

Comparison of the analytical performance of EDXRF and FAAS techniques in the determination of metal species concentrations using protocol 3050B (USEPA)

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ABSTRACT

Sediments are active environmental compartments capable of interchanging the chemical species with the water column, degrading their quality and influencing the toxicity of the matrix. The average concentrations of sediment-associated metallic species have been used to evaluate the extent of their contamination. The approaches used have progressed considerably over the last few decades and different instrumental techniques have been employed in quali-quantification of metal compounds associated with sediments. This study aimed to evaluate the accuracy of the technique of Energy Dispersive X-Ray Fluorescence Spectrometry (EDXRF) performed on the equipment Shimadzu (model Rany, Series EDX-720) in the validation process, adopting as reference the technique of Flame Atomic Absorption Spectroscopy (FAAS), appliance GBC (model Avanta) to quantify the species: Zn, Fe, Ni, Cu, Pb and Cr in solution, in chemically available fraction (3050B Protocol-United States Environmental Protection Agency), extracted from sediments of the River Barigüi, metropolitan region of Curitiba, southern Brazil. The samples were collected according to the clean techniques protocols. The analytical figures of precision, accuracy and determination limit of the method were evaluated using the two techniques separately and on the same samples. Statistically significant differences were observed between the two methods.

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1. Introduction

Sediments are complex environmental matrices, important in storage and dissemination of compounds and in the functioning of the aquatic ecosystem, but it can also act as environmental stressors (Araújo *et al.* 2008, Burton and Johnston 2010, Hortellani *et al.* 2013). This compartment of porous structure comprises solid fractions (organic and inorganic), liquid fractions (interstitial water) and gases, as a result of interactions that occur in the aquatic ecosystems (Mozeto and Zagatto 2008, Fagnani *et al.* 2011, Esteves and Camargo 2011).

The sediment exchange contaminant species with the water column and may remain active for a long period of time (Burton and Johnston 2010, Fagnani *et al.* 2011, Hortellani *et al.* 2013). The metal species in trace order are among the most dangerous pollutants of the sediment, mainly because they are not degradable, of their easy accumulation along the trophic chain and of their influence on the toxicity of the environmental matrices, causing harmful effects (Esteves and Guariento 2011, Santos *et al.* 2012).

The quantification of metal species is a subject of great interest in the environmental area (Jardim and Sodr e 2009, Margu i *et al.* 2014) and usually the analytical procedures employed in these determinations are based on Flame Atomic Absorption Spectroscopy, known as FAAS; on Inductively Coupled Plasma Atomic Emission Spectrometry (ICPAES) and on Induced Coupled Plasma Mass Spectrometry (ICP-MS). However, techniques such as Dispersive X-Ray Fluorescence Spectrometry, known as EDXRF, also comply and

have been employed, mainly in the quantification of major compounds. The multielementary EDXRF technique allows the direct analysis in solid samples of environmental character, dispensing opening sample processes (Pyle *et al.* 1995, Akbulut *et al.* 2014).

Recent advances in the EDXRF instrumentation, such as the development of semiconductor detectors Si(Li), the creation of specific software and the commercialization of easy operation equipment, have expanded the applications of this technique in terms of increase in sensitivity, accuracy and reproducibility of instrumental (Nascimento Filho 1999, Margu i *et al.* 2014). Accordingly, several research have been dedicated to perform the comparison of the EDXRF with traditional analytical techniques emphasizing the reduction in time, cost and facilities in sample preparation (Cust odio *et al.* 2011, Miskolczi *et al.* 2011, Ivosevic *et al.* 2014, Peruchi *et al.* 2014).

As regards the quantification of metal species, several authors have demonstrated the efficiency of the EDXRF, when compared to other instrumental techniques, in the analysis of metals in the total fraction of soil and sediment (Pyle *et al.* 1995, Radu and Diamond 2009, Popescu *et al.* 2011, Almeida *et al.* 2012, Akbulut *et al.* 2014). However, when the quality of sediments is evaluated, usually the overall fraction of the matrix is not of interest, but what is slightly connected and chemically available (Burton and Johnston 2010, Fagnani *et al.* 2011, Hortellani *et al.* 2013).

