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Geochemical interactions study in surface river sediments at an artisanal mining area by means of Canonical (MANOVA)-Biplot

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ABSTRACT

This paper analyzes trace elements concentrations from surface detrital sediments corresponding to 4 rivers located in the artisanal gold mining area of Ponce Enríquez (southern Ecuador) to assess the contamination levels. Moreover, their potential environmental threats were evaluated using both the enrichment factors (EFs) approach and sediment quality guidelines (SQGs). The study showed extremely high concentrations of Hg in certain locations of the Villa river (up to 50 mg/kg), which exceeded the probable effect levels (PELs) for Hg up to 50 times. Similarly, average EFs for As elements reached average values of 87, exceeding up to 80 times the SQGs. Moreover, Cr and Cu were also significant contributors to sediment pollution.

In this study, the Canonical/MANOVA-Biplot, a technique to properly represent the multivariate differences among locations, is introduced as an alternative to the more descriptive approach provided by the most popular Principal Components Analysis. The technique can be viewed as a graphical representation of MANOVA, the adequate technique to stablish the statistical significance of the differences. The procedure established clear differences among the contamination patterns of the 4 river locations.

1. Introduction

Potentially toxic metal(loid)s are naturally occurring elements that meet the following conditions: a) cannot be degraded or destroyed (Tchounwou et al., 2012); b) are persistent in the environment (their concentration remains constant in time); c) can be bioaccumulated (they incorporate into organisms at a rate greater than that at which they are expelled) (e.g. Majer et al., 2014); and d) biomagnificate (higher concentrations are found in organisms higher up in the food chain) (e.g. Smith, 2009; Appenroth, 2010; Wuana and Okieimen, 2011).

The toxicity of these elements depends on a number of factors, namely, dose, route, exposure, and chemical species, as well as the age, gender, genetics, and nutritional status of exposed individuals (Tchounwou et al., 2012). Among all these elements, As, Cd, Cr, Hg and Pb are prominent due to their public health significance because they are considered systemic toxicants, that is to say, that even at low levels of exposure their effects extend through the entire body rather than a specific organ (Leikin and Paloucek, 2008).

Among the potentially toxic elements, As is the most common, ranking 20th in abundance in the Earth's crust (Smedley, 2007). Arsenic can exist as a native mineral, although its presence is more common in pyrites, arsenopyrite, arsenides and sulfosalts (Garelick et al., 2009). Furthermore, As is the only human carcinogen deeply proven to be carcinogen both by inhalation and ingestion (Centeno et al., 2002). Liberation of As into the environment, unlike other carcinogens, usually comes from sources connected with the As-rich geologic strata; such is the case of volcanogenic related activities and mining operations that unearth the As-containing minerals to oxygen (Henke, 2009). In this respect, As desorption from Fe oxyhydroxide (FeOOH) as a consequence of its reduction by bacteria (Mahimairaja et al., 2005; Smedley, 2007) plays a major role in its release. Similarly, in petroleum deposits, Fe^{+3} reduction can be coupled with the oxidation of the organic matter, thus liberating the sorbed As (Henke, 2009). On the other hand, pyrometallurgical processes such as Cu or Hg smelting are frequently a major anthropogenic source (Sierra et al., 2011; Gallego et al., 2015).

Regarding Cr, major sources comprise release from electroplating processes and waste disposal (Wuana and Okieimen, 2011). Chromium may exist in two principal forms: Cr (III) and Cr (VI). Between them, Cr (IV) is the most common at polluted sites, the most mobile and toxic,

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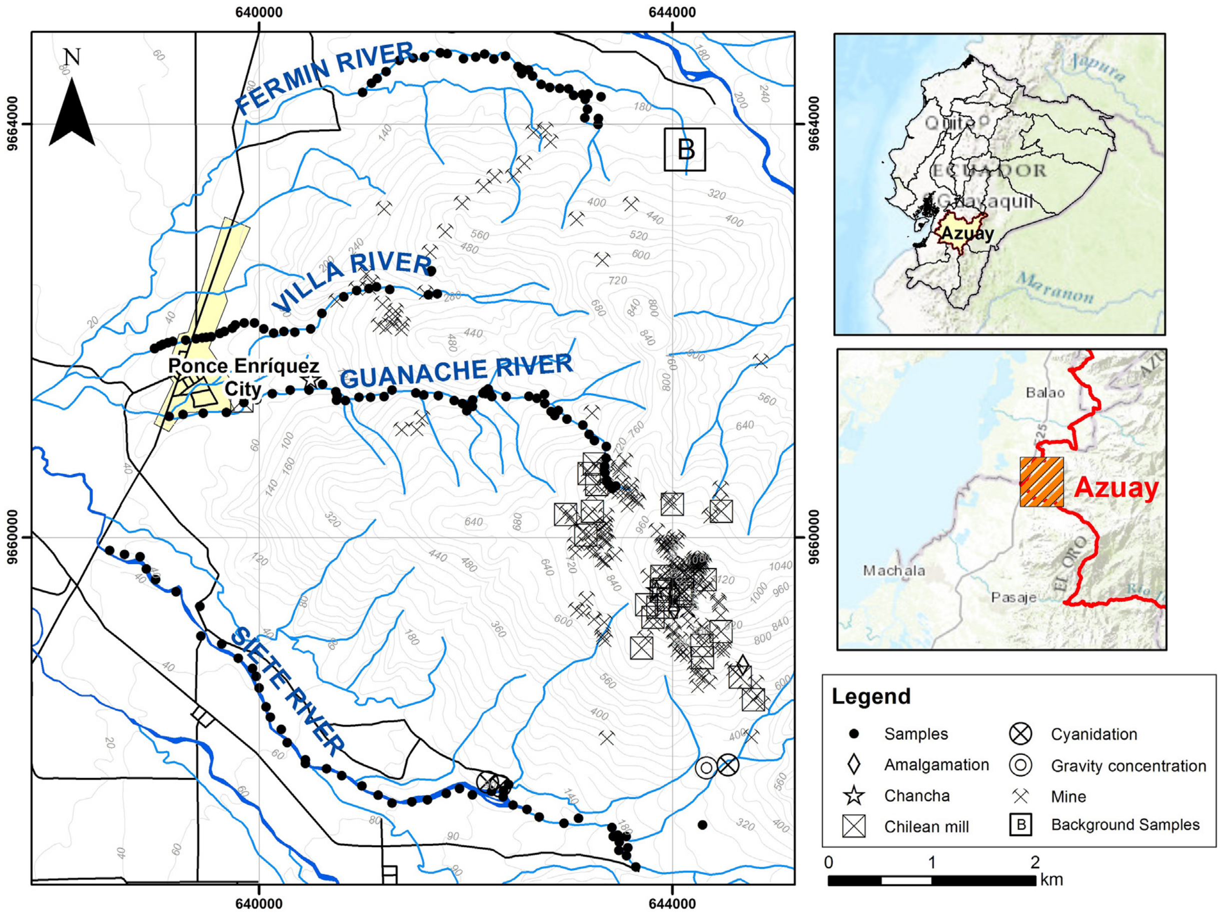

