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Development of site-specific sediment quality guidelines for North and South Atlantic littoral zones: Comparison against national and international sediment quality benchmarks

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ABSTRACT

We aimed to develop site-specific sediment quality guidelines (SQGs) for two estuarine and port zones in Southeastern Brazil (Santos Estuarine System and Paranaguá Estuarine System) and three in Southern Spain (Ría of Huelva, Bay of Cádiz, and Bay of Algeciras), and compare these values against national and traditionally used international benchmark values. Site-specific SQGs were derived based on sediment physical–chemical, toxicological, and benthic community data integrated through multivariate analysis. This technique allowed the identification of chemicals of concern and the establishment of effects range correlatively to individual concentrations of contaminants for each site of study. The results revealed that sediments from Santos channel, as well as inner portions of the SES, are considered *highly polluted* (exceeding SQGs-high) by metals, PAHs and PCBs. High pollution by PAHs and some metals was found in São Vicente channel. In PES, sediments from inner portions (proximities of the Ponta do Félix port's terminal and the Port of Paranaguá) are *highly polluted* by metals and PAHs, including one zone inside the limits of an environmental protection area. In Gulf of Cádiz, SQGs exceedences were found in Ria of Huelva (all analysed metals and PAHs), in the surroundings of the Port of Cádiz (Bay of Cádiz) (metals), and in Bay of Algeciras (Ni and PAHs). The site-specific SQGs derived in this study are more restricted than national SQGs applied in Brazil and Spain, as well as international guidelines. This finding confirms the importance of the development of site-specific SQGs to support the characterisation of sediments and dredged material. The use of the same methodology to derive SQGs in Brazilian and Spanish port zones confirmed the applicability of this technique with an international scope and provided a harmonised methodology for site-specific SQGs derivation.

1. Introduction

Dredging activities can cause several negative impacts to the aquatic ecosystems, such as the elimination of benthic habitats and resuspension of nutrients and contaminants. Special concern arises on the disposal of the dredged material; the simple discharge in marine waters implies several environmental consequences, including physical disturbance (burrowing, smothering) of benthic communities [1] and chemical contamination [2].

There are different options to deal with dredged material, which include [3,4]: (i) beneficial uses—land creation and improvement, beach nourishment, agricultural uses, wetlands restoration, creation of nesting islands, etc.; (ii) disposal in ocean or continental waters; (iii) treatment, such as the separation of sediment contaminated fractions; and (iv) discharge into confined disposal facilities. The selection of the best management option is in a great extent dependent on the quality of the dredged material. Therefore, a reliable assessment of the sediments to be dredged is needed to assure that the disposal of such material will be environmentally harmless as well as cost-effective.

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Despite experts have been claiming that the use of biological testing is crucial to adequately understand the hazard posed by contaminated sediments [5–7], decision-making on the management of dredged materials commonly relies on a simple comparison between levels of contaminants measured in the sediments against national sediment quality criteria or classical sediment quality guidelines (SQGs) (e.g. effects range-low and effects range-median – ERL and ERM; threshold effect level and probable effects level – TEL and PEL).

The SQGs provide a basis to identify the concentrations of chemicals that can potentially cause adverse biological effects [8]. Nevertheless, the bulk concentrations of contaminants may not correlate well to the bioavailability [9] inasmuch as several factors affect the availability of contaminants from sediments to the biota (and consequently the toxicity), such as sediment grain size, pH, salinity, organic matter content, acid volatile sulfides (AVS) contents, among others [10–13]. Consequently, national guidelines, which are intended to predict toxic effects of contaminant levels for different environments and sediment types, may not suitably address the specificities of each local and situation in national and wide geographic areas. In the other hand, sediment quality guidelines derived based on site-specific data is able to better predict the toxicity of contaminants in each specific coastal environment.

The development of the SQGs can be performed by employing different approaches, which can be divided in the two broad categories [14]: (i) mechanistically or theoretically, based on theoretical understanding of the partitioning of chemicals in the sediments and the toxicity of the dissolved contaminants in the interstitial water (e.g. equilibrium partitioning – EqP [15]); (ii) empirically based, derived from databases of concentrations of specific contaminants and their correspondence with observed biological effects (e.g. ERL and ERM [16,17]; TEL and PEL [18]; apparent effects thresholds – AET [19]). Besides, a third approach, so-called “consensus approaches”, was developed recently with the attempt of providing a synthesis of multiple guidelines into a single SQG or a range of SQGs [14], mainly focused on polycyclic aromatic hydrocarbons [20] and polychlorinated biphenyls [21].

In Brazil, sediment quality criteria to orientate dredged material management are given by the Resolution no. 344/2004 from the National Council for the Environment – CONAMA [22]. Such values were established based on the American and Canadian SQGs [23–25]. In Spain, the document *Recommendations for the management of dredged material in ports of Spain* [26] proposes sediment quality guidelines based on geochemical considerations [27] and it has been applied in the characterisation of the sediments dredged in Spanish ports; however, this document does not establish statutory contaminant concentration limits.

The aim of this work was to develop site-specific SQGs through the integration of sediment physical, chemical, ecotoxicological, and macrobenthic invertebrate community data using multivariate analysis for two estuarine and port zones in Southeastern Brazil (Santos Estuarine System and Paranaguá Estuarine System) and three in Gulf of Cádiz, Southern Spain (Ría of Huelva, Bay of Cádiz, and Bay of Algeciras), and compare these values against national and traditionally used international benchmark values. The areas under study are ecologically important and they are affected by different sources of pollution, such as domestic sewage, industrial effluents, urban runoff, as well as contamination due to the port activities [5,28–30]. The establishment of site-specific ranges of contaminants concentrations related to biological responses (ecological and toxicological) will better subsidise the management of the dredged material in the studied zones and the comparison of site-specific SQGs against general SQGs gives an insight into the adequacy of the use of national criteria or international guidelines for assessing dredged material and sediment quality in different coastal environments in South and North Atlantic. Furthermore, the use of the same method to derive SQGs for Brazilian and Spanish port zones aimed to assess the viability of application of this technique with an international scope and providing an internationally harmonised methodology for site-specific SQGs derivation.

2. Material and methods

2.1. Approach

In this study, site-specific sediment quality guidelines were derived for two areas in Southeastern Brazil: Santos Estuarine System (SES) and Paranaguá Estuarine System (PES) (Fig. 1a and b); and three areas in Gulf of Cádiz (GC), Southern Spain: Ría of Huelva, Bay of Cádiz, and Bay of Algeciras (Fig. 2a–c).

All areas of study present prominent port activities besides ecologically important ecosystems (especially mangroves and Atlantic Rainforest in Brazil and salt marshes in Spain). In SES, dense industrialisation and urbanisation has affected the quality of the environment, as reported before [5,31–36]. In PES, the major environmental threats are port activities, uncontrolled landfills, untreated domestic sewage as well as agricultural practices. Among Spanish areas, previous studies reported that Ría of Huelva is heavily contaminated mainly by industrial and mining activities [5,29,37]; in Bay of Cádiz, despite the presence of activities such as shipyard industry, industrial aquaculture as well as the urban concentration, previous studies revealed that sediments from the bay are not toxic. However, some contamination (PCBs) was found in the vicinities of the Port of Cádiz [5]. The Port of Algeciras is the most important Spanish port, situated in Bay of Algeciras, at the estuary of the Guadarranque River. The stream receives the discharges of industrial effluents from Algecira’s petrochemical industrial complex. Previous investigations reported high sediment toxicity caused by metals and PAHs in this zone [5,38].

