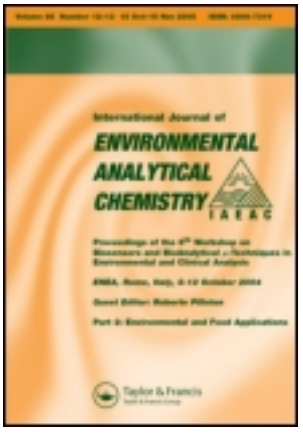

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/geac20

Pendimethalin in surface waters of rivers in the proximity of irrigated paddy fields by solid phase microextraction and gas chromatography

Léa L. Freitas [a b], Ernani S. Sant'Anna [a], Eliane A. Suchara [c], Vanira S. Benato [b d] & Eduardo Carasek [d]

[a] Department of Food Science and Technology, Federal University of Santa Catarina, Rod. Admar Gonzaga, 1346, Florianópolis, SC, Brazil, CEP: 88034-001

[b] State Health Secretary of Santa Catarina, Central Public Health Laboratory, Av. Rio Branco, 152, Florianópolis, SC, Brazil, CEP: 88015-201

[c] Federal University of Mato Grosso, Pontal do Araguaia, MT, Brazil, CEP: 78600-000

[d] Department of Chemistry, Federal University of Santa Catarina, Trindade, Florianópolis, SC, Brazil, CEP: 88040-900

Available online: 20 Oct 2011

To cite this article: Léa L. Freitas, Ernani S. Sant'Anna, Eliane A. Suchara, Vanira S. Benato & Eduardo Carasek (2012): Pendimethalin in surface waters of rivers in the proximity of irrigated paddy fields by solid phase microextraction and gas chromatography, International Journal of Environmental Analytical Chemistry, 92:3, 313-323

To link to this article: http://dx.doi.org/10.1080/03067310903582309

Intern. J. Environ. Anal. Chem.
Vol. 92, No. 3, 15 March 2012, 313–323

Taylor & Francis
Taylor & Francis Group

Pendimethalin in surface waters of rivers in the proximity of irrigated paddy fields by solid phase microextraction and gas chromatography

Léa L. Freitas[ab], Ernani S. Sant'Anna[a]*, Eliane A. Suchara[c], Vanira S. Benato[bd] and Eduardo Carasek[d]

[a]*Department of Food Science and Technology, Federal University of Santa Catarina, Rod. Admar Gonzaga, 1346, Florianópolis, SC, Brazil, CEP: 88034-001;* [b]*State Health Secretary of Santa Catarina, Central Public Health Laboratory, Av. Rio Branco, 152, Florianópolis, SC, Brazil, CEP: 88015-201;* [c]*Federal University of Mato Grosso, Pontal do Araguaia, MT, Brazil, CEP: 78600-000;* [d]*Department of Chemistry, Federal University of Santa Catarina, Trindade, Florianópolis, SC, Brazil, CEP: 88040-900*

(*Received 20 April 2009; final version received 12 December 2009*)

The aim of this study was to develop an analytical methodology for the determination of the herbicide pendimethalin in river waters in the towns of Turvo and Meleiro in the southern region of Santa Catarina State, Brazil. The method, based on solid phase microextraction (SPME) followed by separation and detection by gas chromatography (GC) and electron capture detection (ECD), respectively, was optimised and validated. The limits of detection (LOD) and quantification (LOQ) of 0.02 and 0.06 $\mu g\,L^{-1}$, respectively, and recovery values in the range of 86.2 (±11.5)% to 103.4 (±9.5)% were obtained. It was verified that 53 river water samples showed contamination by pendimethalin at levels that ranged from 0.06 to 0.38 $\mu g\,L^{-1}$.

Keywords: pendimethalin; SPME; river water; herbicides; analytical method

1. Introduction

Pesticides include an enormous variety of chemical compounds which differ from one another not only structurally, but also in their mode of action, metabolism and toxicity to humans [1]. The indiscriminate use of pesticides has led to the appearance of their residues in the different environmental compartments (water, soil and air) and in food products. As a result of this, given the hazardous nature of pesticides in terms of human health and the maintenance of biodiversity, there is currently an urgent necessity for studies of efficient monitoring of possible environmental contamination. Water contamination problems must be solved at source, because, on reaching natural waters, little can be done to reverse the harm to the water quality, which, in this case, has serious consequences [2].

