



Effects of organic matter fraction and compositional changes on distribution of cadmium and zinc in long-term polluted paddy soils[☆]



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ABSTRACT

Soil particulate organic matter (POM) has rapid turnover and metal enrichment, but the interactions between organic matter (OM) and metals have not been well studied. The present study aimed to investigate changes in the OM concentration and composition of the POM fraction and their corresponding effects on metal distribution and extractability in long-term polluted paddy soils. Soil 2000–53 μm POM size fractions had higher contents of C–H and C=O bonds, C–H/C=O ratios and concentrations of fulvic acid (FA), humic acid (HA), cadmium (Cd) and zinc (Zn) than the bulk soils. Cadmium and Zn stocks in soil POM fractions were 24.5–27.9% and 7.12–16.7%, respectively, and were more readily EDTA-extractable. Compared with the control soil, the 2000–250 μm POM size fractions had higher organic carbon concentrations and C/N ratios in the polluted soils. However, there were no significant differences in the contents in C–H and C=O bonds or C–H/C=O ratios of POM fractions among the control, slightly and highly polluted soils. In accordance with the lower contents of C=O bonds and FA and HA concentrations, the Cd and Zn concentrations in 250–53 μm POM size fractions were lower than those in 2000–250 μm POM size fractions. Enrichment of Cd in POM fractions increased with increasing soil pollution level. These results support the view that changes in the OM concentration and the size and composition of POM fractions play a key role in determining the distribution of Cd and Zn in paddy soils.

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1. Introduction

There has been growing public concern over metal pollution in agricultural soils, including paddy soils, in south China (Niu et al., 2013; Chen et al., 2015). Cadmium (Cd) is a priority control metal in soils due to its relatively high health risks and the large areas polluted (Chen et al., 2015; Zhao et al., 2015). Zinc (Zn) tends to occur together with Cd at many polluted sites, and excessive Zn accumulation and intake are also recognized as a main threat to environmental and human health (Giller et al., 1998; Chen et al., 2015). Remediation of Cd/Zn polluted farmlands through manipulation of metal bioavailability is therefore critical for national food safety and human health (Bolan et al., 2014; Zhao et al., 2015). Soil available metal concentrations are usually extracted with the weak neutral salt solutions CaCl_2 , NaNO_3 and NH_4NO_3 that provide the closest relationship with plant uptake (Ure, 1996; Black et al., 2011).

The complexing agent ethylenediaminetetraacetic acid (EDTA) dissolves not only the exchangeable metal fractions but also the metal fractions forming complexes with organic matter, fixing on Fe and Mn oxy-hydroxides and binding to carbonates (Ure, 1996). Wu et al. (2004) and Cornu et al. (2017) found that metal-EDTA complexes are likely taken up undissociated by Indian mustard and sunflower, suggesting that the EDTA-extracted metals are potentially able to move into the plant root system.

In general, metal mobility and availability are controlled by soil properties such as pH, soil organic matter content (SOM), cation exchange capacity (CEC), clay minerals and iron and manganese oxides (Lair et al., 2007; Park et al., 2011; Bolan et al., 2014). In addition to pH, which is the factor influencing the mobility and availability of metals to the greatest extent, SOM is considered to play an important role in determining the solubility and speciation of metals. Organic materials have large negatively charged interfaces that compete strongly with inorganic ligands to readily immobilize metal ions through the formation of stable complexes, thereby decreasing their phytoavailability to crops (Guo et al., 2006; Mohamed et al., 2010; Ok et al., 2011). In addition,

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dissolved organic matter (DOM) and fulvic/humic acids can form soluble chelates with metals to increase metal mobility, extractability and phytoavailability under certain soil conditions (Evangelou et al., 2004; Salati et al., 2010; Hu et al., 2016). Interactions between metals and amended OM have been utilized in the remediation of polluted soils including the immobilization of metals unavailable for plant uptake and mobilization of metals for removal using hyperaccumulator plants (Salati et al., 2010; Park et al., 2011; Wu et al., 2012; Bolan et al., 2014). The quantity and quality of the native SOM may also have significant effects on metal availability and distribution.

The quantity and quality of SOM are important in the management of soil fertility, nutrient supply and carbon dynamics (Paul, 2016), and SOM quantity and quality can change in long-term metal polluted soils (Viventsova et al., 2005; Zhou et al., 2016). Particulate organic matter (POM) is the part of SOM that can be physically size-fractionated into different labile pools in water and used as an index of labile SOM status (Balesdent, 1996; Benbi et al., 2014). It consists mainly of identifiable animal and plant residues, root fragments, fungal hyphae and fecal pellets, and has a more rapid turnover than the OM associated with mineral components (Christensen, 2001; Benbi et al., 2014). Previous studies have found significant enrichment of metals in POM fractions in slightly and highly polluted upland soils, and metal enrichment differs greatly in different size fractions of POM (Balabane and van Oort, 2002; Zhang and Ke, 2004; Labanowski et al., 2007; Mohamed et al., 2010). Metal enrichment of POM fractions may be due to higher adsorption by functional groups favoring metal fixation (Balabane and van Oort, 2002; Labanowski et al., 2007) but the composition of POM fractions has been omitted from earlier studies. Long-term and spiked metal pollution of bulk soils from forests results in overall decreases in the adsorption of all functional groups of SOM studied (Viventsova et al., 2005). Artificial Cd, Cu and Pb pollution by spiking leads to slight decreases in the FTIR absorbance of the peaks of carboxyl and hydroxyl groups of POM fractions (Guo et al., 2006). However, metal spiking experiments cannot fully explain the status of microbial decomposition of OM and sorption behaviors of metals in long-term polluted soils (Giller et al., 1998; Lair et al., 2007). Hence, studies on native SOM quality changes and metal-POM interactions are needed to better understand metal behaviors in the environment and implement repair strategies in different polluted soils.

The objectives of the present study were to learn how the concentration and composition of OM change in different POM size fractions and metal pollution levels, and then to assess their feedback effects on the Cd and Zn enrichment and availability of POM fractions in long-term polluted paddy soils. This information should enhance our understanding of the role of SOM in metal stocks and dynamics which may have very important implications for the maintenance of soil fertility and the remediation of metal-polluted soils.

