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TESIS DOCTORAL

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UNIVERSIDAD DE CÁDIZ

FACULTAD DE CIENCIAS DEL MAR Y AMBIENTALES

ARMONIZACIÓN DEL PROTOCOLO DE EVALUACIÓN DE CALIDAD DE SEDIMENTOS Y MATERIALES DRAGADOS EN ZONAS ESTUARINAS Y PORTUARIAS DEL ATLÁNTICO

Rodrigo Brasil Choueri

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Esta Tesis Doctoral ha sido realizada en el Departamento de Química-Física de la Facultad de Ciencias del Mar y Ambientales de la Universidad de Cádiz, como parte de las actividades de la Cátedra UNESCO/UNITWIN/WiCop. El trabajo que se resume en esta memoria ha sido financiado principalmente por los siguientes proyectos: “Harmonización de los métodos para gestión de material de dragado en zonas costeras internacionales (Europa y Latino America), incluso zonas naturales protegidas” (CAPES-Brazil #099/06/MEC-Spain PHB 2005-0100-PC), cooperación CAPES y Ministerio de Educación y Ciencia; “Plan Nacional I+D+I. Desarrollo y Mejora del análisis integrado para la evaluación de la calidad de sedimentos litorales, incluidos los materiales de dragado portuario” (CTM2005-07282-C03-C01/TECNO), Ministerio de Educación y Ciencia; “Caracterización de la calidad de ecosistemas costeros afectados por vertidos de petróleo: comparación entre casos de vertidos accidentales (impacto agudo) frente a derrames continuos (impacto crónico)” (VEM2003-20563/INTER), Ministerio de Ciencia y Tecnología.

Memoria presentada para optar al titulo de

Doctor en Ciencias del Mar

Rodrigo Brasil Choueri

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HACEN CONSTAR:

Que esta memoria, titulada "Armonización del protocolo de evaluación de calidad de sedimentos y materiales dragados en zonas estuarinas y portuarias del Atlántico", presentada por D. Rodrigo Brasil Choueri, resume su trabajo de Tesis Doctoral y, considerando que reúne todos los requisitos legales, autorizan su presentación y defensa para optar al grado de Doctor en Ciencias del Mar por la Universidad de Cádiz.

Cádiz, Enero de 2006

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Capítulo 1.

Introducción, objetivos e hipótesis, zonas de estudio y organización de la tesis

1.1 Introducción

La evaluación de calidad de sedimentos es, así como los tradicionales análisis de calidad de agua, una de las apreciaciones más adecuadas para el seguimiento y control del estado de degradación los ambientes acuáticos. Esto se debe al hecho de que los sedimentos son particularmente sensibles a los impactos antropogénicos, puesto que, dependiendo de sus características físico-químicas, los elementos tóxicos pueden ser acumulados por tiempos relativamente largos y en concentraciones muy superiores a aquellas encontradas en la columna de agua (Petrovic y Barceló, 2004; Ingersoll, 2003). Los sedimentos actúan como sumidero de contaminantes y pueden también actuar como fuente de contaminantes hacia la columna de agua (DelValls et al., 2004; Salomons y Brils, 2004; U.S.EPA, 1999; Chapman, 1989) ante ciertos cambios en las condiciones físico-químicas del medio (por ejemplo, periodos de anoxia o eventos de removilización).

Los sedimentos poseen gran importancia ecológica en los ecosistemas acuáticos. En este compartimiento ecológico suceden gran parte de las actividades microbiológicas asociadas a la remineralización de la materia orgánica, un proceso fundamental para la recomposición de los nutrientes disueltos en la columna de agua. Los sedimentos también proveen una rica variedad de *habitats*, sitios de alimentación y reproducción para diversos organismos acuáticos, especialmente para los bentónicos.

Por tanto, debido a su importancia ecológica, los sedimentos son objeto principal de innumerables estudios de evaluación de la calidad de ambientes acuáticos (Riba et al., 2005; Riba et al, 2004a, b; Anderson et al., 2001; Carr et al., 1996; DelValls, 1994).

La contaminación de los sedimentos representa una grave amenaza al funcionamiento armónico de los ecosistemas acuáticos. Los organismos bentónicos expuestos a los sedimentos contaminados pueden presentar efectos tóxicos letales y subletales (por ejemplo, alteraciones en tasas de supervivencia, crecimiento y reproducción). Además, algunos contaminantes pueden acumularse en los tejidos de los organismos bentónicos. Los niveles de contaminación llegan a acumularse en niveles tróficos superiores (proceso conocido como biomagnificación). Por lo tanto, estos contaminantes una vez incorporados por organismos los bentónicos pueden acceder a toda la cadena trófica de un ecossitema, afectando no solamente la biota en contacto directo con los sedimentos, sino también a peces, pájaros y mamíferos, incluyendo seres humanos (McDonald e Ingersoll, 2002).

Los sedimentos contaminados pueden afectar directamente a los seres humanos mediante el consumo de organismos contaminados. Al mismo tiempo, los sedimentos polucionados también llevan asociadas implicaciones de tipo económico, afectando a la pesca, turismo, ocio y especialmente a las actividades portuarias. El tema de los materiales de dragado portuarios es actualmente preocupante para diferentes sectores de la sociedad; los sedimentos contaminados han amenazado la viabilidad de muchos puertos comerciales a través de la imposición de restricciones en las operaciones de dragados y disposición final del material dragado. Por ejemplo, recientemente en Brasil, las actividades de dragados en el puerto de Santos (el más grande de América Latina) fueron suspendidas por motivo de disposición inadecuada de los sedimentos contaminados de la zona del puerto y canal de acceso. Las operaciones fueron liberadas tres años después, en el año 2005 (Codesp, 2005).

Los impactos relacionados con las actividades de dragados son numerosos y diversos, de corto y largo plazo, y pueden afectar el ambiente principalmente durante la fase de ejecución, con el transporte del material y la disposición final de los sedimentos. Durante las operaciones de dragados, la remoción de los sedimentos afecta directamente a las comunidades bentónicas, llegando a producirse la destrucción de sus *habitats*. En consecuencia del proceso de dragado, también se produce impacto negativo al medio ambiente debido a la resuspensión de materiales finos. La fracción fina del sedimento puede ser transportada por corrientes marítimas, destruyendo comunidades bentónicas por soterramiento y/o por sofocamiento; al mismo tiempo, el incremento de la turbidez en la columna de agua afecta a las comunidades fitoplanctônicas, a través de la disminución de la extensión de la zona eufótica, produciéndose una reducción de las tasas de productividad primaria. Alteraciones en los parámetros físico-químicos de la columna de agua, como la reducción del pH y disminución de la concentración del oxígeno disuelto, también ocurren y afectan a todo el ecosistema. La resuspensión de los sedimentos también puede provocar la redisolución de nutrientes y contaminantes. Estos nutrientes pueden asociarse a procesos de eutrofización y, dependiendo de la extensión del proceso, el incremento de la producción primaria puede llevar a eventos de florecimientos fitoplanctónicos. La resolubilización de contaminantes como metales, hidrocarburos policiclícos aromáticos y bifeniles policlorados puede causar efectos tóxicos agudos, crónicos, letales y subletales en los organismos afectados.

La disposición final del material dragado también es agresiva al ambiente. Normalmente los puertos se localizan en zonas de concentraciones urbanas e industriales, donde actividades humanas afectan negativamente el ambiente natural. Los sedimentos de estas zonas acumulan contaminantes provenientes de efluentes industriales, urbanos y rurales, bien como originarios de las actividades portuarias. De esta forma, las áreas de disposición de materiales dragados son impactadas tanto físicamente, por la disposición de grandes volúmenes de sedimentos, como, muchas veces, químicamente, a través del descarte de material contaminado.

Durante los últimos treinta años, científicos ambientales, ingenieros y autoridades legislativas han invertido recursos considerables para desarrollar métodos y técnicas para evaluar, gestionar y remediar la contaminación química de los sedimentos. A principios de la década de los 70, convenciones internacionales como la "Convención de Londres" (LC) en 1972 (http://www.londonconvention.org), y la "Convención de Oslo-Paris" (OSPAR) (http://www.ospar.org) establecieron protocolos generales para la evaluación de la calidad ambiental y manejo de materiales de dragado. De acuerdo con estas convenciones, la gestión de los materiales de dragado es determinada considerando la cantidad y la naturaleza de estos materiales. Así, los sedimentos de dragado pueden tener usos beneficiosos, vertidos libremente al mar, o dispuestos en compartimentos aislados.

Evaluaciones de calidad de sedimentos

Uno de los componentes clave en las herramientas de tomada de decisión para el manejo de sedimentos y materiales de dragado es el proceso de caracterización de estos materiales. Tradicionalmente, la evaluación de la calidad de los sedimentos se determina mediante la caracterización química de éste. En este sentido, se determinan los niveles de contaminación y se comparan con guías de calidad de sedimento. Sin embargo, actualmente se han desarrollado diversos métodos para la evaluación de la calidad ambiental de los sedimentos. Estas técnicas incluyen, por ejemplo, aquellas consideradas por la U.S.EPA: (i) la comparación con zonas de referencia, (ii) la partición de equilibrio entre el nivel de contaminantes y las características del sedimento, (iii) análisis de residuos de contaminantes en tejidos biológicos, (iv) toxicidad del agua intersticial, (v) exposición de los organismos al sedimento integral, (vi) análisis de la estructura de la comunidad bentónica (Ingersoll, 1995). Evidentemente, cada uno de estos métodos posee un grado de incertidumbre por si mismos. En los estudios llevados a cabo *in situ* (ej. análisis de la estructura de la comunidad bentónica), el grado de incertidumbre es alto, principalmente en ambientes complejos como son los estuarios. Por otro lado, si los estudios son exclusivamente de contaminación, no es posible conocer la biodisponibilidad de los contaminantes (Burton Jr. et al., 2003). De esta forma, para minimizar las deficiencias de cada método, la integración de diferentes técnicas de evaluación es considerada más efectiva en el sentido de suministrar información fiable sobre las condiciones ambientales de los sedimentos (Abessa et al., 2005; Carr et al., 1996; Long y Chapman, 1985), puesto que la naturaleza diversa de su composición y la compleja mezcla de los agentes tóxicos dificultan la identificación de los contaminantes que producen el efecto biológico (Riba et al., 2004b).

El modelo basado en el "peso de evidencia" (WOE, del inglés *weight of evidence*), la cual consiste en la integración de diferentes métodos de evaluación de la calidad del sedimento (líneas de evidencia – LOE), fue inicialmente propuesta por Long y Chapman en 1985. Este concepto surge de la necesidad de integrar toda información que pudiera proporcionar una visión completa del estado de los sistemas acuáticos, y así establecer su grado de calidad ambiental (Figura 1). Este tipo de modelo ofrece la posibilidad de responder a las tres preguntas principales que se planteen en los estudios de evaluación de calidad ambiental de los ecosistemas acuáticos (Riba et al, 2004a):

1. ¿Qué contaminantes están presentes en la zona de estudio, y en qué concentraciones?
2. ¿Están los contaminantes disponibles para la biota?
3. ¿Qué efectos biológicos están asociados a estos contaminantes?

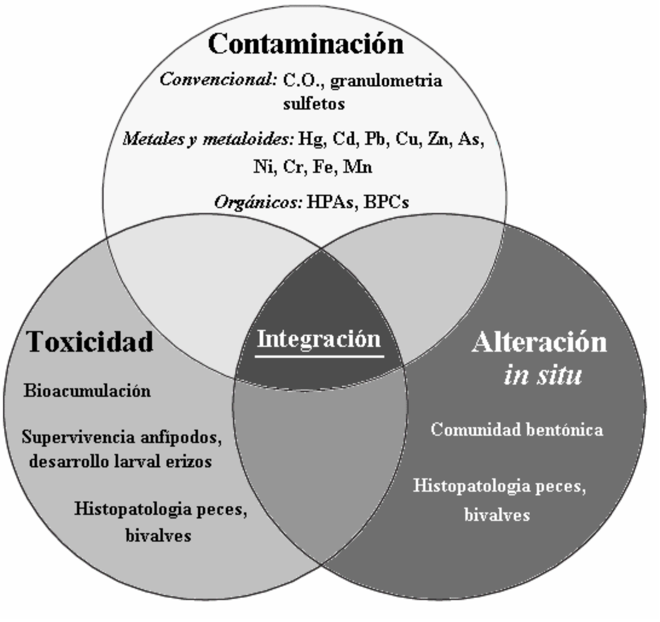


Figura 1: Representación esquemática de la integración de diferentes métodos de evaluación de sedimentos y materiales dragados.

Posterior al estudio inicial de Long y Chapman (1985), financiado por la U.S.EPA, que desarrolló y aplicó el enfoque integrado en la evaluación de la calidad de los sedimentos de *Puget Sound* (WA, EEUU), otros estudios se realizaron, aplicados a diversos sistemas costeros de EEUU y Canadá (Chapman et al., 1991; Chapman et al., 1987). En la década de los 90, investigadores de otros países se interesaron por el modelo: el Gobierno Español financió la aplicación del método integrado en estudios de calidad de sedimento en tres ecosistemas litorales del Golfo de Cádiz (DelValls et al., 1998a, b, c, d, e, 1997, 1996; DelValls e Chapman, 1998). Más recientemente Cesar et al. (2004) utilizaran el método en la evolución de la calidad ambiental de la Bahía de Portmán. En Brasil, el enfoque WOE se ha iniciado con el estudio de Abessa (2002) de evaluación de la calidad de los sedimentos del Sistema Estuarino de Santos (São Paulo) y actualmente la FAPESP (Fundação de Amparo à Pesquisa do Estado do Estado de São Paulo) financia un proyecto para la elaboración de valores-guía de calidad de sedimento para metales y compuestos orgánicos xenobióticos en embalses del Rio Tietê (Proyecto QualiSed), utilizando para ello la caracterización geoquímica de los sedimentos, y los resultados de los análisis de comunidad las bentónica y tests de toxicidad (http://www.dq.ufscar.br/Labs/ biogeoquimica/qualised.htm).

Los resultados llevados en éxito de la evaluación integrada de la calidad de sedimentos se deben al hecho de que cada un de estos estudios suministró información exclusiva referente al sistema; sin embargo, si se hubiese empleado de forma aislada, el resultado hubiese sido limitado y la información ambiental parcial, con un alto grado de incertidumbre (Salomons y Brils, 2004). La determinación de las características físico-químicas cuantifica niveles de contaminantes específicos, pero no informa sobre los efectos interactivos con otros químicos (antagonismo, sinergismo), tampoco sobre la biodisponibilidad de estos contaminantes (Burton Jr. et al., 2003). En el fin de solventar esta deficiencia, estos estudios se completan con ensayos de toxicidad que permiten obtener información referente a la biodisponibilidad de los contaminantes, que sean de simples ejecución, bajo costo y proporcionen datos de fácil interpretación. Sin embargo, es complejo extrapolar los resultados obtenidos bajo condiciones controladas de laboratorios. Las respuestas a las alteraciones *in situ* son mejor identificadas a través de estudios ecológicos en campo, como el análisis de la estructura de la macrofauna bentónica, por ejemplo; este análisis, a su vez, puede presentar variaciones espacio-temporales o verse afectado por perturbaciones no relacionadas a la contaminación. La integración de estas diferentes líneas de evidencia técnicas minimizan las limitaciones de cada modelo por sí solo técnica, de modo que la información integrada de la calidad del sedimento tenga más peso que a los resultados obtenidos individualmente (DelValls, 1994).

Integración de los datos

Existen diferentes formas de integrar los resultados obtenidos en cada línea de evidencia utilizada en un estudio integrado de calidad ambiental. Los métodos comparativos no estadísticos, a pesar de su de fácil interpretación, no son recomendables si son empleados de modo aislado puesto que el tratamiento de datos en esta metodología implica una gran parcela de subjetividad, con la exclusión de algunas variables. Esto puede suponer una perdida de información relevante (Riba et al., 2004a).

Otro método simple y frecuentemente utilizado para la integración de datos ambientales es el "*Triade de calidad de sedimentos*" (Riba, 2004a; Abessa, 2002; DelValls et al., 1998; Chapman, 1996) (Figura 2). Este método se basa en la normalización de las variables determinadas en estudios de contaminación, toxicidad y alteración *in situ* frente a los valores mínimos (establecidos a partir de una zona de referencia) y máximos (los valores máximos de cada variable en los distintos casos de estudio). Con los valores normalizados se calcula tres índices distintos: contaminación, toxicidad y alteración *in situ*. Estos índices son representados gráficamente en un sistema isométrico de tres ejes, representando en cada vértice cada uno de los índices. De este modo queda definido un triángulo para cada uno de los casos de estudio y un triángulo de lado (1, 1, 1) para la estación de referencia.

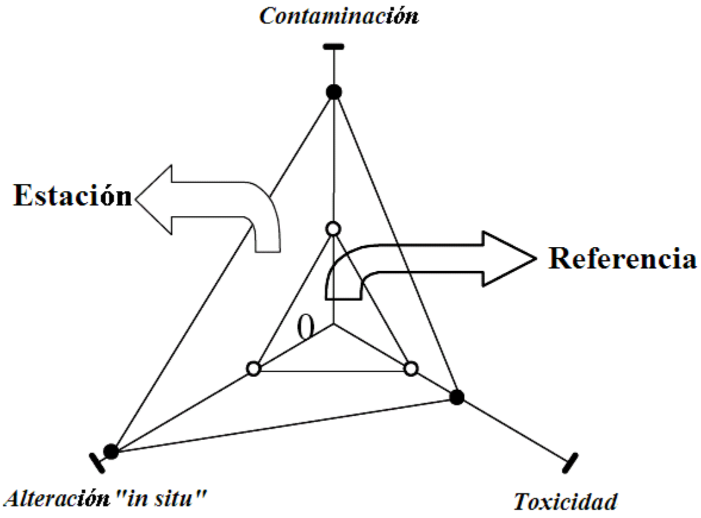


Figura 2 – El triad de calidad de sedimentos (Riba et al., 2004a)

Otra representación de fácil visualización es el diagrama de sectores (Figura 3), que incorpora un análisis estadístico (Riba, 2004a; Abessa, 2002; DelValls et al., 1998). El método se basa en la aplicación de tests estadísticos adecuados para identificar diferencias significativas entre los resultados obtenidos en las zonas de estudio y la zona de referencia. El grado de significancia es representado en los diagramas de sectores por una gradación de colores, desde el blanco (las variables cuyos resultados no presentan diferencias significativas con relación a la zona de referencia; p<0,01), pasando por gris (resultados moderadamente similares a los valores de la estación de referencia; 0,01<p<0,1) y hacia el negro (variables cuyos resultados tienen menor similitud con la zona de referencia; p>0,1) (Figura 3b).

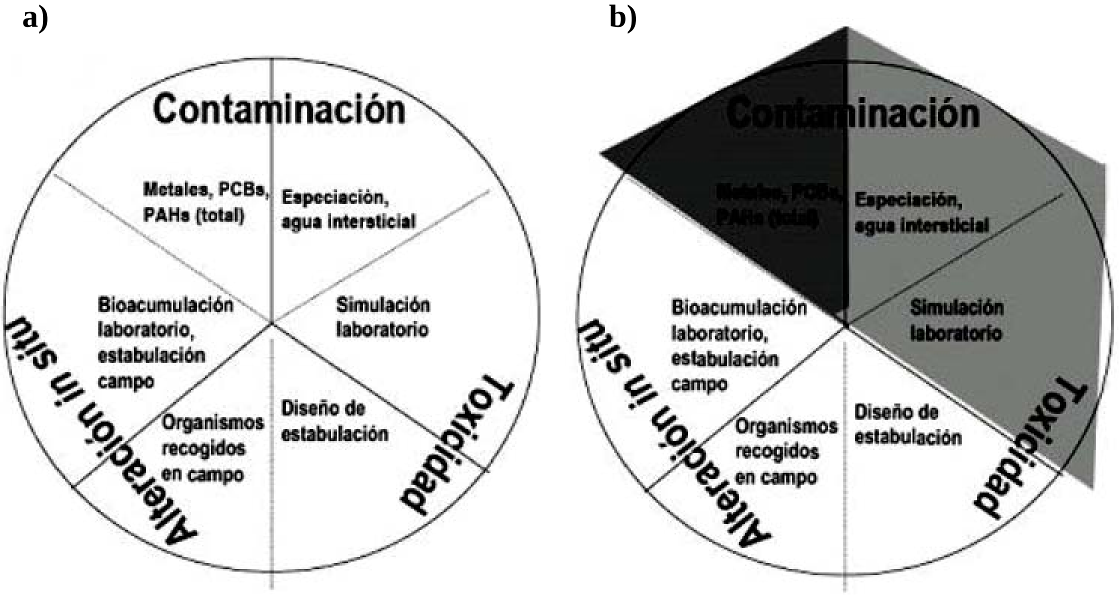


Figura 3: Diagrama de sectores – los colores representado en el diagrama de la derecha representan el nivel de similitud con la estación de referencia. Blanco: sin diferencias estadísticas (p<0,01); Gris: moderadamente similar a la estación de referencia (0,01<p<0,1); Negro: estadísticamente diferente con relación a la estación de referencia (p>0,1).

Actualmente se están adoptando métodos estadísticos más sofisticados que permitan la integración de datos ambientales y que impliquen una menor perdida de información. Las técnicas basadas en el análisis multivariantes (Riba et al., 2004a; Anderson et al., 2001; Hunt et al., 2001; Del Valls e Chapman, 1998; Del Valls et al., 1997; Chapman et al., 1996) permiten obtener conclusiones adicionales (DelValls et al., 1997). En este sentido, el análisis de componentes principales (PCA, del ingles *Principal Component Analysis*) se están utilizando con bastante éxito en los estudios basados en la integración de resultados ambientales (Riba et al., 2004 a, b; DelValls et al., 2002; DelValls y Chapman, 1998). Este método permite identificar qué variables están asociadas al efecto tóxico e interpretar los resultados obtenidos.

Los estudios integrados se están utilizando ampliamente para estudiar la calidad ambiental de los ecosistemas ya que, a pesar de llevaren asociado un alto coste y ser complejos debido a su carácter multidisciplinar, permiten obtener un elevada calidad de la información obtenida y una correcta interpretación de los resultados (Chapman, 1992). Según Chapman (1992), las principales ventajas del método son: (1) el suministro de datos fiables (basados en observaciones) de calidad de sedimentos; (2) la posibilidad de una interpretación ecológica de propiedades físicas, químicas y biológicas del ambiente; (3) la utilización de diferentes enfoques conjuntamente, utilizar técnicas aisladas; (4) la generación de datos adecuados para ser empleados en la obtención de índices de calidad de sedimentos.

El suministro de datos fiables para la obtención de guías de calidad de sedimento (SQGs, del inglés *Sediment Quality Guidelines*) es de gran importancia para disponer correctamente el material de dragado. Hoy en día se recomienda que estos valores sean calculados teniendo en cuenta los efectos biológicos esperados (calculados de forma teórica mediante los coeficientes de partición obtenidos teniendo en cuenta los contaminantes y las características del sedimento) (McCauley et al., 2000) o bien empíricamente (mediante la observación de los efectos biológicos asociados a un rango de concentraciones de los contaminantes) (Long and Morgan, 1990; Long et al. 1998;

MacDonald et al., 1996). De esta forma, el enfoque WOE debe ser aplicado en el desarrollo de valores-guía de calidad de sedimento para poder correlacionar las concentraciones químicas con los efectos biológicos.

En Brasil, la resolución del Consejo Nacional de Medio Ambiente (CONAMA) nº 344 de 25 de marzo de 2004, establece las directrices y procedimientos mínimos para la evaluación y manejo del material dragado, así como indica valores orientativos de calidad de sedimentos. Estos valores son basados en publicaciones internacionales (EC, 2002; Long et al., 1995; FDEP, 1994). Debido a las características únicas de cada ambiente litoral y a la multitud de factores que afectan a la biodisponibilidad de los compuestos químicos en los sedimentos (granulometría, pH, salinidad, el contenido de materia organica y sulfuros volátiles) (Riba et al., 2004c; Riba et al., 2003; Simpson, 2001; Meyer et al., 1994), en muchos casos los valores de calidad de sedimentos (internacionales o nacionales) no son adecuados para cada ambiente específico (Wenning y Ingersoll, 2002). En España, el documento "Recomendación para la Gestión del Material Dragado en los Puertos Españoles" (CEDEX, 1994), presenta guías de calidad de sedimento provisionales, únicas para todas las costas españolas y no tienen en cuenta los efectos asociados. Como futuro plan de acción, el mismo documento recomienda el desarrollo de SQGs basado en tests biológicos y que sean más específicos para los diferentes tipos litorales de la costa de España.

1.2 Objetivos e hipótesis

En este estudio se propone la aplicación de un método de evaluación integrado para estimar la calidad de los sedimentos y materiales de dragado. El método, desarrollado en el ecosistema bentónico, tiene como objetivo evaluar el nivel de polución de los sedimentos. Para esto se llevó a cabo la determinación simultánea de los niveles de contaminación, los efectos tóxicos sobre los organismos bajo condiciones de laboratorio y los efectos adversos que se producen sobre las comunidades bentónicas en condiciones de campo. El objetivo principal de este proyecto es la **armonización de protocolos para la caracterización ambiental de los sedimentos y material de dragado portuario entre Brasil y España**, integrándose la herramienta biológica y posibilitando la gestión de este material mediante un método escalonado para una correcta toma de decisiones, común a los países objeto de estudio. El trabajo consta de tres fases:

1) una primera basada en la caracterización físico-química y toxicológica de los sedimentos en Brasil (Sistema Estuarino de Santos y Sistema Estuarino de Paranaguá) y en España (Ría de Huelva, Bahía de Cádiz y Bahía de Algeciras) para determinar la contaminación y grado de polución existente en las estaciones elegidas de cada zona costera;

2) en la segunda fase se aplicó el método completo de forma simultánea para todas las zonas de estudio, integrando los resultados de los análisis físico-químicos, de los tests ecotoxicologicos y de la estructura de la comunidad bentónica;

3) por último se incorporó la determinación de los índices de calidad ambiental y el cálculo de guías de calidad ambiental (SQVs) para cada una de las zonas estudio. Estos criterios (SQVs) fueron comparados con los niveles de acción que se utilizan

habitualmente en las recomendaciones para la gestión de dragados portuarios en Brasil, España y otros países.

La hipótesis de partida establece que los métodos integrados son válidos para la caracterización del material de dragado y para su gestión en sistemas litorales del hemisferio norte y del hemisferio sur. La inclusión de diferentes líneas de evidencia, como la determinación de las concentraciones de contaminantes en sedimentos, sus efectos tóxicos y la modificación de la estructura de la macrofauna bentónica permite establecer niveles de acción para la cuantificación de la calidad ambiental de sus sedimentos y con base a ellos, establecer su correcta gestión. Se considera que en las zonas estuarinas y portuarias sujetas a diversos tipos de contaminación industrial y domestica – existe una correlación entre el nivel de contaminación de los sedimentos (medido a través de la cuantificación de los niveles de metales, hidrocarburos policiclícos aromáticos y bifenilas policloradas), la toxicidad (medida en laboratorio a través de la exposición de organismos marinos al sedimento estudiado) y las alteraciones en el ecosistema bentónico (investigado a través del análisis de la estructura de la comunidad de la macrofauna bentónica).

En este trabajo se pretende una optimización y aplicación de un método integrado para la adecuada evaluación de la calidad de los sedimentos en distintos sistemas estuarinos y portuarios del Atlántico. A través de este método integrado se desarrolló un protocolo de caracterización de material de dragado amplio y efectivo, lo que posibilita su aplicación en ambas áreas de estudio.

1.3 Zonas de estudio

Sistema Estuarino de Santos

El sistema estuarino de Santos (23º30’ a 24º Sur; 46º05’ a 46º30’ Oeste) (Figura 4) es una amplia región estuarina compuesta por diversos ríos rodeados por ecosistemas de manglares que representan un 43% de todo el área de manglares del Estado de São Paulo (Lamparelli et al., 2001). Esta zona abriga el principal puerto de Latinoamérica, el Puerto de Santos; además de su proximidad con la región metropolitana de São Paulo, las facilidades de transporte y disponibilidad de energia favorecieron la instalación de industrias como metalúrgicas, petroquímicas y fertilizantes. La gran concentración de industrias de este tipo dio lugar al pólo petroquímico de Cubatão, el segundo más grande complejo industrial brasileño (UNEP, 2002). La importancia económica de esta zona incluye las actividades de pesca y su vocación natural para el turismo.

Estudios anteriores demostraron el deterioro ambiental al que se ha visto sometida esta zona, sobre todo debido a la contaminación por metales, hidrocarburos policiclícos aromáticos y bifenilas policlorados. La mayor parte de los estudios están enfocados principalmente a la contaminación química (Lamparelli et al., 2001; Bonetti, 2000; Prósperi et al., 1998; Boldrini y Navas-Pereira, 1987; CETESB, 1985, 1981, 1978; Tommasi, 1985, 1979; Fúlfaro et al., 1983). Recientemente se ha investigado la toxicidad del agua y de los sedimentos (Cesar et al., 2007, 2006; Abessa, 2002; Rachid, 2002; Abessa et al, 1998). La degradación ambiental es mayor en las partes internas del estuario, en la salida del emisario del alcantarillado submarino de Santos (Abessa, 2002;

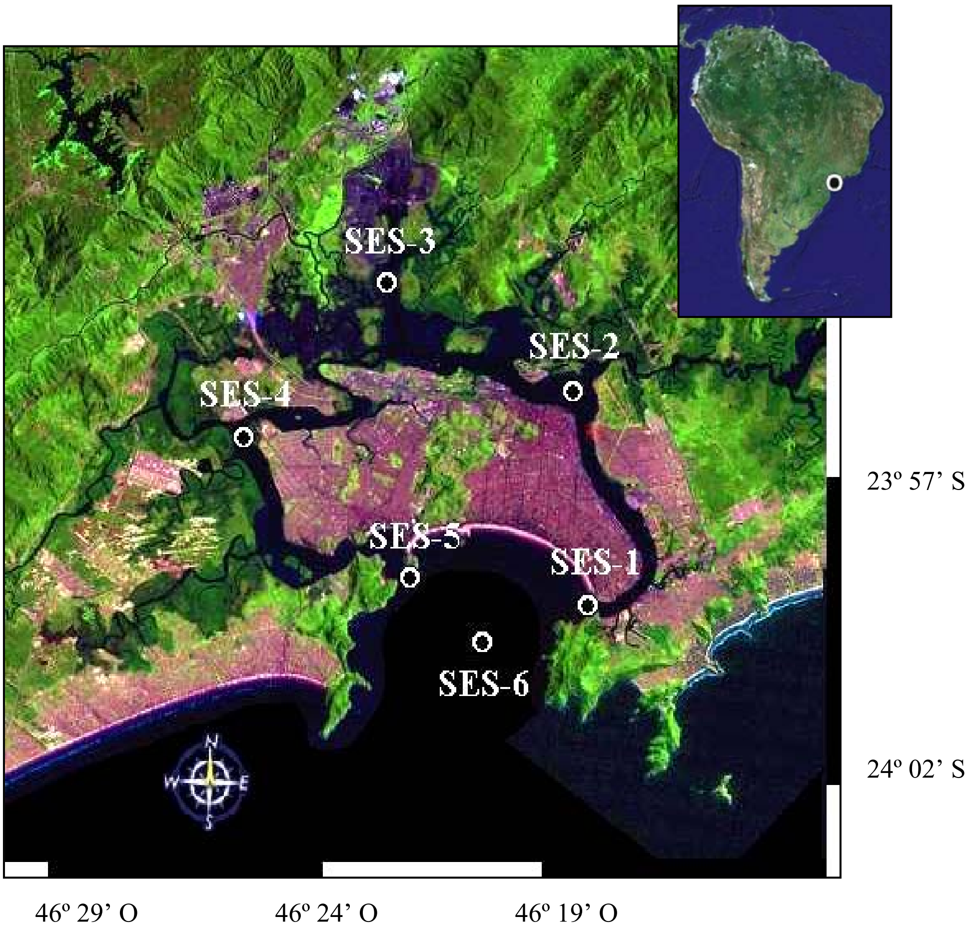
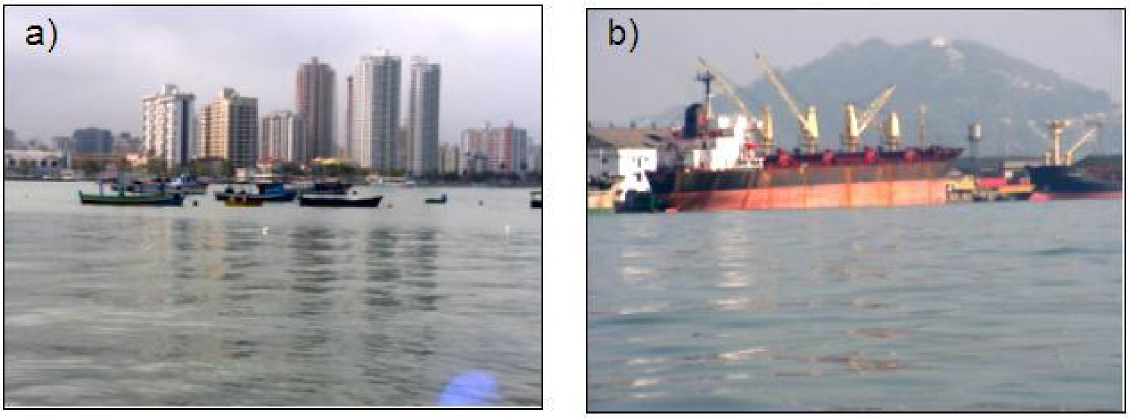


Figura 4: Sistema Estuarino de Santos (SP) y estaciones de muestreo. Imagen extraída de http://www.cdbrasil.cnpm.embrapa.br/

Lamparelli et al., 2001) y en la zona proxima a la Isla de la Moela, probablemente debido a la disposición del material de dragado del Puerto de Santos (Lamparelli et al., 2001). Las principales fuentes de contaminación son los efluentes industriales del pólo petroquímico de Cubatão, la contaminación del puerto, los emisarios y la disposición inadecuada de residuos urbanos e industriales.

Los puntos de muestreo establecidos en el sistema estuarino de Santos fueron diseñados con la finalidad de incluir las diferentes fuentes contaminantes en esta zona:

- Estación SES-1: localizada en la parte externa del Canal de Santos, es la entrada del puerto de Santos, donde las operaciones de dragado son continuas (Figura 5a);
- Estación SES-2: localizada en el interior del puerto de Santos. Estación sometida a una fuerte influencia de las actividades portuarias (Figura 5b);
- Estación SES-3: localizada en la zona más interna del estuario, incluye la parte final del puerto y se ve fuertemente afectada por el polo petroquímico de Cubatão (Figura 5c);
- Estación SES-4: localizada también en el interior del estuario, frente al municipio de São Vicente (Figura 5d);
- Estación SES-5: está localizada en la salida del estuario (Figura 5e);
- Estación SES-6: localizada en el interior de la Bahía de Santos, en la desembocadura del emisario de alcantarillado submarino de Santos (Figura 4f);



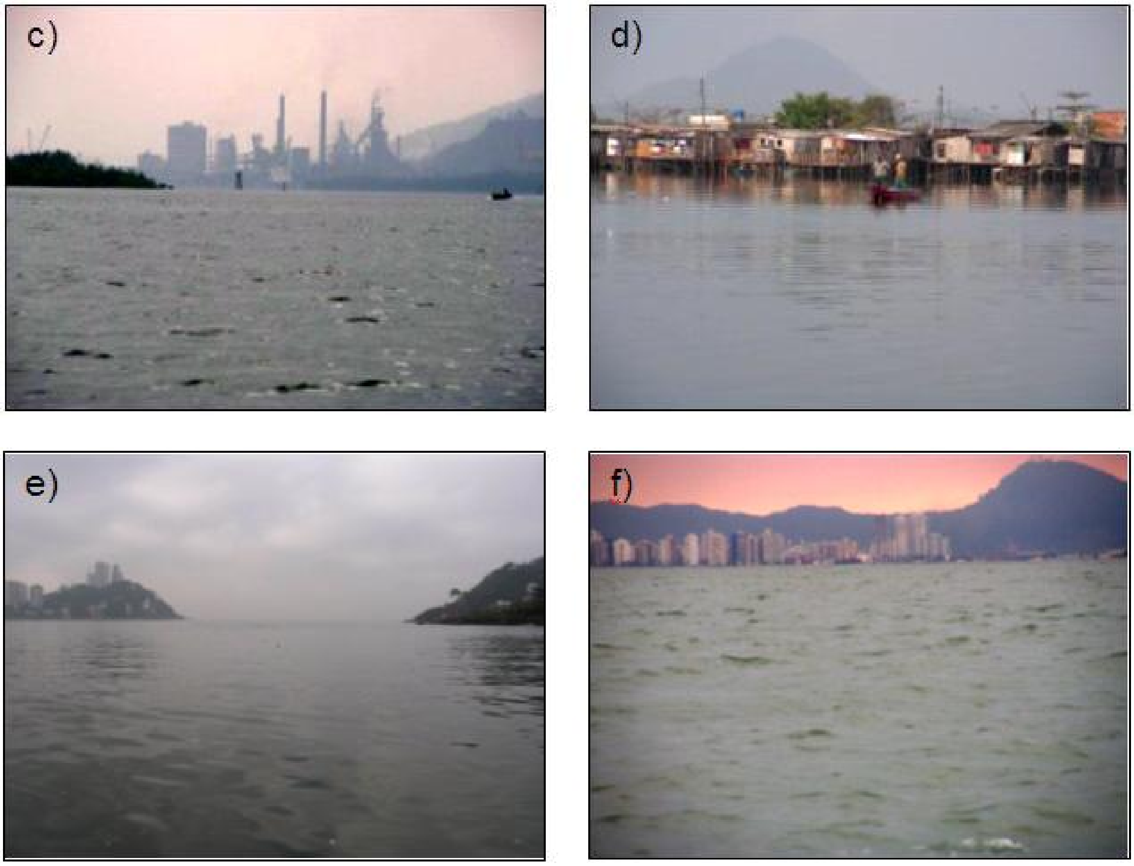


Figura 5: Estaciones de muestreo en el sistema estuarino de Santos. a) SES-1; b) SES-2; c) SES-3; d) SES-4; e) SES-5; f) SES-6. Fotos: Choueri, R.B.

Sistema Estuarino de Paranaguá

El sistema estuarino de Paranaguá (SEP) (25º16’ a 25º34’ Sur; 48º17’ a 48º42’ Oeste) (Figura 6) está formado por importantes ecosistemas, como marismas, manglares, restingas y Foresta Atlántica. En estos ecosistemas se destacan las actividades portuarias, concentraciones urbanas, actividades de pesca comercial y artesanal, y zonas de interés turístico (Noernberg, 2001).

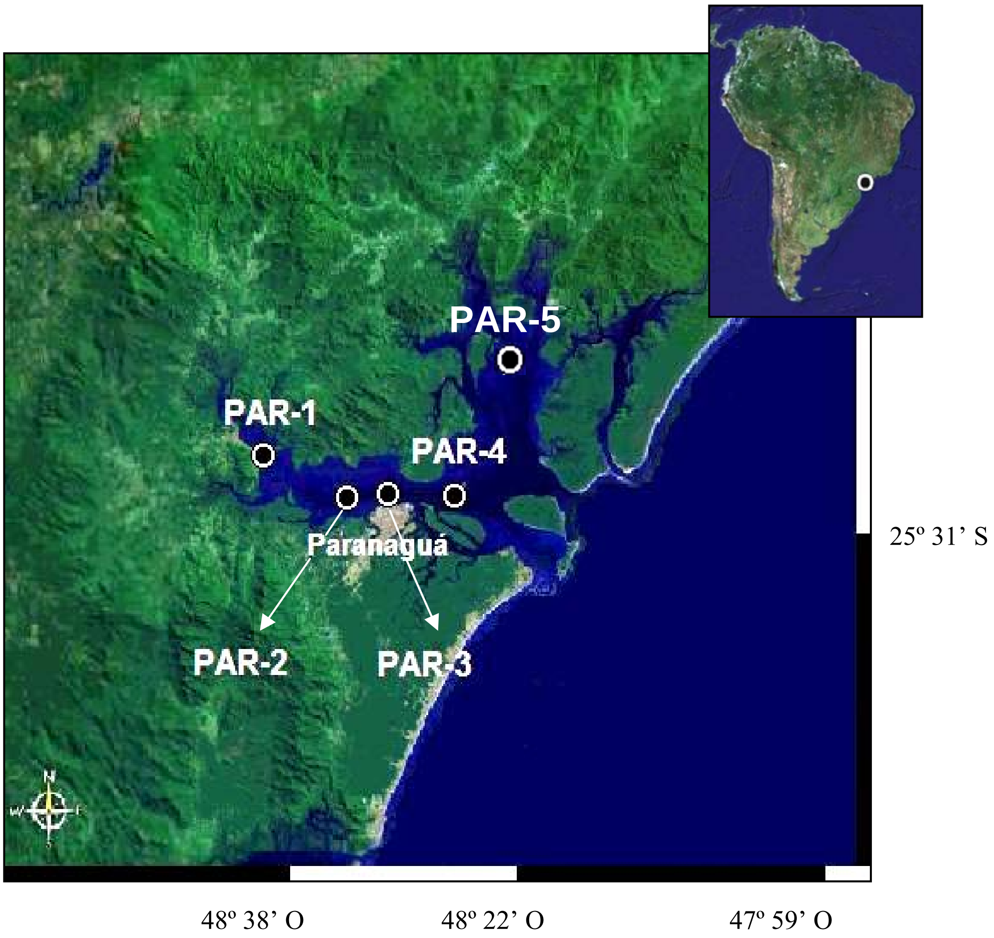


Figura 6: Localización de las estaciones de muestreo en el sistema estuarino de Paranaguá. Imagen: MDA EarthSat 2006; DigitalGlobe 2006. ©GoogleEarth.

El área en que se sitúa el SEP considerase poco polucionada si se compara a otras zonas del litoral Sur-Sureste brasileño. En la región de Cananéia y Iguape, en el Sur del Estado de São Paulo, se forma el “Complejo Estuarino Lagunar Paranaguá-Cananéia-Iguape”. Esta fue la primera zona de Foresta Atlántica definida como Reserva de la Biosfera por parte de la UNESCO (decreto de 1995).

Una potencial fuente de degradación para el ambiente del SEP es el Puerto de Paranaguá, el más grande del Sur de Brasil y también utilizado por Paraguay para el transporte de todos sus produtos (importación y exportación). El principal producto del Puerto de Paranaguá son los graneles sólidos, especialmente productos agrícolas (soja, maíz, trigo, cebada, malte), fertilizantes, sal y minerales. Existe también un terminal petrolífero de la Petrobrás conectado a la refinaría de Araucária, localizada más en el interior, por un oleoducto.

