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# Relation factor: A new strategy for quality control in the determination of pesticides in environmental aqueous matrices

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ABSTRACT

The effects promoted by environmental aqueous matrices on pesticide determinations have been assessed, and for the first time, a simple, low-cost and efficient strategy for the correction of analytical results has been determined. This method can be useful as a parameter of quality control in a quality assurance programs. Evaluation of the matrix effect showed that environmental aqueous matrices, e.g., estuarine water, promote a distinctive and significant effect on the determination of pesticides. The picloram, atrazine and methyl parathion pesticides suffered the smallest effects promoted by the estuarine matrix, whereas chlorpyrifos and cypermethrin suffer a significant effect. For picloram, the matrix effect was a function of its physiochemical properties. However, for atrazine, methyl parathion, chlorpyrifos and cypermethrin, the matrix effect was promoted by environmental matrix components. As strategy for analytical quality control, it has been determined that there are relation factors (RFs) between pesticides and the selected surrogates standards. These RFs are not altered by the complexities and compositions of simple and complex aqueous matrices. Predetermined RFs was applied to the picloram, atrazine and methyl parathion assessment in a real sample from the estuary of the Jaguaribe River, and the results showed that when no quality control was applied, the concentration levels would be underestimated, leading to incorrect results and inaccurate conclusions.



## 1. Introduction

There is an ongoing need for the production of equipment with higher sensitivities and also efficient extraction procedures for the determination of lower levels of organic chemicals that are considered environmental pollutants. Classical analyses of organic compounds have for a time involved several steps, which cause drawbacks when trace or ultra-trace concentrations are involved with raw complex matrices, such as environmental matrices (sediment, soil, water, and air) [1].

Currently, there is a great movement toward the development of procedures that use little or no solvent extraction, a small amount of material (e.g., adsorbent) and samples. This movement has resulted in reduced extraction times, improved quantifications, minimal laboratory routine or easy automation, greener analytical methodologies and reduced analysis costs [2–5]. These methods denoted a need for the miniaturization of basic principles or classical methods (liquid–liquid, solid–liquid and liquid–solid extractions) while also decreasing the number of steps between sampling and determining/quantifying the analytes of interest [6–8]. Although these advances have been developed, the study of organic contaminant levels using traditional or miniaturized methods, especially for pesticide determinations in environmental samples, involves many steps: the collection, transport and storage of samples; sample preparations; chromatographic determinations (final analyte determinations); calculations and interpretations of the data; and the quality assurance and quality control QA/QC of the analytical measurements and results [9]. In both procedures (traditional or miniaturized methods), quality control often receives less attention or is sometimes not even considered in many academic works that focus on the quantification of an analyte of interest, the quality of materials as well as adsorption, toxicological or biodegradation studies. The greatest care is instead directed toward systematic sample preparations and chromatographic detections.

The quality assurance or quality assessment (QA) program represents the global procedures for quality assurance in laboratory operations and aims to achieve high efficiency in the process of chemical analysis. A laboratory can apply a QA program for all or part of its operations that are related to chemical analysis [10]. Several guides are produced by various government agencies, and in

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most cases, a QA program includes several parameters that need to be reported from the sampling stage to the final result, leading to high-quality measures [11]. In addition to the various parameters involved in the QA program, the most important information needed is the quality control (QC) procedures. QC is defined by CITAC and EURACHEM [10] as "the operational techniques and activities that are used to fulfill the requirements for quality". QC is also necessary to achieve accurate and precise results [12] and is usually applied in the steps of sample preparation and chromatographic determination because high precision and accuracy are required for both extraction and chromatography methods. QC procedures can be used to ensure quality when analyzing a specific sample or batch of samples using the following methods:

- The analysis of reference materials/measurement standards;
- The analysis of blind samples;
- The use of quality control samples and control charts;
- The analysis of blanks (reagent or sample blanks);
- The analysis of spiked samples;
- Performing the analysis in duplicate or triplicate;
- Proficiency testing.