Of the many herbicides used on crops, pendimethalin [N-(1-ethylpropyl)-2,6-dinitro-3,4-xylidine] is significant. The occurrence of pendimethalin and its metabolites in soil are the result of direct application, whereas an aquatic presence is most often due to indirect exposure, which because of evaporation and leaching, may be potentially present in air

*Corresponding author. Email: ernanis@cca.ufsc.br

ISSN 0306–7319 print/ISSN 1029–0397 online

http://dx.doi.org/10.1080/03067310903582309
http://www.tandfonline.com

and water, including groundwater [3]. These herbicides could be phytotoxic when runoff water is used in irrigation and have an adverse environmental impact [4].

In Brazil, there are few studies that have investigated the occurrence of the herbicide pendimethalin in surface waters. International organisations such as the United States Environmental Protection Agency (USEPA) and the European Union (EU) have begun to implement some control, establishing limits in relation to the concentrations of pesticides found in waters. Also, these institutions have organised hazard lists of these compounds. The levels permitted by the EU are determined by the Drinking Water Directive 80/778/EEC [5], which establishes that the Maximum Admissible Concentration (MAC) of individual and total pesticide concentrations in potable water must not exceed $0.1\,\mu g\,L^{-1}$ and $0.5\,\mu g\,L^{-1}$, respectively. In Brazil, there is the directive n° 518 of the Health Ministry of 25 March 2004 [6], which introduced maximum admissible limits for new pesticides for human water consumption, being $20\,\mu g\,L^{-1}$ for pendimethalin.

In general, environment waters cannot be analysed without sample pretreatment because of their complexity. A sample preparation step is necessary to extract traces of pesticides, in order to bring the analytes to a suitable concentration and to remove the compounds that interfere in the matrix. The solid-phase microextraction (SPME) technique was developed by Pawliszyn [7] and its original form is based on the sorption of analytes by a chemically modified silica fibre, with subsequent thermal desorption of analytes in a gas chromatograph. It is a relatively simple technique from the experimental point of view, and has many advantages over traditional techniques, for example, the analytical procedure is simpler and faster than liquid-liquid extraction (LLE), and solid phase extraction (SPE). In general, SPME requires a comparatively small volume of sample, cleaner extracts are obtained, and solvents are not used for the elution [8]. The number of experimental parameters to be optimised and controlled is much higher than in other sample preparation techniques. The main factors which affect the quantity of analyte extracted by the fibre are: choice of fibre coating; extraction mode, temperature and time; sample pH, stirring speed; ionic strength of the medium; and desorption time [7]. These parameters must be evaluated and adjusted during method development and are often matrix-specific, and can influence SPME efficiency. The SPME method has been successfully applied to the trace determination of pollutants in waters, such as pesticides [9–12].

The objective of this study was to develop, optimise and validate an analytical method using the SPME-GC-ECD technique for the determination of pendimethalin in surface waters, as well as to evaluate the contamination by this herbicide in samples of river waters of the southern region of Santa Catarina, Brazil.

2. Experimental

2.1 *Samples*

Samples were collected in the municipalities of Turvo (latitude 28°55′34″ and longitude 49°40′45″) and Meleiro (latitude 28°49′43″ and longitude 49°38′09″) in the southern region of Santa Catarina. Collections were performed each month during the period of February to May 2007. A total of 82 samples were collected, 26 being from the River Amola Faca, 31 from the River Manoel Alves, 14 from the River Itoupava and 11 from the River Jundiá. The collection was carried out manually using one litre amber glass flasks, conditioned in polystyrene boxes and kept under refrigeration in ice. The samples were transported directly to the Central Public Health Laboratory of Santa Catarina, where

they were filtered through cellulose acetate membranes (0.45 μm). Samples that were not immediately analysed were kept, for a maximum time of 5 days, at −18°C until analysis.

2.2 *Reagents*

The pendimethalin standard was purchased from Sigma-Aldrich® (USA) with a grade of purity higher than 98.3%. Sodium hydroxide and sodium chloride p.a. (99%) and sulfuric acid p.a. were obtained from Synth® (Brazil).

The intermediate and working solutions were prepared in HPLC grade acetonitrile (Merck®, Germany) and used in the sample spiking and in the obtainment of the analytical curves.

