ARTICLE IN PRESS

Marine Pollution Bulletin xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Marine Pollution Bulletin

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

Spatial and temporal variations of heavy metals in marine sediments from Liaodong Bay, Bohai Sea in China

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ARTICLE INFO

Keywords:
Sediment
Spatial distribution
Trend
Heavy metals
Source analysis

ABSTRACT

An integrated analysis has been carried out using surface sediment monitoring data in order to characterize the spatial distributions and temporal trends of heavy metals within ten years from 2004 to 2013 in the entire Liaodong Bay. Hg, Cd and As were predominant contaminants with their median concentrations of 0.04–0.15, 0.01–0.65, and 1.80–30.3 mg/kg respectively. Both areas and levels of Cu and Pb contamination were low. Cd contents exhibited an obvious decreasing trend and As presented a similar law during these 10 years. Further, emissions from different sources were analyzed to identify the possible reasons contributing to the metal pollution. Dramatic descending of waste water might be the top reason for Cd and As variations. Local flue gases and smoke emissions might not be the main sources contributing to Hg pollution, whereas atmospheric deposition at a larger scale was supposed to be the leading factor.

1. Introduction

Liaodong Bay is located in the northeast of Bohai Sea, China, which is a nearly closed interior sea (37°07′-41°N and 117°35′-122°15′E). The surroundings of Liaodong Bay has now become one of the regions in China with the highest quantity and density of population, the most developed economy, culture and education, and the strongest scientific and technological force and industrial base (Zheng et al., 2014). Liaodong Bay is an important fishery resources base in the north of China, and also one of most important spawning grounds in Bohai Sea. Totally 13 heavily polluted rivers with over 500 km^2 watershed area drained into Liaodong Bay, including Fuzhouhe river, Xiongyuehe river, Shahe river, Daqinghe river, Dahanhe river, Daliaohe river, Liaohe river, Dalinghe river, Xiaolinghe river, Lianshanhe river, Wulihe river, Xingchenghe river and Liuguhe river. Among them, Liaohe River is one of the most heavily polluted rivers in China.

Large amounts of pollutants from river, runoff and atmospheric deposition assemble in the Liaodong Bay and exert great stresses on the local ecosystem. As an important part of the marine environment, the sediment attracts great interests and emphasis from many researches. Marine sediment is a complex system affected by the interaction of geological, hydrological, physicochemical and biological factors and acts as reservoirs of the adsorbed nutrients, pesticides, toxic materials and heavy metals. These pollutants can affect the health of human being through the food chains. Under favorable conditions, the sediments can be resuspended and then result in a second round of contamination of water. Therefore, residues of pollutants in sediment provide valuable records of pollution and denote potential environmental risks. It is meaningful to pay attention to the quality of sediment, variation and indication to the marine environmental conditions (Chau, 2005).

To date, there were many investigations focused on intertidal sediment quality in Liaodong Bay, concerning heavy metals, organic pollutants and sediment particle characteristics (Ma et al., 2013; Wang et al., 2014; Xu et al., 2009; Dou et al., 2014; Liu et al., 2014). Yet, there was still poor understanding of variation trends of pollutants, especially on recent years since economic booming. Most existing studies used only sediment cores, which often covered hundreds of years (Zhao et al., 2014; Liu et al., 2011; Spencer et al., 2006) and it was very hard to depict the variation of pollutants for the recent decades. So the objective of this study was aiming to investigate and assess spatial distributions and temporal trends of heavy metals in the entire Liaodong Bay using regular surface sediment monitoring data from 2004 to 2013. The higher sedimentation rates in this area, a same methodological guideline for sample collection and analysis, and almost fixed sampling locations guaranteed the comparability of data between years and then more precise analysis of the variation of sediment quality was allowed. Also the variations of the possible pollutants sources affecting the sediment quality would be discussed expecting to find a certain relationship between them.

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http://dx.doi.org/10.1016/j.marpolbul.2017.07.021
Received 12 January 2017; Received in revised form 6 July 2017; Accepted 7 July 2017
0025-326X/