2. Materials and methods

2.1. Site description and sample collection

Soil samples were collected on 22 April 2014 from paddy fields in Guangdong province, south China (25°05'58" N, 113°39'33" E) where the cropping regime is dominated by double-rice cropping systems. The local paddy soils are classified as "Stagnic Anthrosols" developed from red sandstone. The region has a subtropical monsoon climate with a mean annual temperature of 19.6 °C and precipitation of 1665 mm. The paddy fields have been heavily polluted by emissions of metals from a Zn smelter over a period of 20 years. Highly and slightly polluted soils were collected from

paddy fields situated about 1.0 and 1.5 km, respectively, from the smelter before the transplantation of early rice. A control soil without discernible metal pollution was collected from a paddy field located 7.0 km from the smelter. The paddy fields selected were located on a transect along the prevailing wind direction (NW to SE in winter, SE to NW in summer) from the smelter. The watering regime, fertilization and other crop management details followed local practice and were maintained consistently across the three fields sampled. Five soil subsamples were taken with a soil corer within a circle 10 m in diameter and were mixed thoroughly to form a composite soil sample of about 1.5 kg. The composite soil samples were collected in triplicate from each field at intervals of 20 m from the top 20 cm of the soil profile. After removal of large roots, residues and macroscopic soil fauna, each composite soil sample was homogenized, air-dried, ground, passed through 2- and 0.15-mm sieves and stored prior to chemical analysis and particle size fractionation.

2.2. Physical fractionation of soil particle sizes

The particle size fractionation procedure described in detail by Balesdent (1996) and Labanowski et al. (2007) was carried out on every composite soil sample in the present study. Each composite soil sample was dispersed (1:5 soil:water ratio) on a rotary shaker for 16 h with glass beads in a plastic tube. The suspension was then wet-sieved over 250- and 53- μm nylon sieves with deionized water to obtain three particle size fractions, namely 2000–250, 250–53 and < 53 μm . The soil was passed through the sieves until the water passing through became clear. We separated the light POM fractions into 2000–250 and 250–53 μm by repeated flotation from the dense mineral fractions in water, and the <53 μm organic-mineral compounds were obtained by centrifugation. The fractions of POM, mineral and organic-mineral compounds of each size were air-dried, weighed and ground prior to chemical analysis. The summed weights of the separated POM fractions (2000–53 μm), mineral fractions (2000–53 μm) and organic-mineral compounds (<53 μm) were calculated as a percentage of the bulk soils to obtain the recoveries of fractionation. Finally, the recoveries of POM fractions, mineral fraction and organic-mineral compounds by the physical fractionation procedure in different soils ranged from 96.4 to 98.7%.

2.3. Soil and particle size fraction analysis

Total concentrations of organic carbon (OC) in the bulk soils and different particle size fractions were determined by wet digestion with potassium dichromate, and total nitrogen (TN) was determined by the Kjeldahl method (Lu, 2000). Soil pH was measured in a 1:2.5 (w/v) soil suspension with a glass electrode in water, and soil texture was determined by the pipette method. EDTA is capable of extracting metals from all non-silicate bound phases in the soil (Ure, 1996), thus 0.05 mol l⁻¹ EDTA was used to study the maximum potential extraction capacity of metal from all isolated soil fractions.

Total Cd and Zn concentrations in the bulk soils, organic-mineral compounds and mineral fractions were digested with 10 ml HCl–HNO₃ (1:1, v/v), and in the POM fractions were digested with 8 ml HNO₃–H₂O₂ (3:1, v/v). The HCl–HNO₃ solution digested the Cd and Zn in samples completely, but HNO₃–H₂O₂ solution dissolved only the metals bound with the organic complex (Chang et al., 2009). The samples and acids were placed inside 50-ml high-pressure polytetrafluoroethylene (PTFE) digestion containers and the sealed containers were placed in a digestion vessel at 105 °C for 6 h. On completion of digestion the sample solutions were placed on an electric evaporation block at 105 °C to remove

acid until about 2 ml solution remained. After cooling, the remaining solution was transferred to a clean polycarbonate tube and made up to 15 ml with deionized water. The final volume of digest solution was filtered through a 0.45- μm syringe filter for elemental analysis. Blank digestions were also carried out following the same procedure. Concentrations of Cd and Zn in the digests and EDTA extracts were determined by atomic absorption spectrophotometry (AAS) using a Varian SpectraAA 220FS or 220Z (Varian, Palo Alto, CA). Certified reference materials comprising shrub leaf material (GSB-23) and ferralsols (GSS-6) were used (National Research Centre for Standards, China) for quality control. As shown in Table S1, the measured concentrations of Cd and Zn in the certified reference materials were all within one standard deviation of the certified values. Acids used were guaranteed grade and double-distilled deionized water (Milli-Q Millipore 18.2 M Ω cm⁻¹) was used. The properties of the soils determined are shown in Table 1.

2.4. FTIR spectroscopic analysis

The Fourier Transform Infrared (FTIR) spectra of OM in the samples of bulk soils and POM fractions were analyzed with a Nicolet iS 10 spectrometer (Thermo Scientific, Waltham, MA) using the KBr technique. The spectra were carried out in the mid-infrared region from 4000 to 400 cm⁻¹ at a resolution of 8 cm⁻¹. Thirty-two individual scans of each sample were recorded and averaged to obtain the spectrum. Each spectrum collected was measured in ambient air against that of pure KBr as the background spectrum. Sample (1 mg) was mixed with 100 mg of KBr, finely ground in an agate mortar, and then pressed into a pellet for FTIR spectral analysis. The spectral data were processed with OMNIC software version 8.0 (Thermo Scientific, Waltham, MA) including baseline correction and atmospheric correction for H₂O and CO₂. The assignments of the absorption peaks observed in the FTIR spectra were based on those reported in the literature for relevant chemical bonds and functional groups of organic and inorganic components (Capriel et al., 1995; Ellerbrock et al., 2009, 2016). The relative contents of C–H and C=O functional groups of OM were measured by the peak heights of these absorption bonds in the FTIR spectra. The details are given in the supplemental materials.

