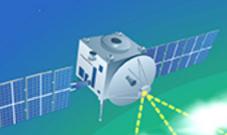


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## **ENVIRONMENTAL SCIENCE**

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PM<sub>2.5</sub>和O<sub>3</sub>污染协同防控区的遥感精细划定与分析 李沈鑫,邹滨,张凤英,刘宁,薛琛昊,刘婧



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# 基于 Meta-analysis 的生物炭对土壤硝态氮淋失和磷酸盐固持影响

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摘要:如何控制农业土壤硝态氮和磷酸盐淋失及其所导致的面源污染是人类社会当前面临的一个重要的全球性环境问题.生物炭因其在土壤改良方面表现出的巨大潜力而备受关注,针对其应用对土壤养分保持、利用的影响也展开了诸多研究.然而,已有的独立实验研究所报道的相关结果之间存在很大的差异,使得生物炭减少土壤硝态氮和磷酸盐淋失的潜在机制以及适宜生物炭制备条件(生物炭类型)等方面尚不明确.基于荟萃分析(MA)方法,通过整合不同文献中的实验结果,系统研究了生物炭对土壤硝态氮淋失和磷酸盐固持影响及其内在机制.总体上,生物炭能够显著减少硝态氮淋失 37.1%,显著提高磷酸盐固持 20.8%;从各影响因素分组的结果来看,生物炭碳氮比、热解温度和添加率对硝态氮淋失响应具有显著影响;而生物炭比表面积、热解温度和土壤有机碳含量对磷酸盐固持响应具有显著影响.基于 MA 得到的结果,分别从不同的角度探讨了生物炭降低土壤硝态氮淋失和提高磷酸盐固持的潜在机制.综合上述结果,秸秆和木质类原料、中高温热解温度(400~600℃)条件下制备的生物炭适宜于减少硝态氮的淋失;秸秆和木质类原料、高温热解温度(>600℃)条件下制备的生物炭适宜于提高磷酸盐的固持.研究结果能够为更好地指导生物炭用于控制土壤硝态氮和磷酸盐面源污染的实践应用提供科学理论依据. 关键词:农业面源污染控制;生物炭,硝态氮淋失;磷酸盐固持,荟萃分析(MA)

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# Influence of Biochar Application on Soil Nitrate Leaching and Phosphate Retention: A Synthetic Meta-analysis

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Abstract: How to control non-point source pollution caused by leaching of soil nitrate and phosphate from agricultural land is currently an extremely important global environmental problem facing human society. Biochar, a carbon-rich material produced from various organic feedstocks using thermochemical technologies, has attracted much attention because of its great potential in soil improvement. Many studies have been carried out to investigate the effects of biochar application on the retention, utilization, and use efficiency of soil nutrients. Unfortunately, the results from individual experimental studies regarding the effects of biochar on soil nitrate leaching and phosphate retention differed greatly. Consequently, the underlying mechanisms related to reduction in nitrate and phosphate leaching/retention by biochar application, as well as the appropriate preparation conditions (or biochar type), remain unclear. In this study, the effects of biochar application on soil nitrate leaching and phosphate retention were systematically examined using the method of Meta-analysis (MA); based on these results, the inhibition mechanisms for nitrate leaching and enhancement mechanisms for phosphate retention were also explored. In total, 149 paired datasets from 41 articles and 180 paired datasets from 36 articles were collected for nitrate and phosphate, respectively. The MA results demonstrated that, regardless biochar and soil properties, biochar application could significantly reduce soil nitrate leaching by 37.1% and increase soil phosphate retention by 20.8%. Furthermore, the C/N ratio of biochar, heating treatment temperature, and biochar application amount indicated a significant effect on the response of soil nitrate leaching to biochar application. The specific surface area of biochar, heating treatment temperature, and soil organic carbon content had a significant effect on the response of soil phosphate retention to biochar application. Based on the results from MA, the potential mechanisms of soil nitrite leaching reduction and phosphate retention enhancement were further explored from different perspectives. Lastly, the biochars prepared from straw or wood materials and pyrolyzed at a medium temperature (400-600℃) or high temperature (>600℃) were recommended for reducing soil nitrate leaching and improving soil phosphate retention, respectively. In sum, the results presented in this study can provide a scientifically theoretical basis for the practical application of biochar in the control of soil non-point source pollution of nitrate and phosphate.

