

Mediterranean Marine Science

Vol 15, No 1 (2014)

Vol. 15, No 1 (unpublished)



Classification of sediments by means of Self-Organizing Maps and sediment quality guidelines in sites of the southern Spanish coastline

O. VESES, R. MOSTEO, M.P. ORMAD, J.L. OVELLEIRO

doi: [10.12681/mms.506](https://doi.org/10.12681/mms.506)

To cite this article:

VESES, O., MOSTEO, R., ORMAD, M., & OVELLEIRO, J. (2013). Classification of sediments by means of Self-Organizing Maps and sediment quality guidelines in sites of the southern Spanish coastline. *Mediterranean Marine Science*, 15(1), 37–44. <https://doi.org/10.12681/mms.506>

Classification of sediments by means of Self-Organizing Maps and sediment quality guidelines in sites of the southern Spanish coastline

O. VESES, R. MOSTEO, M. P. ORMAD and J. L. OVELLEIRO

University of Zaragoza, Department of Chemical Engineering and Environmental Technology, C/ Pedro Cerbuna 12, 50009 Zaragoza, Spain

Corresponding author: themachineiq@hotmail.com

Handling Editor: Aris Karageorgis

Received: 4 October 2012; Accepted: 18 June 2013; Published on line: 2 August 2013

Abstract

This study was carried out in order to classify 112 marine and estuarine sites of the southern Spanish coastline (about 918 km long) according to similar sediment characteristics by means of artificial neural networks (ANNs), such as Self-Organizing Maps (SOM) and sediment quality guidelines, from a dataset consisting of 16 physical and chemical parameters, including sediment granulometry, trace and major elements, total N and P and organic carbon content. The use of ANNs such as SOM allowed classification of the sampling sites according to their similar chemical characteristics. Visual correlations between geochemical parameters were extracted due to the powerful visual characteristics (component planes) of the SOM, thus revealing that ANNs are an excellent tool to be incorporated in sediment quality assessments. Besides, almost 20% of the sites were classified as medium-high or high priority sites for future remedial action due to their high mean Effects Range-Median Quotient (m-ERMQ) value. Priority sites included the estuaries of the major rivers (Tinto, Odiel, Palmones, etc.) and several locations along the eastern coastline.

Keywords: sediments, trace elements, SQG, organic carbon, m-ERMQ, SOM.

Introduction

Trace elements such as cadmium, copper, nickel, lead, zinc, mercury, arsenic and chromium can be found naturally in estuarine and marine sediments. However, these sediments can be exposed to significant anthropogenic trace element loads from point and non-point sources leading to environmental degradation (Rodríguez-Barroso *et al.*, 2009). In Europe, Directive 2008/105/EC states that the concentrations of these pollutants in sediments must not significantly increase with time but no threshold concentration that protects aquatic fauna is provided. In Spain, the Andalusian Water Agency (AWA) is in charge of the management of part of the aquatic environment in the south of Spain and keeps track of trace element concentrations in sediments from this area.

The southern Spanish coastline extends over 918 km. It includes the Odiel-Tinto estuary, which is one of the most polluted estuaries in the world and has been extensively studied (Ruiz, 2001; Santos Bermejo *et al.*, 2003; Sainz & Ruiz, 2006; Vicente-Martorell *et al.*, 2009). Besides, areas hosting certain industrial activities such as the Bay of Cadiz, the Guadiana estuarine, the Bay of Algeciras and the ports of Málaga and Almería are located along this coastline. Consequently, trace element inputs to the local aquatic environment can be greatly increased.

Artificial neural networks (ANNs), such as the Kohonen Self-Organizing Map (SOM), are capable of discerning contamination patterns in large environmental datasets acquired from environmental monitoring programs (Kohonen, 2001; Álvarez-Guerra *et al.*, 2008; Coz *et al.*, 2008; Kalteh *et al.*, 2008). The SOM is an unsupervised learning method that can be used to analyze and cluster large datasets. High dimensional data is clustered in groups of similar input patterns into a two-dimensional lattice of neurons in an output layer. Besides, its powerful visualization tools (component planes) are very effective in classifying data according to their similar characteristics. However, the use of ANNs is not very common in sediment quality assessments in spite of being an excellent tool for the visualization of high dimensional data (Vesanto *et al.*, 2000; Álvarez-Guerra *et al.*, 2008).

In order to assess sediment quality, different sediment quality guidelines (SQGs) have been widely used by many scientists to identify contaminants of concern in aquatic ecosystems and to rank areas of concern on a regional basis (MacDonald *et al.*, 2000). The Effects Range-Low (ERL) value represents a concentration below which adverse effects on sediment-dwelling fauna would be expected infrequently. The Effects Range-Median (ERM) value sets a concentration above which, adverse biological effects on sediment-dwelling organisms

frequently occur. Concentrations equal to or greater than ERL, but less than ERM, represent a range within which biological effects occur occasionally (Long *et al.*, 1995). Therefore, comparing current concentrations with the values set by these guidelines for each element of concern can be helpful in determining the potential toxicity of the sediment sample for benthic fauna inhabiting the sediment. McCready *et al.* (2006) and Wade *et al.* (2008) have evaluated the quality of estuarine and marine sediments according to these guidelines in Sydney Harbour, Australia and in Casco Bay, Maine, U.S.A., respectively. Moreover, the mean ERM quotients (m-ERMQ) provide reasonable estimates of the likelihood of toxicity if mixtures of chemicals are present in different concentrations that may have additive toxicity effects. It should be noted that the higher the values of the quotient, the higher the probabilities of toxicity (Long & MacDonald, 1998; Long *et al.*, 2002; Roach, 2005; Gao & Chen, 2012).

