

生物质炭输入影响土壤氮素转化与氧化亚氮排放的研究进展

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摘要: 全球气候变暖的持续性和不确定性显著影响人类社会的可持续发展。大气氧化亚氮 (N_2O) 的持续增加是导致全球气候变暖的主要原因之一。土壤是氮素转化的重要场所和氮循环生物化学反应库, 也是 N_2O 的重要排放源, 土壤 N_2O 排放速率的变化会显著影响大气 N_2O 含量。生物质炭是指生物质在完全或部分缺氧的情况下经热裂解制备而成的芳香类化学物质, 具有多孔性、强吸附性、化学稳定性、高 pH 和较大阳离子交换量等特性。生物质炭施入土壤后, 会直接或间接影响土壤氮素的转化, 并对土壤 N_2O 排放产生显著影响。本研究综述了生物质炭输入对土壤生态系统氮素转化与 N_2O 排放的研究进展, 分别阐述了生物质炭输入对土壤无机氮动态变化、硝化作用、反硝化作用以及 N_2O 排放的影响, 并从生物质炭吸附和减少氮素淋滤、影响土壤理化性质、土壤氨氧化菌的丰度和多样性以及反硝化菌功能基因等方面具体分析了影响上述过程的作用机制。在此基础上, 对今后生物质炭在土壤增汇减排以及缓解温室效应方面的进一步理论研究和相关技术推广进行了展望。参 109

关键词: 土壤学; 生物质炭; 土壤氮素; 硝化作用; 反硝化作用; N_2O 排放

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Effects of biochar application on soil nitrogen transformation and N_2O emissions: a review

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Abstract: The sustainability and uncertainty of global climate warming have a profound impact on the sustainable development of human society. The continuous increase of atmospheric N_2O concentration is one of the major contributions to the global climate warming. Soil is an important site of nitrogen transformation and a biochemical reaction reservoir of the nitrogen cycle, and also an important source of N_2O emissions. Therefore, changes in soil N_2O emission rate will significantly affect atmospheric N_2O concentration. Biochar refers to the aromatic chemicals prepared by pyrolysis of biomass under the condition of complete or partial hypoxia. Biochar has the characteristics of porosity, strong adsorption, chemical stability, high pH and large cation exchange capacity. After it is applied to soils, biochar will directly or indirectly affect the transformation process of soil nitrogen and significantly affect the soil N_2O emissions. This article reviewed the research progress of biochar effects on nitrogen transformation and N_2O emission in the soil ecosystem, elaborated the effects of biochar input on the dynamic changes of soil inorganic nitrogen, nitrification, denitrification and N_2O emission. Further, in terms of biochar's absorption and reduction of nitrogen leaching, effects on soil

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physicochemical properties, abundance and diversity of soil ammonia oxidizing bacterial, along with functional genes of denitrifying bacteria, the mechanisms influencing the processes above-mentioned are specifically elucidated in details. The future research of biochar in increasing soil sinks, reducing emissions and mitigating the greenhouse effect, as well as the related technology promotion, have been prospected. [Ch, 109 ref.]

Key words: soil sciences; biochar; soil nitrogen; nitrification; denitrification; N_2O emissions

氧化亚氮 (N_2O) 是仅次于二氧化碳 (CO_2) 和甲烷 (CH_4) 的第三大强效温室气体, 百年尺度下的全球变暖潜能值 (GWP) 是 CO_2 的 300 倍^[1]。据估计, 大气 N_2O 每年约增加 0.2%~0.3%, 不仅加剧全球气候变暖, 也对生态系统功能产生显著负面影响^[2]。作为平流层臭氧消耗的因素之一, N_2O 在臭氧层破坏的过程中起着重要的催化作用, 严重威胁大气环境和人类生存安全^[3-4]。因此, 如何缓解 N_2O 持续增加是目前国内外研究关注的重点和难点问题^[5]。生物质炭 (biochar) 是指生物质在完全或部分缺氧的情况下经高温热裂解产生的芳香类化学物质^[6-7], 具有多孔、强吸附力、高化学稳定性、高酸碱度和较大阳离子交换量等特性^[7-8]。作为土壤改良剂, 高孔隙度的生物质炭可以吸附持留氮素 [铵根 (NH_4^+) 和硝酸根 (NO_3^-)] 并显著改变土壤的理化性质, 从而直接或间接影响参与土壤氮循环相关的微生物群 (如硝化菌、反硝化菌和固氮菌) 的丰度和多样性, 最终影响土壤氮循环^[9-11]。因此, 对近年来国内外关于生物质炭对土壤无机氮动态、硝化和反硝化作用以及 N_2O 排放影响及其机制等研究现状进行综述, 可为生物质炭的资源化利用、土壤生态系统增汇减排技术的开发提供参考。