Key words; agricultural non-point source pollution control; biochar; soil nitrate leaching; soil phosphate retention; Meta-analysis (MA)

土壤氮、磷是植物正常生长所必需的营养元素.农业生产过程中施加的氮、磷等化肥中硝态氮和磷酸盐极易溶于水,易随降水和灌溉等过程流失,不仅导致养分利用率低,而且还导致严重的水体富营养化面源污染 $^{[1,2]}$ .据估计,全球每年约有  $3.00 \times 10^6 \sim 4.00 \times 10^6$  t  $P_2O_5$  排放到地下水中,径流中农业生产系统年流失无机氮总量已超过  $1.70 \times 10^6$ 

 $t^{[3]}$ . 在中国,农业系统的净氮和净磷损失强度分别为 0.78~23.7 kg·hm<sup>-2</sup>和 0.03~0.31 kg·hm<sup>-2[4]</sup>. 中国长江入海溶解性无机磷年通量已从 1972 年的

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7.60×10³ t 增长至 2007 年的 3.50×10⁴ t; 同一时期入海溶解无机氮通量从 2.00×10⁵ t 增长至 1.30×10⁶ t [5]. 中国非点源导致的氮、磷环境污染事件占比分别达 81% 和 93% [6]. 综上, 农业生产过程中施肥所导致的氮、磷面源污染现已成为全球性的环境问题. 因此, 提高农业土壤的氮和磷固持能力及其利用效率,减少它们的淋失是当前研究的热点问题.

以生物质为原料,在无氧(或限氧)条件高温热 解制备的生物炭,因其独特的理化特性和良好的吸 附性能,被广泛应用于土壤改良和污染修复等领 域[7~10].有研究表明,生物炭能够通过介导土壤物 理条件(如持水能力、土壤颗粒团聚特性等)[9,11]、 土壤化学特性(如离子交换量、pH 和物质/元素组 分等)[9,11,12]和土壤微生物群落结构[13]等方面的变 化,进而对氮、磷在土壤中的迁移和循环过程产生 影响. 前期不同独立实验研究中,由于所选择的受试 土壤和生物炭类型、生物炭添加率等实验条件的差 异,导致现有的关于生物炭对土壤氮和磷淋失/固持 等影响的结果之间存在很大的差异,如对土壤硝态 氮和磷酸盐淋失的影响既有正向的[14,15] 和负向 的[16,17],也有无影响的[18].因此,利用文献整合分析 方法系统研究生物炭对土壤硝态氮和磷酸盐淋溶损 失(或保持能力)的影响,并阐明主要影响因素(生 物炭和土壤特性、实验条件等)的作用规律和机制, 对于更好地指导生物炭的实践应用十分必要. Borchard 等<sup>[19]</sup>和 Glaser 等<sup>[20]</sup>利用荟萃分析(Metaanalysis, MA) 方法分别研究了生物炭对土壤硝态氮 淋失和土壤可利用性磷含量的影响. 但在上述两项 研究中,受所报道文献数量的限制,无论从所收集数 据的规模,还是所考察影响因素指标的全面性等方 面都存在一定欠缺. 因此,随着相关研究的增长,十 分有必要进行 MA 的更新研究,通过更大数据规模 和更加全面的研究以提高相关 MA 研究结果的科学 性和可靠性.

本研究利用 MA 方法,针对以下 3 个方面开展了研究:①明确生物炭添加对土壤硝态氮淋失及磷酸盐固持的总体影响;②进一步明确相关考察因素(包括生物炭和土壤特性、实验条件等)对总体结果的影响;③探讨生物炭降低硝态氮淋失和提高磷酸盐固持的主要过程机制,并提出适宜的生物炭制备条件和特性.