Although the Tinto-Odiel estuarine and areas such as the Bay of Cadiz or the Bay of Algeciras have been studied thoroughly over the last two decades (Ruiz, 2001; Carrasco *et al.*, 2003; Díaz-de Alba *et al.*, 2011), this study was carried out in order to improve comprehension of pollution patterns and sources of risk related to trace and major elements in all sediment samples currently being monitored by the AWA. Consequently, the purposes of this study are: (a) to classify sites according to similar sediment characteristics by means of ANNs such as SOM, a relatively new tool allowing to extract valuable information from all data including 16 physical and chemical variables from 112 sampling points (sediment samples collected in 2009), (b) to assess sediment quality in these marine and estuarine sediments of the southern Spanish coastline by means of SQGs, and (c) to evaluate the effectiveness of the SOM analysis in exploring and clustering large geochemical data sets.

Materials and Methods

Study area

The southern Spanish coastline comprises several estuarine systems in both the Atlantic Ocean and the Alboran and Mediterranean Seas (Fig. 1). The Atlantic coast extends from the vicinity of the Guadiana estuarine down to the Strait of Gibraltar, including areas such as the Tinto-Odiel estuary or the Bay of Cadiz, among others. Guadiana River drains the Iberian Pyrite Belt (Huelva province, southwest Spain), one of the largest metal sulphide mining areas of the world. It is an important river of the Iberian Peninsula with intense mining activities carried out in the past near its mouth. Thus, Guadiana estuary was exposed to significant heavy metal pollution from the São Domingos Mine (1857 to 1966). Nowadays, mining activities are less intense but metal leaching from mine residues is still important (Delga-

do *et al.*, 2010). Both Odiel and Tinto Rivers also flow across the Iberian Pyrite Belt. The mouth of these rivers forms the so-called Tinto-Odiel estuary. These two rivers cross an area with intense mining activity in the past but fewer important exploitations remain currently (Santos Bermejo *et al.*, 2003). Other significant sources of pollution of this estuary include Huelva harbour, a large paper mill, fertilizer production, chlorine and TiO₂ manufacturing, petroleum refinery and municipal wastewater inputs, among others (Santos Bermejo *et al.*, 2003; Pérez-López *et al.*, 2011).

Guadalquivir River is Spain's second longest river with a drainage area of 57,527 km². The main activity carried out between Seville and the Guadalquivir estuary is agriculture. However, navigation up to the inland port of Seville also causes a serious environmental problem due to erosion and pollution (Mendiguchía *et al.*, 2007). The estuary has an enormous ecological value due to the presence of the Doñana National Park, a major protected marsh area in Europe. In 1998, the National Park of Doñana and the Guadalquivir estuary were impacted by an accidental mine spill (Aznalcóllar accident) that produced the release of 6 million cubic meters of acid waste containing heavy metals, causing a significant negative impact in the estuarine ecosystem (Riba *et al.*, 2002). The Bay of Cadiz is an urban area hosting a number of industrial hubs. The main industries located in the Bay of Cadiz include ship, car and aerospace manufacturing. The area also receives urban wastewater discharges from the cities of Cadiz and Jerez de la Frontera (Ligero *et al.*, 2002; Carrasco *et al.*, 2003).

The Alboran coastline extends from the Strait of Gibraltar to Cabo de Gata, including sites located next to the estuaries of Guadalmedina, Chico or Andarax Rivers, among others. This coastline receives wastewater inputs from urban areas such as Marbella, Málaga, Fuengirola and Almería. Although agriculture is important, significant industrial activities are also carried out in some areas. The main industrial activities are located in the Bay of Algeciras, an urban and industrial area with a high population density. The Bay of Algeciras receives great amounts of urban sewage from the cities surrounding the bay. Besides, Algeciras harbour, one of the largest Spanish ports, is another source of pollution. In addition to this, several industries including stainless steel manufacturing, petrochemical and petroleum refineries, paper mills, thermal power plants, ironworks, and shipyards operate in the area. The bay also receives the water discharge of Guadarranque and Palmones Rivers (Díaz-de Alba *et al.*, 2011). The Mediterranean coastline extends from Cabo de Gata to San Juan de los Terreros. The presence of past mining activities located in the proximity of San José, a coal-burning plant near Carboneras and a chemical factory next to Palomares, all located in the province of Almería, should be noted.

