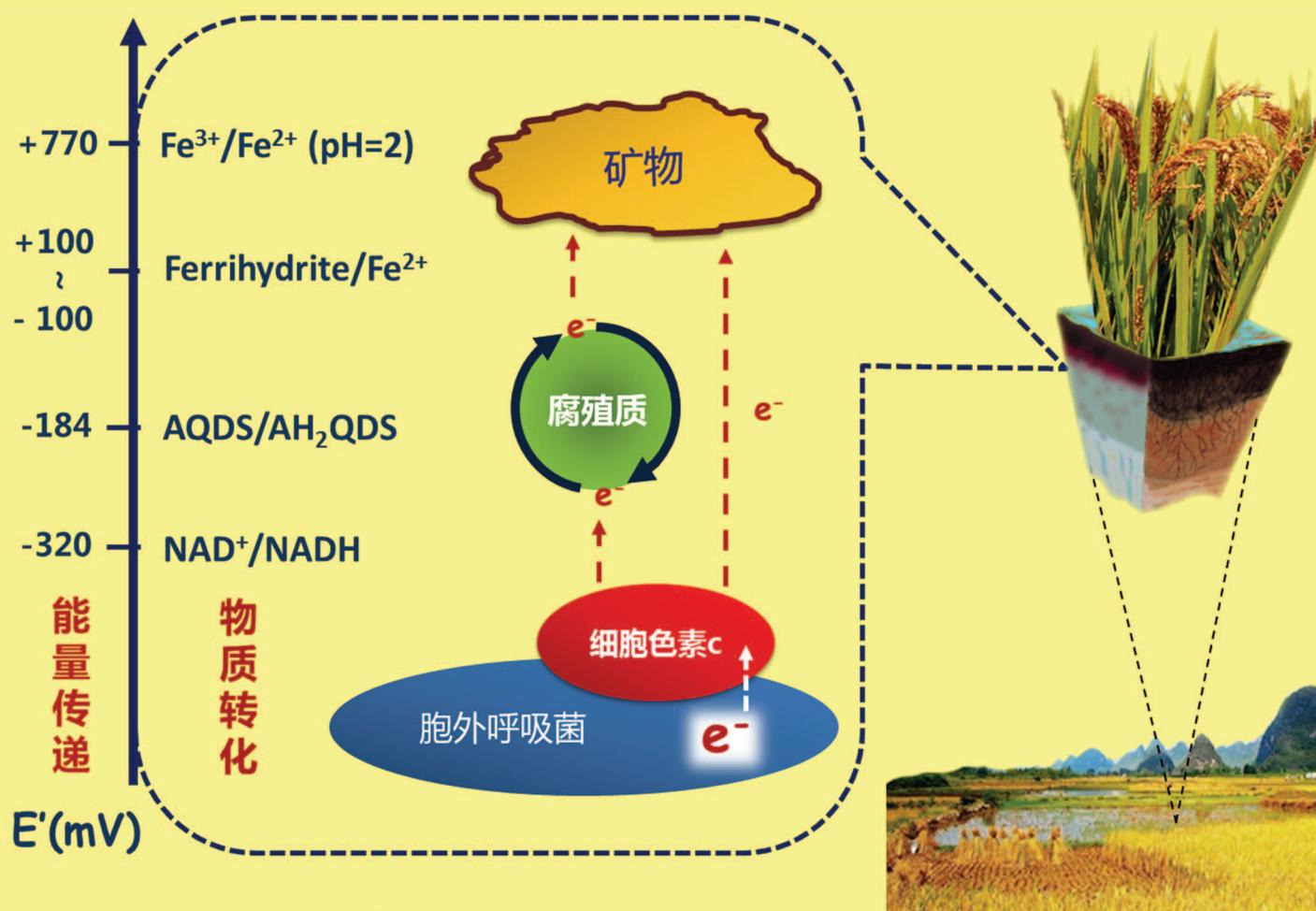


Acta Pedologica Sinica 土壤学报

Turang Xuebao



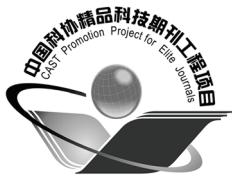
中国土壤学会
科学出版社

主办
出版

2016

第53卷 第2期

Vol.53 No.2



土壤学报

(Turang Xuebao)



