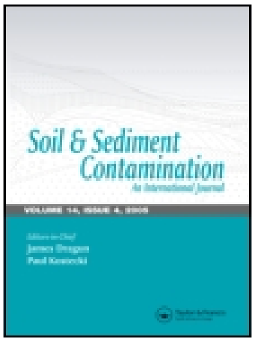

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Differential Distribution of Metals and Enzymes in Quanzhou Bay Estuarine Wetland Soils under Three Mangrove Species

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ABSTRACT

This study aimed to investigate the effects of three dominant mangrove species (*Avicennia marina*, *Aegiceras corniculatum*, and *Kandelia obovata*) on the distribution of the metal elements Fe, Mn, Cu, and Zn and the enzymes urease, phosphatase, polyphenol oxidase, and catalase. Concentrations of the metallic elements and enzymatic activities were quantified in soils under the three mangrove species in the Quanzhou Bay estuarine wetland, a typical coastal wetland in China. Results showed that *A. corniculatum* promoted aggregation of Mn, urease, and phosphatase, while *K. obovata* contributed to accumulation of Cu, urease, and phosphatase. Furthermore, *A. marina* induced activation of Zn and accumulation of urease, phosphatase, and catalase. The characteristic enzyme and metal distributions induced by the different mangrove species are likely to result from different planting times, root systems, and soil pH and salinity. Moreover, the three mangrove species were found to influence the diversity of elemental and enzymatic stoichiometry through differences in the soil microenvironment, which can promote biodiversity in wetland ecosystems. These findings provide a useful guideline to develop strategies for restoration of estuarine wetlands.

KEYWORDS
Ecological restoration; wetland microenvironment; heavy metals; enzymes; stoichiometry diversity

Introduction

Pollution by heavy metals in natural environments is a serious global problem (Irabien and Velasco, 1999). With rapid industrialization and economic development in coastal regions, heavy metals have been continually introduced to estuarine and coastal environments through rivers, runoffs, and land-based point sources where metals are produced as metal refinishing by-products (Yu *et al.*, 2008). Most metals that enter the marine environment settle down and become incorporated into sediments together with organic matters, Fe/Mn oxides, sulphides, and clay (Wang and Chen, 2000). Sediments are the main repository and source of heavy metals in the marine environment and play an important role in the

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transport and storage of potentially hazardous metals (Ribeiro *et al.*, 2005). However, trace metal contents of sediments can also reflect the quality of coastal wetland to some extent. Although sediments act as ultimate sinks for heavy metals in aquatic environments, they cannot fix metals permanently. Furthermore, metal deposits in sediments pose significant ecological risk to the surrounding environment (Yu *et al.*, 2010; Hu *et al.*, 2011).

Heavy metals have significant influence on the physiological processes and growth of plants. High concentrations of Cu, Pb, and Zn destroy leaf structure; for example, heavy metal accumulation lowers the chlorophyll and carotenoid contents of *Avicennia marina* leaves, consequently affecting coastal ecosystems (Macfarlane and Burchett, 2000). In a natural wetland, heavy metals regulate the community structure of benthic fauna and biodiversity (Amin *et al.*, 2009). Fe, Mn, Cu, and Zn accumulate to high concentrations in plant organisms and exert toxic effects on mangrove wetland ecosystems through the food chain; therefore, the contents of these heavy metals in mangrove wetland sediments often serve as useful indexes of the degree of heavy metal pollution in an ecosystem (Macfarlane and Burchett, 2001; Macfarlane *et al.*, 2007; Ravikumar *et al.*, 2007; Agoramoorthy *et al.*, 2008).

Mangrove species play important roles in the distribution of metals in coastal ecosystems. Different mangrove species exhibit a diversity of metal retention capacities and cumulative efficiencies even in the same mangrove wetland ecosystem because of differences in their utilization of nutrients such as Fe, Mn, Cu, and Zn (Krishnan *et al.*, 2007; Agoramoorthy *et al.*, 2008; Hoque, 2010). A mangrove wetland ecosystem has strong retention capacity and cumulative efficiency for heavy metals (Tam and Wong, 1995; Quan *et al.*, 2010; Zhou *et al.*, 2010) and is an important source or sink for heavy metal contamination (Ray *et al.*, 2006). In recent years, mangroves have attracted interest from biogeographers because of their unusual purifying effect on heavy metals (Yim and Tam, 1999; Machado *et al.*, 2009). Mangrove species have even been used to remediate metal pollution in coastal regions (Machado *et al.*, 2002). Several studies have shown that mangrove rhizospheres influence soil metal distribution, which is in turn influenced by the surrounding soil microenvironment. Specifically, low pH promotes Zn accumulation in the surrounding root system, and redox potential and organic matter decomposition control metal concentration by regulating the circulation of Fe and Mn (Song *et al.*, 1990; Marchand *et al.*, 2006).

Soil enzymes from plant root systems and the surrounding environment, such as soil microorganism and fauna, are important driving forces of ecosystem metabolism. These enzymes influence the function of wetland ecosystems and are important indexes in characterizing the cyclic process of substance decomposition (Sinsabaugh, 2010). Surrounding environment properties, such as tides, salinity, pH, redox potential, hydrodynamics, and nutrients, affect enzymatic activities in wetland soils (Fenner *et al.*, 2005; Rejmánková and Sirová, 2007; Song *et al.*, 2007). Drying–wetting alternation environments increase hydrolase activity by stimulating soil microbial community activities (Song *et al.*, 2007). High soil pH restrains acidic phosphatase (P-P) activity but promotes catalase (CAT) and polyphenol oxidase (PPO) activities. In addition, the effect of salinity on enzymatic activities depends on the type of enzyme (Williams *et al.*, 2000; Huang and Morris, 2005).