Existen diversos estudios referentes a la evaluación de los riesgos de operaciones portuarias (Bassfeld, 1998; Soares et al., 1996), incluyendo la carga y descarga de petróleo y sus derivados en el Puerto de Paranaguá (Soares y Marone, 2004). Sin embargo el SEP sufrió importantes accidentes de hidrocarburos. Cabe destacar el accidente tuvo lugar en 2001, cuando 392 mil litros de Nafta fueron vertidos del buque petrolero 'Norma'. En 2004 se vertieron entre 3 y 4 millones de litros de metanol, IFO y por el buque chileno 'Vicuña', después de tener lugar diversas explosiones ocasionadas por un fallo en la descarga de los combustibles.

Todas las estaciones de muestreo en el SEP están localizadas en el canal de navegación del Puerto de Paranaguá y Puerto de Antonina. Este canal es dragado periódicamente para permitir el pasaje de buques de gran porte. Las estaciones de muestreo se disponen a lo largo de un transecto de sentido Oeste-Este, adecuado para el establecimiento de un gradiente de contaminación desde las zonas más internas del estuario hacia zonas con mayor influencia marina (Figura 6):

- Estación PAR-1: es la estación más interna del estuario, localizada en las proximidades del terminal portuario Ponta do Félix (Figura 7a);
- Estación PAR-2: localizada al Este de PAR-1 y más próxima del municipio y puerto de Paranaguá;

- Estación PAR-3: localizada enfrente al puerto de Paranaguá. Esta estación está sometida a una fuerte influencia del puerto y municipio de Paranaguá (Figura 7b);
- Estación PAR-4: la estación mas externa del estuario, bajo influencia de aguas oceánicas;

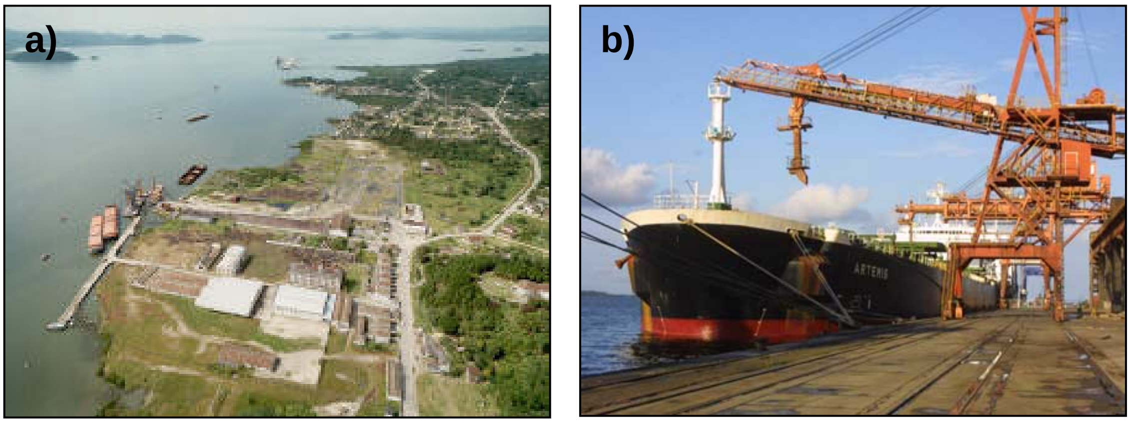


Figura 7: Vista general del a) Terminal Portuário Ponta do Félix (PAR-1); b) Puerto de Paranaguá (PAR-3).

Ría de Huelva

La Ría de Huelva (Figura 8) constituyen dos estuarios formados por las desembocaduras de los rios Tinto y Odiel. Esta zona está históricamente sujeta a contaminación de origen minera desde el início de la ocupación Romana en la Península Ibérica (Riba et al., 2004a). La mayor parte de los contaminantes (sobre todo metales)

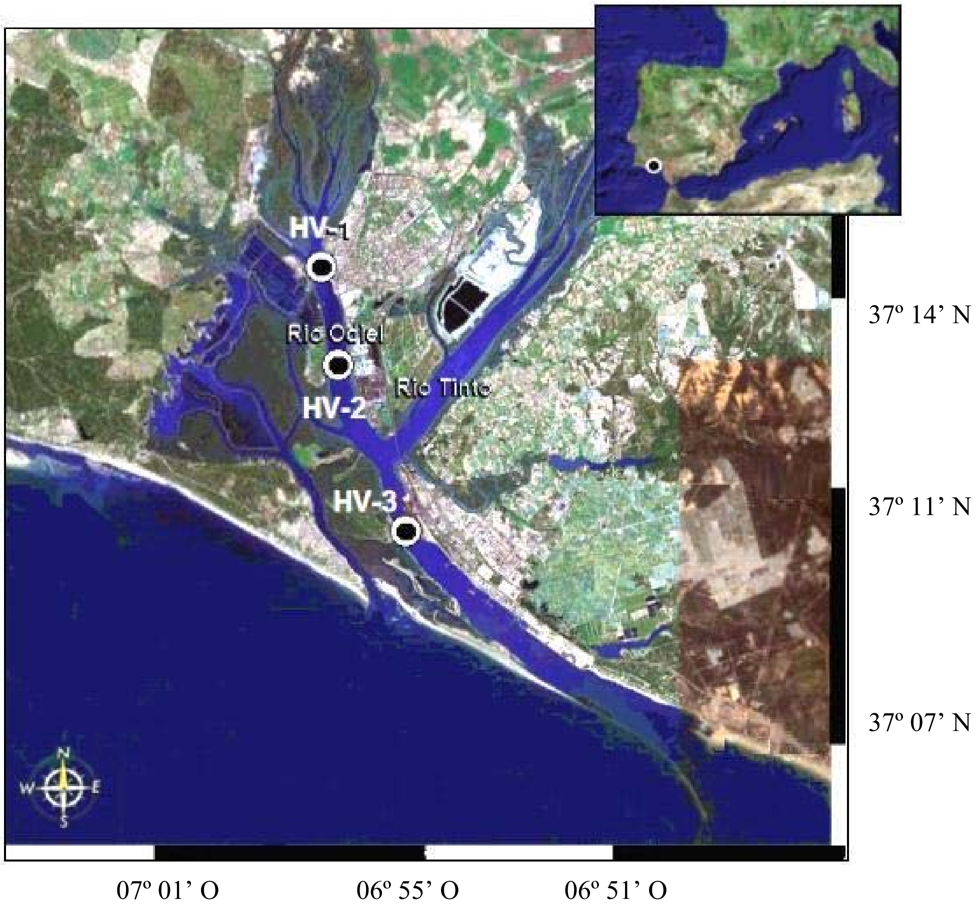


Figura 8: La Ria de Huelva y los puntos de muestreo. Imagen: MDA EarthSat 2006; DigitalGlobe 2006. ©GoogleEarth.

llegan al estuario a través del río Tinto, pero también se puede observar altos niveles de metales en el río Odiel, resultado de lavados piríticos curso arriba. La región abriga un denso polo industrial localizado en la margen izquierda del canal de acceso al puerto de Huelva (Canal del Padre Santo), donde son vertidos efluentes industriales directamente o a través de emisarios submarinos. El puerto de Huelva contribuye al deterioro ambiental de la ría debido a la constante necesidad de dragar el Canal del Padre Santo para poder permitir el acceso al interior del puerto.

El análisis integrado de la polución se llevó a cabo con anterioridad en esta zona haciendo uso de datos físico-químicos, histopatológicos y bioacumulación (Riba et al., 2005), y incluyendo tests de toxicidad (Riba et al., 2004a, b). Estos trabajos manifestaran la degradación ambiental a la que está sometida la Ría de Huelva.

Fueron definidas tres estaciones de muestreo para la determinación del gradiente de contaminación en la Ría de Huelva (figura 8). Todos los puntos de muestreo están sujetos a contaminación de origen minera: HV-1 y HV-2, bajo influencia de los contaminantes provenientes del rio Odiel y HV-3, tanto del rio Odiel como del rio Tinto.

- Estación HV-1: localizada en el rio Odiel, es la estación de muestreo más interna en la Ría de Huelva;
- Estación HV-2: localizada en el puerto de Huelva, esta estación sufre frecuentemente operaciones de dragados (Figura 9a);
- Estación HV-3: localizado en el canal del Padre Santo, en el terminal de descarga de CEPSA S.A., aguas abajo del puerto de Huelva y del puerto de Mazagón. Este punto también sufre operaciones de dragados frecuentemente (Figura 9b).

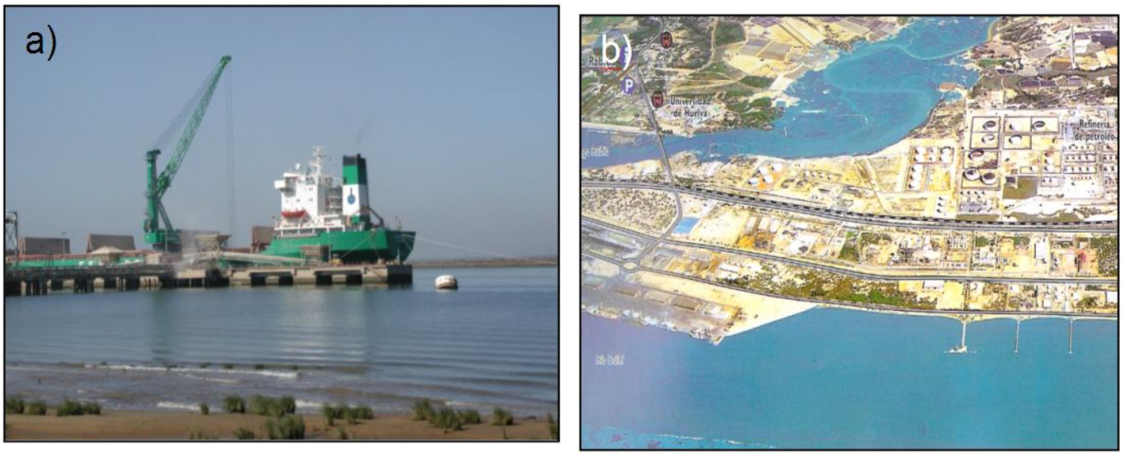


Figura 9: a) Vista general del puerto de Huelva (HV-2) (Foto: Cesar, A.); b) Vista aérea del canal del Padre Santo (HV-3) (Imagen: aeroguía del litoral Andaluz).

Bahía de Cádiz

La bahía de Cádiz (Figura 10) y sus marismas corresponden a un área de 30.000ha entre las latitudes 36º 23' y 36º 37' Norte y longitudes 6º 08' y 6º 15' Oeste. Desde el punto de vista hidrológico, esta zona está dividida en cuatro regiones:

- Bahía externa, con fuerte influencia oceánica, o sea, más expuesta a olas, vientos y mareas;
- Saco interno de la Bahía, localizada al Sur y Sureste de la bahía externa, con aguas rasas y menos expuestas a la acción de olas, pero con fuerte influencia de las mareas;

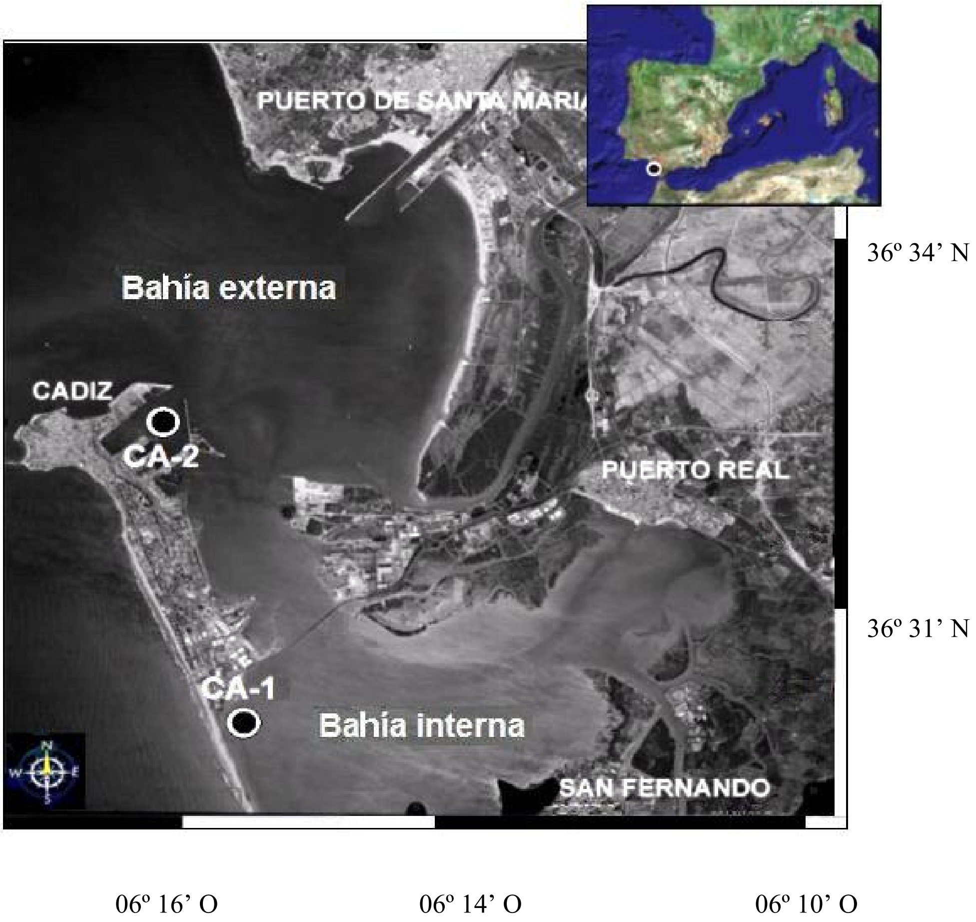


Figura 10: La bahía de Cádiz, las municipalidades en sus márgenes y las estaciones de muestreo. Imagen: modificada de Ligero *et al.*, 2004.

- Las zonas de marismas, las cuales ofrecen una rica variedad de ecosistemas, aunque estos ambientes han quedado deteriorados por la acción humana;
- La parte terrestre, de vital importancia por presentar una gran variedad de organismos y también por presentar sedimentos que garantizan el equilibrio sedimentario de este ambiente costero;

Cerca de 400.000 personas viven en los municipios en el borde de la bahía (Cádiz, El Puerto de Santa Maria, Rota, Puerto Real y San Fernando) y apenas parte de los efluentes provenientes de las zonas urbanas son tratados adecuadamente. Las principales industrias instaladas en esta zona son las industrias naval, automovilística y aerospacial. En el saco interno de la bahía también están situadas instalaciones de la industria de acuicultura. Asimismo la Bahía de Cádiz puede considerarse poco impactada por actividades antrópicas. Estudios anteriores, como Carrasco et al. (2003), identificaron contaminación por zinc, cromo, y también focos puntuales de contaminación industrial y doméstica. Estudios más recientes, demostraron no encontrar respuestas tóxicas relacionadas a los sedimentos de la bahía de Cádiz (Riba et al., 2004a).

Las estaciones de muestreo están representadas en la Figura 11 y brevemente descriptas a continuación:

- Estación CA-1: localizada en el canal navegable de la parte interna de la bahía;
- Estación CA-2: localizada en la bahía externa, en el interior del puerto de Cádiz (Figura 11a y 11b);

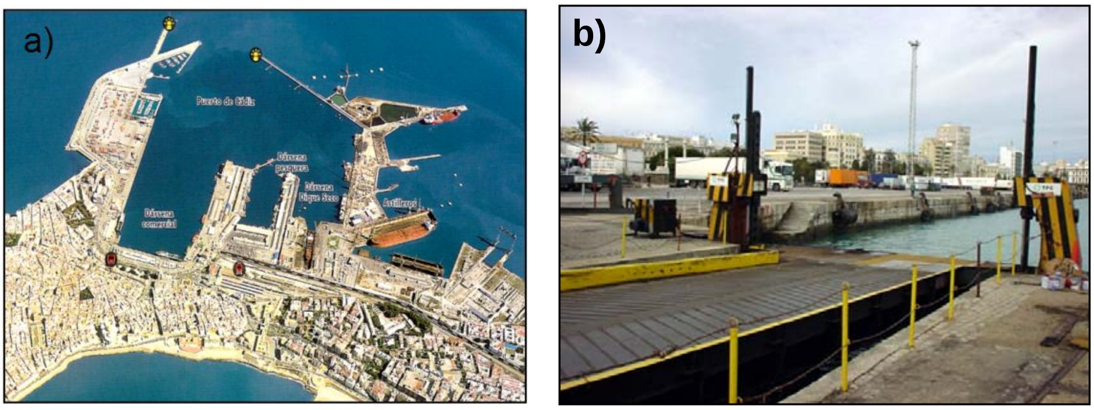


Figura 11: El puerto de Cádiz (CA-2). a) Vista aérea (Imagem: Aeroguía del litoral Andaluz); b) Vista general (Foto: http:www.uca.es)

Bahía de Algeciras

La bahía de Algeciras (Figura 12) está situada en el extremo Sur de España, al Este del Estrecho de Gibraltar. En esta bahía confluyen los ríos Palmones y Guadarranque. El municipio de Algeciras posee una población de fija de 111.283 habitantes (INE, 2005), a parte de una relevante población variable debido al importante puerto y el extenso polo industrial petroquímico instalados en esta zona.

Debido a su posición estratégica, el puerto de Algeciras uno de los más importantes de España, siendo punto de convergencia de las principales rutas marítimas que atraviesan el Mediterráneo y el Canal de Suez. También es el segundo puerto del Mediterráneo en abastecimiento de embarcaciones, suministrando 1,5 millón de toneladas de combustibles al año, lo que frecuentemente genera accidentes de vertidos de hidrocarburos.

Otra fuente de polución importante en la bahía es el polo industrial petroquímico instalado en las cercanías de la refinaría REPSA. Este complejo industrial está entre los cuatro más grandes de España (Duarte, 2000). Los Principales contaminantes producidos en esta zona son los metales y los contaminantes orgánicos persistentes.

A parte de su importancia portuaria e industrial, la bahía de Algeciras abriga tres importantes zonas de preservación ambiental: el Parque Natural de los Alcornocales, el Parque Natural del Estrecho de Gibraltar y el Parque Natural de las Marismas de Palmones, de importancia para el resguardo de la flora y fauna, especialmente a los pájaros que cruzan el estrecho durante las migraciones.

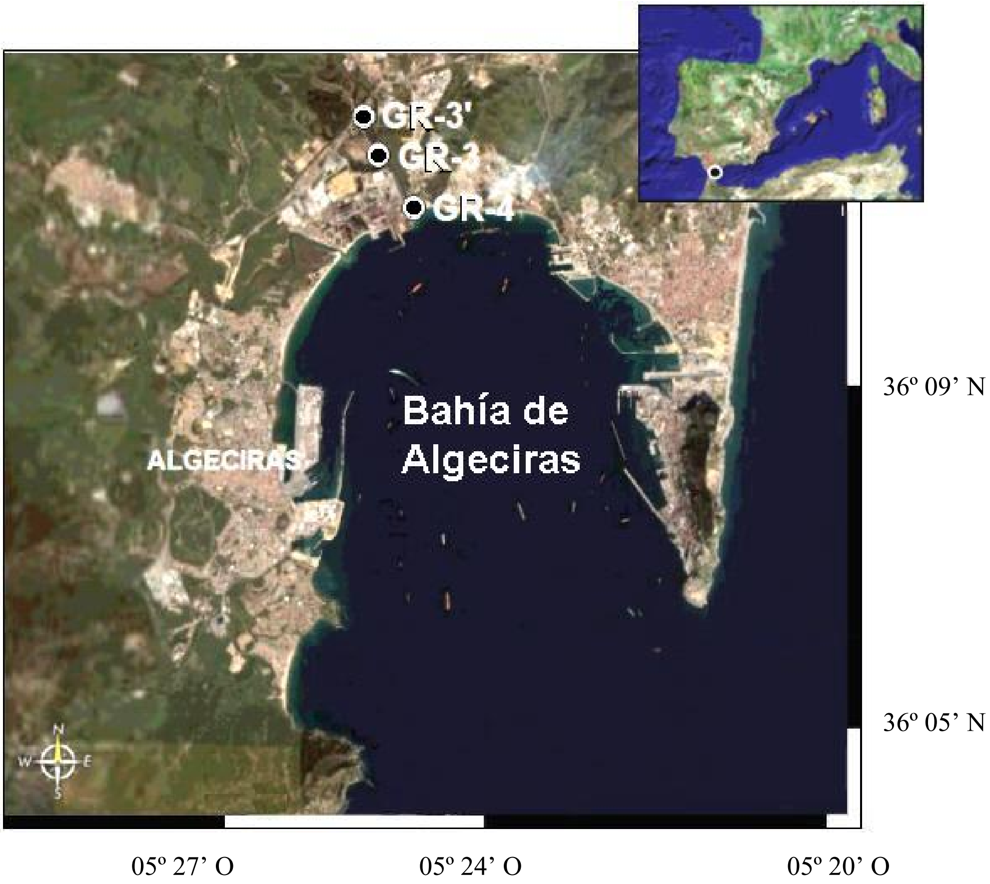


Figura 12: La bahía de Algeciras y las estaciones de muestreo. Imagen: DigitalGlobe 2006. ©GoogleEarth.

Las estaciones de muestreo localizadas en la bahía de Algeciras (GR-3’, GR-3 y GR-4 – Figura 12) están localizadas en la desembocadura del río Guadarranque. Este río recibe la mayor parte de los efluentes del polo industrial de Algeciras (Figura 12a).

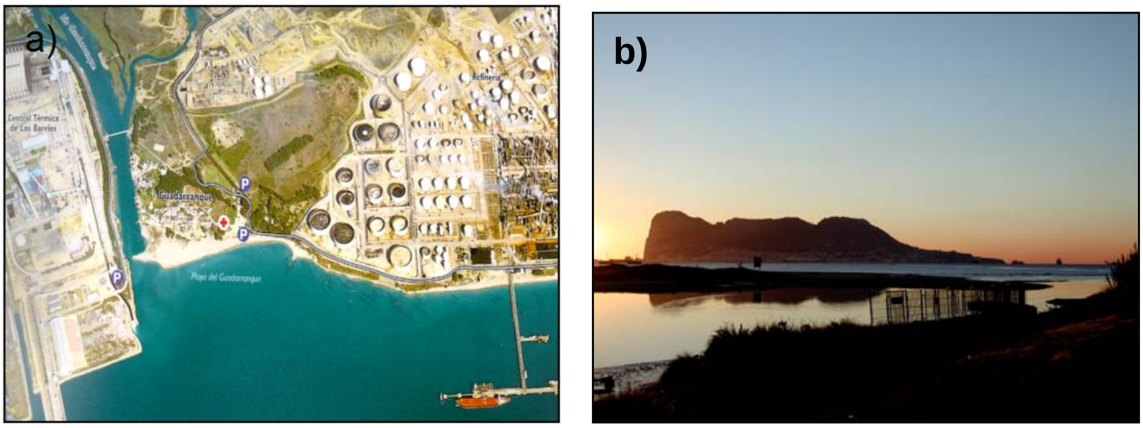


Figura 12: Estuario del río Guadarranque, en la bahía de Algeciras. a) Vista aérea (Aeroguía del litoral Andaluz); b) Vista general (Foto: Cesar, A.)

1.4 Estructura de la tesis

Esta tesis doctoral esta estructurada en cuatro capítulos: el **primer capítulo** es una **presentación del tema** que da unidad al estudio: el método de integración de diferentes líneas de evidencia para evaluar la calidad de sedimentos. En este capítulo quedan también descritos los **objetivos**, las **hipótesis planteadas** y una breve **descripción de las zonas de estudio**. Cada uno de los capítulos principales (capítulos 2 y 3), donde esta presentada la memoria, incluye una breve introducción en español del tema principal desarrollado en el capítulo, junto con los trabajos de investigación. Estos trabajos están presentados en el formato de publicación. Se presentan los trabajos, aceptados o enviados para revistas científicas incluidas en el SCI.

El **capítulo 2**, denominado '**Determinación de la calidad ambiental en zonas del Atlántico Norte y del Atlántico Sur mediante diferentes líneas de evidencia:**

contaminación, toxicidad y alteración' incluye los trabajos I, II y III; el primero de ellos presenta los resultados de la integración de datos de toxicidad y contaminación de los sedimentos del Sistema Estuarino de Santos y el calculo de valores-guía de calidad de sedimento para esta zona. El segundo trabajo presenta la integración de datos de toxicidad y contaminación de los sedimentos en las zonas de estudio de Brasil y España. El trabajo III está enfocado en el análisis de la estructura de la comunidad bentónica en las zonas de estudio y como éstas responden a la contaminación en Brasil y España;

El **capítulo 3 – "Armonización de un método integrado basado en el peso de la evidencia para determinar la calidad de los sedimentos y la gestión de los dragados en zonas del Norte y Sur del Atlántico"**, incluye la aplicación del método integrado de forma completa (datos de contaminación, toxicidad y de estructura de comunidad bentónica) en una zona de estudio (capítulo IV), el cálculo de valores-guía de calidad de sedimentos para cada zona de estudio, considerando los efectos biológicos observados (capítulo V) y, en el capítulo VI, se propone un protocolo de ámbito internacional para la evaluación del riesgo ambiental de sedimentos y materiales dragados.

El **capítulo 4** de esta memoria finaliza con las **conclusiones** obtenidas tras la consecución de los objetivos planteados para esta tesis doctoral.

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Capítulo 2.

Determinación de la calidad ambiental en zonas del Atlántico Norte y del Atlántico Sur mediante diferentes líneas de evidencia: contaminación, toxicidad y alteración

2.1 Introducción

La determinación de la calidad de los sedimentos es uno de los temas más importantes para determinar la calidad ambiental de un ecosistema acuático. Esto se debe a las características y propiedades únicas de los sedimentos: dependiendo de las condiciones ambientales, este compartimiento de los ambientes acuáticos puede actuar como depósito o fuente de contaminantes para el ecosistema.

Las evaluaciones de la calidad de los sedimentos están tradicionalmente basadas en uso de análisis químicos de estos materiales para determinar cuales son los contaminantes que están presentes y cuales son sus concentraciones. El riesgo potencial de los contaminantes asociados al sedimento se evalua a través de comparaciones con guías numéricas (SQGs) (Casado-Martinez, 2006). Sin embargo, en algunos casos la concentración total de los contaminantes en los sedimentos no se correlaciona con la biodisponibilidad de estos químicos (Ingersoll et al., 1997). Otros factores pueden afectar a la disponibilidad de los contaminantes para los organismos acuáticos, como pH, salinidad, la granulometria del sedimento, el contenido de materia orgánica y de sulfuro ácidos volátiles (SAV) (Riba et al., 2004; Riba et al., 2003; Simpson, 2001; Meyer et al., 1994).

Actualmente se reconoce que el empleo de diferentes líneas de evidencia (como por ejemplo los análisis químicos, análisis toxicológicos y de alteraciones de estructura de comunidades biológicas *in situ*) es necesaria para una evaluación global de la calidad de los sedimentos. Los análisis químicos identifican y cuantifican los contaminantes presentes en los sedimentos; los tests de toxicidad determinan el daño biológico de estos contaminantes bajo condiciones de laboratorio; las evaluaciones de estructura de comunidad bentónica refleja fuentes de estrés a lo largo del tiempo y considera diferentes especies bentónicas, que poseen diferentes niveles de tolerancia a la contaminación química y que ocupan diferentes nichos ecológicos en los sedimentos, esclareciendo los efectos biológicos bajo condiciones de campo. De este modo, para obtener una estimación realista de la calidad del sedimento y para reducir la incertidumbre de la aplicación de cada línea de evidencia individualmente, se ha recomendado la integración de las diferentes evaluaciones para la caracterización de la calidad ambiental (DelValls et al, 2004; Mozeto et al., 2004; Chapman, 2002).

En este capítulo se presenta tres artículos en los cuales se emplearon diferentes líneas de evidencia para la determinación de la calidad ambiental. En el primer trabajo (I) se investigó la calidad de los sedimentos del Sistema Estuarino de Santos, en Brasil, a través de la integración de los datos físico-químicos y de toxicidad de los sedimentos. La técnica estadística de integración de las variables conlleva la aplicación de un análisis de factores con una extracción de componentes principales. Se calcularon Valores-guía de calidad de sedimento a partir de estos resultados. En el segundo trabajo (II) la técnica de integración de datos físico-químicos y de toxicidad se llevó a cabo en diferentes ecosistemas litorales: en el Atlántico Norte (Golfo de Cádiz) y Atlántico Sur (Sistema Estuarino de Santos). Este estudio identificó los contaminantes que se asociaban con los efectos tóxicos en las zonas de estudio y comprobó la utilidad de la herramienta de integración de los datos para ecosistemas litorales distintos, incluso sin la necesidad de seleccionar una zona de referencia.

En el tercer trabajo se utilizó la técnica de integración para datos físico-químicos y de estructura de comunidad bentónica de los sedimentos del Golfo de Cádiz y del Sistema Estuarino de Santos. El objetivo fue estudiar como responden a la contaminación las comunidades bentónicas en estas zonas. Para eso, a parte de la integración de datos de contaminación y descriptores bentónicos, se han empleado otras técnicas estadísticas como el MDS y el análisis de *cluster* que van a ayudar en la discusión de los resultados. Los resultados indicaron que las comunidades bentónicas en las zonas de estudio presentan señales de estrés (baja diversidad y riqueza de especies, dominancia de poliquetos). Las comunidades están particularmente estresadas en zonas con baja influencia de aguas oceánicas (partes internas de los estuarios) y en las proximidades de fuentes de contaminación (industrias, puertos, actividades mineras, emisarios de vertidos urbanos). En la zona brasileña, los análisis MDS y cluster mostraran la heterogeneidad del sistema estuarino de Santos; la complejidad ambiental y las diferentes fuentes de contaminación contribuyen en la baja similitud entre las distintas partes del estuario. En el Golfo de Cádiz, las comunidades bentónicas muestran una mayor similitud entre las estaciones de la Bahía de Cádiz (en mejores condiciones) y entre las estaciones de la Bahía de Algeciras, formando dos grupos claros. El análisis multivariante reveló que las comunidades bentónicas en el Golfo de Cádiz están afectadas por una mayor variedad de contaminantes, mientras en el sistema estuarino de Santos solamente HPAs, V y Ni afectaron negativamente a las comunidades bentónicas.

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ECOTOXICOLOGICAL ASSESSMENT OF SEDIMENTS FROM THE SANTOS AND SÃO VICENTE ESTUARINE SYSTEM – BRAZIL

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ABSTRACT

Sediments represent an important repository of pollutants and a source of contamination for the aquatic food web. Toxicity tests using amphipods as test-organisms have been employed in the assessment of marine and estuarine sediments, together with chemical analyses. The present work aimed to evaluate the quality of sediments from six stations situated in the Santos and São Vicente Estuarine and Harbour System (São Paulo - Brazil) using acute whole sediment toxicity tests with amphipods (*Tiburonella viscana*) and chemical analyses of metals, PCB's, and PAH's. Other sediment parameters, such as organic carbon and grain size distribution were also analysed. Higher contamination levels were observed in the internal portion of the estuary, where Santos harbour and the industrial zone are located. The toxicity tests showed significant adverse results for most of the samples tested, and the sediments from the internal portion of the estuary presented the highest toxicity. The principal component analyses (PCA) indicated a close relationship between sediment contamination and toxicity. Positive correlation of these factors in the samples studied was used to establish the ranges of the chemical concentrations associated with adverse effects. Such ranges allowed the estimation of preliminary effect threshold values for sediment contamination, by means of multivariate analysis. These suggested values are: Cu, 69.0; Pb, 17.4; Zn, 73.3 (mg.kg^{-1}); PAHs, 0.5 (mg.kg^{-1}) and PCBs, 0.1 (µg.kg^{-1}).

RESUMO

O sedimento representa um importante depósito de contaminantes e uma fonte de contaminação para a cadeia alimentar aquática. Testes de toxicidade usando anfípodos como organismos-teste são empregados para avaliar sedimentos marinhos e estuarinos, juntamente com análises químicas. O presente trabalho tem como objetivo avaliar a qualidade de sedimentos de seis estações situadas no Sistema Estuarino e Portuário de Santos e São Vicente (São Paulo-Brasil), usando testes de toxicidade aguda com sedimento com anfípodos (*Tiburonella viscana*) e análises químicas de metais, PCB, e PAH. Outros parâmetros do sedimento foram analisados, como carbono orgânico e granulometria. Foram observados níveis de contaminação mais altos na porção interna do estuário onde se localiza o Porto de Santos e a zona industrial. Os testes de toxicidade mostraram resultados adversos significantes para a maioria das amostras testadas, e os sedimentos da porção interna do estuário apresentaram toxicidade mais alta. As análises de componentes principais indicaram uma relação forte entre contaminação do sedimento e toxicidade. As correlações positivas destes fatores nas amostras estudadas foram usadas para estabelecer os pesos das concentrações químicas que estão associadas com os efeitos adversos. Tais análises permitiram estimar valores limiares de efeito para a contaminação de sedimento através de análises multivariadas, identificando os contaminantes associados com o efeito biológico. Estes valores sugeridos são: Cu, 69.0; Pb, 17.4; Zn, 73.3(mg.kg^{-1}); PAHs, 0.5 (mg.kg^{-1}) e PCBs, 0.1 (µg.kg^{-1}).

Descriptors: Toxicity tests, Contamination; Multivariate analysis, Sediment quality values, Santos and São Vicente Estuarine System.
Descritores: Testes de toxicidade, Análises multivariadas, Valores de qualidade de sedimento, Sistema Estuarino de Santos e São Vicente.

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INTRODUCTION

Most of the anthropogenic chemicals and waste materials, including toxic organic and inorganic chemicals, contribute to the degradation of aquatic environments. This is particularly important for the coastal and estuarine ecosystems, which are constantly affected by multiple contamination sources.

The Santos and São Vicente Estuarine System (Fig.1) is located on the coast of the State of São Paulo, Brazil (23°30'5''S - 24°S; 46°05'W - 46°30'W), and in the centre of the *Baixada Santista* Metropolitan Region. The largest Brazilian industrial complex is installed in this densely urbanized region, with the predominant presence of its petrochemical, steel, and fertilizer industries – the major Latin American port that of Santos, is also to be found here. This region is economically important not only because of its industrial development, but also because of its natural tourist and fishery activities. Apart from its outstanding economic importance, the region has also considerable environmental relevance since the Santos and São Vicente Estuarine System is surrounded by mangrove swamps, which account for 43% of the total mangrove area of the state of São Paulo (Lamparelli *et al.,* 2001).

Although it is of great ecological importance, the high density of its urbanization, the presence of multiple potentially polluting industries and its port activities all greatly affect the environmental quality of the Santos and São Vicente Estuarine System. Large quantities of contaminants are discharged into this estuary, resulting in high sediment contamination and toxicity (Lamparelli *et al,* 2001; Abessa *et al.,* 1998; Abessa, 2002; Weber & Bícego, 1987; Boldrini & Navas-Pereira, 1987; CETESB, 1985; Fúlfaro *et al.,* 1983).

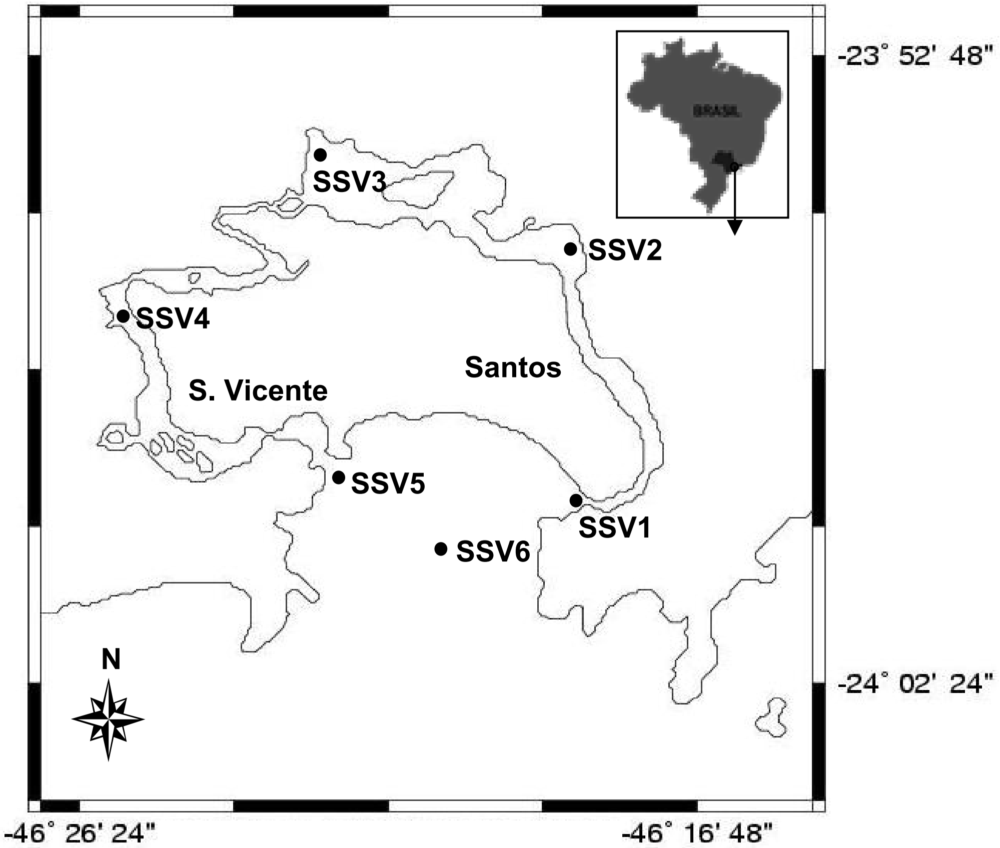

Fig. 1. Geographical location and position of the sampling points in the Santos and São Vicente estuarine system.

Sediments may accumulate contaminants in concentrations higher than those observed in the water column, thus producing harmful effects on the benthic biota and the organisms that feed on the benthos or the sediment. Due to its ecological importance and the persistence of pollutants in this environmental compartment, the sediment is more adequate for monitoring in environmental evaluations (Swartz *et al.,* 1982).

Many different approaches may be used in sediment quality assessment. Among them, chemical analyses and toxicity tests are the most commonly used around the world. Chemical analyses consist of listing the contaminants and quantifying their respective concentrations, and provide information on the presence of substances at such levels as may cause problems (Burton Jr., 1992). Toxicity tests are considered effective tools for providing direct, quantifiable evidence of the biological consequences of contamination, and can be used to estimate the interactive toxic effects of complex contaminant mixtures in the aquatic environment (Burton Jr., 1992). Infaunal amphipods are suitable and are strongly recommended as test organisms in sediment toxicity bioassays (U.S. EPA, 1994; ASTM, 1997), being used world wide in ecotoxicological evaluations of marine sediments (Gannon & Beeton, 1971; Swartz *et al.,* 1982; Nipper *et al.,* 1993; Carr *et al.,* 1996; Abessa *et al.,* 1998; 2001; DelValls *et al.,* 1998; Cesar *et al.* 2000; Hunt *et al.,* 2001a; b).

The main objective of this study was to evaluate the quality of sediments from different sites affected by different sources of contamination, using an integrated method that applies both sediment chemistry and toxicity assessment. A further objective was to derive preliminary site-specific quality values for the Santos and São Vicente Estuarine System using multivariate analysis, for the ranges of chemical concentrations associated with adverse biological effects.

Material and Methods

Approach

This study was conducted at 6 sediment sampling sites along the Santos and São Vicente Estuary (Fig. 1). Three sites were located in the Santos Channel in the zone directly affected by the harbour and the industrial pole (SSV-1 to SSV-3); two were located in the São Vicente Channel (SSV-4 and SSV-5), that is affected mainly by non-treated sewage; and one was located in the central portion of the Santos Bay (SSV-6), near the Santo's Submarine Sewage Outfall (SSOS). Thus distributed, the sampling sites used in this study reflect the different sources and origins of contamination.

Sediment samples were collected synoptically at depths ranging from 4 to 8 m, in March 2004. The spatial sampling was designed on the basis of the results of previous studies (Abessa *et al.,* 2001; Lamparelli *et al.,* 2001) that showed the existence of sediment quality degradation gradient from the upper to the lower parts of the estuarine system. Replicate samples (n=3) were collected from all stations. External control sediment was collected for the amphipod tests (*Engenho D´Água* Beach - *Ilha Bela - São Paulo*). Intact sediment cores were collected by SCUBA divers, carefully capped and sealed underwater and held on ice in the dark during the transport to the laboratory. Only the top 3-5 cm layer of the superficial sediment was used. Sediments were stored at 4ºC in the dark for no longer than two weeks, prior to toxicity testing. The control and dilution water used in the experiments consisted of natural seawater (35) collected in unpolluted areas (where the organisms were also collected) and filtered through a GFC Watman® filter.

Sediment Physical-Chemical Analysis

The sediment was dried at 60 ^{o}C prior to chemical analysis. Dried sediments were gently homogenized. Afterwards, the samples were totally digested in accordance with the method described by Loring & Rantala (1992).

The concentrations of Zn, Cd, Pb, Cu, Ni, Co and V in the sediments were determined by differential pulse anodic stripping voltametry (DPASV). Measurements were taken with a hanging mercury drop electrode (HMDE), using a Methrom 693 processor and the respective applications bulletins (nº147-Methrom for Zn, Cd, Pb and Cu; Methrom Application nº V-81 for V). The quantification of the metal concentration was performed using the standard addition procedure by means of standard solutions for each metal (Titrisol, Merck). The analytical procedure for solid extracts was checked with the use of reference material (MESS-1 NRC and CRM 277 BCR), allowing agreement values greater than 90% for the certified sediments. Polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) were analyzed by using gas chromatography equipment fitted with an electron capture detector (ECD) (U.S. Environmental Protection Agency method 8080). All the analytical procedures were checked with reference materials (Marine Sediment References Material for Trace Metals–1, National Research Council (NRC), Certified Reference Material, 277 BCR, and Conceil National de Researches Canada, 277 BCR, for heavy metals; and NRCpCNRC HS-1 for organic compounds) and allow agreement with certified values higher than 90 %.

Grain size distribution was determined by standard mechanical dry sieve-shaker techniques to determine the sand, silt and clay fractions (Buchanan, 1984). Organic carbon (OC) content was determined using the titration method in accordance with of El Rayis´s (1985) modification based on the acidification of the sediment sample.