第 53 卷 第 2 期 2016 年 3 月

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DOI: 10.11766/trxb201508090330

臭氧污染对麦田土壤不同活性有机碳库的影响*

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摘要 近年来大气臭氧危害加剧, 臭氧浓度升高影响植物—土壤系统进而影响土壤有机碳库周转。本研究在开放条件下, 采用Chan修订的Walkley-Black方法, 研究了连续5年增加稻—麦轮作系统大气臭氧浓度(较周围大气高50%)对麦季农田土壤不同活性有机碳库的影响。结果表明, 大气臭氧浓度升高致使0~3 cm、10~20 cm土层土壤有机碳含量显著降低, 累积导致耕层(0~20 cm)土壤有机碳含量下降18.4% ($p < 0.05$)。臭氧浓度升高显著降低了0~3、3~10、10~20 cm 3个土层中的活性有机碳含量; 臭氧升高使0~3 cm土层的受保护缓性有机碳含量增加了10.8% ($p < 0.05$), 并使未受保护缓性有机碳含量降低了59.7% ($p < 0.05$); 臭氧升高条件下10~20 cm土层的受保护缓性有机碳含量降低了59.6% ($p < 0.05$)。臭氧升高对不同活性碳占总有机碳比例的影响受活性碳类型和土壤层次的制约, 显著降低了3~10 cm土层活性有机碳所占比例 ($p < 0.05$), 未对耕层各层次上的稳定有机碳含量及其分配产生显著影响。臭氧升高导致土壤中占土壤有机碳比重59.3%~69.8%的活性碳库的库容变小, 应是土壤有机碳库下降的直接原因。本研究表明长期大气臭氧浓度增加具有降低土壤有机碳含量并改变不同活性有机碳库分配与周转的态势。

关键词 臭氧; 有机碳; 活性碳库; 农田土壤

中图分类号 S152.3 **文献标识码** A

土壤有机碳库是全球碳循环中重要的碳库, 其储量约是大气碳库和植被碳库的2.5倍~3.0倍, 它既是CO₂的排放源, 也是主要的碳汇^[1], 理解气候变化对土壤有机碳库的影响极其重要。生物地球化学循环模型根据土壤有机碳在土壤中的平均驻留时间差异将土壤有机碳库分成活性碳库、受保护的缓性碳库、未受保护的缓性碳库和稳定的有机碳库^[2]。不同活性碳库间存在着动态变化, 理解大气组分变化对各有机碳库间转化的影响, 有助于评价与理解气候变化对土壤碳周转的影响。当前, 近地层大气中臭氧(O₃)污染持续增加, 其对陆地生态系统产生的危害备受关注。东亚区域对流层中O₃

浓度已超过危害植物生长的阈值(40 nL L⁻¹), 且仍呈增加态势^[3], 20世纪80年代曾预计到2020年将增加50%^[4]。O₃污染能降低光合作用、抑制植物生长、导致作物和林木减产^[5-7], 势必影响有机碳向土壤的输入量^[8], 进而影响土壤有机碳库的容量。现有研究针对O₃污染下作物生产^[5, 6, 9-11]、作物物质积累与分配^[12]、土壤微生物活性^[13]与土壤结构^[14]的响应方面获得了丰硕成果。尽管先前研究表明, O₃污染影响温室气体CO₂和CH₄交换^[15]以及土壤碳固持^[16], 但由于O₃污染对农田土壤不同活性有机碳库的影响研究缺乏, 阻碍了系统理解O₃污染下土壤碳库的周转机制。因此, 本文

* 国家自然科学基金项目(41003030)和河南科技大学创新团队项目(2015TTD002)共同资助 Supported by the National Natural Science Foundation of China (No. 41003030) and Henan University of Science and Technology Innovation Team (No. 2015TTD002)

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收稿日期: 2015-08-09; 收到修改稿日期: 2015-10-15

利用我国定位的稻—麦轮作系统O₃-FACE (Free-air O₃ concentration enrichment) 试验平台, 研究了连续5年O₃浓度增加对麦季农田土壤不同活性有机碳库的影响, 以期进一步理解高O₃浓度下碳库周转机制, 并为建立农田碳素管理措施提供科学依据。

