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Non-proportional bioaccumulation of trace metals and metalloids in the planktonic food web of two Singapore coastal marine inlets with contrasting water residence times

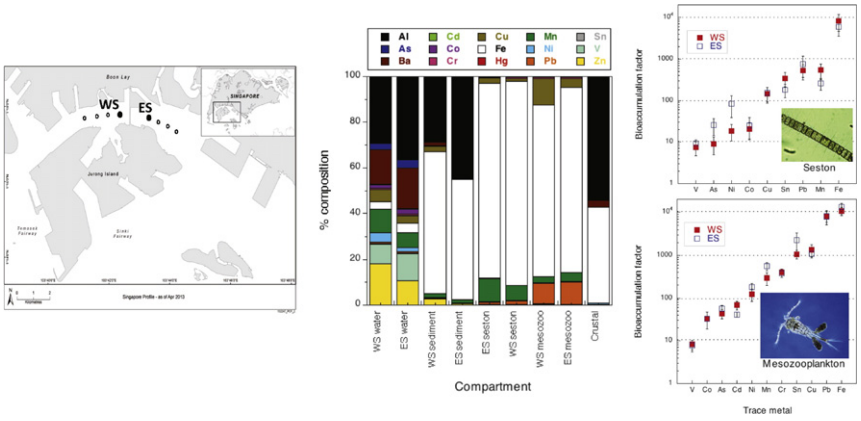
Albert Calbet [a,*], Claire Schmoker [b], Francesca Russo [b], Aurore Trottet [b], Mohamed-Sofiane Mahjoub [b], Ole Larsen [b,c], Hor Yee Tong [d], Guillaume Drillet [b]

[a] Institut de Ciències del Mar, CSIC, Passeig Marítim de la Barceloneta 37-49, 08003 Barcelona, Spain
[b] DHI-NTU Research Centre and Education Hub, 1 CleanTech Loop, #03-05 CleanTech1, 637141, Singapore
[c] DHI Water and Environment-Denmark, Agern Allé 5, 2970 Hørsholm, Denmark
[d] National Parks Board HQ, 1 Cluny Road, Singapore Botanic Gardens, 259569, Singapore

HIGHLIGHTS

- First report of bioaccumulation of trace elements in marine plankton from Singapore
- We found more trace metals/metalloids in the site with longer water residence time
- Most trace metals/metalloids were of anthropogenic origin
- High trace metal concentrations in water/seston were not reflected in zooplankton

GRAPHICAL ABSTRACT



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ABSTRACT

We analyzed the concentrations of trace metals/metalloids (TMs) in the water, sediment and plankton of two semi-enclosed marine coastal inlets located north of Jurong Island and separated by a causeway (SW Singapore; May 2012–April 2013). The west side of the causeway (west station) has residence times of approximately one year, and the east side of the causeway (east station) has residence times of one month. The concentrations of most of the TMs in water and sediment were higher in the west than in the east station. In the water column, most of the TMs were homogeneously distributed or had higher concentrations at the surface. Preliminary evidence suggests that the TMs are primarily derived from aerosol depositions from oil combustion and industry. Analyses of TMs in seston (>0.7 μm; mostly phytoplankton) and zooplankton (>100 μm) revealed that the seston from the west station had higher concentrations of most TMs; however, the concentrations of TMs in zooplankton were similar at the two stations. Despite the high levels of TMs in water, sediment and seston, the bioaccumulation detected in zooplankton was moderate, suggesting either the presence of effective detoxification mechanisms or/and the inefficient transfer of TMs from primary producers to higher

Abbreviations: TM, trace metal/metalloid; CCC, criterion of continuous concentration.

* Corresponding author.
E-mail address: acalbet@icm.csic.es (A. Calbet).

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Sediment
Bioaccumulation

trophic levels as a result of the complexity of marine planktonic food webs. In summary, the TM concentrations in water and seston are not reliable indicators of the bioaccumulation at higher trophic levels of the food web.

1. Introduction

At low concentrations, trace metals/metalloids (TMs) are essential for physiological processes, and the absence of these molecules has harmful ecological consequences. In marine systems, the clearest example of this phenomenon occurs in the equatorial and subarctic Pacific and Southern Oceans in which high-nutrient low-chlorophyll areas shown an iron (Fe) deficiency that limits phytoplankton growth (Martin and Fitzwater, 1988; Morel et al., 1991a, 1991b; Pitchford and Brindley, 1999; Kearney et al., 2015). Other TMs, including cadmium (Cd), cobalt (Co), copper (Cu), manganese (Mn), nickel (Ni) and zinc (Zn), play key biological roles as cofactors of enzymes and might also become limiting for phytoplankton growth (Morel et al., 1991a; Twining and Baines, 2013). However, above a certain threshold, these metals become toxic to marine life and might severely impact the ecosystem. In turn, the cycling of these elements is also influenced through biological activity. Phytoplankton accumulate TMs and transfer these particles up the food web via zooplankton (González-Dávila, 1995; Rejomon et al., 2010). When ingested by zooplankton, a portion of the TMs is returned to the water through excretion and the production of fecal pellets (Lee and Fisher, 1992; Wang and Fisher, 1998). Another portion of the TMs accumulates in zooplankton, becoming available for fish and eventually reaching humans. Moreover, zooplankton inhabiting polluted waters can accumulate TMs through passive diffusion (Wang and Fisher, 1998; Tan and Wang, 2011). Although TM contamination in seawater and sediment has been comprehensively studied, there is little information on the levels and bioaccumulation factors in phytoplankton and zooplankton (Chen et al., 2000; Ho et al., 2007; Qiu, 2015). Given the relevance of these groups as major trophic links, moving pollutants up the food web, it is crucial to understand the mechanisms underlying this process and determine whether there is a limit the carrying capacity of these organisms. Considering the diverse detoxification mechanisms of zooplankton (Xu and Wang, 2001; Ho et al., 2007; Rossi and Jamet, 2008), whether these organisms will accumulate proportionally more or less pollutants compared with phytoplankton remains unknown. Thus, we selected an area with a potentially high presence of TMs to examine this premise.