The fractions chemically available from the sediment are obtained through acid extractions according to standardized

protocols from international agencies and subsequent quantification of chemical species. Thus, it is necessary to make compatible extraction processes for samples when, for example, working with the Guide Values of Sediment Quality (VGQS). The VGQS are protection and management strategies for freshwater ecosystems, developed by the Canadian Environmental Agency (Silvério *et al.* 2006, Silva *et al.* 2012, Hortellani *et al.* 2013).

Thus, this research seeks to evaluate the closeness of the results obtained by different techniques, using the same matrix. This study compared the analytical performance of the EDXRF technique (Shimadzu, EDX-720) adopting as reference the FAAS technique (GBC, Avanta) in order to quantify the metal species: Zn, Fe, Ni, Cu, Pb and Cr in solution extracted by specific protocols of sediment samples from River Barigüi, metropolitan region of Curitiba, southern Brazil.

2. Materials and methods

2.1. Area of study

The sub-basin of the Barigüi river is located in the metropolitan region of Curitiba, southern Brazil (area of 279 km² 66 km long), crossing the boundaries of the municipalities of Almirante Tamandaré, the location of the headwaters, Curitiba and Araucária, where the estuary is located (Iap 2009, Sema 2013, Machado *et al.* 2014). The central portion of the river, in the municipality of Curitiba, located in the district of Santa Felicidade (25°24'37,4''S and 49°18'24,7''W), was chosen because it is a region with high-density urban occupation, with various shops and services. The downstream region, in the municipality of Araucária (25°33'20,56''S and 49°20'32,70''W), has predominance of industrial use and is located the Industrial City of Curitiba (CIC), a part of the Industrial City of Araucária (*) and the Refinery of the Petrobras (REPAR). Apart from this, the industrial zones have

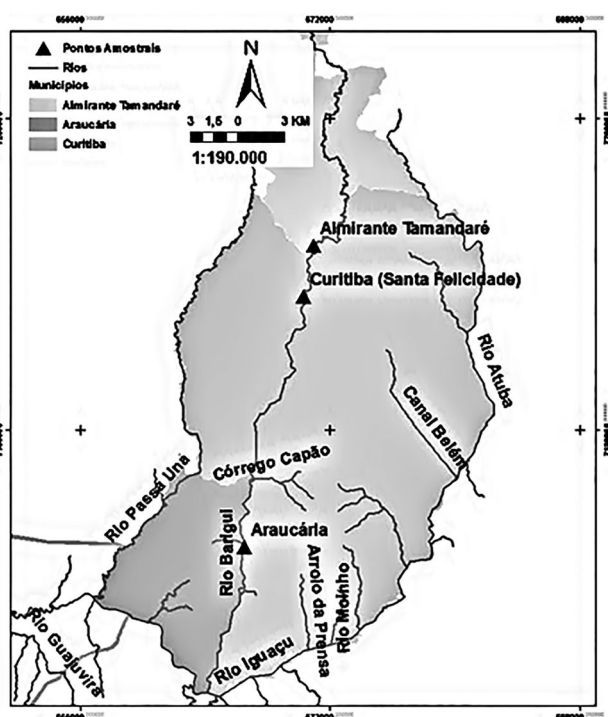


Figure 1. Location of sampling points of the Barigüi River.

attracted several regular and irregular occupations, small metalworks and companies providing services (Froehner and Martins 2008, Iap 2009, Sema 2013).

Figure 1 shows the Barigüi River-Paraná and the indications of the sampling stations where the analysis of superficial sediment samples was carried out.

2.2. Collection, handling and preparation of the samples

The superficial sediment samples were collected according to the technical clean protocols (Cetesb 2011) using a dredge Petersen, stored in double bags of polypropylene and identified with labels. Preservation of the collected samples up to the analysis lab (transport) was done in a cooled thermal box.