Until now, the effect of enzymes on metals has been uncertain; however, the regulation of enzyme activity by metals has been confirmed by many studies. Manganese (Mn) is an important nutrient because it is involved in activation of enzymes such as polyphenol oxidase and superoxide dismutase (SOD) (Carvalho *et al.*, 2014). It has been reported that zinc acts as an inhibitor of phosphatase (Maret, 2013). Copper is associated with a large number of enzymes that catalyze oxidative reactions in a variety of metabolic pathways (Marschner, 1995), while Cu alone or its mixtures with Cd have been found to increase the activities of superoxide dismutase and peroxidase in *Chlorella vulgaris* (Qian *et al.*, 2011). Mourato *et al.* (2009) reported that excess Cu in soils boosts PPO activity. In wetland environments, enzymatic activities control plant growth while plants, in turn, affect enzymatic activities through the influence of their metabolic processes on rhizosphere microorganisms.

Previous studies have shown that enzymatic activity regulates metal distribution in soils, and microenvironment differentiation improves wetland ecosystem biodiversity. However, the interaction between metals and enzymes in mangrove ecosystems remains unclear to date. The present study investigated the effects of region-dominant mangrove species (*Avicennia marina, Aegiceras corniculatum*, and *Kandelia obovata*) on the distribution of Fe, Mn, Cu, Zn, urease (U), phosphatase (P-P), polyphenol oxidase (PPO), and catalase (CAT) in estuarine wetlands. Specifically, we analyzed the correlation of metals with hydrolases and oxidases in soils under different mangrove species to elucidate the mechanism by which metal-enzyme interactions affect the diversity of nutritional mode and enzymatic stoichiometry. Our results provide novel insights into the influences and interaction mechanisms that regulate elemental and enzymatic stoichiometry in soils under different mangrove species. Our findings may serve as a basis for differential restoration in coastal districts in the future.

Materials and methods

Study site and plant species

Quanzhou Bay, Fujian, China, is situated at 118°38′–118°52′E and 24°47′–24°58′ N and covers an area of 136.42 km^2. The study site has a tidal flat area of 568.5 hm^2 and a water area of 308.4 km^2. It is dominated by a subtropical climate, with a mean annual temperature of 20.4°C. The mean monthly temperature is the lowest in January (11.9°C) and the highest in July (28.3°C). The mean annual precipitation is 1095.4 mm, and the annual sunshine duration is 2200 h, with alternating arid and humid seasons. Soil salinity and pH in downstream regions are higher than those in midstream and upstream regions (Wu and Liu, 2011). *A. marina, A. corniculatum*, and *K.obovata* are the dominant plants in estuarine wetlands.

Soil sampling and analysis

Three regions were selected as upstream, midstream, and downstream regions, where native mangrove species including *A. marina* (*Am*), *A. corniculatum* (*Ac*), and *K. obovata* (*Ko*) were mainly distributed (Figure 1). Test soils under *A. marina* (*Am*), *A. corniculatum* (*Ac*), and *K. obovata* (*Ko*) were labelled. Bare land (*Bl*) in each region served as the control. In each region, three similar soil cores were randomly selected. Sampling in each mangrove was done at five soil depths (0–10 cm, 10–20 cm, 20–30 cm, 30–40 cm, and 40–50 cm) and repeated three times at each site on the following dates: 15–17 April 2007 (spring), 8–10 November 2007 (autumn), 6–10 January 2008 (winter), and 1–3 August 2008 (summer). Plant debris and roots were removed from each sample. Each soil sample was collected, air-dried, ground, sieved through a 2 mm mesh, and then analyzed to determine its chemical composition.

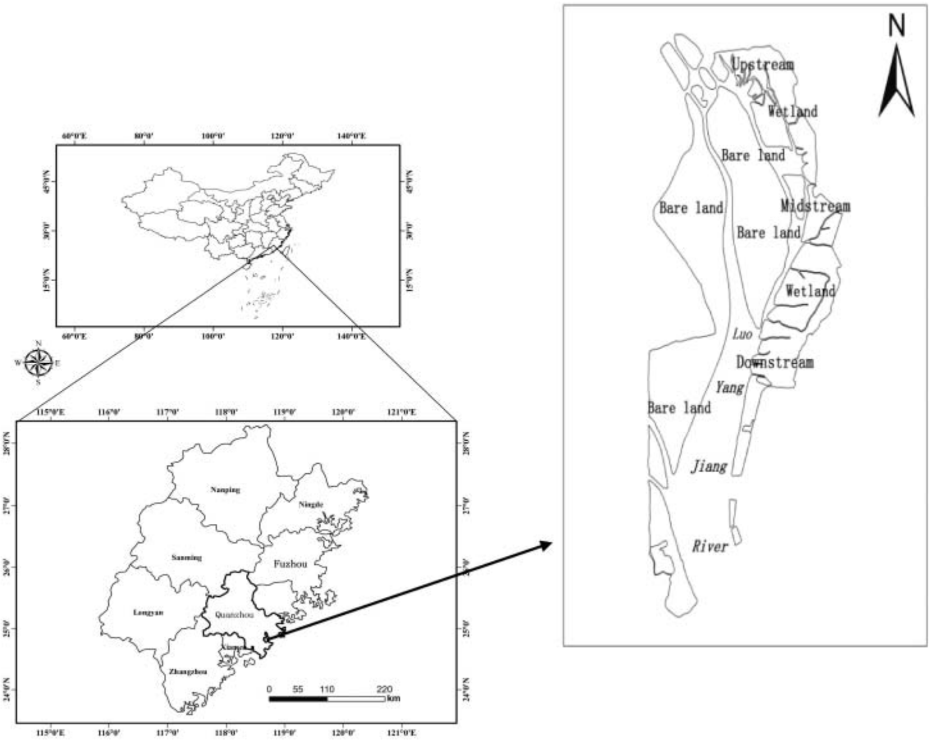

Figure 1. Map of the study area.

