



Estimating the uncertainty from sampling in pollution crime investigation: The importance of metrology in the forensic interpretation of environmental data



Cristina Barazzetti Barbieri^{a,b,*}, Jorge Eduardo de Souza Sarkis^a

^a Centro de Química e Meio Ambiente/Instituto de Pesquisas Energéticas e Nucleares (IPEN), São Paulo, SP, Brazil

^b Departamento de Criminalística/Instituto-Geral de Perícias (IGP/SSP-RS), Porto Alegre, RS, Brazil

ARTICLE INFO

Article history:

Received 26 November 2017

Received in revised form 27 March 2018

Accepted 3 April 2018

Available online 11 April 2018

Keywords:

Uncertainty

Sampling

Pollution

Metals

Sediment

Leachate

ABSTRACT

The forensic interpretation of environmental analytical data is usually challenging due to the high geospatial variability of these data. The measurements' uncertainty includes contributions from the sampling and from the sample handling and preparation processes. These contributions are often disregarded in analytical techniques results' quality assurance. A pollution crime investigation case was used to carry out a methodology able to address these uncertainties in two different environmental compartments, freshwater sediments and landfill leachate. The methodology used to estimate the uncertainty was the duplicate method (that replicates predefined steps of the measurement procedure in order to assess its precision) and the parameters used to investigate the pollution were metals (Cr, Cu, Ni, and Zn) in the leachate, the suspect source, and in the sediment, the possible sink. The metal analysis results were compared to statutory limits and it was demonstrated that Cr and Ni concentrations in sediment samples exceeded the threshold levels at all sites downstream the pollution sources, considering the expanded uncertainty U of the measurements and a probability of contamination >0.975 , at most sites. Cu and Zn concentrations were above the statutory limits at two sites, but the classification was inconclusive considering the uncertainties of the measurements. Metal analyses in leachate revealed that Cr concentrations were above the statutory limits with a probability of contamination >0.975 in all leachate ponds while the Cu, Ni and Zn probability of contamination was below 0.025. The results demonstrated that the estimation of the sampling uncertainty, which was the dominant component of the combined uncertainty, is required for a comprehensive interpretation of the environmental analyses results, particularly in forensic cases.

© 2018 Elsevier B.V. All rights reserved.

1. Introduction

The interpretation of environmental analytical data is often a hard task since these data usually demonstrate great variability. This variability implies that a thorough assessment of the contamination with high statistical significance is difficult to achieve in most environmental investigations [1]. For this reason, metrology tools were adopted in this environmental forensics case study to estimate the uncertainties, including those inherent to the sampling process, and its impact in the interpretation of the data obtained from environmental samples analysis. Recently, especially around the turn of the past century, there has been an

increasing concern with the quality of analytical techniques results. The publication of the “*Guide to the Expression of Uncertainty in Measurement*” by the International Standards Organization (ISO) [2] updated in JCGM 100 (2008) Evaluation of measurement data – Guide to the Expression of Uncertainty in Measurement (GUM 2008) by the Joint Committee for Guides in Metrology (Sèvres Cedex), and the following “*Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results*” [3] demonstrate this concern.

Although the International Standard ISO/IEC 17025, first issued in 1999, reports that the uncertainty of sampling is a factor to be considered as a contributor to the total uncertainty of measurement [4], the focus of the quality control procedures was more directed towards the analytical methodologies, and the uncertainties associated with sampling and sample preparation were still not fully taken into consideration [5]. This is particularly troublesome when dealing with environmental samples where

* Corresponding author at: Departamento de Criminalística/Instituto-Geral de Perícias (IGP/SSP-RS), Porto Alegre, RS, Brazil.

E-mail address: cristinabarbarieri@usp.br (C. Barazzetti Barbieri).

systematic and standardized procedures are more difficult to be carried on and, for this, require more research efforts. Before that, there were some articles on the subject of sampling uncertainty, mostly in the field of applied geochemistry (e.g. [6–10] until 2007, when two major publications were released, the NORDTEST Handbook “*Uncertainty from sampling – A Nordtest handbook for sampling planners on sampling quality assurance and uncertainty estimation*” [11] and the guidance upon which this is based, the EURACHEM/CITAC Guide “*Measurement uncertainty arising from sampling: a guide to methods and approaches*” [12]. After that, there were few publications addressing the topic of uncertainty of sampling in environmental investigations (e.g. [1,13–18]).

The forensic science community also experienced a paradigm shift with the Supreme Court decision admitting the uncertainty in scientific testimony in *Daubert v. Merrell Dow Pharmaceuticals, Inc.*, 509 US 579, 589 (1 US 579, 589 (1993)). Pyrek [19] further explored the ‘post-Daubert’ challenges to forensic science. Later, in 2009, the National Research Council of the National Academies released the report *Strengthening Forensic Science in the United States: A Path Forward* pushing farther the boundaries of uncertainties acknowledgement in experts’ testimony [56]. This report triggered changes in the forensic science scenario in the United States and around the world with the development and validation of new and more accurate methods to help criminal investigations including quantifiable measures of uncertainty in the conclusions of forensic analyses [20].

The main purpose of most measurements is to support decisions based on them [11]. For this, the awareness of the ‘range of certainty’ where the true value of the analyte lie is essential for environmental investigations. To obtain this ‘range of certainty’ or ‘reliance interval’ as proposed by Thompson [21], the assessment of the uncertainty of the measurement, including the sampling uncertainty is required, particularly in pollution investigations where sampling is the first step of the measurement process that will determine the concentrations of pollutants in the affected media. Environmental systems studies have shown that effects between samplers and between protocols are sometimes much smaller than are those derived from the spatial heterogeneity [10]. Ramsey and Ellison [12] propose that quantitative evidence of the quality of sampling can be obtained with the duplicate methods and this is more reliable than the assumption that the samples are representative if they are collected following a conventional protocol.

Solid waste landfills generate leachate, a significant source of contamination of groundwater and surface water [22,23]. The composition of the leachate is highly variable among different landfill sites [24]. In general, landfill leachate is enriched in metals [25,26] and this particular hazardous waste landfill metal contamination in groundwater and soils has been the subject of previous studies [23,27]. Sediments are particularly useful in identifying and monitoring pollution sources since they can accumulate and integrate contaminants present in the water column even at low concentrations [28,29]. Several studies have recorded high levels of metals in fluvial sediments caused by industrial sources [30–33]. In addition, unlike organic compounds, for example, metals are not subject to degradation, so their associations/correlations can be used to obtain the signature or ‘fingerprint’ of the contamination and track it to its probable origin [34].

The definition of acceptable levels of uncertainty is a balance between the need of quality assurance and how much one is willing to pay for it, as the reduction of these levels implies, necessarily, increased operational costs. Skøien and Blöschl [35] point that the number of samples often rely on the budget available rather than on scientific analyses of what would be needed to sample the variable of interest accurately. This highlights the importance of studying methods to estimate the sampling

uncertainties to achieve the best cost-benefit relationship possible. Several studies [36–38] report spatial variation of sediments’ geochemical features, as is intuitively expected, so the question is how to deal with this spatial variability in the context of the limitations on the number of samples to be taken to assess the mean value of the studied parameters. Since the uncertainty of measurements of many systems is dominated by the intrinsic heterogeneity of sampling target [12,39], the use of simple duplicate methods can provide a reliable estimate of uncertainty both in the small and large scale.

Therefore, the objectives of this work were: (a) to determine the levels of metals in freshwater sediments of a stream impacted by landfill leachate discharge and in the leachate itself; (b) to compare the concentrations of metals in sediments and leachate with statutory limits to verify if the suspected pollution was above those values; (c) to assess the uncertainty generated by sampling and analytical procedures of these measurements and its impact on the interpretation of the results, within the environmental forensics framework.

2. Material and methods

2.1. Study area

This study area is located in the Sinos River Watershed (South Brazil) that is densely populated and industrialized with an important presence of the leather and shoemaking industries, in the southern part of Brazil. The studied watercourse, Portão stream, is severely impacted by industrial effluents and sewage. In addition to the tanneries’ effluents, leachate from the hazardous waste landfill was allegedly discharged directly in the Portão stream.

The study area comprised a stretch of Portão stream where the sediment was sampled, and also the hazardous waste landfill where the leachate was taken from leachate ponds (Fig. 1). This landfill started its operation in the early 1990s, receiving hazardous industrial waste, predominantly chromium-tanned leather residues, from tanneries and shoe-making factories, and the volume of residues disposed on this site was estimated in 2,000,000 m³.

