



Changes in soil carbon sequestration in *Pinus massoniana* forests along an urban-to-rural gradient of southern China

H. Chen^{1,3}, W. Zhang¹, F. Gilliam², L. Liu¹, J. Huang¹, T. Zhang¹, W. Wang¹, and J. Mo¹

¹Key Laboratory of Vegetation Restoration and Management of Degraded Ecosystems, South China Botanical Garden, Chinese Academy of Sciences, Guangzhou 510650, China

²Department of Biological Science, Marshall University, Huntington, WV 25755-2510, USA

³University of Chinese Academy of Sciences, Beijing 100039, China

Correspondence to: J. Mo (mojm@scib.ac.cn)

Received: 30 April 2013 – Published in Biogeosciences Discuss.: 9 July 2013

Revised: 9 October 2013 – Accepted: 11 October 2013 – Published: 22 October 2013

Abstract. Urbanization is accelerating globally, causing a variety of environmental changes such as increases in air temperature, precipitation, atmospheric CO₂, and nitrogen (N) deposition. However, the effects of these changes on forest soil carbon (C) sequestration remain largely unclear. Here, we used urban-to-rural environmental gradients in Guangdong Province, southern China, to address the potential effects of these environmental changes on soil C sequestration in *Pinus massoniana* forests. In contrast to our expectations and earlier observations, soil C content in urban sites was significantly lower than that in suburban and rural sites. Lower soil C pools in urban sites were correlated with a significant decrease in fine root biomass and a potential increase in soil organic C decomposition. Variation of soil C pools was also a function of change in soil C fractions. Heavy fraction C content in urban sites was significantly lower than that in suburban and rural sites. By contrast, light fraction C content did not vary significantly along the urban-to-rural gradient. Our results suggest that urbanization-induced environmental changes may have a negative effect on forest soil C in the studied region.

1 Introduction

Urbanization is accelerating globally, with 50 % of the world's population currently living in cities, with a projected increase to 70 % by 2050 (UNFPA, 2007). Rapid urban development has the potential to alter regional carbon (C) budgets through urbanization-induced environmen-

tal changes (Trusilova and Churkina, 2008; Pouyat et al., 2002). Urbanization-induced environmental changes include a variety of environmental changing factors caused by accelerating urbanization, such as increases in air temperature, precipitation, atmospheric CO₂, and nitrogen (N) deposition (Shen et al., 2008). Numerous studies have shown air temperature (Jones et al., 1990), precipitation (Botkin and Beveridge, 1997; Gilbert, 1989), atmospheric CO₂ (Idso et al., 2002; Pataki et al., 2003), and N deposition (Lovett et al., 2000; Fenn et al., 2003) to be higher in urban areas than in rural surroundings. This environmental gradient may even be a useful tool for investigating how global environmental change influences forest ecosystem structure and function, since such changes in cities are also known to be major drivers of global change (Carreiro and Tripler, 2005; Shen et al., 2008).

The current scientific evidence supports the belief that urbanization-induced environmental changes should increase soil C sequestration of urban forests. Results from long-term N addition experiments in the United States and Europe have shown that N deposition can increase forest soil C sequestration from 0.51 to 0.69 Mg C ha⁻¹ yr⁻¹ (Hyvonen et al., 2008; Pregitzer, et al., 2008). Using a meta-analysis of experiments carried out over > 2 yr periods, Jastrow et al. (2005) reported that elevated CO₂ concentration would increase soil C sequestration by 0.19 Mg C ha⁻¹ yr⁻¹. If combined with N addition, this positive effect of elevated CO₂ on soil C storage would be more pronounced (van Groenigen et al., 2006; Hungate et al., 2009). This belief was also supported by recent direct field measurements along an urban-to-rural

gradient in New York red oak (*Quercus rubra* L.) forests (Pouyat et al., 2002) and in a semi-arid tropical desert ecosystem in Phoenix, Arizona (Koerner and Klapetek, 2010). However, besides the above-mentioned two direct measurements, this belief has not been tested in other cities, forests and (or) climate zones (Pouyat, 2003); Yesilonis and Pouyat, 2012). Soil warming induced by elevated urban air temperature may reduce soil C storage in the short-term by increasing decomposition. This may be offset by increasing C input and SOM stabilization in the long-term (Conant et al., 2008; Giardina and Ryan, 2000). As a result, diversity in the responses of forest soil C to urbanization-induced environmental changes may also be existent.

China has undergone rapid urbanization, largely resulting from economic reform and the “open door policy” initiated in late 1978 (Chen et al., 2006). The population of Guangdong Province, southern China, increased nearly two-fold from 1982 to 2010 (i.e., from 53.6 million to 104.3 million persons) (SBGP, 2011). Despite this notable increase, no data are available that relate the response of forest soil C to these urbanization-induced changes.

To address this, we established urban-to-rural gradients in Guangdong Province, beginning with the Pearl River Delta (PRD) economic region at the center of development; the PRD covers nearly 25% of the provincial area and supports ~54% of the population (SBGP, 2011). The purpose of this study was to assess the potential effects of urbanization changes on forest soil C in southern China utilizing this urban-to-rural gradient. Masson pine (*Pinus massoniana* L.) plantations were chosen because of their wide distribution in southern China, accounting for 45% of the total plantation area in Guangdong Province (Kuang et al., 2008). In addition, Masson pine forests have relative structural and spatial homogeneity, eliminating the confounding of other factors. We hypothesized that urbanization-induced environmental changes would increase soil C sequestration in these pine forests.

