Article

Mangrove Soil-Borne Trace Elements in Qi’ao Island: Implications for Understanding Terrestrial Input of Trace Elements into Part of the Pearl River Estuary

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Abstract: An investigation was conducted to characterize the trace element status of mangrove soils of Qi’ao Island in the Pearl River estuary. The results show that the spatial variation in the soil-borne trace elements in the investigated area was minor and most of the trace elements were at a level higher than those in other mangrove wetlands around the world, suggesting the mangrove soils of Qi’ao Island were heavily contaminated by trace elements transported from the Pearl River in the past two decades. Zn was closely related to Pb, Cu, Cd, and As, while some trace elements were not closely related to each other, indicating that they were derived from different sources. An integrated Nemerow pollution index of the surface soils at the 17 sampling locations ranged from 7.53 to 48.42, values which all fall within the highest pollution category. Among the 17 sampling locations, six locations had an ecological risk index (ERI) greater than 300, and 12 locations had an Ecological Risk Index (ERI) greater than 600, indicating that most of the investigated locations were at high or very high ecological risk. The findings obtained from this study have implications for understanding the terrestrial inputs of trace elements into part of the Pearl River estuary. This understanding can be used to guide the development of management strategies for controlling the discharges of trace elements from the catchment area and managing the aquatic ecosystems in the Pearl River Estuary.

Keywords: mangrove; estuary; trace elements; soil; river; contamination

1. Introduction

Mangrove soils act as a sink for trace elements transported from inland areas by coastal rivers [1–4]. The elevated levels of trace elements in the mangrove soils could have adverse impacts on the mangrove growth, aquatic biota, and microbial activities in the mangrove habitats [5–8]. Understanding the level and spatial variation of trace elements in mangrove sediments/soils is essential for environmental risk assessment of the mangrove ecosystems. The relevant contamination information can also be used to indicate trace element loads of the river discharging into the estuary, thus helping environmental regulators and policy-makers to ensuring better environmental pollution control in the upstream catchment.

The Pearl River delta is one of the heavily industrialized areas in China, with petrochemical, electronic, electroplating, manufacturing, and textile industries being the major industrial sectors. These have resulted in discharge of substantial amounts of industrial wastewater into the Pearl River Estuary [9,10].

The Pearl River is the third longest river in China, draining a total area of 453,690 km². The large catchment size, coupled with a humid subtropical climate, makes the sediment load of the river great,
resulting in the rapid growth of the Pearl River delta in the estuarine embayment. The sedimentation rate in the deltaic areas is generally very high and consequently disfavors colonization of mangrove plants. Therefore, mangroves are limited to islands or small bays along the coastline of the estuarine embayment that are far from the active distributaries. In the Pearl River estuary, trace element contamination in mangrove soils has been investigated in Mai Po and Futian in the Shenzhen Bay [7,11,12]. However, these locations are far from the active distributaries of the Pearl River and the trace elements in the contaminated mangrove soils are of local sources, such as discharges of municipal and industrial wastewater.

In this study, Qi’ao Island, which faces two major distributaries of the Pearl River, was selected to investigate the level and distribution of trace elements in the mangrove wetlands. The natural mangrove forest was largely cleared during the period from the early 1950s to the late 1990s. Since the establishment of the Qi’ao Natural Reserve in 1999, replanting of mangroves has resulted in an increase in the area of mangrove wetland from 32 ha to 600 ha. This has created favorable conditions for trapping suspended sediments discharged from the Pearl River. Therefore, the status of trace elements in the mangrove soils could, to a certain extent, reflect the characteristics of the riverine sediment-bearing trace elements. The aim of this study was to characterize the soil-borne trace elements in the mangrove soils and, based on the findings, evaluate their environmental risk and explore the links with the terrestrial input of the trace elements.

2. Materials and Methods

2.1. Study Area

Qi’ao Island (113°36'41” E–113°39'16” E; 22°23'41” N–22°27'39” N) has a total area of 23.8 km². The area experiences a subtropical monsoon climate with annual average temperature and precipitation of 23.5 °C and 1948.9 mm, respectively. It has a mixed semidiurnal tidal cycle and the annual average salinity of the seawater is 1.82%. Major types of rocks in the island include granite and granodiorite. The soils in the investigated area were classified as salic gleic fluvisols according to the World Reference Base (WRB) soil classification system [13]. Major mangrove species include Sonneratia apetala, Sonneratia caseolaris (Linn.) Engl., Kandelia candel (Linn.) Druce, Heritiera littoralis Dryand., Parmentiera cerifera Seem., Bruguiera gymnorrhiza (Linn.) Savigny, Excoecaria agallocha Linn., Thespesia populnea (Linn.) Soland. ex Corr. and Acanthus ilicifolius Linn. Sp. [14–16].

