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Assessing heavy metal contamination in Sado Estuary sediment: An index analysis approach

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Abstract

The Sado Estuary in Portugal is a good example of a site where human pressures and ecological values collide with each other. An overall contamination assessment has never been conducted in a way that is comprehensible to estuary managers. One of the aims of this work was to select different types of index to aggregate and assess heavy metal contamination in the Sado Estuary in an accessible manner. Another aim was to use interpolation surfaces per metal to compare and gauge the results of the indices and to assess the contamination separately per metal. Seventy-eight stations were sampled within the main bay of the estuary and a set of heavy metals and metalloids was established, Cd, Cu, Pb, Cr, Hg, Al, Zn and As. The sediment fine fraction content, organic matter and redox potential were also analysed. Various indices for contamination, background enrichment and ecological risk were used, tested, compared and performance-evaluated. All metals and metalloids were strongly correlated, and the indices appear to reflect heavy metal variability satisfactorily. Difficulties were found in some indices regarding boundary definition (minimum and maximum) and comparability with other estuaries, thus better methods of standardization should be a priority issue. According to the index that has the highest performance score within the group of ecological risk indices – the Sediment Quality Guideline Quotient – only 3% of the stations are highly contaminated and register a high potential for observing adverse biological effects, whereas 47% display moderate contamination. This index can be complemented with the contamination index, which allows more site-specific and accurate information on contaminant levels. If the aim of work on contamination evaluation is to assess the overall contamination of a study area, the indices are highly appropriate. For spatial and source evaluation per metal, interpolation surfaces should also be used.

Keywords: Indicators and indices; Heavy metal assessment; Estuarine management; Sediment; Pollution

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1. Introduction

Estuaries receive significant anthropogenic inputs from both point and non-point upstream sources and from metropolitan areas, tourism and industries located along the estuarine edges. Estuarine sediment contamination is receiving increasing attention from the scientific community, since it is recognized as a major source of ecosystem health stress (Chapman and Wang, 2001; Riba et al., 2002b). Thus, the proper assessment of sediment contamination in estuaries and its biological and ecological significance is crucial.

For better management of estuarine ecosystems their contamination assessment should be easily communicated to local managers and decision-makers. Environmental quality indicators and indices are a powerful tool for processing, analyzing and conveying raw environmental information to decision-makers, managers, technicians or the public (Ramos et al., 2002). Their spatial visualization through maps using a Geographical Information System makes their transmission even easier and more successful.

In recent decades different metal assessment indices applied to estuarine environments have been developed. Each one of them aggregates the concentration of metal contaminants and can be classified in three types—(i) *contamination indices*: which compare the contaminants with clean and/or polluted stations measured in the study area or simply aggregate the metal concentrations; (ii) *background enrichment indices*: which compare the results for the contaminants with different baseline or background levels, available in literature, that can be used for any study area; and (iii) *ecological risk indices*: which compare the results for the contaminants with Sediment Quality Guidelines or Values—SQG. They also differ in the aggregation methods used. Table A.1 (see Appendix A) presents an overview of indices to assess contaminants on the basis of their chronological evolution, their description and some comments and/or drawbacks.

When using summary indices, normalized for example to a reference value, substantial loss of information can occur during the conversion of multivariate data into single proportional indices, including spatial information. However, such indices have provided useful information in the past and continue to do so. They also provide a single and highly visual data presentation, which can be explained to and understood by non-scientists (Chapman, 1996).

SQGs are very useful to screen sediment contamination by comparing sediment contaminant concentration with the corresponding quality guideline. These guidelines evaluate the degree to which the sediment-associated chemical status might adversely affect aquatic organisms and are designed to assist sediment assessors and managers responsible for the interpretation of sediment quality (Wenning and Ingersoll, 2002). They have been largely developed for marine waters (e.g. Long et al., 1995) but a few have been specifically developed for estuarine waters (Chapman and Wang, 2001). The work by Wilson and Jeffrey (1987) is a rare example of SQGs developed specifically for estuaries. Donze et al. (1990) listed background concentration for several estuaries in Europe and the USA.

The Sado Estuary in Portugal is a good example of a site where human pressures and natural values compete with each other and where the degree of metal contamination has not been subject to overall assessment, for the outer estuary, in a way that managers can understand. The Sado Estuary is the second largest in Portugal, with an area of approximately 24,000 ha. It is located on the west coast of Portugal. Most of the estuary is classified as a natural reserve but it also plays an important role in the local and national economy. There are many industries, mainly on the northern margin of the estuary. The most polluting industries are those involving pulp and paper, pesticides, fertilizers, yeast, food and shipyards (Catarino et al., 1987). Furthermore, harbor-associated activities and the city of Setúbal, along with the copper mines on the Sado watershed, use the estuary for waste disposal purposes without suitable treatment. In other areas around the estuary intensive farming, mostly of rice, represents the main use for the land, together with traditional salt pans and increasingly intensive fish farms. The Sado Estuary is characterized by a North Channel with weaker residual currents and shear stress. This enhances the accumulation of sediment allowing locally introduced pollutants to settle rather than be transported away. The southern channel, separated from the North Channel by sand banks, is highly dynamic, with tides being the main cause of water circulation. Geomor-

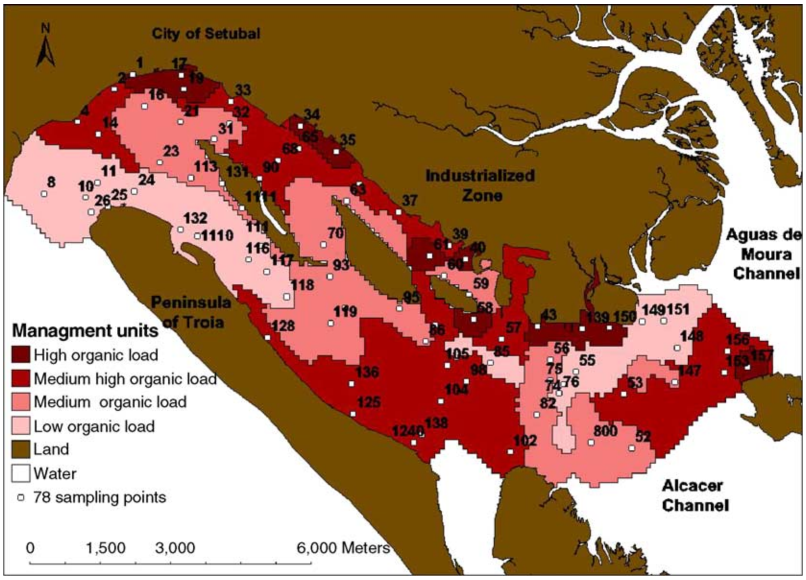

Fig. 1. Location of the sampling points in the Sado Estuary and the management units. These areas are divided into four groups according to their organic load (adapted from Caeiro et al. (2003)).

phological characteristics distinguish the outer estuary (our study area) from the inner one, which corresponds to a narrow channel (Alcacel Channel). The inner part of the outer estuary (entrances to Águas de Moura and Alcacer Channels) is quite shallow, with tidal flats (Neves, 1985).

