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

Seasonal dynamics of trace elements in sediment and seagrass tissues in the largest *Zostera japonica* habitat, the Yellow River Estuary, northern China

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ARTICLE INFO

Keywords:
Cumulative risk
Seasonal change
Trace elements (TEs)
Seagrass
Zostera japonica
Yellow River Estuary

ABSTRACT

Trace element accumulation is an anthropogenic threat to seagrass ecosystems, which in turn may affect the health of humans who depend on these ecosystems. Trace element accumulation in seagrass meadows may vary temporally due to, e.g., seasonal patterns in sediment discharge from upstream areas. In addition, when several trace elements are present in sufficiently high concentrations, the risk of seagrass loss due to the cumulative impact of these trace elements is increased. To assess the seasonal variation and cumulative risk of trace element contamination to seagrass meadows, trace element (As, Cd, Cr, Cu, Pb, Hg, Mn and Zn) levels in surface sediment and seagrass tissues were measured in the largest Chinese *Zostera japonica* habitat, located in the Yellow River Estuary, at three sites and three seasons (fall, spring and summer) in 2014–2015. In all three seasons, trace element accumulation in the sediment exceeded background levels for Cd and Hg. Cumulative risk to *Z. japonica habitat* in the Yellow River Estuary, from all trace elements together, was assessed as "moderate" in all three seasons examined. Bioaccumulation of trace elements by seagrass tissues was highly variable between seasons and between above-ground and below-ground biomass. The variation in trace element concentration of seagrass tissues was much higher than the variation in trace element concentration of the sediment. In addition, for trace elements which tended to accumulate more in above-ground biomass than below-ground biomass (Cd and Mn), the ratio of above-ground to below-ground trace element concentration peaked at times corresponding to high water discharge and high sediment loads in the Yellow River Estuary. Overall, our results suggest that trace element accumulation in the sediment may not vary between seasons, but bioaccumulation in seagrass tissues is highly variable and may respond directly to trace elements in the water column.

1. Introduction

Seagrass is regarded as a coupled social–ecological system (Cullen-Unsworth et al., 2014), and thus the condition of seagrass ecosystems affects human health (Lamb et al., 2017). However, seagrass habitats are degrading worldwide (Waycott et al., 2009). For example, large-scale decline of the seagrass species *Zostera japonica* has been reported at various locations within Asia (Abe et al., 2009; Hodoki et al., 2013; Zhang et al., 2015). Seagrass decline has been attributed to many factors that include natural causes, but in > 70% of the cases anthropogenic factors are thought to be responsible (Hemminga and Duarte, 2000). Seagrass meadows are sensitive ecosystems that show variations in their distribution both seasonally and spatially (Boudouresque et al., 2009).

With rapid urbanization and industrialization, coastal areas in China are now facing great challenges in regard to trace metal contamination. Large volumes of suspended sediment comprising particulate trace elements (TEs), organic matter, nutrients, and minerals are transported to the ocean by rivers every year (Milliman and Meade, 1983). TEs from both natural and human activities have been shown to accumulate in marine habitats through atmospheric and terrestrial contributions (Halpern et al., 2008), and can negatively impact the health of seagrasses (Macinnis-Ng and Ralph, 2002).

For example, the Yellow River Estuary in northern China is well known to be subjected to high sediment loads but relatively low water discharge to the sea (Milliman and Meade, 1983). According to the most recently available data (Lijin station, 2014–2015), the sediment load is approximately 3×10^7 tons per year, and the water discharge is

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https://doi.org/10.1016/j.marpolbul.2018.02.043
Received 30 March 2017; Received in revised form 16 February 2018; Accepted 23 February 2018

Please cite this article as: Lin, H., Marine Pollution Bulletin (2018), https://doi.org/10.1016/j.marpolbul.2018.02.043

only 1.14×10^{10} m^3 (http://www.yellowriver.gov.cn/nishagonggao). Hence, the Yellow River Estuary is characterized by a sediment to water ratio of 0.0026. This value is almost 20 times higher than the sediment to water ratio in the Yangtze River (Qiao et al., 2007), the third largest river in the world which itself is a huge sediment source and is heavily polluted (Dong et al., 2014). However, sediment loads and water discharges differ in magnitude throughout the year, and hence there may be seasonal patterns in the threat to coastal areas posed by sediments and the TEs they carry.

Contamination of aquatic ecosystems by TEs has been a focus of study in recent years because TEs tend to concentrate, via bioaccumulation and sedimentation, in coastal vegetated ecosystems such as mangroves, salt marshes (Weis and Weis, 2004) and seagrasses. Some elements play a key role in biological processes in living organisms (Cu, Fe, Mn, Zn and Ni), but others such as As, Pb, Hg, Cr and Cd are toxic non-essential elements (e.g. Chang et al., 1996). Thus, at sufficiently high concentrations, certain TEs can act as environmental stressors for the local ecology. Environmental stress due to individual TEs depends on their individual concentrations, but this stress can become cumulative when multiple TEs are present in sufficiently high concentrations. TE accumulation and impact on physiological and biochemical processes is known for some seagrass species (Malea and Kevrekidis, 2013). Previous studies indicate that TEs act on CO_2 fixation and therefore can negatively impact seagrass photosynthetic physiology (Macinnis-Ng et al., 2004). However, TEs may also impact on seagrass physiology in several other ways (reviewed in Richir and Gobert, 2016).