QC is dependent on the work objectives and cost availabilities of the user; therefore, it can be used in different ways. QC can be applied in the form of a figure of merit, only with regard to chromatographic methods (for the evaluation of precision, accuracy and detection limit) [13], as an assessment of the influence of seasonal conditions on the separation efficiency and chromatographic detection, by checking the signal from a single point calibration curve. QC can also be used to evaluate the performance of sample preparation on the efficiencies of extraction methods. The lack of QC can result in the underestimation of an analyte of interest, leading to false results and inaccurate conclusions.

The accuracy of the overall analysis for an analyte of interest is dependent on the degree of agreement between the individual results found in a particular test and the reference value accepted as true [14]. The processes commonly used to evaluate the accuracy of an extraction method are as follows: reference material comparison, comparison of methods, recovery tests and standard additions [15,16]. The recovery test is the most commonly used method due to the difficulty in obtaining certified reference materials (CRMs) that are comparable with the analytes of interest. The measurements for the recovery test are expressed in terms of percentage and are based on the sampling quantity measured for the substance in relation to the amount added in the matrix (blank or placebo). The acceptable range of recovery for the determination of the analyte of interest is generally between 70 and 120% with an accuracy of ±20%. However, depending on the analytical complexity and the sample, this value can be 50–120%, with an accuracy of ±15% [16,17]. The recovery, expressed as a recovery factor (%*R*), is defined as a ratio of quantities for the substance of interest, which are present or added to the analytical portion of the test material and are capable of being extracted and quantified [16,18]. The efficiency of recovery can be determined from the use of CRMs (when available), standards or surrogates. A surrogate standard (SS), synthetic or natural, is defined as a pure compound or element added to the investigated matrix (by fortification or spiking) that has similar physical and chemical characteristics to the analyte of interest [19]. By knowing the recovery of the surrogate standard and by determining the recovery factor (%*R*), the concentration determined for the analyte of interest can be corrected [16,18], which improves the accuracy of the process.

According to IUPAC [20], the combined effects for all of the components of the sample included in measurement, other than the analytes of interest, are denoted as the "matrix effect" in analytical chemistry. In environmental matrices, their complex composition is the main cause of problems in the determination of various environmental organic contaminants [21]. The matrix effect can be pronounced in both the extraction method and the chromatographic method. For instance, in studies using liquid–liquid, solid–liquid or liquid–solid extraction methods, several authors reported negative results caused by the matrix effect [22,23]. Furthermore, a lack of accuracy achieved during a chromatographic method can be associated with the matrix effect. This phenomenon is known as the matrix-induced chromatographic response effect (matrix effect) [24]; it can occur in the line of a chromatograph [25], in the column of a chromatograph [26] and during the detection step [25,27]. This effect is often observed in pesticide quantifications by gas chromatography when the chromatographic signals of standards prepared in solvents are compared with those of the analyte in extracts of complex matrices [28,29]. Furthermore, organic matter fractions (e.g., humic and fulvic substances), which are commonly found in the environment, can reduce extraction efficiencies when used in solid phase extraction techniques [30]. This result occurs because these substances are easily extracted using liquid or solid phase extraction techniques, and they can co-elute with the analytes of interest when used in liquid and gas chromatography for pesticide determinations on environmental aqueous matrices [22,30].

Currently, several papers report matrix effects problems using liquid chromatography coupled to a mass spectrometer (LC–MS), when using both electrospray ionization (ESI) and atmospheric pressure chemical ionization (APCI) [31,32]. The mechanisms involved in these effects are diverse, and only some of these mechanisms have been identified. One of the factors implied from the reports indicate that the presence of non-volatile compounds in the additives of the mobile phase or in the components of the sample could hinder the ionized analyte microdrops from converting to gases [32,33].

The matrix effect is less pronounced in environmental aqueous matrices with minor complexities (river, drinking, ground and rain waters) [34,35]; however, it is significant when there is an increase in the complexity of the environmental matrix [1,36]. Thus, the need for a rigorous QC procedure is required for the determination of pesticides in environmental aqueous matrices, especially in studies involving complex environmental matrices, such as estuarine and oceanic waters.