Fig. 1. Location of the sampling points and main mining and metallurgy facilities in the surroundings of Fermín, Villa, Guanache and Siete rivers in Azuay (Ecuador).

and it is considered to cause health concerns including infertility, birth defects, and tumor formation, in animals and only under specific conditions (Wuana and Okieimen, 2011). Moreover, Cr (VI) is considered toxic to plants hindering their growth (Nagajyoti et al., 2010).

Copper is a known essential micronutrient required by both plants and animals. For instance in humans, it assists in the production of blood hemoglobin (Nagajyoti et al., 2010) and in plants, it aids in seed production, disease resistance, and water regulation (Wuana and Okieimen, 2011). However, high doses of this element may cause anemia, liver, kidney and stomach problems in mammals, as well as oxidative stress, plant growth retardation and leaf chlorosis among other issues in plants (Nagajyoti et al., 2010). Although it can be transported

Table 1
Descriptive statistics and enrichment factors (EF) for the potentially toxic trace elements of the different river samples (mg/kg). Mercury statistical values correspond only to those above detection limit (0.5 mg/kg).

Site	Variable	Mean	SD	Min.	Max.	Skew.	Kurt.	Shapiro-Wilk	p (unilateral D)	EF
Fermín	As	205.35	68.80	45.00	311.00	−1.11	0.25	0.8574	$4.12 \cdot 10^{-4}$	20.37
	Cr	67.97	9.00	55.00	103.00	2.02	5.26	0.8307	0.0001	4.78
	Cu	159.82	17.28	134.00	226.00	1.85	4.58	0.8559	$3.80 \cdot 10^{-4}$	5.98
	Hg	BDL								
Guanache	As	383.64	273.17	44.00	1525.00	2.32	6.52	0.7807	$9.87 \cdot 10^{-8}$	38.55
	Cr	121.71	26.46	49.00	168.00	-0.89	0.73	0.9156	0.0008	8.67
	Cu	592.52	255.97	143.00	1371.00	0.56	1.04	0.9082	$4.33 \cdot 10^{-4}$	22.45
	Hg	BDL								
Siete	As	842.88	506.91	71.00	2489.00	1.33	2.42	0.8796	$1.47 \cdot 10^{-4}$	86.64
	Cr	114.81	32.08	41.00	199.00	0.18	1.06	0.9451	0.025	8.37
	Cu	483.71	258.91	56.00	1359.00	1.39	2.80	0.8953	$4.45 \cdot 10^{-4}$	18.75
	Hg	BDL								
Villa	As	298.38	88.66	180.00	482.00	0.94	−0.53	0.8463	$3.46 \cdot 10^{-4}$	51.56
	Cr	67.00	12.09	34.00	80.00	−0.95	−0.05	0.8868	0.0029	4.12
	Cu	533.09	138.05	367.00	821.00	1.01	−0.50	0.8170	$8.66 \cdot 10^{-5}$	22.70
	Hg	1.16	0.45	1.00	3.00	3.05	7.83	0.6743	$1.9 \cdot 10^{-4}$	28.43
4 rivers	As	516.74	823.76	44.00	9890.00	8.99	96.67	–	–	50.62
	Cr	98.42	34.57	34.00	199.00	0.38	−0.64	–	–	6.83
	Cu	494.33	474.09	56.00	5638.00	7.68	79.33	–	–	18.26
	Hg	BDL								

Table 2
Common reference values for fresh water sediments from different sediment quality guidelines (Buchman, 2008) and 10 sediment samples from an upstream tributary of Fermín River.

Element	Reference value (mg/kg)									
	Background (Buchman, 2008)	Fermin upstream sediments	ARCS	TEC	TEL	LEL	PEC	PEL	SEL	UET
As	1.1	11.2	10.798	9.79	5.9	6	33	17	33	17
Cr	13	15.8	36.286	43.4	37.3	26.0	111	90	110	95
Cu	25.0	29.7	28.012	31.6	35.7	16.0	149	197	110	86
Hg	0.004–0.051	0.04	–	0.18	0.174	0.2	1.06	0.486	2	0.56