1 生物质炭输入对土壤无机氮的影响

生物质炭对不同无机氮形态 (NH_4^+ 和 NO_3^-) 吸附程度不同^[11-12]。DOYDORA 等^[13]发现: 与纯畜禽堆肥相比, 生物质炭与畜禽堆肥混合处理, 可以使土壤氨气 (NH_3) 挥发损失降低一半以上, 表明生物质炭可以一定程度上缓解氨挥发损失。董玉兵等^[14]研究追施生物质炭对稻麦轮作中麦季氨挥发和氮肥利用率的影响时发现: 与单施氮肥 ($250 \text{ kg} \cdot \text{hm}^{-2}$) 相比, 氮肥 ($250 \text{ kg} \cdot \text{hm}^{-2}$) 和生物质炭 ($20 \text{ t} \cdot \text{hm}^{-2}$) 混合施用降低了水稻 *Oryza sativa* 土 36.6% 的 NH_3 挥发累积量, 并使氮肥利用率提高 30.1%, 小麦 *Triticum aestivum* 产量增加 55.6%。王峰等^[15]发现: 施氮显著增加酸性茶园土壤氨挥发量; 增施生物质炭, 氨挥发量则显著降低 (降幅为 26.25%~28.21%)。进一步研究表明: 生物质炭富有酸性官能团, 电荷密度高, 表面负电荷多, 比表面积大, 对土壤中以可交换态形式存在的铵态氮 ($\text{NH}_4^+\text{-N}$) 和硝态氮 ($\text{NO}_3^-\text{-N}$) 具有较强的吸附能力, 即酸性官能团可以通过离子交换对 NH_3 产生吸附固定作用^[9, 16]。SARKHOT 等^[17]发现: 施入硬木生物质炭的土壤 $\text{NH}_4^+\text{-N}$ 含量显著降低。KAMEYAMA 等^[18]通过研究发现: 5 种不同热解温度 (400、500、600、700、800 $^{\circ}\text{C}$) 制备的甘蔗 *Saccharum spp.* 渣生物质炭均可以吸附土壤 $\text{NO}_3^-\text{-N}$, 随热解温度升高, 蔗渣炭化率增加, 吸附效果在 700 $^{\circ}\text{C}$ 时达到最大, 但热解温度对生物质炭的微孔体积影响不大, 尽管后者被认为与物理吸附能力有很大关系, 表明物理吸附不是蔗渣生物质炭吸附土壤 NO_3^- 的主要原因。进一步研究发现: 热解温度影响生物质炭表面功能性质, 低温形成酸性官能团, 高温形成碱性官能团^[19]。高温下甘蔗渣 pH 值升高, 生物质炭形成的碱性官能团, 成为其吸附土壤 NO_3^- 的主要原因。肖永恒等^[20]研究了竹叶及其生物质炭对板栗 *Castanea mollissima* 林土壤 N_2O 通量的影响, 发现竹叶处理后土壤 $\text{NH}_4^+\text{-N}$ 和 $\text{NO}_3^-\text{-N}$ 含量分别增加 8.3% 和 13.0%, 而生物质炭处理后土壤 $\text{NH}_4^+\text{-N}$ 和 $\text{NO}_3^-\text{-N}$ 分别降低了 14.1% 和 18.0%。孙贇等^[21]将 3 种不同类型的生物质炭 (小麦秸秆、柳 *Salix babylonica* 枝、椰 *Cocos nucifera* 壳) 施入酸化茶园土壤, 发现 3 类生物质炭均降低了土壤 $\text{NH}_4^+\text{-N}$ 含量。NGUYEN 等^[12]在研究生物质炭的性质以及生物质炭、土壤和肥料的相互作用如何影响土壤无机氮时发现: 与单施铵态氮肥相比, 生物质炭与铵态氮肥混施可以显著降低土壤无机氮含量; 与单施生物质炭相比, 生物质炭与有机肥料配施会增加土壤无机氮含量。由此可以推断: 生物质炭对土壤无机氮具有吸附持留作用, 并且这种作用效果可能在生物质炭与某些铵态氮肥混施下被强化。此外, 生物质炭尤其是木质生物质炭还能促进某些固氮生物的生物固氮能力。RONDON 等^[22]向豆科 Leguminosae 植物土壤添加适量的木质生物质炭, 发现豆科植物的生物固氮能力显著提高。