In this study, the effects promoted by environmental aqueous matrices on pesticide determinations have been assessed, and for the first time, a simple, low-cost and efficient strategy for the correction of analytical results has been determined. This method can be useful as a parameter of quality control in a quality assurance programs.

## 2. Materials

### 2.1. Chemicals and reagents

Hexane, ethyl acetate and dichloromethane (DCM) were obtained from Merck (São Paulo, Brazil) and TEDIA (São Paulo, Brazil). Pesticides (picloram, atrazine, methyl parathion, chlorpyrifos and cypermethrin) were obtained from Supelco-Aldrich (São Paulo, Brazil), and chromatographic standards, such as *E*-diphenyldiazene (*E*-diph), 1,1-diphenylmethanone (BF), bis(pentafluorophenyl)methanone (DFBF) and methyl octadecanoate (ME), were also obtained from Supelco-Aldrich (São Paulo, Brazil).

### 2.2. GC analysis

Pesticides were determined on a Trace GC–MS Focus-Polares-G with an autosampler (AS3000) that was coupled to a quadruple

**Table 1**
Analytical figures of merit and chromatographic data of the studied pesticides.

| Analytes | Linearity | | | | | Repeatability[a] | |
|---|---|---|---|---|---|---|---|
| | Regression equation | Calibration range ($\mu g\,mL^{-1}$) | Correlation coefficient ($R$) | LOD ($ng\,mL^{-1}$) | $t_R$ (min) | Peak area | $t_R$ |
| Picloram | $y = 0.5742x - 0.692$ | 0.5–50 | 0.9954 | 0.398 | 13.66 | 4.19 | 0.01 |
| Atrazine | $y = 1.1783x - 0.8589$ | 0.1–50 | 0.9974 | 0.333 | 15.29 | 5.26 | 0.01 |
| Methyl parathion | $y = 0.6773x - 1.0384$ | 0.5–50 | 0.9913 | 0.629 | 16.33 | 3.88 | 0.01 |
| Chlorpyirifos | $y = 2.177x - 2.1003$ | 0.1–50 | 0.9944 | 0.215 | 16.96 | 2.94 | 0.01 |
| Cypermethrin | $y = 14.007x - 17.054$ | 0.1–50 | 0.9932 | 0.105 | 21.64 | 4.02 | 0.02 |

[a] RSDs of retention time and peak areas ($n = 10$).

ion-trap mass spectrometer (GC-iontrap-MS) (Thermo Electronic Corporation, Milan, Italy). The electron impact ionization conditions were as follows: the ion energy was 70 eV, and the selected-ion monitoring (SIM) acquisition was performed by monitoring the base peak of each pesticide. The MS was auto-tuned to $m/z$ 69, 219 and 502 for EI. The data were acquired with an Xcalibur equipped with the mass spectral libraries of NIST and MAINLIB, which were used to compare the experimental spectra obtained. The separations were performed in a Thermo TR–5 ms column (30 m × 0.25 mm i.d., 0.25-μm film thickness) using the splitless mode. The initial oven temperature was 60 °C for 5 min and then increased to 300 °C at 15 °C $min^{-1}$. The injector and detector temperatures were 280 °C and 300 °C, respectively. A 2-μL aliquot was injected, and argon was used as the carrier gas at a flow rate of 1.0 mL $min^{-1}$.

Validation of the gas chromatographic method was performed by measurements of repeatability, sensibility, linearity and detection limits (Table 1). Repeatability, determined by applying the same operational conditions during a short time interval, was expressed as a relative standard deviation (RSD). It is important to assess the repeatability of at least two parameters in the gas chromatographic method: the retention time (confirming the identity of the analyte of interest) and the peak area or height (quantifying the analyte of interest). The repeatability of the method ranged from 2.94 to 5.26% of the peak area (quantitative analysis) and from 0.01 to 0.02% of the retention time (qualitative analysis), showing satisfactory precision. Intra-day repeatability, expressed as RSD, was also evaluated during two consecutive weeks, and no significant alteration was observed. Analytical curves containing picloram, atrazine, methyl parathion, chlorpyrifos and cypermethrin at different concentrations (between 0.1 and 50 $\mu g\,mL^{-1}$) were obtained by plotting the peak area against the analyte concentration for each compound. The figures of merit for the calibration curves (the correlation coefficient ranged from 0.9913 to 0.9974) are summarized in Table 1, and good linearities for the calibration curves were obtained. The values for the limit of detection (LOD) (0.105–0.629 $ng\,mL^{-1}$) were calculated using the following formula: LOD = $3s_{blank}$/slope of calibration graphs, where $s_{blank}$ is the standard deviation of the ten blank concentration values from the five linear fits for the individual analytes of interest (Table 1) [37].

