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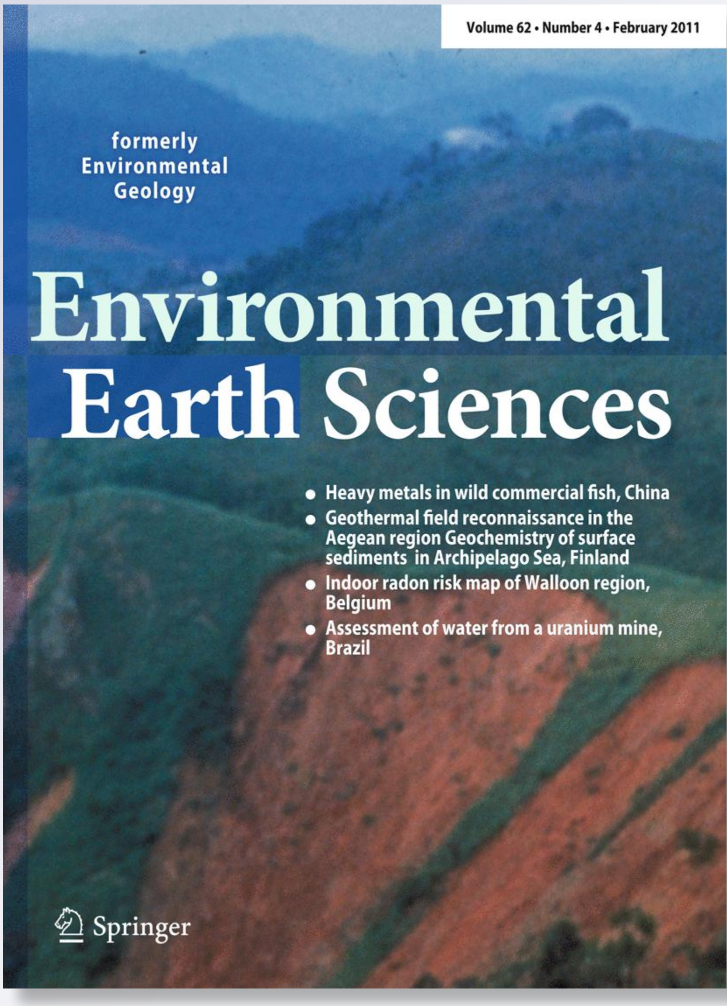

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ORIGINAL ARTICLE

Different spontaneous plant communities in Sanmen Pb/Zn mine tailing and their effects on mine tailing physico-chemical properties

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Abstract Different plant communities have established spontaneously on Sanmen Pb/Zn mine tailing. The site was inspected and four different plant communities were identified according to their species composition. To understand the effects of different communities on mine tailing physico-chemical properties, a community survey was carried out in Sanmen Pb/Zn mine tailing, and the physico-chemical properties and heavy metal (Cu, Pb, Cd and Zn) distribution of mine tailings were determined. Results showed that there were four types of communities (I, II, III and IV) in Sanmen Pb/Zn mine tailing. From community I to IV, the number of plant species and community characteristics (aboveground biomass, underground biomass, coverage and height) consistently increased. Moreover, the nutrient pool and physico-chemical properties of mine tailing consistently reestablished from community I to IV, while the total heavy metal content consistently decreased. The contents of residual fractions, Fe–Mn oxide fractions for Pb, Zn, Cu and Cd and exchangeable fractions for Pb and Zn also consistently decreased. However, the contents of organically bound fraction had no obvious change from community I to IV. Moreover, the contents of Cu organically bound fraction reversely increased. Results demonstrate that communities I, II, III and IV should be a progressive community succession. Moreover, along with the progressive community succession, phytostabilization and phytoextraction of mine tailings are more and more effective.

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Keywords Heavy metal fraction · Mine tailing · Physico-chemical properties · Plant communities

Introduction

Anthropogenic activities such as mining and smelting of metal ores have increased the prevalence and occurrence of heavy metal contamination at the earth's surface. Specifically, opencast mining activities have a serious environmental impact on soils and water streams, generating millions of tons of mine tailings (Bhattacharya et al. 2006). In general, mine tailings are mechanically, physically, chemically and biologically deficient (Vega et al. 2006), characterized by instability and limited cohesion, with low contents of nutrients and organic matter and high levels of heavy metals (He et al. 2005).