土壤淋溶是土壤养分流失的重要原因之一^[23]。土壤中的氮素淋溶主要包括2个过程：①在降雨和灌溉水的作用下，土壤中的氮素以化合物的形式流失；②土壤中可溶性的无机氮（铵态氮和硝态氮）流失到土壤下层^[24-25]。大量淋溶实验表明：生物质炭处理可以显著降低土壤氮素的淋滤损失。DEMPSTER等^[26]发现：25 t·hm⁻²生物质炭处理可以显著降低砂质土壤表层（0~10 cm）铵态氮（14%）和硝态氮（28%）的淋失。SIKA等^[27]发现：生物质炭所降低的铵态氮和硝态氮量与生物质炭质量和土壤质量比值（炭土质量比）成正相关，炭土质量比为0.5%、2.5%和10.0%时，铵态氮累积淋出量分别降低12%、50%和86%，硝态氮累积淋出量分别降低26%、42%和96%。不同类型的生物质炭对氮素的固持效果也不相同。相较于不添加生物质炭的对照组，土壤中添加由玉米 *Zea mays* 秸秆制成的生物质炭（100 t·hm⁻²）可以显著降低土壤总氮淋失量（74%）^[28]，而添加稻草生物质炭（50 t·hm⁻²）所降低的土壤总氮淋失值仅为11%^[29]。当添加炭土质量比为0.5%和1.0%的稻草生物质炭时，总氮的淋失量分别减少28%和44%；而添加炭土质量比为0.5%和1.0%的毛竹 *Phyllostachys edulis* 生物质炭时，总氮的淋失量则减少20%和31%。由此可以推断，添加适量合适类型的生物质炭可以大幅度减少土壤中氮素的淋失^[28]。生物质炭的输入能实现氮素淋失降低的原因很可能与生物质炭改善土壤物理性质有关，如增大土壤颗粒间孔隙度、降低土壤容重，从而增强土壤对氮素的固定作用，达到减少氮素流失的效果^[30-31]。也有研究认为生物质炭本身具备吸附养分、有效持留土壤中氮素的能力^[32]。