#### 1 材料与方法

#### 1.1 数据收集

为研究生物炭添加到土壤中对硝态氮淋失、磷酸盐固持的影响,分别从 Science Direct、Springer、百

度学术和中国知网等数据库以"生物炭(biochar or BC or charcoal)"、"土壤(soil)"、"硝态氮 (nitrate)"、"磷酸盐(phosphate)"、"淋溶 (leaching)"、"固持(retention)"和"阻截 (interpretation)"等为关键词搜索经同行评审的文 献. 对检索到的文献按照以下标准进行筛选[21]. ① 研究为室内或田间实验性质; ② 实验设计包括 对照组(无生物炭添加)和处理组(生物炭添加),且 每组数据仅以有无生物炭添加为唯一变量;③每 个实验处理须有3个及以上重复. 所收集的每条成 对数据(对照组和处理组)中除了硝态氮和磷酸盐 指标(其中的一个或者两个)外,还包括其他土壤特 性[质地、黏粒含量、pH、阳离子交换量(cation exchange capacity, CEC)、有机碳(soil organic carbon, SOC)、总氮(total nitrogen, TN)和有效磷含 量〕、生物炭特性「原料、热解温度(heating treatment temperature, HTT)、pH、CEC、灰分含量 (ash content, AC)、比表面积(specific surface area, SSA)、总碳(total carbon, TC)和 TN]和实验条件 (生物炭添加率和是否配施化肥),见表1.土壤中氮 的存在形态众多,且在非生物和生物等过程作用下, 硝态氮能够被转化为气态氮(如 N,、N,O和 NH,), 用土壤中硝态氮含量的变化无法表征生物炭对土壤 硝态氮固持的影响. 而对于磷酸盐而言,其在土壤中 的存在相对比较稳定. 因此,本研究以硝态氮的淋失 量(淋溶液中硝态氮的浓度)的变化来表征生物炭 对土壤硝态氮固持的影响,与对照处理相比,生物炭 处理淋失量越低,表明生物炭越能提高土壤硝态氮 的固持. 而对于生物炭对磷酸盐固持的影响,既可通 过土壤中磷酸盐含量,也可以通过淋溶液中磷酸盐 浓度进行表征,但需要将这两个指标进行统一.本研 究将报道的淋溶液磷酸盐浓度变化换算为土壤磷酸 盐含量变化,认为生物炭降低(增加)磷酸盐淋失量 等于生物炭增加(降低)土壤磷酸盐含量,例如:生 物炭降低磷酸盐淋失为20%,则认为土壤磷酸盐含 量增加20%,即土壤的磷酸盐固持提高20%.经筛 选和数据收集,用于硝态氮的相关研究共有41篇文 献,收集149条成对实验数据,符合磷酸盐的相关研 究共有36篇文献,收集180条成对实验数据.

数据收集过程中,对于部分以图形式展示的文献数据利用 Plot Digitizer 软件(www. plotdigitizer. sourceforge. net)进行数值数据提取. 此外,部分数据还存在不同文献中单位不同或缺失等情况,对于不同情况按照以下方式进行统一和补充:① 将 pH (CaCl<sub>2</sub>)利用公式 pH(H<sub>2</sub>O) =  $1.65 + 0.86 \times pH$  (CaCl<sub>2</sub>)转化为 pH(H<sub>2</sub>O) [22];② 若文献只报道了

土壤有机质(soil organic matter, SOM),通过 SOC = SOM × 0.58 确定 SOC 含量,其中 0.58 为 Bemmelen 经验指数<sup>[23]</sup>;③ 若文献报道方差分析结果为标准误(SE),标准差(SD)可用 SD = SE(n 为处理的重复数)确定<sup>[21,24]</sup>;④ 若文章中未报道 SD,可按照指标值的 ± 10% 确定<sup>[21]</sup>;⑤ 若文献报道的生物炭添加率为t·hm<sup>-2</sup>,可通过土壤容重(文章若未提及,采用统一数值 1.3 g·cm<sup>-3</sup>)和施用土壤深度(文章若未提及,采用 20 cm)转化为添加率(%).

#### 1.2 数据分析

本研究利用 MA 方法定量研究土壤硝态氮淋失和磷酸盐固持对生物炭添加的响应.为了进一步考察不同因素(土壤特性、生物炭特性和实验条件)对生物炭介导的变量响应的影响,综合不同 MA 研究中的分类标准和方法 $^{[20-22]}$ ,将各考察因素分成不同的组,具体分组及其标准见表 1. 重采样测试在 999次迭代中完成,并采用罗森塔尔法(Rosenthal's method)检测发表偏倚和 MA 结果的稳健性 $^{[21]}$ . 当统计数据显著时(Kendall's Tau 或 Spearman Rankorder 的 P 值其中之一或两者均小于 0.05),则认为存在发表偏倚,需进一步比较失安全系数 N 与 5n+10 时,认为发表偏倚不影响数据趋势;反之,当统计数据不显著时(Kendall's Tau 与 Spearman Rank-order

的 P 值均大于 0.05),则认为不存在发表偏倚,不影响数据趋势<sup>[22]</sup>. 用组间异质性指数  $(Q_b)$  和 P 值检验组间异质性(表 2). 若某一分组指标的  $Q_b$  处于显著性水平上 (P < 0.05),说明该指标不同组之间的结果存在显著性差异. 根据检验结果 ( 表 2 ),虽然部分考察因素存在发表偏倚,但都通过了失安全系数检验,表明 MA 所得结果具有高的稳健性.