Many techniques are available in remediation of mine tailings (i.e., soil washing, vitrification, soil flushing), but most of them are expensive and the structure and microorganism diversity in soil are greatly degraded (Simon 2005). In comparison to these techniques, phytostabilization is cost effective and friendly to soil and natural landscape (Mench et al. 2003; Conesa et al. 2007). Phytostabilization can reduce the bioavailability of metals and prevent wind and rain erosion (Cunningham et al. 1995). Moreover, vegetation can improve nutrient conditions in the soil (Cobb et al. 2000).

The selection of plant species to carry out the phytostabilization of mine tailings must be site specific, since, besides being tolerant to metal pollution, they must be adapted to the local climate. In this sense, it is useful to search plants that have spontaneously colonized mine tailings from ancient times and therefore are completely adapted to these polluted environments (Conesa et al.

2007). In China, there are numerous heavy metal mines, and the mining activities produce huge amounts of Pb/Zn mine tailings (Wong and Bradshaw 2002; Wong 2003). Successful establishment and colonization of several pioneer plant species, such as *Paspalum distichum, Cynodon dactylon* (Shu et al. 2002a), *Sesbania rostrata* (Yang et al. 1997; Wong 2003) and *Leucaena leucocephala* (Zhang et al. 2001), on Pb/Zn mine tailings have been already identified. Many of the previous studies on these pioneer plant species mainly focused on their respective uptake and translocation of heavy metals (Shu et al. 2002b; Freitas et al. 2004), and only few were related to the initial primary succession of pioneer plant species on these mine tailings (Chambers and Sidle 1991; Raskin and Ensley 2000). Moreover, the effects of these initial communities on the physico-chemical properties of mine tailings are still unclear.

This study was carried out on typical Pb/Zn mine tailings at Sanmen of Zhejiang Province, south China, where a number of pioneer plant species have been observed. Also, different communities have developed from these initial pioneer species. The objective of this work was to investigate how the initial community developed on mine tailing and to study the effects of different communities on the physico-chemical properties and heavy metal distribution of mine tailings. It is expected that the results generated from this study may aid in the understanding of natural plant community establishment on mine tailings and their effects on the soil conditions of mine tailings.

Materials and methods

Site description

Sanmen Pb/Zn mine tailing (28°3668N, 120°5575E) is located in Zhejiang Province, China. The region has a semitropical climate with an annual rainfall of 1827.7 mm, occurring mostly during spring and summer. The annual average temperature is 19.5°C. Large-scale exploitation and processing of minerals led to the widespread environmental deterioration in the region, especially of agricultural lands. Sanmen Pb/Zn mine tailing originated from the Sanmen Pb/Zn mine. The mine tailings, typically of grain size 102 μm, are the by-products of Pb–Zn mining operation, in which the major constituents of the ore body are sphalerite, galena, pyrite and calcite. Mine tailings produced from the mining process were deposited in a valley adjacent to the mine area. The surrounding bedrock includes sandstone, siltstone and limestone. The surface of the tailings is dry and almost completely devoid of vegetation except for some pioneer plant species.

Community survey

A community survey was conducted at Sanmen Pb/Zn mine tailing in October 2006. In the mine tailings, plant communities were separated into four different types (I, II, III and IV) according to the diversity and composition of the species. *Miscanthus floridulus* and *Imperata cylindrical* were pioneer species and appeared in all plant communities, while other species inhabited specific communities. The results of a community survey showed that there were four types of relatively stable communities with different diversity and composition of species (Fig. 1): "I" type of communities comprised two species (*M. floridulus* and *I. cylindrica*); "II" type had three species (*M. floridulus*, *I. cylindrica* and *Pueraria lobata*); "III" type included six species (*M. floridulus*, *I. cylindrica*, *P. lobata*, *Aster ageratoides*, *Equisetum ramosissimum* and *Erigeron annuus*); "IV" type had the most number of plant species and consisted of eight species (*M. floridulus*, *I. cylindrica*, *P.* lobata, *A. ageratoides*, *E. ramosissimum*, *E. annuus*, *Conyza Canadensis* and *Lysimachia clethroides*).

