

# Ecological risk assessment of sediment management areas: application to Sado Estuary, Portugal

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**Abstract** The purpose of this work was to integrate different methodologies to assess the potential ecological risk of estuarine sedimentary management areas, using the Sado Estuary in Portugal as case study. To evaluate the environmental risk of sediment contamination, an integrative and innovative approach was used involving assessment of sediment chemistry, sediment toxicity, benthic community structure, human driving forces and pressures and management areas organic load levels. The basis for decision-making for overall assessment was a statistical multivariate analysis appended into a score matrix tables, using a best

expert judgment. The integrated approach allowed to identify from the 19 management areas analyzed, three with no risk but other three with high risk to cause adverse effects in the biota, related with the contaminants analyzed. The methodologies used showed to be effective as a support for decision making leading to future estuarine management recommendations.

**Keywords** Sediment quality · Ecological risk assessment · Ecosystems disturbance · Sado estuary · Pollution effects

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## Introduction

It has long been recognized that sediments accumulate persistent and toxic chemicals, therefore contaminated sediments continue to be a major concern to regulators, managers and the public. The assessment of the extent of contamination in sediments by characterizing the potential impact of contaminants on aquatic biota is a fundamental issue within a ecological risk assessment process that evaluate the likelihood that adverse ecological effects can occur as a result of exposure to one or more stressor.

The use of sediment quality values or guidelines (SQG) alone is not sufficient for decision-making and multiple lines of evidence (LOE) should be used to support sediment management decisions. Additionally there is no consensus on a single process to evaluate the multiple LOE in sediment quality, a process called weigh of evidence (WOE) approach is the appropriate framework to provide a meaningful interpretation of ecological significance and to make sound management decision (Wenning et al. 2005).

One of the first WOE approaches to marine pollution assessment is the sediment quality triad (SQT). Major advances have been made in gathering and assessing the different components of the SQT: sediment chemistry, toxicity and benthic community structure (Long and Chapman 1985). However, a key issue remains the integrated use of such information for informed and realistic decision-making, including determining when sufficient data has been gathered to allow for a decision. Such integration should involve best professional judgment (BPJ, expert opinions and judgments) to address the complexity of ecological system and the limitation of field and laboratory investigations (Chapman et al. 2002). Formalized use of WOE in the environmental sciences is relatively recent. The first formalized WOE framework for contaminated sediments, SQT, was based only in summary indices, where the stations values were divided by the ones of the reference stations (Long and Chapman 1985). Although these indices are still been successfully used, the single use of these indices result in information compressions that can negate full use of WOE (Chapman et al. 2002), since they do not allow to highlight multi associations between the different contaminants and the adverse effects.

Although there is no “one-size-fits-all” the basis for decision-making should be statistical multivariate analyses incorporated into logic systems. BPJ will always be necessary, and scoring systems can assist the logic systems. Such a sound basis for decision-making is particularly important for sites background contamination/effects, variable substrate types and complex contamination patterns, all of which increase the complexity of the analyses and create potential for confounding effects (Chapman et al.

2002). The tabular decision matrix, a mean to assess sediment quality WOE remains an effective basis (a logic system) for sediment management decision-making (Burton et al. 2002a). Tabular decision matrices can reasonably incorporate a limited level of ordinal response, but should emphasize a strong quantitative evaluation within LOE (like statistical summarization) prior to merging into the more qualitative matrix table (Chapman et al. 2002). Grapentine et al. (2002) used a ranking procedure summing the LOE allowing the comparison and classification among stations. MacDonald et al. (2000) also used a ranking to classify sediment management areas. A tabular ranking approach can be moderately robust, as methodology, but has high degrees of sensitivity, appropriateness/applicability and transparency (Burton et al. 2002b).

The aim of this work is to integrate different methodologies to assess the potential ecological risk of sediment management areas in a innovative and understandable way for decision makers. The Sado Estuary was used as case study. To evaluate the environmental risk of sediment contamination an integrative burden-of-evidence approach was used involving assessment of sediment chemistry, sediment toxicity, benthic community structure, human driving force and pressures and management areas organic load levels (these last two only in a qualitative way). The basis for decision-making, for overall assessment, was statistical multivariate analysis added into logic systems.