1 材料与方法

1.1 试验地概况

本试验地位于江苏省江都市宗村良种场中国O₃-FACE (119°42'0" E, 32°35'5" N) 系统平台。该区年均降水量980 mm左右, 年均蒸发量>1 100 mm, 年均温度14.9℃, 年日照时间>2 100 h, 年无霜期220 d; 土壤类型为下位砂姜土(中国土壤分类); 耕种方式为水稻—冬小麦轮作。试验区土壤理化性质为: 有机碳18.4 g kg⁻¹, 全氮1.5 g kg⁻¹, 全磷0.6 g kg⁻¹, 全钾14.0 g kg⁻¹, 砂粒(2~0.02 mm) 578.4 g kg⁻¹, 粉粒(0.02~0.002 mm) 285.1 g kg⁻¹, 黏粒(<0.002 mm) 136.5 g kg⁻¹, 容重1.2 g cm⁻³, pH 7.2。

1.2 试验平台

O₃-FACE试验平台系统于2007年3月开始运行, 分臭氧(O₃-FACE)和对照(Ambient)两个处理, 各4个重复, O₃-FACE圈内目标臭氧浓度高于Ambient圈臭氧浓度50%。O₃-FACE处理臭氧释放通过8根直径15 mm置于冠层上方30~60 cm的布气管进行, Ambient圈无布气管道, 环境条件与自然状态完全一致。稻、麦季均在作物生长季放气直至成熟, 每天放气时间为上午9:00至日落时间; 因高浓度臭氧在下雨、露水时会造成叶片急性损伤, 故下雨时系统将暂停放气。平台控制详情见文献[17]。

1.3 样品采集与分析

2012年5月底在小麦收获后水稻种植前, 于臭氧和对照两个处理各重复圈均随机选取5个点, 分别按0~3 cm、3~10 cm、10~20 cm、0~20 cm采集土壤样品, 各重复圈同层次均采集一个混合样, 利用四分法采集土壤样品1 kg。将土壤样品带回室内, 去除可见杂质, 将新鲜土样过5 mm筛后自然风干、研磨、过筛处理。土壤总有机碳利用重铬酸钾容量法测定。活性有机碳(F1)、受保护的缓性有机碳(F2)、未受保护的缓性有机碳(F3)、稳定有机碳(F4)四个不同活性的有

机碳组分按Chan^[18]修订的Walkley-Black法, 利用重铬酸钾容量法-外加热法, 在不同硫酸浓度即浓硫酸-水溶液配比(酸水比为: 0.5:1、1:1、2:1、1:0)下的氧化环境中测定区分。其中F1含量为酸水比0.5:1条件下所测有机碳; F2含量为在酸水比1:1与0.5:1条件下所测有机碳差值; F3含量为酸水比2:1与1:1条件下所测有机碳差值; F4含量为酸水比1:0与2:1条件下所测有机碳差值。

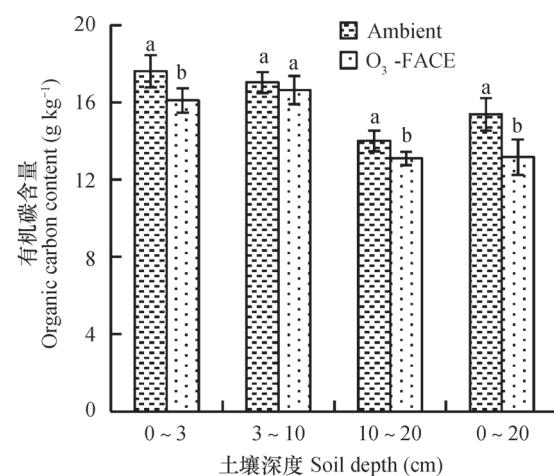
1.4 数据处理

数据通过SPSS 17.0统计软件, 采用Tukey HSD对不同大气臭氧浓度的效应进行统计分析, 显著水平为p<0.05, 利用Microsoft Office Excel 2003制图。

2 结果

2.1 臭氧浓度升高对不同土层土壤有机碳含量的影响

对照与臭氧处理中, 土壤有机碳含量在土壤表层(0~10 cm)含量较高, 而在土壤下层(10~20 cm)含量较低(图1)。与对照相比, 臭氧浓度升高显著降低了0~3 cm、10~20 cm、0~20 cm土层的土壤有机碳含量, 但未显著改变3~10 cm土层的土壤有机碳含量。