Eh

Platinum electrode and saturated calomel electrode potential were used to measure the Eh value. After the tide, the platinum and saturated calomel electrodes were connected to the positive and negative terminals, respectively, of a millivolt meter. Then, the mV files were selected and two electrodes were inserted 5 cm apart into the soil at about 5 cm depth. The instrument was allowed to become stable for 10 min, after which the Eh value was recorded. Temperature and pH values were also measured simultaneously.

The diethylenetriaminepentaacetic acid (DTPA) extraction method was used to measure the concentration of Cu, Zn, Fe, and Mn. Before the start of the experiment, the DTPA extraction agent and standard stock solutions of Cu, Zn, Fe, and Mn were prepared. A total of 25 g air-dried soil was passed through a 1 mm sieve and placed in a 100 ml plastic jar. Then, 50 ml DTPA extraction solvent was added and shaken on a reciprocating shaker at 25°C for 2 h, after which the extract was filtered into a 100 ml volumetric flask. The concentrations of Cu, Zn, Fe, and Mn in the filtrates, blank solution, and standard solution were measured by flame atomic absorption spectroscopy (PE-5100PC, Perkin Elmer Co., USA). The concentration of these four elements in soils was calculated using the equation Cu (Zn, Fe, Mn) (mg kg^{-1}) = $\rho^{*}V/m$, where ρ is the mass concentration (μg mL^{-1}) of test solution obtained from the standard curve; V is the volume of DTPA extraction solvent in mL; m represents the mass of the measured soils.

Routine soil chemical parameters, including U, P-P, PPO, and CAT, were analyzed following the methods suggested by Guan (1986).

Urease

A total of 10.0 g air-dried soil was placed in a 200 mL volumetric flask. Then, 10 mL phosphate buffer solution (pH 7) and 10 mL 2% urea solution were added. The mixture was shaken well and stoppered with a bottle stopper, then incubated at 30°C for 24 h. Next, 70 mL distilled water was added and the mixture was shaken well before filtering with quantitative filter paper into another volumetric flask. Then, 30 ml of the filtrate was transferred into a 50 mL beaker, and four drops of sodium hydroxide solution (10 mol L^{-1}) were added until the pH reached 11. Finally, ammonia-sensitive electrodes in an ion concentration meter with pH 3330 were used to measure the concentration of ammonia in filtrates. Urease activity (EUu) was calculated as the amount of organic matter in NH_3 in 100 g air-dried soil after incubation for 24 h at 30°C.

Phosphatase

A total of 5.0 g air-dried soil was placed in a 50 mL volumetric flask, and five drops of toluene and 20 mL 0.5% $C_6H_5Na_2O_4P$ were added successively (citrates with pH 7 served as buffer solution). The mixture was shaken well and incubated at 37°C for 2 h. Then, 5 mL of filtrates were sampled and the free phenol content was measured by the colorimetric method. Phosphatase activity (EUpp) was calculated as the number of milligrams of P_2O_5 in 100 g air-dried soil after 24 h.

Catalase

A total of 2.00 g air-dried soil was placed in a 100 mL volumetric flask, then 40 ml distilled water and 5 ml of 0.3% hydrogen peroxide solution were added. The mixture was shaken with a reciprocating shaker for 20 min. After this, 5 mL H_2SO_4 at 1.5 mol L^{-1} concentration was added to stabilize undecomposed hydrogen peroxide in the volumetric flask. The suspension in the volumetric flask was filtered with a slow-type filter. Then, 25 mL of filtrates was titrated with $KMnO_4$ (0.005 mol L^{-1}) until the color changed to pink and remained stable for at least 30 min. The activity of catalase (EUcat) was calculated as the number of milliliters of 0.1 mol L^{-1} $KMnO_4$ consumed by 1.00 g air-dried soil per 20 min.

Polyphenol oxidase

A total of 1.00 g air-dried soil was placed in a 50 mL volumetric flask, to which 10.0 mL 1% $C_6H_6O_3$ was added. The mixture was shaken well and incubated at 30°C for 2 h. H_2O (10.0 mL) was used instead of stroma as the control. Then, 4 mL citrate-phosphate buffer solution (pH 4.5) and 25 mL $C_4H_{10}O$ were added to the volumetric flask, it was shaken a few times, and the solution was extracted for 30 min. Colorimetric analysis was done by determining absorption at 430 nm. The activity of polyphenol oxidase (EUppo) was calculated as the number of milliliters of gallnut element released by 1.0 g soil per 2 h.

Fumigation-extraction was used to determine microbial biomass C as described in Medina-Roldán and Bardgett (2011). Total organic carbon (TOC) and total organic nitrogen (TON) were determined by the Walkley–Black method (Nelson and Sommers, 1982) and the Kjeldahl method (Bai *et al.*, 2012), respectively.

Statistical analysis

The mean and standard errors of means were calculated for each condition. One-way ANOVA and pair-wise comparison tests (Tukey's HSD) were used to compare the contents

Table 1. Substrate type and Eh of the soils covered by mangrove species.

