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Occurrence of red clay horizon in soil profiles of the Yellow River Delta: Implications for accumulation of heavy metals

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ABSTRACT

The source-area weathering and pedogenesis processes in the alluvial soil profiles might affect depth distribution of heavy metals. Red clay horizon (RCH) with a thickness of 5–50 cm in a 1 m soil profile has been found ubiquitously in the Yellow River Delta (YRD). The occurrence of this RCH was supposed to be related with the frequent shifting of the Yellow River tail channel in the Yellow River Delta (YRD). The geochemical features of the RCH were distinct from its upper or lower yellow silt horizon (YSH). The average median grain size of the RCH (10.5 μm) was almost three times lower than that of the YSH (29.9 μm). Meanwhile, the RCH was characterized of higher chemical index of alteration (CIA), magnetic susceptibility (χ_{lf}) and frequency-dependent magnetic susceptibility (χ_{fd}) values than the YSH, which implied a stronger source-area weathering and pedogenesis intensity of the RCH. Besides the distinctive characteristics of the RCH, it also accumulated significantly ($p < 0.05$) higher mean contents of Cu, Zn, Pb, Cr, Ni and Co, and maximum content of Cd in the RCH than that in the YSH. The principal component analysis (PCA) suggested that distribution of the heavy metals in the YRD soil profiles was significantly related to the content of aluminosilicates, oxides, clay fraction, χ_{lf} and χ_{fd}, however, such a correlation was not found except for Pb in the YSH. In addition, result of BCR sequential extraction indicated that a higher percentage of Fe–Mn oxides associated fraction was in the RCH than in the YSH for the heavy metals of Pb and Co. Cadmium was observed at higher percentage of exchangeable fraction in the RCH than in the YSH, implying a higher environmental risk of the Cd in the RCH.

1. Introduction

Heavy metal pollution in soils has received extensive attention due to its covert, persistent and irreversible properties (Cheng et al., 2014). In general, the fate and speciation of heavy metals in soils are controlled by a variety of physico-chemical properties, including pH, organic matter, clay minerals, cation exchange capacity (CEC), carbonates, phosphates and Fe–Mn oxides (Bai et al., 2011; Selim, 2013). Therefore, different types of soil horizons might affect the content of heavy metals greatly because of their variation in physico-chemical characteristics formed in different environment conditions. Sterckeman et al. (2000) demonstrated that higher concentrations of heavy metals were accumulated in the deeper mineral soil horizons than the humus rich soil horizons. Lamy et al. (2006) presented that the concentrations of the metals were markedly diminished blow a plow pan in soil profile. Burkhardt et al. (2011) reported that high heavy metal concentrations occurred both in solid phase and in the pore water of an oxidized, iron-rich Btlc horizon of a Luvic Gleysol. Vacca et al. (2012) presented that the soils with the presence of buried horizons in the flooded areas were significantly contaminated by heavy metals.

The accumulation level of heavy metals in soils is usually assessed by the measurement of total heavy metal content. However, it cannot provide sufficient information to evaluate the mobility of actually and potentially mobile metals in soil profiles, and consequently the environmental risk (Kabala and Singh, 2001). As a consequence, sequential extraction procedure by using different mild chemical reagents was developed to evaluate the heavy metal fractions (Tessier et al., 1979; Luo and Christie, 1998a). Hence the heavy metal fractions can be used to assess the mobility in soils (Luo and Christie, 1998b; Nemati et al., 2011).

Previous studies on the heavy metal pollution in soils of the YRD mainly focused on the wetland, which showed unpolluted or moderately polluted levels of heavy metals (Bai et al., 2012; Xie et al., 2014; Yao et al., 2015). These studies also showed that soil organic matter, moisture and clays were key factors to influence the distribution of heavy metals in this area. Liu et al. (2015) applied sequential extraction method to show that most heavy metals in sediments at the Yellow River estuary were presented in the residual fraction.

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However, little information is available on geochemical variability of heavy metals in soil profiles with different weathering features at the whole-delta scale.

In this study, 33 soil profiles were collected from the YRD in November 2012. Among them, 28 soil profiles were found with a special soil horizon named red clay horizon (RCH). Therefore, the objectives of this study were (1) to understand the geochemical characteristics of the different alluvial horizons in soil profiles, especially focusing on the red clay horizon; (2) to infer the factors influencing the accumulation of heavy metals in the different soil horizons; and (3) to assess the mobility of heavy metals in the typical soil profiles by using the sequential extraction procedure.

2. Materials and methods

2.1. Study area

Study area is located at the Yellow River Delta, one of China's three major river deltas, has been undergoing extensive development of industry and agriculture according to plans of Chinese central government. The Yellow River, which historically carries a huge amount of sediment (1.08×10^9 t yr^{-1}) from the erosion of Loess Plateau in central China (Milliman and Syvitski, 1992), has been discharging into the western Bohai Sea since 1855 and forming the modern Yellow River Delta (YRD) with expanding by about 20 km^2 per year (Pang and Si, 1980). Due to high sediment concentration, the unstable Yellow River distributary channels on the delta has shift their courses for a total of 11 times, resulting in the formation of different sedimentary successions with fine grained layers at weak hydrodynamics and coarse grained layers at strong hydrodynamics (Xue et al., 2009; Qiao et al., 2011a). The main geomorphologic classes built by Yellow River channel movements and sediment deposition in the YRD are distributary channel, crevasse splay, natural levee and flood plain. The textures of deltaic sediment are generally classified as brown clayey silt for flood plain and yellow silt for other landforms (Yi et al., 2003). The region of the red clay horizon with 5–50 cm thick occurred in 1 m soil profiles in the study area stretches from the Majia River in the north to the Xiaoqing River in the south, including Dongying City and Binzhou City (Fig. 1a).