注: 不同字母表示同一土层有机碳含量在不同O₃浓度处理中差异显著(p<0.05); O₃-FACE为臭氧处理, Ambient为对照, 下同

Note: Different letters indicate differences at the 0.05 level in the organic carbon content within the same depth class between different O₃ concentrations; O₃-FACE is the treatment of free-air O₃ concentration enrichment, Ambient is the Control, the Same below

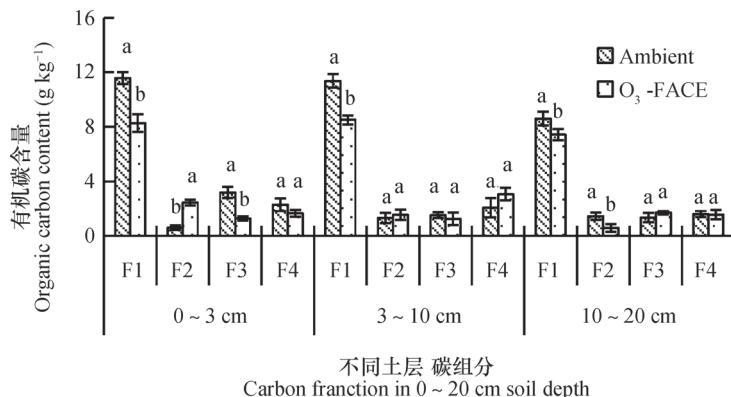
图1 不同土层有机碳含量

Fig. 1 Soil organic carbon content in different soil layers

2.2 臭氧浓度增加对土壤不同活性有机碳含量的影响

在0~20 cm耕层的三个不同层次中,对照与臭氧处理均以活性有机碳为主,臭氧浓度升高对不同活性碳库的影响受土层深度制约(图2)。与对照相比,臭氧浓度升高分别降低了0~3 cm土层的活性有机碳、未受保护缓性有机碳和稳定有机碳含量28.5% ($p < 0.05$)、59.7% ($p < 0.05$)和27.5%,显著增加了受保护缓性有机碳库含量303.3%

($p < 0.05$)。臭氧浓度升高显著降低了3~10 cm土层的活性碳含量25.2% ($p < 0.05$),但未显著改变其他三种活性碳的含量。臭氧浓度升高分别降低了10~20 cm土层的活性碳和受保护缓性有机碳含量13.7%与59.6% ($p < 0.05$),但未显著改变未受保护缓性有机碳与稳定有机碳含量。尽管臭氧污染对不同土层的不同活性碳库影响不完全一致,但显然臭氧污染将影响土壤不同活性有机碳库的容量,甚至周转。



注: 不同字母表示同一土层同一活性有机碳库含量在不同O₃浓度处理中差异显著($p < 0.05$) Note: Different letters indicate differences at the 0.05 level in the same active organic carbon content within the same depth class between different O₃ concentrations

图2 臭氧污染对土壤不同活性有机碳含量的影响

Fig. 2 Effects of elevated O₃ on contents of different fractions of soil active organic carbon

2.3 臭氧浓度升高对不同活性碳占总有机碳库比例的影响

对照与臭氧处理中,0~3 cm、3~10 cm、10~20 cm土层土壤的不同活性有机碳含量占总有机碳含量比例见表1。各处理中,活性有机碳所占比重最大,占总有机碳的59.3%~69.8%。与对照相比,0~3 cm土层中,臭氧浓度升高使受保护缓性碳的比例提高了419.3% ($p < 0.05$),未受保护缓性碳的比例降低了47.8% ($p < 0.05$),但对活性

碳与稳定有机碳库所占比例的影响未达显著水平。3~10 cm土层中,臭氧浓度升高使活性碳的比例降低了15.1% ($p < 0.05$)并使稳定有机碳库的比例增加了67.8% ($p < 0.05$),未显著影响受保护与未受保护缓性有机碳所占比例。10~20 cm土层中,臭氧浓度升高使受保护缓性有机碳的比例降低了54.0% ($p < 0.05$),未受保护缓性有机碳的比例增加了47.9% ($p < 0.05$),对稳定有机碳库与活性碳所占比例无显著影响。