2.3 *Instrumentation*

The analysis was carried out with a Varian CP 3800 (USA) gas chromatograph, coupled to an ECD detector. The capillary column used was CP SIL 8CB 50 m × 0.53 mm, with a film thickness of 5.0 μm (Varian®, USA). The injections were carried out manually in *splitless* mode with the injector at 280°C. The carrier gas flow of nitrogen (99.999%) was 1 mL min^{-1} at the initial temperature of the column oven. The temperature programme of the chromatographic column used for the separation of the herbicide under study was: 60°C (4 min) heating to 140°C at 30°C min^{-1}, at 10°C min^{-1} up to 270°C (5 min), and heating to 280°C at 50°C min^{-1} (5 min). The detector temperature was 300°C.

The identity of the herbicide pendimethalin found in the environmental samples was confirmed using a Saturn 2100 GC coupled to a mass selective detector and a *split-splitless* manual injector. A VF-5 ms capillary column, 30 m × 0.25 mm, with a film thickness of 0.25 μm was used for the herbicide separation. The carrier gas used was helium with a flow of 1 mL min^{-1} at the initial oven temperature of the column (60°C). The temperature programme of the chromatographic column was: 60°C (4 min), heating to 140°C at 30°C min^{-1}, at 10°C min^{-1} to 270°C (5 min), and a new heating of 50°C min^{-1} up to 280°C (5 min). The injector and detector temperatures were 280°C and 300°C, respectively. The data were obtained using the software MS Workstation 6.0.

2.4 *Solid phase microextraction procedure*

The SPME holder and fibres were purchased from Supelco (USA), being fibres previously conditioned following manufacturer's recommendations for time and temperature. For pendimethalin extraction, analytical parameters were standardised on univariate mode, in duplicate, at a concentration of 100 μg L^{-1}. Parameters evaluated were: type of fibre (Polyacrylate – PA, Carbowax-Divinylbenzene – CW-DVB, Polydimethylsiloxane – PDMS, and Carboxen-Polydimethylsiloxane – CAR-PDMS); extraction method (direct and headspace), pH (2, 4, 5, 6, and 8), sample agitation (0, 500, 750 and 1000 rpm), saline concentration (0, 5, 10, 15 and 30%), temperature (22, 40, 70 and 80°C), sample volume (5, 10, 15 and 45 mL) and extraction time (20, 40, 70, 100 and 130 min).

2.5 *Method validation*

The linearity for the herbicide pendimethalin was evaluated at concentrations of 0.05; 0.1; 0.25; 0.5 and 0.74 $\mu g\,L^{-1}$, in triplicate. The limit of detection of the method was calculated as 3.3 × standard deviation (SD) of the blank sample divided by the angular coefficient of the calibration curve (LOD = 3.3 × SD a/b) and the limit of quantification of the method was considered as 10 × SD of the blank sample divided by the angular coefficient of the calibration curve (LOQ = 10 × SD a/b), where: SD = estimated standard deviation, a = standard deviation of the linear coefficient, b = angular coefficient. Standard deviation of blank was determined by using the area of 7 consecutive extractions. The recovery was evaluated in two matrices, river water and tap water, in concentrations of 0.18 and 0.37 $\mu g\,L^{-1}$, in triplicate. The repeatability ($n = 5$) was also evaluated at concentrations of 0.18 and 0.37 $\mu g\,L^{-1}$.

3. Results and discussion

Considering the innumerable experimental variables, which may interfere with the analyte extraction procedure, an optimisation of these variables is necessary in order to improve the efficiency of the extraction process. For the determination of pendimethalin the following parameters, which are the main interferents in analyte extraction, were evaluated in the univariate mode (one variable each time): type of fibre, extraction mode, time and temperature, pH and saline concentration of the sample, sample agitation speed and desorption time. As an initial optimisation procedure of the methodology some variables were fixed and the optimisation was started using a sample volume of 15 mL, direct extraction mode, extraction time of 70 min; agitation of 750 rpm; pH 8; and temperature of 70°C. Values were stipulated according to previous experiments and literature data [7,13,14]. After the optimisation of each variable, the parameter which gave the best result was defined and fixed for the subsequent procedures.

3.1 *Type of fibre*

Four different types of commercial fibres were tested: Polyacrylate (PA) 85 μm, Carbowax-Divinylbenzene (CW-DVB) 65 μm, Polydimethylsiloxane (PDMS) 100 μm and Carboxen-Polydimethylsiloxane (CAR-PDMS) 75 μm, in order to carry out the pendimethalin extraction in water samples. The PA (100 ± 8.6%) and PDMS (88 ± 5.2%) fibres showed the best analyte extraction values. These results are in agreement with Guan *et al*. [14] and it has been reported that the dinitroanalines have been analysed using PDMS and PA fibres [9]. The other fibres studied (CAR-PDMS and CW-DVB) gave low recovery results for the compound studied: 56.9 ± 21.5% and 3.6 ± 1.9% respectively. Thus, considering that the PDMS fibre gave good extraction results and that the PA fibre has a shorter useful working lifetime than the PDMS fibre, the latter was chosen for the extraction of pendimethalin in water. Recovery of PDMS fibre was about 70 extractions.