2.2. Soil Sampling Method

Soil samples were collected from 17 selected locations with varying surface elevations (Figure 1). At each location, three replicate soil samples were collected from each of the three different soil layers (0–10 cm, 10–20 cm, and 20–30 cm). A total of 153 soil samples was collected from the investigated area. Sampling Locations S1–S5 were within the upper intertidal zone; Sampling Locations S6–S13 were within the mid intertidal zone; and S14–S17 were within the lower intertidal zone. At each sampling location, 3 soil cores were taken to a depth of 30 cm using a soil corer. Soil samples were collected at 10 cm intervals (i.e., 3 samples from each soil profile) and put in sealable plastic bags. In the laboratory, the soil samples were air-dried, ground, and passed through a 0.149 mm sieve prior to analysis.
2.3. Laboratory Methods

The soil-borne trace elements were determined by inductively coupled plasma mass spectrometry (ICP-MS Agilent 7700) after digesting 0.13 g of soil with 8 mL of HNO₃ and 2 mL of HF in a microwave digestion system (MARS™6). The soil analysis was performed by the accredited laboratory of the Nanjing Soil Research Institute Analytical Service, Chinese Academy of Sciences.

2.4. Evaluation of Soil Environmental Quality

The environmental quality of the mangrove soils was assessed by a modified integrated Nemerow pollution index. The Nemerow pollution index (NPI) was calculated using the following formula [17]:

\[
NPI = \frac{C_i}{B_i}
\]  

where \(C_i\) is the observed concentration of a trace element in the investigated soil, while \(B_i\) represents the regional background value of that trace element.

By taking into account all the trace elements contained in the soil, the integrated Nemerow pollution index (INPI) can be obtained as follows [18]:

\[
INPI = \left[ \left( \frac{NPI_{\text{ave}}}{} \right)^2 + \left( \frac{NPI_{\text{max}}}{} \right)^2 \right]^{0.5}
\]  

where \(NPI_{\text{ave}}\) denotes the mean value of the Nemerow pollution index for all the trace elements of concern while \(NPI_{\text{max}}\) represents the maximum value of the Nemerow pollution index among these trace elements. Five pollution categories were set (Table 1) according to Hou et al. [18].

| Pollution Category | INPI | Degree of Pollution |
|--------------------|------|---------------------|
| 1                  | <0.7 | No pollution        |
| 2                  | 0.7-1| Alert               |
| 3                  | 1-2  | Slight pollution    |
| 4                  | 2-3  | Medium pollution    |
| 5                  | >3   | Heavy pollution     |

The soil environmental quality was also assessed against the ecological risk index (ERI) using the following formula [19,20]:

\[
ERI = \sum E_i
\]  

**Figure 1.** Maps showing the geographical location of the study area within the Pearl River estuary and the sampling locations within the study area.
\[ \sum E_i^{r} = \sum T_i \times C_i / B_i \] (4)

where \( E_i^{r} \) represents an individual ecological risk factor, \( C_i \) is the observed concentration of a trace element in the investigated soil, and \( B_i \) represents the regional background value of that trace element. \( T_i \) is the toxicity coefficient of a trace element. For Hg, Cd, As, Ni, Cu, Pb, Cr and Zn, \( T_i \) is set at 40, 30, 10, 5, 5, 5, 2, and 1, respectively [21]. Four ERI categories were set for this study (Table 2) according to Guo et al. [20].

Table 2. Classification system for ecological risk of the mangrove soils based on ecological risk index.

| Category | ERI | Ecological Risk Level |
|----------|-----|-----------------------|
| 1        | <150| low                   |
| 2        | 150–300| medium              |
| 3        | 300–600| high              |
| 4        | >600 | very high             |

3. Results

3.1. Upper Intertidal Zone

On average, the concentration of the investigated trace elements was in the following decreasing order: Zn > Cr > Pb > Cu > As > Ni > Cd > Hg. In general, both horizontal and vertical variations in all the investigated trace elements were not remarkable, although exceptional high or low values were observed at some locations or soil layers. For example, Cd was several times higher in the surface soil layer at Location S1 than in the bottom soil layer at the same location and the soil layers at other locations. Similarly, Hg was several times higher in the surface soil layer at Location S4 than in the bottom soil layer at the same location and the soil layers at other locations (Table 3).