2.5. Extraction of humic and fulvic acids

Humic (HA) and fulvic (FA) acids were extracted from bulk soils and POM fractions with 0.1 mol l⁻¹ NaOH and 0.1 mol l⁻¹ Na₄P₂O₇ using a solid:solution ratio of 1:20 (LY/T 1238–1999). The HA was separated from FA by acidification of the solution to pH 2 with 0.5 mol l⁻¹ H₂SO₄. The precipitated HA was collected by centrifugation at 3000 rpm and was then re-dissolved by adding hot 0.05 mol l⁻¹ NaOH. Concentrations of OC in the HA + FA and HA

solutions were determined by wet digestion with potassium dichromate. The concentration of OC in FA was calculated as the difference between HA + FA and HA.

2.6. Statistical analysis

Data are expressed as mean \pm SD of triplicate determinations. Student's t-test or one-way analysis of variance (ANOVA) followed by the LSD (least significant difference) post hoc test was used to test the differences in each variables among different size fractions and pollution levels ($p < 0.05$). If the residuals from ANOVA were not normally distributed or heteroscedasticity was detected by Levene's test the data were transformed to natural logarithms, but the mean and SD values presented are those of the non-transformed data.

3. Results

3.1. Distributions of OC and TN in the POM fractions

The POM fractions were present in much lower percentages than the mineral fractions in the soils (Fig. 1 and Fig. S1). The mass of POM fractions (2000–250 + 250–53 μm) accounted only for 6.86% (1.11 + 5.75), 4.38% (0.52 + 3.87) and 3.86% (0.42 + 2.98) in the control, slightly and highly polluted soils, respectively. Organic-mineral compounds (<53 μm) represented 31.6%, 51.6% and 57.3% of the total fraction mass in the control, slightly and highly polluted soils. The OC and TN concentrations and C/N ratios were higher in the POM fractions than the bulk soils. By comparison, OC and TN concentrations and C/N ratios of POM were higher in 2000–250 μm size fractions than 250–53 μm size fractions. Organic-mineral compounds had slightly higher OC and TN concentrations but lower C/N ratios than bulk soils ($p < 0.05$).

The relative changes in OC and TN concentrations of soil fractions were calculated due to the slight differences in OC and TN concentrations of bulk soils among the three pollution levels. Compared with their corresponding bulk soils, the relative increases in OC and TN concentrations of 2000–250 μm POM size fractions were lower in control soils (742% and 495%) than in slightly (1184% and 572%) or highly (1292% and 621%) polluted soils (Fig. 1). However, the relative increases in OC and TN concentrations of 250–53 μm POM size fractions were not significantly different among the three soils. Relative increases in OC and TN concentrations in the organic-mineral compounds were higher in controls (43.5 and 74.1%) than in slightly (17.2 and 31.9%) or highly (10.1 and 25.0%) polluted soils ($p < 0.05$). Although there were no discernible differences in the C/N ratios of the bulk soils among the three pollution levels, the 2000–250 μm POM size fractions showed higher C/N ratios in polluted soils than the control.

The percentage distributions of OC and TN stocks in various soil fractions were assessed taking into account the weight of each size fraction of bulk soil (Fig. S2). The percentage distributions of OC and TN stocks were larger in <53 μm organic-mineral compounds than 2000–53 μm POM size fractions ($p < 0.05$). In the 250–53 μm POM size fractions, the percentage distributions of OC and TN stocks were higher (23.3–38.5% and 18.6–19.4%) than in 2000–250 μm POM size fractions (6.28–10.1% and 3.18–6.93%). In addition, the percentage distributions of OC and TN stocks were greater in POM fractions but smaller in organic-mineral compounds of the control soils compared with the slightly and highly polluted soils ($p < 0.05$).

3.2. Composition and quality of the POM fractions

The FTIR spectra of OM in bulk soils, POM fractions and organic-mineral compounds are presented in Fig. 2. The absorption peaks at

Table 1
Selected physicochemical properties and total Cd and Zn concentrations of control, slightly and highly polluted soils.

Variable	Control	Slightly polluted	Highly polluted
SOC/g kg ⁻¹	21.8 \pm 0.5	18.1 \pm 0.2	18.8 \pm 0.2
TN/g kg ⁻¹	1.56 \pm 0.10	1.34 \pm 0.04	1.30 \pm 0.02
C/N	13.9	13.5	14.4
pH	5.71 \pm 0.04	5.37 \pm 0.02	5.42 \pm 0.01
Sand/%	49.2	47.8	47.2
Silt/%	26.8	29.4	29.0
Clay/%	24.0	22.8	23.8
Cd/mg kg ⁻¹	0.48 \pm 0.08	3.50 \pm 0.07	9.93 \pm 0.20
Zn/mg kg ⁻¹	71.5 \pm 3.3	1167 \pm 66	1848 \pm 32

SOC: soil organic carbon; data are expressed as mean \pm SD, n = 3.

