

# Assessment of metal contamination in dredged sediments using fractionation and Self-Organizing Maps

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## Abstract

Although total metal content is frequently the initial approach for measuring pollution, no information is provided about mobility and environmental risk. In this paper, a metal fractionation (sequential extraction) technique and artificial neural networks (Self-Organizing Maps, SOMs) have been used jointly to evaluate the pollution level of the sediments dredged from the dry dock of a former shipyard in the Bilbao estuary (Bizkaia, Spain). The load pollution index (LPI) for the upper, middle and bottom layers of the sediments was 7.65, 8.22 and 10.01, respectively, for six metals (Cu, Mn, Ni, Cr, Pb and Zn). This showed that upper sediments were less polluted than the lower ones. Consequently, a reduction in the pollution level of metal discharged into the river in recent years was confirmed. According to fractionation results, the most mobile minor elements were Cu, Pb and Zn, as they are mainly associated with the non-residual fractions. The statistical approach of Self-Organizing Maps (SOMs) revealed that Ni, Pb and Zn amounts in the residual fraction followed the same pattern associated with simultaneous discharges of slags into the river. However, other hazardous discharge sources are responsible for the high accumulation of those metals in the non-residual fractions. © 2007 Elsevier B.V. All rights reserved.

**Keywords:** Metal speciation; Sediments; Fractionation; Self-Organizing Maps; Artificial neural networks

## 1. Introduction

Dredged river or marine sediments may constitute hazardous materials that should be handled according to the pollutant content and disposal site. Many rivers have to be dredged periodically to prevent the risk of flooding or to allow navigation. The alternatives for dredged sediments are ocean disposal, artificial islands or controlled landfills. The adverse effects on water quality and aquatic organisms with ocean disposal on one hand, and the difficulty in finding suitable land sites, on the other, makes this waste management difficult [1,2].

When river sediments are landed, changes in redox conditions affect the distribution and availability of the contaminants. Metals are commonly present in sediments and their mobilization through bioturbation and resuspension constitutes a potential threat [3].

It is widely recognized that the total metal content in soils and sediments does not provide relevant information about bioavailability, mobility or toxicity [4–8]. An alternative tool for obtaining this information is based on the distribution of metals in “operationally defined fractions”, called “operational speciation”. This speciation comprises the application of extractants in order of increasing reactivity, whereby the consecutive fractions obtained correspond to metal association with lesser mobility. Nevertheless, the application of operational speciation has certain significant limitations, such as the limited selectivity of extractants, the redistribution of metals during the extraction process, the deficiency of a reagent dose, if metal content is too high [9] and the inability to distinguish between metal associations with organic matter and sulphides [10,11].

One of the more popular and long-standing extraction schemes was the one proposed by Tessier et al. [12], but the wide variety of methods published subsequently has hindered the comparison of results, unless the same extracting conditions and reagents are used. In order to harmonise extraction methodology, the Standards, Measurements and Testing Programme—SM&T (formerly Community Bureau of Reference, BCR) established a

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common procedural scheme consisting of a three-step extraction method (BCR method). This was published in detail by Ure et al. [13], although later modifications have been carried out [14,15]. Mossop and Davidson [7] compared the original and modified BCR sequential extraction procedures and concluded that the revised version provides a better attack on the iron-based components of the reducible matrix for a wide range of soils and sediments. However, van Hullebusch et al. [8] concluded that the modified Tessier scheme was the most suitable scheme for studying metal partitioning in anaerobic granular sludges.

This paper presents the distribution of metals into “operationally defined fractions” in the sediments from a former shipyard in the Bilbao estuary (North Spain). A selective sequential extraction procedure and a statistical tool (artificial neural networks) have been used to identify specific associations between metal content and sediment phases or fractions. Selective extraction techniques may therefore provide information about the mobility and bioavailability of metals in dredged and discharged river sediments.

