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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

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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 ($> 0.7 \mu\text{m}$; mostly phytoplankton) and zooplankton ($> 100 \mu\text{m}$) 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 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.

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

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/metalloid concentrations in water/seston were not reflected in zooplankton

Keywords: Singapore; plankton; trace metals and metalloids; heavy metals, sediment; bioaccumulation

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,b; 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 et al., 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°N17.949'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 (Broglia 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., submitted). 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. Known amounts of these samples were separated into 6 replicates after thorough rinsing with filtered seawater; two of these replicates were processed for TM determinations, two replicates were filtered and dried for 24 h at 60°C for dry weight estimation, and the other two replicates were preserved in formaldehyde for counting and sizing the organisms under a microscope. Using parallel samples obtained from the same stations, we determined the relationship between the fresh and dry weights of the zooplankton.

The TMs were estimated in the laboratory following a standard protocol (EPA 3015) using an APHA 3125B – Inductively Coupled Plasma Mass Spectrometer (ICP MS, Thermo Scientific X Series II). The elements determined were aluminum (Al), chromium (Cr), iron (Fe), manganese (Mn), cobalt (Co), nickel (Ni), copper (Cu), zinc (Zn), arsenic (As), cadmium (Cd), tin (Sn), barium (Ba), mercury (Hg), lead (Pb), and vanadium (V). The following limits of detection were used ($\mu\text{g L}^{-1}$): Al = 5.0; Fe = 2.0; V, Mn and Ba = 1.0; Ni, Co, Cu, Zn, As = 0.5; Sn = 0.2; Cr, Cd, Pb = 0.1; and Hg = 0.05. The samples of seston and zooplankton were not analyzed for Al, Ba or Zn. For sediment samples, 200 mg were weighed and transferred to a microwave vessel for digestion following EPA Method 3051 through the addition of 10 mL of nitric acid and 2 mL of hydrochloric acid in the presence of 3 mL of hydrofluoric acid. The following micro-assisted digestion parameters were used:

maximum power 500 W and temperatures reaching 175 °C within 5 min and remaining between 170 and 180°C for another 10 min. Upon the completion of digestion, the vessels were cooled to room temperature. The digested sample was diluted and filtered through a 0.45- μ m membrane prior to analysis. For seston samples, we used EPA 3052, following oxidation with dihydrogen dioxide and without hydrofluoric acid addition. An SRM 1515 (apple leaves) was used as reference material. Recovery rates ranged between 86 and 100%.

3. Results

3.1. Physicochemical water characterization

Both stations followed similar temperature patterns (Fig. 2) during the sampling year, with minima observed in February-March 2012 and maxima detected above 30°C from April to June. Secondary temperature maxima were detected at the beginning of October in the west station and less conspicuously, in the east station. Salinity variations (Fig. 2) showed similar patterns at both stations, although with some notable differences. The west station exhibited an abrupt decline at the end of May 2012, and subsequently gradually increased to a maximum by the end of November. In the east station, the lowest values were measured during monsoon periods, while the highest occurred during inter-monsoons.

3.2. Trace metals/metalloids in the water column

Year-round average TM concentrations were typically higher in the west station than in the east station (Annex tables 2 and 3), although each of the TM concentrations were positively correlated with its counterpart at the other station. For the station with a longer water residence time (west station), we observed significant differences in

the TM concentrations among seasons (one-way ANOVA; $p < 0.05$), with higher concentrations observed during the southwest monsoon for Al, Ba, Cd, Co, Cu, Mn, and Ni and during the inter-monsoon periods, for As, Cr, Fe, and V. In the east station, Cd, Co, and Mn showed significantly higher concentrations during the southwest monsoon, while As, Cr, Fe, and V were significantly higher during the inter-monsoon periods, and Al, Ba, and Zn were highly concentrated during both the southwest monsoon and inter-monsoons compared with the northeast monsoon phase. Copper, Ni, and Pb did not show any clear seasonal patterns at this station. Neither temperature nor salinity explained more than 25% of the temporal variation of any TM at both stations. Regarding the vertical distribution in the water column, in the west station we observed significantly higher concentrations (one-way ANOVA; $p < 0.05$) at 1 m for Ba, Cr, Cu, Ni, Pb and Zn. Only Mn was more concentrated near the bottom. The remaining elements showed a homogeneous vertical distribution. No major heterogeneities in the vertical distribution of TMs were observed in the east station. Similarly, no clear differences were observed in the TM concentrations in the water column along transects from the stations towards the mouth of the harbor (Annex tables 2 and 3).

3.3. Trace metals/metalloids in sediment

Overall, the TM concentrations were significantly higher (t-test; $p < 0.05$) in the west station sediments (Annex table 3), where many elements showed a clearly decreasing trend toward the mouth of the harbor. This gradient was not observed in the east station. We determined whether the TMs in the sediment originated from natural or anthropogenic sources using enrichment factors (EF; Duce et al., 1975). These ratios

associate the observed concentrations of TMs with those naturally occurring at the Earth's crust:

$$EF(TM) = (TM/Al)_{\text{sediment}} / (TM/Al)_{\text{crust}},$$

for which the crustal composition was obtained from <http://education.jlab.org>.

Considering that the Al in the sediments of the studied stations is near crustal concentrations, any enrichment factor close to one could be considered to result from natural origins. However, bearing in mind the heterogeneous distribution of elemental compositions in the crust, it has been suggested that the threshold for differentiation between naturally and anthropogenically sourced elements should be > 10 (Kaya and Tuncel, 1997). Using this higher threshold, the nine TMs in the west station were clearly derived from anthropogenic sources (Fig. 3; Hg, Zn, Cu, Pb, Mn, Cd, Sn, and As), whereas only four were detected in the east station (Fig. 3; Hg, Pb, Mn, and As).

3.4. Bioaccumulation of trace metals/metalloids in plankton

We did not observe any clear seasonal pattern in the concentrations of TMs in seston (phytoplankton) at both stations, as the concentrations are typically higher in stations with longer water residence times (Table 2; $p < 0.01$ for Co, Cu, Mn, Sn and V). Most TMs in phytoplankton showed a homogeneous vertical distribution in the water column. No significant relationships were observed between the concentrations of TMs in seston and those dissolved in the water. The concentrations of TMs in zooplankton tissues were similar at both stations and lower than that in phytoplankton (Table 3). We observed significantly positive relationships between the TMs in water and zooplankton for As, Co, and V in the west station and for As, Co, Cr, and V in the east station. A few significant correlations were also evident between the TMs in

seston and zooplankton for As and Mn in the west station and for As, Fe, Mn, Ni and V in the east station. For seston, the order of TM bioaccumulation for the combined stations was $\text{Fe} > \text{Mn} > \text{Pb} > \text{Sn} > \text{Cu} > \text{Co} > \text{Ni} > \text{As} > \text{V}$ (Fig. 4). For zooplankton the order of TM bioaccumulation was $\text{Fe} > \text{Pb} > \text{Cu} > \text{Sn} > \text{Cr} > \text{Mn} > \text{Ni} > \text{Cd} > \text{As} > \text{Co} > \text{V}$ (Fig. 4).