Table 3. Mangrove soil-borne trace elements (mg/kg) in the upper intertidal zone.

| Location | Depth  | Cr      | Ni      | Cu      | Zn      | As      | Cd      | Hg      | Pb      |
|----------|--------|---------|---------|---------|---------|---------|---------|---------|---------|
| S1       | 0–10 cm| 115.59 ± | 31.57 ± | 63.62 ± | 94.63 ± | 56.78 ± | 5.51 ±  | 0.53 ±  | 59.90 ± |
|          |        | 17.82   | 4.23    | 5.37    | 7.63    | 33.11   | 2.90    | 0.03    | 19.54   |
|          | 10–20 cm| 104.03 ± | 28.97 ± | 59.67 ± | 107.18 ±| 100.00 ±| 3.83 ±  | 0.69 ±  | 58.51 ± |
|          |        | 0.07    | 1.66    | 3.62    | 33.22   | 49.75   | 1.89    | 0.27    | 15.08   |
|          | 20–30 cm| 92.52 ±  | 25.53 ± | 39.67 ± | 97.84 ± | 20.37 ± | 0.46 ±  | 0.41 ±  | 31.90 ± |
|          |        | 4.81    | 1.87    | 3.05    | 6.05    | 2.38    | 0.04    | 0.12    | 4.50    |
| S2       | 0–10 cm| 89.19 ±  | 26.50 ± | 35.82 ± | 122.37 ±| 20.92 ± | 0.49 ±  | 0.16 ±  | 36.32 ± |
|          |        | 2.88    | 0.31    | 1.99    | 13.55   | 0.67    | 0.02    | 0.01    | 0.40    |
|          | 10–20 cm| 90.08 ±  | 26.09 ± | 35.44 ± | 102.21 ±| 21.12 ± | 0.51 ±  | 0.56 ±  | 36.69 ± |
|          |        | 2.48    | 0.77    | 1.99    | 4.76    | 0.38    | 0.01    | 0.45    | 1.40    |
|          | 20–30 cm| 94.39 ±  | 26.88 ± | 41.62 ± | 107.18 ±| 23.25 ± | 0.59 ±  | 0.37 ±  | 40.21 ± |
|          |        | 2.02    | 0.42    | 3.00    | 0.80    | 1.22    | 0.05    | 0.22    | 1.17    |
| S3       | 0–10 cm| 80.93 ±  | 22.24 ± | 35.78 ± | 93.23 ± | 20.90 ± | 0.41 ±  | 0.22 ±  | 31.97 ± |
|          |        | 1.69    | 0.00    | 1.77    | 11.35   | 0.76    | 0.01    | 0.00    | 0.55    |
|          | 10–20 cm| 86.15 ±  | 29.00 ± | 45.88 ± | 122.37 ±| 25.73 ± | 0.74 ±  | 0.24 ±  | 38.20 ± |
|          |        | 3.41    | 1.72    | 7.41    | 2.62    | 6.18    | 0.14    | 0.03    | 5.06    |
|          | 20–30 cm| 93.79 ±  | 39.70 ± | 47.96 ± | 128.05 ±| 23.28 ± | 0.90 ±  | 0.20 ±  | 45.85 ± |
|          |        | 2.39    | 11.42   | 4.63    | 1.86    | 0.20    | 0.30    | 0.04    | 8.72    |
As compared to the surface soil layer (0–10 cm) and the bottom soil layer (20–30 cm) at most of the locations, the subsoil layer (10–20 cm) tended to have a higher concentration of Zn and As, whereas the surface layer (0–10 cm) had the highest concentration of Hg. An unusually high concentration of Hg was detected at Location S11. The mean values of various trace elements observed at the locations were as follows:

