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Baseline

Tungsten- and cobalt-dominated heavy metal contamination of mangrove sediments in Shenzhen, China

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ABSTRACT

A baseline investigation into heavy metal status in the mangrove sediments was conducted in Shenzhen, China where rapid urban development has caused severe environmental contamination. It is found that heavy metal contamination in this mangrove wetland is characterized by the dominant presence of tungsten and cobalt, which is markedly different from the neighboring Hong Kong and other parts of the world. The vertical variation pattern of these two metals along the sediment profile differed from other heavy metals, suggesting an increasing influx of tungsten and cobalt into the investigated mangrove habitat, as a result of uncontrolled discharge of industrial wastewater from factories that produce or use chemical compounds or alloys containing these two heavy metals. Laboratory simulation experiment indicated that seawater had a stronger capacity to mobilize sediment-borne tungsten and cobalt, as compared to deionized water, diluted acetic, sulfuric and nitric acids.

Mangrove wetlands are crucial parts of estuarine ecosystems in tropical and sub-tropical regions, providing nursery sites for fishes and crustaceans (Robertson and Duke, 1987). However, there has been increasing contamination of mangrove areas as a result of various human activities that introduce pollutants into mangrove ecosystems. Heavy metal contamination of mangrove sediments has been reported at many locations around the world (Shriadah, 1999; Che, 1999; Tam and Wong, 2000; Defew et al., 2005; Cuong et al., 2005; Marchand et al., 2006, 2011; Agoramoorthy et al., 2008; Sarika and Chandramohanakumar, 2008; Usman et al., 2013). A recent review indicated that at least 22 trace metals have been reported in mangrove sediments (Lewis et al., 2011). Heavy metals commonly found in mangrove sediments include Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn.

We report here a mangrove habitat with markedly elevated concentration of tungsten (W) and cobalt (Co) in the tidal sediments. The investigated site is part of the tidal flat adjacent to the Shenzhen City that shares a border with Hong Kong in the southern China region (Fig. 1). Shenzhen is a "purpose-built" city, which has grown from a largely rural area to a modern city with a population of approximately 15 million people within just about three decades.

The tidal sediments mainly originate from the Shenzhen River, which serves as a natural border between Shenzhen and Hong Kong. Shenzhen River has a catchment area of about 300 km^2 with a length of 33 km. The river has been badly contaminated for decades as a result of industrial development and urbanization, particularly in the Shenzhen part of the catchment.

The investigated area of mangrove tidal flat covers an area of about 1 km^2. Discharges of municipal wastewater into the mangrove wetlands are not controlled and the investigated mangrove wetland has received municipal wastewater for at least more than a decade.

Surface sediment samples (0–10 cm) were collected from 27 locations within the investigated area (Fig. 1). At selected locations (S5, S7 and S13(3)), samples were also taken from sub-surface sediments to a depth of 30 cm. The sediment samples were oven-dried at 60 °C, ground and passed through a 2 mm sieve. A portion of each oven-dried sample was pulverized and used for determination of a wide range of elements. An aqua regia digestion method was used to extract various elements from the sediment samples, followed by measurements using an inductively coupled plasma atomic emission spectrometer (ICP–AES).

Table 1 shows the analytical results of various elements contained in the 27 surface sediment samples. It is interesting to note that the sediments in the investigated area had a mean W concentration of 377 mg/kg with a range of 10–1390 mg/kg, which was much higher than that of Cd (under detection limit), Co (129 mg/kg), Cr (33.8 mg/kg), Cu (52.9 mg/kg), Mn (331 mg/kg), Ni (21.8 mg/kg), Pb (48.3 mg/kg) and Zn (182 mg/kg).

Table 2 shows the correlation coefficient between each of the selected trace metals and each of a wider range of the elements detected in this study. It can be seen that the correlation coefficient was greater

