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Application of two- and three-way principal component analysis to the interpretation of chemical fractionation results obtained by the use of the B.C.R. procedure

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Abstract

This paper describes as two- and three-way principal component analysis (PCA) can be advantageously used to interpret the results originating from the B.C.R. fractionation scheme, an operationally defined speciation procedure used to study the availability and mobility of trace elements and heavy metals present in environmental solid samples. The application of this procedure to find the fractionation of 11 trace elements and heavy metals (Al, As, Cd, Cr, Cu, Mn, Mo, Ni, Pb, V and Zn) in 13 sediments collected at the Mejillones del Sur bay (Antofagasta, Chile) generated a three-dimensional data set $\underline{\mathbf{X}}$ (13 × 11 × 4). Although classical two-way PCA applied to the unfolded $\mathbf{X}_b$ matrix (52 × 11) can yield valuable information about the pattern of fractionation of the chemical elements amongst the B.C.R. fractions, a more profound insight can be found when applying three-way PCA procedures, such as Parafac, that take into account the true tri-dimensional structure of the data set. In this study, Parafac has allowed to classify the sediments according to their associated environmental hazard by means of the A-mode loadings of two significant factors. By plotting these factors into the physical space of the Mejillones del Sur bay, the most hazardous areas of the bay have been located.

Keywords: B.C.R. fractionation; Two-way PCA; Three-way PCA; Parafac; Sediment; Heavy metals

1. Introduction

The B.C.R. extraction/lixiviation procedure is an operationally defined speciation sequential scheme [1–3], developed under the auspices of the European Bureau Communautaire de Référence, used to study the fractionation of trace elements and heavy metals in environmental solid samples (sediments, soils, waste residues, etc.), which are sequentially extracted with three reagents of increasing reactivity giving four fractions (1, 2, 3 and residual). The philosophy behind sequential procedures is that each successive reagent will dissolve different components, so from the study of fractionation patterns of the elements one can infer information (1) about the mobility, pathways or bioavailability of the studied chemical element [4] or (2) to assess the potential hazard that the samples can pose to the environment [5]. These studies are usually carried out by univariate ways, i.e., element to element or sample to sample, but multivariate methods such as principal component analysis (PCA) can provide further interpretation. PCA is a data reduction procedure whose main goal is to provide an easy visualization of the relationships existent amongst objects or variables determined in large or complex data sets such as those found in fractionation studies.

Classical (two-way) PCA is an exploratory data analysis procedure applied when n_{var} variables are measured on n_{obj} objects, originating a ($n_{obj} \times n_{var}$) two-way data array. Two-way PCA allows the extraction of useful information, not available at a first glance, about the interrelationships existing between the objects and/or variables of two-way data

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sets and can be considered today as a routine technique in multivariate environmental studies [5–8]. In some occasions, however, one or more additional dimensions must be taken into account, thus originating a three-way or *n*-way data array. B.C.R. fractionation studies are such a case, because n_{cond} results (corresponding to the four operationally defined fractions) are obtained for each sample and each variable, so a three-way ($n_{obj} \times n_{var} \times n_{cond}$) data array is generated. Such complex data arrays can be still studied by classical (two-way) PCA, by unfolding [9–11] and/or by dividing the three-way array into one or several two-way matrices, which are then separately analysed [5]. However, the results can be difficult to interpret, because the information about the three different dimensions becomes mixed.

The alternative approach is *N*-way PCA [12] an extension of PCA to higher orders, and several *N*-way methods, such as Tucker3 [13,14] and Parafac [15–17], have been devised with this purpose and applied to the study of *N*-way problems of different nature: spectroscopic [17], food chemistry [18,19] or environmental [20,21] studies.

The aim of this paper is to show how the application of two- and three-way PCA can significantly improve the visualization and interpretation of the information existent in data sets generated by B.C.R. fractionation studies, and also that three-way PCA allows to find additional information that classical two-way PCA is unable to extract. The data set corresponds to a study carried out on sediments collected at the Mejillones del Sur Bay (Antofagasta, Chile), an area in which pollution problems caused by trace elements and heavy metals have been reported [22].