## 2. Materials and methods

### 2.1. Sampling location and history

The Nervión estuary (Bilbao, North Spain) was once the largest estuary area on the Cantabrian coast, although it has been drastically reduced by urban, industrial and port developments. Nowadays, the estuary is 15 km long, at an average of 100 m wide, and its channel depth ranges from 2 m in the upper estuary to 9 m at the mouth. The estuary is formed by the tidal part of the main river, the Nervión. The river's average discharge is estimated at  $35.56 \text{ m}^3 \text{ s}^{-1}$  and the predicted suspended sediment load ranges from 143,208 to 1,043,358 tonnes year<sup>-1</sup> [16].

In 1900, the Euskalduna shipyards were founded in the heart of Bilbao, where the Nervión River was still navigable (Fig. 1). Its slipways and facilities covered 90,000 m<sup>2</sup> and many large ships graced its dry docks, particularly during the first 50 years of activity. However, the industrial recession of the 1970s led to its closure in 1984. The dry docks and part of the site of the former Euskalduna shipyards were reassigned to recreational and cultural use, and today the Guggenheim Museum, the Music and Congress Centre (Euskalduna Palace) and the Maritime Museum of Bilbao are situated on the site of the now defunct company. The Maritime Museum is located near the dry docks, where exhibition ships can be visited (Fig. 2). With a view to making further use of the docks, a major refurbishment of the second dry dock was carried out in 2002, involving the dredging of sediments.

Before disposal, samples of these sediments were collected to determine metal content and fractionation, as well as for risk assessment.

### 2.2. Sample collection, storage and preservation

Three 30 cm long sediment cores were collected in the dry dock using a polyvinylchloride (PVC) probe (5 cm diameter, 35 cm deep). The sediments were stored in the probes, which were sealed with a plastic cover. Once the plastic cover was removed in the laboratory, individual cores were extruded immediately after sampling and cut into three 10-cm slices, called A (upper), B (middle) and C (lower or bottom) slices or layers. Consequently, nine samples from three sediment cores were studied. After drying, the samples were sieved through a 2-mm stainless sieve for further analysis.

### 2.3. Analytical methods

The distribution of the metals in the sediment samples was studied by the sequential extraction method proposed by Ure et al. [13], which was adapted for this study. Although the original extraction protocol published by Ure et al. [13] is a three-step procedure, a fourth fraction (residual phase) is proposed. This fraction includes the amount of metals bound to the mineral lattice of the sediments or, in other words, the amount of metals not measured in the previous three steps and bound strongly to the sediment. For this last (fourth) step, we used a method of total acid digestion, explained below, although authors, such as Mossop and Davidson [7] used an aqua regia attack to compare the sum of the four steps with the results of a separate aqua regia digestion.

The consecutive steps of the BCR sequential extraction procedure are as follows:

**Step 1** In this study, 1 g of each sample was introduced into 100 ml centrifuge tubes and weighed. About 40 ml of an acetic acid solution 0.11 M were added into the centrifuge tube and extracted by shaking for 16 h at room temperature (overnight). The liquid phase was subsequently separated from the solid residue by centrifugation at 3500 rpm ( $2000 \times g$ ) for 30 min. After filtration, the supernatant was stored at 4 °C prior to analysis. The solid residue was washed twice with double-distilled water before the next step. The metal content measured in the acetic acid solution is referred to as the exchangeable + carbonatic fraction.



Fig. 1. Geographic location of the sampling site.

