# Sediment Quality Assessment of two Industrialized Areas of Spain

Veses, O.\*, Mosteo, R., Ormad, M.P. and Ovelleiro, J. L.

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

Received 2 Oct. 2012;	Revised 10 June 2013;	Accepted 25 June 2013
-----------------------	-----------------------	-----------------------

**ABSTRACT:** Pollution deriving from trace elements (Cd, Cu, Ni, Pb, Zn, Hg, As and Cr) in sediment samples (collected in 2009), belonging to rivers located in Catalonia and the Basque Country (Spain), was assessed according to sediment quality guidelines. Sediment samples were ranked in terms of a pollution index that takes into account the presence of multiple pollutants such as trace elements. While only about 10% of samples located in rivers of Catalonia showed significant potential toxicity related to trace elements, about 53% of samples located in rivers of the Basque Country showed several potential toxicity issues related to these pollutants. Extremely high trace element concentrations were measured in some samples from this latter region, constituting a clear potential risk to the benthic fauna. The use of Artificial Neural Networks (ANNs) such as Self-Organizing Map (SOM) to classify sites according to their similar quality was found to be a reliable tool that can be incorporated in sediment quality assessments that include large datasets.

Key words: TEC, PEC, Quality guidelines, Sediment, SOM

#### INTRODUCTION

Since the beginning of the industrial revolution in the nineteenth century, rivers from all over the world have received significant amounts of inputs coming from industrial activities (Pekey, 2006; Ye et al., 2012). This rapid industrialization carried out over past decades has contributed to a deterioration of the aquatic environment due to the presence of trace elements such as Cd, Cu, Ni, Pb, Zn, Hg, As or Cr in those inputs. It is well known that these elements may be transfered from the water column to the bottom sediment, leading to an accumulation in this matrix which acts as a sink of these pollutants (Rodríguez-Barroso et al., 2009). Due to their persistent and bioaccumulative nature, taking into account the presence of these elements in sediments is considered of extreme importance in order to carry out sediment quality assessments. In Europe, Directive 2008/105/EC aims to control the concentration of these pollutants in water, sediments and biota. Although environmental quality standards for these pollutants are provided for surface waters, no criteria or guidelines are given for either sediments or biota. In Spain, either Hydrographical Confederations or Water Agencies keep track of these pollutants in sediments through control networks. Despite these pollutants are monitored in Catalonia and the Basque Country through Water Agencies, these organizations do not interpret the data obtained (in part due to the lack of regulation in Spain and Europe). Therefore, this is an important issue that needs to be addressed. Several researchers have proposed different sediment quality guidelines based on empirical data relating contaminant concentrations to harmful effects on sedimentdwelling microorganisms. One of the most used guidelines related to freshwater systems are those developed and provided by MacDonald et al. (2000). Two concentrations are given: one concentration below which, adverse effects are expected to occur only rarely (Threshold Effect Concentration, TEC) and a second one above which, adverse effects are expected to occur frequently (Probable Effect Concentration, PEC). Previous studies have assessed sediment quality based on these guidelines (Olivares-Rieumont et al. 2005; Chibunda et al. 2010; Marcus et al. 2010). Based on the PEC guideline, mean-Probable Effect Concentration Quotients (m-PECQs) provide an overall measure of chemical contamination and support an evaluation of the combined effects of multiple contaminants on sediments (Ingersoll et al., 2001; Long et al., 2006). Moreover, these quotients may help to classify samples as toxic or non-toxic according to reference values found by other researchers and allow for sample comparisons. Previous studies have used these quotients to predict the potential toxicity of sediment samples (Rippey et al. 2008; Ingersoll et al. 2009; MacDonald et al. 2011). On the other hand, artificial neural networks (ANNs) such as the Kohonen Self-Organizing Map (SOM) are based on

<sup>\*</sup>Corresponding author E-mail:themachineiq@hotmail.com

unsupervised training and can be used for clustering datasets (Kohonen, 2001). Groups of similar input patters from high dimensional datasets are clustered into a two-dimensional lattice of neurons in an output layer (Kalteh *et al.*, 2008). Despite the SOM has been extensively used in fields such as signal recognition or process modeling, its implementation in sediment quality assessments is scarce (Álvarez-Guerra *et al.*, 2008; Coz *et al.*, 2008; Kalteh *et al.*, 2008).