Three plots (5×5 m^2) were selected in each type of community. In each plot, five subplots (1×1 m^2) were randomly selected. In each subplot, the aboveground and underground plant tissues were collected. Plant tissues were thoroughly washed with running tap water and rinsed with distilled water to remove any soil particles attached to the plant surfaces. The aboveground and underground tissues were separated and oven dried (80°C) to constant weight and then weighed again. The average community height was measured using rulers (20 plants were measured in each plot). The community coverage was determined using iron gridding (1 m^2 was divided into 100 grids). In each plot, five subplots (1×1 m^2) were randomly selected, and the area of plant canopy in the subplots was measured using iron gridding. In total, in each type of community, 15 subplots of biomass and coverage were measured, and 60 plants (all in three plots) were selected to measure the average community height (20 plants in each plot were used to determined the average community height).

Soil sampling and analysis

Soil samples were collected in October 2006. After the survey of community characteristics, five samples were collected randomly using soil corers in each plot (64 mm in diameter and 100 mm in length). Each sample was collected at a depth of 0–10 cm and with a 20-cm interval from the rhizosphere [the rhizosphere was defined as the soil attached to roots after gentle shaking by hand (Baudoin et al. 2002)] of plants in order to avoid the influence of the rhizosphere. In total, in each community type, 15 samples

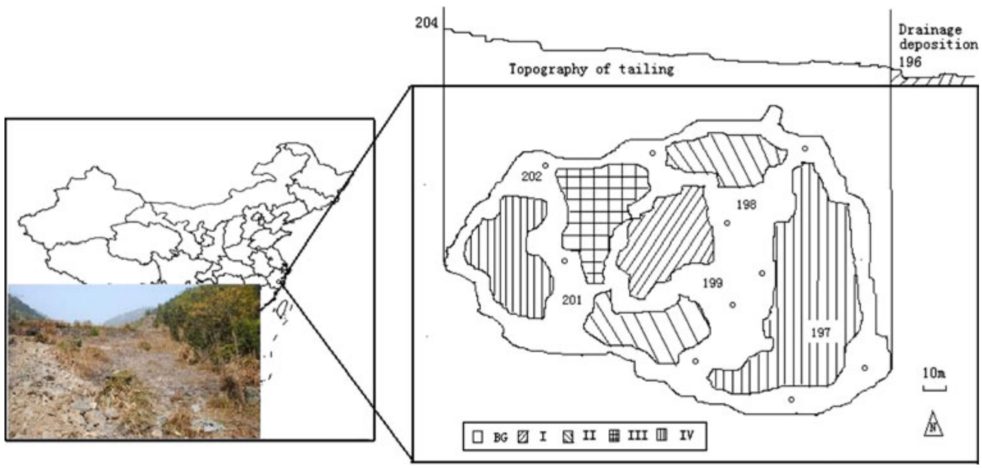

Fig. 1 The basic scheme of different communities (I, II, III and IV) growing on Sanmen Pb/Zn mine tailing and the distribution of these communities. *BG* indicates the bare mine tailing. *Numbers* on the map represent altitudes above sea-level. *Open circle* indicates the sampling position of bare tailing (BG)

of soil were collected from plant communities and 10 samples from bare tailings (BG) (Fig. 1).

Soil pH (solid: distilled water = 1:5) was measured using a pH meter. Organic matter content in soil was determined using the Walkley–Black methods (Nelson and Sommers 1982). For the analysis of total N and total P, 1.0 g of K_2SO_4 catalyst mixture and 5 ml of concentrated H_2SO_4 were added to the 0.5 g air-dried ground tailing in 100-ml digestion tubes. After heating, followed by the addition of 20 ml of distilled water and filtration, the digests were transferred to 50-ml volumetric flasks. Total N in the filtrates was determined using the Berthelot reaction method and total P was determined using the molybdenum blue method (Page et al. 1982). Available phosphorus was determined using the method of Bray and Kurtz (1945). Ammonia N and nitrate N were determined using a steam distillation method (Keeney and Nelson 1982). Fresh field-moist tailing was saturated with water and then the surplus water was allowed to seep out through a sand bath. The remaining water in the tailing represented the water-holding capacity (WHC). Aggregate stability (AS) was determined by using the method of Blake and Hartge (1986).

