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Distribution and Evolution of Soil Organic Carbon, Total Nitrogen and Isotopes in Shanghai, China

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Abstract: The characteristics of soil organic carbon and nitrogen pools and changes in urban territories play a key role in the alteration of the global carbon biogeochemical cycles in the quickening urbanized world. The aim of this study is to assess the spatial distribution of soil organic carbon, total nitrogen and $\delta^{13}\text{C}$, $\delta^{15}\text{N}$ signatures in different urbanized territories in Shanghai, China and provide information on evolution trend of C, N cycling with urban ecosystem evolving. The contents of organic carbon, total nitrogen and $\delta^{13}\text{C}$, $\delta^{15}\text{N}$ in soil profiles (0~100 cm) of urban area vary in the ranges of 4.30-16.40, 0.50-1.80 g kg⁻¹ and -26.72~-21.16%, 2.05~5.89%, respectively. Soil organic carbon, total nitrogen and ^{15}N obviously accumulate while ^{13}C is significantly depleted in the central urban area. The organic carbon, total nitrogen contents decrease with soil profiles depth increasing. The $\delta^{13}\text{C}$ values increase from the top layer to a certain depth and then decrease. The carbon isotopic fractionation effects are more evident in the central urban area. The $\delta^{15}\text{N}$ is at a higher value in the central urban area than the urbanized area. Soil organic carbon, total nitrogen and $\delta^{13}\text{C}$, $\delta^{15}\text{N}$ signatures are correlated with urbanized periods of the studied urban ecosystem. Differences in different urbanized territories and associated environmental impacts are clearly reflected via C, N fractions and $\delta^{13}\text{C}$, $\delta^{15}\text{N}$ signals. The data and information on spatial-temporal distribution and evolution in urban territories of Shanghai will be offered which may be useful to push forward C and N cycles research on urban soils.

Key words: Soil organic carbon, nitrogen, $\delta^{13}\text{C}$, $\delta^{15}\text{N}$, urbanization

INTRODUCTION

The characteristics of C and N pools and change are very important in the global change research (Batjes, 1996; Houghton, 2009; IPCC, 2007; Janzen, 2004). Urban area has enlarged rapidly with social and economic development in the world which means urban soils play an increasingly important role in the global biogeochemical cycles (Svirejeva-Hopkins *et al.*, 2004; Grimm *et al.*, 2008; Kaye *et al.*, 2006; Lorenz and Lal, 2009). Urbanization can directly and indirectly affect soil C and N pools resulting in highly variable C and N contents compared to natural soils and urban soils may become one of the important places to sequester atmospheric greenhouse gases (Svirejeva-Hopkins *et al.*, 2004; Batjes, 1996; Lorenz and Lal, 2009; Pouyat *et al.*, 2006; Takahashi *et al.*, 2008). Therefore, urban area is becoming a hot spot in soil science and global change study and C and N dynamics in urban territories is one of the most active fields of the global biogeochemical cycles.

Urbanized territories is a specific component and C, N cycles in urban soils is significantly different from that in natural soils which is strongly influenced by land-use

and management activity (Svirejeva-Hopkins *et al.*, 2004; Lorenz and Kandeler, 2005; Lorenz and Lal, 2009; Sun *et al.*, 2010; Takahashi *et al.*, 2008; Xu *et al.*, 2012). Urban soils may have higher fluxes of both C and N relative to native soils (Lorenz and Lal, 2009; Pataki *et al.*, 2006). The C and N isotopic fractionation effects are appear during the process of biogeochemical cycles which leads to characteristic isotopic distribution in soils through different source or evolutionary process (Pataki *et al.*, 2006). ^{13}C and ^{15}N isotopes, as ideal tracers in carbon nitrogen cycle research, are sensitive to trace the biogeochemical process which are widely applied in C and N cycle of ecosystems (Ansley *et al.*, 2006; Cheng *et al.*, 2008; Ci *et al.*, 2007; Ge *et al.*, 2007; Liu *et al.*, 2008, 2010; Ma *et al.*, 2008; Sun *et al.*, 2008; Xie *et al.*, 2011; Zhou *et al.*, 2007). Presently, a mass of studies on C and N distribution and evolution focused on agricultural and forest ecosystems to keep higher production capacity (Ansley *et al.*, 2006; Cheng *et al.*, 2008; Ci *et al.*, 2007; Groffman *et al.*, 2006; Liu and Zhang, 2010; Ma *et al.*, 2008; Nguyen *et al.*, 2008; Tu *et al.*, 2008), only in a minority of the studies were concerned with urban ecosystems (Chen *et al.*, 2010;

