



# Statistical evaluation of biogeochemical variables affecting spatiotemporal distributions of multiple free metal ion concentrations in an urban estuary



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## HIGHLIGHTS

- We measured free ion levels of 5 metals over time at 5 inshore sites with Gellyfish.
- Significant correlations which varied over season were found among metals.
- We regressed free metal concentrations against 10 biogeochemical variables.
- pH, salinity, temperature & rainfall were key contributors to free ion variability.
- Free ion concentrations varied significantly over both season and location.

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## ABSTRACT

Free metal ion concentrations have been recognized as a better indicator of metal bioavailability in aquatic environments than total dissolved metal concentrations. However, our understanding of the determinants of free ion concentrations, especially in a metal mixture, is limited, due to underexplored techniques for measuring multiple free metal ions simultaneously. In this work, we performed statistical analyses on a large dataset containing repeated measurements of free ion concentrations of Cu, Zn, Pb, Ni, and Cd, the most commonly measured metals in seawater, at five inshore locations in Boston Harbor, previously collected using an in-situ equilibrium-based multi-metal free ion sampler, the 'Gellyfish'. We examined correlations among these five metals by season, and evaluated effects of 10 biogeochemical variables on free ion concentrations over time and location through multivariate regressions. We also explored potential clustering among the five metals through a principal component analysis. We found significant correlations among metals, with varying patterns over season. Our regression results suggest that instead of dissolved metals, pH, salinity, temperature and rainfall were the most significant determinants of free metal ion concentrations. For example, a one-unit decrease in pH was associated with a 2.2 (Cd) to 99 (Cu) times increase in free ion concentrations. This work is among the first to reveal key contributors to spatiotemporal variations in free ion concentrations, and demonstrated the usefulness of the Gellyfish sampler in routine sampling of free ions within metal mixtures and in generating data for statistical analyses.

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## 1. Introduction

Metal speciation determines the bioavailability, bioaccumulation, and toxicity of trace metals. Of all metal species in aquatic systems, the free ion is recognized as a form most readily taken up by organisms (Verweij et al., 1992; Sunda and Huntsman, 1998). In seawater, free ion metal concentration greatly impacts metal bioavailability and toxicity (Di Toro et al., 2001) and is a better

indicator of ecological risk than the total dissolved metal concentration (Ardestani et al., 2015). This has significant implications on environmental regulation of coastal water quality and ecological health (Paquin et al., 2002; Niyogi and Wood, 2004). Therefore, direct monitoring of free ion concentrations rather than total dissolved concentrations would provide more relevant information for ecological risk assessment and water quality management.

Free ion concentrations of metals, however, can be influenced by many biological, physical and chemical factors, such as the dissolved organic matter (DOM), pH, salinity, and temperature (Kester, 1986; Arakel and Hongjun, 1992). There has been extensive research regarding the interaction of DOM with metal speciation and its protective effect against metal toxicity (Meador, 1991; Schwartz et al., 2004; Seitz et al., 2015). For instance, humic substances, a major fraction of DOM in natural waters, were found to lower the concentrations of Cd and Zn ions by forming metal-humic acid complexes, reducing the bioavailability and toxicity of Cd and Zn to a green alga (Koukal et al., 2003). The formation of these binding complexes is strongly pH dependent, since hydrogen ion is a major cationic species that competes with free metal ions (Byrne et al., 1988). Salinity may also affect the binding of DOM and free metal ions through competition from the major ions, and metal toxicity has generally been found to decrease with increasing salinity (McLusky et al., 1986), which could not be accounted for by osmotic stress alone (Coglianese, 1982). Although direct temperature effects on complexation and speciation of most trace metals is only moderate (Byrne et al., 1988), free metal ion concentrations may be influenced indirectly by temperature as well as seasonal variations in biological production and natural ligand loading. Furthermore, along with the effects on metal speciation, there can be large spatiotemporal variations in these biogeochemical factors, leading to changes in free ion concentrations over space and time (Lathouri and Korre, 2015). For example, source-based DOM differences in streams influenced by both location characteristics and seasonal loading patterns were shown to cause variability in modeled free Cu concentrations (Cuss et al., 2010). Therefore, elucidating the key factors contributing to variability of free ion concentrations will be helpful in the application of biotic ligand model (Di Toro et al., 2001; Paquin et al., 2002; Niyogi and Wood, 2004; Campbell and Fortin, 2013) to predict aquatic toxicity and guide water quality regulations in marine systems.