As much as 0.5 g of air-dried soil was digested [concentrated HCl + concentrated $HClO_4$ (4:1, v/v) (Mcgrath and Cunliffe 1985)] using the US EPA Method 3051 in a microwave oven (Multiwave 3000, Anton Paar, Ashland, VA, USA). The total heavy metal content of tailing was then determined using an inductively coupled plasma optical emission spectrometer (ICP/OES, Optima 2100DV, Perkin Elemer, USA). Tailing samples were fractionated using the sequential extraction procedure of Tessier et al. (1979). Contents of different heavy metal fractions were also determined using an inductively coupled plasma optical emission spectrometer (ICP/OES, Optima 2100DV, Perkin Elmer, USA). The chemical reagent, extraction conditions and corresponding fraction can be found in Table 1.

Data analysis

Differences in community characters, soil physico-chemical properties and heavy metal contents between bare tailing and the four types of communities were determined by analysis of variance (ANOVA) with Newman–Keuls multiple comparisons. The variation in data of duplicate samples was presented by box plots. Data analyses were performed by using SPSS 12.0 for Windows.

Results and discussion

Plant communities

In the Pb/Zn mine tailing, the communities were classified into four types (I, II, III and IV) based on the composition of species. The number of plant species consistently increased from community I to IV. Community characteristics determined in this study significantly and consistently increased from I to IV (aboveground biomass: $F_{3,\ 59} = 237.53$, $P \leq 0.01$; underground biomass: $F_{3,\ 59} = 313.13$, $P \leq 0.01$; coverage: $F_{3,\ 59} = 357.16$, $P \leq 0.01$; average height: $F_{3,\ 239} = 3795.22$, $P \leq 0.01$; Fig. 2). The increasing coverage can provide physical protection to prevent wind erosion and surface runoff, and reduce pollution to vicinities (Norland and Veith 1995; Prasad and Freitas 2003). The increasing underground biomass can reduce heavy metal mobility through immobilization of root exudates (Blaylock and Huang 2000; Maiti 2007), which decreases the potential migration of heavy metals to the surface of mine tailings (Stoltz and Greger 2002). Results indicated that from community I to IV, phytostabilization of mine tailings seemed to be more effective. *M. floridulus* and *I. cylindrical* were the dominant species and formed most part of the community aboveground biomass. Moreover, previous study had reported that they can accumulate

Table 1 Sequential extraction procedure and the corresponding fraction

Steps	Fractions	Extraction procedures
1	Exchangeable	1 g of soil sample, 8 mL 1 mol L^{-1} $MgCl_2$, pH 7, shake for 1 h, at room temperature
2	Carbonate	8 ml 1 mol L^{-1} CH_3COONa, adjusted pH to 5.0 with CH_3COOH, shake for 5 h at room temperature
3	Fe–Mn oxide	20 ml 0.04 mol L^{-1} $NH_2OH{\cdot}HCl$ in 25% CH_3COOH, pH 2.0, water bath at 96°C for 6 h with occasional shaking
4	Organically bound	3 ml 0.02 mol L^{-1} HNO_3, 30% H_2O_2 (adjusted to pH 2.0), water bath at 85°C, for 5 h, 3.2 mol $L^{-1}$$CH_3COONH_4$ in 20% (v/v) HNO_3, shake for 30 min
5	Residual	3 ml HNO_3 + $HClO_4$ + HF under high pressure and 170°C