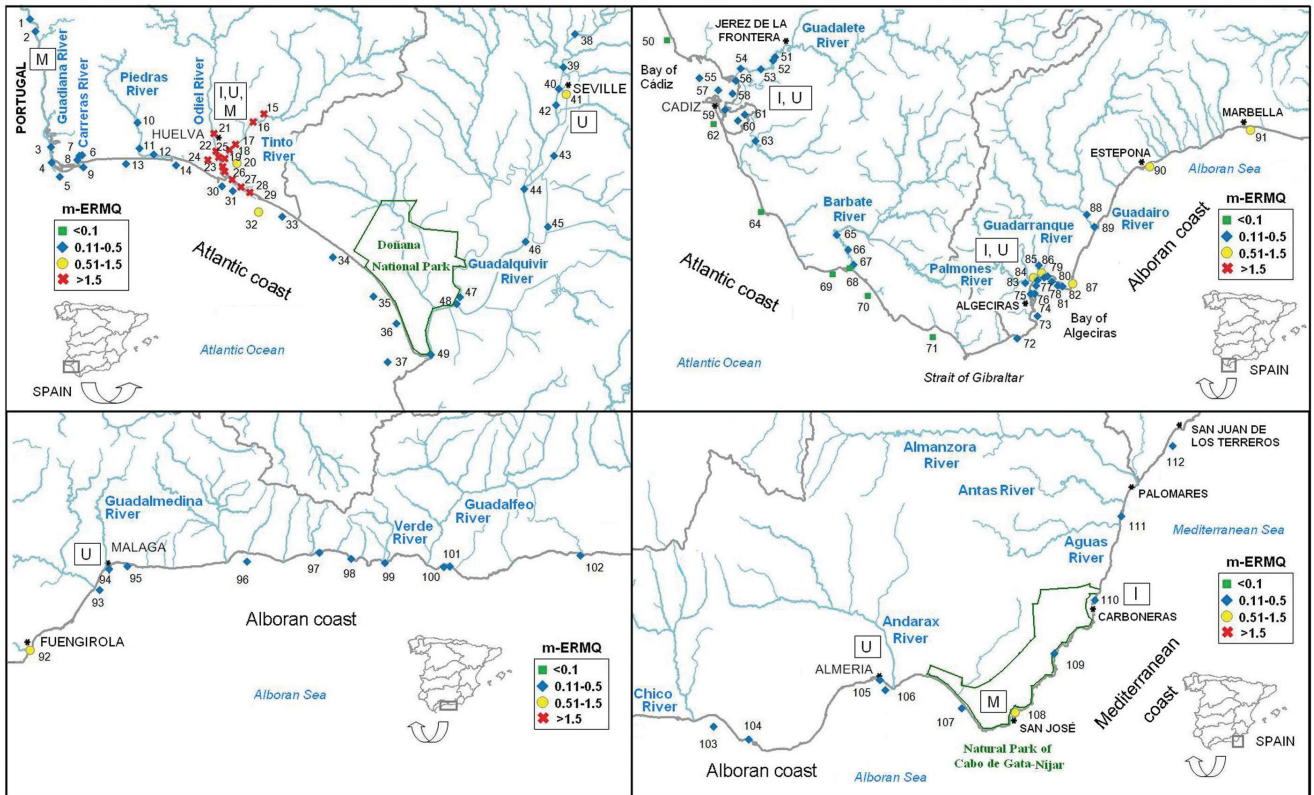


Fig. 1: Sediment quality assessment of the 112 estuarine and marine sites located in the Spanish southern coastline. I, U and M indicate industrial, urban and mining activities, respectively. For a much detailed explanation of potential sources of pollution, the reader is referred to the text.

Data acquisition

All data necessary for this study were obtained from the Consejería de Medioambiente, Andalucía region, and are accessible through their webpage (<http://www.juntadeandalucia.es/medioambiente/site/web/>). These data included total Cd, Cu, Ni, Pb, Zn, Hg, As, Cr, Li, Al, Mn, Fe, N and P concentrations and organic carbon content, all determined in the $63 \mu\text{m}$ grain-size fraction of the sediment. Data also included sediment granulometry and sampling point coordinates. Samples were acid-digested prior to trace and major element analysis. All measurements were carried out following standard procedures, including Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES), in order to determine major and trace element concentrations except Hg, which was determined by Cold Vapour Atomic Absorption (CVAA) spectrometry. Organic carbon content was determined by loss on ignition (LOI). Further details can be checked on the above-mentioned website. All sediment samples were collected in 2009. Concentration ranges of these variables in the study areas as well as the numerical value of the ERL and ERM guidelines are included in Table 1. Additional information including all data used in this study can be found in the Appendix (Table A.1), available in the online edition.

Creation of SOM

The free downloadable version of Matlab SOM Toolbox version 2.0 (Helsinki University of Technology, Finland) was used to create the SOM: <http://www.cis.hut.fi/projects/somtoolbox/>. The SOM algorithm was created to visualize non-linear relations of multidimensional data. The SOM consists of neurons organized on a 2-dimensional hexagonal grid. The neighbourhood relation (typically Gaussian) that connects the neurons dictates the topology or structure of the map. Each neuron (represented by a weight vector) has as many components as the dimension of the input variables. In order to train the SOM, batch training algorithm was selected (further details can be found in Kohonen, 2001). The SOM is trained iteratively to obtain the neuron with the weight vector closest (minimum distance) to all the weight vectors of the neurons of the SOM, which is called the best-matching unit (BMU). After the BMU is found, the weight vectors of the SOM are updated and the BMU is moved closer to the input vector in the input space. Therefore, the final map will show similar data samples close to each other and non-similar data samples far from each other.

The interpretation of SOM results was carried out by the so-called component planes. Qualitative correlations between variables when all component planes are plotted together (positive correlations can be detected by parallel gradients) can be visualized because each component

plane shows the values of one variable in each map unit. As no data normality assumption is needed to create the SOM, raw data were used as input data. However, all variables were previously standardized by subtracting the mean and dividing by the standard deviation to treat all variables as equally important despite their scale of measurement. When concentration values were lower than their method detection limit, half the detection limit was used. In our study, map-size optimization was done by using the heuristic rule (also implemented in the Tool-box) suggested by Vesanto *et al.* (2000) since this rule provides a minimal topographic and quantization error.

