ARTICLE IN PRESS

MPB-08121; No of Pages 11

Marine Pollution Bulletin xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Marine Pollution Bulletin

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

Baseline

Ecological risk assessment of a coastal zone in Southern Vietnam: Spatial distribution and content of heavy metals in water and surface sediments of the Thi Vai Estuary and Can Gio Mangrove Forest

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ARTICLE INFO

Article history:
Received 29 August 2016
Received in revised form 13 October 2016
Accepted 17 October 2016
Available online xxxx

Keywords:
Metals enrichment
Sediment quality criteria
Pollution indices
C/N ratios
Nutrients
Biosphere reserve

ABSTRACT

Enrichment of heavy metals was assessed in the Thi Vai Estuary and in the Can Gio Mangrove Forest (SE, Vietnam). Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn contents in water and in sediments were measured. Total organic carbon, nitrogen, phosphorus and C/N ratios were determined. Cu and Cr values were higher than threshold effect level of toxicity, while Ni exceeded probable effect level, indicating the risk of probable toxicity effects. Enrichment factors (EF), contamination factor (CF) and Geo-accumulation index (I-geo) were determined. CF reveals moderate to considerable pollution with Cr and Ni. EF suggests anthropogenic sources of Cr, Cu and Ni. I-geo indicates low contamination with Co, Cu and Zn and moderate contamination with Cr and Ni. Overall metal contents were lower than expected for this highly industrialized region, probably due to dilution, suggesting that erosion rates and hydrodynamics may also play a role in metal contents distribution.

Southeast Asia has experienced a rapid and colossal economic growth (OECD, 2016) with Vietnam being one of the fastest growing countries since the reform of the foreign trade policy ("Đổi Moi' Policy") and the adoption of a market-oriented economy established in 1986 (Nguyen and Sloper, 1995). Most development activities (e.g. industry, agriculture, human settlement, tourism, transport) take place in coastal zones, which are among the most exploited areas worldwide (Post and Lundin, 1996) and being subject to the impact of multiple stressors, such as eutrophication, increase in erosion and pollution by chemicals. This hazard is increased by the high vulnerability of these areas to environmental changes (Nicholls et al., 2007; Tuan et al., 2003). In Southern Vietnam both Đồng Nai and Bà Rịa–Vũng Tàu provinces are among the most developed and populated areas, with 2.8 and $1.1.10^6$ inhabitants, respectively, and they house the largest number of industrial parks, with oil and gas production as key economy besides heavy industry, nitrogenous urea fertilizer, steel and harbours operation (Nhan, 2006).

The Thi Vai Estuary and the Can Gio Mangrove Forest are located between both provinces and experience several ecological pressures such as water pollution due to industrial wastewater discharges, erosion, sedimentation and oil spills (Meon and Phuoc, 2014). Until 2006, over 60% of the industrial zones had not implemented an adequate wastewater treatment system (Prilop et al., 2014). The Thi Vai Estuary because illegal untreated wastewater discharged directly into the river, reached extreme pollution levels, thus in 2008, local companies were fined and inquired to implement wastewater treatment systems that meet the national standard (Prilop et al., 2014). Although heavy metal contents in the sediments were evaluated in that time (Phuong et al., 2011), the potential of biological effects and ecological risk of heavy metals were not assessed.

Sediment quality guidelines (SQG's) have been developed to assist the evaluation of contaminated sediments and have been applied worldwide (Burton, 2002), aiding to a better understanding of the significance of heavy metal concentrations (MacDonald et al., 1996). In Asia several studies using this approach have been done (e.g. Chatterjee et al., 2009; Kumar and Patterson Edward, 2009; Kim et al., 2011; Udayakumar et al., 2011; Veerasingam et al., 2012), but with main focus on China (e.g. Zhang et al., 2013; Li et al., 2014; Wu et al., 2014). In Vietnam, most studies dealt with Mekong Delta (Wilbers et al., 2014), central Vietnam (Koukina et al., 2016) or with the coastal

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http://dx.doi.org/10.1016/j.marpolbul.2016.10.046
0025-326X/

areas in the north (Ho et al., 2010; Nguyen et al., 2010). To our knowledge the SQG's approach was still not applied in the coastal zone covering the Đồng Nai and Bà Rịa–Vũng Tàu provinces, which play a significant role for the economic development of Vietnam, besides their huge ecological and social importance, their sensitive ecosystems such as mangroves and high population density (Nhan, 2006).