One of the aims of this work is to select different types of indices to aggregate and assess the heavy metal contamination of the Sado Estuary sediment. The different types of indices are compared and discussed. Another aim is to evaluate the contamination per metal, also using interpolation surfaces to compare and gauge the results of the indices on the basis of a qualitative sensitivity analysis. The sediment metal assessment will be represented and evaluated in management units (spatially contiguous and homogeneous regions of sediment structure), which are to be part of a broad environmental data management framework applied to the Sado Estuary, though that is beyond the scope of this work. The support infrastructure of this framework is a set of management units delineated using multivariate geostatistical tools and sediment parameters like total organic matter (TOM), fine fraction (FF) and redox potential (Eh). These tools and this data allowed the computing of 19 management units, classified into four groups according to the increase in organic load (Fig. 1) (Caeiro et al., 2003).

2. Methods

2.1. Sampling design and analytical procedures

From November 2000 to January 2001, sediment samples were collected at 153 sites according to a systematic unaligned sampling design (500 m $\times$ 750 m), located using the Global Positioning System (Garmin GPS 12 $\times$ L). A systematic unaligned sampling design was adopted to provide pairs of close observations, required for modeling the short-scale variability, and uniform coverage of the area. This tends to reduce the average extrapolation error (Caeiro et al., 2003). For contaminant assessment, due to budget constraints, 78 locations were selected from the 153, using an optimization model to select the appropriate spatial distribution within the study area and within each type of management unit (Caeiro et al., 2004) (Fig. 1). At each location three replicates were taken with a *Petit Ponar*® grab (six in Scoopes 00890) and a composite sediment sample was formed. A set of concentrations of totally recoverable heavy metals: Cd, Cu, Pb, Cr, Hg, Al, Zn and the metalloid As was established. Accurately weighted aliquots of about 1 g of sediment were digested according to USEPA (1996) methods. The analytical technique used was inductively coupled plasma atomic emission spectroscopy (ICP–AES). In the case of mercury a CMA (concomitant metals analyser) system was used in the ICP–AES for an improvement in the detection limit. Certified reference material (like SPEX-QC-21-16-85AS-traceable to NIST) and spiked samples were used to evaluate the accuracy of the analytical methods. The maximum value for precision data ($n = 10$) was 5% and the bias data range was −20 to +6%. Total organic matter and sediment fine fraction (FF) and redox potential were also determined for each location (in the total 153-location dataset). Fine fraction was obtained by hydraulic separation (<63 μm), after organic matter destruction and disaggregation of particles. Redox potential was measured in situ using an electrode (Hanna Instruments, model H 13111). Total organic matter corresponds to the amount lost on ignition at 500 ± 25 °C for 4 h. The replicates had standard deviations lower than 20% (Caeiro et al., 2003).

2.2. Indices calculation

The indices used in this study were chosen from Table A.1 according to the following criteria: (i) input data was available (no data available for q, EQUATION, SQG-Q1 and NI_{geo}); (ii) all contaminants were integrated into a single value (p, SEF and ERF do not aggregate all metals into one value); and (iii) whenever there were two similar ones, only one was chosen (SQG-Q′ is the same as SQG-Q if the contaminants are only metals). The selected indices were then: DC (Eq. (A.2)), PLI (Eq. (A.6) and Eq. (A.7)), I (Eqs. (A.8) and (A.9)), MPI (Eq. (A.10)), NI (Eqs. (A.11) and (A.12)), SQG-Q (Eqs. (A.13) and (A.14)) and MSPI (Eq. (A.18)). A new pollution index, PIN (a background enrichment index), was adapted from PI, based on the Portuguese legislation on the classification of dredged materials (DR, 1995):

$$\mathrm{PIN} = \sum_{i=1}^{n} \frac{W_i^2 C_i}{B_{1i}} \qquad (1)$$

where W_i is the class of the contaminant i considering the degree of contamination (from 1 to $n = 5$); C_i the concentration of the contaminant i; B_{1i} the concentration of contaminant i in Class 1 (baseline value – clean sediments).

The guidelines used for the selected indices are listed in Table 1.

According to the legislation mentioned above, the sediments (and the index) can be classified into five categories, from clean to highly contaminated sediments (Table 2). PIN values were normalized in a nominal scale from 1 to 5, according to the threshold classification values. Each index threshold was calculated using the W_i and C_i values for the corresponding class—Class 1 (clean): [0–7] Class 2 (trace contaminated): [7–95.1] Class 3 (lightly contaminated): [95.1–518.1] Class 4 (contaminated): [518.1–2548.6] and Class 5 (highly contaminated): [2548.6–∞].

For the indices I and NI, stations inside the management area at the entrance to the estuary were chosen as the reference stations (8, 10, 11, 24, 25, 26, 111, 116, 117, 118, 132, 1110). This area was considered as a clean reference area since it has high hydrodynamics, has a direct connection with the clean water coming from the sea and has no direct influence from any anthropogenic point and non-point sources. The concentrations of the heavy metals found in these stations are in accordance with, or even lower than, those reported in earlier work carried out in clean areas of the Sado Estuary (e.g. Quevauviller et al., 1989; Quintino, 1993) and are also equal to or less than estuarine baseline values (Wilson and Jeffrey, 1987; see Table 1). An ANOVA test was used to test differences between reference sites and the other stations (Chapman, 1996), after normality assumptions were tested. A cluster analysis was also computed using the seven heavy metals studied, As, Eh, FF and OM, to confirm that the reference stations were grouped together. The concentration values of each metal in the reference sites were calculated using the median values of those 12 stations.

For the PLI calculation the minimum found in all stations was used as the baseline value for each contaminant, since in our sampling points some metal concentrations were lower than the baseline values proposed by Wilson and Jeffrey (1987). Otherwise, the use of baseline values would produce an error in the index calculation (Table 1).