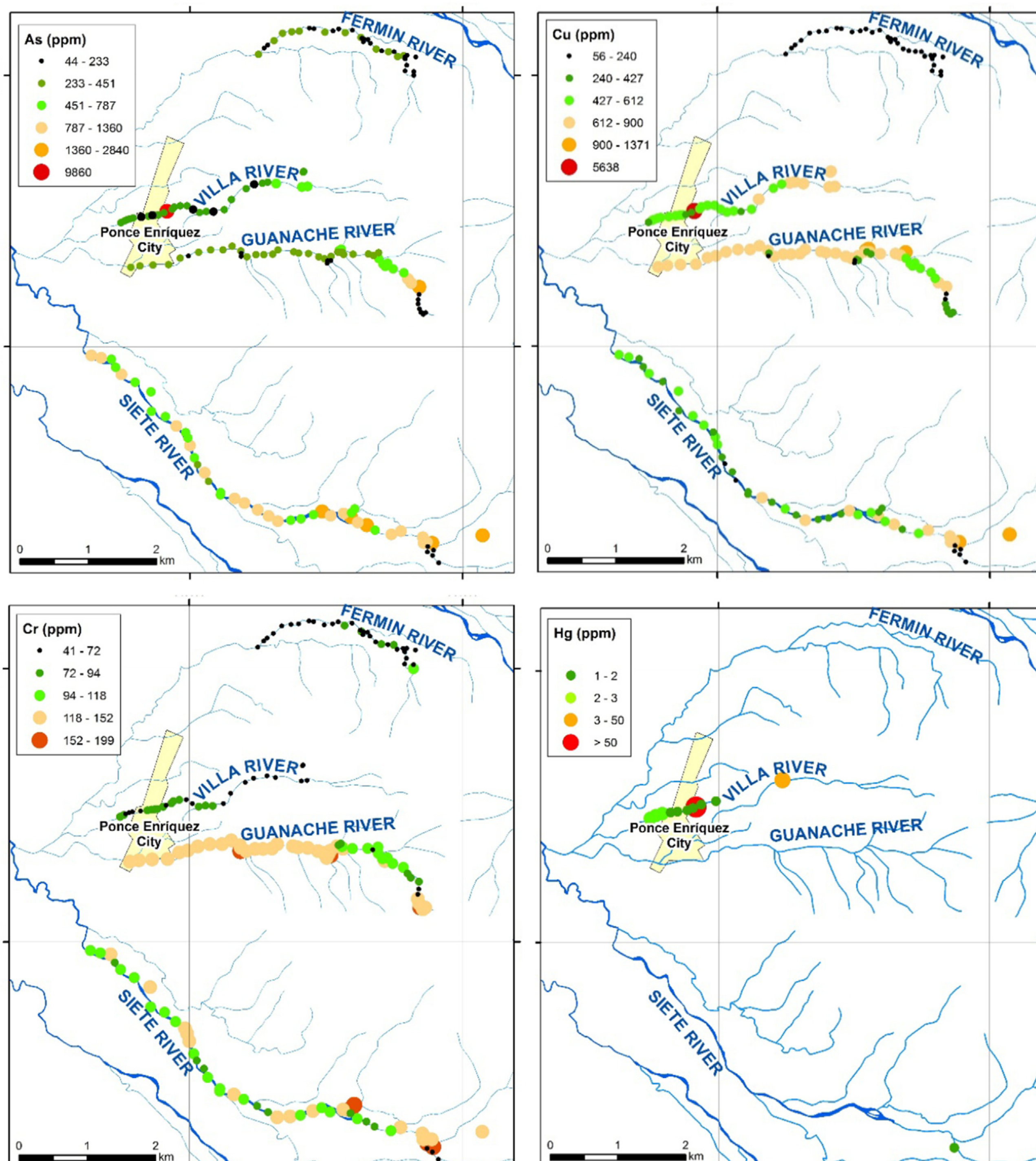

Fig. 2. Spatial distribution As, Cu, Cr and Hg along the 4 rivers. Note that the size of the dot is proportional to the trace element concentration. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 3
Univariate analysis of variance for each separated variable.

Dependent variable	Type III sum of squares	df	Mean square	F	Sig.
Ag	5.648e	3	1.883	12.341	0.000
Al	8.195s	3	2.732	19.269	0.000
As	10,403,203.428j	3	3,467,734.476	34.717	0.000
Ca	5.081n	3	1.694	71.529	0.000
Co	4986.561g	3	1.662.187	9.735	0.000
Cr	106,384.735p	3	35.461.578	62.571	0.000
Cu	4,242,145.594b	3	1,414,048.531	31.915	0.000
Fe	232.236i	3	77.412	38.699	0.000
K	0.019u	3	0.006	22.523	0.000
La	161.397o	3	53.799	84.975	0.000
Mg	15.079q	3	5.026	119.678	0.000
Mn	21,679,986.036h	3	7,226,662.012	39.241	0.000
Mo	1595.739a	3	531.913	134.516	0.000
Na	0.002t	3	0.001	19.637	0.000
Ni	11,974.160f	3	3.991.387	33.134	0.000
Pb	1937.390c	3	645.797	8.478	0.000
S	9.859v	3	3.286	25.438	0.000
Sb	5783.460l	3	1.927.820	130.290	0.000
Sr	5821.632k	3	1.940.544	112.382	0.000
Ti	0.551r	3	0.184	167.021	0.000
V	726,987.122m	3	242.329.041	128.090	0.000
Zn	132,326.401d	3	44.108.800	46.382	0.000

long distances in surface water, either attached to the particles of the stream or in the form of ions, it is not as mobile in soils and sediments as it tends to attach to the organic matter and minerals and it does not commonly enter groundwater (Cerqueira et al., 2011).

Mercury occurs naturally in mineral deposits, sediments, and volcanoes, but it is also released into the environment by coal burning, waste incineration and metallurgy (WHO, 2013). Mercury exists in several forms, namely: elemental, inorganic, and organic (Sierra et al., 2011). Elemental Hg can evaporate in the form of invisible, odorless toxic vapor, and its inhalation can cause serious health issues (WHO, 2013). Once in the environment Hg can transform in the presence of certain microscopic organism into methylmercury, which can be bio accumulated (Baughman, 2006; WHO, 2013). Mercury is documented as a hazardous material to both humans and the environment (Counter et al., 2006; WHO, 2013).

Artisanal gold mining has been a widespread practice throughout the world, and particularly important in Latin America (Tarras-Wahlberg et al., 2000; Kumah, 2006; Seccatore et al., 2014). These mining operations are usually performed without any environmental concern or control, and they are the main cause of many environmental problems (Veiga et al., 2014; Hrubá et al., 2012). This fact is particularly relevant in Ecuador, were years of uncontrolled gold mining has created severe environmental problems mainly concerning cyanide and potentially toxic metals releases (Miserendino et al., 2013).

Within this context, the recent geochemical record in detrital sediments of 4 rivers of the Ponce Enriquez mining district were analyzed. Although Hg and cyanides pollution in gold artisanal mining areas has been widely covered by several authors, less attention has been paid to other potentially toxic trace elements such as As, Cu and Cr. Thus, the specific objectives were as follows:

a) Study the geochemical interaction between some trace elements, so that the specific relevant anthropogenic sources of pollution can be established.
b) Provide relevant information from a geochemical perspective on the spatial distribution of the contamination.