As a visual summary, we compared (Fig. 5) the proportions of TMs in the different constituents with the crustal composition. Figure 5 provides a comparison of the major trace elements among water, sediment, seston, zooplankton and natural sources. The changes in the different compartments are obvious. The TMs in water primarily comprised Al, Ba, Mn, V, and Zn, whereas those in the sediments mostly contained Al and Fe. The TMs in seston comprised Fe and Mn and those in zooplankton mostly comprised Fe, Cu, and Pb. Moreover, the crustal composition of the Earth is dominated with Al and Fe.

4. Discussion

4.1. Sources of trace metals/metalloids in the area

There are diverse sources of TMs in marine environments, including riverine inputs, industrial waste-water discharges, re-suspension of the sediment, antifouling paints, aerosol deposition, leaching from sands used in reclamation of lands, etc. Considering that each TM was positively correlated with its counterpart at the other station, a common origin is expected. Thus, the same freshwater reservoir drains to both sides of the causeway, and the magnitude of the discharges is insignificant with respect to the overall volume of the sites. Moreover, there are no major industries located on the

perimeter of this reservoir, and we did not observe any consistent gradients in the concentrations of dissolved TMs from the inner inlets (zone of discharge of the reservoir) towards open waters. The re-suspension of sediments could explain the high levels and similarities of the dissolved TMs in the waters of the two inlets, suggesting that the wind-driven re-suspension of sediments could have the same timing at both sites. However, if sediments were important in driving the concentrations of TMs in water, then higher concentrations should be observed near the bottom (or a homogeneous distribution when water is well mixed because winds), which was not the case.

Most of the elements measured are commonly observed in aerosols over urban Singapore, resulting from oil-fired power plants, metal processing industries, land reclamation and construction activities, municipal solid waste incinerators and traffic emissions (Balasubramanian and Qian, 2000). The wet deposition of TMs is high in Singapore, with average fluxes of $14,560 \mu\text{g m}^{-2} \text{yr}^{-1}$ of Cu, $7,280 \mu\text{g m}^{-2} \text{yr}^{-1}$ of Mn, $8,840 \mu\text{g m}^{-2} \text{yr}^{-1}$ of Pb, or $18,720 \mu\text{g m}^{-2} \text{yr}^{-1}$ of Zn (Hu and Balasubramanian, 2000). These fluxes are orders of magnitude above those of most other regions (except the North Sea; Injuk et al., 1997). The magnitude of wet deposition is insignificant when solely considering the area of the harbor. However, by accounting for the entire basin, this value could well explain the concentrations observed in the water.

4.2. Effects of water residence time on the TM concentrations

Overall, these data were consistent with our original hypothesis predicting that the TMs in water and sediment should be higher at sites with longer water residence times (west station). Frequent flushing with less polluted waters from the Singapore Strait help reduce the TM concentrations at the east station, whereas at the west

station, the intensity of flushing is much lower (DHI MIKE21 FM Advection Dispersion Model, www.mikepoweredbydhi.com). Moreover, as a result of the western entrance, any open waters entering the west station should be greatly influenced by the Johor Strait, which is more polluted than the Singapore Strait (Goh and Chou, 1997).

Knowing the concentration of a given substance in water or sediment is meaningless without an adequate comparison with the concentrations detected at other sites and without also knowing the levels of that substance posing a threat to marine life. Thus, Table 4 presents the data gathered for other estuaries and ports to better frame the results obtained in the present study. We selected Cd, Cu, Ni, and Zn, which have been most widely studied for their potential toxicity. The Criterion of Continuous Concentration (CCC, U.S. Environmental Protection Agency, 2006), an estimate of the highest concentration of a substance in water to which an aquatic community can be indefinitely exposed without resulting in a deleterious effect, are also shown in Table 4. Cadmium, Ni and Zn were not above their CCC values in the samples examined in the present study or in samples obtained from most other estuaries and ports. However, the Cu concentrations were above the CCC during some sampling periods. This situation was more frequent observed in the west station, where water is less renewed. Other sites, such as the Weser Estuary in Germany (Turner et al., 1992), the Mersey Estuary in UK (Comber et al., 1995) and Macquarie Harbor in Australia (Mackey et al., 1996), also presented concentrations above the CCC value for Cu. Copper is an essential nutrient in trace amounts, but becomes toxic at high concentrations (Knops et al., 2001; Debelius et al., 2010; Prosnier et al., 2015). After long-term exposure to any pollutant, species selection and local adaptations might favor the development of resistant populations (Gächter and Máres,

1979). The development of resistant populations might be the case observed in the present study, as a parallel study described rich and abundant populations of both zooplankton and phytoplankton in this area (Schmoker et al., submitted).

Consistent with their longer residence times, high atomic weights and relatively low solubility, most TMs accumulate in sediments at much higher concentrations than in water. Table 5 presents some TM concentrations observed in other ports and estuaries for comparison with the sampling sites in the present study. We selected the same TMs as listed in Table 4 for comparative purposes. The concentrations of TMs in the sediments of the west station and east station rank relatively high, yet these values were comparable to or were even surpassed at many other sites. According to the Consensus-Based Sediment Quality Guidelines SQG (in Sany et al., 2011), the east station could be classified as moderately contaminated with respect to Cu and Zn, whereas the west station can be classified as heavily polluted for Cu, Zn and Ni. However, Cu and Zn have been identified as major pollutants at both stations. High concentrations of both metals have previously been detected in other areas of Singapore with elevated ship transport, potentially reflecting the leaching of anti-fouling paints and occasional discharges of diesel oil (Goh and Chou, 1997). The west station does not have higher ship transport than the east station; however, the west station is adjacent to many oil refineries.

4.3. Bioaccumulation

Phytoplankton incorporate TMs through adsorption onto the cell surface and intracellularly through the passive and active uptake of dissolved elements (González-Dávila, 1995; Ho et al., 2007; Sakata et al., 2012). Mesozooplankton take up TMs

through these mechanisms and the ingestion of polluted prey (Rejomon et al., 2010; Wright et al., 2010). Therefore, the relationships between the water TM concentrations and those observed in zooplankton could indicate direct absorption/adsorption. In contrast, correlated TM concentrations between prey and zooplankton grazers could denote the incorporation of TMs through ingestion (Chen et al., 2000). We only observed a few significant relationships between TM concentrations in zooplankton and those in water and seston. Cobalt and Cr might have been acquired in soluble forms, whereas Mn, Fe, and Ni were likely acquired by zooplankton through feeding, and As and V were incorporated through both mechanisms. We did not obtain conclusive information for the remaining metals. Indeed, we are aware that confounding factors can interfere with these correlations. For example, incorporation through diffusion shows saturation thresholds above those at which the intake is constant (Fisher et al., 1984). Thus, there was no correlation between the organismal and water contents at high ambient concentrations. In addition, the exclusion of specific metals from uptake is likely an adaptive strategy to avoid toxicity (Foster, 1977). Moreover, the speciation of the elements, which was not considered in the present study, might also determine incorporation levels (Sunda and Guillard, 1976; Chen et al., 2008).

