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# The vertical distribution and their relationship of dissolved organic carbon and exchangeable metals in Chinese old-growth forest soils

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Many unmanaged temperate and tropical old-growth forests are shown to retain their capability to sequester carbon (C) from the atmosphere, but the C sequestration mechanisms in the soil were unknown. Seven thin soil layers within a depth of 20 cm were sampled from one unmanaged tropical seasonal old-growth rain forest and three unmanaged temperate old-growth forests (e.g. *Betula ermanii*, *Picea jezoensis*, and *Pinus koraiensis* mainly mixed with *Tilia amurensis, Fraxinus mandshurica* and *Quercus mongolica*) in southwest and Northeast China, respectively, to study the vertical distribution and their relationships of dissolved and total organic matter, microbial biomass C and nitrogen (N), and exchangeable metals concerned in forest soils. There were larger concentrations of all C and N pools and higher pH values in uppermost soil layers under three temperate old-growth forests than in corresponding layers of tropical forest soil, and the concentrations in temperate forest soils decreased more with increasing soil depth. Among the three temperate forests, the soils at less than 10 cm depth under the pine and broadleaf mixed forest had the smallest total C -to -N ratio, and the largest dissolved organic N concentration occurred in the 0 - 2.5-cm soil. Contrary to the exchangeable Al and Pb, the concentrations of exchangeable Ca, Mg and Ba in the 0 to 20 cm profile soils under the three temperate old-growth forests were larger than those under the tropical old-growth rain forest, and the largest values were observed in the profile soils under the pine and broadleaf mixed forest. Hence, the concentration ratios of Ca to Al and (Ca+Mg) to Al in the temperate forest profile soils were larger than those in the tropical forest profile soils. Maximal concentrations of all tested metals (excluding Al and Pb) were observed in uppermost soil layers under the four old-growth forests and varied with tree species. According to the principal component analysis and regression analysis, the vertical distribution of dissolved organic C and organic N concentrations in the soil at the various depths is a function of the decreasing microbial activity and is partly associated with the metals of concern. Together with the soil C availability and microbial metabolic quotient reported earlier, the results would improve our understanding of the C sequestration mechanisms involved in these old-growth forest soils.

**Key words:** Dissolved organic matter, metals, microbial biomass carbon and nitrogen, old-growth forest soil.

## INTRODUCTION

Decomposition of litter under different forest floors and climatic conditions has a vital impact on the release of dissolved organic matter (DOM) into the soil, soil microbial properties and acidification (Raulund-Rasmussen and Vejre, 1995; Ahokas, 1997; Yang et al., 2004; Xu et al., 2006, 2007), which can in turn affect the vertical distribution of soil carbon (C) pools and

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exchangeable metals in forest soils at the varying depths. Metal ions are strongly bound to the soil, which can be associated with soil acidity and DOM. There is a good relationship between the extents to which the metals and DOM are mobilized in forest soils (McBride, 1989; Jansen et al., 2003, 2004; Andersen et al., 2004; Rieuwerts, 2007), and this may affect the vertical distribution of dissolved organic C (DOC) concentration in soil (McDowell, 2003).

The metal/C ratio of DOM has been considered to be an important parameter for its stability against microbial breakdown (Boudot et al., 1989; Shoji et al., 1993; Schwesig et al., 2003; Huygens et al., 2005), thus affecting the sequestration of soil organic C (Six et al., 2002; Jandl et al., 2007) . The increase in concentrations of exchangeable metals has an important impact on the adsorption of DOC on soil surface, which can decrease the biodegradation of absorbed DOC in subsurface mineral soil and increases soil C sequestration capacity (Kalbitz et al., 2003). In temperate volcanic forest soils, it has been recognized that metal-humus complexes are resistant to microbial decomposition and can offer protection against microbial breakdown (Shoji et al., 1993). In addition, volcanic soils generally contain a larger concentration of organic C than non-volcanic soils (Shoji et al., 1993; Morisada et al., 2004). Hence, it is important to study the vertical distribution and interaction of dissolved and total organic C and exchangeable metals in volcanic forest soils, which improves our understanding of the mechanisms involved in carbon sequestration in such soil (McBride, 1989; Six et al., 2002; Morisada et al., 2004; Xu et al., 2007).

In tropical zones, high temperature and rainfall can result in high mineralization of soil organic C and the leaching of the (earth)alkali ions such as Ca and Mg, and thus decreasing soil acidity leads to the accumulation of metals such as Al and Pb in forest soils (Bai et al., 2002; Rieuwerts, 2007). In comparison with temperate forest soils, tropical forest soils generally contain smaller concentrations of dissolved and total organic C, which can affect the relationships between DOM and exchangeable metals in forest soils. Recent observations using the eddy-covariance technique have reported that unmanaged temperate and tropical old-growth forests can retain their capability to sequester C from the atmosphere (Knohl et al., 2003; Loescher et al., 2003; Desai et al., 2005), which is probably resulted from the high C sequestration unknown in such soils (Zhou et al., 2006). Previous studies have shown that the soils at less than 20 cm depth under temperate and tropical old-growth forests contain a high microbial efficiency in carbon utilization and soil properties such as metal concentrations can affect this efficiency and soil C availability (Xu et al., 2007). However, there is rather limited knowledge about the vertical distribution and their relationships of different soil C pools and exchangeable metals in the soils at the various depths under these old-

growth forests.

The objective of this work was to study the vertical distribution and their relationships of dissolved and total organic C and exchangeable metals concerned in the soils at the various depths under four unmanaged temperate and tropical old-growth forests in China. Together with the soil C availability and microbial metabolic quotient reported earlier (Xu et al., 2007), the results would improve our understanding of the C sequestration mechanisms involved in these old-growth forest soils.