2 生物质炭输入对土壤硝化作用和反硝化作用的影响

2.1 生物质炭输入对土壤硝化作用的影响

土壤硝化作用是指土壤微生物将铵（NH₄⁺）、氨（NH₃）等还原态氮转化为亚硝酸根（NO₂⁻）或硝酸根（NO₃⁻）等氧化态氮的过程^[33]，通常分为自养硝化和异养硝化2种类型。一般来说，自养硝化作用是土壤N₂O产生的主要途径^[34]。自养硝化过程会产生羟胺（NH₂OH），氧化生成的中间产物[NOH]会通过化学分解或酶促反应产生N₂O^[35-38]。自养硝化有氨氧化作用和亚硝化作用2个阶段。氨氧化作用通过氨氧化细菌（AOB）和氨氧化古菌（AOA）在氨单加氧酶和羟胺氧化还原酶的催化下完成氨的氧化过程，此阶段中NH₂OH被分解，释放出N₂O^[39-40]。生物质炭处理会对土壤氨氧化菌的丰度和多样性产生显著影响。研究表明：土壤、湿地和海洋等生态系统的氮循环过程中，AOA和AOB均发挥着非常重要的作用^[41-43]。以土壤AOA和AOB为例，随着土壤氨浓度、氧分压、温度、pH值、含水量、养分等变化，AOA和AOB的丰度和活性波动较大^[44-45]。BALL等^[46]测定了不同燃烧史（分别发生于1910、1934和1992年，不同燃烧史产生木质生物质炭质量不等）的爱达荷州北部温带针叶林土壤中的AOB丰度，发现不同土层不同燃烧史的火烧土AOB丰度均显著高于非火烧土。TAKETANI等^[47]提取了富含生物质炭的土壤，发现其中AOA的基因拷贝数比对照高出约1/3到1/2。SONG等^[48]研究了在沿海碱性土壤中施用生物质炭（质量分数分别为5%、10%和20%）后土壤AOB和AOA的反应，结果发现：土壤中AOB分别增加了15.9%、121.0%和28.6%，但AOA无显著变化。也有研究发现生物质炭对土壤氨氧化作用具有一定的抑制效果^[49-50]。CLOUGH等^[51]在对土壤施用牛尿（氮肥760 kg·hm⁻²）后添加生物质炭（20 t·hm⁻²），检测发现生物质炭处理的土壤硝化率显著低于对照；进一步研究发现生物质炭在土壤中能够释放一种名为“α松萜”的硝化抑制剂^[52]，影响土壤N₂O-N和NH₃-N通量及无机氮转化。DELUCA等^[53]在富含生物质炭的森林土壤中发现：生物质炭处理抑制土壤氨氧化作用，原因在于吸附固定了土壤NH₄⁺-N。因此，生物质炭对土壤氨氧化作用的影响具有多样性和复杂性^[54-55]，影响机制主要包括3点：①生物质炭通过改变土壤pH值、氧分压、团聚体和孔隙度等理化性质，显著影响氨氧化功能微生物的丰度和种群结构^[46-48, 51, 56]；②生物质炭通过吸附固定土壤中的NH₄⁺-N，显著降低土壤氨氧化作用^[53, 57]；③生物质炭可以吸附为增加缓释效果而在化肥中添加的硝化抑制剂，部分生物质炭还在降解后释放萜类等硝化抑制剂，抑制土壤的氨氧化作用^[51, 58-62]。

亚硝化作用是亚硝酸盐氧化菌在亚硝酸盐氧化还原酶催化下将亚硝酸盐氧化成硝酸盐的过程^[63]。一般认为参与亚硝化作用的酶活性较低^[64]，氨氧化作用处于硝化作用的限速步骤（第1步反应）^[65]，因此对亚硝化菌的研究较少，有关生物质炭输入对土壤亚硝化功能微生物的研究更是鲜见报道。现有研究表

明：亚硝化作用功能微生物的丰度、活性及多样性与 CO_2 、温度、降水和氮浓度等环境因子有关^[66]。根据生物质炭对土壤氨氧化作用产生影响推测，生物质炭同样会对亚硝化作用产生较大影响。因此，探究生物质炭对土壤亚硝化作用的影响及其机制是未来生物质炭输入对土壤氮素转化研究的主要方向之一。此外，现有对土壤氮素转化的研究大多立足于适宜环境，而对于极端环境（如干旱、湿冷）或特殊状态（如熏蒸）下生物质炭对土壤的影响过程和作用机制鲜有涉及^[9, 67-68]。