	The average content of each granule /%				
	Gravel	Sand	Silts	Clay	Eh
Ac	0	2.18±0.47	68.19±0.62	28.01±0.28	225.38±13.07a
Ko	0	2.30±0.75	68.87±0.81	28.80±1.34	219.04±14.39a
Am	0	2.48±0.76	67.36±1.06	30.17±1.16	202.94±17.37a
Bl	0	0.90±0.21	68.60±0.56	30.51±0.60	222.62±15.18a

The mean values followed by different letters in the same row differ significantly at $p < 0.05$, according to one-way ANOVA and t-test. *Ac-Aegiceras corniculatum*, *Ko-Kandelia obovata*, *Am-Avicennia marina, Bl*-bare land.

of essential elements in the different mangrove plants. Relationships among nutritional elements, hydrolytic enzymes, and oxidases were determined by correlation analysis. All statistical analyses were performed using SPSS 13.0 (SPSS Inc., Chicago, IL, USA).

Results

Substrate type and Eh of soils under different plant species

The soil under mangrove species was found to be dominated by silt, indicating that the soil in the whole region belonged to the same sedimentary type, namely clayey silty sand. No significant difference in Eh value was detected among the soils under *Ac*, *Am*, and *Ko* (Table 1).

Difference in MBC, TOC, and TON contents of soils under different plant species

The content of MBC in soils covered by mangrove species was significantly higher than those in soil without plants. However, no significant difference was observed among soils under the three mangrove species (Table 2). Likewise, the TOC and TON contents of the soils were not different in soils under the three mangrove species.

Difference in metal contents of soils under different plant species

Bl had lower contents of Fe, Mn, Cu, and Zn than samples with vegetation (Table 3). No significant difference in Fe content was detected among the soils under *Ac*, *Am*, and *Ko*. The Mn content of the soil under *Ac* was significantly higher than that of the soils under the

Table 2. Contents of MBC, TOC, and TON in soils under different mangrove species.

	MBC (mg kg-1)	TOC (g kg-1)	TON (g kg-1)
Ac	40.19±4.66a (n=155)	9.03±0.24a (n=157)	1.13±0.02a (n=155)
Ko	35.85±3.83a (n=116)	8.88±0.18a (n=113)	1.09±0.05a (n=116)
Am	37.12±3.75a (n=114)	8.1±0.11a (n=114)	1.11±0.02a (n=111)
Bl	25.58±3.08b (n=153)	8.94±0.20a (n=153)	1.07±0.03a (n=150)

The mean values followed by different letters in the same row differ significantly at $p < 0.05$, according to one-way ANOVA and t-test. *Ac-Aegiceras corniculatum*, *Ko-Kandelia obovata*, *Am-Avicennia marina, Bl*-bare land.

Table 3. Contents of Fe, Mn, Cu, and Zn in the soil under different mangrove species.

	Fe (mg kg-1)	Mn (mg kg-1)	Cu (mg kg-1)	Zn (mg kg-1)
Ac	44.20±1.63a (n=167)	27.81±1.46b (n=152)	6.84±0.30a (n=151)	9.62±0.40b (n=153)
Ko	41.55±1.37a (n=110)	21.17±1.31a (n=110)	9.07±0.46b (n=110)	8.18±0.33a (n=110)
Am	51.31±3.49a (n=111)	25.83±1.36ab (n=112)	7.17±0.39ab (n=111)	9.51±0.50b (n=110)
Bl	40.24±1.65a (n=127)	20.12±1.32a (n=128)	6.19±0.33a (n=128)	7.11±0.33a (n=128)

The mean values followed by different letters in the same row differ significantly at $p < 0.05$, according to one-way ANOVA and t-test. *Ac-Aegiceras corniculatum*, *Ko-Kandelia obovata*, *Am-Avicennia marina, Bl*-bare land.

other two species. The soil under *Ko* had the highest Cu content of 9.07 mg kg^{-1}. The Zn contents of the soils under *Ac* (9.62 mg kg^{-1}) and *Am* (9.51 mg kg^{-1}) were significantly higher than that of the soil under *Ko*. Thus, the mangrove species covering the soil modified the distribution of metal elements, except for Fe, to different extents (Table 3). *Ac* principally affected the distribution of Mn and Zn, *Ko* mainly affected the distribution of Cu, and *Am* primarily influenced the distribution of Zn.

Difference in enzyme activities of soils under different plant species

As observed in the case of metals, distributions of the enzymes U, P-P, PPO, and CAT were also affected by vegetation. All three enzymes were lower in soils without vegetation than in soils with vegetation. The U activity in the soils under vegetation was significantly higher than that in the soil without vegetation. No significant difference in U activity was observed among the three species. The P-P activity in the soil under *Ac* was significantly higher than those in the soils under the other two species. The CAT activity in the soil under *Am* (0.54 EUcat) was significantly higher than that in the soils under the other two species. No significant difference in PPO activity was observed among the soils under the three mangrove species. Thus, our results indicate that the mangrove covering the soil modified the distribution of enzymes to different extents, except for PPO, which was unaffected (Table 4). Both *Ac* and *Ko* significantly affected the distribution of U and P-P, while *Am* affected the distribution of U, P-P, and CAT.

Table 4. Activities of urease, phosphatase, polyphenol oxidase, and catalase in the soil under different mangrove species.

	U(EUu)	P-P(EUpp)	CAT(EUcat)	PPO(EUppo)
Ac	7.90±0.20b (n=180)	6.27±0.17c (n=150)	0.40±0.01a (n=165)	18.44±0.71a (n=165)
Ko	8.95±0.31b (n=120)	5.99±0.11b (n=120)	0.34±0.01a (n=120)	19.25±1.02a (n =110)
Am	8.99±0.29b (n=120)	5.58±0.09b (n=120)	0.54±0.03b (n=120)	18.80±0.96a (n =120)
Bl	5.67±0.19a (n=180)	4.19±0.14a (n=80)	0.38±0.01a (n=140)	17.57±1.12a (n =135)

The mean values followed by different letters in the same row differ significantly at $p < 0.05$, according to one-way ANOVA and t-test. *Ac-Aegiceras corniculatum*, *Ko-Kandelia obovata*, *Am-Avicennia marina, Bl*-bare land.