Sediment Quality Assessment

Sediment quality assessment was carried out in terms of the m-ERMQ for trace element mixtures and both the ERL and ERM guidelines for individual trace elements. Following Long & MacDonald (1998), the m-ERMQ was calculated by Eq. (1).

$$m - ERMQ = \left(\sum_i [tr.elem_i] / ERM_i \right) / i \quad \text{Eq. (1)}$$

where i is the number of trace elements considered (8) and $[tr.elem_i]$ and ERM_i represent the individual concentration of each trace element considered and its corresponding ERM concentration. Trace element concentrations include cadmium, copper, nickel, lead, zinc, mercury, arsenic and chromium. For calculation purposes, half the detection limit was used for concentrations below their method detection limit. In order to classify sites, four levels of the m-ERMQ were used as suggested by Long & MacDonald (1998): Low priority sites (m-ERMQ<0.1); Medium-low priority sites (m-ERMQ=0.11–0.5); High-medium priority sites (m-ERMQ=0.51–1.5); High priority sites (m-ERMQ>1.5). These levels relate to the likelihood that 12%, 30%, 46% and 74% of sediments with these ERMQ values, respectively, were toxic in amphipod survival bioassays (Roach, 2005).

Results and Discussion

Overview of geochemical parameters

There is a great variation between the study areas with regard to sediment granulometry. While some areas are sandy, others contain a great proportion of fine grain sizes. The fine fraction (silt and clay, <0.63 μm) ranged from <0.1% to 96.9%. Organic carbon content did not show such variability with values ranging from 0.1% to 3.6%.

It should be pointed out that concentrations of elements associated with pyrite (Cu, Pb, Zn and As) are much higher at sites located in the Tinto-Odiel estuary compared to the rest of the sites (Table 1). With respect to Cd, most of the samples showed concentrations below the corresponding method detection limit. Cu concentrations

were relatively low except in samples from the western coastline. Regarding Ni, the highest concentrations were observed in samples located in Palmones River, Guadarranque River and the coastline between Algeciras and Málaga with values of up to 472 mg/kg dw. Pb concentrations were found to be low except for some high concentrations observed in the Tinto-Odiel estuary and Guadalquivir River near Seville. Samples located along the western coastline (sites 1 to 55) showed the highest Zn concentrations. Hg concentrations were generally low along the eastern coastline but relatively high in riverine samples of the western coastline as well as in the Bay of Cadiz and the Bay of Algeciras. Moreover, high concentrations of this element (up to 8.1 mg/kg dw) were observed in some samples from the Tinto-Odiel estuary. Several samples from the western (sites 1 to 37) and the eastern coastline (sites 90-112) presented As concentrations greater or equal to 8 mg/kg dw. Cr concentrations were low in most samples with punctual higher concentrations in some samples of the Tinto-Odiel estuary and the Bay of Algeciras and its surrounding area.

The percentage of iron ranged from 0.6 wt% to 13.0 wt%. It is noteworthy that samples with the highest trace element concentrations (Tinto-Odiel estuary) showed the highest Fe percentages as well. Significant Fe content was also detected in samples of the eastern Mediterranean coast. The Al content was found to be within the range 0.9-8.3 wt%. Some samples from the Guadiana River and the Tinto-Odiel estuary showed the highest content of this element. With respect to Li, a great variability between samples was found; it is noteworthy that, in general, lower concentrations were measured in marine samples both in the Atlantic Ocean and the Alboran Sea. On the contrary, Mn seemed to be more equally distributed among samples. Total N and P content ranges were as follows: <0.05-0.360 wt% and <0.01-1.40 wt%, respectively. The highest values of these elements were found in samples from the Tinto-Odiel estuary.

Site classification according to SOM

Figure 2 shows the distribution of the sites according to the SOM of 11x5 units and the 6 clusters obtained after applying the k -means algorithm to the trained SOM. Component planes (Fig. 3) should be visualized in conjunction with Fig. 2 for the interpretation of the clusters obtained by the k -means algorithm.

Cluster I and II group all sites of the Tinto-Odiel estuary. From all sites studied, the highest Fe, Li and Al concentrations were measured in some of the sites of this estuary. The high major and trace element concentrations can be attributed mainly to past mining activities as suggested by Pérez-López *et al.* (2011). Besides, highly intensive industrial activities carried out in the area including chemical, petrochemical or paper industry, among others, contribute to the pollution of this estuary.

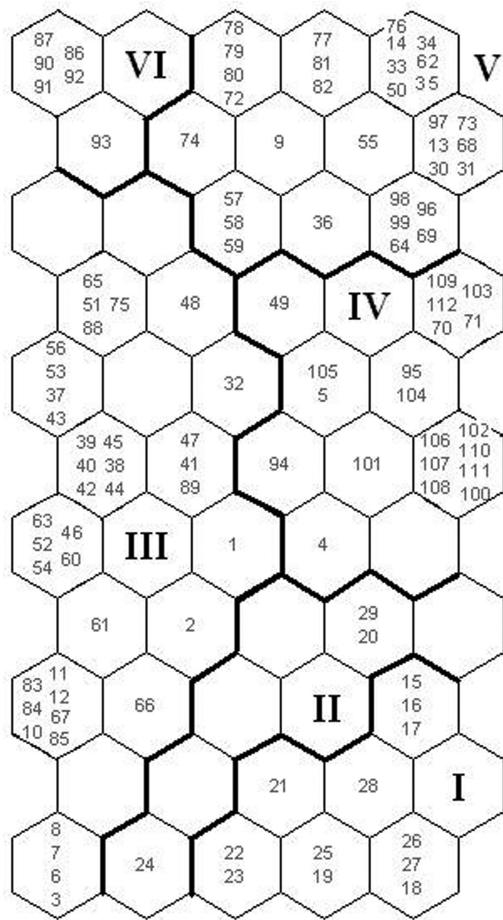


Fig. 2: Distribution of sites on the Self-Organizing Map (SOM). After the SOM was trained, the application of the *k*-means algorithm produced 6 clusters.