2.2. Soil sampling

Thirty three soil profiles were collected from inland to coast at the YRD in November 2012. Soils were sampled by pedogenic horizons from bottom to top in 1 m depth. Samples from thin or discontinuous horizons were added to the horizon above or below. A total of 42 RCH samples were identified in 28 soil profiles (Fig. 1a, marked in red). According to the lithologic characteristics, the soil profile could be divided into three parts (Fig. 1b), the RCH, which have reddish brown color and abundant clay. The upper and lower parts of the RCH with 52 and 26 horizon samples, which have yellow color and abundant silt, were classified as yellow silt horizon (YSH). All soil samples were collected using a stainless steel hand auger and then placed into polyethylene bags.

2.3. Sample analysis

All soil samples were air dried at room temperature for one week and sieved through a 2-mm nylon sieve to remove coarse debris, plant roots and other waste materials. They were then ground with a pestle and mortar until all particles passed a 0.149-mm nylon sieve. The 2-mm samples were used for the determination of soil grain size, salinity and pH. The 0.145-mm samples were used for the measurement of soil organic matter (SOM), total nitrogen (TN), cation exchange capacity (CEC), $CaCO_3$, magnetic properties, major elements and heavy metals.

Soil grain size was measured using a Malvern Mastersizer 2000 instrument after removing organic matter and carbonates using 15% H_2O_2 and 4 M HCl. Soil salinity and pH was determined in supernatant of 1:5 and 1:2.5 soil–water mixtures, respectively. SOM was measured using dichromate oxidation. TN was analyzed on a Vario MACRO cube elemental analyzer. Soil CEC was determined using sodium acetate–ammonium acetate extraction. The $CaCO_3$ equivalent was determined by neutralization with HCl and back titration with NaOH. Soil magnetic susceptibility was measured at low (0.47 kHz) (χ_{lf}) and high (4.7 kHz) frequency (χ_{hf}) using a Bartington MS2 meter. Frequency dependent susceptibility (χ_{fd}%) was calculated as $(\chi_{lf} - \chi_{hf}) / \chi_{lf} \times 100\%$.

Major and trace elements, including K, Ca, Na, Al, Si, Cu, Zn, Cr, Ni, Pb and Co in the soil, were determined by X-ray fluorescence spectroscopy (XRF, Philips Magix Pro PW2440 instrument). Briefly, 4.0 g of each soil sample was weighed and backing with 2.0 g boric acid in the mold, then pressed it into a 32-mm diameter pellet at 30 t pressure for 10 s. The prepared powder pellets were directly measured on XRF. Cd was determined by ICP-MS (ELAN DRC II, Perkin Elmer) after high-pressure Teflon bomb digestion with strong acids such as HF (5 mL), HNO_3 (2 mL) and $HClO_4$ (1 mL) at 180 °C for 12 h (Pretorius et al., 2006). Quality assurance and quality control were assessed using duplicates and standard reference materials (GSS-1, GSS-4, GSS-6, GSS-8) from National Research Center for Certified Reference Materials of China with 10% of the samples. The recoveries for the major elements and heavy metals in the standards were ranged from 95 to 105%.

The optimized BCR sequential extraction procedure was performed to determine chemical fractionations of heavy metals in the soil samples. This method was described in detail by Nemati et al. (2011). The chemical fractions obtained in each step by the BCR method are shown in Table 1. It was applied to 1 g soil samples in duplicate into a centrifuge tube. The tube was shaken for 16 h at room temperature. The extract was separated from the solid phase by centrifugation at 3000 rpm for 20 min. The metal concentrations of the extracts were analyzed by ICP-MS (ELAN DRC II, Perkin Elmer).

2.4. Geoaccumulation index and pollution index

The geoaccumulation index (I_{geo}) and pollution index (I_{POLL}) were utilized to assess the intensity of heavy metal pollution in soil profiles. The I_{geo} was calculated using the equation developed by Müller (1979):

$$I_{geo} = \mathrm{Log}_2[C_n/(1.5 \times B_n)]$$

where C_n is the measured concentration of the element n in a sample and B_n is the natural background concentration of this element. These geochemical background values were obtained based on the mean values of environmental background concentrations of the A and C horizons of Shandong Province (China National Environmental Monitoring Center (CNEMC), 1990).

The I_{POLL} was computed using the equation developed by Karbassi et al. (2008):

$$I_{POLL} = \mathrm{Log}_2(B_c/L_p)$$

where I_{POLL}, B_c and L_p are indicative of pollution intensity, bulk concentration and lithogenous portion, respectively. The residual fraction of heavy metals in BCR sequential extraction was categorized as the lithogenous portion of metals.

2.5. Statistical analysis

All multivariate statistical analyses, including ANOVA analysis and principal component analysis (PCA), were conducted using SPSS 20.0 for windows. ANOVA analysis was employed to test the differences among three soil genetic horizons. Differences are considered to be significant if $p < 0.05$. Varimax with Kaiser normalization was applied as the rotation method in the PCA.

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