Few field studies have reported TM concentrations in phytoplankton or microplankton (Twining and Baines, 2013). For pristine waters of the equatorial Pacific Ocean, Twining et al. (2011) detected phytoplankton concentrations of Mn, Fe, Co, Ni, and Zn of several orders of magnitude lower than observed in the present study. In a protected glacial lake in the Patagonia, Argentina, Arribére et al. (2010) reported As, Co, and Fe values one order of magnitude lower than those reported in the present study. Moreover, in the South China Sea and in Shimizu Port (Japan), Ho

et al. (2007) and Sakata et al. (2012), respectively, also detected ca. ten-fold lower metal concentrations than in the smallest size-fractions of plankton reported herein. The higher concentrations of TMs detected in the seston/phytoplankton in the present study did not denote any special capability to bioaccumulate compared with other reports; instead, these values reflected higher elemental concentrations in the waters sampled. With respect to zooplankton, the absolute magnitudes of the TMs in the different fractions analyzed here do not differ much from previous records (El-Din and Abdel-Moati, 2001; Ho et al., 2007), or these concentrations were even lower than the results of Hsiao et al. (2005) and Rejomon et al. (2015). Lower biomass-specific values in zooplankton than in phytoplankton are common for some TMs, reflecting increased detoxification and excretion efficiencies (Xu et al., 2001; Ho et al., 2007; Rossi and Jamet, 2008). Furthermore, for particulate incorporation, the transfer of an element through the food chain is not necessarily proportional to the ingested amounts. In marine copepods, the assimilation efficiency for some elements is not proportional to the amounts in the diet (Schmidt et al., 1999, Xu et al., 2001). Thus, copepods and other crustaceans regulate the amount of metal in their bodies (Martin, 1974; Xu et al., 2001). The mechanisms enabling this control are diverse, including enhanced excretion rates and inhibited uptake (Nugegoda and Rainbow, 1989; Chan and Rainbow, 1993). Consequently, the accumulation of TMs in the different compartments of the food web is not consistent with a proportional/linear model. Thus, there is a saturation threshold over which the concentration of TMs in zooplankton does not further increase. Whether this threshold reflects efficient detoxification mechanisms in zooplankton or the attenuation mediated through complex lateral trophic pathways in pelagic food webs (Stemberger and Chen, 1997) remains an open question. Nevertheless, despite the lower bioaccumulation capacity

of zooplankton compared with that of phytoplankton, some potentially toxic TMs have been observed at high concentrations. For instance, Cu and Pb showed an average 20 and 25 $\mu\text{g g}^{-1}$ dry weight, respectively, at both stations for the studied period. These values are orders of magnitude higher than those commonly observed in fish (see review by Monsefrad et al., 2012). Fortunately, these TMs do not biomagnify in aquatic ecosystems (Cardwell et al., 2013).

4.4. Conclusions

In the present study, we reported on the concentrations of TMs in the water, sediment and plankton of two semi-enclosed coastal sites with contrasted water residence times. As expected, the concentrations of TMs in water, sediments and seston were higher at sites with longer water residence times (west station). Regarding the biological compartments, phytoplankton presented higher concentrations of TMs than zooplankton, representing differences in the elemental bioaccumulation factor sequence for both groups. This difference reflects either effective detoxification mechanisms in zooplankton or/and the inefficient transfer of TMs from primary producers to higher trophic levels, and the complexity of marine planktonic food webs, with many lateral links, might attenuate the transfer of TMs. Consequently, the TM concentrations in water and seston are poor indicators of the bioaccumulation at higher trophic levels of the food web, and the bioaccumulation of TMs in the marine food webs does not follow a linear model.

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Table 1. Summary of the sampling dates for trace metals/metalloids (TMs) in each compartment of the ecosystem.

Date	TMs in water	Transect	TMs in sediment	TMs in plankton
May 23, 2012	X			
June 1, 2012	X			
June 19, 2012	X			
June 29, 2012	X			
July 26, 2012	X			
August 7, 2012	X			
August 23, 2012	X			
August 29, 2012	X		X	
September 5, 2012	X			
September 18, 2012	X			
October 4, 2012	X	X	X	
October 9, 2012	X			
November 8, 2012	X			X
November 22, 2012	X			X
December 7, 2012	X			
December 18, 2012	X			X
January 16, 2013	X			
January 30, 2013	X			X
February 21, 2013	X			X
March 5, 2013	X	X	X	X
March 13, 2013	X			X
March 26, 2013	X			
April 2, 2013	X			X
April 9, 2013	X			X
April 23, 2013	X			X

Table 2. Trace metals/metalloids in seston ($> 0.7 \mu\text{m}$) in $\mu\text{g g}^{-1}$ dried weight. Note that the analyses did not include Al, Ba and Zn. Cadmium, Cr, and Hg were under detection limits. SE: standard error.