Correlation among heavy metals under different plant species

Fe, Mn, Cu, and Zn positively correlated with *Bl*, which suggested that the metal content of the soil without any plants was relatively homogeneous. However, the mangrove species modified this distribution (Table 5). No clear relationship was observed between Cu and Fe or Cu and Mn in the soils under mangrove plants, except for *Ko*. Zn and Mn showed significant positive correlation in the soils under *Ko* and *Am* but no clear correlation was observed in the soil under *Ac*. These results indicate that the mangrove plants modified the distribution of metals in this region. Neither *Ac*, *Ko*, nor *Am* significantly modified the relationship between Cu and Fe or Cu and Mn. However, *Ko* had a significant effect on the correlation between Zn and Mn.

Correlation among hydrolytic enzymes and oxidases under different plant species

Mangrove species modified the distribution of enzymes and oxidases in the wetland. As shown in Table 6, the hydrolytic enzymes and oxidases positively or negatively correlated in *Bl*. However, the enzymes and oxidases showed different correlations in the soils under different plants. PPO and U exhibited no clear correlation in the soils under *Ac*, *Ko*, and *Am*. PPO and P-P showed significant negative correlation in the soil under *Ko* but exhibited no clear relationship in the soils under *Ac* and *Am*. CAT and U were positively correlated in the soil under *Ko* but displayed no clear relationship in the soils under the other two species. Therefore, neither *Ac*, *Ko*, nor *Am* had significant effect on the relationship between U and PPO. However, both *Ac* and *Am* affected the relationship between U and CAT as well as that between P-P and PPO. *Am* modified the relationship between PPO and CAT.

Correlation among heavy metals, hydrolytic enzymes, and oxidases

The correlation coefficients among Fe, Mn, Cu, Zn, U, P-P, PPO, and CAT are shown in Table 7. The relationship between metals and enzymes in the test soils was unique for each mangrove species. Weak correlation was observed between Fe and U, Fe and P-P, Zn and CAT, and Cu and P-P in *Bl*. However, the mangrove plants modified the relationship

Table 5. Pearson's correlation coefficient among Fe, Mn, Cu, and Zn in four soils.

		Fe	Mn	Cu
Ac (n=180)	Mn	0.50^{**}		
	Cu	0.01	-0.06	
	Zn	0.31^{**}	0.14	0.57^{**}
Ko (n=120)	Mn	0.58^{**}		
	Cu	-0.21^{*}	-0.20^{*}	
	Zn	0.19^{*}	0.26^{**}	0.32^{**}
Am (n=120)	Mn	0.32^{**}		
	Cu	-0.17	-0.13	
	Zn	0.60^{**}	0.29^{**}	0.29^{**}
Bl (n=180)	Mn	0.68^{**}		
	Cu	0.24^{**}	0.26^{**}	
	Zn	0.52^{**}	0.48^{**}	0.56^{**}

Ac-Aegiceras corniculatum, Ko-Kandelia obovata, Am-Avicennia marina, Bl-bare land.
*Correlation is significant at the 0.05 level (2-tailed).
**Correlation is significant at the 0.01 level (2-tailed).

Table 6. Pearson's correlation coefficient among urease, phosphatase, polyphenol oxidase, and catalase in four soils.

		U	P-P	PPO
Ac (n=180)	P-P	0.63**		
	PPO	-0.04	-0.00	
	CAT	0.06	0.44**	-0.22**
Ko (n=120)	P-P	0.48**		
	PPO	-0.14	-0.76**	
	CAT	0.52**	0.50**	-0.28*
Am (n=120)	P-P	0.70**		
	PPO	-0.02	-0.16	
	CAT	-0.02	0.38**	-0.01
Bl (n=180)	P-P	0.70**		
	PPO	0.36**	-0.28*	
	CAT	-0.22**	0.68**	-0.40**

Ac-Aegiceras corniculatum, Ko-Kandelia obovata, Am-Avicennia marina, Bl-bare land.
*Correlation is significant at the 0.05 level (2-tailed).
**Correlation is significant at the 0.01 level (2-tailed).

between Mn and P-P in the soils under *Ac* and *Ko* and that between Fe and P-P in the soils under *Ko* and *Am*. Taken together, these results indicate that different mangrove species exert different influences on the distribution of metals and enzymes in the soil around them.

Discussion

Differential distribution of metals

Aerobic environments control the circulation of Fe and Mn in wetland ecosystems (Otero *et al.*, 2009). The present study indicates that mangrove principally influences the distribution of Mn but not Fe in wetlands. Periodic flooding influences ventilation in wetland soils, and aerobic environments control the cycle of Fe and Mn through redox potential

Table 7. Pearson's correlation coefficient among metals, hydrolytic enzymes, and oxidases in four soils.

		Fe	Mn	Cu	Zn
Ac (n=180)	U	-0.28**	-0.01	0.02	-0.40**
	P-P	-0.36**	-0.61**	0.09	-0.26*
	PPO	-0.11	-0.27**	0.03	0.20*
	CAT	-0.16*	-0.17*	0.22**	-0.07
Ko (n=120)	U	0.09	0.06	0.17	-0.14
	P-P	-0.60**	-0.67**	0.53**	0.45
	PPO	-0.05	0.19*	-0.38**	0.01
	CAT	-0.11	-0.05	0.59**	-0.09
Am (n=120)	U	-0.37**	-0.14	0.32**	-0.31**
	P-P	-0.44**	-0.60*	0.18	-0.22
	PPO	-0.28**	-0.01	-0.15	-0.16
	CAT	0.08	0.13	0.03	0.10
Bl (n=180)	U	-0.21*	-0.06	-0.05	0.05
	P-P	-0.43**	-0.25	0.49**	0.18
	PPO	-0.07	0.05	0.09	0.19*
	CAT	-0.08	-0.10	0.16	-0.23*

Ac-Aegiceras corniculatum, *Ko-Kandelia obovata*, *Am-Avicennia marina*, *Bl*-bare land; U-urease, P-P-phosphatase, PPO-polyphenol oxidase, CAT-catalase.
*Correlation is significant at the 0.05 level (2-tailed).
**Correlation is significant at the 0.01 level (2-tailed).