South East Asia is one of the most densely populated and industrialized areas of the world. Several mega-cities and mega-harbors, including Singapore, are located in this region (Chou, 2006). To support this development, the geography and landscape of this island area at the tip of the Malay Peninsula have been drastically changed. These changes were primarily achieved through land reclamation, joining several small islands. Jurong Island is such an area, created since the 1930s through the combination of 17 original islands. The new island is linked to mainland Singapore via a causeway that separates two water bodies with no water exchange between them. To our knowledge, there are no studies concerning the concentrations of trace elements in Jurong waters or the bioaccumulation of these molecules in the planktonic food web. There are, however, two records of TM concentrations in Singapore marine waters, both corresponding to northern locations (Nayar et al., 2004; Cuong et al., 2008), and there is only one study on marine sediments around this island (Goh and Chou, 1997). However, the conclusions from these studies are contradictory. While Nayar et al. (2004) reported toxicity associated with dredged and re-suspended sediments on the phytoplankton of the Ponggol Estuary, Cuong et al. (2008) and Goh and Chou (1997) concluded that the TM concentrations in both the water column and sediments of coastal Singapore were relatively lower than those of other industrialized countries. Notably, none of the previous studies evaluated biological constituents as potential TM reservoirs. Nevertheless, Singapore is a highly industrialized country with surrounding waters susceptible to high pollution loads. How these pollutants might move up the food web is, therefore, a major concern.

In the present study, we selected coastal seawaters located north of Jurong Island and sampled to the west and east of the above-mentioned causeway separating the inlets with different water residence times. Assuming similar sources of TMs in both inlets, we hypothesized that the water, sediment and seston from the western inlet should show increasing TM concentrations with longer water residence times. We also hypothesized that there is a limit to the amount of TMs that zooplankton might accumulate, making the former hypothesis invalid for zooplankton. Therefore, we expect a non-linear relationship between TMs in water/prey and zooplankton. The objectives of the present study were (1) to determine the concentrations and potential sources (anthropogenic vs. natural) of the most abundant TMs in the area; (2) to examine how different water residence times affect the accumulation of TMs in the biotic and abiotic compartments of the two inlets; and (3) to assess the bioaccumulation of TMs in the planktonic food web. We propose that these data will contribute to the resolution of broader questions on how water residence times affect the extent of pollution and the current understanding of the model of transference of pollutants among different compartments of the ecosystem.

2. Methods

We examined two marine harbor areas, one on each side of the Jurong causeway, located on the western coast of Singapore (Fig. 1; west station; 01°17.949′N, 103°42.383′E and east station; 01°17.694′N, 103°43.340′E). The west station has residence times of ca. one year, while the east station has a residence time of one month (DHI MIKE21 FM Advection Dispersion Model, www.mikepoweredbydhi.com). To obtain basic environmental descriptors and determine the TM concentrations in the water column, we sampled both stations every two weeks (Table 1) from May 2012 to April 2013 at three depths: 1 m (surface), 10 m, and 15 m (near bottom). Additionally, on eight separate occasions, from November 2012 to April 2013 (Table 1), we collected samples for TM quantifications in seston >0.7 μm (mostly phytoplankton) and zooplankton >100 μm. On three separate occasions, August and October 2012 and March 2013, we also sampled water and gathered sediments using a hand-pulled drag along a transect (4 sampling points per transect) from the station to the mouth of the harbor (Table 1).

We measured the temperature and salinity using a YSI 6920 S2 multi-probe sensor. The microplankton samples (250 mL of seawater) were fixed with homemade acidic Lugol's solution (2% final concentration). Subsamples of 10 mL were settled for 6 h in Utermöhl chambers, and the microplankton/phytoplankton in the entire chamber were counted and sized. The volumes of these organisms were approximated to the closest geometrical shapes, and a 30% volume was added to the estimate to compensate for losses resulting from preservation (Broglio et al., 2004; Jakobsen and Carstensen, 2011); an additional 25% volume was added to account for cells <10, which were not properly quantified using this methodology (Schmoker et al., unpublished). To convert volume to dry weight, we assumed volume wet weight equivalence and subsequently converted the wet weight to dry weight by a factor of 0.2 (Strickland, 1960).

We collected zooplankton from the bottom to the surface using vertical, hand-pulled plankton hauls with 100 μm-mesh nets. The samples were fixed in 4% formaldehyde. Approximately 1000 individuals were counted per sample. Additional net hauls of unpreserved material were used to quantify the concentration of TMs in zooplankton.