# Factors controlling cadmium and lead activities in different parent material-derived soils from the Pearl River Basin

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## HIGHLIGHTS

- Cd and Pb in paddy soils are more labile than in dry soils due to stable equilibrium.
- Pb activity is very sensitive to pH change in limestone soils.
- High sand content enhances Cd activity in granite soils.
- DOM greatly impacts Cd and Pb activities in sand shale, diluvium, and alluvium soils.

## ARTICLE INFO

## ABSTRACT

Labile metals in agricultural soils are available to crops and thus pose a great health risk for human beings. Therefore, factors influencing heavy metal activity are of interest to researchers. In this study, a total of 142 soil samples representing 5 typical parent materials in the Pearl River Basin (PRB), China were collected to investigate factors impacting the distribution of labile Cd and Pb in the soils. The results showed that the labile fractions accounted for 0.03%–14.7% for Cd and 0.01%–0.39% for Pb of the total metals, and the labile fractions were linearly correlated to their corresponding total contents. The step regression analyses suggested that the key factors impacting labile Cd and Pb varied in different parent material soils. Pb activity was highly sensitive to pH in alkaline limestone soils. The quartz sand remained in granite-produced soils enhanced Cd activity. And dissolved organic matter (DOM) compositions considerably influenced Cd and Pb activities in sand shale, diluvium, and alluvium soils. Land use impacts heavy metal activities. The labile Cd and Pb in paddy soils were higher than those in non-paddy soils, although total metals in the soils were comparable. It could be ascribed to the long-term equilibrium of metals between the solution and solid phases of the paddy soils. The results provide a theoretical basis for preliminary prediction of heavy metal activity and provide a technical support for heavy metal activity management and pollution control based on soil parent materials.

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## 1. Introduction

Heavy metal contamination in the environment, especially the agricultural soils, is drawing a great attention due to its high risk to human beings (Yang et al., 2013; Qayyum et al., 2017). Relative to the total metal, the activity of heavy metal in soils is considerably associated with the uptake of crop and thus human health (Sastre et al., 2004; Tai et al., 2013). Therefore, illustrating the factors affecting the heavy metal activity in agricultural soils is significant for the evaluation of their environmental risks.

The activities of heavy metals are influenced by soil properties and compositions, such as pH, organic matter, and iron oxides (Sauve et al., 2000a, 2000b; Lu et al., 2003; Chen et al., 2008; Yu et al., 2016a, 2016b). Sauve et al. (2000a) reported that pH, soil organic matter (SOM), and total contents of Ni, Cu, Cd, Zn can be

used to predict the percentages of labile fraction based on a big dataset. In the heavily contaminated soils, the metals cannot be effectively fixed due to limited sorption capacities, resulting in high activities of ions (Tsang and Lo, 2006). However, the heavy metals tightly bound to varying matrices of soil have lower risks for transportation to plants (Jacquat et al., 2009). Parent rocks substantially influence both the properties and trace metal remaining of soils. Weathering of parent rocks produces the soil primary and secondary minerals such as, quartz, kaoline, and montmorillonite. The minerals are different in particle size, cation exchange capacity, metal species, etc. which endows soils with corresponding properties. For some areas without any pollution source, the metal compositions and contents are determined by the parent materials (Mico et al., 2006). Besides, the behaviors of the remaining metals can be notably influenced by the parent material-related features. For instance, calcareous soil is originated from limestone or dolomite and contains high carbonates and organic matter (Chen et al., 2000). As carbonates form precipitates with heavy metals and organic matters fix heavy metals with functional groups such carboxyl and hydroxyl, they would enhance the accumulation of heavy metals. Considering the important and complex role of parent materials on soil properties and heavy metals, it is significant to understand the effects of parent materials on the activities of heavy metals, as well as the factors impacting metal activities in different parent material-derived soils.

In this work, the Pearl River Basin (PRB) in China is selected for investigating the heavy metal distributions in different parent material-derived soils of different pollution levels and related impacting factors. On one hand, many mines and related industries, such as, Dabaoshan Mine, Fankou Mine and Dongguan industrial district, are located in the study area (Wong et al., 2002; Yin et al., 2016). Consequently, heavy metal pollution in the agricultural soils, especially Cd and Pb, is severe in its tributaries due to wastewater irrigation, atmospheric deposition, etc. On the other hand, various parent rocks (residual and transported) including limestone, granite, sand-shale, diluvium, and alluvium are extensively distributed in this area (Chen et al., 2000).

The aims of the present study were to investigate the distributions of labile Cd and Pb in five representative parent material soils from the PRB; and more importantly, to unveil the factors affecting Cd and Pb activities in the soils.