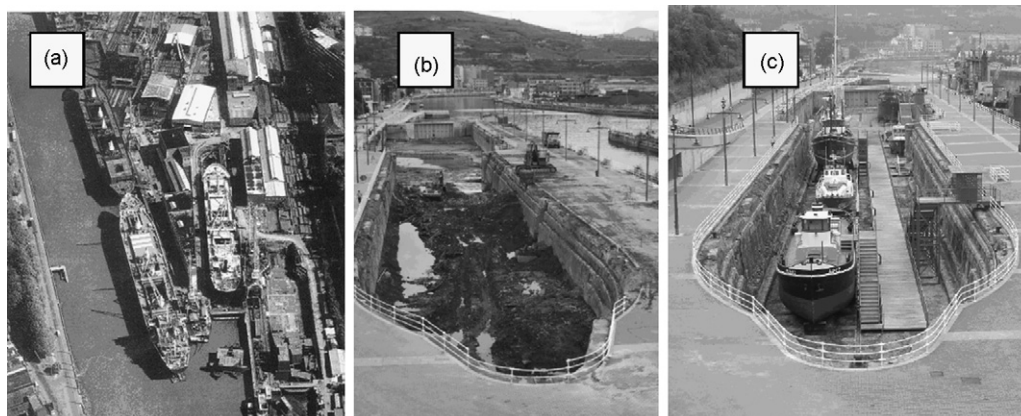


Fig. 2. Precise location of the sampling point: (a) the two dry docks of the active Euskalduna shipyards; (b) the dredging of the sediments in the refurbished dock; (c) the current recreational use of the refurbished dry dock.

**Step 2** The solid residue from the previous step was extracted with 40 ml of a solution of hydroxylamine hydrochloride or hydroxylammonium chloride 0.1 M acidified with nitric acid to pH 2. The extraction procedure was carried out in the same way as in step 1. The metal content measured in the extracting solution is referred to as Fe/Mn oxide fraction.

**Step 3** The solid residue from step 2 was extracted with a 10 ml solution of  $H_2O_2$  as supplied by the manufacturer (acid-stabilized to pH 2). This solution was added carefully in order to avoid losses through violent reaction. After heating at 85 °C for 1 h, a new addition of 10 ml of the  $H_2O_2$  solution was carried out and the liquid volume was reduced by heating at 85 °C. Finally, 50 ml of ammonium acetate 1 M were added and the extraction was again carried out as explained in step 1. The metal content measured in the extracting liquid is referred to as organic fraction.

**Step 4** The solid residue from step 3 was transferred to a polytetrafluoroethylene (PTFE) vessel and 6 ml of HF were added. After 3 h, 20 ml of HF, 6 ml of  $HClO_4$  and 2 ml of  $HNO_3$  were added to the previous solution and acid digestion was maintained overnight. The acid mixture

was heated at 300 °C until dense drop. After adding 10 ml of HF, 2 ml of  $HNO_3$ , 2 ml of  $HClO_4$  and 10 ml  $H_3BO_3$  (saturated), the solution was heated again at 200 °C until dense drop. After adding 6 ml of  $HNO_3$  and 2 ml of  $H_2O_2$ , the extraction was again carried out as explained in step 1. The liquid solution contained the residual metal amount not extracted in the previous steps.

The metals measured were Cu, Co, Mn, Ni, Cr, Pb, Zn, Fe, Mg, Ca, K and Na. The quantification of the metal content in the digested samples of each step was carried out using an air/acetylene flame atomic absorption spectrophotometer (AAS, Perkin-Elmer 1100B). Instrument calibration was carried out using standard solutions in each extracting solution. The nine samples were processed in triplicate and stored at 4 °C until analysis. All reagents were of analytical-reagent grade unless otherwise stated.

#### 2.4. Statistical methods

The possible associations among metals in the different fractions are not easily established, as many factors should be taken into account at the same time; for example, the influence of

Table 1  
Pseudototal metal content in each of the three layers and in the whole sample of the dredged sediments

Metal	A layer	B layer	C layer	Whole sample	Background values <sup>a</sup>	SQL <sup>b</sup>
Cu (mg kg <sup>-1</sup> )	284	216	301	267	18	50
Co (mg kg <sup>-1</sup> )	36.4	38.3	48.4	41.0	n.a.	n.a.
Mn (mg kg <sup>-1</sup> )	387	299	502	396	175	350
Ni (mg kg <sup>-1</sup> )	67.1	124.7	123.5	105.0	12	50
Cr (mg kg <sup>-1</sup> )	166	257	248	224	11	100
Pb (mg kg <sup>-1</sup> )	328	315	353	332	34	60
Zn (mg kg <sup>-1</sup> )	1308	1244	1612	1388	175	250
Fe (%)	4.42	4.15	5.55	4.71	1.9	4
Mg (%)	0.95	0.85	0.82	0.87	n.a.	n.a.
Ca (%)	6.64	7.52	6.07	6.74	n.a.	n.a.
K (%)	1.54	1.54	1.45	1.51	n.a.	n.a.
Na (%)	2.18	2.04	3.51	2.57	n.a.	n.a.

n.a., Not available; SQL, sediment quality levels.