### Table 4. Mangrove soil-borne trace elements (mg/kg) in the mid intertidal zone.

| Sample | Depth   | Cr   | Ni   | Cu   | Zn   | As   | Cd   | Hg   | Pb   |
|--------|---------|------|------|------|------|------|------|------|------|
| S6     | 0–10 cm | 95.45 ± 2.52 | 31.66 ± 0.32 | 41.39 ± 7.39 | 90.20 ± 1.60 | 26.06 ± 0.52 | 0.62 ± 0.16 | 0.19 ± 0.04 | 39.62 ± 5.41 |
|        | 10–20 cm| 100.84 ± 1.57 | 29.00 ± 0.88 | 37.78 ± 1.93 | 106.08 ± 4.56 | 32.15 ± 9.64 | 0.60 ± 0.04 | 0.18 ± 0.02 | 40.38 ± 1.83 |
|        | 20–30 cm| 92.82 ± 2.31 | 29.02 ± 1.49 | 34.91 ± 0.91 | 82.33 ± 3.44 | 21.85 ± 0.58 | 2.32 ± 1.89 | 0.14 ± 0.01 | 41.27 ± 10.87 |
| S7     | 0–10 cm | 93.31 ± 1.79 | 27.53 ± 0.05 | 33.48 ± 0.99 | 103.08 ± 2.81 | 20.40 ± 0.96 | 0.49 ± 0.01 | 0.15 ± 0.01 | 37.84 ± 0.38 |
|        | 10–20 cm| 101.17 ± 4.47 | 30.61 ± 0.43 | 46.08 ± 6.83 | 181.25 ± 72.36 | 106.00 ± 83.20 | 2.26 ± 1.63 | 0.16 ± 0.04 | 41.36 ± 81.20 |
|        | 20–30 cm| 100.95 ± 1.15 | 28.31 ± 0.53 | 43.14 ± 6.83 | 92.49 ± 4.69 | 22.68 ± 0.85 | 0.48 ± 0.02 | 0.13 ± 0.03 | 35.67 ± 0.62 |
| S8     | 0–10 cm | 90.07 ± 2.68 | 29.98 ± 1.50 | 44.21 ± 7.37 | 109.70 ± 9.83 | 30.36 ± 8.56 | 4.03 ± 3.46 | 0.39 ± 0.06 | 64.78 ± 24.19 |
|        | 10–20 cm| 94.22 ± 4.34 | 27.89 ± 1.68 | 43.36 ± 5.46 | 128.33 ± 7.07 | 51.37 ± 27.64 | 4.68 ± 3.38 | 0.33 ± 0.03 | 74.49 ± 29.23 |
|        | 20–30 cm| 95.21 ± 1.74 | 27.33 ± 0.35 | 37.14 ± 1.69 | 107.32 ± 8.56 | 24.66 ± 3.04 | 2.26 ± 1.61 | 0.25 ± 0.06 | 47.33 ± 12.18 |

### 3.2. Mid Intertidal Zone

In general, marked horizontal and vertical variations in the investigated trace elements were not observed. However, the subsoil layer (10–20 cm) tended to have a higher concentration of Zn and As, as compared to the surface soil layer (0–10 cm) and the bottom soil layer (20–30 cm) at most of the sampling locations. An unusually high concentration of Cd was recorded at Location S8 and an unusually high concentration of Hg was detected at Location S11. The mean values of various trace elements were comparable to those in the upper intertidal zone with a similar decreasing order being observed: Zn > Cr > Pb > Cu > As > Ni > Cd > Hg (Table 4).
The soil-borne trace elements were only slightly variable horizontally. No clear pattern of vertical variation in the soil-borne trace elements was observed. An unusually high concentration of Cd was observed for the surface soil layer at Location S17 (Table 5).