2.2. Sampling

The sampling points were georeferenced in geographic coordinates system and geodetic datum SIRGAS 2000 using a Garmin brand, Etrex Vista HCX model handheld navigation GPS receiver. The spatial data was processed for the elaboration of the map in Fig. 1 using the GIS software QGIS, version 2.12 – Lyon [40].

Sediments were sampled at eight locations, identified as S1 through S8, for at least eight targets are needed to get a reliable estimate of uncertainty from sampling [11,41]. Although the higher the number of replicates the better the estimated standard deviation will be, budget limitations are often a restraint in environmental forensic investigations, making this minimum sample design a practical strategy. The sampling points were located around the headwaters of the stream (S1), used as a reference for background values, upstream from the leachate discharge sites (S2), near the discharge sites (S3 through S7) and about 50 m downstream the discharges (S8). At each sampling point, two 20–30 cm depth cores of sediment were taken, using a different tubular device made of PVC with a 40 mm diameter inner tube. Each sediment core was considered a sampling target duplicate and they were spaced 10–30 cm one from each other for this was the minimum practicable distance between the sampling spots. The 16 sediment samples obtained were pre-homogenized and stored in plastic containers.

A total of 16 leachate grab samples were taken from eight leachate ponds (L1 through L8) at the landfill leachate treatment

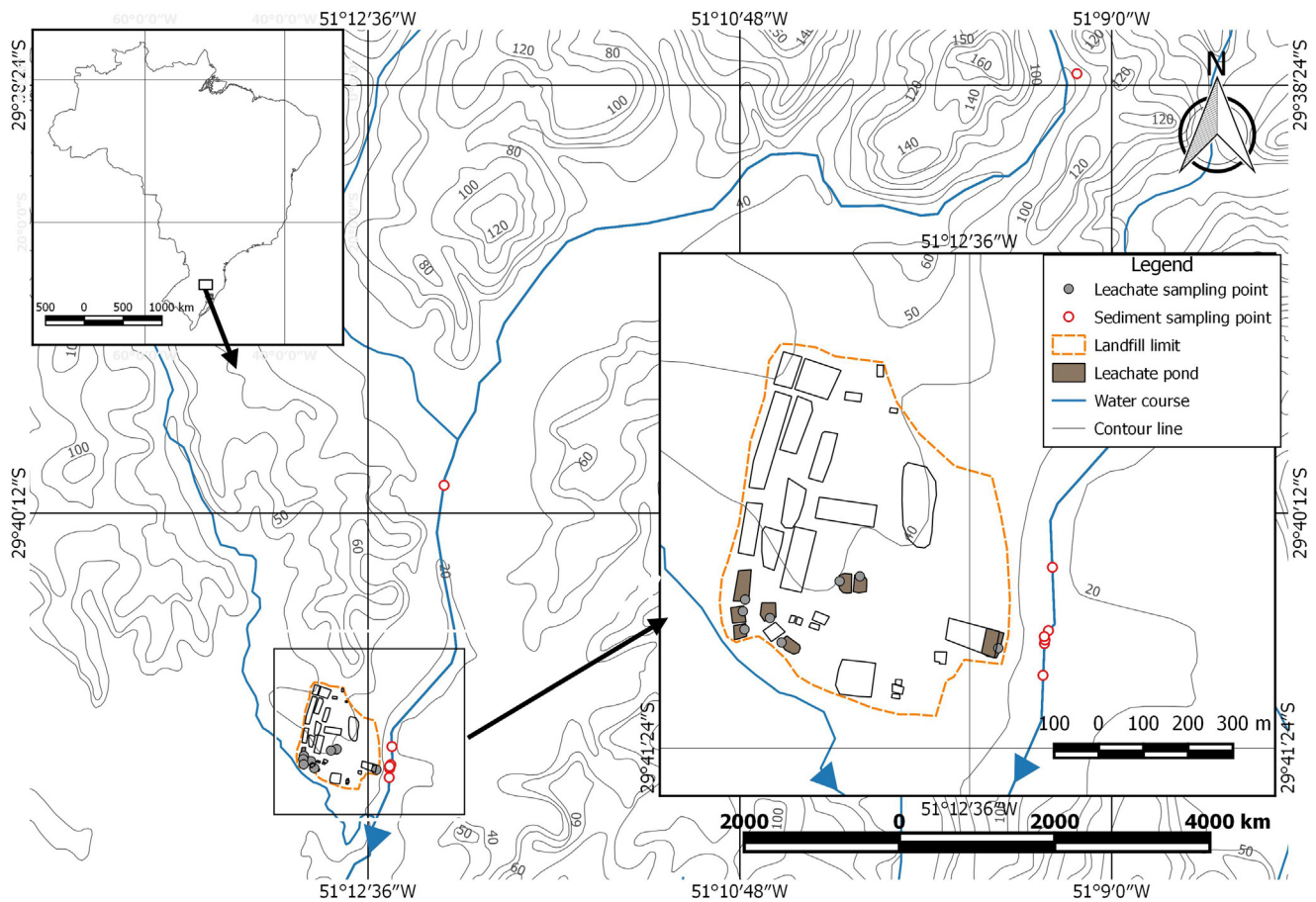


Fig. 1. Study area showing sediment and leachate sampling points locations.

system facilities. At each pond, a stainless steel water sampler was submerged and its content, approximately 1 L, was transferred to a plastic bottle. This procedure was performed twice in each pond to obtain the sampling duplicates.

All samples (sediment and leachate) were refrigerated during transportation to the laboratory and stored frozen in previously acid washed containers as described in CETESB [42] until analysis.

2.3. Sample preparation and analysis

Sediment samples were freeze-dried and passed through a 2 mm nylon sieve to homogenize and remove debris and larger stones and after that, through a 63 μm nylon sieve. Metal analysis was carried on the <63 μm fraction as a homogenizing and normalization procedure to allow comparison among sampling sites since there is a preferential association of pollutants with fine grain sized particles [43,28]. The samples were digested using a Microwave Accelerated Reaction System, Model Mars 6 (CEM Corporation). The acid extraction solution was a mixture containing 9 mL of HNO_3 and 3 mL of HCl sub-boiling, according to recommendations of 3051A USEPA method. This mixture was added to microwave tubes Xpress containing 0.5–1.0 g of sediment sample or the certified reference material. The digestion was performed according to the following parameters: power of 850–1800 W, ramp time of 5 min 3 s up to 175 $^\circ\text{C}$ and hold time of 4 min 30 s. After cooling, the contents of the tube were transferred to a 50 mL centrifuge vial and completed up to 40 g with high purity water (Milli-Q) with a resistivity of 18 $\text{M}\Omega\text{cm}^{-1}$ at 25 $^\circ\text{C}$. Metal analysis was performed after decanting the residues of the vial. The validation of this method was performed by analyzing certified

reference material (SRM 2704 Buffalo River Sediment) three times. The analysis steps were replicated for each sample.

The leachate samples were acid extracted according to EPA 3015a method adapted [44] adding 3 mL of HNO_3 sub-boiling and 1 mL of HCl sub-boiling to a subsample of 20 g previously homogenized by vigorous shaking and weighed into Xpress microwave tubes. The samples were digested using a Microwave Accelerated Reaction System, Model Mars 6 (CEM Corporation). The digestion was performed according to the following parameters: power of 1030–1800 W, ramp time of 20 min up to 120 $^\circ\text{C}$ and hold time of 5 min. After cooling, the contents of the tube were transferred to a 50 mL centrifuge vial and completed up to 30 g with high purity water (Milli-Q) with a resistivity of 18 $\text{M}\Omega\text{cm}^{-1}$ at 25 $^\circ\text{C}$.

Metal analysis (Cr, Cu, Ni, Zn) was performed after decanting the residues of the vial.

Metal concentrations in leachate and sediment extracts were measured using Flame Atomic Absorption Spectrometer (FS-FAAS, Varian, model Spectr-AAS-220-FS). All glassware was cleaned in 10% HNO_3 (w/v) prior to each experiment. Chemicals used for digestion and extraction experiments were analytical reagent grades. The validation of this method was performed by analyzing the spiked matrix in three replications. The analysis steps were duplicated for each sample.

