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Integrated approach to assess ecosystem health in harbor areas

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HIGHLIGHTS

- PAHs, PCBs and HCB were not high compared with sediment and dredging guidelines.
- Metal in sediments within the range where adverse effects can occur.
- IBR index was able to discriminate site 4 as the most impacted area.
- Assessment of the health status by WOE approach proved to be a good approach.

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ABSTRACT

Harbors are critical environments with strategic economic importance but with potential environmental impact: health assessment criteria are a key issue. An ecosystem health status approach was carried out in Portimão harbor as a case-study. Priority and specific chemical levels in sediments along with their bioavailability in mussels, bioassays and a wide array of biomarkers were integrated in a biomarker index (IBR index) and the overall data in a weight of evidence (WOE) model. Metals, PAHs, PCBs and HCB were not particularly high compared with sediment guidelines and standards for dredging. Bioavailability was evident for Cd, Cu and Zn. Biomarkers proved more sensitive namely changes of antioxidant responses, metallothioneins and vittellogenin-like proteins. IBR index indicated that site 4 was the most impacted area. Assessment of the health status by WOE approach highlighted the importance of integrating sediment chemistry, bioaccumulation, biomarkers and bioassays and revealed that despite some disturbance in the harbor area, there was also an impact of urban effluents from upstream.

Capsule abstract: Environmental quality assessment in harbors.

1. Introduction

Coastal areas are affected by a variety of anthropogenic pressures, among which harbors represent critical environments with strategic economic importance, often with limited hydrodynamism, poor water quality and low biodiversity. Stressors in harbors arise from anthropogenic sources and from economic and commercial activities, such as transport, ship repair or painting, loading and bunkering operations, shipyards, accidental spills, wastewater emissions (Bocchetti et al., 2008). These activities contribute to the generation of chemical inputs such as metals, oxidized and alkylated PAHs, petrol fuel additives and antifoulants which can pose a risk to aquatic organisms residing in harbor areas. In addition, ports are not independent entities since they are integrated in population centers and can have direct influence on surrounding environments and related interests (i.e., fishing, recreation, etc.) (Grifoll et al., 2011). In this respect, there is concern on the environmental impact caused by port activities and how these should be properly managed (Darbra et al., 2009).

Within the European Water Framework Directive (WFD, 2000/60/EC and Directives 2008/105/EC and 2013/39/EU), the recognized economic and social value of harbors can justify hydro-morphological changes of the water bodies, classified as heavily modified (HMWB) because they fail to meet the good ecological status. The explicit recognition of the importance and development of specific economic activities strongly support an integrative approach to assess the environmental health in harbor areas within the WFD and the development of new environmental management tools aimed to identify which end points are better suited as proxies for quality evaluation.

Multidisciplinary approaches are required in chronically polluted harbor areas to assess the chemical, biological and toxicological impact of complex mixtures of stressors in different environmental matrices, i.e., water, sediments and biota (Viarengo et al., 2007). Sediments act as sink of contaminants and provide precise records about the type and magnitude of the disturbance (Ondiviela et al., 2012): however, changes of physicochemical characteristics (redox potential, pH,

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dissolved oxygen) or desorption during dredging activities can remobilize contaminants, affecting their mobility, bioavailability and risk for marine organisms (Bocchetti et al., 2008; Ondiviela et al., 2012). Therefore, a particular attention should be paid to the presence of priority and specific substances in sediments despite that bulk chemical analyses alone do not necessarily reflect the bioavailability and the toxic action of measured compounds (Annicchiarico et al., 2007; Prato et al., 2010). In this respect, ecotoxicological bioassays are important complementary tools to evaluate synergistic effects of contaminant mixtures in sediments. In addition, organisms such as the blue mussels *Mytilus galloprovincialis* are good bioindicators to assess environmental bioavailability, bioaccumulation and biological responses of anthropogenic pressures in the water column: at cellular level, biomarkers are excellent early warning signals that can indicate the exposure to specific groups of contaminants, or different levels of cellular unbalance and toxicity due to complex mixtures of chemicals not necessarily identified as being of concern (Cajaraville et al., 2000). Therefore, an integration of well-established biomarkers and bioassays in current EU decision making criteria is thus expected to be an important component to assess the environmental quality of harbor areas and to establish the link between contaminants and ecological responses.