The use of SQG's is a helpful tool to identify contaminants of concern (MacDonald et al., 1996) but they had been mostly developed for North America (Burton, 2002). Therefore, the use of heavy metal enrichment indices together with sediment quality criteria can be a useful tool to evaluate heavy metal contamination (e.g. Abrahim and Parker, 2008; Wang et al., 2015). Thus, this study aims to: (1) assess heavy metals in the surface sediments and in the water of the Thi Vai Estuary and in the Can Gio Mangrove Forest; (2) determine total nitrogen, total phosphorus and total organic carbon in the sediments; (3) identify organic matter sources using C/N ratios; (4) assess sediment contamination through SQG's and enrichment indices (contamination factor, enrichment factor and geo-accumulation index) in order to (5) assess the potential ecological risk and determine (6) the actual ecological status of these systems and their level of contamination.

Thi Vai Estuary and the Can Gio Mangrove Forest (10°27′48.3″N - 106°49′25.9″ E to 10°41′38.2″N - 106°58′30.7″ E) are located in Southern Vietnam ca. 40 km southeast of Ho Chi Minh City, Vietnam's biggest industrial city, located between the highly industrialized and populated Đồng Nai and Bà Rịa–Vũng Tàu provinces.

The area is situated in the tropical monsoon zone characterized by a single rainy season from May to October with annual rainfall exceeding 1000 mm (Meon and Phuoc, 2014).

The Thi Vai Estuary has a catchment area of ca. 625 km^2, and it is about 76 km long. The tidal regime is irregular semi-diurnal with high amplitudes of 3.3–4.1 m. Around 14 industrial zones which were established mainly after 1996 are located in the catchment area (Prilop et al., 2014). Because of the discharge of untreated wastewater by several companies located along the estuary, the Thi Vai was considered ecologically dead until about ~2008, particularly, due to the release of untreated wastewater (~105,600 m^3 per month) from a local monosodium glutamate company between 1994 and 2008 (Meon and Phuoc, 2014).

The Thi Vai was classified in 2006 into three regions, each characterized by different pollution levels based on water quality monitoring: Upstream; extremely polluted; central region; strongly polluted and downstream; strongly polluted to moderately polluted depending on tide (Prilop et al., 2014). In 2008 a wastewater treatment system was implemented and consequently, a decrease of pollution levels of the water quality was observed. The estuary is still subject to several other environmental pressures such as illegal sand excavation, tannery plants, rubber plantations and agriculture (Prilop et al., 2014; Lorenz et al., 2014).

Adjacent to the Thi Vai Estuary basin in the West the Can Gio Mangrove Forest is located (Tuan and Kuenzer, 2012). It covers an area of 72,000 ha, and forms the delta of the Saigon- Đồng Nai River system which is the second largest river system in southern Vietnam after the Mekong Delta (Nguyen, 2011).

The Can Gio Mangrove Forest was destroyed during the Second Indochina War (1954–1975) due to application of herbicides and defoliants, mainly known as "agent orange". A reforestation program started in 1978, making the Can Gio Mangrove Forest one of the most extensively restored mangrove forests in the world, and received the nomination by Unesco as "Biosphere Reserve" in 2000.

The surface area is covered mostly by alluvium, fluviomarine, kukersite sediments (Huynh and Nguyen, 2003) with soils dominated by acidic soil types such as acrisols, rhodic ferrasol and thionic fluvisols (Lorenz et al., 2014). Of concern are the high sedimentation and erosion rates in the area, which have been increasing due to shipping activities, impacts from aquaculture farming, oil spills, among others (Huynh and Nguyen, 2003; Meon and Phuoc, 2014).