2.4. Uncertainty estimation

The empirical approach described by Grøn et al. [11] was employed to assess the uncertainties of the measurements. In this study, relative range statistics with duplicate measurements in a

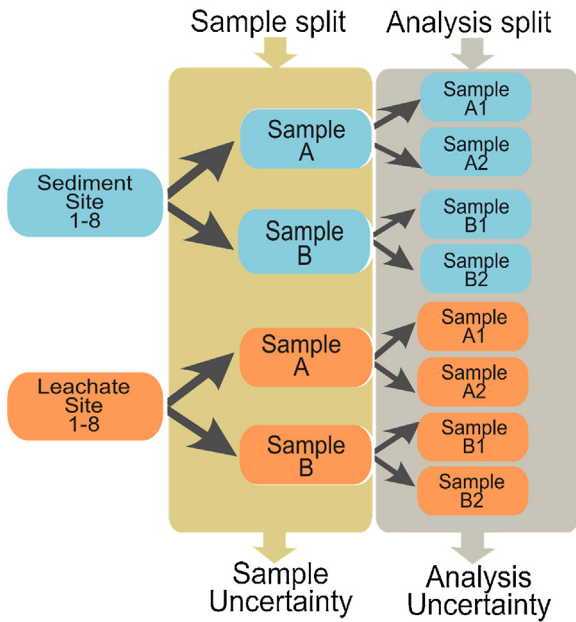


Fig. 2. Scheme of the two level balanced design applied to leachate and sediment samples.

balanced design with eight different targets (sampling sites S1 to S8 for sediments and L1 to L8 for leachate) were applied. This method of calculation using range statistics was chosen for it is easily implemented using spreadsheet applications and the results obtained provides statistical estimates only slightly different from those obtained with ANOVA and RANOVA methods [12]. The metal analyses in sediment and leachate were implemented with double split design (duplicate method), replicating the sampling target and the analytical procedures (Fig. 2).

The Relative Standard Deviation (RSD) of the measurement represents the uncertainty of the whole measurement, which includes the process of sampling and analysis of each variable/parameter. The measurement RSD corresponds to the combined standard uncertainty u for the purposes of this study and, according to Grøn et al. [11], the confidence interval to report a sampling uncertainty based directly on one standard deviation ($X = x \pm u$) corresponds to $\approx 67\%$. The authors indicate that the expanded uncertainty, $U (U = 2u)$, would increase the confidence interval to $\approx 95\%$, as expected in a normal distribution when two

standard deviations (σ) are considered. Fig. 3 shows the equations used to calculate the Relative Standard Deviations of the measurement, and its components, which are the sampling and analysis RSDs. The relative standard deviation, RSD, for measurement is calculated using a statistical factor of 1.128 because duplicates are being analyzed [11,45].

3. Results and discussion

3.1. Sediment analysis

The results of the Buffalo River Sediment analysis can be viewed in Supplementary material 1, as well as the Detection Limits for each metal. Zn displayed the highest recovery rate (94%) and Cr the lowest (55%). The relatively low recovery values for Cr are possibly because the USEPA 3051a Method is not intended to accomplish total decomposition of the sample and the Buffalo River Sediment is certified for total extraction of metals. Furthermore, this study's recoveries were in accordance with the ones reported in USEPA 3051a and the results of other authors [46–48]. The determinations of the studied metals in the Buffalo River Sediment were suitable for the validation of the methodology, but not for the analytical bias estimation. This is because the chromium predominantly present in the matrix analyzed in this work may be in a different form of that in the SRM, so the bias would not be applicable.

The results of Cr, Cu, Ni, and Zn determinations in sediment samples are shown in Fig. 4. The results presented for each sampling target duplicate (sample A and B) are the mean values of the analysis duplicates (A₁, A₂ and B₁, B₂). Thus, sample xA_i is, in fact, the mean value of subsamples' xA₁ and xA₂ determinations. The complete dataset of the metals' determinations in sediment can be found in Supplementary material 2. Data reveals an important metal enrichment in the stream sediments (sites S2 to S8) in comparison to the site near the headwaters (S1).

Metal concentrations in sediments were compared to statutory limits established by CONAMA Resolution n° 454/2012 [49] which are based on the levels defined by Canadian Sediment Quality Guidelines for the Protection of Aquatic Life [50] and known as TEL (Threshold Effect Level) and PEL (Probable Effect Level) levels. Cr, Cu, Ni, and Zn were found in concentrations above these limits in most sampling sites downstream of S1. As shown in Fig. 4, Cr and Ni values were above the PEL at all impacted sites as well as Cu in sites S5 (Sample A) and S8 and Zn in sites S5, S7 (sample B) and S8. The other sites exhibited Cu and Zn concentrations predominantly between TEL and PEL.

target	Sample A					Sample B					$\bar{x}_i = \frac{\bar{x}_{iA} + \bar{x}_{iB}}{2}$	$d_{\bar{x}_i} = \frac{ x_{iA} - x_{iB} }{\bar{x}_i}$		
	x_{iA1}	x_{iA2}	$D_{iA} = x_{iA1} - x_{iA2} $	\bar{x}_{iA}	$d_{iA} = \frac{D_{iA}}{\bar{x}_{iA}} \cdot 100$	x_{iB1}	x_{iB2}	$D_{iB} = x_{iB1} - x_{iB2} $	\bar{x}_{iB}	$d_{iB} = \frac{D_{iB}}{\bar{x}_{iB}} \cdot 100$				
1	x_{1A1}	x_{1A2}	$D_{1A} = x_{1A1} - x_{1A2} $	\bar{x}_{1A}	$d_{1A} = \frac{D_{1A}}{\bar{x}_{1A}} \cdot 100$	x_{1B1}	x_{1B2}	$D_{1B} = x_{1B1} - x_{1B2} $	\bar{x}_{1B}	$d_{1B} = \frac{D_{1B}}{\bar{x}_{1B}} \cdot 100$	$D_1 = \frac{\bar{x}_{1A} + \bar{x}_{1B}}{2}$	$d_{\bar{x}_1} = \frac{ x_{1A} - x_{1B} }{\bar{x}_1}$		
2	x_{2A1}	x_{2A2}	$D_{2A} = x_{2A1} - x_{2A2} $	\bar{x}_{2A}	$d_{2A} = \frac{D_{2A}}{\bar{x}_{2A}} \cdot 100$	x_{2B1}	x_{2B2}	$D_{2B} = x_{2B1} - x_{2B2} $	\bar{x}_{2B}	$d_{2B} = \frac{D_{2B}}{\bar{x}_{2B}} \cdot 100$	$D_2 = \frac{\bar{x}_{2A} + \bar{x}_{2B}}{2}$	$d_{\bar{x}_2} = \frac{ x_{2A} - x_{2B} }{\bar{x}_2}$		
3	x_{3A1}	x_{3A2}	$D_{3A} = x_{3A1} - x_{3A2} $	\bar{x}_{3A}	$d_{3A} = \frac{D_{3A}}{\bar{x}_{3A}} \cdot 100$	x_{3B1}	x_{3B2}	$D_{3B} = x_{3B1} - x_{3B2} $	\bar{x}_{3B}	$d_{3B} = \frac{D_{3B}}{\bar{x}_{3B}} \cdot 100$	$D_3 = \frac{\bar{x}_{3A} + \bar{x}_{3B}}{2}$	$d_{\bar{x}_3} = \frac{ x_{3A} - x_{3B} }{\bar{x}_3}$		
					$n_{iA} = 3$						$n_{iB} = 3$	$n_i = 3$		
					$\bar{d}_{analysis} = \frac{\sum d_{iA} + \sum d_{iB}}{n_{iA} + n_{iB}}$					$RSD_{analysis} = \frac{\bar{d}_{analysis}}{1.128}$				
					$\bar{d}_{measurement} = \frac{\sum d_{\bar{x}_i}}{n_i}$					$RSD_{measurement} = \frac{\bar{d}_{measurement}}{1.128}$				
$RSD_{sampling} = \sqrt{RSD_{measurement}^2 - \left(\frac{RSD_{analysis}}{\sqrt{2}}\right)^2}$														

Fig. 3. Range statistics calculations in double split design investigation for sampling targets (i). To obtain the replicates, two samples (A and B) were collected at each sampling site (target) and each sample was divided into two subsamples (1 and 2) for analysis. The calculation of the RSD for measurement, analysis, and sampling is demonstrated with three sampling targets. Adapted from Grøn et al. [11].