ary. This fact has also been suggested and reported by other authors (Ruiz, 2001; Santos Bermejo *et al.*, 2003; Sainz & Ruiz, 2006). The high values of Fe may be due to the presence of pyrite and weathering products (Fe-oxo-hydroxides). The relative similarity between N and P component planes (Fig. 3) suggests a positive correlation. Historical fertilizer production and the accumulation of phosphogypsum wastes stored in a stack over salt marshes of the Tinto-Odiel estuary might explain both the P and N enrichment measured and also contribute to the contaminant load of the estuary. Cluster II is formed by the 3 sites of the estuary with lowest pollution level, but still classified as medium-high or high priority sites.

Cluster III includes sites mainly presenting a great proportion of fine grain sizes and organic carbon content. It is noticeable that most of these sites belong to the lower parts of the rivers studied. As fine particles are likely to be accumulated in areas of relatively low turbulence (lower parts of rivers), river samples present a greater proportion of fine particles than marine samples, which are exposed to tidal action. Inputs of organic wastes from the surrounding urban areas might explain part of the organic carbon content observed at these sites. Most of these samples also presented medium Cu and Zn concentrations as well as significant Mn concentrations. It must also be noted that the Al gradient suggests that sites of this cluster (especially those located in the left bottom of the SOM) are rich in aluminosilicates (Fig. 2, Fig. 3).

Clusters IV, V and VI are mainly constituted by marine sites. Cluster IV and cluster V group sites with both medium-to-low major and trace element concentrations,

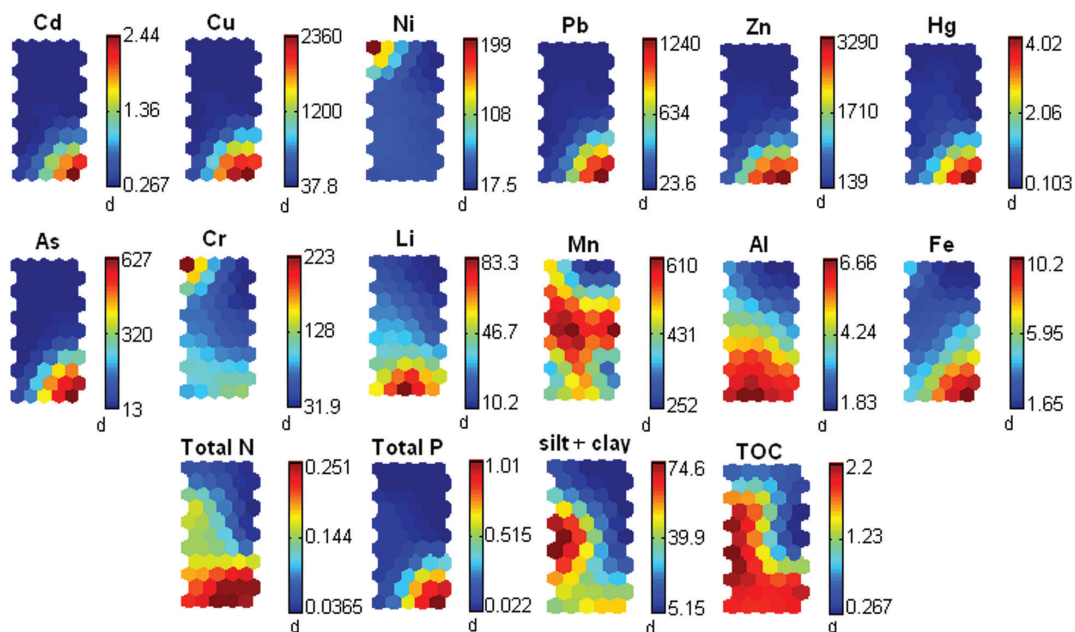


Fig. 3: Component planes of the SOM for the chemical variables (input variables or components): trace and major elements, TOC% and fine grain fraction (<0.63 μm). Hexagons in a certain position in each plane correspond to the same map unit in Figure 2. The value of the component in the weight vector (distance) of each unit of the map is represented by the colours in the scale bar (right side of each component plane).

suggesting relatively low pollution. Cluster IV is formed by sites showing significant major element concentrations (mainly Mn and to a lesser extent Fe). It is noticeable that all sites (100-112) of the eastern coastline are included in this cluster. This suggests that sediment samples from this coastline present similar chemical composition. This area is characterized by the presence of volcanic rocks and mining activities including Zn and Pb extraction (mainly in the 19th century and the beginning of the 20th century). The difference between cluster IV and cluster V consists in the different concentrations of Mn and Fe leading to different mineral compositions. Besides, higher As concentrations were measured in samples belonging to cluster IV. One possible source of these enrichments in the samples of cluster IV may originate from long-term inputs from mining activities carried out in this area but may also be due to a natural origin. It must be pointed out that most of the sites of the Bay of Cadiz and the Bay of Algeciras showed similar sediment characteristics and were grouped in this cluster V.