The matrices of data for SQGs derivation included sediment physical–chemical characteristics (granulometry, levels of metals and organic contaminants), toxicity (elutriates, sediment–water interface and whole sediment) and benthic community structure information of each area of study. In SES, data from thirty one sampling stations were utilised (Fig. 1a); in PES, five sampling stations were set (Fig. 1b); in GC, three sampling stations were located at Ría of Huelva (Fig. 2a), two at Bay of Cádiz (Fig. 2b), and three at Bay of Algeciras (Fig. 2c). Details of sediment and benthic macrofauna sampling, analytical procedures, methodology employed for the toxicity tests, and quality assurance/quality control procedures were described in Cesar et al. [5], Choueri et al. [28], and Abessa et al. [39].

2.2. Multivariate analysis

The integration of different Lines-of-Evidence was performed by means of a Factor Analysis, with the application of Principal Component Analysis (PCA) (Varimax normalised rotation) as an extraction procedure. This methodology establishes and quantifies the correlations among the variables in the original data set in order to reduce the number of variables to a smaller set of components and therefore making easier the interpretation of the data [40].

Two different data sets (SES ‘a’ and SES ‘b’) were used to derive SQGs for Santos Estuarine System and PCA was applied individually in each of the original data matrix. Thus, some contaminants’ SQGs are duplicated for this area. The following variables were integrated in the analyses: (i) SES ‘a’—number of species (S), density of organisms (N), Margaleff’s richness (R), Pielou’ evenness (J'), Shannon’s diversity (H'), and Simpson’s dominance (D) values, concentrations of Cu, Ni, Pb, V, Zn, PAHs, and PCBs, total organic carbon (TOC), % of fines, and amphipods mortality (%). Concentrations of Cd and Co were measured but not included in the PCA because their concen-

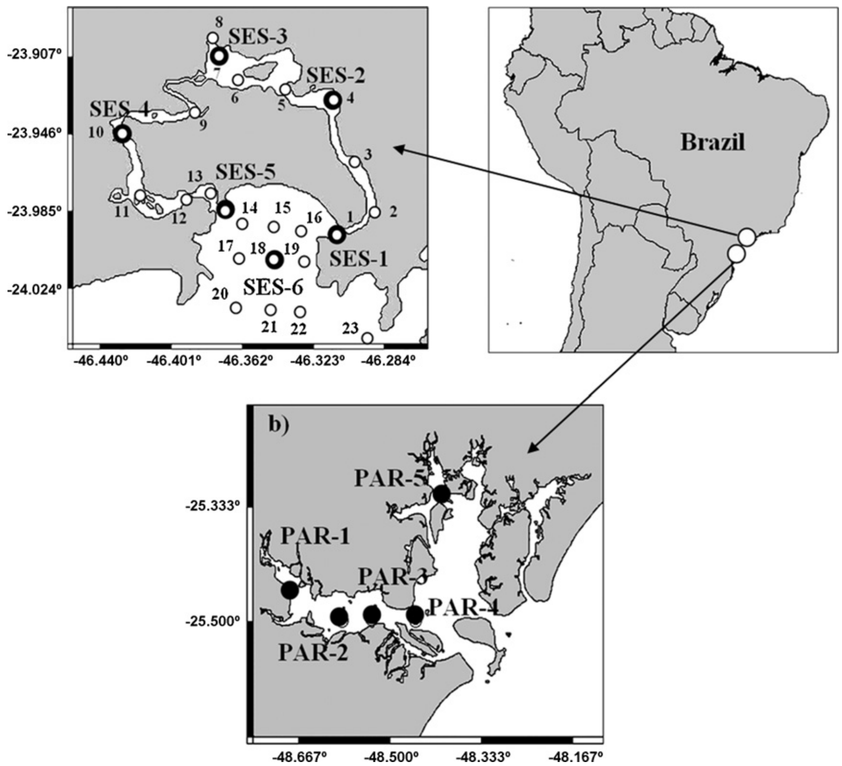

Fig. 1. Localisation of the sampling stations in (a) Santos Estuarine System (black circles represent sampling stations of Cesar et al. [5]; white circles represent sampling stations of Abessa et al. [39]) and (b) Paranaguá Estuarine System and their disposition in Southeastern Brazil.

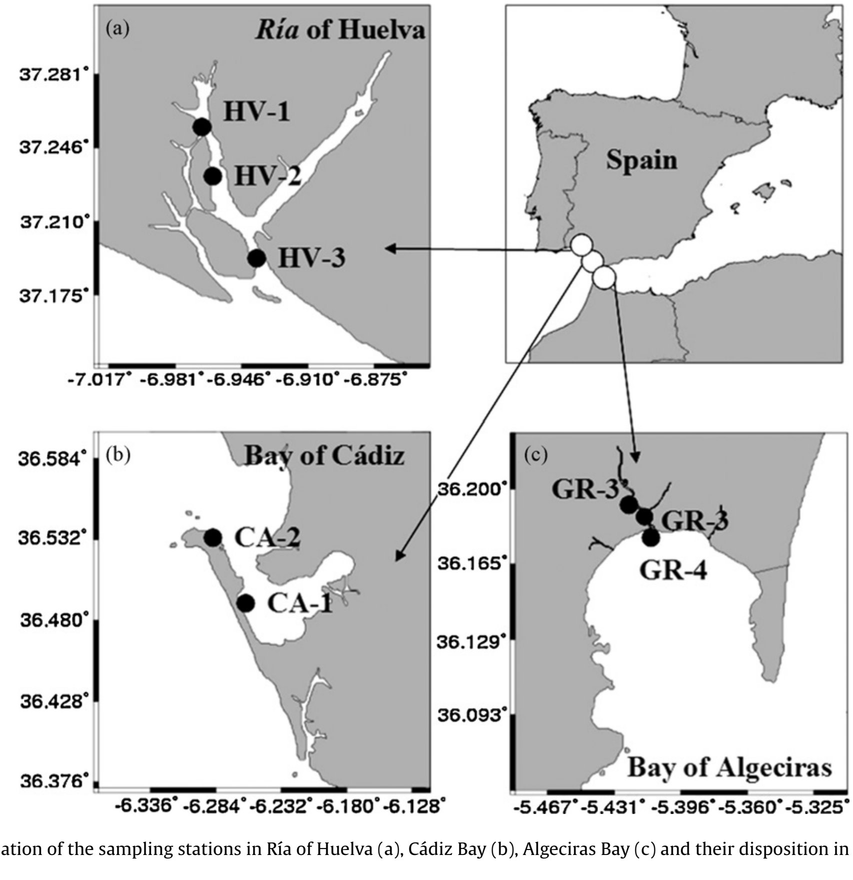

Fig. 2. Localisation of the sampling stations in Ría of Huelva (a), Cádiz Bay (b), Algeciras Bay (c) and their disposition in Southern Spain.

trations were below the limit of quantification (LQ) of the method and (ii) SES ‘b’—S, N, R, J', H', and D values, levels of Cd, Co, Cr, Ni, Pb, Hg, Zn, and PAHs, % of OC, % of fines, and amphipods mortality (%). For PES, data included in the PCA analysis were the benthic community descriptors cited above, concentrations of As, Cr, Cu, Ni, Pb, Zn, PAHs, PCBs, TOC, % of fines, % of abnormal embryo-larval development of sea-urchin exposed to sediment elutriates and SWI, and amphipods mortality (%). Levels of Ag, Cd, and Se were not detected in the chemical analysis of the sediments and hence such contaminants were not included in the PCA. Gulf of Cádiz’s original dataset for the PCA analysis comprised: the set of benthic community descriptors used in this work, concentrations of Cd, Co, Cu, Ni, Pb, V, Zn, PAHs, PCBs, TOC, % of fines, % of abnormal embryo-larval development of sea-urchin exposed to sediment elutriates and SWI, and % of amphipods mortality. For all four data matrices the values of benthic community descriptors were transformed as the inverse (i.e. multiplied by -1) in order to show an increase with increasing environmental alteration.