### Table 4. Cont.

| Sample | Depth | Cr     | Ni     | Cu     | Zn     | As     | Cd     | Hg     | Pb     |
|--------|-------|--------|--------|--------|--------|--------|--------|--------|--------|
| S9     | 0–10 cm | 97.92 ±2.59 | 26.90 ±1.89 | 34.77 ±0.33 | 95.15 ±0.47 | 21.47 ±0.47 | 0.48 ±0.16 | 0.33 ±0.02 | 37.19 ±0.08 |
| 10–20 cm | 98.50 ±4.37 | 29.08 ±0.78 | 41.45 ±2.14 | 177.89 ±32.77 | 78.47 ±31.50 | 2.58 ±1.06 | 0.23 ±0.04 | 62.33 ±12.11 |
| 20–30 cm | 98.95 ±5.53 | 29.41 ±1.66 | 38.98 ±2.98 | 102.79 ±5.64 | 22.19 ±0.85 | 0.66 ±0.03 | 0.22 ±0.04 | 37.00 ±0.49 |
| S10    | 0–10 cm | 90.08 ±0.76 | 25.59 ±0.88 | 37.30 ±2.07 | 105.57 ±9.01 | 21.03 ±1.42 | 0.50 ±0.12 | 0.37 ±0.00 | 40.07 ±4.72 |
| 10–20 cm | 100.86 ±5.97 | 26.89 ±1.13 | 35.79 ±2.08 | 106.34 ±10.38 | 20.52 ±0.90 | 0.53 ±0.10 | 0.32 ±0.04 | 36.49 ±2.20 |
| 20–30 cm | 98.85 ±3.83 | 27.64 ±0.56 | 39.26 ±2.08 | 97.24 ±2.00 | 21.03 ±1.75 | 0.58 ±0.04 | 0.28 ±0.02 | 37.86 ±1.33 |
| S11    | 0–10 cm | 91.48 ±6.88 | 25.98 ±0.29 | 32.51 ±0.89 | 128.32 ±32.57 | 19.82 ±1.06 | 0.50 ±0.05 | 2.84 ±0.24 | 36.42 ±2.21 |
| 10–20 cm | 98.17 ±4.36 | 27.82 ±1.24 | 36.72 ±2.38 | 124.35 ±27.78 | 49.26 ±28.19 | 0.53 ±0.37 | 0.32 ±0.42 | 47.11 ±10.30 |
| 20–30 cm | 159.26 ±56.12 | 34.98 ±8.21 | 37.11 ±2.29 | 110.31 ±12.89 | 22.35 ±0.87 | 0.92 ±0.16 | 0.49 ±0.19 | 40.52 ±0.47 |
| S12    | 0–10 cm | 90.15 ±9.27 | 30.10 ±5.03 | 32.75 ±1.79 | 104.86 ±2.56 | 17.86 ±1.80 | 0.49 ±0.03 | 0.31 ±0.04 | 36.01 ±3.13 |
| 10–20 cm | 107.01 ±2.19 | 32.14 ±2.67 | 37.97 ±1.16 | 108.61 ±5.50 | 19.92 ±0.44 | 0.71 ±0.06 | 0.35 ±0.04 | 44.19 ±0.12 |
| 20–30 cm | 103.50 ±3.03 | 32.20 ±0.53 | 40.53 ±0.90 | 115.91 ±3.32 | 23.56 ±0.64 | 0.83 ±0.01 | 0.32 ±0.03 | 46.89 ±0.93 |
| S13    | 0–10 cm | 95.03 ±6.05 | 30.16 ±2.46 | 44.76 ±3.44 | 118.77 ±6.86 | 23.11 ±1.50 | 0.60 ±0.03 | 0.12 ±0.02 | 40.40 ±1.88 |
| 10–20 cm | 99.64 ±6.54 | 32.35 ±0.37 | 43.79 ±1.12 | 115.31 ±14.37 | 22.60 ±0.39 | 0.80 ±0.08 | 0.12 ±0.02 | 44.69 ±0.87 |
| 20–30 cm | 93.22 ±5.56 | 29.44 ±2.14 | 40.58 ±0.71 | 105.90 ±1.81 | 22.60 ±0.77 | 0.66 ±0.02 | 0.11 ±0.01 | 38.80 ±1.92 |
| Average | 99.44 ±2.59 | 29.25 ±0.47 | 38.99 ±0.75 | 113.96 ±4.55 | 31.02 ±4.44 | 1.23 ±0.24 | 0.38 ±0.11 | 45.36 ±2.55 |

### 3.3. Lower Intertidal Zone

The average concentration of the investigated trace elements showed the decreasing order: Zn > Cr > Pb > Cu > Ni > As > Cd > Hg, which is different to those in the upper and mid intertidal zones. The soil-borne trace elements were only slightly variable horizontally. No clear pattern of vertical variation in the soil-borne trace elements was observed. An unusually high concentration of Cd was observed for the surface soil layer at Location S17 (Table 5).
This can be used to indicate that the trace element loadings in the Pearl River distributaries were relatively constant amounts of trace elements from the Pearl River catchment in the past two decades. Due to the very small local catchment size, it was unlikely that soil erosion from the hill slopes contributed significantly to the tidal sediments. Most of the sediments deposited during the past two decades. Due to the very small local catchment size, it was unlikely that soil erosion from the hill slopes contributed significantly to the tidal sediments. Most of the sediments present in the tidal zone should have been deposited from the suspended materials discharged into the Pearl River estuary from the Pearl River. It is clear from the results that spatial variation in the investigated soil-borne trace elements was minor, suggesting that the whole intertidal zone received relatively constant amounts of trace elements from the Pearl River catchment in the past two decades. This can be used to indicate that the trace element loadings in the Pearl River distributaries were generally stable during the recent two decades.

