Regional Studies in Marine Science ▮ (▮▮▮▮) ▮▮▮–▮▮▮

Contents lists available at ScienceDirect

Regional Studies in Marine Science

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

Composition of metals in suspended particulate matter of Alfonso basin, southern Gulf of California

Cristian Hakspiel-Segura [a], Aída Martínez-López [a,*], Paulina Pinedo-González [b], Gerardo Verdugo-Díaz [a], Juan David Acevedo-Acosta [a]

[a] Centro Interdisciplinario de Ciencias Marinas-IPN (CICIMAR), Av. Instituto Politécnico Nacional s/n, Col. Playa Palo de Santa Rita, La Paz, B.C.S. 23096, Mexico

[b] Department of Earth Sciences, University of Southern California, Los Angeles, CA 90089-0740, United States

HIGHLIGHTS

- Vertical profiles of particulate metals varied according hydrographical periods.
- Most of particulate metals present higher concentrations in the euphotic strata.
- Some particulate metals seem to be highly related to phytoplankton abundances.
- Phytoplankton is suggested as an important reservoir of particulate metals.

ARTICLE INFO

Article history:
Received 4 March 2015
Received in revised form
23 June 2015
Accepted 7 July 2015
Available online xxxx

Keywords:
Particulate metals
Particulate phosphorus
Alfonso basin
Hypoxic layer
Phytoplankton

ABSTRACT

Suspended particulate matter residues collected by 0.4 μm pore size filters were analyzed for 9 trace metals (M_p) and phosphorus (P_p) from seawater samples taken from depths ranging from 0–300 m. The samples were obtained from a marginal basin located in southwestern Gulf of California. Four different sampling trips occurred during the year to coincide with periods of known contrasting hydrographic conditions. The depth-integrated concentration values followed the sequence Fe > P_p > Zn > Cu > Ni > Mo > Cd > Pb > V > Co. Temporal and vertical distribution of the largest concentrations of M_p and M_p/P_p trace metals with their concentrations normalized to phosphorus were consistent with enrichment processes in March and May. These were respectively associated with intense mixing and a submesoscale cyclonic eddy. The highest abundances of autotrophic picoplankton and nanoplankton, diatoms and dinoflagellates and chlorophyll *a* concentrations were also noted at this time. Wind speed was the only environmental variable that correlated positively (Spearman, $p < 0.05$) with the temporal distribution of most of the M_p trace metals (except Cd, Co and V) in the euphotic zone, which was attributed to increases in the eolic contribution, sediment resuspension and horizontal transport towards the basin. The biological significance of Fe, Cu, Ni, Mo and V is discussed within the document based on the detected significant correlations with phytoplankton-assessed components. Our observations suggest a link between environmental forcing, the entrainment of metals and phytoplankton response as a reservoir of these metals in the euphotic zone, and as a possible source of replenishment for remineralization in the deeper layer. Future research should corroborate the assumptions about the origin and dynamics of dissolved and particulate fractions of metals and influence the biological activity and biogeochemistry of these elements in the basin.

1. Introduction

Particulate trace metals (M_P) and Particulate phosphorus (P_p) are key components in the biogeochemical cycles of many elements of the water column (Morel et al., 2003). They represent an intermediate stage in the transport of the chemical components in seawater to the seafloor sediments (Satyanarayana et al., 1990). M_P enters the marine environment through waterways, runoff, eolic transport, groundwater and submarine volcanic eruptions to name a few (Bruland and Lohan, 2004; Palenik et al., 2007; Tiefenthaler et al., 2008). However, within the water column, M_P are often regulated by physical ocean dynamics, which include

* Corresponding author. Tel.: +52 612 1234658x82434; fax: +52 612 122 53 22.
E-mail address: amartin@ipn.mx (A. Martínez-López).

http://dx.doi.org/10.1016/j.rsma.2015.07.001
2352-4855/

the overall circulation, currents, resuspension of continental shelf sediments, etc.; chemical remobilization (precipitation and dissolution) caused by changes in the redox conditions of the water column and sediments; and/or by the active participation of microorganisms through the assimilation of dissolved inorganic compounds and the remineralization of suspended organic matter (Bruland et al., 1991; Hutchins and Bruland, 1994; Holden and Adams, 2003).

Chemical properties of trace metals and their association with particulate matter enable their use as tracers of nutrient inputs, oceanographic conditions and biological processes (Burton and Stratham, 1988; Boehme-Terrana, 2007). In living organisms, some trace metals (e.g. Cu, Fe, Mn, Mo, Ni) are essential for proper physiological functioning, as they are key components of enzymes that catalyze biochemical reactions involved in organic matter production (photosynthesis and chemosynthesis) and nutrient cycling (Bruland, 1983; Sunda, 2012). Studies in marine environments and experimental systems reveal that iron and other metals play a key role in the composition of the plankton structure, the regulation of phytoplankton primary productivity, and nitrogen fixation in diazotrophs, among other processes (Howarth et al., 1989; Ho et al., 2003; Sunda, 2012). Under certain circumstances, the biological uptake of these elements can exceed their utilization and, thus, the capacity to store or bioaccumulate metals into compounds or organelles constitutes a strategy to isolate their toxic effects on cell components (Morel et al., 2003; Wright et al., 2010), and as a reservoir for maintaining metabolic activity in spite of limiting environmental levels of trace metals (Wilhelm and Trick, 1994; Marchetti et al., 2009). These relationships between trace metals and microbial physiological processes make of the plankton component a key reservoir of these elements in the particulate fraction. Despite the above, most studies on the dynamics of M_P have not provided detailed information on their interrelationships with the biological productivity of ecosystems.