2. Experimental

2.1. Sampling zone

The Mejillones del Sur bay (see Fig. 1) is located in the administrative Chilean second region, 64 km away from Antofagasta, in the coastal area of the Atacama Desert (23°00′S; 70°27′W). It has a semi-closed morphology bordered by a large peninsula, with a 14.8 km north-oriented mouth, 7.4 km of sack and depths of ca. 120 m. It is the most important bay along northern Chilean coasts, characterized by heavy coastal upwelling systems, low oxygen concentrations and very rich in nutrients that makes it very productive [23], supporting rich marine biota and biodiversity. Important fish, bivalves and crustaceans populations inhabiting the area sustain a great variety of marine birds and mammals. The town of Mejillones was an important industrial center during the nitrate mining period (19th and early 20th centuries), but later its most important economic activities have been artisan and industrial fishing and marine aquaculture. Actually there is a huge industrial development related to mining services (explosives, energy, etc.) and future industrial actuations such as a mega-harbor and metallic melting industries. Trace elements and heavy metals are being continually incorporated into the marine environment from multiple productive processes, affecting the ecological balance and introducing risks for the human population health. Pollution problems have been already reported in the close fish industries and in the migratory birds nesting areas near the bay.

A 36-points sampling grid was designed but only the 13 more polluted points, found in previous works [22], were chosen to carry out the fractionation study. The samples were collected with a Phleger mini-box core sampler (7.6 cm diameter) and only the superficial layer (7 cm deep) was taken. Samples were stored in closed plastic bags refrigerated at 4 °C until their analysis.

2.2. Fractionation procedure

The B.C.R. scheme [3] is a sequential extraction procedure with three steps: (1) 0.11 M acetic acid at 20 °C overnight and a extractant/sample ratio of 40 mL g^{-1}; (2) 0.5 M hydroxylamine hydrochloride (pH = 1.5 with nitric acid) at 20 °C overnight (40 mL g^{-1}); (3) 8.8 M hydrogen peroxide

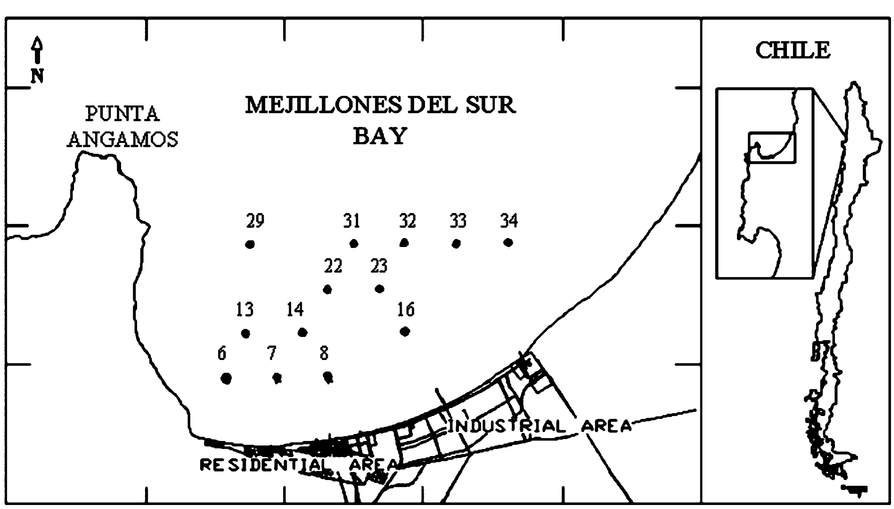

Fig. 1. Schematic map of the Mejillones del Sur bay with the sampling grid superposed.

(pH = 2–3 with nitric acid) during 1 h at room temperature (10 mL g^{-1}) and 1 h at 85 °C to reduce the volume; then 1 M ammonium acetate (pH = 2 with nitric acid) at 20 °C and overnight (50 mL g^{-1}). The procedure was applied to 1 g refrigerated humid sediment samples. 'Pseudo-total' contents were determined separately by USEPA 3051 norm [24], consisting of a microwave-aided wet digestion of the sediment with concentrated nitric acid.

2.3. Determination of trace elements and heavy metals

The concentrations of Al, Cr, Cu, Mn, Mo, Ni, Pb, V and Zn were determined in the liquid extracts by inductively coupled plasma atomic emission spectrometry (PHILIPS PU 7000/01 System), whereas As and Cd were determined by electro thermal atomic absorption spectrometry (Varian GTA 100 SpectraAA-800). Quantification was with respect to reagent-matched multielement standards. All results are the mean of three replicates and are given for dried sample.

All calculations were made by using MINITAB 13.0 and MATLAB 6 packages. Parafac analysis was carried out by using the *N*-way toolbox for MATLAB [25,26]. The contour plots were drawn with SURFER 8.00.

3. Results and discussion

3.1. Univariate interpretation

Table 1 shows the experimental results grouped according to their respective B.C.R. fraction. The residual fraction of each sediment was found by subtracting the sum of B.C.R. fractions from its 'pseudo-total' contents determined separately. In this work, we have preferred the use of acid-extractable 'pseudo-total' contents in opposition to true totals found after treatment of the samples with hydrofluoric-based mixtures. The reason behind this choice is that the goal of the study is to evaluate the potential hazards derived from the presence of polluted sediments in the Mejillones del Sur bay, and true total contents does not allow to discriminate between natural (i.e., mineralogical) or anthropogenic sources.