2 Materials and methods

2.1 Study region

This study comprised sites located throughout Guangdong Province, southern China (Fig. 1). The PRD economic region is the fastest developing area in the province. The following environmental gradients have been related to patterns of urbanization extending from the core of PRD to its surrounding areas: (1) air temperature is approximately 0.5–2.0 °C higher in the core of PRD than in its surroundings due to the effect of “urban heat island” (Mai et al., 2011; Dou and Zhao, 2011); (2) CO₂ emissions are relatively elevated in PRD, accounting for 70% of total emissions in Guangdong Province (Liu, 2009); (3) rates of N deposition vary from approximately 46 kg ha⁻¹ yr⁻¹ toward the core of PRD to <20 kg ha⁻¹ yr⁻¹

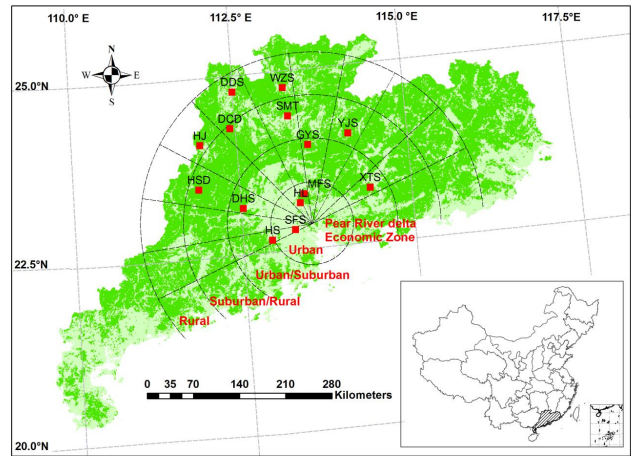


Fig. 1. Location of our study sites in Guangdong Province of southern China. A total of fourteen Masson pine forests were selected along the transect. The detailed information for each forest is listed in Table S1.

in the most distant rural areas (Huang et al., 2012; Kuang et al., 2011); and (4) annual average precipitation is also higher in urban areas than in surrounding areas (Li et al., 2009).

Because the pattern of urbanization of this region is not always linear, we combined both distance from center and land-use status to determine our gradients. We initially used distance to define four urbanization classes in this study region: (1) urban, 0–65 km from the urban core; (2) urban/suburban, 65–130 km from the urban core; (3) suburban/rural, 130–195 km from the urban core; (4) rural, 195–260 km from the urban core (Fig. 1). We further divided each class into 10 subzones of equal area. In each class we randomly chose 3 or 4 subzones to locate our sampled forests based on a land-use map. In total, 14 forests were selected in this study – three in the urban class (Huolushan, Maofengshan, and Shunfengshan, abbreviated to HLS, MFS, and SFS, respectively), four in the urban/suburban class (Heshan (HS), Dinghushan (DHS), Guanyinshan (GYS), and Xiangtoushan (XTS)), four in the suburban/rural class (Heishiding (HSD), Shimentai (SMT), Yunjishan (YJS), and Dachouding (DCD)), and three in the rural class (Huaiji (HJ), Dadongshan (DDS), and Wuzhishan (WZS)) (Fig. 1). Longitude of these forests ranges from 111°54′19.78″ E to 114°25′37.54″ E, and latitude ranges from 22°40′13.31″ N to 24°46′40.25″ N (Table S1). Annual precipitation ranges from 1566 to 2133 mm, and mean annual air temperature ranges from 19.45 to 22.2 °C in the study region (Table S1).

All pine plantations used in this study had remained unmanaged following planting. Several criteria were used in site selection to ensure comparability among forests: (1) no disturbance after planting, including fire, insect infestations, logging, and fertilization; (2) stand age between 40 and 60 yr; (3) stand density between 600 and 800 trees ha⁻¹ (Table S1); (4) soils of lateritic red earth (Ultisols in USDA soil

taxonomy or Acrisols in the FAO soil classification). In addition, sampling was carried out in the center of the selected site to avoid edge effects.

2.2 Soil sampling

Soil sampling was conducted from January to May 2011. In each forest site, three random subplots (5 m × 5 m) were selected to sample soil from three soil layers (0–10, 10–20 and 20–40 cm depths) using a 10 cm inside diameter (ID) corer. Soil samples passed through a 2 mm sieve, and roots and plant residues were removed. Soil organic carbon (SOC) was determined by dichromate oxidation and titration with ferrous ammonium sulfate (Walkley and Black, 1934). Soil total nitrogen (TN) was measured using the micro-Kjeldahl method (Jackson, 1964). For bulk density determination, soil was collected in a 0.25 m² × 0.5 m deep pit in each subplot, using a 5 cm ID corer. Bulk density measures were used to calculate SOC content.

Soil microbial biomass carbon (MBC) was estimated by the chloroform fumigation extraction technique (Vance et al., 1987). Soluble C was extracted using a 0.5 M K₂SO₄ solution from 10 g soil samples before and after fumigation. Extracts were analyzed for total dissolved C using a total C analyzer (Shimadzu model TOC-500, Kyoto, Japan). Soil MBC was calculated as the difference in extractable C between fumigated and non-fumigated soil, divided by 0.45. Soil extractable dissolved organic carbon (DOC) was measured on the same samples used for the analysis of MBC, and calculated as the K₂SO₄-extractable C concentration.

