Chemosphere 155 (2016) 564–572

Contents lists available at ScienceDirect

Chemosphere

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

Contribution of the upper river, the estuarine region, and the adjacent sea to the heavy metal pollution in the Yangtze Estuary

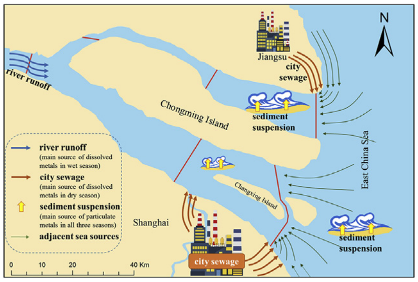
Su Yin [a], Yuehan Wu [b], Wei Xu [a], Yangyang Li [b], Zhenyao Shen [a, b], Chenghong Feng [a, b, *]

[a] State Key Laboratory of Water Environment Simulation, School of Environment, Beijing Normal University, Beijing 100875, PR China
[b] The Key Laboratory of Water and Sediment Sciences, Ministry of Education, School of Environment, Beijing Normal University, Beijing 100875, PR China

HIGHLIGHTS

- City sewage and sediment suspension dominate metal pollution in the Yangtze Estuary.
- River runoff significantly affects dissolved metal pollution only in the wet season.
- Particulate metals were mainly from sediment suspension in the Yangtze Estuary.
- Section fluxes and statistical analysis methods provide identical metal sources.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 21 November 2015
Received in revised form
10 February 2016
Accepted 24 April 2016
Available online 4 May 2016

Handling Editor: Martine Leermakers

Keywords:
Heavy metals
Flood-ebb tides
Section flux
Contribution
Yangtze Estuary

ABSTRACT

To determine whether the discharge control of heavy metals in the Yangtze River basin can significantly change the pollution level in the estuary, this study analyzed the sources (upper river, the estuarine region, and the adjacent sea) of ten heavy metals (As, Cd, Co, Cr, Cu, Hg, Ni, Pb, Sb, and Zn) in dissolved and particulate phases in the surface water of the estuary during wet, normal, and dry seasons. Metal sources inferred from section fluxes agree with those in statistical analysis methods. Heavy metal pollution in the surface water of Yangtze Estuary primarily depends on the sediment suspension and the wastewater discharge from estuary cities. Upper river only constitutes the main source of dissolved heavy metals during the wet season, while the estuarine region and the adjacent sea (especially the former) dominate the dissolved metal pollution in the normal and dry seasons. Particulate metals are mainly derived from sediment suspension in the estuary and the adjacent sea, and the contribution of the upper river can be neglected. Compared with the hydrologic seasons, flood-ebb tides exert a more obvious effect on the water flow directions in the estuary. Sediment suspension, not the upper river, significantly affects the suspended particulate matter concentration in the estuary.

1. Introduction

Heavy metal pollution in estuaries has received much attention because of its toxicity, wide sources, non-biodegradable properties, and accumulation behaviors (Yu et al., 2008; Wei et al., 2009). Identifying the sources of pollution has become a popular research topic in recent years, and many different methods, e.g., multivariate statistical analysis, the Pb isotope tracer technique and the spatial distribution method, were used in previous studies. (Qi et al., 2010; Adokoh et al., 2011; Pope and Langston, 2011; Legorburu et al.,

---

* Corresponding author.State Key Laboratory of Water Environment Simulation, School of Environment, Beijing Normal University, Beijing 100875, PR China.
E-mail address: fengchenghong@hotmail.com (C. Feng).

http://dx.doi.org/10.1016/j.chemosphere.2016.04.095

2013; Xu et al., 2014). Emphasis was mainly placed on differentiating the proportion of heavy metals from natural or anthropogenic sources (Adokoh et al., 2011; Xu et al., 2014). Studies have also addressed the origin of the anthropogenic heavy metals (e.g., domestic sewage, industrial sewage, agricultural sewage, etc.) (Li et al., 2013; Gu et al., 2014). However, based on the metal source identification methods, it remains unclear whether the discharge control of heavy metals in river basins can significantly change the pollution level in estuaries.

Estuaries are often subject to marine influences (e.g., tides and saline water) and riverine influences (e.g., flows of fresh water and sediment). The inflows of sea water and fresh water provide high levels of heavy metals in the water and sediment phases, making estuaries among the most heavily polluted areas of the world. Moreover, approximately 60% of the population of the world lives along estuaries. The ever-increasing human activities also dramatically deteriorate the estuarine environment (Li et al., 2012a). The premise for the recognition of heavy metal pollution in estuaries is to specify their sources. To date, there is no report to synthetically elucidate the roles of upper river runoff, the estuarine region (including estuarine cities, sediment suspension, etc.), and the adjacent sea regarding heavy metal pollution in estuaries.

Tidal currents are the main physical features of estuarine circulation flows (Meerhoff et al., 2013). The rise and fall of tides influence the structure and spreading of water current by straining and stirring effects (Zu et al., 2014). The tide carries an influx of particles (Schindler et al., 2013) and is a means for pollutants to move into and out of estuaries (Meerhoff et al., 2013). To fully examine the contributions of river runoff, the estuarine region and the adjacent sea, the role of tides must be seriously considered. Analyzing tidal pollutants fluxes in key sections of estuary might be an effective method to infer the contributions of the three different source ways.