The main objective of this study is to assess trace element pollution in freshwater sediments of two of the most industrialized and populated areas of Spain providing an overall view of sediment quality in these areas. Moreover, the issue of lack of regulation is addressed by providing interpretation of the dataset collected by both Catalan Water Agency (CWA) and Basque Country Water Agency (BCWA). Finally, classification of sampling sites according to their similar sediment quality was carried out by means of ANNs such as SOM, a tool scarcely used in sediment quality assessments but proven to extract relevant information from large datasets.

## MATERIALS & METHODS

The Basque Country and Catalonia are highly industrialized and populated areas from the north of Spain. A brief description of the main river basins of these two areas is provided as follows.

Catalonia is a region situated in the northeast of Spain bordering to the north by France and to the east by the Mediterranean Sea (Fig. 1). Numerous rivers flow through this territory. Llobregat River (156 km) is situated in the middle of Catalonia and receives several urban and industrial inputs along its course. Cardener and Noya Rivers are its main tributaries. Cardener River crosses Manresa, a town hosting several electrochemical industries. Some issues related to industrial pollution (galvanic, tanning and textile) in Nova River have been previously reported (Rosas, 2001). Chemical, metallurgical and textile industries operate in the Besos River basin. This basin also receives water from Congost and Mogent Rivers. Ter River is 208 km long and receives inputs from textile, tannery, metallurgic and pulp-mill industries as well as agricultural activities and urban discharges from the cities of Vic and Girona (Carafa et al., 2011). Fluvia River is located in the northeast of Catalonia. Previous Cr and Zn issues have been reported in this river due to the presence of textile and tanning industries along its course. Tordera, Foix and Muga Rivers are small rivers. A previous study did not show any pollution problems in sediments collected from these rivers (Roig et al., 2011). Francoli River is 60 km long and flows through the petrochemical area located in Tarragona.

A previous study reported relatively high Pb and Zn concentrations in sediments from this river (Roig *et al.*, 2011). Ebro River is the largest river in Spain (930 km) and its lower course and delta are located in Catalonia. Previous studies have reported pollution issues due to mercury or pesticides such as DDT (Terrado *et al.*, 2006; Veses *et al.*, 2012). The main tributary of Ebro River is Segre River. Industry along its course is scarce, prevailing agricultural activities.

The Basque Country is located in north of Spain bordering the north by the Cantabrian Sea and France. Numerous small rivers such as Nervion or Deba Rivers flow through this territory (Fig. 2). The so-called Ria de Bilbao is a 15-km estuary part of Nervion River (72 km) that has received urban and industrial inputs since the nineteenth century (Saiz-Salinas et al., 1997). This Ria also receives waters from tributaries such as Asua and Cadagua Rivers (Fernández et al., 2008). The upper part of Oria River (74 km) is characterized by metallurgic industries, paper mills, weapon and artificial fiber manufacturing and production of machinery for the chemical industry. Deba River basin receives industrial (mainly metal processing industry and precision engineering) and domestic water inputs from the surrounding urban and industrial areas (BCWA, 2002).

Urola River basin is located between the Oria River basin and the Deba River basin. The main industrial activities include metal, wood, textile and food. Oka River is a very short river (20 km) located in an area of relative low population density. The main industrial activities are: manufacture of cutlery, kitchen utensils, electrical equipment, plastics, weapons and transformation of wood. Intensive agricultural land use is also important. Arakil River basin is located in the south part of the Basque Country. Metal, wood and chemical industries operate in the area (BCWA, 2002). Jaizubia River is a tributary of Bidasoa River located in the northeast of the Basque Country. Discharges from urban and industrial activities (mainly metal and food processing) have contributed to the deterioration of this hydrological unit (BCWA, 2002). Oiartzun River is a short river characterized by the presence of industrial activities such as paper mills, textile, metal and electrical processing and the exploitation of Arditurri mines until 1984, where silver, iron, lead and zinc, among others were extracted (BCWA, 2009). Consequently, urban and industrial inputs to the local aquatic environment under study can lead to a negative impact in the aquatic life. All data related to trace element concentrations in freshwater sediment samples were acquired by checking the websites of CWA (http://aca-web.gencat.cat/aca/ appmanager/aca/aca?profileLocale=es) and BCWA (http://www.uragentzia.euskadi.net/u81-0002/es/).