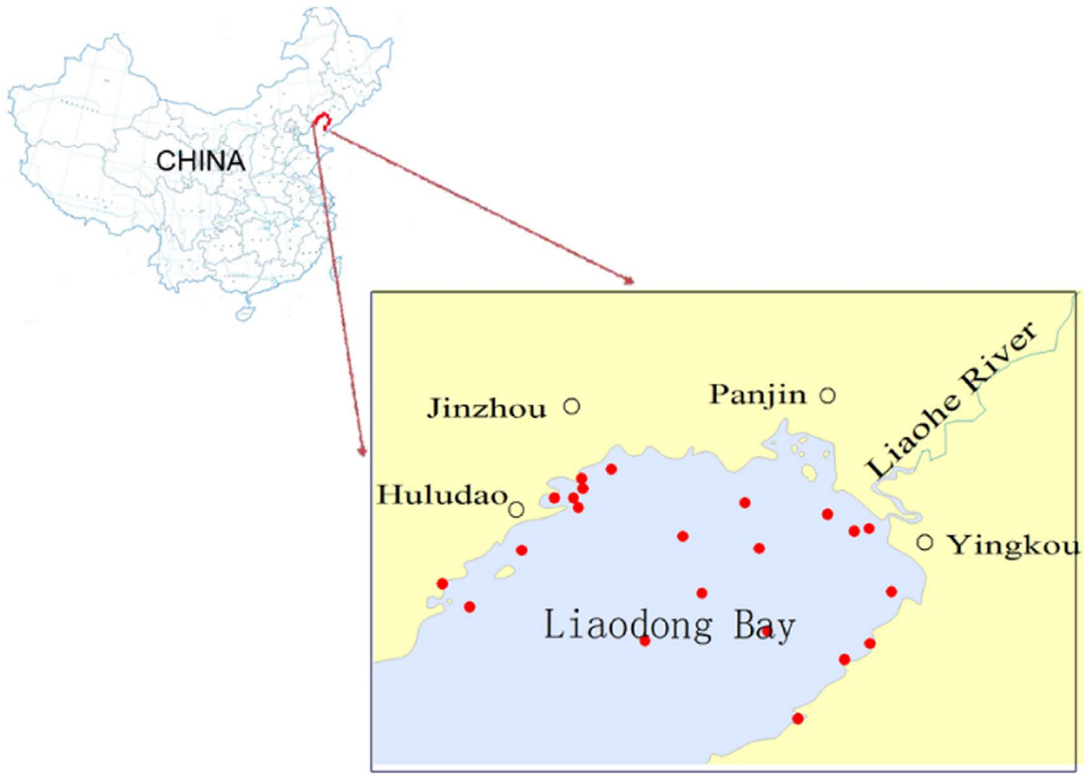

Fig. 1. Sampling stations of sediment in Liaodong Bay in 2009.

2. Materials and methods

2.1. Field sampling and laboratory analysis

Historical monitoring data in this area was used in this paper for assessment of spatial distribution and temporal trends. The time span was 10 years from 2004 to 2013 and totally 155 sampling sites (10 years) were covered. The sampling design followed principles of higher density in the coastal area and lower density far from the shore. No matter which area was concerned, the sampling sites were basically evenly distributed since the objective of sediment investigation was describing sediment quality, not examining contaminants transport. Taking 2009 for example, the sampling locations were shown in Fig. 1.

Surface sediment samples (0–2 cm) were collected with a grab sampler in September each year following the methods GB17378.3 (2007) "The speciation for the marine monitoring-part 5: sediment analysis". After returning lab, sediment samples were freeze-dried, lightly disaggregated using a pestle and mortar, and then sieved through 63 μm nylon sieve since most metals were often associated with fine grains. Totally five kinds of pollutants as Hg, Cd, Pb, As and Cu were measured.

The contents of Pb, Cd, Cu and As were determined by digesting the samples (0.1–0.5 g) using a mixture of concentrated HNO_3 (5 ml) and $HClO_4$ (2 ml) on a electric heating plate at temperature 180–200 °C. The measurements of Pb, Cd and Cu were carried out using atomic absorption spectrometry (AAS) and in some cases (low concentrations) using graphite furnace atomic absorption spectrometry (GFAAS). The As concentration was determined using atomic fluorescence spectrometry (AFS). Hg contents were measured using direct mercury analyzer (DMA80, Milestone) based on EPA method 7473. Sediment samples were weighed and introduced in the Hydra C. They were initially dried, then thermally decomposed in an oxygen flow and then further decomposed in hot catalyst bed. Mercury vapors were trapped on gold amalgamator and then desorbed for quantization. The accuracy of analytical procedures for total metal determinations was checked using sediment standard reference materials (SRM) GBW07314. Replicate measurements of SRMs showed good accuracy, with recovery rates ranging from 95% to 105%. SRMs mess-3(NRCC) was chosen to calibrate Hg analysis.

2.2. Statistical analyses

Statistical data treatment was carried out with SPSS (11.5 package version). Concentration ranges, means, medians, lower and upper quartiles for each metal were identified to characterize the populations. The frequency histograms by means of Kolmogorov-Smirnov test were performed using this software. Since concentrations values were not normally distributed, non-parametric statistics were applied. The Mann-Kendall non-parametric test was used to identify the trend, which statistically assessed if there was a monotonic upward or downward trend of variables of interest over time. A monotonic upward (downward) trend meaned that the variable consistently increased (decreased) through time, but the trend may or may not be linear. Super map software (Super map Deskpro 6) was used to map the spatial distributions and origin8 was employed to analyze the temporal variations of pollutants using a scatter diagram. The first class standard values (marine sediment quality criteria GB18668, 2002) were used to assess the over standard rates.

3. Results and discussions

3.1. Assessment of data gathered

Totally 155 sediments samples were collected in Liaodong Bay within 10 years in order to obtain monitoring data of each metal (Table 1). As far as Cu was concerned, monitoring was not implemented in 2006 and 2008 and only 110 samples were covered. Table 1 presented information on the average concentration ranges, median concentration ranges, and sample ratios exceeding the first class marine sediment quality standard values. Hg median concentrations ranged