The main goal of the PORTONOVO project (www.portonovoproject.org) was the selection, development and validation of indicators and methodological procedures for the definition of the good ecological potential and management in ports of the Atlantic Area. Within this project, an ecosystem health assessment was carried out in Portimão harbor (Portugal) to identify and quantify spatial variations of WFD priority and specific substances in water, sediments and biota from several sites differently impacted by port activities (Directives 2000/60/EC and 2008/105/EC). Based on the most relevant European and national normative a set of physico-chemical (water and sediments), hydro-morphological and biological indicators was selected. Physico-chemical indicators were transparency, oxygenation and nutrients conditions. Bioavailability and biological effects of contaminants were assessed by integrating levels of priority and specific substances (metals and organic compounds) detected in sediments and accumulated in mussels *M. galloprovincialis* with a wide array of bioassays and biomarkers reflecting specific effects of classes of contaminants at different levels of biological organization. The biomarkers selected included biomarkers of oxidative stress (superoxide dismutase (SOD), catalase (CAT), glutathione peroxidase (GPX), lipid peroxidation (LPO)), biomarkers of exposure (metallothioneins (MT), δ-aminolevulinic acid dehydratase (ALAD), acetylcholinesterase (AChE)) and of estrogenic effect (alkali-labile phosphates (ALP)). Besides biomarkers, bioassays (sediment toxicity with amphipods, Microtox solid-phase and Stress on Stress (SoS) tests) were integrated to assess the toxicity of contaminant's mixtures trapped in sediments and accumulated in the biota. Data was integrated in the Integrated Biomarker Response (IBR) index (Beliaeff and Burgeot, 2002; Serafim et al., 2012) to rank sites according to the disturbance levels and provide environmental managers with a decision-support tool to evaluate the environmental quality of Portimão harbor. The IBR index provides useful information about the effects of multiple stressors and has been widely used in laboratory, in caged and transplant experiments, as well as in the field to assess health effects of contaminants using mussels and clams (Brooks et al., 2011; Cravo et al., 2012; Marigómez et al., 2013a,b; Tlili et al., 2013; Brenner et al., 2014; Devin et al., 2014).

All the chemical and biological data were further elaborated within a quantitative weight of evidence (WOE) model (Sediqualsoft) which combines various typologies of studies (or lines of evidence, LOEs), including sediment chemistry, ecotoxicological bioassays, bioaccumulation and biomarker results (Piva et al., 2011). Independent elaborations for different LOEs allow to consider different criteria which better apply to various typologies of data; the hazards for sediment chemistry and bioavailability are based on the number, magnitude and potential toxicity of chemicals which exceed a set of Sediment Quality Guidelines or natural concentrations measured in control organisms, while biomarkers and bioassays are evaluated considering the biological relevance of measured endpoints ("weight") and the entity of variations compared to specific "thresholds" defined for several species and tissues (Piva et al., 2011). The use of weighted criteria overcomes the limits of qualitative pass-fail approaches toward normative values, in line with recent European Directives which require classifying the health status of water bodies integrating different quality indicators. The Sediqualsoft model was previously applied to different multidisciplinary studies for the characterization of industrial and harbor sediments, the assessment of environmental hazards in coastal and brackish areas and the ecological risk of the Costa Concordia wreck (Benedetti et al., 2012, 2014; Piva et al., 2011; Regoli et al., 2014).

2. Materials and methods

2.1. The Portimão harbor

The Portimão harbor, located in the Arade river, is the main freshwater input in the South West coast of Portugal and has an area of approximately 987 km^2. The Arade river crosses several urban areas (Ferragudo/Parchal and Portimão with around 45,000 inhabitants) and the main contamination sources come from municipal and industrial effluents, harbor, marina and all sort of fishing-related activities (shipyards, industries), fish farms, husbandry, agricultural and urban runoff. Located near the river mouth are small harbors for recreational and fishing vessels and the Portimão harbor (DGPA, 2004). Ship facilities exist near the city of Portimão and the port itself is a gateway to the southern region of Portugal and lies on the route to or from the Mediterranean Sea or from the North Atlantic and also on the route of cruise ships that cross the Atlantic Ocean. The port of Portimão offers excellent conditions to dock large vessels and international cruise ships, after appropriate dredging activities were carried out since 2008. The port accommodates commerce and tourist quays, several socio-economic activities (maritime traffic, ferry boats, ship building industry, marine culture, beach and tourism) and actively contributes to the increase of transport and tourism. Nevertheless, the areas inside and outside the harbor are affected by the port water quality.

2.2. Sampling sites

Seven sites were selected along the Portimão harbor numbered downstream to upstream (Fig. 1). The coordinates of these sites are listed in Table 1 along with abiotic parameters (temperature, salinity, pH and dissolved oxygen) measured in situ with an YSI probe and turbidity with a turbidimeter. Water, sediments and mussel *M. galloprovincialis* were also collected at these sites between November 2010 and February 2011. Due to the inexistence of representative species of sediment toxicity, mussels were used as representative of the water column pollution.

Nutrient (silicates, nitrates, nitrites, phosphates and ammonia) concentrations were determined in 0.45 μm filtered seawater by spectrophotometric methods described by Grasshoff et al. (1983) and data accuracy assessed using reference standard solutions (Marine Nutrient Standard Kit — OSI). Chlorophyll *a* and phaeopigment were analyzed in seawater filtered with a glass fiber filter (0.7 μm) by spectrophotometry, according to the method described by Lorenzen (1967).

2.3. Sediment analyses

Surface sediment samples were collected in triplicate with the aid of a "Van Veen" grab, transported to the laboratory at 4 °C and stored at −20 °C for subsequent use for bioassays and for the determination of metal and organic contaminant concentrations. Sediment organic content was determined in three replicates from each site as the percentage of weight loss by combustion at 450 °C and drying at 100 °C for 24 h. Total metal content was determined in the <63 μm fraction