

Comparison on soil organic carbon and nitrogen dynamics between urban impervious surfaces and vegetation

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18 **Abstract**

19 The soil carbon (C) and nitrogen (N) dynamic was usually considered as a minor change
20 based on a static process in the sealed soil under decades of impervious surface (IS).
21 However, no systematic studies concerning the soil organic carbon (SOC) and nitrogen
22 (SON) dynamic were conducted under IS in contrast with urban vegetation (i.e., forest,
23 grass). Here we utilized fractional distillation of soils as well as stable isotopic analysis to
24 examine soil C&N cycles after 20 and 30 years of vegetation planting and IS construction in
25 Guangzhou and Shenzhen, Pearl River Delta, China. Soil samples including bare soil (CK)
26 and four land use treatments were split into different chemical fractions. Then we analyzed
27 the C&N content, C/N ratio, $\delta^{13}\text{C}$, $\delta^{15}\text{N}$, C&N recalcitrant indices (RIC, RIN), and the mean
28 residence time (MRT). We found that the soil C&N increased first (i.e., 20 years) because of
29 enhanced C&N stocks in both labile (LP) and recalcitrant pool (RP), and then stabilized or
30 decreased (i.e., 30 years) with the IS ages in both cities. IS had a lower SOC decomposition
31 rate and thus resulted in the five to ten times longer MRT (about 259–465 years) than that in
32 vegetated soils (about 39–55 years). Moreover, the SOC&SON always showed a decoupling
33 relation in labile pools (i.e., LC and LN) in forests in both cities. The study showed the IS
34 remarkably altered the soil C&N dynamics, showing a great difference in SOC&SON
35 fractions composition and turnover compared with vegetation.

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37 *Keywords: Impervious surface; Urban forest; Grass; $\delta^{13}\text{C}$ & $\delta^{15}\text{N}$; SOC turnover*

1. Introduction

Urban expansion has changed the natural landscape by transforming the natural and/or semi-natural lands into impervious surface (IS), which are characterized by high spatiotemporal heterogeneity in both structure and function (Majidzadeh et al., 2017; Xu et al., 2018; Wang et al., 2018; Canedoli et al., 2020). By 2010, IS has spread to 600,000 km² all over the world (Liu et al., 2014; Lu et al., 2020). The conversion to the IS would result in high soil bulk densities, and a decrease in ecosystem service offered by native ecosystems, reduce plant species and finally disturb the terrestrial carbon (C) and nitrogen (N) cycles (Raciti et al., 2012; Chen et al., 2013; Majidzadeh et al., 2017). The construction of IS, possessed of more than 50% of soil organic carbon (SOC) reserves in urban (Yan et al., 2015), usually involved the removals of aboveground plant biomass and the top soil layer, thus causing soil compaction as well as sealings (Yan et al., 2015). Generally, soil sealing may immensely impede the energy transfer, exchanges of water, gases, material inputs and microbial activity between impervious-covered soils and atmosphere, and could substantially alter the biogeochemical properties as well as C&N processes of natural soils (Cambou et al., 2018; Lu et al., 2020).

The SOC was widely perceived as a central part of terrestrial ecosystem C pools (Xu et al., 2016; Xu et al., 2020). The conversions of land uses, as an important factor, substantially impact an equilibrium of soil C between new C additions and SOC loss, then result in sequestrations and carbon dioxide release in ecosystem (Yu et al., 2017). In urban forests and grasses, SOC&SON stocks represent the balances between continuous soil organic matter (SOM) increases derived from above- and below-ground additions of plant materials and microbial activity-driven soil C&N loss (Meng et al., 2016; Dou et al., 2017). By comparison, soil C and N beneath the IS which was sealed without vegetation cover, and certainly blocked the C&N exchange between soil and the atmosphere, was still at the initial stage (Zhang et

al., 2012; Xu et al., 2018).

Few studies concerning the C&N dynamics in IS soils were conducted owing to its inaccessibility (Yan et al., 2015; Majidzadeh et al., 2017). Moreover, a variety of factors might together determine the C&N stocks in the sealed soils (Yan et al., 2015; Majidzadeh et al., 2017). For one thing, the accumulative evidences proved that impervious-covered soils might be capable of storing abundant SOC, because of hindering the release of CO₂. For another, construction of IS may remove the topsoil with rich SOM (Yan et al., 2015), and substantially limit the input of organic matter (i.e., aboveground plant leaves and litter), eventually lowering the regional soil C reserves. For example, previous studies indicated a clear decline in soil C&N contents because of the topsoil removals and being sealed for long term (Yan et al., 2015; Majidzadeh et al., 2017; Lu et al., 2020). In any case, soils beneath IS might be remain used as habitats for microorganism as well as invertebrates, then provided spaces for microbial degradation and leaching, which could lead to a loss of soil C&N (Lehmann and Stahr, 2007). The above inconsistency might be as a result of multiple factors, and historical land-use, disturbance, climatic factors and sealed ages are likely to cause the differences in soil C&N reserves under IS land-use type (Majidzadeh et al., 2017).

Thus, the mechanisms controlling soil C dynamics under impervious soils sealed by asphalt cement with inaccessibility are much more unclear than those for vegetated soils. Therefore, quantifying and tracking SOM pools beneath IS can be difficult, for the SOM was composed of labile pool (LP) and recalcitrant pool (RP) based on various microbial degradation and turnovers (Dou et al., 2018; Jia et al., 2019). Consequently, the mean residence time (MRT) of SOC for these SOM fractions could be distinct substantially due to discrepancy in physicochemical stability (Rovira and Vallejo, 2002; Dou et al., 2013). Generally, variations in new additions of C into soils would easily affect the labile fractions which could be sensitive to external environment changes and turnover rapidly. By contrast,

the recalcitrant fractions are less active and occupy a great proportion of soil C stocks (Dou et al., 2018; Sainepo et al., 2018). In addition, a mean $\delta^{13}\text{C}$ in organic soils reveals the $\delta^{13}\text{C}$ signals derived from plant biomass inputs (Van Kessel et al., 2000; Throop et al., 2013; Li et al., 2021). The conversion of land use types like impervious- and vegetation-covered (forests, grasses) types means the dramatic transformation of vegetation types, hence current SOC inputs and its turnover could be estimated utilizing ^{13}C stable isotope technique under the changes in $\delta^{13}\text{C}$ of SOM originated from plant residuals (Van Kessel et al., 2000; Cheng et al., 2013). Besides, those $\delta^{15}\text{N}$ values could be used in the study concerning the process for N cycles, which would be influenced by land use conversions (Marin-Spiotta et al., 2009; Dou et al., 2013). For example, forest plantations have been widely presumed to reduce both inorganic N contents and net N mineralization, leading to a low ^{15}N value in forest soils (Li et al., 2014). Thus, a $\delta^{15}\text{N}$ value has been utilized as a quota to evaluate the SOM decomposition level (Cheng et al., 2013). For urban ecosystem, the soils with a certain proportion of isotope constitution originated from current plant materials being sealed (i.e. incompletely decomposed plant materials beneath IS) or the losses of C&N owing to decomposition and leaching to a certain extent, enables researcher to concurrently track the depletions or enrichments of $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ after the sealing of soils, and then the relative soil turnover rates as well as MRT of SOC pools can be estimated under IS. Thus, SOM fractionation together with the isotope technique with natural abundance have been acknowledged as a feasible approach for estimating SOM dynamics under decades of sealed soils in urban ecosystems.