Amphipod Toxicity Test

The Platyischnopid amphipod *Tiburonella viscana* inhabits the upper layers of clean or muddy sands from midwater level to 65 m depths and is common on the coast of São Paulo State. Organisms and negative control sediment were collected from sand-banks along the *Engenho D'Água* Beach, *São Sebastião* Island (23°48'S-45°22''W) and acclimated for 3 days in the laboratory. Amphipod sediment toxicity tests were conducted in accordance with the method described by Melo & Abessa (2002). The test chambers were filled to 2 cm depth with the test sediments and filtered seawater up to 750 ml and then maintained overnight at 25 ± 2°C with gentle aeration. On the next day, 10 adult, healthy amphipods were added to each test chamber and the test begun. Four replicates per test sediment were prepared. The tests were conducted at 25 ± 2°C, under constant aeration and lighting. After ten days, the contents of the chambers were gently sieved through a 0.5 mm screen and the surviving amphipods counted. Missing organisms were considered dead. The dissolved oxygen concentration, salinity and pH of the overlying water in the test chambers were measured at the beginning and end of the test.

Statistical Analysis and Multivariate Approach

Toxicity data were checked for normality and homoscedasticity assumptions with Shapiro-Wilk's and Bartlett's tests, respectively. The amphipod mortalities were compared by the one-way analysis of variance (ANOVA), followed by Dunnet´s t'test. These analyse were carried out with the statistical package Toxstat® V.3.3 (Gulley *et al.,* 1991).

Contamination and toxicity data were analyzed by factor analysis using principal component analysis (PCA), a multivariate statistical technique for the exploration of variable distributions as the extraction procedure. The original data set used in the analysis included nine chemical concentrations, one toxicity endpoint, organic carbon and fines. Factor analysis was performed on the correlation matrix, that is, the variables were autoscaled (standardized) so as to be treated as of equal importance. All 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). For such analyses, the following data were used: total concentrations of Zn, Cd, Pb, Cu, Ni, Co, V, PCBs and PAHs, OC content, grain size distribution and toxicity (amphipod mortality).

RESULTS AND DISCUSSION

Sediment Physical-Chemical Analysis

Results obtained for sediment contamination and physical-chemical parameters are summarized in Table 1. Sediment samples tended to present relatively similar granulometric characteristics, with percent of fines ranging between 2 and 5%, excepting the sediments from SSV-3 and SSV-6, which presented higher contents of fines (approximately 10%). The result for the sediments from SSV-2 and SSV-3 differs from those obtained previously by Abessa (2002) for the same region. For other samples, both studies agreed, especially as regards SSV-6, where the higher levels of fines are due to the precipitation of particles discharged by the SSOS. According to Abessa *et al.* (2005), the sewage outfall emits suspended solids at above the maximum rate permitted for effluents under Brazilian law. Organic carbon contents in the sediments ranged from 0.8% to 4 %. Higher levels were found in the sediments collected in the estuary, indicating the influence of the mangroves and the sewage disposal in the organic enrichment of the sediments in the system.

The concentrations of metals in the sediments from the internal portion of the estuary (SSV-2; SSV-3 and SSV-4), where the Santos harbour and the industrial zone are located, were higher than those measured in the samples from the lower estuary and Santos Bay (SSV-1; SSV-5 and SSV-6). The metals contents exceeded the limits established by the Brazilian Legislation for Dredged Sediments (CONAMA nº.344; Brazil, 2004) for the samples from stations SSV-2 (Cu, Pb and Zn) and SSV-3 (Cu). These results corroborate those obtained previously (Abessa, 2002; Lamparelli *et al*., 2001), which showed the same distribution pattern of pollutants for this area.

According to Lamparelli *et al.* (2001), the most internal portion of the estuary (represented by SSV-3 in this study) is affected by the Cubatão River, which receives most of the effluents from the Cubatão industrial complex. Thus this area receives the major contribution of chemicals. Moreover, Abessa (2002) found high concentrations of metals in the area close to the SSV-2, suggesting that such levels were due to industrial discharges. Other sources of the pollutants of the estuary are the old industrial and domestic landfills, nowadays considered contaminated by the State Environmental Agency (Lamparelli *et al.,* 2001).

Table 1. Results of amphipod toxicity test and physical-chemical analysis in the sediments from Santos and São Vicente Estuary.

Sampling sites	Amphipod* Mortality (%)	Trace Metals (mg.kg^{-1})							Organics		Sediment properties	
	Mean (± sd)	Cd	Co	Cu	Ni	Pb	V	Zn	PAH's (mg.kg^{-1})	PCB's (µg.kg^{-1})	O.C (%)	Fines (%)
SSV-1	25.0 ± 5.8	<0.1	<0.1	<0.1	4.85	17.4	36.0	73.3	0.106	0.66	3.75	3.96
SSV-2	72.5 ± 5.0	<0.1	<0.1	167.2	2.96	66.2	24.0	154.2	0.518	4.00	1.24	4.46
SSV-3	77.5 ± 12.6	<0.1	<0.1	157.7	4.49	22.1	87.8	110.4	0.425	2.61	2.78	9.68
SSV-4	80.0 ± 11.5	<0.1	<0.1	69.0	3.83	14.9	104.8	66.8	0.950	0.94	2.82	2.67
SSV-5	40.0 ± 8.2	<0.1	<0.1	<0.1	3.89	8.69	18.6	32.6	0.163	0.58	0.85	1.42
SSV-6	67.5 ± 9.6	<0.1	<0.2	<0.1	6.02	14.6	<0.1	53.2	0.600	<0.1	1.00	11.56

* Amphipod species – *Tiburonella viscana*.

These landfills, a consequence of illegal industrial and domestic waste disposal in recent decades, are scattered around the estuary and may be another considerable source of contamination – via superficial drainage or leachates – of the inner parts of the estuary. The central portion of the Santos Channel also receives a constant influx of chemical contaminants because of the activities of Santos harbour (Lamparelli *et al.,* 2001). Abessa (2002) proposed that both regions should be considered highly polluted as regards metal contamination, and our data corroborate that author's suggestion.

The results obtained for PAHs and PCBs showed the same trend as that observed for the metals. According to Lamparelli *et al.* (2001), the sources of PCBs for the Santos and São Vicente Estuarine Complex may be the substances used or produced by the industrial processes (such as Ascarel and Arochlor) and the atmospheric deposition of PCBs released into the air by factories. In the present study, the sediments collected in the areas close to the industrial complex (stations SSV-2 and SSV-3) showed the highest values of PCBs, thus corroborating the results obtained by Lamparelli *et al*. (2001).

The highest concentration of PAHs was measured in the sediments from station SSV-4, located at the mouth of the Piaçabuçu River. Abessa (2002) also found a high concentration of PAHs in sediments in the same area. This river (Piaçabuçu) receives domestic sewage *in natura* and the river basin drains areas affected by old illegal industrial landfills, which are contaminated by a variety of chemicals. According to Lamparelli *et al.* (2001), both sources may contribute to the introduction of PAHs into this area. Moreover, sediments from stations SSV-2 and SSV-3 also presented high concentrations of PAHs, probably due to industrial and port activities. The contamination of these areas has already been registered in previous works (Abessa *et al.,* 2001; Lamparelli *et al.,* 2001; Medeiros & Bícego, 2004).

Amphipod Toxicity Test

Results of the whole sediment toxicity test using *Tiburonella viscana* are given in Table 1. Mean amphipod mortality (10-day exposure) ranged from 80% at SSV-4 to 25% at SSV-1. Sediments from almost all the stations were considered toxic to *T. viscana* ($p<0.05$), excepting the sample from station SSV-1, which was not significantly different from the negative control (*Engenho D´água* beach). Water quality data (TºC, D.O., salinity, and pH) were kept constant and within the acceptable limits (Melo & Abessa, 2002) during the experiment.

The results obtained in this investigation for sediment toxicity are in accordance with previous data for the Santos and São Vicente Estuary (Abessa, 2002; Abessa *et al.,* 1998; 2001). The toxicity of the sediments from SSV-2 and SSV-3 was clearly related to the port operations and industrial activity. According to the authors mentioned above, the sediments from the Santos Channel have frequently been toxic, even since the first studies conducted in this area and despite the removal of superficial sediments from the channel by routine dredging. Moreover, these two sites presented the highest levels of contaminants in the present study, which explains the toxic effects on the amphipods. The toxicity of the sediments from SSV-4 was probably related to the contamination sources previously mentioned for the São Vicente Channel (i.e., untreated domestic sewage released into the Piaçabuçu River and waste disposal landfills). This sample presented the highest levels of PAHs, which may have caused the toxicity. Among the significant toxic sediments, SSV-1 and SSV-5 showed the lowest mortality. Although the contamination levels at this site were not high, Abessa *et al.* (2005) found the toxicity to be associated with the high levels of detergents in the sediments from that place, thus evidencing that the discharge of untreated sewage affects the sediment quality. Thus, the sewage was probably a further cause of the toxicity of the sample from station SSV-6, located close to the SSOS diffusers. Rachid (2002) conducted a Phase 1 TIE study using porewater from that site, and showed that toxicity was mainly caused by volatile substances, metals, ammonia and organic compounds, whereas Abessa (2002) and Lamparelli *et al.* (2001) attributed the toxicity to some specific contaminants such as chlorines, detergents, ammonia, sulphur and mercury. The results of our study partially corroborate with those previous findings above.

Multivariate Analysis Approach

The multivariate method (factor analysis) provides a deeper insight into the structure of complex and diverse data (Riba *et al.,* 2003). For example, this multivariate tool has revealed groupings of varying degrees of correlation between chemical concentrations in sediment and their biological effects. Chemical concentrations in sediments have been associated by PCA with toxicity to amphipods, the indicator of biological effects (Table 2). Such factors have been used to explain 84.7% of the variance in the original data set. The first principal factor, PC1 accounted for 41.9% of the variance. This factor is correlated with the chemical concentrations of PCBs, Cu, Pb, Zn and toxicity. The second factor, PC2, accounted for 24.28% of the variances and combined O.M. and V contents. This factor represented the association of the organic carbon and vanadium in sediments (with higher loadings) but not those associated with biological response. Finally, the third factor accounted for the lowest variance (18.41%) and associated the toxicity (higher than in factor 1), PAHs and fines with higher loadings. This factor suggested that the biological effect could be related to the concentrations of PAHs associated with fines, although their concentrations are below those established by Brazilian Legislation for Dredged Sediments (CONAMA nº.344; Brazil, 2004) as toxic.

To confirm these factor descriptions and to establish preliminary effect threshold values for sediment contamination for the Santos and São Vicente Estuary and Bay, the representation of estimated factor scores from each station was used (Fig. 2). Factor 1 scores were negative for stations SSV-1, SSV-4, SSV-5 and SSV-6. On the other hand, the positive scores of factor 3 measured at stations SSV-3, SSV-4 and SSV-6, confirmed that this factor was related to the association of biological effect with PAH concentrations.

Table 2. Sorted rotated factor loadings (pattern) of the original 10 variables. The loading matrix has been rearranged so that the columns appear in decreasing order of variance explained by factors. Loadings greater than 0.32 are highlighted (bold type). Factors are numbered consecutively from left to right in order of decreasing variance explained.

Variable	Factor 1	Factor 2	Factor 3
% Variance	41.99	24.28	18.41
Cu	**0.88**	0.15	**0.37**
Ni	-0.82	-0.10	**0.35**
Pb	**0.91**	-0.24	-0,04
V	0.19	**0.84**	0.31
Zn	**0.91**	0.07	0.21
PAHs	0.14	0.15	**0.76**
PCBs	**0.97**	-0.02	0.11
O.C.	-0.07	**0.94**	-0.07
Fines	-0.20	-0.22	**0.76**
Toxicity	**0.42**	0.16	**0.87**

For the chemicals grouped with their highest loadings in factor 1 (PCBs, Cu, Pb and Zn) and in factor 3 (PAHs), the estimation of such effect threshold values in accordance with the procedures reported by DelValls *et al.* (1998) for Sediment Quality Values (SQVs). This approach is based on the comparison of the chemicals and the toxicity of their respective groups, i.e., in this case, factors 1 and 3. The assumption is that these chemicals are presumably correlated in a cause-and-effect relationship. Thus, when the scores of factors 1 and 3 (probable correlation between the chemicals and biological adverse effects) are 0 or below (Fig. 2), the maximum

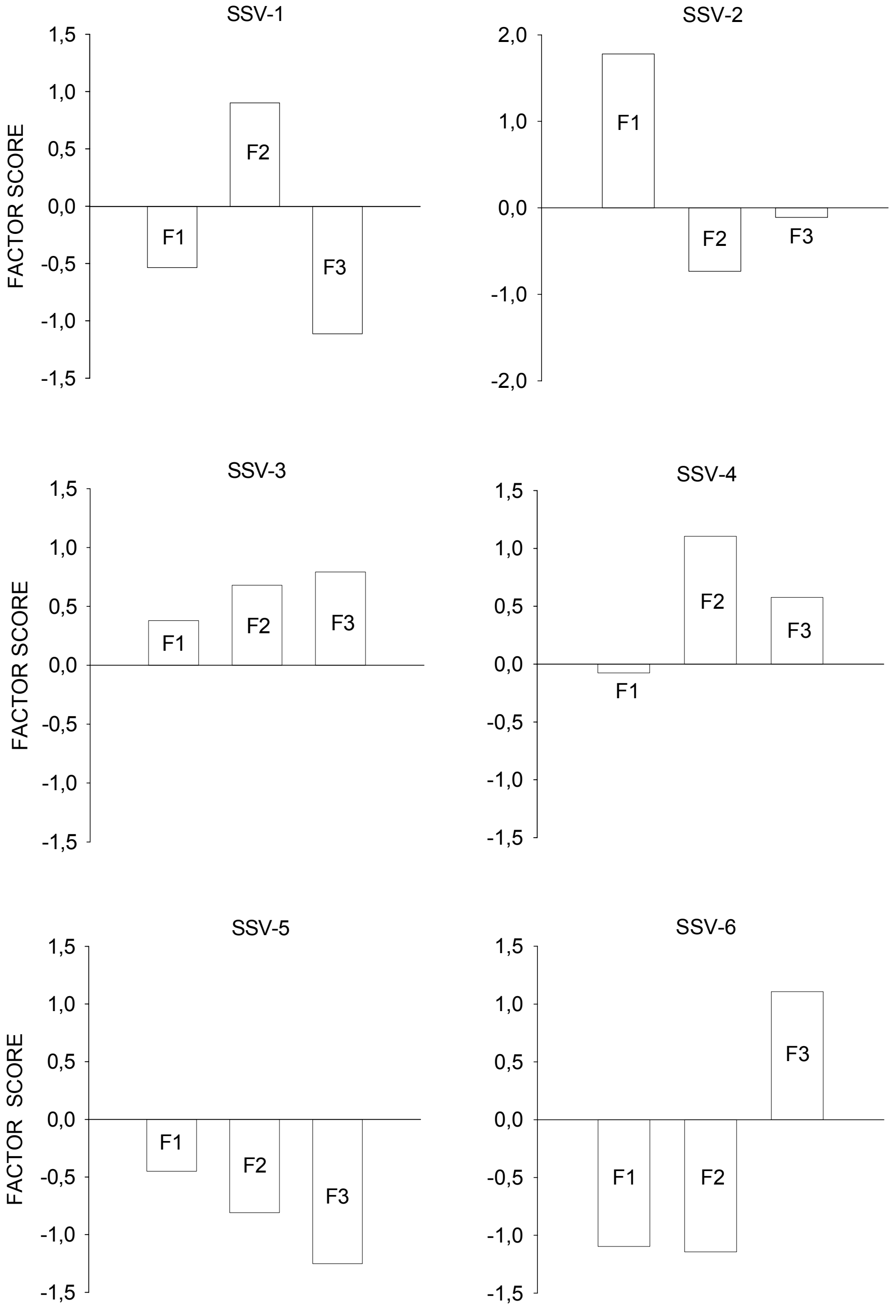

Fig. 2. Estimated factor scores to the centroid from each of six stations. The factor scores quantify the influence of each component (contaminant) on the toxicity at each station and are used to confirm the factor description.

concentrations of toxic chemicals at any of those stations represent the maximum chemical concentrations that are not associated with adverse effects. These are considered to be concentrations below which biological effects are low or minimal and are here indicated as not polluted. By contrast, to establish the minimum concentrations above which biological effects are always high, those minimal concentrations where factor scores from factors 1 and 3 were higher than 0 were selected and described here as highly polluted. Also, an intermediate range of chemical concentrations representing an area of uncertainty, between the high and low concentrations, is described as moderately polluted. These three classes of sediment toxicity-contamination associations may be better identified from Table 3.

Table 3. Summary of the estimated effect threshold values for sediment contamination in the Santos and São Vicente Estuarine System for the metals Cu, Pb and Zn (mg.kg^{-1}), total polycyclic aromatic hydrocarbons (ΣPAHs; mg.kg^{-1}) and total polychlorinated biphenyls (ΣPCBs; µg.kg^{-1}).

Chemical study	Sediment quality guideline		
	Polluted	Not polluted	Area of uncertainty
Cu	> 157.7	≤ 69.0	157.7 – 69.0
Pb	> 22.1	≤ 17.4	22.1 – 17.4
Zn	> 110.4	≤ 73.3	110.4 – 73.3
ΣPAHs	> 0.6	≤ 0.5	0.6 – 0.5
ΣPCBs	> 4.0	≤ 0.9	4.0 – 0.9

The results of this investigation showed that toxicity was closely related to the physical-chemical data, confirming the poorer sediment quality in the internal portions of the estuary, followed by the vicinity of the SSOS. Such results were in agreement with the literature on for this region (Lamparelli *et al.,* 2001; Abessa, 2002). As a consequence, the dredging operations and the oceanic disposal of sediments from the Santos Channel should be monitored to estimate the effective damage of these activities to local marine ecosystems. Moreover, the factorial analysis used in this study to estimate effect threshold values for sediment contamination was considered useful and should continue to be used to derive Sediment Quality Values and/or Guidelines.

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Comparative sediment quality assessment in different littoral ecosystems from Spain (Gulf of Cadiz) and Brazil (Santos and São Vicente estuarine system)

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Abstract

The goal of this work was to establish comparisons among environmental degradation in different areas from Southern Spain (Gulf of Cádiz) and Brazil (Santos and São Vicente estuary), by using principal component analyses (PCA) to integrate sediment toxicity (amphipods mortality) and chemical–physical data (Zn, Cd, Pb, Cu, Ni, Co, V, PCBs, PAHs concentrations, OC and fines contents). The results of PCA extraction of Spanish data showed that Bay of Cádiz, CA-1 did not present contamination or degradation; CA-2 exhibited contamination by PCBs, however it was not related to the amphipods mortality. *Ría* of Huelva was the most impacted site, showing contamination caused principally by hydrocarbons, in HV-1 and HV-2, but heavy metals were also important contaminants at HV-1, HV-2 and HV-3. Algeciras Bay was considered as not degraded in GR-3 and -4, but in GR-3′ high contamination by PAHs was found. In the Brazilian area, the most degraded sediments were found in the stations situated at the inner parts of the estuary (SSV-2, SSV-3, and SSV-4), followed by SSV-6, which is close to the Submarine Sewage Outfall of Santos — SSOS. Sediments from SSV-1 and SSV-5 did not present chemical contamination, organic contamination or significant amphipod mortality. The results of this investigation showed that both countries present environmental degradation related to PAHs: in Spain, at *Ría* of Huelva and Gudarranque river's estuary areas; and in Brasil, in the internal portion of the Santos and São Vicente estuary. The same situation is found for heavy metals, since all of the identified metals are related to toxicity in the studied areas, with few exceptions (V for both Brazil and Spain, and Cd and Co for Brazilian areas). The contamination by PCBs is more serious for Santos and São Vicente estuary than for the investigated areas in Gulf of Cádiz, where such compound did not relate to the toxicity.

Keywords: Sediment toxicity; Sediment contamination; Estuary; Multivariate analysis

1. Introduction

Most of the anthropogenic chemicals and waste materials, including toxic organic and inorganic chemicals, contribute to the degradation of aquatic environments. This is particularly important for the coastal and estuarine ecosystems around the world, which are constantly affected by multiple contamination sources.

Sediments may accumulate contaminants in concentrations higher than those observed in the water column, producing negative effects to the benthic biota and to the organisms that feed on the benthos or on the sediment. Due to the ecological importance and the persistence of pollutants in this environmental compartment, sediments are more appropriate to be monitored in environmental evaluations (Swartz et al., 1982).

Many different approaches can be used in the sediment quality assessment. Among them, chemical analyses and toxicity tests are the most used around the world (Acosta and

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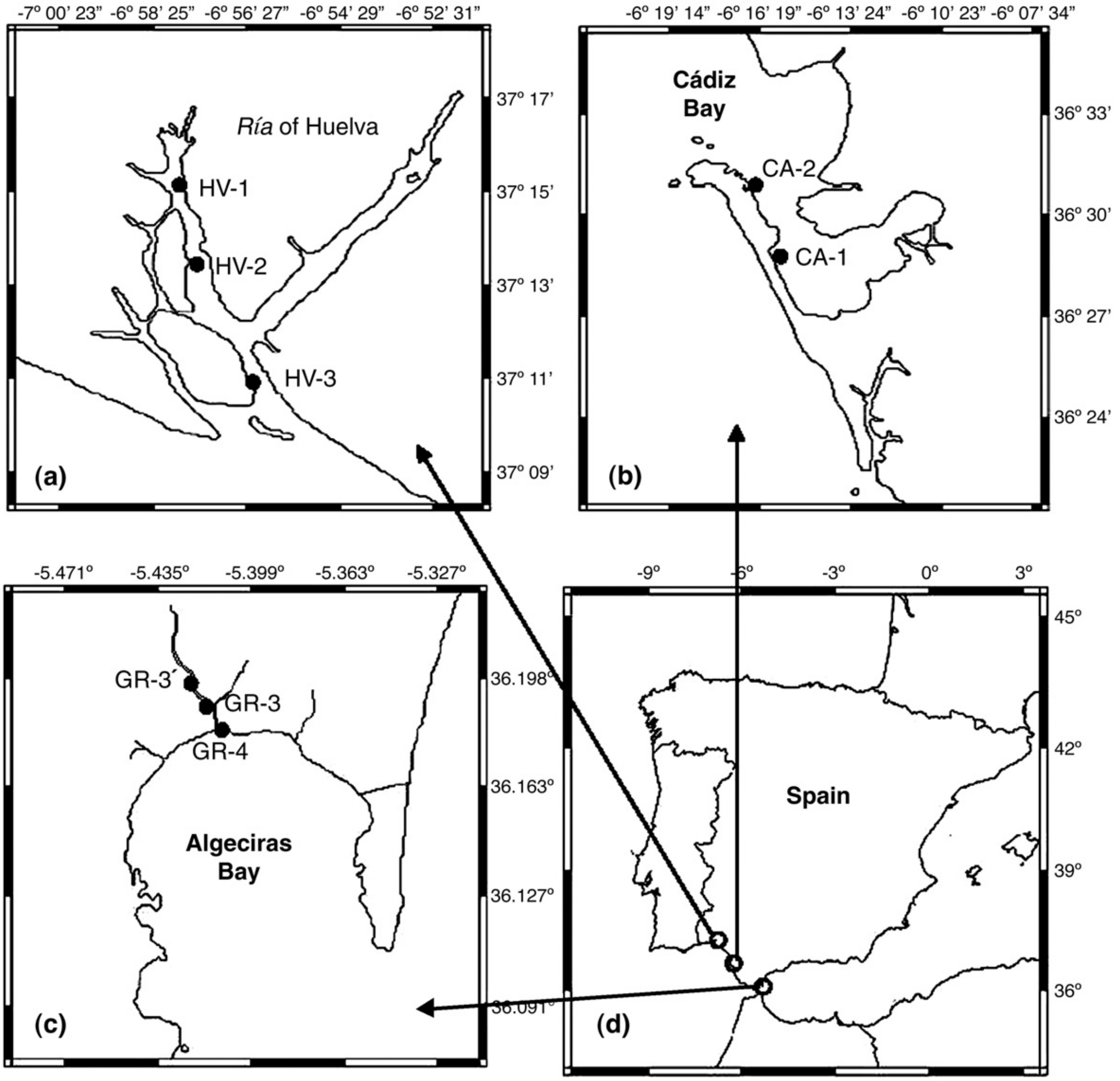

Fig. 1. Localization of the sampling stations in *Ría* of Huelva (a), Cádiz Bay (b), Algeciras Bay (c) and their disposition in Southern Spain (d).

Lodeiros, 2004; León et al., 2004; Evangelista et al., 2005). Such approaches, when applied alone, may result in lack of realism and/or great uncertainties; but when they are used in an integrative way, more reliable information about the environmental condition is provided.

There are several studies utilizing principal component analysis (PCA) to integrate environmental data (Riba et al., 2004a,b; DelValls et al., 2002; DelValls and Chapman, 1998). Thus, by using such multivariate tool, the goal of this work was to determine the environmental degradation in different coastal areas from Spain and Brazil, which are affected by different contamination sources.

Three areas from the Gulf of Cádiz, Southern Spain, were studied: *Ría* of Huelva, Bay of Cádiz, and Guadarranque River's estuary, in the Bay of Algeciras. *Ría* of Huelva and Bay of Algeciras are affected by industrial and harbour activities, whereas Bay of Cádiz is considered a low contaminated area, according to some recent studies (Riba et al., 2004a,b). In Brazil, the studied area was the Santos and São Vicente estuarine system, located in the São Paulo State, South-Eastern Brazil. This area comprises a dense urbanization area, the biggest Brazilian industrial complex – with predominant presence of petrochemical, siderurgy, and fertilizers industries – and also the major Latin American port, so called Port of Santos. There is a vast literature showing high sediment contamination and toxicity in this area (Cesar et al., 2006; Abessa, 2002; Abessa et al., 2001; Lamparelli et al., 2001; CETESB, 1985, 1978).

2. Materials and methods

2.1. Approach

This study was carried out in 8 sediment sampling sites distributed in 3 different regions (*Ría* of Huelva, Bay of Cádiz, and Guadarranque River's mouth) in Southern Spain (Fig. 1); and 6 sediment sampling sites distributed along the Santos and São Vicente estuarine system, in the Brazilian coast (Fig. 2). In Spain, 3 sampling sites were located in *Ría* of Huelva (HV-1, HV-2 and HV-3), an ancient mining area where nowadays an industrial zone and a harbour are installed; 2 sampling sites were positioned at the Bay of Cádiz (CA-1 and CA-2), an area with low level of sediments contamination (Riba et al., 2004a,b); 3 sampling sites were located at the mouth of Guadarranque River, in Bay of Algeciras (GR-4, GR-3 and GR-3′). Such river receives industrial effluents from

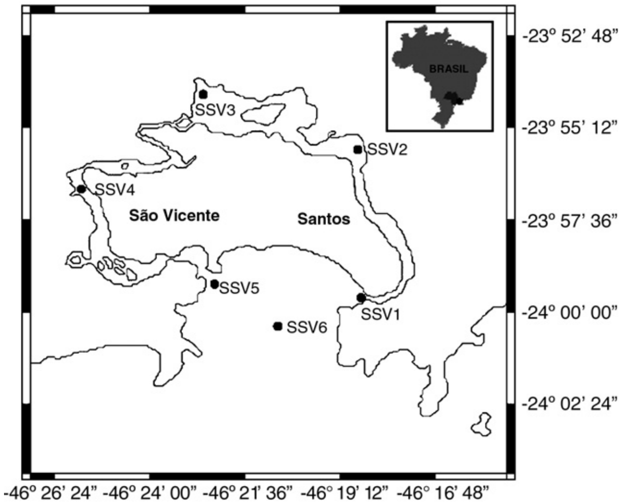

Fig. 2. Localization of the sampling stations in Santos and São Vicente estuarine system — Brazil.

the Algeciras industrial zone. In the Santos and São Vicente estuarine system, 3 sampling sites were located in the Santos Channel, in the influence zone of the harbour and industrial complex (SSV-1, SSV-2 and SSV-3); 2 sampling sites were situated in the São Vicente Channel (SSV-4 and SSV-5), which is mainly influenced by nontreated sewage; and 1 site was located on the central portion of the Santos Bay (SSV-6), near the Submarine Sewage Outfall of Santos (SSOS). Distributed in this way, the sampling sites in Spain and Brazil represent different sources and origins of contamination.

Sediment samples were collected synoptically in each study area, in depths ranging from 1 to 5 m at each site, and stored at 4 °C in the dark. The following examinations were made with the collected sediments: (a) whole sediment toxicity test using the amphipods *Tiburonella viscana* for the Brazilian estuary (Melo and Abessa, 2002) and *Corophium voluntator* for the Spanish areas (Riba et al., 2003), and (b) chemical analysis of homogenized surface sediment for determination of heavy metals (Zn, Cd, Pb, Cu, Ni, Co and V) by DPASV with HMDE (Riba et al., 2002); polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) by using gas chromatography equipped with an electron capture detector (ECD) (U.S. Environmental Protection Agency method 8080); grain size distribution, by standard mechanical dry sieve-shaker techniques, to determine the sand, silt and clay fractions (Buchanam, 1984); and organic carbon (OC) content, using the titration method modified by El Rayis (1985), which is based on the acidification of the sediment sample.

The physical–chemical results of the sediment analyses from both Brazilian and Spanish sites were compared to the Canadian Sediment Quality Guidelines — SQGs (TEL — "Threshold Effect Level" and PEL — "Probable Effect Level") (Environment Canada, 1999), with exception of the nickel concentrations, which were compared to the guidelines proposed by the Florida Department of Environmental Protection (FDEP, 1994). According to the concept of SQG, adverse biological effects are not expected when the concentrations of contaminants are below the TEL values, whereas concentrations of contaminants higher than the PEL values will probably result in adverse biological effects.

2.2. Multivariate analysis

Toxicity and contamination data were integrated by factor analysis, using a principal components analysis as the extraction procedure. This is a multivariate technique to explore variable distributions. The original data set used in this analysis, as for the Spanish sites as for the Santos and São Vicente estuary, included 1 toxicity parameter (amphipods mortality) and 11 physical–chemical parameters (Zn, Cd, Pb, Cu, Ni, Co, V, PCBs, PAHs, %OC, and % of fines). Factor analysis was performed on the correlation matrix, that is, the variables were autoscaled (standardized) so as to be treated with equal importance. All analyses were performed using the PCA option of the *multivariate exploratory technics* procedure, followed by the basic set-up for *factor analysis* procedure from the STATISTICA software tool (Stat Soft, Inc., 2001; version 6).

3. Results

3.1. Sediment toxicity and physical–chemical data

Results of amphipods mortality responses, geochemical matrix characteristics and sediment chemistry are summarized in Table 1 for the Spanish sites and in Table 2 for the Brazilian sites.

The results of the toxicity test with sediments from Southern Spain showed higher toxicity at the *Ría* of Huelva sites and GR-3′ in Bay of Algeciras. Low amphipods mortality was found in Bay of Cádiz sediments, especially in CA-1. In Santos and São Vicente Estuarine System, sediments from the inner estuary (SSV-4, SSV-3, SSV-2) were toxic, as well as the sample collected close to the SSOS (SSV-6). The sediments from SSV-1 and SSV-5 exhibited the lower amphipods mortalities.

The comparison of the chemical data of sediments from Spanish areas to the SQG values (Environment Canada, 1999; FDEP, 1994) showed TEL exceedences for Cd in sediments from Bay of Cádiz (CA-2) and *Ría* of Huelva (HV-1, HV-2, and HV-3); Cu and Zn in Bay of Algeciras (GR-3 and GR-3′, respectively); Ni, at Bay of Cádiz (CA-2) and *Ría* of Huelva (HV-1 and HV-2); PAHs, at Bay of Algeciras (GR-3); and PCBs in Bay of Cádiz (CA-2). Concentrations of contaminants higher than the PEL values were found for Cu and Zn, in Bay of Cádiz (CA-2) and *Ría* of Huelva (HV-1, HV-2, and HV-3); Ni, at *Ría*of Huelva (HV-3) and Bay of Algeciras (GR-3′); Pb, at *Ría* of Huelva (HV-2 and HV-3); and PAHs at the mouth of Guadarranque river, in Bay of Algeciras (GR-3′).

In the Santos and São Vicente Estuarine System, two samples presented contaminants in concentrations higher than TEL: the one collected at the São Vicente Channel (SSV-4) (Cu and PAHs) and that from the Santos Channel (SSV-2), close to the Port of Santos (Pb and Zn). Levels of Cu, at SSV-2 and SSV-3 sediments, exceeded the PEL.

Table 1
Summary of amphipod toxicity test results and physical–chemical characteristics of the sediments for the Spanish stations

Sampling sites	Amphipod* mortality (%)	Trace Metals (ppm)							Organics		Sediment properties	
	Mean (±SD)	Cd	Co	Cu	Ni	Pb	V	Zn	PAH's (ppm)	PCB's (ppb)	O.C. (%)	Fines (%)
CA1	3.3±5.8	0.65	6.80	15.60	8.9	12.20	11,50	18,3	0.074	<0,01	1,10	6,8
CA2	26.7±5.8	1.20	18.30	169.00	29.3	99.20	132,10	360,0	0.096	161,00	2,60	66,4
HV1	100.0±0.0	3.90	26.00	1989.00	42.3	406.00	90,00	1945,0	0.298	3,50	2,10	88,3
HV2	96.7±5.8	2.50	10.00	1543.00	21.2	335.00	111,00	2010,0	0.191	4,60	2,90	89,5
HV3	76.7±5.8	1.60	14.00	789.00	97.2	198.00	76,00	987,0	0.100	1,10	3,90	74,5
GR3	66.7±5.8	0.29	<0.01	20.80	15.5	19.10	24,60	66,0	2.103	<0,01	3,44	75,4
GR4	43.3±5.8	0.10	5.59	3.67	13.1	6.21	0,01	35,3	0.712	<0,01	3,19	54,2
GR3′	100.0±0.0	0.17	12.80	5.01	74.7	21.60	26,10	138,0	12.003	<0,01	2,15	90,5

Table 2
Summary of amphipod toxicity test results and physical–chemical characteristics of the sediments for Santos and São Vicente estuarine system stations

Sampling sites	Amphipod* mortality (%)	Trace metals (ppm)							Organics		Sediment properties		
	Mean (±se)	Cd	Co	Cu	Ni	Pb	V	Zn	PAH's (ppm)	PCB's (ppb)	O.M. (%)	O.C. (%)	Fines (%)
SSV-1	25.0±2.9	<0.1	<0.1	<0.1	4.85	17.4	36.0	73.3	0.106	0.66	6.45	3.75	3.96
SSV-2	72.5±2.5	<0.1	<0.1	167.2	2.96	66.2	24.0	154.2	0.518	4.00	2.13	1.24	4.46
SSV-3	77.5±6.3	<0.1	<0.1	157.7	4.49	22.1	87.8	110.4	0.425	2.61	4.79	2.78	9.68
SSV-4	80.0±5.8	<0.1	<0.1	69.0	3.83	14.9	104.8	66.8	0.950	0.94	4.84	2.82	2.67
SSV-5	40.0±4.1	<0.1	<0.1	<0.1	3.89	8.69	18.6	32.6	0.163	0.58	1.47	0.85	1.42
SSV-6	67.5±4.8	<0.1	<0.2	<0.1	6.02	14.6	<0.1	53.2	0.600	<0.1	1.72	1.00	11.56

3.2. Multivariate analysis

3.2.1. Southern Spain sites

By means of the application of a PCA, the physical–chemical and toxicity data were represented by four new variables, or principal factors (Table 3), which explains 93.12% of the variance in the original data set. Table 3 gives the loadings following varimax rotation for the four factors. Each factor is described according to the dominant group of variables. The first principal factor (F1) is predominant and accounts for 48.88% of the variance; this factor relates almost all heavy metals (excepting Ni) to toxicity responses in the whole sediment toxicity test with amphipods. The second factor (F2) accounts for 20.46% of the variance and shows correlation among PAHs, Ni, percentage of fines, and amphipods mortality. The correlation between chemicals and amphipods mortality is higher in F2 than in F1. The third factor (F3), accounting for 13.02% of the variance, aggregates only PCBs (with a high value), Co and V, without relation to amphipods mortality. Finally, the fourth factor (F4), which accounts for 10.76% of the variance, shows the expected relation between organic carbon and concentration of fines.

3.2.2. Santos and São Vicente estuary sites

Chemical concentrations in sediments were associated by PCA with amphipods mortality, resulting in three principal factors (Table 4). The loadings following varimax rotation for the three factors are found in Table 4. Such factors explained 84.7% of the variance in the original data set. The first principal factor, F1, was predominant and accounted for 41.9% of the variance. This factor combines concentrations of PCBs, Cu, Pb, Zn and lethality to amphipods. The second factor (F2) accounts for 24.28% of the variance and combines organic matter, organic carbon and vanadium in sediments (with higher loadings), but the concentration of this metal and organic characteristics were not associated with biological response. Finally, the third factor (F3) accounts for the lowest variance (18.41%) and associates amphipods mortality (higher than in F1), PAHs and concentration of fines with higher loadings. This factor suggests that the biological effect could be related to the concentrations of PAHs associated to the fine particles of the sediment.

4. Discussion and conclusions

4.1. Sediment toxicity and physical–chemical data

The results of amphipods mortality are coherent to the concentrations of contaminants in the sediments from both Spanish and Brazilian areas. Low amphipods mortality was found in sediments from Bay of Cádiz, especially in CA-1. In CA-2, despite the low sediment toxicity, high concentrations of some metals (particularly Cu and Zn) and PCBs were detected. In Southern Spain, high toxicity was found at *Ría* of Huelva sediments, where the concentrations of all metals exceed either TEL or PEL values. Sediments were also very toxic in GR-3′ (Bay of Algeciras), where the concentration of PAHs exceeded the PEL.

Table 3
Sorted rotated factor loadings (pattern) of the original 14 variables on the four principal factors of Spanish stations

Variable	Factor 1	Factor 2	Factor 3	Factor 4
% Variance	48.88	20.46	13.02	10.76
Cd	0.98	–	–	–
Co	0.64	–	0.51	–
Cu	0.99	–	–	–
Ni	–	0.78	–	–
Pb	0.99	–	–	–
V	0.63	–	0.71	–
Zn	0.98	–	–	–
PAHs	–	0.81	–	–
PCBs	–	–	0.97	–
O.C.	–	–	–	0.97
Fines	0.43	0.72	–	0.43
Toxicity	0.53	0.73	–	–

The loading matrix has been rearranged so that the columns appear in decreasing order of variance explained by factors. Only loadings greater than 0.35 are shown. Factors are numbered consecutively from left to right in order of decreasing variance explained.

Table 4
Sorted rotated factor loadings (pattern) of the original 14 variables on the four principal factors of Santos and São Vicente estuary stations

Variable	Factor 1	Factor 2	Factor 3
% Variance	41.99	24.28	18.41
Cd	–	–	–
Co	–	–	–
Cu	0.88	–	0.37
Ni	–	–	0.35
Pb	0.91	–	–
V	–	0.84	–
Zn	0.91	–	–
PAH's	–	–	0.76
PCB's	0.97	–	–
O.M.	–	0.94	–
O.C.	–	0.94	–
Fines	–	–	0.76
Toxicity	0.42	–	0.87

The loading matrix has been rearranged so that the columns appear in decreasing order of variance explained by factors. Only loadings greater than 0.35 are shown. Factors are numbered consecutively from left to right in order of decreasing variance explained.

In the Santos and São Vicente Estuarine System, some contaminants showed concentrations above TEL and/or PEL values. Copper was the only contaminant found at concentrations higher than PEL (SSV-2 and SSV-3); sediments from these sites were highly toxic to amphipods. The sediment sample collected at the São Vicente Channel (SSV-4) was also toxic to *T. viscana*; in this area, Cu and PAHs concentrations exceeded the TEL values. According to Abessa (2002), 80% sediments exceeding TEL for at least one contaminant produced toxicity. The sediment from SSV-6 showed toxicity, which may be due to the discharges from the Submarine Sewage Outfall of Santos. Abessa (2002) demonstrated that the toxicity of sediments from this area is caused by detergents, sulphur, ammonia, and eventually, metals. Samples collected at areas more influenced by marine waters (SSV-1 and SSV-5) showed lower toxicity.

4.2. Multivariate analysis

Besides the analysis of the variables aggregated by PCA, a representation of estimated factor scores from each station to the centroid of all cases for the original data was done in the present work, in order to confirm the factor descriptions and to characterize the quality of the sediment at each Spanish and Brazilian studied site, as can be seen in Fig. 3 for the Spanish sites and Fig. 4 for Santos and São Vicente estuary sites.

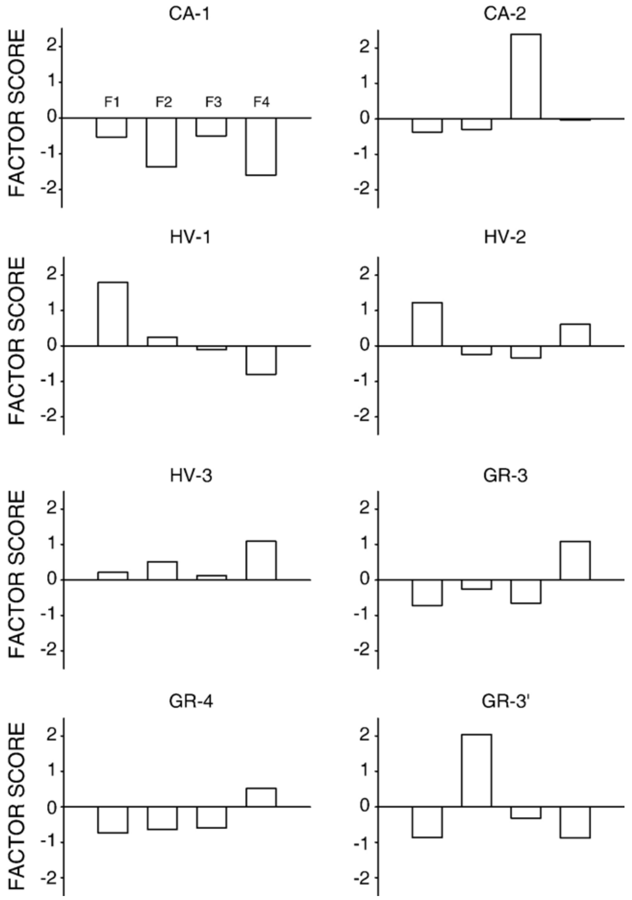

Fig. 3. Estimated factor scores from each of eight cases to the centroid of cases for the original data from Spanish stations. The factor scores quantify to the prevalence of every component for each station and are used to confirm the factor description.