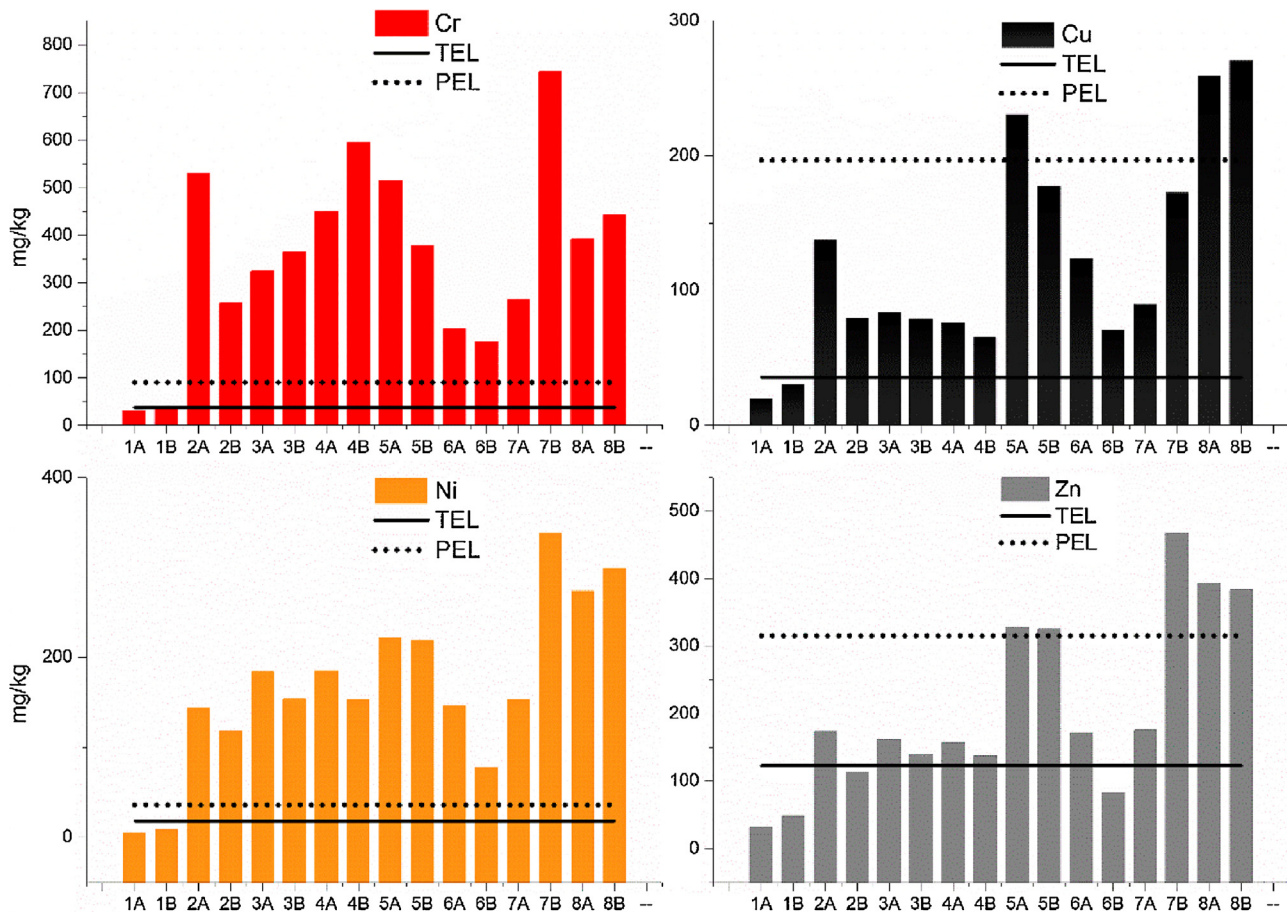


Fig. 4. Cr, Cu, Ni and Zn concentrations in sediment samples (sites S1–S8) in double split design showing the mean values of the analysis split for each sampling replicate identified as A and B compared to sediment legislation based on Canadian Sediment Quality Guidelines (TEL and PEL).

3.2. Leachate analysis

The recoveries of spiked samples and Detection Limits for metal analysis in leachate can be found in Supplementary material 1 and complete dataset of the metals' determinations in leachate is displayed in Supplementary material 3. The results presented for each sampling target duplicate (sample A and B) are the mean values of the analysis duplicates as the sediments were. The metals' concentrations exhibited variations among the leachate ponds, revealing the compositional differences between them (Fig. 5). These differences were probably a consequence of the distinct types of waste contained in the various cells of the landfill in which the leachate directed to these ponds was produced. The most abundant metal, detected in all samples, was chromium, and its levels ranged from 2.91 mg/L in sample 1A to 31.6 mg/L in sample 2B, with an average of 16.08 mg/L and a standard deviation of 10.58 mg/L. This high Cr content was expected since the landfill cells are predominantly filled with chromium-tanned leather residues that contains roughly 3% chrome on a dry matter basis [51].

The leachate was considered wastewater from the studied Hazardous Waste Landfill since it was released in the watercourse, therefore the statutory limits for metal concentrations in it are given by CONAMA Resolution n° 430/2011 [52]. The concentration limit for Cr on this Resolution is 0.5 mg/L, so this makes the maximum value found in one sample from pond L2 more than 60 times higher than the regulation allowance. This highlights the pollution potential of the landfill leachate. Cu was identified in ponds L2, L5, L7, L8 and L6 and, in the latter, only in one of the

analysis duplicates and at levels near the detection limit of the method. The Cu maximum concentration was 0.33 mg/L, which is below the statutory limits for this metal, set at 1 mg/L. Ni was detected in all samples in levels from 0.11 mg/L (L1) to 0.87 g/L in L2, with a mean value of 0.44 mg/L. Zn was detected in L2, L5, L7, and L8 and in one sample from pond L6 with concentrations ranging from 0.12 mg/L in sample L4 to 1.61 mg/L in L8. The latter metals (Ni and Zn) showed concentrations below the statutory limits for effluents (2 mg/L for Ni and 5 mg/L for Zn).

3.3. Uncertainty estimation

The double split design performed with the metal analysis in leachate and sediment allowed the discrimination of the components of the uncertainty from the measurement. In this case, these components were the analytical process and the sampling. The calculations of the RSD representing the uncertainty for each determination were performed according to the equations presented in Fig. 3 and the results are shown in Table 1.

The total expanded uncertainty $U(k=2)$ of the measurement for metals in sediments ranged from 56% for Ni to 63% for Cr. The highest value of the analytical component of the uncertainty was registered for Cu (4.5%) and the smallest for Zn (3.2%) in the same environmental compartment. The sampling component of uncertainty was higher for Cr (63%) and lower for Ni (56%). The total expanded uncertainty $U(k=2)$ of the measurement, obtained with the results of metal determinations in leachate samples, ranged from 17% for Cr to 41% for Zn. The highest value of the analytical component of the uncertainty in leachate was registered for Cu