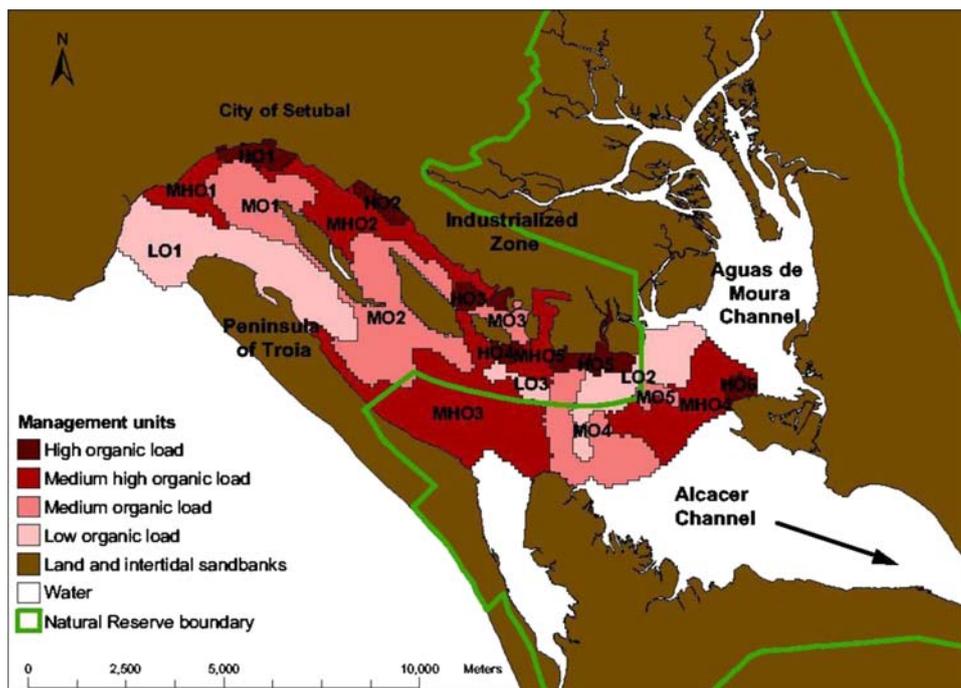
## Methods

### Study area

The Sado Estuary, with an area of approximately 24,000 ha, is located in the West Coast of Portugal. Most of the estuary is classified as a Natural Reserve, but there are many industries mainly on the northern margin of the estuary. Furthermore the harbor-associated activities and the city of Setúbal along with the copper mines on the Sado watershed use the estuary for waste disposal. In other areas around the estuary intensive farming, mostly rice fields, and also tomatoes, are the main land use together with traditional salt-pans and increasingly intensive fish farms.

In previous work the Sado estuary bay was divided in 19 management sedimentary areas based on sediment parameters: Fine Fraction contents (FF), total organic matter (TOM) and redox potential (Eh), measured in an extensive systematic unaligned sampling design (500 × 750 m—153 locations) and using multivariate geostatistical tools. Those areas were classified in 4 types according to enriched levels of organic load (Caeiro et al. 2003a; Fig. 1).

**Fig. 1** Nineteen management areas of Sado Estuary and natural reserve boundary



### Sediment sampling

A sampling survey of seventy-seven locations was previously designed for metal contamination assessment using an optimisation model to select the appropriate spatial distribution within the study area and in each management area type, based on the first 153 locations campaign (Caeiro et al. 2004b). The same optimization model was used to select a subset of stations that best represented the management areas based on the metal and metalloids data in the seventy-seven locations (Caeiro et al. 2003b). A new sub-set of 19 selected locations were then used to conduct toxicity bioassays and pesticides analysis, representing the more contaminated locations of each management area. These 19 stations campaign (second campaign) occurred from July to October 2003. At each location, sub-samples were taken with a Petit Ponar grab in the first campaign and with a Van Veen in the second campaign, and a composite sediment sample was formed.

### Sediment chemistry

A set of metals and metalloids, Cd, Cu, Pb, Cr, Hg, Al, Zn and As, were earlier determined (Caeiro et al. 2005a). These contaminants were chosen taking into account earlier work conducted in the estuary and estuarine pollution sources. TOM, FF, sand and gravel contents, and Eh were also determined for each location (Caeiro et al. 2003a). The values of these parameters were calculated in each management area using the median values of locations belonging to each area.

The following organochlorine pesticides were also determined: aldrin, dieldrin, pp' DDD, pp' DDE, pp' DDT, endosulfan I, endosulfan II, endrine, heptachlor, heptachlor epoxide,  $\alpha$ -BHC,  $\gamma$ -BHC,  $\delta$ -BHC. The organochlorine pesticides are of major concern due to their wide human use, persistence and bioaccumulation. The sediment samples for pesticides were Soxhlet extracted with a mixture of hexane/acetone 1:1 for 10 h. Sulphur was eliminated with copper. The extract was filtered and concentrated in rotative evaporator at 50°C until a volume of about 20 ml and concentrated in Nitrogen flow until a final volume of 1 ml. This extract was filtered over activated carbon for removal of colored impurities. The adsorbent was washed with 5 ml of hexane and 5 ml of acetone. The filtrate and the washing solvents were concentrated in nitrogen flow until a final volume of 3 ml. Analysis was performed on a gas chromatograph equipped with an electronic capture detector and a capillary column (DB608). Calibration and peak identification were performed using standard solutions containing the analyzed pesticides in a range of 5–100 ppb. The recoveries of the concentration and clean-up steps were evaluated at the 30 ppb level and the final results were corrected with the respective recoveries.

The average sediment quality guideline quotients (SQG-Q; Long and MacDonald 1998) was calculated separately for metals and metalloid, and pesticides, using probable effect level (PEL) for each contaminant, that means chemical concentrations above which adverse biological effects are likely to occur (Macdonald et al. 1996). These guidelines were originally developed for coastal waters and have been largely used in estuarine and coastal sediment quality

assessment studies (e.g., Long and MacDonald 1998; Car-dellicchio et al. 2007). A classification of potential impact to cause adverse effects was performed according to (MacDonald et al. 2000). For organic compound only the pesticides where PEL values were available were used ( $\gamma$ -BHC, p,p'-DDE, dieldrin, p,p'-DDD and p,p'-DDT).

#### Sediment benthos structure

A benthic biotope index ( $BI_{\text{bio}}$ ) was calculated earlier in the seventy-seven sampling points. The values of the index in each management area were calculated using the median values of the locations belonging to each management area (Caeiro et al. 2005b). The benthos communities were classified in: 1 to 1.4—Marine; 1.5 to 2.4—Transition; 2.5 to 3.4—Estuarine; 3.5 to 4.4—Estuarine enriched; 4.5 to 5—Estuarine impoverished.

#### Sediment toxicity testing

Two toxicity bioassays were performed in whole and elutriate sediment in the 19 sampling point's representative of each management area. One of the bioassay was an acute test with mortality as the endpoint (10 days) with juveniles of marine amphipod *Gammarus locusta* from a laboratory standard culturing according to the procedure of Costa et al. (1998). The other bioassay was conducted in the sediment elutriate with embryos of the Atlantic sea urchin *Paracentrotus lividus*. The toxicity was based on abnormal larvae development (72 h) and according to Rolland et al. (1999) procedure.