## MATERIALS AND METHODS

### Site description and soil sampling

Temperate and tropical forest soils at the various depths and with a wide range of organic carbon contents were sampled near the Changbai Mountain Forest Ecology Research Station (128°28´E, 42°24´N) and the Xishuangbanna Tropical Rain Forest Ecosystem Research Station (101°16´E, 21°56´N), respectively. The area around the Changbai Mountain is a temperate, continental climate, with a long-term cold winter and warm summer. Annual mean temperature varies from 2.8°C at the bottom of the mountain to -7.3°C near the volcanic lake on the top, and annual mean precipitation varies from 750 to 1340 mm. Recent small-scale volcano eruptions occurred in 1597, 1668, 1702 and a very larger-scale eruption occurred during 1000 to 1410 (Zhao, 1981; Liu et al., 1992). Three typical unmanaged temperate forests in a vertical distribution along the northern slope were selected: Korean pine and broadleaf mixed forest (*Pinus koraiensis* mainly mixed with *Tilia amurensis, Fraxinus mandshurica* and *Quercus mongolica)*, >200 years old, altitude 740 m; spruce ( *Picea jezoensis*), >200 years old, altitude 1680 m; and birch (*Betula ermanii* ), >200 years old, altitude 1910 m. A tropical unmanaged seasonal rain forest was selected near the tropical forest station. Some tree species in the seasonal rain forest (*Pometia tomentosa, Terminalia myriocarpa, Barringtonia macrostachya, Myristica yunnanensis, Homalium laoticum* and *Shorea chinensis* as main species, >200 years old, altitude 720 m) are deciduous under the monsoon climate, although they do not shed all leaves in the same season (Cao and Zhang, 1997). In the tropical zone, the annual mean temperature is approximately 22°C, and annual mean precipitation is approximately 1400 mm, with pronounced dry and wet seasons over the year. The depth of the A-horizon in the soils under the temperate and tropical old-growth forests was approximately 10cm and 5 cm, respectively. There was no humus layer under the tropical forest, but three temperate forests had humus layers of 3 to 5 cm at depth.

Soil sampling in the tropical and temperate zones was done respectively in May and July, 2005, after selection of three 4 × 4 m plots under each forest stand, which were about 1 m away from large trunks. Within each plot, a soil profile with more than 1 m depth and 80 cm width was formed after the above-ground litters had been removed, and the uppermost soil layer (0-2.5-cm) with a length of approximate 40 cm and a width of approximate 10 cm was sampled by using a thin stainless steel spade. After sampling of the 0- 2.5-cm soil layer, samples of the other six soil layers such as 2.5 to 5.0, 5.0 to 7.5, 7.5 to 10.0, 10.0 to 12.5, 12.5 to 15.0 and 15.0 to 20.0 cm along the soil profile were collected separately, as previously mentioned. Hence, in total, 84 soil samples were taken. All samples were kept separately in air-tight plastic bags and transported to the laboratory within 48 h. The fresh moist soils were sieved (2 mm, or 4 mm for 0-2.5-cm temperate soils) to remove small stones and roots, and stored in the dark at 4°C prior to the

analysis.

## Analysis of soil properties

Temperate and tropical forest soils were classified as Andosols and Oxisols (FAO soil classification), respectively. The textures of the temperate and tropical forest soils were loam and clay loam, respectively. Soil water-holding capacity (WHC) was determined by saturating each soil in glass funnels with water and allowing drainage under cover for two to three hours at ambient temperature. Duplicate soils were dried at 105°C for 24 h to determine gravimetric water content. Soil total C and N contents were measured with a CN analyzer (MT- 700 with an Auto Sampler MTA-600, Yanaco, Kyoto, Japan). Fresh soil pH (soil/water, 1/2.5, w/w) was measured with a portable pH meter. Exchangeable metals were extracted by shaking 10-g fresh soil with 50 ml of 1 mol $L^{-1}$ KCl solution for 60 min on an end-over-end shaker, and then filtered to 50-ml plastic bottles via cellulose-acetate membrane filter (0.45 µm pore size). The concentrations of metals such as Na, Ca, Mg, Ba, Al, Mn, Fe and Pb in the filtrates were measured by using an inductively coupled plasma-mass spectrometry (VG PlasmaQuard III, Fisons Instruments, UK). The instrument was operated at a sampling dose of 1.0 ml $min^{-1}$ with a measuring time of 40 s. Indium ($In^{115}$) was used as an internal standard for calibrating the instrument. The concentrations of organic C and total N in the filtrates were measured by using a TOC/TN-analyzer (Shimadzu TOC-V$_{CSH}$/TN, Kyoto, Japan). The concentrations of $NH_4^+$-N and $NO_3^-$-N in the filtrates were measured colorimetrically by the nitroprusside and hydrazine-reduction methods, respectively (Kim, 1995). Concentrations of dissolved organic N (DON) in the filtrates were calculated as the differences between total N and ($NH_4^+$+$NO_3^-$)-N concentrations.

To stabilize soil conditions for the measurement of microbial biomass C (SMBC) and N (SMBN), 40-g soils in 250-ml glass bottles were adjusted to about 45% WHC and incubated for 7 days at 25°C under toxic conditions. This consistency of soil water content reduces the uncertainties about the proportion of soil microbial biomass released by the fumigation and extraction. After the incubation, each forest soil in duplicate (5.0 g) was fumigated in a vacuum desiccators containing ethanol-free $CHCl_3$ in a small beaker and with a little hot water at the bottom for 24 h in the dark at 25°C. All the fumigated and unfumigated soils (5.0 g) were extracted by shaking with 25 ml of 0.5 mol $L^{-1}$ $K_2SO_4$ solution for 60 min on an end-over-end shaker. The suspensions were centrifuged at 6400 $g$ for 5 min and then filtered to 50-ml plastic bottles via cellulose-acetate membrane filter (0.45 µm pore size). The concentrations of organic C and total N in soil extracts were analyzed using a TOC/TN-analyzer (Shimadzu TOC-V$_{CSH}$/TN, Kyoto, Japan). Microbial C and N concentrations of the soils were calculated using the equation: $y = E/0.45$, where $E$ is the difference in organic C or total N concentrations between fumigated and unfumigated soil extracts, $y$ is the SMBC or SMBN concentration, and the factor for correcting SMBC and SMBN concentrations is 0.45 (Jenkinson, 1988; Wu et al., 1990).