Date	Statio	Depth	As	SE	Co	SE	Cu	SE	Fe	SE	Mn	SE	Ni	SE	Pb	SE	Sn	SE	V	SE
November 8, 2012	west	1	7.2	4.1	3.2	0.47	192	84.2	6052	855	718	56	7.2	0.1	162	138.2	8.0	1.3	13.8	1.8
	west	10	16.6	6.1	5.7	0.36	391	170.7	9097	1314	1655	86	15.5	5.2	54	12.9	11.7	5.1	22.0	2.5
	west	15	20.3	2.3	4.5	0.82	908	44.2	10933	1343	738	18	76.4	60.1	63	38.2	12.4	0.7	34.0	0.5
November 8, 2012	east	1	28.1	6.4	24.3	2.05	155	32.4	54850	5055	3995	129	19.9	10.5	4691	4294.0	83.0	63.1	149.9	38.3
	east	10	122.6	0.0	108.4	9.43	615	169.7	264185	20393	14120	282	2402.3	544.6	1063	473.9	417.3	172.1	703.7	76.6
	east	15	265.7	16.7	79.9	39.02	2243	1261.7	184890	52996	14405	1977	414.4	117.1	8587	2016.1	475.7	453.4	739.6	115.2
November 22, 2012	west	1	3.5	1.4	0.6	0.62	32	17.8	400	342	98	68	9.1	4.3	37	33.9	1.2	1.2	2.5	2.5
	west	10	22.1	3.0	8.6	0.16	229	19.2	6463	119	1258	17	65.0	12.7	67	1.2	10.5	0.3	22.3	2.8
	west	15	90.5	4.2	35.6	2.63	880	96.4	31319	3724	7256	99	285.5	73.6	327	14.3	93.4	28.1	90.8	10.5
November 22, 2012	east	1	6.4	0.3	0.5	0.00	25	3.2	798	18	101	0	16.6	2.1	19	4.3	1.1	0.0	2.9	0.1
	east	10	45.9	6.8	6.9	1.43	151	24.9	6915	550	621	2	170.2	42.8	49	10.3	6.7	1.5	20.3	3.4
	east	15	94.8	3.4	35.2	15.55	474	139.6	24479	3419	1511	142	941.6	570.3	319	56.6	20.7	2.9	64.0	9.7
January 16, 2013	west	1	17.0	9.7	8.2	1.24	132	29.9	4419	1682	936	19	U.D.L.		95	70.0	10.0	2.2	9.2	4.7
	west	10	11.5	5.5	10.1	0.65	90	28.4	3170	602	1013	46	U.D.L.		73	5.2	3.4	0.7	4.3	0.7
	west	15	117.6	1.4	90.0	2.38	1248	71.9	51444	22383	9320	314	U.D.L.		917	678.6	93.3	15.2	68.6	68.6
January 16, 2013	east	1	118.8	25.0	5.3	1.92	580	10.9	37219	85	2537	38	U.D.L.		697	27.4	82.7	6.2	34.4	4.7
	east	10	801.9	26.0	64.7	29.96	2911	31.5	293240	9462	15137	1347	U.D.L.		1820	189.2	503.1	86.7	97.8	17.3
	east	15	2528.1	45.6	141.2	4.56	7407	45.6	908932	4555	33166	23	U.D.L.		6487	1266.3	1407.5	232.3	546.6	4.6
January 30, 2013	west	1	118.8	33.1	120.0	7.35	3871	568.4	150765	27561	14692	1218	211.9	211.9	1131	371.2	139.6	12.2	584.6	15.6
	west	10	46.3	46.3	174.8	3.43	6612	1221.7	238140	16792	25288	1148	682.0	116.5	1491	72.0	222.8	37.7	656.3	12.0
	west	15	251.6	147.4	244.4	14.38	8456	957.9	345207	37562	30387	935	154.6	154.6	2309	483.4	336.1	37.7	918.4	80.9
January 30, 2013	east	1	47.8	8.1	27.5	7.29	1166	153.1	53349	8427	3094	297	14.6	14.6	985	104.1	51.5	15.8	164.1	35.2
	east	10	34.9	7.4	12.6	0.00	563	0.0	23398	968	1552	93	31.7	3.8	167	34.2	16.0	9.2	82.1	0.2
	east	15	57.1	15.6	28.7	4.73	909	0.0	51081	2982	3009	146	U.D.L.		404	66.9	22.2	4.7	156.7	3.3
February 21, 2013	west	1	22.6	22.6	12.6	5.66	698	179.9	11864	6203	1416	275	72.9	38.4	204	85.2	0.0	0.0	66.5	16.7
	west	10	3.3	3.3	63.2	0.83	1713	136.3	57713	3116	6778	249	12.9	12.9	413	51.1	68.1	9.1	174.1	6.2
	west	15	127.6	29.0	140.1	3.91	3599	12.5	149658	3444	14576	133	18.8	18.8	916	43.8	117.4	12.5	416.4	11.0
February 21, 2013	east	1	U.D.L.		1330.1	0.00	713	617.2	5321	0	495	69	U.D.L.		572	250.6	8.0	8.0	U.D.L.	

March 5, 2013	east	10	85.3	85.3	11.3	4.83	2253	239.9	27263	7971	3862	163	U.D.L.		114	57.2	40.3	12.9	49.9	19.3
	east	15	U.D.L.		60.4	4.53	1202	685.6	108850	6645	6496	262	U.D.L.		593	40.0	49.1	0.8	286.9	34.7
	west	1	23.8	17.1	79.0	9.52	925	79.0	26326	5773	4297	38	18.7	18.7	370	33.9	83.4	20.0	69.5	11.7
	west	10	206.1	80.3	246.7	7.60	3496	292.3	107214	422	13138	524	U.D.L.		885	48.2	232.3	44.8	272.9	4.2
March 5, 2013	west	15	1084.7	32.2	1087.0	34.58	25497	483.0	1038384	21586	63070	1491	893.2	138.3	5553	189.0	1691.1	102.6	2277.2	35.2
	east	1	U.D.L.		U.D.L.		U.D.L.		306	29	37	6	1.9	1.9	5	0.4	0.1	0.0	1.6	0.1
	east	10	1.4	1.4	U.D.L.		U.D.L.		3090	374	147	33	U.D.L.		2	1.9	0.3	0.3	8.1	1.7
	east	15	2.9	0.8	U.D.L.		39	3.4	4621	30	194	3	7.0	1.0	2	1.8	2.4	1.2	11.8	0.3
March 13, 2013	west	1	U.D.L.		5.5	0.20	158	7.2	3715	351	281	7	27.3	0.3	17	3.1	7.1	1.6	14.0	1.3
	west	10	U.D.L.		10.6	0.18	184	27.5	7082	1016	608	44	32.7	23.7	50	18.5	9.7	1.0	20.6	4.5
	west	15	U.D.L.		111.5	12.08	1728	227.6	84843	15564	6538	616	118.0	65.0	77	72.0	127.8	28.8	242.5	61.3
	east	1	U.D.L.	0.3	0.3	0.02	3	0.9	345	90	59	4	0.4	0.4	26	1.7	0.0	0.0	1.9	0.3
March 13, 2013	east	10	3.3	3.3	2.8	0.96	4	4.4	5237	1112	309	52	3.6	3.6	U.D.L.		1.2	0.2	15.3	3.4
	east	15	U.D.L.		1.4	0.33	U.D.L.		2808	811	120	23	2.0	2.0	34	6.3	0.1	0.1	7.5	3.3
	west	1	443.3	81.6	257.6	14.40	11168	625.7	115541	2881	17571	16	U.D.L.		6182	216.0	284.9	35.2	283.3	8.0
	west	10	47.6	29.0	25.9	0.00	121	9.0	16074	1878	3842	5	U.D.L.		84	7.6	23.2	1.7	14.9	0.2
April 2, 2013	west	15	50.0	7.3	56.8	4.69	347	18.2	68481	2656	9754	208	U.D.L.		317	21.4	98.4	7.8	219.8	125.0
	east	1	0.9	0.2	0.4	0.04	10	0.3	408	38	70	4	U.D.L.		8	1.2	0.5	0.2	1.2	0.3
	east	10	6.5	2.5	4.6	0.68	68	3.0	6326	173	377	8	U.D.L.		74	2.3	2.8	0.0	15.3	1.8
	east	15	U.D.L.		5.7	0.15	84	18.7	9723	132	499	15	U.D.L.		173	44.9	6.7	3.0	21.2	1.8
April 9, 2013	west	1	6.9	0.1	2.3	0.32	84	12.7	2305	376	181	22	1.2	1.2	152	1.2	7.4	0.6	4.5	1.4
	west	10	46.1	5.8	44.5	6.59	650	114.0	29698	10846	4170	300	50.6	46.5	202	3.7	60.5	7.4	72.0	23.5
	west	15	155.8	1.0	35.9	4.21	967	400.6	48090	9650	4875	327	54.7	48.3	295	78.4	251.9	214.1	129.5	23.3
	east	1	86.9	13.2	5.9	0.35	313	258.4	12090	1679	1030	83	14.5	8.7	123	14.5	41.9	1.4	39.3	5.0
April 9, 2013	east	10	587.7	109.3	53.0	7.58	1857	848.5	103751	27599	8028	596	53.0	53.0	378	208.9	123.4	17.3	277.1	84.4
	east	15	1332.1	35.4	207.0	32.69	4329	1446.6	345594	73826	25714	2313	351.4	346.0	3923	806.4	332.4	168.9	907.2	231.6
	west	1	0.8	0.1	0.3	0.02	12	0.4	268	18	27	2	0.5	0.0	6	0.8	0.3	0.1	2.1	0.1
	west	10	0.7	0.3	0.7	0.03	10	2.0	376	56	109	4	0.6	0.2	4	0.8	0.3	0.1	1.7	0.1
April 23, 2013	west	15	0.4	0.1	0.5	0.01	7	0.2	408	0	88	3	0.7	0.1	5	0.3	0.2	0.0	1.3	0.2
	east	1	3.2	1.3	2.8	0.04	57	16.5	3620	117	476	1	20.5	13.4	63	6.3	1.5	1.5	13.4	0.0
	east	10	3.0	3.0	5.6	0.90	247	23.1	7989	843	1084	43	23.3	20.3	54	2.6	U.D.L.		25.4	3.1
	east	15	0.6	0.6	9.1	0.29	357	0.0	13698	1000	1529	50	23.4	4.9	48	6.4	7.6	7.6	34.2	0.1