Groffman *et al.*, 2006; Han *et al.*, 2009; Lorenz and Kandeler, 2005; Pouyat *et al.*, 2002, 2006; Takahashi *et al.*, 2008; Xu *et al.*, 2011, 2012), A little data of $\delta^{13}\text{C}$, $\delta^{15}\text{N}$ in surface soil is offered in understanding urban environments (Boeckx *et al.*, 2006; Norra *et al.*, 2005). In the context, the distribution and evolution of C, N and their isotopes are uncertain during the urbanization process.

Beginning from the 1980s, the process of urbanization in China has accelerated and urban area enlarged rapidly (Liu *et al.*, 2003; Xu *et al.*, 2011). This study conducts research on the distribution and evolution of organic carbon, total nitrogen and $\delta^{13}\text{C}$, $\delta^{15}\text{N}$ in soil profiles of different territories according to urbanized periods in Shanghai, the typical urbanized metropolitan in China. The study of C and N spatial distribution in urban territories extends to deeper soil profiles than any previous research and research of $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ in different urbanized territories is a new contribution to

urban soils also which may be useful to push forward C and N cycle research and provide a database for urban soil management.

MATERIALS AND METHODS

Study area: Shanghai, the largest economic city in China, extends between 30°41'-31°50' N latitude and 120°51'-121°45' E longitude with a total area of 6,341 km², in the east of Chinese Mainland (Fig. 1). The climate is generally subtropical monsoon with warm and humid climate. Monthly temperature ranges from 2.0-3.5°C in January to 26-28°C in July, with mean annual temperature of 14-17°C, respectively (She and Luo, 2007). Rainfall is also highly seasonal, with mean annual total of 1,000-1,500 mm, about 60-70% falling in spring and summer (She and Luo, 2007). The major soil types in this region include paddy soil, tidal soil, yellow brown soil and coastal saline soil (National Soil Survey Office, 1993).