Fig. 1. Sediment quality assessment results according to the m-PECQ value of the 29 sites located in Catalonia. Numbers correspond to sampling sites. For complete analytical data and sampling site location, the reader is referred to Table 1

Trace elements are monitored once a year and their concentrations were measured by standard methods. Analytical data are showed in Table 1.

Sediment quality assessment was carried out by means of the m-PECQ and the comparison of concentrations measured with the TEC and PEC values provided by MacDonald et al. (2000). The numerical values of these guidelines are outlined in Table 1. Although TEC and PEC values set for Hg are not considered completely reliable by their authors (MacDonald *et al.*, 2000), these values can still be used as a screening value for the risk assessment of this element. The m-PECQ was calculated by equation 1 as suggested by Ingersoll et al. (2001).

$$m - PECQ = \left(\sum_{i} (tr.elem_{i} / PEC_{i})\right) / i \qquad (1)$$

where [tr.elem<sub>i</sub>] corresponds to the individual concentration of each trace element, PEC<sub>i</sub> represents the individual PEC and *i* is the number of trace elements considered. Mercury was not included in the calculation of the m-PECQ as suggested by Ingersoll et al. (2001). Half the detection limit was used for elements reported below the method detection limit. As suggested by Ingersoll et al. (2001), five ranges of the m-PECQ were used for ranking samples in terms of incidence of toxicity: <0.1; 0.1-<0.5; 0.5-<1.0; >1.0;

>5.0. These levels relate to the likelihood that 10%; 17%; 56%; 97%; 100% of sediments with these m-PECQ values, respectively, were toxic in amphipod survival bioassays (*Hyalella azteca* 28- to 42-day tests in freshwater sediments from North America).

The SOM was created with the Matlab SOM Toolbox version 2.0 (this version can be freely downloaded from the Helsinki University of Technology, Finland: http://www.cis.hut.fi/projects/ somtoolbox/). It is a type of artificial neural network, used to produce two dimensional visualizations sets of multi-dimensional data using unsupervised training with certain characteristics that help to preserve the topological properties of the original data. It consists of components called neurons arranged in a regular spacing in a hexagonal grid which are associated to a weight vector of the same dimension as the input data vectors (Kohonen, 2001).

The topology of the map is provided by the neighborhood relation (typically Gaussian) that connects the neurons. Batch training algorithm was selected to train the SOM iteratively. Each training step consists of choosing randomly a sample input data vector from the input data set and measuring the distances between it and all the weight vectors of the SOM. The neuron whose weight vector is closest to the input vector is called the best-matching unit



Fig. 2. Sediment quality assessment results according to the m-PECQ value of the 15 sites located in the Basque Country. Numbers correspond to sampling sites. For complete analytical data and sampling site location, the reader is referred to Table 1

(BMU). After finding the BMU the weight vectors of the SOM are updated moving the BMU closer to the input vector in the input space (Kalteh *et al.*, 2008). The property of topology preserving means that the mapping preserves the relative distance between the points. Data samples near each other in the input space are located in nearby units in the SOM. Therefore, non-linear relations of multidimensional data can be visualized in the SOM (Vesanto *et al.*, 2000).

Despite the SOM algorithm can deal with some missing data, as Hg concentrations were not reported in almost all samples belonging to sites managed by CWA, this element was discarded in SOM analysis. As no normal distribution on data is needed to create the SOM, raw data were used as input data. However, previous data standardization was carried out to treat all variables as equally important despite their scale of measurement. As in m-PECQ calculations, half the detection limit was used when concentration values were lower than the method detection limit.

Component planes were used to interpret the SOM results. The values of one variable in each map unit are showed in the component planes. Thus, qualitative correlations between variables when all component planes are plotted together can be visualized (positive correlations are detected by parallel gradients).