Finally, cluster VI groups 6 sites sharing the same feature, i.e. parallel gradients for the component planes of Ni and Cr (Fig. 3). This might suggest possible relationships between the sources of pollution of Cr and Ni. The metal industry (steel manufacturing) located near Guadarranque River (sites 85 and 86) could explain both the high Ni and Cr concentrations observed and the shape of their component planes. Furthermore, this fact is in concordance with Díaz-de Alba *et al.* (2011) whose results showed associations between the sources of pollution for Cr and Ni in sediment samples collected at sites of the same area. The rest of the samples of this cluster (91, 92, and 93) are located along the coastline, from the Bay of Algeciras to close to the city of Málaga. As there are no human inputs associated with either Cr or Ni along this coastline, Usero *et al.* (2004) suggested a geogenic origin of these high concentrations in a previous study. In fact, the presence of ultrafamic rocks such as Peridotite in the area (López-Casado *et al.*, 2001) could explain these high Ni and Cr concentrations observed.

Site classification based on the m-ERMQ

In order to quantify the relationships encountered in SOM analysis, site classification according to the m-ERMQ value was calculated and is shown in Fig. 1. About 82% of all sites were classified as low or medium-low priority sites. However, 22 sites were classified as high-medium or high priority sites.

Clusters I and II from the SOM output grouped sites located in the Tinto-Odiel estuary and its adjacent littoral area. Most of the sites (14 out of 15) of the Tinto-Odiel estuary presented high m-ERMQ values (greater than 2) and were classified as high priority sites. All sites presented extremely high trace element concentrations (especially Cu, Pb, Zn, Hg, As but Ni and Cr to a much

lesser extent). Moreover, Cu, Pb, Zn, Hg and As concentrations exceeded their ERM values by up to 11-, 12-, 10-, 11- and 13-fold respectively, clearly representing a significant risk to the benthic fauna. Most sites (3 out of 4) of the adjacent littoral area of the Tinto-Odiel estuary were classified as medium-low priority sites. However, 1 site in this area was classified as a high-medium priority site (sites 30-33, Fig. 1). This implies a significant decrease of the toxicity in samples from this area probably due to the dilution of the contaminant load coming from the estuary when it reaches the sea.

Cluster III included sites belonging mainly to the lower parts of all the rivers studied. Moreover, all sites of this cluster presented an m-ERMQ lower than 0.5 and were classified as medium-low priority sites. The 4 sites belonging to Guadiana River showed m-ERMQ values of less than 0.5 suggesting relatively low potential risk. However, Zn and As concentration values were found to be greater than their ERL value. This possible enrichment of Zn and As in these sediments could be related to the past mining activities carried out in this area.

Sites located in Carreras and Piedras Rivers presented similar analytical values for all variables and showed similar sediment quality (m-ERMQ<0.5). Cu, Ni, Zn, Hg and As concentrations exceeded their ERL in all samples. As there is no potential source of pollution for these elements in these areas, the explanation of these slightly high concentrations is not an easy task. The main source of pollution is located southeast, the Tinto-Odiel estuary. The influence of the North Atlantic Surface Water current might transport pollutants from this estuary in a south-easterly direction but a north-westerly direction is unlikely. However, the existence of a littoral countercurrent in shallow waters of the coastline (small but not negligible) has been reported previously (Moreira & Ojeda, 1992). Therefore, this littoral countercurrent could be a source of pollution at sites situated in the Carreras and Piedras Rivers.

In general, sites located in Guadalquivir River were classified as medium-low priority sites. However, site 41 located near Seville showed an m-ERMQ> 0.5 and was classified as a medium-high priority site. High Pb and Zn concentrations explain this relatively high m-ERMQ. Intense agricultural activities (mainly rice, cotton and beet) constitute the main pollution source of the basin. This results in relatively high total N and P values along its basin. Besides, this river also receives urban effluents from the city of Seville and other settlements. It must be pointed out that sites located in the neighbourhood of Doñana (47-49, Guadalquivir River) showed m-ERMQ values of less than 0.5 suggesting low potential risk. A previous study carried out by Gómez-Parra *et al.* (2000), showed high Zn concentrations of up to 744 mg/kg at the confluence of Guadiamar and Guadalquivir Rivers, which were related to the Aznalcóllar accident. Sites 47 and 48, located in the same area, showed Zn concentrations of 319 and 224 mg/kg respectively, indicating a

clear downward trend for this metal in those sediments. However, Cu and Zn concentrations were found to be greater than the ERL value at those sites, suggesting that adverse effects on the benthic fauna should be verified by conducting toxicological tests.

All sites of the Guadalete River were classified as medium-low priority sites ($m\text{-ERMQ} < 0.5$). Cu and Zn concentrations exceeded their ERL value at all sites and Ni concentrations exceeded its ERM value at two sites (51 and 53). Moreover, relatively high total P and N concentrations were observed at all sites. This river receives inputs from urban (Jerez de la Frontera) and agricultural activities mainly, as well as industries such as distilleries, wineries and sugar manufacturing that could explain the origin of the high P and N content observed.

Sites located in the estuary of the Barbate River showed $m\text{-ERMQ}$ values of less than 0.5 and were classified as low-medium priority sites. However, Ni, Zn, Cr or total N levels could be a cause of concern. Agricultural runoff is the main source of pollution of this estuary and thus, fertilizer usage might explain part of this pollution. Moreover, another source of pollution could be marine currents since the Barbate estuary is directly influenced by the "metal plume" carried from the Tinto-Odiel estuary to the Strait of Gibraltar. Palmones, Guadarranque and Guadairo Rivers presented $m\text{-ERMQ}$ values of less than 0.5. However, site 84, located in Palmones River, presented high Cr, Ni and Zn concentrations exceeding or nearly exceeding their ERM and was classified as a medium-high priority site.

