Science of the Total Environment 626 (2018) 307–318

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Trace metals and macroelements in mussels from Chinese coastal waters: National spatial patterns and normalization

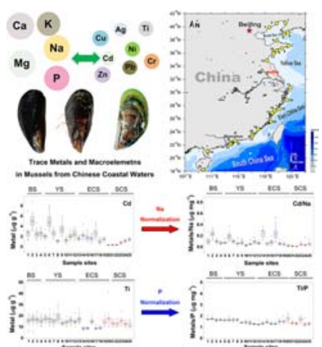
Guang-Yuan Lu, Wen-Xiong Wang *

Marine Environmental Laboratory, Shenzhen Research Institute, The Hong Kong University of Science and Technology (HKUST), Shenzhen 518000 Shenzhen, China
Division of Life Science, HKUST, Clearwater Bay, Kowloon, Hong Kong, China

HIGHLIGHTS

- Trace metals in mussels displayed differential patterns in the Chinese seawaters.
- Na and P normalization reduced the variability of metals in mussels from different locations.
- Na/P and body dry weight co-determined metal bioaccumulation in mussels.
- Nonlinear optimization of metals was necessary to assess bioaccumulation.
- Metal stoichiometry in bivalves showed elemental sources and accumulation mechanisms.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 12 November 2017
Received in revised form 1 January 2018
Accepted 3 January 2018
Available online xxxx

Editor: F.M. Tack

Keywords:
Mussels
Biomonitors
Metals
Non-linear analysis
Normalization

ABSTRACT

Metal contamination is one of the most ubiquitous and complex problems in the Chinese coastal environment. To explore the large-scale spatial patterns of bioavailable metals, we sampled three major mussels, including 784 blue mussels (*Mytilus edulis* Linnaeus, 1758) of 14 sites, 224 hard-shelled mussels (*Mytilus unguiculatus* Valenciennes, 1858) of 4 sites, and 392 green mussels (*Perna viridis* (Linnaeus, 1758)) of 7 sites, ranging from temperate to tropical coastlines of China, during August and September 2015. The concentrations of macroelements (Na, K, Ca, Mg, and P) and toxic trace metals (Ag, Cd, Cr, Cu, Ni, Pb, Ti, and Zn) in the mussel's whole soft tissues were determined. Among the four Chinese coastal basins, Cd, Ti and Cr in the mussel tissues were the highest at Bohai Sea (BS) and Yellow Sea (YS), and Cu, Ni, Pb and Ag in the mussel tissues were the highest at East China Sea (ECS) and South China Sea (SCS). Zinc concentrations in mussels from YS were significantly higher than those from the other regions. Given the variability of environmental conditions such as salinity and nutrients, we further normalized the measured tissue metal concentrations with tissue Na and P levels. After Na normalization as the salinity proxy, the variability of Cd, Cu, Zn, Ag, and Ni was reduced. Trace elements accumulation in the mussel tissues was significantly related to both macroelements (Na or P) and body dry weight. The present study demonstrated that nonlinear optimization of different elements was necessary in assessing metal bioaccumulation patterns in marine mussels at a large spatial scale.

1. Introduction

Metal contamination is one of the most ubiquitous, persistent and complex problems in aquatic environments (Pan and Wang, 2012;

* Corresponding author.
E-mail address: wwang@ust.hk (W.-X. Wang).

https://doi.org/10.1016/j.scitotenv.2018.01.018
0048-9697/

Wang et al., 2013; Le et al., 2016; Liu and Wang, 2016; Lu et al., 2017). Bivalves are often used as biomonitors of coastal water quality at different spatio-temporal scales, mainly because of their specific bioaccumulation characteristics as well as sessile lifestyle and filtering behavior (González-Fernández et al., 2015; Farrington et al., 2016; Hu et al., 2016; Capolupo et al., 2017). “Mussel Watch” or bivalve sentinel programs at local, regional, national and international scales have been well established to assess the geographic status and temporal trends of contaminants of environmental concern in the coastal ecosystems (Beyer et al., 2017; Chandurvelan et al., 2015; Zhou et al., 2008). Farrington et al. (2016) summarized the key attributes of bivalves as excellent candidates of sentinel organisms. With their wide distribution, filter-feeding ability and relatively robustness under conditions of moderate levels of pollution, mussels can accumulate metals from seawater by factors of 10^2–10^5. As primary consumers, they act as the vehicles for the transfer of anthropogenic pollutants from abiotic and biotic (phytoplankton) phases to higher trophic levels (Guitart et al., 2012; Baltas et al., 2017; Beyer et al., 2017; Bilgin and Uluturhan-Suzer, 2017). Mussels are also the commercially important seafoods in China, amounting to 70% of the total global production (data from 2017 Fisheries Statistics Yearbook of China).

Over the past decades, many studies have measured the metal concentrations in different bivalve species, waters and sediments in coastal environments (Pan and Wang, 2012; Chen et al., 2014; Baltas et al., 2017; Bilgin and Uluturhan-Suzer, 2017; Wang and Lu 2017). The effects of environmental and biological factors on different physiological aspects of metal bioaccumulation in bivalves have been extensively investigated (Chandurvelan et al., 2015; Wenne et al., 2016; Cunha et al., 2017; Bonnefille et al., 2018). Metal bioaccumulation in mussels are profoundly related to the environmental conditions, among which salinity is an important key factor (Heugens et al., 2001; Brown et al., 2004; Bussell et al., 2008). An important question is how to scientifically identify and assess the baseline concentration of bioavailable metals in the mussels. However, given the tremendous complexity of national coastal waters due to anthropogenic and naturally hydrographic variability, it is extremely challenging to compare the contamination levels (including metals) accumulated in mussels from different coastal ecosystems (Lu et al., 2017). Alarmingly high metal concentrations of Cd, Cu, Zn, Cr, Ni, and As in the sediments, water and marine bivalves from Chinese coastal areas were reported over the past few years, especially in the estuaries and bay areas (Pan and Wang, 2012; Wang et al., 2013; Lu et al., 2017).