<sup>a</sup> Ref. [22].

<sup>b</sup> Ref. [23].

variables, such as organic content, pH, temperature and the interactions between metals during the extraction procedures. In such cases, statistical approaches render useful information that should be carefully analysed.

One alternative to detect patterns in a set of data is the application of the Self-Organizing Maps. This statistical tool is a group of artificial neural networks based on the topological properties of the human brain [17–20]. SOMs are also known as Kohonen networks in honour of the author who first developed them [17].

SOMs are primarily intended to identify groups or detect patterns in a set of data. This statistical tool is designed for unsupervised learning and is trained using the Kohonen algorithm. This algorithm does not require any examples of the output variable in the data set. The neurons of the output layer are arranged on a topological map, forming a two-dimensional lattice. The Kohonen training algorithm is designed to encourage the formation of clusters of similar cases at nearby positions in the lattice. This allows independent clusters to be identified and labelled, even in the absence of labelled training data. Class labels are assigned to neurons, and it is the class label of the “winning” neuron during execution that forms the class or grouping estimation of the SOM [21]. The Kohonen algorithm assigns centers to a radial hidden layer by attempting to recognize clusters within the training cases. Cluster centers close to one another in pattern-space tend to be assigned to units that are close to each other in the network (topologically ordered).

SOMs can also be understood as a non-linear mapping of a multi-dimensional hyperspace onto a two-dimensional plane. Points, which are close to each other in the hyperspace, can also be expected to be close to each other (i.e. assigned to the same neuron) in the two-dimensional lattice. Accordingly, clusters of points or patterns can be identified because they can reasonably be assigned to the same neuron. The ultimate aim of this neuronal tool here is to discover similar patterns among the metals and their fractions.

### 3. Results and discussion

#### 3.1. Pseudototal metal content

Contaminants from both natural and anthropogenic sources are deposited in rivers at the same time, and total metal content is frequently the first approach for pollution measurement. In this study, total metal content was determined by the sum of the content in each fraction of the sequential extraction, and was referred to as the pseudototal content.

Table 1 shows the pseudototal metal content in each layer and in the whole sample. A comparison with background levels and sediment quality levels has also been included. Three metals (Cu, Pb and Zn) clearly exceeded the sediment quality level (SQL), and also exceeded the background levels. As far as Ni and Cr are concerned, the metal content in the bottom layers (B and C layers) is more than twice the SQL value; however, the decrease in these metal levels for A layer reveals that the source of Ni and Cr has been considerably reduced in recent years, as a consequence of the pollution abatement measures implemented by the authorities. García-Barcina et al. [24] also found

an important improvement in the quality of Bilbao estuary water in recent years. No reference values are shown for Fe, Mg, Ca, K and Na, as they are not considered hazardous metal pollutants, but their content may be related to other metal associations.

In order to estimate the overall pollution level of the samples, the load pollution index (LPI) was defined by Tomlinson et al. [25] as:

$$\text{LPI} = \prod_{n=1}^{n=x} (\text{EF}_n)^{1/x} \quad (1)$$

where EF is the enrichment factor defined as  $\text{EF} = C_n/B_n$ ;  $C_n$  represents the measured concentration of the metal  $n$  and  $B_n$  is the background concentration of the metal  $n$ ;  $x$  is the number of metals considered. The  $x$  value in this study is 6 and it only includes the minor metals Cu, Mn, Ni, Cr, Pb and Zn. Co has been excluded because its background value in the area is not available (Table 1).