Cluster IV grouped all sites (100-112) of the eastern coastline. All these samples were ranked as low or medium-low priority sites except site 108, located in San José (Natural Park of Cabo de Gata-Níjar), which was ranked as a medium-high priority site. Both high Pb (>250 mg/kg) and Zn ($>1,200$ mg/kg) concentrations were measured at this site, representing a potential risk to benthic fauna. Although part of this high Pb and Zn concentrations might be attributed to a natural origin, past mining activities could provide a reasonable explanation for these high Pb and Zn concentrations. Although the $m\text{-ERMQ}$ value at sites 110, 111 and 112 was found to be less than 0.5, Ni, Pb and As concentrations exceeded their ERL value. Although these concentrations could be explained by a natural origin, the presence of a coal-burning plant near Carboneras (site 110) and a chemical factory in the proximity of Palomares (sites 111 and 112) might account for part of this potential pollution.

Cluster V included most of the sites of the Bay of Cadiz and the Bay of Algeciras, both showing similar sediment quality ($m\text{-ERMQ} < 0.5$). These sites were classified as medium-low priority sites. However, Hg concentrations exceeded its ERL at all sites located in the Bay of Cadiz area. Moreover, ERM for Ni was exceeded at site 57 and Cu, Ni, Zn or As values were found to be above their ERL at some sites of this bay. This suggests that

the industrial activities (metal processing sector) carried out in the area might contribute to the relatively moderate pollution recorded at some sites of the bay. Cluster VI grouped 6 sites located along the coastline from the Bay of Algeciras to close to the city of Málaga. Site 90, located in the Alboran Sea (Estepona) showed an $m\text{-ERMQ}$ value greater than 1.5 suggesting potential toxicity issues mainly due to the high concentration of Cr and Ni measured and previously suggested by the shape of their component planes. Site 86 located in Guadarranque River presented high Cr, Ni and Zn concentrations exceeding or nearly exceeding their ERM and was classified as a medium-high priority site. Sites 87, 91 and 92 situated in the surrounding area of the Bay of Algeciras, Marbella and Fuengirola presented an $m\text{-ERMQ} > 0.5$, all showing high concentrations of these two elements as well.

Conclusion

Incorporating tools such as SOM in sediment quality assessments was found to be very useful due to its powerful visual characteristics (component planes), allowing to extract valuable information from the dataset such as visual correlations between all geochemical parameters. Moreover, the SOM correctly classified the study areas according to their similar chemical characteristics, identifying potential pollution issues in a visual and user-friendly way, thus revealing that ANNs are an excellent tool to be incorporated in sediment quality assessments.

The use of a pollution index such as the $m\text{-ERMQ}$ allowed for the creation of a site ranking in terms of potential toxicity of the samples to benthic fauna. Although a large number of sites were ranked as low or medium-low priority sites, some sites of the southern and eastern coastline and, especially, the Tinto-Odiel estuary, were found to be medium to highly polluted and ranked as medium-high to high priority sites requiring future remedial action. Moreover, trace element pollution was related to the human activities carried out near the sampling points. Site ranking according to this index provided a quantification of the potential toxicity of the samples. This index revealed that areas most likely to have potential toxicity issues, such as those previously identified by the SOM, were, in fact, classified as high priority sites. However, further research including toxicological tests or use of empirical models such as the Equilibrium partitioning Approach (EpA) is encouraged, especially for the most polluted samples.

Acknowledgements

This research was supported by MICINN-FEDER funding through CTM2008-01876/TECNO project and DGA-FSE. We wish to thank the University of Zaragoza as well as the Consejería de Medioambiente from the region of Andalucía for additional support in collecting all data.