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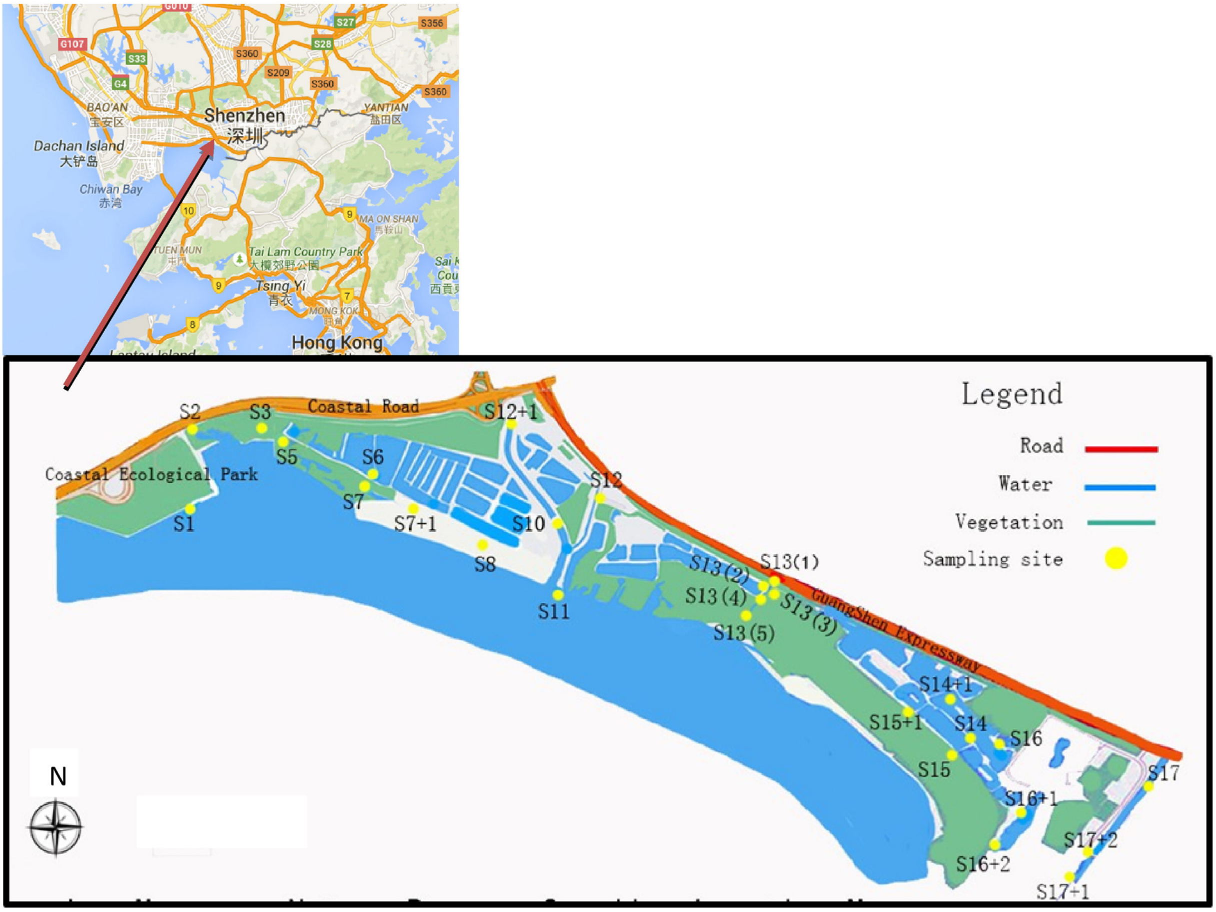

Fig. 1. Location map showing the study area and sampling sites.

than 0.45 for most of the element pairs except for those involving B, Ba, Ca, P and Sr as a part of the pair. It is interesting to note that either Co or W had consistent negative relationship with any of other elements, suggesting that these dominant contaminants were largely derived from the same source, which differs from those that contributed to fluxes of other trace metals into the tidal sediments.

Principal component analysis shows that the first principal component accounted for more than 60% with the second principal component only accounting for about 12% of total data variation (Fig. 2). It is clear that some sampling locations that were likely to receive contaminants from the same source had the similar composition of trace elements e.g. sampling location groups of (a) 13(1), 13(2) and 13(3), (b) S1, S2 and S3, and (c) S11, S12, and S12 + 1. Further work is currently underway to obtain better understanding of the pollution sources.

Tam and Wong (2000) investigated heavy metal distribution in the mangrove sediments in the neighboring Hong Kong and found that the sediment-borne heavy metals were around 80 mg/kg for Cu, 240 mg/kg for Zn, 40 mg/kg for Cr, 30 mg/kg for Ni, 3 mg/kg for Cd and 80 mg/kg for Pb. These were largely similar to but slightly higher than the mean values of the corresponding heavy metals in the sediment samples investigated in the current study except for Cd. Tungsten and cobalt were not investigated in their study and therefore no comparison can be made. The mean concentration of sediment-borne Mn, Cu, Zn, Ni, Pb, Fe, Cr was comparable to that in the Punta Mala Bay of Pacific Panama (Defew et al., 2005). Shriadah (1999) investigated 8 heavy metals in mangrove sediments along the shoreline of United Arab Emirates and the results showed that the concentration of these metals was much lower than that observed in this study except for Cd.

The vertical variation in concentration of a few selected heavy metals along the sediment profile is shown in Fig. 3. There are 2 distribution patterns: W and Co gently increased from the 0–10 cm layer to the 10–20 cm layer and then sharply decreased to a much lower value in the 20–30 cm layer while La, Mn, Sr and Zn decreased from the 0–10 cm layer to the 10–20 cm layer and then started increasing from the 10–20 cm layer to the 20–30 cm layer. The vertical variation in the concentration of a heavy metal in the mangrove sediments may, to a large extent, reflect temporal change in influx rate of that heavy metal in the receiving mangrove wetland. Therefore, the difference in the vertical variation pattern between the two different groups of heavy metals in the sediments appears to suggest that the heavy metal composition in the municipal wastewater discharged into the investigated area changed substantially with time during the period when the upper 30 cm of the sediments was deposited; tungsten and cobalt loads tended to increase over time. Tungsten and cobalt are not common pollutants in typical domestic wastewater but more likely to be associated with industrial sources such as factories that produce or use chemicals or alloy that contain these heavy metals. The dominance of tungsten and cobalt in heavy metals contained in the mangrove sediments may also give a hint about the possibly heavy contamination by these two metals of other environmental compartments such as air, soils and fishponds that could directly or indirectly affect human health in the city.

The environmental impacts of tungsten contamination on mangrove wetland systems are not clear. There have been increasing concerns over the potentially adverse impacts of tungsten on ecosystems and human health (Koutsospyros et al., 2006; Braida et al., 2007; Gbaruko and Igwe, 2007). Recent experiments have demonstrated that soil-borne W at a dose less than 500 mg/kg could have certain toxic effects on cabbage and snail, and also cause bioaccumulation of W in these test organisms (Kennedy et al., 2012). The bioavailability of tungsten

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