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Metal release from contaminated coastal sediments under changing pH conditions: Implications for metal mobilization in acidified oceans

Zaosheng Wang [a,*], Yushao Wang [b], Peihong Zhao [a], Liuqin Chen [a,c], Changzhou Yan [a,*], Yijun Yan [a], Qiaoqiao Chi [a]

[a] *Key Laboratory of Urban Environment and Health, Institute of Urban Environment, Chinese Academy of Sciences, 1799 Jimei Boulevard, Xiamen City 361021, China*
[b] *Key Laboratory of Tropical Marine Environmental Dynamics, South China Sea Institute of Oceanology, Chinese Academy of Sciences, Guangzhou 510301, China*
[c] *School of Environment, Northeast Normal University, Changchun 130117, China*

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ABSTRACT

To investigate the impacts and processes of CO_2-induced acidification on metal mobilization, laboratory-scale experiments were performed, simulating the scenarios where carbon dioxide was injected into sediment–seawater layers inside non-pressurized chambers. Coastal sediments were sampled from two sites with different contamination levels and subjected to pre-determined pH conditions. Sediment samples and overlying water were collected for metal analysis after 10-days. The results indicated that CO_2-induced ocean acidification would provoke increased metal mobilization causing adverse side-effects on water quality. The mobility of metals from sediment to the overlying seawater was correlated with the reduction in pH. Results of sequential extractions of sediments illustrated that exchangeable metal forms were the dominant source of mobile metals. Collectively, our data revealed that high metal concentrations in overlying seawater released from contaminated sediments under acidic conditions may strengthen the existing contamination gradients in Maluan Bay and represent a potential risk to ecosystem health in coastal environments.

1. Introduction

From the era when the industrial revolution began, CO_2 concentrations in the atmosphere have increased from 275 to 390 ppm. Notably, CO_2 levels above 400 ppm have been recorded recently at the National Oceanic and Atmospheric Administration's (NOAA's) Mauna Loa observatory (Rodriguez-Romero et al., 2014a). The oceans absorb CO_2 from the atmosphere which results in a reduction of oceanic pH by changing ocean carbonate chemistry leading to ocean acidification (OA). OA presents a threat of unprecedented scale to the marine environment, potentially causing great adverse impacts on the ecosystem. Based on this, carbon capture and storage (CCS) is proposed as one of the better strategies for the near-term reduction of atmospheric CO_2 emissions in order to avoid the abrupt and irreversible repercussions of global climate change (GCC) and OA. Nevertheless, practical implementation of this technological option could have significant impacts on marine ecosystems because CO_2 leakages deriving from the capture facilities, transport pipelines, and offshore installations would react with seawater and provoke more extreme acidification and significant changes in oceanic pH. Furthermore, some of potential subterranean structures for CO_2 storage are located near to the coastal areas of continental shelf, where sediments are contaminated with high concentrations of a wide variety of metals and organics (Payan et al., 2012a, 2012b). In this context, broad changes in seawater pH may enhance metal transfer from solid matrices to the liquid phase and metal concentrations in the seawater column may reach undesirable levels at a local scale producing serious negative effects in dynamic coastal systems (Khosrovyan and Riba, 2014). Consequently, in order to provide a more accurate and confident assessment of concurrent stressors related to metal release from marine sediments exposed to changes in pH, it is essential to preferably characterize how a reduction of pH in scenarios of ocean acidification, as well as in extreme and/or accidental CO_2 leakages, could influence the behaviors and release of metals bound to coastal sediments (Roberts et al., 2013).

Although functioning as a sink in polluted environments, the sediment system is not a final repository for metal contaminants. Metals in the sediment can reside in different geochemical fractions, i.e., exchangeable and water soluble, carbonate-, organic-, Fe–Mn oxide-bound and residual, showing a high variation in changing factors (pH, granulometry, temperature, etc.). In addition to the direct effects of a decrease of pH and increases in dissolved carbon dioxide (pCO_2), changes related to the CO_2-induced acidification would most likely lead to metal mobilization resulting from the dissolution of carbonates, sulfides and Fe–Mn oxide fractions, as well as by adsorption/desorption reactions at the sediment–water interface, and by ion exchange in sediments, which means that the release processes regarding the fate of metals in sediments as well as the magnitude of release are phase-

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[*] Corresponding authors.
E-mail addresses: zswang@iue.ac.cn (Z. Wang), czyan@iue.ac.cn (C. Yan).

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specific under changing environmental conditions (Apps et al., 2011). Previous studies have demonstrated that seawater acidification caused by an increase of CO_2 levels in the marine environment may produce metal mobilization from the surface of sediments to the seawater column (Ardelan et al., 2009), while limited studies have focused explicitly on the effect of pH on metal partitioning behavior in different geochemical fractions in contaminated sediments. Therefore, a better understanding of the complex mechanisms of metal release process to changing pH conditions is needed when the impacts of acidification on coastal contaminated sediments are being evaluated.

Maluan Bay (24°32′47″N, 118°00′38″E), a large embayment lagoon along the southeastern coast of China (Fig. 1), is subjected to a high spatial and temporal heterogeneity in abiotic conditions and to a multitude of anthropogenic pressures making this bay zone vulnerable to ocean acidification. Not limited to this, the levels of metal contamination in bay environments have increased notably as a result of anthropogenic activities over the past 30 years, especially in recent decades (Wang et al., 2015). This contributes, in particular, to the accumulation of metals in coastal sediments. When acidification is coupled with other anthropogenic factors, particularly with the presence of metals in sediment, it is very important to determine how a reduction in pH resulting from CO_2-induced acidification affects the behavior of sediment metals. Thus, these characteristics make this one of the most interesting areas for the study of interaction mechanisms between acidification processes and heavy metals.