The Factor Analyses were performed on the correlation matrix, i.e. the variables were auto-scaled (standardised) so as to be treated as of equal importance (varimax normalised). The sorted rotated factor loadings which arose from the Factor Analysis consisted of coefficients correlating the original variables and the principal factors. The selected variables to be interpreted were those associated with a factor loading ≥ 0.38 [41]. The analyses were performed using the PCA option of the “Multivariate Exploratory Techniques” procedure, followed by the basic set-up for “Factor Analysis” procedure from the STATISTICA software tool (Stat Soft, Inc. 2001; version 6).

2.3. Development of SQGs

The SQGs derived in this study yield two thresholds, termed “SQG-low” and “SQG-high”. Chemical concentrations lower than SQG-low were considered not harmful to aquatic biota; thus, sediments bearing chemicals below such level is considered as *not polluted*. In the other hand, the concentrations of contaminants above SQG-high are potentially harmful to the ecosystem; whether sediments present chemical levels higher than this level, then it is considered as *polluted* by these contaminants. Lastly, biological responses are not predictable in the concentration range in between these two thresholds (“uncertainty area”)—sediments containing contaminants levels which fall into this interval are considered as *moderately polluted*.

The calculation of SQGs followed the methodology presented in DelValls and Chapman [42] slightly modified. Basically, chemical concentrations associated to biological effects were established by identifying correlations among sediment chemical concentrations, toxicity endpoints, and benthic community descriptors through the application of Factor Analysis followed by PCA. Chemicals significantly correlated to biological effects were considered chemicals of concern and SQGs were derived for these contaminants. Besides, the calculation of the prevalence of factors (factor scores) for each station in relation to all stations allowed us to detect in what stations the correlation between biological effects and contaminants is significant. This was important because the SQG-high of a given chemical of concern was determined by identifying its minimal measured concentration in the station where the factor (or factors) that associates this particular chemical as well as biological effects is relevant; above SQG-high all concentrations were related to negative biological effects in this study. The SQG-low of a chemical of concern was established through the identification of its highest measured concentration in the stations where the significant factors are not related to biological effects; below SQG-low, biological effects were not observed in this study. The “uncertainty area” (chemical levels in between SQGs-high and SQGs-low) included a range of concentrations in which biological effects were observed in some instances, and other instances were not. For a better understanding of the derivation process, a hypothetical case is presented: chemical “X” is significantly associated with a biological effect (toxicity or benthic community impairment) in the first factor (F1); to simplify the explanation, “X” is not associated to any other factor. The calculation of prevalence of factors showed that F1 is prevalent in stations “A” and “B”. Thus, SQG-high for “X” will be its lowest concentration considering only stations “A” and “B”. SQG-low for “X” will be its highest concentration among the other stations (excluding A and B).

3. Results

3.1. Sediment physical–chemical characteristics, toxicity and benthic community structure data

Results of sediment physical–chemical and toxicity data are summarised in Appendix A.

Detailed description of chemical, toxicity and benthic community results were previously reported in Cesar et al. [5], Choueri et al. [28], and Abessa et al. [39]. In general for Brazilian and Spanish areas, higher sediment contamination and toxicity were found at inner parts of the estuaries as well as associated to contamination sources (urban sewage outfall, industrial areas, ports). Among GC areas, the highest sediment toxicity was found in Ría of Huelva (together with the highest metals concentrations), followed by Bay of Algeciras (with higher levels of PAHs). Both in Southeastern Brazilian and Gulf of Cádiz estuaries, benthic community presented low species richness, diversity, evenness, and high Simpson’s dominance, with a gradient of impoverishment of benthic communities from outer towards inner estuaries.

3.2. Multivariate analysis

The use of the PCA and the Factor Analysis on the SES ‘a’ data matrix rearranged the set of original data in three new factors, which together explained 86.11% of the total variance (Table 1).

The predominant factor (F1) accounted for 42.50% of the variance and grouped Cu, V, PAHs, amphipods’ mortality, and macrobenthic’s number of species, Margaleff’s species richness, Pielou’s evenness, Shannon’s diversity, and Simpson’s dominance. Therefore, F1 showed the significant correlation between biological effects (toxicity and benthic community alteration) and some chemicals (vanadium and PAHs with higher loadings, and some

Table 1
Sorted rotated factor loadings of the original 16 variables on the three principal factors of the SES (a) sampling stations. Only loadings greater than 0.38 are shown. The variance of the principal factors is given in percentage of the total variance in the original data matrix.

Variable	Factor 1	Factor 2	Factor 3
% Variance	42.50	24.66	18.95
Cu	0.38	0.89	–
Ni	–	−0.70	0.55
Pb	–	0.95	–
V	0.90	–	–
Zn	–	0.95	–
PAHs	0.78	–	–
PCBs	–	0.98	–
TOC	–	–	−0.39
Fines	–	–	0.90
Amphipods’ mortality	0.73	0.44	0.40
S	0.86	–	0.47
N	–	–	0.90
R	0.92	–	–
J'	0.76	–	−0.58
H'	0.99	–	–
D	0.97	–	–

Table 2

Sorted rotated factor loadings of the original 17 variables on the three principal factors of the SES (b) sampling stations. Only loadings greater than 0.38 are shown. The variance of the principal factors is given in percentage of the total variance in the original data matrix.

Variable % Variance	Factor 1 37.49	Factor 2 19.52	Factor 3 10.91
Cd	0.57	–	–
Co	0.90	–	–
Cr	0.87	–	–
Ni	0.92	–	–
Pb	0.55	–	0.45
Hg	0.81	–	–
Zn	0.87	–	–
PAHs	0.75	–	–
TOC	0.53	–	–
Fines	0.64	–	–
Amphipods' mortality	0.57	–	–
S	–	0.94	–
N	–	–	−0.65
R	–	0.96	–
J'	–	0.54	0.63
H'	–	0.91	–
D	–	–	0.81

Table 3

Sorted rotated factor loadings of the original 20 variables on the three principal factors of the PES sampling stations. Only loadings greater than 0.38 are shown. The variance of the principal factors is given in percentage of the total variance in the original data matrix.

Variable % Variance	Factor 1 79.84	Factor 2 10.41	Factor 3 7.30
As	0.69	0.62	0.37
Cr	–	0.87	0.41
Cu	0.66	–	0.71
Ni	–	0.87	0.38
Pb	0.45	0.82	–
Zn	0.45	0.72	0.52
Hg	0.81	0.55	–
PAHs	0.94	–	–
PCBs	–	−0.88	–
TOC	0.56	0.45	0.70
Fines	0.64	–	0.68
Abnormal sea-urchin (elutriates)	–	–	0.91
Abnormal sea-urchin (SWI)	–	–	0.93
Amphipods' mortality	–	0.46	0.86
S	0.55	0.64	0.53
N	0.58	0.66	0.46
R	0.54	0.59	0.59
J'	0.55	0.36	0.72
H'	0.55	0.51	0.65
D	0.54	0.39	0.71

contribution of copper, with lower loading). Second factor (F2) explained 24.66% of the variance and showed correlations of Cu, Pb, Zn, PCBs, amphipods mortality, and Ni with negative values. Consequently, F2 indicated significant association between some contaminants (metals and PCBs) and sediment toxicity. The third factor (F3) accounted for 18.95% of the total variance and showed loadings higher than 0.38 for Ni, percentage of fines, amphipods mortality, number of species and abundance of individuals; this factor represented toxicity and some benthic community alteration correlated mainly to the fine characteristics of the sediments (higher loading) and levels of nickel. In summary, the contaminants of concern identified in SES 'a' data matrix, i.e. those chemicals related to toxicity and/or degradation on benthic community structure, were copper, nickel, lead, vanadium, zinc, PAHs, and PCBs.