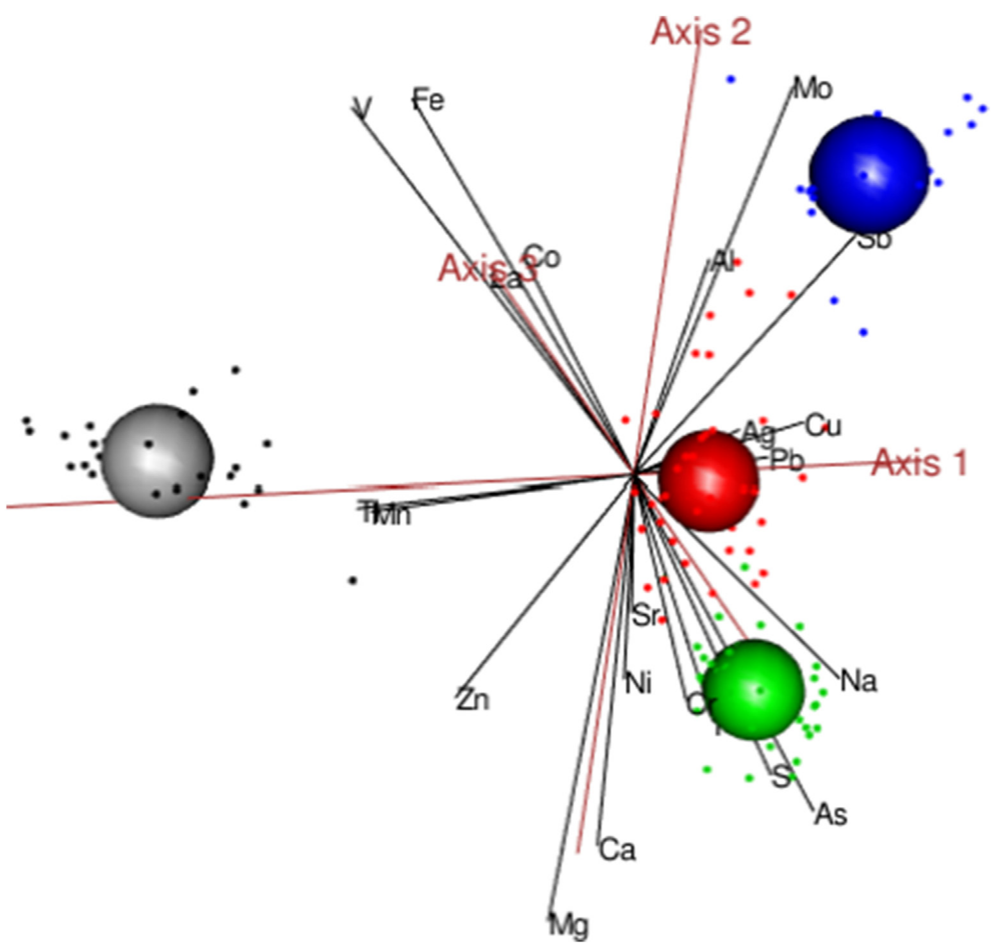

Fig. 3. 3D-biplot of the most informative canonical scores, canonical axes 1, 2 and 3.

Table 4
Summary of the variables with higher concentrations for each location obtained from the biplot representation.

Location	Higher concentrations
Fermín	La, Mn, Ti, V, Zn,
Guanache	Ag, Co, Cu, Pb
Siete	S, Ca, Cr, K, Mg, Na, Ni, Sr
Villa	Al, La, Mo, Sb, V

c) Introduce to the geochemical community the Canonical (MANOVA)-Biplot as an alternative to Principal Components when a group structure exists in a geochemical dataset.

2. Materials and methods

2.1. Regional setting and sediment sampling

The most affected areas by mining pollution in Ecuador are located in Zaruma, Portovelo and Ponce Enríquez (PRODEMINCA, 2000a, 2000b), of which the present study focuses in the later.

Mining and metallurgical activities started intensively in the early 1980s, and since then, several environmental issues have been reported. In this sense, anomalous concentrations of As, Cu, Zn were detected in drinking water (Appleton et al., 2001; Carling et al., 2013) and pollution problems were reported in shrimp farms and banana plantations located downstream of certain mining areas of Ecuador (Sandoval, 2001; Velásquez-López et al., 2010; Velásquez-López et al., 2011).

The geology of the mining area consists of basalts, andesitic basalts, basaltic andesites and andesites of Paleocene-Eocene age (Fm. Macuchi) that are fractured by Miocene intrusive bodies of gabbro and granodiorite (PRODEMINCA, 1996, 2000a). This intrusion developed massive Cu sulphides (pyrite, chalcopyrite, bornite, covellite) with Au-Ag-Mo. Moreover, minerals including galena, stibnite and quartz are also present (PRODEMINCA, 2000b). Other occurring rocks include sandstones and shales bodies (Fm. Yunguilla). The gold exploited in the area corresponds to high temperature arsenopyrite-chalcopyrite hydrothermal veins (Appleton et al., 2001). The river sediments are mainly composed of alluvial sediments of the Holocene transported from the Cordillera Central.

Gold amalgamation is the most common gold processing practice performed by the artisanal and small-scale miners (ASM) of the area. Amalgamation takes place in two types of facilities, namely “chilean mills” and “chanchas”. “Chilean-mill” processing includes grounding, concentration and amalgamation; whereas “chanchas” processing, just consists of milling in small ball mills to which Hg is added (Velásquez-López et al., 2010).

Formal metallurgy includes gravity separation, floatation, cyanide leaching, and activated carbon adsorption/elution. “Chanchas” and “chilean-mill” tailings are frequently sent to formal facilities to be leached with cyanides. Mine tailings are frequently discharged directly to the rivers. An inventory of processing centers is provided in Fig. 1.