## **RESULTS & DISCUSSION**

In general, Cd concentrations were low. However, medium and high concentrations were measured in some samples belonging to rivers located in the Basque Country. Regarding Cu, About 63% of samples showed concentrations above the TEC value for this element. Two samples, located in Oria and Jaizubia Rivers, surpassed the PEC value set for this element. Ni concentration varied among samples, being noteworthy that the higher concentrations were measured in samples belonging to rivers located in the Basque Country. Medium and High concentrations of Pb were measured in samples sited in rivers managed by the BWA. Samples located in eastern rivers of Spain presented medium-to-low concentrations of this element. Zn concentrations showed a great variability among samples. While some samples presented extremely high concentrations (>18000 mg/kg dw), others presented values less than 10 mg/kg dw. With respect to Hg, medium-to-high concentrations of this element were measured in sediments of rivers belonging to the Basque Country. Almost all samples showed As concentrations above its TEC value and some of them exceeded its PEC value. The highest Cr concentrations were measured in two samples located in Noya and Congost Rivers, both managed by the CWA. Concentration values between the TEC and PEC of this element were measured in 7 samples.

Site	Location	Cd	Cu	Ni	Pb	Zn	Hg	As	Cr
1	Segre River	0.1	9.7	20.0	10.6	76.5	NDA	21.2	15.3
2	Segre River	0.2	30.5	19.0	16.5	76.9	NDA	19.8	32.4
3	Segre River	0.2	21.3	12.4	13.6	62.8	NDA	17.6	17.6
4	Ebro River	0.3	12.8	16.6	16.8	46.3	NDA	19.6	25.6
5	Ebro River	0.2	6.5	7.6	10.8	26.4	NDA	17.9	13.6
6	Francoli River	0.25	45.65	13.2	28.35	111.45	< 0.25	9.5	45.95
7	Francolí River	0.2	21.25	12.9	34.45	85.25	< 0.25	12.1	19.9
8	Foix River	< 0.5	36.5	11.3	20.5	59.9	NDA	15.0	6.8
9	Cardener River	< 0.5	31.8	16.6	24.6	109.9	NDA	14.5	22.5
10	Llobregat River	0.4	20.5	16.6	17.6	73.0	NDA	15.1	23.8
11	Llobregat River	< 0.5	30.0	20.2	21.5	89.0	NDA	19.7	25.8
12	Llobre gat River	0.2	<i>33</i> .8	20.0	24.0	89.4	NDA	22.3	24.7
13	Noya River	0.2	24.5	14.5	12.4	71.7	NDA	19.2	136.1
14	No ya River	< 0.5	51.1	24.3	26.4	95.9	NDA	27.0	48.9
15	Besos River	0.3	70.5	28.5	44.4	197.8	NDA	14.3	87.9
16	Besos River	0.2	45.0	19.6	28.4	145.8	NDA	11.4	50.9
17	Besos River	< 0.5	85.3	39.9	57.6	270.1	NDA	27.5	84.0
18	Besos River	0.3	39.3	38.0	33.9	185.1	NDA	11.9	33.9
19	Congost River	< 0.5	18.6	9.3	30.5	71.6	NDA	9.5	19.6
20	Congost River	< 0.5	68.9	31.5	58.2	254.3	NDA	21.7	145.4
21	Mogent River	< 0.5	32.7	15.1	35.2	132.1	NDA	10.8	24.5
22	Tordera River	< 0.5	8.5	8.0	25.7	61.5	NDA	<1.25	11.0
23	Tordera River	< 0.5	< 0.5	2.8	<1.25	9.9	NDA	<1.25	6.0
24	Ter River	<1.35	41.95	19.6	25.6	108.8	< 0.25	18.45	21.8
25	Ter River	<1.0	38.9	19.8	26.45	94.9	< 0.25	15.8	65.8
26	Ter River	< 0.5	122.7	25.9	81.8	259.6	NDA	26.0	36.8
27	Fluvia River	0.1	37.6	18.7	18.6	102.9	NDA	20.1	30.5
28	Fluvia River	0.1	7.1	9.6	8.5	29.8	NDA	16.6	16.1
29	Muga River	0.1	11.7	16.1	14.5	46.2	NDA	19.7	28.6
30	Zadorra River	0.501	14.27	13.74	20.45	123.5	0.402	4.115	8.994
31	Arakil River	0.525	59.12	20.09	54.87	260	0.492	3.72	11.82
32	Nervion River	0.215	91.21	29.21	142.3	4821	0.112	22.8	37.41
33	Nervion River	0.328	44.25	30.42	58.08	166.2	0.098	15.24	43.00
34	Cadagua River	< 0.201	81.44	21.16	1760	221.9	0.247	30.27	10.77
35	Asua River	1.029	121.9	53.76	206.3	318.2	7.043	47.77	84.40
36	Butroe River	< 0.201	23.26	19.3	55.56	94.35	0.51	17.84	15.99
37	Oka River	< 0.201	50.88	64.51	28.51	85.13	0.228	6.393	39.01
38	Lea River	< 0.201	28.47	23.19	55.02	99.17	0.76	15.61	11.84
39	Artibai River	< 0.201	62.6	33.47	68.6	213.1	0.117	22.81	15.15
40	Deb a River	0.323	100.7	61.53	88.93	400.7	0.267	18.87	35.70
41	Urola River	0.627	75.91	55.45	229	412.5	0.65	26.4	28.61
42	Oria River	0.53	153.3	30.4	221.5	434.1	0.179	41.85	59.44
43	Oiartzun River	7.42	103.3	27.57	924.6	3372	0.262	34.46	23.18
44	Jaizubia River	2.34	354.8	46.12	3013	18084	0.83	37.69	21.90
TEC	NA	0.99	31.6	22.7	35.8	121	0.18	9.79	43.4
PEC	NA	4.98	149	48.6	128	459	1.06	33.0	111