3.2 *Sample agitation*

In order to determine the influence of sample agitation on the extraction efficiency, four stirring speeds were evaluated: no agitation, 500, 750 and 1000 rpm. An increase in the diffusion of the analyte in the sample matrix to the extraction fibre was observed.

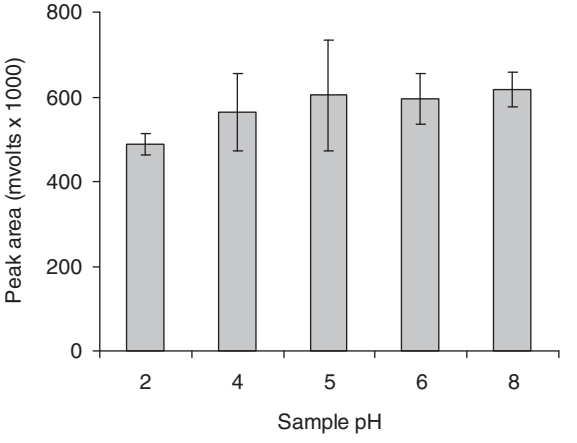

Figure 1. Sample pH optimisation in pendimethalin extraction (peak area) in water samples. Vertical bars represent means ± S.D.

Analyte was extracted at the proportions of 10, 72.6, 81.4 and 100%, respectively. With the increase in the agitation an equilibrium state is reached more rapidly. In spite of the equilibrium time decreased progressively with the increase in the agitation rate, very fast agitation speeds tend to be uncontrollable and a fast rotation speed may lead to low precision measurements [15]. Thus, the speed of 750 rpm was defined for the optimisation of the subsequent parameters, since this speed also gave good extraction results.

3.3 *Influence of pH*

The adjustment of some physico-chemical characteristics of the matrix can affect significantly the efficiency and reproducibility of the extractions. Among the parameters that promote a change in sample conditions, the influence of pH is of great importance. In this study the pH levels of 2, 4, 5, 6 and 8 were evaluated. Care should be taken regarding the pH extremes (lower than 2 and higher than 11), which may damage the fibre coating. The results obtained for each pH value studied are shown (Figure 1). Considering the results obtained, it can be observed that for pH 2 less recovery in the pendimethalin extraction was obtained in comparison to the higher pH values. In the range of 4 to 8 no significant difference in the extraction was found, and a pH of 8 was defined for the methodology under study, considering that extraction was efficient at this pH value and several reports indicating that better results for extraction are achieved at neutral or basic pH. According to literature data, when pH values are neutral and basic, extraction yields are higher than in acidic pH [12,13]. Boyd-Boland *et al*. [13] studied the influence of pH on the extraction of dinitroanilines and did not observe significant effects on the extraction varying the pH from 4 to 11.

3.4 *Influence of salt addition*

In order to determine the influence of salt (NaCl) on the extraction procedure five levels of saline concentration were investigated: 0, 5, 10, 15 and 30%. It was observed that on increasing the salt concentration in the sample, a decrease in the quantity of pendimethalin

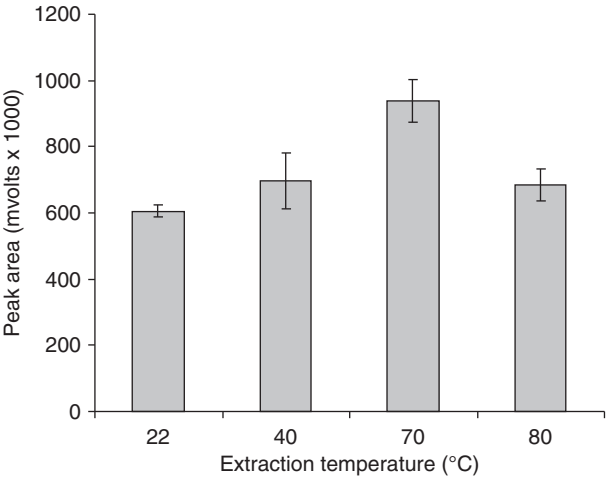

Figure 2. Optimisation of pendimethalin (peak area) extraction temperature in water samples. Vertical bars represent means ± S.D.