The probable effect level (PEL) was used for the SQG-Q index calculation. Although the PEL was originally developed for coastal waters, it can be used in the Sado estuarine study area with more confidence due to the low range of salinity (from 29 to 37‰)

Table 1
Indices calculated in this study and guidelines used

Index	Classification	Guidelines (mg/kg)							
		Cd	Pb	Zn	Cu	As	Cr	Hg	TOM
New pollution index (PIN)	Clean sediments (DR, 1995)	1	50	100	35	20	50	0.5	–
Degree of contamination (DC)	Pre-industrial reference level (Hakanson, 1980)	1	70	175	50	15	90	0.25	–
Pollution load index (PLI)	Baseline (Wilson and Jeffrey, 1987)	0.5	10	20	5	5	5	0.05	1
	Minimum value in this study	0.2	2	2.1	1	1.1	0.6	0.02	0.5
	Threshold (Wilson and Jeffrey, 1987)	1.5	100	100	50	100	50	1.5	7.5
Sediment quality guideline-quotient (SQG-Q)	PEL (MacDonald et al., 1996)	4.21	112	271	108	41.6	160	0.7	–
Metal pollution index (MPI)	–	–	–	–	–	–	–	–	–
Index for ratio-to-reference (I)	Reference stations (LO1 management unit)	0.6	3.09	9.52	3.5	7.41	1.85	0.066	–
Index for new maximum RTR (NI)	Maximum RTR value	13.3	22.3	53.27	54.57	7.8	34	10.5	–
Marine sediment pollution index (MSPI)	Percentile 0–20	0.6	3.3	15.4	3.0	7.0	2.0	0.060	–
	Percentile 21–40	1.0	5.0	34.0	6.0	8.0	5.0	0.070	–
	Percentile 41–60	1.5	8.0	57.0	12.0	10.2	9.2	0.080	–
	Percentile 61–80	2.9	18.2	101.6	30.6	21.0	19.6	0.232	–
	Percentile 81–100	8.0	69.0	507.0	191.0	58.0	63.0	0.7	–

(Rodrigues and Quintino, 1993). The effects range-median (ERM) (Long et al., 1995) or other sediment quality guidelines could also be used.

For index performance evaluation the indices were scored on the basis of qualitative expert knowledge and judgment (the project research team), using the following criteria:

i. Comparability: the existence of a target level or threshold against which to compare it so that users are able to assess the significance of the values associated with it.
ii. Representativity: ability to provide a spatially representative picture of estuarine environmental states and impacts.
iii. Credibility: a good theoretical basis in technical and scientific terms; applicability to estuaries.
iv. Simplicity: ease of calculation and interpretation.
v. Sensitivity and robustness: responsiveness to change in the environment.
vi. Acceptable levels of uncertainty.

Each index was scored from 1 (lowest performance) to 3 (highest performance) for every criterion

Table 2
Classification of dredge material in coastal zones according to DR, 1995

Classes/contaminants (mg/kg)	Cd	Pb	Zn	Cu	As	Cr	Hg
Class 1: clean dredged material	<1	<50	<100	<35	<20	<50	<0.5
Class 2: trace contaminated dredged material	1–3	50–150	100–600	35–150	20–50	50–100	0.5–1.5
Class 3: lightly contaminated dredged material	3–5	150–500	600–1500	150–300	50–100	100–400	1.5–3.0
Class 4: contaminated dredged material	5–10	500–1000	1500–5000	300–500	100–500	400–1000	3.0–10
Class 5: highly contaminated dredged material	>10	>1000	>5000	>500	>500	>1000	>10

Table 3
Score of the metal assessment indices, based on several criteria

	Contamination and background enrichment indices						Ecological risk indices	
	MPI	PIN	DC	I	NI	MSPI	PLI	SQG-Q
Simplicity	3	3	3	3	3	2	3	3
Representative	1	3	3	2	2	3	3	3
Credibility	2	3	1	3	3	3	2	3
Comparability	1	3	3	1	2	2	3	3
Sensitivity and robustness	1	2	3	3	3	3	3	2
Acceptable levels of uncertainty	2	2	2	2	2	3	2	3
Total	16	10	15	14	15	16	16	17

presented above, and a total performance score was summarized for all the indexes used (see Table 3).

In each management unit the indices were calculated using the median values of chemical concentration in all the locations belonging to each management area. This mode was also used where the index was nominal. These measures of the central tendency were used instead of an arithmetic mean as the objective of the analysis is to show the main trend in the index values for each management area. Moreover, the arithmetic mean should only be used for normal distributions and should not be used in the present of outliers (Wheater and Cook, 2002).

To gauge the results of the indices per management unit and evaluate sediment contamination separately per metal, a co-kriging interpolation for each heavy metal was computed. Sediment FF, a variable strongly correlated with all the heavy metals, was used as an auxiliary variable using the complete 153-location dataset. This interpolation method estimates the contaminants at an unmonitored location using a linear combination of neighboring index and FF values. The weights are such that the variance of the estimation error is minimal, under the constraint that the estimation is unbiased (Goovaerts, 1997). Co-kriging usually improves the prediction when secondary and well-correlated information is available and it explicitly accounts for the spatial cross-correlation between primary and secondary variables.

Statistical analyses were conducted using Statistica® 6.0 software. Data transformation was only performed for interpolation surfaces and multivariate analyses like principal component analysis (PCA) and hierarchical analysis, after normality was tested. When necessary, $\log(x + c)$ (where c = the lowest non-zero value found for each metal) was then computed (Chapman, 1996). To visualize the index results within the coastal area of the Sado Estuary and in management units, ArcGIS 8.0® GIS software was used. The classification of the classes for visualizing the indices was defined on the basis of the literature, when available (in the case of DC, SQG-Q and MSPI, see Table A.1). For I and NI an equal three interval was used for values above the reference stations and a classification from clean to highly contaminated given. In the case of MPI and PLI a geometric increment was employed, divided into four classes. MPI used a classification from clean to highly contaminated (as it is only a contamination index); for PLI a classification from unimpacted to highly polluted was given, according to the index author's classification (see Table A.1). The kriging interpolations of the contaminant concentrations were computed with the Geostatistical Analyst® ArcGiS 8.0 extension. The classification of the classes for visualizing the surfaces areas of the metals and metalloids were computed according to the Portuguese legislation on the classification of dredged materials (see Table 2).

3. Results and discussion

Metal and metalloid frequency distributions were positively skewed, so log transformation was used for interpolation surfaces of the contaminants and for further multivariate statistics. For the interpolation surfaces the contaminant and FF semivariogram models were fitted visually, using a linear model of coregionalization (Goovaerts, 1997). A geometric anisotropy model allowed the longer range to be captured in the direction of azimuth 120°, which corresponds to the water flow.

A PCA was computed with the metals and metalloid, Al, TOC, FF and Eh. The first PCA component, strongly correlated with all variables (loading values greater than 0.8), explained 79.6% of the total variance in the dataset, while explaining only 5.8% of the second component. These correlations indicate that all the contaminants should be strongly correlated with each other and with the organic charge of the sediment. When only the contaminants Cd, Pb, Zn, As, Cu, Cr and Hg are included in the analysis, the first component explained 83.6% of the variance, also strongly correlated with all the variables (loading values greater than 0.85). Each of the other components only explained less than 5% of the variance. These later PCA factor loadings were used for the MSPI calculation and the PCA factor scores were used to compare the differences between the references and impact stations (for I and NI indices). The reference stations were different from the other stations (ANOVA, $F = 20.36$, $p = 0.000023$) and clustered in the same group.

3.1. Index comparison

The results of the indices per location and per area are shown in Fig. 2. Since the computed indices have different aims, their discussion will be divided into two groups: (i) contamination and background enrichment indices, which measure the contamination or enrichment levels and (ii) ecological risk indices, which evaluate the potential for observing adverse biological effects. Their performance scores (Table 3) will be compared within each group.