U.D.L. Under detection limit

Table 3. Trace metals/metalloids in zooplankton (> 100 µm) in µg g⁻¹ dried weight. Note that the analyses did not include Al, Ba or Zn. Mercury was under detection limits. SE: standard error.

Date	Station	As	SE	Cd	SE	Cr	SE	Cu	SE	Fe	SE	Mn	SE	Ni	SE	Pb	SE	Sn	SE	V	SE
November 8,	west	1.02	0.00	0.05	0.000	1.94	0.00	34.7	0.00	417	0.0	19.6	0.00	0.98	0.00	22.2	0.00	1.33	0.00	1.52	0.00
	east	0.98	0.02	0.03	0.002	2.04	0.23	10.0	0.08	627	30.3	32.4	1.30	1.07	0.07	24.5	1.37	0.59	0.02	1.78	0.08
November 22,	west	1.71	0.24	0.14	0.071	1.99	0.48	25.5	5.25	468	51.9	24.5	9.89	1.03	0.22	24.2	19.34	1.45	0.14	1.35	0.47
	east	2.22	0.41	0.02	0.001	3.05	0.34	8.3	1.25	410	72.0	18.7	3.73	1.97	0.32	26.7	1.20	0.56	0.11	1.43	0.06
January 16, 2013	west	1.14	0.18	0.06	0.011	1.74	0.51	24.7	5.09	246	71.6	6.1	1.21	2.92	1.68	69.3	2.13	1.51	0.24	0.78	0.09
	east	0.59	0.03	0.05	0.003	0.54	0.02	11.2	0.47	96	65.5	3.5	1.61	0.17	0.08	3.0	1.39	0.18	0.04	0.02	0.01
January 30, 2013	west	0.02	0.00	0.02	0.004	0.34	0.00	9.2	1.46	137	62.3	1.6	0.99	2.76	1.55	9.2	3.65	0.50	0.13	N.A	
	east	0.23	0.00	0.02	0.005	0.29	0.20	23.0	5.26	211	5.4	4.9	0.22	0.81	0.12	46.2	4.64	3.24	0.00	N.A.	
February 21,	west	0.71	0.12	0.04	0.002	1.82	0.73	119.1	16.63	237	60.2	5.8	1.48	1.10	0.55	41.8	6.33	0.96	0.05	0.35	0.05
	east	0.69	0.12	0.03	0.004	0.09	0.00	9.0	0.64	60	38.5	1.5	0.57	0.20	0.02	90.7	77.92	0.68	0.60	0.18	0.02
March 5, 2013	west	0.19	0.07	0.13	0.051	0.74	0.27	13.4	2.33	53	14.7	1.7	0.03	0.46	0.06	9.9	1.91	0.28	0.14	0.14	0.02
	east	0.56	0.03	0.05	0.013	0.48	0.03	4.7	0.05	182	11.8	5.7	0.78	0.37	0.02	3.6	2.95	0.30	0.14	0.33	0.01
March 13, 2013	west	0.35	0.02	0.02	0.002	0.39	0.03	10.1	0.12	72	7.6	1.7	0.08	0.34	0.02	2.5	1.13	0.17	0.01	0.20	0.00
	east	0.44	0.04	0.03	0.007	0.75	0.06	7.1	0.30	69	4.1	2.0	0.03	0.67	0.22	9.8	1.34	0.19	0.01	0.19	0.01
April 9, 2013	west	N.A.		0.04	0.022	0.53	0.05	8.6	0.12	62	21.8	1.6	0.18	0.49	0.07	9.0	0.73	0.25	0.05	0.14	0.04
	east	0.39	0.10	0.03	0.010	0.38	0.26	8.6	0.48	75	22.2	9.8	6.22	0.37	0.02	3.8	0.48	0.11	0.02	0.19	0.06

N.A. Not acquired; U.D.L. under detection limit.

Table 4. Water concentration ($\mu\text{g L}^{-1}$) of Cd, Cu, Ni, and Zn in other harbor and estuary areas around the world.

Site of study	Cd	Cu	Ni	Zn	Reference
Juru estuary, Malaysia	0.6-0.8	0.6-0.8	1.6-1.8	4-10	Seng et al. (1987)
Weser estuary, Germany	0.16	2.98	3.75	7.03	Turner et al. (1992)
Six estuary, Texas, USA	N.A.	0.1-3.2	N.A.	0.3-1.9	Benoit et al. (1994)
Mersey estuary, UK	0.01-0.11	0.8-4.95	2-10.5	6.5-28	Comber et al. (1995)
Humber estuary, UK	0.05-0.45	1.8-10.1	2.5-12	3-20.5	Comber et al. (1995)
Tweed estuary, UK	0.049-0.22	0.49-4.7	N.A.	3.6-15	Laslett (1995)
Macquarie harbor, Australia	0.005-0.028	2.35-6.99	0.28-0.55	0.39-2.03	Mackey et al. (1996)
Bathurst harbor, Australia	0.002-0.007	0.14-0.24	0.14-0.29	0.39-2.94	Mackey et al. (1996)
Archelos estuary, Greece	N.A.	0.31-0.31	2.76-2.76	2.05-2.05	Dassenakis et al. (1997)
Gironde estuary, France	0.024-0.131	0.39-1.35	0.27-0.54	0.47-2	Kraepiel et al. (1997)
Tay estuary, Scotland	0.002-0.12	0.45-1.9	0.23-0.9	0.4-8	Owens and Balls (1997)
Scheldt estuary, Netherlands	0.01-0.03	0.3-2.22	N.A.	0.6-23	Zwolsman et al. (1997)
N. Australia coast and estuary	0.002-0.034	0.15-1.04	0.12-0.55	0.018-0.50	Munksgaard and Parry (2001)
Port Jackson, Australia	0.006-0.104	0.93-2.55	0.175-1.61	3.27-9.66	Hatje et al. (2003)
Ponggol estuary, Singapore	U.D.	10	20	N.A.	Nayar et al. (2004)
Northern Singapore	0.013-0.109	0.23-1.16	0.28-0.78	0.97-3.66	Cuong et al. (2008)
Jurong East, Singapore	0.047-0.256	0.61-7.01	0.064-1.78	0.72-14.65	This study
Jurong West, Singapore	0.055-0.304	1.49-8.11	0.62-7.46	4.42-47.8	This study
CCC*	8.7	2.6	7.7	76.6	US EPA (2006)