extracted occurred. Boyd-Boland *et al.* [13] also observed that the efficiency of the dinitroanilines decreased with an increase in ionic strength. Thus, it was defined that the extraction would be carried out without the addition of salt to the sample, since it has a negative effect. The effect of the addition of salt is dependent on the polarity of the analyte, the salt concentration and the sample matrix. Increasing of ionic strength aims to reduce interaction between the analyte and water. However, in some cases when highly polar analytes are involved, it can ionically dissociate in aqueous solution, tending to remain in solution and, consequently, present lower affinity for PDMS fibre, which presents apolar characteristic. Thus, a lower extraction efficiency will be observed [16]. Compounds with low hydrophobicity can present decreased extraction efficiency with the increasing in NaCl concentration [12].

3.5 *Sample temperature*

The extraction temperatures evaluated were 22, 40, 70 and 80°C and the results obtained can be seen in Figure 2. This study showed that an increase in the extraction occurred up to a temperature of 70°C after which a drop in the pendimethalin extraction was observed. A similar result was observed by Guan *et al.* [14] where a decrease in the extraction efficiency occurred at above 70°C when analysing blood samples and at above 90°C when analysing water samples. Thus, it was verified that an excessive extraction time at high temperatures may lead to analyte loss. This is because the process of analyte absorption by fibre is an exothermic process and the high temperature may decrease the quantity extracted. An extraction temperature of 70°C was defined for the optimisation of the subsequent parameters.

3.6 *Sample volume*

The extraction efficiency for different sample volumes (5, 10, 15 and 45 mL) was studied. It was observed that with an increase in the sample volume there was an increase in the

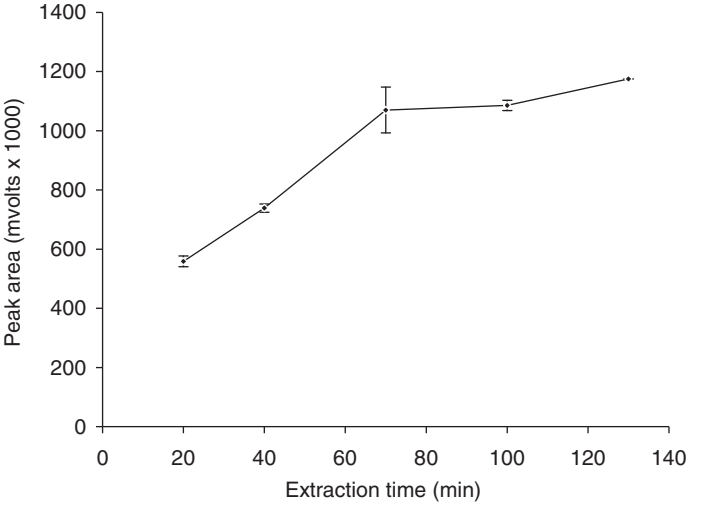

Figure 3. Optimisation of pendimethalin (peak area) extraction time in water samples. Vertical bars represent means ± S.D.

quantity of analyte extracted. However, although the volume of 45 mL gave the best extraction result, the volume of 15 mL was selected due to the laboratory conditions, such as vial availability, it is worth noting that the volume of 15 mL also gave good extraction values. In general, amount of analyte absorbed at stationary phase increases with the increasing of sample volume and, as a consequence, sensitivity also increases [9]. According to González-Barreiro *et al.* [17], in a study where volumes were optimised, better results were found to be between 4 to 120 mL.

3.7 *Extraction time*

The extraction was optimised in order to determine the time required for an analyte to reach the equilibrium between the sample matrix and the stationary phase [9]. Thus, to establish the extraction profile the extraction times of 20, 40, 70, 100 and 130 min were evaluated. It was observed (Figure 3) that after 130 min of extraction the equilibrium had not been reached, thus, in order to achieve a greater analytical frequency (which is desirable in routine procedures) a time of 70 min was defined for the pendimethalin extraction.

Several studies have shown that a shorter time than the equilibrium time can be selected provided that the extraction are timed carefully to prevent from deviations of the amount extracted [18]. For some compounds the time required to establish the equilibrium is long, in this case although the SPME has a maximum sensitivity at the point of equilibrium, the complete equilibrium is not necessary due to the linear relation between the quantity of analyte extracted by the fibre and the initial concentration of the sample under non-equilibrium conditions. However, care should be taken to ensure that the exposure of the fibre to the sample is precise, in order to provide reproducible results [15]. In many applications where SPME is performed with an auto sampler, extraction times are often equal to the time required for the analysis. Thus, extraction of a sample occurs

during the GC run of the previous one. Typical extraction times are in a range from 20 to 40 min, when several pesticides are to be determined in the same sample [18].