## 3. Experimental procedures

This work was developed in two stages. First, the matrix effect was investigated using selective liquid–liquid extraction as the extraction method. Second, a strategy was developed for the first time for the correction of the analytical results, which was then used as a parameter for quality control of pesticide determinations in a real sample from the Jaguaribe River estuary.

### 3.1. Liquid–liquid extraction-selective (LLE-S)

The extraction solvents were selected based on the solubilities and relative polarities of the pesticides, which depended on the physiochemical properties of the pesticides studied. Additionally, the extraction and chromatographic determinations were performed according to the protocol developed by Lima [37]. Briefly, an aliquot of 200 mL of the samples studied were spiked with the standard surrogates selected (BF, DFBF and ME; concentration of 100 $ng\,mL^{-1}$), and the samples were then extracted with 10 mL of extracting mixture (hexane/ethyl acetate/DCM (1:1:1)) three times. Next, the extracted solution was passed through a column of $Na_2SO_4$ to remove any trace of water, and the eluent was concentrated to 1 mL with $N_2$. *E*-diph was added as an internal standard (IS), and pesticides concentrations were determined by gas chromatography (Fig. 1).

### 3.2. Matrix effect

To evaluate the influence of the aqueous matrix on the analysis, the samples were spiked (50 $ng\,mL^{-1}$) and analyzed. The matrix effect was evaluated in terms of the recovery, the pesticide concentrations were determined in pure solvent (Milli-Q high-purity water) and in an environmental matrix (estuarine water) (Table 2). The matrix effect was calculated using Eq. (1).

$$\%ME = \frac{\left(50\,ng\ ml^{-1} - \text{concentration after extraction}\right) - \text{blank concentration}}{\text{concentration spiket}} \times 100 \quad (1)$$

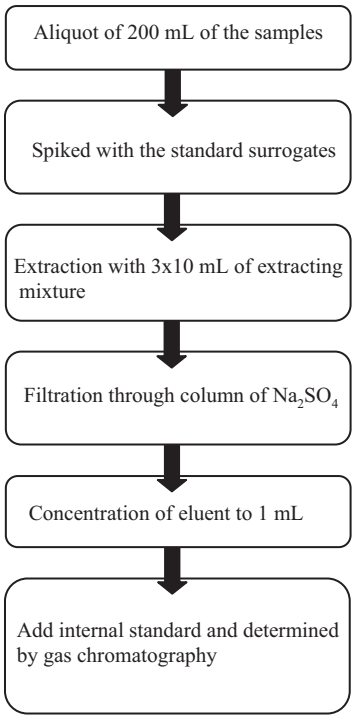


**Fig. 1.** Schematic diagrams of extraction protocol.

**Table 2**
Characteristics of the studied waters.

| Water | pH | Conductivity ($mS\,cm^{-1}$) | Total suspended matter ($mg\,l^{-1}$) | Salinity (‰) |
|---|---|---|---|---|
| Pure solvent | 7.2 | 0.1 | 0.01 | 0 |
| Estuarine | 8.2 | 43.1 | 10 | 31 |

### *3.3. Quality control applied to the study of pesticides in a real sample (Jaguaribe River)*

All data were subject to rigorous quality control procedures. Surrogates were used throughout the analytical procedure to compensate for losses and contamination during the extractions of the samples and instrumental analyses. Analysis of the reagent blanks demonstrated that the analytical system and glassware used were free of contamination. The pesticide determinations were performed in triplicate, and the pesticide concentrations were corrected using their relation factors, which were created for the pesticides studied (see below).