2.3 Soil density fractions

Soil C was separated into two fractions using a density fraction method: (1) light fraction (LF), which tends to have younger soil C pools and include undecomposed or partly decomposed organic residues and micro-biomass (Christensen, 2001); and (2) heavy fraction (HF), which generally contains older soil C pools and includes C associated with mineral surfaces or concealed within micro-aggregates (Trumbore, 1993). Methodology for soil C fractionation followed McLauchlan and Hobbie (2004), with alterations as noted. Approximately 15 g of air-dried soil was weighed into a 100 mL centrifuge tube with 50 mL NaI (a density of 1.7 g cm⁻³). Tubes were centrifuged at 1000 rpm for 10 min. The materials floating on the surface of tubes (LF) were decanted into a vacuum filter unit with 0.45 μm nylon filter paper. This process was repeated until no floating material remained. The materials remaining at the bottom (HF) of the centrifuge tube were also rinsed into the vacuum filter unit. All samples on the filter paper were washed with 75 mL of 0.01 mol L⁻¹ CaCl₂, followed by at least 75 mL of distilled water. The light and heavy materials were dried at 60 °C for 48 h and weighed. All samples passed through a 60-mesh

sieve and were analyzed for SOC and TN concentration as previously described.

2.4 Fine root biomass

Root cores were collected from the 0–10 cm soil layer using a 10 cm ID corer. Fine roots (≤ 2 mm diameter) were sorted from washed cores by hand into living and dead components following procedures from Silver and Vogt (1993). Root samples were washed with distilled water, oven dried, and measured for living and dead fine root biomass. The SOC and TN of living fine root samples were also analyzed as described.

2.5 Statistical analysis

All data analyses were carried out using SAS software (SAS Institute Inc., Cary NC, USA). One-way analysis of variance (ANOVA) was performed to compare the differences between four urbanization classes (urban, urban/suburban, suburban/rural, and rural) in fine root biomass, fine root C and N concentration, and soil respiration. Two-way ANOVA was used to test differences between urbanization classes and soil depths in the variables, which were measured in multiple soil layers. Correlation and regression analyses were used to examine relationships between variables and distances from urban to rural centers. Statistically significant differences were set at $P < 0.05$, unless otherwise stated. Mean values are expressed ± 1 standard error of the mean.

3 Results

3.1 SOC and TN concentrations

Both SOC and TN concentrations varied significantly with the urbanization class, with both increasing from urban to rural conditions (Table 1). Significant and positive correlations existed between SOC concentrations, soil TN concentrations and the distance from urban to rural in all soil depths ($0.52 \leq R^2 \leq 0.66$, all $P < 0.001$). Distance explained approximately 24–31 % and 21–36 % of changing for SOC and soil TN among sites, respectively. Two-way ANOVA showed that urbanization-induced environmental changes significantly reduced SOC and TN concentrations in urban sites compared with those in suburban and rural sites, in all soil depths (Table 1, all $P < 0.05$). As a result, no significant differences between gradient classes were shown for the soil C : N ratio in any soil layer (Table 1, all $P > 0.05$).

3.2 SOC content

When SOC was calculated as content (i.e., as Mg ha⁻¹), it increased significantly from urban to rural conditions, exhibiting a positive linear relationship with distance across all soil depths (Fig. 2a, $R^2 = 0.717$, $P < 0.001$). Two-way ANOVA

Table 1. Comparison of SOC %, TN %, soil C : N ratio and soil bulk density (g cm^{-2}) (in 0–10, 10–20, and 20–40 cm soil layers) among four urbanization gradient classes.

Soil depth (cm)	Urbanization classes	SOC (%)	TN (%)	C : N ratio	Soil bulk density (g cm^{-3})
0–10 cm	Urban	2.10 (0.13) a	0.19 (0.02) a	10.92 (1.05)	1.25 (0.17) a
	Urban/Suburban	2.63 (0.47) a	0.23 (0.03) ab	12.03 (2.09)	1.22 (0.14) a
	Suburban/Rural	3.75 (0.40) b	0.28 (0.04) bc	13.47 (2.91)	1.04 (0.13) b
	Rural	3.99 (0.63) b	0.31 (0.03) c	12.91 (2.52)	1.03 (0.05) b
10–20 cm	Urban	1.33 (0.16) a	0.10 (0.01) a	14.28 (2.55)	1.41 (0.10) a
	Urban/Suburban	1.59 (0.48) ab	0.11 (0.02) a	14.98 (3.12)	1.34 (0.12) ab
	Suburban/Rural	2.04 (0.40) ab	0.15 (0.03) ab	14.18 (2.92)	1.15 (0.08) ab
	Rural	2.19 (0.06) b	0.15 (0.01) b	15.46 (1.07)	1.19 (0.03) b
20–40 cm	Urban	0.81 (0.09) a	0.05 (0.02) a	18.05 (1.23)	1.48 (0.10) a
	Urban/Suburban	0.93 (0.20) a	0.05 (0.02) a	18.23 (1.02)	1.41 (0.06) ab
	Suburban/Rural	1.47 (0.20) b	0.08 (0.01) ab	18.28 (1.03)	1.21 (0.13) ab
	Rural	1.51 (0.12) b	0.08 (0.02) b	18.34 (0.94)	1.26 (0.01) b

The different letters indicate significant differences at $P < 0.05$ level, and no letters indicate no significant differences between different urbanization gradient classes, respectively (SNK test). Values are means with S. E. in parentheses ($N = 3$ for urban and rural, $N = 4$ for urban/suburban and suburban/rural).