Within this context, 34 sampling points from Fermín, 32 from Villa, 56 from Guanache, 48 from Siete River, and 10 more from a small upstream Fermin River tributary (Fig. 1) were selected. At each sampling point 3 subsamples (roughly 200 g each) were collected from the upper 0–20 cm of sediment by means of a modified Van Veen grab sampler. Subsamples were mixed and quartered, and the resulting sample

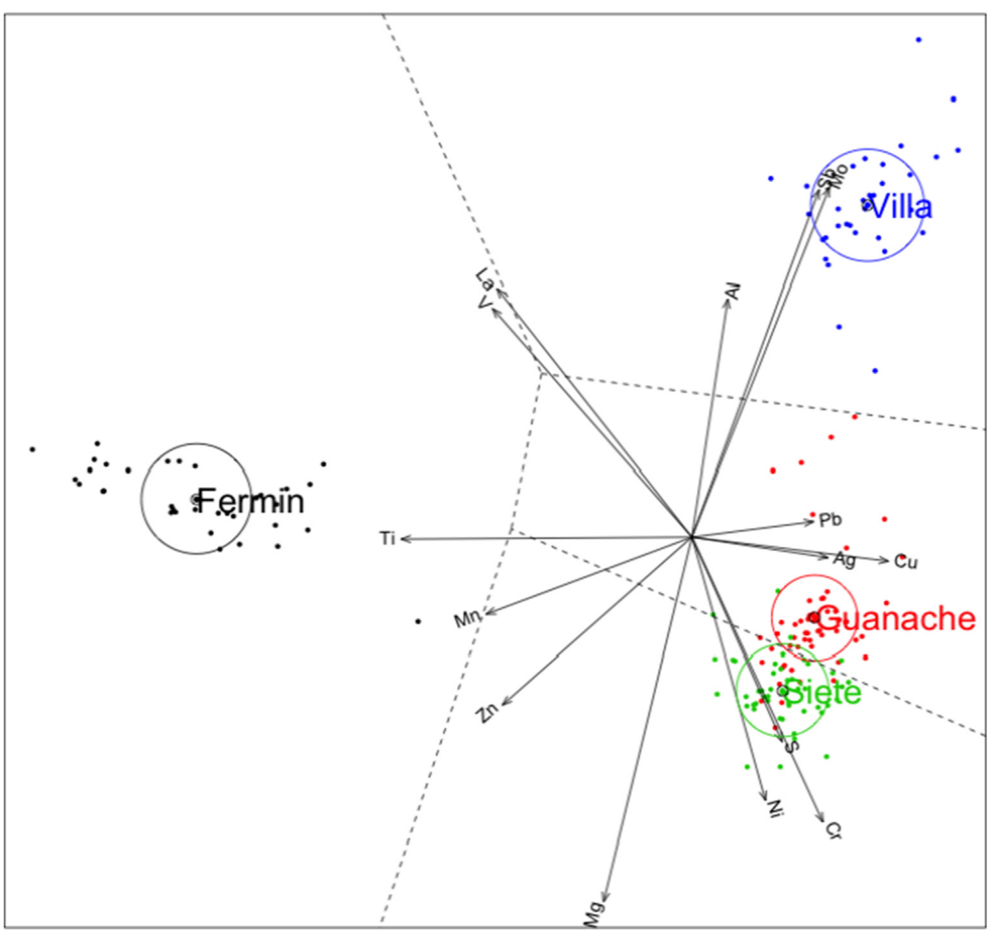

Fig. 4. Partial representation using canonical variates 1 (x-axis) and 2 (y-axis).

(roughly 200 g) was screened in the field through a 2 mm sieve. Then, samples were packed in polyethylene bags and dried at room temperature in order to minimize the loss of volatile elements.

2.2. Chemical analysis

Samples were quartered and ground using an agate mortar and pestle to a grain size of <125 μm. The milled samples were shipped to the accredited ISO 9001 and ISO/IEC 17025:2005 ACME-Bureau Veritas Mineral Laboratories (Vancouver, Canada). Therein, 0.5-g representative sub-samples of the ground product were leached by means of a hot 'Aqua regia' digestion ($HCl + HNO_3$). The concentrations of the elements (Ag, Al, As, Au, B, Ba, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, Hg, K, La, Mg, Mn, Mo, Na, Ni, P, Pb, S, Sb, Sc, Se, Sr, Te, Th, Ti, Tl, V, W, Zn) were determined for the digested material by inductively coupled plasma optical emission spectrometry (ICP-OES). Seven blanks, the same number of duplicates and standard reference materials (STD DS9 and *STD OREAS45EA*) were employed in the laboratory as a means of controlling background noise, accuracy and precision.

2.3. Pollution levels assessment

The local background values for the aforementioned trace elements were established based on samples collected in areas not directly affected by any mining or metallurgical operations. Thus, 10 extra samples from a small upstream tributary of the Fermin River (the least polluted river), wherein no mining activities take place, were selected as local background. The obtained values were coherent with previous studies of the area e.g. Tarras-Wahlberg et al. (2000).

Accordingly, Enrichment Factors (EFs) were calculated as follows: $EF = (E / N)_{site} / (E / N)_{background}$, wherein E is the element of interest, and N the concentration of the normalizer (e.g. Sierra et al., 2015).

In using this criterion, an appropriate normalizer, which aims at compensating grain size effects, has to be chosen. This element is required to be evenly introduced by geological activities into the studied sediments over the past years, and not to be affected by human pollution (Sakan et al., 2011). These normalizers are expected to follow a straight line when their values are plotted against the concentration of the pollutant or its logarithm.

In this sense, a complete suite of normalizers commonly used in literature (e.g. Sierra et al., 2015) have been considered (Supplementary material (SM2)). This material depicts the correlations for Al, Ti and Fe with the potentially toxic elements.

The sediment quality guidelines (SQGs) are numerical values designed to assist in the interpretation of the adverse effects of contaminant concentrations in sediments that may affect sediment-dwelling organisms, wildlife, or humans. The following reference values (Buchman, 2008) have been used for assessment purposes, namely: assessment and remediation of contaminated sediments (ARCS), threshold effect concentration (TEC), threshold effects levels (TELs) and, lowest effect level (LEL), probable effect concentration (PEC), probable effect levels (PELs), severe effect level (SEL) and UET (upper effects threshold).