Management area LO1 was considered the reference area, since this area has high hydrodynamics, is directly connected to the ocean and has no direct effluent disposal (Fig. 1). The baseline concentrations of the metals found in this area are in accordance or are even lower compared to earlier data of Sado Estuary clean areas (e.g., Quevauviller et al. 1989).

One-tailed analysis of variance (ANOVA) followed by a Tukey test was computed in order to compare the sediments bioassays against the reference area (LO1) and the negative control. The negative control corresponds to the amphipods culture sediment and was obtained at the amphipod collection site; or the exposure of sea urchin fertilized cells to filtered seawater only. The Quality Analysis/Quality Control requirement for the negative control was 10% mean mortality (ASTM 1993). No reference control sediment was used for the amphipod bioassay since sediment type does not influence the bioassays results using these species (Costa et al. 1998). In both bioassays the stations responses were corrected by the mean response in the negative control. Prior to ANOVA analysis the toxicity test data were tested according to requirements for normality and homogeneity of variance.

#### Ecological risk assessment

The data for chemicals, benthos and toxicity bioassays were analysed using the multivariate statistical analysis factor analysis (FA) using the principal component analysis (PCA) extraction procedure to explore variables distribution in accordance with Cesar et al. (2007) procedure. The data was transformed (square root transformation in case of toxicity bioassays,  $\log(x + 1)$  for chemical and biotic index data and  $\log(x + 400)$  for Eh) to satisfy the test requirements for normality. The variables were standardized (centered and scaled) to be treated with equal importance.

Tabular Decision Matrix was used for WOE using the improved SQT (Graptentine et al. 2002; Chapman et al. 2002). Each LOE was judged on the basis of a graduation (a scoring system) to rate each measurement endpoint as high, moderate, or negligible/low impact for adverse effects (Table 1). The LOE were summarized in SQG-Qs, toxicity bioassay results and  $BI_{\text{bio}}$  index. The classification of the toxicity bioassay to use in the ordinal ranking scheme was based on ANOVA significant differences (value of  $p$  and tested the differences among the group of stations classified as low, moderate and high potential impact).

The management area type classification was also added has a forth LOE in the tabular matrix (see Table 1) but only as BPJ as qualitative information, to address the stability of surface contaminated sediment in accordance with Graptentine et al. (2002).

The fifth LOE added in the tabular analysis as qualitative data was the main *Driving Forces* (D) and *Pressures* (P) of each management area, including the potential main pollutants, in accordance with DPSIR model—*Driving Forces, Pressures, State, Impacts and Responses* (RIVM 1995). The D reports to the “needs” of individuals and institutions that lead to activities that exert pressures on the estuary. This category understood as the social needs that require the existence of a given economic activity (e.g., urban areas, industry). The “intensity” of the P depends on the nature and extent of the D and also on other factors which shape human interaction with ecological systems (e.g., pollutants discharged by industry or urban waste water). Their selection and spatial location within each management area were based on an extensive data search on Sado Estuary characterization, literature review and expert knowledge (Caeiro et al. 2004a).

An overall risk assessment was scored for each management area as no significant, potential significant or high significant ecological adverse effects, according to the FA results and expert knowledge and judgment also taking into account qualitatively the management area type and the main D and P.

Statistical analyses were conducted using Statistica<sup>®</sup> 6.0 software. To visualize and overlay the LOE results in the

**Table 1** Ranking scheme applied for weight of evidence categorization

Risk assessment				
		No significant adverse effects	Potential significant ecological effect	High significant adverse ecological effects
Chemistry	Metals and metalloid	SQG-Q ≤ 0.1 (low potential impact for adverse effects)	1 < SQG-Q < 0.1 (moderate potential impact for adverse effects)	SQG-Q ≥ 1 (high potential impact for adverse effects)
	Pesticides	SQG-Q ≤ 0.1 (low potential impact for adverse effects)	1 < SQG-Q < 0.1 (moderate potential impact for adverse effects)	SQG-Q ≥ 1 (high potential impact for adverse effects)
Toxicity	Amphipod mortality (whole sediment)	No toxic (stations no statistically different from reference area $p \geq 0.1$ )	Moderate toxicity (stations statistically different from reference for $0.0001 < p < 0.1$ )	High toxic (stations statistically different from reference for $p \leq 0.0001$ )
	Sea urchin larvae abnormality (elutriate sediment)	No toxic (stations no statistically different from reference area $p \geq 0.1$ )	Moderate toxicity (stations statistically different from reference for $0.001 < p < 0.1$ )	High toxic (stations statistically different from reference for $p \leq 0.001$ )
Benthos	Biotic index	1–2.5 (marine and transition benthos assemblages)	2.6–4.5 (estuarine type and enriched benthos assemblages)	4.5–5 (estuarine impoverish assemblages)
Management area type		<i>High organic load</i> management areas were classified as “Stable”; <i>Medium organic load</i> and <i>Medium high organic load</i> management areas were classified as “Medium Stable” and <i>Low organic load</i> management areas were classified as “Unstable”		
Main driving forces/pressure and pressures components (potential pollutants)		Defined for each management area based on literature and expert knowledge		

management areas, within Coastal line of Sado Estuary, and Driving Forces/Pressures ArcGIS 8.0<sup>®</sup> GIS software was used.