The rearrangement of the variables of the matrix SES 'b', through the application of the PCA and the Factor Analysis resulted in three factors, which together accounted for 67.92% of the variance in the original data set (Table 2).

The first factor (F1) explained 37.49% of the variance and grouped metals (Cd, Co, Cr, Ni, Pb, Hg, Zn), PAHs, TOC, fines, and amphipods' mortality. This factor demonstrates the significant correlation between sediments toxicity, levels of all analysed contaminants (metals and PAHs), as well as organic carbon content and finer characteristics of the sediments. Factor 2 described 19.52% of the variance and showed the relationship among benthic community descriptors (S, R, J', and H'), but with no relation to either toxicity or contaminants. Previous studies reported that the environmental parameters (water, temperature, salinity and OD contents, sediment grain size distribution, TOC, % carbonates, etc.) are primarily responsible to the benthic community structure in SES [39]. Factor 3 (10.91% of the variance) demonstrated significant correlation between some benthic community structure indicators (evenness and dominance) and lead contamination. In the case of SES 'b', contaminants of concern were as follows: cadmium, cobalt, chromium, nickel, lead, mercury, zinc, and PAHs.

The original matrix of sediment data of PES was reorganised through the multivariate analysis into three new variables (factors) which explained 97.55% of the total variance (Table 3).

The predominant factor (F1) described 79.84% of the variance and showed significant statistical correlation among the most of the analysed metals (excepting chromium and nickel), PAHs, TOC, percentage of fines, and benthic community descriptors (S, N, R, J', H', and D). F1 therefore indicated high correlation between contaminants (As, Cu, Pb, Zn, Hg, PAHs), natural sediment characteristics (TOC content and percentage of fines), and *in situ* alterations on benthic communities. Factor 2 (F2) accounted for 10.41% of the total variance and showed sediment amphipods' mortality and benthic community alterations (S, N, R, J', H', and D) significantly correlated to metals (with the exception of copper) and organic carbon content. The third factor (F3) described 7.30% of the variance in the original data set and showed sediment toxicity variables (amphipods' mortality test, and elutriates and SWI sea-urchin embryo-larval development tests) and benthic community alterations associated to metals (As, Cr, Cu, Ni and Zn). For PES, the list of contaminants significantly correlated to toxicity and/or benthic community stress were arsenic, chromium, copper, nickel, lead, zinc, mercury, and PAHs.

Two new variables (F1 and F2) were extracted from the original data set of GC, following the application of the PCA and the Factor Analysis. Together, these two factors corresponded to 73.48% of the total variance in the original data set (Table 4).

Nickel, PAHs, elutriates and SWI sea-urchin embryo-larval development tests, amphipods' mortality test, and benthic community descriptors (S, N, R, J', H', and D) were significantly associated in the prevalent factor (F1) (54.24% of the variance); F1 demonstrated variables representing sediment toxicity and benthic community alterations associated with Ni and PAHs. The second factor (F2) (19.23% of the total variance) related metals (Cd, Co, Cu, Pb, V and Zn), fines, amphipods' mortality, and some benthic community descriptors (evenness, diversity and dominance); hence F2 showed significant correlation between the variables of sediment toxicity, benthic community alterations and levels of metals. The chemicals of concern identified in GC were cadmium, cobalt, copper, nickel, lead, vanadium, zinc, and PAHs.

The results of the analyses of prevalence of each factor for each sampling station were presented in Tables 5 and 6 for SES 'a' and 'b', respectively; Table 7 for PES; and Table 8 for GC.

3.3. Developed SQGs

Because in all cases each factor is related to at least one negative biological response (toxicity, benthic community alterations, or both), only those sampling stations where factor scores ≤0 were not associated to negative biological effects. Thus, SQG-low of a

Table 4
Sorted rotated factor loadings of the original 20 variables on the two principal factors of the Gulf of Cádiz sampling stations. Only loadings greater than 0.35 are shown. The variance of the principal factors is given in percentage of the total variance in the original data matrix.

Variable % Variance	Factor 1 54.24	Factor 2 19.23
Cd	–	0.97
Co	–	0.78
Cu	–	0.92
Ni	0.55	–
Pb	–	0.95
V	–	0.81
Zn	–	0.92
PAHs (ppm)	0.61	−0.41
PCBs (ppb)	−0.50	–
TOC	0.42	–
Fines	0.80	0.39
Abnormal sea-urchin (elutriates)	0.84	–
Abnormal sea-urchin (SWI)	0.84	–
Amphipods' mortality	0.90	0.39
S	0.93	–
N	0.87	–
R	0.94	–
J'	0.52	0.58
H'	0.82	0.50
D	0.68	0.55

Table 5
Factor scores estimated for each of the six sampling stations evaluated in the SES (a) to the centroid of all cases for the original data.

Station	F1	F2	F3
SES-1	−0.87	−0.55	−0.94
SES-2	−0.53	1.84	−0.26
SES-3	0.81	0.44	1.15
SES-4	1.64	−0.34	−0.98
SES-5	−0.69	−0.59	−0.28
SES-6	−0.36	−0.80	1.30

given contaminant was defined as the highest concentration of this contaminant among those stations where the related factor score ≤ 0. Likewise, the concentration of a chemical above which there is association to major biological effects (SQG-high), was designated as the lowest concentration among those stations where the related factor score present value >0.

Table 6
Factor scores estimated for each of the 25 sampling stations evaluated in the SES (b) to the centroid of all cases for the original data.

Station	F1	F2	F3
1	0.02	−0.71	0.52
2	0.10	−1.00	−0.50
3	0.05	−0.36	−0.56
4	1.07	1.32	2.32
5	1.31	1.45	−0.83
6	1.07	0.00	−0.89
7	1.62	−0.27	1.17
8	2.82	0.29	−0.90
9	0.51	1.05	−0.21
10	−0.87	0.72	−1.06
11	0.00	−0.08	−0.45
12	−1.35	1.51	−0.03
13	−1.27	1.58	1.18
14	−0.80	0.37	−0.65
15	−0.70	0.25	−0.45
16	−0.56	−2.56	0.07
17	−0.58	0.37	−0.35
18	0.03	0.24	0.48
19	−0.15	−0.91	−0.44
20	−0.96	0.65	−0.70
21	−0.43	−0.38	−0.46
22	−0.42	−0.75	3.07
23	−0.59	−1.14	−0.21
24	0.91	−1.27	0.03
25	−0.83	−0.37	−0.13

Table 7
Factor scores estimated for each of the five sampling stations evaluated in the PES to the centroid of all cases for the original data.

Station	F1	F2	F3
PAR-1	−0.22	0.43	1.64
PAR-2	1.43	0.27	−0.04
PAR-3	0.57	−0.61	−0.69
PAR-4	−0.88	−1.34	−0.01
PAR-5	−0.90	1.25	−0.90

Table 8
Factor scores estimated for each of the eight sampling stations evaluated in the GC to the centroid of all cases for the original data.

Station	F1	F2
HV-1	0.37	1.66
HV-2	0.43	1.11
HV-3	0.42	0.11
CA-1	−1.70	−0.48
CA-2	−1.25	0.40
GR-4	0.15	−1.00
GR-3	0.15	−0.98
GR-3′	1.42	−0.81

Table 9 for SES 'a' and SES 'b', Table 10 for PES, and Table 11 for GC present the SQGs derived for the chemicals of concern in each of the study areas.