Z. japonica is one of the most widely distributed seagrass species in the world, and occurs in temperate and subtropical coastal regions (Fan et al., 2011). The distribution of *Z. japonica* in China, based on a nationwide survey, has been recently reported (Fan et al., 2011; Zheng et al., 2013; Zhang et al., 2015). However, larger *Z. japonica* beds are very rare, due to rapid declines resulting from increasingly severe habitat destruction (Lee, 1997; Lee et al., 2005; Abe et al., 2003, 2009; Fan et al., 2011; Mach et al., 2014; Zhang et al., 2015). In 2015, a large and continuous *Z. japonica* bed with an area ca. 1000 ha was found in the Yellow River Estuary of Shandong province in China (Zhou et al., 2016). Whilst the sediment and seagrass accumulation of TEs in this *Z. japonica* bed has been previously investigated (Lin et al., 2016a), the seasonal distribution of this accumulation, and the biological risk to this seagrass habitat due to cumulative contributions from all TEs together, has not yet been established.

Thus, the main aims of this study were to (i) assess the seasonal variation in sediment TE concentration, and seasonal variation in ecological risk due to sediment TEs (As, Cd, Cr, Cu, Pb, Hg, Mn and Zn) in the Yellow River Estuary; (ii) assess the seasonal variation in seagrass tissue TE concentrations, for above-ground biomass, below-ground biomass, and their ratio; and (iii) develop hypotheses for how seasonal variation in seagrass TE concentration is affected by TE concentrations in the environment.

2. Materials and methods

2.1. Study area

The *Z. japonica* habitat is located in the Yellow River Estuary, within the northeastern Gulf of China (Fig. 1). This intertidal seagrass bed extends along the coast, from lines A to B shown in Fig. 1, with a length ca. 30 km and an area ca. 1000 ha. The seagrass bed is adjacent to a *Spartina alterniflora* habitat, forming a unique ecological landscape. The main direction of the current along this coastal habitat is southeast, due to anticlockwise circulation in the southern part of the Bohai Sea (Zhang, 2015).

Although we do not have data for TE loading in the Yellow River during our study period (Bi et al., 2014), monitoring of sediment load and water discharge is carried out at a nearby hydrometric station (Lijin station; Xu et al., 2016; data available online at: http://www.yellowriver.gov.cn/nishagonggao). During summer months, large volumes of suspended sediment, which are highly likely to comprise particulate TEs, are transported along the Yellow River to the ocean every year (Fig. 2).

2.2. Field sampling and analyses

Three seagrass sampling sites S1, S2 and S3 were chosen in a single linear transect running northwest to southeast along the coast (from N 38°00′, E 119°15′ to N 37°43′, E 119°30′). For the seagrass sites, S1 was located in the coastal area north and furthest from the mouth of the Yellow River, S2 was located north of the river mouth and midway along the transect, and S3 was located south and closest to the river mouth. The *Z. japonica* meadow inhabits intertidal sandy or muddy bottoms at depths of approximately 1–2 m.

Z. japonica samples were collected from the three seagrass sites (4 replicates per site, replicates separated by a distance of 50 m), in three seasons: fall (August to September 2014), spring (April 2015) and summer (July 2015). As shown in Fig. 2, these sampling times coincide with times of high, low and high sediment discharge in the Yellow River, respectively. The *Z. japonica* samples were washed, cleaned of sediments, and separated into above-ground and below-ground plant compartments. Epiphytes, where present, were removed from leaves by wiping them off with a paper towel, or scraping them off with a razor blade. Samples of seagrass were dried at 60 °C for 24 h, manually ground to a coarse powder, and freeze-stored before being transferred to the laboratory for TE analysis. In addition, surficial sediment samples were collected from the top 5 cm of the *Z. japonica* stands ($n = 4$ per site), using an acrylic plastic corer to avoid contamination. The samples were dried and then freeze-stored until TE analyses were conducted. All containers were new and had been washed with acid.

Seagrass and sediment samples were analyzed for eight TEs: As, Cd, Cr, Cu, Pb, Hg, Mn and Zn. Individual TE concentrations were measured and analyzed at the Institute of Geology, Chinese Academy of Sciences (Langfang, Hebei, China), following the protocol described in Lin et al. (2016b). In this paper, when we discuss TE concentration, we are always referring to total concentration. When performing statistical analyses, we considered each TE separately rather than cumulatively, because any statistically significant effects identified in all eight TEs pooled together would be more difficult to interpret. Prior to all statistical analyses, the distribution of the data was tested using the Shapiro-Wilk test.

2.3. Assessing trace element contamination in the sediment

Sediments are a suitable indicator of TE pollution in estuarine and coastal areas (Batley, 1989). Assessing seasonal variation in ecological risk in the Yellow River Estuary due to sediment TEs, which is the first aim of our study, was accomplished by:

(1) Statistical tests of the differences in TE concentration between sites and seasons using ANOVA and repeated measures ANOVA respectively, and post-hoc Tukey tests, all with a significance of $p < 0.05$, and.

(2) Calculation of two indices of TE contamination – the geoaccumulation index (I_{geo}) and the ecological risk index *(RI)* – for each trace element and season, averaged over the three sites. The second index, *RI*, was also used to assess cumulative risk from all trace elements together, averaged over the three sites, for each of the three seasons tested.

The first index – the geoaccumulation index (I_{geo}) – quantifies TE contamination in the sediment according to (Muller, 1981)

$$I_{geo} = \log_2\left[\frac{[\mathrm{TE}]_{\mathrm{sediment}}}{1.5[\mathrm{TE}]_{\mathrm{background}}}\right], \tag{1}$$

where $[\mathrm{TE}]_{\mathrm{sediment}}$ is the TE concentration in the sediment (mg/kg), $[\mathrm{TE}]_{\mathrm{background}}$ is the geochemical background concentration of the