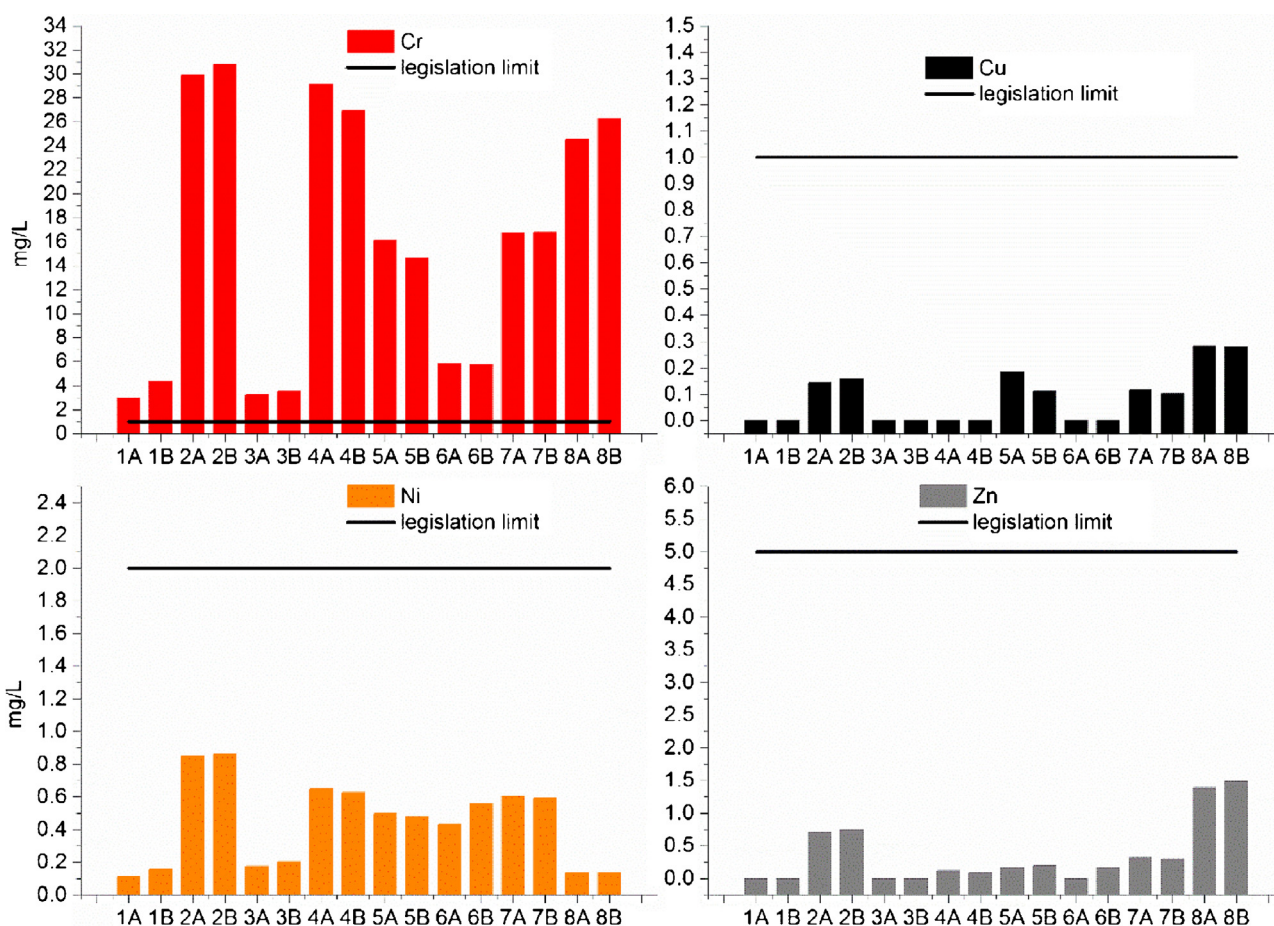


Fig. 5. Cr, Cu, Ni and Zn concentrations in leachate samples (ponds L1–L8) in double split design showing the mean values of the analysis split for each sampling replicate identified as A and B compared to wastewater legislation limit.

(26%) and the lowest for Cr (7.8%). The highest uncertainty from sampling in leachate was found for Zn determinations (38%) and the lowest for Cr (16%). The uncertainty of measurement was overall lower in the matrix leachate, which could be considered a type of wastewater. This is expected since the leachate, as an aqueous matrix, exhibits greater uniformity in the distribution of its components compared to particulate substances as the sediments [57].

Leachate analyses showed a relatively larger interval of uncertainty among the parameters determined, ranging from 17% for Cr to 41% for Zn. In general, the uncertainties of the analytical process were relatively higher in the analysis of leachate in comparison to the sediments.

The duplicate method is applied to estimate the uncertainties (standard/random error) introduced by the sampling (sampling precision). The dominant factor for this error is the spatial

heterogeneity [10]. The heterogeneity of particulate samples was studied by Gy, who divided it into two classes: heterogeneity of constitution and heterogeneity of the distribution [53–55]. The heterogeneity of the constitution refers to the fact that natural materials are heterogeneous because they consist of aggregates of different types of particles (e.g. molecules, ions, grains). On the other hand, the heterogeneity of distribution occurs because particles of the analyte are not evenly distributed in the sample target, but rather forming clusters. This is particularly important in the case of solids, powders or other particulate materials like the sediments studied. Unlike those, fluids, as either gases or liquids, tend to display a more homogeneous distribution of components.

Addressing of uncertainty of measurements is critical for proper decision making in any field of activity in which they are used [12]. In environmental forensics, these are of particular significance, since in many circumstances these measures may define a situation as an environmental crime or another legislation breach, with its implications of associated penalties. In this study, the uncertainty of the measurement lied around 30% in sediment, leading to an expanded uncertainty ($k=2$) to achieve 95% confidence of around 60%. This implies that information about the uncertainty from the measurement is essential for the interpretation of the analyses' results. Taking as an example the results of Cu determination at samples from site S5 of 230 mg/kg in replicate 5A and 177 mg/kg in 5B (Table 2), knowing the legislation guidelines for this metal in sediment (197 mg/kg) and the calculated expanded uncertainty of Cu measurements in sediment of 59%, the range of certainty in the results of sample 5A, with a confidence interval of 95%, would lie from 94 mg/kg to 367 mg/kg

Table 1

Expanded measurement uncertainty U ($k=2$, i.e. 95% confidence) estimates for the double split design performed with the results of metals (Cr, Cu, Ni, and Zn) in sediment and leachate samples from eight sampling points (targets).

	Sediment			Leachate		
	Analysis (%)	Sampling (%)	Total (%)	Analysis (%)	Sampling (%)	Total (%)
Cr	4.1	63	63	7.8	16	17
Cu	4.5	59	59	26	34	39
Ni	3.6	56	56	17	18	22
Zn	3.2	61	61	23	38	41

Table 2Cr, Cu, Ni, and Zn concentrations in sediment and leachate reporting the expanded measurement uncertainty U (95% confidence).

	Sediment			Leachate				
	Cr (mg/kg)	Cu (mg/kg)	Ni (mg/kg)	Zn (mg/kg)	Cr (mg/L)	Cu (mg/L)	Ni (mg/L)	Zn (mg/L)
1A	30.2 ± 19.1	19.5 ± 11.6	4.6 ± 2.6	31.1 ± 19.1	2.95 ± 0.5	<0.05	0.11 ± 0.0	<0.04
1B	38.5 ± 24.3	30.4 ± 18.0	8.5 ± 4.8	48.2 ± 29.7	4.36 ± 0.7	<0.05	0.15 ± 0.0	<0.04
2A	529.3 ± 334.5	137.4 ± 81.5	143.3 ± 80.7	173.3 ± 106.6	29.9 ± 5.0	0.14 ± 0.1	0.85 ± 0.2	0.7 ± 0.3
2B	256.5 ± 162.1	79.4 ± 47.1	118.5 ± 66.7	112.6 ± 69.3	30.8 ± 5.1	0.16 ± 0.1	0.86 ± 0.2	0.7 ± 0.3
3A	324.1 ± 204.8	83.6 ± 49.6	183.9 ± 103.5	161.7 ± 99.4	3.25 ± 0.5	<0.05	0.17 ± 0.0	<0.04
3B	364.2 ± 230.1	79.2 ± 47.0	153.4 ± 86.3	139.3 ± 85.7	3.49 ± 0.6	<0.05	0.20 ± 0.0	<0.04
4A	449.8 ± 284.3	75.8 ± 44.9	185.2 ± 104.3	156.6 ± 96.3	29.1 ± 4.9	<0.05	0.65 ± 0.1	0.1 ± 0.0
4B	594.9 ± 376.0	65.3 ± 38.7	152.2 ± 85.7	137.0 ± 84.2	26.9 ± 4.5	<0.05	0.63 ± 0.1	0.1 ± 0.0
5A	515.0 ± 325.5	230.7 ± 136.8	221.9 ± 124.9	327.5 ± 201.4	16.1 ± 2.7	0.18 ± 0.1	0.50 ± 0.1	0.2 ± 0.1
5B	377.8 ± 238.8	177.3 ± 105.2	218.5 ± 123.0	324.7 ± 199.7	14.6 ± 2.4	0.11 ± 0.0	0.48 ± 0.1	0.2 ± 0.1
6A	202.4 ± 127.9	124.0 ± 73.5	146.4 ± 82.4	170.9 ± 105.1	5.87 ± 1.0	<0.05	0.43 ± 0.1	<0.04
6B	174.5 ± 110.3	70.6 ± 41.8	77.6 ± 43.7	83.0 ± 51.1	5.74 ± 1.0	<0.05	0.56 ± 0.1	0.2 ± 0.1
7A	264.2 ± 167.0	89.9 ± 53.3	152.9 ± 86.1	175.4 ± 107.9	16.7 ± 2.8	0.12 ± 0.0	0.60 ± 0.1	0.3 ± 0.1
7B	743.1 ± 469.7	172.7 ± 102.4	338.4 ± 190.5	467.5 ± 287.5	16.8 ± 2.8	0.10 ± 0.0	0.59 ± 0.1	0.3 ± 0.1
8A	391.0 ± 247.1	259.2 ± 153.7	273.6 ± 154.1	393.2 ± 241.8	24.5 ± 4.1	0.28 ± 0.1	0.13 ± 0.0	1.4 ± 0.6
8B	441.5 ± 279.0	270.4 ± 160.4	298.8 ± 168.2	383.0 ± 235.5	26.3 ± 4.4	0.28 ± 0.1	0.14 ± 0.0	1.5 ± 0.6