使用软件 MetaWin 2.1 中的随机-效应模型进行结果处理,通过将实验结果标准化为效应量来对各实验结果进行综合分析,MA 允许对不同实验变量的多个研究结果进行精确的统计比较.效应量是响应值(RR)的自然对数:

$$\ln(RR) = \ln(X_1/X_c) \tag{1}$$

式中,  $X_{\epsilon}$  为生物炭处理组均值,  $X_{\epsilon}$  为对照组均值.

土壤硝态氮淋失量和磷酸盐固持的变化率表示为:

变化率(%) = 
$$RR \times 100\% - 100\%$$
 (2)

对每个变量组来说, ln(RR) = 0 表示无效应, ln(RR) > 0 表示为增强效应, ln(RR) < 0 表示为减弱效应. 经对数转换的数据用于计算总体响应值及每个组的95%置信区间. 若两组95%置信区间不存在重叠,表明其间存在显著差异;若置信区间不与零重叠,表明生物炭添加组与对照组之间存在显著差异

表 1 土壤硝酸盐淋失和磷酸盐固持对生物炭响应的 Meta-analysis 中各考察因素分组及其标准<sup>1)</sup>

Table 1 Groups and classified standard for each examined factor in the Meta-analysis of responses

of soil nitrate leaching and phosphate retention to biochar application

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因素分类	因素名称	分组及其标准	因素名称	分组及其标准
	原料类型	秸秆类、有机废弃物类和木质类	SSA/m <sup>2</sup> ⋅g <sup>-1</sup>	硝酸盐:≤50、50~100 和≥100 磷酸盐:≤100 和>100
11- 11-lm 12-	HTT∕℃	≤400、400~600 和≥600	TC/g·kg <sup>-1</sup>	硝酸盐:≤300、300~500、500~700 和≥700 磷酸盐:≤500、500~700 和≥700
生物炭 特性指标	рН	硝酸盐: ≤8、8~10 和≥10 磷酸盐: ≤7、7~8、8~10 和≥10	TN ∕g•kg <sup>-1</sup>	硝酸盐: ≤5、5~10、10~15 和≥15 磷酸盐:未考察
	CEC/cmol·kg <sup>-1</sup>	≤50 和 >50	C/N	硝酸盐: ≤50、50 ~100 和≥100 磷酸盐:未考察
	AC/%	≤10、10~25 和≥25		
	质地	黏土(砂粒>50%,黏粒<30%)、壤土 (砂粒20~50%,黏粒<30%)和砂土 (砂粒<20%,黏粒>30%)	CEC/cmol·kg <sup>-1</sup>	硝酸盐: ≤20 和 >20 磷酸盐: ≤10、10 ~20 和 ≥20
土壤特性	黏粒含量/%	≤15、15~30 和≥30	SOC/g·kg <sup>-1</sup>	硝酸盐:≤10 和>10 磷酸盐:≤10、10~20 和≥10
	рН	<6、6~7、7~8 和≥8	TN/g·kg <sup>-1</sup>	硝酸盐: ≤1、1~2 和≥2 磷酸盐: 未考察
	有效磷/mg·kg <sup>-1</sup>	硝酸盐:未考察 磷酸盐:≤10、10~20 和≥20		
实验条件	生物炭添加率/%	≤1、1~3和≥3	是否配施化肥	硝酸盐:配施化肥和不配施化肥 磷酸盐:未考察