Chromium was not related to any other investigated trace elements (Table 6). This appears to suggest that this trace element was not largely derived from the same water pollution sources as the other seven investigated trace elements. The major water pollution sources of Cr include chrome plating, leather tanning, and textile industries [23–25], which do not release substantial amounts of other trace elements.

| Sample | Depth   | Cr (mg/kg) | Ni (mg/kg) | Cu (mg/kg) | Zn (mg/kg) | As (mg/kg) | Cd (mg/kg) | Hg (mg/kg) | Pb (mg/kg) |
|--------|---------|------------|------------|------------|------------|------------|------------|------------|------------|
| S14    | 0–10 cm | 79.60 ± 0.74 | 24.20 ± 0.56 | 34.20 ± 4.12 | 109.30 ± 9.33 | 39.79 ± 22.99 | 4.02 ± 3.70 | 0.07 ± 0.00 | 33.68 ± 3.22 |
|        | 10–20 cm| 82.70 ± 7.25 | 27.90 ± 0.37 | 36.20 ± 3.35 | 101.99 ± 7.16 | 18.51 ± 0.97 | 0.42 ± 0.03 | 0.07 ± 0.01 | 33.69 ± 2.40 |
|        | 20–30 cm| 107.00 ± 18.10 | 32.80 ± 3.68 | 45.20 ± 6.78 | 138.67 ± 21.62 | 40.15 ± 15.17 | 1.54 ± 0.88 | 0.10 ± 0.02 | 51.64 ± 7.93 |
| S15    | 0–10 cm | 81.60 ± 6.28 | 27.40 ± 0.23 | 38.90 ± 0.93 | 65.74 ± 47.90 | 12.66 ± 7.04 | 2.26 ± 1.90 | 0.08 ± 0.00 | 34.33 ± 3.96 |
|        | 10–20 cm| 106.00 ± 24.5 | 34.60 ± 6.24 | 39.60 ± 2.98 | 112.05 ± 4.54 | 20.55 ± 1.71 | 0.47 ± 0.05 | 0.08 ± 0.01 | 32.75 ± 2.77 |
|        | 20–30 cm| 99.30 ± 9.77 | 31.90 ± 1.81 | 53.00 ± 9.39 | 312.17 ± 173.62 | 17.74 ± 5.84 | 1.08 ± 0.43 | 0.10 ± 0.02 | 45.59 ± 4.72 |
| S16    | 0–10 cm | 83.50 ± 13.20 | 30.60 ± 2.27 | 43.50 ± 7.94 | 119.37 ± 0.90 | 21.71 ± 0.90 | 0.51 ± 0.10 | 0.10 ± 0.00 | 34.98 ± 4.71 |
|        | 10–20 cm| 151.00 ± 68.10 | 48.30 ± 17.20 | 44.70 ± 5.16 | 126.34 ± 8.33 | 21.39 ± 0.72 | 0.59 ± 0.04 | 0.08 ± 0.01 | 38.28 ± 2.74 |
|        | 20–30 cm| 91.30 ± 1.68 | 30.90 ± 0.74 | 60.80 ± 12.00 | 190.22 ± 1.81 | 21.79 ± 0.49 | 1.02 ± 0.04 | 0.10 ± 0.02 | 39.54 ± 1.65 |
| S17    | 0–10 cm | 91.30 ± 2.97 | 32.00 ± 1.31 | 39.20 ± 2.07 | 120.63 ± 15.90 | 40.38 ± 19.91 | 0.87 ± 0.36 | 0.09 ± 0.03 | 45.68 ± 9.21 |
|        | 10–20 cm| 95.30 ± 3.03 | 30.00 ± 0.42 | 42.30 ± 1.64 | 113.64 ± 5.59 | 21.69 ± 0.85 | 0.54 ± 0.04 | 0.08 ± 0.02 | 41.54 ± 1.49 |
|        | 20–30 cm| 95.80 ± 5.41 | 32.70 ± 3.11 | 48.70 ± 1.76 | 131.08 ± 2.42 | 22.61 ± 1.31 | 0.65 ± 0.06 | 0.08 ± 0.02 | 42.34 ± 3.19 |
| Average |        | 101.55 ± 2.74 | 30.37 ± 0.75 | 40.76 ± 1.08 | 124.84 ± 8.93 | 26.26 ± 2.16 | 0.94 ± 0.13 | 0.28 ± 0.08 | 43.35 ± 1.40 |

4. Discussion

The sedimentation rate in the tidal zone of Qi’ao Island was approximately 1.68 cm/year [22]. Therefore, the mangrove soils (0–30 cm) investigated in this study were mostly derived from sediments deposited during the past two decades. Due to the very small local catchment size, it was unlikely that soil erosion from the hill slopes contributed significantly to the tidal sediments. Most of the sediments present in the tidal zone should have been deposited from the suspended materials discharged into the Pearl River estuary from the Pearl River. It is clear from the results that spatial variation in the investigated soil-borne trace elements was minor, suggesting that the whole intertidal zone received relatively constant amounts of trace elements from the Pearl River catchment in the past two decades. This can be used to indicate that the trace element loadings in the Pearl River distributaries were generally stable during the recent two decades.

