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Multivariate analysis of heavy metal contaminations in seawater and sediments from a heavily industrialized harbor in Southern Taiwan

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ABSTRACT

Heavy metal pollution, including chromium, zinc, arsenic, cadmium, mercury, copper, lead, and aluminum, in the largest industrial harbor in southern Taiwan was investigated. Increasing metal contamination was observed by monitoring heavy metal concentrations in seawater and sediments and estimating the enrichment factors, particularly those inside the harbor. Compared to other metal-polluted harbors worldwide, the presence of chromium in the sediments was relatively high. Excluding the background contribution, the harbor area was polluted by outflows from river mouths, wastewater discharging pipes, and point sources near industrial activities within the harbor. It is shown by principal component and cluster analyses that metal contamination was affected by a wide range of different and complex contamination mechanisms inside and outside the harbor, suggesting managing the pollution using straightforward strategies, i.e., solutions that only consider a single source or single pathway of metal emissions, is problematic.

1. Introduction

Translocation, deposition, remobilization, and accumulation of heavy metals have been important issues for the marine environment and ecology. Recognitions regarding contamination and relative magnitudes from different sources, including natural and anthropogenic activities, have been widely discussed and reported (Rainbow, 1995; Guerra-Garcia and Garcia-Gomez, 2005). One reason for heavy metals to be of concern is their deleterious effects on the environment and public health, especially if present at levels above a toxicity threshold (MacDonald et al., 1996; O'Connor, 2004). For example, copper (Cu) and zinc (Zn) are two metals that can be transported and accumulated in marine sediments and organisms like many other metal elements (Miao et al., 2005; Lin et al., 2011). High levels of Cu and Zn in water have been found to damage marine life by reduced cell division rates, oxidative damage, interference with cellular events, and cell death, causing damage to gills, liver, kidneys and nervous systems (Flemming and Trevors, 1989; Stohs and Bagchi, 1995). At low concentrations, chronic exposure to water or sediments contaminated with these metals can result in reduced growth and photosynthesis of flora and changes in the abundance and taxonomic composition of fauna (Morrisey et al., 1996). Many other heavy metals, including chromium (Cr), arsenic (As), cadmium (Cd), mercury (Hg), and lead (Pb), also cause various acute or chronic toxicities; the bioaccumulation potential of these heavy metals enhances their environmental problems (Bryan and Langston, 1992).

Heavy metals in aquatic environments are increasingly recognized as important intermediate sources for subsequent pollution in aquatic ecosystems or public health. Considerable efforts have been expended to assess their presence in harbors and estuaries. After being released from natural background or anthropogenic sources near the land surface, e.g., rivers carrying significant metal loadings, soluble heavy metal species are immobilized and deposited onto the sediment surfaces through various mechanisms. These immobilization mechanisms include adsorption onto soil/sediments by ion exchange, coagulation with dissolved or suspended species in water (e.g., organic matter), incorporation into the lattice structure of minerals, and precipitation by forming insoluble species of heavy metals (Bryan and Langston, 1992; Du Laing et al., 2009). The high salinity of seawater enhances the aggregation of suspended particles, resulting in more rapid sedimentation of heavy metals (Du Laing et al., 2009). As a consequence, the water and soil/sediments in harbors and estuaries serve as a pool for heavy metals to be adsorbed, accumulated, and released to nearby and overlying areas (Guerra-Garcia and

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Garcia-Gomez, 2005; Chen et al., 2007). While many marine organisms, particularly those bound to marine sediments, may uptake heavy metals and play important roles in the food chain, the adverse effects of heavy metals in aquatic environments on the ecosystem and public health may be further enhanced (Bryan and Langston, 1992; Chapman and Wang, 2001).