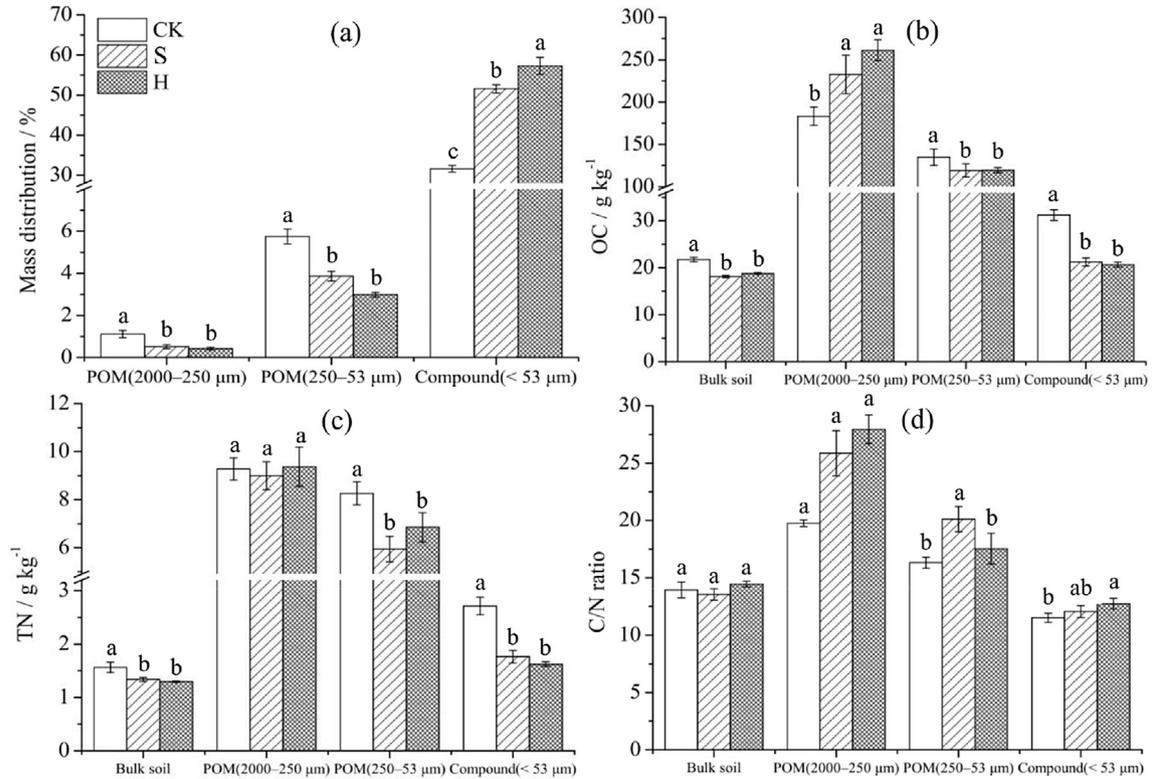


Fig. 1. (a) Distribution of soil fractions expressed as a percentage of the mass soil (%), (b) OC and (c) TN concentrations (in mg kg⁻¹ fraction) and (d) C/N ratios in different particle size fractions in control (CK), slightly (S) and highly (H) polluted soils, respectively. The bars represent the standard deviation of three replicates, and different lowercase characters for each fraction indicate significant differences among the control, slightly and highly polluted soils ($p < 0.05$).

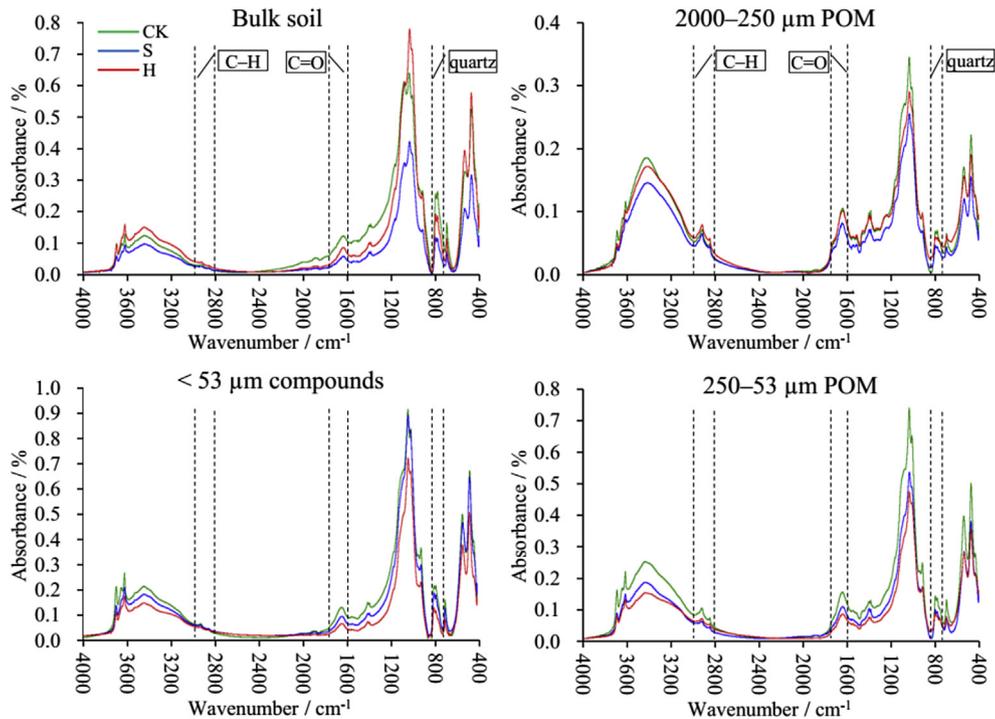


Fig. 2. FTIR spectra of bulk soils, 2000–250 μm and 250–53 μm POM size fractions and <53 μm organic-mineral compounds from (green) control, (blue) slightly and (red) highly polluted soils, respectively. C–H bonds in the 3020–2800 cm⁻¹ region, C=O bonds in the 1740–1600 cm⁻¹ region and quartz bonds in the 820–730 cm⁻¹ region. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

2928–2922 and 2856–2851 cm^{-1} correspond to C–H bonds of asymmetric and symmetric stretch vibration and the peaks at 1704–1703 and 1647–1632 cm^{-1} correspond to C=O bonds of carboxyl and ester groups, respectively. In the present study the absorption peaks for quartz were at 799–795 cm^{-1} . The peak heights of C–H and C=O bonds were normalized relative to the internal reference of quartz (Table 2). In the POM fractions the ratios of peak heights of C–H/quartz, C=O/quartz and C–H/C=O were 0.38–0.84, 1.58–2.61 and 0.21–0.32, respectively, which were higher than those for bulk soils and organic-mineral compounds regardless of the fraction size or pollution level. In addition, the ratios of peak heights of C–H/quartz, C=O/quartz and C–H/C=O were 30.9–122%, 19.3–52.0% and 9.40–49.6% higher in 2000–250 μm POM size fractions than in 250–53 μm POM size fractions. Compared with control soils, the ratios of C–H/quartz and C=O/quartz were lower in the metal polluted bulk soils and organic-mineral compounds. No significant differences were observed in the ratios of C–H/quartz, C=O/quartz or C–H/C=O in the POM fractions among control, slightly and highly polluted soils regardless of fraction size.