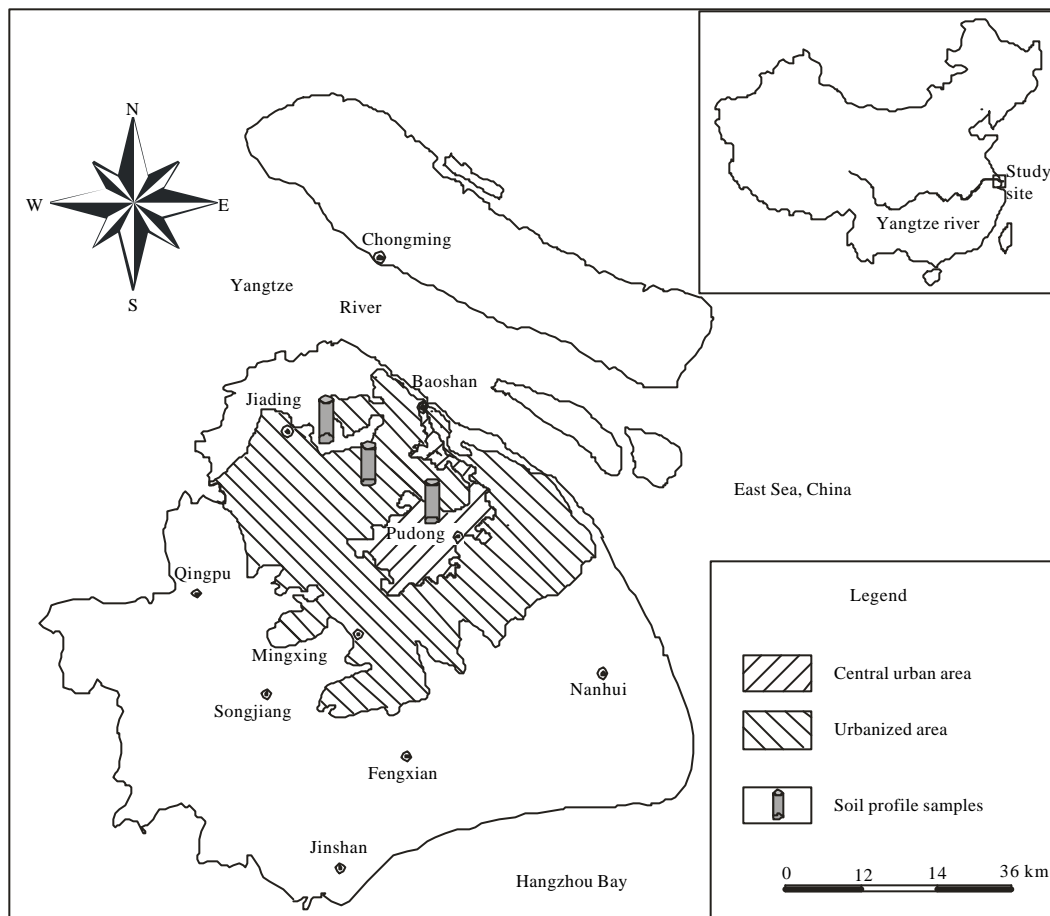


Fig. 1: Geographical map of Shanghai, China and sampling location (soil profiles)

Urbanization process in Shanghai has been quickening greatly since the 1980s. The urban area expanded from 193 km² in 1980 to 1,571 km² in 2005, or up from 3.05 to 24.77% in the past 25 years and the urban expansion circled the central city region according to the RS images (Xu *et al.*, 2012). With urban area expanding rapidly, vegetation types, soil ecological environment and soil management have changed. The spatial characteristics of soil organic carbon distribution and evolution in Shanghai, China showed significant differences occurred between the urban territories according to different urbanized periods. The soil organic carbon obviously accumulated in the central urban area while soil organic carbon density in the newly urbanized area decreased (Xu *et al.*, 2012).

Site sampling and methods: Urban area includes uncovered land (mostly urban green space such as park, forestry, etc.) and covered land (covered by building, road, etc). Urban green space system is a main type of urban landscape and plays a key role in maintaining and improving urban environment which generally become the primary object of study on C and N cycles (Svirejeva-Hopkins *et al.*, 2004; Grimm *et al.*, 2008; Lorenz and Lal, 2009). Urban green coverage in Shanghai was 289 km², or 37.00% in 2005 (SBS, 2007).

In order to indicate the characteristics of C, N cycles in urban soils, the urban area is divided into 3 regions according to urbanized periods which are central urban area, urbanized area and suburban, respectively. The central urban area is urbanized before the year 1980, urbanized area is urbanized territories in the period of 1980-2012 and suburban is defined as the region around urban area. Land use in urban area is mostly for construction uses and the land use in suburban area mostly agricultural uses. The urbanized territories are mainly transformed from agricultural land.

The 8 soil profiles (mostly 1-m depth) were located in the central urban area, urbanized area and suburban which included 3 green spaces in parks, 3 attached to urban road and 2 garden lands in suburban. Stratification samples were taken at 20 cm intervals in the soil profiles and all samples adding up to 128. The samples are prepared a list of tests after the process of drying, cleaning and milling. The contents of soil organic carbon and total nitrogen are

determined by Flash EA1112HT elementary analyzer and the abundance of ¹³C and ¹⁵N by MAT253 isotope mass spectrometry.

The $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ http://www.sciencedirect.com/science?_ob=ArticleURL&_udi=B6V67-4MM8BMY-1&_user=1915929&_coverDate=02%2F15%2F2007&_ali d=703152030&_rdoc=48&_fmt=full&_orig=search&_cdi =5807&_sort=d&_st=13&_docanchor=&_ct=187&_acc t=C000055340&_version=1&_urlVersion=0&_userid=19 15929&md5=240ad10f2430f94af25a386d72c6b72e-hit104 is calculated as follows:

$$\delta^{13}\text{C}(\%) = [(R_{\text{sample}}/R_{\text{standard}})-1] \times 1000, R = {}^{13}\text{C}/{}^{12}\text{C}$$

$$\delta^{15}\text{N}(\%) = [(R_{\text{sample}}/R_{\text{standard}})-1] \times 1000, R = {}^{15}\text{N}/{}^{14}\text{N}$$

where, R_{sample} stands for the abundance of test samples and R_{standard} stands for the abundance of standard samples. The $\delta^{13}\text{C}$ determining adopts international standards of PDB (Pee Dee Belemnite) which has detection limit of 0.1% and $\delta^{15}\text{N}$ determining adopts the standard of atmospheric nitrogen which has detection limit of 0.2%, respectively.