In the lab, the sediment samples were homogenized in polypropylene trays with plastic spatulas and sent for drying in circulation kilns at the temperature of 50°C for 48 h. Then the dried samples were disaggregated into a mortar and directed for separation of grain size through a magnetic sieve shaker, where the fine fraction (<63 µm) was sent to the opening via protocol 3050B (United States Environmental Protection Agency [USEPA], 1996) that allows the evaluation of the fractions chemically available. Protocol 3050B was used to extract the matrix compounds that would be available in environmental conditions, without changing the structures of the silicate type. This protocol involves a process of digestion with nitric acid (65%), hydrogen peroxide (30%) and 1 g dry sediment (fractions <63 µm) in a beaker of 250 mL, placed on a heating plate (95°C for 15 min) and covered with a watch glass (Silva *et al.* 2012, Hortellani *et al.* 2013, Akbulut *et al.* 2014).

Sampling openings were carried out in triplicate for sampling point, resulting in 300 mL of solution that was mixed, shaken and divided into two aliquots (150 mL), stored in polypropylene bottles and directed to instrumental analysis (Figure 2). This procedure was employed to minimize any possible discrepancies in the opening process by ensuring that each of the devices gets the same samples for the analytical performance evaluation. Thus, this study evaluated the degree of proximity of the results obtained by two methods, through analyses carried out in replicates, using the instrumental methods FAAS and EDXRF separately, on the same samples (Inmetro 2011).

2.3. Instrumental analysis

The conditions for the analyses with the EDXRF technique were: equipment Shimadzu, model EDX-720, radiation

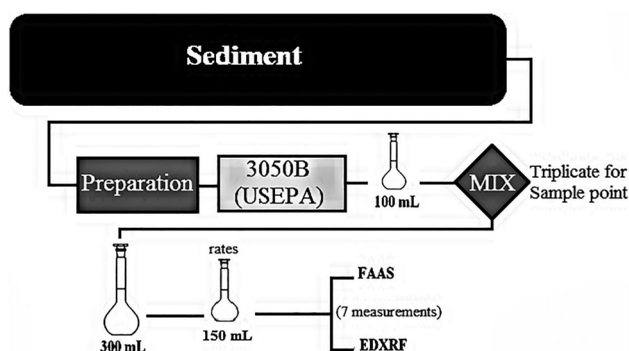


Figure 2. Flow chart of the process of preparation of sediment samples.

Table 1. Figures of analytical merit used in comparison of instrumental techniques.

Term	Description
Precision	The accuracy was expressed as relative standard deviation, accordingly, $(DP/CMD) \times 100$, where DP is the standard deviation and CMD is the average concentration determined.
Accuracy	Determined in relation to the reference values and can be expressed as analytical recovery: $(VO/VE) \times 100$, where VO is the observed value and VE is the expected value.
Limit of determination of the analytical method	Lower concentration of analyte in a sample which can be quantified by an analytical method with a greater confidence level of 95%, given by the expression: $LDM = 2 \times \sqrt{\frac{\sum_{m=1}^n (C_m - \bar{C})^2}{(n-1)}}$ where C_m is the concentration of m analysed replicates of a standard containing the species of interest in known concentration, \bar{C} is the average concentration and n is the number of replicates.

Data source: (Rousseau 2001, Anvisa 2003, Bona *et al.* 2007, Inmetro 2011).

200s, air atmosphere, rhodium source (Rh) with an applied voltage of up to 50 keV, semiconductor detector Si(Li) with a resolution of 0–40 keV, collimator 10 mm, quantitative routine, and analytical curve with a matrix of correlation with linear regression. For comparison of the techniques, the FAAS technique was adopted as a reference. The analysis conditions were as follows: appliance GBC model Avanta, acetylene fuel flame and air-oxidant, temperature 2100°C, speed of 226 cm s⁻¹ and hollow cathode lamps.