(Marchand *et al.*, 2006). *Ac* has a better root system compared with *Ko* and *Am* because of its longer planting time. The broad rhizosphere environment of *Ac* provides a well-oxidized environment that strengthens its redox potential for increasing Mn content. High pH is an important factor that affects the degree of redox potential in wetlands (Song *et al.*, 1990). Our previous study revealed that the average pH of soils is 7.06 under *Ac*, 6.96 under *Ko*, and 6.87 under *Am* (Wu and Liu, 2011). Hypoxic environment leads to loss of Mn because of decline in redox potential (Otero *et al.*, 2009). Differential root systems change the reaction pattern in response to flooding environments by changing the oxygen condition of soils, and such environments in turn increase the Mn content of the soil. In this study, the Mn content of the soil under *Ac* was found to be significantly higher than that in the soils under the other two species because of high pH and strong redox potential. The metal contents of soils are determined by microbial activation, root activation, and biomass absorption and utilization. However, no significant difference in MBC was observed among the three species in this study (Table 2). Root activation and biomass absorption and utilization may be the factors driving differential distribution of metals. Although *Ko* has been reported to have strong activation ability owing to its developed root system (Wu and Liu, 2011), its smaller aboveground biomass may account for its weak absorption amount, which may explain the lower total metal content observed in the soil covered by *Ko* compared with *Ac* and *Am*. *Am* was planted in the 1970s, and *Ac* was planted at the end of the twentieth century. *Ko* was planted in this region only in 2005, so it has the shortest planting time of the three species. *Ko* had the smallest average biomass with 2.13 kg plant^{-1}, compared with 2.63 kg plant^{-1} under *Ac* and 2.84 kg plant^{-1} under *Am* in this region (Fu and Wu, 2011). Due to the difference in planting density and planting time, the biomass per hectare of *Ac, Am,* and *Ko* was estimated to be 59,175 kg, 85,200 kg, and 15,975 kg, respectively. The biomass in the rhizosphere increases Zn content by activating soluble Zn. This explains why the Zn contents of the soils under *Ac* and *Am* were significantly higher than that of the soil under *Ko*. The differential distribution of Cu in the soil under different mangrove species can be explained in part by differences in biomass—biomass can influence plants to absorb more soluble Cu, thereby lowering Cu retention in soils. Thus, Cu content of the soil is dependent on the biomass of the mangrove species.

Compared with *Bl*, the distribution of Cu in the soils under the other mangrove species was different. This may account for the observed variations in correlation between Fe and Cu. In the present study, both Cu and Mn contents were found to be influenced by the mangrove species covering the soil, which likely account for the observed differences in interactions between them. In addition, differences in interactions among metal elements likely result from variations in redox potential, salinity, and pH in the soils under *Ac*, *Ko*, and *Am* (Song *et al.*, 1990; Reddy, 1997; Liang *et al.*, 2003). Compared with *Bl*, *Ko* and *Am* did not change the relationship between Zn and Mn in the soils around them. One reason for this may be that the changes in distribution of Zn and Mn were in the same direction.

Differential distribution of enzymes

Biomass increases the hydrolase activity in soils (Pancholy and Rice, 1973; Taylor *et al.*, 2002). As shown in Table 4, the U and P-P activities in the vegetated soils were significantly higher than those in *Bl*. This result can be attributed to the higher organic matter supply and ventilation provided by the developed root systems of vegetated soils, which can promote the metabolism and respiration of microorganisms. Drying–wetting alternation environments increase P-P activity by significantly stimulating the activity of the soil microbial community (Song *et al.*, 2007). The different root systems of the different mangrove species likely support the growth of diverse species in response to the surrounding environment. Salinity is an important factor that affects CAT activity (Sinsabaugh, 2010). In this region, the average salinity in the soils was 14.15 under *Ac*, 13.98 under *Ko*, and 14.72 under *Am* (Wu and Liu, 2011). Thus, CAT activity in the soil under *Am* was significantly higher than those in the soils under the other two species because of higher salinity in the former. The different planting times of these three species account for their variations in the root system, organic matter content in the roots, and salinity distribution. Thus, mangrove species have unique soil microenvironments that exert different effects on soil enzyme activities and relationships.

Diversity of stoichiometry

In the present study, different mangrove species were found to have clearly different influences on metal distribution and enzyme activity. In addition, these influences were found to have interactive and stoichiometric relationship with nutrient and enzymatic composition in each district. As shown in Table 7, the interactive relationship between metals and enzymes in the soils under each species varied, and the relationship among soils under all species differed significantly from that in *Bl* because of differences in the soil microenvironments. These results indicate that microenvironments formed by different mangrove species that influence metal and enzyme distribution in the soil have distinctive differences. In particular, the soil under *Ac* has high pH, medium biomass content, and medium salinity, while that under *Ko* has medium pH, low biomass content, and low salinity, and that under *Am* has low pH, high biomass content, and high salinity. These variations lead to diverse interactive patterns and elemental and enzymatic stoichiometry. These patterns and relationships likely promote biodiversity in the wetland ecosystem. Thus, microenvironment diversity fostered by different plant species is likely to be the major factor that regulates elemental and enzymatic stoichiometry in estuarine wetlands.