2.4. Univariate statistical analysis

A univariate exploration of the data set was conducted in order to thoroughly analyze the possible relationships between the elements (mean, standard deviation, maximum, minimum, skewness, kurtosis, correlation coefficients and normality tests). All calculations were

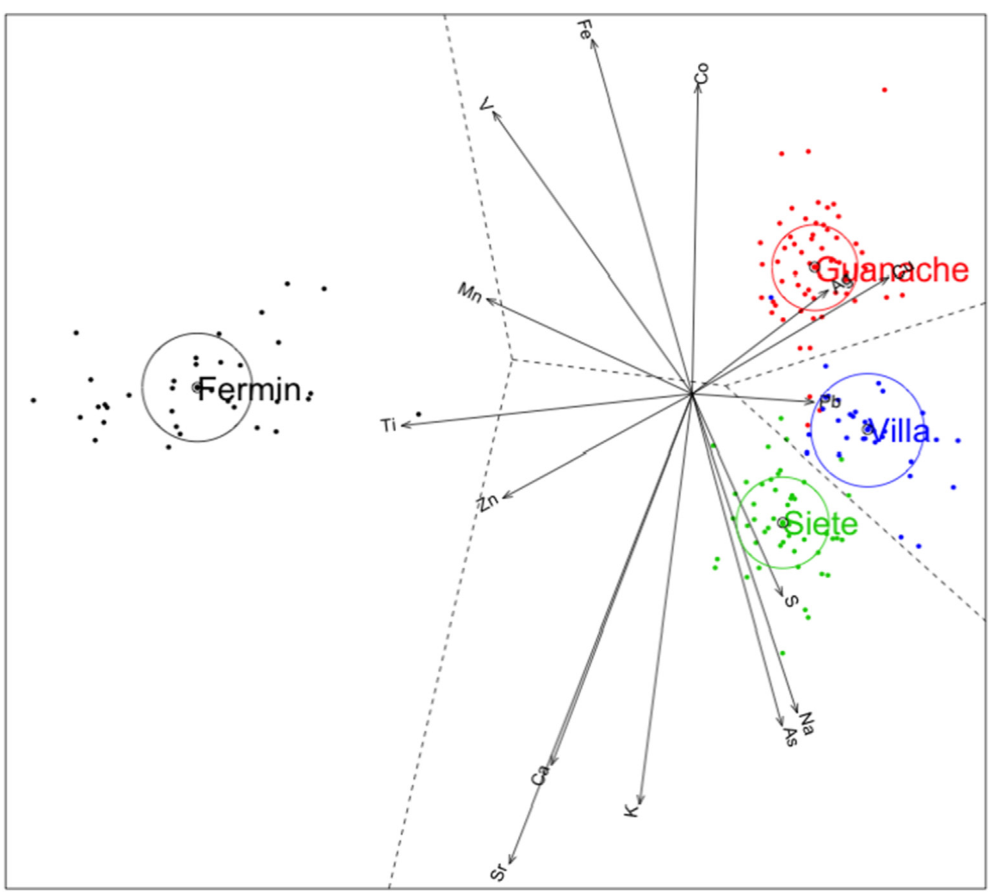

Fig. 5. Partial representation using canonical variates 1 (x-axis) and 3 (y-axis).

Table 5
Qualities of the representation of the group means for each canonical variate.

River	Dimension		
	CV1	CV2	CV3
Fermín	**99.39**	0.59	0.02
Guanache	**39.70**	17.44	**42.86**
Siete	16.86	**48.85**	**34.29**
Villa	21.54	**77.55**	0.91

performed by means of R freeware program (R Development Core Team, 2016).

2.5. Canonical (MANOVA)-Biplot

The most popular technique to analyze multivariate data is, probably, Principal Components Analysis (PCA). This procedure allows for summarizing a (large) number of observed variables into a smaller number of synthetic principal components (PC), obtained as linear combinations of the observed ones, and explaining as much of their variability as possible.

Although PCA is always useful to describe a multivariate sample, from a statistical point of view, it is not the most adequate technique when the individuals have a group structure and the aim is to study that structure and the statistical significance of the differences among groups. In that case, Multivariate Analysis of Variance (MANOVA) can be used to study the significance of the differences and Canonical Variate Analysis (CVA) to study the dimensionality of the alternative hypothesis when the null in MANOVA is rejected (Mardia et al., 1979).

Moreover, there are many other statistical advantages of using CVA over PCA in addition to the pervious. In that way:

- The directions that account for most of the total variability if a dataset does not coincide, in general, with the directions that better show the differences among groups. PCA uses the former and CVA the latter.
- The importance of the between-groups differences depends on the within-groups variability as in ANOVA or MANOVA. In this respect, PCA does not consider the within-groups variability and the observed difference may not be statistically important (significant) and even spurious; CVA does.
- PCA is scale dependent, CVA is scale invariant (Gower et al., 2011).
- In PCA the groups' structure is not directly used in the calculations while in CVA is (Gower et al., 2011).

Table 6
Qualities of the representation of the variables to explain the group means and qualities of the sum for each 2 dimensional partial representations. The cases in which the dimensions and the plane variables are better interpreted are highlighted in bold.

