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Baseline

Highly contaminated areas as sources of pollution for adjoining ecosystems: The case of Augusta Bay (Central Mediterranean)

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ABSTRACT

An assessment of trace element and polycyclic aromatic hydrocarbon (PAH) contamination based on surface sediments collected in summer 2012 was carried out in Priolo Bay adjoining one of the most polluted areas of the Mediterranean Sea, the industrial Augusta harbour (Italy, Central Mediterranean). Inorganic and organic contaminants were generally not remarkable. Occasional elevated concentrations of Hg, Cd, Ni and PAHs exceeding sediment quality guidelines were detected in the northern sector of Priolo Bay, close to Augusta harbour, possibly as a result of water drainage of industrialised and urbanised areas and/or potential direct export of contaminated material from Augusta harbour, whose influence on the adjoining Priolo Bay ecosystem cannot be ruled out. By domino effect, Priolo sediments may therefore become a potential source of pollutants and may represent a threat to the biota.

Coastal marine areas are sensitive environments and their natural equilibrium can often be perturbed as an effect of numerous anthropogenic stressors (Gao et al., 2014). Major concerns originate from contaminants released from both point (*e.g.*, effluent discharges; Yuan et al., 2007) and non-point pollution sources (*e.g.*, cultivated and urbanised land runoff; La Jeunesse et al., 2002). After entering a confined area from different sources, contaminants tend to move between media, for example through bioaccumulation up the food chain, burial in bottom sediments, and/or escape through atmospheric evasion. By readily trapping contaminants, marine sediments are an important source of information about the occurrence, magnitude and trend of human-associated environmental contamination. In addition to being a contaminant sink, sediments can act as a source through contaminant mobilisation from solid to liquid phase when changes in environmental variables (*e.g.*, pH, Eh, organic ligand concentration) occur. This may lead to speciation processes in sediments, which may cause the release of even more toxic compounds (Yuan et al., 2004). Thus, sediments play an important role in geochemical cycles through the release of their bioavailable constituents into the overlying water column, which may affect the biota (Roberts, 2012). Indeed, contaminants can cause alterations at different levels of the hierarchy of biological organisation (*e.g.*, organism, population, community). Among the hazardous environmental contaminants, trace elements and polycyclic aromatic hydrocarbons (PAHs) are of particular concern, most of them being toxic even at low concentrations.

Augusta Bay is a semi-enclosed basin located on the eastern coast of Sicily (Ionian Sea, southern Italy), covering an area of approximately 4000 ha (Fig. 1). Following the construction of the breakwaters in the early 1960s, the northern sector of the bay (Augusta harbour) is connected to the open sea through two artificial inlets in the south and in the east, called Scirocco (300 m wide and 13 m deep) and Levante (400 m wide and 40 m deep) inlets, respectively. Since the late 1950s Augusta harbour has been affected by marine pollution from industrial and petrochemical plants, but also from agriculture and urban waste, with consequent risks to the ecosystem and human health (Sciacca and Fallico, 1978; De Domenico et al., 1994; ICRAM, 2005; Nicotra et al., 2007; Ausili et al., 2008; ENVIRON International Team, 2008; Romano et al., 2009; Sprovieri et al., 2011). The most important environmental issue is Hg contamination, deriving mainly from waste from the chlor-alkali plant, which was discharged untreated until the 1970s, when direct discharge from the industrial plant was reduced by demercurisation and a waste treatment plant in response to a national anti-pollution law of 1976 (G.U.R.I., L.319/1976). Recently, Bellucci et al. (2012) reported that the original environment was considerably modified not only by direct contaminant discharge from the industries, but also by navigation and dredging of polluted sediments from 1958 up to 1997. Thus, dredging has affected at least 3/5 of the harbour surface sediments. The environmental degradation was not confined to the harbour since, as suggested by Di Leonardo et al. (2007,

