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Zooplankton from a North Western Mediterranean area as a model of metal transfer in a marine environment

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ABSTRACT

We monitored the concentration of 21 trace elements in zooplankton samples collected in a Northwestern Mediterranean coastal ecosystem (Italy). In the last 20 years, this area has been the target of important anthropogenic impacts including maritime traffic and substantial industrial activities. Zooplankton contributes to the transfer of trace metals to higher trophic levels and constitute one of the recommended groups for the baseline studies of metals in the marine environment. The essential trace elements (As, Cu, Mn, Zn, Fe, Mo, Co, Cr, Se, Ni) and the nonessential trace elements (Al, Be, Cd, Pb, Sb, Sn, V) were generally found at concentrations of no concern in the analyzed zooplankton samples, but showed important variations between seasons and different water depths. The zooplankton was found to be a significant accumulator of metals, and bioaccumulation factors were in the range of 28 (Co) to 10,9015 (Fe) in marine surficial waters, with increasing values at increasing water depth. Zooplankton is a useful bioindicator to assess metal contamination and its impact in the marine environment.

1. Introduction

The Mediterranean Sea is characterized by a rich biodiversity, but the presence of chemical and mining industries in the majority of coastal areas threatens this ecosystem by producing significant amounts of chemical waste, of which trace metals constitute an important part (EEA, 2006; Lafabrie et al., 2008). Some of these trace metals, such as copper (Cu), zinc (Zn), manganese (Mn), iron (Fe), and chromium (Cr) are essential for the metabolism of the organisms while others, like cadmium (Cd), lead (Pb), and mercury (Hg), are nonessential. All metals, essential or not, are toxic above a threshold bioavailability and can be considered as serious pollutants of aquatic environments because of their toxicity, persistence, and tendency to concentrate in organisms (Ikem and Egiebor, 2005).

Plankton is a determinant for metal transfer in marine food webs and trace metals are included in plankton biochemical cycles (Whitfield, 2001). Zooplankton is particularly critical to the functioning of ocean food webs because of their sheer abundance and vital ecosystem roles. Zooplankton is mainly composed of copepods, the most abundant animal taxon on the Earth (Schminke, 2007); copepods are the major grazers in ocean food webs, providing the principal pathway for energy from primary producers to consumers at higher trophic levels (Richardson, 2008; Fernández-Severini et al., 2013). Additionally, zooplankton plays an important role in the biogeochemical cycling of trace metals in marine ecosystems. In fact, in surface pelagic waters, plankton can strongly affect the vertical transport of elements; biogenic particle flux accounts for a lot of the vertical flux and hence controls the residence times of particle-reactive elements in the sea (Fisher et al., 1991).

Metals may be adsorbed onto organic films or colloidal materials at the particle surface or by crossing the plankton cell (Fisher and Reinfelder, 1995). Adsorption of metals to plankton varies greatly in the first trophic levels. In general, plankton with higher surface: volume ratio has higher concentration factors, especially for non-reactive particles. Once aggregated or incorporated into plankton, elements may be transferred along the web chain and transformed by successive organisms, either enhancing or alleviating their toxicity (Watras and Bloom, 1992).

Metals that are egested by sinking fecal pellets from zooplankton are exported out of the surface waters, enriching the deep-water dissolved-metal pool through re-mineralization and release (Fisher et al., 1991). Cellular metals regenerated in the dissolved state during grazing may be recycled many times and re-utilized by the phytoplankton community. In assessing environmental quality with respect to trace elements in seawater, the

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bioavailable fraction is of major importance as toxicity is dependent on the bioavailable exposure concentration (Kahle and Zauke, 2003). This bioavailable fraction can only be assessed by determining the amount of metals incorporated into organisms, which is the main goal in biomonitoring (Rainbow, 1993).

Because of their wide geographic distribution, trophic position, rapid turnover, huge biomass and high capacity to accumulate trace metals, zooplanktonic organisms can be used as biomonitors for trace metals in marine environments (Barka et al., 2001; Kahle and Zauke, 2003; Fang et al., 2006; Hsiao et al., 2011).

Coastal areas receive large amounts of contaminants introduced by domestic, industrial and agricultural activities, either directly, via rivers or through atmospheric deposition (Usero et al., 2005). Costal marine ecosystems are important for the fate of contaminants and are therefore worth studying.

Data regarding metal concentrations in zooplankton communities of Mediterranean coastal environments are very scarce and usually report just a few metals, for example, rare earth elements (Gulf of Lion, France; Strady et al., 2015); Cu, Pb, and Cd (Toulon Bay, France; Rossi and Jamet, 2008); Zn, Cu, and Cd (estuary of Var, France; Hardstedt-Roméo and Laumond, 1980). No previous studies have analyzed the concentrations of this many trace elements, reported here, in zooplankton from a Northwestern Mediterranean area, specifically from an Italian coastal region.