## 4. Results and discussion

### *4.1. Matrix effect investigation*

Several studies report the influences of matrix effects caused by using environmental matrices in the determination of several hydrophobic organic contaminants [23,38–40] with techniques such as liquid-phase [41] and solid-phase extractions [22,42,43] as well as the latest miniaturized techniques, such as SDME [35], SPME [44] and SBSE [45–47].

Although studies on the class of pesticides are scarce, the majority of matrix effects are promoted by the complex chemical composition of the environmental matrix, especially changes in pH and salinity, as well as increases in humic and fulvic substance concentrations and other classes of substances, both natural or anthropogenic [21–23,30,34,35,41,44,47]. In general, these matrices are quite different from aqueous matrices, such as river water, rainwater, groundwater or drinking water, and thus, the matrix effect in estuarine and oceanic waters is even more pronounce [34,41].

The matrix effect in the studied samples is presented in Fig. 2. Each result corresponds to the mean value of three replicate runs, and the error bars correspond to the relative standard deviations (RSDs). The results show that the pure solvent promoted a small matrix effect in the determination of most of the investigated pesticides ($R = 65–95\%$), except for picloram ($R = 44\%$). In estuarine water, this effect is quite significant in the determination of the investigated pesticides (Fig. 2), and this effect is greatly influenced from effects promoted by the physiochemical properties and by the composition of the environmental matrix. In the case of picloram, there was no difference between the pure solvent and estuarine waters

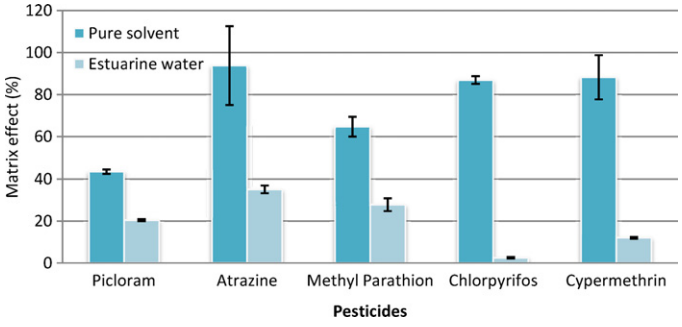


**Fig. 2.** Matrix effects on the studied samples.

values. Therefore, the composition of the aqueous matrix did not influence the determination of this pesticide. However, the recovery of picloram was greatly reduced in both of the aqueous matrices studied, suggesting this reduction was due to the physiochemical properties of picloram, especially its $K_{o/w}$ and $K_{oc}$ constants and high dissolution and polarity indices, which do not favor partition into organic solvents. The reduction in the extraction of picloram, using the adsorption phase (e.g., SPE), is also attributed to the disadvantage in partition [34].

The picloram, atrazine and methyl parathion pesticides suffered minor effects that were promoted by the estuarine matrix (Fig. 2). Picloram displayed the smallest variation for the matrix effect between the pure solvent and the estuary matrix, followed by methyl parathion and atrazine. According to Albanis and Hela [34], the matrix effect in ascending order and based on the recovery determinations of picloram, atrazine and methyl parathion was as follows: distilled water < underground water < river water < sea water. Interestingly, in a saline matrix study, the recoveries were 16.9% (picloram), 58.4% (atrazine) and 61.5% (methyl parathion) [34], which are similar to the results observed in our study.