The results of Table 1 are usually studied to find mean fractionation patterns for each trace element and heavy metal, as it is shown in Fig. 2. From a close inspection of this figure it is possible to extract only very general conclusions about the mobility of the analysed chemical elements in the sediments. Thus it can be seen that As, Cd and Ni present their greater fractionation percentages in the fraction 1, and Pb, Co and V in fraction 2. On the other hand, Cr appears mainly in fraction 3, and Al, Mn, Mo and Zn in the residual fraction. Since As, Cd and Ni are very toxic elements and are mainly associated to the more easily released fractions, we can conclude that the sediments pose a high environmental hazard. This way of data analysis does not provide further insight on the fractionation behaviour of trace elements and heavy metals, and does not allow to extract any conclusion about individual sediments either because mean results are employed.

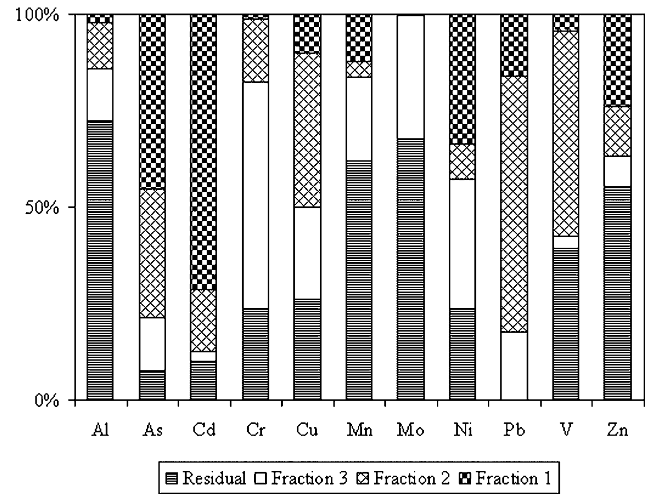

Fig. 2. Mean fractionation pattern of trace elements and heavy metals in sediments of the Mejillones del Sur bay.

3.2. Two-way PCA

In B.C.R. fractionation studies a two-way table, such as Table 1, is not enough to describe the structure of the data set, because there is a third mode, the B.C.R. fraction, that becomes necessary to represent the whole data set. This can be imagined as $\underline{\mathbf{X}}$, a parallelepiped of size ($n_{\text{obj}} \times n_{\text{var}} \times n_{\text{cond}}$), $n_{\text{obj}} = 13$ being the number of objects (sediments or sampling sites), $n_{\text{var}} = 11$ the number of variables (trace elements and heavy metals), and $n_{\text{cond}} = 4$ the number of B.C.R. fractions.

These three-way data arrays can be still analysed by two-way PCA if they are previously reordered to obtain a two-way data array. This reordering, usually known as unfolding, can be carried in three different ways according to the main goal of the study [11]. In our case, we are interested to study the behaviour of the B.C.R. fractionation scheme, i.e., each fraction, so the unfolding was made to obtain a $\mathbf{X}_b$ matrix having $n_{\text{obj}} \times n_{\text{cond}} = 52$ rows and $n_{\text{var}} = 11$ columns. These $\mathbf{X}_b$ data were j-scaled (i.e., the data were auto-scaled or z-transformed) so all variables have a mean of zero and variance unity. By this technique, differences amongst variables arising from their different ranges and magnitudes are removed whereas the differences between objects and conditions are preserved [22].

Two-way PCA decomposes the $\mathbf{X}_b$ matrix according to:

$$x_{ij} = \sum_{f=1}^{\text{NF}} a_{if} b_{jf} + e_{ij}$$

where a_{if} and b_{jf} are the elements of the scores and loading matrices $\mathbf{A}$ and $\mathbf{B}$ of (($n_{\text{obj}} \times n_{\text{cond}}$) × NF), ($n_{\text{var}}$ × NF) dimensions respectively, and e_{ij} is the error term of the element x_{ij} of the j-scaled $\mathbf{X}_b$ data array. The number of components NF is chosen so small as possible, but still allowing for the explanation of the greater amount of variance by the model.