Table 1. Trace element concentrations of freshwater sediment samples used in this study (2009). All values are expressed in mg/kg dw (dry weight). Sediment quality guidelines (TEC and PEC) were extracted from MacDonald et al. (2000) and expressed in mg/kg dw

NA: Not Applicable; NDA: No Data Available

Numerical values of all variables are expressed as originally reported by each Water Agency

TEC: Threshold Effect Concentration (below which harmful effects are unlikely to be observed)

PEC: Probable Effect Concentration (above which harmful effects are likely to be observed)

Interpretation of analytical values: below TEC: regular, between TEC and PEC: italics and above PEC: bold.

Sample classification according to the m-PECQ value obtained is showed in the maps presented in Fig. 1 and Fig. 2. These maps were created by using the MapWindow 4.8.6 software in order to provide an overall view of the sediment quality in terms of the m-PECQ in the study areas.

There is a great variability in the results obtained. The lowest m-PECQ value was obtained in sample 23 (Tordera River) and the highest value was obtained in sample 44 (Jaizubia River). It must be noted that higher quotient values are generally obtained in samples located in rivers belonging to the Basque Country. While only about 10% of samples located in rivers of Catalonia showed m-PECQ values greater than 0.5, about 53% of samples located in rivers of the Basque Country presented m-PECQ values greater than 0.5.

In general, samples located in rivers near Barcelona and its surroundings presented concentrations of some elements above the TEC (Cu, Ni, Pb, Zn and As) or PEC (Cr) value suggesting anthropogenic influences on the sediment quality of those samples. The TEC value for Cu is surpassed in most samples, a characteristic of river systems hosting densely populated and industrialized centers. Samples 15 (Besos River), 17 (Besos River), and 20 (Congost River) showed the worst quality probably due to the high industrialization presented along their curses. These results are in concordance with a previous study that also reported some pollution issues related to trace elements in rivers from this area (Roig *et al.*, 2011).

The upper course of Ter River appears to be less polluted (samples 24 and 25) than the lower part (sample 26) according to their m-PECQ values. Contaminant load from several industries and urban discharges might contribute to the deterioration of the quality of this river. Samples located in Ebro and Segre Rivers were found to be relatively low polluted despite the potential sources of pollution identified in these two river systems. Only As concentrations were measured above this TEC value, a fact not only observed in these two systems but in almost all samples in rivers located in Catalonia. Despite these moderately high As concentrations might suggest anthropogenic influences, part of these concentrations might be attributed to a natural origin. Samples located near the metropolitan area of Bilbao (35, 32, 34 and 33 to a much lesser extent) presented high values of the m-PECQ, probably due to the high industrial pressure of the area. The m-PECQ value obtained in sample 44 (Jaizubia River) was greater than 9, clearly indicating a significant potential risk to the benthic fauna. High trace element concentrations (especially Pb and Zn) might be explained by the presence of metal processing industries along its basin. Samples 40 (Deba River) and 41 (Urola River) presented m-PECQ values between 0.5 and 1.0 suggesting a potential risk. The presence of metal-related industries might explain the trace element content (especially Cu, Ni, Pb and Zn) in those samples. Paper and metal industries next to the location of samples 42 (Oria River) and 43 (Oiartzun River) could explain the medium-to-high m-PECQ values obtained. With respect to mercury assessment, about 57% of samples where this element was measured exceeded its TEC value, all of them belonging to rivers situated in the Basque Country. This suggests that industrial activities could be the origin (or at least part of it) of the Hg enrichment in those sediments. Besides, sample 35 (Asua River) exceeded the PEC value up to 6-fold, clearly suggesting an anthropogenic origin and a significant risk to the benthic fauna.