References

- Álvarez-Guerra, M., González-Piñuela, C., Andrés, A., Galán, B., Viguri, J.R., 2008. Assessment of Self-Organizing Map artificial neural networks for the classification of sediment quality. *Environment International*, 34 (6), 782-790.
- Carrasco, M., López-Ramírez, J.A., Benavente, J., López-Aguayo, F., Sales, D., 2003. Assessment of urban and industrial contamination levels in the bay of Cádiz, SW Spain. *Marine Pollution Bulletin*, 46 (3), 335-345.
- Coz, A., Rodríguez-Obeso, O., Alonso-Santurde, R., Álvarez-Guerra, M., Andrés, A., et al., 2008. Toxicity bioassays in core sediments from the Bay of Santander, northern Spain. *Environmental Research*, 106 (3), 304-312.
- Delgado, J., Nieto, J.M., Boski, T., 2010. Analysis of the spatial variation of heavy metals in the Guadiana Estuary sediments (SW Iberian Peninsula) based on GIS-mapping techniques. *Estuarine, Coastal and Shelf Science*, 88 (1), 71-83.
- Díaz-de Alba, M., Galindo-Riaño, M.D., Casanueva-Marengo, M.J., García-Vargas, M., Kosore, C.M., 2011. Assessment of the metal pollution, potential toxicity and speciation of sediment from Algeciras Bay (South of Spain) using chemometric tools. *Journal of Hazardous Materials*, 190 (1-3), 177-187.
- Gao, X., Chen, C-T.A., 2012. Heavy metal pollution status in surface sediments of the coastal Bohai Bay. *Water Research*, 46 (6), 1901-1911.
- Gómez-Parra, A., Forja, J.M., DelValls, T.A., Sáenz, I., Riba, I., 2000. Early contamination by heavy metals of the Guadalquivir Estuary after the Aznalcóllar mining spill (SW Spain). *Marine Pollution Bulletin*, 40 (12), 1115-1123.
- Kalteh, A.M., Hjorth, P., Berndtsson, R., 2008. Review of the self-organizing map (SOM) approach in water resources: Analysis, modelling and application. *Environmental Modelling & Software*, 23 (7), 835-845.
- Kohonen, T., 2001. *Self-Organizing Maps*. Springer-Verlag, Berlin, 501 pp.
- Ligero, R.A., Barrera, M., Casas-Ruiz, M., Sales, D., López-Aguayo, F., 2002. Dating of marine sediments and time evolution of heavy metal concentrations in the Bay of Cádiz, Spain. *Environmental Pollution*, 118 (1), 97-108.
- Long, E.R., MacDonald, D.D., 1998. Recommended uses of empirically derived, sediment quality guidelines for marine and estuarine ecosystems. *Human and Ecological Risk Assessment*, 4 (5), 1019-1039.
- Long, E.R., Hameedi, M.J., Sloane, G.M., Read, L.B., 2002. Chemical contamination, toxicity, and benthic community indices in sediments of the lower Miami River and adjoining portions of Biscayne Bay, Florida. *Estuaries and Coasts*, 25 (4), 622-637.
- Long, E.R., MacDonald, D.D., Smith, S.L., Calder, F.D., 1995. Incidence of adverse biological effects within ranges of chemical concentrations in marine and estuarine sediments. *Environmental Management*, 19 (1), 81-97.
- López-Casado, C., Sanz de Galdeano, C., Molina Palacios, S., Henares Romero, J., 2001. The structure of the Alboran Sea: an interpretation from seismological and geological data. *Tectonophysics*, 338 (2), 79-95.
- MacDonald, D.D., Ingersoll, C.G., Berger, T.A., 2000. Development and evaluation of consensus-based sediment quality guidelines for freshwater ecosystems. *Archives of Environmental Contamination and Toxicology*, 39 (1), 20-31.
- McCready, S., Birch, G.F., Long, E.R., Spyrikis, G., Greely, C.R., 2006. Predictive abilities of numerical sediment quality guidelines in Sydney Harbour, Australia, and vicinity. *Environment International*, 32 (5), 638-649.
- Mendiguchía, C., Moreno, C., García-Vargas, M., 2007. Evaluation of natural and anthropogenic influences on the Guadalquivir River (Spain) by dissolved heavy metals and nutrients. *Chemosphere*, 69 (10), 1509-1517.
- Moreira, J.M., Ojeda, J., 1992. Aplicaciones temáticas de la teledetección espacial en Andalucía. p. 169-191. In: *Andalucía, una visión inédita desde el espacio*. Agencia de Medio Ambiente (Ed.), Junta de Andalucía, Sevilla. (In Spanish)
- Pérez-López, R., Nieto, J.M., López-Cascajosa, M.J., Díaz-Blanco, M.J., Sarmiento, A.M., et al., 2011. Evaluation of heavy metals and arsenic speciation discharged by the industrial activity on the Tinto-Odiel estuary, SW Spain. *Marine Pollution Bulletin*, 62 (2), 405-411.
- Riba, I., DelValls, T.A., Forja, J.M., Gómez-Parra, A., 2002. Influence of the Aznalcóllar mining spill on the vertical distribution of heavy metals in sediments from the Guadalquivir estuary (SW Spain). *Marine Pollution Bulletin*, 44 (1), 39-47.
- Roach, A.C., 2005. Assessment of metals in sediments from Lake Macquarie, New South Wales, Australia, using normalisation models and sediment quality guidelines. *Marine Environmental Research*, 59 (5), 453-472.
- Rodríguez-Barroso, M.R., Benhamou, Y., El Moumni, B., El Hatimi, Y., García-Morales, J.L., 2009. Evaluation of metal contamination in sediments from north of Morocco: geochemical and statistical approaches. *Environmental Monitoring and Assessment*, 159 (1-4), 169-181.
- Ruiz, F., 2001. Trace metals in estuarine sediments from the southwestern Spanish coast. *Marine Pollution Bulletin*, 42 (6), 481-489.
- Sainz, A., Ruiz, F., 2006. Influence of the very polluted inputs of the Tinto-Odiel system on the adjacent littoral sediments of southwestern Spain: a statistical approach. *Chemosphere*, 62 (10), 1612-1622.
- Santos Bermejo, J.C., Beltrán, R., Gómez Ariza, J.L., 2003. Spatial variations of heavy metals contamination in sediments from Odiel river (Southwest Spain). *Environment International*, 29 (1), 69-77.
- Usero, J., Morillo, J., Gracia, I., Leal, A., Ollero, C., et al., 2004. *Evaluación de la calidad de las aguas y sedimentos del litoral de Andalucía. Años 1999-2003*. Junta de Andalucía. Consejería de Medio Ambiente, Sevilla, 150 pp. (In Spanish)
- Vesanto, J., Himberg, J., Alhoniemi, E., Parhankangas, J., 2000. *SOM Toolbox for Matlab 5*. Technical Report A57. Neural Networks Research Centre, Helsinki University of Technology, Helsinki, Finland.
- Vicente-Martorell, J.J., Galindo-Riaño, M.D., García-Vargas, M., Granado-Castro, M.D., 2009. Bioavailability of heavy metals monitoring water, sediments and fish species from a polluted estuary. *Journal of Hazardous Materials*, 162 (2-3), 823-836.
- Wade, T.L., Sweet, S.T., Klein, A.G., 2008. Assessment of sediment contamination in Casco Bay, Maine, USA. *Environmental Pollution*, 152 (3), 505-521.