3.2. Contamination and background enrichment indices

Special care must be taken when comparing the different threshold and index classifications (Fig. 2). For example since MPI does not compare the contaminants with any value, the defined classes were classified according to earlier knowledge of the sampling station contaminant status and according to the other index classifications. That is why it has a low performance score according to the comparability and sensitivity criteria (Table 3). The PIN index has the advantage of being simple to compute and giving the results according to the dredged material classes of the Portuguese legislation. This allows comparison with other ecosystems. The problem is the low sensitivity to contamination of the thresholds defined in the sediment classifications of the legislation. Using the PIN index the stations analysed are only classified up to the level of ‘‘lightly contaminated’’, when in the other indices higher contamination levels are found. The DC index classifies most of the estuary management units with low impact. Although already tested successfully in coastal areas, the use of background levels defined for lakes may have induced underestimation. Also, the problem concerning natural background levels has already been well examined, with the discussion ranging from general geological reference levels to a pre-industrial or pre-civilization level for every location (Kwon and Lee, 1998). (See the low score for credibility criteria in Table 3.) However for the calculation of the DC index local reference data is not necessary, as with I and NI. Similarly to MPI, I and NI do not allow comparison of the classifications with other ecosystems and their class definition is also biased. Compared with I, NI has the advantage of normalizing the index values for the most contaminated station (maximum) and masking outlier values (DelValls et al., 1998b). Even so, its map visualization is equivalent in terms of area classification (Fig. 2).

MSPI has the advantage over the earlier indices that it gives different weights to each contaminant. The application of a PCA to identify important variables from a monitoring program can reduce sampling resources. Parameters that do not show significant spatial variations can be analysed with lesser frequency than those that have been identified as more important from the results of the PCA (Shin and Lam, 2001). Also the use of the PCA allows successful assessment of the source of the contamination, since this multivariate analysis tool does not need any linear assumption and establishes and quantifies the correlations among the original variables in the dataset when the goal is to reduce the number of variables (DelValls et al., 1998a). Given that our stations vary from unpolluted to highly polluted and can be rated from best to worst quality on the basis of dataset percentiles, it allows a more accurate index classification. The problem arises when comparing the results with other ecosystems with different contamination-range datasets. For example, if in a study area dataset there are

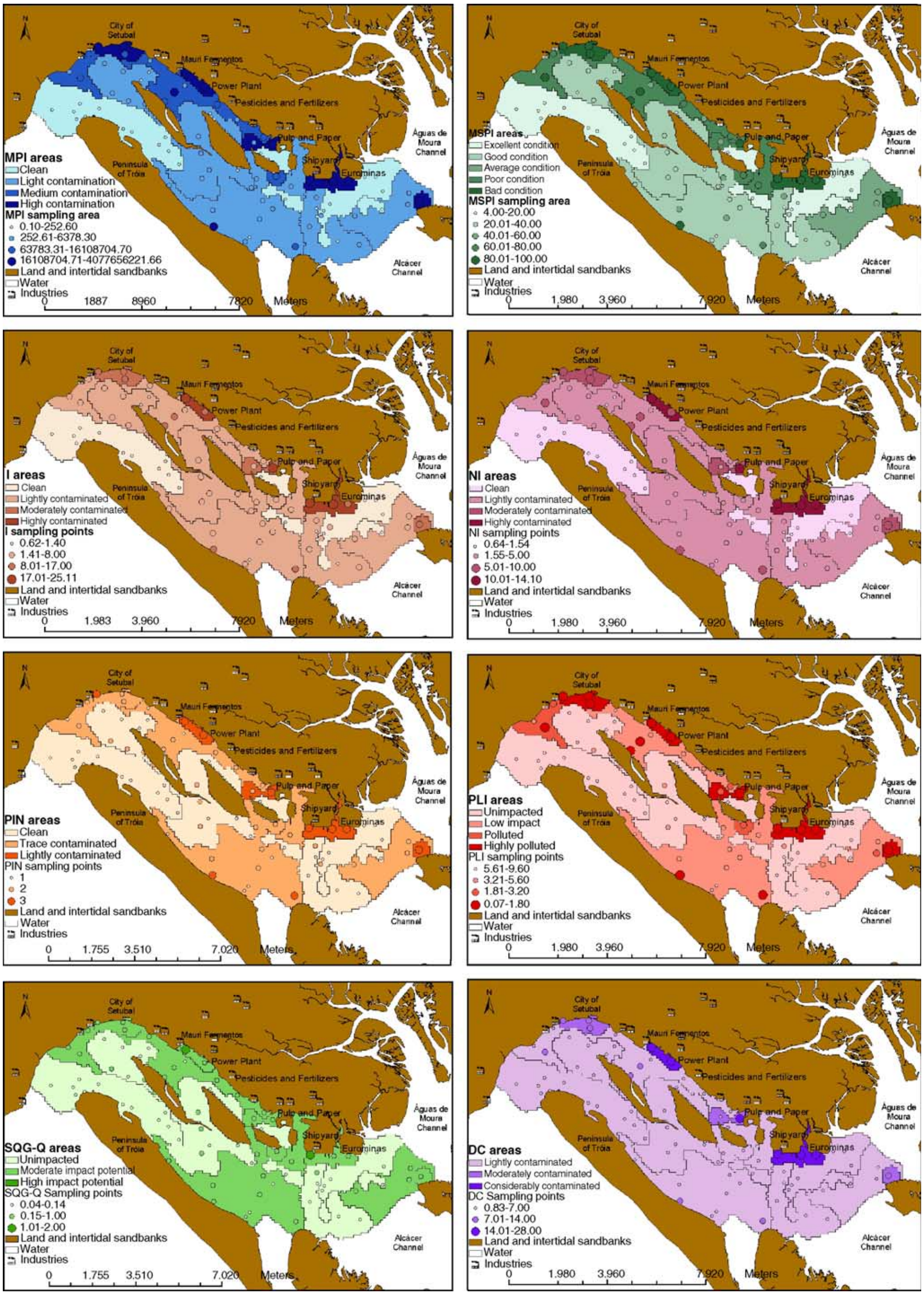

Fig. 2. Results of the contaminants indices for the sampling points and management units in the Sado Estuary.

only clean or lightly contaminated concentrations, the MSPI values in the category 80–100 will always be considered as sediment in a bad condition.

In an overall comparison of the contamination and background enrichment indices the PIN and MSPI indices have the highest performance scores, according to the indicator criteria and above discussion (Table 3), PIN due to its simplicity and comparability and MSPI due to its sensitivity, robustness and acceptable level of uncertainty. MPI has the lowest performance score since it does not allow comparison between ecosystems and has low sensitivity and limited ability to provide a representative picture of the environmental state of an estuary or any environmental impact on it.

3.3. Ecological risk indices

The PLI and SQG-Q indices are the two ecological indices calculated in this work, both of which allow the results to be compared with other ecosystems. In the case of PLI, for example, the most polluted station has a value of 0.07 (Station 43; Figs. 1 and 2). This value is low when compared with other highly contaminated European estuaries like the Tolka or Avoca in Ireland where stations with a PLI value equal to 4.3×10^{-3} and 10^{-6} can be found (Wilson and Elkaim, 1991).