The chemicals of concern identified in the SES 'a' data matrix were copper, nickel, lead, vanadium, zinc, PAHs, and PCBs; in SES 'b', cadmium, cobalt, chromium, nickel, lead, mercury, zinc, and PAHs were related to toxicity. SQGs-low for Cu in SES 'a', and Cd and Cr in SES 'b' were not derived because the levels of these contaminants which were not associated to biological effects corresponded to the limit of quantification of the analytical chemistry procedure. Nevertheless, maximum guidelines for these chemicals were possible to be identified and they were presented in Table 9 together with the SQGs for the other chemicals of concern. In PES, arsenium, chromium, copper, nickel, lead, zinc, mercury, and PAHs were identified as chemicals of concern and then SQGs were calculated to these contaminants (Table 10). The minimum guidelines for Cr and Pb were not presented because they corresponded to the limit of quantification of the analytical chemistry method. The SQGs derived for Gulf of Cádiz included the contaminants: cadmium, cobalt, copper, nickel, lead, vanadium, zinc, and PAHs (Table 11).

4. Discussion

As mentioned afore, two different data matrices were used to derive SQGs for SES, and consequently some contaminants' SQGs are duplicated for this study area; namely, nickel, lead and zinc were the contaminants of concern in SES 'a' which are in common with SES 'b'. There was a slight difference between the SQGs derived for these contaminants, which could be expected since the data were taken from different studies, i.e. samples were taken in different periods, different sampling methods were used, and the chemical analyses employed in each of these studies were not the same. Nevertheless, differences between SQGs derived from the two data sets were smaller than differences found in the comparison against national and international benchmark SQGs, as we will discuss further in this article. The application of the SQGs of SES 'a' and 'b' data matrices in the classification of the sediments of SES showed sediments highly polluted by several metals (Cu, Co, Cr, Ni, Pb, Zn, Hg), PAHs and PCBs at inner parts of the estuarine system, where the Cubatão industrial complex is installed, as well as in the Santos channel, where the Port of Santos is located. São

Table 9
Sediment quality guidelines for the chemicals of concern of SES. All concentrations are expressed in mg kg^{-1} of dry sediment, except for PCBs, expressed in µg kg^{-1} of dry sediment.

Chemicals	Sediment quality values		
	Not polluted	Moderately polluted	Highly polluted
Cd (ppm)			
SES (a)	–	–	–
SES (b)	–	–	≥0.75
Co (ppm)			
SES (a)	–	–	–
SES (b)	≤4.1	>4.1 and <10.3	≥10.3
Cr (ppm)			
SES (a)	–	–	–
SES (b)	–	–	≥65.8
Cu (ppm)			
SES (a)	–	–	≥69.0
SES (b)	–	–	–
Ni (ppm)			
SES (a)	≤3.89	>3.89 and <6.02	≥6.02
SES (b)	≤5.9	>5.9 and <21.2	≥21.2
Pb (ppm)			
SES (a)	≤17.4	>17.4 and <22.1	≥22.1
SES (b)	≤10.3	>10.3 and <19.2	≥19.2
V (ppm)			
SES (a)	≤36.0	>36.0 and <87.8	≥87.8
SES (b)	–	–	–
Hg (ppm)			
SES (a)	–	–	–
SES (b)	≤0.08	>0.08 and <0.32	≥0.32
Zn (ppm)			
SES (a)	≤73.3	>73.3 and <110.4	≥110.4
SES (b)	≤37.9	>37.9 and <61.7	≥61.7
PAHs (ppm)			
SES (a)	≤0.163	>0.163 and <0.950	≥0.950
SES (b)	≤0.015	>0.015 and <1.660	≥1.660
PCBs (ppb)			
SES (a)	≤0.94	>0.94 and <2.61	≥2.61
SES (b)	–	–	–

(–) Not possible to calculate.

Vicente channel was classified as highly polluted by PAHs according to both SQGs; this chemical is probably originated from non-treated domestic sewage and drainage from former irregular industrial landfills [5,31]. In addition, SQGs based on SES ‘a’ data showed high pollution by copper and vanadium and in this area, and SES ‘b’ SQGs showed high pollution by some metals (Pb, Hg and Zn) in São Vicente channel sediments. Different to upstream zones, sediments from downstream zones of the estuarine system were considered moderate to not polluted.

Table 10
Sediment quality guidelines for the chemicals of concern of PES. All concentrations are expressed in mg kg^{-1} of dry sediment.

Chemicals	Sediment quality values		
	Not polluted	Moderately polluted	Highly polluted
As	≤3.40	>3.40 and <5.45	≥5.45
Cr	≤27.85	>27.85 and <48.80	≥48.80
Cu	–	–	≥6.55
Ni	≤10.98	>10.98 and <19.10	≥19.10
Pb	–	–	≥17.63
Zn	≤26.95	>26.95 and <41.33	≥41.33
Hg	≤0.013	>0.013 and <0.051	≥0.051
PAHs	≤0.02	>0.02 and <0.03	≥0.03

(–) Not possible to calculate.

Table 11
Sediment quality guidelines for the chemicals of concern of Gulf of Cádiz. All concentrations are expressed in mg kg^{-1} of dry sediment.

Chemicals	Sediment quality values		
	Not polluted	Moderately polluted	Highly polluted
Cd	≤0.65	>0.65 and <1.20	≥1.20
Co	≤6.80	>6.80 and <14.00	≥14.00
Cu	≤20.80	>20.80 and <169.00	≥169.00
Ni	≤8.9	>8.9 and <42.3	≥42.3
Pb	≤21.60	>21.60 and <99.20	≥99.20
V	≤26.10	>26.10 and <76.00	≥76.00
Zn	≤138.0	>138.0 and <360.0	≥360.0
PAHs	≤0.097	>0.097 and <0.100	≥0.100

The application of site-specific SQGs to PES showed that inner parts of PES were highly polluted by all analysed metals and PAHs, including the area in the vicinities of the Ponta do Félix port’s terminal. Sediments in the proximities of the Port of Paranaguá presented some chemicals (As, Pb, Zn, Hg, and PAHs) exceeding the SQGs-high derived for PES. Sediments from inner Laranjeiras Bay (PAR-5), at the sampling station situated inside the limits of “Guaraqueçaba Environmental Protection Area” and away from contaminant sources, were classified as highly polluted by metals (excepted copper). Therefore, in the light of the classification of PES’ sediment quality rendered by the SQGs derived in this study, an area of the estuarine system that is legally recognised as a high priority area for conservation was identified as environmentally degraded. This fact demands the attention of the authorities, government and society in order to encourage the development of a management plan to improve the pollution control efforts in Paranaguá Estuarine System as a whole. Finally, downstream portions of PES were considered as not polluted.

The classification of GC sediments based on the site-specific SQGs showed that sediments of Ría of Huelva were highly polluted by all analysed metals and PAHs. In Bay of Cádiz, sediments from the vicinities of the Port of Cádiz (CA-2) were classified as highly polluted by all analysed metals (excepted Ni), and sediments from inner Bay of Cádiz were classified as not polluted. In Bay of Algeciras, sediments were classified as highly polluted by Ni and PAHs.