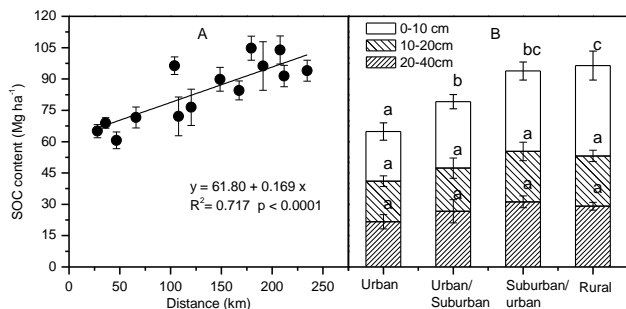


Fig. 2. Change in SOC content in the top 40 cm soil. (A) correlation analysis of bulk SOC content (in the 0–10 cm, 10–20 cm, and 20–40 cm soil layers) and the distance from urban to rural; (B) comparisons of SOC content among four urbanization gradient classes. Error bars indicate ± 1 S. E. ($N = 3$ for urban and rural, $N = 4$ for urban/suburban and suburban/rural). Different letters denote significant differences ($P \leq 0.05$) between gradient classes (SNK test).

showed that SOC content increased significantly from urban sites to rural sites at 0–10 cm depth (Fig. 2b, $P < 0.001$), but not at 10–20 and 20–20 cm depths (Fig. 2b, $P = 0.5060$ and 0.0821 , respectively). When calculating SOC content to 40 cm depths, the mean SOC contents were 64.87 ± 4.17 , 79.12 ± 11.7 , 93.83 ± 8.71 , and $96.43 \pm 6.60 \text{ Mg ha}^{-1}$ in urban, urban/suburban, suburban/rural and rural sites, respectively.

3.3 Soil density fractions

LF and HF showed different patterns along the urban-to-rural gradient. HF comprised $> 94\%$ of total soil mass and contained the majority of soil C content (approximately 70–85 %) for all sites combined (Table 2). Mass proportions of LF and HF, LF organic carbon (LF-OC) concentrations, and the LF-OC content did not vary significantly along the gradi-

ent (Table 2). By contrast, HF organic carbon (HF-OC) concentrations increased from urban to rural conditions in the 0–10 and 10–20 cm soil layers (Table 2, both $P < 0.0001$). N concentrations in LF showed no significant differences among four urbanization classes, but significantly increased in HF from urban to rural in both the 0–10 and 10–20 cm soil layers (Table 2, $P = 0.0001$ and 0.0244 , respectively). No significant change was observed for the C : N ratio of LF and HF in two soil layers (Table 2, both $P > 0.05$).

3.4 Fine root, microbial biomass C, and extractable DOC

Living and dead fine root biomass exhibited similar patterns along the urban-to-rural gradient. Living fine root biomass was significantly higher than dead root biomass ($P < 0.001$, $n = 14$), and comprised approximately 70 % of the total fine root biomass (living plus dead). Living, dead and total fine root biomass were all significantly lower in urban sites than in other urbanization classes (Fig. 4a). Living fine root C concentration exhibited no significant difference among four gradient classes, but N concentrations of living fine root increased significantly from urban sites to rural sites (Fig. 5, $P < 0.0001$). C : N ratios declined from 44 ± 4 in urban sites to 40 ± 3 , 33 ± 2 and 28 ± 4 in urban/suburban, suburban/rural, and rural sites, respectively ($P < 0.0001$).

Microbial biomass C decreased significantly from urban to rural sites in the 0–10 cm soil layer (Fig. 4b, $P < 0.05$), but not significantly in 10–20 and 20–40 cm (Fig. 4b, both $P > 0.05$). Conversely, the extractable DOC was not significantly different among urbanization classes in any soil layer (Fig. 4c, $P > 0.05$ for each layer).

Table 2. Characteristics of two soil fractions.

Soil fraction	Depth (cm)	Urban classes	C (%)	N (%)	C:N ratio	Percent of bulk soil mass (%)	Percent of bulk soil C (%)
LF	0–10	Urban	25.96 (3.66)	0.93 (0.11)	28.04 (0.91)	3.62 (0.53)	28.80 (4.02)
		Urban/Suburban	21.50 (3.84)	0.87 (0.13)	25.29 (4.01)	3.54 (0.99)	28.25 (5.34)
		Suburban/Rural	26.72 (5.89)	0.91 (0.09)	29.48 (4.31)	4.10 (1.34)	27.22 (5.47)
		Rural	21.68 (2.92)	0.81 (0.05)	26.46 (2.46)	5.87 (1.33)	26.40 (4.04)
	10–20	Urban	25.29 (3.97)	0.64 (0.03)	40.67 (7.68)	1.06 (0.06)	19.81 (1.48)
		Urban/Suburban	21.72 (2.50)	0.57 (0.02)	38.09 (5.52)	1.35 (0.21)	20.14 (1.40)
		Suburban/Rural	27.23 (5.30)	0.66 (0.11)	41.27 (5.43)	1.19 (0.24)	17.91 (1.62)
		Rural	25.55 (7.24)	0.69 (0.12)	36.74 (7.03)	1.55 (0.56)	15.06 (2.59)
HF	0–10	Urban	1.66 (0.10) a	0.12 (0.02) a	14.30 (2.99)	96.37 (0.48)	71.20 (4.02)
		Urban/Suburban	1.99 (0.40) a	0.15 (0.03) ab	14.21 (2.12)	96.45 (0.99)	71.75 (5.34)
		Suburban/Rural	2.93 (0.54) b	0.19 (0.04) bc	14.97 (1.91)	95.90 (1.34)	72.78 (3.42)
		Rural	3.16 (0.44) b	0.25 (0.07) c	16.67 (3.10)	94.12 (1.33)	73.95 (4.49)
	10–20	Urban	1.15 (0.18) a	0.09 (0.01) a	13.77 (2.32)	98.94 (0.06)	80.28 (1.48)
		Urban/Suburban	1.21 (0.25) ab	0.09 (0.02) a	13.46 (2.93)	98.64 (0.21)	79.83 (1.40)
		Suburban/Rural	1.52 (0.36) bc	0.13 (0.03) ab	11.71 (2.06)	98.80 (0.24)	82.54 (1.62)
		Rural	1.75 (0.22) c	0.17 (0.09) b	15.45 (4.14)	98.44 (0.56)	84.94 (1.15)

The different letters indicate significant differences at $P < 0.05$ level, and no letters indicate no significant differences between different urbanization gradient classes, respectively (SNK test).