The Pearl River Delta (PRD), with the urbanization ratio raised from 70% during 1990 to 85% in 2015, is a critical urban agglomeration in China, which has gone through a great change in land-covers and landscape pattern after carrying out the reform and opening up policy (Liu et al., 2019). Thus, massive IS areas set up, but little has been focused on quantifying SOC dynamics beneath IS in cities of PRD region (Bae and Ryu, 2015). In this

paper, owing to the highest urbanization in Guangzhou and Shenzhen within PRD, the impervious soils inside and outside of urban parks in contrast to vegetation-covered area (i.e., forest, grasses) were selected in two cities to investigate the SOM pools (to 20 cm depth). The study has far-reaching implications for land-use changes, especially in fast urbanization region globally. In the paper, we gave the hypothesis as follows: the currently aboveground inputs of vegetation biomass were zero when the soil was sealed under IS. However, there was still a certain amount of residual additions derived from incompletely decomposed plant materials beneath the IS, as a potential plant C source to supply soil C pool. Thus, the alterations in soil $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ were likely to depend on these incompletely decomposed residuals beneath IS. The purposes of the present research are followed as: how urban IS has potentially altered (1) dynamics of the SOC&SON pools; and (2) current C additions, turnover rates and MRT of the native SOM fractions; and (3) utilizing the results to evaluate the future impact on C&N reserves under IS soils in urban ecosystem.

2. Materials and methods

2.1. Site description

PRD region (21.29°N–23.93°N, 111.99°E–115.42°E) locates in the south of Guangdong, China, which is mainly formed by alluvial deposits (Liu et al., 2019). The PRD covers an area of 5.77×10^6 ha of mountains, hills, croplands, plains as well as cities. Plain is located at center of PRD, while mountain and hill are in surrounding regions (Wang et al., 2019). Climatic type of PRD belongs to the subtropics. The dominant plant species is subtropical evergreen broadleaf monsoon forest (Xu et al., 2018). Annual precipitation ranges from 1600–2000 mm, and 80 % occurs between April and September, whereas the average annual temperature during daytime exceeds 20°C. The total sunshine days are 79–92 each year. Laterite soils predominate PRD area and are formed from the sandy shales of southern part of

China, which belongs to the classification of fine loamy, hyperthermic, and acidic Udic Cambisol in Chinese Soil Taxonomy (Wang et al., 2019). Rapid population growth and urbanization in the PRD area have caused dramatic land use changes, which have had tremendous influences on terrestrial C cycles. Thus, Guangzhou and Shenzhen, as the most typical cities for rapid urban expansion in the PRD area, were selected to investigate the SOM dynamics in response to decades of IS.

The study was conducted in impervious-covered soils inside and outside of urban parks in contrast to adjacent vegetation-covered area (i.e., forest, grasses) at South China Botanical Garden (SCBG), Chinese Academy of Sciences in Guangzhou, and the Lotus Hill Park (LHP) in Shenzhen, lying at the center of the PRD. The SCBG was established in 1929 with the tourist area of 333 ha, whereas LHP was built in 1992 with the total area of 194 ha. The two grand and comprehensive parks as a typical representative were selected because that there existed (1) no excessive human disturbance due to regulations on social protection; (2) clear land use history, horticulture measure application for various land covers; (3) containing various land use types such as forests and grasses, helping to reveal the ecological effects under decades of IS. A chronosequence research for IS (i.e., 20 yr, 30 yr) is imperative to clarify the knowledge gaps. The experiment included five treatments in Guangzhou: (1) bare soil, i.e., open areas with no inputs of organic matter from plant debris for decades, CK1; (2) 20 years forests, F1-20; (3) 20 years grasses, G1-20; (4) 20 years impervious surface, IS1-20; (5) 30 years impervious surface, IS1-30. Notably, the 30-yr IS was difficult to find in the two parks and thus we found the near one was 1-2 km away from SCBG and LHP. Moreover, no suitable sampling plot for 20-yr IS was found around the LHP in Shenzhen and therefore four treatments were contained: (1) bare soil, CK2; (2) 20 years forests, F2-20; (3) 20 years grasses, G2-20; (4) 30 years impervious surface, IS2-30. 30-yr ago, an extensive uncultivated land was converted to IS (i.e., IS-30) adjacent to parks. In addition, after the park/botanical

garden was established, the forests and grasses were artificially planted under uncultivated lands. Thus, 20-yr forest plantations dominated by *Schima superba* Gardn accompanied with *Memecylon nigrescens*, *Psychotria rubra* and *Evodia lepta* and a 20-yr grass plantation dominated by mixed planting of herbs (*Alternanthera philoxeroides*, *Cynodon dactylon*, and *Lindernia crustacea*) were selected in SCBG, whereas a forest plantation dominated by *Roystonea regia* and a grass plantation dominated by *Wedelia chinensis* in LHP were used as a comparative study. The IS represented the road surface that was established by a mixture of sand, asphalt and cement at the sampling plots. The IS sample plots were selected under the damaged road surface under reconstruction in LHP, whereas the soil samplings were collected using an electric drill and soil corer under the abandoned pavement area for reconstruction in SCBG. According to our investigation and survey, the top soil (about 0-10 cm) was removed during the road construction because the surface ground contained litter, debris and gravels. Moreover, the experimental plots such as forests and grasses were not fertilized and pruned and grew naturally since cultivation.

2.2. Sample collection

The completely randomized design of the experiment was carried out with 3 randomly selected experimental sites. The interval between each site (i.e., containing 20-yr forests and grasses) was about 1-2 km. Each land use type was approximately 400 m² size (20 m×20 m). In August 2017, 3 quadrats (2 m×2 m) were randomly selected close to the rhizospheric areas in each land type (i.e., forests and grasses) and the distance between each quadrat was about 5 m. Meanwhile, we chose the bare soil (CK) adjacent to other treatment plots as the control (i.e., CK, bare soil in radius >1 m, making sure that there was no organic matter input from vegetation for decades according to the investigation from garden staff and field observation). Soils from sampling quadrats were sampled in surface 20 cm depth by a 2.5 cm radius soil

core sampling kits. Systematic censuses for plant community and soils were carried out to guarantee the comparabilities under different land cover types (i.e., similarities for soil type and texture, topographic features and land use history) for a sampling quadrat in each park/garden. Aboveground plant such as leaves and litter were sampled in every quadrat. Belowground plant sample of roots were collected inside a 30×30 cm quadrat in surface 0-30 cm soils. The cleaned leaves, litter and roots were dried in the oven to an unchanged biomass at 60°C and were further weighed in laboratory. The pH and density of bulk soils were determined by common methods conducted for each land cover according to Dou et al. (2016a, b). Afterward manually removing big roots and rocks, then soils were open-air drying.