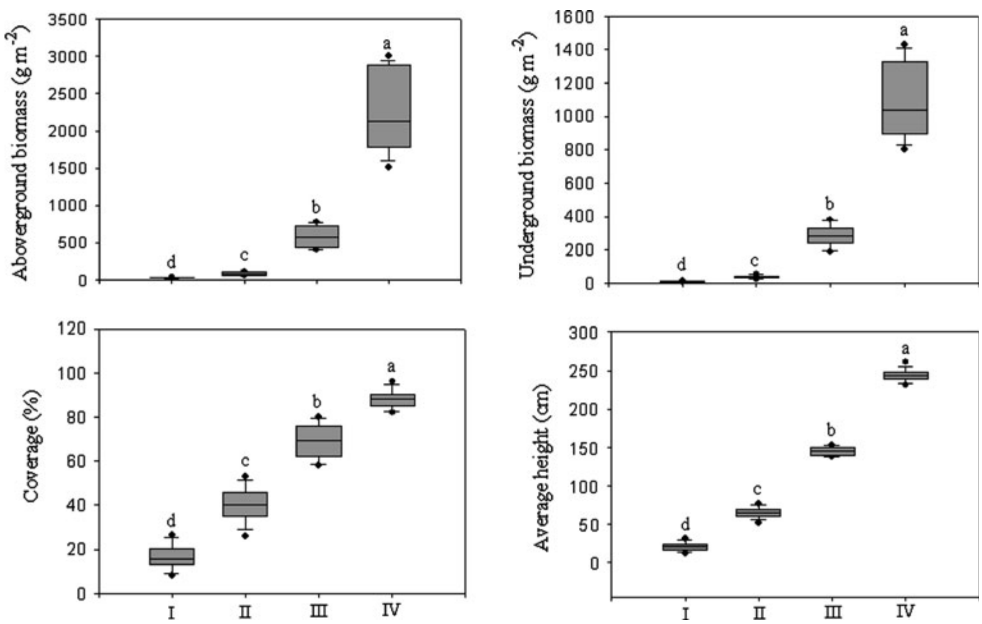

Fig. 2 The characteristics determined in each type (I, II, III and IV) of community. *Different small letters* indicate significant differences in the community characteristics between different types of communities at 0.05 level. Aboveground biomass ($n = 15$); underground biomass ($n = 15$); coverage ($n = 15$); average height ($n = 60$)

high contents of heavy metals in the aboveground tissues (Wang et al. 2008). Consequently, the increasing aboveground biomass confirmed the more effective phytoextraction of mine tailings from community I to IV.

Ecological studies reveal that mine tailings can also be colonized as a consequence of primary succession, which can start with seeds or vegetative propagules either from the surrounding vegetation or by long-distance transport by wind or water (Chambers and Sidle 1991; Marrs and Bradshaw 1993). In Sanmen Pb/Zn mine tailings, *M. floridulus* had the highest cover percentage (>50%) and aboveground biomass (>60%). Consequently, it was the common dominant species in different plant communities of Sanmen Pb/Zn mine tailing. Moreover, *M. floridulus* has been proved to be the initial pioneer species for many mine tailings and has high tolerance to heavy metal toxicity (Wang et al. 2008). We suppose that the initial plant establishment on Sanmen Pb/Zn mine tailing may depend on rhizome strategy (Shu et al. 2005), i.e., clonal growth by rhizomatous extension of *M. floridulus* (*M. floridulus* belongs to clonal plants). Moreover, more species (*M. floridulus* and *I. cylindrical* may be the initial pioneer species) had continuously established from community I to IV. The productivity (increasing aboveground and underground biomass) and resource utilization [increasing coverage for light resource and increasing average height for space resource (Spehn et al. 2000)] also significantly increased from community I to IV. Consequently, these communities (community I to IV) should belong to a progressive succession (Sun et al. 2006). In many mine tailings of China, as in the studied site, established communities usually (just as from I to IV) developed step by step from several common initial pioneer species. A more complete understanding of natural colonization succession of these communities should help achieve self-sustained vegetation on mine tailings quickly and cheaply by accelerating the natural succession process (Dobson et al. 1997). In our study, *M. floridulus* and *I. cylindrica* were the ideal pioneer species, which could be used to remediate Pb/Zn mine tailings at the initial stage. Then, other tolerant species may be artificially transplanted according to inhabitation succession and simultaneously small artificial measures taken to ameliorate soil physico-chemical properties. Thus, a mature and self-sustained plant community will be constructed on mine tailings in a relatively short time.