Values are means with S. E. in parentheses ($N = 3$ for urban and rural, $N = 4$ for urban/suburban and suburban/rural).

4 Discussion

SOC content ranged along the urban-to-rural gradient from 64.87 to 96.43 Mg ha^{-1} in top 40 cm soil, well within the range (41.74 to 102.17 Mg ha^{-1}) reported for pine forests in Guangdong Province and other subtropical regions of China (Fang and Mo, 2002; Kang et al., 2006; Zheng et al., 2008; Jiang et al., 2011). Our results suggest that urbanization-induced environmental change has significantly decreased soil C content (Fig. 2b), rejecting our initial hypothesis and contradicting results from other studies. Pouyat et al. (2002) analyzed soil in New York red oak (*Quercus rubra* L.) forests and showed that soil C content significantly increased in urban sites compared with that in rural sites. In a semi-arid tropical desert ecosystem, similar results were also found by Koerner and Klpatsek (2010) along an urban-to-rural gradient in Phoenix, Arizona.

Although the reasons for our observed pattern are not clear, we suggest two possible explanations. First, C input may be decreased in urban sites due to the reduction in below-ground root input to the soil. We found that fine root biomass was significantly lower in urban sites than that in suburban and rural sites (Fig. 4a). Indeed, C input via fine roots can equal C input from above-ground production (Nadelhoffer and Raich, 1992). Furthermore, because annual productivity of fine roots typically decreases with excess N availability (Nadelhoffer, 2000), it is likely that decreased fine root production arose from higher N deposition in more urbanized areas (Gilliam, 2006, 2007).

Second, soil C loss from urban sites may be enhanced by increasing SOM decomposition. Decomposition of SOM can be influenced by a variety of factors, including organic matter quality, microbial activity, and microclimate (Chapin et al., 2002). In our study, organic matter quality did not appear to change with degree of urbanization, since there were no sig-

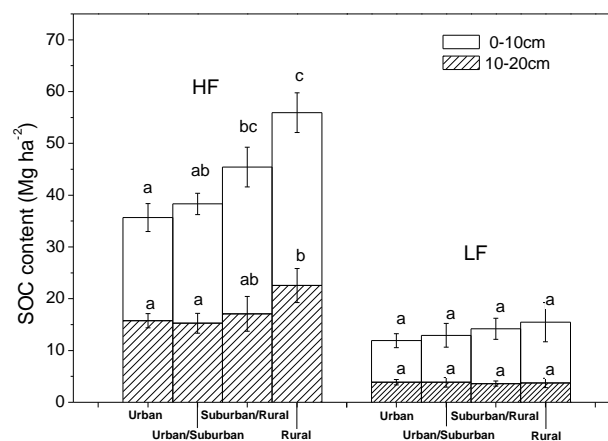


Fig. 3. Comparisons of HF-OC and LF-OC content (in 0–10 and 10–20 cm soil layers) among four urbanization gradient classes. Error bars indicate ± 1 S. E. ($N = 3$ for urban and rural, $N = 4$ for urban/suburban and suburban/rural). Different letters denote significant differences ($P \leq 0.05$) between gradient classes (SNK test).

nificant differences in the soil C:N ratio along the urban-to-rural gradient (Table 1). There was, however, a significant increase in microbial biomass in urban sites (Fig. 4b), indicating a potential increase in microbial activity. Meanwhile, the elevated air temperatures associated with urban sites would also increase SOM decomposition. Pouyat et al. (2002) suggested that the elevated temperature in urban areas increased litter decay rate, and that the magnitude can even offset increased litter input to the soil.

Although there were no significant differences in DOC between four gradient classes (Fig. 4c), some studies have reported that land-use change and land management can increase DOC fluxes in urban areas (Aitkenhead-Peterson et

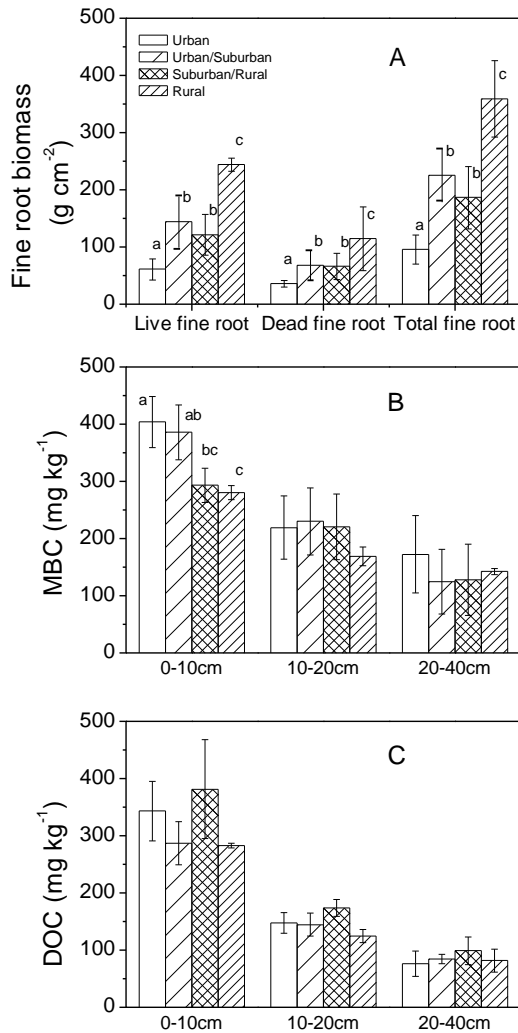


Fig. 4. Comparisons of fine root biomass (A), MBC (B), DOC (C) among different urbanization gradient classes. Error bars indicate ± 1 S. E. ($N = 3$ for urban and rural, $N = 4$ for urban/suburban and suburban/rural). Different letters indicate significant differences ($P \leq 0.05$) between gradient classes, and no letters indicate no significant differences ($P > 0.05$) between different urbanization gradient classes, respectively (SNK test).

al., 2009; Williams et al., 2005). Compared with such anthropogenic influences, our results suggest that the effects of urbanization-induced environmental changes on soil DOC flux may be negligible.