The Analytic Curves (expression of the relationship between a sign and the corresponding measured value) were obtained with mono-elemental spectroscopic standards (Zn, Fe, Ni, Cu, Pb and Cr), at concentrations of 1, 2, 3, 4 and 5 (mg L⁻¹) for FAAS. For EDXRF, the instrumental intensity curves were prepared with the following concentrations: 2, 5, 10, 30 and 50 (mg L⁻¹).

Analytical techniques were applied separately on each sample solution and seven repetitions were performed, thus generating a data set of the matrix on each of the analytical instruments, enabling the realization of a statistical modeling. Technical definitions of analytical elements such as accuracy, precision and limit of determination of method (LDM) are presented in Table 1.

The figures of analytical merit were established from the results of seven recoveries of standard solutions of Cu, Ni, Fe, Cr, Zn and Pb with a concentration of 5 (mg L⁻¹), measured from mono-elemental spectroscopic standards.

2.4. Statistical tests and graphical constructions

Statistical treatment of the data began with the test of Grubbs on the system QuickCalcs – *Outlier Calculator* (GraphPad Software 2014) for the identification and elimination of outliers. Later, the data were tested in the Action 2.7 system (Estatcamp 2014), consisting of (i) the Kolmogorov–Smirnov

Normality Test; (ii) the *F*-test, (iii) the Paired *t*-test and (iv) the Dunnett test. For creating the graphics, we used the *software* SciDAVis (Sourceforge 2014).

3. Results and discussion

In comparing performance, the results related to the analytical curves are shown in Table 2.

The linear correlation coefficients of analytical curves were up 0.98, stating the linear relationship between the sign and the concentration. The figures of analytical merit are shown in Table 3.

The figures of analytical merit LDM and Precision showed higher values in the EDXRF technique, when compared to the FAAS, showing the best analytical performances of the second technique. According to Wood (1999), variation up to 16% is acceptable in the accuracy of results obtained with environmental samples. In this sense, the results of the FAAS and EDXRF analyses can be considered accurate, except the result for Pb by the EDXRF technique.

For environmental matrices, the accuracy of the analytical methods can vary between 90% and 110%. In this sense, the result of the FAAS and EDXRF analyses can be considered accurate (Brito *et al.* 2003).

Table 4 shows the average concentrations of the metal species obtained in samples of sediment from Araucária and Santa Felicidade. These results are obtained after the removal of significant outliers ($p < .05$) by the Grubbs test.

The chemical element nickel was not detected by any of the techniques studied in any of the sample points, and the largest concentrations obtained were for iron and zinc. In general, the average concentrations of metallic species obtained by using the techniques were equivalent, but with greater standard deviations observed with the use of the EDXRF.

Table 2. Analytical curves obtained by FAAS and EDXRF techniques.

Metals	FAAS		EDXRF	
	Standards (mg L ⁻¹)	Analytical curve	Standards (mg L ⁻¹)	Analytical curve
Cu	1, 2, 3, 4, 5	$y = 0.06x + 0.0057$ $R^2 = 0.99$	2, 5, 10, 30, 50	$y = 0.029x + 0.051$ $R^2 = 0.99$
Ni	1, 2, 3, 4, 5	$y = 0.03x + 0.0078$ $R^2 = 0.99$	2, 5, 10, 30, 50	$y = 0.017x + 0.057$ $R^2 = 0.99$
Fe	1, 2, 3, 4, 5	$y = 0.03x - 0.025$ $R^2 = 0.98$	2, 5, 10, 30, 50	$y = 0.014x - 0.14$ $R^2 = 0.99$
Cr	1, 2, 3, 4, 5	$y = 0.02x + 0.0012$ $R^2 = 0.99$	2, 5, 10, 30, 50	$y = 0.027x + 0.020$ $R^2 = 0.99$
Zn	1, 2, 3, 4, 5	$y = 0.10x + 0.12$ $R^2 = 0.99$	2, 5, 10, 30, 50	$y = 0.035x + 0.22$ $R^2 = 0.99$
Pb	1, 2, 3, 4, 5	$y = 0.05x - 0.011$ $R^2 = 0.99$	2, 5, 10, 30, 50	$y = 0.057x - 0.041$ $R^2 = 0.99$

Table 3. Figures of analytical merit obtained by FAAS and EDXRF techniques.