2.3. Soil chemical fractionation

Acidolysis process consulted by Rovira and Vallejo (2002) was used for soil fractionations such as soil labile and recalcitrant fractions. About dekagram of air-dried soils was processed using 1 mol/L hydrochloric acid at approximately 25°C for 24h with the purpose of removing the inorganic C. Then, unhydrolyzed residues were defined as SOM pools. Using the 20 ml of 2.5 mol/L sulfuric acid hydrolyzed about 0.5 g of the SOM samples at 105 °C for 30 min in closed Pyrex tubes. Hydrolyzate was retrieved after being centrifuged and filtrated. Washings were mixed in previous hydrolyzate after the residues were rinsed using 20 ml of deionized water. Hydrolyzates were described as active pools (1). Then the residues were performed a stoving at 65 °C. Remainings were hydrolyzed using 2 ml of 13 mol/L sulfuric acid at approximately 25°C overnight with continuously shakings. The next step is to dilute the sulphuric acid to 1 mol/L, then hydrolyzing the samples at 105 °C for 3 hours under periodic shakings. Hydrolyzate was retrieved after centrifugation and filtration. Washings were moved to the hydrolyzate after the remains were rinsed using 20 ml of water.

213 The hydrolyzates were regarded as active pools (2). The total labile pools were obtained from
 214 the sum of active pools (1) and active pools (2). The residues were moved to a crucible after
 215 it was rinsed twice with water, and stoving at 65 °C. The fractions were regarded as the
 216 recalcitrant pools.

217 Recalcitrant indexes of C and N (i.e., RIC, RIN) were estimated as follows (Rovira and
 218 Vallejo, 2002):

$$219 \quad RIC (\%) = (non-hydrolyzed\ C / total\ SOC) \times 100 \quad (1)$$

$$220 \quad RIN (\%) = (non-hydrolyzed\ N / total\ SON) \times 100 \quad (2)$$

221

222 2.4. SOC&SON content, Natural abundance isotope analyses for C&N

223 After the oven-dry treatment, plants and soil samples were levigated and then passed
 224 through 20-mesh sieve (Dou et al., 2016a, b). Then, SOC, SON, $\delta^{13}C$ as well as $\delta^{15}N$ values in
 225 plant leaves, roots and litter and soil fractions were determined by the isotope ratio mass
 226 spectrometer (IsoPrime 100, IsoPrime, Manchester, UK). The SOC&SON storage were
 227 estimated from area-weighted, rectifying for the depths and densities of soils. Isotopic ratios
 228 of C&N in the plant-derived residues and soil fractions were presented as follows:

$$229 \quad \delta^h X = \left[\frac{\left(\frac{X^h}{X^l} \right)_{sample}}{\left(\frac{X^h}{X^l} \right)_{standard}} - 1 \right] \times 1000 \quad (3)$$

230 Specifically, X represents C or N, h refers to the heavy isotopes, l represents the light
 231 isotopes. The isotopic ratio of C (^{13}C) reflects the comparative value of PeeDee Belemnite
 232 Standard ($\delta^{13}C = 0.0112372\%$), while N stable isotopic ratio (^{15}N) are presented as the
 233 comparative value of atmosphere ($\delta^{15}N = 0.0\%$). Standard samples are measured for each 10
 234 samplings; and the accuracy of the measurement is $\pm 0.13\%$ for $\delta^{13}C$ and $\pm 0.21\%$ for $\delta^{15}N$,
 235 respectively.

Concerning various land cover plots (i.e., IS, forests, grasses), the $\delta^{13}\text{C}$ values were utilized to estimate a percentage of current C (f_{cur} , that is, the plant-derived current C residue in vegetation-covered soils, or the SOC originated from incompletely decomposed plant residual in humus horizon beneath IS, if there indeed existed new addition in impervious-covered soils) and of aged C ($f_{aged}=1-f_{cur}$, C in soils before land cover changes) as follows (Del Galdo et al., 2003; Rong et al., 2020):

$$f_{cur} = \frac{\delta_{cur} - \delta_{aged}}{\delta_{veg} - \delta_{aged}} \times 100\% \quad (4)$$

Specifically, δ_{cur} represents current $\delta^{13}\text{C}$ values for SOC pool under IS, forests and grasses, δ_{aged} refers to $\delta^{13}\text{C}$ data of SOC from control (CK), on the basis of the presuming there is little change of residues return under CK; where δ_{veg} refers to $\delta^{13}\text{C}$ data of mixture from leaves, litter and roots of vegetation under forest and grass plots. Besides, because of being sealed for decades and no aboveground addition into the soil under IS, we presumed that the setting value of δ_{veg} was 0‰ with the purpose of approximatively calculating the relative turnover rate of SOC pool under IS.

Decomposition rate constants (k) of an aged SOC (that is, SOC previous to land use conversion) from SOM was calculated according to Cheng et al (2013):

$$\ln(f_{aged}) = -kt \quad (5)$$

where $f_{aged} = (1 - f_{cur})$ represented the percentage of aged SOC, k referred to the relative decay rate constants for aged SOC, t referred to the period for land-cover conversion (i.e., for 20yr, 30yr).

The mean residence time (MRT) of SOC under different land covers was estimated according to the following formula:

$$MRT = 1/k \quad (6)$$

259

260 2.5. statistical analysis

261 The C&N stores, $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ in soils, the current SOC return and aged SOC
262 decomposition rates, RIC&RIN, and C/N ratio in SOM and MRT were determined by
263 averaging the replications of the plots under specific land covers. Gaussian distributions and
264 homogeneity of variance were checked for all variables before further analyses. An analysis
265 of variance (ANOVA) was conducted to examine the discrepancies in SOC&SON, the $\delta^{13}\text{C}$
266 and $\delta^{15}\text{N}$ values, the C/N ratio, the f_{cur} , k and MRT between different land uses ($P = 0.05$; 0-
267 20 cm). ANOVA of multi-comparisons were performed to verify influences between different
268 types of land uses on pH, bulk density, C&N in whole soil, SOC&SON level, C/N ratios, the
269 $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ data, RIC&RIN, f_{cur} , k as well as MRT of the SOM pools (LSD; $P = 0.05$).
270 The statistic was conducted using the software of OriginPro (v 8.0) and SPSS (v 16.0).