**Results**

**Sediment chemistry**

None of the areas was classified with high chemical impact potential of adverse effects (Fig. 2a, b). Metals index have areas with SQG-Q values near one and more areas classified as unimpacted compared with SQG-Q pesticide index. However, it should be taken into account that SQG-Q for pesticides were only evaluated for the pesticides with available PEL values. All metals have similar spatial distribution and are mainly related with deposition areas near industrialized zones (e.g., near areas HO2, HO5). Pesticides showed different patterns. The areas LO2 and MHO4 at the entrance of Águas de Moura Channel have the highest impact potential according to SQG-Q pesticides index. Some management areas have different classification levels of metals and pesticide SQG-Q indices,

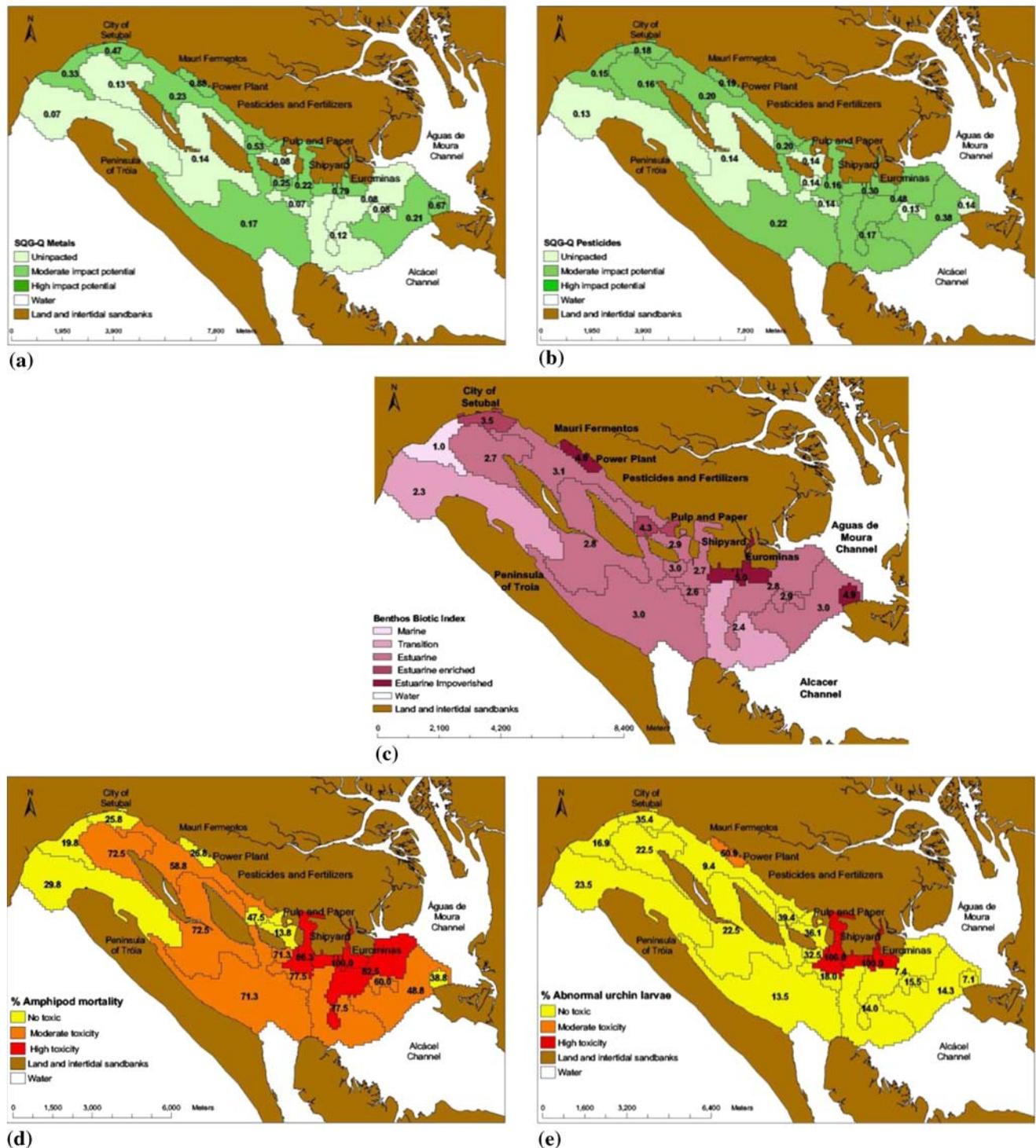
reflecting different contaminant sources (e.g., HO6, LO2 and HO4). These facts are further confirmed in the FA interpretation where the metals are all together in the same factor and appear only associated with two pesticides concentrations. The pesticides are spread over the different factors (Table A1 Supplementary Material).

**Sediment benthos structure**

The in situ benthos alteration, evaluated through the biotic index showed clean and undisturbed communities at the entrance of the estuary, i.e., a marine type community at the north side of the estuary mouth and a transition region spreading over a large area through the Southern Channel. The more disturbed and organic enriched communities are found in the North Channel and in a small area at the entrance of Águas de Moura Channel (Fig. 2c).

**Sediment toxicity**

In general amphipods bioassay assigned more pessimistic scenarios when compared with the sea urchin larvae. This



**Fig. 2** a Metals SQG-Q; b pesticides SQG-Q; c biotic index; d amphipod toxicity bioassay and e sea urchin larvae toxicity bioassay, in the Sado Estuary management areas

can be not only related with the high sensitivity of this amphipod species but also with higher levels of toxicity in sediment, associated with insoluble contaminant's forms (like the organochlorine pesticides). Nevertheless in both bioassays the areas near pulp and paper industry and

shipyard at the North Channel correspond to sediments with high toxicity and the sediment areas at the entrance of the estuary, small area at the entrance of Águas de Moura Channel and HO3 and MO3 areas at the North Channel showed no toxicity (Fig. 2d, e).