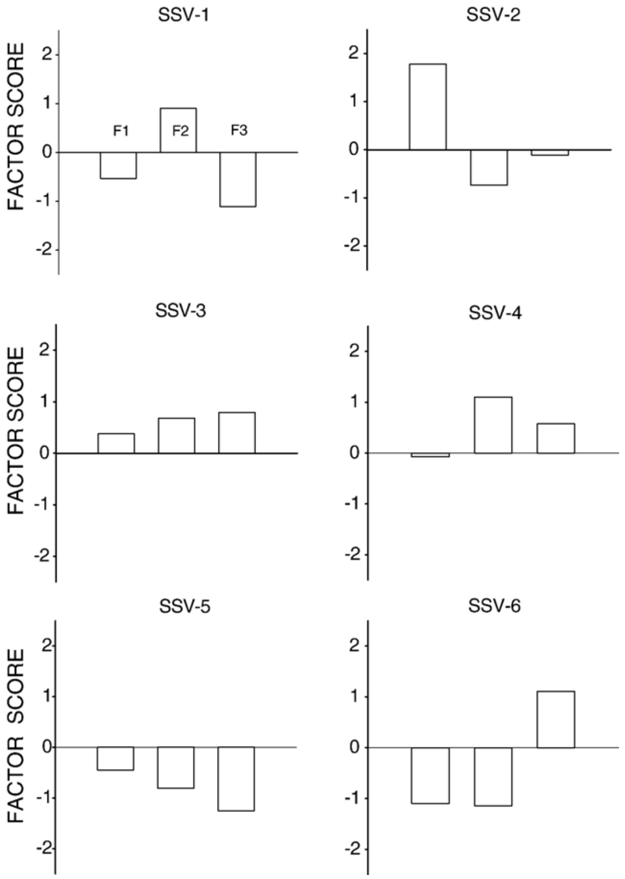

Fig. 4. Estimated factor scores from each of six cases to the centroid of cases for the original data from Santos and São Vicente estuary stations. The factor scores quantify to the prevalence of every component for each station and are used to confirm the factor description.

4.2.1. Southern Spain areas

The first Factor (F1) shows environmental degradation caused by metals, since the loadings of all heavy metals, in exception of Ni, are related to high mortality in amphipods toxicity test. Indeed, F1 is representative (it has positive factor score) only at *Ría* of Huelva sites (HV-1, HV-2 and HV-3), where the contamination of the sediments by heavy metals is well known (Riba et al., 2004a,b). HV-1 and HV-3 also show a strong environmental alteration due to PAHs and Ni, which were aggregated in the second Factor (F2). Riba et al. (2004b) also found hydrocarbons contamination in sediments from *Ría* de Huelva. One site at Bay of Algeciras (GR-3′) shows positive factor score to F2; it is located at the inner part of Guadarranque River’s mouth, receiving directly effluents from the Algeciras industrial complex. The degradation caused by PAHs and Ni can be considered higher than that caused by heavy metals and showed by F1, since the toxicity response loadings are higher in F2. The third factor (F3) demonstrates contamination caused by PCBs, Co, and V; however, this is not related amphipods mortality. Such Factor is positive in CA-2 and HV-3, corroborating with the work of Riba et al. (2004b), which reported PCBs contamination in sediments from Bay of Cádiz and *Ría* of Huelva. The fourth Factor (F4) represents the natural sedimentary matrix with high percentage of fines and organic carbon in *Ría* of Huelva and Bay of Algeciras.

4.2.2. Santos and São Vicente estuary

The first factor (F1) shows environmental degradation related to some heavy metals (Cu, Pb and Zn) and PCBs, since such contaminants were aggregated to the toxicity response, by the PCA analysis. Only for SSV-2 and SSV-3 this factor presents positive scores; indeed, such sites are under influence of Santos harbour and Cubatão industrial complex. PAHs, fines contents and amphipods toxicity are strongly associated to third factor (F3); Cu and Ni also appear to be aggregated, but with lower loadings. It means that the high level of PAHs is leading to environmental degradation at the sites where this factor has positive scores. Such situation is found at SSV-3, SSV-4 and SSV-6. As discussed earlier, SSV-3 in under the influence of the Santos harbour and the Cubatão industrial complex, the probable sources of hydrocarbons for this site; SSV-4 is located on *Mariana* River's mouth, which receives untreated domestic sewage and its river basin drains areas influenced by old irregular industrial landfills, which are contaminated by several chemicals. According to Lamparelli et al. (2001) both sources can contribute to the introduction of PAHs in this area. SSV-6 is located close to the diffusers of the submarine sewage outfall of Santos (SSOS), probably the source of the PAHs found at this site.

In summary, the high degraded environments were found at the inner parts of the Santos and São Vicente Estuary (SSV-2, SSV-3, and SSV-4), confirming existing literature (Medeiros and Bícego, 2004; Abessa, 2002; Prósperi, 2002; Lamparelli et al., 2001), followed by SSV-6, which is near to the SSOS. SSV-1 and SSV-5 did not present chemical contamination, organic contamination or significant toxicity.

The results of this investigation shows that the contamination by PAHs is closely related to amphipods mortality, as in Spanish (*Ría* of Huelva and Gudarranque river's estuary) as in Brazilian areas (inner parts of the estuary); it means that both countries present environmental degradation related to hydrocarbons in those areas. Similar situation was observed for the heavy metals; almost all of the identified metals were related to lethal toxicity in *Ría* of Huelva and Gudarranque river's estuary areas, and the internal zone of Santos and São Vicente estuary. Few exceptions for this pattern were V for both Brazil and Spain, and Cd and Co, only for the Brazilian areas. The presence of PCBs is more serious for Santos and São Vicente estuary than for the studied areas in Gulf of Cádiz, because in Spain such results were not related to amphipods mortality.

Because of the environmental degradation in the studied ecosystems, in special for the Santos and São Vicente Estuarine System, it was difficult to find a satisfactory reference area. By using the Principal Component Analysis technique, such problem was minimized, and thus inferences could be made about the sediment quality of both ecosystems, with or without a reference area.

Finally, the multivariate analysis approach was considered a very useful and reliable tool to identify the contamination and its associated effects in two different ecosystems in the North and in the South Atlantic Ocean. Also, the results demonstrate their feasibility to compare the sediment quality in both ecosystems, with or without the selection of a reference area.

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Comparative benthic community structure assessment in different littoral ecosystems of South Atlantic (Southeastern Brazil) and North Atlantic (Southern Spain)

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ABSTRACT

Benthic community structure was assessed in Santos and São Vicente Estuarine System, Southeastern Brazil, and Ría of Huelva, Bay of Cádiz, and Bay of Algeciras, Southern Spain. Biological data were analysed employing classical community descriptive parameters (Margaleff's species richness, Shannon-Wiener's diversity, Pielou's evenness, and Simpson's dominance), Polychaeta's dominance, and multivariate techniques (cluster and MDS analysis). Factor analysis followed by PCA extraction was used in the integration of data of benthic community structure and sediment physical-chemistry (levels of trace metals, PAHs, PCBs, percentage of fines and organic carbon). The results indicate that benthic communities are in general under stressed conditions, particularly in areas with low influence of sea waters. Multivariate analysis revealed that benthic community degradation increases with enhancing contamination. In addition, such analysis revealed that benthic communities in Spanish areas are negatively affected by a wide variety of contaminants, whilst in Brazilian areas only PAHs and few metals are associated to altered benthic communities. The methodology utilised in this study to compare the condition of benthic communities in different littoral zones permitted the understanding of how benthic communities from different littoral environments respond to diverse sources of anthropogenic and natural stressors, especially in areas with such environmental relevance and where port and industrial activities take place.

Key words: Benthos; Contamination; Multivariate analysis; Santos and São Vicente Estuarine System; Gulf of Cádiz.

1. INTRODUCTION

Benthic communities are assemblages of organisms that live inside sediments (infauna) or on the surface of sediments (epifauna). Such communities play a fundamental role in estuarine and marine ecosystems, since they influence surface productivity, alter physical and chemical characteristics of the sediment and sediment-water interface, and transfer energy to higher trophic levels (Simpson et al., 2001; Gaston et al., 1998). Besides their ecological significance, some benthic species are socio-economically important because they are target of artisan and/or industrial fisheries.

In general, the ecological significance and holistic responses to environmental contaminants makes benthic communities an important and viable tool for sediment quality assessment (Bilyard, 1987). Many methods for assessing the sediment quality used by environmental agencies worldwide (as U.S. EPA, Environmental Canada, Environmental Australia) rely on benthic community structure assessments.

There are a number of parameters commonly utilized to describe the structure of the benthic macrofauna, such as species richness, diversity, evenness, and dominance. However, misjudgements may rise up when the interpretation of this kind of data relies exclusively on univariate analyses, since the natural spatial and temporal variation of benthic communities may have strong influence on these results (DelValls et al., 1998a). Multivariate analyses, based on ordination (as MDS - Multi Dimensional Scaling) or similarity indices (as Cluster analysis) are more complex and allow identifying groups of stations derived from their species-abundance’s closeness. Such techniques have been applied in previous studies, providing more consistent conclusions than those obtained with only descriptive parameters (Marín-Guirao et al., 2005a; Marín-Guirao et al., 2005b; Drake et al. 1999; DelValls, 1998). Other multivariate techniques permit the integration of data from different natures to the benthic macrofauna analysis (e.g. benthic community descriptors and chemical concentrations on sediments), resulting in a wider analysis that allows a deeper and more robust interpretation of the environmental data. One of them, so-called PCA (Principal Component Analysis), has been successfully applied in the integration of different kinds of environemtnal data

(Cesar et al. 2007; Riba et al. 2004a; Riba et al. 2004b; DelValls et al. 2002; DelValls et al. 1998b; DelValls & Chapman, 1998).

In this study we conducted a comparative analysis of the benthic community structure from port and estuarine zones of Southeast Atlantic (Santos and São Vicente Estuarine System, Brazil) and from Gulf of Cádiz (Southern Spain) and how they are affected by chemical contamination. To do so, benthic community structure were analysed by means of univariate and multivariate methods, and benthic community descriptors were integrated with sediment physical-chemical data by using PCA. The initial hypothesis is that this technique of data integration will show a positive correlation between chemical concentrations of contamiants in sediments and benthic community degradation, i.e. in those areas further affected by chemical contamination, benthic communities present characteristics of impaired communities (low species diversity, richness, evennes, and high *Polychaeta*'s dominance). The PCA must permit the discrimination of chemicals os concern (those related to negative biological effects) in the study areas in both countries. The application of this technique in different estuarine areas in Brazil and Spain is useful to appraise its aplicability in litoral systems with dissimilar natural characteristics and affected by different sources of pollution (domestic sewage, industrial effluents, urban runoff, and contamination by port's activities)

2. METHODOLOGY

2.1 STUDY AREAS

2.1.1 *Santos and São Vicente Estuarine System (SSVES) stations*

The Santos and São Vicente Estuarine System (SSVES) (23°30’5’’S to 24°S; 46°05’W to 46°30’W) is located in Southeastern Brazilian coast (Figure 1). The ecosystem in the estuarine system is complex and heterogeneous, formed by a vast net of rivers that ramifies in the coastal plain, which, together with the sea, mould the São Vicente Island (where the cities of Santos and São Vicente are situated) and numerous small estuarine islands. This area is covered predominantly by mangrove vegetation.

The SSVES is the most industrialized region in Brazilian coast, comprising the Cubatão industrial complex, with petrochemicals, siderurgy, and fertilizers industry; the Port of Santos – the major port in Latin America; and a large urban concentration, so-called *Baixada Santista*. The area is also important because of its touristy characteristics and fisheries resources (Abessa et al., 2001). The urban/industrial effluents and landfills, and the Port of Santos’ activities provoke a major impact in the regional environment. Previous works showed high sediment contamination by metals, PAHs, and PCBs (Lamparelli et al., 2001; Prósperi, 1998; Fúlfaro et al., 1983; Tommasi, 1979; CETESB, 1978; 1981; 1985). Recent investigations on sediment toxicity found that the contaminants in the sediments are bioavailable to aquatic biota (Abessa et al., 2001), especially in inner parts of the estuarine system, closer to Cubatão industrial complex (Cesar et al. 2007; Cesar et al., 2006). However, there is a lack of publications about the benthic macrofauna in SSVES; one existent work states that the benthic community structure in the estuarine system is controlled mainly by natural factors, but there are evident signals of stress caused by anthropogenic activities in some zones of the estuary (Abessa, 2002).

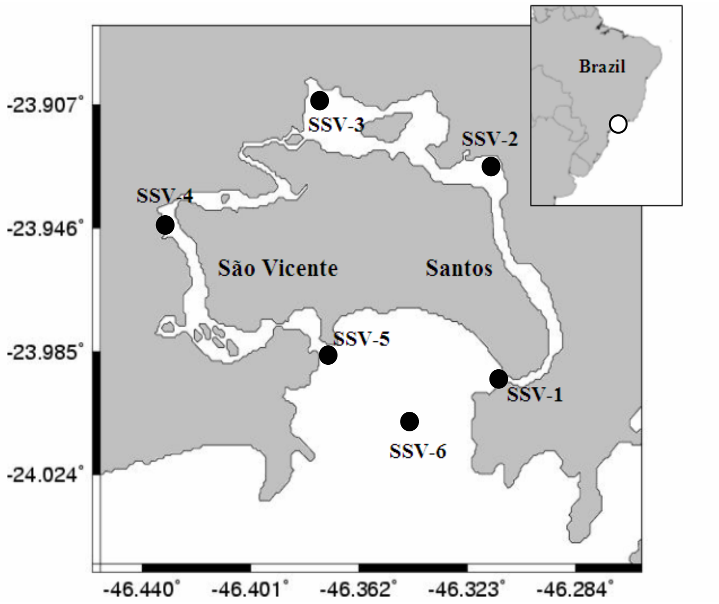

Figure 1. Localization of the sampling stations in Santos and São Vicente estuarine system – Brazil.

The 6 sampling stations in SSVES were distributed in a way that sediments impacted by different pollution sources were embodied in the investigation (Figure 1). Three sampling sites were located in the Santos Channel, in the zone influenced by the Port of Santos and Cubatão industrial complex (SSVES-1 to SSVES-3); two sampling sites were located in the São Vicente Channel (SSVES-4 and SSVES-5), mainly influenced by untreated sewage and by irregular domestic and industrial landfills; SSVES-6 was located on the central portion of the Santos Bay, near the Santos and São Vicente sewage outfall.

2.1.2 *Southern Spain stations*

In general, the 8 sampling stations in Southern Spain encompass different sources of pollution. Three different regions were sampled (Figure 2): three stations

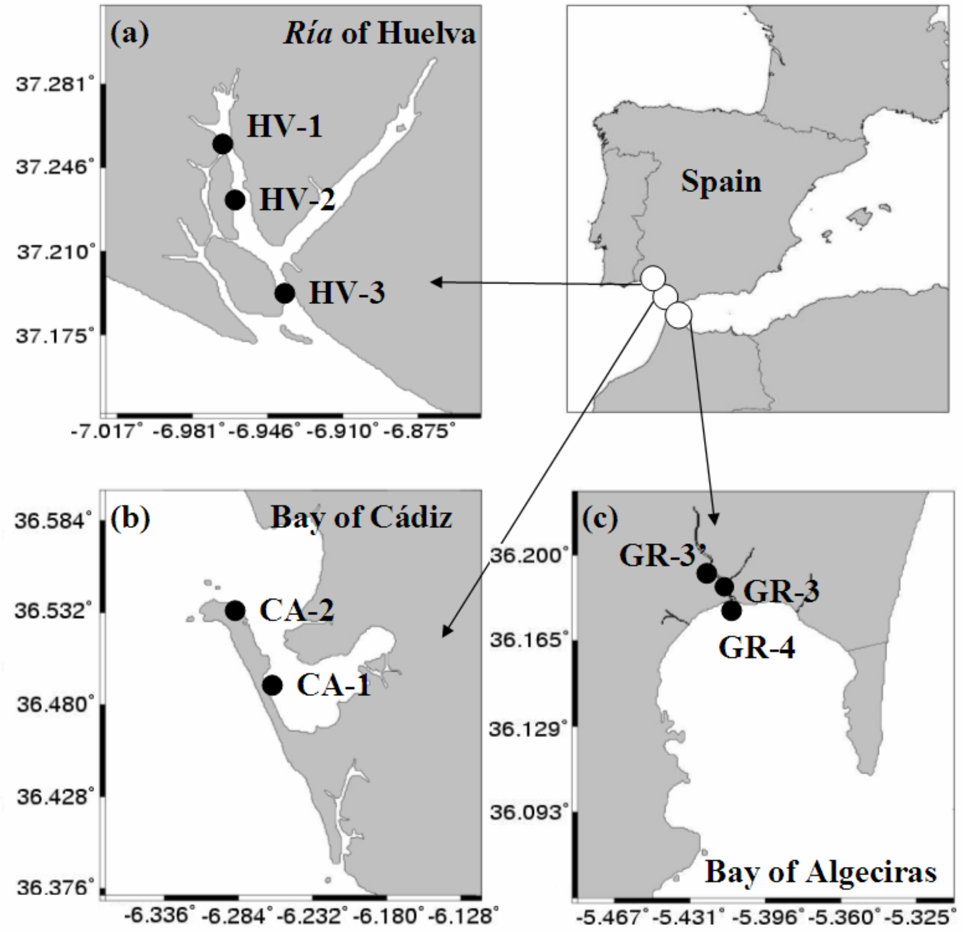

Figure 2. Localization of the sampling stations in Ría of Huelva (a), Cádiz Bay (b), Algeciras Bay (c) and their disposition in Southern Spain.

were situated in *Ría* of Huelva (HV-1, HV-2, and HV-3), a zone affected by mining activities since Roman Age until today. Besides mining, industrial activities and the Port of Huelva contribute to the environmental degradation in this zone (Cesar et al., 2007; Riba et al. 2004a). Two stations were located at Bay of Cádiz (CA-1 and CA-2), an urban and industrial area with a total population of about 400 000 inhabitants (Drake et al., 1999); in addition, intensive marine aquaculture industry is placed in the salt marshes at the margins of the bay. Sediments of Bay of Cadiz have been considered as not degraded since they did not show toxic effects in previous investigations (Cesar et al., 2007; Riba et al. 2004a; Riba et al., 2004b). Other 3 stations were placed at *Guadarranque* river's mouth at Bay of Algeciras (GR-3, GR-3', and GR-4). This bay shelters the Port of Algeciras, the most important Spanish port, and also the Algeciras industrial zone, formed by petrochemical industrials. Cesar et al. (2007) reported environmental degradation in this area, caused by high levels of PAHs and trace metals in the sediments.

2.2 APPROACH

2.2.1 *Sediment collection*

Sediments were collected synoptically for benthic community structure and chemical analyses in Brazil and Spain, in order to permit the integration of the results further ahead. Intact sediment cores were collected by SCUBA divers, capped and sealed carefully underwater and retained throughout storage. Three replicates were collected in each station and only the top 3-5 cm layer of the superficial sediment was used. For benthic community structure analyses samples were sieved through a 0.05mm mesh net and the residues were fixed with 4% buffered formalin. Subsequently, the material was transferred to 70% isopropyl alcohol prior to sorting and identification of the macroinvertebrates. For physical-chemical analysis the sediments were kept in coolers chilled with ice until their transportations to laboratory, where they were stocked at 4ºC in the dark.

2.2.2 *Physical-chemical analyses*

Samples of each replicate were homogenized until no color or textural differences could be detected prior to the following analyses: (a) grain-size distribution, by standard mechanical dry sieve-shaker techniques, to determine sand, silt, and clay fractions (Buchanam, 1984); (b) metals content (Zn, Cd, Pb, Cu, Ni, Co and V) were determined following methods outlined by Riba et al. (2002). Briefly, the samples were firstly totally digested using an acid mixture, as described in Loring and Rantala (1992), and then metals concentrations were determined by differential pulse anodic stripping voltammetry (DPASV) with static drop mercury electrode (SMDE), using a processor Metrohm 693. The quantification of the metals concentrations was performed by the use of standard addition procedure; (c) PAHs and PCBs concentrations were measured by extracting the samples with cyclohexane and dichloromethane and subsequent concentration and purification by column chromatography technique. The determinations were made by gas chromatography equipped with electron capture detector (ECD) (US EPA SW-846 Method 8270) (Riba et al., 2002) (d) organic carbon (O.C.) content, using the titration method based on the acidification of the sediment sample (El Rayis, 1985).

All the analytical procedures were checked with reference materials (Marine Sediment References Material for Trace Metals–1, National Research Council (NRC), Certified Reference Material, 277 BCR, and Conceil National de Reserches Canada, 277 BCR, for heavy metals; and NRCpCNRC HS-1 for organic compounds) and allow agreement with certified values higher than 90%.

2.2.3 *Benthic infaunal analysis*

The organisms were sorted and identified to the lowest possible taxon level (species level, or family in case of *Polychaeta*). The biological data set was analysed by means of different univariate, graphical/distributional, and multivariate methods. Univariate methods included classical community descriptive parameters, such as Margalef's species richness ($R = (S\text{-}1)\ (\text{LogN})^{-1}$), where 'S' is the species richness (*i.e.* number of species), and 'N' is the total number of all individuals; Shannon's diversity ($H' = -\sum(P_i \ \text{Log}_e P_i)$), where '$P_i$' is the relative abundance of each species; Pielou's evenness ($J = H'\ (\text{LogS})^{-1}$); and Simpson's dominance ($D = 1\text{-}\sum\{N_i\ [N_i\text{-}1]\ [N\ (N\text{-}1)]^{-1}\}$), where '$N_i$' is the abundance (*i.e.* number of individuals). Significant differences among sampling stations were tested by one-way Analysis of Variance (ANOVA) ($p<0.05$). Since numerical contribution of major taxa is widely utilised to evaluate pollution effects (DelValls, 1998a; Chapman et al., 1996), an abundance analysis was carried out by calculating the proportion of major taxa's (*Polychaeta*, *Mollusca*, *Crustacea*) abundance to the total abundance for each sample.

Multivariate analyses were carried out based on a similarity matrix calculated using the Bray-Curtis coefficient for fourth square-root transformed taxa abundance data (Clarke and Warwick, 1994). From this matrix, clustering analysis was made by hierarchical, agglomerative method using group average sorting, and the results were displayed in a dendrogram. An ordination analysis was executed by using a non-metric Multi-Dimensional Scaling (MDS) based on the similarity matrix, and the results were presented graphically. PRIMER 5 for Windows (PRIMER-E Ltda, 2001, version 5.2.0) software was employed for the univariate and multivariate procedures.

Relationship amongst variables was assessed using a Factor Analysis followed by Principal Component Analysis (PCA), applied as the extraction procedure. The matrixes of data were based on the benthic community descriptive parameters (Margaleff's species richness, Shannon-Wiener's diversity, Pielou's evenness, and Simpson's dominance) and contaminants concentrations (PAHs, PCBs, Cd, Co, Cu, Ni, Pb, V, Zn, % O.C. and % fines) for each country. The biological data sets were transformed in order to exhibit an increase according to the biological damage, i.e. the parameters calculated from the *in situ* biological effects were transformed as the inverse (values of S, N, *R*, *J'*, *H'*, and *D* were multiplied by -1). The objective of PCA is to derive a reduced number of new variables as linear combinations of the original variables. This provides a description of the structure of the data with the minimum loss of information. The variables were autoscaled (standardized) to be treated with equal importance. All analyses were performed using the PCA option of the MULTIVARIATE EXPLORATORY TECHNICS procedure, followed by the basic set-up for FACTOR ANALYSIS procedure from the STATISTICA software (Stat Soft, Inc. 2001; version 6).

3. RESULTS

3.1 SANTOS AND SÃO VICENTE ESTUARINE SYSTEM STATIONS

Results of sediment chemistry, sediment physical characteristics, and descriptive parameters of benthic community are detailed in Table 1. Sediments on SSVES-2 and SSVES-3 were highly contaminated by copper, with a concentration exceeding the

Table 1. Benthic community descriptive parameters and sediment physical-chemical characteristics of SSEVS sampling stations.

Variables	**Sampling stations**					
	SSVES-1	**SSVES-2**	**SSVES-3**	**SSVES-4**	**SSVES-5**	**SSVES-6**
Benthic descriptors (mean ± sd)						
Number of taxa (S)	5.00±2.00	4.67±1.15	1.33±0.58	2.33±1.15	4.00±2.00	3.00±1.73
Number of individuals (N)	8.67±5.69	7.00±3.61	1.33±0.58	7.33±4.04	5.00±2.65	3.67±2.31
Margaleff's richness (*R*)	1.90±0.41	1.97±0.26	1.44	0.88±0.91	1.92±0.75	1.86±0.00
Evenness (*J'*)	0.90±0.06	0.96±0.03	1.00	0.77±0.32	0.94±0.10	0.96±0.00
Diversity (H')	1.38±0.30	1.46±0.18	0.23±0.40	0.57±0.55	1.21±0.55	0.89±0.77
Dominance (D)	0.82±0.04	0.91±0.08	1.00	0.45±0.51	0.90±0.16	0.90±0.00
Chemicals						
Cd (ppm)	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Co (ppm)	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Cu (ppm)	<0.1	167.2	157.7	69.0	<0.1	<0.1
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	<0.1

Table 1 - Continued

Variables	**Sampling stations**					
	SSVES-1	**SSVES-2**	**SSVES-3**	**SSVES-4**	**SSVES-5**	**SSVES-6**
Chemicals						
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	<0.1
Sediment characteristics						
O.C. (%)	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

probable effect level (PEL) utilised by the agency Environment Canada (EC, 1999). High concentration of copper was found on SSVES-4 sediments as well, at a level superior to the *threshold effect level* (TEL) proposed by the above mentioned Canadian sediment quality guidelines. Chemical concentrations between TEL and PEL represent the range in which toxic effects are occasionally observed. Other chemicals also exceeded TEL in SSVES-2, such as Pb and Zn, and in SSVES-4, such as PAHs.

The descriptive parameters of benthic infaunal community structure did not vary significantly among the SSVES stations (ANOVA, $p<0.05$). In general, the Brazilian estuary presented low taxa richness (S), Margaleff's richness (R) and Shannon-Wiener diversity (H'); and high evenness (Pielou's J) and low dominance (values of D Simpson are close to 1). The dominance pie-charts (Figure 3) reveal that *Polychaeta* was the most abundant group in most of the stations (SSVES-3, SSVES-4, SSVES-5, and SSVES-6). The results of cluster and MDS analysis were graphically represented in Figure 4 'a' and 'b', respectively.

Sediments chemical concentrations and physical characteristics were integrated with benthic community descriptive parameters by PCA. The PCA over the original data set reorganized the data in three principal factors, which together explained 85.82% of the total variance in the original matrix. The loadings following varimax rotation for the first three principal factors are found in Table 2. The first principal factor (F1) represented 32.42% of the total variance and combined benthic community descriptors, PAHs, V, and organic carbon content. The second factor (F2), accounting for 28.53% of the total variance, combined PCBs, Cu, Pb, and Zn. Lastly, third factor accounted for 24.88% of the total variance, combined number of taxa, abundance, specie's diversity, concentration of Ni and fines' percentage. Specie's evenness and dominance were negatively correlated to this group.

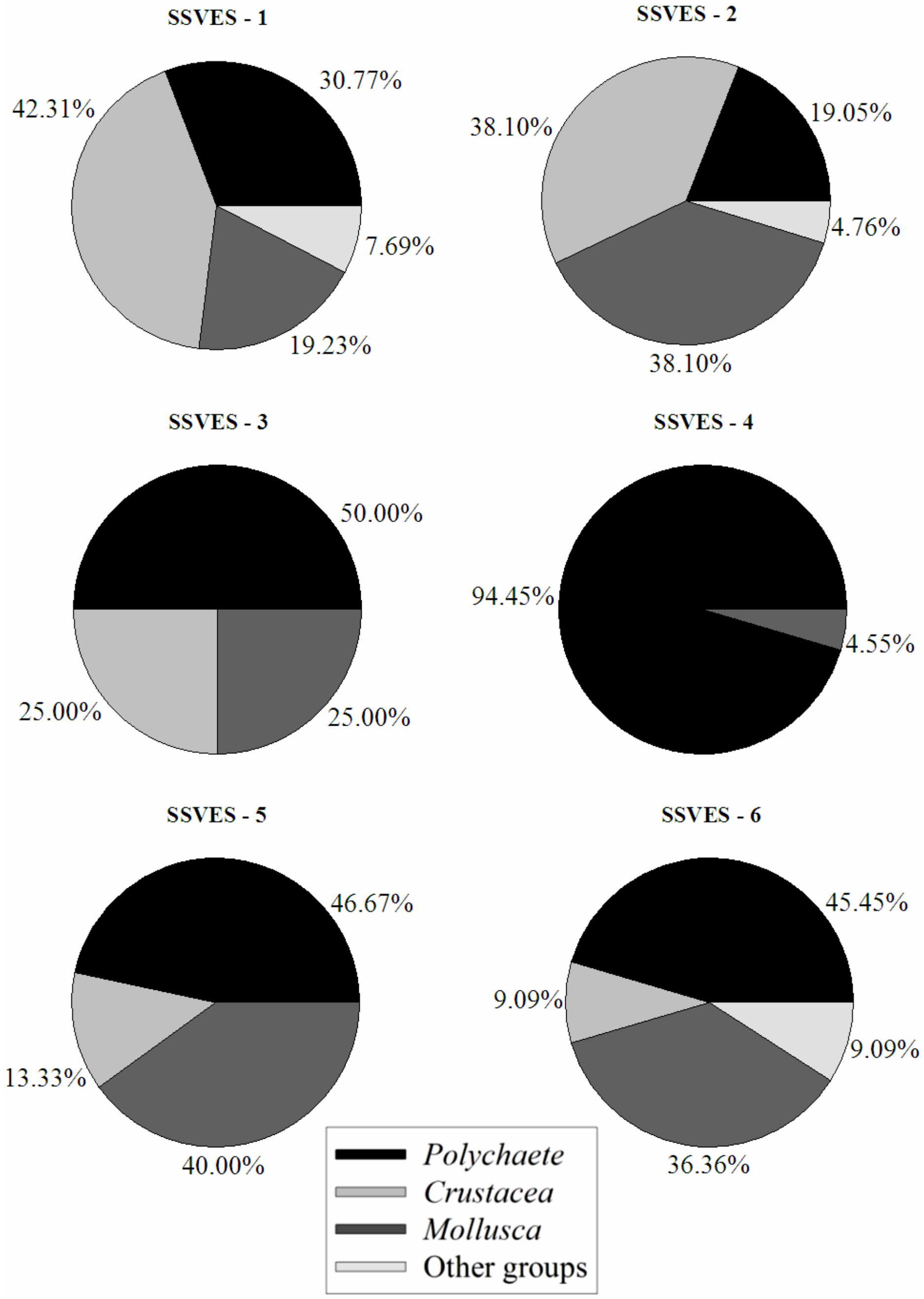

Figure 3. Dominance distribution of the main taxa in sediments from SSVES stations.

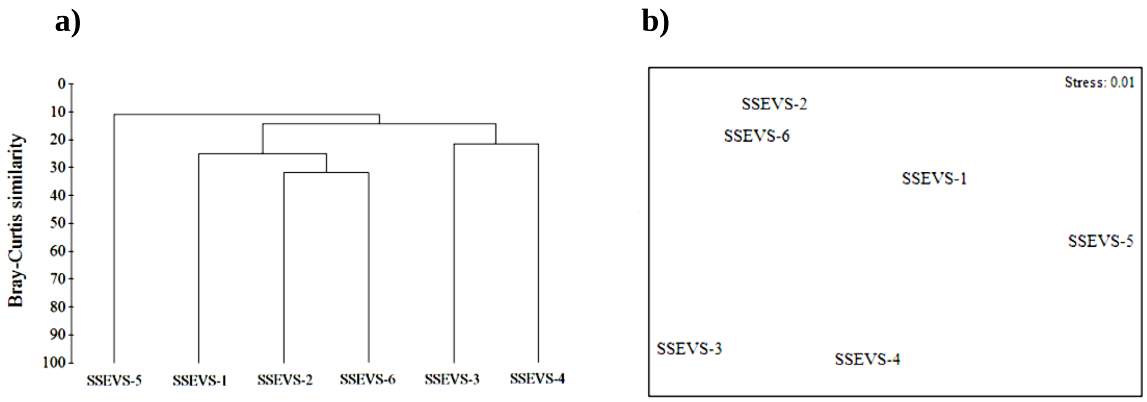

Figure 4. Dendrogram showing classification of SSVES stations (a) and two-dimensional non-metric multi-dimensional scaling (MDS) plot of stations based on a Bray-Curtis similarity matrix of taxa abundance (b).

Table 2. Sorted rotated factor loadings (pattern) of the original 15 variables on the three principal factors of SSVES stations. The loading matrix has been rearranged so that the columns appear in decreasing order of variance explained by factors. Only loadings equal or greater than 0.40 are shown. Factors are numbered consecutively from left to right in order of decreasing variance explained.

Variable	**Factor 1**	**Factor 2**	**Factor 3**
% Variance	32.42	28.52	24.88
S	0.61	------	0.78
N	------	------	0.95
R	0.99	------	------
J’	0.75	------	-0.57
H’	0.66	------	0.74
D	0.80	------	-0.49

Table 2. Continued.

Variable	**Factor 1**	**Factor 2**	**Factor 3**
PAHs	0.73	------	------
PCBs	------	0.99	------
Cu	------	0.93	------
Ni	------	-0.71	0.49
Pb	------	0.91	------
V	0.91	------	------
Zn	------	0.96	------
O.C.	0.50	------	------
Fines	------	------	0.85

3.2 SOUTHERN SPAIN STATIONS

Results of sediment chemistry, sediment physical characteristics, and descriptive parameters of benthic community are summarized in Table 3. High contamination by metals was found at *Ría* of Huelva (Cu, Pb, Zn, and Ni concentrations exceeded PEL; Cd exceeded TEL), vicinities of the Port of Cádiz at Bay of Cádiz (CA-2) (Cu and Zn exceeded PEL; Cd and Ni exceeded TEL), and upper stream of *Guadarranque* River's mouth on Bay of Algeciras (GR-3 and GR-3') (Ni exceeded PEL; Cu and Zn exceeded TEL). PCBs were found at high levels on the vicinities of Port of Cádiz (concentration

Table 3. Benthic community descriptive parameters and sediment physical-chemical characteristics of Southern Spain sampling stations

Variables	Sampling stations							
	HV-1	HV-2	HV-3	CA-1	CA-2	GR-4	GR-3	GR-3’
Benthic descriptors (mean ± sd)								
Number of taxa (S)	0.33±0.58	1.00±0.00	2.00±1.00	13.67±5.03	8.33±1.53	4.67±1.15	4.67±1.15	0.67±0.58
Number of individuals (N)	0.33±0.58	1.67±1.15	5.33±2.89	136.67±65.49	50.33±12.34	21.33±6.03	19.67±5.69	1.33±1.15
Margaleff’s richness (*R*)	-	0	0.51±0.51	2.57±0.78	1.87±0.30	1.21±0.36	1.25±0.42	0
Evenness (*J’*)	-	-	0.87±0.00	0.64±0.04	0.8±0.02	0.85±0.07	0.81±0.05	-
Diversity (*H’*)	0	0	0.52±0.48	1.64±0.32	1.69±0.17	1.29±0.23	1.24±0.26	0
Dominance (*D*)	-	0	0.38±0.34	0.66±0.09	0.78±0.03	0.72±0.09	0.68±0.09	0
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	0.10	12.80
Cu (ppm)	1 989.00	1 543.00	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	<0.01	24.60	26.10

Table 3 - Continued

Variables	**Sampling stations**							
	HV-1	**HV-2**	**HV-3**	**CA-1**	**CA-2**	**GR-4**	**GR-3**	**GR-3'**
Chemicals								
Zn (ppm)	1 945.0	2 010.0	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	<0.01	161.00	<0.01	<0.01	<0.01
Sediment characteristics								
O.C. (%)	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

higher than TEL) and sediments from upper stream of *Guadarranque* River's mouth on Bay of Algeciras were highly contaminated by PAHs (concentrations exceeding PEL on GR-3' and higher than TEL on GR-3).

Figure 5 shows the pie-charts representing the relative dominance of each main group of organism in the Spanish areas.

Differences were found among the benthic community structure of the Southern Spain areas under study. At *Ría* of Huelva stations, very few organisms were collected, preventing the calculation of most of the indices in HV-1 and HV-2. Species' diversity (*H'*) was equal to 0 in these two stations and presented very low value at HV-3. Only *Nereidae* (*Polychaeta*) was collected in HV-2; in HV-3, *Cerastoderma edule* was the main specie that accounted for the dominance of *Mollusca* group. Stations at Bay of Cadiz exhibited the highest numbers of taxa richness (*R*) and diversity (*H'*) among the Southern Spain sampling areas. *Mollusca* was the dominant group in this area, with high predominance of *Hydrobia sp* in CA-1, and *Abra tenuis* and *Cobula giba* in CA-2. *Crustacea*, mainly *Amphipoda* speices, was found in Bay of Cádiz as well. In Bay of Algeciras, the number of organisms collected in GR-3' prevented the calculation of species' richness, evenness and dominance indices. However, in the other stations, values of species' richness were similar to those values found in Bay of Cadiz (ANOVA, $p<0.05$). Evenness (*J*) numbers in GR-3 and GR-4 were significantly higher than those found for CA-1 (ANOVA, $p>0.05$), but not significantly different from the CA-2 values (ANOVA, $p<0.05$). *Polychaeta* was the most abundant group in Bay of Algeciras sampling stations. Figure 6 'a' and 'b' present graphically the results of cluster and MDS analysis, respectively.

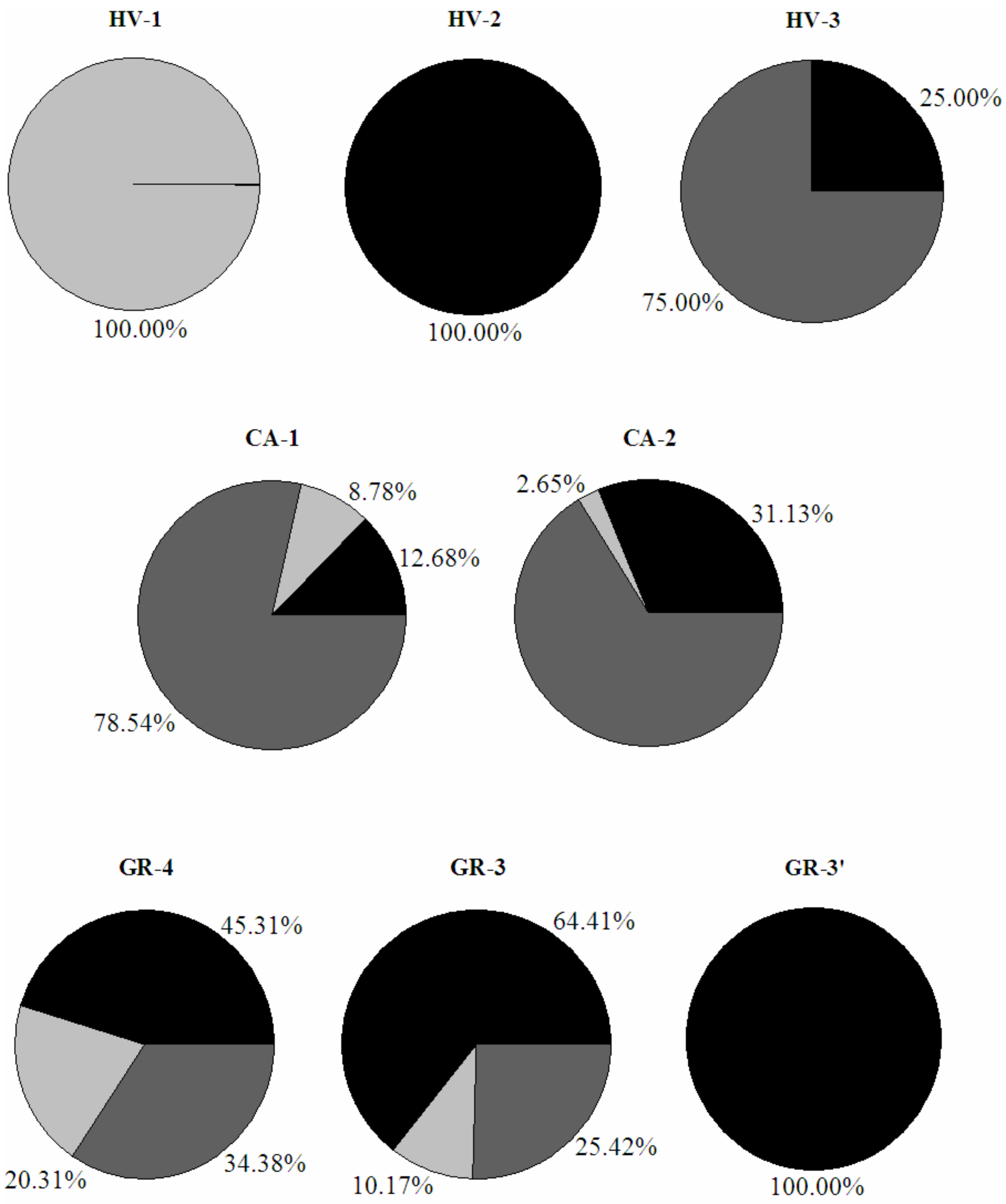

Figure 5. Dominance distribution of the main taxa in sediments from Southern Spain stations.

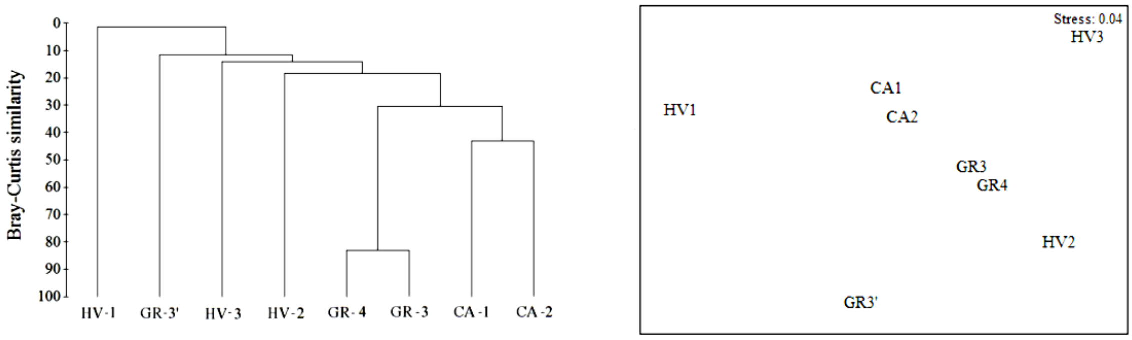

Figure 6. Dendrogram showing classification of Southern Spain stations (a) and two-dimensional non-metric multi-dimensional scaling (MDS) plot of stations based on a Bray-Curtis similarity matrix of taxa abundance (b).