RESULTS AND DISCUSSION

Distribution of soil organic carbon, total nitrogen, $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ in urban soils: The soil organic carbon content shows a significant positive correlation at the 0.01 level with total nitrogen content in urban soils of Shanghai with Pearson correlation coefficient of 0.787 but which shows a significant negative correlation with $\delta^{13}\text{C}$ with Pearson correlation coefficient of -0.690. The total nitrogen content shows a weak correlation with $\delta^{15}\text{N}$ with Pearson correlation coefficient of -0.343. The mean content of organic carbon in urban soil profiles (1-m depth) is 9.07 g kg⁻¹, with the coefficient of variation (CV) of 0.53 and the mean content of total nitrogen is 0.90 g kg⁻¹, with the CV of 0.39 which shows obvious spatial variability (Table 1).

The mean $\delta^{13}\text{C}$ in urban soil profiles is -24.24%, with a range of -26.72~-21.16% and the mean $\delta^{15}\text{N}$ is 3.78%, with a range of 2.05~5.89%. The mean $\delta^{13}\text{C}$ in urban surface layer (0~20 cm) is -24.87%, with a range of

Table 1: Data analysis and sampling distribution of soil profiles (1-m depth) in Shanghai, China

Sampling site	$\delta^{13}\text{C}(\%)$		C (g kg ⁻¹)		$\delta^{15}\text{N}(\%)$		N (g kg ⁻¹)	
	Mean	Range	Mean	Range	Mean	Range	Mean	Range
Central Urban Area	-24.64	-26.04~-22.91	12.06	5.40~16.40	4.45	3.23~5.89	1.10	0.60~1.70
Urbanized Area	-23.97	-26.72~-21.16	7.08	4.30~15.80	3.33	2.05~4.92	0.77	0.50~1.80
Suburban	-23.21	-24.14~-22.39	4.88	1.90~9.00	3.96	1.71~6.86	0.68	0.40~1.20

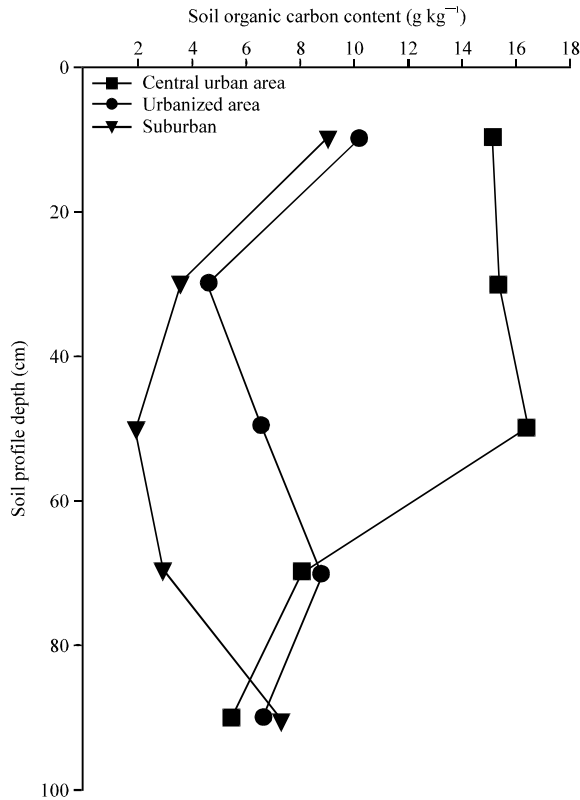


Fig. 2: Distribution of organic carbon in soil profiles of the central urban area, urbanized area and suburban in Shanghai, China