Ecological risk assessment

The FA computed eight factors explaining 89.8% of the total variance although the first four explained the main variance. In Supplementary Material it is available the detail FA interpretation, including the factor loading (Table A1) and the factor scores estimated for each management unit (Fig. A1).

Discussion

From the factor analyses results and from all the contaminants analyzed only the pesticides:  $\gamma$ -BHC, dieldrin and endolssulfan I, seem not to be associated with adverse biological effects. Aldrin was not included in the FA due to all levels in the stations being below detection limit. Nevertheless FA consider each variable by themselves and it is important to keep in mind that biological effects are the result of interactions between geochemical features and forms and levels of the contaminants and moreover toxicity of a complex mixture is not necessarily the sum of their components toxicity.

It can be also noticed that the metal’s concentrations are associated together and with the organic load of the

sediment (FF and TOM) and the benthos index (that was also based on sediment characteristics), and less associated with toxicity. It is well-established that granulometry and organic matter contents are important controlling factors in the abundance of metals in natural environment (Zhang et al. 2007). Release of metals from estuarine sediments is determined primarily by sediment physico-chemical characteristics and secondarily by the level of resuspension energy (Turner et al. 2002). Since in our study area their higher levels are associated with high organic loads and low levels of hydrodynamics their retention is expected what should be responsible for low bioavailability. Most of these areas where the metals and metalloid are contaminants of concern correspond to areas in the North Channel near industries and urban sewages responsible for discharging these contaminants (Fig. 3; Table 2 as an example for few number of management areas, in Table A2 in Supplementary Data there is available the complete tabular matrix for all areas). The potential for metals release from sediments by bioturbation should be negligible on those areas due to the presence of estuarine impoverished benthos community’s (Fig. 2c). According to Turner et al. (2002) trace metals in highly contaminated or organic-rich environments may be “squeezed out” of aqueous solution, suggesting that the effects might be a common characteristic of certain

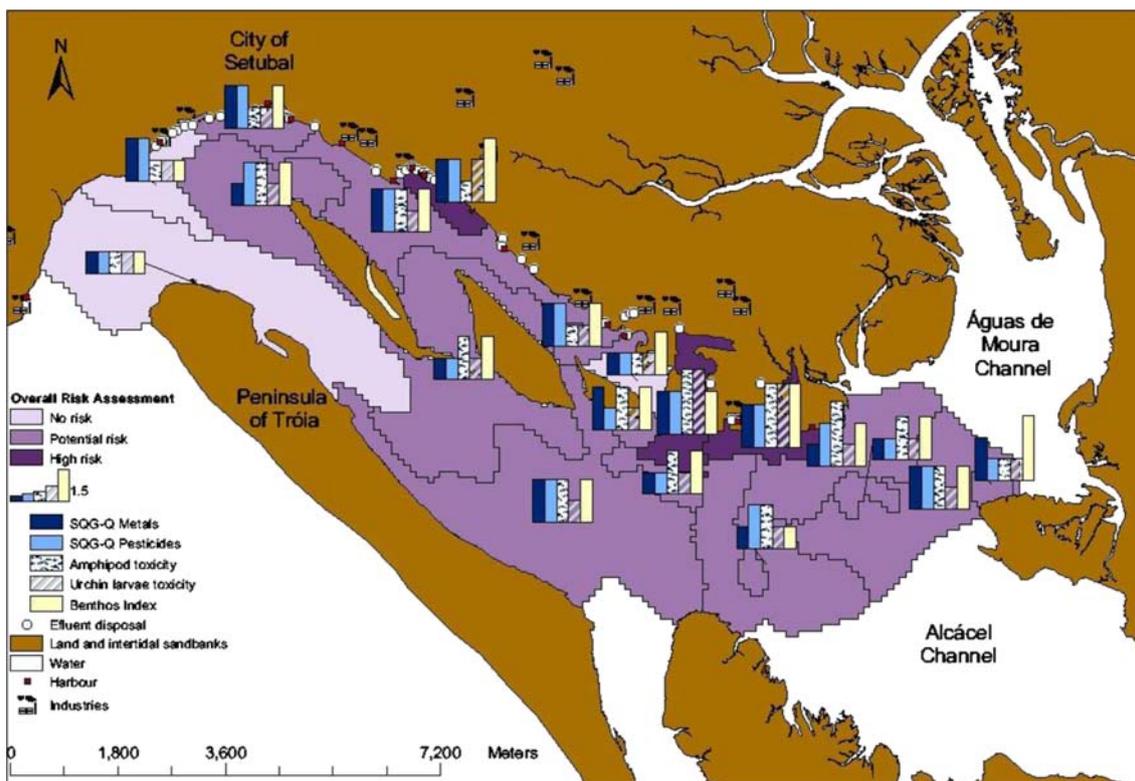


Fig. 3 Overall ecological risk assessment and LOE scores for each management area, according to Table 2-support information. Industries adapted from Araujo et al. (2002), effluents disposal from Correia and Florêncio (2002) and harbours from APSS 2003