*National Recommended Water Quality Criteria. N.A. not acquired, U.D. under detection.

Table 5. Sediment concentration ($\mu\text{g g}^{-1}$) of Cd, Cu, Ni, and Zn in other harbor and estuary areas around the world.

Site of study	Cd	Cu	Ni	Zn	Reference
Chao Phya estuary, Thailand	1.2	26	N.A.	140	Menasveta and Cheevaparanapiwat (1981)
Juru estuary, Malaysia	U.D.-6.80	9.3-13.8	24.8-46.7	73.5-110	Seng et al. (1987)
Tokyo Bay, Japan	0.53-1.40	16.6-79.9	16.4-44.1	106-405	Fukushima et al. (1992)
Restronguet Creek, UK	1.53	2398	58	2821	Bryan and Langston (1992)
Fal estuary, UK	0.78	648	23	750	Bryan and Langston (1992)
Tamar estuary, UK	0.96	330	44	452	Bryan and Langston (1992)
Gannel estuary, UK	1.35	150	38	940	Bryan and Langston (1992)
Tyne estuary, UK	2.17	92	34	421	Bryan and Langston (1992)
Johor strait, Singapore	0.18	30.7	30.2	132	Wood et al. (1997)
Darling Harbour, Australia	N.A.	95.7	8.6	614	Hatje et al. (2001)
Barcelona harbor, Spain	0.43-2.76	70.6-531	18.3-34.3	213-1133	Guevara-Riba et al. (2004)
Haihe estuary, China	0.4-2.1	21-246	N.A.	N.A.	Liu et al. (2006)
Pearl river estuary, China	2.8-4.7	15-141	24.8-122	240-346	Li et al. (2007)
Hongkong	0.10-5.3	1-4000	5.0-220	17-790	Zhou et al. (2007)
Yangtze river estuary, China	0.06-0.3	12-47	N.A.	45-125	An et al. (2010)
Ponggol estuary, Singapore	0.24	34.7	6.07	N.A.	Nayar et al. (2004)
Kranji, Singapore	0.19	17.3	26.1	62.1	Cuong and Obbard (2006)
Pulau Tekong, Singapore	0.06	7.7	17.1	49.8	Cuong and Obbard (2006)
Northern Singapore	0.07-0.22	6.3-21.0	13.3-26.6	48.2-52.0	Cuong et al. (2008)
Jurong East, Singapore	0.04-0.13	14.8-43.8	4.9-10.7	48.3-152	This study
Jurong West, Singapore	0.5-1.1	146.1-852	17.4-41.7	247-740	This study

CBSOG SQG					Consensus-Based Sediment Quality Guidelines SQG 2003
Non-polluted	<0.99	<25	<23	<90	
Moderately polluted	0.99-3	25-75	23-36	90-200	
Heavily polluted	>3	>75	>36	>200	

N.A. not acquired

Figure Legends

Figure 1. Study area showing the position of the sampling stations. The dark circles correspond to routine sampling sites. The open circles and numbers indicate the positions of the stations along the transects. ES: east station; WS: west station.

Figure 2. Time series of the vertical profiles of temperature (A, B; °C) and salinity (C, D) for the two stations sampled at the west station (WS) and east station (ES). The dots correspond to sampling events. The South West Monsoon (SWM) and the North East Monsoon (NEM) are indicated as solid bars in the upper region of each plot.

Figure 3. Enrichment factor for the sediment TMs relative to the crustal composition normalized to the Al concentration. The data were ordered based on the west station values. The lines for 1 and 10 enrichment factors are indicated. ES: east station; WS: west station.

Figure 4. Bioaccumulation factor for seston (A) and zooplankton (B). The factors were calculated based on wet weight. ES: east station; WS: west station.

Figure 5. Proportions of the different elements in the studied samples compared with the crustal composition. ES: east station; WS: west station.

References

- An Q, Wu YQ, Wang JH, Li ZE. Assessment of dissolved heavy metals in the Yangtze River Estuary and its adjacent sea, China. *Environ Monit Assess* 2010; 164: 173-187.
- Arribère MA, Campbell LM, Rizzo AP, Arcagni M, Revenga J, Ribeiro Guevara S. Trace Elements in Plankton, Benthic Organisms, and Forage Fish of Lake Moreno, Northern Patagonia, Argentina. *Water, Air, Soil Pollut* 2010; 212: 167-182.
- Balasubramanian R, Qian WB. Characterization and source identification of airborne trace metals in Singapore. *J Environ Monit* 2004; 6: 813-8.
- Benoit G, Oktay-Marshall SD, Cantu A, Hood EM, Coleman CH, Corapcioglu MO, et al. Partitioning of Cu, Pb, Ag, Zn, Fe, Al, and Mn between filter-retained particles, colloids, and solution in six Texas estuaries. *Mar Chem* 1994; 45: 307-336.
- Broglio E, Saiz E, Calbet A, Trepát I, Alcaraz M. Trophic impact and prey selection by crustacean zooplankton on the microbial communities of an oligotrophic coastal area (NW Mediterranean Sea). *Aquat Microb Ecol* 2004; 35: 65-78.
- Bruland KW, Donat JR, Hutchins DA. Interactive influences of bioactive trace-metals on biological production in oceanic waters. *Limnol Oceanogr* 1991; 36: 1555-1577.
- Bryan GW, Langston WJ. Bioavailability, accumulation and effects of heavy metals in sediments with special reference to United Kingdom estuaries: a review. *Environ Pollut* 1992; 76: 89-131.
- Cardwell RD, Deforest DK, Brix KV, Adams WJ. Do Cd, Cu, Ni, Pb, and Zn biomagnify in aquatic ecosystems? *Rev Environ Contam Toxicol* 2013; 226: 101-22.
- Chan H-M, Rainbow PS. The accumulation of dissolved zinc by the shore crab *Carcinus maenas*. *Ophelia* 1993; 38: 13-30.
- Chen C, Amirbahman A, Fisher N, Harding G, Lamborg C, Nacci D, et al. Methylmercury in marine ecosystems: spatial patterns and processes of production, bioaccumulation, and biomagnification. *Ecohealth* 2008; 5: 399-408.