The rest of the samples of both regions presented m-PECQ values lower than 0.5 indicating a low potential toxicity to the benthic fauna. However, some of these samples presented one or more trace element concentration above its respective TEC (e.g. samples 8, 9, 31 and 39 among others) and toxic effects might appear. Further sediment quality assessments including toxicological tools are suggested in order to clarify this issue.Sample distribution on the SOM and component planes for each variable (trace elements) are showed in Fig. 3. The application of the *k*-means algorithm on the trained SOM produced 5 clusters, making sample classification easier to interpret.

Clusters I, II and III include samples belonging to highly industrialized areas. All these samples share the same feature of presenting high-to-very high m-PECQ values. Cluster I is formed by 3 samples where concentrations of Cd, Cu, Pb, Zn and As prevail, as suggested by the gradient of their component planes (Fig. 3). These samples presented the highest m-PECQ values of all samples highlighting its bad sediment quality. The presence of metal-related activities in the proximities of the sampling sites where these samples where collected explains this cluster. Due to the extremely high m-PECQ values and hence, the significant potential toxicity to the benthic fauna, these sites should be classified as high priority sites in order to take future remediation actions. Cluster II is constituted of 7 samples, all except 1 situated in rivers of the Basque Country. These samples are characterized by medium-to-high values of the m-PECQ. Medium and high Ni concentrations as well as significant Cu, Zn and Cr content were measured in samples of this cluster, a fact suggested by the shape of their component planes (Fig. 3). Metal industries, especially those associated with Ni and Cr to a lesser extent, are located in sites near the sampling point locations. Cluster III groups 5 samples, all belonging to rivers located in Catalonia. They have in common the medium-to-high Cr concentrations measured. These



Fig. 3. (a) Sample distribution on the SOM. After training the SOM, 5 clusters were obtained by the application of the *k*-means algorithm on the trained SOM. (b) Component planes of the SOM for trace elements (input variables or components). Each hexagon located in the same position in each plane represents the same map unit. The scale bar located in the right side of each component plane represents the value of the component in the weight vector (distance) of each unit of the map

samples also presented medium Ni concentrations, a fact suggested by the component plane of this element (Fig. 3). These samples are located in rivers such as Besos, Congost, Ter and Noya Rivers, all hosting activities related to Cr and Ni. Clusters IV and V are constituted of samples where anthropogenic influences are much more attenuated. Cluster IV groups samples mainly characterized by medium As concentrations, as suggested by the gradient of the component plane for this element (Fig. 3). Besides, some samples located in the upper right corner of this cluster presented medium Cr or Ni concentrations. As the concentrations of these 3 elements are between the TEC and PEC values in most of the samples, this might indicate some anthropogenic influences. Despite the m-PECQ value of 0.5 is never exceeded for these samples and it does not represent a clear risk to the benthic fauna, further monitoring of these elements (especially As) is encouraged. Cluster V is formed by samples with the lowest pollution. Most of the trace element concentrations are below its respective TEC clearly indicating none or very low anthropogenic influences. However, some trace element concentrations between TEC and PEC were found in samples 6 (Zn) 30 (Zn) and 31 (Cu, Pb and Zn). Despite that, the m-PECQ values were low (<0.5 in all samples), indicating a low potential risk to the benthic fauna.