Chromium was not related to any other investigated trace elements (Table 6). This appears to suggest that this trace element was not largely derived from the same water pollution sources as the other seven investigated trace elements. The major water pollution sources of Cr include chrome plating, leather tanning, and textile industries [23–25], which do not release substantial amounts of other trace elements.
Table 6. Correlation matrix showing the correlation coefficients between the investigated trace elements.

|       | Cr   | Ni  | Cu  | Zn  | As  | Cd  | Hg  | Pb   |
|-------|------|-----|-----|-----|-----|-----|-----|------|
| Cr    | 1    |     |     |     |     |     |     |      |
| Ni    | 0.129| 1   |     |     |     |     |     |      |
| Cu    | -0.163| 0.549**| 1   |     |     |     |     |      |
| Zn    | -0.317| 0.007| 0.459*| 1   |     |     |     |      |
| As    | -0.382| -0.049| 0.389| 0.965**| 1   |     |     |      |
| Cd    | -0.082| -0.163| 0.396| 0.550**| 0.495*| 1   |     |      |
| Hg    | 0.316| -0.394| -0.079| 0.017| 0.010| 0.270| 1   |      |
| Pb    | 0.171| -0.267| -0.089| 0.450*| 0.384| 0.360| -0.054| 1    |

** significant at \( p < 0.01 \). * significant at \( p < 0.05 \).

Mercury was also not related to any other trace elements (Table 6). Mining is a major source of mercury in many places [26]. However, Hg discharge related to mining activities is always accompanied with discharges of heavy metals and metalloids [27]. Therefore, Hg discharged into Pearl River was likely to be due to other sources, such as pulp and paper industries [28].

There was a close relationship between Pb and Zn in the investigated mangrove soils (Table 6). This can be explained by the close association between lead sulfide and zinc sulfides in lead–zinc deposits [29]. Mining and smelting of lead–zinc ores result in simultaneous discharge of both Pb and Zn.

The close relationship between Ni and Cu (Table 6) could be attributed to their concurrent presence in nickel–copper sulfide ores [30]. The sources of nickel include nickel plating, non-Ni ore mining, burning of coal and oil, nickel–cadmium batteries, sewage, phosphate fertilizers, and pesticides, which also involve other trace elements [31]. The fact that Ni was only closely related to Cu but not to other trace elements suggests that these are not major contributors to the Ni loading in the Pearl River system.

It is interesting to note that Zn was not only closely related to Pb but also to Cu, Cd, and As (Table 6). Zn discharge can be caused by a wide range of economic activities, including mining, smelting, coal burning, manufacturing, and the use of pesticides and fungicides [32–34], which frequently involve other trace elements.

It is also interesting to note that there is a trend showing that the concentration of Cd and Hg decreased from the upper intertidal zone to the lower intertidal zone. This suggests that these two elements tended to be retained in the upper part of the tidal zone and their seaward transport was relatively weak. The extremely high concentration of Cd and Hg in the surface soil layer at some locations was accompanied by a large standard deviation, indicating the significant variation among the three replicate samples collected at the same location. This can be attributed to unusual contamination by local sources at certain isolated spots. Further investigation is needed to understand the causes of these observations.

The background concentrations of Cr, Ni, Cu, Zn, As, Cd, Hg, and Pb were 50.5, 14.4, 17, 47.3, 8.9, 0.05, 0.078, and 36 mg/kg, respectively. It can be seen from Figure 2 that the concentrations of the eight investigated soil-borne trace elements were all greater than the respective background concentration of each trace element.
Figure 2. Concentration of the investigated soil-borne trace elements (Cr, Cu, As, Hg, Ni, Zn, Cd and Pb) compared to their respective background values.

The INPI of the surface soils at the 17 sampling locations ranged from 7.53 to 48.42, values which all fall within the highest pollution category (Category 5), i.e., heavy pollution (Table 7).