Conclusions

This study is the first to investigate the differential distribution of Fe, Mn, Cu, Zn, U, P-P, PPO, and CAT under different mangrove species in Quanzhou Bay. Results showed that mangrove species regulated the stoichiometry of soil metals in this estuarine wetland ecosystem. The influences of the same species on the distribution of various metals and enzymes were different. The influences of different species on the same metal and enzyme also differed. The mangroves that covered the soil modified the distribution of metals (except for Fe) and enzymes (except for PPO) to different extents. Thus, different mangrove species influenced the distributions of metals and enzymes by distinct mechanisms. Differences in the microenvironments influenced by mangrove species and the surrounding environment resulted in diversity of elemental and enzymatic stoichiometry, which can promote biodiversity in the wetland ecosystem. This study may serve as a basis for long-term management and differential intervention of heavy metal pollution in estuarine wetlands.

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References

Agoramoorthy, G., Chen, F. A., and Hsu, M. J. 2008. Threat of heavy metal pollution in halophytic and mangrove plants of Tamil Nadu, India. *Environ. Pollut.* **155**, 320–326.

Amin, B., Ismail, A., Arshad, A., Yap, C. K., and Kamarudin, M. S. 2009. Gastropod assemblages as indicators of sediment metal contamination in mangroves of Dumai, Sumatra, Indonesia. *Water, Air, Soil Pollut.* **201**, 9–18.

Bai, Y., Wu, J., Clark, C. M., Pan, Q., Zhang, L., Chen, S., Wang, Q., and Han, X. 2012. Grazing alters ecosystem functioning and C: N: P stoichiometry of grasslands along a regional precipitation gradient. *J. Appl. Ecol.* **49**, 1204–1215.

Carvalho, E. R., Oliveira, J. A., Von Pinho, É. V. D. R., and Costa Neto, J. 2014. Enzyme activity in soybean seeds produced under foliar application of manganese. Ciênc. agrotec. **38**, 317–327.

Fenner, N., Freeman, C., and Reynolds, B. 2005. Observations of a seasonally shifting thermal optimum in peat land carbon-cycling processes: Implications for the global carbon cycle and soil enzyme methodologies. *Soil Biol. Biochem.* **37**, 1814–1821.

Fu, W., and Wu, Y. 2011. Estimation of aboveground biomass of different mangrove trees based on canopy diameter and tree height. *Procedia Environ. Sci.* **10**, 2189–2194.

Guan, S. Y. 1986. *Soil Enzyme and Study Method*, Agricultural Press, Beijing.

Hoque, S. 2010. Chemical composition of leaves of a mangrove tree (*Sonneratia apetala* Buch. Ham) and their correlation with some soil variables. *Bangladesh J. Bot.* **39**, 61–69.

Hu, G., Yu, R., Zhao, J., and Chen, L. 2011. Distribution and enrichment of acid-leachable heavy metals in the intertidal sediments from Quanzhou Bay, southeast coast of China. *Environ. Monit. Assess.* **173**, 107–116.

Huang, X., and Morris, J. T. 2005. Distribution of phosphatase activity in marsh sediments along an estuarine salinity gradient. *Mar. Ecol-Prog. Ser.* **292**, 75–83.

Irabien, M. J., and Velasco, F. 1999. Heavy metals in Oka River sediments (Urdaibai National Biosphere Reserve, Northern Spain): Lithogenic and anthropogenic effects. *Environ. Geol.* **37**, 54–63.

Krishnan, K. P., Fernandes, S. O., Chandan, G. S., and Bharathi, P. A. 2007. Bacterial contribution to mitigation of iron and manganese in mangrove sediments. *Mar. Pollut. Bull.* **54**, 1427–1433.

Liang, C., Das, K. C., and McClendon, R. W. 2003. The influence of temperature and moisture contents regimes on the aerobic microbial activity of a biosolids composting blend. *Bioresour. Technol.* **86**, 131–137.

Macfarlane, G. R., and Burchett, M. D. 2000. Cellular distribution of copper, lead and zinc in the grey mangrove, *Avicennia marina* (Forsk.) Vierh. *Aquat. Bot.* **68**, 45–59.

Macfarlane, G. R., and Burchett, M. D. 2001. Photosynthetic pigments and peroxidase activity as indicators of heavy metal stress in the grey mangrove, *Avicennia marina* (Forsk.) Vierh. *Mar. Pollut. Bull.* **42**, 233–240.

Macfarlane, G. R., Koller, C. E., and Blomberg, S. P. 2007. Accumulation and partitioning of heavy metals in mangroves: A synthesis of field-based studies. *Chemosphere.* **69**, 1454–1464.

Machado, W., Moscatelli, M., Rezende, L. G., and Lacerda, L. D. 2002. Mercury, zinc, and copper accumulation in mangrove sediments surrounding a large landfill in southeast Brazil. *Environ. Pollu.* **120**, 455–461.

Machado, W., Santelli, R. E., Carvalho, M. F., Molisani, M. M., Barreto, R. C., and Lacerda, L. D. 2009. Relation of reactive sulfides with organic carbon, iron, and manganese in anaerobic mangrove sediments: Implications for sediment suitability to trap trace metals. *J. Coastal Res.* **24**, 25–32.

Marchand, C., Lallier-Verges, E., Baltzer, F., Alberic, P., Cossa, D., and Baillif, P. 2006. Heavy metals distribution in mangrove sediments along the mobile coastline of French Guiana. *Mar. Chem.* **8**, 1–17.

Maret, W. 2013. Inhibitory zinc sites in enzymes. *BioMetals*. **26**, 197–204.