The use of the PCA over the original data set reorganized the data in three principal factors, which together explain 84.71% of the total variance in the original matrix. Table 4 gives the loadings of the variables following varimax rotation for these three factors. The predominant factor (F1) represented 52.40% of the variance and related number of species, number of individuals, species' richness and diversity, Ni concentration, percentage of organic carbon and fines. Second factor (F2) accounted for 19.62% of the variance and showed correlation among species' richness, evenness, diversity, species dominance, Cd, Co, Cu, Pb, V, Zn and, with negative value, PAHs concentrations. Finally, F3, representing 12.69% of the total variance, grouped species' richness, evenness, diversity, species dominance, PAHs, and, with negative values, PCBs, V, and organic carbon.

Table 4. Sorted rotated factor loadings (pattern) of the original 17 variables on the three principal factors of Southern Spain stations. The loading matrix has been rearranged so that the columns appear in decreasing order of variance explained by factors. Only loadings equal or greater than 0.40 are shown. Factors are numbered consecutively from left to right in order of decreasing variance explained.

Variable	Factor 1	Factor 2	Factor 3
% Variance	52.40	19.62	12.69
S	0.85	------	------
N	0.93	------	------
R	0.74	0.42	0.51
J'	------	0.55	0.77
H'	0.55	0.49	0.67
D	------	0.56	0.73
PAHs	------	-0.41	0.70
PCBs	------	------	-0.66
Cd	------	0.98	------
Co	------	0.76	------
Cu	------	0.93	------
Ni	0.61	------	------
Pb	------	0.95	------
V	------	0.77	-0.40
Zn	------	0.92	------
O.C.	0.82	------	-0.45
Fines	0.85	------	------

4. DISCUSSION

4.1 SANTOS AND SÃO VICENTE ESTUARINE SYSTEM

4.1.1 *Benthic community description*

Low values of species richness and low diversity are expected for aquatic ecosystems like estuaries, where the variation of environmental conditions (salinity, pH, temperature) is stressing to the biota. In fact, the observed values of taxa richness (S), Margaleff´s richness (*R*), Shannon-Wiener diversity (*H*’) in SSVES were low, as well as the total number of organisms collected in each station. Additionally, in stressing environments (either natural and/or anthropogenic stress), a high dominance of few better adapted species is expected (Salomons and Brils, 2004; DelValls, et al. 1998a; McLusky and Martins, 1998); however, in SSVES the situation was opposing (high evenness and low dominance), probably because of the small number of organisms collected per sample. Therefore, the results for these two descriptors may be a mathematical artefact and do not represent exactly the responses to the environmental conditions, or at least must be considered with caution – the same was observed by Abessa (2002). Despite no statistical differences (ANOVA; $p<0.05$) in the descriptive benthic community parameters were detected among the sampling stations, it can be detected a general tendency of lower taxa richness and diversity for the stations at the inner parts of the estuary and nearer to Cubatão industrial complex (SSVES-3 and SSVES-4), as well as at the station closer to the submarine sewage outfall (SSVES-6). Abessa (2002) also reported negative gradient of taxa richness and diversity of benthic fauna from outer to inner parts of SSVES. Moreover, the same study, later corroborated by Cesar et al. (2007), found higher environmental degradation (toxicity associated to chemical contamination) of sediments at the inner SSVES and vicinities of submarine sewage outfall, which can explain the lower values of taxa richness and diversity.

The communities in SSVES were, in general, dominated by *Polychaeta*, group of organisms considered more tolerant to pollution (Yüksek, et al., 2006; Horne et al. 1999; DelValls, 1998a). *Cirratulidae* was the most abundant family, but this was found in only one station (SSEVS-4); this family is considered as an indicator of stressed environments with high organic loads (Diaz-Castañeda and Harris, 2004; Khan et al., 2004). *Onuphidae* was the most conspicuous *Polychaeta* group, found in four of the six sampling stations.

Exceptions to the *Polychaeta* dominance were SSVES-1 and SSVES-2; in the first station *Crustacea* was the most abundant group, with higher contribution of amphipods. Abessa (2002) also found amphipods in the same portion of SSVES. Such situation may indicate a good sediment condition in SSVES-1, since this group of crustaceans is one of the most sensitive infaunal groups to contaminants (Anderson et al. 2004; U.S. EPA, 1991). In SSVES-2, *Crustacea* and *Mollusca* were the dominant groups. This area is highly hydrodynamic, which may prevent thus the deposition of finer particles and contaminants associated to them.

4.1.2 *Faunistic ordination*

The cluster and MDS analyses evidenced the heterogeneity of the different parts of the SSVES. Different sources and degrees of pollution, and also the natural environmental complexity of the estuary contributed to the low similarity among the sampling stations. The complexity and environmental heterogeneity in the Santos and

São Vicente estuarine system was previously reported (Abessa et al., 2002; Tommasi, 1979). In addition, the analyses were affected by the low density of organisms in the samples. At species-level, maximum Bray-Curtis similarity was about 30%, between SSVES-2 and SSVES-6. *Owenidae* polychaetes, the mollusk *Mulinia cleryana*, and the ophiurida *Microphiopholis* sp were the common species in these two stations. Roughly, one group of stations includes SSVES-1, SSVES-2, and SSVES-6. Other group comprises SSVES-3 and SSVES-4. Finally, SSVES-5 was placed isolated in the cluster and MDS analysis.

4.1.3 *Principal component analysis (PCA)*

Besides the analysis of the variables aggregated by PCA, a representation of estimated factor scores from each station to the centroid of all cases for the original data was done in order to confirm the factor descriptions and to explain the benthic community structure characteristics at each of the Santos and São Vicente estuary system stations, as can be seen in Figure 7.

Factor scores were all negative for stations SSVES-1 and SSVES-5, which means that the benthic community structure was not moulded by chemical contamination in the external parts of the estuary. The lower contamination and toxicity of the sediments at the external SSVES was vastly documented (Cesar et al., 2007; Medeiros and Bícego, 2004; Abessa, 2002; Lamparelli et al., 2001). SSVES-2 presented positive factor score only for the Factor 2, which associates some metals (Cu, Pb, and Zn) and PCBs, but not with any benthic community descriptor. This indicates that despite sediments from SSEVS-2 exhibit relatively high concentrations of those metals (Cu, Pb and Zn exceeding TEL) and PCBs (comparatively to other areas in the SSVES),

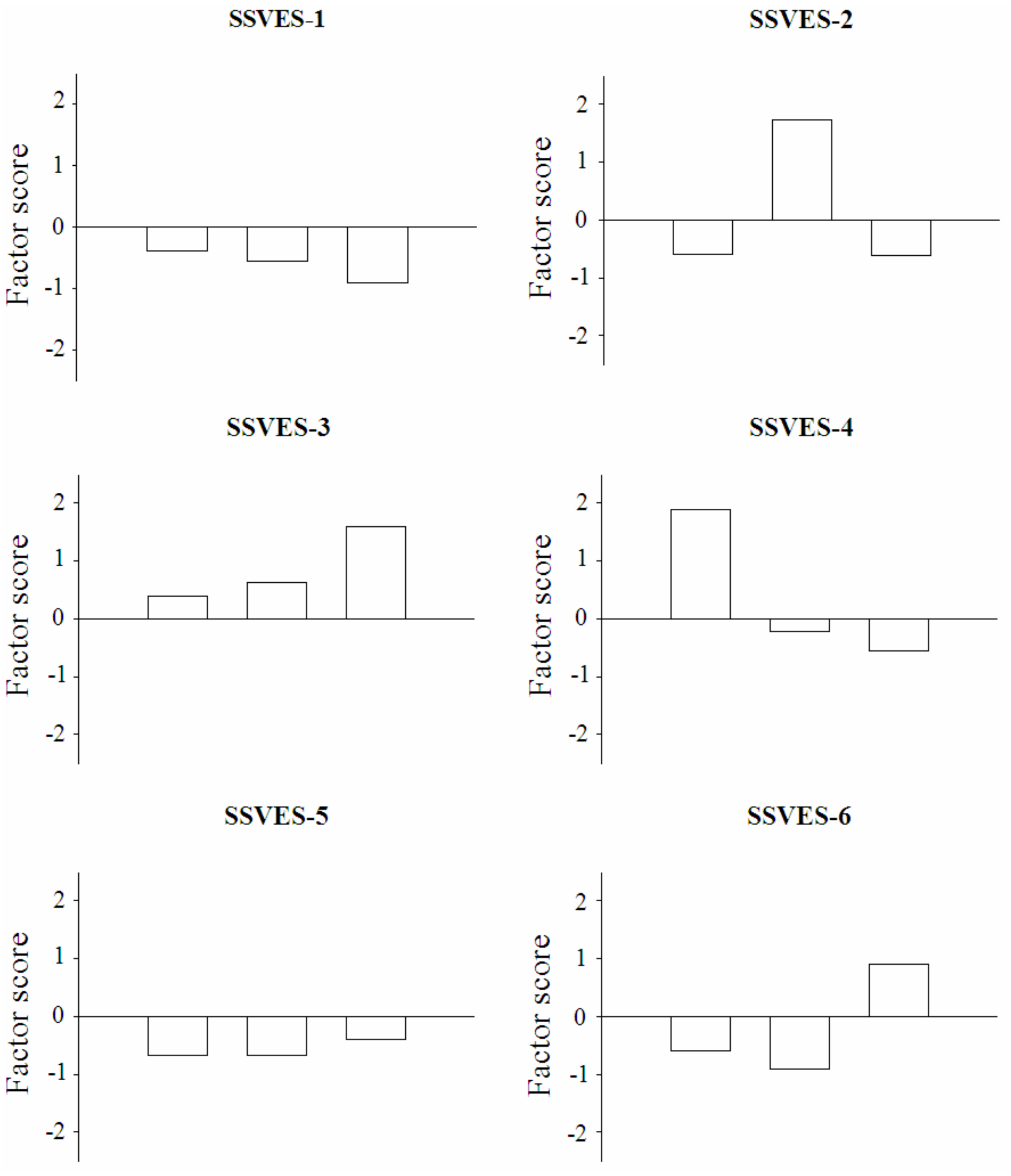

Figure 7. Estimated factor scores from each of six cases to the centroid of cases for the original data of SSVES stations.

probably resultant of the Port of Santos and industrial activities, they are not affecting benthic community structure. SSVES-3 is the station located at the most internal part of the estuary, under high influence of the Cubatão industrial complex; the three factors showed positive scores in this station, indicating chemical contamination by Cu, Pb, Zn, and PCBs, and alterations in benthic community caused by high levels of PAHs, V, Ni, and organic carbon. In addition, the natural characteristic of the sediments seems to play important role in this station, since percentage of fines was also related to stress on benthic community in F3. Factor 1 (F1) was positive for SSVES-4, suggesting that benthic community in this station was mainly affected by V and PAHs, and organic carbon content in a lesser extent. The probable source of the pollution in SSVES-4 is untreated domestic sewage, the drainage from old irregular industrial landfills and the mangrove vegetation (Cesar et al. 2007; Lamparelli et al., 2001). Lastly, the benthic community in SSVES-6 seems to be affected mainly by fine characteristic on the sediments and others contaminants not measured in this study, because the concentration of nickel, the only metal related to F3, is not expressive in this area. Abessa et al. (2005) suggested that the fine characteristic of the sediments in this area is because of the discharges of particulate material from the Santos submarine sewage outfall; these authors also found high sulphur and detergent concentrations in these sediments.

4.2 SOUTHERN SPAIN STATIONS

4.2.1 *Benthic community description*

The values of the benthic community parameters clearly indicate a better environmental condition in Bay of Cádiz, with higher values of number of species, number of specimens collected, species' richness and diversity. The presence, sometimes with high relative dominance, of pollution-sensitive groups, principally some *Mollusca* and *Amphipoda* species, also indicates low stress of sediments from Bay of Cádiz. *Ría* of Huelva showed the lowest values of benthic community parameters considering the areas under study. Only one specimen was sampled in HV-1, and very few individuals were found in HV-2; both stations showed Shannon diversity equal to 0, and some parameters were not possible to calculate for these two stations. The dominance of pollution resistant organisms as *Nereidae* in HV-2 and *Cerastoderma edule* in HV-3 (according to classification made by Grall and Glémarec, 1997) confirms the poor condition of sediments in *Ría* of Huelva. Previous works also found low alteration of sediments from Bay of Cadiz and high environmental degradation of sediments from *Ría* of Huelva (Cesar et al. 2007; Riba et al., 2004a).

The stations in Bay of Algeciras showed differences among them: few organisms were collected in the station placed upper stream (GR-3') of the *Guadarranque* river and the values of benthic community descriptors in this station presented no statistical differences in relation to *Ría* of Huelva stations (ANOVA, $p>0.05$). Unlike GR-3', the stations closer to the *Guadarranque* river's mouth seems to be in better environmental condition, since much of the benthic community parameters showed no statistical differences (ANOVA, $p<0.05$) in relation to Bay of Cadiz stations. The dominance distribution of taxa in Bay of Algeciras reveals that pollutant resistant groups – according Grall and Glémarec (1997) classification – are more abundant. *Polychaeta* (*Capitellidae* and *Nereidae*) was the most common taxa, followed by *Mollusca* (only pollution-resistant species, as *Cerastoderma edule* and *Abra tenuis*).

4.2.2 *Faunistic ordination*

Cluster and MDS analysis was prejudiced by the low number of specimens collected in *Ría* of Huelva stations and GR-3' station in Bay of Algeciras. These stations presented low values of Bray-Curtis similarity in the cluster analysis and they were placed scattered in the MDS chart.

Nevertheless, the others stations could be divided in 2 clear groups: one for Bay of Algeciras stations, with the strongest similarity, and the other for Bay of Cádiz. In Bay of Algeciras, taxa in common between GR-3 and GR-4 were *Capitellidae* and *Nereidae* (*Polychaeta*), *Anthura gracilis* and *Carcinus maenas* (*Crustacea*), and *Cerastoderma edule* (*Mollusca*). In Bay of Cadiz, taxa in common between CA-1 and CA-2 were mainly *Polychaeta*, being *Capitellidae* the most common taxa found in these two stations.

4.2.3 *Principal component analysis (PCA)*

A representation of estimated factor scores from each Southern Spain station to the centroid of all cases for the original data was carried out to verify the factor descriptions and to explain the benthic community structure characteristics, as showed in Figure 8.

The positive factor score to F1 indicates that Ni contamination and natural characteristics of the sediments (O.C. and fines) are the principal variables in this factor, correlated with benthic community descriptors; this situation was found in *Ría* of Huelva (HV-2 and HV-3) and Bay of Algeciras (GR-3', GR-3, and GR-4). Positive

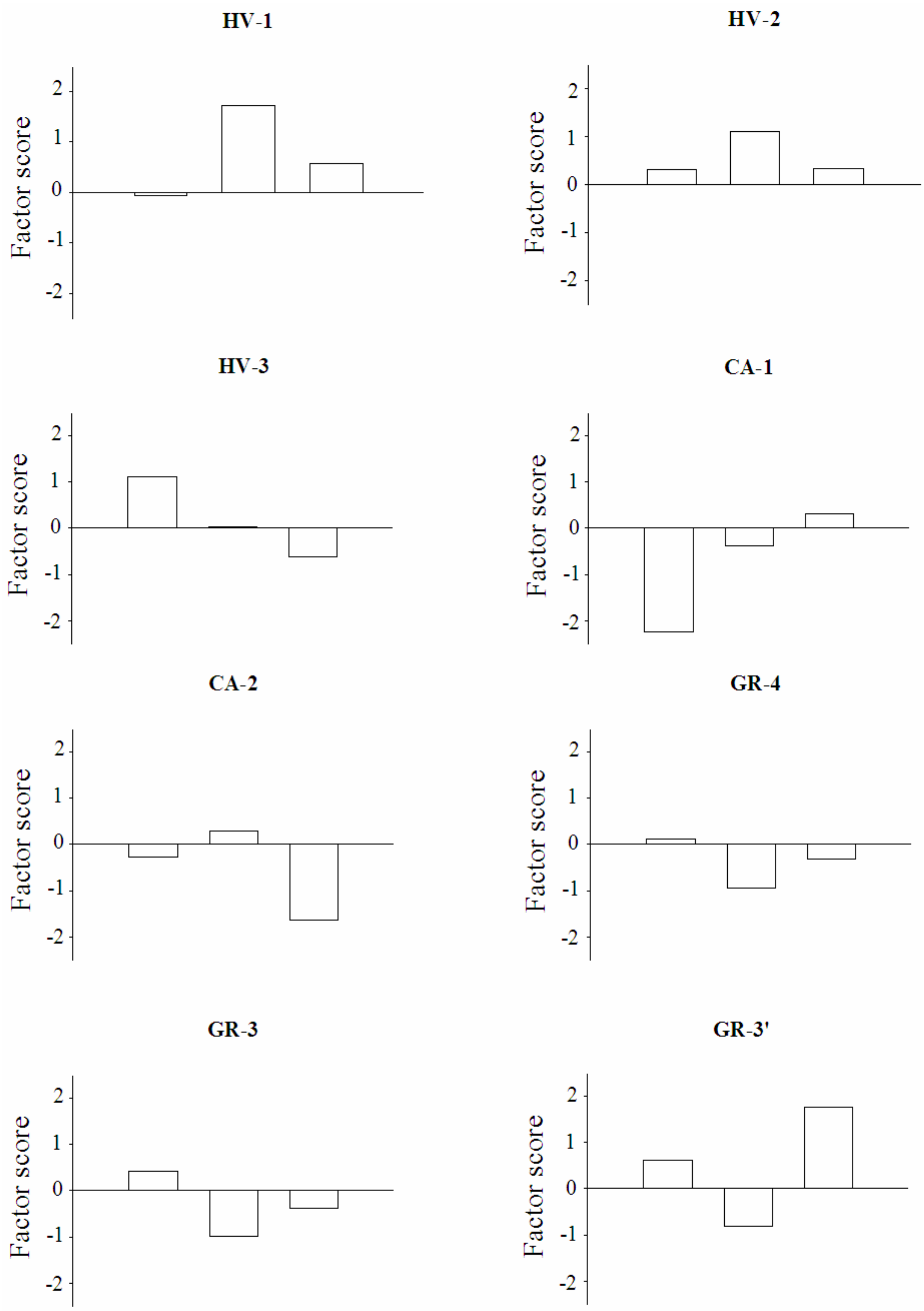

Figure 8. Estimated factor scores from each of eight cases to the centroid of cases for the original data of Southern Spain stations.

score to F2 signifies that benthic community is structured as a function of trace metal concentrations (Cd, Cu, Pb, Zn, Co and V); this is found in all stations of *Ría* of Huelva and in the vicinities of port of Cádiz (CA-2), in Bay of Cadiz. Previous works reported that sediments from *Ría* of Huelva produce adverse biological effects, such as biomarkers responses (Martin-Díaz et al., 2007), trace metals bioaccumulation (Riba et al., 2005a), severe histological lesions on benthic organisms (Riba et al., 2005b), as well as acute and chronic toxicity responses (Riba et al., 2004a), mainly caused by PAHs and trace metals from mining activities in the area. Finally, positive score to F3 means that benthic community structure is strictly correlated with the concentration of PAHs. This situation is found in internal stations in *Ría* of Huelva (HV-1 and HV-2), CA-1 in Bay of Cádiz, and GR-3' in Bay of Algeciras. The environmental degradation caused mainly by PAHs contamination in GR-3' is probably originated from the discharge of effluents from the Algeciras industrial complex into the *Guadarranque* river. In *Ría* of Huelva, PAHs contamination was reported before by Riba et al. (2004a); furthermore, Cesar et al. (2007) found that PAHs concentration was related to sediment toxicity in this area.

The positive score of F3 in HV-1, HV-2, and GR-3' indicated that the benthic community was altered in these stations by the high concentrations of PAHs. Unlike in *Ría* of Huelva and Bay of Algeciras, in CA-1 Factor 3 was significant not because the high PAHs concentration is disturbing benthic community structure, but, as opposite, because of the lowest value of PAHs concentration and the highest values of the benthic community descriptors in this station.

4.3 COMPARATIVE APPROACH

Chemical contamination in SSVES, Southeastern Brazil, and *Ría* of Huelva, Bay of Cádiz, and Bay of Algeciras in Southern Spain, was highest in those areas nearer to contamination sources (ports, industrial areas, sewage outfall) as well as in areas more protected from the action of sea waters, as internal parts of the estuaries. In these low-energy-water areas, sediments tend to contain a higher proportion of finer particles, which accounts for their well-known capacity of trapping contaminants (Queralt et al., 1999; Horowitz, 1991; Förstner, 1989). Conversely, sediments more exposed to sea action, with higher content of sand particles, tended to bear lower concentrations of contaminants.

Similarities were identified on the pattern of benthic community alteration among studies areas in Brazil and Spain. As typically found in estuarine areas, benthic community structure in SSVES, Brazil, and *Ría* of Huelva and Bay of Algeciras, Spain presented low individuals' abundance and number of taxa, low species richness, diversity, evenness, and high dominance of *Polychaeta*. In SSVES, as well as Southern Spain areas, a gradient of enrichment of benthic community from upper stream zones towards outer areas, under higher influence of the sea, was found.

The integration of benthic community structure and sediment physical-chemical data revealed that benthic community degradation increases with enhancing contamination by metals and organics, especially for Spanish areas (all analysed metals and PAHs were correlated to impaired benthic communities in some stations). In SSVES there was relationship between stressed benthic communities and concentrations of few metals (V and Ni), PAHs, organic matter, and percentage of fines, predominantly on areas upper estuary. As reported before, sediment contamination may impact macrobenthic infauna on several ways, such as by retarding larval settlement and metamorphosis of new settlers, inhibiting early juvenile growth and causing deleterious effects on adults (Trannum et al., 2004; Lu and Wu, 2003; Lotufo, 1998; Olsgard and Gray, 1995; Hill and Nelson, 1992; Chandler and Scott, 1991).

5. CONCLUSIONS

In general, in SSVES and Southern Spanish areas, the benthic communities followed a gradient of enrichment from upper stream zones towards zones more affected by sea action. Stressed benthic communities were also found closer to anthropogenic contaminant sources, such as ports, industrial and mining areas, and sewage outfalls. In some Spanish areas all analysed trace metals and PAHs were correlated to alterations on benthic communities, whilst in the most degraded zones of SSVES, the degradation of benthic communities were found correlated mainly to PAHs. Fine sediments were affecting benthic community in *Guadarranque* River in Bay of Algeciras, Spain, and in the vicinities of submarine sewage outfall in Santos Bay, Brazil. Nevertheless, whilst the finer characteristic of the sediments in the Spanish area is a natural feature of this environment, it was suggested by Abessa et al. (2005) that the higher percentage of fines in this area of SSVES is caused by sewage discharges from the outfall, *i.e.* an anthropogenic source of stressor.

In summary, in SSVES the integration of sediment physical-chemical and benthic community descriptors data revealed contamination by trace metals and PCBs in sediments close to the Port of Santos, but not affecting benthic community. Inner parts of the estuary are contaminated by metals, but benthic communities are affected mainly by Ni, V and PAHs. In the surroundings of the urban sewage outfall of Santos and São

Vicente, contents of Ni and others urban contaminants (not measured in this work) can be affecting the benthic communities, as well as the high percentage of fine particles in these sediments probably stemmed from the sewage discharges. The benthic community seems to be not affected by pollutants downstream the estuarine system. In Southern Spain stations, integrated data of benthic community structure and physical chemical characteristics of the sediments demonstrated that benthic community are negatively affected by chemical contamination in *Ría* of Huelva (trace metals and PAHs), in the proximities of Port of Cadiz in Bay of Cadiz (trace metals), and in the *Guadarranque* river, close to Algeciras industrial complex in Bay of Algeciras (PAHs). Natural characteristics of the sediments besides of Ni concentration are affecting the structure of benthic community upper stream *Guadarranque*'s River mouth in Bay of Algeciras.

This was the first comparative study between South and North Atlantic estuaries and areas subjected to port activities on the assessment of benthic community structure related to chemical contamination. The successful application of a unique technique (PCA) in the integration of sediment physical chemistry data and benthic community descriptors of different environments allowed the understanding of how benthic communities behaved according to chemical contamination, as well as identifying the chemicals which account for the benthic community disturbs in both countries. Moreover, the methodology utilised in this study to compare the condition of benthic communities in different littoral zones permitted the understanding of how benthic communities from different littoral environments respond to diverse sources of anthropogenic and natural stressors, especially in areas with such environmental relevance and where port and industrial activities take place.

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Capítulo 3.

Harmonización de un método integrado basado en el peso de la evidencia para determinar la calidad de los sedimentos y la gestión de los dragados en zonas del Norte y Sur del Atlántico

3.1 Introducción

Como se ha demostrado en el capítulo anterior, para una mejor comprensión de la contaminación de los sedimentos y de los potenciales riesgos ecológicos, la evaluación de calidad de los sedimentos deben sustentarse sobre investigaciones multidisciplinares que incluyan informaciones físico-químicas sobre el sedimento, sus efectos tóxicos asociados en laboratorio y sus efectos sobre comunidades *in situ*. La consideración de distintas líneas de evidencia también es recomendada para la caracterización del material de dragados (London Convention, 1996; GIPME, 2000; PIANC, 2006). El análisis integrado permite una correcta gestión de estos materiales, con el fin de evitar decisiones que llevasen a una degradación ambiental y que se recomienden una incorrecta disposición en locales confinados, estructuras onerosas y de baja aceptación social.

En la última década se han desarrollado diversas herramientas de toma de decisiones para evaluación y gestión de sedimentos y materiales de dragados y utilizadas por agencias legislativas. Sin embargo, estas herramientas conservan algunas similitudes, como la recomendación de la utilización de diversas líneas de evidencia, su utilización de forma escalonada y la abertura de la estructura para un proceso de refinamiento de los análisis con nuevas evaluaciones que suministren nuevas informaciones concernientes a la calidad del material bajo investigación (Wenning y Ingersoll, 2002).

A pesar de existir acuerdo entre especialistas sobre la estructura básica de estas herramientas de toma de decisiones, todavía se busca la estandardización internacional de las técnicas y evaluaciones empleadas en estos procesos (bioensayos, procedimientos químicos analíticos, técnicas de integración de los datos). El desarrollo de un protocolo para evaluación de sedimentos y material de dragados armonizado internacionalmente garantizaría la uniformidad en las evaluaciones y en la gestión de estos materiales entre países y así se permitiría la estandarización de las técnicas empleadas y comparación de los resultados obtenidos (Salomons y Brils, 2004; Petrovic y Barceló, 2004).

En este contexto se presentan en este capítulo tres artículos: el primer trabajo (IV) muestra la aplicación del método integrado completo, basado en la utilización de datos físico-químicos, de toxicidad y de la estructura de comunidad bentónica relativos al sedimento del Sistema Estuarino de Paranaguá, lugar de gran interés interese ecológico que sufre diversos impactos antrópicos, entre ellos, intensa actividad portuaria. La utilización del análisis multivariante permitió identificar que las zonas más internas del estuario están degradadas, o sea, los sedimentos llevaban asociados efectos tóxicos y que las comunidades bentónicas estaban sometidas a un estrés debido a la contaminación antropogénica (principalmente metales).

En el segundo trabajo (V) de este capítulo fueron calculados valores-guía de calidad de sedimentos específicos para las zonas de estudio (Sistema Estuarino de Santos, Sistema Estuarino de Paranaguá y Golfo de Cádiz). La comparación de los niveles de contaminación de los sedimentos con valores-guía preestablecidos es un importante escalón en los estudios de evaluación de la calidad ambiental de sedimentos y materiales de dragados. Sin embargo, los valores referenciales establecidos para utilización en nivel nacional difícilmente se adecuan a las características ambientales locales. Los valores-guía (SQVs) específicos para cada zona presentados en este trabajo, fueron desarrollados considerando los efectos tóxicos observados y la influencia de los contaminantes sobre las comunidades bentónicas de campo. Estas informaciones fueron integradas a través de análisis multivariante.

La aplicación de los SQVs obtenidos en las zonas de estudio permitió clasificar los sedimentos localizados en el saco interno del estuario de Santos como *altamente polucionado* por metales y contaminantes orgánicos. Además, se clasifica como *altamente polucionado* los sedimentos del canal de São Vicente, en la porción Oeste del sistema estuarino (HPAs y V) y de las proximidades del emisario de alcantarillado submarino de Santos (HPAs y Ni). En el sistema estuarino de Paranaguá los sedimentos localizados en el interior del estuario fueron clasificados como *altamente polucionados* por metales y HPAs. En el Golfo de Cádiz, sedimentos de la Ría de Huelva fueron considerados *altamente polucionados* (metales y orgánicos), así como los de las proximidades del Puerto de Cádiz (metales), en la Bahía de Cádiz, y los de la Bahía de Algeciras (Ni, Co y HPAs). Estos SQVs específicos de cada zona, comparados frente Valores-Guía utilizados nacionalmente en Brasil y España y en otros países (Canada, UK), son más restrictivos, lo que confirma la aplicación inadecuada de los valores-guía de calidad de sedimentos generales. Además, la aplicación de la misma metodología para derivar los SQVs en ecosistemas litorales brasileños y españoles confirma la viabilidad de la aplicación de esta técnica de obtención de valores-guía de calidad de sedimento, integrándose datos químicos, toxicológicos y de comunidad bentónica, en cualquier zona litoral.

El ultimo articulo (VI) de esta memoria propone un protocolo armonizado para la evaluación del riesgo ambiental de sedimentos y materiales de dragados de Brasil y España. El objetivo final fue la construcción de una herramienta escalonada de toma de decisiones suficientemente amplia para su aplicación en los dos países, pero también que se ajustara a las características locales de cada zona. El protocolo propuesto en este trabajo aportó el desarrollo de nuevos estudios en comparación con otras herramientas de evaluación del riesgo ambiental de sedimentos como, por ejemplo, la posibilidad de identificación de las muestras tóxicas y/o que causasen estrés en comunidades bentónicas, y la capacidad de discriminación de los contaminantes responsables por los efectos biológicos. Al mismo tiempo, la herramienta presentada en este trabajo no implica la utilización de una zona sin contaminación como zona de referencia. La herramienta fue aplicada en las zonas de estudio y garantizó ser adecuada para la aplicación internacional. De este modo, el protocolo armonizado permite la estandardización de los procedimientos, técnicas y procesos de toma de decisiones para la evaluación del riesgo ambiental de sedimentos y materiales dragados de zonas estuarinas y portuarias del Atlántico Norte y Sur.

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Integrated sediment quality assessment in *Paranaguá* Estuarine System, Southern Brazil

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ABSTRACT

Sediment quality from *Paranaguá* Estuarine System (PES), a highly important port and ecological zone, was evaluated by assessing three lines-of-evidence: (1) sediment physical-chemical characteristics; (2) sediment toxicity (elutriates, sediment-water interface, and whole sediment); and (3) benthic community structure. Results revealed a gradient of increasing degradation of sediments (*i.e.* higher concentrations of trace metals, higher toxicity, and impoverishment of benthic community structure) towards inner PES. Data integration by PCA showed positive correlation between metals (As, Cr, Ni, Pb, and Zn) and toxicity on samples collected form stations located in upper estuary and one station placed away from contamination sources. Benthic community structure seems to be affected by both pollution and natural fine characteristics of the sediments, which reinforces the importance of a Weight-of-Evidence Approach to evaluate sediments of PES.

Key words: Weight-of-Evidence Approach; Multivariate analysis; sediment toxicity; sediment contamination; macrobenthic community;

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The authors declare that this study was conducted in accordance with the national and institutional guidelines for the *protection of human subjects and animal welfare*.

1. INTRODUCTION

Many port managers deal with the continuous effort of dredging waterways in order to keep the necessary water depth to allow safe navigation. Dredging activities can cause severe environmental impacts, especially when the sediments to be removed are contaminated. For example, the resuspension of the bottom during such operations may turn the settled contaminants soluble again (DelValls et al., 2004); moreover, high concentrations of chemicals in the dredged material may be toxic to the biota at the disposal area (Stronkhorst et al., 2003; Sousa et al., 2007). Since sediment contamination affects severely the management of dredged material (Salomons and Brils, 2004), the proper assessment of the sediment quality is essential in areas where dredging operations are executed.

Many specialists have endorsed the idea of using different lines of evidence (LOE) in sediment quality assessments, such as toxicity tests and benthic community structure surveys rather than using only the traditional chemical analyses. Whilst the aim of chemical analyses is only to quantify the contaminants present in the sediments, sediment toxicity tests are used to determine whether contaminated sediments are potentially harmful to the biota, including measurements of the interactive toxic effects of complex chemical mixtures in sediment (McDonald and Ingersoll, 2003). *In situ* benthic community surveys are, in turn, useful to indicate impacts of in-place pollutants in aquatic environments, reflecting sources of stress over time, and taking into account the effects of contaminants over a number of different benthic species, which occupies different niches and have different tolerances to chemical contamination. Therefore, in order to obtain a realistic estimation of the sediment quality, and to reduce uncertainties, specialists recommend the integration of different lines of evidence in sediment quality assessments (Cesar et al., 2007; DelValls et al, 2004; Mozeto et al., 2004; Chapman, 2002).

The integration of environmental data can be performed through different univariate and multivariate techniques; multivariate analyses permit the integration of data from different natures (e.g. chemical concentrations on sediments, toxicity endpoints, benthic community descriptors), resulting in a wider analysis that allows a deeper and more robust interpretation of the data. Principal Component Analysis (PCA) is one of the most common forms of combining environmental data by multivariate analysis (Landis and Yu, 1999) and it has been successfully utilized in integrating sediment data for sediment quality assessments (Cesar et al., 2007; Riba et al. 2004a; Riba et al. 2004b; DelValls et al. 2002; DelValls et al. 1998b; DelValls & Chapman, 1998).

The *Paranaguá* Estuarine System is an ecologically relevant site that shelters the Port of *Paranaguá*. Potentially dangerous products such as petroleum derivatives, fertilizers and minerals, as well as grains are handled in the port. This study is important to provide ecologically reliable information about the sediment quality in this area, and therefore subsidize the management of dredged material from the navigational channel of the Port of *Paranaguá*.

In order to assess the sediment quality of *Paranaguá* Estuarine System (PES) (*Paraná* State, Brazil) three lines of evidence were investigated: (1) sediment physical-chemical analyses; (2) toxicity tests; and (3) benthic community structure. These data were integrated by PCA analysis.

2. MATERIALS and METHODS

2.1 STUDY AREA

Paranaguá Estuarine System (PES) (25º16’ – 25º34’ S; 48º17’ – 48º42’ W) is located on the Coast of the *Paraná* state, Southern Brazil (Figure 1). This ecosystem is formed by two main bays: the *Paranaguá* Bay, with W-E orientation, and the *Laranjeiras* Bay, with N-S orientation. The estuarine system is bordered by the Atlantic Ridge and its coastal zone is divided into five environmental units: mangrove plain, coastal plain with forest, coastal plain with agriculture and urban facilities, fluvial plain with forests and fluvial plain with agriculture (MMA, 1996). Approximately 19% of the Atlantic rainforest remnants of Brazil are situated in this area, which has its ecological importance asserted by the 16 especially protected areas, besides the definition as “Biosphere Reserve” by UNESCO in 1995.

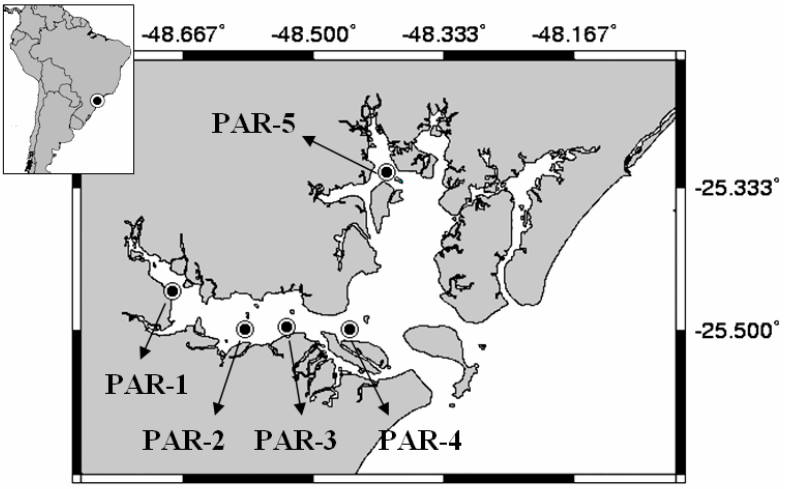

Figure 1. Localization of the sampling stations in the Paranaguá Estuarine System (PES).

The major Southern Brazilian port, the Port of *Paranaguá*, is placed in the *Paranaguá* Bay. This is the biggest port in grain export in South America (Marone et al., 2000) but also other products, such as fertilizers, minerals, and petroleum derivatives, are handled in the Port of *Paranaguá*. Additional environmental pressures in the area of the PES include the *Ponta do Félix* Port Terminal, an uncontrolled urban landfill in *Paranaguá*, which receives 130 tons of residues per day without any treatment (http://www.pr.gov.br), non-planned urban development bordering the estuary (and the consequent discharges of nontreated sewage), as well as agriculture (with wide use of agrichemicals).

2.2 APPROACH

Sediment collection

Four sampling stations were set along the navigational channel of Port of *Parangué* and *Ponta do Félix* Terminal, in the *Paranaguá* Bay, in order to identify the gradient of contamination along the channel; one additional station was situated in *Laranjeiras* Bay, in a zone considered as low contaminated (Figure 1). Sediment samples were collected synoptically for physical-chemical, toxicity, and macrobenthic community structure analyses. Three replicates sediments were collected in each station by using a 0.02 m^2 Petit-Ponar grab sampler. For physical-chemical analysis and toxicity tests, the sediments were kept in coolers with ice until their transportations to laboratory, where they were stocked at 4ºC in the dark. For benthic community structure analysis, samples were sieved through a 500 µm mesh bag. Macroinvertebrates retained on the screen were fixed with 4% buffered formalin, subsequently washed, and then transferred to 70% isopropyl alcohol prior to sorting and identification. Each sieved sample had individual taxa identified and enumerated by using stereoscope microscopy, in order to assess species richness and abundance. All organisms were sorted and identified to family level and their abundance was calculated.

Physical-chemical analyses

Grain size analysis was performed by the wet sieving process according to Mudroch and MacKnight (1994). This technique consists of a series of sieves for sandy sediments and a flocculation and pipette determination for silts and clays.

Total organic carbon (TOC) was analyzed by combustion at 900°C for total carbon (TC) and phosphoric acid addition for inorganic carbon (IC), which are transformed to CO_2 and determined by an infra-red (IR) detector on a Shimadzu TOC 5000 attached to a Solid Sample Module SSM 5000A (Standard Methods, 2000).

Metals (Ag, Cd, Cu, Cr, Ni, Pb and Zn) and metalloids (As and Se) were extracted from sediment samples according to the Method 3050B (USEPA, 1996a) in which an aliquot of 2g of sediment is weighted (± 0.0001g) and subjected to an acid extraction with concentrated HNO_3 and H_2O_2 30% and heated to about 90°C. Concentration were determined by flame atomic absorption spectrophotometry (F-AAS) for Cu, Cr, Ni, Pb and Zn, graphite furnace (GF-AAS) for Ag and Cd and hydrate generation (HG-AAS) for As and Se. Mercury was extracted by a mixture of the Methods 245.5 and 245.6 from USEPA (1991a) which employs concentrated HNO_3 and H_2SO_4, with $KMnO_4$ 7.5%, $K_2S_2O_8$ 8% and $NH_2OH.HCl$ 15% heated on a water bath to

95°C. Mercury concentration determination was done by cold vapor spectrophotometry (CV-AAS). Detection limits varied from 0.02 to 5mg kg^{-1} depending on the metal and equipment used on the analysis.

Organic compounds analyses were conducted as follows: 10g (± 0.0001g) of sediments were ultrasound extracted on a 50mL mixture of n-hexane/acetone 1:1 twice. The extract was concentrated on a rotary evaporator to a volume of 2mL and on a nitrogen flux to 1mL (an USEPA Method 3550B; USEPA, 1996b). After that, it was passed through a clean-up column with silica gel, eluted with 50mL of dichloromethane/hexane 2:3 mixture, and concentrated to 1mL on rotary evaporator and nitrogen flux (USEPA Method # 3630C; USEPA, 1996c).

Extracts were analyzed on a GC-MS Shimadzu model QP 2010 with methods prepared for each compound class that was being evaluated. Polycyclic aromatic hydrocarbons (PAHs) were analyzed according to Method 8270C (USEPA, 1996d). Following this method, the compounds analyzed were: Naphthalene, Acenaphthylene, Acenaphthene, Fluorene, Phenanthrene, Anthracene, Fluoranthene, Pyrene, p-terphenyl-d14, Benz[a]anthracene, Chrysene, Benzo[b]fluoranthene, Benzo[a]pyrene, Indeno[1,2,3-cd]pyrene, Dibenz[a,h]anthracene and Benzo[ghi]perylene. Standard solution from Supelco was obtained on a concentration of 2000mg L^{-1}. The method was created in SIM mode (Selected Ions Monitoring), with an initial temperature of 45°C heating gradually to 250°C with splitless mode on the first minute followed by a split ratio of 1:15 and solvent cut of 3.5 minutes with helium flux of 1.2mL/min and 66.4 kPa of pressure. n-alkanes method was almost the same, except that the temperature curve started on 50°C and ended on 320°C and was prepared in SCAN mode in order to obtain an unresolved complex mixture (UCM) overview.

The methods for polychlorinated biphenyls (PCBs) were adapted from Methods 8081B, 8082A and 8275A from USEPA (USEPA, 1998; 2000; 1996e, respectively). Methods were built on SIM mode. PCBs started to be analyzed at 100°C ending at 250°C with a splitless mode for 2 minutes and a split ratio of 1:30 and solvent cut of 6 minutes. Pressure and helium flow are the same for PAHs.

Detection limits were calculated by visual methods on all cases (Ribani et al., 2004). Since the calibration curve was constructed with the first concentration point equal to 1ppb, detection limits are calculated on 0.1 µg kg^{-1} and quantification limits calculated on 0.3 µg kg^{-1} for PAHs, n-alkanes, PCBs and organochlorine pesticides. All calibration curves were constructed with the following concentration points: 1, 10, 50, 100, 500 and 1000ppb (µg L^{-1} or kg^{-1} depending on the matrix, water or sediment).