Metals	FAAS			EDXRF		
	Precision (%)	Accuracy (%)	LDM (mg L ⁻¹)	Precision (%)	Accuracy (%)	LDM (mg L ⁻¹)
Cu	0.95	98.77	0.06	3.89	97.04	2.27
Ni	3.27	96.73	0.19	4.02	100.50	2.42
Fe	5.84	90.20	0.32	6.34	95.04	3.63
Cr	1.34	102.00	0.08	11.33	102.25	2.32
Zn	1.11	102.33	0.07	4.82	102.03	2.95
Pb	1.72	98.90	0.10	19.44	91.59	8.90

Note: LDM = Limit of determination of the method.

Table 4. Average concentrations of the metal species in Araucária and Santa Felicidade.

Metals (mg kg ⁻¹)	FAAS		EDXRF	
	(Araucária)	(Santa Felicidade)	(Araucária)	(Santa Felicidade)
Cu	24.70 ± 0.50	19.04 ± 0.40	24.84 ± 205.13	18.80 ± 164.42
Ni	ND ^a	ND ^a	ND ^a	ND ^a
Fe	591.84 ± 33.49	708.16 ± 7.91	529.26 ± 9.22	716.20 ± 34.32
Cr	22.51 ± 5.14	29.33 ± 5.07	16.86 ± 3.84	17.37 ± 5.44
Zn	394.23 ± 1.65	243.81 ± 2.70	411.77 ± 129.40	118.55 ± 44.24
Pb	38.57 ± 1.22	27.82 ± 11.94	35.07 ± 8.34	38.29 ± 9.73

^aUndetected.

Figure 3 shows the comparative chart of concentrations of the metal species, determined by different analytical techniques (FAAS and EDXRF) in sediment samples of Araucaria.

Figure 3 shows a trend of approximation of the average concentrations for all metal species and the existence of high standard deviations for Cu and Zn using the EDXRF technique. These high variations show the presence of errors in data acquisition, since this data set is not classified as an outlier by the Grubbs test.

Added to this, one can infer that the techniques follow the variations in concentrations of elements in a similar way.

Figure 4 shows the comparative chart of concentrations of the metal species, determined by different analytical techniques (FAAS and EDXRF) in sediment samples of Santa Felicidade. It can be observed that zinc was the species that suffered the greatest variance between the techniques studied.

Figure 4 shows the repetition of the behaviour of data acquisition of the techniques, that is, approximation of the sample averages and high variances related to Cu and Zn by the EDXRF technique. The Kolmogorov–Smirnov Normality test was applied to the sample data set generated by the two techniques.

The purpose of this procedure was to evaluate the existence of normal distribution of data that would enable statistical parametric modelling. Tables 5 and 6 show the results of

the Kolmogorov–Smirnov Normality test for the FAAS and EDXRF techniques, respectively.

There is evidence that the data obtained using the FAAS and EDXRF techniques follow a normal distribution (with 95% confidence, $p > 0.05$). In this sense, the data distribution follows a Gaussian function and allows the application of parametric statistics.

To evaluate if the two methods have significant differences between them, can use the application of the calculation of the value F (ratio of the variances of the two methods), by determination statistic of the F -Test. One should compare the F value obtained with the value list of distribution F (critical values for a bilateral test with $\alpha = 0.05$); if $F_{\text{Calculado}} \leq F_{\text{tabelado}}$, the two methods do not present significant differences between them (Inmetro 2011).