Marschner, H. 1995. *Mineral Nutrition of Higher Plants*, Academic Press, London.

Medina-Roldán, E., and Bardgett, R. D. 2011. Plant and soil responses to defoliation: A comparative study of grass species with contrasting life history strategies. *Plant Soil*. **344**, 377–388.

Mourato, M. P., Martins, L. L., and Campos-Andrada, M. P. 2009. Physiological responses of Lupinus luteus to different copper concentrations. *Biol. Plant.* **53**, 105–111.

Nelson, D. W., and Sommers, L. E. 1982. Total carbon, organic carbon and organic matter. In: *Methods of Soil Analysis*, Part 2, pp. 539–579 (A. L. Page, R. H. Miller, D. R. Keeney, eds.), Chemical and Microbiological Properties Agronomy Monograph, American Society of Agronomy Inc., Madison, WI.

Otero, X. L., Ferreira, T. O., Huerta-Diaz, M. A., Partiti, C. S. M., Souza, V., Vidal-Torrado, P., and Macias, F. 2009. Geochemistry of iron and manganese in soils and sediments of a mangrove system, Island of Pai Matos (Cananeia-SP, Brazil). *Geoderma*. **148**, 318–335.

Pancholy, S. K., and Rice, E. L. 1973. Soil enzymes in relation to old field succession: Amylase, cellulose, invertase, invertase, dehy drogenase and urease. *Soil. Sci. Soc. Amer. Proc.* **37**, 47–50.

Qian, H., Li, J., Pan, X., Sun, L., Lu, T., Ran, H., and Fu, Z. 2011. Combined effect of copper and cadmium on heavy metal ion bioaccumulation and antioxidant enzymes induction in *Chlorella vulgaris*. *Bull. Environ. Contam. Toxicol.* **87**, 512–516.

Quan, W., Shi, L., Han, J., Ping, X., Shen, A., and Chen, Y. 2010. Spatial and temporal distributions of nitrogen, phosphorus and heavy metals in the intertidal sediment of the Chang Jiang River Estuary in China. *Acta Oceanol. Sin.* **29**, 108–115.

Ravikumar, S., Williams, G. P., Shanthy, S., Anitha Gracelin, N., Babu, S., and Parimala, P. S. 2007. Effect of heavy metals (Hg and Zn) on the growth and phosphate solubilising activity in halophilic phosphobacteria isolated from Manakudi mangrove. *J. Environ. Biol.* **28**, 109–114.

Ray, A. K., Tripathy, S. C., Patra, S., and Sarma, V. V. 2006. Assessment of Godavari estuarine mangrove ecosystem through trace metal studies. *Environ. Int.* **32**, 219–223.

Reddy, K. R. 1997. Biogeochemical indicators to evaluate pollutant removal efficiency in constructed wetlands. *Water Sci. Technol.* **35**, 1–10.

Rejmánková, E., and Sirová, D. 2007. Wetland macrophyte decomposition under different nutrient conditions: Relationships between decomposition rate, enzyme activities and microbial biomass. *Soil Biol. Biochem.* **39**, 526–538.

Ribeiro, G. S., Rizzo, A., Sánchez, R., and Arribére, M. 2005. Heavy metal inputs in northern Patagonia lakes from short sediment core analysis. *J. Radioanal. Nucl. Chem.* **265**, 481–493.

Sinsabaugh, R. L. 2010. Phenol oxidase, peroxidase and organic matter dynamics of soil. *Soil Biol. Biochem.* **42**, 391–404.

Song, J. M., Li, Y., and Zhu, Z. B. 1990. Relationship between Eh value and redox environment in marine sediments. *Soil Biol. Biochem.* **9**, 33–30.

Song, K. Y., Zoh, K. D., and Kang, H. 2007. Release of phosphate in a wetland by changes in hydrological regime. *Sci. Total Environ.* **380**, 13–18.

Tam, N. F. Y., and Wong, Y. S. 1995. Spatial and temporal variations of heavy metal contamination in sediments of a mangrove swamp in Hong Kong. *Mar. Pollut. Bull.* **31**, 254–261.

Taylor, J. P., Wilson, B., Mills, M. S., and Burns, R. G. 2002. Comparison of microbial numbers and enzymatic activities in surface and subsoil using various techniques. *Soil Biol. Biochem.* **34**, 387–401.

Wang, F., and Chen, J. S. 2000. Relation of sediment characteristics to trace metal concentration: A statistical study. *Water Res.* **34**, 694–698.

Williams, C. J., Shingara, E. A., and Yavitt, J. B. 2000. Phenol oxidase activity in peatlands in New York State: Response to summer drought and peat type. *Wetlands*. **20**, 416–421.

Wu, Y. Y., and Liu, R. C. 2011. *The Plants' Adaptability to Environment of Quanzhou Bay Estuary Wetland*, Science Press, Beijing.

Yim, M. W., and Tam, N. F. Y. 1999. Effects of wastewater-borne heavy metals on mangrove plants and soil microbial activities. *Mar. Pollut. Bull.* **39**, 179–186.

Yu, R., Hu, G., and Wang, L. 2010. Speciation and ecological risk of heavy metals in intertidal sediments of Quanzhou Bay, China. *Environ. Monit. Assess.* **163**, 241–252.

Yu, R. L., Yuan, X., Zhao, Y. H., Hu, G. R., and Tu, X. L. 2008. Heavy metal pollution in intertidal sediments from Quanzhou Bay, China. *J. Environ. Sci.* **20**, 664–669.

Zhou, Y. W., Zhao, B., Peng, Y. S., and Chen, G. Z. 2010. Influence of mangrove reforestation on heavy metal accumulation and speciation in intertidal sediments. *Mar. Pollut. Bull.* 60, 1319–1324.