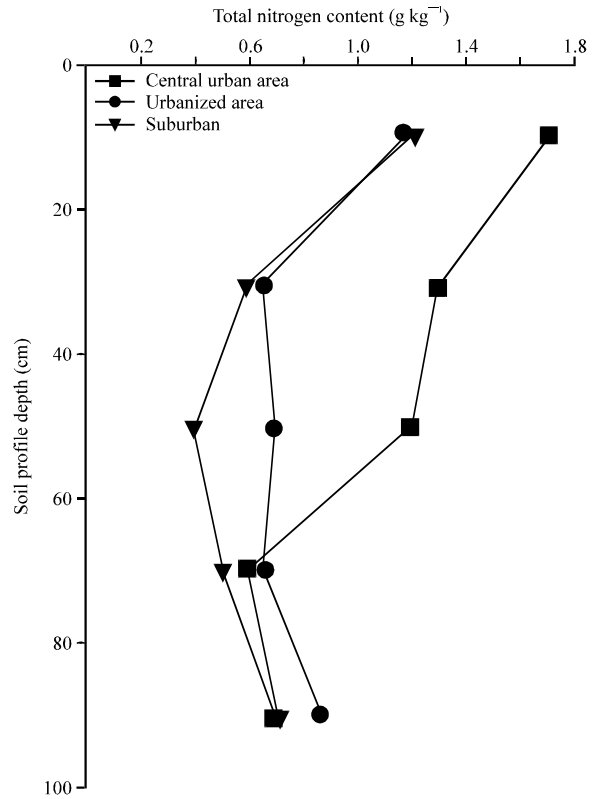


Fig. 3: Distribution of total nitrogen in soil profiles of the central urban area, urbanized area and suburban in Shanghai, China

-26.04~-22.76% and mean $\delta^{15}\text{N}$ is 3.83, with a range of 2.05~5.89%. The $\delta^{13}\text{C}$ values in the topsoil of Gent, Belgium, vary between -30.7 to -12.0‰, with an average of -27.2‰ and $\delta^{15}\text{N}$ between 1.5‰ to 11.7‰, with an average of 4.4‰, respectively (Boeckx *et al.*, 2006). The average $\delta^{13}\text{C}$ value in urban surface layer in this study is about 2‰ more enrichment and $\delta^{15}\text{N}$ less than 1‰ depletion.

Distribution of organic carbon, total nitrogen, $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ in soil profiles: The formation of soil profile is by a series of biochemical processes and the characteristics of organic carbon and total nitrogen in soil profiles are coupled with the sources of carbonaceous, nitrogenous material and soil profile development. The contents of organic carbon and total nitrogen generally decrease gradually with soil profile depth increasing. The distribution of C and N shows abrupt variation vertically in urban soils due to soil mixing, sealing and translocation resulting in burying of topsoil rich in C or N (Lorenz and Kandeler, 2005; Lorenz and Lal, 2009). The range of soil organic carbon and total nitrogen contents in urban soil profiles are 4.30~16.40 and 0.50~1.80 g kg⁻¹, more than the

counterpart of 1.90~9.00 and 0.40~1.20 g kg⁻¹ in suburban, respectively. The contents of soil organic carbon in the central urban area, urbanized area and suburban decrease with depth increasing while no evident variation is present in the upper layer of 0~60 cm in the central urban profiles (Fig. 2). The contents of total nitrogen decrease with depth increasing (Fig. 3). The contents of total nitrogen in the upper layer of the central urban area are higher than that in urbanized area and suburban, therefore the contents decline drastically in the soil profiles of central urban area.

The characteristics of $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ in soil profiles are mainly controlled by the mass sources and C, N-isotope fractional process (Benner *et al.*, 1987; Connin *et al.*, 2001; Ci *et al.*, 2007; Liu *et al.*, 2010; Tu *et al.*, 2008). Generally, plant species is an important affecting factor for $\delta^{13}\text{C}$ variation and $\delta^{13}\text{C}$ value in the surface layer depends on the $\delta^{13}\text{C}$ of vegetation. $\delta^{13}\text{C}$ value increases due to microbiological decompose of ^{12}C preferentially (Benner *et al.*, 1987; Connin *et al.*, 2001; Ci *et al.*, 2007; Tu *et al.*, 2008). Furthermore, since the Industrial Revolution of 1850, burning of massive fossil