## Calculation and statistical analysis

Three replicate composite samples were used to calculate means and standard errors of each soil property at each depth, according to the basis of soil dry weight. Least significant differences (LSD) were calculated at the 5% level to assess the differences in the tested soil properties among forest types at each soil depth, by using SYSTAT software for Windows (version 12.0). A principal component analysis and regression analysis were performed to identify their relationships between the concentrations of dissolved and total organic C and N and exchangeable metals concerned in

these forest soils.

## RESULTS AND DISCUSSION

### Vertical distribution of C and N pools in forest soils

Figure 1 shows concentrations of C and N pools and total C-to-N ratios as well as pH values of forest soils at the various depths. There were larger concentrations of DOC, DON and total C and N as well as greater pH values in uppermost soil layers under the three temperate forests than in corresponding soil layers under the tropical forest $P < 0.05$). Both microbial biomass C and N concentrations of the soils at less than 10 cm depth were larger under the three temperate forests than under the tropical forest $(P<0.05)$, and their maximal concentrations occurred in the 0- 2.5-cm soil. More than 80% of the variability in DOC concentrations across soil depths under temperate and tropical forests was accounted for by the concentrations of total C and microbial biomass C (Figure 2). Hence, the decrease of dissolved organic C concentrations in the soils with increasing soil depth is a function of the decreasing microbial activity.

The concentrations of these C and N pools in the temperate forest soils decreased more with increasing soil depth than those in the tropical soils (Figure 1). Among the three temperate old-growth forests, there were the largest concentrations of DOC and total C in the 0 - 2.5-cm soil under spruce. The pine and broadleaf mixed forest soils at less than 10 cm depth had a smaller total C-to-N ratio and a larger DON concentration compared to the spruce and birch forest soils at high altitude $(P<0.05)$ (Figure 1). Andersen et al. (2004) reported that Norway spruce had larger concentrations of soil organic C and DOC than adjacent stands of beech and grand fir in Denmark. The concentrations of soil organic C and total C-to-N ratios in uppermost soil layers under the four unmanaged old-growth forests (Figure 1) were smaller than those under non- polluted montane coniferous forests with 7500 years old in Chile (Zarin et al., 1998). Probably, the C sequestration capacity of the soil under these unmanaged old-growth forests is associated with the sites of location and the growth of forests.

Different tree species produce different types of litters and this can lead to a build-up of forest floors with different compositions and pH. The differences of organic C in the litters and changes in soil microbial activities sustained by tree species (Xu et al., 2007) can partly account for the vertical distribution of dissolved organic C concentrations in the soils under these old-growth forests.

### Vertical distribution of exchangeable metals in forest soils

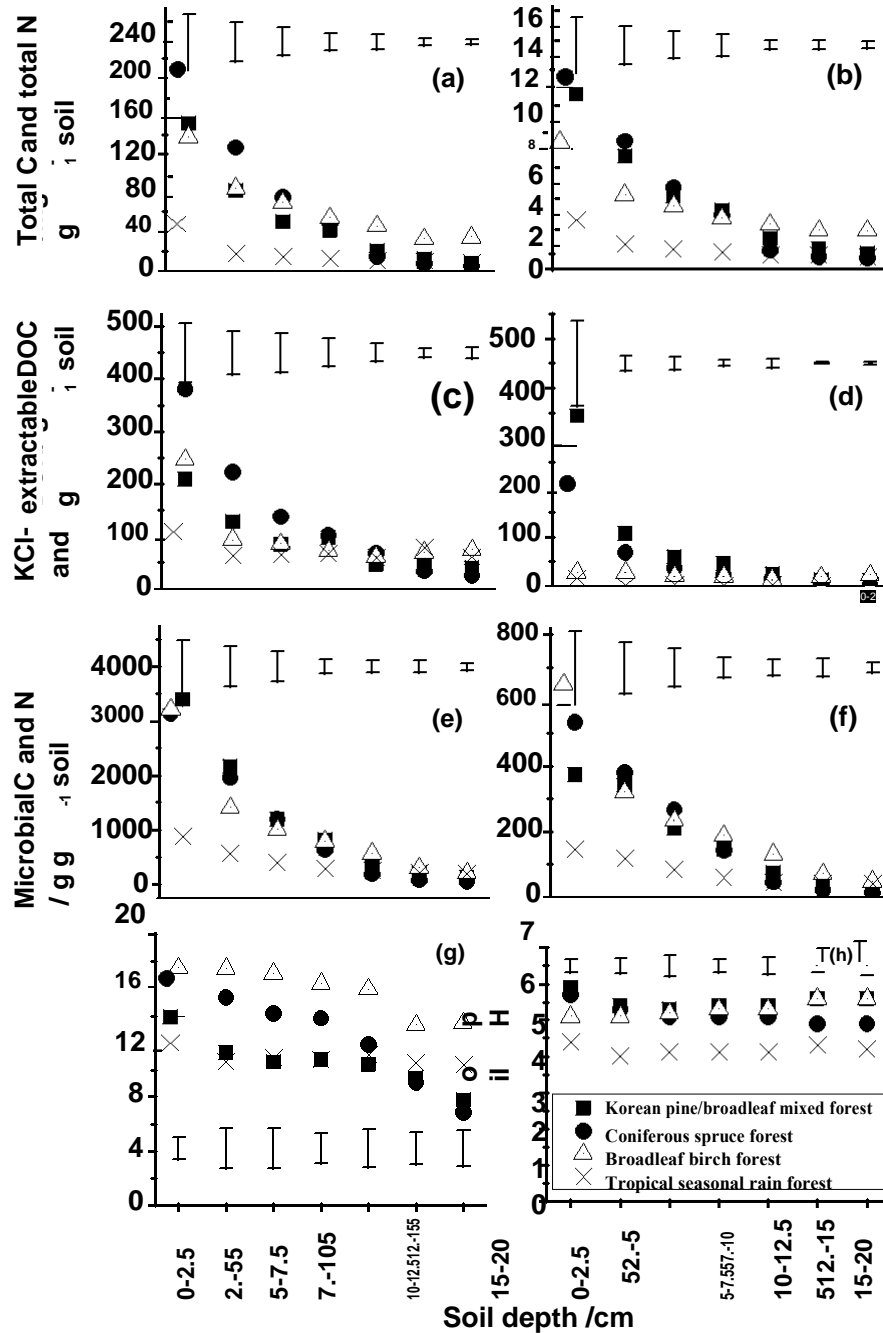The concentrations    of all tested exchangeable metals