and in sample 5 B from 72 mg/kg to 282 mg/kg. As absolute values, sample 5A would classify the sediment above the legislation threshold and sample 5B, which was collected at the 'same' sampling site, would be considered below it. Nevertheless, acknowledging this reliance interval, it is evident that each single result alone would not be able to classify the sediment according to the statutory limits and this expresses the importance of this approach to the interpretation of environmental analysis results in the forensic context. Therefore, if this were the only evidence of an alleged pollution crime it would be difficult to sustain a judgment of conviction or acquittal of the author. On the other hand, if a measure with a degree of uncertainty so high was used as an absolute value and integrated a piece of evidence like an expert report, this could lead a Justice to a decision based on speculative premises. This corroborates the importance of incorporating this uncertainty from sampling assessment in environmental studies to inform the extent of the focused parameter variability in the domain of the studied environment.

To deal with the uncertainty, Ramsey and Argyraki [10] proposed the probabilistic classification for contaminated land. Summarizing, this classification defines four probabilistic categories, which are: *uncontaminated* (when the measured value plus the uncertainty is below a certain threshold), *possibly contaminated* (when the measured value is below the threshold, but the

measured value plus the uncertainty is over this threshold), *probably contaminated* (when the measured value is above the threshold, but the measured value minus the uncertainty is below this threshold) and *contaminated* (when the measured value minus the uncertainty is over this threshold). The probability of contamination ($P(C)$) assigned to these categories using the expanded uncertainty is then <0.025 for *uncontaminated*, 0.025–0.500 for *possibly contaminated*, 0.500–0.975 for *probably contaminated* and >0.975 for *contaminated*. The classification of the sediment and leachate samples regarding the respective statutory thresholds for the metals analyzed in these environmental compartments using the probabilistic approach is depicted in Table 3. The classification of the targets' duplicates according to this method demonstrates that sampling site S5 results for Cu determinations, that were discussed above, are indeed not conclusive as sample 5A is Probably Contaminated (probability of contamination from 0.500 to 0.975) and sample 5B Possibly Contaminated (probability of contamination from 0.025 to 0.500). Such results would clearly demand further investigations in that sampling site, or, if not possible, caution on the decisions regarding its Cu contamination. The values displayed visually in Fig. 4, suggest that even though the sampling uncertainty at some locations (e.g. locations 2 and 7) is very high, overall it is small enough to ensure that the Cr concentration in sediments exceeds

Table 3

Probabilistic classification [10] applied to sediment and leachate determinations regarding the statutory limits.

	Sediment				Leachate			
	Cr	Cu	Ni	Zn	Cr	Cu	Ni	Zn
1A	Uncont.	Uncont.	Uncont.	Uncont.	Cont.	Uncont.	Uncont.	Uncont.
1B	Uncont.	Uncont.	Uncont.	Uncont.	Cont.	Uncont.	Uncont.	Uncont.
2A	Cont.	Poss. Cont.	Cont.	Uncont.	Cont.	Uncont.	Uncont.	Uncont.
2B	Cont.	Uncont.	Cont.	Uncont.	Cont.	Uncont.	Uncont.	Uncont.
3A	Cont.	Uncont.	Cont.	Uncont.	Cont.	Uncont.	Uncont.	Uncont.
3B	Cont.	Uncont.	Cont.	Uncont.	Cont.	Uncont.	Uncont.	Uncont.
4A	Cont.	Uncont.	Cont.	Uncont.	Cont.	Uncont.	Uncont.	Uncont.
4B	Cont.	Uncont.	Cont.	Uncont.	Cont.	Uncont.	Uncont.	Uncont.
5A	Cont.	Prob. Cont.	Cont.	Prob. Cont.	Cont.	Uncont.	Uncont.	Uncont.
5B	Cont.	Poss. Cont.	Cont.	Prob. Cont.	Cont.	Uncont.	Uncont.	Uncont.
6A	Prob. Cont.	Poss. Cont.	Cont.	Uncont.	Cont.	Uncont.	Uncont.	Uncont.
6B	Prob. Cont.	Uncont.	Prob. Cont.	Uncont.	Cont.	Uncont.	Uncont.	Uncont.
7A	Cont.	Uncont.	Cont.	Uncont.	Cont.	Uncont.	Uncont.	Uncont.
7B	Cont.	Poss. Cont.	Cont.	Prob. Cont.	Cont.	Uncont.	Uncont.	Uncont.
8A	Cont.	Prob. Cont.	Cont.	Prob. Cont.	Cont.	Uncont.	Uncont.	Uncont.
8B	Cont.	Prob. Cont.	Cont.	Prob. Cont.	Cont.	Uncont.	Uncont.	Uncont.

Uncont.: Uncontaminated ($P(C) < 0.025$), Poss. Cont.: Possibly Contaminated ($P(C) = 0.025 - 0.500$), Prob. Cont.: Probably Contaminated ($P(C) = 0.500 - 0.975$), Cont.: Contaminated ($P(C) > 0.975$).

the PEL at most locations, with a probability above 0.975, thus indicating that the sampled targets could be considered polluted with this metal.

Regarding the sediment sampling targets, it is noted that site S8 was revealed as the most consistently contaminated by all the metals determined. It is worth mentioning that this site was the one downstream the landfill, consequently receiving the total contribution of leachate emissions. The classification of leachate was able to characterize all sampling targets as contaminated with Cr and uncontaminated regarding Cu, Ni, and Zn.

These uncertainties estimates are specific to this study's parameters and matrices as well as analysis methodology and cannot be directly applied to other cases, even similar ones. Nevertheless, they can be regarded as a reference of the uncertainty comprised in metal analyses in sediments and leachate using this methodology.

The duplicate method could be further explored in environmental forensics and also applied to estimate the uncertainties in other forensic fields in order to comply with the recommendations of the Committee on Identifying the Needs of the Forensic Sciences Community, National Research Council [56] that require quantifiable measures of uncertainty in the conclusions of forensic analyses.

4. Conclusions

The metal determination in sediment samples demonstrated that Cr and Ni concentrations exceeded the statutory limits (PEL) at all sites downstream from the pollutions sources (S2–S8). This can be stated considering the expanded uncertainty U ($k=2$) of the measurements and with $P(C) > 0.975$ at most sites. Cu and Zn concentrations were above the *Probable Effect Level* (PEL) at site S8 and S5, but the classification was inconclusive due to the uncertainties of the measurements.

Metal analyses in leachate, considering the expanded uncertainty U ($k=2$) of the measurements, revealed that Cr concentrations were above the statutory limits with $P(C) > 0.975$ in all leachate ponds and that the leachate, despite containing Cu, Ni, and Zn, could be classified as uncontaminated by these metals with $P(C) < 0.025$.

The uncertainty from sampling was the most important component of the combined uncertainty that also included the uncertainty originating from the analysis. The sampling uncertainty estimates indicate that it is a function of the environmental matrix and on the parameters analyzed. The uncertainties of metals' determinations were higher in sediment samples, however, the variation of the parameters was relatively low, unlike the leachate, where the measurement uncertainties were relatively lower, on the other hand, greater variation was observed among the parameters. This sampling uncertainty estimation approach also allows inter-site comparison, and it was noticed that the pristine site S1 showed lower variations between the replicates. The relatively higher heterogeneity of sediments in polluted sites emphasizes the importance of the uncertainty estimation in sites affected by anthropogenic inputs.