So far, attempts to link M_p, as a component of environmental variability, to the activity and distribution of plankton populations has not been explicitly articulated as a definitive relationship. The value of this information has been underestimated compared to what is known about dissolved fractions of metals. This is partly derived from the inability to discern the origin or formative process of particulate matter (Dessai et al., 2011). However, this uncertainty has been reduced by implementing some specific procedures, which facilitates the postulation and defense of a number of hypotheses on the ecological role of metals in marine environments.

Procedures are currently available for efficiently removing trace metals that are adhered to or adsorbed onto the surfaces of minerals and organic matrices (including cell membrane surfaces), prior to the analysis of environmental samples, which would otherwise affect the actual concentration of metals in the particulate fraction (Tovar-Sánchez et al., 2004; Hassler and Schoemann, 2009). This has allowed a more accurate assessment of the contribution of this reservoir and, under certain conditions, of its relationship with the nutritional requirements and elemental stoichiometry of microbial populations (Tovar-Sánchez et al., 2004). However, in some cases (environments) these procedures fail to discriminate between the intracellular metal content and the natural contribution of inert particles, especially in coastal systems influenced by various inputs.

Marginal systems such as the Alfonso basin, La Paz Bay, comprise environments that are particularly interesting for investigating the distribution of M_P across the water column, since topographic features, ocean dynamics, oxygenation conditions of the water column and high biological productivity jointly lead to a broad range of redox conditions from the surface to bottom waters (Jacobs et al., 1985; Ho et al., 2004a; Dellwig et al., 2010).

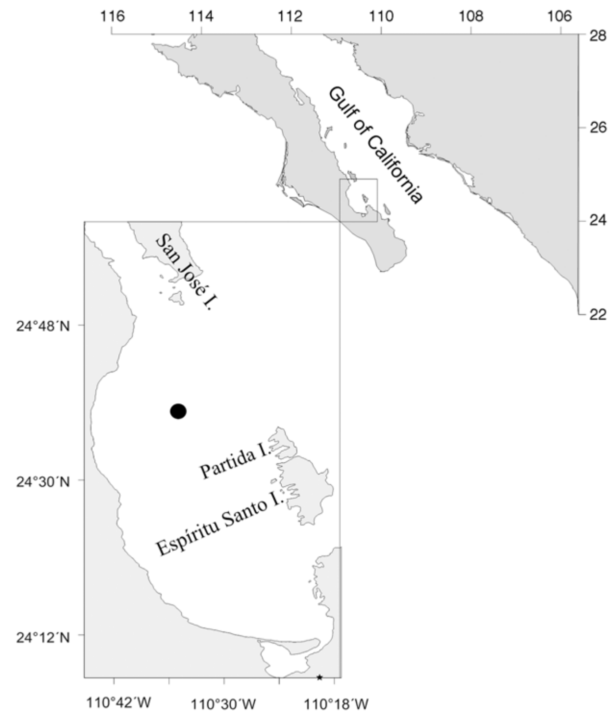

Fig. 1. Location the sampling station (●) in Alfonso basin, Bahía de La Paz.

Studies on particulate matter in La Paz Bay have examined and quantified the composition of some trace elements, including several M_P, in shallow coastal sediments (Choumiline, 2011; Pérez-Tribouillier and Choumiline, 2013), in sinking and suspended materials (Romero-Bañuelos, 2003; Rodríguez-Castañeda, 2008; Choumiline et al., 2010), and in sediments from the basin's deep portions (Pérez-Cruz, 2013). Nevertheless, the contribution and temporal behavior of M_P in the water column are still poorly known, as well as the chemical and biological processes that may affect them.

In this investigation, the concentration of several M_P (Fe, Cd, Co, Cu, Mo, Ni, Pb, V and Zn) and particulate phosphorus (P_p) were measured by means of High-Resolution Inductively-Coupled Plasma Mass Spectrometry in samples collected from the surface down to 300 m deep in the Alfonso basin during four periods of contrasting hydrographic processes, in order to examine potential interactions of these M_P with the abundance of some plankton fractions as a tracers for environmental conditions and the state of biological production and exportation along a dissolved-oxygen concentration gradient as an indicator of redox conditions.

2. Material and methods

2.1. Study site

The study site, within Alfonso basin, corresponds to a single monitoring station of oceanographic, biological and sedimentological variables since 2002 and is located in the northern part of one of the largest bays on the eastern edge of the Baja California peninsula (Fig. 1). This system is partially enclosed by the Espíritu Santo and La Partida islands, which allow water exchanges with the Gulf of California through two main inlets. The north mouth inlet is the largest and closest to the basin, which includes a threshold at a depth of ~275 m that prevents the entry of deeper water to the bay (Nava-Sánchez et al., 2001).

Three different water masses have been described for the basin, based on its topographic and oceanographic features: water masses from the Gulf of California, Subtropical Subsurface

Please cite this article in press as: Hakspiel-Segura, C., et al., Composition of metals in suspended particulate matter of Alfonso basin, southern Gulf of California. Regional Studies in Marine Science (2015), http://dx.doi.org/10.1016/j.rsma.2015.07.001