However, the chlorpyrifos and cypermethrin pesticides had considerable effects promoted by the estuarine matrix, greater than that reported by Wang et al. [43] when studying lake water ($R = 40\%$). Despite favoring partition with organic solvents due to their low solubilities and high $K_{o/w}$ constants, which could provide high extraction efficiencies in the case of the chlorpyrifos and cypermethrin pesticides, their high $K_{oc}$ constants seemed to govern their non-availabilities for extraction. According to Cortada et al. [48], one of the main effects promoted by environmental aqueous matrices is their adsorption of pesticides into their suspended particulate matter (SPM), especially hydrophobic contaminants. For example, endosulfan and HCH insecticides have been significantly correlated with total organic carbon (TOC) in water, suggesting that these chemicals are strongly bound and concentrated by water-soluble organic carbon. Therefore, as expected, high concentrations of endosulfan and HCH insecticides are also associated with SPM [49]. When metals are complexed with dissolved organic matter, adsorption is increased, especially with hydrophobic contaminants at low concentrations [50]. Another fact about estuarine matrices is that they are rich in minerals that have high adsorption capacities, which decrease their chances of extracting contaminants from the matrices during extraction processes. To Peng et al. [51], the sorption of endrin increases with an increase in ionic strength, and pH has an effect on the sorption of both montmorillonite and kaolinite. Additionally, geosorbents are natural adsorbents able to "sequester" or "capture" chemical substances and elements that are considered contaminants. Therefore, these materials in aquatic environments exhibit strong adsorption sites and are responsible for the mobility and fate of contaminants in various environments [52,53].

Another relevant matrix effect is an increase in ionic strength, especially in polar and volatile chemicals [44,45,54]. An increase in ionic strength that corresponds to the addition of salt, also known as the salting out effect, induces a decrease in the apparent polarity of the molecules of water and, therefore, decreases the solubility of the polar molecules [55]. For instance, when increasing the ionic strength (to seawater level), an increase in the overall sorption coefficient (55%) was observed compared with that of freshwater [56]. Therefore, depending on the technique used for sample preparation, the effect of salt in the matrix can be used favorably to increase the extraction efficiency [40,45]. However, for most chemicals with moderate to high $K_{o/w}$ (e.g., PAHs, PCBs and some pesticides), an increase in salt concentration decreases the extraction efficiency, which is one of the main matrix effects on the determinations of organic contaminants in the environmental aqueous matrices [45,47,57].

### 4.2. Strategy for quality control

Various strategies have been proposed with the aim to minimize or eliminate matrix interferences [32]. In aqueous matrix determinations, to compensate for the matrix effects when matrix suppression phenomena cannot be eliminated, different calibration techniques are used, such as quantifications with matrix-matched calibration curves or alterations of the samples by dilution [58]. Casas et al. [59] cite dilution as an option to reduce the matrix effect caused in the determination of pyrethroid pesticides (e.g., cypermethrin) in runoff water and wastewater. This practice has shown success in simple matrices; however, in complex matrices, such as estuarine and marine waters, co-precipitation reactions occur due to changes in the physiochemical properties of the sample. Therefore, as the matrix effect is mainly derived from the constituents of the sample (natural or unnatural), and as its elimination is costly, it is suitable to know with certainty what influences the analysis procedure.

The quality control parameters commonly used to improve the accuracy of an analysis for organic contaminants in environmental matrices are the additions of (fortifications/spikes) and calculated recoveries of a surrogate standard. Unfortunately, there is a great lack of surrogate standards for comparison with pesticides on the market, suggesting surrogate standards are not commonly used to achieve these quality control parameters. For instance, other studies have used surrogate standards from different chemical classes for the study of pesticides (e.g., deuterated PAHs). However, the use of a surrogate standard from a different chemical class to correct for the losses of the contaminants of interest is inappropriate because of their different physiochemical properties, which provide different behaviors for the evaluated sample and in the extraction ratio. However, the recovery of a surrogate standard can be used to correct for the losses of the contaminants of interest, it is interesting to see when a 1-to-1 correction is realized using QC (Eq. (2)), a result suggesting that errors of the same or greater magnitude are likely present for those works that do not use quality control parameters. The scarcity of methods for pesticide determinations in complex environmental matrices is mainly because of the wide variation in the molecular structures of the pesticides, their physiochemical properties and low efficiencies of extraction in the liquid and solid phase methods, promoted primarily by the matrix effect, as observed earlier.

$$Cc = \frac{Ce \times 100}{\%R_{SS}} \quad (2)$$

In Eq. (2), Cc is the corrected concentration of the pesticide of interest, Ce is the found concentration of the pesticide of interest and $\%R_{SS}$ is the percent recovery of surrogate standard (SS) in the sample, when used.