In our study, the result is expressed by the ratio of the square of the sample standard deviation (S_{FAAS}) obtained in the FAAS technique, as default, and the value of the square of the relative sample standard deviation (S_{EDXRF}) of the EDXRF technique, proposed method, for each chemical species of the study individually. The results are obtained by using the following equation:

$$F = \frac{(S_{\text{FAAS}})^2}{(S_{\text{EDXRF}})^2}. \quad (1)$$

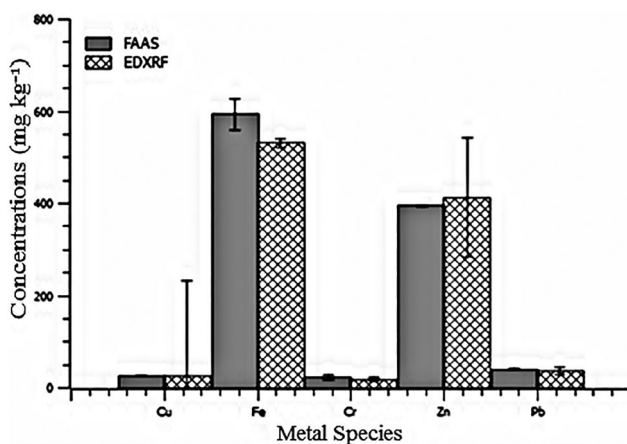
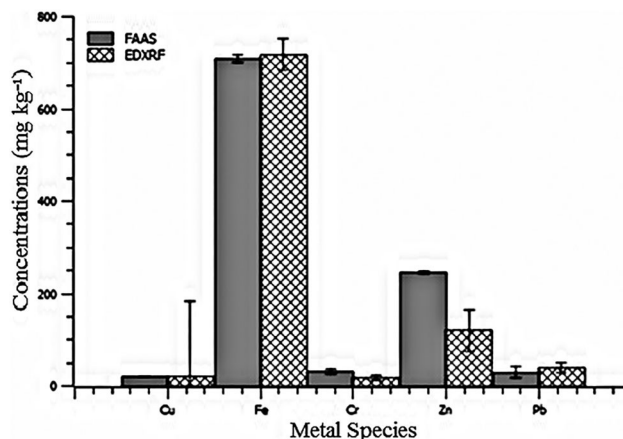
**Figure 3.** Average concentrations of the metal species in Araucária.**Figure 4.** Average concentrations of the metal species in Santa Felicidade.

Table 5. Kolmogorov–Smirnov Normality Test (FAAS).

	Araucária		Santa Felicidade	
	(Kolmogorov–Smirnov)	(<i>p</i> -value)	(Kolmogorov–Smirnov)	(<i>p</i> -value)
Cu	0.225	.446	0.224	.355
Fe	0.245	.232	0.151	.900
Cr	0.143	.935	0.169	.788
Zn	0.139	.951	0.201	.533
Pb	0.227	.339	0.264	.146

Table 6. Kolmogorov–Smirnov Normality Test (EDXRF).

	Araucária		Santa Felicidade	
	(Kolmogorov–Smirnov)	(<i>p</i> -value)	(Kolmogorov–Smirnov)	(<i>p</i> -value)
Cu	0.215	.422	0.179	.711
Fe	0.178	.721	0.260	.163
Cr	0.184	.669	0.287	.084
Zn	0.280	.099	0.265	.208
Pb	0.260	.164	0.299	.100

In this sense, Table 7 shows the values of the statistical analysis of the *F*-test, when subjected to data generated by FAAS and EDXRF. In Table 7, the *p*-value corresponds to the level of significance required in the statistical test (95%); the degree of freedom (gl) corresponds to the statistical dimension of the sample size, the number of parameters measured in the sample population and the $F_{\text{tabulated}}$ values of a distribution *F* bilateral table (Callegari-Jacques 2008).

The metal species in this study showed reasons of calculated *F* variance lower than the *F* tabulated. The reasons of variance show little expressive values for Cu and Zn; this fact can be linked to greater variance of the sample data obtained in the EDXRF compared to the FAAS.

The Paired t-test was applied to the sample data generated by the two techniques, to carry out the comparison of the averages of the set, because this test can also be used to evaluate if the average of the results of the two methods can be considered statistically equal (Inmetro 2011) (Table 8).

Table 7. Evaluation of the reasons for variance of the instrumental data.