3.8 *Desorption time*

Desorption time study was carried out at a temperature of 270°C (maximum temperature recommended for PDMS fibre by manufacturer) and evaluated desorption times of 3 and 5 min. The fibre was injected in three consecutive runs. It was found that the pendimethalin was rapidly removed from the fibre and transferred to the chromatographic column. When the desorption time of 3 min was evaluated, it was observed that in the second injection of the fibre for 3 min there was a residual area of 0.22% and in the third of 0.11% of the area obtained in the first injection. For the desorption time of 5 min, an area of 0.16% was observed for the second run and after the third run no residual area was observed. Therefore, both times can be used for desorption, since residual areas were less than 10%. The time of 5 min was taken as the standard for desorption in the following analysis.

After the optimisation of all of the parameters the methodology was defined as the extraction in direct mode using PDMS fibre, the sample adjusted to pH 8, without addition of salt and using a 15 mL volume, the extraction temperature was 70°C, stirring speed was 750 rpm and extraction time was 70 min.

3.9 *Analytical features*

Based on the optimised methodology the validation of the method was carried out. The linearity of the parameters, LOD, LOQ, recovery and repeatability were investigated. Analytical curve was performed routinely, at each sample collection, and a significant matrix effect was not observed. For river water, linearity was found within the range of 0.06 to 0.74 $\mu g\,L^{-1}$ and the correlation coefficient (R^2) was 0.9938. The LOD and LOQ values found for pendimethalin were 0.02 and 0.06 $\mu g\,L^{-1}$, respectively. These values are considered acceptable and well below the admissible limit of 20 $\mu g\,L^{-1}$ in water for human consumption [6]. In the literature, linearity has been reported for pendimethalin in water samples in the range of 0.1 to 10 $\mu g\,L^{-1}$ using SPME [14] and in the range of 0.025 to 0.2 $\mu g\,L^{-1}$ in water samples using SPE [19]. Also, LOD values in water using the SPME technique of 0.1 $\mu g\,L^{-1}$ by GC-ECD [14] and of 0.02 $\mu g\,L^{-1}$ using NPD, and 0.0001 $\mu g\,L^{-1}$ by MS [13] have been reported.

Recovery ranged from $86.2 \pm 11.5\%$ to $102.3 \pm 16.1\%$ and from $97.7 \pm 9.6\%$ to $103.4 \pm 9.5\%$ for river and tap water, respectively. The precision was evaluated through the repeatability ($n = 5$) in the concentrations of 0.18 and 0.37 $\mu g\,L^{-1}$, the RSD values found being between 14.6 and 15.3%, respectively. These values are considered acceptable; since they are below the maximum of 20% defined for repeatability tests [20]. Guan *et al.* [14] obtained RSD values of 7.7 to 12% using SPME.

The SPME technique in direct extraction mode showed results better than the values found in the literature. Recovery values reported for pendimethalin in water obtained through the SPME technique in headspace mode are $58 \pm 8.3\%$ for a concentration of 0.5 $\mu g\,L^{-1}$ and $59 \pm 5.1\%$ for a concentration of 1.0 $\mu g\,L^{-1}$ [14] and a recovery of 86.8% for a concentration of 0.025 $\mu g\,L^{-1}$ using the SPE technique with the use of C18 cartridges [19].

3.10 *Environmental samples*

A total of 82 surface water samples were analysed, which were collected from the Amola Faca, Jundiá, Itoupava and Manoel Alves rivers. The samples were analysed according to the previously optimised and validated method.

Of the samples analysed, it was verified that 53 had pendimethalin contamination at levels that varied from 0.06 to 0.38 $\mu g\,L^{-1}$. A contamination of 65% of the total number of samples analysed was observed. Of the four rivers from which the samples were collected, the River Amola Faca had the highest percentage of contaminated samples (81%) and the levels varied from 0.06 to 0.24 $\mu g\,L^{-1}$. It was also observed that in all of the rivers studied, the highest levels found were for the third collection carried out in April 2007. In the River Itoupava, 57% of the samples had pendimethalin at levels between 0.06 and 0.16 $\mu g\,L^{-1}$. The river which showed the lowest number of contaminated samples was the River Jundiá, with pendimethalin being detected in only 27% of samples, and contamination was only found in the month of April, with levels varying from 0.14 to 0.19 $\mu g\,L^{-1}$. The River Manoel Alves showed contamination in 68% of the samples analysed, in the range of 0.06 to 0.38 $\mu g\,L^{-1}$, and the highest levels of contamination were found in the months of April and May.