The effects of these biogeochemical factors on free ion concentrations may also be modified by the presence of other metals, since different metals are usually present in natural waters concurrently. For example, competition from other metals for binding sites on natural ligands could decrease its binding propensity, resulting in a higher free ion concentration (Di Toro et al., 2001). Despite the importance of examining metal speciation in metal mixtures, the effect of biogeochemical parameters on free metal concentrations and interactions among metals have largely been understudied (Qiu et al., 2015), partly due to the lack of a reliable field sampling tool to simultaneously measure the free ion concentration of multiple metals. Although a few passive samplers are available for studying metal speciation, such as the diffusive gradient in thin films (DGT; Zhang and Davison, 1995) and the Chemcatcher passive sampler (Huang, 2006; Knutsson et al., 2013), the application in metal mixtures have been underexplored and multi-metal data are limited (Persson et al., 2001; Allan et al., 2007). To address this need, we developed the Gellyfish sampler, an in-situ equilibrium-based sampling device capable of determining free metal ion concentrations for multiple metals simultaneously in marine ecosystems (Senn et al., 2004; Dong et al., 2015). A brief description of the mechanism and structure (Supplementary Material, Figure S1) of the Gellyfish sampler is provided in the Supplementary Material.

Boston Harbor is an urban estuary located in a densely

populated area, with a history of organic and metal contamination primarily sourced from industrial effluents and urban sewage (Bothner et al., 1998). The inner harbor receives input from the Charles River, Mystic River and Chelsea Creek, and has a freshwater residence time of 2–10 days (Hilton et al., 1998). The outer harbor extends to the south and east of the inner harbor and is discharged by several rivers, including the Neponsett and Weymouth Rivers. In this work, we aimed to examine the spatial and seasonal variations in free metal ion concentrations of Cu, Zn, Pb, Ni and Cd in Boston Harbor, to evaluate correlations among metals, and to explore the effect of a variety of biogeochemical variables on free ion concentrations, based on previous Gellyfish measurements collected biweekly over ten months. This work is among the first to evaluate the effect of biogeochemical factors on free ion concentrations using a statistical approach. Our results revealed the key controls on the spatiotemporal variability of free metal ions and may be useful for identifying sites and time of the year with potentially higher free ion concentrations as monitoring priorities. Our work also demonstrated the usefulness of the Gellyfish in routine sampling of multiple free ion concentrations in coastal waters.

## 2. Materials and methods

### 2.1. Sampler preparation

The manufacturing of Gellyfish samplers was described in detail in previous publications (Senn et al., 2004; Lewis, 2006; Dong et al., 2015). The binding samplers contained 15  $\mu$ L of resin beads coated with iminodiacetic acid (IDA), embedded in a polyacrylamide gel matrix of 400  $\mu$ L (unhydrated volume). Blank samplers were constructed in a similar way as the binding samplers, but contained blank beads without IDA coating. Hydrated samplers were sandwiched between two Supor polysulfone membrane filters (Pall Corporation, East Hills, NY) with a pore size of 0.45  $\mu$ m, to protect them against biofouling during deployment. The hydrated samplers were round gel discs with an approximate thickness of 3 mm and a volume of 0.83 mL (Lewis, 2006). They were then assembled in a specially designed filter holder (Air Diagnostics and Engineering, Harrison, ME). This sampler configuration was shown to achieve 90% equilibrium within 3.3 days (Lewis, 2006).

### 2.2. Sampling procedures

The data used in this study were collected at two-week intervals from March to December 2005, at five inshore locations in Boston Harbor, including three sites in the inner harbor: Mystic River (MR), Inner Harbor (IH), Fort Point Channel (FPC), and two sites in the outer harbor: Savin Hill Cove (SHC), and the Marina Bay (MB) (Fig. 1). These sites were chosen based on their relative distance, proximity to potential contaminant sources, and ease of access.

A detailed description of our sampling process for free metal ions and total dissolved metals (operationally defined as species passing through a 0.45  $\mu$ m filter) was provided in Dong et al. (2015). Briefly, triplicate Gellyfish binding samplers and duplicate blank samplers were deployed in a plastic basket every two weeks at each of the five sites on the same day. All samplers were retrieved after six days of exposure and transported in sealed plastic bags to the Trace Metals Laboratory at Harvard T.H. Chan School of Public Health within 3 h, for subsequent extraction and chemical analysis. Upon retrieval, a 1 L seawater grab sample was collected at each site for subsequent determination of total dissolved metal and organic carbon concentrations.

Water temperature and salinity were measured in the field at the same time as the retrieval. Water pH was determined in the seawater samples immediately after they were brought back to the

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