表1 不同处理下不同活性碳占总有机碳库的比例

Table 1 Percentage of different fractions of active carbon to total organic carbon under different treatments

处理 Treatment	深度 Depth (cm)	各不同活性碳库有机碳占总有机碳比例 Percentage of different active carbon to total organic carbon (%)			
		F1	F2	F3	F4
对照Ambient	0~3	65.5 ± 2.9ab	3.5 ± 1.0d	18.1 ± 2.2a	12.9 ± 2.1bc
	3~10	69.8 ± 3.3a	8.1 ± 2.0bc	9.4 ± 1.5b	12.7 ± 4.2b
	10~20	66.0 ± 3.4ab	11.2 ± 2.0b	10.3 ± 2.3b	12.4 ± 1.7b
臭氧O ₃ -FACE	0~3	60.5 ± 2.4b	17.9 ± 0.7a	9.4 ± 1.2b	12.1 ± 1.1b
	3~10	59.3 ± 5.3b	10.7 ± 2.1b	8.7 ± 2.8b	21.3 ± 2.5a
	10~20	66.0 ± 2.9ab	5.2 ± 2.4cd	15.2 ± 1.5a	13.8 ± 2.7b

注: 同列不同小写字母表示差异显著($p < 0.05$) Note: Different lowercase letters in the same column mean significant differences at the 0.05 level

3 讨 论

臭氧浓度升高显著降低耕层(0~20 cm)土壤有机碳含量, 可能是臭氧污染致两个层次(0~3 cm、10~20 cm)土壤有机碳含量显著降低及3~10 cm层土壤有机碳呈降低趋势的叠加结果。Felzer等^[19]也发现长期臭氧污染将降低森林与农田系统的土壤有机碳含量。土壤有机碳含量受制于外源碳输入量与土壤碳输出量, 农田土壤碳输入主要源于根茬碳的归还, 而碳输出主要表现为异养呼吸。现有研究发现, 高浓度臭氧通过植株气孔来抑制植物的光合作用, 导致植物合成碳水化合物能力减弱^[5-8], 减少向根系的碳分配与抑制根系生长^[20-21]。同一研究平台, 已发现了臭氧浓度升高显著降低小麦的根茬碳量^[8], 也会使水稻根茬输入量降低8.8% (未刊资料), 但增加了土壤碳分解排放的CO₂和CH₄^[15]。稻-麦农田系统中根系输入碳的减少和碳分解排放的增加共同导致土壤有机碳库容量的下降。臭氧污染导致0~3 cm和10~20 cm土层有机碳含量下降, 主要由于臭氧污染减少了根系归还碳量及其在各层的分配。由于作物种植深度多在3~5 cm, 根系多分布于0~15 cm耕层的中间部分^[22], 0~3 cm因过浅而10~20 cm因犁底层(15~20 cm)过于紧实均不利于根系下扎, 该两层的根茬归还碳量远低于根茬主要归还在3~10 cm土层的量^[22]。在3~10 cm土层中, 由于大量新鲜碳的补充基本满足了微生物的分解需求, 致使土壤有机碳含量对臭氧污染响应不显著; 另两个层次由于新鲜碳归还量的减少, 导致微生物对土壤原有碳的分解增加, 使臭氧污染下的土壤碳含量降低。

本研究中, 臭氧污染导致耕层中(0~20 cm)三个层次中所占比例最大的活性有机碳含量均显著降低, 这可能由于臭氧污染降低了土壤微生物生物量碳^[13, 23]、破坏了土壤物理结构^[14]、降低了碳的土壤固持并增加了土壤呼吸^[15]进而促进了活性碳的分解。王春乙等^[24]也认为臭氧污染可以直接氧化有机物质, 促进有机物分解。由于活性有机碳最易被微生物利用或最易被氧化, 因此活性碳库较其他碳库组分对臭氧污染的响应更显著。本研究中臭氧处理下三个土层中活性有机碳含量均较对照减少, 表明臭氧污染将减少易被利用碳的数量。随着易利用碳数量的降低, 导致臭氧污染环境土壤微生物量减少^[23]。