Decreases in soil C storage in urban areas appears largely driven by the change in the HF-OC pool (often considered passive C) rather than in the LF-OC pool (labile C) (Fig. 3). Contrary to our results, other work has found higher total passive C and lower labile C in soil from urban forests compared with soil from rural forests (Groffman et al., 1995), which was attributed to decreasing SOM recalcitrance, which was strongly linked to the reduction in air pollution and earthworm activity.

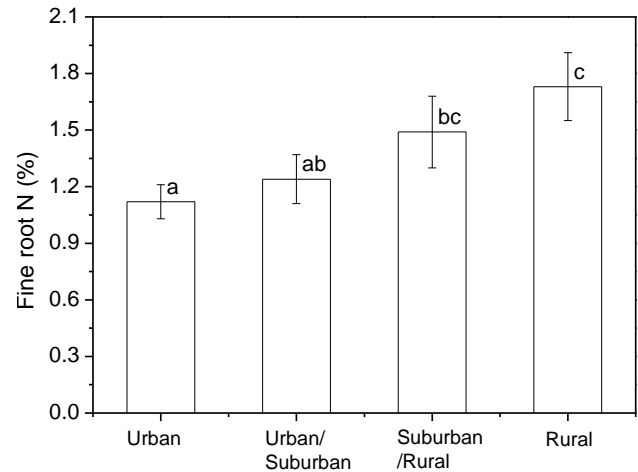


Fig. 5. Comparisons of N concentration in living fine root (0–10 cm soil layer) among four urbanization gradient classes. Error bars indicate ± 1 S. E. ($N = 3$ for urban and rural, $N = 4$ for urban/suburban and suburban/rural). The different letters denote significant differences ($P \leq 0.05$) between gradient classes (SNK test).

It has been suggested that the recalcitrance of SOM would increase with the formation of stable organo-mineral complexes via adsorption reactions (Sollins et al., 1996). We found that N concentration of HF was higher in rural sites than in suburban and urban sites (Table 2), suggesting that increasing amounts of N-rich material were adsorbed into mineral soil, possibly forming stable organo-mineral complexes in rural areas. N-rich proteinaceous compounds are important in the formation of organo-mineral complexes (Kleber et al., 2007). We suggest that these N-rich materials may arise from dead roots, considering that both dead fine root biomass and root N concentrations increased toward rural sites (Fig. 5). In addition, the enzyme-kinetic hypothesis predicts that degradation of low-quality substrate (recalcitrant molecular structure) has a higher temperature sensitivity compared with labile substrate, because the former requires higher total activation energy to fully mineralize substrate (Bosatta and Agren, 1999). Therefore, higher temperature in urban areas is likely to cause accelerated decomposition of HF-C and may be another reason for the lower HF-C content in urban sites.

In conclusion, we measured the forest SOC content along an urban-to-rural gradient in Guangdong Province, southern China. We found that the SOC content was significantly lower in urban areas than that in suburban and rural areas. It was suggested that decreased fine root biomass and potentially increased SOC decomposition were the possible reasons for this lower soil C pool in urban forests. We further found that HF-OC content also increased from the urban sites to rural sites, which was the main driver of the change in the total soil C pool. By contrast, LF-OC had no significant change in this study. These results are contrary to the general belief and the earlier studies, suggesting that

urbanization-induced environmental changes may decrease soil C sequestration in the studied forests. Our findings would be typical for tropical plantation forests; however, the results and corresponding control mechanisms should be further validated in various ecosystems and regions in the future.

Supplementary material related to this article is available online at <http://www.biogeosciences.net/10/6609/2013/bg-10-6609-2013-supplement.pdf>.

Acknowledgements. This study was supported by the National Natural Science Foundation of China (nos. 41273143 and 31000236) and the National Key Basic Research 973 Program (2010CB833502). The authors wish to acknowledge C. Ma and F. Zhu for their skilful assistance in field work, X. Chen for her assistance in laboratory work, and P. Gundersen, W. Zhu, Y. Fang, and X. Lu for their invaluable suggestions in earlier versions of the manuscript.