**Table 2** Tabular matrix with the SQT LOE for 4 of the 19 management areas

Management areas/Triad components	Chemistry		Toxicity		<i>In situ</i> alteration		Management area type	Main Driving Forces/Pressures	Pressure components (potential pollutants)	Overall risks assessment	Explanation/contamination of concern
	Metals and metaloids	Pesticides	Amphipod mortality	Urchin abn. larvae	Biotic Index						
HO1							Stable	<ul style="list-style-type: none"> <li>Urban (city of Setúbal) sewages and harbors</li> </ul>	<ul style="list-style-type: none"> <li>•BOD, COD, SS, Nutrients, FOG, HC, acids, pathogens</li> </ul>		<ul style="list-style-type: none"> <li>• Potential significant adverse effects (benthos alteration) caused by heavy metals and metalloid and δ-BHC.</li> </ul>
HO2							Stable	<ul style="list-style-type: none"> <li>• Urban (city of Setúbal) Industrial (Ferments, pyrites, power plant) TBT pathogens and harbors</li> </ul>	<ul style="list-style-type: none"> <li>•BOD, COD, SS, Nutrients, FOG, HC, acids and bases, TBT pathogens</li> </ul>		<ul style="list-style-type: none"> <li>• High significant adverse effects (toxic and benthos alteration) caused by heavy metals and metalloid (Cd, Cu, and As exceed PEL levels) and δ-BHC. Higher concentration of α-BHC. Toxicity more associates with soluble compounds.</li> </ul>
LO1							Unstable	<ul style="list-style-type: none"> <li>• Tourism, harbour</li> </ul>	<ul style="list-style-type: none"> <li>•FOG, HC, metals, acids, pathogens, TBT, COD</li> </ul>		<ul style="list-style-type: none"> <li>• This sediment does not present a risk. Reference area. Although with some pressure near the harbour this is a big area with high hydrodynamic with direct contact with the ocean, with no industrial pressure.</li> </ul>
MHO3							Medium stable	<ul style="list-style-type: none"> <li>• Tourism, military harbor, Non-point source (rice-fields and agriculture) and contamination from sediment transport. It is inside the RNES</li> </ul>	<ul style="list-style-type: none"> <li>•Pesticides, nutrients, FOG, HC, metals, acids, pathogens, BOD, COD, TBT, SS</li> </ul>		<ul style="list-style-type: none"> <li>• Potential significant adverse effects (toxic and benthos alteration) caused by unmeasured chemicals. Higher concentration of endosulfan I and II, but maybe not bioavailable. Further chemical investigations are needed.</li> </ul>

*BOD* biological oxygen demand, *COD* chemical oxygen demand, *Nut.* nutrients, *SS* total suspended solids, *PAH* polynuclear aromatic hydrocarbons, *PCB* polychlorinated biphenyls, *TBT* tributyltin, *FOG* fat, oil and grease, *HC* hydrocarbons. Complete tabular matrix in Supplementary Materials—Table A2

metals in the presence of a specific pool of organic ligands. These facts can explain the low association between the metals and the elutriate sediment bioassay. However, the meaning of interactions between sediment-bound metals and sediment-ingesting organism remains to be determined and further analysis of hazard identification, exposure, effects and risk characterization should be conducted for a correct ecological risk assessment (Chapman et al. 2003).

As noticed by the FA interpretation, the different organochlorine pesticides have shown different behaviors and were found in different areas. From the 14 pesticides analyzed the ones of highest concern in the study area are the DDT and its metabolites, and BHC isomers. Also the pesticides heptachlor and heptachlor epoxid, isodrin, endosulfan II and endrin were associated with levels of toxicity. For some of these pesticides there aren't available PEL values, what makes it difficult to determine their adverse effect evaluation. Nevertheless these pesticides are used as insecticides usually in crops like rice and other cereal and vegetables (Laws 1993), and are considered dangerous substances due to their toxicity, persistence and bioaccumulation, particularly of fish (Donze et al. 1990).

The concentrations of the pesticides, p,p'-DDE, p,p'-DDD and p,p' DDT were all below PEL levels but associations with toxicity levels and biotic index were found what could be related with synergetic effects.

The areas where the pesticides associated with toxicity were found are mainly on the North Channel or at the entrance of Águas de Moura (Fig. 3). Their presence and deposition can be not only associated with the sediment transport from the rice-fields (e.g., lindane (BHC isomer) is used in rice-field crops in the Sado watershed—Pereira 2003), the aquacultures and other agriculture crops but also from atmospheric deposition, non farm use or incidental release from chemical manufacturing plants (Nowell et al. 1999; like fertilize and pesticide industry located near management area MHO2).

From the 19 management areas analyzed three didn't present any ecological risk (18.5% of the study area). The areas of more concern are only 5.6% of the study area (Fig. 3). These areas of high or medium high organic load are located in the North Channel and suffer high human pressure mainly because of industrial activities. In particular the areas HO5 and MHO5 can also accumulate the contamination coming from Águas de Moura Channel, since particles coming from that channel can settle near Lisnave and Eurominas industries due to residual flow (hydrodynamics according to Neves 1985). These areas have also low hydrodynamics, thus are associated with high levels of deposition. In addition they are just located near the limit of the Natural Reserve. In these areas the contaminants of concern, from the ones analyzed, are the metals and metalloids, in particular Cd, Cu, Zn and As exceeded the PEL

guidelines, and the pesticides BHC isomers, heptachlor, isodrin, DDT and metabolites, endosulfan II and endrin.

In some management areas classified with potential risk assessment, adverse biological effects were detected, however they were not related with the contaminants analyzed. Further chemical analysis should be conducted to measure other contaminants (e.g., PAH, PCB, TBT, other pesticides, emerging pollutants like pharmaceuticals). PAH and PCB are released in to the marine environment through several human activities and are a threat to human health, namely PAH are well known to be carcinogens and mutagens (Cardellicchio et al. 2007). However, the quantification of these pollutants were not possible due to technical laboratory problems. Also other geochemical features such as the ammonia and sulfide contents in sediment, the contaminate-binding capacity of acid volatile sulphide and total organic carbon can affect the toxicity results (Nipper 2000).