因不同碳库组成之间相互保持平衡, 故臭氧污染直接或间接作用于土壤不同活性碳库, 进而影响不同层次土壤中不同活性碳库间的转化。不同有机碳库在土壤中的保持与稳定机制存在差异, 受保护缓性有机碳闭蓄于团聚体内并参与团聚体的形成, 未受保护缓性有机碳游离填充于团聚体孔隙间, 而稳定有机碳则是黏粉粒矿物结合态有机碳^[25]。在0~3 cm土层中, 受保护缓性有机碳含量显著增加, 而未受保护缓性有机碳与稳定有机碳含量显著降低, 这主要是由于臭氧污染增加了麦田耕层团聚体的形成而减少了粉黏粒的含量^[14], 团聚体的形成使闭蓄于团聚体内的受保护缓性有机碳含量增加, 但粉黏粒含量减少使得矿物结合态的稳定有机碳含量下降。由于臭氧污染增加了土壤呼吸, 随着0~3 cm土层活性有机碳含量的下降, 未受保护的缓性有机碳被微生物利用并导致其下降。在10~20 cm土层中, 受保护缓性有机碳含量显著降低, 可能是臭氧污染下耕层(0~15 cm)的根茬碳归还量减少^[8], 相应减少了在10~20 cm土层的分配, 随外源碳输入的减少, 微生物可利用碳源的不足导致团聚体被破坏, 闭蓄于团聚体内部的受保护缓性碳被释放并转化为活性碳和未受保护缓性有机碳为微生物分解利用^[14, 25], 降低了其含量, 而未受保护缓性有机碳由于获得补充未出现显著减少。除活性碳含量外, 臭氧污染对3~10 cm层其他碳库无显著影响, 这可能由于该层有大量的根残茬与分泌物等活性碳输入, 为微生物提供了充足的碳源, 减少了对团聚体的破坏和粉黏粒含量的影响, 保护了受保护与未受保护的缓性碳、稳定有机碳。此外, 也可能与不同活性碳库在土壤中的响应稳定机制、作物的生长需求等有关, 需要结合土壤有机碳的物理、化学与生物化学循环机制开展深入研究。

本研究发现臭氧污染稻-麦轮作系统5年后, 降低了麦季土壤有机碳含量, 且不同程度影响耕层土壤不同活性碳库有机碳含量和分配转化。麦季旱作主要提升土壤活性有机碳的降解速率, 降低土壤活性碳库, 而稻季厌氧条件有利于碳的保持^[26]。但余永昌等^[27]研究发现臭氧浓度升高条件下稻田土壤活性有机碳含量下降。现有结果显示, 臭氧污染将不利于稻-麦轮作系统土壤的活性碳库。然而, 未来高大气臭氧浓度条件下, 稻-麦轮作系统中稻季土壤不同活性碳库的转化特征、稻-麦轮作

系统中不同活性碳库周转变化对全球碳循环的影响仍需进一步研究。

4 结 论

臭氧浓度升高显著降低了0~20 cm表层土壤有机碳含量，在0~3 cm、3~10 cm、10~20 cm不同层次上显著降低了活性有机碳含量，并在3~10 cm土层中显著降低了活性碳占总有机碳的比例。臭氧污染导致土壤中占土壤有机碳比例在60%以上的活性碳库的库容变小，并改变了各活性有机碳库的分配与转化特征，应是导致土壤有机碳下降的主要原因。

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Effects of Ozone Pollution on Different Active Organic Carbon Stocks in Wheat Farmland Soil

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Abstract Ozone (O_3) is one of the best-documented air pollutants in East Asia and in many parts of the world. Tropospheric O_3 concentration has rapidly increasing in East Asia since the 1990s, and the global average tropospheric O_3 concentration is expected to have increased by 50% by 2020 relative to the 1980s. Since the concentration of tropospheric $O_3 > 40 \text{ nL L}^{-1}$ would cause visible leaf injury, plant damage