Edited by: P. Stoy

References

- Aitkenhead-Peterson, J. A., Steele, M. K., Nahar, N., and Santhy, K.: Dissolved organic carbon and nitrogen in urban and rural watersheds of south-central Texas: land use and land management influences, *Biogeochemistry*, 96, 119–129, 2009.
- Bosatta, E. and Agren, G. I.: Soil organic matter quality interpreted thermodynamically, *Soil Biol. Biochem.*, 31, 1889–1891, 1999.
- Botkin, D. B. and Beveridge, C. E.: Cities as environments, *Urban Ecosystems*, 1, 3–19, 1997.
- Carreiro, M. M. and Tripler, C. E.: Forest remnants along urban-rural gradients: Examining their potential for global change research, *Ecosystems*, 8, 568–582, 2005.
- Chapin, F. S. I., Matson, P. A., and Mooney, H. A.: *Principles of terrestrial ecosystem ecology*, Springer, New York, USA, 159–168, 2002.
- Chen, X. L., Zhao, H. M., Li, P. X., and Yin, Z. Y.: Remote sensing image-based analysis of the relationship between urban heat island and land use/cover changes, *Remote Sens. Environ.*, 104, 133–146, 2006.
- Christensen, B. T.: Physical fractionation of soil and structural and functional complexity in organic matter turnover, *Eur. J. Soil Sci.*, 52, 345–353, 2001.
- Conant, R. T., Steinweg, J. M., Haddix, M. L., Paul, E. A., Plante, A. F., and Six, J.: Experimental warming shows that decomposition temperature sensitivity increases with soil organic matter recalcitrance, *Ecology*, 89, 2384–2391, 2008.
- Dou, H. Y. and Zhao X. Y.: Climate change and its human dimensions based on GIS and meteorological statistics in Pearl River Delta, Southern China, *Meteorol. Appl.*, 18, 111–122, 2011.
- Fang, Y. T. and Mo, J. M.: Study on carbon distribution and storage of a pine forest ecosystem in Dinghushan Biosphere Reserve, *Guihaia*, 22, 305–310, 2002 (in Chinese with English abstract).
- Fenn, M. E., Haeuber, R., Tonnesen, G. S., Baron, J. S., Grossman-Clarke, S., Hope, D., Jaffe, D. A., Copeland, S., Geiser, L., Rueth, H. M., and Sickman, J. O.: Nitrogen emissions, deposition, and monitoring in the western United States, *Bioscience*, 53, 391–403, 2003.
- Giardina, C. P. and Ryan M. G.: Evidence that decomposition rates of organic carbon in mineral soil do not vary with temperature, *Nature*, 404, 858–861, 2000.
- Gilbert, O. L.: *The ecology of urban habitats*, Chapman and Hall, London, 25–32, 1989.
- Gilliam, F. S.: Response of the herbaceous layer of forest ecosystems to excess nitrogen deposition, *J. Ecol.*, 94, 1176–1191, 2006.
- Gilliam, F. S.: The ecological significance of the herbaceous layer in temperate forest ecosystems, *Bioscience*, 57, 845–858, 2007.
- Groffman, P., Pouyat, R., McDonnell, M. J., Pickett, S., and Zipperer, W. C.: Carbon pools and trace gas fluxes in urban forest soils, in: *Advance in soil science: soil management and greenhouse effect*, edited by: Lai, R., Kimble, J., Levine, E., and Stewart, B. A., CRC press, Boca Raton, 147, 1995.
- Huang, L., Zhu, W., Ren, H., Chen, H. F., and Wang, J.: Impact of atmospheric nitrogen deposition on soil properties and herb-layer diversity in remnant forests along an urban-rural gradient in Guangzhou, southern China, *Plant Ecol.*, 213, 1187–1202, 2012.
- Hungate, B. A., van Groenigen, K. J., Six, J., Jastrow, J. D., Luo, Y. Q., de Graaff, M. A., van Kessel, C., and Osenberg, C. W.: Assessing the effect of elevated carbon dioxide on soil carbon: a comparison of four meta-analyses, *Glob. Change Biol.*, 15, 2020–2034, 2009.
- Hyvonen, R., Persson, T., Andersson, S., Olsson, B., Agren, G. I., and Linder, S.: Impact of long-term nitrogen addition on carbon stocks in trees and soils in northern Europe, *Biogeochemistry*, 89, 121–137, 2008.
- Idso, S. B., Idso, C. D., and Balling Jr., R. C.: Seasonal and diurnal variations of near-surface atmospheric CO₂ concentration within a residential sector of the urban CO₂ dome of Phoenix, AZ, USA, *Atmos. Environ.*, 36, 1655–1660, 2002.
- Jackson, M. L.: *Soil chemical analysis*, Prentice-Hall Inc, Englewood cliffs, New York, 86–92, 1964.
- Jastrow, J. D., Miller, R. M., Matamala, R., Norby, R. J., Boutton, T. W., Rice, C. W., and Owensby, C. E.: Elevated atmospheric carbon dioxide increases soil carbon, *Glob. Change Biol.*, 11, 2057–2064, 2005.
- Jiang, P. K., Meng, C. F., Zhou, G. M., and Xu, Q. F.: Comparative study of carbon storage in different forest stands in subtropical China, *Bot. Rev.*, 77, 242–251, 2011.
- Jones, P. D., Groisman, P. Y., Coughlan, M., Plummer, N., Wang, W. C., and Karl, T. R.: Assessment of urbanization effects in time-series of surface air-temperature over Land, *Nature*, 347, 169–172, 1990.
- Kang, B., Liu, S., Zhang, G. J., Chang J. G., Wen, Y. G., Ma, J. M., and Hao, W. F.: Carbon accumulation and distribution in *Pinus massoniana* and *Cunninghamia lanceolata* mixed forest ecosystem in Daqingshan, Guangxi, China, *Acta Ecologica Sinica*, 26, 1320–1329, 2006 (in Chinese with English abstract).
- Kleber, M., Sollins, P., and Sutton, R.: A conceptual model of organo-mineral interactions in soils: self-assembly of organic molecular fragments into zonal structures on mineral surfaces, *Biogeochemistry*, 85, 9–24, 2007.