Sampling and analytical processes may alter sediment chemistry and bioavailability. Assessment tools provide useful information, but some (like SQGs, laboratory toxicity and benthic indices) are prone to distortion without the availability of specific in situ exposure and effect data (Pekey et al. 2004). Other LOE can be used like field toxicity (e.g., Nipper 2000), "in situ" alteration (e.g., Riba et al. 2004) or biomarkers or more complete studies of bioavailability (e.g., Costa et al., in press). Although implementation and interpretation of these LOE are still complex and expensive they could be measured only at locations with chemicals of concern. WOE methods should in future contribute to further improvements to this integrated approach to the characterization of environmental quality in highly dynamic systems like estuaries.

Due to the ecological importance and the persistence of pollutants in sediments, it is appropriate to monitor this compartment in environmental evaluations and to conduct sediment ecological risk assessment studies. Interpretative tools and multiple approached are required to determine if sediment-associated contaminants are present at concentrations which could potentially, impair the designated uses of the aquatic environment (Riba et al. 2004; Cardellicchio et al. 2007; Zhang et al. 2007).

This work integrated different methodologies of LOE for sediment quality assessment using already published and new chemical (organic pesticides) and toxicological data. The latest statistics methods for WOE to assess sediment quality were used and human activities, their pressures and sediment stability were added into the tabular decision matrix to complement the statistical analysis as BPJ, supporting the definition of future management recommendation. GIS and spatial analysis tools characterizing management areas and not isolated points also helped the overall estuarine sediment risk assessment integrating stressors and adverse effects in the ecosystem and

visualizing it in an understanding way for decision-makers. Easily-understood representations of results permit easier interpretation in comparison with presenting the results of complicated statistical techniques. Although integrative assessment methods is both time and money consuming, it presents some strengths that render it extremely cost effective for the level of information provide in evaluating sediment adverse potential to cause ecological adverse effects in estuarine environments. Providing managers with a defensible science-based recommendation in which they can be confident is crucial to moving to risk management decisions when factors beyond science have to be considered (Grapentine et al. 2002). Nevertheless the innovative integration of the different tools used in this study can contribute to the ecological risk assessment associated with estuarine contaminated sediments, and can be developed in other ecosystems.

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## References

- American Society for Testing and Material – ASTM (1993) Standard guide for conducting 10-day static sediment toxicity testes with marine and estuarine amphipods. E 1367–92, Vol. 11.04. Annual Book of ASTM Standard, ASTM, Philadelphia, PA, pp 1138–1163
- APSS (2003) Porto de Setúbal. Available via <http://www.portodese.tubal.pt/foto/FOTOS/Fotos.htm>. Accessed 20 February 2003
- Araujo R, Vasconcelos L, Painho M (2002) SADIND-Sistema de Visualização Interpretativa para a Gestão Ambiental do Estuário do Sado. *Biologia* 20:97–107
- Burton GA, Batley EG, Chapman PM, Forbes VE, Smith EP, Reynoldson T, Schlegel CE, Besten PJ, Bailer AJ, Green AS, Dwyer RLA (2002a) Weight-of-evidence framework for assessing sediment (or other) contamination: improving certainty in the decision-making process. *Hum Ecol Risk Assess* 8:1675–1696
- Burton GA, Chapman PM, Smith EP (2002b) Weight-of-evidence approaches for assessing ecosystem impairment. *Hum Ecol Risk Assess* 8:1657–1673
- Caeiro S, Goovaerts P, Painho M, Costa MH (2003a) Delineation of estuarine management areas using multivariate geostatistics: the case of Sado estuary. *Environ Sci Technol* 37:4052–4059
- Caeiro S, Nunes LM, Goovaerts P, Painho M, Costa MH (2003b) Optimization of sediment estuarine monitoring program using contamination data. In: Proceedings of Fifth International Symposium on GIS and Computer Cartography for Coastal Zone Management. GISIG- Geographical Information System International Group and International Center of Coastal and Ocean Policy Studies. Genova, Italy, pp 1–9
- Caeiro S, Mourão I, Costa MH, Painho M, Ramos TB, Sousa S (2004a) Application of the DPSIR model to the Sado Estuary in a GIS context—social and economical pressures. In: Toppen F, Prastacos P (eds) Proceedings of 7th Conference on Geographic Information Science. Crete University Press. AGILE, Crete, pp 391–402
- Caeiro S, Nunes L, Goovaerts P, Costa MH, Cunha MC, Painho M, Ribeiro L (2004b) Optimization of an estuarine monitoring program: selecting the best spatial distribution. In: Soares A, Gomez-Hernandez J, Froidevaux R (eds) *GeoENV IV Geostatistical for Environmental Applications*. Kluwer Academic Press, Dordrecht, pp 355–366
- Caeiro S, Costa MH, Ramos TB, Fernandes F, Silveira N, Coimbra AP, Medeiros G, Painho M (2005a) Assessing sediment heavy metals contamination in Sado Estuary: a index analysis approach. *Ecol Indic* 5:151–169
- Caeiro S, Costa MH, Goovaerts P, Martins F (2005b) Benthic biotope index for classifying habitats in the Sado Estuary: Portugal. *Mar Environ Res* 60(5):570–593
- Cardellicchio N, Buccolieri A, Giandomenico S, Lopez L, Pizzulli F, Spada L (2007) Organic pollutants (PAHs, PCBs) in sediment from the Mar Piccolo in Taranto (Ionian Sea, Southern Italy). *Mar Pollut Bull* 55:451–458
- Cesar A, Choueri RB, Riba I, Morales-Caselles C, Pereira CDS, Santos AR, Abessa DMS, DelValls TAA (2007) Comparative sediment quality assessment in different littoral ecosystems from Spain (Gulf of Cadiz and Brazil (Santos and São Vicente estuarine system)). *Environ Int* 33:429–435
- Chapman PM, McDonald BG, Lawrence GS (2002) Weight-of-evidence issues and frameworks for sediment quality (and other) assessments (2002). *Hum Ecol Risk Assess* 8:1489–1515
- Chapman PM, Wang F, Janssen CR, Goulet RR, Kamunde CN (2003) Conducting ecological risk assessments of inorganic metals and metalloids: current status. *Hum Ecol Risk Assess* 9:641–697
- Correia R, Florêncio M (2002) Estudo da Sensibilidade Ambiental do Estuário do Sado face às actividades antropogénicas nele desenvolvidas. Trabalho de Projecto da Licenciatura em Engenharia do Ambiente. Escola Superior de Tecnologia de Setúbal. Instituto Politécnico de Setúbal. Setúbal, Portugal
- Costa FO, Correia AD, Costa MH (1998) Acute marine sediment toxicity: a potential new test with the Amphipod *Gammarus locusta*. *Ecotoxicol Environ Saf* 40:81–87
- Costa PM, Caeiro S, Diniz MS, Lobo J, Martins M, Ferreira AM, Caetano M, Vale C, DelValls TA, Costa MH (in press) Biochemical endpoints on juvenile *Solea senegalensis* exposed to estuarine sediments: the effect of contaminant mixtures on metallothionein and CYP1A induction. *Ecotoxicology*. doi: 10.1007/s10646-009-0373-7
- Donze M, Nieuwendijk C, Boxel A, Quak M (1990) Shaping the Environment: Aquatic Pollution and Dredging in the European Community. Delwel Publishers Hague, The Netherlands
- Grapentine L, Anderson J, Boyd D, Burton A, DeBarros C, Johnson G, Marvin C, Milani D, Painter S, Pascoe T, Reynoldson T, Richman L, Solomon K, Chapman PM (2002) A decision making framework for sediment assessment developed for the great lakes. *Hum Ecol Risk Assess* 8:1641–1655
- Laws EA (1993) *Aquatic Pollution*. Wiley, USA
- Long ER, Chapman PM (1985) A sediment quality triad: measures of sediment contamination, toxicity and infaunal community composition in puget sound. *Mar Pollut Bull* 16:405–415
- Long ER, MacDonald DD (1998) Recommended uses of empirically derived, sediment quality guidelines for marine and estuarine ecosystems. *Hum Ecol Risk Assess* 4:1019–1039
- Macdonald D, Carr S, Clader FD, Long ED, Ingersoll CG (1996) Development and evaluation of sediment quality guidelines for Florida coastal waters. *Ecotoxicology* 5:253–278
- MacDonald DD, Lindskoog RA, Smorong DE, Greening H, Pribble R, Janicki T, Janicki S, Grabe S, Sloane G, Ingersoll CG, Eckenrod S, Long ER (2000) Development of an Ecosystem-Based Framework for Assessing and Managing Sediment