As shown in Table 2, the concentrations of FA and HA were higher in POM fractions than in bulk soils and organic-mineral compounds. We also observed higher FA and HA concentrations in 2000–250 μm POM size fractions than in 250–53 μm POM size fractions, especially in the slightly and highly polluted soils. Although the FA concentrations in the polluted bulk soils were lower than the controls, the FA concentrations in 2000–250 μm POM size fractions were higher in polluted soils than control soils. Both in the bulk soils and POM fractions, the HA concentrations were lower in polluted soils than control soils. In comparison to their corresponding controls, the HA/FA ratios decreased by 41.7% and 54.5% of 2000–250 μm POM size fractions but increased by 12.1% and 32.5% of 250–53 μm POM size fractions in slightly and highly polluted soils, respectively.

3.3. Distribution of Cd and Zn in the POM fractions

Total and EDTA-extractable Cd and Zn concentrations and the percentage of EDTA-extractable Cd and Zn in each size fraction are shown in Table 3. Total and EDTA-extractable Cd and Zn concentrations in soil fractions increased with significantly increasing pollution level. At control, slight and high pollution levels, total Cd

concentrations were 2.91–3.98, 4.99–23.7 and 4.94–18.6 times higher in 2000–53 μm POM size fractions than in bulk soils, and Zn concentrations were 1.78–1.85, 1.44–1.76 and 1.76–2.12 times higher than in bulk soils, respectively. In organic-mineral compounds, total Cd and Zn concentrations were 1.11–1.66 and 1.44–1.85 times higher than in bulk soils. In contrast, total and EDTA-extractable Cd and Zn concentrations were lower in mineral fractions than in bulk soils (Table S2). The percentages of EDTA-extractable Cd and Zn were 77.3–93.5% and 30.5–60.6% in 2000–53 μm POM size fractions and did not change greatly among the control, slightly and highly polluted soils. Compared with other soil components, the percentages of EDTA-extractable Cd and Zn increased in POM fractions except for the Cd in slightly polluted soil.

Except the Zn in control soils, total and EDTA-extractable Cd and Zn concentrations were higher in 2000–250 μm POM size fractions than in 250–53 μm POM size fractions among the three soils (Table 3). The extraction percentages for Zn with EDTA were higher in POM size fractions 2000–250 μm than 250–53 μm but there were no significant differences between 2000–250 and 250–53 μm POM size fractions in the percentages of Cd extractability. By comparison, the percentages of Cd extractability were higher than those of Zn in POM fractions ($p < 0.05$).

The percentage distributions of total Cd and Zn stocks in different soil fractions are shown in Fig. S2. Organic-mineral compounds had the largest soil Cd and Zn stocks. Despite the lower mass distributions of POM fractions than mineral fractions, the 24.5–27.9% and 7.12–16.7% distributions of Cd and Zn stocks in POM fractions were higher than the 9.42–14.5% and 3.81–8.52% distributions of mineral fractions. Compared with control soils, the percentage distributions of Cd stocks increased but Zn stocks decreased in the POM fractions of slightly and highly polluted soils. The percentage distributions of Cd and Zn stocks in the POM fractions were lower in the size range 2000–250 μm than in 250–53 μm ($p < 0.05$).

4. Discussion

4.1. Characteristics of OC, TN and C/N ratio in POM fractions

The mass distributions of 2000–53 μm POM size fractions in the paddy soils were 3.86–6.86%, higher values than the 0.47–1.20%

Table 2
Mean ratios of peak heights of C–H/quartz, C=O/quartz and C–H/C=O from FTIR spectra, concentrations (in g C kg^{-1} fraction) of fulvic acids (FA) and humic acids (HA), and ratios of HA/FA in different size fractions of control, slightly and highly polluted soils.

Pollution level	Peak height			Concentration		
	C–H/quartz	C=O/quartz	C–H/C=O	FA	HA	HA/FA
Bulk soil						
Control	0.054 ± 0.000 a	0.82 ± 0.04 a	0.065 ± 0.003 a	7.02 ± 0.14 a	6.26 ± 0.45 a	0.89 ± 0.08 a
Slightly	0.048 ± 0.013 ab	0.68 ± 0.04 b	0.070 ± 0.015 a	5.83 ± 0.46 b	4.78 ± 0.62 b	0.83 ± 0.15 ab
Highly	0.033 ± 0.007 b	0.62 ± 0.01 b	0.053 ± 0.012 a	5.98 ± 0.57 b	3.82 ± 0.31 b	0.65 ± 0.12 b
POM (2000–250 μm)						
Control	0.60 ± 0.08 a	2.14 ± 0.21 a	0.28 ± 0.01 a	55.5 ± 2.4 c	53.8 ± 5.4 a	0.97 ± 0.12 a
Slightly	0.84 ± 0.19 a	2.61 ± 0.33 a	0.32 ± 0.03 a	72.9 ± 0.6 b	41.3 ± 4.1 b	0.57 ± 0.05 b
Highly	0.75 ± 0.10 a	2.40 ± 0.26 a	0.31 ± 0.01 a	87.6 ± 5.5 a	38.6 ± 1.4 b	0.44 ± 0.03 b
POM (250–53 μm)						
Control	0.46 ± 0.02 a	1.79 ± 0.08 a	0.26 ± 0.01 a	40.9 ± 0.8 a	41.6 ± 0.9 a	1.02 ± 0.04 b
Slightly	0.38 ± 0.09 a	1.77 ± 0.09 a	0.21 ± 0.04 a	28.6 ± 0.7 b	32.5 ± 1.0 b	1.14 ± 0.06 ab
Highly	0.38 ± 0.03 a	1.58 ± 0.16 a	0.24 ± 0.00 a	28.5 ± 1.8 b	38.0 ± 5.5 ab	1.35 ± 0.28 a
Compound (<53 μm)						
Control	0.092 ± 0.004 a	0.83 ± 0.05 a	0.11 ± 0.01 a	5.42 ± 0.19 a	4.07 ± 0.40 b	0.75 ± 0.05 a
Slightly	0.050 ± 0.020 b	0.67 ± 0.02 b	0.075 ± 0.029 a	6.18 ± 0.51 a	4.69 ± 0.14 a	0.76 ± 0.08 a
Highly	0.045 ± 0.017 b	0.62 ± 0.09 b	0.072 ± 0.024 a	5.69 ± 0.41 a	4.07 ± 0.19 b	0.72 ± 0.09 a