The main objective of this study is to investigate the effects of simulated CO_2-induced acidification on the release and fate of metals incorporated in two coastal sediments with different physical properties and contamination levels under different scenarios of acidification. "Sediment–seawater–CO_2 contact systems" were examined in laboratory-scale experiments. These involved the direct release of CO_2 into samples of sediment overlain by seawater in non-pressurized chambers, mimicking both ocean acidification due to the uptake of CO_2 (pH: 7.3–7.7) and acidified seawater in possible scenarios of leakages from a CO_2 storage site (pH: 6.5–6.9), with pH = 6.5 as the expected local "worst-case" scenario.

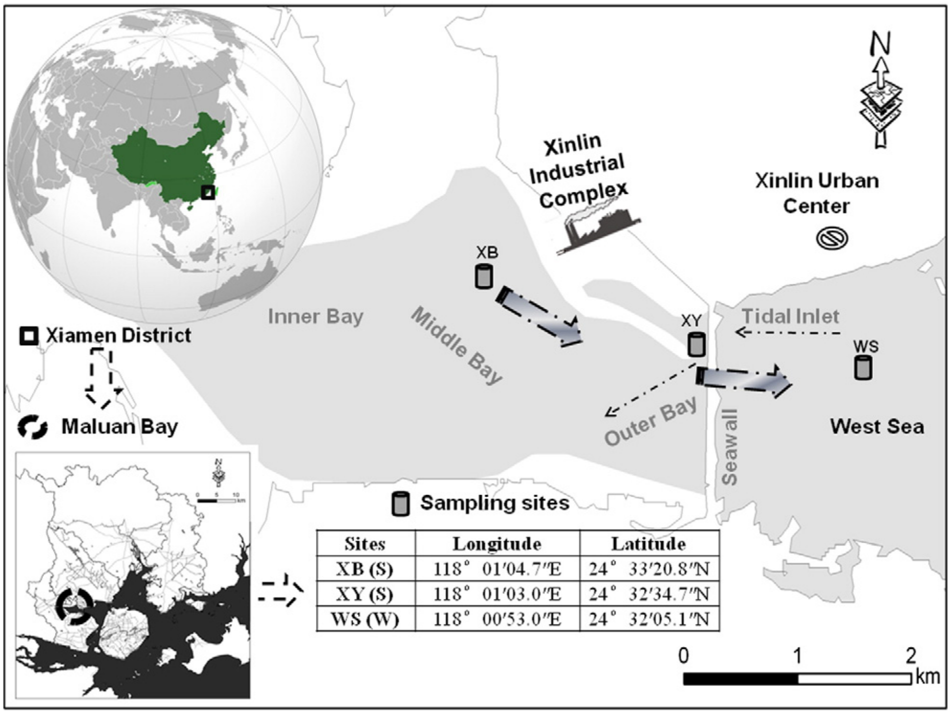
2. Materials and methods

2.1. Collecting sediment samples

Sediment samples were collected from two sites in Maluan Bay, a semi-enclosed lagoon located in the northwest of Xiamen promontory, on the southeastern coast of China (Fig. 1). The sites are mainly affected by industrialization, urban discharges, marine aquaculture and other anthropogenic activities such as the ship-building industry and aircraft manufacturing, causing different degrees of metal contamination in the bay area.

Specifically, site XB (XingBin) was subjected to intensive anthropogenic activities, receiving effluents from the heavily industrialized Xinlin complex of hundreds of industries, and the sediment from this site was heavily enriched by metal pollutants and could retain high amounts in the geochemical matrix. Thus, this site was believed to represent an ideal case for studying the effects of acidification on metal behavior and bioavailability. Another sediment sampling site selected in this work, nearest to the West Sea, site XY (XingYang) is representative of the whole narrow and shallow tidal coast of Maluan Bay. Considering that Maluan Bay daily receives tidal currents from the West Sea, the sediment from XY site was considered as a relatively uncontaminated reference site, although an artificial seawall constructed in 1960s restricts the exchange of seawater, and its seawater renovation is controlled by semi-diurnal tidal cycles. Further detailed information of the studied area and the characterization of sampling locations are presented in Fig. 1.

Approximately top 10 cm deep samples of surface sediments were collected using a stainless steel grab sampler and/or plastic spatula at each site. The samples were placed in acid-rinsed plastic containers with no head space and transported to the laboratory in a cooler box with ice packs at 4 °C. In the laboratory, they were stored below −20 °C in darkness until further processing and analysis. The seawater used in the experiments was collected from the surface of West Sea (WS) during high tide, transported to the laboratory, and placed in a 1000-L tank. The seawater was continuously filtered using a high-power external filter containing nitrate-removal stones. The seawater



Sites	Longitude	Latitude
XB (S)	118° 01′04.7″E	24° 33′20.8″N
XY (S)	118° 01′03.0″E	24° 32′34.7″N
WS (W)	118° 00′53.0″E	24° 32′05.1″N

Fig. 1. Schematic map of the Xiamen and Maluan Bay, showing the main geographical characterization of the general area sampled and locations of the sampling sites. The co-ordinates are given in the central table. Dashed black arrows indicate tidal flow directions and bold rectangular arrows represent directions of metal mobilization (see the parts of Results and discussion).