For the PLI index calculation, the threshold and baseline values (see Table 1) were determined specifically for estuaries in which these values were found for sediment contamination in conjunction with depleted biological communities. The problem is that the guidelines were never updated after initial publication (1985). Also, the baseline values defined by the authors are higher than those found in our reference stations, which resulted in erroneous calculations and led us to make use of our own baseline values (from reference stations). In comparison, the guidelines used in the SQG-Q index are recent and their predictive ability has been widely tested (e.g. MacDonald et al., 1996; DelValls and Chapman, 1998; Long et al., 1998, 2000; Long and MacDonald, 1998; Hyland et al., 1999). However for the SQG-Q index no maximum level is defined, in contrast to the PLI. Hyland et al. (1999) found degraded benthic assemblages with a mean SQG-Q of <0.1, i.e. with a much lower range in concentrations of sediment contaminants. Regional variations in the magnitude of sediment contamination, the relatively insensitive bioindicators of toxicity used by Long et al. (1998) (amphipod survival test with bulk sediments), the measure of benthic community conditions that reflect the sensitivities of multiple-component species to longer-term exposures and potential interactions, may explain some of the differences that were observed in bioeffect levels. Although the use of empirically derived SQG in sediment monitoring and assessment has been the subject of debate, recent studies suggest SQG continues to be widely used to predict when chemical concentrations are likely to be associated with a measurable biological response (Fairey et al., 2001). In summary, according to the index performance criteria, SQG-Q has a higher score compared to PLI, due to the credibility and the acceptable level of uncertainty of the guidelines (Table 3).

In an overall evaluation of indicator criteria performance, SQG-Q evaluates the potential for adverse biological effects more effectively while MSPI measures the contamination level more satisfactorily. Nevertheless, most of these indices gave the same weights to the contaminant mixture, with the exception of MSPI, or did not account for synergies between contaminants as they exist in nature.

An assessment of Sado contamination will mainly be based on those two indices, in addition to the interpolation areas for an assessment per metal also used for indices and management unit gauging. Use of the many indices and approaches available is recommended for a better assessment of the quality of sediments and its development. They are fast and relatively simple to apply (Kwon and Lee, 1998). The use of these kinds of tool raises confidence when decisions about ecosystem and human health protection are being made.

3.4. Assessment of Sado Estuary metal contamination

The index classifications per management unit showed spatial patterns similar to those of the heavy metals, which led to the identification of the same ‘clean’ or ‘showing levels do concern’ (Figs. 2 and 3). In general, metals have similar spatial patterns and are associated with similar urban and industrial point

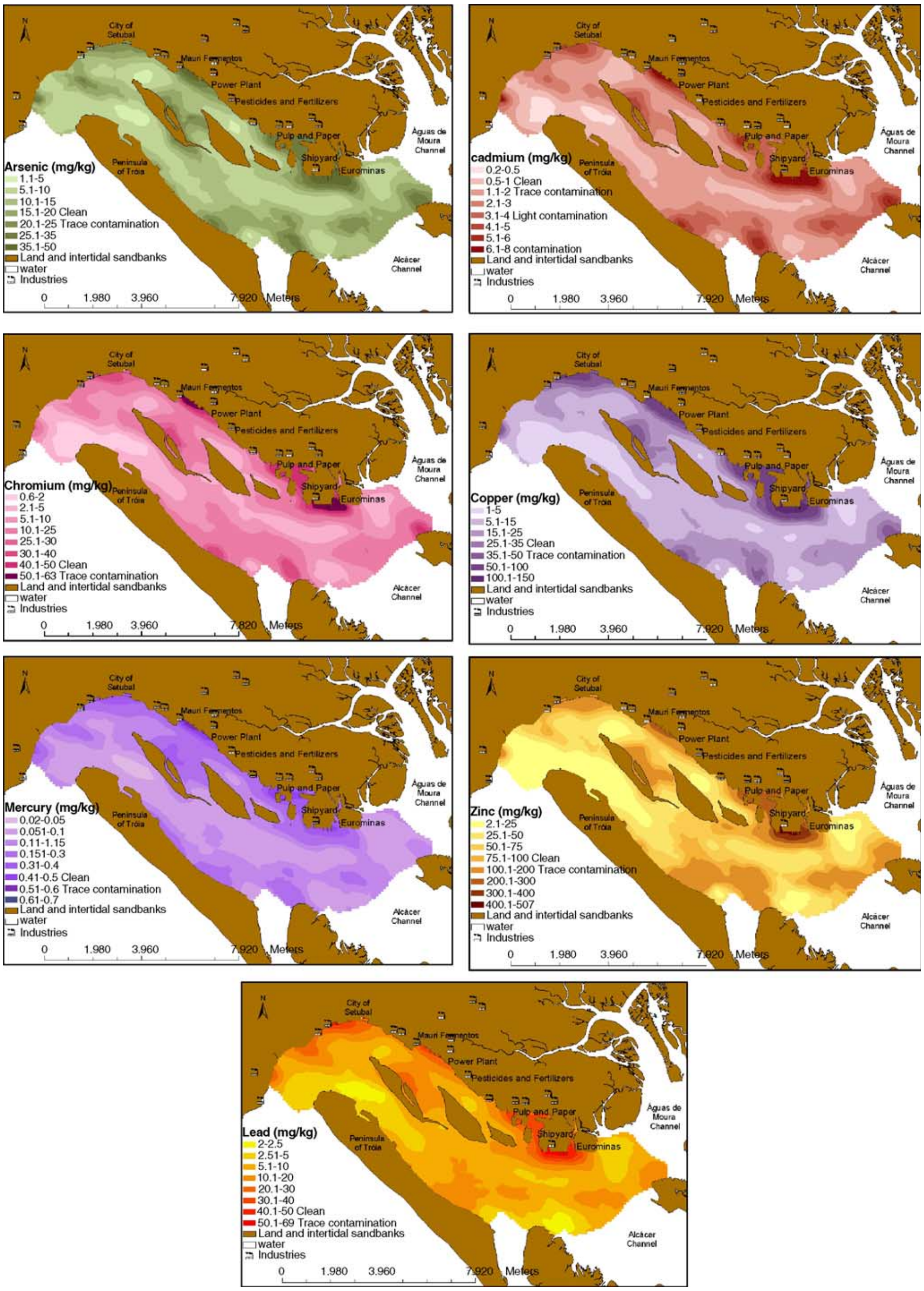

Fig. 3. Spatial distribution of the metals in the Sado Estuary. Classification according to DR (1995) (see Table 3). Industries adapted from Araujo et al. (2002).

sources, as can be seen in Fig. 3. This fact is also confirmed by the strong correlation of all the metals in a single principal component in the PCA. Cd showed levels of concern followed by As and Cu; Zn, Pb, Cr, and Hg showed only trace contamination (Fig. 3 and Table 2).