Different lowercase characters in the same column for one variable indicate significant difference by one-way analysis of variance at $p < 0.05$. Data are expressed as mean ± SD, $n = 3$.

Table 3

Total and EDTA-extracted Cd and Zn concentrations (in mg kg⁻¹ fraction) and the EDTA extracted percentage (EDTA/total, %) of different soil size fractions in control, slightly and highly polluted soils.

Variable	Pollution Level	Bulk soil	POM/ μm		Compound <53 μm
			2000–250	250–53	
Cd					
Total	Control	0.48 \pm 0.08 Dc	1.91 \pm 0.18 Ac	1.39 \pm 0.07 Bc	0.80 \pm 0.01 Cc
	Slightly	3.50 \pm 0.07 Db	82.8 \pm 11.5 Ab	17.4 \pm 1.4 Bb	4.68 \pm 0.21 Cb
	Highly	9.93 \pm 0.20 Da	185 \pm 10 Aa	49.0 \pm 5.8 Ba	11.0 \pm 0.1 Ca
EDTA	Control	0.35 \pm 0.02 Dc	1.58 \pm 0.15 Ac	1.15 \pm 0.19 Bc	0.52 \pm 0.05 Cc
	Slightly	3.07 \pm 0.09 Cb	65.8 \pm 11.8 Ab	13.5 \pm 2.1 Bb	4.31 \pm 0.07 Cb
	Highly	8.77 \pm 0.23 Ca	167 \pm 12 Aa	45.8 \pm 5.1 Ba	9.22 \pm 0.27 Ca
Percentage	Control	74.2 \pm 10.1 Ab	82.8 \pm 5.5 Aab	82.9 \pm 13.8 Aa	65.7 \pm 5.0 Ac
	Slightly	87.7 \pm 2.5 Aa	79.1 \pm 3.3 Bb	77.3 \pm 6.4 Ba	92.1 \pm 2.7 Aa
	Highly	88.3 \pm 3.2 ABa	90.1 \pm 5.9 ABa	93.5 \pm 1.7 Aa	83.9 \pm 1.8 Bb
Zn					
Total	Control	71.5 \pm 3.3 Bc	128 \pm 17 Ac	133 \pm 5 Ac	136 \pm 6 Ac
	Slightly	1167 \pm 66 Cb	2054 \pm 86 Ab	1678 \pm 117 Bb	1715 \pm 57 Bb
	Highly	1848 \pm 32 Da	3915 \pm 83 Aa	3244 \pm 123 Ba	2660 \pm 35 Ca
EDTA	Control	23.4 \pm 0.2 Cc	59.2 \pm 0.9 Ac	58.5 \pm 2.8 Ac	39.1 \pm 0.3 Bc
	Slightly	258 \pm 5 Db	1102 \pm 118 Ab	513 \pm 59 Bb	314 \pm 3 Cb
	Highly	491 \pm 5 Ca	2371 \pm 10 Aa	1260 \pm 168 Ba	546 \pm 25 Ca
Percentage	Control	32.8 \pm 1.5 Ca	50.9 \pm 1.2 Ab	44.1 \pm 0.9 Ba	28.8 \pm 1.2 Da
	Slightly	22.1 \pm 0.8 Cc	53.6 \pm 5.3 Ab	30.5 \pm 1.5 Bc	18.3 \pm 0.5 Db
	Highly	26.6 \pm 0.2 Cb	60.6 \pm 1.5 Aa	38.7 \pm 3.7 Bb	20.5 \pm 0.9 Db

Different lowercase characters in the same column for one variable and different uppercase characters in the same row indicate significant difference by one-way analysis of variance at $p < 0.05$. Data are expressed as mean \pm SD, $n = 3$.

reported in French soils (Balabane and van Oort, 2002; Labanowski et al., 2007; Sebastia et al., 2008) but similar to the 4.14–4.51% found in soils in Zhejiang province, east China (Zhang and Ke, 2004). Total POM fractions represented a small part of the mass of soils, but the 2000–53 μm POM size fractions retained over 29.6% of soil OC. Similar findings regarding the OC stocks (25–47%) of POM fractions were reported by Sebastia et al. (2008) in vineyard soils. By comparison, OC and TN concentrations and C/N ratios were found to be consistently lower in 250–53 μm POM size fractions than 2000–250 μm POM size fractions. This agrees with previous studies in which OC and TN concentrations decreased with decreasing POM size, indicating an increasing level of decomposition (Balabane and van Oort, 2002; Labanowski et al., 2007; Fels et al., 2014). However, the loss of C is more rapid than that of N because of microbial immobilization of N which decreases the C/N ratios of small POM size fractions during decomposition (Christensen, 2001). Generally, OC and TN concentrations and C/N ratios are higher in plant residues than in soil biota or microbial products associated with soil minerals (Paul, 2016). In contrast to the small POM size fractions, the large POM size fractions were expected to contain the least decomposed OM and therefore to be most closely related to the original OC, TN and C/N ratios of OM inputs from plant residues and/or organic material amendments in soils (Christensen, 2001; Sebastia et al., 2008; Rennert et al., 2017). Due to the smaller weight as a percentage of the soils, the percentage distributions of OC and TN stocks in POM size fractions 2000–250 μm were lower than in 250–53 μm .