Thirty-three water and surface sediment samples were collected in January 2013. Using a Petite Ponar® dredge during low tide, the top 2 cm sediments were taken representing 31 samples along the Thi Vai Estuary. Due to difficulties of sampling and permission restriction only two samples were collected in the Can Gio Mangrove Forest (Fig. 1). Coordinates were recorded using Lowrance GPS®. Samples were labeled as follow: Samples 1 to 31 (Thi Vai Estuary), and the samples 32 and 33 represent the Can Gio Mangrove Forest (Fig. 1).

In the Laboratory of the Institute for Environment and Resources in Vietnam (IER) the following elements were analyzed in the water: calcium (Ca), cadmium (Cd), chromium (Cr), cupper (Cu), iron (Fe), manganese (Mn), nickel (Ni), lead (Pb) and zinc (Zn). All elements were in mg L^{-1} determined following the National Technical Regulation on Water Quality (QCVN10:2008/BTNMT) and the Standard Methods Examination of Water and Wastewater (APHA, 2005). The analytical method detection limit (MDL) for each dissolved metal (mg L^{-1}) was: 0.001 for Cd; 0.005 for Cr; 0.004 for Cu; 0.06 for Fe; 0.02 for Mn; 0.009 for Ni and Pb; 0.003 for Zn.

Surface sediments were pre-treated in the laboratory of the Institute of Geosystems and Bioindication (IGeo), Technische Universität Braunschweig, in Germany. Sediments were sieved through a 2-mm sieve, and then separated into the fractions sand-sized (2 mm–63 mm) and fine-grained size (<63 μm). Dried samples were weighed and ground into powder with agate pestles and mortars. In the Institut für Physische Geographie, Freie Universität Berlin, the following elements were analyzed: Cd, Cr, cobalt (Co), Cu, Fe, Mn, Ni, Pb and Zn, as well as total phosphorus (TP). Elements were analyzed for fine-grained (<63 μm) and total fractions (<2 mm–63 μm) through ICP-OES (Perkin Elmer Optima 2100 DV) following DIN EN 13346 (Anonymous, 2001) and diluted using an aqua regia dilution. Most elements were in μg g^{-1} determined. Fe and Mn were determined in mg g^{-1}.

Total nitrogen (TN) and total organic carbon (TOC) in the sediments were analyzed using an elemental analyzer LECO TruSpec CHN Macro. TOC was determined after removing inorganic carbon with chloridric acid (HCl 10%). The calibration followed certified and internal laboratory standards (e.g. $CaCO_3$; EDTA; LECO 502-309 Soil; Sediment LKSD-1 to −4 (Lynch, 1990)). The standard deviation, determined by multiple measurements, is for all elements <2%. C/N ratios were calculated by dividing TOC by TN (Meyers and Teranes, 2001).

SQG's – also known as sediment quality criteria – is a tool that provides useful information about sediment contamination, and therefore, has been adopted by various regulatory agencies, because this approach attempts to incorporate biological effects (Burton, 2002). Two threshold levels are set: Threshold effect levels (TEL) and probable effect level (PEL). TEL represents the concentration below which adverse biological effects are expected to occur rarely, and PEL defines the level above which adverse effects are expected to occur frequently (MacDonald, 1994).

The degree of metal enrichment in the sediments was assessed through the following numerical methods: Contamination Factor (Håkanson, 1980), Enrichment Factor (Sinex and Wright, 1988) and Geo-accumulation Index (I-geo) (Müller, 1979). These methods were calculated as follow:

Contamination Factor (CF) (Håkanson, 1980):

$$CF = (Me_s/Me_b)$$

where Me_s refers to the metal concentration in the sediment sample, and Me_b refers to the background value. The CF pollution rating classification proposed in Håkanson (1980) is: CF values equal to 1 (low contamination); ≤1 CF < 3 (moderate contamination); ≤3 CF < 6 (considerable contamination) and ≥6 (very high contamination).

Enrichment Factor (EF): To reduce the variability associated with grain size variations, this method normalizes the metal content with a reference metal, usually Al or Fe, because these elements are not expected to be enriched from anthropogenic sources due to their relatively