The approach demonstrated the importance of metrology tools in addressing the heterogeneity of the environmental media, which is often ignored in most assessments. The awareness of the uncertainties, including those derived from sampling that usually reflects the small-scale patchiness of the contaminants' distribution, may be crucial to the interpretation of environmental assessments' results in forensic investigations. This is of special relevance since the uncertainties comprised in the environmental analysis results can modify the interpretation of these data and could lead to inaccurate decisions and/or understandings if not taken into account.

The probabilistic classification is a valuable benchmark and deserves further discussions in order to be applied to sediments and wastewater for regulatory and liability purposes, as this study demonstrated. This, along with the duplicate method that provides an uncertainty estimation tailored to the projects/studies context covering the geospatial, the matrix, the analyte and the analytical method variabilities, are noteworthy tools in environmental pollution investigations' experimental design and in the conclusions of environmental forensic analyses.

Acknowledgement

This work was supported by the CNPq – National Council of Technological and Scientific Development in Brazil (grant number 484248/2011-1).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.forensicint.2018.04.005>.

References

- [1] K.A. Boon, M.H. Ramsey, Judging the fitness of on-site measurements by their uncertainty, including the contribution from sampling, *Sci. Total Environ.* 419 (2012) 196–207, doi:<http://dx.doi.org/10.1016/j.scitotenv.2011.12.001>.
- [2] ISO, Guide to the Expression of Uncertainty in Measurement, International Organization for Standardization (ISO), Geneva, 1993.
- [3] B.N. Taylor, C.E. Kuyatt, Guidelines for Evaluating and Expressing Uncertainty in NIST Measurement Results, NIST Technical Note 1297, National Institute of Standards and Technology, 1994.
- [4] ISO/IEC 17025:1999, General Requirements for the Competence of Testing and Calibration Laboratories, International Organization for Standardization (ISO), Geneva, 1999.
- [5] P. De Zorzi, M. Belli, S. Barbizzi, S. Menegon, A. Deluisa, A practical approach to assessment of sampling uncertainty, *Accredit. Qual. Assur.* 7 (2002) 182–188, doi:<http://dx.doi.org/10.1007/s00769-002-0447-1>.
- [6] R.G. Garrett, The determination of sampling and analytical errors in exploration geochemistry, *Econ. Geol.* 64 (1969) 568–569.
- [7] R.G. Garrett, Sampling methodology, in: R.J. Howarth (Ed.), *Handbook Of Exploration Geochemistry*, v. 2: Statistics and Data Analysis in Geochemical Prospecting, Elsevier, Amsterdam, 1983.
- [8] M.H. Ramsey, Sampling and analytical quality Control (SAX) for improved error estimation in the measurement of Pb in the environment using robust analysis of variance, *Appl. Geochemistry* 8 (1993) 149–153, doi:[http://dx.doi.org/10.1016/S0883-2927\(09\)80027-9](http://dx.doi.org/10.1016/S0883-2927(09)80027-9).
- [9] M.H. Ramsey, A. Argyraki, M. Thompson, Estimation of sampling bias between different sampling protocols on contaminated land, *Analyst* 120 (1995) 1353–1356.
- [10] M.H. Ramsey, A. Argyraki, Estimation of measurement uncertainty from field sampling: implications for the classification of contaminated land, *Sci. Total Environ.* 198 (1997) 243–257, doi:[http://dx.doi.org/10.1016/S0048-9697\(97\)05456-9](http://dx.doi.org/10.1016/S0048-9697(97)05456-9).
- [11] C. Grøn, J.B. Hansen, B. Magnusson, A. Nordbotten, M. Krysell, K.J. Andersen, U. Lund, Uncertainty from Sampling – A Nordtest Handbook for Sampling Planners on Sampling Quality Assurance and Uncertainty Estimation, Nordic Innovation Centre, Oslo, Norway, 2007.
- [12] M.H. Ramsey, S.L.R. Ellison (Eds.), *Eurachem/EUROLAB/CITAC/Nordtest/AMC Guide: Measurement Uncertainty Arising from Sampling: a Guide to Methods and Approaches*, Eurachem, 2007 ISBN 978 048926 26 6. Available from the Eurachem secretariat.
- [13] M.H. Ramsey, M. Thompson, Uncertainty from sampling, in the context of fitness for purpose, *Accredit. Qual. Assur.* 12 (2007) 503–513, doi:<http://dx.doi.org/10.1007/s00769-007-0279-0>.
- [14] M.H. Ramsey, K. Boon, New approach to geochemical measurement: estimation of measurement uncertainty from sampling, rather than an assumption of representative sampling, *Geostand. Geoanal. Res.* 34 (2010) 293–304.
- [15] F. Botta, B. Lepot, E. Leoz-Garziandia, A. Morin, Estimation of sampling uncertainty in lake-water monitoring in a collaborative field trial, *TrAC Trends Anal. Chem.* 36 (2012) 176–184, doi:<http://dx.doi.org/10.1016/j.trac.2011.12.007>.
- [16] J.L. Zhou, E. Siddiqui, H.H. Ngo, W. Guo, Estimation of uncertainty in the sampling and analysis of polychlorinated biphenyls and polycyclic aromatic hydrocarbons from contaminated soil in Brighton, UK, *Sci. Total Environ.* 497–498 (2014) 163–171, doi:<http://dx.doi.org/10.1016/j.scitotenv.2014.07.097>.
- [17] N. Guigues, M. Desenfant, B. Lalere, S. Vaslin-Reimann, D. Eyl, P. Mansuit, E. Hance, Estimating sampling and analysis uncertainties to assess the fitness for