The effectiveness of the SQGs derived in this study was assessed through a method, presented by Shine et al. [43], that elucidates the ability of the SQGs to correctly classify a toxic sample as toxic (sensitivity) as well as the ability to correctly classify a nontoxic sample as nontoxic (specificity). From the values of sensitivity and specificity it is possible to estimate the “positive predictive value” (the likelihood that a sample exceeding the threshold is in fact toxic), the “negative predictive value” (the likelihood that a sample below the threshold is nontoxic), and the “overall efficiency” (the likelihood of making a correct prediction of toxicity or nontoxicity) of the SQGs. The value of all these measures ranges from zero to one, with values closer to one being most desirable. Gulf of Cádiz’s SQGs showed high sensitivity (0.96) and specificity (0.93), as well as high positive and negative predictive value (0.94 and 0.95, respectively), and a overall efficiency of 0.95 when applied over a dataset containing sediment contamination levels and related biological effects (toxicity, benthic community alterations, and histopathological lesions) from Gulf of Cádiz (data from the present study and previous ones: Morales-Caselles et al. [44]; and Riba et al. [29,30]). For Santos’ SQGs assessment, results of the present investigation and data from previous studies were employed as well; nevertheless, these previous studies were carried out in different occasions, and they were based on either sediment contamination [34] or sediment toxicity [33,45,46]. The SQGs of SES showed high sensitivity (higher than 0.90 for SES “a” and “b”) but lower specificity (0.50 and 0.75, for “a” and “b”, respectively). The reduced number of previous sediment assessments in SES may have accounted for the lower specificity of

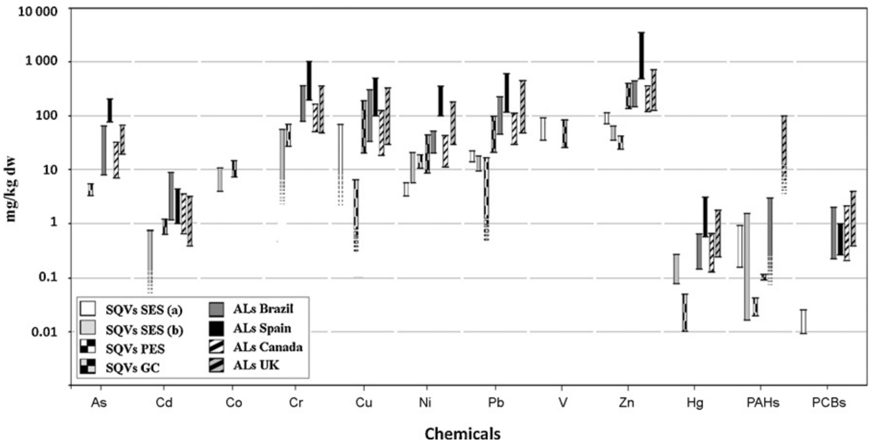

Fig. 3. Comparison of the sediment quality values derived in this study for SES, PES, GC, against national and international Action Levels (ALs) for dredging material characterisation in current use. Fading bars represent those chemicals which minimum guidelines were not derived or provided.

Santos Estuarine System SQGs. In case of PES, since false positive and false negative cases were prevented in the derivation of the SQGs of this study, the indicators of sensitivity, specificity, positive and negative predictive values, and overall efficiency of Paranaguá's SQGs were all equal to 1.0. Therefore, more data would be desirable to certificate the efficiency of these SQGs.

The derived SQGs for SES, PES and Gulf of Cádiz were compared against general benchmark SQGs applied in Brazil and Spain, as well as Action Levels in current use in Canada and United Kingdom (Fig. 3). Brazilian and Spanish SQGs were developed based on different approaches: Brazilian dredging benchmark SQGs, defined by CONAMA no. 344 [22], were established using a combination of the effects range-low and effects range-median (ERL/ERM) [24] and the Canadian threshold effect level and probable effects level (TEL/PEL) [23]; Spanish standards for dredging material classification, recommended by CEDEX [26], are based on sediment geochemical considerations [27]; the Canadian Council of Ministers of the Environment (CCME) uses the TEL/PEL approach, which is derived from geochemistry, toxicity and benthic community data; United States employs the ERL/ERM approach, as a recommendation of the US-NOAA (National Oceanographic and Atmospheric Administration); in the UK there are no statutory contaminant concentration limits, although CEFAS (Centre for Environmental, Fisheries and Aquaculture Science) uses a set of guidelines developed based on sediment chemistry and ecotoxicological information from datasets to aid the assessment of disposal of dredged material at sea [47].

As it is clearly showed in Fig. 3, the SQGs derived in this study for Brazilian and Spanish areas are more restrictive than the SQGs applied in their respective countries. In Brazilian areas, the SQGs-high derived for several chemicals are lower than the SQGs-low currently used by national and international legislations. These findings corroborate the information obtained by Abessa et al. [48], which reported that 80% of the sediments from SES were toxic when the Canadian TEL is exceeded. In Gulf of Cádiz, despite the SQGs derived in this study are more restricted than the guidelines recommended in CEDEX for all identified chemicals of concern, some SQGs are similar to dredging benchmark standards currently applied in Canada, and UK (cases of Cu, Pb and Zn). The similarity of some GC's SQGs to classical SQG's could be expected since the latter are based on data from temperate zones. Nevertheless, other SQGs derived for the chemicals of concern in GC are more restrictive than the classical SQGs (cases of Cd, Ni, and PAHs).

The fact of the site-specific SQGs derived in this study were more restrictive than the proposed sediment quality guidelines utilised in Brazil and Spain, indicates that, at least in the areas of this study, the management decisions based on the current regulation or recommendation in Brazil and Spain may be too permissive. This situation can lead to severe environmental impacts since the capacity of these sediments to buffer the pollution may be, in general, overestimated in these areas.

Discrepancies were also found between the derived SQGs for Brazilian and Spanish areas, as well as between Brazilian areas. Main differences among Brazilian site-specific SQGs and GC-SQGs were found for Cu, being PES-SQG much lower than GC-SQG for this contaminant; Pb and Zn, being both SES and PES-SQGs lower than GC-SQGs; and PAHs, being GC-SQG higher than PES-SQG but lower than SES-SQG for the organic contaminant. Comparing SES against PES-SQGs, major differences were found for Cu, Hg, PAHs (these SQGs were higher in SES), and Cr (SQG higher in PES). The differences among the SQGs derived for each site, including the dissimilarities between SQGs for different sites in the same country, are consequence of the particular environmental conditions of each study area. According to Chapman and Mann [49], many factors can affect the bioavailability of contaminants, such as site-specific sediment characteristics (e.g., grain size, organic carbon, pH, redox potential, acid volatile sulfides) and biotic factors (e.g., bioturbation, bioirrigation); in addition, different mixtures of contaminants also influence the toxic responses of aquatic organisms as well as the effects on benthic organisms at community level. Thus, each site presents a different range of concentrations of chemicals in which biological effects are observed, and consequently, different SQGs were derived.

Estuaries are highly dynamic environments; factors such as river flow, tidal flushing, and sediment resuspension can affect contaminants' bioavailability by changing conditions such as salinity and redox potential in the sediments [50]. Consequently, SQGs based solely on toxicity tests under relatively static conditions may not mimic well the bioavailability of contaminants in the field. As recommended by Chapman et al. [51], "there is a need to develop estuarine-specific SQGs that more appropriately account for low and variable salinities". In this study we derived SQGs not only to predict potential sediment toxicity in the environment, but also to support dredged material management since the study areas are important port zones both in Brazil and Spain. Because much of the material removed may require disposal at sea, SQGs based on standardised saltwater toxicity tests can better address the conditions at disposal site. Although laboratory-controlled exposure-response data may not account for the variable environment in the estuaries, the guidelines derived in this study do not rely on laboratory toxicity tests alone, but also includes *in situ* biological surveys which minimises potential differences between laboratory toxicity tests and the actual environmental condition in each study area.

According to Batley et al. [14], the ultimate objective of SQGs might be stated as the protection of the natural structure and function of benthic ecosystems. Most empirical SQGs are based in large part on laboratory toxicity tests, and, as reported by Hyland et al. [50], benthic degradation is often observed at chemical concentrations substantially below SQGs values. Therefore, there is a research priority on developing SQGs that include the *in situ* effects of sediment contaminants on benthic ecosystems, with care of discriminating effects of toxic chemicals from those natural of stressors [14]. The use of different Lines-of-Evidence to investigate the biological effects related to a range of chemical concentrations specifically to each study area gives robustness to the SQGs derived in this study. The use of multivariate analysis to analyse correlation among the results tend to minimise the uncertainties inherent to each technique (e.g. influence of natural stressors on benthic communities' structure; lack of correspondence to *in situ* conditions on laboratory-controlled toxicity tests).

