of the method was evaluated at three concentration levels: 3, 10, and 18 μg L⁻¹. It is worth noting that relative standard deviation (RSD) was less than 12%, indicating high precision of the SPE-HPLC/DAD method. According to the European Commission, RSD should not exceed 20% for the analysis of pesticide residues.

To the alachlor recovery, at concentrations of 3, 10, and 18 μg L⁻¹, it was observed the ranged from 89.56 ± 7.27 % to 103.59 ± 11.65 % in the surface water samples. Thus, the alachlor recoveries are within the acceptable recovery range of 70–120 %, established by the European Commission. RSD should not exceed 20 % for the analysis of pesticide residues.

Table 1. Alachlor concentration obtained in the surface water samples

| Points | Campaign 1 | Campaign 2 |
|--------|------------|------------|
|        | Mean concentration (μg L⁻¹) | RSD (%) | Mean concentration (μg L⁻¹) | RSD (%) |
| P1     | ND         | -         | 3.33 ± 0.03 | 0.87 |
| P2     | ND         | -         | ND         | -     |
| P3     | ND         | -         | 8.40 ± 0.44 | 5.22 |
| P4     | 9.65 ± 2.60| 26.97     | 7.48 ± 0.27 | 3.61 |

ND: not detected

In the first sampling campaign, it was observed that only point P4 presented quantifiable values of alachlor. In the second sampling campaign, alachlor concentration was detected in points P1, P3, and P4. Point 4 presented alachlor in the two sampling campaigns. The occurrence caused by diffuse pollution makes the origin unclear to us, that is, if it is caused by use in agricultural activities or by handling in the local pesticide company. The company, currently, does not produce alachlor, but have handled it in previous years.

The value greater than 20 % to RSD, obtained in the first campaign, refers to an environmental sample subject to variations in its characteristics, these can provide changes in the results of analysis of compounds in very low concentrations, as is the case of alachlor. Despite the variation obtained, the concentration value is in the same range as in the second campaign.

Precipitation may influence the results. For the first campaign there was the occurrence of 34 mm of rainfall, 5 days before the sampling procedure. For the second sampling campaign, within the five days before sampling, there was 27; 66; and 44 mm of precipitation. In rainy periods alachlor may have undergone leaching from soil to surface water. Therefore, surface runoff is a significant route of entry of pesticides in surface water.

According to Thomatou et al., pesticide content in surface waters depends on the frequency of rainfall, on the application and use of pesticides in agricultural activities; and on the physicochemical properties of the soil and of the substance, such as: solubility in water, vapor pressure, and partition coefficients.

Thomatou et al. evaluated samples in Amvrakia Lake (Western Greece) and found a maximum alachlor concentration of 807 ng L⁻¹ and the mean was 66.4 ng L⁻¹ with detection in 50.5 % of the samples evaluated. Cruzheiro et al. evaluated the presence of pesticides in the Estuary of the Mondego River (Portugal); surface water samples were collected between 2010 and 2011, and the annual mean values obtained for alachlor were 100 ng L⁻¹.

The alachlor concentration obtained by Abrantes et al., in surface water from Vela Lake, in Portugal, ranged from 1.13 to 3.47 μg L⁻¹ in the summer of 2004. After application of pesticides, in the fall of 2004, the concentrations ranged from 1.68 to 7.61 μg L⁻¹, during the first seasonal rains. The maximum alachlor concentration observed by Papadakis et al. in Pinos River, in northern Greece,
was 0.27 μg L⁻¹, detected after application. Vryzas et al.¹⁴ observed concentrations of pesticides after the rainy season during the month of application of pesticides. The alachlor concentration was 0.52 μg L⁻¹.

Herrero-Hernandez et al.¹⁶ carried out 4 campaigns in surface and groundwater, in the vineyard area of La Rioja (Spain), for 3 different collection points, and found that the occurrence of alachlor was greater than 50 % of the samples analyzed in one of the campaigns, for all the collection points. The highest value obtained was 11.98 μg L⁻¹ and the highest average was 1.27 μg L⁻¹. Silva et al.¹³ verified the presence of alachlor in 2 Mediterranean river basins in Portugal, with 19 % of the samples collected in the Tagus river showing values above the maximum acceptable concentration of 0.7 μg L⁻¹, referring to the environmental quality standards established by the 2013/39/EU of the European Parliament and the Council of the European Union.²⁶

The samples analyzed in this study presented alachlor concentrations higher than those obtained by Thomatou et al., Cruzeiro et al. and Vryzas et al.,⁷,¹⁰,¹⁴ and similar to that obtained by Abrantes et al. and Herrero-Hernandez et al.⁹,¹⁶ However, the alachlor concentration in the points analyzed was below the maximum concentration allowed in Brazilian legislation of 20 μg L⁻¹ for class I and II water bodies.²⁷

### 3.3 Evaluation of alachlor persistence in the environment

This evaluation was carried out to determine the behavior of alachlor over time, in two distinct media. For the study in ultrapure water, there was no significant trend resulting from storage time. Note that, after 15 days, there was a 21 % decrease in alachlor concentration in the surface water sample. After 30, 44, and 225 days, alachlor concentration decreased to 12.7; 11.7 and 9.6 μg L⁻¹, respectively. It is worth mentioning that, after 225 days, alachlor was still present in the aquatic environment; therefore, its persistence in the environment is subject of concern.

The results obtained in this study are consistent with those obtained by Mouvet et al.²⁸ Mouvet and colleagues studied alachlor recovery in surface water samples and observed significant loss of 47 % of alachlor after 30 days, for an initial concentration of 0.5 μg L⁻¹. The authors suggest that biological transformation may be involved in the alachlor loss observed in surface water.

Paule et al.²⁹ evaluated the alachlor stability using the suspension of natural phototrophic biofilms from two distinct lotic environments, using an initial concentration of 20 μg L⁻¹ and incubation time of 10 days, half-life values of 8 ± 0.4 and 30.8 ± 12.1 days were obtained. The authors found that the half-life, degradation of alachlor, is dependent on the initial concentration of the compound, the environmental and operational conditions and the nature of the alachlor.

The half-life of alachlor as a function of time is shown in Figure 2, it is observed that the test time condition is extremely relevant in the evaluation of alachlor half-life, Paule et al.,²⁹ in only 10 days of testing, verified a half-life around 30 days, in the present study, in 15 days of assay the half-life was 43 days, however, when the test time is extended to 30; 44 and 225, the half-life increases to 60; 71 and 249 days, respectively. These results fall within the range presented by the Rotterdam Convention⁸, according to the document, DT50 (time taken for 50 percent of the parent compound to disappear from water by transformation) values to Alachlor in the range of 200-500 days in river water.

### Conclusions

Thus, the presence of alachlor in surface water, from a region with suspected contamination of environmental matrices by pesticides, was confirmed in this study, and
its concentration is below the maximum allowed value, of 20 μg L⁻¹, established by Resolution 357 of CONAMA of 2005, for class I and II fresh surface waters. It is also pointed out that, considering the reduction in the marketing and use of alachlor in Brazil, it is expected a gradual decrease in its concentration in environmental matrices. Besides that, the persistence of alachlor in water was assessed, under controlled conditions, it was found that this pesticide has a high persistence, confirming previous studies, and indicating that the evaluation period is extremely relevant in the study of the half-life of alachlor, using times of up to 225 days, it was observed that the greater the contact time between the pesticide and the surface water, the higher the calculated value for the half-life.

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