271

272 3. Results

273 3.1. Physicochemical properties of soils, isotopic characteristic of plants

274 On the whole, there was no significant difference in soil C/N ratios ($P > 0.05$; Table 1)
275 among the urban land uses. The soil bulk density and pH were the highest in IS soils among
276 all the land uses in Guangzhou and Shenzhen (Table 1). The $\delta^{13}\text{C}$ of leaves, litter and roots
277 varied from -27.36 to -34.65 ‰ under forests in two cities and under grasses in LHP,
278 tallying with the feature of C_3 plant, while the $\delta^{13}\text{C}$ value of leaves and roots was -19.65 ‰
279 under grasses in SCBG, most likely representing the characteristic of mixed C_3 and C_4 plants
280 (Table 2). The $\delta^{15}\text{N}$ values of plant were from 1.04 to 5.18 ‰ in forests, which were more
281 enriched than those in grasses with averaged $\delta^{15}\text{N}$ values from -3.04 to 0.57 ‰ (Table 2).
282 Clearly, the greater C:N ratios were found in root than those in leaf and litter under the

forests.

3.2. Natural abundance of C&N stable isotopes in SOM

The IS markedly altered the abundance of stable isotopes for the soil C and N ($P < 0.05$), which eventually enriched the $\delta^{13}\text{C}$ with the range from -25.98‰ to -22.87‰ in SOM pools in both cities as well as from -26.16‰ to -25.57‰ in RP in SCBG, but depleted $\delta^{15}\text{N}$ with the range from 2.42‰ to 4.92‰ in SOM pools as well as from -0.75‰ to 2.80‰ in RP across the IS soils compared with the bare soils (Table 3). By contrast, urban vegetations such as forests and grasses depleted the $\delta^{13}\text{C}$ in both SOM pools and RP in the two cities except for that in 20-yr grass soils in SCBG of Guangzhou, which was markedly more enriched in $\delta^{13}\text{C}$ than that in bare soils (Table 3). Meanwhile, the lower $\delta^{15}\text{N}$ values occurred in IS soils than that in vegetated soils on the whole.

3.3. SOC&SON stocks

Urban land use for decades significantly altered the soil C&N stocks and C/N ratio ($P < 0.001$; Table 4). Clearly, 20-yr IS significantly increased the C&N stocks compared with CK, while minor changes even substantial decreases in C&N of SOMP and RP occurred under 30-yr IS (Table 4; Fig. 1). Forests had greater SOC&SON and RC&RN contents and stocks than those in grasses in SCBG of Guangzhou, while the opposite trend of C&N in SOMP and RP was showed in the LHP of Shenzhen (Table 4; Fig. 1). By contrast, the greater LC stocks were found in forests than those in grasses, while the substantially more LN reserves occurred in grasses compared with forests in both cities (Fig. 1). Overall, the largest C&N stored in vegetated soils across all the land covers while the least C&N occurred in IS soils, especially under 30-yr IS.

3.4. SOM turnover and the mean residence time (MRT), RIC and RIN

Clearly, the IS resulted in a less soil C input as well as a decreased C decomposition rate (k) relative to forest and grasses, thus markedly slowing the SOC turnover rates ($P < 0.05$; Fig. 2). Accordingly, the substantially longer residence time of SOC occurred in IS soils (i.e., 259–465 years) compared with vegetated soils (i.e., 39–55 years) in both cities. Meanwhile, there was a longer SOC residence time in 20-yr IS soils than that in 30-yr IS soils in SCBG of Guangzhou (Fig. 2).

The land use conversions remarkably changed the RN proportion in SCBG ($P < 0.001$) as well as the RC proportion in LHP ($P = 0.001$), resulting in different RIC and RIN values under various land use covers (Fig. 3). Moreover, the forest soil had the highest RIN (75.39 %), followed by bare soil (52.36 %) and 30-yr IS soil (48.16 %), then by 20-yr IS soil (43.67 %), while the grass soil had the lowest RIN (16.09 %) in SCBG of Guangzhou. Moreover, the highest RIC was found in grass soil (88.14 %) and 30-yr IS soil (78.13%), and followed by bare soil (64.76%) and forest soil (60.71 %) in LHP of Shenzhen (Fig. 3).

4. Discussion

4.1. The C&N dynamics in IS soils (IS-20 vs. IS-30)

In our study, the urban land use conversions such as IS notably altered the soil C&N dynamics and therefore resulted in different SOC&SON stabilities and turnover rates under the impervious-covered and vegetated soils. The higher the C&N content and stock of total SOM pools, recalcitrant and labile pools were found under 20-yr IS in contrast with bare soils, while 30-yr IS caused a minor change of SOC&SON in SCBG of Guangzhou even with a remarkable reduction in LHP of Shenzhen (Table 4; Fig. 1). Moreover, the SOC stocks at 0–20 cm soil were about 0.95–2.69 kg m⁻² beneath 20–30 yr IS in two cities, being similar to the previous researches (Wei et al., 2014; Cambou et al., 2018). However, the results are not

consistent with the previously increasing evidences that soil C&N might have a significant decrease after soil sealing such as IS (Raciti et al., 2012; Wei et al., 2014; Cambou et al., 2018; Lu et al., 2020). For instance, Wei et al. (2014) showed that SOC was markedly lower in the sealed soils (2.35 kg m^{-2} for 0–20 cm) than that in bare soils (4.52 kg m^{-2} ; $P < 0.05$). Likewise, Cambou et al. (2018) indicated that SOC stocks were lower in sealed soils compared with bare soils in New York and Paris. Previous studies were supported by the fact that, in some cases the construction of IS might be involved in the topsoil removals where was rich in SOM, and concurrently impeded organic material additions into the soils (Cambou et al., 2018); in other cases, the soil beneath IS might serve as habitats for decomposer biota, still existing soil degradation and leaching process, which would finally cause a certain amount of loss (Lehmann and Stahr, 2007; Majidzadeh et al., 2017). Besides, other research showed that the soil C contents were reducing beneath IS for the first 50 years, and then increased afterward (Majidzadeh et al., 2017), which was also inconsistent with our results. By contrast, our results emphasized a relationship between the age of soil sealing and SOC&SON stocks, and indicated the soil C&N increased first and then stabilized or decreased with the IS ages. The controversy could be explained that humus layer might still exist in the sealed soils, containing a massive incompletely decomposed woody and/or herbaceous material, which eventually caused the abundant organic matter inputs and thus enhanced soil C&N in the present study. After all, IS soils were capable of continuing to provide spaces for rooting (Lehmann and Stahr, 2007), proving the existence for plant residual. Moreover, a slower SOC decomposition rate was found in IS plots than in forest and grasses, which was more conducive to increased SOC accumulation (Fig. 2), as it was sealed for decades. In short, continuous inputs in short-term to a certain extent and deceleration of turnover rates might eventually result in the increment of soil C&N under IS (Table 4 and Fig. 2).