**Figure 1.** Concentrations of C and N pools and pH values of the soils at the various depths under temperate and tropical old-growth forests. Values are the means of three replicates (standard errors were removed), and LSD$_{0.05}$ bars represent differences in the tested soil properties across forest types at the *P<0.05* level. (a), (c) and (e) represent the total C, KCl-extractable DOC and microbial biomass C concentrations of the soil, respectively. (b), (d) and (f) represent the total N, KCl-extractable DON and microbial biomass N concentrations of the soil, respectively.

except Al and Pb in the soils decreased remarkably with increasing soil depth under the three temperate forests, and the reduction varied with tree species and the metals of concern (*P<0.05)* (Figure 3). The concentrations of exchangeable Ca, Mg and Ba in uppermost layers of the

soil under the three temperate old-growth forests were larger than those under the tropical old-growth forest *(P<0.05)* (Figures 3a, d and h). The tropical forest profile soils contained larger concentrations of exchangeable Al and Pb than the temperate forest profile soils, except for
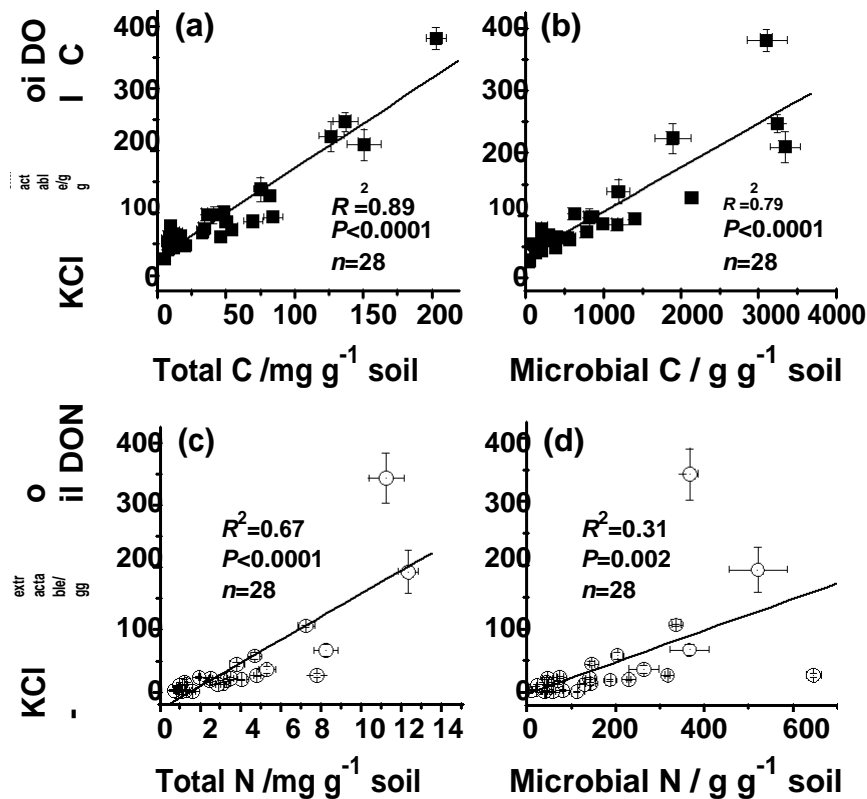
**Figure 2.** Relationships between KCl-extractable organic C (DOC) and organic N (DON) concentrations versus the concentrations of (a) total C, (b) microbial biomass C, (c) total N or (d) microbial biomass N in the soils at the various depths. Coefficients of determination for linear regressions $(R^2)$ and $P$ values were calculated. Error bars indicate standard errors of three replicates.

the 0-2.5-cm birch soil ($P < 0.05$) (Figure 3c and g). Hence, the logarithms of concentration ratios of Ca to Al and (Ca+Mg) to Al in the temperate forest soils were larger than those in the tropical forest soils ($P < 0.05$) (Figures 3j and k). Under the tropical forest and the temperate pine and broadleaf mixed forest, the concentrations of soil exchangeable Al and Pb increased with increasing soil depth, whereas the maximal concentrations of both occurred in uppermost and subsurface layers of the soils under spruce and birch, respectively ($P < 0.05$) (Figures 3c and g).

The tropical forest soils contained a smaller pH value than the temperate forest soils (Figure 1h). Contrary to the exchangeable Ca, Mg and Ba, there was a significant negative correlation between soil pH and concentrations of exchangeable Al ($r = -0.77$, $P < 0.001$) and Pb ($r = -0.77$, $P < 0.001$) in the soils at the various depths across forest types. The decreased soil pH could promote an accumulation of exchangeable Al and Pb in deep layers of the soil and the leaching of the (earth) alkali ions such as Ca and Mg under these forest floors (Figure 3). The pH values of forest floors are usually smaller under conifers than under hardwoods (Raulund-Rasmussen and Vejre, 1995). Spruce was observed to acidify the

uppermost mineral soil more than pine and ash (Binkley and Valentine, 1991). Ahokas (1997) reported that spruce stands acidify more than fir and birch stands. The solubility of Pb and Al in the soil can increase as pH decreases (McBride, 1989; Bai et al., 2002; Jansen et al., 2003). This could partly explain the different vertical distribution of exchangeable Al and Pb in the soils under the three temperate old-growth forests (Figures 3c and g).