In the present study, the relative increases in OC and TN concentrations and C/N ratios in the 2000–250 μm POM size fractions were higher in long-term polluted soils than control soils. This can be attributed mainly to the toxic effects of metals on the OM decomposer community limiting C and N losses, and then a shift in the OC and TN concentrations and C/N ratios closer to the original OM inputs increasing OC and TN concentrations and C/N ratios of the 2000–250 μm POM size fractions (McEnroe and Helmisari, 2001; Zhou et al., 2014). The toxic effects of metals on SOM decomposition may not only originate from the source of soil but also from the source of OM input associated metal pollution (Boucher et al., 2005; Zhou et al., 2014). Consequently, metal

pollution decreased the amounts of available C and N released from the decomposition of large POM size fractions and then decreased C and N adsorption by clay minerals, resulting in smaller relative increases in OC and TN concentrations of organic-mineral compounds in polluted soils than control soils. In a meta-analysis study, Zhou et al. (2016) reported that C/N ratios in bulk soils were higher after long-term metal pollution than controls. According to the results of Zhou et al. (2016), higher C/N ratios in 2000–250 μm POM size fractions might be explained not only by the inhibitory effects of metals on OM decomposition taking the large POM size fractions closer to the original OM inputs with high C/N ratios but also by decreased plant N utilization efficiency, resulting in larger mineral N losses from polluted soils. However, the relative changes in OC and TN concentrations or C/N ratios in the 250–53 μm POM size fractions were not significant between metal polluted and control soils. Compared with control soils, these results suggest that the increases in OC and TN concentrations and C/N ratios occurred mainly in the large POM size fractions of the metal polluted paddy soils. Although OC and TN concentrations tend to be higher in polluted soils, the percentage distributions of OC and TN stocks in 2000–250 μm POM size fractions were smaller than those in the control soils because of the smaller weight of the POM fractions.

4.2. Changes in OM composition and quality of POM fractions

Study of the composition and quality of SOM is important rather than considering only the quantity of SOM fractions. Using FTIR spectroscopy the hydrophilic functional group of the C=O bond is responsible for OM adsorption properties and the hydrophobic functional group of the C–H bond is related to OM wettability, and the relative contents of these functional groups are positively related to soil OC concentrations (Capriel et al., 1995; Ellerbrock et al., 2009; Bernier et al., 2013; Rennert et al., 2017). In addition, FA and HA are major constituents of SOM and HA is higher in molecular weight and contains less phenol and carboxylic acid functional groups compared with FA (Melo et al., 2016). In the present study the higher peak heights of C–H and C=O bonds and concentrations of FA and HA in 2000–53 μm POM fractions were mainly due to the higher OC concentrations compared with the

bulk soils. The larger C–H/C=O ratios indicate an increase in C–H content accompanied by a relative decrease in C=O content in POM fractions than in bulk soils, corresponding to the more hydrophobic characters and susceptibility to decomposition of labile SOM present (Ellerbrock et al., 2009; Rennert et al., 2017).

From the 2000–250 μm POM size fractions to 250–53 μm , the significant decreases in peak heights of C–H and C=O bonds and in concentrations of HA and FA were due to the decreasing OC concentration with increasing level of POM decomposition. During maize straw decomposition, Hu et al. (2016) observed lower contents of C–H and C=O functional groups in degraded DOM than in fresh DOM using FTIR spectral analysis. The higher C–H/C=O ratios in 2000–250 μm POM size fractions than 250–53 μm indicate a lower decrease in the abundance of functional groups for C=O than C–H with increasing level of OM decomposition. Therefore, decreasing POM size due to degradation processes will lead to more hydrophilic characters of SOM. Increases in HA/FA ratios in small POM size fractions compared with large POM size fractions further indicate that humification progress was enhanced with increasing level of OM decomposition, especially in polluted soils.

As a result of large decreases in biomass inputs and soil organic carbon (SOC) concentrations due to the long-term effects of metal pollution on soil microorganisms and vegetation, Viventsova et al. (2005) found that SOM had greater diversity and bond intensity of functional groups in unpolluted soils than in polluted soils. Capriel et al. (1995) also observed that hydrophobic functional group of the C–H correlated positively with SOC concentrations. In the present study, the slightly lower SOC concentrations in metal polluted soils could explain the significant reductions in peak heights of C–H and C=O bonds compared with control soil. In contrast, there was a slightly higher OC concentration of 2000–250 μm POM size fractions in polluted soils than in control soil. Therefore, these changes in OC concentration would contribute greatly to the lack of significant differences in the contents of C–H and C=O groups of 2000–250 μm POM size fractions among control, slightly and highly polluted soils in the present study. However, freshly added Cd, Cu and Pb ions can cause slight decreases in the contents of carboxyl and hydroxyl groups of POM fractions (Guo et al., 2006). Nevertheless, results from metal spiking experiments are not representative of long-term polluted soils because of the different responses of microbial decomposition of OM and sorption behavior of metals to acute and chronic toxicities and the associated changes in soil properties and plant growth (Giller et al., 1998; Lair et al., 2007). In addition, the C–H/C=O ratios in POM fractions were also similar among control, slightly and highly polluted soils. These results therefore suggest that the contents of hydrophobic and hydrophilic functional groups in the 2000–53 μm POM size fractions will not change significantly in soils after long-term metal pollution. In the present study, the higher FA concentrations of 2000–250 μm POM size fractions in metal polluted soils than control soil might also be due mainly to the higher OC concentrations of 2000–250 μm POM size fractions in polluted soils. In addition, metal polluted soils had lower HA/FA ratios in 2000–250 μm POM size fractions and higher HA/FA ratios in 250–53 μm POM size fractions. Overall, we conclude that the responses of OM functional groups and humic substances to metal pollution were inconsistent in the present study.