Table 7. The integrated Nemerow pollution index (INPI) of the surface soils at the 17 sampling locations.

| Sampling Location | INPI   | Degree of Pollution |
|-------------------|--------|---------------------|
| S1                | 12.74  | Heavy pollution     |
| S2                | 11.41  | Heavy pollution     |
| S3                | 14.52  | Heavy pollution     |
| S4                | 16.38  | Heavy pollution     |
| S5                | 14.29  | Heavy pollution     |
| S6                | 48.42  | Heavy pollution     |
| S7                | 16.45  | Heavy pollution     |
| S8                | 7.53   | Heavy pollution     |
| S9                | 11.72  | Heavy pollution     |
| S10               | 9.31   | Heavy pollution     |
| S11               | 9.56   | Heavy pollution     |
| S12               | 9.90   | Heavy pollution     |
| S13               | 17.69  | Heavy pollution     |
| S17               | 22.70  | Heavy pollution     |
| S18               | 15.18  | Heavy pollution     |
| S19               | 8.02   | Heavy pollution     |
| S20               | 9.35   | Heavy pollution     |

Using the ecological risk assessment method of Hakanson [19], among the 17 sampling locations, six locations had an ERI greater than 300 and 12 locations had an ERI greater than 600 (Figure 3), indicating that most of the investigated locations were at high or very high ecological risk.
By comparison with some other mangrove wetlands around the world, the concentration of soil-borne Cr, Zn, As, Cd, and Hg was higher at this study site than in the majority of the reference sites (Table 8). Qi’ao Island is the island closest to the mouths of two major active distributaries of the Pearl River. Therefore, the mangrove tidal zone was directly exposed to the sediment-borne trace elements discharged from the Pearl River. Although a firm conclusion cannot be drawn from the data obtained at this study site alone, the special location of Qi’ao Island does allow some level of confidence to suggest that Pearl River is amongst the heavily contaminated rivers around the world.

Table 8. Levels of heavy metals in mangrove wetland soils.

| Study Area                          | Cr   | Ni  | Cu   | Zn  | As  | Cd  | Hg  | Pb  |
|-------------------------------------|------|-----|------|-----|-----|-----|-----|-----|
| Sanya, China [35]                   | 61.5 | -   | 21.0 | 126 | 14.3| 0.09| -   | 42.3|
| Luoyang Bridge, China [35]          | 18.6 | -   | 34.0 | 106 | 5.31| 0.06| -   | 167 |
| Dongzhai Harbor, China [36]         | 75.8 | 31.0| 19.6 | 44.8| 8.67| 0.62| -   | 20.7|
| Yingluo Harbor, China [37]          | 56.7 | -   | 7.76 | 31.9| -   | 0.11| 0.04| 14.2|
| Shenzhen Bay, China [7]             | 96.2 | 44.6| 88.8 | 358 | 172 | 0.94| 0.14| 72  |
| Zhangjiang River Estuary, China [38]| -    | -   | 21.04| -   | -   | 0.33| 0.03| 63.2|
| Sunderban mangrove, India [39]      | 41.8 | 47.4| 60.06| 88.3| -   | 0.48| 0.24| 52.9|
| Guanabara Bay, Brazil [40]          | 42.4 | -   | 98.6 | 483 | 1.32| 1.32| -   | 160 |
| Kottuli, India [41]                 | 0.26 | 0.38| 69.3 | 384 | -   | 0.03| -   | 6.91|
| Hong Kong, China [11]               | 40.0 | 3.00| 240  | 40.0| -   | 3.00| -   | 80  |
| Pichavaram, India [42]              | 530  | 253 | 150  | 108 | -   | 34.5| -   | 133 |
| Brisbane River, Australia [43]      | 7.6–116| 2.4–57.6| 3.1–34.1| 40–144| 0–13.0| 0–2.0| 7.7–84.7|
| This Study                          | 99.5 | 29.2| 40.8 | 116 | 30.0| 1.16| 0.41| 44.0|

5. Conclusions

The mangrove soils of Qi’ao Island were heavily contaminated by trace elements transported from the Pearl River. These soil-borne trace elements pose a high risk to the mangrove ecosystem. The whole intertidal zone received relatively constant amounts of trace elements from the Pearl River catchment in the past two decades. Zn showed common sources with many other trace elements while some trace elements were not closely related to each other. The findings obtained from this study have implications for understanding the terrestrial inputs of trace elements into part of the Pearl River estuary. Although a firm conclusion cannot be drawn from the data obtained at this study site alone, the special location of Qi’ao Island does allow some level of confidence to suggest that Pearl River is amongst the heavily contaminated rivers in the world. This will provide useful information for
decision-makers to better control the discharge of trace elements from the catchment area and manage the aquatic ecosystems in the Pearl River Estuary.

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