



Heavy metal pollution in the surface water of the Yangtze Estuary: A 5-year follow-up study



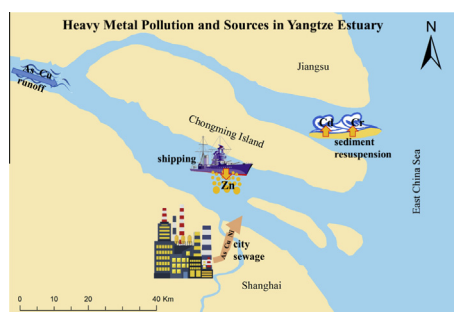
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HIGHLIGHTS

- Heavy metals were divided into two groups with different temporal–spatial distribution.
- Each heavy metal source was synthetically and clearly differentiated.
- Health indices of the eight metals fall within three gradients.

GRAPHICAL ABSTRACT



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ABSTRACT

The temporal–spatial changes in the concentration and health risk of eight dissolved heavy metals in the Yangtze Estuary over a 5-year period were discussed based on large-scale sampling data. Special attention was paid to the differentiation of metal sources. Concentrations of the metals were present in the following order: $Zn \gg As > Cu > Cr > Ni > Pb > Cd > Hg$, but the hazard quotient indices could be obviously divided into three gradients. More attention should be paid to As, Ni, Pb, and Cr because they increased yearly. Cu, Ni, Pb and As had higher health risks in the nearshore zones, while higher health risks of Zn, Cr, Cd, and Hg were observed in the estuarine channel. Correlations and hierarchical cluster analysis results of metal sources were consistent well with those obtained by temporal–spatial distributions. Shipping activities were the largest contributor to the elevated Zn concentrations in the estuary, while Megacity Shanghai significantly affected the Ni, Cu and As pollution. Yangtze River runoff was the primary source of Cu and As in the estuary. Cd and Cr pollution were closely related to the sediment release under the drive of the “salt-out effect”.

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1. Introduction

Estuary is one of the most productive environments, supporting many different ecosystem goods and services (Savage et al., 2012). However, estuaries have been universally degraded by increasing pressure caused by population growth and development of anthropogenic activities, making these systems peculiarly susceptible to

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various types of contaminations (Mathews and Fisher, 2008). Thus, estuaries have drawn increasing attention and have been the research focus all over the world in the past several decades.

The Yangtze Estuary in China receives approximately 90% of terrestrial materials entering the East China Sea (Zhou et al., 2010). It also acts as an important water source of the Megacity Shanghai, providing uses such as irrigation, navigation, and other functions (An et al., 2010). However, the Yangtze River has been listed as one of the World's Top 10 Rivers at Risk by the World Wild Fund for Nature (WWF), and the water environment in the estuary has been shown to be significantly altered (Dai et al., 2010). It is urgent

and significant to investigate the current pollution levels and the evolution trend of the estuary.

In the past decade, extensive endeavors have been made to investigate the distribution, source and risk of estuarine heavy metal pollution because of its ubiquity, recalcitrance, bioaccumulation, and toxicity (Kalloul et al., 2012; Yang et al., 2012). To date, researches have primarily focused on the pollution of metals in the surface sediments (Li et al., 2013) and sediment cores (Feng et al., 2014). However, relatively few efforts have addressed heavy metals dissolved in the surface water of the estuary, though the water-soluble metals possess more direct and significant environmental threats.

Previous research focuses were mainly on the concentration changes of dissolved heavy metals across a salinity gradient of surface water or in the surface, middle, and bottom water layer in the Yangtze Estuary (Wang et al., 2009). Generally, investigations were focused on metal distribution in a portion of the estuary at a certain time period, which cannot reflect the overall and long-term status of heavy metal pollution in the estuary. To our knowledge, there is no report that comprehensively analyzes the continuous concentration changes of dissolved metals in the past decade, although the Yangtze River and its estuary suffered serious impacts from anthropogenic activities such as water impoundment of the Three Gorges Dam and large-scale channel dredging. Moreover, a comprehensive investigation into the temporal–spatial differences of the sources and the health risks of heavy metals in the entire estuary in the past decade is lacking.

Therefore, in this study, water samples were taken at 50 sites (including nearshore zone, estuarine channel and adjacent sea) and 7 typical geographic positions in three hydrologic seasons (i.e., wet, normal and dry) in the past 5 years (2010–2014) to analyze the concentration distribution of eight ubiquitous metals (As, Cd, Cr, Cu, Ni, Pb, Zn and Hg) with statistical analysis and correlation analysis

methods. The temporal–spatial changes of the heavy metal health risk evaluated with hazard quotient indices were also studied. Special attention has been paid to the source differences of each metal in the estuary, with the main purpose of providing comprehensive information on metal pollution changes in the entire estuary.