- Quality Conditions in Tampa Bay, Florida. Tampa Bay Estuary Program, Florida
- Neves RJJ (1985) Biodimensional model for residual circulation in coastal zones: application to the Sado Estuary. *Ann Geophys* 3:465–472
- Nipper M (2000) Current approaches and future direction for contaminant-related impact assessment in coastal environments: Brazilian perspective. *Aquat Ecosyst Health Manag* 3:433–447
- Nowell LH, Capel PD, Dileanis PD (1999) Pesticides in Stream Sediments and Aquatic Biota - Distribution, Trends and Governing Factors. CRC Press, Boca Raton Pesticides in the Hydrological System series
- Pekey H, Karakas D, Ayberk S, Tolun L, Bakoglu M (2004) Ecological risk assessment using trace elements from surface sediments of Izmit Bay (Northeastern Marmara Sea) Turkey. *Mar Pollut Bull* 48(9–10):946–953
- Pereira TPM (2003) Impacte da Utilização de Pesticidas em Ecosistemas Orizícolas sobre a Qualidade de Águas superficiais. Doctoral Thesis. Universidade Técnicas de Lisboa. Instituto Superior de Agronomia, Lisbon
- Quevauviller P, Lavigne R, Cortez L (1989) Impact of industrial and mine drainage wastes on the heavy metal distribution in the drainage basin and Estuary of the Sado River (Portugal). *Environ Pollut* 59:267–286
- Riba I, Forja J, Gómez-Parra A, DelValls A (2004) Sediment quality in littoral regions of the Gulf of Cádiz: a triad approach to address the influence of mining activities. *Environ Pollut* 132:341–353
- Rolland G, Guedes L, Quintino V (1999) Comparative toxicity of experimental effluent eucalyptus pulp kraft bleaching. *Ecotoxicol Environ Restor* 2:19–25
- RIVM (1995) General Strategy for Integrated Environmental Assessment at the European Environmental Agency. The Netherlands National Institute of Public Health and Environmental Protection, Bilthoven
- Turner A, Martino M, Roux SM (2002) Trace metals distribution coefficients in the Mersey Estuary, UK: evidence for salting out of metals complexes. *Environ Sci Technol* 36:4578–4584
- Wenning RJ, Batley GE, Ingersoll CG, Moore DW (eds) (2005) Use of sediment quality guidelines and related tools for the assessment of contaminated sediments. SETAC Press, USA
- Zhang L, Xin Y, Feng H, Jing Y, Ouyang T, Xingtian Y, Liang R, Gao C, Chen W (2007) Heavy metal contamination in western Xiamen Bay sediments and its vicinity, China. *Mar Pollut Bull* 54:974–982