Recently, it has been proposed that normalization based on Na (as a proxy for salinity) and P (as a proxy for nutrient) is a potential step to conduct realistic mapping of coastal contamination in complicated environmental settings (Lu et al., 2017). Liu and Wang (2015) reported a significant association between trace metal and major cations (Na, Mg, K, Ca) concentrations in blue mussels (*Mytilus edulis*) and green mussels (*Perna viridis*), and firstly suggested that simultaneous quantification of major cations with trace elements could benefit the assessment of metal bioaccumulation during biomonitoring. Yin and Wang (2017) applied sodium (Na) calibration of metals against salinity effect in oysters (*Crassostrea hongkongensis*) in the Pearl River Estuary from Southern China, and verified the feasibility of such method. At a national scale, Lu et al. (2017) successfully used Na-normalization of Cd and Ni, and P-normalization of Ti and Pb in the oyster tissues of China to assess metal contamination. Their study also identified the need of conducting non-linear analysis between macroelements and metals during biomonitoring. The aims of the present study were to conduct spatial analysis of metal contamination in the entire Chinese coastal waters using three common marine mussel species as monitoring organisms. Given the complexity of coastal environmental conditions, we applied the similar approach as reported earlier for oysters by normalizing the metals with Na (as salinity proxy) and P (as nutrient proxy) (Lu et al., 2017). We measured five macroelements and eight toxic trace metals in these mussels collected from 25 representative sites along the entire coastal waters of China, from temperate to tropical coastlines (109.7°E to 122.1°E, 18.2°N to 40.6°N). Finally, we conducted stoichiometric analysis of trace elements with an aim to further understand the elemental balance and nutritional status of marine mussels.

2. Materials and methods

2.1. Sampling

In this study, we identified 25 sites from the four Chinese coastal seas: Bohai Sea (BS), Yellow Sea (YS), East China Sea (ECS), and South China Sea (SCS), spanning from 109.7°E to 122.1°E, 18.2°N to 40.6°N. At each site, 50–60 mussels (average of 56 mussels) were collected from the surface and crevices of intertidal to shallow subtidal rocks and reefs during August to September 2015 (see details in Fig. 1 and Table 1; BS: LB, CZ, XKE, CI; YS: GLD, DSI, SGB, XQDI, ASB, JZB, GB, and HZB; ECS: SSI, YSI, NJI, SCH, SCT, LST, HMI, and DCB; SCS: NAI, DSV, GSI, MZ, and TLH). Three mature ordinary species of 784 blue mussels (common temperate species, *Mytilus edulis* Linnaeus, 1758, which may be confused with the Mediterranean mussel *Mytilus galloprovinvialis* Lamarck, 1819) of 14 sites, 224 hard-shelled mussels (endemic northwestern Pacific species, *Mytilus unguiculatus* Valenciennes, 1858) [unaccepted name as *Mytilus coruscus* Gould, 1861, corrected in World Register of Marine Species, WoRMS] of 4 sites, and 392 green mussels (common subtropical and tropical species, *Perna viridis* Linnaeus, 1758) of 7 sites with similar shell sizes (6.74 ± 1.12 cm Length, 3.48 ± 0.50 cm Height, and 2.41 ± 0.44 cm Width) were collected and ice-fresh transported to the Shenzhen Marine Environmental Laboratory within 24 h. Before elemental analysis, we selected healthy mussels and depurated them in clear seawater at 25 °C for two days to clear their gut materials.

2.2. Chemical analysis

After depuration of gut contents, the whole soft tissues of 1–3 mussels were dissected as one composite sample, and then washed with Milli-Q water. The soft tissues of 25 individual samples from each site were firstly measured for their wet weights, and then freeze-dried to constant weight at −45 °C (FDU-1200, Eyela, Japan) for at least 96 h, and recorded for their dry weights. For pretreatment, each 0.1 g homogenous sample was digested with 65% HNO_3 (Sigma-Aldrich) in Thermo tubes (polypropylene, USA) at 80 °C for 12 h. We used inductively coupled plasma-optical emission spectrometry (Optima 7000, ICP-OES, PerkinElmer, USA) to measure the macroelements concentrations (P, Na, Mg, K, and Ca) and inductively coupled plasma-mass spectrometry (NexION 300X, ICP-MS, PerkinElmer, USA) to measure the trace elements concentrations (Ag, Cd, Cr, Cu, Ni, Ti, Pb, and Zn). The accuracy of elements was checked using similar wet digestion of the standard reference materials of mussel tissue (SRM 2976) and oyster tissue (SRM 1566b) from the National Institute of Standards and Technology (NIST, Gaithersburg, Maryland, USA), and the reference marine sediment of IAEA-158 (for trace elements and methylmercury) from the International Atomic Energy Agency. The recoveries of all elements were within 98 to 104% of the reference values. Details of analysis procedure were described by Liu and Wang (2015) and Lu et al. (2017). Concentrations of all elements in mussel tissues were based on dry tissue weight.

2.3. Data analysis

We normalized the trace elements in the mussel tissues by Metals/Na and Metals/P due to their important roles in the balance of osmosis and nutrition in cells (Liu and Wang, 2015; Lin et al., 2016; Lu et al., 2017). Concentrations in each site were averaged for all 25 individual samples for the regional representatives. All statistical analysis and multivariate fitting were based on Origin 9.0 and IBM SPSS Statistics 22. Two