We carried out two-way PCA by using the eigenvalue decomposition of the correlation matrix as implemented in

Table 1
Results of BCR fractionation (all results in mg kg^{-1})

Sample ID	Al	As	Cd	Cr	Cu	Mn	Mo	Ni	Pb	V	Zn
Fraction 1											
6	103.7	8.36	8.33	0.83	14.83	11.50	0.01	4.83	0.01	0.01	12.33
7	135.4	11.76	4.46	1.43	18.93	12.32	0.01	3.39	0.01	0.01	11.96
8	119.5	7.79	18.04	0.89	14.64	12.86	0.01	3.75	1.43	0.01	7.50
13	168.8	10.73	10.25	0.50	26.75	12.25	0.01	12.00	0.01	0.01	13.00
14	153.2	10.10	7.50	0.01	30.00	12.95	0.01	8.18	3.64	0.01	15.23
16	94.4	6.21	18.28	0.01	7.50	11.88	0.01	3.44	0.01	0.01	6.88
22	130.3	8.98	40.00	0.01	31.25	13.13	0.01	13.75	0.01	14.06	10.63
23	167.6	10.58	26.58	1.05	41.05	15.79	0.01	12.89	0.01	10.79	12.89
29	203.6	6.71	38.33	0.28	37.78	17.22	0.01	15.00	0.01	15.28	16.11
31	122.2	6.58	30.31	0.01	15.31	9.06	0.01	10.63	14.38	21.25	16.88
32	165.8	7.66	15.00	0.01	41.94	10.56	0.01	8.89	7.78	1.94	10.83
33	155.2	10.79	3.80	0.01	21.20	11.60	0.01	5.40	4.80	0.01	8.80
34	93.3	10.14	28.15	0.01	8.70	15.37	1.11	8.52	1.48	0.01	23.70
Fraction 2											
6	871.7	5.34	1.83	6.00	91.17	5.33	0.01	0.01	13.83	16.67	17.50
7	825.0	6.96	0.89	6.07	99.46	4.64	0.01	2.68	20.54	9.46	5.54
8	767.9	4.89	7.32	5.18	90.89	5.00	0.01	3.75	12.86	25.54	7.86
13	790.0	7.45	1.75	6.00	92.50	5.00	0.01	1.75	27.00	26.75	5.75
14	815.9	9.68	1.14	8.41	113.18	5.23	0.01	0.01	14.09	27.50	5.68
16	634.4	3.89	8.59	6.09	54.84	5.78	0.01	0.94	8.75	30.63	3.75
22	765.6	7.06	6.56	5.94	106.25	3.44	0.01	1.25	19.06	85.00	5.00
23	844.7	9.01	4.47	6.84	131.84	3.68	0.01	2.89	9.47	78.16	6.32
29	741.7	7.84	4.17	5.56	105.28	5.28	0.01	5.28	8.61	91.39	9.72
31	491.3	3.03	4.69	1.56	47.19	0.94	0.01	2.50	0.01	78.44	0.01
32	934.4	9.84	3.06	3.06	113.06	2.50	0.01	0.83	1.11	62.78	0.01
33	904.8	10.20	1.60	5.20	104.00	3.00	0.01	5.20	9.40	22.60	13.80
34	740.7	3.38	7.96	5.37	71.11	5.00	0.01	2.41	17.59	33.70	9.81
Fraction 3											
6	518.0	1.58	0.01	14.17	42.50	12.83	4.67	4.67	10.83	0.01	0.01
7	563.9	1.61	0.01	16.07	47.50	13.93	4.46	1.61	5.00	0.01	0.01
8	481.8	1.58	0.71	12.68	38.21	11.96	6.96	6.79	3.57	0.01	0.01
13	1202.5	2.67	0.01	19.50	55.75	22.50	10.50	6.75	7.25	0.01	0.01
14	1395.5	3.15	1.14	20.68	63.18	28.86	9.09	10.00	3.41	0.01	0.01
16	895.3	2.45	1.09	15.00	30.78	20.00	9.69	6.41	0.01	0.01	0.01
22	915.3	4.36	0.63	28.44	77.50	29.69	15.63	9.69	5.63	13.75	0.01
23	1015.5	4.27	0.01	27.89	84.21	31.32	13.16	20.79	0.01	13.42	0.01
29	958.1	3.24	0.01	26.11	79.44	31.94	12.78	10.00	0.01	13.89	0.01
31	666.9	2.16	0.94	17.81	51.25	17.50	17.50	15.00	0.01	0.01	30.63
32	1009.4	2.95	0.56	23.61	67.50	24.17	13.06	8.06	6.67	0.01	6.39
33	1086.8	2.47	0.60	24.80	61.20	25.80	5.20	6.60	5.80	0.01	11.80
34	847.8	2.46	0.93	19.07	37.22	21.85	5.37	5.74	1.85	0.01	2.41
'Pseudo-total' contents											
6	6534.4	19.74	10.68	34.02	205.24	117.09	15.88	16.97	24.68	59.16	50.23
7	6674.9	22.98	17.89	35.43	248.71	118.66	22.44	18.74	25.55	73.50	65.47
8	8497.9	18.11	26.44	39.35	211.82	136.30	21.66	20.79	17.87	58.39	54.37
13	5573.8	21.13	12.05	26.05	175.20	62.84	19.27	20.57	34.28	38.56	35.84
14	7059.3	22.93	9.86	30.48	216.96	90.25	22.62	18.24	21.19	55.08	55.44
16	4553.7	12.67	28.06	25.94	133.96	91.20	21.14	16.70	8.79	44.80	49.41
22	7101.2	25.30	47.19	42.41	303.23	124.84	49.27	32.52	24.70	112.89	76.32
23	6079.5	24.06	31.11	35.79	263.36	107.36	40.16	36.59	9.50	102.38	63.12
29	6215.9	18.42	42.56	33.37	239.65	106.28	52.67	30.30	8.68	120.57	62.74
31	5756.1	13.92	35.98	34.70	240.12	97.85	48.83	32.51	14.40	143.32	47.53
32	6555.4	20.62	18.64	40.61	342.36	117.54	44.53	29.67	15.57	107.27	56.55
33	7894.8	23.71	13.08	38.39	285.23	121.61	32.66	25.85	20.00	72.39	62.77
34	8028.9	16.42	37.09	36.87	236.23	127.84	24.98	22.65	20.96	65.44	48.35

