Estuarine, Coastal and Shelf Science 151 (2014) 302–309

Contents lists available at ScienceDirect

Estuarine, Coastal and Shelf Science

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

Assessing metal toxicity in sediments of Yellow River wetland and its surrounding coastal areas, China

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ARTICLE INFO

Article history:
Accepted 16 July 2014
Available online 24 July 2014

Keywords:
metals
toxicity
sediments
pollution
equilibrium partitioning model
Bohai Sea

ABSTRACT

Seventy one surface sediments were collected from Yellow River (YR) wetland and its surrounding coastal areas, mainly in Laizhou Bay, China. The equilibrium partitioning (EqP) model and empirical sediment quality guidelines (SQGs) were applied to assess the potential metal toxicity in the collected sediments. The results show that, based on the EqP model, 15% of stations exhibited potential metal toxicity. Several metals (Cu, Ni and Cr) exceeded the empirical SQGs (59–100% of the time), however these guidelines may not be suitable for use in the Bohai Sea owing to the background concentrations. As a result, the EqP model is found to be a more useful method for assessing potential metal toxicity in Bohai Sea sediment than the empirical SQGs. Additionally, we have provided new insights on assessing metal toxicity in sediment of low organic carbon and acid volatile sulfide concentrations, which may be useful for other coastal areas in China.

1. Introduction

The Bohai Sea, with an area of 77 000 km^2, is the largest inland sea in northeastern China. The area along the coast has witnessed rapid industrial and population growth in the past 30 years, and, as a result, the Bohai Sea is under intense pressure (SOA, 2012). Increasing quantities of wastewater have been discharged into coastal waters, with the result that sediments have become a repository for contaminants (Shaw et al., 1990; Chapman and Wang, 2001; Audry et al., 2004). Contaminants such as heavy metals are easily adsorbed to sediments; they do not degrade and are potential threats to benthic organisms and human health.

To facilitate assessment of the metal contamination levels in sediments, a number of sediment quality guidelines (SQGs) have been developed. These can be categorized into two forms, empirical and mechanistic. Empirical SQGs have been derived from existing datasets of sediment chemistry and corresponding adverse biological effects (Long et al., 1995; Macdonald et al., 1996; ANZECC, 1997; Chapman et al., 1999). Among the empirical SQGs, the threshold/probable effect level (TEL/PEL) and the effect range low/median (ERL/ERM) are the most commonly used worldwide to assess sediment toxicity. China also drafts SQGs in 2002. In these guidelines, sediment quality is categorized into 3 classes, and 5 metals (Cu, Pb, Cr, Cd, Ni) are included (CEPA, 2002). The assessment of empirical SQGs is based on the bulk (total) metal content in sediments. However, increasing experimental evidence has shown that the total metal content does not reflect the bioavailability of metal in sediment (Swartz et al., 1986; Ankley et al., 1996; Vink, 2002; USEPA, 2005; Campana et al., 2013).

The other group of SQGs uses a mechanistic approach; a representative is the equilibrium partitioning (EqP) model. This model was developed as an attempt to include the bioavailability of chemicals in sediment, and was initially used to assess organic contaminants in sediment (Di Toro et al., 1990; Adams, 1992). The EqP model proposed that the dissolved metal concentration in pore water can be controlled by acid volatile sulfide (AVS, in μmol/g *dw*) in sediment. AVS can react with simultaneously extracted metals (SEM, in μmol/g *dw*) to form metal sulfides, which are non-bioavailable to benthic organisms. Under the EqP concept, two approaches, AVS − ΣSEM (ΣSEM is the sum of SEM concentrations) and (ΣSEM − AVS)/*foc* (f_{OC} is the total organic carbon (TOC) content, in g OC/g *dw*), were proposed in order to assess the potential metal toxicity (USEPA, 2005). The former has been applied mainly for assessment conducted under anoxic environment, and proved highly effectively for predicting the absence of metal toxicity when AVS − ΣSEM > 0 (Hare et al., 1994; Ankley et al., 1996; Boothman et al., 2001; Han et al., 2005; Campana et al., 2013). The latter is an extension of the formal assessment and it is mainly for application under suboxic or oxic environment, and can help predicting the onset of the metal toxicity. Experimental results showed that the inclusion of the TOC as a normalizer resulted in improved

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http://dx.doi.org/10.1016/j.ecss.2014.07.010
0272-7714/

predictions of the onset of toxicity (Burton et al., 2005; Vandegehuchte et al., 2007; Besser et al., 2008; Nguyen et al., 2011; Costello et al., 2012).

The Yellow River (YR) wetland and its surrounding coastal areas, mainly the Laizhou Bay, are important wetland and fishing grounds in Bohai Sea. With a water depth of 5–20m, the study area is relatively shallow. The Yellow River, a river with high suspended particle concentration, is the biggest river that discharges into the study area, bringing approximately 1.5×10^{10} m^3 of freshwater and 1×10^9 tons of sediments into the bay annually (Wang et al., 2006; Qiao et al., 2010; Miao et al., 2011). The freshwater discharged from the Yellow River was observed to go northward in a counter-clockwise direction and southward in a clockwise direction (Mao et al., 2008; Qiao et al., 2010). Previous studies have reported AVS and ΣSEM data in Laizhou Bay and several surrounding rivers (Gao et al., 2013; Zhuang and Gao, 2013), but due to the relatively high AVS found in sediments, the (ΣSEM-AVS)/*foc* assessment was never employed to further assess the metal toxicity in sediments, nor in other coastal areas in China. We collected surface sediment samples in YR wetland and its surrounding coastal areas, mainly in Laizhou Bay. Sediment samples were analyzed for AVS, SEM, TOC, and total metal concentrations. Sediment toxicities were assessed using the EqP model and several empirical SQGs. The assessment results were compared and discussed.

