Abstract

Heavy metal contamination was compared for soils with different land use (cropland and wetland) in the reclaimed region of the Pearl River estuary. A sequential extraction technique was used to produce five chemical fractions (exchangeable (F1), carbonate (F2), Fe–Mn hydroxide (reducible) (F3), organic (F4) and residual (F5)) to study the effects of reclamation and tillage on the distribution and mobility of the heavy metals Cr and Ni. The results revealed that generally the contamination levels increased with a longer history of reclamation (100> 40> 30> 10 years) whilst an undisturbed reference wetland was least affected. The most substantial quantities of both Cr and Ni were observed in the residual fraction, which may be a consequence of the mixing effects of soil tillage and planting. With the exception of the 20-30cm layers from the wetland and 10 year old cropland samples, the total concentration of Cr and Ni at all sites and all soil layers exceeded the moderately polluted level according to the SQGs of the US EPA.

1. Introduction

The Pearl River estuary is one of the largest estuaries in China and home to over 42 million people. Land reclamation of tidal wetlands became a common practice around the Pearl River estuary more than one hundred years ago and has continued until the present day [1]. Heavy metal contamination as a result of urbanization and industrial development of the Pearl River estuary has recently come under scrutiny [2-
4). Although several studies have been conducted in the Pearl River estuary, few have focused on development of metal contamination in the reclaimed cropland soils. This information is critical to aid coastal zone management and plan industrial and urban development [5]. The primary objective of this study was therefore to compare the concentrations of the metals chromium (Cr) and nickel (Ni) appearing in the different fractions of soils derived from croplands with different histories of reclamation and from an undisturbed referencing wetland.

2. Materials and methods

The study was conducted in an area north to south along the Wanqingsha reclaimed land, south of the Pearl River (22°36’39” to 22°44’36”N and 113°23’42” to 113°38’34”E), in early August of 2010. The interval between sampling sites was about 2500 m which corresponded to croplands with different histories of reclamation either: 100, 40, 30 or 10 years. The referencing tidal wetland was located close to the sea at the same site. In each case soil cores were taken in triplicate from the top 30 cm of soil. The cores were immediately sectioned at 10 cm intervals. All the soil samples were placed into polyethylene bags, transferred to the laboratory and preserved in a refrigerator at 4°C. The soil samples were then air-dried and homogenized for heavy metal fractionation analysis.

The Cr and Ni were sequentially extracted following the five step method proposed by Tessier et al. (1979) into five fractions operationally defined as exchangeable (F1), carbonate (F2), Fe–Mn hydroxide (reducible) (F3), organic (F4) and residual (F5). It can be considered that these fractions decrease in lability from exchangeable to residual (Jain et al., 2010). After each successive extraction the samples were centrifuged at 4000 rpm for 15 minutes to separate the extract from the soil samples. The concentrations of Cr and Ni in each of the leachates were determined by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP/AES). The quality assurance and quality control were assessed using duplicates, method blanks and standard reference materials (GBW07401) from the Chinese Academy of Measurement Sciences with each batch of samples (1 blank and 1 standard for each 10 samples). The recoveries of samples spiked with standards ranging from 95 to 105%.

3. Results and discussion

3.1. Heavy metal fractionation in soil profiles

The heavy metal concentrations of the 10 year old cropland and reference wetland were lower than those obtained from the older samples (100, 40 and 30 years), at all depths. The highest metal concentrations were observed in the 100 year old cropland, which indicated that the most severe pollution occurred in cropland with the longest history of reclamation, where runoff and urban sewage had been irrigated for a long time. This is probably a result of a long history of tillage and the heavy application of agrochemicals that caused the metals to settle in the soil profile [5].

3.1.1. Chromium contamination

The highest concentration of Cr was observed in the surface soil and the concentration generally decreased slightly with depth. However it was noted that the surface and subsurface soil of the reference wetland had almost the same Cr concentration. For the surface soil, the total concentration of Cr decreased corresponding to the age of the cropland from the oldest to most recent and finally the reference wetland. However for the subsurface and bottom layers of soil, the 40 year old cropland showed the highest accumulation of Cr, though the lowest concentration was still observed in wetland.
The total Cr concentration in most of the soil samples exceeded the “heavily-polluted” level (75 mg/kg), according to the Sediment Quality Guidelines (SQGs) developed by the United States Environmental Protection Agency [6], and even the lowest concentration (60.55 mg/kg) from the 20-30 cm soil layer of the wetland sample was classified as “moderately polluted” (25 mg/kg ~ 75 mg/kg) (Table 1). For all samples Cr was predominantly found in the residual fraction of the soil cores (residual Cr/total Cr > 84%). This was consistent with the results of Cai et al. [7] who also found Cr was mostly in the residual fraction (>65%) of river sediments obtained from the Pearl River delta.

### 3.1.2. Nickel contamination

The surface soils from the older croplands (100, 40 and 30 years) had total Ni concentrations close to or above the “heavily-polluted” level (50 mg/kg), however their subsoils below 10 cm in depth were only “moderately polluted” (Table 1). All the samples from the 10 year old cropland and reference wetland also fell into this category. The total Ni concentration at all five sampling sites generally decreased with soil depth. However, the difference in Ni concentrations between the 10-20 cm and 20-30 cm layers of the 30 and 10 year old croplands was not significantly different. The total proportion of exchangeable and carbonate bound Ni contributed less than 6.6% of the total Ni, while similar to Cr, the residual form was predominant, having a ratio of >68% in all the soils sampled.

|               | Cr            | Ni            |
|---------------|---------------|---------------|
| Measured values in this study | 60.55 ~ 104.18 | 22.67 ~ 54.60 |
| SEPAC         |               |               |
| Class I       | ≤ 90          | ≤ 40          |
| Class II      | ≤ 250         | ≤ 60          |
| Class III     | ≤ 300         | ≤ 200         |
| Class I (%)   | 66.7          | 66.7          |
| Class II (%)  | 33.3          | 33.3          |
| Class III (%) | 0.0           | 0.0           |
| USEPA         |               |               |
| Non-polluted  | < 25          | < 20          |
| Moderate-polluted | 25-75       | 20-50         |
| Heavily-polluted | > 75        | > 50          |
| Non-polluted (%) | 0.0         | 0.0           |
| Moderate-polluted (%) | 20.0        | 86.7          |
| Heavily-polluted (%) | 80.0        | 13.3          |

### 4. Conclusions

The distribution of the heavy metals Cr and Ni between the 5 different fractions varied by depth but seemed to be unaffected by reclamation and tillage. However, tillage history was an important factor related to the absolute accumulation of heavy metals, particularly of Ni in the cropland soils. The
pollution assessment based on total concentrations of heavy metals according to the Chinese National Environment Quality Standards (CNEQS) set by the State Environmental Protection Administration of China (SEPAC) [8] and the SGQs of the US EPA indicated that Cr, and Ni were always present at concentrations considered moderately or heavily polluted in the first case or class 1 or 2 in the second.

Acknowledgements

This work was supported financially by the Key Project of National Natural Science Foundation (No.U0833002), Program for New Century Excellent Talents in University (NECT-10-0235), National Natural Science Foundation (No. 50879005 and 51179006) and special fund of State Key Lab of Water Environment Simulation (11Z01ESPCN). We wish to express our thanks to all our colleagues within this research group for their assistances in field work.

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