2.2 生物质炭输入对土壤反硝化作用的影响

土壤反硝化作用是土壤反硝化功能微生物在缺氧条件下将 NO_3^- 还原为一氧化氮（ NO ）、 N_2O 与氮气（ N_2 ）的过程。反硝化作用过程是指土壤中的硝酸盐在微生物分泌酶（硝酸盐还原酶、亚硝酸盐还原酶、 NO 还原酶和 N_2O 还原酶）的催化下转化为亚硝酸盐，并最终转化为含氮气体（ NO 、 N_2O 与 N_2 ）^[69]。土壤反硝化作用是土壤产生 N_2O 的主要来源，因此，反硝化作用速率和影响机制一直是土壤 N_2O 减排研究的重要内容。为了量化研究土壤反硝化作用的效果与强度，引入了排放比率（ $\text{N}_2\text{O}/\text{N}_2$ ）的概念，而 $\text{N}_2\text{O}/\text{N}_2$ 往往与土壤诸多环境因子密切相关。从微观角度上来看，研究影响土壤反硝化作用的机制，可以理解为研究土壤反硝化菌对土壤环境因子动态变化的响应^[70]。亚硝酸盐还原酶将亚硝酸盐还原成 NO 是反硝化过程中的第 1 步，也是区分硝酸盐呼吸菌和反硝化菌的关键节点，可采用标记反硝化菌的方法来研究其种群结构和多样性^[71]。*NosZ*、*nirK*、*nirS* 是反硝化菌功能基因研究中最常见的 3 类基因，土壤反硝化作用对生物质炭输入的响应，可以体现为上述 3 类微生物功能基因的丰度和多样性对生物质炭输入的响应。生物质炭输入显著增加了土壤反硝化功能基因丰度和活性^[72-73]。WANG 等^[73]发现：生物质炭提高了 *nosZ/nirK*，使得 $\text{N}_2\text{O}/\text{N}_2$ 降低，实现 N_2O 减排。NELISSEN 等^[74]发现：生物质炭对土壤反硝化功能基因丰度的增加具有普遍性，不同施入量的生物质炭（质量分数分别为 1%、2% 和 10%）均能实现。综合国内外的研究，生物质炭对土壤反硝化作用的影响机制可能有：①生物质炭具有多孔性的特性，输入生物质炭可以显著提高土壤通气状况，抑制厌氧条件下氮素微生物酶活性^[52, 69, 75-77]；②施用生物质炭改变了土壤 pH 值，从而影响反硝化过程的排放比率^[57, 73, 78]；③生物质炭所含有的有机物质对土壤反硝化菌的群落结构及其功能基因的丰度产生了一定影响^[72-74, 79-80]。

3 生物质炭输入对土壤 N_2O 排放的影响

CAYUELA 等^[81]在对数据整合分析后发现：生物质炭具有降低土壤 N_2O 排放的潜力，平均降幅约为 54%。然而，由于生物质炭制备原料、气候类型、土壤质地、施用时间和田间管理方式等条件的不同，其对土壤 N_2O 排放的效应各异^[82-84]。一般来讲，草本或木本炭能减少 N_2O 排放，但畜禽粪便炭无此效果^[85]。热带、亚热带地区施用生物质炭对 N_2O 的减排作用小于温带地区^[81]。生物质炭对强酸性土壤（ $\text{pH} < 5$ ） N_2O 减排作用较小，对 $\text{pH} > 5$ 土壤的 N_2O 减排作用较大^[86]。以往对农田土壤的研究表明：施用生物质炭可以减少旱地土壤 N_2O 排放^[87]。TAGHIZADEH-TOOSI 等^[88]施用 $30 \text{ t} \cdot \text{hm}^{-2}$ 的松木 *Pinus* 生物质炭，降低了粉砂土壤 N_2O 的排放；ZHANG 等^[89]施加小麦秸秆生物质炭，降低了壤土土壤 N_2O 的排放。生物质炭输入对森林土壤 N_2O 排放的研究相对较少，但研究者认为减排效果最为显著的^[90-91]。SUN 等^[91]发现：在松林土壤中施用生物质炭（ $30 \text{ t} \cdot \text{hm}^{-2}$ ）可显著减少 N_2O 排放累积量（25.5%）。MALGHANI 等^[90]发现：生物质炭（质量分数为 1%）处理可以使云杉 *Picea asperata* 林土壤 N_2O 排放速率显著降低。肖永恒等^[20]发现：与对照相比， $5 \text{ t} \cdot \text{hm}^{-2}$ 的生物质炭可使板栗林土壤 N_2O 年平均通量和年累积排放量分别减少 27.4% 和 20.5%。SONG 等^[77]发现：施用生物质炭显著降低毛竹林土壤 N_2O 排放（降幅为 28.8%~31.3%），关键机制在于生物质炭降低了土壤活性氮浓度和土壤氮循环相关酶活性。JI 等^[92]研究了中国亚热带茶园土壤 N_2O 排放对生物炭添加的响应，发现添加生物质炭降低了土壤 N_2O 排放通量（24%），导致 *nirK* 和 *nosZ* 基因丰度显著增加。贺超卉等^[79]也发现：添加质量分数为 1% 的生物质炭可显著提高 *nirS* 和 *nosZ* 基因丰度，增大 $\text{N}_2/(\text{N}_2\text{O}+\text{N}_2)$ ，促进 N_2O 彻底还原成 N_2 从而实现减排。总体来讲，生物质炭输入降低土壤 N_2O 排放的作用机制主要包括 4 个方面：①生物质炭处理显著提高土壤通气状况，抑制土壤反硝化过程^[93-95]；②生物质炭可吸附土壤硝化作用的底物（ NH_4^+ ），降低土壤中 NH_4^+ 有效性，从而降低土壤 N_2O 的排放速率^[12, 20, 78, 93-94]；③生物质炭输入使得土壤 pH 值升高，提高了土壤 N_2O 还原酶活性，并抑制了参与 NO_3^- 和 NO_2^- 向 N_2O 转化的酶活性^[95-100]；④生物质炭处理提高了土壤活性有机碳（如水

