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Magnetic characterization of distinct soil layers and its implications for environmental changes in the coastal soils from the Yellow River Delta

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ABSTRACT

The soils in the Yellow River Delta (YRD) were formed through the deposition of the Yellow River sediments under complicated hydrodynamic conditions, resulting in large variability in soil properties. In this study, environmental magnetic analyses were conducted on four typical soil profiles and one high resolution soil profile with distinct soil layers to examine the soil formation process and to track the environmental changes. The results showed that the red clay layer (RCL) in the YRD soil profiles had unique magnetic properties, which could be clearly separated from the yellow silt layer (YSL) at frequency dependent susceptibility (χ_{fd}%) > 6%, susceptibility of anhysteretic remanent magnetization (χ_{ARM}) > 250 × 10^{-8} m^3 kg^{-1}, χ_{ARM}/magnetic susceptibility (χ_{lf}) > 5, χ_{ARM}/saturated isothermal remanent magnetization (SIRM) > 45 × 10^{-5} m A^{-1} and SIRM/χ_{lf} < 12 × 10^3 A m^{-1}. The magnetic enhancement of the RCL could be attributed to the presence of fine superparamagnetic (SP)/single domain (SD) ferrimagentic grains sourcing from hydrodynamic sorting of old sediments (e.g., paleosol in the Chinese Loess Plateau). It was hard to discriminate the RCL and YSL in the < 2 μm fraction by magnetic bi-plots, suggesting that the abundance of clays with higher contents of secondary ferrimagnetic minerals contributed significantly to the magnetic variability of different soil layers in the YRD. Three units were identified in a high resolution soil profile based on the changes of magnetic curves, including a steady deposition process in the upper unit, a strong hydrodynamic process with varied provenance in the middle unit and a heterogeneous deposition process in the lower unit with the RCL. The three units were closely linked to the variation of nutrients (carbon and nitrogen) and metals (chromium (Cr), copper (Cu), nickel (Ni), lead (Pb), zinc (Zn), titanium (Ti) and zirconium (Zr)) in the soil profile, indicating the influence of provenance and sorting during sediment transportation and deposition. The magnetic method is sensitive to characterize soil formation and environmental changes in the coastal zone.

1. Introduction

Magnetic minerals occurring as iron oxides (e.g., magnetite, maghemite, haematite), oxyhydroxides (e.g., goethite, ferrihydrite, lepidocrocite), and sulphides (e.g., greigite, pyrrhotite) (Roberts, 2015), are ubiquitous components in soil, sediment, dust and peat (Oldfield, 1999). These minerals are sensitive to a range of environmental processes, and the magnetic measurements can provide information on the concentration, domain state, and mineralogy of magnetic particles in a simple, rapid and nondestructive way (Thompson and Oldfield, 1986; Liu et al., 2012), which makes magnetic parameters extremely useful in investigating the soil formation, sediment provenance, hydrodynamic sorting, postdepositional diagenesis, paleoclimatic change and pollution assessment in a variety of environments (Magiera et al., 2006; Li et al., 2012; Dong et al., 2014; Chen et al., 2015; Roberts, 2015).

The Yellow River, which transported approximately 1.1 × 10^9 t yr^{-1} of sediments to the sea before dam construction (Milliman and Meade, 1983), has been well known for frequent channel migrations in its lower reaches due to the high sediment loads and steep river-channel gradients (Saito et al., 2000). Since 1855, when the river began flowing into the Bohai Sea, the river channel has shifted 10 times in the Yellow River Delta (YRD) area (Pang and Si, 1979; Xue, 1993). The effects of changes of the sedimentary environments on the delta have attracted many researchers because it is both "drivers" and "recorders" of natural and anthropogenic environmental change (e.g., drought, port and dam construction, water diversion work, and

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reclamation) (Turner and Rabalais, 1994; Bianchi and Allison, 2009; Kong et al., 2015).