- Chen CY, Stemberger RS, Klaue B, Blum JD, Pickhardt PC, Folt CL. Accumulation of heavy metals in food web components across a gradient of lakes. *Limnol Oceanogr* 2000; 45: 1525-1536.
- Chou LM. Marine habitats in one of the world's busiest harbours. In: Wolanski E, editor. *The Environment in Asia Pacific Harbours*. Springer, New York, 2006, pp. 377-391.
- Comber SDW, Gunn AM, Whalley C. Comparison of the partitioning of trace metals in the Humber and Mersey estuaries. *Mar Poll Bull* 1995; 30: 851-860.
- Cuong DT, Karuppiyah S, Obbard JP. Distribution of heavy metals in the dissolved and suspended phase of the sea-surface microlayer, seawater column and in sediments of Singapore's coastal environment. *Environ Monit Assess* 2008; 138: 255-72.
- Cuong DT, Obbard JP. Metal speciation in coastal marine sediments from Singapore using a modified BCR-sequential extraction procedure. *Appl Geochem* 2006; 21: 1335-1346.
- Dassenakis M, Scoullou M, Gaitis A. Trace metals transport and behaviour in the Mediterranean estuary of Archelous River. *Mar Poll Bull* 1997; 34: 103-111.
- Debelius B, Forja JM, DelValls Á, Lubián LM. Toxic effect of copper on marine picophytoplankton populations isolated from different geographic locations. *Scien Mar* 2010; 74: 133-141.
- Duce RA, Hoffman G, Zoller H. Atmospheric trace metals at remote northern and southern hemisphere sites: Pollution or natural? *Science* 1975; 187: 59-61.
- El-Din NMN, Abdel-Moati MAR. Accumulation of Trace Metals, Petroleum Hydrocarbons, and Polycyclic Aromatic Hydrocarbons in Marine Copepods from the Arabian Gulf. *Bull Environ Contam Toxicol* 2001; 66: 110-117.
- Fisher NS, Bohé M, Teyssié JL. Accumulation and toxicity of Cd, Zn, Ag, and Hg in four marine phytoplankters. *Mar Ecol Prog Ser* 1984; 18: 201-213.
- Foster PL. Copper exclusion as a mechanism of heavy metal tolerance in a green alga. *Nature* 1977; 269: 322-323.
- Fukushima K, Saino T, Kodama Y. Trace metal contamination in Tokyo Bay, Japan. *Sci Total Environ* 1992; 125: 373-389.
- Gächter R, Máres A. MELIMEX, an experimental heavy metal pollution study: Effects of increased heavy metal loads on phytoplankton communities. *Schweiz Z Hydrol* 1979; 41: 228-246.

- Goh BPL, Chou LM. Heavy metal levels in marine sediments of Singapore. *Environ Monit Assess* 1997; 44: 67-80.
- González-Dávila M. The role of phytoplankton cells on the control of heavy metal concentration in seawater. *Mar Chem* 1995; 48: 215-236.
- Guevara-Riba A, Sahuquillo A, Rubio R, Rauret G. Assessment of metal mobility in dredged harbour sediments from Barcelona, Spain. *Sci Total Environ* 2004; 321: 241-155.
- Hatje V, Apte SC, Hales LT, Birch GF. Dissolved trace metal distributions in Port Jackson estuary (Sydney Harbour), Australia. *Mar Pollut Bull* 2003; 46: 719-730.
- Ho T-Y, Wen L-S, You C-F, Lee D-C. The trace-metal composition of size-fractionated plankton in the South China Sea: biotic versus abiotic sources. *Limnol Oceanogr* 2007; 52: 1776-1788.
- Hsiao SH, Fang TH, Hwang JS. The bioconcentration of trace metals in dominant copepod species off the northern Taiwan coast. *Crustaceana* 2006; 79: 459-474.
- Hu G-P, Balasubrahmanian R. Wet deposition of trace metals in Singapore. *Water Air Soil Pollut* 2003; 144: 285-300.
- Injuk J, Van Grieken R, De Leeuw G. Deposition of atmospheric trace elements into the North Sea: Coastal, ship, platform measurements and model predictions. *Atmos Environ* 1997; 32: 3011-3025.
- Jakobsen HH, Carstensen J. FlowCAM: Sizing cells and understanding the impact of size distributions on biovolume of -planktonic community structure. *Aquat Microb Ecol* 2011; 65: 75-87.
- Kaya G, Tuncel G. Trace element and major ion composition of wet and dry deposition in Ankara, Turkey *Atmos Environ* 1997; 31: 3985-3998.
- Kearney KA, Tommasi D, Stock C. Simulated ecosystem response to volcanic iron fertilization in the subarctic Pacific ocean. *Fish Ocean* 24: 395-413.
- Knops M, Altenburger R, Segner H. Alterations of physiological energetics, growth and reproduction of *Daphnia magna* under toxicant stress. *Aquat Toxicol* 2001; 53: 79-90.
- Kraepiel AML, Chiffoleau J-F, Martin J-M, Morel FMM. Geochemistry of trace metals in the Gironde estuary. *Geochim Cosmochim Acta* 1997; 61: 1421-1436.

- Kuss J, Kremling K. Spatial variability of particle associated trace elements in near-surface waters of the North Atlantic (30°N/60°W to 60°N/2°W), derived by large volume sampling. *Mar Chem* 1999; 68: 71-86.
- Laslett RE. Concentrations of dissolved and suspended particulate Cd, Cu, Mn, Ni, Pb and Zn in surface waters around the coasts of England and Wales and in adjacent seas. *Estuar Coast Shelf Sci* 1995; 40: 67-85.
- Lee B-G, Fisher NS. Decomposition and elemental release from zooplankton debris. *Mar. Ecol. Prog. Ser.* 1992; 88: 117-128.
- Li QS, Wu ZF, Chu B, Zhang N, Cai SS, Fang JH. Heavy metals in coastal wetland sediments of the Pearl River Estuary, China *Environ Pollut* 2007; 149: 158-164.
- Liu L, Xiong DQ, Gao XH, Song CY, Li FS. Characteristics of heavy metals contamination and distribution in surficial sediment of Haihe River and the adjacent sea area. *Mar Environ Sci* 2006; 25: 40-44.
- Mackey DJ, Butler ECV, Carpenter PD, Higgins HW, O'Sullivan JE, Plaschke RB. Trace elements and organic matter in the pristine environment: Bathurst Harbour, Southwestern Tasmania. *Sci Total Environ* 1996; 191: 137-151.
- Martin JH, Fitzwater SE. Iron deficiency limits phytoplankton growth in the north-east Pacific subarctic. *Nature* 1988; 331: 341-343.
- Martin JL. Metals in *Cancer irroratus* (Crustacea: Decapoda): Concentrations, concentration factors, discrimination factors, and correlations. *Mar Biol* 1974; 28: 245-251.
- Menasveta P, Cheevaparanapiwat V. Heavy metals, organochlorine pesticides and PCBs in green mussels, mullets and sediments of river mouths in Thailand. *Mar Pollut Bull* 1981; 12: 19-25.
- Monsefrad F, Imanpour Namin J, Heidary S. Concentration of heavy and toxic metals Cu, Zn, Cd, Pb and Hg in liver and muscles of *Rutilus frisii kutum* during spawning season with respect to growth parameters. *Iran J Fish Scien* 2012; 11: 825-839.
- Morel FMM, Hudson RJM, Price NM. Limitation of productivity by trace metals in the sea. *Limnol Oceanogr* 1991a; 36: 1742-1755.
- Morel FMM, Rueter JG, Price NM. Iron nutrition of phytoplankton and its possible importance in the ecology of ocean regions with high nutrients and low biomass. *Oceanography* 1991b; 4: 56-61.