Furthermore, the higher SOC&SON stocks of RP occurred under 20-yr IS, but that didn't occur under 30-yr IS (Fig.1). In general, the recalcitrant pool was regarded as a considerable C reservoir with the stable composition, and was not sensitive to changes in external environment (Dou et al., 2018). Thus, we could conclude that the IS-20 had the great potentials for C sequestration due to the enhanced SOC and RC, while the IS-30 was not capable of retaining soil C in urban ecosystem in both cities. By contrast, it is well known that the soil C&N stocks will definitely decrease when no plant material inputs into soils but ongoing microbial decomposition continued. Thus, the 30-yr IS significantly resulted in the loss or no net changes in SOM and its fractions in both cities under the PRD region (Fig. 2), probably because that the plant materials sealed were completely decomposed beneath IS soils over time and thus there was little leftover input into the soil.

In general, the IS could severely alter soil physicochemical properties such as bulk density, temperature, and moisture (Yan et al., 2015; Majidzadeh et al., 2017), which might be due to the topsoil removals, the original disturbances and/or long-range soil sealing. Indeed, we found the IS led to the highest pH and bulk density (Table 1). Due to high density, little change in RC&RN content but remarkable decreases in RC&RN storage occurred in LHP of Shenzhen (Table 4 and Fig. 1). Non-hydrolyzable SOM is acknowledged as a characteristic for the recalcitrant fractions, which is usually used for estimating the inactive SOM pools (Cheng et al., 2013). Analysis from the recalcitrant index indicated that the IS didn't alter the recalcitrant indices of SOC&SON except for markedly increased RIC in contrast to CK under 30-yr IS in LHP (Fig. 3). However, the study using enzyme assay in soils suggested that recalcitrant compounds dominated the SOM pools beneath IS plots (Raciti et al., 2012). Our study showed that no significant difference was found in C&N between LP and RP in 20–30 year IS plots in SCBG of Guangzhou, while the C&N in RP was substantially greater than that in LP in LHP of Shenzhen (Fig. 1). Based on the above, we could draw the conclusion

that on the whole IS plots could not result in the increased recalcitrant proportions of C&N induced by vegetation owing to soil sealing in short-term, but it might have an increment when the labile C was probably decomposed gradually in long-term (i.e., IS-30; Fig. 3). Indeed, soil fractions analysis showed that the decreased SOC&SON contents were mainly because of markedly reduced C&N content in labile pools under the 30-yr IS (Table 4). Moreover, the increased SOC&SON was attributed to the enhanced C&N stocks in both recalcitrant and labile pools under the 20-yr IS (Table 4; Fig. 1).

Nevertheless, IS in urban ecosystem affected the way as to how soil C and N were stabilized, retained and decomposed by shifts in active and recalcitrant compositions of SOC&SON as well as the microbial processes (Majidzadeh et al., 2018; Lu et al., 2020), probably eventually leading to the losses of soil C&N stocks in future and certain negative consequences for C&N dynamics, and even offsetting the C&N sequestration under other urban landscapes (Raciti et al., 2012; Wei et al., 2014).

4.2. Comparisons for SOC&SON in IS and vegetated soils

Urban plants are generally recognized as a considerable soil C sink (Velasco et al., 2016). Therefore, assessing and comparing the soil C potentials for sequestration between urban green space and IS, is playing a vital role in sustainable C management and evaluations in urban ecosystem. Altogether, we found the soil total C&N, SOC&SON contents and stocks were larger in vegetated soils than that in IS soils, especially for forests (Table 1; Fig. 1), though the faster turnover rates occurred in forest and grass soils in contrast to IS soils (Fig. 2). This finding was supported by the evidence that the averaged soil C&N contents (0–10 cm) were substantially lower under the IS in house compared to urban grasses (Majidzadeh et al., 2017). Usually, additions of labile C substrate into the soils were capable of prominently arousing the SOM decompositions in vegetation plots (Fig. 2; Zhu and Cheng, 2012). Thus,

our results were well illustrated by the fact that the effects resulted from rapid decomposition rate were overshadowed by the impacts derived from a massive C inputs of plant biomass with high C/N ratios in SOM pool under forests and grasses, therefore resulting in the greater C&N in vegetation plots in contrast to the IS plots (Table 2; Table 4). Besides, the IS system represents the removals of the topsoil with rich SOM, then the soil is sealed using the constructing materials with devoid C&N, and thus little plant material transformed into current C addition into IS soils, which would eventually lead to the relatively less C&N (Table 4; Majidzadeh et al., 2017, 2018; Lu et al., 2020). As expected, we found the soils under IS had a slower turnover rate and could significantly prolong the mean residence time (MRT) of C in SOM pools (Fig. 2), leading to five to ten times longer (about 259–465 years) than that in vegetated soils (about 39–55 years). Increases in litter production may accelerate C cycling (Fang et al., 2015) and thus reduced inputs under IS probably lead to the slow C decomposition rate.

Analysis from the soil fractionation found that the greatest soil C&N contents and stocks occurred in forests (4726.68 g C m⁻², 194.90 g N m⁻²) in SCBG mainly owing to RC, RN and LC, while largest C&N occurred in grass plots (6086.64 g C m⁻², 422.59 g N m⁻²) in LHP primarily due to the enhanced C&N in RP (Table 4; Fig. 1). The results suggested an obvious space-time heterogeneity and these inconsistencies might be attributed to multiple factors, such as land cover history, disturbances, microclimate conditions, types of plants and soil nutrient status. Here we found that the *Roystonea regia* were the dominant species under forests in LHP of Shenzhen, which had a lower soil C&N than that in grasses. The result was similar to the previous studies that the lower soil C and SOM storage was usually found under palm plants compared with natural forest and grasses (Fujii et al., 2020; Hairiah et al., 2020; Málaga et al., 2020). Generally, *Roystonea regia* primarily grew in sandy soil with rich carbonate and thus little difference in total C&N but dramatic distinction in SOC&SON were

found (Fig. 1). Moreover, the above result was explained by the fact that the leaves of palm plants were usually low-quality and consequently very difficult to decompose owing to high structural compound in leaf (Chellaiah et al., 2018). In addition, no obvious change was found in RIC (60.71%) between forest and CK (64.76%; Fig. 3) in LHP, further indicating that palm plant such as *Roystonea regia* didn't have a remarkable C sequestration capacity and potential. Besides, the lowest stock of soil labile N was found in forest and 30-yr IS in both cities (Fig. 1). This result further confirmed that our previous research in the same experimental site which demonstrated a decoupled C&N dynamic in soil labile pool under forests. It might be caused by increased N use of plants and/or leaching of labile N in SOM pools (Montane et al., 2007) and the fact that the plant materials with the greater C/N ratios (i.e., lower N content) might offset an abundant residue addition into forest soils (Table 2). Accordingly, decades for forests eventually resulted in the highest RN proportion (i.e., RIN, 75.39%) in SCBG of Guangzhou (Fig. 3). Based on above analysis, we could draw the conclusion that the vegetated soils had a greater storage capacity for C&N than IS soils, even with the rapid decay rates, while the IS extended the turnover period of SOC pools.