#### CONCLUSION

In general, samples belonging to rivers located in Catalonia presented moderately low pollution. However, some samples collected from Besos, Congost, Ter and Noya Rivers, showed potential toxicity issues related to Cr. Moreover, most of the samples from this region showed moderately high concentrations of As. Further tracking of this element is recommended due to its potential toxicity in aquatic systems. More than half of the samples belonging to rivers located in the Basque Country presented high-to-very-high pollution. Some of these samples showed trace element concentrations extremely high, constituting a clear potential risk to the benthic fauna. The use of biological tools such as toxicological tests, the inclusion of empirical models such as the Equilibrium partitioning Approach (EpA) or the application of the Geoaccumulation Index in further quality assessments is encouraged, especially in the most polluted samples.

SOM visual properties made possible the identification of samples sharing similar chemical characteristics. Therefore, using artificial neural networks such as SOM to rank sites according to their similar quality was found to be a reliable tool that can be incorporated in sediment quality assessments, especially in those resulting from large collections of datasets.

# ACKNOWLEDGEMENTS

This research was supported by MICINN-FEDER funding through CTM2008-01876/TECNO project. We wish to thank the University of Zaragoza as well as Catalan Water Agency and Basque Water Agency for the support in collecting all data.

# REFERENCES

Álvarez-Guerra, M., González-Piñuela, C., Andrés, A., Galán, B. and Viguri, J. R. (2008). Assessment of Self-Organizing Map artificial neural networks for the classification of sediment quality. Environ. Int., **34**,782-790.

BCWA, (2002). Basque Country Water Agency, Red de vigilancia de la calidad de las masas de agua superficial. Informe de resultados 2002. (In Spanish)

BCWA, (2009). Basque Country Water Agency, Red de seguimiento del estado químico de los ríos de la comunidad autónoma del país Vasco. Informe de resultados. Campaña 2009. (In Spanish)

Carafa, R., Faggiano, L., Rea, I M., Munné, A., Ginebreda, A., Guasch, H., Flo, M., Tirapu, L. and von der Ohe P. C. (2011). Water toxicity assessment and spatial pollution patterns identification in a Mediterranean River Basin District. Tools for water management and risk analysis. Sci. Total Environ., **409**, 4269-4279.

Chibunda, R. T., Pereka, A. E., Phiri, E. C. J. and Tungaraza, C. (2010). Ecotoxicity of Mercury Contaminated Sediment Collected from Mabubi River (Geita district, Tanzania) to the Early Life Stages of African Catfish (*Clarias* gariepinus). Int. J. Environ. Res., **4**, 49-56.

Coz, A., Rodríguez-Obeso, O., Alonso-Santurde, R., Álvarez-Guerra, M., Andrés, A., Viguri, J.R., Mantzavinos, D. and Kalogerakis, N. (2008). Toxicity bioassays in core sediments from the Bay of Santander, northern Spain. Environ. Res. **106**, 304-312.

Directive 2008/105/EC, (2008). of the European Parliament and of the Council of 16 December 2008 on environmental quality standards in the field of water policy, amending and subsequently repealing Council Directives 82/176/EEC, 83/ 513/EEC, 84/156/EEC, 84/491/EEC, 86/280/EEC and amending Directive 2000/60/EC of the European Parliament and of the Council.

Fernández, S., Villanueva, U., de Diego, A., Arana, G. and Madariaga J. M. (2008). Monitoring trace elements (Al, As, Cr, Cu, Fe, Mn, Ni and Zn) in deep and surface waters of the estuary of the Nerbioi-Ibaizabal River (Bay of Biscay, Basque Country). J. Marine Syst., **72**, 332-341.

Ingersoll, C. G., MacDonald, D. D., Wang, N., Crane, J. L., Field, L. J., Haverland, P. S., Kemble, N. E., Lindskoog, R. A., Severn, C. and Smorong D. E. (2001). Predictions of sediment toxicity using consensus-based freshwater sediment quality guidelines. Arch. Environ. Contam. Toxicol., **41**, 8–21.

Ingersoll, C. G., Kemble, N. E., Kunz, J. L., Brumbaugh, W. G., MacDonald, D. D. and Smorong, D. (2009). Toxicity of sediment cores collected from the Ashtabula River in Northeastern Ohio, USA, to the amphipod *Hyalella azteca*. Arch. Environ. Cont. Tox., **57**, 826–827.