The study area is a highly productive coastal region characterized by remarkable commercial maritime traffic and several industrial plants. Moreover, in the last twenty years, due to its peculiar geomorphology, the area has been the target of important anthropogenic impacts, such as the discharges of Leghorn harbor mud (1,873,000 m^3) contaminated by Cu, Zn and Pb (ARPAT, 2006). Up until the 1990s, the chloralkali plant of Solvay (Rosignano) built in 1918, discharged about 8000 $m^3 h^{-1}$ of industrial effluents directly into the sea (Balestri et al., 2004). Contamination by Hg has been reported in areas close to this plant (Balestri et al., 2004; Lafabrie et al., 2007a,b). The Arno River drains a wide inland area, transporting Al, Fe, Hg and other trace elements at high concentrations toward the sea (Cortecci et al., 2009). In addition, three coastal towns (Pisa, Leghorn and Cecina), discharge partially treated effluent into the rivers (Renzi et al., 2009). Furthermore, this coastal area also experiences summer tourism, which leads to a substantial increase in inhabitants. Therefore, municipal wastewater treatment plants show effluents characterized by worsened water quality and an increase in the nutrient concentration of marine water (Renzi et al., 2009).

The main objectives of the present study were:

(i) to analyze the concentrations of aluminum (Al), antimony (Sb), arsenic (As), beryllium (Be), cadmium (Cd), cerium (Ce), cobalt (Co), chromium (Cr), iron (Fe), manganese (Mn), mercury (Hg), molybdenum (Mo), lanthanum nickel (Ni), lead (Pb), copper (Cu), selenium (Se), tin (Sn), thallium (Tl), vanadium (V) and zinc (Zn) in zooplankton samples collected in all four seasons at three different depths.
(ii) to verify if this marine ecosystem, which was heavily influenced in the past by anthropogenic activities, is still compromised by the presence of high concentrations of metals.
(iii) to evaluate the relevance of zooplankton (and in particular of copepods) as a metal bio-indicator.

2. Materials and methods

2.1. Sampling area

The sampling area was located offshore from the Italian coast, at the border between the Northern Tyrrhenian Sea and the Ligurian Sea (Fig. 1). Station 1 (43°29′40″ N–10°01′45″ E), Station 2 (43°28′10″ N, 10°01′55″ E) and Station 3 (43°27′10″ N, 10°03′00″ E) were located at 12.5 nautical miles off the coast, over the continental shelf toward the strongly impacted neritic zone close to Solvay-Rosignano. The study area was in fact in the Ligurian Sea, within the "Cetacean Sanctuary" where the number of cetaceans is at least twice as high as anywhere else in the Mediterranean (Ambrose, 1999). The Ligurian sea is situated at the north east border of the Western Mediterranean and is connected to the southern basin (Tyrrhenian Sea) across the Corsica Channel. The major large-scale feature of the water dynamic of the Ligurian Sea is a cyclonic circulation that is active all year round, but more intense in winter than in summer, involving both deep and surface layers (Aliani et al., 2003). Climatic forcing can greatly change the intensity of fluxes, but the general pattern can be considered permanent (Molinero et al., 2005a,b). Southern waters flowing toward the Ligurian sea occur by means of two main currents running along each side of Northern Corsica. The West Corsica Current (WCC) runs along the western side of Corsica while the warm and salty Tyrrhenian current (TC) goes through the Corsica Channel (Artale et al., 1994) (Fig. S1). The two waters merge at the north of Corsica and flow together along the Ligurian coast toward the Gulf of Lions. The Tyrrhenian current permits warm species from the south to reach the Ligurian basin, passing through the Corsica Channel. The investigated sector is characterized by the large extension of the continental shelf and limited depth (100 m), even at remarkable distances from the coast (18 miles) (Chiocci and La Monica, 1996).

2.2. Sample collection

Zooplankton samples were collected during four expeditions in May, August, and November 2014 and February 2015. The same neritic areas were investigated across all seasons. The three sampling stations were aligned along a transect parallel to the coast (12.5 NM offshore), as shown in Fig. 1. Stations 1–3 (Fig. 1) were located on the continental shelf above bottom depths ranging from 109 to 114 m. The entire water column was sampled by three hauls: one surface haul, and two vertical hauls (5–50 m, 50–100 m depth, respectively); zooplankton samples were taken with a WP-2 standard net, with a mesh size of 300 μm and a diameter of 60 cm. The horizontal sampling time was approximately 15 min at a vessel cruising speed of 2 knots, while during the vertical sampling the net was hauled at 0.7 $m s^{-1}$.

Each net was fitted with a flow meter (KC Denmark model 23.090) to measure the volume of water filtered, which ranged from 14 to 422 m^3. The net hauls were consistently carried out at night to minimize variability due to vertical migration. One whole sample of each net was divided into two aliquots using a Folsom splitter immediately after sampling; one aliquot was used for estimating biomass and analyzing zooplankton composition, and the second aliquot was immediately frozen at −20 °C onboard for subsequent analysis of for trace element concentrations (Fang et al., 2014; Fernández de Puelles et al., 2014). Samples used for estimating biomass (mg of dry weight m^{-3}) were collected on pre-weighed glass fiber filters and heated at 60 °C for 24–36 h (Lovegrove, 1996). Samples for composition analysis were fixed in 4% neutralized formaldehyde buffered with borax and kept in the dark (Boltovskoy, 1981). Subsamples of mesozooplankton were obtained using a Folsom Plankton Splitter, and at least two subsamples were counted completely to determine the abundance, presented as ind. m^{-3}, of the main zooplankton groups (Boltovskoy, 1981). Considering the quail-quantitative importance of copepods, the adults were identified to species level and juvenile stages to genus level, wherever possible (Vives and Shmeleva, 2007, 2010). In addition to the entire Mediterranean Sea, in the Ligurian and Tyrrhenian Seas, the bulk of copepod populations are