5. Conclusions

By and large, the urban IS had severely altered soil physicochemical properties and C&N dynamics (i.e., stabilization, turnover) in ecosystem. We found the soil C&N increased first (i.e., 20 years) because of enhanced C&N stocks in both LP and RP, and then stabilized or decreased (i.e., 30 years) with the IS ages in both cities, emphasizing a relationship between the age of soil sealing and soil C&N stocks. The results could be explained that a certain amount of incompletely decomposed woody and herbaceous materials most likely still existed in the short term and meanwhile IS had a slower SOC decomposition rate owing to being sealed, but were gradually depleted with time until 30 years of sealing. Accordingly,

analysis from the recalcitrant index indicated that the increased RIC in contrast to CK under 30-yr IS in LHP, because that it might have an increment when the labile C was probably decomposed gradually in long-term. The SOC&SON stock was larger in vegetated soil than that in IS soil, indicating that forests and grasses had a greater storage capacity for C&N than IS, even with the rapid decay rates. Moreover, the IS was capable of extending the turnover period of SOC pools. Besides, our study emphasized that the soil C&N stocks were varied with strong heterogeneity depending on tree species under forest in comparison with grasses in two cities. However, the SOC&SON, whether in Guangzhou or Shenzhen, always showed a decoupling relation in labile pools (i.e., LC and LN) in forests. In conclusion, we found IS for decades remarkably altered the soil C&N dynamics under the sealed condition in PRD region, showing a different composition for C&N fractions and a difference in SOC turnover in contrast to vegetation. Moreover, estimating C cycles and potentials in soil ecosystem because of rapid urbanization is urgently demanded with the intention of estimating the influences on terrestrial ecosystems in the long term. Accurate evaluation of soil C&N dynamics following the land use conversions, is essential to explore the impacts from human activities in response to the global C balance, then to take valid management strategies in urban ecosystem.

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609 Figure legends
610

611 **Fig. 1** Responses of SOC&SON, RC&RN, LC&LN stocks (mean \pm SD, n = 9) to land use
612 conversions at 0-20 cm depth layer in Guangzhou (a, b) and Shenzhen (c, d). Result
613 accompanying with different letters above the columns represents significantly different ($P <$
614 0.05) between land covers.

615 **Fig. 2** Current C input (f_{new}) (a, b), decay rate (k , yr⁻¹) of aged C (c, d) and the mean residence
616 time (MRT) of C (e, f) (mean \pm SD, n=9) in SOM pools following land use conversions in
617 Guangzhou and Shenzhen. Result accompanying with different letters above the columns
618 represents significantly different ($P < 0.05$) between land covers.

619 **Fig. 3** Variations in recalcitrance indices for SOC (RIC), SON (RIN) following land use
620 conversions at 0-20 cm depth layer in Guangzhou (a, b) and Shenzhen (c, d) (mean \pm SD, n =
621 9). Result accompanying with different letters above the columns represents significantly
622 different ($P < 0.05$) between land covers.

623

624 **Table 1** Mean values ($n = 9$) for the soil properties (0–20 cm) under different land covers.
625 Mean \pm SD with different letters for a variable represent significant differences ($P < 0.05$).
626 BD: bulk density; CK: bare soil; F: forest; G: grass; IS: impervious surface; 20: 20 years; 30:
627 30 years; 1: Guangzhou; 2: Shenzhen.

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Land use	C:N ratio	BD (g cm ⁻³)	pH
Guangzhou			
CK1	15.27 \pm 3.77 ^{ab}	1.35 \pm 0.09 ^b	4.60 \pm 0.39 ^b
F1–20	16.77 \pm 0.98 ^{ab}	1.49 \pm 0.14 ^b	4.40 \pm 0.74 ^b
G1–20	13.83 \pm 0.72 ^b	1.64 \pm 0.15 ^a	4.47 \pm 0.27 ^b
IS1–20	17.66 \pm 2.37 ^a	1.71 \pm 0.05 ^a	7.95 \pm 0.27 ^a
IS1–30	17.04 \pm 1.50 ^{ab}	1.78 \pm 0.07 ^a	7.72 \pm 0.08 ^a
Shenzhen			
CK2	13.80 \pm 0.89 ^b	1.84 \pm 0.07 ^a	4.78 \pm 0.16 ^c
F2–20	15.88 \pm 2.09 ^b	1.35 \pm 0.06 ^b	6.41 \pm 0.26 ^b
G2–20	12.02 \pm 0.94 ^b	1.30 \pm 0.15 ^b	4.56 \pm 0.27 ^c
IS2–30	23.87 \pm 3.94 ^a	1.82 \pm 0.04 ^a	9.31 \pm 0.27 ^a

631 **Table 2** Mean values (mean \pm SD, n = 9) for the natural abundance stable C&N isotopes and
632 C/N ratios of leaf, litter, root of plants under different land covers and ages. The *abbr* for land
633 covers and years are the same as shown in Table 1.

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Land use		$\delta^{13}\text{C}$ (‰)	$\delta^{15}\text{N}$ (‰)	C:N ratio
Guangzhou				
F1-20	Leaf	-30.98 ± 4.42	3.70 ± 0.89	20.25 ± 3.71
	Litter	-31.18 ± 3.21	5.18 ± 1.62	35.45 ± 2.25
	Roots	-29.80 ± 3.62	3.24 ± 1.46	75.00 ± 18.65
G1-20	Leaf + Root	-19.65 ± 2.78	-3.40 ± 1.35	46.68 ± 5.24
Shenzhen				
F2-20	Leaf	-32.29 ± 4.72	1.12 ± 0.42	38.04 ± 4.52
	Roots	-27.36 ± 3.16	1.04 ± 0.35	92.87 ± 23.32
G2-20	Leaf	-34.65 ± 4.64	-0.12 ± 0.05	12.83 ± 4.21
	Litter	-31.01 ± 4.48	0.57 ± 0.22	20.67 ± 5.14

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Table 3 Mean values (n = 9) for the $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ of SOM pools (0–20 cm) under different land covers. The *abbr* for land covers and years are the same as shown in Table 1. Mean \pm SD with different letters for a variable represent significant differences ($P < 0.05$). Note: * $P < 0.05$; ** $P < 0.01$; *** $P < 0.001$.