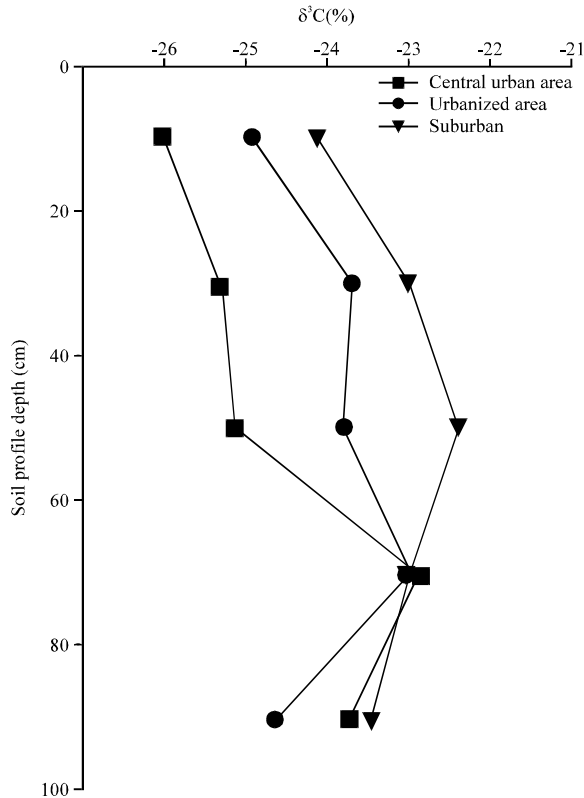


Fig. 4: Distribution of $\delta^{13}\text{C}$ in soil profiles of the central urban area, urbanized area and suburban in Shanghai, China

fuels with low ^{13}C leads to $\delta^{13}\text{C}$ of atmospheric CO_2 decrease which make $\delta^{13}\text{C}$ biomass decrease (Benner *et al.*, 1987; Connin *et al.*, 2001). This so-called “Suess effect” could be partly responsible for depletion of $\delta^{13}\text{C}$ isotope in surface layer. Therefore, the $\delta^{13}\text{C}$ value increases with depth increasing in soil profiles of long history with same plant community. Probably, urban area is affected by fossil fuel burning than the suburban. As a longer urbanized territory, urban soils in the central urban area accumulated more carbonaceous compounds with $\delta^{13}\text{C}$ depletion. This could explain the more depleted $\delta^{13}\text{C}$ values in the city centre.

The $\delta^{13}\text{C}$ values in the central urban area of Shanghai increase from -26.04 to -22.91% in upper 0~80 cm depth, those in the urbanized area from -24.68 to -22.91% and then decrease to -23.77 and 24.68%, respectively; The $\delta^{13}\text{C}$ values in the suburban show a more random distribution, increasing from -24.14 to -22.91% in upper 0~60 cm depth and then decrease to -23.48%, respectively (Fig. 4). The rising extent of $\delta^{13}\text{C}$ values in urban soils is $1.71 \pm 3.03\%$. The variation extent of $\delta^{13}\text{C}$ values reveal the degree of carbon isotopic fractionation effect in soil

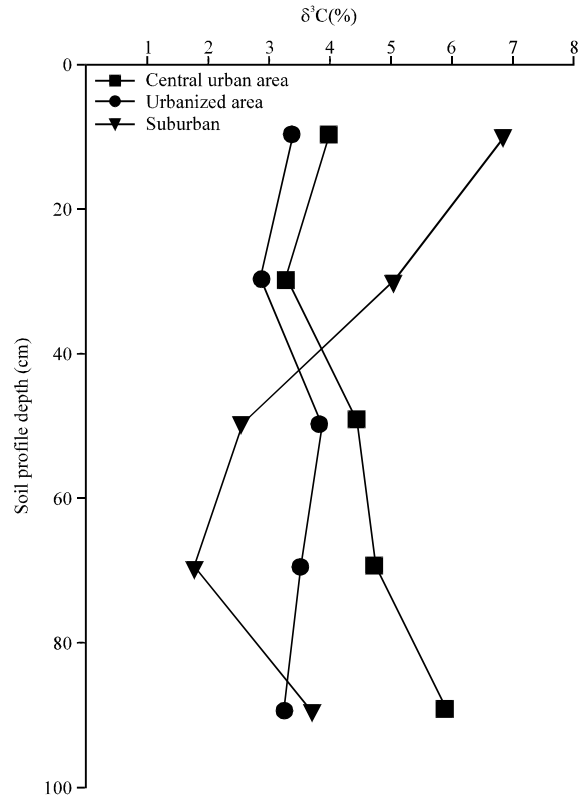


Fig. 5: Distribution of $\delta^{15}\text{N}$ in soil profiles of the central urban area, urbanized area and suburban in Shanghai, China

profiles which means larger rising extent of $\delta^{13}\text{C}$ values show stronger carbon isotopic fractionation effect and vice versa. The stronger carbon isotopic fractionation effect is appearing in the upper soil profiles of the central urban area due to the evident increase of $\delta^{13}\text{C}$ values.