	Araucária				Santa Felicidade			
	(Calculated <i>F</i>)	(<i>p</i> -value)	(gl)	(Tabulated <i>F</i>)	(Calculated <i>F</i>)	(<i>p</i> -value)	(gl)	(Tabulated <i>F</i>)
Cu	5.9×10^{-6}	8.7×10^{-13}	5 × 6	5.99	5.9×10^{-6}	4.1×10^{-15}	6 × 6	5.82
Fe	13.2	6.3×10^{-3}	6 × 6	5.82	5.3×10^{-2}	2.4×10^{-3}	6 × 6	5.82
Cr	1.8	4.9×10^{-1}	6 × 6	5.82	8.7×10^{-1}	8.7×10^{-2}	6 × 6	5.82
Zn	1.6×10^{-4}	8.5×10^{-11}	6 × 6	5.82	3.7×10^{-3}	1.1×10^{-6}	6 × 5	6.98
Pb	2.1×10^{-2}	1.8×10^{-3}	6 × 6	5.82	1.5	6.7×10^{-2}	6 × 5	6.98

Table 8. Evaluation of methods by the Paired t-test.

	Araucária		Santa Felicidade	
	(Paired t-test)	(<i>p</i> -value)	(Paired t-test)	(<i>p</i> -value)
Cu	−0.002	.998	0.004	.997
Fe	4.448	.004	−0.614	.561
Cr	2.214	.069	4.550	.004
Zn	−0.362	.729	7.912	.002
Pb	1.034	.341	−2.441	.050

Table 9. Dunnett's multiple comparisons test.

	Araucária				Santa Felicidade			
	(Average)	(LI)	(LS)	(<i>p</i> -value)	(Average)	(LI)	(LS)	(<i>p</i> -value)
Cu	0.143	−168.787	169.072	.999	−0.243	−135.665	135.179	.997
Fe	−62.580	−91.182	−33.977	.000	8.040	−20.966	37.046	.557
Cr	−5.656	−10.939	−0.372	.038	−11.961	−18.083	−5.840	.001
Zn	17.543	−88.997	124.083	.726	−125.164	−158.493	−91.836	.000
Pb	−3.500	−10.436	3.436	.293	10.472	−1.781	22.724	.087

For the sample set submitted to the Paired t-test, note that the model describes the compatibility between the instrumental FAAS and EDXRF techniques, for the chemical species Cu, Cr, Zn and Pb in Araucária and Cu, Fe and Pb in Santa Felicidade, with 95% significance ($P > .05$).

Another comparison between the EDXRF and FAAS techniques was conducted with the Dunnett multiple comparisons test, to evaluate the levels of a sample set with a reference level (or control) of another sample set, allowing the comparison of the data (Table 9).

It is showed that the table contains upper bounds (LS) and lower bounds (LI) that serve as intervals of comparison between the sample concentrations obtained using the instrumental techniques FAAS and EDXRF. The results significant ($\alpha = 0.05$) for the sample data do not allow us to reject the hypothesis of equality between the data generated by the two techniques ($p > 0.05$), for Zn and Pb in Araucária and Zn in Santa Felicidade.

4. Conclusions

The results point to the infeasibility of direct use (without sample preparations) of the EDXRF technique for the quantification of metal species chemically available extracted by protocol 3050B (USEPA 1996). In a study by Marguí *et al.* (2014), it was stated that the direct analysis of solutions by EDXRF could be influenced by background dispersions, resulting in poor signal-to-noise ratios, because usually, to perform the analysis by EDXRF, a few millilitre of liquid sample is placed on a glass with a thin film fund, in chamber of samples without vacuum, and that due to heating bubbles are released from the solutions, giving rise to problems in reproducibility. It is believed that mistakes of this order may have influenced the process of obtaining data for the chemical species in our EDXRF analysis, mainly for Cu and Zn, providing the high deviations from the average

concentrations. It should be noted that any kind of pre-treatment was not used in the solutions coming from the opening of sediments by 3050B protocol (USEPA 1996), a fact that could minimize the discrepancies in obtaining data.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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