Changes in physico-chemical properties of mine tailings

Although the physico-chemical properties and heavy metal distribution of mine tailings were not recorded in the pre-colonization stage, the tailings produced from flotation processes often had homogeneous substrate. Moreover, the physico-chemical properties of bare tailings (BG, Fig. 1) were also relatively homogenous. However, the physico-chemical properties of mine tailings colonized by different communities (I, II, III and IV) exhibited significant difference (Fig. 3) and all of them were higher than those in bare tailings. Results indicated that the nutrient pools and the soil characteristics of mine tailings were improved by establishment of plant communities. Moreover, the physico-chemical properties of mine tailing consistently improved from community I to IV. The improvement in physico-chemical properties may be the result of exudates released by the roots and microbial metabolites (Marschner and Romheld 1983; Leyval and Berthelin 1993), as the underground biomass increased significantly from community I to IV. Vangronsveld et al. (1996) and Zhang et al. (2006) also found that nutrient pools and physico-chemical properties of mine tailings gradually reestablished along with the consequent community succession or inhabitation succession. Consequently, we speculate that I, II, III and IV communities may be different succession stages that developed from initial pioneer species (*M. floridulus* and *I. cylindrical*), and physico-chemical properties of mine tailing were simultaneously improved along with the community succession.

The heavy metal distribution of mine tailing

The total contents of Cu, Pb, Cd and Zn in bare tailing (BG) were significantly higher than those of mine tailings colonized by different communities ($P < 0.05$; Fig. 4). Moreover, from community I to IV, the total contents consistently decreased. In these communities, *M. floridulus* and *I. cylindrical* can accumulate high contents of heavy metals (Gong et al. 1997; Peng et al. 2006; Wang et al. 2008). Moreover, the increasing aboveground biomass confirmed the increasing phytoextraction of mine tailings from community I to IV. Therefore, the phytoextraction of plants will have a certain effect on the decrease of total heavy metal contents of mine tailings. However, the distribution of heavy metal contents in mine tailings was not recorded at the pre-colonization stage and a inhabitation strategy may exist: more plant species prefer to inhabit in an area with low contents of heavy metals that have little bio-toxicity to plants. Although we cannot completely attribute the decrease of total heavy metal contents to the phytoextraction of plants, from our results, we confirmed that the species diversity of communities is a sensitive bio-indicator of total heavy metal contents of mine tailings.

The total content of heavy metals can indicate the extent of contamination, but it usually is not an accurate indication of phytotoxicity. Hence, many recent studies investigated the fractions of heavy metals in mine soils (Li et al. 2005; Remon et al. 2005; Vega et al. 2004) to evaluate the phytotoxic risk along a remediation process. In the Sanmen Pb/Zn mine tailings, the carbonate fraction in bare tailings and soils of different communities had very low contents (Fig. 4). This is a special character, which may be related to the ore composition. From bare tailing to community I, II, III to IV, the contents of residual fraction significantly decreased, which may be related to the exudates released by the roots and increasing microbial metabolites, making the heavy metals change from a tight-bound to a loose-bound phase (Marschner and Romheld 1983; Leyval and Berthelin 1993). Compared to Cu and Cd, Pb and Zn had significantly higher contents of exchangeable fraction in the bare tailing, but significantly decreased from community I to IV. The successive decrease of exchangeable fraction may be due to the plant uptakes, as the exchangeable fraction is the easily bio-available fraction (Tao et al. 2003). Moreover, *M. floridulus* takes large portion of community biomass that had been proved to accumulate high contents of Pb and Zn (Wang et al. 2008). Differing from the change in other fractions, the contents of organically bound fraction for Cu, Pb, Cd and Zn had no significant decrease, especially the contents of organically bound fraction of Cu inversely increased. The change in the organically bound fraction may be the reason for the increase in organic matter, with the tendency of transition heavy metals to form stable complex with organic ligands (Chen 1996). Moreover, Cu mainly formed stable Cu–organic complex (Fuentes et al. 2004). Therefore, its contents of organically bound fraction exhibited increasing trend with the increase in organic matter. The decreasing content of Fe–Mn oxide fractions may also be related to the increase of organic matter, which interferes with the Fe–Mn oxides matter combining with heavy metals (García et al. 2005). Results demonstrated that the establishment of different communities greatly changed the composition of heavy metals fraction, and more information about this