溶性有机碳、微生物量碳等)相对含量,刺激了微生物的生长,从而提高土壤硝化程度,最终导致 N_2O 排放降低^[72, 79, 92, 101-102]。

也有研究表明:生物质炭处理对土壤 N_2O 排放无显著影响或促进 N_2O 排放。如HAWTHORNE等^[103]发现:在森林土壤中施用质量分数10%的生物质炭会显著增加 N_2O 排放,但施用质量分数1%的生物质炭后却未观察到明显的影响。SACKETT等^[104]也发现:在温带阔叶林中使用生物质炭($5\text{ t}\cdot\text{hm}^{-2}$)不会改变土壤 N_2O 排放。因此,生物质炭添加对土壤 N_2O 排放的影响十分复杂,作用机制也需进一步研究。

4 总结与展望

综上所述,生物质炭输入对土壤氮素转化的影响主要是通过作用于土壤氮循环过程及其相关功能微生物的丰度和活性来实现的。生物质炭通过影响土壤无机氮的有效性、土壤pH值、团聚体和孔隙度等理化性质,进而影响土壤氨氧化功能微生物的丰度和多样性。此外,生物质炭还为硝化菌、固氮菌等好氧微生物提供良好的生长繁殖条件,从而提高土壤氮素转化效率,促进土壤氮循环,有力维系了土壤生态系统的健康与稳定。另外,阐明生物质炭减少土壤 N_2O 排放的重要机制对于开发缓解土壤温室气体排放的有效方法至关重要^[72, 105]。施加生物质炭降低土壤 N_2O 排放主要是通过增加土壤通气度和氧气浓度,抑制低氧条件下微生物对土壤的反硝化作用、吸附 NH_4^+ 或 NO_3^- 从而减少作为硝化或反硝化作用底物的无机氮库来实现。

生物质炭对于土壤生态系统氮循环的作用显著。土壤氮素转化与 N_2O 排放是土壤生态系统氮循环的2个重要过程。但现有条件下的研究大多在实验室或模拟温室中进行,即使存在少部分的野外控制试验,也大多为短期研究(少于3a)。同样,生物质炭输入对土壤 N_2O 排放的影响机制复杂,结果也不同程度地受到生物质炭类型、施用剂量、土壤类型以及 N_2O 测定时间等因素的影响,因此,有必要开展对不同类型生物质炭应用于不同土壤类型的系统长期定位实验的研究。当前关于生物质炭对土壤氮素转化的影响机制分析大多局限于生物质炭自身的理化特性或者推测生物质炭对土壤中某些物质的影响,而对土壤氮循环功能微生物丰度和多样性的关联研究却不多。因此,生物质炭输入影响土壤 N_2O 排放的微生物学机制尚不清晰^[10, 106]。一部分研究认为生物质炭降低土壤 N_2O 排放可能与反硝化菌能源物质的减少有关^[107],另一部分研究则认为生物质炭影响 N_2O 排放是通过改变反硝化菌和硝化菌的种类来实现的^[89, 108]。因此,今后需重点关注生物质炭输入对土壤氮素转化与 N_2O 排放的微生物生态学机制尤其是涉及分子生物学等领域的研究。越来越多的研究表明,单施生物质炭或氮肥均无法实现氮素吸收利用的最大化,两者配合施用在促进氮素利用上存在着一定的协同作用^[109]。生物质炭特殊的理化性质使其具有成为肥料增效载体的可能,以生物质炭为原料制备的炭基缓释肥逐渐成为当下生物质炭研究的热门。生物质炭和全球气候变化(增温和氮沉降)的交互作用正在受到越来越多的关注,在全球气候变化背景下,研发基于生物质炭材料的土壤 N_2O 减排技术也将成为生物质炭应用的又一新方向。

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