- purpose of a water quality monitoring network, *Accredit. Qual. Assur.* (2015) 101–112, doi:<http://dx.doi.org/10.1007/s00769-015-1186-4>.
- [18] S. Dołęgowska, A. Gałuszka, Z.M. Migaszewski, Assessing soil sampling uncertainty in heterogeneous historic metal ore mining sites, *Accredit. Qual. Assur.* 20 (2015) 163–170, doi:<http://dx.doi.org/10.1007/s00769-015-1109-4>.
- [19] K. Pyrek, *Forensic Science Under Siege: The Challenges of Forensic Laboratories and the Medico-Legal Investigation System*, Academic Press (Elsevier), Burlington, MA, 2007.
- [20] J.M. Butler, U.S. initiatives to strengthen forensic science & international standards in forensic DNA, *Forensic Sci. Int. Genet.* 18 (2015) 4–20, doi:<http://dx.doi.org/10.1016/j.fsigen.2015.06.008>.
- [21] M. Thompson, Rationality in an Uncertain World, *Analyst* 120 (1995) 117–118.
- [22] S.S. Castañeda, R.J. Sugang, R.V. Almoneda, N.D.S. Mendoza, C.P.C. David, Environmental isotopes and major ions for tracing leachate contamination from a municipal landfill in Metro Manila, Philippines, *J. Environ. Radioact.* 110 (2012) 30–37, doi:<http://dx.doi.org/10.1016/j.jenvrad.2012.01.022>.
- [23] M.T.G. Oliveira, S.B.A. Rolim, P.C. Mello-Farias, A. Meneguzzi, C. Lutckmeier, Industrial pollution of environmental compartments in the Sinos River Valley, RS, Brazil: geochemical-biogeochemical characterization and remote sensing, *Water Air Soil Pollut.* 192 (2008) 183–198, doi:<http://dx.doi.org/10.1007/s11270-008-9645-8>.
- [24] H. Mohammadzadeh, I. Clark, Degradation pathways of dissolved carbon in landfill leachate traced with compound-specific ¹³C analysis of DOC, *Isotopes Environ. Health Stud.* 44 (2008) 267–294, doi:<http://dx.doi.org/10.1080/10256010802309814>.
- [25] T.H. Christensen, P. Kjeldsen, P.L. Bjerg, D.L. Jensen, J.B. Christensen, A. Baun, H. J. Albrechtsen, C. Heron, Biogeochemistry of landfill leachate plumes, *Appl. Geochem.* 16 (2001) 659–718.
- [26] P. Kjeldsen, M.A. Barlaz, A.P. Rooker, A. Baun, A. Ledin, T.H. Christensen, Present and long-term composition of MSW landfill leachate: A review, *Crit. Rev. Environ. Sci. Technol.* 32 (2002) 297–336.
- [27] E.I.F. Krieger, *Avaliação da Contaminação das Águas Subterrâneas na Área de Influência da Evaluation of groundwater contamination in the area of influence of waste treatment plant—UTRESA S/A, in Estância Velha (RS)*, Dissertation (Master Degree) — Graduate Program in Ecology at the Federal University of Rio Grande do Sul. (in Portuguese) (2000).
- [28] W. Salomons, U. Förstner, *Metals in the Hydrocycle*, Springer-Verlag, Berlin, 1984 349p.
- [29] H.M.V.M. Soares, R.A.R. Boaventura, A.A.S.C. Machado, J.C.G. Esteves da Silva, Sediments as monitors of heavy metal contamination in the Ave river basin (Portugal): multivariate analysis of data, *Environ. Pollut.* 105 (1999) 311–323.
- [30] S. Ramamoorthy, B.R. Rust, Heavy metal exchange process in sediment water systems, *Environ. Geol.* 2 (3) (1978) 165–172.
- [31] J. Rule, Assessment of trace element geochemistry of Hampton Roads Harbor and Lower Chesapeake Bay area sediments, *Environ. Geol.* 8 (4) (1986) 209–219.
- [32] K.P. Singh, D. Moan, V.K. Singh, A. Malik, Studies on distribution and fractionation of heavy metals in Gomti River sediments — a tributary of the Ganges, India, *J. Hydrol.* 312 (2005) 14–17.
- [33] M.S. Islam, M.K. Ahmed, M. Raknuzzaman, M. Habibullah-Al-Mamun, M.K. Islam, Heavy metal pollution in surface water and sediment: a preliminary assessment of an urban river in a developing country, *Ecol. Indic.* 48 (2015) 282–291, doi:<http://dx.doi.org/10.1016/j.ecolind.2014.08.016>.
- [34] I.G. Petrisor, *Environmental Forensics Fundamentals: A Practical Guide*, CRC Press, Boca Raton, FL, 2014 374p. ISBN: 978-1-4665-7158-7.
- [35] J.O. Sköien, G. Blöschl, Sampling scale effects in random fields and implications for environmental monitoring, *Environ. Monit. Assess.* 114 (2006) 521–552, doi:<http://dx.doi.org/10.1007/s10661-006-4939-z>.
- [36] R.T. Rytty, S.L. Reneau, D. Katzman, Investigations of contaminated fluvial sediment deposits: merging of statistical and geomorphic approaches, *Environ. Manage.* 35 (2005) 632–648, doi:<http://dx.doi.org/10.1007/s00267-004-0098-6>.
- [37] A. Farkas, C. Erratico, L. Viganò, Assessment of the environmental significance of heavy metal pollution in surficial sediments of the River Po, *Chemosphere* 68 (2007) 761–768, doi:<http://dx.doi.org/10.1016/j.chemosphere.2006.12.099>.
- [38] M.R. Ghanbarpour, M. Goorzadi, G. Vahabzade, Spatial variability of heavy metals in surficial sediments: Tajan River Watershed, Iran, *Sustain. Water Qual. Ecol.* 1–2 (2013) 48–58, doi:<http://dx.doi.org/10.1016/j.swaqe.2014.04.002>.
- [39] P.D. Taylor, M.H. Ramsey, P.J. Potts, Spatial contaminant heterogeneity: quantification with scale of measurement at contrasting sites, *J. Environ. Monit.* 7 (2005) 1364–1370.
- [40] QGIS Development Team, Version 2.12 — Lyon. Quantum GIS Geographic Information System. Open Source Geospatial Foundation Project, 2015. URL <http://qgis.osgeo.org>. (Accessed 10 May 2015).
- [41] J.A. Lyn, M.H. Ramsey, D.S. Coad, A.P. Damant, R. Wood, K.A. Boon, The duplicate method of uncertainty estimation: are eight targets enough? *Analyst* 132 (2007) 1147–1152, doi:<http://dx.doi.org/10.1039/b702691a>.
- [42] CETESB (São Paulo State Environmental Technology Company), National Guide to collecting and preserving samples: water, sediment, aquatic communities and wastewaters. Organizers: BOTELHO, C.J.B.; COELHO, M.J.; SATO, ZANOLI, M.I.; LAMPARELLI, M.C., São Paulo: CETESB; Brasília; ANA, 2011. 326 p.il., 2011. URL <http://laboratorios.cetesb.sp.gov.br/wp-content/uploads/sites/47/2013/11/guia-nacional-coleta-2012.pdf>. (Accessed 5 June 2016) (in Portuguese).
- [43] S. Miserocchi, L.G. Bellucci, M. Marcaccio, G. Matteucci, V. Landuzzi, G. Quarantotto, G. Rovatti, Sediment composition and normalisation procedures: an example from a QUASH project sediment exercise, *J. Environ. Monit.* 2 (2000) 529–533, doi:<http://dx.doi.org/10.1039/b002760j>.
- [44] US EPA (United States Environmental Protection Agency), Method 3015. Microwave assisted acid digestion of aqueous samples and extracts, 2007. URL <http://www3.epa.gov/epawaste/hazard/testmethods/sw846/pdfs/3015a.pdf>. (Accessed 15 September 2015).
- [45] A.J. Duncan, Quality Control in Industrial Statistics, Richard D. Irwin Inc., 1974.
- [46] M.E. Cox, M. Preda, Trace metal distribution and relation to marine sediment mineralogy, Gulf of Carpentaria, Northern Australia, *Mar. Pollut. Bull.* 46 (12) (2003) 1623–1629, doi:<http://dx.doi.org/10.1016/j.marpolbul.2003.08.010>.
- [47] M. Rodrigues, M. Formoso, Geochemical distribution of selected heavy metals in stream sediments affected by tannery activities, *Water Air Soil Pollut.* 169 (2006) 167–184.
- [48] I.C.A.C. Bordon, J.E.S. Sarkis, G.M. Gobatto, M.A. Hortellani, C.M. Peixoto, Metal concentration in sediments from the Santos Estuarine system: a recent assessment, *J. Braz. Chem. Soc.* 22 (2011) 1858–1865, doi:<http://dx.doi.org/10.1590/S0103-50532011001000005>.
- [49] Brasil. National Council for the Environment (CONAMA). Resolution # 454, November, 1st 2012. Establishes the general guidelines and procedures for managing material to be dredged in waters under national jurisdiction. Repeals the resolutions #344 of 2004 and #421 of 2010. URL <http://www.mma.gov.br/port/conama/legiabre.cfm?codlegi=620>. (Accessed 5 June 2016) (in Portuguese).
- [50] CCME (Canadian Council of Ministers of the Environment), Canadian Sediment Quality Guidelines for the Protection of Aquatic Life [WWW Document], 2001. URL <http://ceqg-rcqe.ccme.ca/en/index.html>. (Accessed 6 October 2016).
- [51] M. Hossain, T. Monir, R. Ul-Haque, A.I. Kazi, S. Islam, S.F. Elahi, Heavy metal concentration in tannery solid wastes used as poultry feed and the ecotoxicological consequences, *Bangladesh J. Sci. Ind. Res.* 42 (2007) 4, doi:<http://dx.doi.org/10.3329/bjsir.v42i4.748>.
- [52] Brasil. National Council for the Environment (CONAMA). Resolution # 430, May, 13th 2011. Rules on the conditions and standards for effluent release, supplementing and amending the Resolution #357, March, 17th 2005, the National Council for the Environment, 2011. URL <http://www.mma.gov.br/port/conama/legiabre.cfm?codlegi=646>. (Accessed 5 June 2016). (in Portuguese).
- [53] P.M. Gy, *Sampling of Heterogeneous and Dynamic Material Systems*, Elsevier, Amsterdam, 1992 654p.
- [54] P.M. Gy, *Sampling for Analytical Purposes*, John Wiley & Sons Ltd., Chichester, 1998 153p.
- [55] P.M. Gy, Proceedings of First World Conference on Sampling and Blending 74 (2004) 7–70 Special Issue of *Chemometr. Intell. Lab.*
- [56] National Research Council — Committee on Identifying the Needs of the Forensic Sciences Community, Strengthening Forensic Science in the United States: A Path Forward, National Academies Press, 2009, doi:[http://dx.doi.org/10.1016/0379-0738\(86\)90074-5](http://dx.doi.org/10.1016/0379-0738(86)90074-5).
- [57] S.L. Simpson, G.E. Batley, A.A. Chariton, J.L. Stauber, C.K. King, J.C. Chapman, R.V. Hyne, S.A. Gale, A.C. Roach, W.A. Maher, *Handbook for Sediment Quality Assessment*, CSIRO: Bangor, NSW, 2005.