**Relationships between C and N pools and exchangeable metals in forest soils**

To quantify the base cation availability per unit soil total C, (exchangeable $Ca^{+2}$ + $Mg^{+2}$ + $Na^+$) values at the various depths under the four old-growth forests were calculated on the basis of soil total C concentrations, and are shown in Figure 3i. The base cation availability of the soil under the four forests increased with increasing soil depth, with one exception of birch soils with the relatively small base cation availability. Among the three temperate old- growth forests, the greatest base cation availability in the soils was observed under the pine and broadleaf mixed forest at low altitude (Figure 3i). There was a good
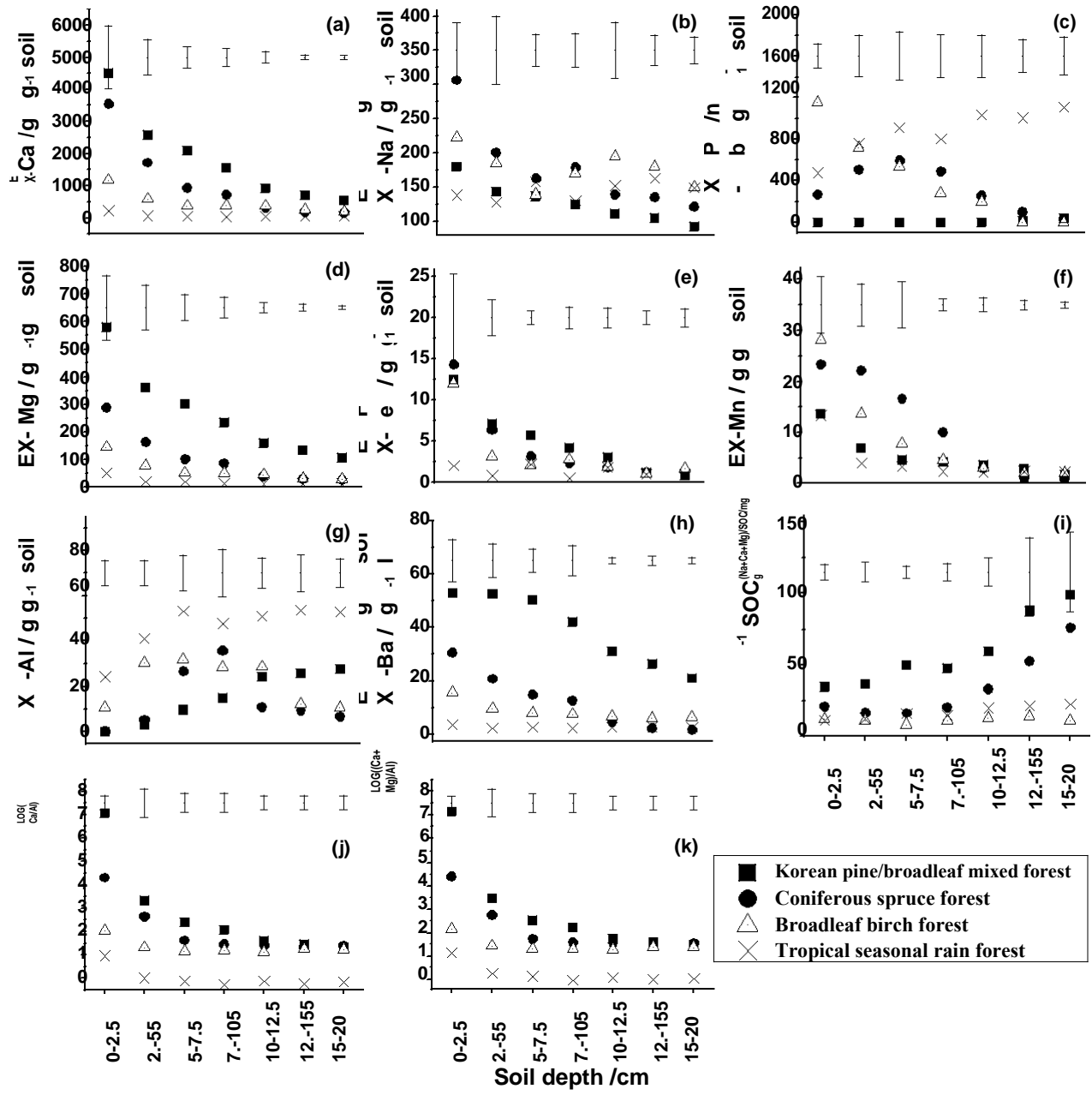
**Figure 3.** Concentrations of exchangeable metals in the soils at the various depths under temperate and tropical old-growth forests. Values are the means of three replicates (standard errors were removed), and LSD$_{0.05}$ bars represent differences in the tested soil properties across forest types at the *P < 0.05* level. Both Ca:Al and (Ca+Mg):Al values are the logarithms of concentration ratios of soil exchangeable Ca, Mg and Al, respectively. SOC, soil total carbon.

positive relationship between soil total C and (exchangeable Ca$^{+2}$ + Mg$^{+2}$ + Na$^+$) under the four old-growth forests ($R^2$ = 0.64, *P < 0.001*). Zarin et al. (1998) had shown that soil organic C is an excellent predictor ($R^2$ = 0.93, *P < 0.001)* of (exchangeable Ca$^{+2}$ + Mg$^{+2}$ + Na$^+$ + K$^+$) in the old-growth montane coniferous forests in Chile. Hence, the contents of the base cations in the soils are associated with the soil C sequestration under these old-growth forests.