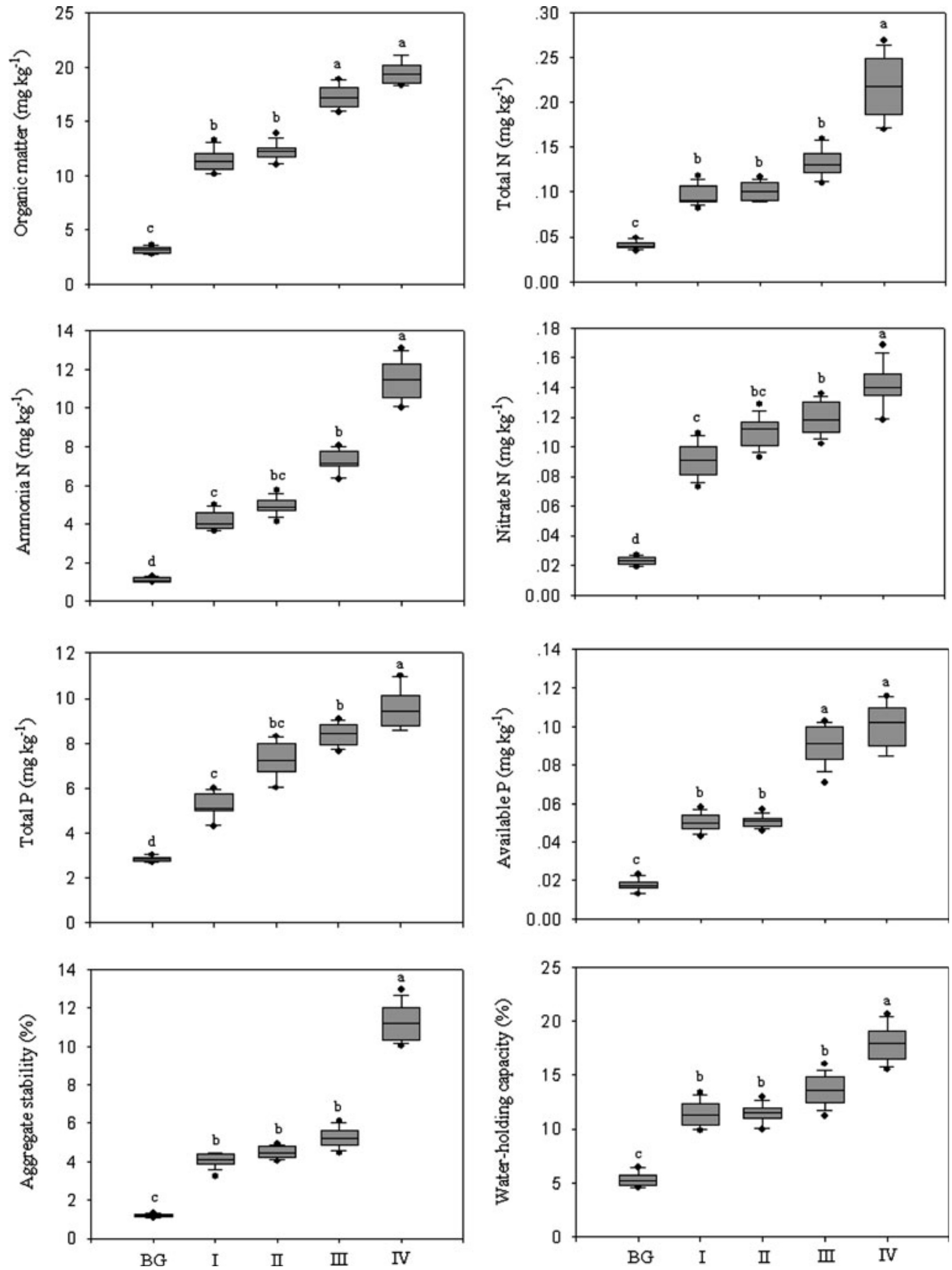

Fig. 3 Physico-chemical properties of soils in sites with different communities (I, II, III and IV; $n = 15$) and bare tailings (BG; $n = 10$). *Different small letters* indicate significant differences in the physico-chemical properties of soils between different types of communities and bare tailing at the 0.05 level

could help us to understand more precisely the heavy metal mobilization and potential risks in the process of phytoremediation (Chlopecka et al. 1996; Sanchez et al. 1999; Kaasalainen and Yli-Halla 2003). Although inhabitation strategy may partially explain the change of heavy metal fractions, different change rates and direction of heavy metal fractions proved that plant establishment plays an important role in the change of composition in soil heavy metal fractions. In our results, with the increase of species diversity and biomass of communities, the bioavailability of heavy metals (exchangeable fraction) in soils significantly decreased, but the mobility of heavy metals (residual fraction) simultaneously increased.