and reduction in crop and forest productions, the effects of tropospheric O₃ on terrestrial ecosystems have aroused considerable attention the world over. Currently many of these studies have focused on effects of O₃ on plants, and most agreed that O₃ inhibits plant growth and accelerates plant senescence. Elevated O₃ has also been demonstrated to reduce photosynthetic rate and productivity of crops and forests, and to alter carbon metabolism and subsequently allocation of resources (e.g. Carbon (C)) underground. The increasing atmospheric O₃ concentration has a negative effect on the plant-soil system, thus further affecting the turnover of soil organic carbon pool. This is important as it is well known that soils are important C sinks within the biosphere. Soil organic carbon in biogeochemical cycling is divided into different fractions of active organic carbon according to the ease and time with which soil organic carbon becomes available in the soil, including easily oxidized organic carbon, protected slow organic carbon, non-protected slow organic carbon, and passive carbon. However, not so much is known about the effect of elevated O₃ on sequestration and stability of the different fractions of soil organic carbon. Thus it is important to better understand C cycles in the context of predicted increases in atmospheric O₃. The paddy fields of the Yangtze River Delta region in Southeast China are one of most heavily O₃-polluted regions of the country. In light of the larger amount of carbon deposition to paddy soils than to other agricultural soils, it is essential to have a understanding of responses of soil organic carbon and sequestrations of different fractions of active organic carbon under elevated O₃. Thus the main objective of this study was to determine whether an increase in atmospheric O₃ concentration would influence soil organic carbon and sequestration of each active carbon fraction. With the Chan-modified free-air O₃ concentration enrichment system and Walkley-Black method, effects of elevated atmospheric O₃ on different active soil organic carbon stocks in paddy soil were investigated. The paddy field under investigation had been under a rice-wheat rotation agroecosystem with elevated atmospheric O₃, 50% higher than the ambient O₃, for five years. Results showed that elevated atmospheric O₃ significantly decreased the contents of soil organic carbon in the 0~3 cm and 10~20 cm soil layer, with a total decrease of about 18.4% in the topsoil (0~20 cm). Elevated atmospheric O₃ significantly decreased the contents of easily oxidized organic carbon in the 0~3 cm, 3~10 cm and 10~20 cm soil layers, but increased the content of protected slow organic carbon by 10.8%, while decreasing the content of non-protected slow organic carbon by 59.7% in the 0~3 cm soil layer, and the content of protected slow organic carbon by 59.6% in the 10~20 cm soil layer. The effects of elevated atmospheric O₃ on the proportions of different fractions of active organic carbon to total organic carbon related to fraction and soil depth. Elevated atmospheric O₃ significantly decreased the proportion of easily oxidized organic carbon to total organic carbon by 15.1% in the 3~10 cm soil layer, did not affect the contents and distributions of passive carbon in all soil layers, but caused the stock of labile organic carbon, accounting for 59.3%~69.8%, in total soil organic carbon pool to decline, which is probably the direct cause leading to decrease in soil organic carbon under elevated atmospheric O₃. It is quite obvious that long-time exposure to elevated atmospheric O₃ would decrease the content of soil organic carbon and change the distribution patterns of different fractions of active organic carbon in soil carbon pool and their turnover.

Key words Ozone; Organic carbon; Labile organic carbon pool; Agricultural soils

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土壤学报

Turang Xuebao

(双月刊, 1948年创刊)

第 53 卷 第 2 期 2016 年 3 月

ACTA PEDOLOGICA SINICA

(Bimonthly, Started in 1948)

Vol. 53 No. 2 Mar., 2016

编 辑 《土壤学报》编辑委员会

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主 管 中 国 科 学 院

Superintended by Chinese Academy of Sciences

主 办 中 国 土 壤 学 会

Sponsored by Soil Science Society of China

承 办 中国科学院南京土壤研究所

Undertaken by Institute of Soil Science,

Chinese Academy of Sciences

出 版 科 学 出 版 社

Published by Science Press

地址：北京东黄城根北街 16 号 邮政编码：100717

Add: 16 Donghuangchenggen North Street,

Beijing 100717, China

印 刷 装 订 北京中科印刷有限公司

Printed by Beijing Zhongke Printing Limited Company

总 发 行 科 学 出 版 社

Distributed by Science Press

地址：北京东黄城根北街 16 号 邮政编码：100717

Add: 16 Donghuangchenggen North Street,

Beijing 100717, China

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国 外 发 行 中国 国际图书贸易总公司

Oversea distributed by

China International Book Trading Corporation

地 址：北京 399 信箱 邮政编码：100044

Add: P. O. Box 399, Beijing 100044, China

国内统一连续出版物号:CN 32-1119/P

国内邮发代号: 2-560

国外发行代号: BM45

定 价: 60.00 元

国 内 外 公 开 发 行

ISSN 0564-3929



03>

9 770564 392163