- Koerner, B. A. and Klopatek, J. M.: Carbon fluxes and nitrogen availability along an urban-rural gradient in a desert landscape – Arizona State University, Urban Ecosystems, 13, 1–21, 2010.
- Kuang, Y. W., Sun, F. F., Wen, D. Z., Xu, Z. H., Huang, L. B., and Li, J.: Nitrogen deposition influences nitrogen isotope composition in soil and needles of *Pinus massoniana* forests along an urban-rural gradient in the Pearl River Delta of south China, *J. Soil. Sediment.*, 11, 589–595, 2011.
- Kuang, Y. W., Sun, F. F., Wen, D. Z., Zhou, G. Y., and Zhao, P.: Tree-ring growth patterns of Masson pine (*Pinus massoniana* L.) during the recent decades in the acidification Pearl River Delta of China, *Forest Ecol. Manag.*, 255, 3534–3540, 2008.
- Li, W., Du, Y., Wang G. D., Wu. M. S., and Xu Y. L.: Urbanization effects on precipitation over the Pearl River Delta based on satellite data, *Chinese J. Atmos. Sci.*, 33, 1259–1266, 2009 (in Chinese with English abstract).
- Liu, Y.: On current CO₂ Emission in Guangdong and Policy Trends, *China Opening Herald*, 40–53, 2009 (in Chinese with English abstract).
- Lovett, G. M., Traynor, M. M., Pouyat, R. V., Carreiro, M. M., Zhu, W. X., and Baxter, J. W.: Atmospheric deposition to oak forests along an urban-rural gradient, *Environ. Sci. Technol.*, 34, 4294–4300, 2000.
- Mai, J. H., Luo, N. X., Lai, W. F., and Lin, W. S.: A simulation about the impact of urbanization on the urban heat island in the Pearl River Delta region, *Tropical Geography*, 31, 187–192, 2011 (in Chinese with English abstract).
- McLauchlan, K. K. and Hobbie, S. E.: Comparison of labile soil organic matter fractionation techniques, *Soil Sci. Soc. Am. J.*, 68, 1616–1625, 2004.
- Nadelhoffer, K. J.: The potential effects of nitrogen deposition on fine-root production in forest ecosystems, *New Phytol.*, 147, 131–139, 2000.
- Nadelhoffer, K. J. and Raich J. W.: Fine root production estimates and belowground carbon allocation in forest ecosystems, *Ecology*, 73, 1139–1147, 1992.
- Pataki, D. E., Bowling, D. R., and Ehleringer, J. R.: Seasonal cycle of carbon dioxide and its isotopic composition in an urban atmosphere: Anthropogenic and biogenic effects, *J. Geophys. Res.-Atmos.*, 108, 4735, doi:10.1029/2003JD003865, 2003.
- Pouyat, R. V.: Soil carbon in urban forest ecosystems, in: The potential of U. S. forest soils to sequester carbon and mitigate the greenhouse effect, edited by: Kinble, J. M., Heath, L. S., Birdsey, R. A., and Lai, R., CRC press, Boca Raton, 347–362, 2003.
- Pouyat, R., Groffman, P., Yesilonis, I., and Hernandez, L.: Soil carbon pools and fluxes in urban ecosystems, *Environ. Pollut.*, 116, 107–118, 2002.
- Pregitzer, K. S., Burton, A. J., Zak, D. R., and Talhelm, A. F.: Simulated chronic nitrogen deposition increases carbon storage in Northern Temperate forests, *Glob. Change Biol.*, 14, 142–153, 2008.
- SBGP (Statistics Bureau of Guangdong Province): The main data bulletin of the sixth national population census in Guangdong province, 2010, (http://www.gdstats.gov.cn/tjgb/t20110511_83329.htm), 2011 (in Chinese).
- Shen, W. J., Wu, J. G., Grimm, N. B., and Hope, D.: Effects of urbanization-induced environmental changes on ecosystem functioning in the phoenix metropolitan region, USA, *Ecosystems*, 11, 138–155, 2008.
- Silver, W. L. and Vogt, K. A.: Fine-Root Dynamics Following Single and Multiple Disturbances in a Subtropical Wet Forest Ecosystem, *J. Ecol.*, 81, 729–738, 1993.
- Sollins, P., Homann, P., and Galdwell, B. A.: Stabilization and destabilization of soil organic matter: Mechanisms and controls, *Geoderma*, 74, 65–105, 1996.
- Trumbore, S. E.: Comparison of carbon dynamics in tropical and temperate soils using radiocarbon measurements, *Global Biogeochem. Cy.*, 7, 275–290, 1993.
- Trusilova, K. and Churkina, G.: The response of the terrestrial biosphere to urbanization: land cover conversion, climate, and urban pollution, *Biogeosciences*, 5, 1505–1515, doi:10.5194/bg-5-1505-2008, 2008.
- UNFPA: United Nations: State of the World Population. United Nations Population Fund, New York, 2007.
- van Groenigen, K., Six, J. J., Hungate, B. A., de Graaff, M. A., van Breemen, N., and van Kessel, C.: Element interactions limit soil carbon storage, *P. Natl. Acad. Sci. USA*, 103, 6571–6574, 2006.
- Vance, E. D., Brookes, P. C., and Jenkinson D. S.: An extraction method for measuring soil microbial biomass-C, *Soil Biol. Biochem.*, 19, 703–707, 1987.
- Walkley, A. and Black, I. A.: An examination of the degtjareff method for determining soil organic matter, and a proposed modification of the chromic acid titration method, *Soil Sci.*, 37, 29–38, 1934.
- Williams, M., Hopkinson, C., Rastetter, E., Vallino, J., and Claessens, L.: Relationships of land use and stream solute concentrations in the Ipswich River basin, northeastern Massachusetts, *Water Air Soil Poll.*, 161, 55–74, 2005.
- Yesilonis, I. D. and Pouyat R. V.: Carbon stocks in urban forest remnants: Atlanta and Baltimore as case studies, in: Carbon sequestration in urban ecosystems, edited by: Lai, R. and Agustin, B., Springer Press, Dordrecht, the Netherlands, 103–102, 2012.
- Zheng, H., Ouyang, Z. Y., Xu, W. H., Wang, X. K., Miao, H., Li, X. Q., and Tian, Y. X.: Variation of carbon storage by different reforestation types in the hilly red soil region of southern China, *Forest Ecol. Manag.*, 255, 1113–1121, 2008.