- Munksgaard NC, Parry DL. Trace metals, arsenic and lead isotopes in dissolved and particulate phases of North Australian coastal and estuarine seawater. *Mar Chem* 2001; 75: 165-184.
- Nayar S, Goh BPL, Chou LM. Environmental impact of heavy metals from dredged and re-suspended sediments on phytoplankton and bacteria assessed in in situ mesocosms. *Ecotoxicol Environ Saf* 2004; 59: 349-369.
- Nayar S, Miller DJ, Hunt A, Goh BP, Chou LM. Environmental effects of dredging on sediment nutrients, carbon and granulometry in a tropical estuary. *Environ Monit Assess* 2007; 127: 1-13.
- Nugegoda D, Rainbow PS. In uptake rate and regulation breakdown in the decapod crustacean *Palaemon elegans* Rathke. *Ophelia* 1989; 30: 199-212.
- Owens RE, Balls PW. Dissolved trace metals in the Tay estuary. *Est Coast Shelf Sci* 1997; 44: 421-434.
- Pitchford JW, Brindley J. Iron limitation, grazing pressure and oceanic high nutrient-low chlorophyll (HNLC) regions. *J Plankton Res* 1999; 21: 525-547.
- Prosnier L, Loreau M, Hulot FD. Modeling the direct and indirect effects of copper on phytoplankton-zooplankton interactions. *Aquat Toxicol* 2015; 162: 73-81.
- Qiu YW. Bioaccumulation of heavy metals both in wild and mariculture food chains in Daya Bay, South China. *Est Coast Shelf Sci* 2015; 163: 7-14.
- Rejomon G, Balachandran KK, Nair M, Joseph T, Dinesh Kumar PK, Achuthankutty CT, et al. Trace Metal Concentrations in Zooplankton from the Eastern Arabian Sea and Western Bay of Bengal. *Environ Forens* 2008; 9: 22-32.
- Rejomon G, Dinesh Kumar PK, Nair M, Muraleedharan KR. Trace metal dynamics in zooplankton from the Bay of Bengal during summer monsoon. *Environ. Toxicol.* 2010; 25(6): 622-633.
- Resources WDoN. SQG-Concensus based sediment quality guideline. Recommendation for use and application. Department of interior, Washington D.C.20240. 2003: 17.
- Rossi N, Jamet JL. In situ heavy metals (copper, lead and cadmium) in different plankton compartments and suspended particulate matter in two coupled Mediterranean coastal ecosystems (Toulon Bay, France). *Mar Pollut Bull* 2008; 56: 1862-70.

- Sany BT, Sulaiman AH, Monazami GH, Salleh A. Assessment of sediment quality according to heavy metal status in the West Port of Malaysia. *World Acad Sci Eng Technol* 2011; 50: 633-637.
- Schmidt MA, Zhang Y, Hutchins DA. Assimilation of Fe and carbon by marine copepods from Fe-limited and Fe-replete diatom prey. *J Plakton Res* 1999; 21: 1753-1764.
- Schmoker C, Russo F, Drillet G, Trottet A, Mahjoub MS, Hsiao SH, et al. Effects of water residence times on plankton succession and food web dynamics in two marine inlets of Singapore. *J. Plakton Res.* submitted.
- Seng C-E, Lim P-E, Ang T-T. Heavy metal concentrations in coastal seawater and sediment off Prai Industrial Estate, Penang, Malaysia. *Mar Poll Bull* 1987; 18: 611-612.
- Stemberger R, Chen C. Fish tissue metals and zooplankton assemblages of northeastern U.S. lakes. *Can J Fish Aquat Sci* 1997; 55: 339-352.
- Strickland JDH. Measuring the production of marine phyto-plankton. *Bull Fish Res Bd Canad* 1960; 122: 1-172.
- Sunda WG, Guillard RRL. The relationship between cupric ion activity and the toxicity of copper to phytoplankton. *J Mar Res* 1976; 39: 567-586.
- Tan Q-G, Wang W-X. Contrasting patterns of cadmium bioaccumulation in freshwater cladocerans. *Limnol Oceanogr* 2011; 56: 257-267.
- Turner A, Millward GE, Schuchardt B, Schirmer M, Prange A. Trace metal distribution coefficients in the Weser estuary (Germany). *Continental Shelf Res* 1992; 12: 1277-1292.
- Twining BS, Baines SB. The trace metal composition of marine phytoplankton. *Ann Rev Mar Sci* 2013; 5: 191-215.
- Twining BS, Baines SB, Bozard JB, Vogt S, Walker EA, Nelson DM. Metal quotas of plankton in the equatorial Pacific Ocean. *Deep Sea Res II* 2011; 58: 325-341.
- Wang W-X, Fisher NS. Accumulation of trace elements in marine copepods. *Limnol Oceanogr* 1998; 43: 273-283.
- Wood AKH, Ahmad Z, Shazili NAM, Yaakob R, Carpenter RC. Geochemistry of sediments in Johor Strait between Malaysia and Singapore. *Cont Shelf Res* 1997; 17: 1207-1228.

- Wright DD, Frazer TK, Reinfelder JR. The influence of river plume dynamics on trace metal accumulation in calanoid copepods. *Limnol Oceanogr* 2010; 55: 2487-2502.
- Xu Y, Wang WX. Individual responses of metal assimilation and regeneration by copepod *Calanus sinicus* to changes in food quantity. *Mar Ecol Prog Ser* 2001; 218: 227-238.
- Zhou F, Guo HC, Hao ZJ. Spatial distribution of heavy metals in Hong Kong's marine sediments and their human impacts: a GIS-based chemometric approach. *Mar Poll Bull* 2007; 54: 1372-1384.
- Zwolsman JJG, Eck BTMs, Van der Weijden CH. Geochemistry of dissolved trace metals in the Scheldt estuary, southwestern Netherlands: Impact of seasonal variability. *Geochim Cosmochim Acta* 1997; 61: 1635-1652.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5