A diversity of factors may have influenced the levels of herbicide found. These include climatic factors such as temperature and pluvial precipitation (rain). It is difficult to correlate with precision the reason for the slightly higher levels of pendimethalin found in April (third collection). It was observed that in the period during which this third sample collection was carried out, the temperature was high and the rivers had large volumes of water (full).

The pendimethalin was found for each sample collection. In the first collection carried out in February, the presence of pendimethalin was only observed in one sample of the River Amola Faca. In the second collection (March) an increase in the number of contaminated samples was observed and the concentration range varied from 0.06 to 0.16 $\mu g\,L^{-1}$. In the second collection no contaminated samples were found in the River Jundiá. Regarding the other rivers studied, the River Amola Faca showed the greatest concentrations of pendimethalin. In the third and fourth collections the highest levels of pendimethalin were found. The levels varied from 0.09 to 0.31 $\mu g\,L^{-1}$ and from 0.08 to 0.38 $\mu g\,L^{-1}$ in April and May, respectively. All samples collected in April showed contamination by pendimethalin. Of all the samples analysed, the highest concentrations found were in the River Manoel Alves (0.38 $\mu g\,L^{-1}$), in April and May.

In Figure 4 it can be observed that the behaviour of pendimethalin during the study period was similar for the three rivers Amola Faca, Jundiá and Manoel Alves, where an increase in the pendimethalin occurred until April, followed by a decrease in the last collection.

For the River Itoupava, this increase was observed in the third collection and remained in the last. It should be noted that for all of the samples which showed pendimethalin contamination, the levels found were well below the maximum admissible limit set by Brazilian legislation [6]. However, it should be considered that according to the Drinking Water Directive 80/778/EE [5], EU legislation only a concentration of 0.1 $\mu g\,L^{-1}$ is allowed in potable water for any individual herbicide and the sum of the herbicides cannot surpass the level of 0.5 $\mu g\,L^{-1}$. Considering the maximum admissible level of the EU of 0.1 $\mu g\,L^{-1}$, 41.5% of the samples were above this value. Although the matrix used in this study was

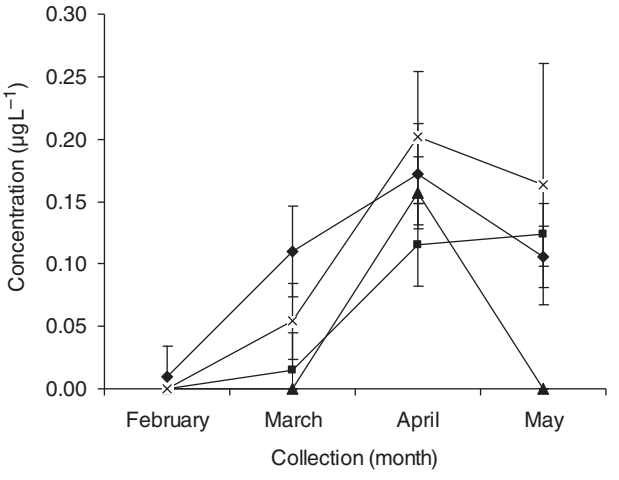

Figure 4. Pendimethalin average concentrations in river water samples according to the river and month of collection. The data points are as follows: -◆- Amola Faca, -■- Itoupava, -▲- Jundiá and -×- Manoel Alves. Vertical bars represent mean ± S.D.

surface water from rivers, it is important to emphasise that these are water bodies which supply the whole region.

In the literature there are reports of pendimethalin in sea water in a concentration of $0.00072\,\mu g\,L^{-1}$ [21], in bay water at levels of $0.018\,\mu g\,L^{-1}$, with only one contaminated sample in this study [22], in lake water levels of $0.004\,\mu g\,L^{-1}$ have been found [23] and in river water a concentration of $0.32\,\mu g\,L^{-1}$ [24]. Hoffman *et al.* [24] on analysing river water samples in the United States in 2000, found that 11% of the samples were contaminated with pendimethalin.