PCB standard solution was from AccuStandard Inc. on a concentration of 10mg L^{-1}. The following PCBs ranging from dichlorobiphenyl to heptachlorobiphenyl were analysed: 8, 28, 37, 44, 49, 52, 60, 66, 70, 74, 77, 82, 87, 99, 101, 105, 114, 118, 126, 128, 138, 153, 156, 158, 166, 169, 170, 179, 180, 183, 187 and 189.

Replicates were done on approximately 30% of the samples, for TOC, metals and organic compounds. Recovery was calculated by spiking some of the samples or an aliquot of $NaSO_4$ and adding certain concentrations of the standard solutions cited above. Percentage recoveries were around 88 to 104 % for PCBs and 92 to 128 for PAHs.

All glassware for organic compounds analysis were washed with Extran (from Merck), rinsed with acetone and methanol PA (Merck or Synth) and set to dry on an oven at 105°C and all reagents used on extraction were HPLC grade from Baker, Merck or Mallinckrodt. Glassware for metals was washed with Extran and set on a bath with

HNO_3 20% for 4 hours and reagents used in the extractions were all PA grade from Baker, Merck and Mallinckrodt.

Toxicity tests

The toxicity of sediments from the four sampling stations along the navigational channel of Port of *Paranaguá Ponta do Félix* Terminal, plus a station placed away from pollution sources, was assessed by analyzing the embryo-larval development of sea-urchin (*Lytechinus variegatus*) and amphipods mortality (*Tiburonella viscana*) exposed to the tested sediments. For better characterization of the sediment toxicity, three routes of exposure were tested:

(i) Elutriate treatment: this method aims to assess the transference of contaminants, and consequently the toxicity, from sediments to the water, after a resuspension process. Elutriations were made according to USEPA (1995) recommendations. Sea urchin embryo-larval development test followed methods described in ABNT NBR 15350 (2006).

(ii) Sediment-Water Interface (SWI) treatment: the sea urchin embryo-larval development (Cesar et al., 2004) was observed, aiming to evaluate the potential toxicity of the sediments for releasing contaminants to the water column through arising fluxes of pore water.

(iii) Whole-sediment: the amphipods mortality was used (Melo and Abessa, 2002), with the objective of assessing the effects caused by the direct contact with the sediments, i.e., with the solid-phase and the pore water together.

Negative control was made for all the treatments by using solely uncontaminated natural seawater. Four replicates were made for each test. Differences in toxicity responses among the sampling stations were statistically assessed by one-way ANOVA (followed by Tukey's test), for the tests with liquid-phase samples and the Student-t' test for whole sediment test.

Benthic infaunal analysis

The organisms were sorted and identified to family level. To integrate in the PCA, classical community descriptive parameters were calculated by using the software PRIMER 5 for Windows (PRIMER-E Ltda, 2001, version 5.2.0), such as: Margalef's species richness (R = (S-1) $(\text{LogN})^{-1}$), where 'S' is the species richness (*i.e.* number of species), and 'N' is the total number of all individuals; Shannon's diversity ($H' = -\sum(P_i \, \text{Log}_e P_i)$), where '$P_i$' is the relative abundance of each species; Pielou's evenness ($J = H' \, (\text{LogS})^{-1}$); and Simpson's dominance ($D = 1-\sum\{N_i \, [N_i-1] \, [N \, (N-1)]^{-1}\}$), where '$N_i$' is the abundance (*i.e.* number of individuals) in each species. In addition, an abundance analysis was carried out by calculating the proportion of major taxa's (*Polychaeta*, *Mollusca*, and *Crustacea*) abundance to the total abundance for each sample.

Principal Component Analysis

The relationship amongst variables was assessed by using a multivariate analysis approach by means of a Factor Analysis. Principal Component Analysis (PCA) (Varimax normalized rotation) was used as an extraction procedure. It was based on the geochemical characteristics of the sediments (PAHs, PCBs, As, Cr, Cu, Ni, Pb, Zn, % O.C., and % fines), results of toxicity bioassays (abnormal development of sea-urchin embryo-larva exposed to sediment elutriates and SWI, and amphipods mortality exposed to whole sediment), and the benthic community descriptive parameters (number of taxa, density of organisms, richness, evenness, diversity, and Simpson's dominance). The concentrations of Ag, Cd, and Se were not included in the PCA since these metals were not detected in the samples of any station. The variables were autoscaled (standardized) so as to be treated with equal importance. All analyses were performed using the *Statistica* software tool (Stat Soft, Inc. 2001; version 6).

3. RESULTS

Physical-chemical, toxicity, and benthic community structure data

The results of physical-chemical characteristics, toxicity and benthic community structure of sediments from PES are summarized in Table 1. Sediments from PAR-1 and PAR-2 were predominantly muddy (>60% fines), whereas the other sediment samples presented lower percentages of fines, between about 15 and 27%. The sediments from PAR-1 and PAR-2 were richer in organic carbon than the other sampling sites; low OC contents were found in sediments from PAR-3 and PAR-5. The OC content in the sample from PAR-4 was very low (0.44%).

The stations located at the inner parts of the PES (PAR-1 and PAR-2) presented higher concentrations of metals in the sediments whereas stations located downstream

Table 1. Physical-chemical characteristics, toxicity tests results, and benthic community descriptive parameters of sediments from Paranaguá Estuarine System (PES).

Chemicals	**Sampling points**				
	PAR-1	**PAR-2**	**PAR-3**	**PAR-4**	**PAR-5**
Ag (mg.kg^{-1})	<0.004	<0.004	<0.004	<0.004	<0.004
As (mg.kg^{-1})	7.40	8.33	5.45	3.40	5.75
Cd (mg.kg^{-1})	<0.001	<0.001	<0.001	<0.001	<0.001
Cr (mg.kg^{-1})	58.00	51.50	27.85	14.50	48.80
Cu (mg.kg^{-1})	16.20	13.80	6.55	<0.04	<0.04
Ni (mg.kg^{-1})	21.90	20.73	10.98	6.65	19.10
Pb (mg.kg^{-1})	29.75	27.70	17.63	<0.30	23.95
Se (mg.kg^{-1})	<0.04	<0.04	<0.04	<0.04	<0.04
Zn (mg.kg^{-1})	80.50	77.75	41.33	26.95	58.00
PAHs total (μg.kg^{-1})	20.95	28.35	26.04	11.17	10.19
PCBs total (μg.kg^{-1})	<0.3	1.09	1.32	1.47	<0.3
Sediment characteristics					
TOC (%)	4.20	3.65	1.53	0.44	1.32
Fines (%)	64.55	64.87	27.34	15.33	20.22
Toxicity endpoints (mean ± SD)					
% of abnormal sea-urchin development (elutriates)	88.75± 7.41	33.25± 3.77	22.25± 3.40	13.75± 4.79	18.75± 9.78
% of abnormal sea-urchin development (SWI)	82.67± 13.58	19.00± 4.24	10.00± 5.35	10.00± 3.16	13.67± 9.81
% of amphipods mortality	90.00± 10.00	63.33± 5.77	40.00± 20.00	36.67± 32.15	46.67± 15.28

Table 1. Continued

Benthic community descriptors					
Number of taxa (S)	1	1	9	13	7
Density of organisms (ind.m^{-2})	7	14	106	207	97
Taxa Richness (Margaleff's *R*)	0.00	0.00	1.72	2.25	1.31
Taxa Evenness (Pielou's *J'*)	-	-	0.90	0.92	0.86
Taxa Diversity (Shannon's *H'*)	0.00	0.00	1.99	2.36	1.68
Simpson's dominance (D = 1-λ')	0.00	0.00	0.85	0.89	0.78

(PAR-3 and PAR-4). PAR-3 and PAR-4 presented metal concentrations lower than those found in PAR-5, the station located away from potential pollutant sources. The levels of PAHs and PCBs were low in all the studied samples, suggesting that such compounds are not the priority contaminants for PES.

PAR-1, the most internal station in the PES, presented the most toxic sediment elutriates, SWI (both sea-urchin embryo-larval development test) and whole sediment (amphipods mortality test). Abnormal sea urchin embryo-larval development were significantly higher in PAR-1 than in the others stations, in both elutriates and SWI tests (one-way ANOVA, $p<0.05$). PAR-2 sediments also showed higher elutriate toxicity than PAR-4 and PAR-5 (one-way ANOVA, $p<0.05$). Toxicity results of PAR-3, PAR-4, and PAR-5 were not significantly different in case of elutriates and SWI tests with sea urchin embryos. For the amphipods mortality test, the sediments from PAR-1, PAR-2 and PAR-5 were significantly toxic (t-student; $p<0.05$).

Concerning benthic community structure, PAR-1, followed by PAR-2, presented the lowest density of organisms (ind.m^{-2}), number of taxa, taxa richness (Margaleff's index), diversity (Shannon-Wiener's index), and Simpson dominance (D = 1-λ') equal to 0 (i.e. highest dominance). In PAR-3 and PAR-4, benthic community descriptors values were higher than those calculated for PAR-5 station. *Polychaeta* was the dominant group at all five stations, with higher predominance at inner estuary stations (Figure 2). This was the unique group found at PAR-1 and PAR-2; *Mollusca* was scarcely found in PAR-3, PAR-4, and PAR-5, and *Crustacea* was found only at PAR-4 station.

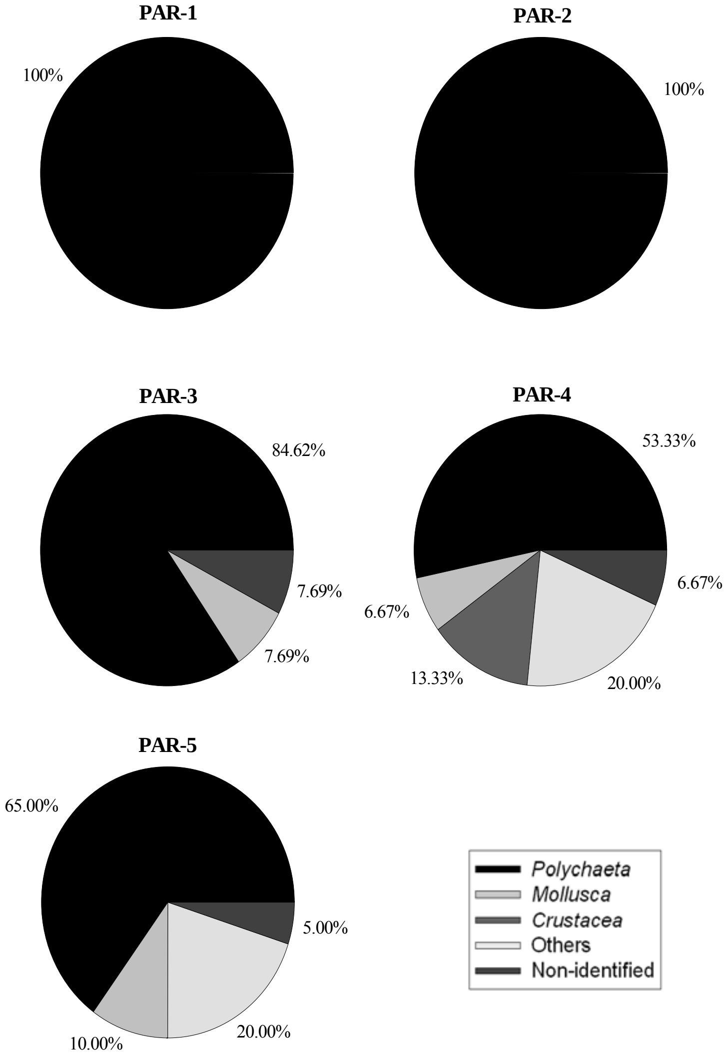

Figure 2. Dominance distribution of the main taxa in sediments from PES stations.

Multivariate Analysis approach (Principal Component Analysis – PCA)

The Factor Analysis reorganized the data of the original data set in three principal factors, which together explained 97.85% of the total variance in the original data. The loadings of the variables following varimax rotation for these three factors are represented in the Table 2. The predominant factor (F1) accounted for 81.07% of the variance and related all five benthic community descriptors, concentrations of PAHs, As, Cu, Pb, Zn, and percentage of fines and organic carbon. Since sediment toxicity tested under laboratory conditions is not related here, F1 represents only the effect of the related contaminants in the benthic communities. Second factor (F2) represented 10.00% of the total variance and correlated all five benthic community descriptors, concentrations of As, Cr, Ni, Pb, Zn, amphipods mortality, and organic carbon percentage. This factor indicates environmental degradation caused by the related metals, since sediment toxicity (amphipods mortality) is correlated in F2, in addition to *in situ* alterations. Lastly, F3 represented 6.78% of the total variance and grouped specie's richness, evenness, and diversity, high Simpson's dominance, concentrations of Cu and Zn, fine characteristics of the sediments, organic carbon content, sea urchin abnormal development exposed in the elutriates and SWI test, and amphipods mortality. The third factor (F3) denotes environmental degradation caused by higher levels of Cu and Zn, once sediment toxicity endpoints and *in situ* alterations are related to these metals in this factor.

Table 2. Sorted rotated factor loadings (pattern) of the original 19 variables on three principal factors. Only loadings greater than 0.40 are shown.

Variable	**Factor 1**	**Factor 2**	**Factor 3**
% Variance	81.07	10.00	6.78
S	0.61	0.69	------
N	0.62	0.69	------
R	0.63	0.64	0.44
J’	0.69	0.41	0.55
H’	0.66	0.55	0.49
D	0.69	0.44	0.54
PAHs	0.94	------	------
PCBs	------	-0.85	-0.43
As	0.71	0.67	------
Cr	------	0.89	------
Cu	0.78	------	0.55
Ni	------	0.89	------
Pb	0.43	0.85	------
Zn	0.51	0.76	0.40
O.C.	0.67	0.49	0.55
Fines	0.77	------	0.50
Abnormal development (elutriates)	------	------	0.89
Abnormal development (SWI)	------	------	0.94
Amphipods mortality	------	0.48	0.79

4. DISCUSSION

Physical-chemical, toxicity, and benthic community structure data

A gradient of increasing contamination was found from outer stations towards inner PES stations, especially for the metals. Chemical concentrations of sediments from PES were compared to the Canadian Sediment Quality Guidelines – SQGs (TEL – "Threshold Effect Level" and PEL – "Probable Effect Level") (Environment Canada, 1999), with exception of the nickel concentrations, which were compared to the guidelines proposed by the Florida Department of Environmental Protection (FDEP, 1994). According to the concept of SQG, adverse biological effects are not expected when the concentrations of contaminants are below the TEL values, whereas concentrations of contaminants higher than the PEL values will probably result in adverse biological effects. The stations located inner estuary (PAR-1 and PAR-2) presented concentrations of some metals higher than the TEL values, namely As and Ni in PAR-1 and PAR-2, and Cr solely in PAR-1. Chromium was found in PAR-2 in a concentration close to TEL value, but not higher than it. In addition, the concentrations of Cu and Pb in sediments from PAR-1 and PAR-2 were slightly higher than in the other samples, but not exceeding the Canadian SQG. In PAR-5, sediments contained high concentrations of Ni (exceeding TEL) and Cr (close to minimum value of TEL). The PAH and PCB levels were low in all samples and the observed concentrations were below the TEL, thus such compounds probably were not directly responsible for the toxicity.

The results of toxicity bioassays followed the pattern of the contamination in the navigational channel of PES, i.e. there is a gradient of increasing toxicity towards inner PES. In the sea-urchin test, toxicity was higher on elutriates than SWI, which suggests that part of the total concentration of contaminants in the sediments of PES are normally unavailable to the biota, although they may happen to be available after a resuspension process, e.g. tides, currents, dredging operations. In any case, sediments from PAR-1 can be considered highly toxic, PAR-2 was moderate to high toxic, PAR-3 and PAR-4 were low to non-toxic, and PAR-5 moderately toxic.

Benthic community structure analysis showed a tendency of impoverishment of benthic community towards upper estuary, following the rising concentration of contaminants, especially metals, in the sediments as well as the increasing proportion of finer sediments. The analysis of the taxa's dominance also shows the pattern of increasing alteration from outer parts of the estuary towards inner PES. At PAR-1 and PAR-2 only *Polychaeta* was found; this group of organisms is considered more tolerant to pollution (Yüksek, et al., 2006; Horne et al. 1999; DelValls, 1998a). At the other stations, besides of *Polychaeta*, other groups were found, as *Mollusca* in PAR-3, PAR-4, and PAR-5, and *Crustacea*, one of the most sensitive infaunal groups to contaminants (Anderson et al. 2004; U.S. EPA, 1991b), solely in PAR-4.

Multivariate Analysis approach

Besides the definition of the new variables by means of Factor Analysis, a representation of estimated factor scores from each station to the centroid of all cases for the original data was done, aiming to confirm the factor descriptions and to characterize the quality of sediments from the PES, as it can be seen in Figure 3.

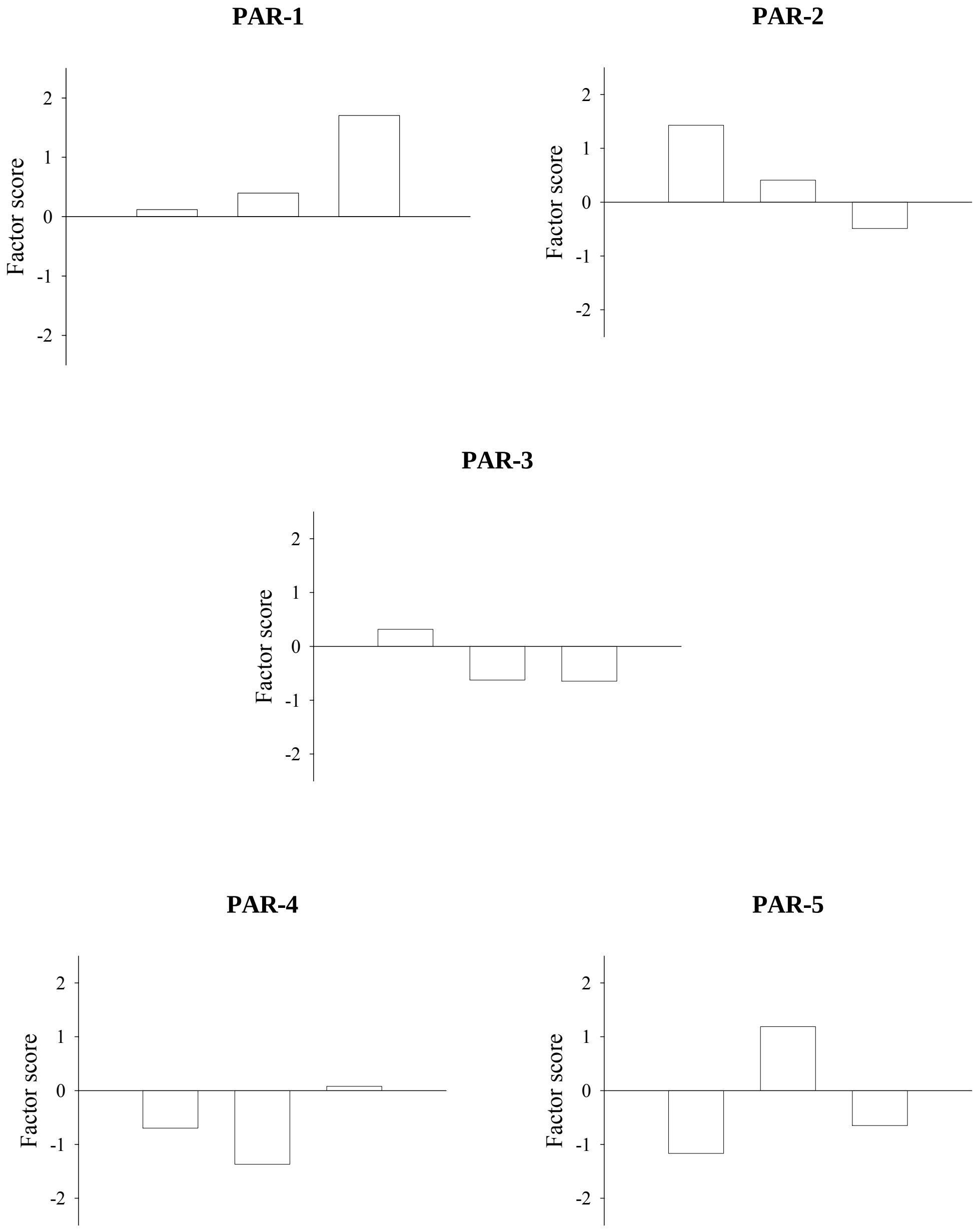

Figure 3. Estimated factor scores from each of five smpling stations to the centroid of cases for the original data from PES. The factor scores quantify to the prevalence of every component for each station and are used to confirm the factor description.

In the light of this analysis, it was found that PAR-1, the most internal sampling point located at the PES navigational channel, is the most environmentally degraded station in this study. All three factors scores were positive for PAR-1, which let us to conclude that some metals (As, Cr, Ni, Pb, and Zn) are causing stress on benthic community in this station as well as toxic effects under laboratory conditions. Even though PAR-1 sediments are mainly composed by mud, and it is expected that benthic diversity and species' variety decrease as the sediments become muddier (Albaryak et al., 2006), the prevalence of F2 and F3, which factors relate the poor benthic community to toxicity endpoints, confirms the state of high environmental degradation of the sediments in PAR-1.

At PAR-2 station, F1 and F2 were the prevalent factors. In F1, chemical concentrations (As, Cu, Pb and Zn) were related only to benthic community alterations; however, the positive score to F2 represents that concentrations of As, Cr, Ni, Pb, and Zn provoked toxicity to biota (since it is related to amphipods mortality) as well as stress on benthic community; therefore, sediments in PAR-2 are polluted (causing benthic community alterations as well as toxcity responses) because of the high concentration of these metals.

Factor 1 (F1) was representative for PAR-3 station. This factor relates benthic community alterations with PAHs, As, Cu, Pb, Zn, percentage of fines and organic carbon content in these sediments. Since the toxicity of such contaminants in PAR-3 sediments were not confirmed by toxicity tests in laboratory, *i.e.* F1 does not relate toxic responses, the condition of the benthic community in this station may be related not only to chemical contamination, but also to natural characteristics of the sediments. Despite PAR-3 is the nearest sampling station to the Port of *Paranaguá*, thus directly affected by pollution from port activities, the low percentage of fine sediments reveals that this zone is subjected to high energy waters, which can constantly transport the contaminants to other parts of the estuary.

In PAR-4 only Factor 3 (F3) was representative, which indicates that the non-stressed conditions of benthic communities natural are related to the sandy characteristics of the sediments, and low organic carbon content. This is the station located more downstream in the PES, consequently, sediments in this zone are exposed to the washing action of the sea, which probably carries off a large part of the contaminants and keeps these sediments in good environmental condition.

Factor 2 presented positive value for PAR-5 station; this denotes that the sediments in this zone are polluted by metals, namely As, Cr, Ni, Pb, and Zn, since these concentrations are affecting negatively the benthic community structure as well as amphipods mortality. PAR-5 is placed away from main contamination sources in PES, which suggests that *Benito* bay, located inside the limits of the Area of Environmental Protection of *Guaraqueçaba*, is being affected by pollution sources located elsewhere.

In general, there is a gradient of degradation of sediments towards inner PES. Higher sediment contamination by As, Cr, Ni, Pb, and Cu, increased toxicity to both sea-urchin larva and amphipods, and poorer benthic communities were found at upper stream parts of the estuarine system. The main source of pollution placed upstream in the estuary is the *Ponta do Félix* Port's Terminal, which handles, among other products, siderurgy products. Additionally, the main sources of pollution in the PES are placed downer at the estuary, the town of *Paranaguá*, especially its uncontrolled landfill, and the Port of *Paranaguá.* The metals which are causing toxicity in PES are commonly found in landfill leachates (Reinhart, 1993) and they were related to pollution caused by urban landfills in other areas (Sanchez-Chardi and Nadal, 2007; Lamparelli et al., 2001). Therefore, the contaminants produced along the estuary may have being physically transported (*e.g.* currents, tides, waves) to internal parts of the estuary, being trapped in the finer sediments of these low water energy zones, causing degradation of the sediments in these zones. Correlations commonly exist between decreasing grain size and increasing metal concentrations (Queralt et al., 1999; Horowitz, 1991; Förstner, 1989), as clay minerals are characterized by large surface areas per mass unit, which accounts for their capacity of adsorbing metals. In the other hand, the parts of the estuary under more intense action of sea waters (waves, tides), which have sediments composed primarily by sand, presented richer benthic communities, low levels of contaminants and no toxicity, therefore, no environmental degradation.

5. CONCLUSIONS

Sediments at internal parts of PES are environmentally degraded because of high levels of metals, namely As, Cr, Ni, Pb, and Cu. Although most of the contaminant concentrations are not infringing international standards of sediment quality, special attention must be taken in the management of dredged material from these zones since the mentioned metals are potentially bioavailable to the biota, *i.e.* causing toxicity and stress on benthic communities.

This was the first sediment quality assessment in PES using the Weight-Of-Evidence approach. Others sediment assessments were carried out in this area, as part of legal requirements to execute dredging operations on the navigational channel and turning base of the Port of *Paranaguá*, but only focusing on sediment chemistry and such results were not published and are not available. The use of three lines of evidence, *i.e.* sediment physical-chemical characteristics, sediment toxicity, and benthic community analysis, integrated by multivariate analysis, was useful to assess the quality of the sediments of PES, giving an insight about the bioavailability of contaminants as well as *in situ* alterations. Such information is valuable to subsidize dredged material management in this particular estuarine system.

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Development of site-specific Sediment Quality Values using the Weight of Evidence approach for North and South Atlantic littoral zones

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Science of the Total Environment (enviado)

ABSTRACT

The aim of this work was to develop site-specific Sediment Quality Values (SQVs) for two estuarine and port zones in Southeastern Brazil (Santos Estuarine System and Paranaguá Estuarine System) and three in Gulf of Cádiz (Ría of Huelva, Bay of Cádiz, and Bay of Algeciras), by linking sediment physical-chemical, toxicological, and benthic community data through the application of multivariate analysis (Factor analysis followed by PCA extraction). This technique permitted the identification of substances 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 as *highly polluted* (exceeding maximum SQVs) by metals, PAHs and PCBs. High pollution by PAHs and V was found in São Vicente channel, and PAH besides Ni in the vicinities of the submarine sewage outfall of Santos. In the PES, sediments from inner portions of PES (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, SQVs exceedences were found in Ria of Huelva (all analysed metals and PAHs), in the area of the Port of Cádiz (Bay of Cádiz) (metals), and Bay of Algeciras (Ni, Co, and PAHs). The site-specific SQVs derived in this study are more restricted than national SQGs applied in Brazil and Spain, as well as international guidelines (Canada, UK). This finding confirms the importance of the development of site-specific SQVs to support the characterization of dredged material. The use of the same methodology to derive SQVs in Brazilian and Spanish port zones confirmed the viability of application of this technique with an international scope and provided an international protocol for site-specific SQVs derivation.

Key Words: Sediment Quality Values, Multivariate Analysis, Dredged Material, Marine Pollution, Estuary.

1. INTRODUCTION

An immeasurable amount of sediments are dredged from waterways, ports, and harbours every year in the world. Dredging is necessary to maintain waterways depths adequate for navigation, as well as to deepen existing facilities in order to allow safe access to larger ships. This is especially needed in estuarine areas, where the processes which cause sediments precipitation are intense.

Dredging activities may 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 in several environmental consequences, including physical disturbance (burrowing, smothering) of benthic communities (Harvey et al., 1998), and chemical contamination (Stronkhorst et al., 2003).

There are different management options to dredged material, which include (IMO, 1996; USEPA and USACE, 2006): (1) beneficial uses (land creation and improvement, beach nourishment, agricultural uses, and environmental purposes – wetlands restoration, creation of nesting islands, etc); (2) disposal in ocean or continental waters; (3) treatment, such as the separation of sediment contaminated fractions; (4) 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 harmless to the environment as well as done in a cost-effective manner.

Despite experts have been claiming that the use of biological testing is crucial to adequately understand the hazard posed by contaminated sediments (Cesar et al. 2007, Petrovic and Barceló, 2004), decision-making on the management of dredged materials in many instances relies on a simple comparison between the levels of contaminants measured in the sediments and the national Sediment Quality Guidelines (SQGs). Nevertheless, one-size-fits-all practices hardly suit adequate sediments/dredged material assessment (Wenning and Ingersoll, 2002; Chapman and Mann, 1999). Several factors affect the availability of contaminants from sediments to the biota, such as sediment grain size, pH, salinity, organic matter content, acid volatile sulfides (AVS) contents, among others (Riba et al., 2004a; Riba et al., 2003; Simpson, 2001; Meyer et al., 1994); therefore, the bulk concentrations of contaminants may not correlate well to the bioavailability (Ingersoll et al., 1997). Consequently, site-specific guidelines rather than national general guidelines may be more suitable to address the specificities of each local and situation and thus to orientate the decision making process.

There are different approaches to develo SQGs, which can be divided in 2 broad categories (Wenning et al. 2005; Alvarez-Guerra et al., 2007): (1) 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 (McCauley et al., 2000) (e.g. Equilibrium Partioning – EqP – DiToro et al. 1991); (2) empirically-based, derived from databases of concentrations of specific contaminants and their correspondence with observed biological effects (e.g. Effects Range-Low and Median – ERL and ERM – Long and Morgan, 1990; Long et al. 1998; Threshold and Probable Effects Level – TEL and PEL – MacDonald et al., 1996). A third category, the "Consensus Approach" combines SQGs from theoretical and empirical approaches to create a consensus threshold of effects concentrations (TEC), median effects concentrations (MEC), and extreme effects concentrations (EEC) (Swartz, 1999). In Brazil, sediment quality values to orientate dredged material management are given by the Resolution n° 344/2004 from the National Council for the Environment – CONAMA (Brasil, 2004). Such values were based on the American and Canadian SQGs (EC, 2002; Long et al., 1995; FDEP, 1994). In Spain, the document *Recommendations for the management of dredged material in ports of Spain* (RMDM) (CEDEX, 1994) has been applied to characterize the sediments dredged in Spanish ports, however, it is a normative document which is not legally valid. These Spanish SQGs are based on geochemical considerations instead of being related to toxicological or biological effects (DelValls et al., 2004).

The aim of this work was to develop site-specific Sediment Quality Values (SQVs) for two estuarine and port zones in Southeastern Brazil (Santos and São Vicente Estuarine System and Paranaguá Estuarine System) and three in Gulf of Cádiz (Ría of Huelva, Bay of Cádiz, and Bay of Algeciras, Southern Spain), by integrating sediment geochemical, ecotoxicological, and benthic community data through the application of multivariate analysis. The areas under study are affected by different sources of pollution, as domestic sewage, industrial effluents, urban runoff, as well as contamination due to the port activities themselves (Choueri et al., in press; Cesar et al, 2007; Riba et al., 2004b, 2004c). The integration of sediment chemistry and toxicity/ecological effect data allows the identification of substances of concern and the establishment of effects range correlatively to individual concentrations of contaminants for each site of study. The establishment of site-specific ranges of contaminants concentrations related to biological responses may better subsidise the management of the dredged material in the studied zones. Furthermore, the use of the same method to derive SQVs for Brazilian and Spanish port zones aimed to assess the viability of application of this technique with an international scope and providing an internationally harmonized protocol for site-specific SQVs derivation.

2. MATERIAL AND METHODS

2.1 *Approach*

In this study, site-specific Sediment Quality Values were derived for two areas in Southern Brazil: Santos Estuarine System (SES) and Paranaguá Estuarine System (PES) (figure 1'a' and 'b'); and three areas in Gulf of Cádiz (GC), Southern Spain: Ría of Huelva, Bay of Cádiz, and Bay of Algeciras (figure 2 'a', 'b' and 'c'). All the areas of study present prominent port activities together with ecologically important ecosystems (in Brazil, mangroves and Atlantic forest; in Spain, salt marshes). In SES, dense industrialization and urbanization has been affecting the quality of the environment, as reported before (Cesar et al., 2007; Cesar et al., 2006; Abessa, et al., 2005; Abessa et al., 2001; Lamparelli et al., 2001; CETESB, 1985, 1978). In PES, the major environmental threats are the 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 by mainly industrial and mining activities (Cesar et al., in press; Cesar et al., 2007; Riba et al, 2005; Riba et al.; 2004b); in Bay of Cádiz, despite the activities of 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) (Cesar et al., 2007) and benthic community structure alterations (Cesar et al., in press) were found in the vicinities of the Port of Cádiz. The Port of Algeciras is the most important Spanish port, situated in Bay of Algeciras, at the estuary of the Guadarranque River. This stream receives the discharges of industrial effluents from the Algecira's petrochemical industrial complex. Previous investigations reported high sediment toxicity and benthic community alterations caused by metals and PAHs (Cesar et al., 2007 and Cesar et al., in press).

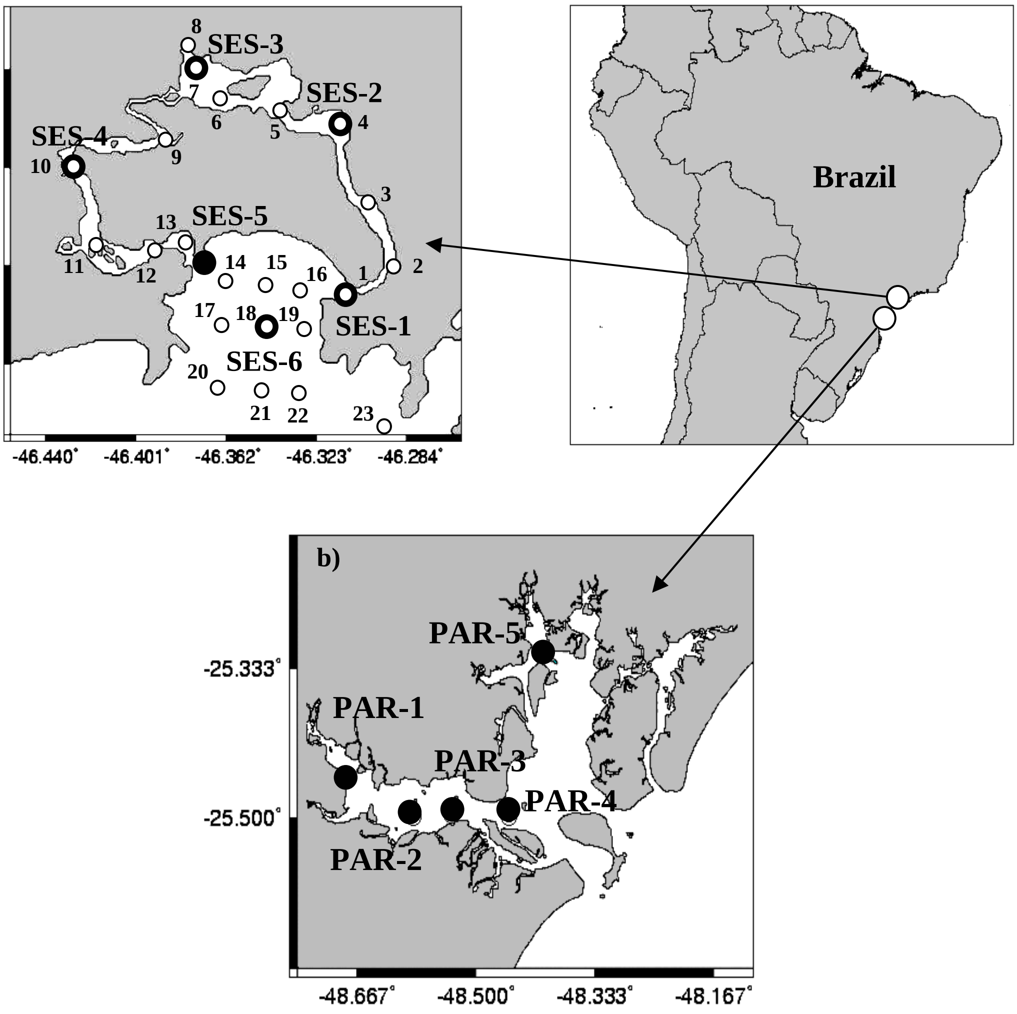

Figure 1. Localization of the sampling stations in (a) Santos Esturine System (black circles represent sampling stations of Cesar et al., 2007; white circles represent sampling stations of Abessa, 2002) and (b) Paranaguá Esturine System and their disposition in Southeastern Brazil.

The data matrix for SQVs derivation included sediment geochemistry, toxicity (elutriates, sediment-water interface, whole sediment) and benthic community structure information of each area of study. In SES, data from thirty one sampling stations were utilised (figure 1a); in PES, five sampling stations were set (figure 1b); in GC, three sampling stations were located at Ría of Huelva (figure 2a), two at Bay of Cádiz (figure

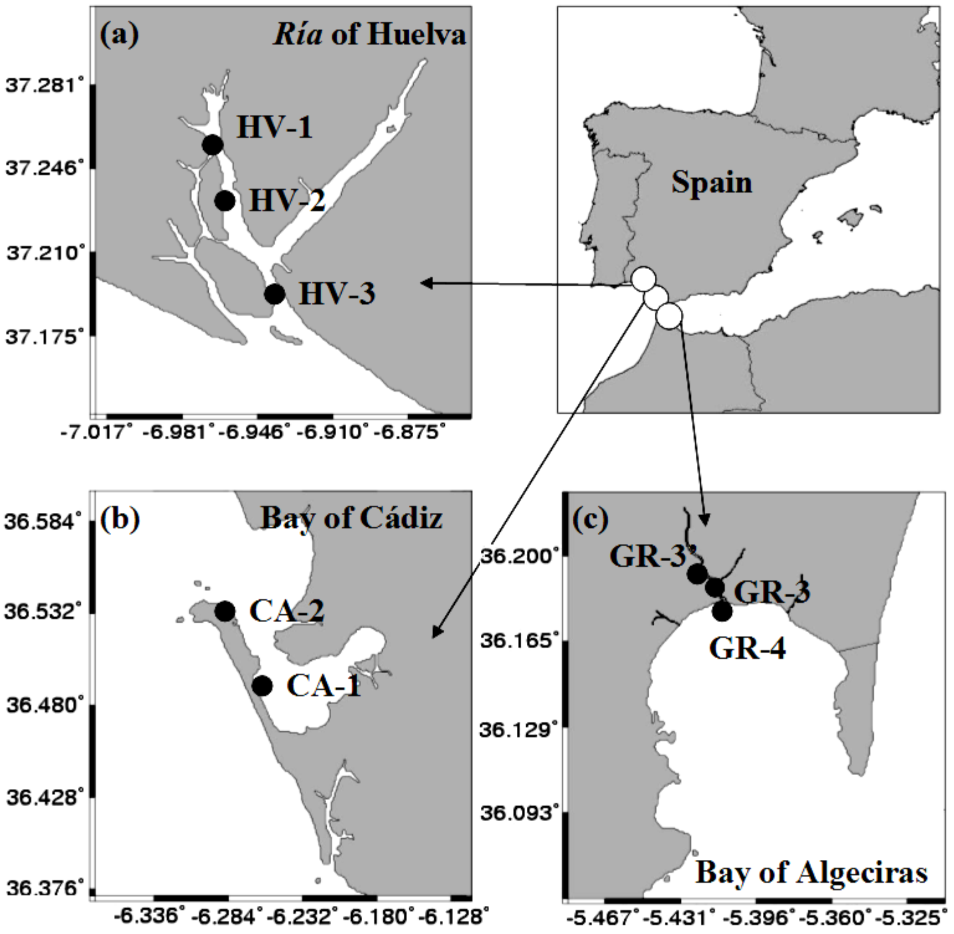

Figure 2. Localization of the sampling stations in Ría of Huelva (a), Cádiz Bay (b), Algeciras Bay (c) and their disposition in Southern Spain.

2b), and three at Bay of Algeciras (figure 2c). Details of sediment and benthic macrofauna sampling, analytical procedures, and the methodology employed on the toxicity tests were described in Choueri et al. (in press), Cesar et al. (in press), Cesar et al. (2007), and Abessa et al. (in press).

2.2 Multivariate Analysis

The integration of different lines of evidence was performed by means of a Factor Analysis, with the application of a Principal Component Analysis (PCA) (Varimax normalized 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 (DelValls et al., 1998).

The original data sets of Brazilian and Spanish areas comprised physical characteristics of the sediments, chemical concentrations (metals and organics), toxicity parameters, and benthic community descriptors. The two different data sets of SES in which PCA was applied contained the following variables: (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, PCBs, % organic carbon TOC), % of fines, and amphipods mortality. Concentrations of Cd and Co were measured but not included in the PCA because their concentrations were below the detection limit of the equipment; and (ii) SES (b) – S, N, *R*, *J'*, *H'*, and *D* values, levels of Cd, Co, Cr, Ni, Pb, Hg, Zn, PAHs, % of TOC, % of fines, and amphipods mortality. For the PES, the data included in the PCA analysis were the benthic community descriptors cited above, concentrations of As, Cr, Cu, Ni, Pb, Zn, PAHs, PCBs, % of TOC, % of fines, % of abnormal embryo-larval development of sea-urchin exposed to sediment elutriates and SWI, and % of amphipods mortality. Levels of Ag, Cd, and Se were not detected in the chemical analysis of the sediments therefore such contaminants were not included in the PCA.

The data set comprised in the PCA analysis for the Gulf of Cádiz areas were as follows: 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. The values of benthic community descriptors were transformed as the inverse (i.e. multiplied by -1) in all four analyses 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 (standardized) so as to be treated with equal importance (varimax normalized). 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 ≥ 0.40, as proposed by Tabachnic & Fidell (1996). The analyses were performed using the PCA option of the MULTIVARIATE EXPLORATORY TECHNICS procedure, followed by the basic set-up for FACTOR ANALYSIS procedure from the STATISTICA software tool (Stat Soft, Inc. 2001; version 6).

2.4 Development of SQVs

The calculation of SQVs followed the methodology presented in DelValls and Chapman (1998). Basically, chemical ranges associated to toxic responses were identified by linking sediment chemical concentrations, toxicity endpoints, and benthic community descriptors through the application of PCA. The calculation of the prevalence of factors (factor scores) for each station in relation to all stations allowed us to detect the stations which showed positive or negative score to the factor(s) related to biological effects. This was important because, in the process of SQVs derivation, the SQVs-high were determined as the minimal measured concentration of chemicals in the stations where the factor (or factors) associated to biological effects shows a positive score. Conversely, SQVs-low were considered as the maximum measured concentration of chemicals in the stations where the factors related to biological effects showed negative scores.