The large area at the entrance to the estuary, the two areas on the right, at the entrance to Aguas de Moura, and two small areas near the smallest sandbank are unimpacted areas classified as in excellent condition.

The areas with contaminants of concern are located on the North Channel near certain industries: one near the shipyard and Eurominas; one near the pulp and paper plant; one near the power plant and yeast factory and one near the outfall of the City of Setubal and the fishing and urban ports. Although the conditions in these areas are considered bad in terms of contamination, according to the MSPI index, their ecological risk is only moderate (see the MSPI and SQG-Q indices in Fig. 2). Nevertheless, Stations 34, near the yeast factory, and 43, near the shipyard, have a high impact potential for adverse biological effects (see Figs. 1 and 2, SQG-Q index). According to the spatial distribution of the metals and metalloid, ‘‘hotspots’’ are found close to those anthropogenic sources (Fig. 3). The station near the power plant and yeast factory (34) has the highest values for Cd (8.0 mg/kg) and Cr (63.0 mg/kg). Sources of chromium are associated with the manufacture of chemicals, chrome plating and cooling towers (McConnell et al., 1996). Anthropogenic sources of cadmium could be pesticides and pigments. The highest mercury values (0.7 mg/kg) are also found in this area (Station 68). This metal is released into the environment by human activities such as the combustion of fossil fuels, waste disposal and industrial activities (Donze et al., 1990). Associated with the power plant is the discharge of heavy metals, oils, salts, acids and alkalines. Associated with the yeast factory are organic acids and sulphates (Catarino et al., 1987).

The station near the shipyard (43) has the highest values for Pb (69.0 mg/kg), Zn (507.0 mg/kg) and Cu (191.0 mg/kg). This area is under the influence of the wastewaters and water-runoff from that industrial activity (rich in heavy metals). The most important uses of Zn are protection against corrosion, Cu is used in construction materials and Pb was formerly used in paints, pigments and glass (Donze et al., 1990).

In the specific case of lead, other enriched stations are located near the outfall of Setubal City and the fishing ports (Fig. 3). Other work conducted in the study area has also related lead with urban contamination (Vale and Sundby, 1980). In addition, the areas near those ports and the pulp and paper factory are enriched with mercury.

The area between the sandbanks is also enriched with arsenic, reaching its highest value at Station 93 (59.0 mg/kg). One of the major sources of arsenic is pesticides and herbicides (Donze et al., 1990). The areas with high arsenic level can be related to currents and a high sediment deposition rate in the area. According to Neves (1985), the residual flow in the outer estuary shows a cyclonic vortex centred at the outer point of the sandbanks. This enrichment has only happened with arsenic so the indices classified these places as in good condition or with moderate impact potential.

A small unit at the entrance to the Águas de Moura channel and a station on the left at the entrance to the Alcacer Channel (Stations 102, 153, 156 and 157—see Fig. 1) have higher contamination levels and moderate ecological risk (MSPI and SQG-Q indices, Fig. 2). These locations register an increase in the concentration of most of the metals, especially Cd, Cr, Cu, As and Zn (Fig. 3). These locations are associated with shallow hydrodynamics and limited depth, so high organic loads can also be associated with non-point pollution runoff and deposition, due to aquaculture and rice field activities located upstream of these channels. Alcacer Channel may also be a source of heavy metals due to pyrite outcrop erosion and old mining activities in the river drainage basin, as has already been stressed by other authors (Quevauviller et al., 1989; Cortesão and Vale, 1995).

The concentrations of metals and metalloids are similar to the results presented in other work recently carried out in different parts of the outer estuary. In these studies, higher contamination was found near the power plant, yeast factory and Eurominas site. Exceptions were the higher cadmium values obtained here when compared with the work of Vale et al. (1997) and Gil et al. (1999). Our concentrations are also similar to measurements of Zn, Cu and Pb made 20 years ago (Vale and Sundby, 1980). Earlier work also associated Cd and Zn with sediments deposited in the upper limit of the estuary, related to river input

(Quevauviller et al., 1989), but this area was not covered by this study. Though the number of industries has increased, cleaner technologies and industrial wastewater treatment improvements can explain the stability of these contamination levels.

4. Conclusions

The tools – interpolation surfaces, GIS and indices – used in this work for the evaluation of estuarine sediment contamination were shown to be very useful for aggregation, data transmission and visualization. Data aggregation in indices and its visualization using GIS, including the full GIS capabilities of overlaying spatial data, have many advantages. These tools are essential for decision-making processes and management involving natural resources. Loss of information can occur during the conversion of multivariate data into single indices. However, such indices offer useful information, provided that their limitations are recognized.

Different metal assessment indices were used and discussed. Some indices give equivalent information but others give complementary information (e.g. contamination or background enrichment indices and ecological risk indices) that can be developed for different purposes. There should be better methods of standardization for indices to allow better comparability between them (as several assess the same information).

According to the evaluation of the index criteria performance, SQG-Q had the highest score particularly in the group of ecological risk indices. This index can be complemented with the MSPI contamination index. MSPI does not evaluate the potential for adverse effects and the results from one ecosystem are more difficult to compare with others, but it allows more site-specific and accurate information on contamination levels. The results of the indices per management unit are in accordance with the surface areas of each metal. If the aim of contamination evaluation is to assess the overall contamination of a study area, the indices are highly appropriate. For spatial and source evaluation per metal, the interpolation surfaces should also be used.

In general the Sado Estuary has a low contamination level and a moderate potential for observing adverse biological effects. Of all the stations analysed, only 3% are highly contaminated and register a high potential for observing adverse biological effects, but 47% have moderate contamination. Nevertheless, some hotspots were found near industrialized zones and in areas with sediments rich in organic matter at the entrance to channels. All metals have similar spatial behavior and are mainly related to deposition areas. Metal with concentrations of concern is Cd, followed by As and Cu, Pb, Zn, Cr and Hg have shown only trace contamination. In the near future a new urban and industrial wastewater treatment plant will start working, so an improvement in water quality can be expected.

To link the index results more effectively with the pressures on the estuary, e.g. urban and industrial wastewater discharges and water-runoff, and thus evaluate them better, a sediment transport model (Painho et al., 2002) should be used to estimate which estuary management unit will suffer an effect caused by a certain pressure and the resulting impact.

Heavy metal assessment indices are not to be used as the only evidence of sediment quality. In future developments, organic compounds (pesticides, PAHs and PCBs) will be integrated into the contamination evaluation, which can be correlated with data on the different sources and spatial distribution of pollution. Furthermore, the integration of contamination assessment with biota and toxicity evaluation will be carried out in each management unit to allow a weigh of evidence for sediment quality assessment.

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Appendix A

See Table A.1.