This study revealed substantial disparities among the SQGs derived for each study area, which confirmed that the local characteristics have evident influence in the biological responses to contamination and suggested that national and international benchmarks are inefficient to predict biological responses on sediments from these areas. The development of site-specific SQGs is strongly recommended to support sediment and dredged material quality assessment in Brazil and Spain. Nonetheless, all SQGs (either site-specific or classical ones) have a certain degree of uncertainty. It is reasonable to consider that classical sediment quality guidelines are derived from ample databases of contaminant levels and their related biological effects from a large number of sampling stations, which confers robustness and reliability to the classical guidelines. The site-specific SQGs presented in this study were derived from much smaller databases; the use of classical SQGs, therefore, should not be disregarded in sediment and dredged material evaluations. Therefore, due to intrinsic uncertainties and variability, SQGs (either site-specific or classical ones) should not be treated as a razor edge separating safe from unsafe or toxic from non-toxic [14]. Both site-specific and classical SQGs have advantages and drawbacks, and they should be used together in decision-making processes of sediment and dredged material assessments. Both general and site-specific SQGs are useful tools to be used together as initial screening values; in instances when initial screening is not sufficient for making decisions, additional investigations may be required to improve certainty to the decision-making process.

5. Conclusions

The site-specific SQGs derived in this study were different from the sediment quality standards employed at national and international level. In general, the site-specific SQGs were more restrictive than the national guidelines applied in their respective countries as well as the classical sediment quality guideline. Thus, this finding confirms that, in some instances, the application of general SQGs may not fully address local particularities of each environment. These results underpin the importance of the development of site-specific SQGs to be used along national SQGs in assessments of sediment quality and characterisation of the dredging material in Santos Estuarine System, Paranaguá Estuarine System and Gulf of Cádiz.

Furthermore, the site-specific SQGs derived from the integration physical–chemical, ecotoxicological, and benthic community structure data were able to indicate the environmental quality of the different areas in all studied Brazilian and Spanish estuarine and port zones, confirming the feasibility of the application of an internationally harmonised methodology to deriving site-specific SQGs based on the WOE approach and integration of LOEs through multivariate analysis.

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Appendix A.

See Table A.1,Tables A.2A and A.2B, Tables A.3 and A.4.

Table A.1

Physical–chemical characteristics, toxicity tests results, and benthic community descriptive parameters of sediments from Santos and São Vicente Estuarine System: SES (a) data matrix.

Variables	Sampling stations					
	SES-1	SES-2	SES-3	SES-4	SES-5	SES-6
Chemicals						
Cd (ppm)	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ
Co (ppm)	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ
Cu (ppm)	<LQ	167.2	157.7	69.0	<LQ	<LQ
Ni (ppm)	4.85	2.96	4.49	3.83	3.89	6.02
Pb (ppm)	17.4	66.2	22.1	14.9	8.7	14.6
V (ppm)	36.0	24.0	87.8	104.8	18.6	<LQ
Zn (ppm)	73.3	154.2	110.4	66.8	32.6	53.2
PAHs (ppm)	0.106	0.518	0.425	0.950	0.163	0.600
PCBs (ppb)	0.66	4.00	2.61	0.94	0.58	<LQ
Sediment characteristics						
TOC (%)	3.75	1.24	2.78	2.82	0.85	1.00
Fines (%)	3.96	4.46	9.68	2.67	1.42	11.56
Sediment toxicity (mean ± S.D.)						
Amphipods mortality (%)	25.0 ± 2.9	72.5 ± 2.5	77.5 ± 6.3	80.0 ± 5.8	40.0 ± 4.1	67.5 ± 4.8
Benthic descriptors						
Number of species (S)	13	10	3	5	10	8
Density of organisms ($\mathrm{N\,m^{-2}}$)	216.7	175.0	33.3	183.3	125.0	91.7
Margaleff's richness (R)	2.23	1.74	0.57	0.77	1.86	1.55
Pielou's evenness (J')	0.91	0.89	0.95	0.45	0.93	0.97
Shannon's diversity (H')	2.34	2.06	1.04	0.73	2.15	2.02
Simpson's dominance ($D = 1 - \lambda'$)	0.88	0.85	0.64	0.32	0.87	0.87

Table A.2A

Physical–chemical characteristics, toxicity tests results, and benthic community descriptive parameters of sediments from Santos and São Vicente Estuarine System: SES (b) data matrix (stations 1–12).

Variables	Sampling stations											
	1	2	3	4	5	6	7	8	9	10	11	12
Chemicals												
Cd (ppm)	<LQ	<LQ	<LQ	0.75	0.92	0.99	0.42	0.98	1.49	<LQ	<LQ	<LQ
Co (ppm)	6.0	5.2	4.2	10.7	10.3	12.3	17.0	15.3	5.1	0.9	4.8	0.2
Cr (ppm)	18.7	17.6	7.5	37.9	44.1	44.8	65.8	97.5	22.8	5.0	53.6	5.0
Ni (ppm)	9.5	8.9	7.0	21.8	22.2	25.0	34.1	44.2	13.2	2.5	10.2	1.3
Pb (ppm)	10.9	11.2	10.8	204.8	23.5	19.2	39.7	89.9	19.6	3.7	10.3	2.5
Hg (ppm)	0.11	0.12	0.36	0.74	0.23	0.32	0.92	0.75	0.50	0.11	0.31	0.04
Zn (ppm)	40.1	47.6	44.5	180.0	284.4	86.9	152.8	312.0	77.6	14.2	37.9	7.6
PAHs (ppm)	0.060	0.190	2.910	1.660	39.820	28.840	10.980	42.390	2.120	1.380	0.030	0.002
Sediment characteristics												
TOC (%)	1.39	2.53	2.37	1.03	2.14	0.79	1.39	2.76	2.62	2.03	2.51	0.31
Fines (%)	85.18	93.60	99.20	80.73	97.88	91.18	88.54	43.59	39.40	6.77	8.84	1.77
Sediment toxicity (mean ± S.D.)												
Amphipods mortality (%)	68.3 ± 28.4	45.0 ± 10.0	45.0 ± 10.0	46.7 ± 5.8	31.7 ± 10.4	33.3 ± 11.5	48.3 ± 12.6	53.3 ± 20.2	55.0 ± 30.4	26.7 ± 20.2	36.7 ± 15.3	21.7 ± 12.6
Benthic descriptors												
Number of species (S)	16	15	9	1	0	5	10	4	3	2	8	0
Density of organisms (N m^{-2})	1012.8	371.8	312.5	12.8	0.0	102.6	756.4	76.9	179.5	25.6	359.0	0.0
Margaleff's richness (R)	3.40	4.16	2.67	–	–	1.92	2.21	1.67	0.76	1.44	2.10	–
Pielou's evenness (J')	0.58	0.88	0.88	–	–	0.97	0.45	0.96	0.60	1.00	0.85	–
Shannon's diversity (H')	1.61	2.38	1.94	0.00	0.00	1.56	1.03	1.33	0.66	0.69	1.77	0.00
Simpson's dominance ($D = 1 - \lambda'$)	0.60	0.89	0.86	0.00	1.00	0.89	0.42	0.87	0.38	1.00	0.82	1.00

Table A.2B

Physical–chemical characteristics, toxicity tests results, and benthic community descriptive parameters of sediments from Santos and São Vicente Estuarine System: SES (b) data matrix (stations 13–25).