Assuming that chemicals and toxicity effects related in the same factor are correlated in a cause-and-effect manner, the analysis above permits the identification of: (1) the maximum concentration not associated to toxic effects, *i.e.* below this concentration for its specific contaminant, sediments are considered as *not polluted*; (2) the minimal concentration above which toxic effects are always found, *i.e.* above this level for its specific contaminant, sediments must be considered as *polluted*; (3) the concentration range in between these two values, where biological responses are not predictable – if the sediments/dredged material contain such levels of contaminants, they must be considered as *moderately toxic*.

3. RESULTS

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

Results of sediment physical-chemical and toxicity data are summarized in table 1 (a) and (b) for SES, table 2 for PES, and table 3 for GC. Detailed description of the

Table 1 (a). 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**					
Chemicals	**SES-1**	**SES-2**	**SES-3**	**SES-4**	**SES-5**	**SES-6**
Cd (ppm)	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Co (ppm)	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Cu (ppm)	<0.1	167.2	157.7	69.0	<0.1	<0.1
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	<0.1
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	<0.1
Sediment characteristics						
OC (%)	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 ± sd)						
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 (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-λ')	0.88	0.85	0.64	0.32	0.87	0.87

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

Variables	**Sampling stations**											
Chemicals	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**
Cd (ppm)	<0.50	<0.50	<0.50	0.75	0.92	0.99	0.42	0.98	1.49	<0.50	<0.50	<0.50
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)	5.88	8.33	44.71	22.97	386.38	357.54	123.82	480.36	0.00	24.73	33.17	0.00
Sediment characteristics												
OC (%)	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 ± sd)												
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 ($D = 1\text{-}\lambda'$)	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 1 (b). Continued.

Variables	**Sampling stations**												
Chemicals	**13**	**14**	**15**	**16**	**17**	**18**	**19**	**20**	**21**	**22**	**23**	**24**	**25**
Cd (ppm)	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	0.85	<0.50
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)	0.00	0.02	0.01	0.00	0.01	0.51	0.01	0.00	0.01	0.01	0.00	0.03	0.00
Sediment characteristics													
OC (%)	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 ± sd)													
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	10564.1	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 2. Physical-chemical characteristics, toxicity tests results, and benthic community descriptive parameters of sediments from Paranaguá Estuarine System.

Variables	**Sampling stations**				
Chemicals	**PAR-1**	**PAR-2**	**PAR-3**	**PAR-4**	**PAR-5**
Ag (ppm)	<0.004	<0.004	<0.004	<0.004	<0.004
As (ppm)	7.40	8.33	5.45	3.40	5.75
Cd (ppm)	<0.001	<0.001	<0.001	<0.001	<0.001
Cr (ppm)	58.00	51.50	27.85	14.50	48.80
Cu (ppm)	16.20	13.80	6.55	<0.04	<0.04
Ni (ppm)	21.90	20.73	10.98	6.65	19.10
Pb (ppm)	29.75	27.70	17.63	<0.30	23.95
Se (ppm)	<0.04	<0.04	<0.04	<0.04	<0.04
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)	<0.3	1.09	1.32	1.47	<0.3
Sediment characteristics					
OC (%)	4.20	3.65	1.53	0.44	1.32
Fines (%)	64.55	64.87	27.34	15.33	20.22
Sediment toxicity (mean ± SD)					
% 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 (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-λ')	0.00	0.00	0.85	0.89	0.78

Table 3. Physical-chemical characteristics, toxicity tests results, and benthic descriptive parameters of sediments from Gulf of Cádiz.

Variables	**Sampling stations**							
Chemicals	**HV-1**	**HV-2**	**HV-3**	**CA-1**	**CA-2**	**GR-4**	**GR-3**	**GR-3’**
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	<0.01	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	<0.01	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	<0.01	161.00	<0.01	<0.01	<0.01
Sediment characteristics								
OC (%)	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 ± sd)								
% 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 (mean ± sd)								
Number of species (S)	1	1	3	23	14	6	6	1
Density of organisms ($N.m^{-2}$)	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

chemical, toxicity and benthic community results were previously reported in Abessa et al. (in press), Cesar et al. (2007), Cesar et al. (in press), and Choueri et al. (in press). Excepting Bay of Cádiz, 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 toxicity was found at Ría of Huelva (together with the highest metals concentrations), followed by Bay of Algeciras (with higher levels of PAHs). Both in Southeastern Brazil 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 application 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 4). The predominant factor (F1) accounted for 42.50% of the variance and grouped Cu, V, PAHs, amphipods' mortality, and benthic's number of species, Margaleff's species richness, Pielou's evenness, Shannon's diversity, and Simpson's dominance. Therefore, F1 represented toxicity and ecological effects possibly associated to vanadium and PAHs (these contaminants presented higher loadings), with some contribution of copper (lower loading). Second factor (F2) explained 24.66% of the variance and related Cu, Pb, Zn, PCBs, amphipods mortality, and Ni with negative values. Consequently, F2 represented sediment toxicity associated to the related metals and PCBs. The third factor (F3) accounted for 18.95 % of the total

Table 4. Sorted rotated factor loadings of the original 16 variables on the 3 principal factors of the SES (a) 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	**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	------
OC	------	------	-0.39
Fines	------	------	0.90
Amphipods' mortality	0.73	0.44	0.40
S	0.86	------	0.47
N	------	------	0.90
R	0.92	------	0.35
J'	0.76	------	-0.58
H'	0.99	------	------
D	0.97	------	------

variance and showed loadings higher than 0.35 for Ni, percentage of fines, amphipods mortality, number of species and abundance of individuals; this factor represented toxicity and some benthic community alteration caused mainly by the fine characteristics of the sediments (higher loading) and levels of nickel. In summary, the contaminants of concern identified in this case, 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 new variables, which accounted for 67.92 % of the variance in the original data set (table 5). 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 suggests that the sediments toxicity was related to the high levels of all analysed contaminants (metals and PAHs), as well as organic carbon 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. Abessa et al. (in press) has 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. Factor 3 (10.91% of the variance) represented some alteration on benthic community structure (evenness and dominance) as a result of lead contamination. In the case of SES (b), contaminants of concern were as follows: cadmium, cobalt, chromium, nickel, lead, mercury, zinc, and PAHs.

Table 5. Sorted rotated factor loadings of the original 17 variables on the 3 principal factors of the SES (b) 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	**Factor 1**	**Factor 2**	**Factor 3**
% Variance	37.49	19.52	10.91
Cd	0.57	------	------
Co	0.90	------	------
Cr	0.87	------	------
Ni	0.92	------	------
Pb	0.44	------	0.46
Hg	0.81	------	------
Zn	0.87	------	------
PAHs	0.77	------	------
OC	0.53	------	------
Fines	0.63	------	------
Amphipods' mortality	0.57	------	------
S	------	0.95	------
N	------	------	-0.64
R	------	0.96	------
J'	------	0.51	0.66
H'	------	0.91	------
D	------	------	0.82

The original matrix of sediment data of PES was reorganized through the multivariate analysis in three new variables which explained 97.55% of the total variance (table 6). The predominant factor (F1) described 79.84% of the variance and showed relationship between the most of the analysed metals (excepting chromium and nickel), PAHs, OC, percentage of fines, and benthic community descriptors (S, N, *R*, *J'*, *H'*, and *D*). Consequently F1 represented *in situ* alterations on benthic communities associated to As, Cu, Pb, Zn, Hg, PAHs, as well as organic carbon and physical characteristics of the sediments. Factor 2 (F2) accounted for 10.41% of the total variance and represented sediment toxicity (amphipods' mortality) together with benthic community alterations (S, N, *R*, *J'*, *H'*, and *D*) associated 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 (amphipods' mortality test, and elutiates 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 related 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 7). The prevalent factor (F1) accounted for 54.24% of the variance and grouped Ni, PAHs, elutiates and SWI sea-urchin embryo-larval development tests, amphipods' mortality test, and benthic community descriptors (S, N, R, J', H', and D). In this case, F1 represented sediment toxicity and benthic community alteration associated with high levels of Ni and PAHs. The second factor (F2) (19.23% of the total variance) related

Table 6. Sorted rotated factor loadings of the original 20 variables on the 3 principal factors of the PES 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	**Factor 1**	**Factor 2**	**Factor 3**
% Variance	79.84	10.41	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	------
OC	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

Table 7. Sorted rotated factor loadings of the original 20 variables on the 2 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	**Factor 1**	**Factor 2**
% Variance	54.24	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	------
%O.C.	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

metals (Cd, Co, Cu, Pb, V and Zn), fines, amphipods' mortality, and some benthic community descriptors (evenness, diversity and dominance); therefore F2 explained the sediment toxicity and benthic community alterations associated to metals. The chemicals of concern identified in GC were: cadmium, cobalt, copper, nickel, lead, vanadium, zinc, and PAHs.

4. DISCUSSION

The results of the analyses of prevalence of each factor for each sampling station in SES, PES and GC were presented in the tables 8 and 9 for SES (a) and (b) respectively; table 10 for PES; table 11 for GC). Because in all cases each factor is related to at least one negative biological response, only those sampling stations where factor scores are ≤0 are not associated to negative biological effects. Thus, for the derivation of the SQVs in each case (SES (a), SES (b), PES, and GC), the concentration of a given chemical below which the adverse biological effects were considered low or minimal, was defined as: the higher concentration of the chemical among those stations where the related factor score was ≤0. Chemical concentrations lower than these values are therefore considered not harmful to the biota, and sediments were considered as not polluted. Likewise, the concentration of a given chemical above which there is association to major biological effects, was designated as: the lowest concentration among those stations where the related factor score present value >0. Sediments presenting chemical concentrations higher than these values were considered highly polluted. Lastly, sediments bearing chemicals at concentrations which fall into the gap in between the two values were considered moderately polluted. Table 12 for SES (a)

Table 8. Factor scores estimated for each of the 6 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

Table 9. 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	0.01	-0.73	0.49
2	0.10	-0.98	-0.55
3	0.07	-0.34	-0.60
4	0.97	1.21	2.38
5	1.30	1.45	-0.66
6	1.14	0.05	-0.93
7	1.61	-0.30	1.18
8	2.86	0.32	-0.81
9	0.50	1.05	-0.09
10	-0.85	0.77	-1.09
11	0.04	-0.04	-0.50
12	-1.35	1.51	-0.04
13	-1.29	1.54	1.17
14	-0.80	0.39	-0.68
15	-0.70	0.27	-0.50
16	-0.60	-2.58	-0.07
17	-0.57	0.39	-0.37
18	0.01	0.23	0.48

Table 9. Continued.

Station	F1	F2	F3
19	-0.16	-0.90	-0.52
20	-0.95	0.68	-0.74
21	-0.43	-0.36	-0.53
22	-0.48	-0.87	2.99
23	-0.61	-1.14	-0.30
24	0.89	-1.27	0.01
25	-0.72	-0.35	0.28

Table 10. Factor scores estimated for each of the 5 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 11. Factor scores estimated for each of the 8 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

and SES (b), table 13 for PES, and table 14 for GC present the SQVs defined for the chemicals of concern in each study area (i.e. those related to negative biological effects).

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. Minimum values (i.e. below which there is no association to biological effects) for Cu in SES (a), and Cd and Cr in SES (b) were not presented in the table 12 because such values corresponded to the detection limit of the analytical chemistry procedure. Nevertheless, maximum values for these contaminants were possible to be identified and presented in the table 12. Nickel, lead and zinc were the contaminants of concern in SES (a) in common with SES (b); there was a slightly difference between the SQVs derived for these contaminants, which could could be expected since the data were taken from different studies (i.e. samples were taken in different periods and the sampling methods were different) and the chemical analyses employed in each of these studies were not the same. Nevertheless, the differences between the SQVs derived from the two data sets were smaller than the differences found in the comparison to national and international benchmark Sediment Quality Guidelines (SQGs), as we will discuss further on this article.

The application of these SQVs in the classification of the sediments of SES showed sediments highly polluted by several metals, PAHs, and PCBs in the 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. The SQVs derived from SES (a) and (b) data matrices classified sediments from São Vicente Channel as highly

Table 12. Sediment quality values 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 <4.2	4.2≥
Cr (ppm)	SES (a)	–	–	–
	SES (b)	–	–	7.5≥
Cu (ppm)	SES (a)	–	–	69.0≥
	SES (b)	–	–	–
Ni (ppm)	SES (a)	≤3.89	3.89> and <4.49	4.49≥
	SES (b)	≤5.9	5.9> and <7.0	7.0≥
Pb (ppm)	SES (a)	≤17.4	17.4> and <22.1	22.1≥
	SES (b)	≤7.8	7.8> and <10.3	10.3≥
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 <0.11	0.11≥
Zn (ppm)	SES (a)	≤73.3	73.3> and <110.4	110.4≥
	SES (b)	≤35.9	35.9> and <37.9	37.9≥
PAHs (ppm)	SES (a)	≤0.163	0.163> and <0.425	0.425≥
	SES (b)	–	–	–
PCBs (ppb)	SES (a)	≤0.94	0.94> and <2.61	2.61≥
	SES (b)	–	–	–

– not possible to calculate

Table 13. Sediment quality values 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 14. Sediment quality values for the chemicals of concer of Gul 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 <10.00	10.00≥
Cu	≤20.80	20.80> and <169.00	169.00≥
Ni	≤8.9	8.9> and <13.1	13.1≥
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≥

polluted by PAHs, probably originated from non-treated domestic sewage and drainage from former irregular industrial landfills. In addition, SQVs based on SES (b) data showed high pollution by metals in São Vicente Channel sediments as well. In general, sediments from outer parts of the estuarine system were considered as not polluted.

In PES, arsenium, chromium, copper, nickel, lead, zinc, mercury, and PAHs were identified as chemicals of concern and then SQVs were calculated to these contaminants (table 13). The minimum values for Cr and Pb were not presented because it corresponded to the detection limit of the analytical chemistry methods. Likewise for SES, inner parts of PES were classified as highly polluted by all analysed metals and PAHs, including the area in the vicinities of the Ponta do Félix port's terminal. The sediments in the proximities of the Port of Paranaguá presented some chemicals (As, Zn, Hg, and PAHs) exceeding the maximum values of the SQVs derived for PES. The sediments collected at inner Laranjeiras Bay (PAR-5), inside the limits of the Guaraqueçaba Protection Area, were classified as highly polluted by metals (copper excepted). Choueri et al. (in press) suggested that this area, placed away from the main contamination sources, is being affected by pollution sources located elsewhere. The SQVs derived for PES were useful to identify the degradation of the sediments at this protected area, and this demands attention of the authorities, government and society to start a management plan to reduce the pollution released in the PES waters. Similarly to SES, the downstream portions of the PES were considered as not polluted.

The SQVs derived for Gulf of Cádiz, included cadmium, cobalt, copper, nickel, lead, vanadium, zinc, and PAHs (table 14). Following this classification, sediments of Ría of Huelva were considered as highly polluted by metals and PAHs. In Bay of Cádiz, sediments from the vicinities of the Port of Cádiz (CA-2) were classified as highly polluted by metals, and sediments from inner Bay of Cádiz were classified as not polluted. In Bay of Algeciras, sediments were classified as highly polluted by Ni, Co, and PAHs.

The derived SQVs for SES, PES and Gulf of Cádiz were compared to general benchmark Sediment Quality Guidelines (SQGs) applied in Brazil and Spain, as well as Action Levels in current use in Canada and United Kingdom (Figure 3). Different approaches were utilized to derive National SQGs: Brazilian dredging benchmark SQGs, defined by CONAMA nº 344 (Brasil, 2004), were based on a combination between the Effects Range – Low and Effects Range – Median (ERL/ERM) (Long et al., 1995) and the Canadian Threshold Effect Level and Probable Effects Level (TEL/PEL) (EC, 2002); Spanish standards for dredging material classification, recommended by CEDEX (1994), are based on sediment geochemical considerations (DelValls et al., 2004); the Canadian Environmental Agency Canada uses TEL/PEL approach (EC, 2002), which is derived from geochemistry, toxicity and benthic community data; USA employs the ERL/ERM approach, as a recommendation of the US-NOAA (National Oceanographic and Atmospheric Administration); British SQGs are provided by CEFAS (Centre for Environmental, Fisheries and Aquaculture Science) and they are based on sediment chemistry and ecotoxicological information from datasets.

As it is clearly showed in the figure 3, the SQVs derived in this study for Brazilian and Spanish areas are more restrict than the SQGs applied in their respective countries. In Brazilian areas, the Maximum Values derived for several chemicals are lower than the Minimum Values currently used by national and international legislations. This was the case of Cd, Cr, Ni, Pb, Zn and PCBs in SES, and Cr, Cu, Pb,

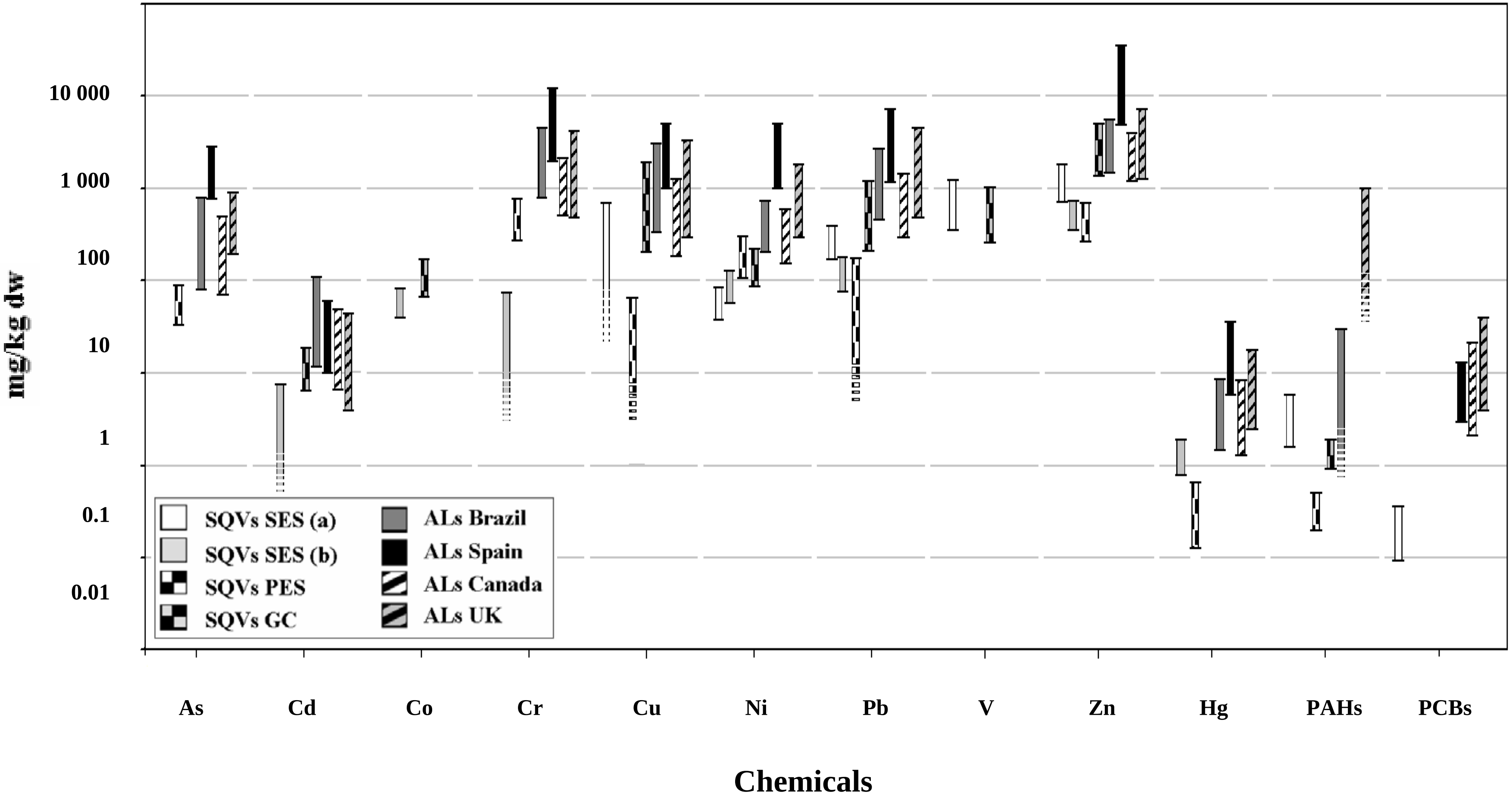

Figure 3. Comparison between the sediment quality values proposed in this study for SES, PES, GC, and national and international action levels (ALs) for dredging material characterization in current use. Fading bars represent those chemicals which minimum values were not derive or provided.

Hg and Zn in PES. These findings corroborate the information obtained by Abessa et al. (2006), which reported that 80% of the sediments from SES were toxic when the Canadian TEL is exceeded. In Gulf of Cádiz, despite the SQVs derived in this study are more restricted than the values recommended in CEDEX (1994) for all identified chemicals of concern, some SQVs are similar to SQGs applied in Brazil, Canada, and UK, as in the cases of Cu, Pb and Zn. Neverthless, other SQVs 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 SQVs 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 among the derived SQVs for Brazilian areas, as well as between Brazilian areas and the Spanish SQVs. Comparing SES and PES-SQVs, major differences were found for Cu, Hg, PAHs (these SQVs were higher in SES), and Cr (SQV higher in PES). Main differences among Brazilian site-specific SQVs and GC-SQVs were found for Cu, being PES-SQV much lower than GC-SQV for this contaminant; Pb and Zn, being both SES and PES-SQVs lower than GC-SQVs; and PAHs, being GC-SQV higher than PES-SQV but lower than SES-SQV for the organic contaminant.

The differences among the SQVs derived for each site, including the dissimilarities between SQVs for different sites in the same country, are consequence of the particular environmental conditions of each study area. According to Chapman and

Mann (1999), 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 sulphides) 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 SQVs are derived.

As shown in this article, site-specific SQVs can be very different from general benchmark values. The first approach brings some advantages, basically, the consideration of the local specificities in the establishment of relationships between chemicals concentrations and biological effects; the disparities among the SQVs derived for each study area confirmed that the local characteristics has evident influence in the biological responses to contamination, and, consequently, the use of site-specific SQVs is strongly recommended in sediment and dredged material quality assessment. Nevertheless, the use of site-specific SQVs does not undermine the application of general benchmark values. Unlike the specific values, the general guidelines are usually derived from ample databases of contamination levels and their related biological effects from a large number of sampling stations, being an important approach to be considered in sediment and dredged material evaluations.

5. CONCLUSIONS

The site-specific SQVs derived in this study were different from the sediment quality standards employed at national and international level. In general, the site-specific SQVs 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 SQVs to be used together with the national SQGs in assessments of sediment quality and characterization of the dredging material in Santos Estuarine System, Paranaguá Estuarine System and Gulf of Cádiz.

Additionally, the site-specific SQVs 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 harmonized protocol for deriving site-specific SQVs based on the WOE approach.

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Harmonization of the protocol of ecological risk assessment of sediments from ports and estuarine zones of the Atlantic

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Science of the Total Environment (enviado)

ABSTRACT

This paper presents a proposal for an international framework of sediment quality assessment and dredging material characterization in estuaries and port zones of the Atlantic. This framework provides a structure and a process for conducting sediment/dredging material assessment that leads to a management decision. This framework is based on the WOE approach, comprising sediment physical-chemical, toxicity and benthic community structure assessments. The main structure consists in several steps to be proceeded and binary decisions ('yes' or 'no') are proposed after each step. The sequence of assessments may be interrupted when the information obtained is judged to be sufficient for a correct characterization of the risk posed by the sediments/dredging material. The framework is conceptually divided into 'Screening assessment' (examination of available data, chemical characterization, comparison to reference values), 'Quantitative assessments' (assessment of sediment toxicity, assessment of benthic community structure, integration of the results, construction of the decision matrix) and the section 'Decision' (is sediments harmful? is sediments harmless? conduct further assessments?), which provides the final evaluation of the sediments/dredging material. This framework brought novel features compared to other frameworks: the proposed technique of data integration (factor analysis followed by PCA extraction) made possible the identification of which samples are toxic and/or related to impaired benthic communities; the data integration permitted the discrimination of which chemicals are causing negative biological effects; the framework dispenses the use of a reference area. We demonstrated the successful application of this framework in different port and estuarine zones of the North (Gulf of Cádiz) and South Atlantic (Santos and São Vicente Estuarine System and Paranaguá Estuarine System) and Spain (Ría of Huelva, Bay of Cádiz, and Bay of Algeciras), which confirms its international scope.

1. INTRODUCTION

Sediments, because of their physical-chemical characteristics, can accumulate contaminants in concentrations much higher than those detected in the water column. In the last decades, due to the increasing anthropogenic activities, the presence of pollutants in sediments has threatened and/or degraded the aquatic ecosystems (lethal and sub-lethal toxicity, bioaccumulation and biomagnification of contaminants throughout the food chain). The sediment contamination cannot be considered exclusively as an environmental problem: it affects directly and indirectly other human activities, as fishing, aquaculture, recreation, among others. Moreover it represents costly economical issue for navigational dredging and environmental restoration projects.

The assessment (and subsequent management and remediation) of chemicals in the sediments have been developed during the past thirty years (Wenning and Ingersoll, 2002). This traditionally relies on measuring the concentrations of selected contaminants and comparing them with numerical sediment quality values (SQVs). However, the total concentration of the contaminants is not always strongly correlated to the bioavailability (Ingersoll et al., 1997). Geochemical features of the sediments, such as grain size, pH, salinity, organic matter content, acid volatile sulfides content may affect the availability of toxicants to aquatic organisms (Riba et al., 2004a; Riba et al., 2003a; Simpson, 2001; Meyer et al., 1994). Additionally, the effects of potential interactions of a mixture of contaminants (synergism, antagonism, or additivity) are not addressed by the simple measurement of the level of contaminants in the sediments.

For a better understanding of the sediment contamination and its associated ecological risks, sediment-quality assessment protocols must be based on a multi-disciplinary research that integrates physical and chemical surveys, assessment of the sediment-toxic effects and ecological assessment techniques (community surveys) (Petrovic and Barceló, 2004). The consideration of different Lines-Of-Evidence (LOE) is being recommended for dredging material assessment as well (London Convention, 1996; GIPME, 2000; PIANC, 2006), in order to obtain a full understanding of the potential ecological risks associated to the disposal of this material. Such integrative analysis permit the correct management of the problem, avoiding permissive decisions which would end up in environmental degradation at the disposal site(s), as well as excessively conservative judgements, which would recommend the unnecessary use of disposal facilities, costly structures with low societal acceptance.

In the last years different frameworks for sediment quality assessment and dredging material characterization have been developed and used by regulatory agencies in different countries. These frameworks share some features, which includes: (a) the use of various LOEs, integrated in a manner to reduce the multivariate data to binary decisions (pass/fail), or ordinal ranks (not/possibly/likely/very different from reference sites) (Grapentine et al., 2002); (b) multiple tiers, being unnecessary to complete all steps if the firsts levels provide sufficient information for an adequate sediment management; (c) and an iteration process that allows the refinement of an assessment as data are collected and analysed (Wenning and Ingersoll, 2002). Despite the agreement on the basic structure of the most utilized frameworks, an international standardisation and harmonization of the tools utilised in such assessments (bioassays, chemical analytical procedures, data integration techniques) still is needed. The development of a harmonized protocol may standardize the procedures for the assessment and management of contaminated sediments among countries, allowing thus inter-comparisons of the techniques and the obtained results (Salomons and Brils, 2004; Petrovic and Barceló, 2004).

In this context, this paper presents a proposal for an international framework of sediment quality assessment and dredging material characterization in estuaries and port zones of the Atlantic, which provides a structure and a process for conducting sediment/dredging material assessment that leads to a management decision. Such framework was developed based on case-studies in Brazil (Santos Estuarine System and Paranaguá Estuarine System) and Spain (Ría of Huelva, Bay of Cádiz, and Bay of Algeciras), in important port zones and ecologically relevant sites are affected by multiple pollution sources. Sediment quality was previously assessed in these zones, focusing on the integration of sediment geochemistry, toxicity and benthic community structure data (Cesar et al., in press; Choueri et al., in press; Cesar et al., 2007; Riba et al., 2004b, c). This is the first attempt to develop an internationally harmonized protocol of sediment quality assessment and dredging material characterization that deploys the integration of different LOEs.

2. STRUCTURE OF THE FRAMEWORK

This framework conserve the basic structure of other frameworks previously proposed by other authors and agencies (Burton et al., 2002; Grapentine et al., 2002; Chapman et al., 2005; EC and OME, 2005), and its main characteristics are presented below (i, ii, iii and iv).

The use of different LOEs in sediment assessments often result in complex matrices, containing data of different natures and thus becoming a challenge for managers to understand the meaning of such information. Therefore, (i) this framework integrates multivariate environmental data and reduce the information to binary decisions (yes/no).

The inclusion of surveys other than chemical analysis, such as sediment toxicity and benthic community investigations, would obviously increment the costs and the time spent to assess the sediment quality and characterize the dredged material, which may generate resistance by the port managers in accepting the integrative analysis. By this reason sediment and dredged material quality assessment protocols must be developed on a tiered fashion, which allows identifying the cases when analyses further than physical-chemical ones are not necessary to complement the evaluation, avoiding the production of redundant information and consequently saving time and economic resources. (ii) This framework is tiered and advances through the following of several steps, being unnecessary to complete all tiers if the previous levels provide enough information for the correct characterization of the material. In addition, this tiered framework allows an (iii) iteration process, which permits the further inclusion of data, either to refine or to adequate the focus of the analysis as new information become available.

The international standardization of the framework for sediment/dredging material quality assessment is sought in order to have evenness in assessments and management of contaminated sediments around the World (Salomons and Brils, 2004). (iv) The internationally harmonized framework developed in this study is intended to be sufficiently prescriptive to standardize the decision-making process but without providing inflexible guidelines or techniques; instead, it is flexible to allow site-specific particularities among different littoral systems. This flexibility also permit the incorporation of scientific and technological advances in the area of sediment quality assessment, such as new chemical analytical procedures, novel methods to measure biological effects, recent statistical approaches to evaluate and integrate data, among others.

3. DESCRIPTION OF THE FRAMEWORK

This framework (figure 1) is based on the WOE approach, comprising different LOEs, namely sediment physical chemical, sediment toxicity, and benthic structure community assessments. Its main structure consists in several steps to be proceeded and binary decisions ('yes' or 'no') are proposed after each step. The sequence of assessments may be interrupted when the obtained information is judged to be sufficient for a correct characterization of the risk posed by the sediments/dredged material. Conceptually, the framework is divided into 'Screening assessment', which comprises 'step 1' and 'step 2' leading to 'decision 1', and 'step 3' that leads do 'decision 2'; 'Quantitative assessments', includes steps '4' and '5', and decisions '3' and '4'; and the section 'Decision', which provides the final evaluation of the sediments/dredged material.

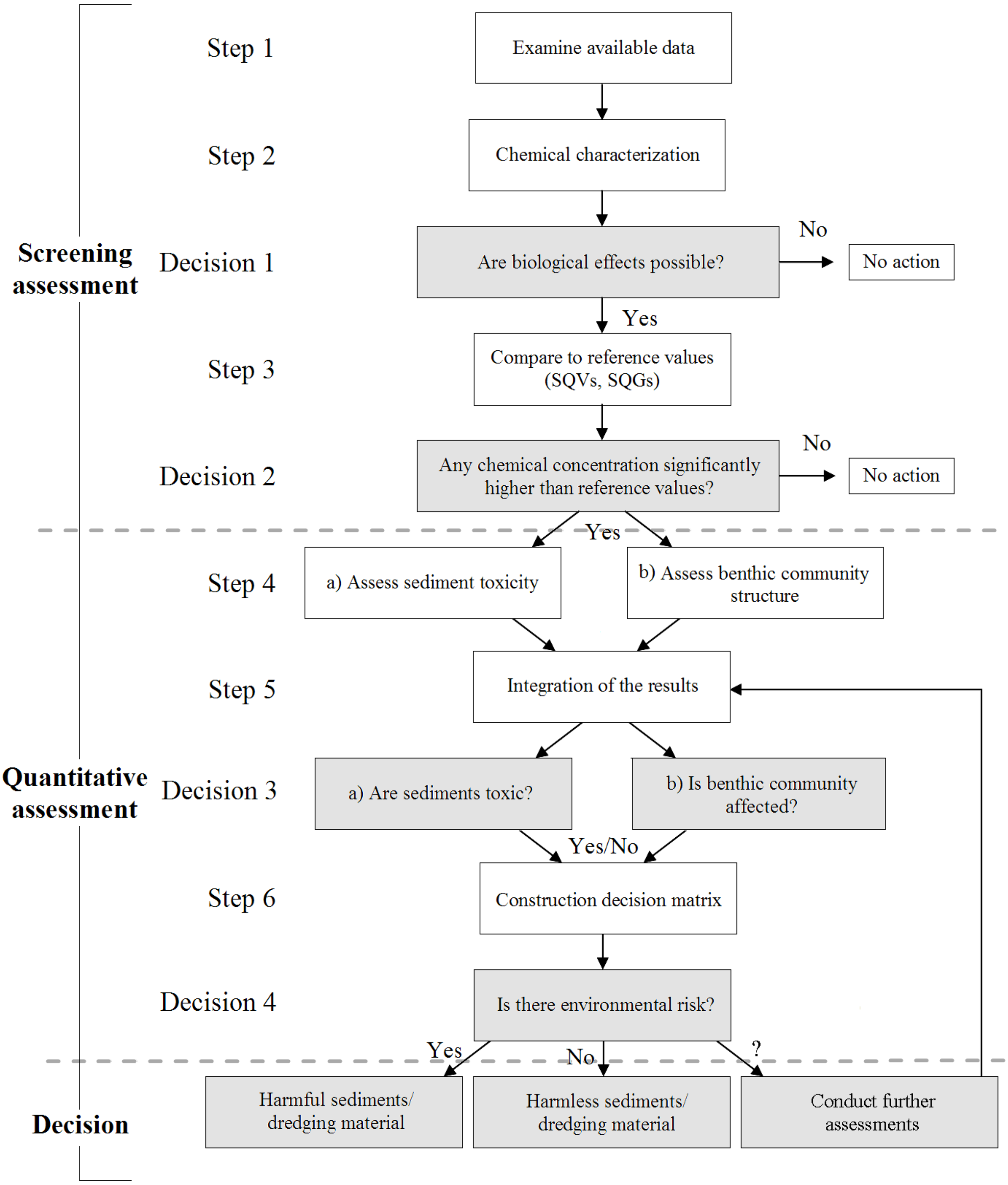

Figure 1. Risk assessment framework for sediment and dredging material based on the Weight-of-evidences approach

3.1 Step 1 (analysis of the available information)

The objective of the first step is to gather historical data in order to construct a conceptual model of the area of concern. Subsequently, such model will guide the sampling and analysis, thus the production of redundant data can be avoided. Relevant information to be raised is (EC and OME, 2005; Burton et al., 2002): (i) the existence of contaminants of potential concern (contaminants that can cause negative effects on the biota; contaminants that can biomagnify through the food chains); (ii) presence of potential pollution sources and which contaminants are related to each one; (iii) the presence of receptors of potential concern (organisms that may be directly or indirectly affected by the contaminants); (iv) identification of critical biological species (threatened or endangered species, keystone species, commercially important species, species of stakeholder concern); (v) exposure pathways by which the contaminants reach the organisms; (vi) the environmental sensitivity of the area of concern (e.g. is it an important feeding or reproduction ground for the biota?; (vi) any human health consumption advisory; (vii) sediment stability; (viii) identification of potential contamination/pollution sources.

3.2 Step 2 (sediment physical-chemical characterization), Decision 1 (are biological effects possible?), Step 3 (comparison to reference values) and Decision 2 (any chemical higher than the reference value?)

Physical-chemical analyses on sediment/dredging material provide the quantification of specific contaminants in the whole sediments, as well as sediments characteristics which could affect the bioavailability of contaminants (e.g. sediment grain size, TOC, carbonates, acid volatile sulfides – AVS, among others). This is necessary to evaluate if sediments/dredged material may pose risk to the environment or not. The decision on which chemicals to be measured is made based on the outcomes of the 'step 1'. The comparison of the levels of contaminants in the sediments/dredged material with reference values (site-specific Sediment Quality Values – SQVs; Sediment Quality Guidelines – SQGs; or specific background levels) provides a rudimentary idea of the potential environmental risk of these chemicals. As SQVs and SQGs are typically conservative by design, the ecological risk may be considered negligible in instances when levels of contaminants are below the minimal reference values (RV-low, i.e. SQV-low, SQG-low) (EC and OME, 2005). In case of measured chemical concentrations being higher than chemical reference values, further assessments are required for an adequate characterization

3.3 Step 4(a) (assess sediment toxicity) and Step 4(b) (assess benthic community structure)

The quantification of contaminants in the whole sediment does not provide information neither on the bioavailability of the contaminants nor on the potential toxic effects of these sediments to aquatic organisms. Sediment quality assessments which integrate different LOEs have been carried out extensively worldwide (Cesar et al., 2007; Riba et al., 2004c; Silva et al., 2004; Nipper et al., 1998; Carr et al., 1996a, 1996b; Chapman et al., 1987; Long and Chapman, 1985) since, as discussed previously, such integrative approach provides a more complete understanding on the environmental quality of sediments compared to assessments that relies on only one assessment technique.

There are many different assessments which may be carried out to evaluate biological effects caused by sediment contamination, such as benthic community structure assessments (Cesar et al., in press; Drake et al., 1999; Van Dolah et al., 1999; Swartz et al., 1986; Warwick, 1986; Reish, 1986), a variety of toxicity bioassays (Nendza, 2002; Burton, 1999; DeWitt et al., 1999; McGee et al., 1993; Meador et al., 1990; Chapman, 1988; Chapman and Long, 1983), analysis of different biomarkers (of exposition and/or effects, "in situ" and/or laboratory bioassays) (Jimenez-Tenorio et al., 2007; Neuparth et al., 2005; Martín-Díaz et al., 2004; Fent, 2004; Vigano et al., 2001; Wells et al., 2001; Timbrell et al., 1994; Simpson, 1992), bioaccumulation and biomagnification assessments (Burton et al., 2005; Riba et al. 2005a; Casado-Martinez et al., 2003; Burton, 1999; Sibley et al., 1999), and others. The decision on which assessment will be incorporated into the framework of assessing sediments/dredged material depends on the purposes of the framework. For an adequate environmental risk assessment, the minimal information required is: (1) which contaminants are present? (2) In which concentrations? (3) Which is the possibility of the contaminants to be in contact to the organisms? In which intensity? (4) Which are the potential effects of these contaminants to the biota? First two questions are answered through sediment chemical analyses; the last two problems are answered by assessments which address biological effects of the sediment contaminants. Other LOEs may be integrated, either to refine the assessment, or to adapt the assessment to other purposes. For example, if the objective in this study was to develop a framework for human health risk assessment of sediments/dredging material, the inclusion of investigations on the potential of bioaccumulation and biomagnification of these contaminants, assessments on feeding behaviour of threatened populations, and relationships between contamination and species for human consume would be essential.

Toxicity tests provide direct and quantifiable evidences of the biological consequences of the sediment contamination (USEPA, 1999). Such tests produce data integrating the toxic effects resulting of complex mixtures of contaminants and provide some inferences on their bioavailability (USEPA, 1999). Test protocols recommend the use of sets of bioassays, including: different pathways of exposure (e.g. interstitial water, whole sediment); the assessment of lethal and sublethal effects (e.g. growth, reproduction); and at least one chronic test. The test-species must be sensitive to contamination; in addition, standardised techniques and quality control criteria must be utilised in the bioassays (DelValls et al., 2004; Casado-Martínez et al., 2006a, b, c, d).

The benthic community analysis brings valuable information to the assessments of the potential ecological risks of sediments/dredged material because: (i) benthic organisms have different habits (swimmers, crawlers and burrowers) and feeding strategies (scavenger, detritus and filter feeders), which makes benthic fauna susceptible to different exposure routes; (ii) it reflects medium- to long-term local conditions, because benthic organisms are relatively sedentary; (iii) the benthic community comprises organisms with different life histories, different tolerances to stress, and that occupy a variety of niches; consequently each species will respond differently to the contaminants and this may be observed in a benthic community structure investigation; (iv) the life-spam of many species reflect sources of stress over time, allowing the integration of this variable in sediment analyses. The methods to assess benthic community structure include the calculation of classical parameters (diversity, species richness, abundance, dominance), advanced techniques (multivariate analysis, Abundance-Biomass Comparison, meta-analysis), and the use of indices which include different community characteristics (e.g. Relative Benthic Index). However, the adequacy of this last technique is still doubtful (DelValls et al., 2007), especially due to natural interferences which affects the benthos.

3.4 Step 5 (integration of the results), Decision 3(a) (are sediments toxic?) and Decision 3(b) (are benthic communities affected?)

The identification of toxic samples and impaired benthic communities are usually accomplished through the comparison with toxicity tests using reference sediments, i.e. non-contaminated sediments with characteristics similar to the sediments under examination (grain size, organic carbon content, pH, etc), or comparison with benthic community structure in reference areas. However, the identification of one reference site (or more than one, as recommended by Underwood, 1996) may become a challenging task, especially in highly polluted areas, areas affected by non-point pollution sources, or ecosystems characterised by a high natural variability (e.g. estuaries). In many instances it is impossible to find areas with sediments that match the minimum requirements to be used as reference sediments. Underwood (1999) emphasise the need of developing new procedures for environmental disturbance assessments “when no data are available before an environmental impact”, i.e., when reference conditions are difficult or impossible to be obtained.

In this framework, the use of advanced techniques for integrating environmental data (multivariate analysis, presented further on this paper) allows to establish correlations among chemical concentrations, toxicity results, and benthic community parameters. Assuming that the statistical correlations correspond to cause-and-effect relations among variables, it is possible to identify in which samples chemical contamination is probably causing toxic effects and/or benthic community impairment. However, in some instances the results of data integration must be analysed with special attention: in cases when all samples present high contamination, or when all samples show low contamination, the multivariate analysis may establish relationships among the variables which do not correspond to cause-and-effect correlations. In any case, cross-checking the results of multivariate analyses with the original data of levels of contaminants, toxicity responses, and benthic structure parameters, can minimise the mistakes based on false conclusions taken from the multivariate analysis.