MINITAB package, so the NF value can be chosen by using a Scree plot or by considering the components with eigenvalues greater than unity, which explain more variance than a single original variable. In our case we have only considered the two first principal components, PC1 and PC2, which explain 57.5% of total variance. This is a relatively high amount of variance, and since the $\mathbf{X}_b$ unfolded matrix does not really describe the real structure of the data set, a further insight into two-way PCA model (taking additional components) is not necessary.

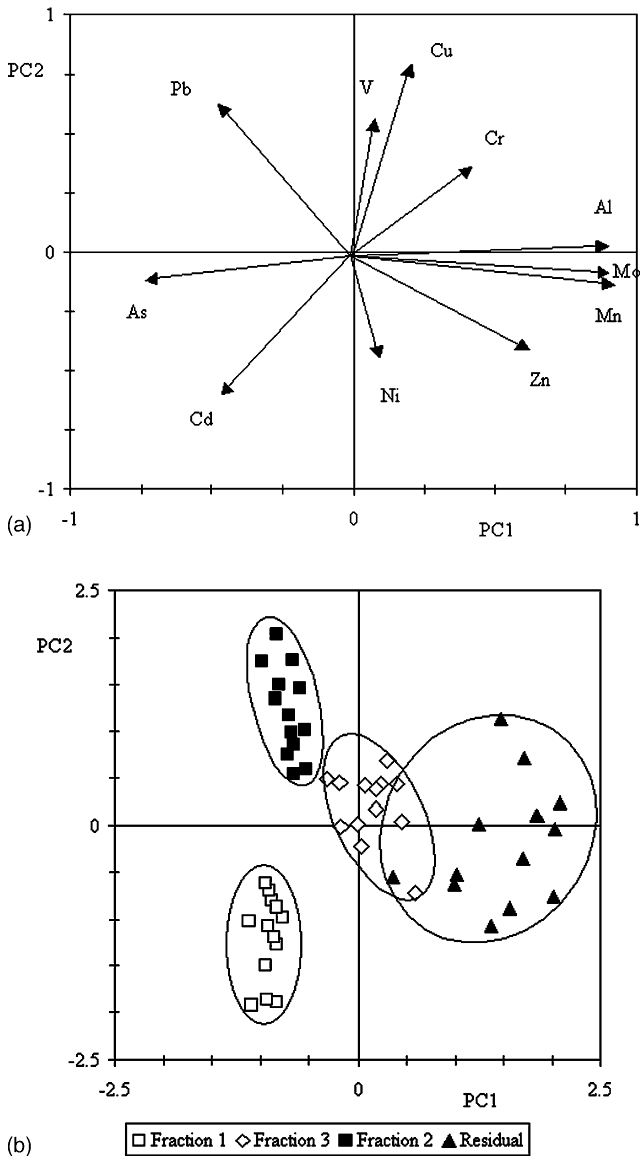

Fig. 3. Two-way PCA applied to the results of the B.C.R. fractionation procedure: (a) loading plot, (b) score plot.