Table A.1
Indices applied to estuarine environments to assess contamination

Author	Index name: type	Description	Comments/drawbacks
Johanson and Johnson (1976) *fide* Ott (1978)	Pollution index (PI): *contamination index*	$\mathrm{PI} = \sum_{i=1}^{n} W_i C_i$ (A.1) W_i is the weight for pollution variable i; C_i the highest concentration of pollution variable i reported in a location of interest. For each pollutant i, the weight was based on the reciprocal of the median of observed concentrations	This index allows the identification of priority contaminations sites for implementation of decontamination action. It requires several measurements in the same sampling location. No threshold classification from unpolluted to high pollution
Hakanson (1980) and Kwon and Lee (1998)	Degree of contamination (DC) (sub-index of an ecological risk index): *background enrichment index*	$\mathrm{DC} = \sum_{i=1}^{n} C_{\mathrm{f}}^{i} = \sum_{i=1}^{n} \frac{\bar{C}_{0-1}^{i}}{C_{n}^{i}}$ (A.2) C_{f}^{i} is the contamination factor; $\bar{C}_{0-1}^{i}$ the mean content of the substance in question (i) from superficial sediment (0–1 cm) from accumulation areas (at least five samples); C_{n}^{i} the reference level (according to Hakanson, 1980); $\mathrm{DC} < n$ (no. of contaminants): low level of contamination; $n < \mathrm{DC} < 2n$: moderate degree of contamination; $2n < \mathrm{DC} < 3n$: considerable degree of contamination; $\mathrm{DC} > 3n$: very high degree of contamination	This was developed and tested for lakes, although it has already been successfully used for coastal areas (Kwon and Lee, 1998). It needs at least five samples, which provide an even area coverage of the study area. Only built for eight contaminants (PCB, Hg, Cd, As, Cu, Pb, Cr)
Satsmadjis and Voutsinou-Taliadouri (1985)	Index of metals pollution in marine sediments (q): *contamination index*	The assessment of the degree of pollution of sediment by an element first requires the relation of its contents, c, to the granulometric composition of the substratum in a clean section of the investigated region, and the metal concentration estimation for uncontaminated sediment is then evaluated on the basis of the grain size composition: $f = g + \frac{t}{0.2g+5}$ (A.3) $c = EKd^{\log f/\log 5}$ (A.4) $q = \frac{C'}{c}$ (A.5) f is the clay equivalent; g the percentages of clay; t the percentages of silt; E and K the constants; d the enrichment constant, expresses the magnitude of the influence of the grain size on the concentration of the metal. The enrichment induced by fine particles is very slight for $d < 1.2$, moderate for $1.2 \leq d < 1.4$, substantial for $1.4 \leq d < 2$ great for $2 \leq d < 4$ and huge for $d \geq 4$; $C'$the true concentration of the metal. If it exceeds 1, measures the extent of the pollution by the metal in question	Calculated on the basis of data from one specific place – Greek gulfs. Not tested in other coastal ecosystems. According to the author it is difficult to find the proper data to set up and to compute Eq. (A.4), since not easily discernible factors may boot? the level of an element in a seemingly virgin zone. It does not incorporate all contaminants into one value. It requires the separate measurement of silt and clay. No threshold for maximum pollution

Table A.1 (*Continued*)

Author	Index name: type	Description	Comments/drawbacks
Wilson and Jeffrey (1987)	Pollution load index (PLI): *ecological risk index*	For each contaminant the PLI is calculated using the formula: $\text{PLI} = \text{anti}\log_{10}\left(1 - \frac{C-B}{T-B}\right)$ (A.6) B is the baseline value—not contaminated; T the threshold, minimum concentrations associated with degradation or changes in the quality of the estuarine system. Wilson and Jeffrey (1987) define B and T for the different contaminants; C the concentration of the pollutant. For each place the PLI calculation takes into account all the n contaminants: $\text{PLI} = (\text{PLI}_1, \text{PLI}_2, \ldots, \text{PLI}_n)^{1/n}$ (A.7) Varies from 10 (unpolluted) to 0 (highly polluted)	This index allows the comparison between several estuarine systems. Easy to implement. It has been applied successfully in European estuaries (Wilson et al., 1987; Wilson and Elkaim, 1991; Ramos, 1996), and US estuaries (Wilson, 2003). Ramos (1996) used this index with other aggregation methods like arithmetic average and minimum sub-index and obtained good results. Evaluates toxicity, as it takes into account SQG comparison. Values of baseline and threshold not defined locally for each coastal zone analysed and not recently revised
Chapman (1990)	Index for chemistry (ratio-to-reference RTR) of the sediment quality triad component (I): *contamination index*	$\text{I} = \frac{\sum_{i=n}\text{RTR}_i}{n} \quad \forall i$ (A.8) $\text{RTR}_i = \frac{v_i}{(v_i)_0}$ (A.9) n is the total variable number; v_i the value of each parameter i; $(v_i)_0$ the value of each parameter at reference site	Useful in time-series monitoring, summarizing changes by time and location. It needs reference site values. It may give imprecise values because of the undue influence of one of the measurements used in the final composite values (DelValls et al., 1998b). No threshold for maximum pollution
Usero et al. (1996)	Metal pollution index (MPI): *contamination index*	$\text{MPI} = (M_1, M_2, M_3, \ldots, M_n)^{1/n}$ (A.10) M_n is the concentration of metal n expressed in mg/kg of dry weight	Simple but does not compare the contaminant concentration with any baseline or guidelines. No threshold classification from unpolluted to high pollution. Geometric average, as stressed by Ott (1978), has advantages when compared with other aggregations methods, since it highlights concentration differences
DelValls et al. (1998b)	Index for chemistry (new maximum RTR) of sediment quality triad component (NI): *contamination index*	$\text{NI} = \frac{\sum_{i=1}^{n}\text{RTM}_i}{(\sum_{i=1}^{n}\text{RTM}_i)_0} \quad \forall i$ (A.11) $\text{RTM}_i = \frac{\text{RTR}_i}{\text{RTR}-m_i}$ (A.12) $(\text{RTR}-m_i)$ is the RTR maximum value obtained for the parameters i; $(\cdot)_0$ the reference site	The use of the maximum reference value (polluted station reference) to normalize a sediment quality triad (SQT) dataset permits the classification of each component variable between maximum and minimum. It needs reference site values. No threshold for maximum pollution