The Yangtze Estuary is one of the largest estuaries in the world, with a mouth approximately 90 km wide (Yan et al., 2013). The complicated topography and influence of tides and saltwater intrusion cause remarkable differences between water currents in the north branch and south branch of the estuary and between different hydrologic seasons (Qiu et al., 2012). Moreover, the World Wild Fund for Nature (WWF) has listed the Yangtze River as one of the World's Top 10 Rivers at Risk, and the estuary bears the largest amount of wastewater in China. It is an ideal estuary to probe the contributions of the river runoff, the estuarine region, and the adjacent sea for heavy metal pollution in estuaries.

Therefore, concentrations of ten heavy metals (As, Cd, Co, Cr, Cu, Hg, Ni, Pb, Sb, and Zn) in the dissolved and particulate phases in seven key sections of the Yangtze Estuary were comprehensively investigated during flood and ebb tides during the wet, normal and dry seasons. The differences of metal fluxes between these sections and the flood-ebb tides were calculated. Furthermore, multivariate statistical analysis methods (i.e., correlation analysis and principal component analysis) and geostatistical approaches were also used to verify and detail the three source proportions. The main purpose is to clarify the contribution of the upper river, the estuarine region, and the adjacent sea to the heavy metal pollution in the surface water of Yangtze Estuary.

2. Materials and methods

2.1. Study area and sample collection

The 16 sampling sites, the seven sections (X, N1–N3 and S1–S3), and the location of the Yangtze Estuary in China are shown in Fig. 1. Surface water and suspended particulate matter (SPM) were collected at the 16 sampling sites with borosilicate glass bottles and home-made filters in July 2013 (2013-07, wet season), October 2013 (2013-10, normal season) and February 2014 (2014-02, dry season). Acoustic Doppler Current Profilers (ADCP) (Fig. 1C) were used to measure the flow velocity, cross sectional area, the flow direction of the water current and the SPM concentration of each section. All of the work was completed during flood and ebb tides. Before analysis, the water samples were filtered through a pretreatment fiberglass membrane (0.45 μm in pore size), and SPM samples were naturally air-dried.

2.2. Heavy metal measurements

The concentrations of heavy metals were measured at the Institute of Geophysical and Geochemical Exploration (IGGE), Chinese Academy of Geological Sciences, which is certificated by the China National Accreditation Board for Laboratories. The concentrations of As and Sb were measured by hydride generation atomic fluorescence spectrometry (HG-AFS, GB/T 7485-1987); the concentrations of Hg were measured by cold vapor atomic fluorescence spectrometry (CV-AFS, GB/T 7468-1987); the concentrations of Cd, Co, Cr, Cu, Ni, Pb, and Zn were measured by high resolution inductively coupled plasma mass spectrometry (HR-ICP-MS, Thermo); and the concentrations of Fe and Mn were measured by inductively coupled plasma-atomic emission spectrometry (ICP-AES). The method accuracies were systematically and routinely examined with standard reference materials (GSF, ULTIMA, HORIBA Jobin Yvon). The laboratory reagent blanks, replicate samples for each batch of 10 samples, standard reference materials, which were designated by IGGE and ratified by Administration of Quality Supervision, Inspection and Quarantine (AQSIQ), were all analyzed to examining the method accuracies. Reproducibility was found to be at the 95% confidence level. The measuring results of heavy metal concentrations in dissolved and particulate phases are briefly detailed in Appendix Table A.1.

2.3. Heavy metal flux calculation and statistical methods

Heavy metal flux in each section was calculated by the following equation, which was reported in previous studies to examine other materials (Liu et al., 2010; Bouchez et al., 2011):

$$F_W = c_W v S$$

$$F_S = c_s c_{spm} v S$$

where F_W and F_S are the flux of the dissolved and particulate metals, respectively; c_w is the concentration of dissolved metals; v is the flow velocity of the section; S is the section area; c_s is the heavy metal content of SPM; and c_{spm} is the average SPM concentration of the section. Correlation analysis and principal component analysis (PCA) were often used for the interpretation of large, complex data (Krishna and Mohan, 2014). The two multivariate statistical analysis were evaluated by PASW 18.0 (SPSS Inc., Chicago, IL, USA) and could be used to determine the heavy metal sources (Swarnalatha et al., 2014; Xie et al., 2014). The spatial variation of SPM concentrations and the factor scores on the principal components were analyzed with the geostatistical method and ArcGIS 9.3. Geostatistics involves describing spatial patterns (semivariograms) and predicting the values of the attributes at locations that have not been sampled (kriging). Ordinary kriging is the most widely used geostatistical technique, and it considers the direction of variations and incorporates trends into the interpolation to create better predictions (Wang et al., 2014). Ordinary kriging is estimated by a linear combination of the observed values with weights, as follows (Wang et al., 2014):