The LPI index for the A, B and C layers is 7.65, 8.22 and 10.01, respectively. These values reveal that upper sediments are less polluted than lower sediments, in accordance with the results published by Franco et al. [26], who studied the evolution of the LPI in the Nervión estuary over 12 years. They found a decreasing pollution trend with time, in keeping with the industrial recession and more efficient abatement measures. The LPI value for the three layers in combination is 8.72, and according to the classification used by Belzunze et al. [27], when the LPI value is between 3 and 12, the sediment can be classified as moderately polluted. Cearreta et al. [1] found that surface sediments in the Bilbao estuary registered some transported living foraminifera of species that are dominant in less heavily polluted estuaries.

#### 3.2. Sequential extraction

Regardless of the moderate pollution level in the sediment samples, the distribution of the metals into fractions illustrates their mobility and possible reactivity. The sequential extraction results revealed that the distribution pattern for Na in the three layers is very similar and thus, the mean value for each fraction is represented in Fig. 3. The same behaviour was found for the other major elements, Mg, Ca and K and consequently, Fig. 3 shows the mean values for the four fractions of each metal. Although Ca, Na and Mg are not classified as dangerous elements, their preferential accumulation in the most mobile form (first step or fraction) reveals that they may be readily transformed, thus liberating cations when pH conditions change slightly. In contrast, K is found mainly in the residual step, which is indicative of the mineral/detrital origin of this metal. Consequently, K does not pose any threat to the biosystem.

A high percentage of Cu, Pb and Cr is bound mainly to the organic fraction, or step 3 (Fig. 4), in contrast to other studies where the preferential adsorption of Pb and Cu on three common iron hydrous oxides (ferrihydrite, hematite and goethite) has been reported [28,29]. In fact, more than the 80% of the total amount of Cu for the three layers is bound mainly to this fraction, which is evidence of the preferential association of

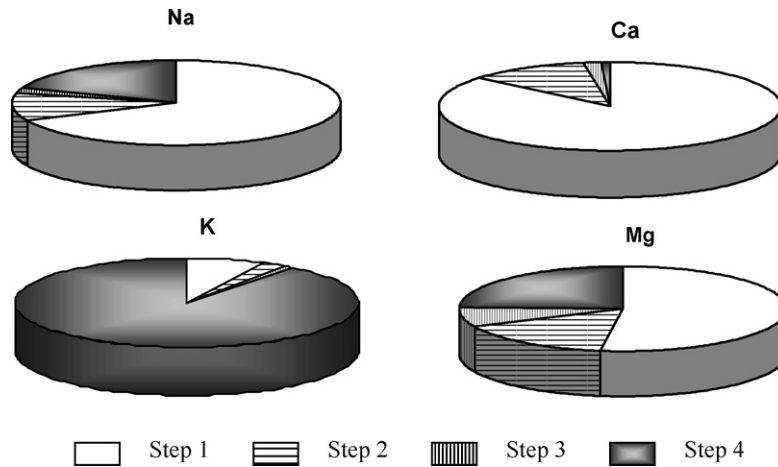


Fig. 3. Percentage distribution of Na, Ca, K and Mg in the four steps of the sequential procedure (step 1 related to the exchangeable + carbonatic fraction; step 2 related to the oxide fraction; step 3 related to the organic fraction and step 4 referred to the residual fraction).

this metal. This element, more than others, shows a tendency towards the organic phase, as it forms strong associations with oxygen and sulphur atoms [30,31]. Although this tendency was also reported in other studies for sediment samples taken in the estuaries and coastal zone of the Basque Country [25], an exception to this pattern was found in the outer samples of the Nervión estuary, where most of the Cu was found to be in residual form [25]. In that study, Cu association to the residual fraction was related to an industrial slag origin, but Cu in the samples of the present research is considered more readily soluble, as organic matter becomes structurally less complex in the case of open-air sediments. It seems likely, therefore, that as the sediment dries, metals would be released from associations with organic matter, contributing to the increase in metal availability [29].

A similar pattern was found for Pb, but some differences were observed among layer distribution. Although the total amount in each layer is very similar (Table 1), Pb in layer A shows a

more preferential accumulation in the organic fraction than in layer C (bottom layer). In contrast, Cr distribution is similar for the three layers, although the upper layer is less polluted than the others.