Kaohsiung Harbor is the largest international industrial port in Taiwan, containing more than one hundred docks, industrial zones, fishing ports, shipyards, and commercial and recreational areas. Since 2000, the harbor has seen more than forty thousand vessels annually (http://www.khb.gov.tw). The pollution in this area originates from local activities and four rivers, i.e., the Love River, the Canon River, the Jen-Gen River, and the Salt River. These rivers are polluted by domestic, agricultural, pasturage, and industrial wastewaters received upstream, directly contributing to and worsening the pollution in Kaohsiung Harbor. Moreover, two other rivers in the north, a southern developing industrial area, and three wastewater discharging pipes outside the harbor provide additional heavy metal contributions to the harbor area. Kaohsiung city is the largest city in southern Taiwan and is closely connected to the harbor area. Because nearly three million people reside in this metropolitan area, the potential impacts of environmental pollution in the harbor have caused great concern for local governments and the general public (Chen and Wu, 1995; Chen et al., 2007).

The objective of this study is to investigate the spatial and temporal distributions of heavy metals in seawater and sediments from this heavily industrialized harbor area and to characterize the pollution by using multivariate statistical methods, including principal component analysis (PCA) and cluster analysis. The heavy metals of interest are Cr, Zn, As, Cd, Hg, Cu, and Pb. Aluminum (Al) in sediments was analyzed to facilitate the estimation of enrichment factors (EFs) of metals at different locations. In total, sixteen sampling locations were selected to comprehensively monitor the harbor area, seven locations inside the harbor and nine sites outside the harbor. The metal profiles of the areas inside and outside the harbor were established by using the respective concentration distributions and variations. Moreover, they were studied using PCA and cluster analysis to determine the important metal species and, more importantly, the inherent characteristics of metal pollution at different locations.

Fig. 1. Map of the investigated area and monitoring sites in this study.

2. Materials and methods

2.1. Study area and monitoring sites

Fig. 1 shows the map of the examined area and monitoring locations in this study. 16 monitoring sites include stations near the four river mouths (sites 1, 2, 10, and 11 for Dian-Bao Creek, Hojing Creek, the Love River, and the Jen-Gen River, respectively), two stations at seawater bathing beaches (sites 3 and 4), stations near the exits of three wastewater discharging pipes (sites 5, 6, and 7), one near a southern industrial park (site 8), one at 2.5 nautical miles away from the coast (site 9), one location at a pier inside the harbor (site 12), one location near several shipbuilding, steel and petroleum industries, and a combustion plant (site 13), one station at the south exit of the harbor and near a coking coal transport service (site 14), and two stations near different fishing ports (sites 15 and 16). Stations 1 through 9 were located outside the harbor and stations 10 through 16 were used to monitor metal pollution inside the harbor.

2.2. Seawater and sediment sampling

For each monitoring site, seawater and sediment samples were collected and analyzed in May and October 2010 (denoted later as seasons 1 and 2, respectively). The environmental conditions of these two seasons are given in Table 1. All containers used to collect and store seawater and sediments were pre-washed using 10% nitric acid and reverse osmosis (RO) water, followed by oven drying at 40 °C. For seawater sampling, water quality parameters including temperature, salinity, and dissolved oxygen were analyzed on-site by using a water quality sensor (Compact-AAQ1183-IF, ALEC Electronics Ltd., Japan). Seawater samples were collected at two different depths (1 or 2 m below the surface and 1 or 2 m above the bed) to test the sensitivity of the results to water depth. For trace metal analysis, 300 ml of seawater was sampled in plastic containers, acidified to pH < 2, and stored in darkness at 4 °C for subsequent analysis in the laboratory. Marine sediments were sampled with an Ekman Dredge grab sampler (6" × 6" × 6", Jae Sung International Co.) (TWEPA, 2003a). After collection, sediment samples were stored in acid-washed plastic bags at 4 °C (24 cm × 34 cm, with a maximum load weight of 10 kg and the bag thickness exceeding 0.1 mm). In the laboratory, samples were kept at −20 °C until further processing and analysis. Samplings were at least triplicated to ensure the representativeness of the samples.

2.3. Sample processing and analysis

For metal analysis in seawater, samples were pre-treated to remove high concentrations of salt in the samples (TWEPA, 2003b).