2. Materials and methods

2.1. Study area and sample collection

The Yangtze Estuary is one of the largest estuaries in the world, with a mouth approximately 90 km wide. The estuary has a complicated topography and is bifurcated into the north branch and the south branch by Chongming Island (Fig. 1). A detailed description of the estuary terrain can be found in our previously published study (Li et al., 2012).

Fifty typical sampling sites are shown in Fig. 1A, including 20 sites in the nearshore zone, 19 sites in the estuarine channel and 11 sites in the adjacent sea. Water samples were collected in August 2010 (2010-08, wet season), November 2010 (2010-11, normal season), February 2011 (2011-02, dry season) and May 2011 (2011-05, wet season). Moreover, 16 sampling sites in seven typical sections within the estuarine channel were taken (Fig. 1B) in July 2013 (2013-07, wet season), October 2013 (2013-10, normal season) and February 2014 (2014-02, dry season). All water samples were filtered with 0.45 μm fiberglass membranes immediately after sampling. The filtrates were stored at 4 $^{\circ}\text{C}$ and analyzed within 2 weeks.

2.2. Measurements of heavy metals

Metal concentrations were measured by the Institute of Geophysical and Geochemical Exploration (IGGE), Chinese

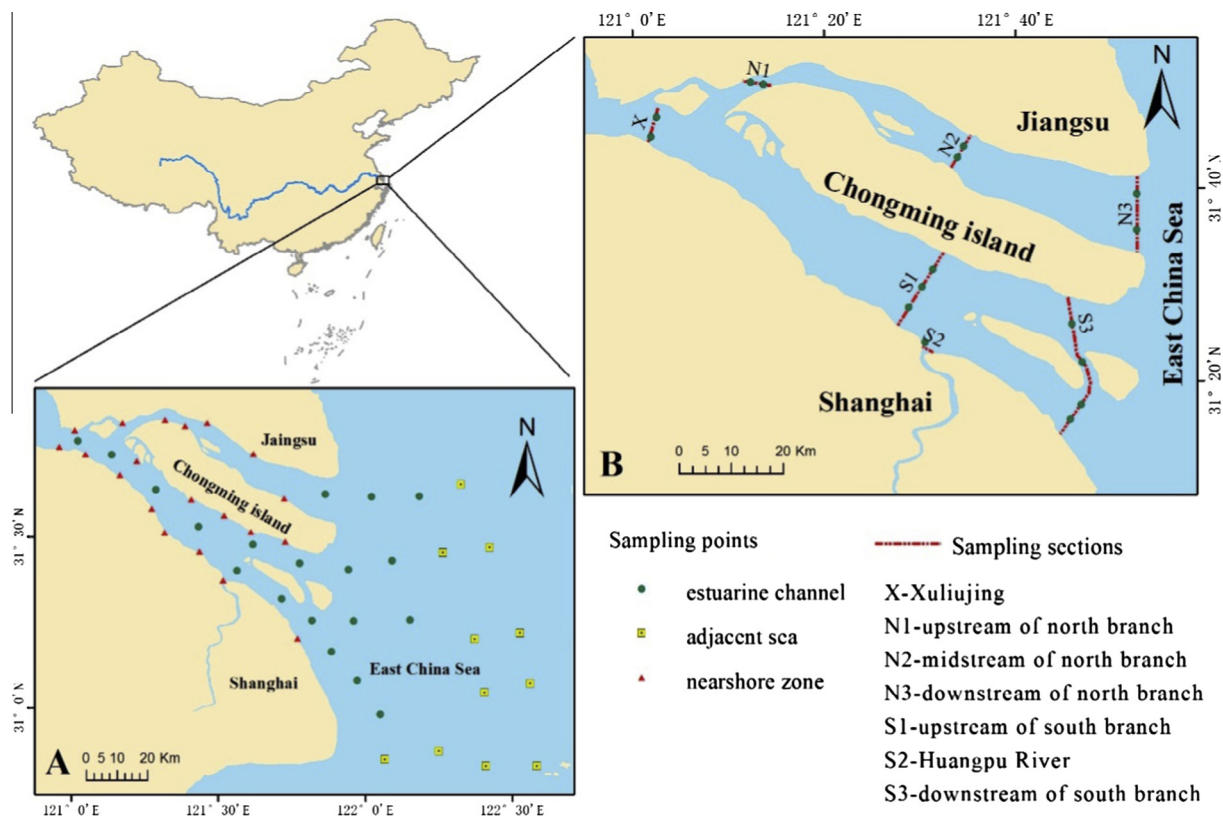


Fig. 1. Study area and geographical location of the sampling sites (A) and sampling sections (B) in the Yangtze Estuary in China. The upper left figure shows the geographical location of the Yangtze River and the estuary in China.

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