Metalliferous ores, especially lead/zinc (Pb/Zn) deposits in China, have been explored over the past century, and lots of mine tailings and waste rock heaps derived from mining activities remain during the initial stage of plant colonization. As in our studied site, different communities developed from the few common initial pioneer species (such as *M. floridulus* in the studied site) in many mine tailings. Consequently, as in our results, the common species appearing in most communities colonized on mine

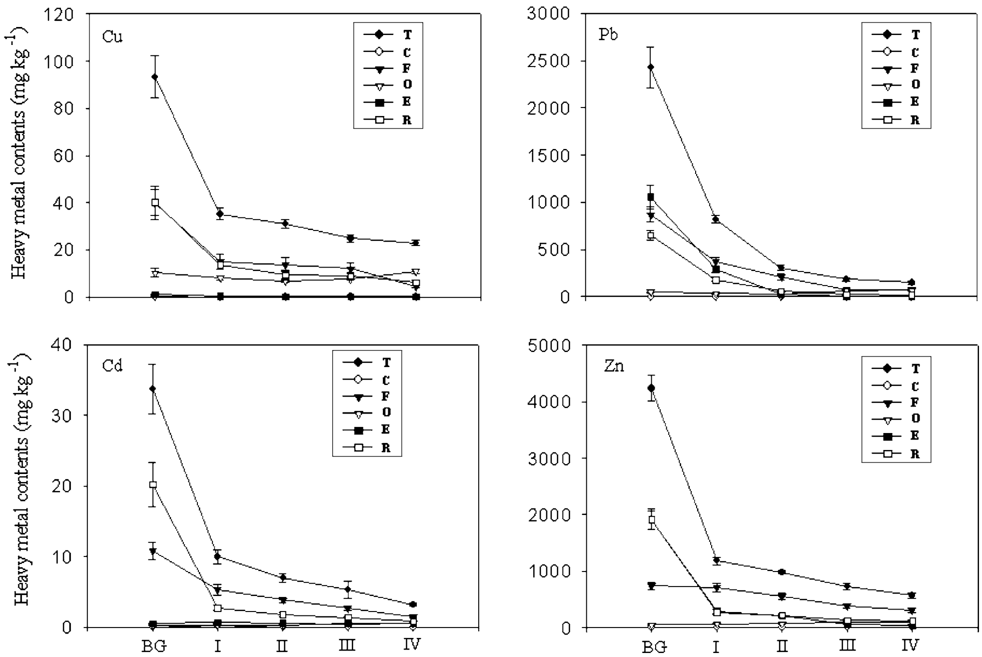

Fig. 4 The contents of total and different heavy metal fractions in bare tailings (BG; $n = 10$) and mine tailings colonized by different communities (I, II, III and IV; $n = 15$). *T* total contents, *C* carbonate fraction, *F* Fe–Mn oxide fraction, *O* organically bound fraction, *E* exchangeable fraction, *R* residual fraction

tailings should be the ideal pioneer species, which can be used to phyto-remediate mine tailings at the initial stage. Other tolerant plant species can be artificially transplanted to accelerate the community succession and enhance the effects of phytostabilization and phytoextraction.

Conclusions

Results showed that different plant communities (I–IV) were established spontaneously on Sanmen Pb/Zn mine tailing. From community I to IV, the number of plant species and characteristics of communities (aboveground biomass, underground biomass, coverage and height) consistently increased and matched with consistent improvement of nutrient pool and physico-chemical properties of mine tailings. The total heavy metal (Pb, Zn, Cu and Cd) contents of mine tailings inversely and consistently decreased from community I to IV. The contents of residual fractions and Fe–Mn oxide fractions for Pb, Zn Cu and Cd and exchangeable fractions for Pb and Zn also consistently decreased. However, the contents of organically bound fraction had no obvious change community I to IV. Moreover, the contents of organically bound Cu fraction reversely increased. Results demonstrate that community I to IV belong to a progressive community succession, along with more and more effective phytostabilization and phytoextraction of mine tailings.

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