A relevant amount of Zn, Ni and Co is accumulated in the first fraction step (Fig. 5). More than 90% of the total amount of Zn was found in the non-residual fraction, which is consistent with the data published by Belzunce et al. [27]. Ni distribution in layer A is slightly different from the distribution in the others, which is related to the significant reduction (to a half) in the total amount measured in the upper layer. The results in Fig. 5 show that the most important fraction for Ni and Co is the residual one, which do not fully ensure their future immobilization. In fact, Stephens et al. [29] found that metals, such as Pb, Ni and Cu initially present in insoluble forms became progressively more soluble/available in anoxic sediments as the samples dried and oxidised in the laboratory (open air) over a few weeks. In contrast to soil samples, dredged sediment disposal should take

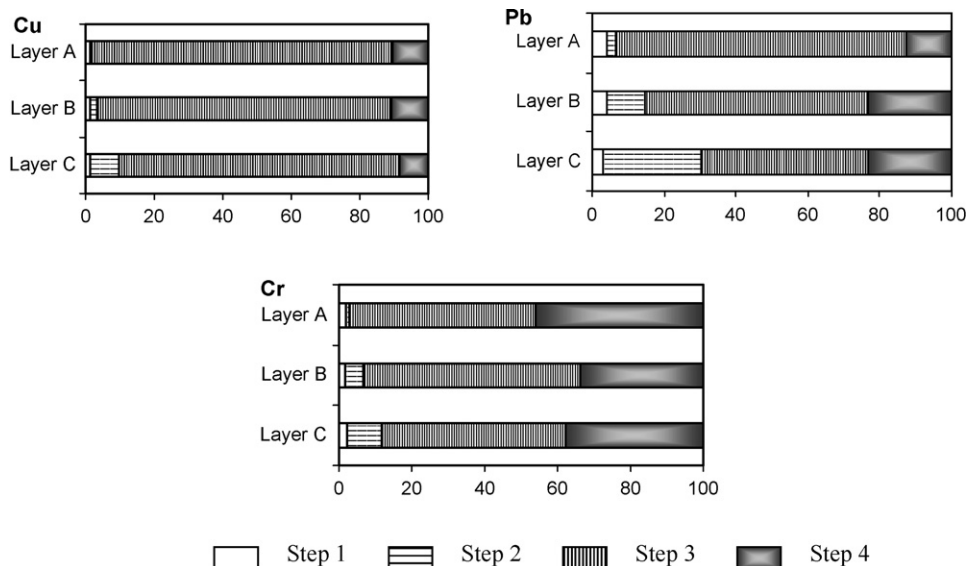


Fig. 4. Percentage distribution of Cu, Pb and Cr in the four steps of the sequential procedure (step 1 related to the exchangeable + carbonatic fraction; step 2 related to the oxide fraction; step 3 related to the organic fraction and step 4 referred to the residual fraction).