To estimate sediment dynamics in the coastal region, the radionuclides ^{210}Pb and ^{137}Cs have been often used to study modern sediment deposition processes (Mabit et al., 2014). Generally, using the excess ^{210}Pb activity to calculate accumulation rate needs a relatively stable sedimentation condition for sufficient time to achieve an exponential curve with decay of ^{210}Pb (Sanchez-Cabeza and Ruiz-Fernández, 2012). However, the frequent shifting of the Yellow River course makes the excess ^{210}Pb activity profiles sometimes displaying segmented or uniform distribution patterns, complicating their use for accumulation rate estimation (Wu et al., 2015; Zhou et al., 2016). Previous studies have shown that sediment particle size plays an important role in affecting the magnetic properties due to the wide range of grain size of each magnetic component, which preferentially resides in a specific particle size fraction (Oldfield et al., 2009; Liu et al., 2012). Therefore, the strong particle size dependence of magnetic properties can be used to infer sediment sources and hydrodynamics in the coastal areas (Hatfield et al., 2010; Zhang et al., 2012; Dong et al., 2014). It is specially suitable for the YRD, where hydrodynamics contributes significantly to the sedimentary changes due to the simple tributary system and the dominant sediment provenance (eroded soil from the Loess Plateau) (Qiao et al., 2011; Li et al., 2012).

The modern YRD consists of several sub-deltas resulting from distributary channel shifts, forming a complicated imbrication pattern in the delta complex (Xue, 1993; Wang et al., 2006). Under this pattern, the sedimentary successions are characterized by cyclic changes of clay-enriched layers and silt-enriched layers, which are useful in the study of delta evolution, climate and environment change in the river basin (Xue et al., 1995; Yi et al., 2003; Qiao et al., 2011; Hu et al., 2012). The clay-enriched layers occurring in soil profiles can also play important roles in the geochemical cycles due to their abilities to stabilize organic matter, to sorb pollutants and to indicate soil formation process (Zhang et al., 2009; Schmidt et al., 2011; Bockheim and Hartemink, 2013). In our field investigation in the YRD, we discovered a ubiquitous distribution of red clay-yellow silt sequence in soil profiles, which showed significant accumulation of nutrients and heavy metals (Li et al., 2014, 2017). However, it still lacks of sensitive methods to characterize the red clay-yellow silt sequence and to provide evidence of environmental changes in the YRD. The present study attempts to characterize the red clay-yellow silt sequence using a wide range of magnetic measurements, and to investigate if the magnetism can provide more insights into the changes of soil nutrients and metals in relationship with the soil formation process, aiming to provide a better understanding of processes that control the environmental changes in the coastal zone.

2. Materials and methods

2.1. Study area

The study area is located at the Yellow River Delta High-efficient Eco-economic Zone (YRDHEZ) (Fig. 1), which is based on the Yellow River Delta (YRD) (region 1) and coastal areas of northern Shandong province (regions 2–4), endorsing by China's government in 2009. The YRD as the core area of the YRDHEZ is unique in its dynamic, ecological and economic character, characterizing as one of the most rapid sedimentation areas in the world, and including the most integrated estuary wetland ecosystem and the second-largest oil production basin (Shengli Oilfield) in China (Xue, 1993; Fang et al., 2005; Kong et al., 2015). Soil types in the YRD are dominated by Gleyic Solonchaks (47.3%) in embanked former back swamps, salt marshes and tidal flats; Salic Fluvisols (30.1%) in embanked former back swamps and abandoned river courses; and Calcaric Fluvisols (17.1%) in embanked former back swamps and present floodplain (Fang et al., 2005). The YRD area has a typical monsoon and warm-temperate climate. The annual mean temperature is 11.7–12.6 °C. The annual mean precipitation and evaporation are about 600 mm and 1944 mm, respectively, with 70% of precipitation occurring between July and August (Zhao and Song, 1995). The YRD is formed by the deposition of the Yellow River sediments since 1855 after a major switch in the lower course to the Bohai Sea. Nearly 90% of the sediments are sourced from the Chinese Loess Plateau, and the annual mean median grain size of the sediments is 18–30 μm at Lijin station, Shandong province, China (Wang et al., 2010). The soils in the YRD are also a kind of loess-like sediments.