Element	Dimension					
	CV1	CV2	CV3	CV1–2	CV1–3	CV2–3
Ag	**61.62**	1.44	36.94	63.06	98.56	4.44
Al	2.19	**97.32**	0.49	99.51	2.68	100.32
As	5.23	22.53	**72.23**	27.76	77.46	25.53
Ca	9.81	21.03	**69.15**	30.84	78.96	24.03
Co	0.03	1.48	**98.48**	1.51	98.51	4.48
Cr	14.71	**70.62**	14.66	85.33	29.37	73.62
Cu	**72.61**	1.12	26.27	73.73	98.88	4.12
Fe	5.94	18.58	**75.48**	24.52	81.42	21.58
K	1.56	1.68	**96.76**	3.24	98.32	4.68
La	37.47	**61.62**	0.91	99.09	38.38	64.62
Mg	4.63	**79.67**	15.69	84.30	20.32	82.67
Mn	**73.34**	10.52	16.13	83.86	89.47	13.52
Mo	12.58	**82.00**	5.42	94.58	18.00	85.00
Na	9.46	2.43	**88.10**	11.89	97.56	5.43
Ni	5.86	**76.04**	18.10	81.90	23.96	79.04
Pb	**97.91**	1.63	0.46	99.54	98.37	4.63
S	8.84	**46.02**	**45.14**	54.86	53.98	49.02
Sb	9.94	**74.77**	15.28	84.71	25.22	77.77
Sr	12.51	3.85	**83.64**	16.36	96.15	6.85
Ti	**98.78**	0.00	1.22	98.78	100.00	3.00
V	22.85	30.39	**46.76**	53.24	69.61	33.39
Zn	**47.71**	**37.82**	14.48	85.53	62.19	40.82

All things considered, it was employed an extension of CVA called Canonical/MANOVA-Biplot that is essentially CVA with added information about the observed variables and the significance of the results.

Canonical/MANOVA Biplot is a joint representation of the group means and variables of a data matrix whose rows are divided into several groups. The group means are projected into the canonical variates, that is the combinations of the observed variables that better account for the differences among groups. The variables are situated on the map in the directions that best predict the actual mean values for each variable. Individual points can also be projected onto the canonical space.

On the plot, we can interpret similarities among groups as an inverse function of Mahalanobis' distances, the variables responsible for the between-groups differences as projections on the group points onto the variable directions and correlations among variables as angles among the vectors; acute angles mean positive relations, obtuse angles mean negative relations and right angles are interpreted as no relation.

A short, but comprehensive, description of Canonical/MANOVA Biplot can be found in Varas et al. (2005) or Santana et al. (2009). Besides, a more complete description of the technique is performed in Gower and Hand (1995) or Gower et al. (2011).

Confidence regions around the means are also situated on the plot using a traditional chi-squared approach as in Mardia et al. (1979) or a Hottelling T2 approach as in Lejeune and Caliński (2000).

The interpretation of the canonical variates is usually made with the correlations among the observed and canonical variables, despite the relationships are not maximized by the technique. We propose the quality of the representation of the group means as a better measure of the accuracy of the result. The quality in the representation of the data was obtained from the Quality Representation Index (QRI) proposed by Demey et al. (2008). This index measures the percentage of the variability of the groups means accounted by the reduced dimension solution, and it corresponds to the squared cosine of the angle between the point/vector in the multidimensional space and its projection onto the low dimensional solution. In this respect, a QRI was calculated for both group means and variables.

All the calculations were automated by means of the software MultBiplot (Vicente-Villardon, 2016), MultBiplotR (Vicente-Villardon, 2016), and InfoStat (Di Rienzo et al., 2015).

3. Results and discussion

3.1. Pollution levels assessment

At the first stage of the investigation a univariate statistical characterization was performed. Among the wide range of elements analyzed, this section focuses on those potentially toxic, of which As, Cr, Cu and Hg have been selected according to the SQGs and enrichment factors criteria.

Along the same lines, Table 1 evidences high differences between the maximum and minimum concentrations, as well as high standard deviations for the aforementioned elements. In addition, according to the shape of their probability density curves (skewness and kurtosis), and the Shapiro–Wilk tests (table 1), their distributions are far from Gaussian (Patel and Read, 1996). Both facts, particularly for the cases of As and Hg emphasize the idea of their presence in sediment of the area as allochthonous natural or anthropogenic input. Boxplots representations for most representative elements are provided in Supplementary material SM1.

Moreover, Supplementary material SM2, shows the correlations between the aforementioned elements and some common normalizers. In this case, it can be observed that the correlations followed a group pattern clearly identifiable for each river. This fact hindered the selection of a unique normalizer, so Al was preferred just for simplicity reasons.

Thus, when mean concentrations for the 4 rivers (Table 1) is compared with the SQGs (Table 2), As and Cu (516.74 and 494.33 mg/kg respectively) exceeded the ARCS, TEC, TEL, LEL, PEC, PEL, SEL and UET reference values, and Cr (mean value 98.42 mg/kg) exceeded all the previous except the PEC and SEL values. Along the same lines, the average EFs for the 4 rivers advocate an abnormal behavior (positive anomalies) for As, Cr and Cu, with enrichment factors of 51, 7 and 18 respectively, clearly suggesting the anthropogenic origin of these elements.

The average concentrations of As were of 205.35 mg/kg in Fermín, 383.64 mg/kg in Guanache, 842.48 mg/kg in Siete, and 298.38 in Villa (Table 1). Furthermore, the Siete River contained the second highest concentration of Cr (114.51 mg/kg) and Cu (483.71 mg/kg), very close to the results of Guanache (Cr: 121.71 mg/kg, Cu: 592.52 mg/kg) (table 1).

Following the preceding considerations for As, Cr and Cu, the most affected rivers seemed to be in the following order: Siete, Guanache, Villa and Fermín. However, when Hg is taken into consideration, Villa River could be considered the most polluted, as Hg concentrations frequently exceed the PEC and even the SEL values.

The spatial distribution of the trace elements is presented in Fig. 2. This figure shows that As, Cu and Hg concentrations are unevenly distributed along the rivers; that is to say, they do not follow any pattern. Within this context, along the course of the 4 streams, a strongly polluted area at the entrance of Ponce Enríquez City (red dots) exists for the 4 trace elements. This geochemical anomaly corresponds to a zone wherein direct discharges from the “chanchas” facilities are observed. Moreover, despite the previous irregular distribution, Cr followed a clear pattern increasing its concentration downstream (Fig. 2).

3.2. Canonical (MANOVA)-Biplot analysis

The existence of a clear group patterns each corresponding to one different river, makes, as stated in the methods section, PCA inadequate (e.g. Varas et al., 2005; Santana et al., 2009). Consequently, a MANOVA followed by a Canonical Biplot, which reduces the dimensionality while at the same time maintains the structure of variation between and within groups, was performed.