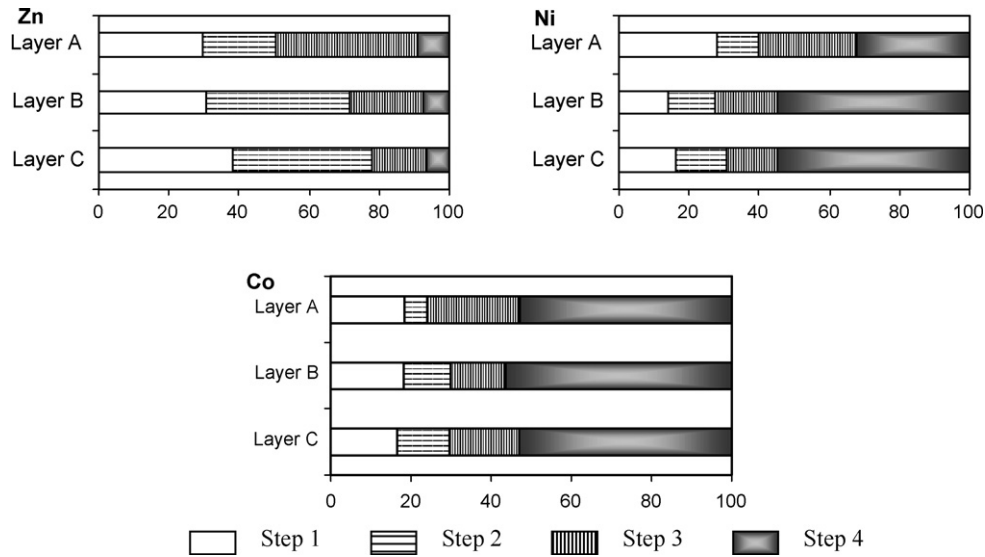


Fig. 5. Percentage distribution of Zn, Ni and Co in the four steps of the sequential procedure (step 1 related to the exchangeable + carbonatic fraction; step 2 related to the oxide fraction; step 3 related to the organic fraction and step 4 referred to the residual fraction).

into account the increase in metal leachability when the anoxic sediments are disposed of on land.

A high percentage of Fe is in a stable association with the mineral matrix of the sediment (residual fraction), which is related to the mineral/detrital origin of this metal (Fig. 6). By contrast, Mn appeared to be associated mainly to the most mobile forms, which was also concluded by other authors [27].

3.3. Self-Organizing Maps (SOM networks)

It was also considered of interest to compare the behaviour of the different metal fractions and detect similar patterns in the samples. Hence, Kohonen networks (SOM networks) were considered as the most appropriate tool. Three analyses were carried out on each of the nine sediment samples (3 points × 3 layers), thus yielding a total of 27 analyses (9 samples × 3 analyses). Furthermore, 4 different amounts were measured for each of the 12 metals, which meant that 48 (12 × 4) fractions were determined in 27 different analyses. Each fraction could thus be represented in a 27-dimension hyperspace.

With the objective being to identify patterns describing similar behaviour of the different fractions, several SOM networks were tested with dimensions in the output layer ranging from (1 × 2) to (4 × 4) neurons. Obviously, the input layer had 27

neurons in all cases. Since the units of the 48 points and their operation ranges were different, all the variables were first standardised and rescaled to have an average of 0 and a standard deviation of 1.

The best SOM network was identified in an interactive way with the help of a classical K-means cluster analysis. A SOM with a 3 × 3 structure (9 neurons) in its output layer yielded meaningful and consistent results, thus grouping similar metal fractions in the same neuron. This 3 × 3 SOM is a structure that can be understood as the most appropriate projection of the 48 points corresponding to the 27-dimension hyperspace onto an easy-to-handle two-dimensional representation. In this representation, those metal fractions that have a similar behaviour are expected to belong to the same neuron of the SOM. The results are shown in Fig. 7, with the metal fractions (48 fractions) distributed into the 9 neurons.

The variables in neurons 2, 4, 5 and 8 (Pb and Mn in step 2, Mn in steps 3 and 4 and Zn in steps 1 and 2) revealed no common tendency with any other metal. The entire distribution of four elements (Mg, K, Na and Fe) into the four fractions is included in the first neuron, which means that they all have the same evolution in the sediments. These metals, classified as major elements, have a natural origin in these sediments, as concluded previously, and presumably they have also been discharged into

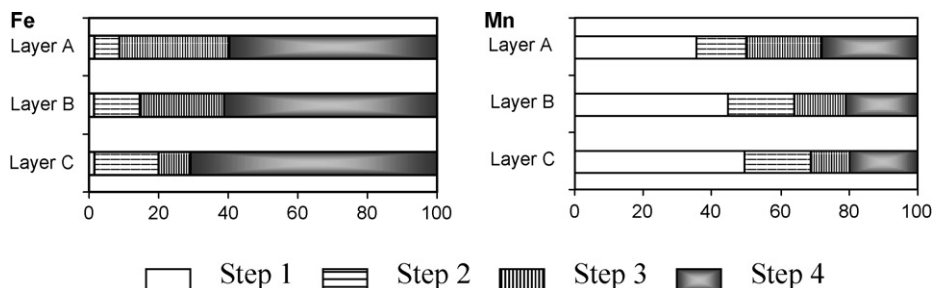


Fig. 6. Percentage distribution of Fe and Mn in the four steps of the sequential procedure (step 1 related to the exchangeable + carbonatic fraction; step 2 related to the oxide fraction; step 3 related to the organic fraction and step 4 referred to the residual fraction).