1)分组及其标准列中对每个指标分别注明硝酸盐和磷酸盐的分组,如未明确注明说明该指标的硝酸盐和磷酸盐分组相同

#### 1.3 结果处理

Excel 2010 和 OriginPro 2017 软件完成. MA 的结果通过森林图展示,森林图给出每组数据的总体平均

#### 表 2 Meta-analysis 中各分组的发表偏倚和组间异质性检验结果

Table 2 Statistical results of publication bias and heterogeneity for each group us	sed in the	Meta-analysis
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					发表偏倚	检验			组间异原	质性检验
分组	土壤/生物炭/实 验条件指标	实验组数 (n)	Kendall's Tau	Spearman Rank-order 相关性	失安全 系数 (N)	5n + 10	是否存 在偏倚	偏倚是否 影响趋势	$Q_{ m b}$	P
	生物炭原料	140	0. 377 50	0. 427 48	1 290 905	710	否	否	1. 058	0.716
	生物炭 HTT	126	0. 623 05	0. 629 93	778 988	640	否	否	18. 557	0.007
	生物炭 pH	118	0. 316 94	0. 346 98	952 406	600	否	否	1. 419	0. 551
	生物炭 CEC	58	0. 164 16	0. 251 87	317 023	300	否	否	0.670	0.501
	生物炭 AC	31	0.00289	0.00784	51 848	165	是	否	1. 037	0.746
	生物炭 SSA	74	0. 270 49	0. 283 57	157 636	380	否	否	3. 943	0. 229
	生物炭 TC	104	0. 206 85	0. 235 69	848 461	530	否	否	9. 352	0.087
	生物炭 TN	106	0. 386 52	0. 422 71	1 017 871	540	否	否	7. 495	0. 222
硝态氮	生物炭 C/N	28	0.00064	0. 002 18	53 792	150	是	否	24. 675	0.002
	土壤质地	107	0. 401 64	0. 423 43	711 158	545	否	否	7. 499	0. 124
	土壤黏粒含量	96	0. 182 00	0. 231 66	631 414	490	否	否	6. 651	0. 171
	土壤 pH	131	0. 196 33	0. 248 70	1 106 925	665	否	否	4. 638	0. 345
	土壤 CEC	58	0. 248 29	0. 351 97	60 605	300	否	否	0.752	0.646
	SOC	47	0.00254	0.00210	162 872	245	是	否	0.858	0. 404
	土壤 TN	90	0. 523 71	0. 598 65	254 918	460	香	否	2. 923	0. 140
	生物炭添加率	146	0. 241 43	0. 292 10	1 372 609	740	否	否	29. 208	0.001
	是否配施化肥	147	0.065 31	0. 104 14	1 359 706	745	否	香	5. 004	0. 086
	生物炭原料	174	0. 751 18	0. 799 98	233 082	880	∥ 否	否	0. 183	0.808
	生物炭 HTT	171	0. 488 79	0. 565 90	205 250	865	否	否	3. 482	0.025
	生物炭 pH	143	0. 629 62	0. 702 88	281 781	725	否	否	1. 677	0. 220
	生物炭 CEC	77	0. 053 78	0. 113 25	9 863	395	香	否	1. 423	0.318
(_	生物炭 AC	58	0. 730 83	0. 810 54	19 193	300	否	否	6. 881	0.061
7	生物炭 SSA	82	0. 309 30	0. 393 01	30 941	420	否	否	15. 838	0.002
磷酸盐	生物炭 TC	149	0. 940 08	0. 963 24	216 911	755	香	否	0. 773	0. 422
IV4 FIX Ini.	土壤质地	123	0. 025 95	0. 057 17	40 305	625	是		0.081	0. 980
0	土壤黏粒含量	93	0. 000 99	0.005 20	21 953	475	是	否	2. 375	0.464
16.0	土壤 pH	168	0. 464 11	0. 553 77	240 188	850	否	否	2. 072	0. 243
10	土壤 CEC	55	0. 204 27	0. 230 27	1 667	285	否	否	5. 134	0. 087
1	SOC	54	0.00000	0.00000	1 874	280	是	否	11. 350	0.018
A	土壤有效磷含量	87	1.00000	0. 983 32	89 090	445	否	否	1. 169	0.302
	生物炭添加率	179	0. 747 17	0. 795 96	239 352	905	否	否	0.340	0.667

响应值及95%置信区间.

#### 2 结果与分析

#### 2.1 生物炭对土壤硝态氮淋滤的影响

#### 2.1.1 生物炭特性对土壤硝态氮淋滤响应的影响

土壤硝态氮淋失对生物炭添加的总体响应及其在不同因素分组中的变化等结果见图 1. 与对照相比,生物炭添加可显著减少硝态氮淋失量为 37. 1% (全组均值,不考虑任何影响因素),表明生物炭对硝态氮的淋失具有积极的抑制效应. 然而,不同生物炭或土壤特性组中的响应值表现出明显差异,说明各考察因素对硝态氮淋失响应具有不同的影响. 如图 1(a)所示,硝态氮淋失响应值在不同的生物炭原料、pH、CEC、AC、SSA、TC 和 TN 等的各自分组之间的变化较小,且它们的组间异质性检验结果 P 值均高于 0. 05(表 2),意味着上述生物炭特性指标的变化不会对硝态氮淋失响应产生显著性影响. C/N

≤50 组与对照相比, 硝态氮淋失量可显著减少68.2% [图 1(a)],表明低 C/N 的生物炭更加有利于减少硝态氮的淋失. 相反,在 HTT <400℃的组中,与对照相比硝态氮淋失量仅显著减少 14.2%,说明低 HTT 制备的生物炭表现出较弱的抑制硝态氮淋失损失的潜力. 在所有生物炭组中, C/N ≤50 组中硝态氮淋失损失减少的潜力最大(-68.2%),其次是 HTT 为 400 ~600℃组(-43.6%). 此外,从不同AC 组间的结果来看,当生物炭 AC ≥10% 时,灰分含量越高,硝态氮淋失的减少潜力越大.