According to the principal component analysis, dissolved and total organic matter concentrations of the soils at the various depths were related with the concentrations of soil exchangeable metals, and this influence differed with the metals of concern (Table 1). The DON rather than DOC concentrations of the soils at the various depths had a better relationship with the concentrations of exchangeable Ca, Mg and Al as well as the logarithms of concentration ratios of Ca/Al and

**Table 1.** Rotated loading matrix (Orthomax, Gamma =1.0000) from a principal component analysis of the standardized attribute data of natural acid forest soils.

|  | Centre | | |
| --- | --- | --- | --- |
|  | 1 | 2 | 3 |
| Total C content | 0.845 | 0.490 | 0.188 |
| Total N content | 0.739 | 0.627 | 0.213 |
| Ratios of total C to N | 0.875 | -0.131 | 0.116 |
| Soil pH (soil/water, 1:2.5) | 0.196 | 0.298 | 0.886 |
| KCl-extractable organic C | 0.836 | 0.462 | 0.039 |
| KCl-extractable organic N | 0.331 | 0.843 | 0.214 |
| Exchangeable Ca content | 0.365 | 0.881 | 0.274 |
| Exchangeable Mg content | 0.177 | 0.933 | 0.279 |
| Exchangeable Ba content | 0.012 | 0.850 | 0.339 |
| Exchangeable Al content | -0.263 | -0.399 | -0.775 |
| Exchangeable Pb content | 0.333 | -0.269 | -0.883 |
| LOG(Ca/Al) | 0.341 | 0.784 | 0.480 |
| LOG((Ca+Mg)/Al) | 0.335 | 0.795 | 0.468 |
| Exchangeable Na content | 0.896 | 0.096 | 0.019 |
| Exchangeable Mn content | 0.885 | 0.269 | -0.018 |
| Exchangeable Fe content | 0.678 | 0.682 | 0.132 |
| Microbial biomass C | 0.746 | 0.636 | 0.066 |
| Microbial biomass N | 0.861 | 0.415 | 0.051 |

Both LOG(Ca/Al) and LOG((Ca+Mg)/Al) values are the logarithms of concentration ratios of soil exchangeable Ca, Mg and Al, respectively.

(Ca+Mg)/Al in the soil, respectively (Figure 4). This indicated that there was a preferable adsorption for dissolved organic N rather than for dissolved organic C in the soils, at the various depths under the four old-growth forests. The concentrations of exchangeable Fe and Mn (Figure 5) and logarithms of concentration ratios of Ca/Al and (Ca+Mg)/Al (Figure 6) in the soils gave a significant positive correlation with the concentrations of soil total C and N, respectively $(P < 0.001)$. The concentrations of total C and N and the total C-to-N ratios in the soils at the various depths across forest types increased with increasing concentration of soil exchangeable Na ($P < 0.001$) (Figure 7).

The dissolved organic matter plays an important role in soil C cycle (McDowell, 2003). Direct sorption of the DOM to solid soil components involves bindings to positively charged sites on solid soil components, which may affect the complexation of metal ions with DOM. Some extractable metals such as Fe, Mn and Al are vital in biogeochemical processes that take place in acid soils. The metal/C ratio of DOM had been recognized as a vital factor for its stability against microbial decomposition (Boudot et al., 1989; Shoji et al., 1993; Schwesig et al., 2003; Huygens et al., 2005). As shown in Figure 5, more than 70% of the variability in concentrations of soil organic matter was accounted for by the concentrations of soil exchangeable Fe and Mn, respectively. Jansen et al. (2004) reported the preferential adsorption of Fe over

Al on solid-phase organic matter in solution. This induces the occurrence of organo-metallic complexes in acid forest soils, which provides chemical protection against microbial breakdown of soil DOM. Hence, the relationships between exchangeable metals and DOM can improve our understanding of the C sequestration mechanisms involved in acid forest soils. As shown in Figure 7c, 55% of the variability in soil total-C-to-N ratios was accounted for by the concentrations of soil exchangeable Na (P < 0.001). Probably, an increase in exchangeable Na concentrations within a range of 100 to 200 μg g$^{-1}$ soil can result in different sequestration of C and N concentrations in the soils under these four old-growth forests (Figure 7). However, at present, this reason is not clear, and further data are needed at more old-growth forest sites to confirm this proposal.