## 2. Materials and methods

### 2.1. Sampling sites

The catchment of PRB is up to $44.21 \times 10^4$ km$^2$. One hundred forty-two (142) surface soil (0–20 cm) samples from the PRB, including 54 samples in Xijiang River Basin, 64 samples in Beijiang River Basin, and 24 samples in Pearl River Delta (Fig. 1) were collected. The sampling sites were so selected to include five representative parent materials (limestone (L), sand shale (S), diluvium (D), alluvium (A), and granite (G)) and reflect different pollution levels (e.g., background level and pollution levels). Three zones including L1 (a background site), L2 polluted by a non-ferrous metals smelter in Hechi City, and L3 slightly polluted zone, were located in the limestone area. Four zones including S1 (a background site), S2 and S3 polluted by the Dachang tin-polymetallic mining and located in the upper and lower catchment of the Diaojiang River, and S4 slightly polluted, were in the sand shale area. Seven zones including D1 and D2 polluted by the Fankou lead-zinc

deposit, D3 and D4 polluted by the Danxia lead-zinc smelter, D5 (a background site), D6 and D7 polluted by the Maba lead-zinc smelter, were in the diluvium area. Three zones including A1 polluted by the Dabaoshan polymetallic sulfide meso-hypothermal deposit, A2 (a background site), A3 slightly polluted, were in the alluvium area. Two zones including G1 and G2 polluted by the industrial activity in Zhongshan City, were in the granite area. In each zone, 6–12 sampling sites were chosen and each site was ~300 m away from the each other. Surface samples (~5 kg) from the paddy (P) and non-paddy (N) soil were collected from May to July 2015. The samples were termed a combination with parent material, land use type, and number (Table 1). The samples were stored by plastic bags and carried back to the laboratory. The air-dried samples were grounded to pass through 2 mm and 0.15 mm sieves for the different analyses.

### 2.2. Soil characterization

Soil pH was measured from a 2.5:1 (v/m) water to soil suspension using a pH detector (PHS-3C, China). Cation exchange capacity (CEC) was analyzed using the ammonium acetate saturation methods (Tan et al., 2017). Particle-size analysis was performed using sedimentation and pipette method. Sands (50–2000 μm), silts (2–50 μm), and clays (<2 μm) were measured (Zhang et al., 2017). Fe and Mn oxides including crystalline and amorphous Fe/Mn were separated and further quantitatively determined by colorimetry (Gleyzes et al., 2002). Soil organic carbon (SOC) was determined by oxidation with dichromate (Zhang et al., 2017). Dissolved organic matter (DOM) in soils was water-extracted (water to solid ratio = 5:1; 1 h) by a shaker. Dissolved organic carbon (DOC) content was detected by a total organic carbon (TOC) analyzer (Elementar vario TOC, Germany). The DOM compositions were characterized by an ultraviolet–visible (UV) spectrophotometer. The absorbances at 250, 254, 365, 400, 436, 465, 600, and 665 nm of the equilibrium solution were measured. Specific UV–vis absorptions at 254 nm (SUVA$_{254}$, L·g$^{-1}$ cm$^{-1}$) and ΔlogK were calculated by Eq. (1) and Eq. (2), respectively (Kumada, 1988).

$$SUVA_{254} = \frac{A_{254}}{l \, DOC} \qquad (1)$$

$$\Delta logK = logA_{400} - logA_{600} \qquad (2)$$

where, $A_i$ is the absorbance at i nm, l (cm) is the cell path length and DOC is the dissolved organic carbon content (mg L$^{-1}$) of the soil solution. SUVA$_{254}$ and ΔlogK are frequently used as the indicators for aromaticity and humification of DOM (Ni et al., 2016). The E2/E3, E2/E4, and E4/E6 are the ratios of the absorbance at 250 nm over 365 nm, 254 nm over 436 nm, 465 nm over 665 nm (Table S1, Supplementary Data). The former two ratios reflect the humification of DOM, meanwhile the latter ratio represents aromaticity of DOM (Helms, 2006).

### 2.3. Heavy metal analysis

The total concentrations of Cd and Pb in soils were measured by the HCl-HNO$_3$-HClO$_4$-HF digestion method (Li et al., 2009). The digestion solution were analyzed by a flame atomic absorption spectrometry (AAS, Hitachi Z-2300, Japan). A six step sequential extraction of heavy metals in soils was carried out based on the modified Tessier method (Ma and Rao, 1997). The extraction methods were detailed in Table S2 (Supplementary Data). The Cd