2. Sampling and analytical method

2.1. Sample collection

Seventy-one surface sediment samples were collected during September and October 2012 (Fig. 1). Fifty-five stations were located in Laizhou Bay and southeastern Bohai Bay. Sixteen stations were located in the YR wetland, which were divided into three groups based on their locations; among them, five were collected very close to the oil rigs located on the wetland; three were collected in the YR riverbed; eight were just randomly collected along the wetland (Fig. 2). The sediments under deep water were collected using a stainless steel box-corer (15 × 15 × 20 cm, Ekman-Berge type, HYDRO-BIOS Inc.), while the others were collected directly using plastic spoon. The surface (<2 cm) sediment was transferred from undisturbed sediments into a polyethylene zipper bag, avoided head space and quickly closed. The bags were placed in the dark in coolers and were transported back to the laboratory, where they were stored in refrigerators at 4 °C until analysis. AVS and SEM analysis were conducted within two weeks of sample collection.

2.2. AVS and SEM analysis

The analytical methodology for AVS is a modified diffusive method (Hsieh and Shieh, 1997; Ulrich et al., 1997). Briefly, sediment (3 g wet weight ± 0.01 g) was weighed and placed in a 500 ml HDPE bottle (Nalgene Inc.). A 15 ml glass tube containing 10 ml of 3% alkaline zinc acetate (in 2 M NaOH) was placed upright inside the reaction bottle. The bottle was flushed with high purity N_2 for 30 s before 50 ml 1 N cold HCl was injected into the reaction bottle. The bottle was tightly closed and sealed, and set aside overnight (more than 17 h). Afterwards, the glass tube with the trap solution was removed. The methylene-blue colorimetric method was chosen for sulfide analysis (Cline, 1969). A standard S^{2-} solution (Beijing Aoke biotechnology Inc.) was used to develop the calibration curve and examine the method recovery, which was within 86–99%. All labware that was in contact with the samples were cleaned by soaking in 10% HNO_3 (trace metal grade, National Chemical Production Inc., China), and then thoroughly rinsed with deionized water. The solutions (zinc acetate, 1M HCl) used in the pretreatment experiment were all deoxygenated with high purity N_2 before use. The method detection limit was 0.3 μg S/g *dw* (0.009 μmol S/g *dw*). The metal blank was 0.002 μmol S/g *dw*.

The remaining sediment suspensions were centrifuged at 3000 rpm for 10 min, after which the supernatant was allowed for 1–2 h before further analysis. The solution was diluted 20 times for trace metal analysis (Cd, Cu, Ni, Pb, Zn, Cr) by ICP-MS (Thermo Fisher XII). The remaining sediments were dried and weighed to obtain the dry weight and to calculate the water contents. The ΣSEM was calculated as the sum of all simultaneously extracted metals, using the equation $\Sigma SEM = SEM_{Cu} + SEM_{Ni} + SEM_{Pb} + SEM_{Zn} + SEM_{Cd}$ (Di Toro et al., 2005). Replicates were analyzed for 20% of samples and the relative standard deviations were within 20%. The average values of AVS and ΣSEM are reported in the results section.

2.3. Other analysis

Sediments were dried, ground and sieved to <2 mm before analysis for total metals (Cu, Pb, Zn, Ni, Cr and Cd) and TOC. For total metal analysis, 0.05 g sample was digested with 1.5 mL HNO_3 and

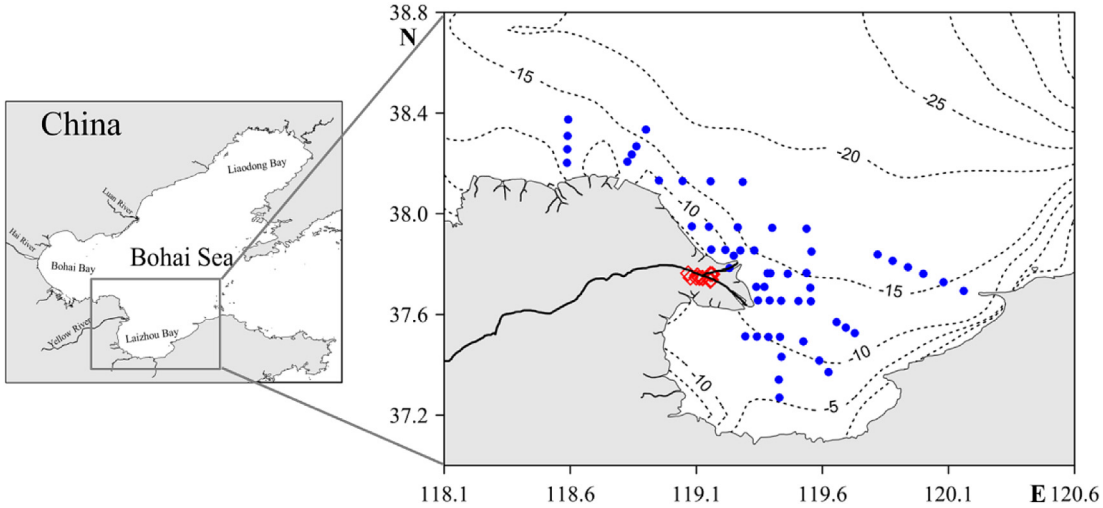

Fig. 1. Sampling stations in in Yellow River wetland (red diamonds) and its surrounding coastal areas (blue dots). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)