2.2. Soil sampling

Forty two soil profiles (Y01–Y42) and fifteen cores (Y45–Y54, Y58–Y62) for chemical analysis and the RCL distribution identification were collected from inland to coast at the YRDHEZ in November 2012 (Fig. 1a). Profiles were sampled according to diagnostic layers from bottom to top in 1 m depth. All soil samples were collected using a stainless steel hand auger and then placed into polyethylene bags. According to the diagnostic characteristics, the typical soil profile in the YRD could be divided into the red clay layer (RCL) and the yellow silt layer (YSL) (Fig. 1b). Previous studies showed that the RCL with similar geochemical features was widely distributed in the YRD (Li et al., 2014, 2017). In this study, four typical soil profiles (Y03, Y16, Y26 and Y34) from the YRD occurring the RCL with different thickness and depth, and seven soil profiles (Y36–Y42) from east of the Mi River without the RCL as comparison were used to investigate the magnetic properties of the RCL-YSL sequence. In addition, one high resolution soil profile (Y16) from the YRD was sampled in May 2015 at an interval of 5 cm in 170 cm depth to investigate the vertical distributions of the magnetic properties and environmental indicators.

2.3. Sample analysis

Soil samples were air dried (typical soil profile samples) or freeze-dried (high resolution soil profile samples) and crushed gently with a pestle and mortar, and then passed through a 2-mm nylon sieve. About 100 g of the 2-mm samples were ground to pass a 0.149-mm nylon sieve. The 2-mm samples were used for the measurement of soil particle size and excess ^{210}Pb ($^{210}Pb_{ex}$), and for the separation of clay particles (< 2 μm fraction). The 0.149-mm samples were used for the measurement of total organic carbon (TOC), total inorganic carbon (TIC), total nitrogen (TN), elements (aluminum (Al), calcium (Ca), sodium (Na), potassium (K), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb), zinc (Zn), titanium (Ti) and zirconium (Zr)), iron oxides, and magnetic properties. The detailed methods for measuring soil particle size, TOC, TIC, TN, elements and iron oxides, and for separating of < 2 μm fraction could be found in Li et al. (2014, 2017) with some modifications. Briefly, soil particle size was measured using a Malvern Mastersizer 2000 instrument after removing organic matter and carbonates using 15% H_2O_2 and 1 M HCl. Total carbon, TN and TOC were measured on a Vario MACRO cube elemental analyzer (Elementar, Germany). For TOC measurement, soil samples were pretreated with 1 M HCl to remove carbonates. TIC was calculated as the difference between total carbon and TOC. Elements were determined by X-ray fluorescence spectroscopy (XRF, Philips Magix Pro PW2440 instrument). Free iron oxides (Fe_d) were extracted by dithionite-citrate-bicarbonate (DCB), and poorly crystalline iron oxides (Fe_o) were extracted by acid ammonium oxalate. The < 2 μm fraction was separated by the settling of particles in standing cylinders according to Stokes' law after removing organic matter and carbonates using 15% H_2O_2 and 1 M HCl.

Measurements of ^{210}Pb activities of the samples were conducted using an EG & G Ortec HPGe GWL gamma-ray spectrometer. The total ^{210}Pb and ^{226}Ra activities were measured at 46.5 keV and 295.2 keV (^{214}Pb), respectively. The excess ^{210}Pb ($^{210}Pb_{ex}$) was calculated by subtracting ^{226}Ra activity from total ^{210}Pb activity. The Constant Rate of Supply (CRS) model was used for the determination of mass accumulation rate (Sanchez-Cabeza and Ruiz-Fernández, 2012).