The concentration ratios of Ca/Al ($R^2 = 0.62$, $P < 0.001$) and (Ca+Mg)/Al ( $R^2 = 0.44$, $P < 0.001$) in these old-growth forest soils increased with increasing soil pH, and the ratios accounted for 58 to 71% of the variability in concentrations of soil total C and N (Figure 6). The variation of pH in the solution and kinds of metals would affect the stability of the complexation with DOM (Jansen et al., 2003). There was a significant positive relationship between the Ca/C ratio of DOM and soil pH ($r = 0.66$, $P < 0.001$), whereas the Pb/C ratio of DOM was correlated negatively to the soil pH ($r = -0.90$, $P < 0.001$). Hence, the variations of soil pH and kinds of metals concerned
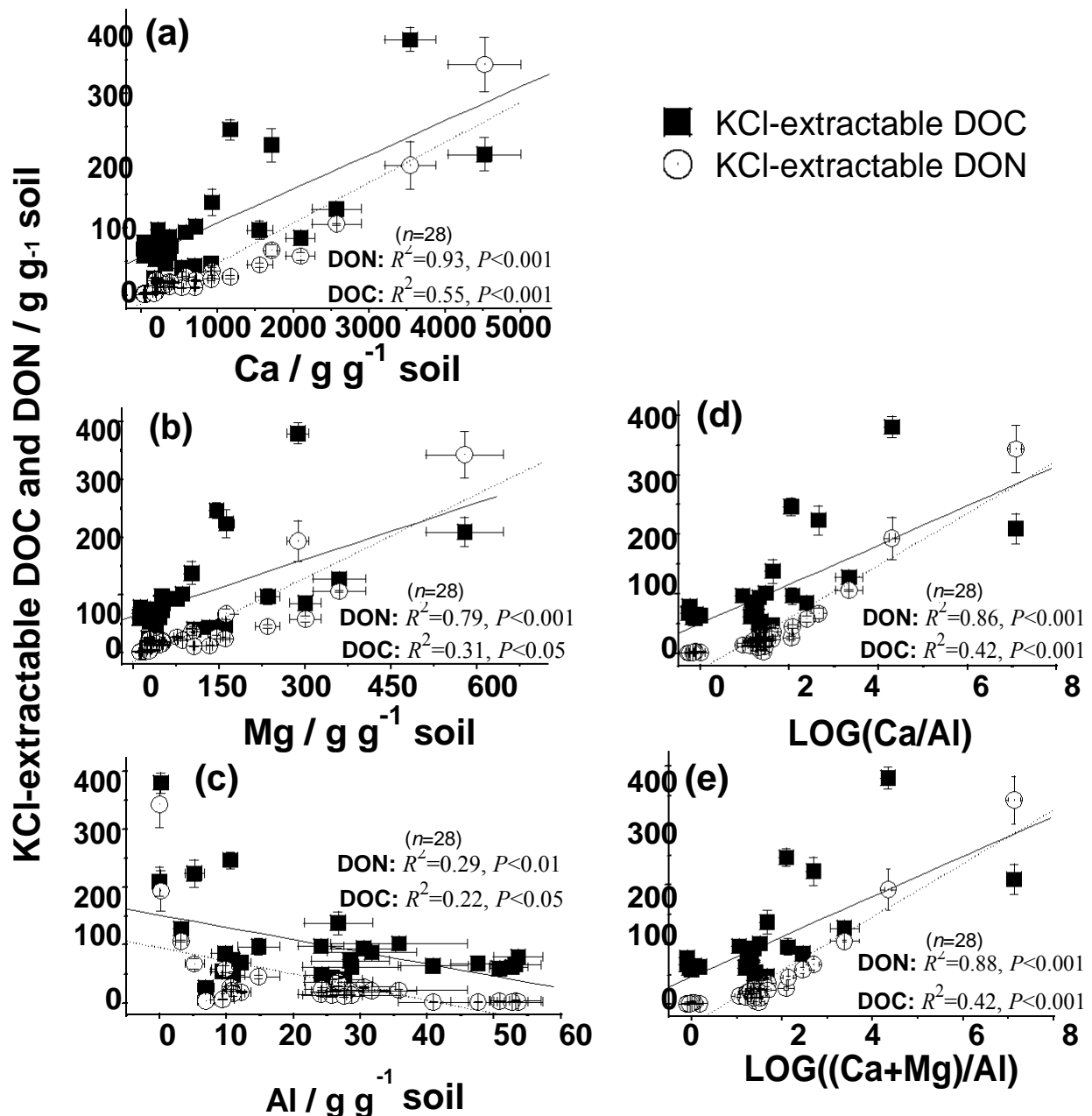
**Figure 4.** Relationships between the concentrations of KCl-extractable organic C (DOC) and organic N (DON) versus the concentrations of (a) soil exchangeable Ca, (b) Mg, (c) Al, (d) LOG(Ca/Al) or (e) LOG((Ca+Mg)/Al). Both LOG(Ca/Al) and LOG((Ca+Mg)/Al) values are the logarithms of concentration ratios of soil exchangeable Ca, Mg and Al, respectively. The linear regression indicates the KCl- extractable DOC or DON concentration, y, against (the soil exchangeable Ca, Mg, Al, LOG(Ca/Al), or LOG((Ca+Mg)/Al)), *x*. Solid lines: for the DOC; dotted lines: for the DON. Coefficients of determination for linear regression ($R^2$) and *P* values were calculated. Error bars indicate standard errors of three replicates.

under the four old-growth forests can contribute to the metal/C ratio of DOM and the C sequestration functions in the soil.