Fig. 3a and b show respectively the loading and score plots for PC1 and PC2. From the interpretation of these Figures we can extract conclusions about the pattern of behaviour of the trace elements and heavy metals according to their fractionation by the B.C.R. scheme. Fig. 3a shows the behaviour of the variables (trace elements and heavy metals). As it can be seen, there is an association of Al, Mn and Mo and in a lesser extension Zn. These elements behave in an opposite way to Cd, As and Pb, whereas the rest of the metals appear more dispersed into the components space, showing a more individualized behaviour. In the Fig. 3b, and due to the previous unfolding, each object (or sediment representative of a sampling point) appears four times according to its fractionation. However, it can be seen that, in general, the points corresponding to different fractions are clustered in different regions of the components space, so the differential behaviour of the fractions is clearly demonstrated.

The superposition of the loading and score plots of Fig. 3 shows the general fractionation pattern of the trace elements and heavy metals amongst the four B.C.R. fractions: Al, Mo, Mn and Zn are mainly related with the residual fraction, Pb with the fraction 2 (oxidizable) and As and Cd with fraction 1 (acid soluble). The other elements appear fractionated amongst several fractions.

The philosophy of the B.C.R. fractionation procedure is that chemical elements associated to the first fractions present a higher environmental hazard. We can see from the score plot (Fig. 3b) that the fractions appear ordered along PC1 axis following the sequence (from left to right) 1 → 2 → 3 → residual, so PC1 could be used as a measurement of environmental hazard. Moreover, the more toxic elements (Cd, As and Pb) are associated to the more easily released fractions 1 and 2, so we can conclude than the sediments are, in general, environmentally hazardous. These conclusions are similar to those obtained by a closer inspection of Fig. 2, and again we cannot extract conclusions about the behaviour of individual sampling points.

3.3. Three-way PCA

As seen above, two-way PCA of $\mathbf{X}_b$ matrix does not allow describing or inferring neither similarity nor general behaviour patterns for the sampling points. Evidently, that information is present and available in the original data set, $\underline{\mathbf{X}}$, but because of the unfolding, it is buried and confounded in the score plot along the information corresponding to the behaviour of the B.C.R. fractions.

On the contrary, three-way PCA allows a much easier interpretation of the information present in the data set since it directly takes into account its three-way structure. Tucker3 and Parafac are the most common models for performing three-way PCA, and their differences and similarities can be summarized as follows.

Tucker 3 model: This method decomposes the three-way data set $\underline{\mathbf{X}}$ according to:

$$x_{ijk} = \sum_{p=1}^{P}\sum_{q=1}^{Q}\sum_{r=1}^{R} a_{ip} b_{jk} c_{kr} g_{pqr} + e_{ijk}$$

where a_{ip}, b_{jk} and c_{kr} are the elements of the loading matrices (the term score is not used in N-way PCA) **A, B** and **C** of ($n_{\text{obj}} \times P$), ($n_{\text{var}} \times Q$) and ($n_{\text{cond}} \times R$) dimensions respectively, g_{pqr} denotes the elements (p, q, r) of the core array $\underline{\mathbf{G}}$ ($P \times Q \times R$) and e_{ijk} is the error term of the element x_{ijk} of the j-scaled $\underline{\mathbf{X}}$ data array. The squared $g_{pqr}{}^2$ element reflects the interactions amongst the three modes, and P, Q and R are chosen so smaller as possible.

Parafac model: The decomposition model is different:

$$x_{ijk} = \sum_{f=1}^{\mathrm{NF}} a_{if} b_{jf} c_{kf} + e_{ijk}$$

where a_{if}, b_{jf} and c_{kf} are the elements of the three loading matrices **A, B** and **C** of ($n_{\mathrm{obj}} \times$ NF), ($n_{\mathrm{var}} \times$ NF) and ($n_{\mathrm{cond}} \times$ NF) dimensions respectively and e_{ijk} and x_{ijk} have the same meanings than above. Parafac can be considered as a constrained version of Tucker3 model with the same number of factors, NF, for each loading matrix and with the superdiagonal elements of the core matrix equal to 1.

In both models a joint visual interpretation of the three modes can be carried out, but Tucker3 model requires in addition that the core matrix $\underline{\mathbf{G}}$ will be sufficiently superdiagonal. In our case, that condition was not fulfilled, so we have preferred the use of Parafac model. The number of factors, NF, of the model was chosen by means of the core consistency tool [19] implemented in the *N*-way toolbox for MATLAB [25,26]. The optimal complexity was found for a two factors model (core consistency = 100%) explaining 54.4% of the data variance, an amount very close to the 57.5% explained by two-way PCA. Fig. 4a–c show respectively the loading plots for A, B and C modes, i.e., for sampling points, chemical elements and B.C.R. fractions. The joint interpretation of these three plots can be carried out directly [27].