The MANOVA to compare the mean vectors in the four groups is highly significant (Wilk's Lambda $= 0.0005574$, F $= 66{,}433.86$, p $= 2.2e-16$), so there is a clear difference among the groups. The univariate analyses of variance for each separate variable are all highly significant; that is to say, there are noteworthy differences among groups for all the contaminants (Table 3).

Once it has been stated that the MANOVA is significant, we may study the structure of the differences using a Canonical Biplot. In such cases, all metal loadings from the different rivers are displayed as 2D or 3D scatterplots in a plane using the scores of groups and locations on the canonical variates. In this study, the rank of the weighted means matrix is 3; therefore, all the differences among groups can be shown in a 3D plot (Fig. 3). In other words, the 3 dimensional solution accounts for 100% of the “between-groups” variability (52.77%, 32.33% and 14.90% for the 1st, 2nd and 3rd canonical variates respectively).

The Euclidean distance between two group means approximates the Mahalanobis distance, the closer the two groups are on the graph the more similar their contaminants profiles are. The same relation is true for individual locations. The correlation between the different contaminants can be inferred from the angles among them, with two elements being more positively correlated the smaller their angle, more negatively correlated the nearer the straight angle, and less correlated the nearer the right angle. The concentrations can be directly read from the graph considering that the longer the arrow that symbolizes an element and the closer to a group, the higher the concentration of the element in the group. Table 4 shows a summary of the variables that have higher values at each location.

In this connection, it is important to highlight the strong correlation between S, As, Cr and Ni, signifying a possible common anthropogenic origin. All this pollution seems to be a probable consequence of the illegal disposal of the processed gold-bearing quartz-arsenopyrite veins, extraction basins and derelict mines. This hypothesis may be corroborated by the fact that the groups better represented by these elements correspond to the most polluted areas. Moreover, the small correlation observed between Al and K can be explained in terms of a low presence of finely ground materials due to the hydrodynamic energy of these rivers, which favors the prevalence of the coarser grained fractions.

Observing the 3D plot it can be noted that there are significant differences among the four locations because they are all substantially separated. The radii of the confidence spheres are very small and do not intersect.

3D plots are usually difficult to interpret (unless seen in movement). Partial 2D views measuring the quality of the representation are usually more useful for interpretation. Figs. 4 and 5 contain the 2D representation of the canonical variates CV1 vs CV2 and CV1 vs CV3 respectively and Tables 5 and 6 present the qualities of the representation of the groups and variables (for the prediction of the groups). Variables with low qualities have been eliminated from the representation in order to simplify the interpretation.

With 4 groups, the effective dimension of the group differences is 3, so all the information concerning the differences among groups is contained in the 3 dimensional representation; meaning that the sum of the qualities to explain the group differences for the three canonical variates are always 100%.

In Table 6 the higher contributions have been highlighted in order to establish the combination of canonical variates that contains more information pertaining to each single group or variable. For example, the variable Pb is mostly related to the first CV and can be interpreted in planes 1–2 (Fig. 4).

If one observes Fig. 4, it permits asserting that the first CV separates Fermín from the other three groups. Fermín has higher concentrations of Ti, Mn and Zn, and lower concentrations of Pb, Cu and Ag as compared to the other three. It should be noted that only variables with high quality for the CV have been considered.

Moreover, the second CV separates the group Villa mainly from Siete, with Guanache and Fermin occupying intermediate positions on the projection onto the CV. Villa has higher concentrations of Mo, Sb and Al, while Siete has higher concentrations of S, Cr, Ni, Mg. For all these variables, Guanache and Fermín have values closer to the average. Variables La and V also have good qualities, and by projection, it can be observed that Fermín and Villa have higher concentrations of such contaminants compared to the other two groups. It should be considered that, as in the previous case, only variables with high quality for CV2 have been considered.

A simple observation of Fig. 5 permits assessing that the third CV separates Guanache from the other three, highlighting the differences with Siete that were hidden in the representation of the planes 1–2. Guanache has higher values of Co, Ag and Cu, being the last two similar to those of Villa. Guanache also has lower values of Ca, Sr, K Na.

All things considered, it can be concluded that since Fermín is the least polluted river, CV1 acts separating the polluted from the least affected areas. Moreover, CV2 separates Villa from the other 3 clusters. This river has higher concentrations of Pb, Mo and Sb and lower concentrations of Zn and Mg. The good correlation of this factorial axis with the aforementioned elements together with Ag may be indicative of the geological background, mainly of the presence of igneous rocks (andesites, basalts, and gabbros) (e.g. Richards, 2003). Finally, factorial axis 3 significantly separates river Siete from the rest (higher concentrations of As, Ca and Na and lower concentrations of Al, Co and Fe)., In this sense, Siete is the river in which more mining and metallurgical activities occur, thus resulting in higher As pollution. Therefore, contamination by As seems to play a major role in the axis.

4. Conclusions

An environmental evaluation of the Ponce Enriquez gold mining area has been conducted, assisted by means of diverse statistical techniques, searching for the presence of potentially toxic trace elements. The intensive mining and metallurgical activity in the site has promoted a clearly anthropised geochemistry in which the differentiation of pollution sources is not easy. In this regard, univariate statistics and the classical SQGs and EFs approach pointed at As, Cu, Cr and Hg as the main toxicants in the zone.

Within this context, the Canonical (MANOVA)-Biplot was introduced to the geochemical studies. The mathematical procedure is a biplot representation associated with a Canonical Discriminant Analysis (CDA). The CDA is performed after a Multivariate Analysis of Variance (MANOVA). This method aims at providing a graphical summary of the multivariate and univariate hypothesis by testing procedures commonly used to compare several groups. Moreover, it can be an alternative in the study multivariate interactions to others such as PCA, when a clear group structure is observed in the data.

The Canonical (MANOVA)-Biplot, when tested to the data set, was fast at creating clear, meaningful and precise information on geochemical interactions and distribution patterns. Moreover, it allowed delimitating the polluted river zones and suggested the possible sources of contamination. As a result, the proposed methodology may be a useful tool for modeling elements data sets in sediment pollution issues.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.gexplo.2017.01.002.

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