Long and MacDonald (1998)	Mean sediment quality guideline quotient (SQG-Q): *ecological risk index*	Takes into account a complex mixture of contaminants in each location (NSTP: National Status and Trend Program) $\text{SQG-Q} = \frac{\sum_{i=1}^{n} \text{PEL-Q}_i}{n}$ (A.13) $\text{PEL-Q} = \frac{\text{contaminant}}{\text{PEL}}$ (A.14) PEL-Q is the probable effect level quotient; PEL the probable effect level for each contaminant (concentration above which adverse effects frequently occur) (MacDonald et al., 1996). Sediment locations are then scored according to their impact level (MacDonald et al., 2000)—SQG-Q $\leq$ 0.1 unimpacted: lowest potential for observing adverse biological effects; 0.1 $<$ SQG-Q $<$ 1: moderate impact potential for observing adverse biological effects; SQG-Q $\geq$ 1: highly impacted potential for observing adverse biological effects	This mixes all contaminants in the same SQG, including metals, PAHs and PCBs. Evaluates toxicity, since it takes into account SQG comparison. It can also be used with other SQGs like the effect range-median (ERM) (Long et al., 1995), or others. Other scores can be used instead of 1. MacDonald et al. (2000) used threshold of 1 and 2.3 and obtained better results with 1
Field et al. (1999, 2002)	Logistic regression models (p): *ecological risk index*	The logistic model evaluates the probability of observing acute toxicity effect (p for a probability of 20, 50 or 80%) for 37 chemicals (metals, PAH, PCB and organochlorine pesticides) based on amphipod mortality tests: $p = \frac{\exp[B0+B1(x)]}{1+\exp[B0+B1(x)]}$ (A.15) $B0$ is the intercept parameter; $B1$ the slope parameter; x the chemical concentration or log chemical concentration. Probability of observing a toxic effect from 0 to 1	Developed using a large dataset of matching saltwater sediment chemistry and toxicity data for field-collected samples compiled from a number of different sources and geographic areas. It does not aggregate all contaminants into one value
Ingersoll et al. (1999) *fide* MacDonald et al. (2000)	Mean sediment quality guideline quotient (SQG-Q′): *ecological risk index*	Same procedure as in earlier SQG-Q, but calculates the quotient separately for each type of contaminant: metals, PCBs and PAHs, then the mean SQG-Q is calculated by determining the average for each SQG-Q type of contaminant (USEPA procedure). Sediment locations are scored in the same way as in NSTP	Evaluates toxicity, since it takes into account SQG comparison. It can also be used with other SQGs like ERM or scored with other thresholds
Ferreira (2000)	Equation sub-index sediment quality (EQUATION): *ecological risk index*	This sub-index is integrated in an estuarine quality index based on key physical and biogeochemical features. The sediment quality sub-index is evaluated through sediment contamination, bioaccumulation and biodiversity descriptors. The sediment contamination is evaluated in terms of area affected according to a probabilistic approach. The system is divided into a set of grid cells, and into contamination levels defined using the PEL. In each grid cell, the median value for each sampling station is determined and if any of the PEL values for indicator contaminants are exceeded, the stations is considered polluted. The contamination of a grid cell is based on the proportion of contaminated stations contained. Five grades are defined, ranging from light contamination (10% of area polluted) to gross pollution (>70% of area)	According to the author, since the rate of change in persistent pollutants in the sediment is usually low, this eliminates the need for dedicated synoptic sampling. Only applicable for gross comparison between estuaries, not for detailed management of a particular system

Table A.1 (*Continued*)

Author	Index name: type	Description	Comments/drawbacks
Fairey et al. (2001)	Mean sediment quality guideline quotient as indicator of contamination and acute toxicity (SQG-Q1): *ecological risk index*	$\text{SQG-Q1} = \frac{[\text{Cd}/4.21]+[\text{Cu}/270]+[\text{Pb}/112.18]+[\text{Ag}/1.77]+[\text{Zn}/410] +[T_{\text{chlordane}}/6]+[\text{dieldrin}/8]+[\text{TPAH}_{\text{oc}}/1800]+[\text{TPCB}/400]}{9}$ (A.16) The constant values correspond to PEL, in the case of Cd, Ag, Pb, ERM in the case of Cu, Zn, total chlordane and Dieldrin; consensus guideline defined by Swartz (1999) *fide* (Fairey et al., 2001) for total PAH and consensus guideline defined by MacDonald et al. (2000) *fide* Fairey et al. (2001) for total PCB. Sediments have a high probability of being toxic to amphipods when SQG-Q1 is high (>1.5) and a low probability of being toxic when SQG-Q1 is low (<0.5)	It is only meant to serve as a central tendency indicator. It minimizes the potential for impact from any one component. It is prudent to consider chemical exposure on an individual chemical basis in addition to the chemical matrix basis described here. SQG-Q1 ranges are themselves currently subject to investigation. It is focused on acute toxicity of sediment to marine amphipods as the sole measure of biological response
Ruiz (2001)	New index of geoaccumulation (NI_{geo}): *background enrichment index*	$\text{NI}_{\text{geo}} = \log_2 \frac{C_n}{1.5\times B_n}$ (A.17) B_n is the concentration of the metal n in unpolluted sediments, according to a list of regional backgrounds for the different grain sizes (medium sand, fine sand or silt and clay); C_n the concentration of the metal. Unpolluted $\text{NI}_{\text{geo}} < 1$; very lightly polluted $1 < \text{NI}_{\text{geo}} < 2$; lightly polluted $2 < \text{NI}_{\text{geo}} < 3$; moderately polluted $3 < \text{NI}_{\text{geo}} < 4$; highly polluted $4 < \text{NI}_{\text{geo}} < 5$; very highly polluted $\text{NI}_{\text{geo}} > 5$	The first version of this index was developed for rivers by Muller (1981), *fide* Ruiz (2001), but this new version has been applied in estuaries. It needs a grain size classification of the sediment. Has the great advantage of using a different background level depending on sediment grain size. C_n only developed for Cr, Cu, Zn and Pb. It does not aggregate all contaminants into one value
Shin and Lam (2001)	Marine sediment pollution index (MSPI): *contamination index*	$\text{MSPI} = \frac{(\sum_{i=1}^{n} q_i w_i)^2}{100}$ (A.18) q_i is the sediment quality rating of the i contaminant; w_i the weight attributed to the i variable (proportion of eigenvalues obtained from the results of a principal component analysis, PCA). For each variable the sediment quality is rated (q_i) on the basis of the percentile in the dataset—MSPI 0-20: sediment in excellent condition; MSPI 21-40: sediment in good condition; MSPI 41-60: sediment in average condition; MSPI 61-80: sediment in poor condition; MSPI 81-100: sediment in bad condition. The index is also scored on this scale	Site-specific, making the index more accurate. It has a complex computation (PCA development). This index has shown significant correlation with benthic and toxicity data
Riba et al. (2002a)	Metal enrichment index (SEF): *contamination index*	$\text{SEF} = \frac{C_i - C_0}{C_0}$ (A.19) C_i is the total concentration of each metal i measured in the sediment; C_0 the heavy metal background level established for the ecosystem studied	It does not aggregate all contaminants into one value. No threshold for maximum pollution

Riba et al. (2002a)	Potential ecological risk index (ERF): *ecological risk index*	$\mathrm{ERF} = \frac{C_i - C_{\mathrm{SQV}}}{C_{\mathrm{SQV}}}$ (A.20) C_i is the total concentration of each metal i measured in the sediment; C_{SQV} the highest concentration of the heavy metal non-associated with biological effects (chemical concentration associated with adverse effects); polluted stations have values equal to or greater than 1	It does not aggregate all contaminants into one value. It uses site-specific sediment quality guidelines (DelValls and Chapman, 1998)

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