Thus, we designed a simple strategy as the parameter for quality control. In this study, surrogate standards (Me, DFBF and BF) of different chemical classes and low in cost were used in the pesticide determinations of the complex environmental aqueous matrix because they have significant matrix effects and are difficult to predict.

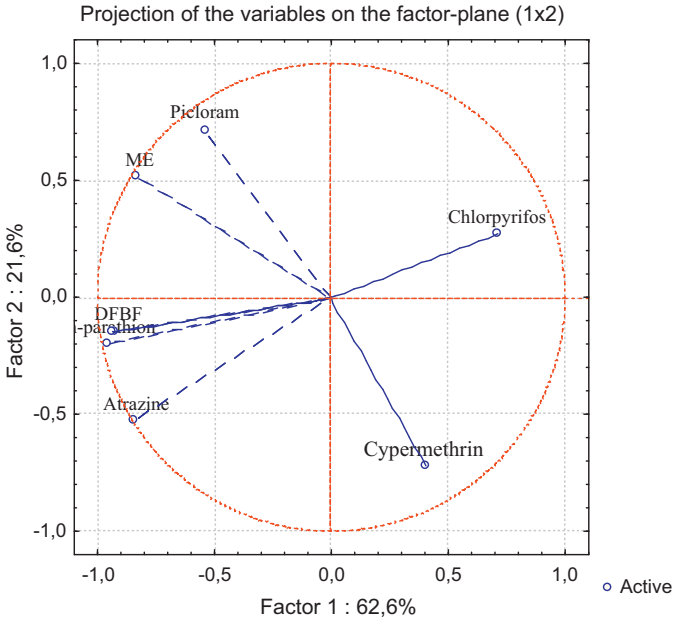


**Fig. 3.** Principal component analysis of the pesticides and surrogate standards studied.

To prepare the synthetic samples, pure solvent and estuarine water spiked with the studied pesticides were first prepared at a concentration that we judged to be present in the environment and in the areas with agricultural activity (50 ng $mL^{-1}$). Next, the synthetic samples were spiked with the surrogate standard, as in a routine protocol for quality control [60]. Both samples were extracted by ELL-S in triplicate, and the results for each recovery are summarized in Table 3.

In terms of recovery, the relationships between the studied pesticides and the substances used as surrogate standards were evaluated using principal component analysis (PCA). As observed in Fig. 3, two main components retained 84.2% of their information. Additionally, picloram correlates well with the Me surrogate standard, whereas atrazine and methyl parathion correlate better with the DFBF and BF surrogate standards. Thus, Me and both DFBF and BF were used as the surrogate standards for the pesticide determinations in the water samples; BF was selected over DFBF due to its better correlation with atrazine and methyl parathion. Unfortunately, chlorpyrifos and cypermethrin both had negative correlations with the three surrogate standards evaluated. Thus, the data for the chlorpyrifos and cypermethrin concentrations could

**Table 3**
Pesticide and surrogate standard recoveries (%) in the studied aqueous samples.

| | Pesticides | | | | | PS | | |
|---|---|---|---|---|---|---|---|---|
| | Picloram | Atrazine | Methyl-parathion | Chlorpyrifos | Cypermethrin | DFBF | BF | ME |
| Estuarine water | 54.8 | 80.0 | 59.9 | 71.0 | 22.2 | 43.1 | 51.2 | 75.7 |
| | 36.8 | 90.7 | 56.8 | 65.8 | 22.8 | 56.7 | 44.4 | 69.1 |
| | 44.3 | 85.0 | 81.0 | 63.5 | 10.4 | 72.4 | 79.3 | 78.6 |
| Average | 45.3 | 82.0 | 65.9 | 66.8 | 18.5 | 57.4 | 58.3 | 74.5 |
| RSD | 9.0 | 13.1 | 13.2 | 3.8 | 7.0 | 14.7 | 18.5 | 4.9 |
| Pure solvent | 41.5 | 99.0 | 79.9 | 63.5 | 55.8 | 66.0 | 70.6 | 70.5 |
| | 67.6 | 96.0 | 86.9 | 64.4 | 10.4 | 81.7 | 80.6 | 102.2 |
| | 53.9 | 98.0 | 88.9 | 52.6 | 9.0 | 72.7 | 75.1 | 96.3 |
| Average | 54.3 | 97.7 | 85.2 | 60.2 | 25.1 | 73.5 | 75.4 | 89.7 |
| RSD | 13.1 | 1.5 | 4.7 | 6.6 | 26.6 | 7.9 | 5.0 | 16.9 |