**Conclusions**

There was a larger concentration of dissolved and total organic C and N in uppermost layers of the soils under the three temperate old-growth forests than under the tropical old-growth forest, and the concentration in the temperate forest soils decreased more with increasing soil depth. These paralleled the change in concentrations of microbial C and N of the soils at the various depths under these old-growth forests. Contrary to the soil exchangeable Al and Pb, the concentrations of
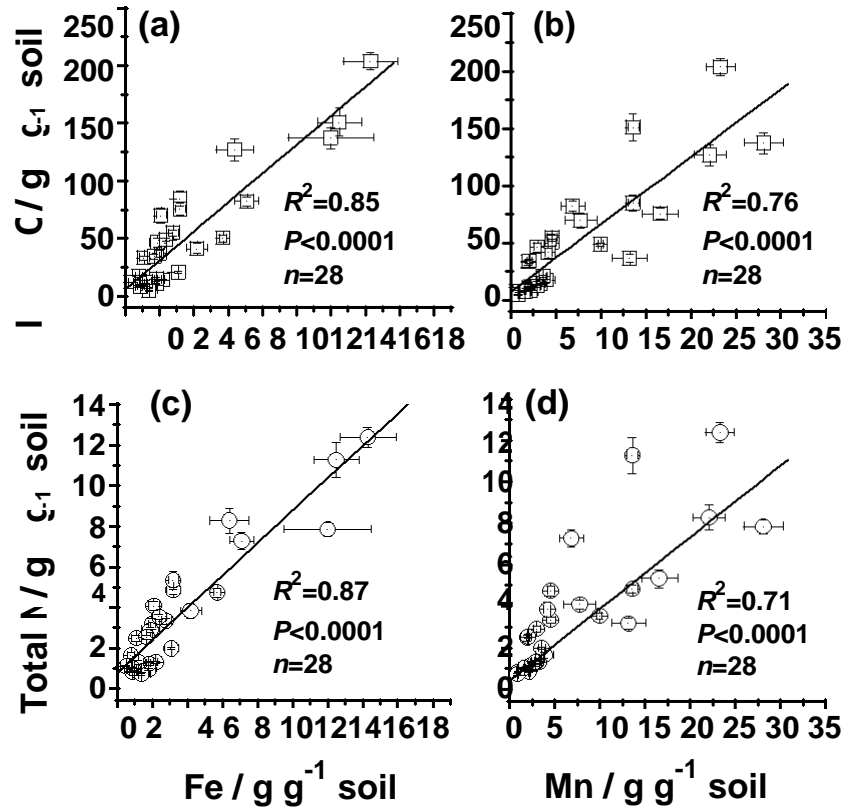
**Figure 5.** Relationships between the concentrations of total C and total N versus the concentrations of (a, c) exchangeable Fe or (b, d) exchangeable Mn in the soils at the various depths. Coefficients of determination of linear regression ($R^2$) and $P$ values were calculated. Error bars indicate standard errors of three replicates.
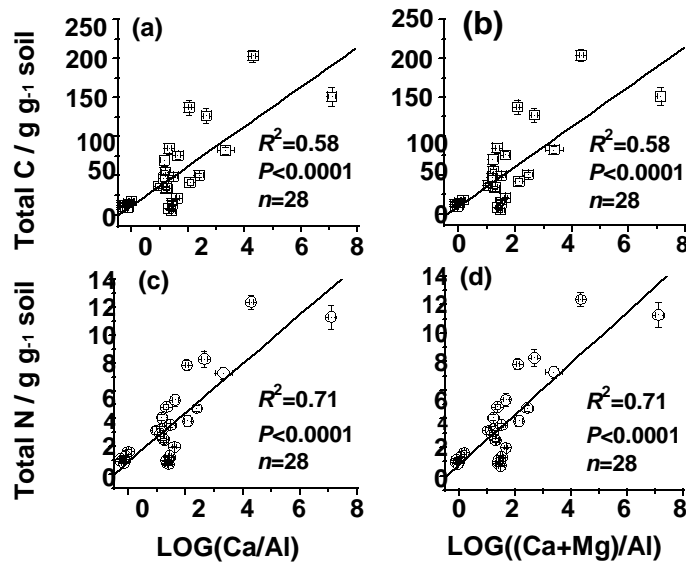


**Figure 6.** Relationships between the concentrations of total C and total N versus the (a, c) LOG (Ca/Al) or (b, d) LOG ((Ca+Mg)/Al) in the soils at the various depths. Both LOG(Ca/Al) and LOG((Ca+Mg)/Al) values are the logarithms of concentration ratios of soil exchangeable Ca, Mg and Al, respectively. Coefficients of determination for linear regression ($R^2$) and $P$ values were calculated. Error bars indicate standard errors of three replicates.
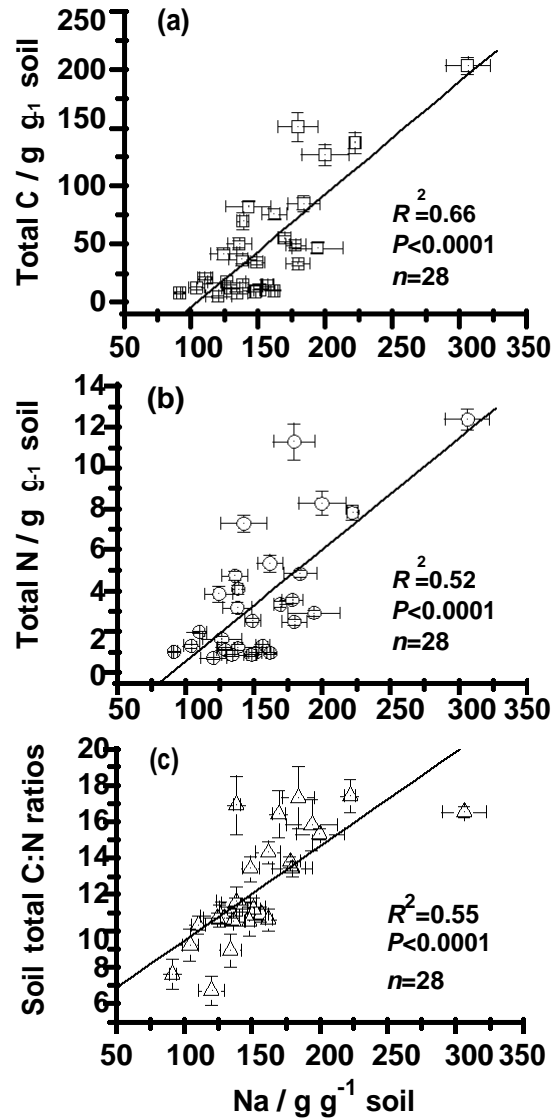
**Figure 7.** Relationships between exchangeable Na concentrations versus the concentrations of (a) total C and (b) total N or (c) the ratios of total C to total N concentrations in the soils at the various depths. Coefficient sof determination for linear regressions ($R^2$) and *P* values were calculated. Error bars indicate standard errors of three replicates.

exchangeable Ca, Mg and Ba in uppermost layers of the soils were larger under the three temperate forests than under the tropical forest. The maximal concentrations of all tested exchangeable metals (excluding Al and Pb) were observed in the 0 - 2.5- cm soil and varied with tree species. The results indicate that the vertical distribution of DOM concentrations in the soil is a function of the decreasing microbial activity and is partly associated with the metals of concern. Further data including soil bulk density should be needed at more old- growth forest sites to confirm the relationships between Na concentration and the C sequestration in soil.

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