Variables	Sampling stations												
	13	14	15	16	17	18	19	20	21	22	23	24	25
Chemicals													
Cd (ppm)	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	0.85	<LQ
Co (ppm)	1.1	4.1	5.8	2.3	5.4	7.1	6.5	3.2	4.1	8.5	3.8	11.6	1.6
Cr (ppm)	5.0	12.5	18.8	10.0	18.4	28.4	29.0	9.5	19.6	40.9	5.0	69.5	5.0
Ni (ppm)	2.4	9.1	11.3	4.9	10.3	12.5	13.4	7.9	14.7	17.9	8.1	21.2	5.9
Pb (ppm)	17.0	6.5	8.3	5.3	7.8	16.8	11.8	5.3	5.8	18.0	5.5	24.5	2.0
Hg (ppm)	0.03	0.05	0.04	0.04	0.04	0.19	0.06	0.04	0.04	0.08	0.03	0.11	0.04
Zn (ppm)	10.9	34.0	41.4	23.8	35.9	61.7	44.7	49.6	32.2	55.5	29.7	74.4	16.8
PAHs (ppm)	0.001	0.015	0.005	0.003	0.006	0.511	0.011	0.001	0.005	0.010	0.001	0.028	0.001
Sediment characteristics													
TOC (%)	1.22	0.12	0.14	0.70	0.23	1.39	1.55	0.14	1.17	0.29	0.21	0.87	0.77
Fines (%)	1.76	2.97	4.27	27.26	7.83	71.16	66.74	2.57	58.03	11.97	54.47	90.18	1.21
Sediment toxicity (mean ± S.D.)													
Amphipods mortality (%)	13.3 ± 11.5	26.7 ± 2.9	16.7 ± 7.6	21.7 ± 2.9	46.7 ± 10.4	51.7 ± 12.6	8.3 ± 7.6	13.3 ± 2.9	10.0 ± 0.0	19.0 ± 5.8	23.3 ± 10.4	56.7 ± 7.6	41.3 ± 10.4
Benthic descriptors													
Number of species (S)	1	3	4	37	3	6	14	2	9	18	18	17	13
Density of organisms (N m^{-2})	25.6	38.5	64.1	859.0	51.3	294.9	320.5	25.6	166.7	10564	538.5	756.4	1435.9
Margaleff's richness (R)	0.00	1.82	1.86	8.56	1.44	1.59	4.04	1.44	3.12	2.53	4.55	3.92	2.54
Pielou's evenness (J')	–	1.00	0.96	0.93	0.95	0.55	0.92	1.00	0.89	0.28	0.91	0.84	0.82
Shannon's diversity (H')	0.00	1.10	1.33	3.36	1.04	0.91	2.43	0.69	1.95	0.81	2.64	2.38	2.11
Simpson's dominance ($D = 1 - \lambda'$)	0.00	1.00	0.90	0.97	0.83	0.46	0.93	1.00	0.87	0.33	0.93	0.89	0.85

Table A.3
Physical–chemical characteristics, toxicity tests results, and benthic community descriptive parameters of sediments from Paranaguá Estuarine System.

Variables	Sampling stations				
	PAR-1	PAR-2	PAR-3	PAR-4	PAR-5
Chemicals					
Ag (ppm)	<LQ	<LQ	<LQ	<LQ	<LQ
As (ppm)	7.40	8.33	5.45	3.40	5.75
Cd (ppm)	<LQ	<LQ	<LQ	<LQ	<LQ
Cr (ppm)	58.00	51.50	27.85	14.50	48.80
Cu (ppm)	16.20	13.80	6.55	<LQ	<LQ
Ni (ppm)	21.90	20.73	10.98	6.65	19.10
Pb (ppm)	29.75	27.70	17.63	<LQ	23.95
Se (ppm)	<LQ	<LQ	<LQ	<LQ	<LQ
Zn (ppm)	80.50	77.75	41.33	26.95	58.00
Hg (ppm)	0.07	0.09	0.06	0.01	0.05
PAHs (ppm)	0.02	0.03	0.03	0.01	0.01
PCBs (ppb)	<LQ	1.09	1.32	1.47	<LQ
Sediment characteristics					
TOC (%)	4.20	3.65	1.53	0.44	1.32
Fines (%)	64.55	64.87	27.34	15.33	20.22
Sediment toxicity (mean ± S.D.)					
% of abnormal sea-urchin (elutriates)	88.7 ± 7.4	33.2 ± 3.8	22.2 ± 3.4	13.7 ± 4.8	18.7 ± 9.8
% of abnormal sea-urchin (SWI)	82.7 ± 13.6	19.0 ± 4.2	10.0 ± 5.3	10.0 ± 3.2	13.7 ± 9.8
% of amphipods mortality	90.0 ± 10.0	63.3 ± 5.8	40.0 ± 20.0	36.7 ± 32.1	46.7 ± 15.3
Benthic community descriptors					
Number of species (*S*)	1	1	9	13	7
Density of organisms ($\mathrm{N\,m^{-2}}$)	7.2	14.5	105.6	206.5	96.6
Margaleff's richness (*R*)	0.00	0.00	1.72	2.25	1.31
Pielou's evenness (*J′*)	–	–	0.90	0.92	0.86
Shannon's diversity (*H′*)	0.00	0.00	1.99	2.36	1.68
Simpson's dominance ($D = 1 - \lambda'$)	0.00	0.00	0.85	0.89	0.78

Table A.4
Physical–chemical characteristics, toxicity tests results, and benthic descriptive parameters of sediments from Gulf of Cádiz.

Variables	Sampling stations							
	HV-1	HV-2	HV-3	CA-1	CA-2	GR-4	GR-3	GR-3′
Chemicals								
Cd (ppm)	3.90	2.50	1.60	0.65	1.20	0.10	0.29	0.17
Co (ppm)	26.00	10.00	14.00	6.80	18.30	5.59	<LQ	12.80
Cu (ppm)	1989.00	1543.00	789.00	15.60	169.00	3.67	20.80	5.01
Ni (ppm)	42.3	21.2	97.2	8.9	29.3	13.1	15.5	74.7
Pb (ppm)	406.00	335.00	198.00	12.20	99.20	6.21	19.10	21.60
V (ppm)	90.00	111.00	76.00	11.50	132.10	<LQ	24.60	26.10
Zn (ppm)	1945.0	2010.0	987.0	18.3	360.0	35.3	66.0	138.0
PAHs (ppm)	0.298	0.191	0.100	0.074	0.096	0.711	2.103	12.003
PCBs (ppb)	3.50	4.60	1.10	<LQ	161.00	<LQ	<LQ	<LQ
Sediment characteristics								
TOC (%)	2.10	2.90	3.90	1.10	2.60	3.19	3.44	2.15
Fines (%)	88.3	89.5	74.5	6.8	66.4	54.2	75.4	90.5
Sediment toxicity (mean ± S.D.)								
% of abnormal sea-urchin (elutriates)	100.0 ± 0.0	63.7 ± 3.9	82.0 ± 4.3	7.2 ± 2.5	7.2 ± 1.0	31.0 ± 2.6	94.2 ± 2.6	94.5 ± 2.5
% of abnormal sea-urchin (SWI)	100.0 ± 0.0	100.0 ± 0.0	87.0 ± 3.6	60.3 ± 9.5	79.0 ± 6.2	98.0 ± 2.0	79.0 ± 7.5	100.0 ± 0.0
% of amphipods mortality	100.0 ± 0.0	96.7 ± 5.8	76.7 ± 5.8	3.3 ± 5.8	26.7 ± 5.8	43.3 ± 5.8	66.7 ± 5.8	100.0 ± 0.0
Benthic descriptors								
Number of species (*S*)	1	1	3	23	14	6	6	1
Density of organisms ($\mathrm{N\,m^{-2}}$)	16.7	83.3	266.7	6833.3	2516.7	1066.7	983.3	66.7
Margaleff's richness (*R*)	0	0	0.36	2.49	1.66	0.72	0.73	0
Pielou's evenness (*J′*)	–	–	0.71	0.63	0.70	0.82	0.81	–
Shannon's diversity (*H′*)	0	0	0.78	1.96	1.85	1.46	1.45	0
Simpson's dominance ($D = 1 - \lambda'$)	0	0	0.46	0.70	0.79	0.74	0.73	0

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