3.5 Step 6 (construction of the decision matrix), Decision 4 (is there environmental risk?) and the Final decision

The decision matrix is fed with information from the previous assessments for each LOE, in a sampling station basis. It is a summary of the decisions taken with basis on the integration of the LOEs, which allows developing different scenarios for the best insight on the potential risks posed by the sediments/dredging material to the biota. The final decision may be definitive (‘harmful’ or ‘harmless sediments/dredged material’) or not. In the second case, when the information obtained is not enough to fully assess the ecological risk of the sediments, the realisation of further studies (including the incorporation of other LOEs, if necessary) is recommended.

4. APPLICATION OF THE FRAMEWORK IN PORT AND ESTUARINE AREAS – CASE STUDIES

4.1 Step 1 – Analysis of the available data

4.1.1 Brazilian areas

Santos Estuarine System (SES) and Paranaguá Estuarine System (figure 2a and b, respectively) are two of the most important port zones in Brazil (Port of Santos and Ports of Paranaguá and Antonina). The first one is also place for heavy industry (petrochemicals, siderurgy and industries of fertilizers) and a large urban concentration. Both areas comprehend ecologically significant ecosystems, such as mangroves and Atlantic rain forest. Whilst for SES there is vast information on the sediment contamination in SES (Abessa, et al., 2005; Lamparelli et al., 2001; CETESB, 1985, 1978) and previous reports showing sediment toxicity (Abessa et al., 2005; Abessa et al. 2001) and alterations on benthic communities (Abessa et al, in press), there is very few available information of PES sediment contamination, toxicity or benthic communities.

4.1.2 Spanish areas

The studied areas are located at Gulf of Cádiz (GC) (Southern Spain): Ria of Huelva, Bay of Cádiz and Bay of Algeciras (figure 3a, b, and c, respectively). All three areas comprise port and industrial activities; the first one is the most impacted site, as reported by Riba et al. (2005b, 2004b, c), affected mainly by mining activities and

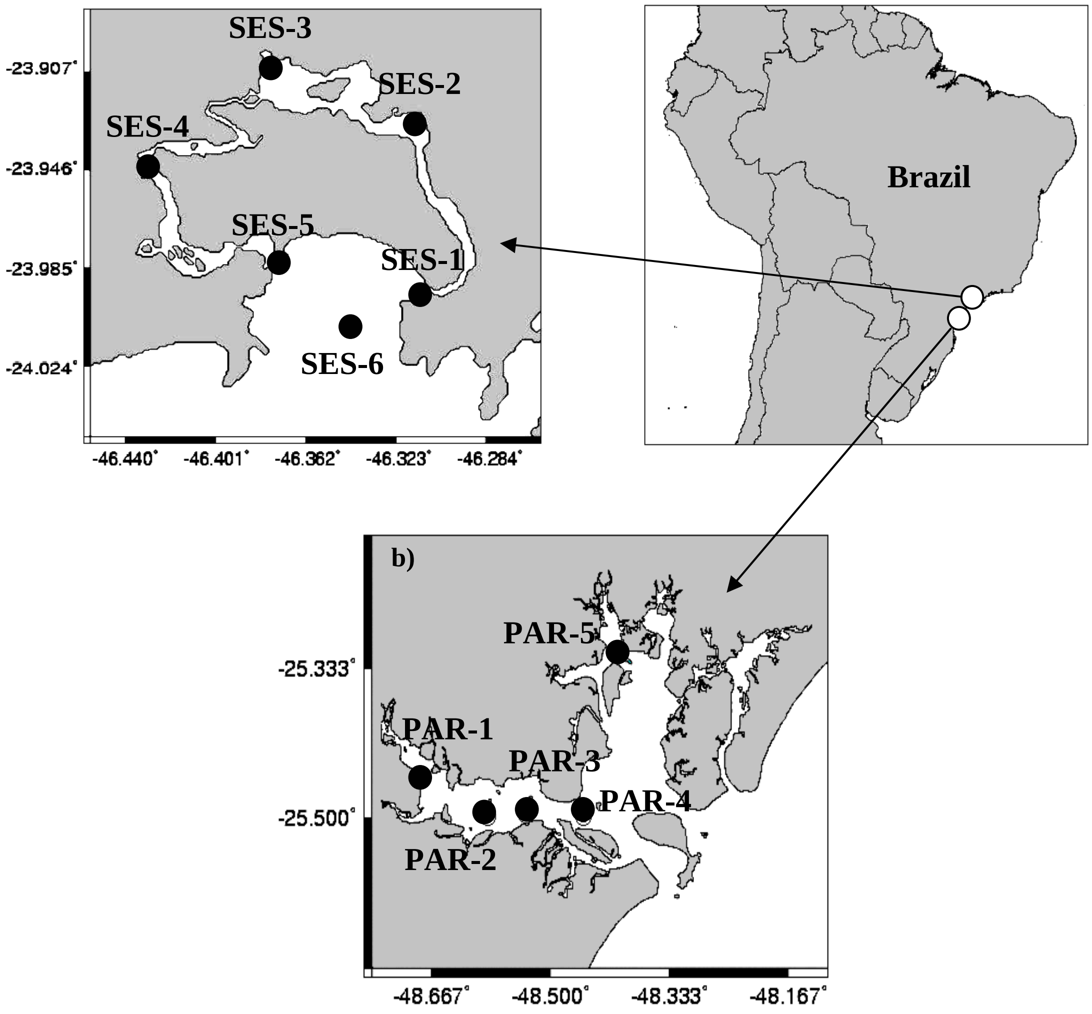

Figure 2. Localization of the sampling stations in (a) Santos Esturine System and (b) Paranaguá Esturine System and their disposition in Southeastern Brazil.

chemical, petrochemical and metallurgic industries; sediments from Bay of Cádiz are not toxic to marine organisms, as reported by Riba et al. (2004b, c), and Bay of Algeciras is environmental degraded by chronic oil spills from the Algeciras industrial complex (Morales-Caselles et al., 2007).

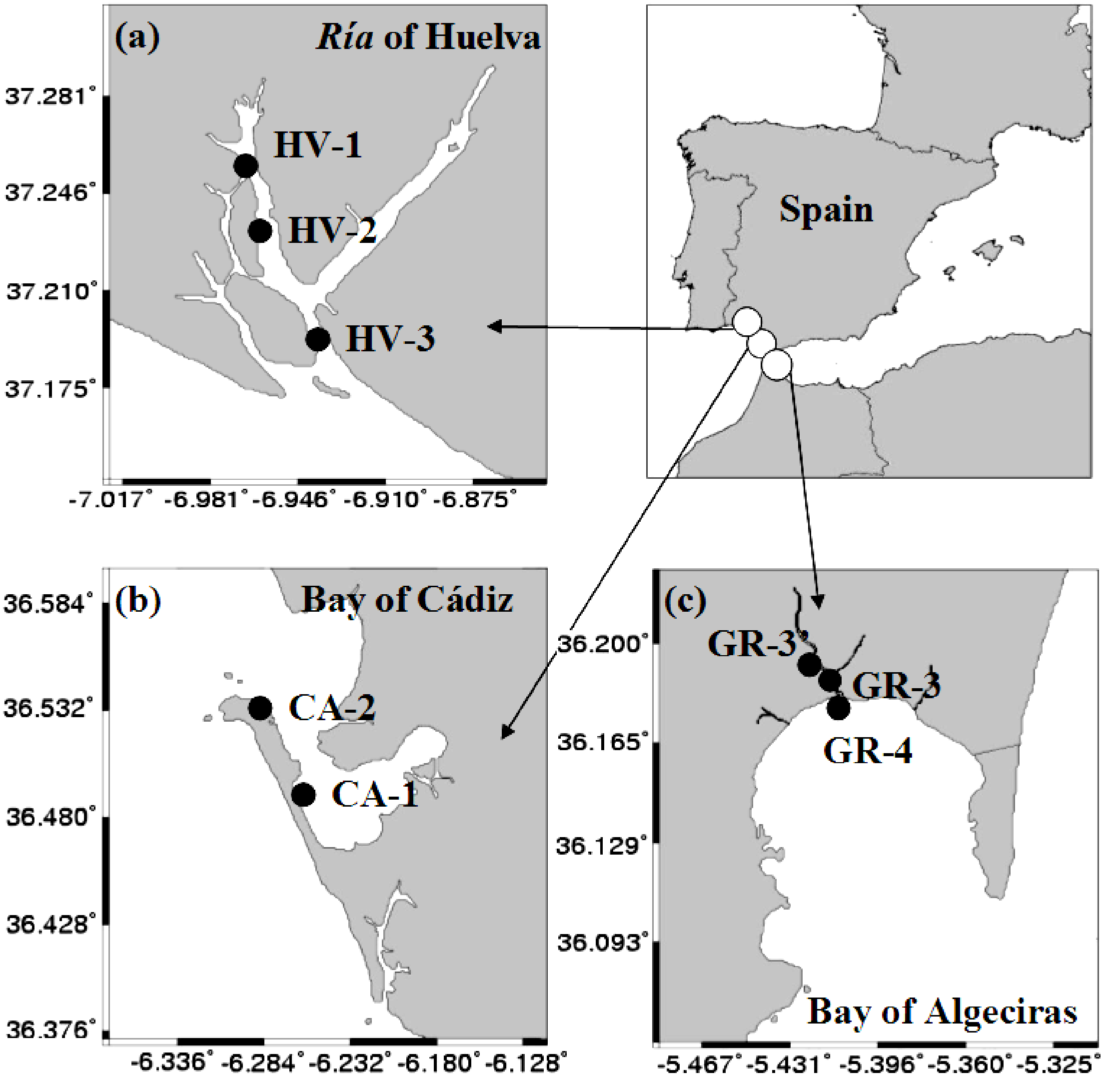

Figure 3. Localization of the sampling stations in Ría of Huelva (a), Cádiz Bay (b), Algeciras Bay (c) and their disposition in Southern Spain.

4.2 Step 2 - Sediment physical-chemical characterization

The sediments from SES and GC were analysed considering: (a) grain-size distribution and Organic Carbon (OC) content; (b) metals content (Zn, Cd, Pb, Cu, Ni, Co and V measured by differential pulse anodic stripping voltammetry (DPASV) with static drop mercury electrode (SMDE); (c) levels of PAHs and PCBs, through gas chromatography equipped with electron capture detector (ECD). All the analytical procedures were checked with reference materials (Marine Sediment References Material for Trace Metals–1, National Research Council (NRC), Certified Reference Material, 277 BCR, and Conceil National de Reserches Canada, 277 BCR, for metals; and NRCpCNRC HS-1 for organic compounds) and allow agreement with certified values higher than 90%. Further details on the analytical procedures can be found in Cesar et al. (2007)

Physical-chemical analyses of sediments of PES were as follows: (a) grain size analysis and OC; (b) levels of metals and metalloids: Cu, Cr, Ni, Pb and Zn were determined by flame atomic absorption spectrophotometry (F-AAS); Ag and Cd by graphite furnace (GF-AAS); As and Se by hydrate generation (HG-AAS); Hg by cold vapor spectrophotometry (CV-AAS). (c) PAHs and PCBs concentrations were determined through gas chromatography. Replicates were done on approximately 30% of the samples, for TOC, metals and organic compounds. Recovery was calculated by spiking some of the samples or an aliquot of NaSO4 and adding certain concentrations of the standard solutions cited above. Percentage recoveries were around 88 to 104 % for PCBs and 92 to 128 for PAHs. The analytical procedures are detailed in Choueri et al. (in press).

The results of sediment physical-chemistry for Brazilian and Spanish areas were presented in the table 1. Potentially toxic chemicals were detected in the samples from SES, PES, and GC; this situation led us to the next step, described below.

4.3 Step 3 – Compare to reference values

Choueri et al. (in press) presented site-specific SQVs for SES, PES, and GC (table 1); therefore, the levels of chemicals measured in the samples were compared to these values. The comparisons revealed that most of the samples in each study area presented one or more chemicals with concentrations exceeding their respective SQV-high. Exceptions were SES-5 and PAR-4 in Brazilian areas, and CA-1 in Gulf of Cádiz: SQV-high exceedences were not found in such stations; however, some chemical concentrations were equal to SQV-low. Therefore, following the assumption that only chemical concentrations lower than reference values are considered as not potentially risky to aquatic biota, all stations required further assessments to evaluate the ecological risk posed by the contaminants in these sediments.

4.4 Step 4(a) – Assess sediment toxicity

For the characterization of the sediment toxicity, one route of exposure was assessed for SES sediments (i), and three routes of exposure were assessed for PES and GC sediments (i, ii and iii): (i) whole-sediment, aiming to assess the toxicity of the sediments in direct contact with aquatic organisms, i.e. solid-phase and pore water together. Amphipods mortality (*Tiburonella viscana* and *Corophium volutator* for Brazilian and Spanish sediments, respectively) was the endpoint for these tests (Melo and Abessa, 2002; Riba et al., 2003b). (ii) Sediment elutriates, in order to assess the toxicity of the contaminants transferred from sediments to water after a resuspension process. Sea-urchin embryos (*Lytechinus variegatus* for PES and *Paracentrotus lividus*

Table 1. Results of sediment physical-chemical characterization and site-specific SQVs for each of the study areas.

	Metals and metalloids (ppm)												**Organics**		**Characteristics**	
Stations	Ag	As	Cd	Cr	Co	Cu	Ni	Pb	V	Se	Zn	Hg	PAHs (ppm)	PCBs (ppb)	OC	Fines
SES-1	Nm[1]	Nm[1]	<0.1	Nm[1]	<0.1	<0.1	4.85	17.4	36.0	Nm[1]	73.3	Nm[1]	0.106	0.66	3.75	3.96
SES-2	Nm[1]	Nm[1]	<0.1	Nm[1]	<0.1	167.2	2.96	66.2	24.0	Nm[1]	154.2	Nm[1]	0.518	4.00	1.24	4.46
SES-3	Nm[1]	Nm[1]	<0.1	Nm[1]	<0.1	157.7	4.49	22.1	87.8	Nm[1]	110.4	Nm[1]	0.425	2.61	2.78	9.68
SES-4	Nm[1]	Nm[1]	<0.1	Nm[1]	<0.1	69.0	3.83	14.9	104.8	Nm[1]	66.8	Nm[1]	0.950	0.94	2.82	2.67
SES-5	Nm[1]	Nm[1]	<0.1	Nm[1]	<0.1	<0.1	3.89	8.7	18.6	Nm[1]	32.6	Nm[1]	0.163	0.58	0.85	1.42
SES-6	Nm[1]	Nm[1]	<0.1	Nm[1]	<0.1	<0.1	6.02	14.6	<0.1	Nm[1]	53.2	Nm[1]	0.600	<0.1	1.00	11.56
SES-specific SQVs																
SQV-low[4]	Nc[2]	Nc[2]	Nc[2]	Nc[2]	4.1	Nc[2]	3.89	17.4	36.0	Nc[2]	73.3	0.08	0.163	0.94	Na[3]	Na[3]
SQV-high[4]	Nc[2]	Nc[2]	0.75	7.5	4.2	69.0	4.49	22.1	87.8	Nc[2]	110.4	0.11	0.425	2.61	Na[3]	Na[3]
PAR-1	<0.004	7.40	<0.001	58.00	Nm[1]	16.20	21.90	29.75	Nm[1]	<0.04	80.50	0.07	0.02	<0.3	4.20	64.55
PAR-2	<0.004	8.33	<0.001	51.50	Nm[1]	13.80	20.73	27.70	Nm[1]	<0.04	77.75	0.09	0.03	1.09	3.65	64.87
PAR-3	<0.004	5.45	<0.001	27.85	Nm[1]	6.55	10.98	17.63	Nm[1]	<0.04	41.33	0.06	0.03	1.32	1.53	27.34
PAR-4	<0.004	3.40	<0.001	14.50	Nm[1]	<0.04	6.65	<0.30	Nm[1]	<0.04	26.95	0.01	0.01	1.47	0.44	15.33
PAR-5	<0.004	5.75	<0.001	48.80	Nm[1]	<0.04	19.10	23.95	Nm[1]	<0.04	58.00	0.05	0.01	<0.3	1.32	20.22
PES-specific SQVs																
SQV-low[4]	Nc[2]	3.40	Nc[2]	27.85	Nc[2]	Nc[2]	10.98	Nc[2]	Nc[2]	Nc[2]	26.95	0.013	0.02	Nc[2]	Na[3]	Na[3]
SQV-high[4]	Nc[2]	5.45	Nc[2]	48.80	Nc[2]	6.55	19.10	17.63	Nc[2]	Nc[2]	41.33	0.051	0.03	Nc[2]	Na[3]	Na[3]

Table 1. Continued.

	Metals and metalloids (ppm)												Organics		Characteristics	
Stations	Ag	As	Cd	Cr	Co	Cu	Ni	Pb	V	Se	Zn	Hg	PAHs (ppm)	PCBs (ppb)	OC	Fines
HV-1	Nm[1]	Nm[1]	3.90	Nm[1]	26.00	1989.00	42.3	406.00	90.00	Nm[1]	1945.0	Nm[1]	0.298	3.50	2.10	88.3
HV-2	Nm[1]	Nm[1]	2.50	Nm[1]	10.00	1543.00	21.2	335.00	111.00	Nm[1]	2010.0	Nm[1]	0.191	4.60	2.90	89.5
HV-3	Nm[1]	Nm[1]	1.60	Nm[1]	14.00	789.00	97.2	198.00	76.00	Nm[1]	987.0	Nm[1]	0.100	1.10	3.90	74.5
CA-1	Nm[1]	Nm[1]	0.65	Nm[1]	6.80	15.60	8.9	12.20	11.50	Nm[1]	18.3	Nm[1]	0.074	<0.01	1.10	6.8
CA-2	Nm[1]	Nm[1]	1.20	Nm[1]	18.30	169.00	29.3	99.20	132.10	Nm[1]	360.0	Nm[1]	0.097	161.00	2.60	66.4
GR-4	Nm[1]	Nm[1]	0.10	Nm[1]	5.59	3.67	13.1	6.21	<0.01	Nm[1]	35.3	Nm[1]	0.711	<0.01	3.19	54.2
GR-3	Nm[1]	Nm[1]	0.29	Nm[1]	<0.01	20.80	15.5	19.10	24.60	Nm[1]	66.0	Nm[1]	2.103	<0.01	3.44	75.4
GR-3’	Nm[1]	Nm[1]	0.17	Nm[1]	12.80	5.01	74.7	21.60	26.10	Nm[1]	138.0	Nm[1]	12.003	<0.01	2.15	90.5
Gulf of Cádiz – specific SQVs																
SQV-low[4]	Nc[2]	Nc[2]	0.65	Nc[2]	6.80	20.80	8.9	21.60	26.10	Nc[2]	138.0	Nc[2]	0.097	Nc[2]	Na[3]	Na[3]
SQV-high[4]	Nc[2]	Nc[2]	1.20	Nc[2]	10.00	169.00	13.1	99.20	76.00	Nc[2]	360.0	Nc[2]	0.100	Nc[2]	Na[3]	Na[3]

Not measured[1]
Not calculated[2]
Not applicable[3]
from Choueri et al. (in press)[4]

for GC sediments) were exposed to elutriates and the percentage of abnormal development was quantified (ABNT NBR 15350, 2006). (iii) Sediment-water interface, with the objective of evaluating the potential toxicity of contaminants released by the sediments to the water column through arising fluxes of pore water. The sea urchin embryo-larval development test was used (see item 'ii'). The results of the toxicity tests described above were presented in the table 2.

4.5 Step 4(b) – Assess benthic community structure

The benthic community structure in SES, PES, and GC was evaluated through the calculation of the classical community descriptive parameters: Margalef's species richness (R = (S-1) $(\mathrm{LogN})^{-1}$), where 'S' is the species richness (*i.e.* number of species), and 'N' is the total number of all individuals; Shannon's diversity ($H' = -\sum(\mathrm{P}_i\ \mathrm{Log}_e\mathrm{P}_i)$), where '$\mathrm{P}_i$' is the relative abundance of each species; Pielou's evenness ($J = H'\ (\mathrm{LogS})^{-1}$); and Simpson's dominance ($D = 1\text{-}\sum\{\mathrm{N}_i\ [\mathrm{N}_i\text{-}1]\ [\mathrm{N}\ (\mathrm{N}\text{-}1)]^{-1}\}$), where '$\mathrm{N}_i$' is the abundance (*i.e.* number of individuals) in each species. The results of benthic structure parameters for each area were presented in the table 2.

4.6 Step 5 – Integration of the results

For each study area, the relationships among variables were evaluated by means of a Factor Analysis followed by a Principal Component Analysis (PCA) as extraction procedure. This technique aims to reduce the number of variables in the original matrix through the identification of linear combinations among them, providing a description of the structure of the data with minimum loss of information.

Table 2. Results of the characterization of the biological effects related to sediments from SES, PES, and Gulf of Cádiz.

	Toxicity resuslts			**Benthic community descriptors**					
	% abnormal sea-urchin		**% Amphipods mortality**	**S**	**N.m^{-2}**	***R***	***J'***	***H'***	***D***
Station	**Elutriates**	**SWI**							
SES-1	-	-	25.0±2.9	13	216.7	2.23	0.91	2.34	0.88
SES-2	-	-	72.5±2.5	10	175.0	1.74	0.89	2.06	0.85
SES-3	-	-	77.5±6.3	3	33.3	0.57	0.95	1.04	0.64
SES-4	-	-	80.0±5.8	5	183.3	0.77	0.45	0.73	0.32
SES-5	-	-	40.0±4.1	10	125.0	1.86	0.93	2.15	0.87
SES-6	-	-	67.5±4.8	8	91.7	1.55	0.97	2.02	0.87
PAR-1	88.7±7.4	82.7±13.6	90.0±10.0	1	7.2	0.00	-	0.00	0.00
PAR-2	33.2±3.8	19.0±4.2	63.3±5.8	1	14.5	0.00	-	0.00	0.00
PAR-3	22.2±3.4	10.0±5.3	40.0±20.0	9	105.6	1.72	0.90	1.99	0.85
PAR-4	13.7±4.8	10.0±3.2	36.7±32.1	13	206.5	2.25	0.92	2.36	0.89
PAR-5	18.7± 9.8	13.7± 9.8	46.7± 15.3	7	96.6	1.31	0.86	1.68	0.78
HV-1	100.0±0.0	100.0±0.0	100.0±0.0	1	16.7	0	-	0	0
HV-2	63.7±3.9	100.0±0.0	96.7±5.8	1	83.3	0	-	0	0
HV-3	82.0±4.3	87.0±3.6	76.7±5.8	3	266.7	0.36	0.71	0.78	0.46
CA-1	7.2±2.5	60.3±9.5	3.3±5.8	23	6833.3	2.49	0.63	1.96	0.70
CA-2	7.2±1.0	79.0±6.2	26.7±5.8	14	2516.7	1.66	0.70	1.85	0.79
GR-4	31.0±2.6	98.0±2.0	43.3±5.8	6	1066.7	0.72	0.82	1.46	0.74
GR-3	94.2±2.6	79.0±7.5	66.7±5.8	6	983.3	0.73	0.81	1.45	0.73
GR-3'	94.5±2.5	100.0±0.0	100.0±0.0	1	66.7	0	-	0	0

Principal Component Analysis (PCA) is one of the most common forms of combining environmental data by multivariate analysis (Landis and Yu, 1999) and it has been successfully utilized on sediment data integration for sediment quality assessments

(Riba et al. 2004b; Riba et al. 2004c; DelValls et al. 2002; DelValls et al. 1998; DelValls & Chapman, 1998).

The data matrix of SES included natural characteristics of the sediments (%OC and % of fines), chemicals concentrations (PAHs, PCBs, Cu, Ni, Pb, V, Zn), % of amphipods mortality, and benthic community parameters (number of species, density of organisms, Margaleff's species richness, Shannon's diversity, Pielou's evenness, and Simpson's dominance). The integration of the variables of SES resulted in three new factors (F1, F2 and F3); the associations between the variables and the new factors are presented in the table 3. The PES data matrix was based on sediment physical-chemical characteristics (PAHs, PCBs, As, Cr, Cu, Ni, Pb, Zn, % OC, and % fines), toxicity results (abnormal development of sea-urchin embryo-larva exposed to sediment elutriates and SWI, and amphipods mortality exposed to whole sediment), and the benthic community descriptive parameters (number of species, density of organisms, Maragaleff's richness, Pielou's evenness, Shannon's diversity, and Simpson's dominance). Three new factors (variables) were established for PES (F1, F2 and F3); the results of the integration of the variables assessed on PES sediments are summarized in the table 4. The matrix of GC data encompassed natural features of the sediments (%OC and % of fines), concentrations of chemicals (Cd, Co, Cu, Ni, Pb, V, Zn, PAHs, PCBs), results of the toxicity bioassays (abnormal development of sea-urchin embryo-larva exposed to sediment elutriates and SWI, and amphipods mortality exposed to whole sediment), and benthic community descriptors (number of species, density of organisms, Margaleff's species richness, Shannon's diversity, Pielou's evenness, and Simpson's dominance). The application of the multivariate analysis in the GC data matrix resulted in two new variables (factors). The loadings showing the associations between the original variables and the factors are

Table 3. Sorted rotated factor loadings of the original 16 variables on the 3 principal factors of the SES 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	**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	------
OC	------	------	-0.39
Fines	------	------	0.90
Amphipods' mortality	0.73	0.44	0.40
S	0.86	------	0.47
N	------	------	0.90
R	0.92	------	0.35
J'	0.76	------	-0.58
H'	0.99	------	------
D	0.97	------	------

Table 4. Sorted rotated factor loadings of the original 20 variables on the 3 principal factors of the PES 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	**Factor 1**	**Factor 2**	**Factor 3**
% Variance	79.84	10.41	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	------
OC	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

summarized in the table 5.

In the multivariate analysis the variables were autoscaled (standardized) so as to be treated with equal importance. In each case the values of benthic community descriptors were transformed in order to exhibit an increase according to the biological damage, i.e. the parameters were transformed as the inverse by multiplying them by -1. All multivariate analyses were performed using the *Statistica* software tool (Stat Soft, Inc. 2001; version 6).

4.7 Decisions 3(a) and 3(b) – Are sediments toxic? Is benthic community affected?

As stated previously, we assume that a high statistical correlation among variables denote a cause-and-effects relation, e.g. if toxicity results are correlated to chemical concentrations we presume that the toxicity is a consequence of the high concentration of the related chemicals. Only loadings showing values equal or higher 0.35 were considered good associations between an original variable and a new factor (Tabachnick and Fidell, 1996).

The PCA extraction for SES showed sediment toxicity caused by Cu, V, Pb, Zn, PAHs and PCBs, and benthic community alterations as consequence of Cu, V, and PAHs contamination. Nickel and percentage of fines were associated to amphipods mortality and benthic community stress, but with lower relevance (only in Factor 3). The results of the PCA applied on PES data showed that levels of As, Cr, Cu, Ni, Pb, Zn and Hg are causing sediment toxicity (whole sediment and/or elutriates and SWI) and impairments on benthic communities. Benthic communities are negatively affected by PAHs as well, but this contaminant is not causing toxicity. The

Table 5. Sorted rotated factor loadings of the original 20 variables on the 2 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	**Factor 1**	**Factor 2**
% Variance	54.24	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	------
%O.C.	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

GC data matrix showed sediment toxicity and benthic communities' degradation as a consequence of Cd, Co, Cu, Ni, Pb, V, Zn and PAHs contamination. The detailed explanation of these analyses for all three areas can be found in Choueri et al. (in press 'b').

The PCA extractions revealed that sediments are toxic and benthic communities were degraded as a consequence of the high levels of contaminants in each study area. To complete the analysis, it was necessary to identify which factors are representative (if any) for each sampling station. This was accomplished through an estimation of the factor scores for each sampling station to the centroid of all stations. These scores quantified the prevalence of each factor for each station; basically we assume that positive factor scores represent existent correlation between the factor and the sampling station; conversely, a negative score for a given factor means that this factor has no correlation to the sampling station.

The results of this analysis are presented in table 6 for SES, table 7 for PES, and table 8 for GC. The calculation of the factor scores for SES showed that the areas downer in the estuary are neither contaminated nor polluted (scores are negative for all factors). In the other hand, inner areas of the SES presented high sediment degradation (sediment toxicity and/or impaired benthic communities) caused by metals and organic contaminants. Santos Channel (Eastern portion of the SES) showed sediment toxicity caused by Cu, Pb, Zn and PCBs, and São Vicente Channel (Western portion of the SES) sediments are degraded (toxicity and damaged benthic communities) by Cu, V and PAHs. In the surroundings of the Santos submarine sewage outfall, nickel is causing toxicity and stress on benthic community. In this area, fine characteristics of the sediments also play an important role on benthic community structure.

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

Stations	**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

Table 7. Factor scores estimated for each of the 5 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 8 sampling stations evaluated in the Gulf of Cádiz 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

In PES, sediments are not contaminated or environmentally degraded in the area under high influence of the sea. However, sediment quality decreased towards inner estuary: benthic communities were negatively affected by metals and PAH in the vicinities of the Port of Paranaguá, sediment toxicity, caused by metals and PAHs, was found in the area between the Port of Paranaguá and the Port of Antonina (located upper stream), and sediment toxicity and impaired benthic communities associated to metals and PAHs were found in the vicinities of the Ponta do Felix Terminal (Port of Antonina). Another area inner PES, Benito bay, which is located away from the main contamination sources, presented sediment toxicity and degraded benthic community caused by metals.

In GC the situation is: sediments of Ria of Huelva are toxic and affecting benthic community structure because of the high contents of all analysed metals and PAHs. In Bay of Cádiz, only the sediments from the vicinities of the Port of Cádiz showed negative effects of metals on the structure of the benthic community. Lastly, high levels of Ni and PAHs were the reason of the sediment toxicity and the degraded benthic communities in Bay of Algeciras.

The integration of the sediment physical-chemical, toxicity and benthic community descriptors answers the questions about the sediment toxicity and the structure of the benthic community made in the ‘Decision 3(a)’ and ‘(b)’. Next step is the construction of the decision matrix in order to summarize the information obtained through the integration of the LOEs and lead to the final decision about the ecological risk posed the sediments/dredging material under investigation.

4.8 Step 6 – Construction of the decision matrix

The decision matrix summarizes the information obtained through the integration of the LOEs and lead to the final decision about the ecological risk posed the sediments/dredging material under investigation. Firstly, it was necessary to categorise the effects (based on each LOE) that the sediments might pose to the ecosystem in an ordinal ranking (table 8), which gives an assessment for each LOE (no/ potential/ significant adverse effects). In this case, one symbol (‘+’) indicates no adverse effects; two symbols (‘++’) indicates possible potential adverse effects (only applicable for sediment chemistry); and three symbols (‘+++’) represents possible significant adverse effects. After the conclusion of the categorization matrix, a new matrix containing eight theoretical responses was constructed, adapted from that proposed by Chapman and Anderson (2006), establishing four different decisions to the different possible scenarios (table 9). As contamination data (chemical concentrations) do not provide information

Table 8. Categorization matrix based on the integrated WOE approach and the quantitative results from each of the lines of evidence used. Ordinal ranks, denoted by the white, light grey and black circle to characterize the possible potential risk of the contaminated sediments.

LOE	+	++	+++
Chemical concentrations	All concentrations below SQVs-low	One or more exceedences for SQVs-low	One or more exceedences for SQVs-high
Toxicity	Negative score for factors that relates toxicity	Na[1]	Positive score for factors that relates toxicity
Benthic community	Negative score for factors that relates benthic community alterations	Na[1]	Positive score for factors that relates benthic community alterations

Not applicable[1]

Table 9. Decision matrix based to determine the ecological risk associated to each scenario. Modified from Chapman and Anderson (2005).

Scenario	Chemical concentrations	Toxicity	Benthic community	Ecological risk assessment
1	+	+	+	Harmless sediments, no risk
2	++ or +++	+	+	Harmless sediments, no risk
3	+	+	+++	Harmless sediments, no risk
4	+	+++	+	Possible risk: identify causes of toxicity.
5	++ or +++	+	+++	Possible risk: conduct further assessments
6	+	+++	+++	Possible risk: conduct further assessments
7	++ or +++	+++	+	Stressed ecosystem: identify causes of toxicity.
8	++ or +++	+++	+++	Harmful sediments, environmental risk.

on the biological effects, this LOE has less influence in the final decision. In the other hand, data obtained from toxicity tests has more weight on the final risk evaluation.

4.9 Decision 4 – Is there environmental risk?

The table 10 is the decision matrix built for the study areas, which provides the final decision on the ecological risk assessment of the sediments from SES, PES, and GC. The sediments from the majority of the sampling stations were considered as ‘harmful sediments’ (twelve stations). This was expected since the study areas present multiple contaminant sources which are potentially dangerous for the environment (industries, mining, ports). ‘Harmless’ sediments were found in the study areas as well (four stations): in Santos Estuarine System, the samples collected downstreamer the estuary were not associated to ecological risks. The same happened in Paranaguá Estuarine System where the station located downer the estuary were considered as ‘harmless’. In Gulf of Cádiz, harmless sediments were found only at Bay of Cádiz, in one site which sediments are usually reported as ‘clean’ (Riba et al., 2005b; Riba et al. 2004b, c).

Therefore, definitive decisions were provided for sixteen from a total of nineteen sampling stations in this study. Three decisions were not definitive, i.e., in spite of the application of the WOE approach, including assessments of sediment geochemistry, toxicity, and benthic community, further studies are still necessary for an adequate assessment of the ecological risks of these sediments. For one SES sediment sample (SES-2), contamination and toxicity were associated but the benthic community did not exhibit evidences of damage; therefore, despite the indication of potential ecological risks (contamination related to toxicity), further studies must be carried out to assess for

Table 10. Decision matrix for the risk assessment of sediments from SES, PES, and Gulf of Cádiz

Stations	**Chemical concentrations**	**Toxicity**	**Benthic community**	**Risk assessment**
SES-1	+++	+	+	Harmless sediments, no risk.
SES-2	+++	+++	+	Stressed ecosystem: identify causes of toxicity.
SES-3	+++	+++	+++	Harmful sediments, environmental risk.
SES-4	+++	+++	+++	Harmful sediments, environmental risk.
SES-5	++	+	+	Harmless sediments, no risk.
SVES-6	+++	+++	+++	Harmful sediments, environmental risk.
PAR-1	+++	+++	+++	Harmful sediments, environmental risk.
PAR-2	+++	+++	+++	Harmful sediments, environmental risk.
PAR-3	+++	+	+++	Possible risk: conduct further assessments.
PAR-4	++	+	+	Harmless sediments, no risk.
PAR-5	+++	+++	+++	Harmful sediments, environmental risk.
HV-1	+++	+++	+++	Harmful sediments, environmental risk.
HV-2	+++	+++	+++	Harmful sediments, environmental risk.
HV-3	+++	+++	+++	Harmful sediments, environmental risk.
CA-1	++	+	+	Harmless sediments, no risk.
CA-2	+++	+	+++	Possible risk: conduct further assessments.
GR-4	+++	+++	+++	Harmful sediments, environmental risk.
GR-3	+++	+++	+++	Harmful sediments, environmental risk.
GR-3’	+++	+++	+++	Harmful sediments, environmental risk.

example, the interferences of confounding factors on the observed toxicity. One sediment sample from PES (PAR-3) and one from Bay of Cádiz (CA-2) showed association between chemical contamination and stressed benthic community, but not toxicity. Again, despite the quality of these sediments seems to be low, variables other than chemical contamination can affect benthic communities (Chapman and Wang, 200; Riba *et al*., 2004b), and their role or influence on the results needs to be examined.

5. CONCLUSIONS

The framework for sediments/dredging material risk evaluation proposed in this article is based on the assessment of different LOEs and integration of the results through multivariate analysis and brought novel features in comparison to other sediment risk assessment frameworks, such as:

(a) the integration of contamination, toxicity and benthic community structure data by the application of a factor analysis followed by PCA extraction revealed correlations among the variables and allows the determination if a sample is toxic and if benthic communities are affected by contaminants or not;

(b) this framework permit the discrimination of which chemicals are probably causing negative biological effects (toxicity and/or impaired benthic communities);

(c) this framework dispenses the use of a reference area; sediment toxicity and benthic community stress are defined by correlations between level of contaminants, toxicity of the samples and level of benthic community description; however, this characteristic is not applicable in any case since, in some instances, the multivariate analysis may identify correlations which do not correspond to cause-and-effect relationships among variables.

In this study we demonstrated the successful application of this framework in different port and estuarine zones of the North and South Atlantic, which confirms its international scope. Therefore, this allows the standardisation of the procedures, techniques and decision-making processes for the ecological risk assessment of sediments and dredged material for Atlantic ports and estuarine zones.

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Capítulo 4.

Conclusiones finales

1) Los principales contaminantes y sus respectivas fuentes fueron identificadas en las zonas de estudio. En el Sistema Estuarino de Santos, la zona próxima al puerto de Santos está polucionada por cobre, plomo, zinc y BPC; en el saco interno del estuario, afectado por el polo petroquímico de Cubatão, cobre, plomo, vanadio, HPA y BPC son los principales contaminantes; en el canal de São Vicente, donde son vertidos residuos domésticos sin tratamiento adecuado, los sedimentos están sometidos a la contaminación por cobre, vanadio y HPA; la macrofauna bentónica en la zona del emisario submarino de Santos se ve afectada posiblemente por contaminantes no incluidos en este estudio.

En el Sistema Estuarino de Paranaguá, los puertos de Paranaguá y Antonina, además de un vertedero clandestino, son las principales fuentes de degradación ambiental. Las partes internas del estuario, con menor influencia de las aguas marinas, son las más afectadas por los contaminantes como metales (As, Cr, Cu, Ni, Pb, Zn, Hg) y HPA.

Entre las zonas del Golfo de Cádiz, la Ría de Huelva está sometida a degradación por metales (Cd, Co, Cu, Ni, Pb, V, Zn) y HPA provenientes de las actividad mineras y industriales que tienen lugar en esta zona; la Bahía de Cádiz posee señales de degradación por metales (Cd, Co, Cu, Pb, V, Zn) en la zona del puerto; en la Bahía de Algeciras, los principales contaminantes son el níquel y los HPA, debido a los vertidos industriales provenientes del polo petroquímico de Algeciras.

2) La integración de los datos de contaminación y toxicidad de los sedimentos del Sistema Estuarino de Santos y del Golfo de Cádiz (Ría de Huelva, Bahía de Cádiz y Bahía de Algeciras) revelaron que, en general, los sedimentos se han visto más degradados en el saco interno del sistema estuarino brasileño y de los estuarios

españoles. En estas zonas, están asociados a efectos tóxicos a anfípodos los siguientes contaminantes: en el Sistema Estuarino de Santos, HPA, BPC y metales (Cu, Ni, Pb, Zn); en la Ría de Huelva, HPA y metales (Cd, Co, Cu, Ni, Pb, V y Zn); en la Bahía de Algeciras, HPA y níquel. Por tanto, estas zonas presentaron degradación ambiental relacionada a estos contaminantes. En la Ría de Huelva y en la Bahía de Cádiz los altos niveles de BPC no estaban asociados a efectos tóxicos.

3) De modo general, las comunidades bentónicas en el Sistema Estuarino de Santos y en el Golfo de Cádiz siguen un gradiente de enriquecimiento desde las zonas más internas de los estuarios en dirección a zonas más afectadas por la acción del mar. Las comunidades bentónicas presentaran estrés significativo ($p<0.05$) en estaciones próximas a las fuentes de contaminación antropicas, como las zonas portuarias, industriales y mineras y emisarios submarinos. En partes internas del estuario de Santos las comunidades bentónicas se han visto afectadas negativamente por Ni, V y HPA. En las proximidades del emisario submarino de Santos, los niveles de Ni y posiblemente otros contaminantes urbanos (no medidos en este estudio) fueron los responsables de la alteración de las comunidades bentónicas. Las comunidades bentónicas encontradas en zonas sometidas a una mayor influencia del mar no se vieron afectadas. En las zonas del Golfo de Cádiz, los resultados mostraron que las comunidades bentónicas están afectadas por la contaminación química en la Ría de Huelva (Cd, Co, Cu, Ni, Pb, V, Zn y HPAs), en las proximidades del puerto de la Bahía de Cádiz (Cd, Co, Cu, Pb, V, Zn) y en la zona cercana al polo industrial de Algeciras (HPA y Ni).

4) La integración de los datos de contaminación, toxicidad y de la estructura de la comunidad bentónica en sedimentos del Sistema Estuarino de Paranaguá reveló un

gradiente creciente de degradación ambiental (sedimentos con contaminación asociada a efectos tóxicos y comunidades bentónicas estresadas) en dirección a las partes internas del estuario, incluyendo una zona de protección ambiental. Aunque la mayoría de los contaminantes analizados no hayan excedido los valores-guía de contaminación de sedimentos establecidos en la legislación brasileña, la gestión de los sedimentos de las zonas internas del estuario requiere una atención especial.

5) El enfoque aplicado en los análisis multivariantes fue considerado una herramienta útil y fiable para identificar la contaminación y sus efectos asociados en diferentes ecosistemas litorales del Atlántico Norte y Sur. Los resultados demostraron la eficacia de la técnica al comparar diferentes ecosistemas, independiente de la utilización de una zona de referencia.

6) Los valores-guía de calidad de sedimentos (SQVs) desarrollados en este estudio para zonas estuarinas y portuarias de Brasil y España son más restrictivos frente a los valores de referencia aplicados a nivel nacional. Estos resultados confirman la aplicación no adecuada de valores-guía generales y la importancia del desarrollo de valores-guía de calidad de sedimentos específicos para una adecuada caracterización del material de dragado. La utilización del mismo método en el desarrollo de los SQVs específicos para zonas litorales de Brasil y España confirmaron la posibilidad de utilizar una técnica común, de aplicación internacional, para este fin.

7) La herramienta desarrollada para la toma de decisiones en la evaluación del riesgo ambiental de sedimentos y materiales dragados propuesta en este estudio fue novedosa si se compara con otras herramientas de este tipo. Sus características

principales son: (a) a través de la técnica de integración de las tres líneas de evidencia (contaminación, toxicidad y alteración en comunidades bentónicas) fue posible identificar qué estaciones presentaban efectos tóxicos y/o alteración de la estructura de comunidad bentónica; (b) la integración de los datos también permitieron la discriminar los contaminantes que estaban causando efectos tóxicos; (c) el protocolo no demanda el uso de una zona descontaminada de referencia, lo que facilitó la aplicación de éste en zonas sujetas a intenso impacto antropogénico. La utilización de la herramienta de toma de decisiones en diferentes ecosistemas de Brasil y España confirmó su aplicabilidad internacional, permitiendo así la estandardización de los procedimientos, técnicas y procesos de tomada de decisión para la evaluación de los riesgos ecológicos asociados a los contaminantes de sedimentos y materiales de dragado de zonas estuarinas y portuarias del Atlántico.