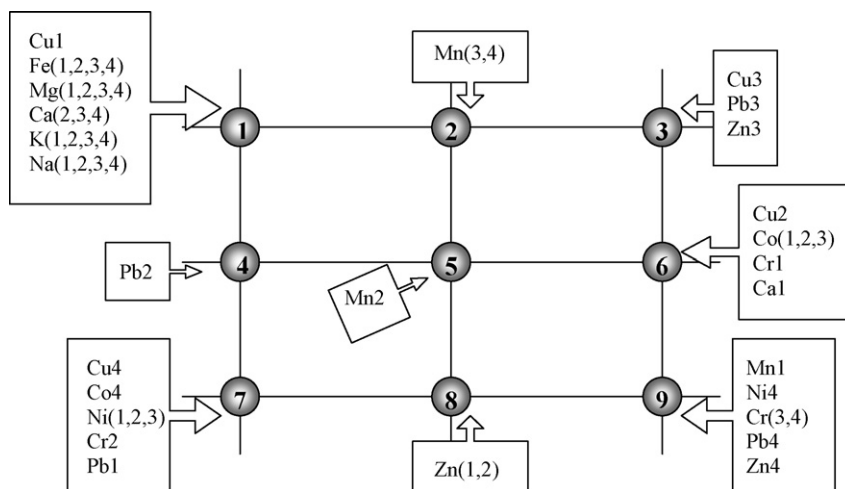


Fig. 7. The nine patterns or groups obtained by Self-Organizing Maps (SOMs) for the metals in the four fractions. The number denotes the step or fraction.

the river simultaneously over time. The third neuron comprises the Cu, Pb and Zn amounts associated with the organic fraction, which means a possible competition to render chelates, regardless of the non-preferential accumulation of Zn in this step. Another similar pattern (neuron 6) showed a relationship among Co, Cr and Ca in step 1, or the exchangeable + carbonatic fraction. Cu and Co associated with oxides (step 2 in neuron 6) and in the residual fraction (step 4 in neuron 7) have a similar evolution due to their close chemical properties, and may be due to the same origin. On the other hand, neuron 7 comprises the most soluble fraction of Ni and Pb and the most recalcitrant fraction of Cu and Co. Finally, Ni, Pb, Cr and Zn in step 4, or the residual fraction, appeared together in neuron 9, which is indicative of a simultaneous discharge of slags containing these metals.

#### 4. Conclusions

It is widely accepted that metal distribution in sediments or soils is indicative of the potential harm to the environment through chemical associations. The more mobile the metal, the higher the risk associated with it. In this study, the sediments dredged from the dry dock of a former shipyard were analysed to establish the distribution of 12 metals into 4 speciation fractions. Regarding the minor metals Cu, Mn, Ni, Cr, Pb and Zn, the load pollution index for the samples collected in the upper, middle and bottom layers is 7.65, 8.22 and 10.01, respectively. These values reveal that the upper sediments are less polluted than the lower ones, which is indicative of a reduction in the pollution level discharged into the river in recent years. However, Cu, Pb and Zn clearly exceeded the sediment quality levels by more than five times.

Fractionation studies showed that these three metals are mobile, as they are preferentially associated with non-residual fractions.

The combination of the fractionation results with the statistical treatment of SOMs rendered conclusions about the behaviour pattern of certain metals. Thus, the association between the neurons and variables showed that Ni, Pb and Zn in the more

resistant fraction (residual fraction) come from slag discharges into the river. However, other discharge sources should also be considered, as in some cases the amount of those metals in the other fractions is as high as 80% of the total. Cu, Pb and Zn have a common pattern as far as association with organic matter is concerned, which may reveal a possible competition to render organic chelates.

To conclude, special attention should be paid to the mobility of Zn, Pb and Cu if these sediments are disposed in the open air without prior treatment.

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