4.3. Effects of POM compositional and quality changes on Cd and Zn distributions

In the present study POM fractions had higher Cd and Zn concentrations than other soil constituents. This corroborates studies in which POM fractions usually showed enrichment of metals in long-term polluted soils (Labanowski et al., 2007; Mohamed et al.,

2010). Despite the relatively low percentages of the bulk soil mass (3.86–6.86%), 2000–53 μm POM size fractions made significant contributions to total metal stocks of bulk soils, 24.5–27.9% for Cd and 7.12–16.7% for Zn. Metal enrichment of POM fractions was due to the initial inputs of metal-enriched residues to soils and was also linked to increasing amounts of metal-reactive sites on POM surfaces such as carboxylic and phenolic functional groups which would inhibit the adsorption of metals by mineral components (Balabane and van Oort, 2002; Guo et al., 2006; Labanowski et al., 2007; Salati et al., 2010; Hu et al., 2016). The FA and HA fractions also have the highest number of carboxylic and phenolic functional groups and therefore can bind metals most efficiently (Melo et al., 2016). In the present study the POM fractions showed higher contents of the hydrophilic groups C=O, FA and HA than did bulk soils, and therefore eventually resulted in greater Cd and Zn absorption capacities in POM fractions. The high EDTA-extractability of Cd (77.3–93.5%) and Zn (30.5–60.6%) in POM fractions supports the hypothesis that the surface sorption of metals was stimulated by metal enrichment (Labanowski et al., 2007), but the affinity of Cd toward POM fractions was lower (Guo et al., 2006).

Previous studies report increasing enrichment of metals with decreasing POM size in long-term polluted soils and explain them on the basis of the larger surface areas and larger number of functional sites for the smaller POM size fractions (Balabane and van Oort, 2002; Zhang and Ke, 2004; Labanowski et al., 2007; Mohamed et al., 2010). However, changes in the functional groups and surface areas of different POM size fractions were not reported concomitantly in these published studies. In other studies specific sorption which formed inner-sphere complexes and non-specific sorption that formed outer-sphere complexes were suggested as the main mechanisms of metal sorption on OM (Guo et al., 2006; Qi et al., 2016). In contrast, POM fractions of decreasing size showed decreasing Cd and Zn concentrations in the present study. Although the surface areas of the POM fractions were not measured, significant decreases in the content of the hydrophilic group C=O with decreasing POM size occurred. Sebastia et al. (2008) found that whatever the size of the POM fraction, the same types of functional groups were metal-reactive. We therefore assume that significant decreases in metal-reactive functional groups might be the main factor responsible for the lower Cd and Zn concentrations in POM size fractions 250–53 μm than 2000–250 μm in paddy soils. The lower FA and HA concentrations in 250–53 μm POM size fractions further demonstrate the low binding capacity of metals compared with 2000–250 μm . Labanowski et al. (2007) found that Cd and Zn were less EDTA-extractable with decreasing POM size in soils planted with maize and wheat. In the soils studied, however, the EDTA-extractability of Cd was not affected by the size of POM fraction. Due to their relatively higher mass percentages, 250–53 μm POM size fractions maintained higher Cd and Zn stocks than 2000–250 μm POM size fractions. Although there were no significant differences in the contents of C–H and C=O bonds or the C–H/C=O ratios in the same POM size fractions between metal polluted and control soils, POM fractions of increasing pollution intensity showed increasing Cd concentrations. This suggests that Cd saturation of POM fractions was not attained under the conditions of our present study.

4.4. Extractability of Cd and Zn in POM fractions

In an arable field polluted by atmospheric fallout from a Zn smelter, Labanowski et al. (2007) observed that the percentages of Cd and Zn extracted with EDTA were 86–100% and 72–98% in 2000–53 μm POM fractions. The extractabilities of Cd and Zn in POM fractions were slightly high compared with the results in the present study. Several studies considered that EDTA-extractable Cd

and Zn were potentially able to move into the root system for plant uptake (Ure, 1996; Wu et al., 2004; Cornu et al., 2017). However, no studies have reported that plants can normally directly utilize the Cd and Zn that are bound with POM. Even so, Li et al. (2014) observed 29.6–80.0% and 3.18–19.7% decreases in the concentrations of Cd and Zn bound to the organic complex or sulfides, respectively, in polluted soils with repeated phytoextraction by the Cd/Zn hyperaccumulator *Sedum plumbizincicola*. This suggests that hyperaccumulator plants might potentially utilize the Cd and Zn bound to POM fractions, and the utilization efficiency might be higher for Cd than Zn due to the greater extractability observed.

Although the masses of POM fractions were low in the bulk soils, we observed that Cd and Zn stocks reached 24.5–27.9% and 7.12–16.7%, respectively. In addition, organic amendments changed metal distribution, caused large metal retention in POM fractions and increased POM fraction contents in polluted soils (Mohamed et al., 2010). In previous studies, Viventsova et al. (2005) and Zhou et al. (2016) also found significant reductions in SOM content in long-term metal polluted soils. Therefore, the study of interactions between metals and POM fractions will be very useful in efforts to increase the efficiency of soil remediation and especially technologies combining organic amendment with phytoextraction of metal polluted soils.

5. Conclusions

The enrichment of Cd and Zn was attributable to the higher concentrations of the hydrophilic group C=O and the humic substances in POM fractions than in bulk soils, and the Cd and Zn in POM fractions were more EDTA-extractable. Soil POM fractions showed decreases in OC, TN, FA and HA concentrations and C/N ratios with decreasing POM size, and higher Cd and Zn concentrations in the POM size fractions 2000–250 μm than 250–53 μm due to a reduction in metal-reactive functional groups of C=O bonds. In the 2000–250 μm POM size fractions, the OC, TN and FA concentrations and C/N ratios were higher in polluted soil than control soil. Despite the higher Cd and Zn concentrations of POM fractions in polluted soils than in control soils, there were no significant differences in the contents of C–H and C=O bonds or C–H/C=O ratios between metal polluted and control soils. Accordingly, the quality and composition of OM fractions can change in the long-term polluted paddy soils and these changes in OM may exert feedback effects on the distribution and extractability of soil Cd and Zn.

Conflict of interest

The authors declare that they have no competing interests.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <https://doi.org/10.1016/j.envpol.2017.09.081>.

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