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Element-specific behaviour and sediment properties modulate transfer and bioaccumulation of trace elements in a highly-contaminated area (Augusta Bay, Central Mediterranean Sea)

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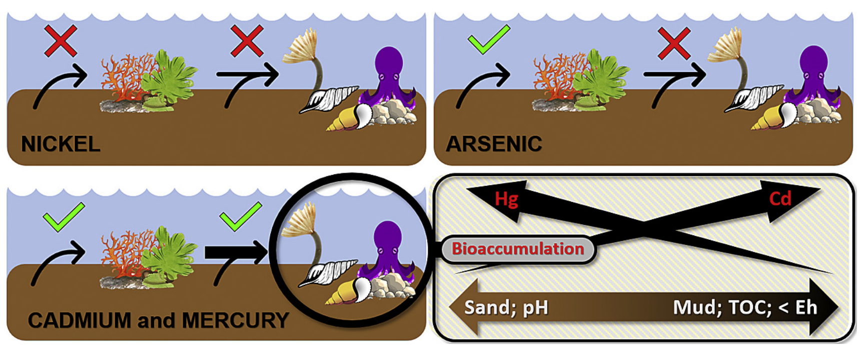
HIGHLIGHTS

- Trace element transfer was not related to sediment contamination spatial pattern.
- Nickel was confined in sediment and arsenic transferred only to macroalgae.
- Cadmium and mercury bio-accumulated in filter feeder and carnivorous invertebrates.
- High TOC, mud content and low Eh promoted Cd transfer and bioaccumulation.
- High TOC, mud content and low Eh promoted Hg transfer but hindered bioaccumulation.

GRAPHICAL ABSTRACT



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ABSTRACT

High sediment contamination in the coastal area of Priolo Bay, adjacent to the highly-polluted Augusta Harbour, poses serious risks for the benthic communities inhabiting the area. Nevertheless, the transfer of trace elements and consequent bioaccumulation in the biota is an overlooked issue. This study aimed to assess the transfer and bioaccumulation patterns of As, Cd, Ni and Hg to the dominant macroalgae and benthic invertebrates of Priolo Bay. Results revealed different patterns among trace elements (TEs), not driven by sediment contamination but rather by element-specific behaviour coupled with sediment physicochemical properties. Specifically, As accumulated in macroalgae but not in invertebrates, indicating bioavailability of dissolved As only, and a lack of effective trophic transfer. Ni was confined to surface sediment and transfer to biota was not highlighted. Cd and Hg showed the highest concentrations in invertebrates and bioaccumulated especially in filter feeders and carnivores, revealing the importance of suspended particulate and diet as transfer pathways. Total organic carbon (TOC), fine-grained sediments and redox potential were the most important sediment features in shaping the sediment contamination spatial patterns as well as those of TE transfer and bioaccumulation. In particular, As and Cd transfer to macroalgae, and especially Hg bioaccumulation in benthic invertebrates was controlled by sediment properties, resulting in limited transfer and accumulation in the most contaminated stations.

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1. Introduction

Mercury (Hg) and other trace elements (TEs), including metals and metalloids, can be released from both natural (e.g. bedrock, volcanoes and forest fires; Nriagu, 1988) and anthropogenic sources (e.g. industrial activities and combustion of fossil fuels; Nriagu, 1988). Due to their worldwide emissions and high persistence, TEs are widespread in all ecosystems. In marine areas, sediment is the main TE storage and may act both as a TE sink and source (Du Laing et al., 2009; Eggleton and Thomas, 2004). Sediment disturbance (e.g. dredging or natural resuspension processes), by changing its physicochemical properties, may lead to contaminant desorption and remobilisation into the water column (Eggleton and Thomas, 2004), increasing the burden of bioavailable fractions. Once TEs become available to aquatic organisms, they may be taken up and bioaccumulated in their tissues, eliciting biological responses (Wilber and Clarke, 2001). Although some TEs, such as Co, Cu, Mn, Ni and Zn, have an important role as micronutrients in trace concentrations, they become toxic if certain thresholds are exceeded. Moreover, other TEs (e.g. Cd, Hg and Pb) are of particular concern, being harmful to biota even at low concentrations (e.g. Mamtani et al., 2011).

Bioaccumulation of TEs by aquatic organisms is a well-documented issue, although complex processes are involved because bioaccumulation patterns differ among elements, species and habitats depending on multiple biological and environmental factors (Eggleton and Thomas, 2004; Luoma and Rainbow, 2005). First, TE bioavailability depends on sediment physicochemical properties such as redox condition, grain size distribution and organic matter content (Cosio et al., 2014; Eggleton and Thomas, 2004; Neff, 2003). Second, bioaccumulation of available TEs in organisms results from several routes of exposure (passively from the surrounding medium through respiratory organs and dermal uptake and actively from food ingestion) whose role is variable among species and trophic groups (Neff, 2003). Third, TE concentration may be regulated through detoxification processes that are species-specific and variable also within species depending on gender and development stage (Eggleton and Thomas, 2004). Thereby, aquatic organisms from the same area may have very different TE concentrations even within related taxa, trophic habit and life style (Rainbow, 2002).