4. Conclusion

The SPME-GC-ECD technique showed good analytical results, regarding the linearity and limit of detection and quantification in the determination of pendimethalin in water. Besides showing advantages in relation to a decrease in the analysis time and non-use of solvent, the method is simple and sensitive. It was verified that 53 samples had contamination at levels that varied between 0.06 and $0.38\,\mu g\,L^{-1}$, with contamination being found in the four rivers studied. The river which had the highest number of contaminated samples was the Amola Faca, followed by the rivers Manoel Alves, Itoupava and Jundiá, respectively. The limits of detection found were sufficiently low to allow the detection of this compound at a level of $0.1\,\mu g\,L^{-1}$, the maximum admissible concentration defined by the European Union for the presence of any pesticide in waters destined for human consumption, without prior treatment. Even though concentration of pendimethalin was not detected above the admissible limit set by Brazilian legislation, it is worth noting the importance of monitoring for this herbicide.

Acknowledgements

The authors wish to thank the *Laboratório Central de Saúde Pública de Santa Catarina*/Central Public Health Laboratory of Santa Catarina State, (LACEN-SC) for financial support.

References

[1] G. Morasso, C. Bolognesi, E. Duglio, and M. Musso, Trends Food Sci. Tech. **11**, 379 (2000).
[2] S.C.N. Queiroz, C.H. Collins, and I.C.S.F. Jardim, Quim. Nova. **24**, 68 (2001).
[3] M. Strandberg and J.J. Scott-Fordsmand, J. Chromatogr. A **733**, 217 (1996).
[4] S.H.J. Tekel, Ecotox. Environ. Safe. **57**, 190 (2004).
[5] European Commission. Drinking Water Directive. http://ec.europa.eu/environment/water/water-drink/index_en.html.
[6] Brasil, Ministério da Saúde, Portaria No. 518 de 25 de março de 2004.
[7] J. Pawliszyn, editor, *Applications of Solid Phase Microextraction* (RSC, Cambridge, UK, 1999), p. 655.
[8] C. L. Arthur and J. Pawliszyn, J. Anal. Chem. **62**, 2145 (1990).
[9] L.J. Krutz, S.A. Senseman, and A.S. Sciumbato, J. Chromatogr. A **999**, 103 (2003).
[10] F.J. Arrebola, S. Cortes Aguado, N. Sánchez-Morito, A. Garrido Frenich, and J.L. Martínez Vidal, Anal. Lett. **37**, 99 (2004).
[11] M. Sakamoto and T. Tsutsumi, J. Chromatogr. A **1028**, 63 (2004).
[12] C. Rocha, E.A. Pappas, and C. Huang, Environ. Pollut. **152**, 239 (2008).
[13] A.A. Boyd-Boland and J. Pawliszyn, J. Chromatogr. A **704**, 163 (1995).
[14] F. Guan, K. Watanake, A. Ishii, H. Seno, T. Kumazawa, H. Hattori, and O. Suzuki, J. Chromatogr. B: Anal. Technol. Biomed. Life Sci. **714**, 205 (1998).
[15] H. Kataoka, H.L. Lord, and J. Pawliszyn, J. Chromatogr. A. **880**, 35 (2000).
[16] F. M. Lanças, *Extração em Fase Sólida* (SPE). Ri Ma, 96 (2004).
[17] C. González-Barreiro, J. Chromatogr. A **896**, 373 (2000).
[18] C. Miège and J. Dugay, Analusis Magazine **26**, 137 (1998).
[19] I.M. Bruzzoniti, C. Sarzanini, G. Costantino, and M. Fungi, Anal. Chim. Acta **578**, 241 (2006).
[20] M. Ribani, C.B.G. Bottoli, C.H. Collins, I.C.S.F. Jardim, and L.F.C. Melo, Quim. Nova. **27**, 771 (2004).
[21] R. Carafa, J. Wollgast, E. Canuti, J. Ligthart, S. Dueri, G. Hanke, S.J. Eisenreich, P. Viaroli, and J.M. Zaldívar, Chemosphere **69**, 1625 (2007).
[22] S.J. Lehotay, J.A. Harman-Fetcho, and L.L. McConnell, Mar. Pollut. Bull. **37**, 32 (1998).
[23] N.D. Camper, T. Whitwell, R.J. Keese, and M.B. Riley, Ecotoxicol. Environ. Saf. **57**, 190 (2004).
[24] R.S. Hoffman, P.D. Capel, and S. Larson, Environ. Toxicol. Chem. **19**, 2249 (2000).