Land use	Soil organic pool		Recalcitrant pool	
	$\delta^{13}\text{C}$ (‰)	$\delta^{15}\text{N}$ (‰)	$\delta^{13}\text{C}$ (‰)	$\delta^{15}\text{N}$ (‰)
Guangzhou				
CK1	-27.20 \pm 0.22 ^c	6.40 \pm 0.52 ^a	-27.48 \pm 0.17 ^c	6.82 \pm 0.19 ^a
F1–20	-28.30 \pm 0.24 ^d	5.22 \pm 0.51 ^b	-28.85 \pm 0.92 ^d	3.99 \pm 0.39 ^b
G1–20	-24.20 \pm 0.86 ^a	5.38 \pm 0.58 ^b	-24.70 \pm 1.12 ^a	6.48 \pm 1.68 ^a
IS1–20	-25.98 \pm 0.38 ^b	2.44 \pm 0.34 ^c	-26.16 \pm 0.15 ^{bc}	1.50 \pm 0.26 ^c
IS1–30	-24.22 \pm 0.12 ^a	2.42 \pm 0.30 ^c	-25.57 \pm 0.94 ^{ab}	2.80 \pm 0.27 ^{bc}
Source of variation				
Land use	***	***	**	***
Shenzhen				
CK2	-24.67 \pm 0.82 ^b	6.12 \pm 0.97 ^a	-25.15 \pm 0.56 ^a	5.30 \pm 1.44 ^b
F2–20	-26.66 \pm 1.16 ^c	6.79 \pm 1.41 ^a	-26.86 \pm 1.69 ^{ab}	8.73 \pm 1.24 ^a
G2–20	-27.98 \pm 0.37 ^c	2.32 \pm 0.36 ^b	-28.84 \pm 0.81 ^c	3.12 \pm 0.82 ^b
IS2–30	-22.87 \pm 0.75 ^a	4.92 \pm 1.26 ^a	-27.35 \pm 0.21 ^{bc}	-0.75 \pm 1.57 ^c
Source of variation				
Land use	***	**	*	***

643 **Table 4** Mean values (n = 9) for the C&N content, C/N ratios of SOM pools (0–20 cm) under different land covers. The *abbr* for land covers
 644 and years are the same as shown in Table 1. Mean ± SD with different letters for a variable represent significant differences ($P < 0.05$). Note:
 645 n.s. = not significant; $**P < 0.01$; $***P < 0.001$.

Land use	Soil organic pool			Recalcitrant pool		
	C (g kg ⁻¹)	N (g kg ⁻¹)	C: N ratio	C (g kg ⁻¹)	N (g kg ⁻¹)	C: N ratio
Guangzhou						
CK1	3.47±0.71 ^{cd}	0.23±0.07 ^c	15.30±2.70 ^b	1.72±0.18 ^c	0.12±0.04 ^c	14.96±4.44 ^c
F1–20	15.86±1.70 ^a	0.65±0.03 ^a	24.22±1.64 ^a	7.94±1.13 ^a	0.49±0.07 ^a	16.08±0.42 ^c
G1–20	5.38±0.19 ^c	0.51±0.09 ^b	10.81±1.57 ^c	2.79±0.66 ^c	0.08±0.02 ^c	18.00±0.77 ^a
IS1–20	7.91±1.95 ^b	0.55±0.13 ^{ab}	14.47±1.43 ^b	4.80±1.42 ^b	0.24±0.09 ^b	20.37±2.93 ^b
IS1–30	3.21±0.95 ^d	0.21±0.07 ^c	15.69±0.94 ^b	1.49±0.34 ^c	0.09±0.02 ^c	15.91±1.87 ^c
Source of variation						
Land use	***	***	***	***	***	***
Shenzhen						
CK2	6.88±1.97 ^c	0.64±0.21 ^b	10.88±1.02 ^b	4.41±1.17 ^{bc}	0.28±0.01 ^{bc}	15.84±3.92 ^{ab}
F2–20	11.01±1.71 ^b	0.59±0.05 ^b	18.57±1.67 ^a	6.76±1.83 ^b	0.45±0.12 ^b	15.05±0.11 ^b
G2–20	23.41±1.10 ^a	1.62±0.15 ^a	14.45±0.77 ^b	20.67±2.04 ^a	1.26±0.19 ^a	16.54±1.12 ^{ab}
IS2–30	2.61±0.27 ^d	0.14±0.02 ^c	19.48±3.46 ^a	2.04±0.19 ^c	0.10±0.00 ^c	19.92±2.05 ^a
Source of variation						
Land use	***	***	**	***	***	n.s.

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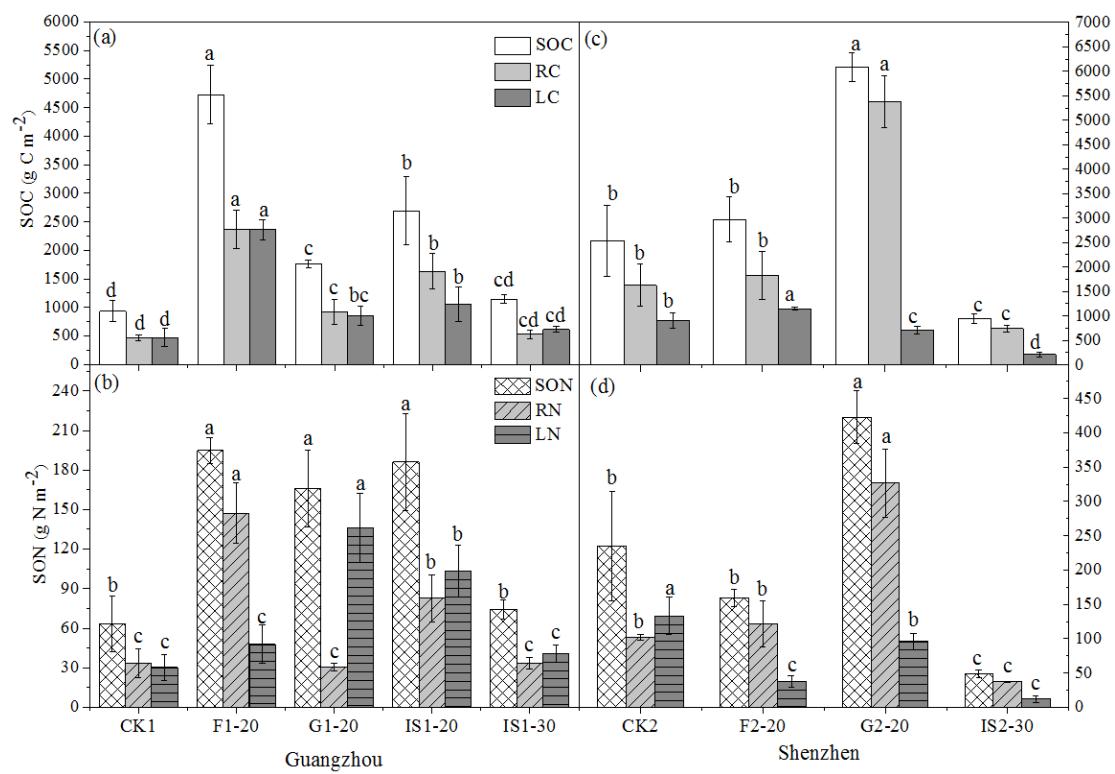