In addition to being the source of atmospheric CO_2 , urban areas are also important sources for reactive N compounds. The major direct N sources in urban soils are N depositions from automobile engines, chemical fertilizers and urine and feces. The results show that significant differences of $\delta^{15}\text{N}$ occur in soil profiles between urban area and suburban (Fig. 5). The mean $\delta^{15}\text{N}$ value in the central urban area is 4.45%, with a range of 3.23~5.89% and that in the urbanized area is 3.33%, with a range of 2.05~4.92%. The $\delta^{15}\text{N}$ is at a higher value in the central urban area than the urbanized area; both reveal similar variation trends in soil profiles. The $\delta^{15}\text{N}$ is higher in the upper layer profiles of suburban.

C, N evolution during urbanization process: The components with carbon or nitrogen in urban soils may contain a mixture of natural substances and

anthropogenic organic particles (Lorenz and Lal, 2009). Thus, the C:N ratios vary widely in the ranges of 6.20~12.75 among urban soils in Shanghai. The C:N ratios in the central urban area, urbanized area and suburban are 11.07, 9.22 and 6.81, respectively. The C:N ratios decrease gradually along the central urban area-urbanized area-suburban gradient which means that the decomposition degree of soil organic matter increases gradually with urban land use duration extending and urban ecosystem evolving.

The contents of organic carbon in top layer (0~20 cm) in the central urban area, urbanized area and suburban are 13.80, 8.40 and 9.00 g kg⁻¹ and those of total nitrogen are 1.45, 0.98 and 1.20 g kg⁻¹, respectively. The soil organic carbon and total nitrogen obviously accumulate in the central urban area in surface layer while which contents in the urbanized area decrease which generally agrees with the previous results interrelated (Xu *et al.*, 2012). The mean values of $\delta^{13}\text{C}$ in the central urban area, urbanized area and suburban are -24.64, -23.97 and -23.21‰ and those of $\delta^{15}\text{N}$ are 4.45, 3.33 and 3.96‰, respectively (Table 1). The ¹⁵N isotope obviously accumulates in the central urban area while ¹³C is significantly depleted in the central and urbanized area. The characteristic distributions of soil organic carbon, total nitrogen content and $\delta^{13}\text{C}$, $\delta^{15}\text{N}$ occur along the central urban area-urbanized area-suburban gradient which reveals the evolution trend of carbon nitrogen cycle with urban land use duration extending and urban ecosystem evolving.

CONCLUSION

Urban regions are major sources of atmospheric CO₂ and reactive N compounds and urban soils is an important part of modern city environment (Svirejeva-Hopkins *et al.*, 2004; Grimm *et al.*, 2008; Lorenz and Lal, 2009). In this context, as urban areas dramatically increase globally, urban areas play a key role in the alteration of the global C and N biogeochemical cycles. In view of the increase in atmospheric CO₂ and reactive N concentrations as a result of urbanization, urban soils may become an important fields to sequester C and N (Svirejeva-Hopkins *et al.*, 2004; IPCC, 2007; Janzen, 2004; Lorenz and Lal, 2009). However, little biogeochemical information about urban soils is available as studies on urban ecosystems have been traditionally neglected by ecologists and soil scientists. Therefore, more studies on the effects of urbanization on C and N biogeochemical cycling are urgently needed.

This study represents a major advance in the use of soil organic carbon, total nitrogen, $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ in understanding urban soil C, N cycling in Shanghai, the

typical metropolitan of rapid urbanization development in the world. The results show that significant differences of soil organic carbon, total nitrogen content and $\delta^{13}\text{C}$, $\delta^{15}\text{N}$ occur at a range of spatial and temporal scales. Along the central urban area-urbanized area-suburban gradient, soil organic carbon, total nitrogen contents and C:N ratios decrease but $\delta^{13}\text{C}$ values increase. The soil organic carbon, total nitrogen and ¹⁵N obviously accumulate while ¹³C is significantly depleted in the central urban area. The organic carbon, total nitrogen contents decrease with soil profiles depth increasing. The $\delta^{13}\text{C}$ values increase from the top layer to a certain depth and then decrease. The carbon isotopic fractionation effects are more evident in the central urban area. The $\delta^{15}\text{N}$ reveal similar variation trends in urban soil profiles but the $\delta^{15}\text{N}$ is at a higher value in the central urban area than the urbanized area.

In general, not only the contents of soil organic carbon, total nitrogen contents but also $\delta^{13}\text{C}$, $\delta^{15}\text{N}$ values are correlated with urbanized period of the studied urban ecosystem. The distinct distributions of soil organic carbon, total nitrogen and their isotopes in different urbanized area indicate the evolution trend of C, N cycles with urban land use duration extending and urban ecosystem evolving.

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