In the Central Mediterranean, Augusta Bay is seriously exposed to large contaminant emissions from the highly industrialized surrounding area. Previous studies highlighted that sediments within the bay are heavily contaminated by some TEs (mainly As, Cd, Hg, Ni) and that this condition is not confined to inside the harbour, because TEs spread to adjoining (i.e. Priolo Bay) and offshore areas (e.g. ICRAM, 2008; Di Leonardo et al., 2008, 2009, 2014a,b; Sprovieri et al., 2011). In particular, exceptionally high Hg concentrations have been found within the bay, due to unregulated discharges from a chlor-alkali plant, making this area notorious as an hotspot for Hg export to the whole Mediterranean basin (Sprovieri et al., 2011). Augusta Bay was also subject to massive sediment dredging activities within the harbour and illegal dumping and discharge offshore (Bellucci et al., 2012). These activities, together with the intense ship traffic, may have resulted in heavy sediment remobilisation, posing high risks to aquatic organisms. Nevertheless, very few studies have been carried out on the biota from Augusta Bay, especially regarding TE behaviour and transfer to benthic organisms. Previous research documented TE accumulation and consequent biological responses in transplanted mussels (Ausili et al., 2008; Signa et al., 2015) and in fish (Ausili et al., 2008; Bonsignore et al., 2013; Scopelliti et al., 2015; Tomasello et al., 2012). A recent study reported Hg trophic transfer and biomagnification in the whole Priolo food web, while Cd biomagnified only in the invertebrate benthic food web (Signa et al., 2017). To our knowledge, information about TE accumulation in local macroalgae and invertebrates is missing.

The main aim of this study was to assess the bioaccumulation patterns in the biota from the highly contaminated area of Augusta Bay, in particular the coastal area of Priolo Bay. To do this, we addressed the following questions: do the most abundant TEs in Priolo Bay (As, Cd, Hg and Ni; Di Leonardo et al., 2014b) transfer to the biota? Do the patterns of TE transfer and bioaccumulation mirror the environmental contamination levels? How do the physicochemical properties of sediments influence TE transfer and bioaccumulation in the biota? What role do the intraspecific variability and trophic habits of benthic organisms play in the patterns of TE transfer and bioaccumulation?

2. Materials and methods

2.1. Study area

Augusta Bay is a coastal marine basin located along the south-eastern coast of Sicily (Ionian Sea, Central Mediterranean) (37°09' − 37°12′ N and 15°10' − 15°14′ E; Fig. 1). In its northern sector it includes the heavily-industrialized Augusta Harbour, a semi-enclosed area with only two connections to the sea, Scirocco inlet to the south (300 m wide, 13 m deep) and Levante inlet to the east (400 m wide, 40 m deep). The most contaminated sediments have been found in the southern part of Augusta Harbour, close to the Scirocco inlet (ICRAM, 2008) and the adjoining coastal ecosystem in the southern part of Augusta Bay, Priolo Bay, has also been found to be adversely affected by industrial activities, being located just outside Augusta Harbour (Catania et al., 2015; Di Leonardo et al., 2014b; ISPRA, 2010). In particular, Hg is the most abundant element in Priolo Bay sediments but also As, Cd and Ni concentrations are considerably high (Di Leonardo et al., 2014b). The mean depth of Priolo Bay is 15 m and the seabed is characterised by *Posidonia oceanica* dead matte mixed with sandy bottoms (Di Leonardo et al., 2014b) and covered with patchy macroalgal beds (pers. obs.).

2.2. Sampling procedures

Macroalgae and invertebrates were sampled in summer 2012 in Priolo Bay along two nearshore to offshore transects (North: N and South: S), in three stations per transect at around 5, 10 and 20 m depth (Fig. 1). The most abundant macroalgae (*Caulerpa prolifera*, *Codium bursa* and *Dictyopteris polypodioides*) and benthic megafaunal organisms (*Cerithium vulgatum, Hexaplex trunculus, Holothuria poli, Pinna nobilis* and *Sabella pavonina*) were manually sampled during scuba diving expeditions. Specifically, the area covered at each sampling station was equivalent to 10 × 10 m^2. Specimens of *Octopus vulgaris* and *Sepia officinalis* were caught respectively with fish traps deployed at each station and with three trammel nets deployed across the bay (Fig. 1). Six sediment samples were also collected in each station using a PVC hand-corer (Ø 4 cm; length: 25 cm): three whole cores were used for grain size analysis and the other three were sliced for total organic carbon (TOC) analysis in the surface layer (0–1 cm). pH and Eh (±mV) were measured in triplicate at the water/sediment interface with a B&C Electronics 152.2 portable meter. All samples were stored and transported to the laboratory in a cool box. Once in the laboratory, macroalgae were rinsed with distilled water to remove coarse residuals and, where present, epiphytes were removed by surface scraping with a disposable scalpel. For each invertebrate species, a number of specimens varying from two to five of similar size, whenever available, were selected and dissected to collect muscle