From the loadings for B and C modes, observations similar to those found in two-way PCA can be made: the loading plot for B-mode (Fig. 4b) shows a similar appearance than the loading plot of two-way PCA (Fig. 3a) and trace elements and heavy metals conserve their relative position, exception made of Pb. In the loading plot of C-mode (Fig. 4c), B.C.R. fractions also lay in the same relative positions than in the score plot of two-way PCA (Fig. 3b), with the more easily released fractions (fractions 1 and 2) placed at lower values of factor 1, and the more strongly retained ones (fractions 3 and residual) located at higher values of factor 1. Therefore, the general pattern of behaviour found by univariate interpretation and two-way PCA is conserved in the three-way analysis, although the Parafac model relies mainly on the behaviour of fraction 2 and residual.

However, three-way PCA permits to extract additional information contained in the loading plot of A-mode (Fig. 4a), which is directly related with the global behaviour of the sediments (or sampling points). In that plot, each point represents a sediment and from the joint observation of Fig. 4a–c, we can see some tendencies in the behaviour of the sampling points. Thus, points 13, 14, 16 and 6 are associated with As, Cd and Ni and with B.C.R. Fraction 1 (the more easily released ones). Points 23, 29 and 22 are associated with Pb, V, Cu and Cr, whereas points 8, 31, 32, 33 and 34 are located with Al, Mo, Mn and Zn and residual fraction. Therefore, the more dangerous sampling points are 13, 14, 16 and 6, because of their association with both the more toxic elements and the more easily released fractions.

The environmental situation, derived from the presence of trace elements and heavy metals in the Mejillones del Sur bay, can be visualized by means of the A-mode loadings of Parafac factors 1 and 2. Sediments with small values of factor 1 will contain high concentrations of toxic elements (As, Cd and Ni), whereas sediments with great values of factor 1 con-