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2008, 2009, 2014), surrounding offshore systems were presumably chosen as dumping sites. Accordingly, numerous studies on recent (surface sediments) and historical (sediment cores up to about 150 years) sediments, evaluating the environmental sources and accumulation features of contaminants in and outside Augusta harbour, confirmed the severe level of trace element contamination reached nowadays (ICRAM, 2008; Sprovieri et al., 2011; Bellucci et al., 2012). In addition, Sprovieri et al. (2011) described the Augusta harbour as an important contributor of Hg to the entire Mediterranean Sea: Hg released from harbour sediments to the sea water can easily be intercepted by the surface Atlantic Ionian Stream (AIS) and the Levantine Intermediate Waters (LIW), representing a risk for the large-scale marine system. However, so far little attention has been paid to the potential export of contaminants from the Augusta harbour to adjoining coastal marine areas. Among them, Priolo Bay, localised outside the artificial dams of Augusta harbour from the southern quay of the breakwater to the Magnisi Peninsula, could presumably be the most directly influenced by the release of contaminants from Augusta harbour, being in direct connection with it. At the same time, Priolo Bay has elevated ecological, heritage and cultural value since it is the location of the Priolo saltworks wildlife reserve, being an important stopover for migrating birds, and it is also recognised as a Site of Community Importance (SCI) by the European Commission Habitats Directive (92/43/EEC). Specifically, Priolo Bay is marked by complex surface water dynamics: a general distal current flows from NE to SW, whereas a local current affected by the incident wave forcing on the coast flows parallel to the coastline alternately to the north or south. By interacting, these currents generate an anticyclonic circulation that characterises the inner sector of this basin (ISPRA, 2010). The sea bed is characterised by *Posidonia oceanica* dead matte (personal observation) interlarded with sandy bottoms (ISPRA, 2010). Three streams, the Canniolo, Priolo and Castellaccio, flow into the bay.

Within this context, the objectives of this study were: (1) to determine the concentrations of important contaminants, trace elements and PAHs, in sediments from Priolo Bay; (2) to provide information on the potential for negative effects on the biota; and (3) to evaluate the possible function of highly contaminated sites such as Augusta harbour as sources of contaminants for adjoining ecosystems.

Sediment samples were collected in summer 2012 along two nearshore to offshore transects (North: N and South: S), in three stations per transect, at depths of -5, -10 and -20 m respectively (Fig. 1). Samples were collected in duplicate from the surface sediments (0–5 cm) by divers using a PVC hand-corer (Ø 4 cm). Simultaneously, Eh (±mV) of each sediment sample was measured in triplicate with a HYDROLAB DS5 multiparametric probe. In the laboratory, the sediments were oven dried at 40 °C, powdered manually in an agate mortar and analysed for bulk geochemistry, total PAH and trace element concentrations. All the analyses were performed on the two sediment replicates per site, apart from major element determination, which was carried out on only one of the two replicates.

Sediment mineralogy was investigated by powder X-ray diffraction using a PW 14 1373 apparatus (Philips, Holland) and Cu Ka radiation filtered by Ni. The relative proportions of quartz, carbonates and alumino-silicates minerals were established according to the methods and data of Schultz (1964).

Major element (Si, Al, Ca, Mg, Na, K, Ti, Fe, Mn and P) concentration was determined by X-ray fluorescence spectrometry (XRF) on pressed, baked boric-acid pellets, using a ZSX primus spectrometer (RIGAKU, Japan). Data reduction was performed according to the method described by Franzini et al. (1975). Analytical accuracy was checked by performing seven analytical replicates of the standard reference material BCR-1 (U.S. Geological Survey). The recovery ranged from 92% to 99% (average 97%). All samples were washed repeatedly in deionized water to avoid contamination with halite.

Total organic carbon was determined with a Flash EA™ 1112 elemental analyser (Thermo Scientific, Germany). Carbonates were eliminated through HCl treatment in silver capsules.