**Table 4**
$R_f$ of the pesticides with the surrogate standards.

| | Relation factor | |
|---|---|---|
| | Pure solvent | Estuarine water |
| Picloram/ME | 0.60 ± 0.05 | 0.61 ± 0.10 |
| Atrazine/BF | 1.30 ± 0.11 | 1.45 ± 0.21 |
| Methyl-parathion/BF | 1.13 ± 0.05 | 1.16 ± 0.13 |

**Table 5**
Data on the concentrations of the pesticides in the estuary of the Jaguaribe River.

| Pesticides | Results ($ng\,mL^{-1}$) | Corrected results ($ng\,mL^{-1}$)[a] |
|---|---|---|
| Picloram | 3.25 | 6.23 |
| Atrazine | <LD | – |
| Methyl parathion | 5.61 | 6.22 |

[a] Eq. (3).

not be corrected using the strategy developed; it is advised that other surrogate standards be studied to perform these corrections.

Despite acknowledging the correlation between the surrogate standards and pesticides, there is a need to know the extraction ratios of the substances studied (pesticides and surrogate standards) and to determine whether these relationships change between simple and complex matrices (e.g., estuarine water). Thus, we created Relation factors ($R_f$) with the surrogate standards and the pesticides that have shown satisfactory correlations by PCA analysis. In Table 4, there is no significant variation between the $R_f$ found for the pesticides (picloram, atrazine and methyl parathion) and their respective surrogate standards in the pure solvent and estuarine water based on the extraction ratios. These data indicate that both the pure solvent and estuarine water promote an effect on the studied pesticides and their corresponding surrogate standards at the same intensity, either due to the inefficiency of the extraction method or due to the effect caused by the environmental matrix. Overall, using these surrogate standards in complex matrices, such as marine or estuarine waters, can be used as a quality control method to make corrections to their respective studied pesticide concentrations (Eq. (3)).

$$Cc = \frac{Ce \times 100}{\%R_{ss}} \times \frac{1}{R_f} \quad (3)$$

In Eq. (3), Cc is the corrected concentration of the pesticide of interest, Ce is the found concentration of the pesticide of interest, $\%R_{ss}$ is the percent recovery of surrogate standard (SS) in the sample and $R_f$ is the relation factor between the investigated pesticide and the surrogate standard selected.

### 4.3. Application on a real sample

Picloram, atrazine and methyl parathion concentrations in a sample from the estuary of the Jaguaribe River, which is located in the largest Brazilian agribusiness complex, were investigated, and their results are summarized in Table 5. As shown, if no quality control (e.g., surrogate standard) was used, an underestimation of the results would occur when compared with the corrected concentration result using the $R_f$.

## 5. Conclusion

Complex environmental aqueous matrices, such as estuaries, promote significant and different effects on pesticide concentration determinations when compared with simple aqueous matrices. The picloram, atrazine and methyl parathion pesticides suffered minor effects promoted by the estuarine matrix, while both chlorpyrifos and cypermethrin were greatly affected. For picloram, the matrix effect was due to its own physiochemical properties; however, for atrazine, methyl parathion, chlorpyrifos and cypermethrin, the matrix effect was promoted by the constituents in the environmental matrix. The result of the pesticide determinations for the real sample showed that an appropriate quality control method on the data is indispensable, and in case of the absence of QC, the data collected could be underestimated, leading to incorrect conclusions.

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