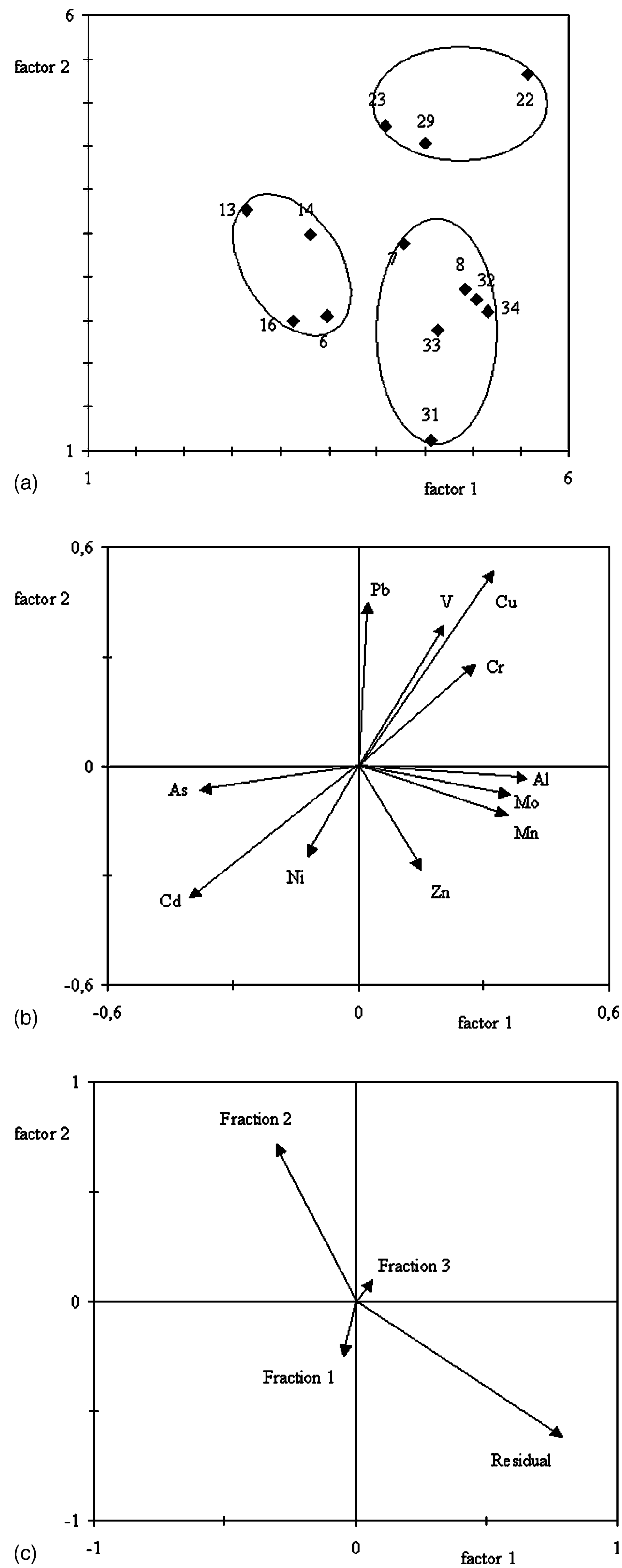

Fig. 4. Loading plots of three-way PCA applied to the results of the B.C.R. fractionation procedure. (a) A-mode: (♦) individual sediments, (b) B-mode, (c) C-mode.

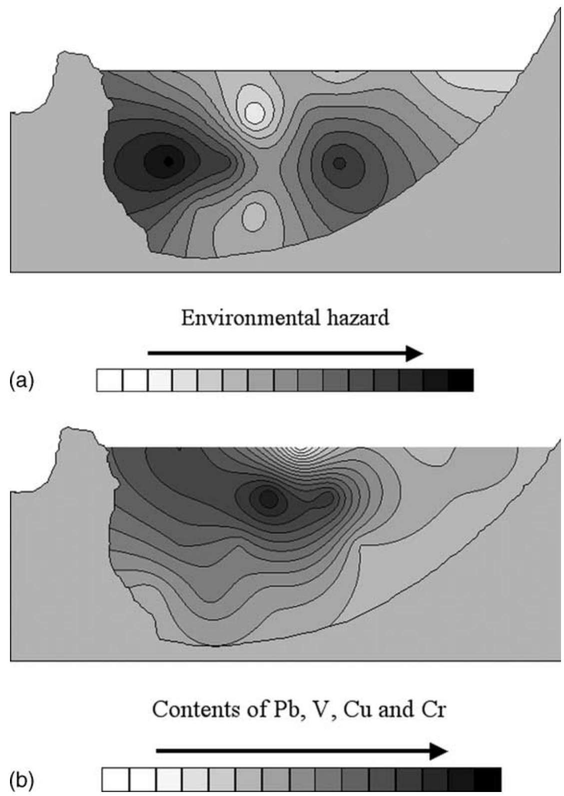

Fig. 5. Contour plots of the A-mode loadings of Parafac model onto the Mejillones del Sur bay showing the zones that pose greater environmental hazard: (a) factor 1, (b) factor 2.

tain less toxic chemical elements (Mn, Mo, Al, Cu, etc.) in the more strongly retained (and consequently less available) residual fraction. Thus Parafac factor 1 can be interpreted in terms of environmental hazard: the more negative the factor 1 A-loading of a sediment is, the higher the potential risk it poses to the environment and, on the contrary, the more positive the factor 1 A-loading of a sediment is, the lower the potential risk. The loadings of Parafac factor 2 also retain useful information about the occurrence of Pb, V, Cu and Cr, which do not seem to be associated to any B.C.R. fraction in particular.

If the A-mode loadings of Parafac factors 1 and 2 are plotted as a function of the GPS coordinates of the sampling points, the resulting contour plots (Fig. 5a and b, respectively) will show environmental information about the Mejillones del Sur bay. In Fig. 5a, the shading intensity is directly related with the environmental hazard (i.e., smaller A-mode loadings of Parafac factor 1): the shaded zones correspond to areas of the bay having sediments whose surface layer is loaded with toxic elements (As, Cd and Ni) which are not strongly retained and therefore could be easily released. In Fig. 5b, the shading is related to the presence of Pb, V, Cu and Cr (i.e., greater A-mode loadings of Parafac factor 2). Therefore the shaded zones of Fig. 5a and b must be of main concern to the local administrations.

4. Conclusions

Results derived from the use of the B.C.R. fractionation procedure are arrayed in a three-mode way (sediments, chemical elements and fractions) and although they can be studied by univariate methods, no decisive conclusions can be extracted from such study.

Classical two-way PCA after previous unfolding of the three-mode array into a two-way matrix, allows to find the general behaviour patterns for both chemical elements and B.C.R. fractions, but no information regarding individual sediments can be found.

On the contrary, three-way PCA takes into account the true structure of the data set and allows to visualize information about the three ways that can be jointly interpreted. A two factors Parafac model has allowed interpreting the data set information. The first factor can be used as a measurement of environmental hazard, whereas the second one also contains useful environmental information about trace metal pollution.

Lastly, it can be concluded than three-way PCA is the most adequate tool to learn all the information contained in data sets obtained by application of the B.C.R. fractionation procedure to environmental samples.

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