Kalteh, A. M., Hjorth, P. and Berndtsson, R. (2008). Review of the self-organizing map (SOM) approach in water resources: Analysis, modelling and application Environ. Modell. Softw., **23**, 835-845.

Kohonen, T. (2001). Self-Organizing Maps. Springer-Verlag.

Long, E. R., Ingersoll, C. G. and MacDonald, D. D. (2006). Calculation and uses of mean sediment quality guideline quotient, a critical review. Environ. Sci. Technol., **40**, 1726–1736.

MacDonald, D. D., Ingersoll, C. G. and Berger, T. A. (2000). Development and evaluation of consensus-based sediment quality guidelines for freshwater ecosystems. Arch. Environ. Contam. Toxicol., **39**, 20–31. MacDonald, D. D., Ingersoll, C. G, Kemble, N. E., Smorong, D. E., Sinclair, J. A., Lindskoog, R. Gaston, G, Sanger, D., Carr, R. S., Biedenbach, J., Gouguet, R., Kern, J., Shortelle, A., Field, L. J. and Meyer, J. (2011). Baseline ecological risk assessment of the Calcasieu Estuary, Louisiana: Part 3. An evaluation of the risks to benthic invertebrates associated with exposure to contaminated sediments. Arch. Environ. Cont. Tox., **61**, 29–58.

Marcus, M. D., Covington, S., Liu, B. and Smith, N. R. (2010). Use of existing water, sediment, and tissue data to screen ecological risks to the endangered Rio Grande silvery minnow. Sci. Total Environ., **409**, 83-94.

Olivares-Rieumont, A., de la Rosa, D., Lima, L., Graham, D. W., D2 Alessandro, K., Borroto, J., Martínez, F. and Sánchez, J. (2005). Assessment of heavy metal levels in Almendares River sediments—Havana City, Cuba. Water Res., **39**, 3945-3953.

Pekey, H. (2006). The distribution and sources of heavy metals in Izmit Bay surface sediments affected by a polluted stream. Mar. Pollut. Bull., **52**, 1197-1208.

Rippey, B., Rose, N., Yang, H., Harrad, S., Robson, M. and Travers, S. (2008). An assessment of toxicity in profundal lake sediment due to deposition of heavy metals and persistent organic pollutants from the atmosphere. Environ. Int., **34**, 345-356.

Rodríguez-Barroso, M. R., Benhamou, Y., El Moumni, B., El, Hatimi Y. and García-Morales J. L. (2009). Evaluation of metal contamination in sediments from north of Morocco: geochemical and statistical approaches. Environ. Monit. Assess., **159**, 169–181.

Roig, N., Nadal, M., Sierra, J., Ginebreda, A., Schuhmacher, M. and Domingo, J. L. (2011) Novel approach for assessing heavy metal pollution and ecotoxicological status of rivers by means of passive sampling methods. Environ. Int., **37**, 671-677.

Rosas, H. (2001). Estudio de la contaminación por metales pesados en la cuenca del Llobregat. Theses, Polytechnic University of Catalonia. (In spanish)

Saiz-Salinas, J. (1997). Evaluation of adverse biological effects induced by pollution in the Bilbao Estuary (Spain). Environ. Pollut., **96**, 351-359.

Terrado, M., Barceló, D. and Tauler, R. (2006) Identification and distribution of contamination sources in the Ebro river basin by chemometrics modelling coupled to geographical information systems. Talanta 2006, **70**, 691-704.

Vesanto, J., Himberg, J., Alhoniemi, E. and Parhankangas, J. (2000). SOM Toolbox for Matlab 5. Technical Report A57. Neural Networks Research Centre, Helsinki University of Technology, Helsinki, Finland.

Veses, O., Mosteo, R., Ormad, M. P. and Ovelleiro, J. L. (2012) Potential toxicity of Polycyclic Aromatic Hydrocarbons and organochlorine pesticides in sediments from the Ebro River Basin in Spain. Bull. Environ. Contam. Toxicol. **88**, 644-650.

Ye, F., Huang, X., Zhang, D., Tian, L. and Zeng, Y. (2012). Distribution of heavy metals in sediments of the Pearl River Estuary, Southern China: Implications for sources and historical changes. J. Environ. Sci., **24**, 579-588.