Fig. 1

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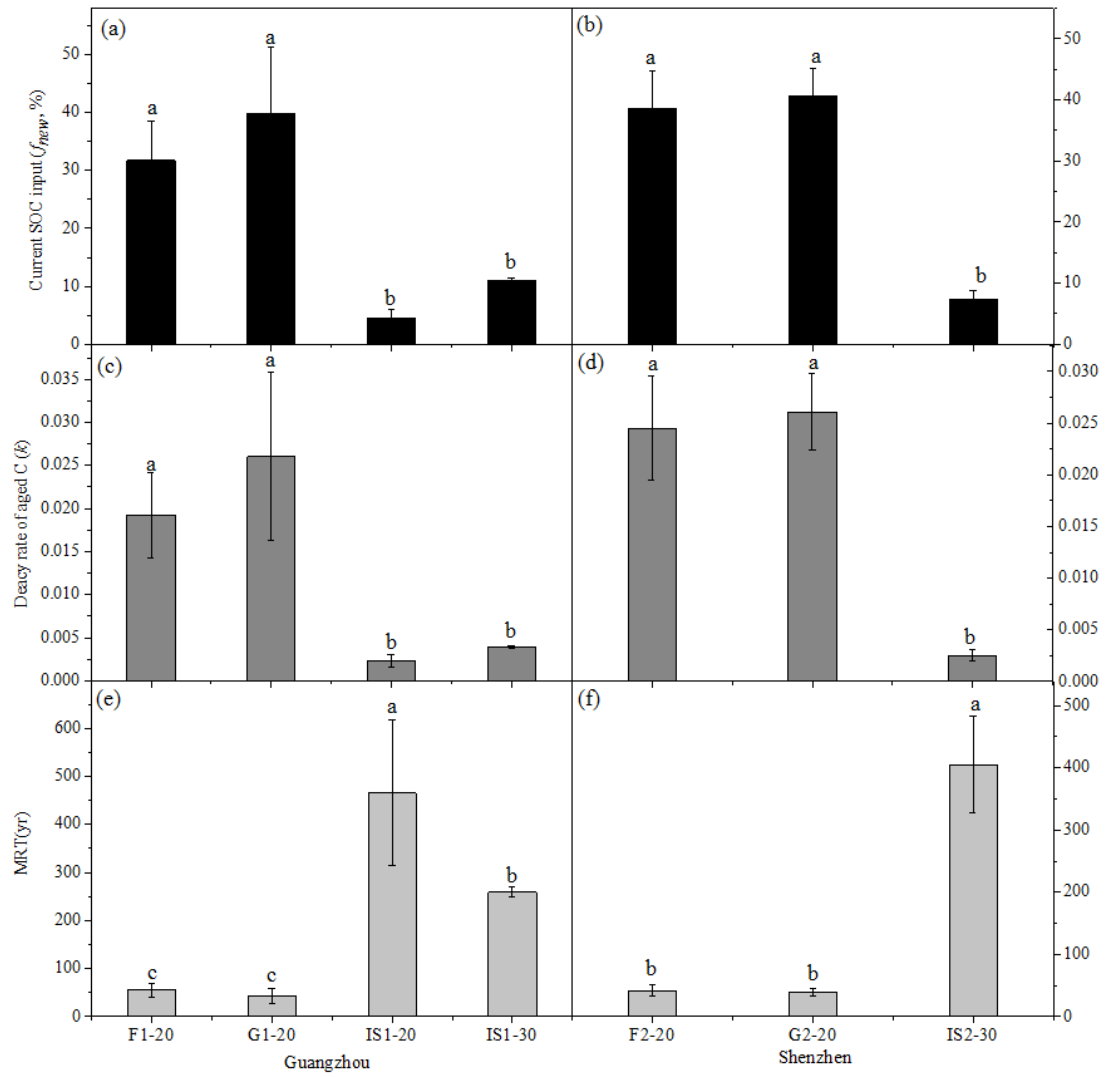


Fig. 2

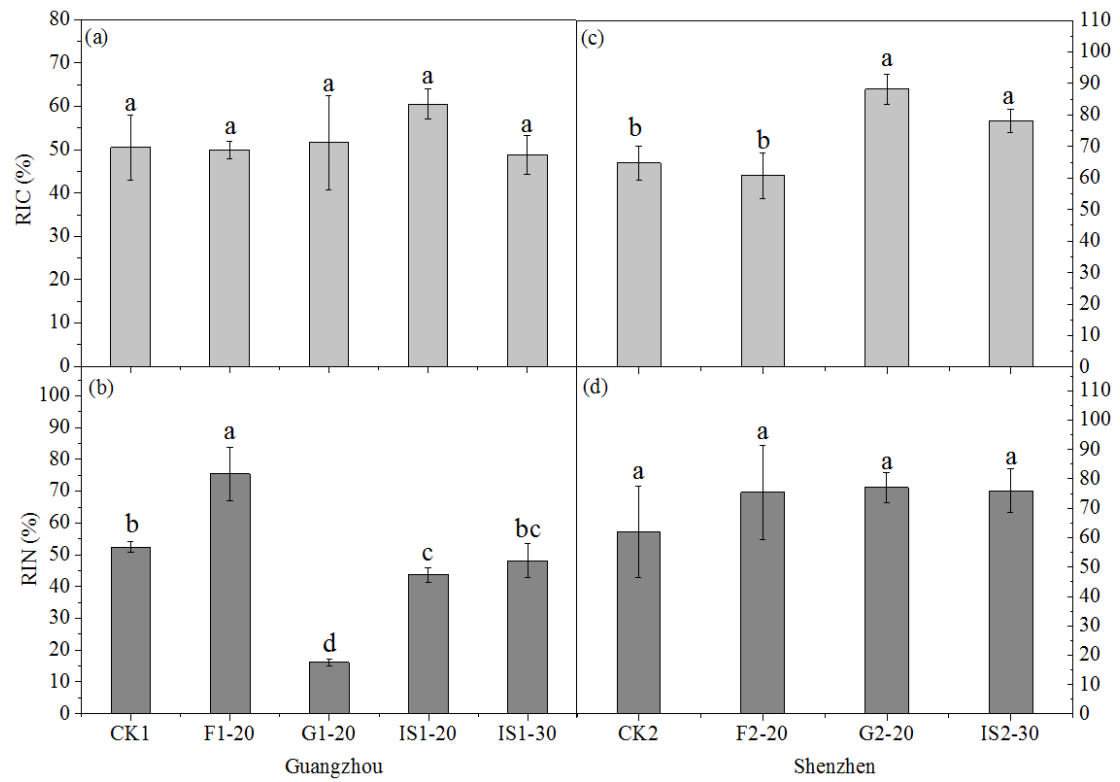


Fig. 3