PAH analysis included the 16 priority PAH congeners defined by the United States Environmental Protection Agency (U.S. EPA): naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Fl), phenanthrene (Phe), anthracene (An), fluoranthene (Flt), pyrene (Py), benzo[a]anthracene (BaAn), chrysene (Ch), benzo[b]fluoranthene (BbFlt), benzo[k]fluoranthene (BkFlt), benzo[a] pyrene (BaPy), indeno[1,2,3-cd]pyrene (IPy), dibenzo[a,h]anthracene (DahAn), benzo[g,h,i]perylene (BghiPe). Benzo[e]pyrene (BePy) and perylene (Pe) were also determined. All chemicals and reagents were of analytical grade with high purity. Dried aliquots of sediment sample were extracted with a Soxhlet apparatus (System B-811 extractor, Büchi, Switzerland) using a modified form of the U.S. EPA 3541 method (U.S. EPA, 1994). A solution of two deuterated surrogate standards was added to the sample before Soxhlet extraction to evaluate recovery efficiency. The extraction was carried out with *n*-hexane/acetone (1:1, v/v) and the extract was then concentrated in a Syncore® Analyst (Büchi, Switzerland) under vacuum pressure. The final extract was dissolved in *n*-hexane and a solution of five deuterated PAH internal standards was added for quantification. Samples were analysed in a GC–MS-QP 2010 Plus instrument (Shimadzu Corporation, Japan) equipped with a fused silica capillary SLB-5ms column (10 m, 0.1 mm i.d., 0.1 μm film thickness, Supelco, USA). The recovery of surrogate standards varied from 70% to 105% (average 92%). The accuracy of PAH quantification was validated by analysing the standard reference material BCR® 535 (freshwater harbour sediment, JCR's Institute for Reference Materials and Measurements). The recovery ranged from 70% to 92% (average 83%). The detection limit was estimated as <2 ng g^{-1} for each PAH. Results are given in ng g^{-1} of dry weight (dw).

Natural and anthropogenic origin of PAH contamination in marine sediments can be interpreted by analysing the complex mixture of PAHs, using molecular indices based on ratios of selected PAH concentrations (Yunker et al., 2002). In the present study, the fingerprints of PAHs from pyrolytic or petrogenic origin in the surface sediments of Priolo Bay were deduced using two selected PAH ratios: the low to high molecular weight (LPAHs/HPAHs) and Flt/(Flt + Py) ratios (Table 1). The first ratio is the sum of six LPAHs (Nap, Acy, Ace, Fl, Phe, and An) to the sum of twelve HPAHs (Flt, Py, BaAn, Chr, BbFlt, BkFlt, BaPy, BePy, DahAn, Pe, BghiPe, and IPy). LPAHs are chiefly proxies of low/moderate temperature combustion processes and petrogenic input, while HPAHs are mainly indicators of high temperature combustion processes and pyrolytic origin: the higher the LPAH/HPAH ratio, the greater the prevalence of petrogenesis on the pyrolytic source of PAHs (Bihari et al., 2006; De Luca et al., 2004). Also, the Flt/(Flt + Py) ratio is considered a reliable tool to check PAH origin in sediments: overall, values <0.40 are characteristic of PAH derived from petroleum, values between 0.40 and 0.50 mark PAHs originating from liquid fossil fuel (vehicle and crude oil) combustion, whereas values >0.50 are characteristic of grass, wood or coal combustion (Yunker et al., 2002).

Trace element concentrations (As, Cd, Co, Cr, Cu, Hg, Mo, Ni, Pb, V and Zn) were determined by digesting 0.2 g of dried sample with a mixture of 67–70% HNO_3, 40% HF, 30% H_2O_2 and MilliQ deionized water using a microwave digestion system (MARS® CEM). Blank, duplicate samples and standard reference material (MESS-3, Marine Sediment Reference Materials, National Research Council of Canada) were prepared using the same composition of reagents for quality-control purposes. The recovery ranged from 79% to