#### 2.1.2 土壤特性对土壤硝态氮淋失响应的影响

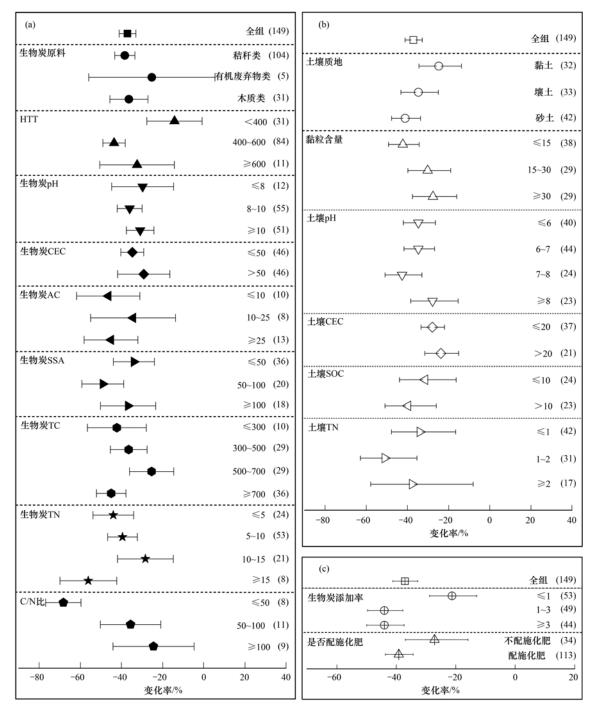
土壤硝态氮淋失对生物炭添加的响应受土壤特性的影响见图 1(b),结合表 2 中组间异质性检验的结果显示,所有土壤特性指标对硝态氮淋失响应均无显著性影响. 从不同土壤质地与黏粒含量两指标各自组间的硝态氮淋失响应值的变化规律来看,随着土壤黏粒含量升高,生物炭减少硝态氮淋失的潜

力下降,如硝态氮淋失减少量从砂土组的 41.1%下降到黏粒组的 24.6%、从黏粒含量  $\leq$  15% 组的 42.2%下降到黏粒含量  $\geq$  15% 组的 27.6%.由此推断土壤黏粒含量越高,越不利于生物炭减少硝态氮的淋失.而在土壤 CEC > 20 cmol·kg<sup>-1</sup>组中,硝态氮淋失减少潜力为 - 23.7%,远低于总体平均响应值 (-37.1%),说明土壤 CEC 较高时,生物炭添加更倾向于促进硝态氮的淋失.土壤 CEC 表现出与生物炭 CEC 较为一致的对硝态氮淋失的影响规律,说明

较高的 CEC 值可能是促进硝态氮淋失的重要因子. 所有土壤指标组,在土壤 pH 为 7~8(-42.6%)和 SOC <10 g·kg<sup>-1</sup>(-39.7%)的组中,生物炭表现出最高的减少硝态氮淋失的作用潜力.

#### 2.1.3 实验条件对土壤硝态氮淋滤响应的影响

土壤硝态氮淋失对生物炭添加的响应受实验条件的影响见图 1(c). 与不配施化肥相比,配施化肥的条件下生物炭减少硝态氮淋失的作用效果更明显. 低生物炭添加率(≤1%)的组中,生物炭降低硝



(a)生物炭特性组,(b)土壤特性组,(c)实验条件组(各因素分组及其标准的详细信息见表1);括号内的数值为该分组的样本数量 图1 土壤硝态氮淋失对生物炭添加响应结果

Fig. 1 Results of the response of soil nitrate leaching to biochar application

态氮淋失的潜力显著低于其他两个高添加两组,这 表明生物炭对硝态氮淋失的作用潜力受一定规模效 应的影响.

#### 2.2 生物炭添加对土壤磷酸盐固持的影响

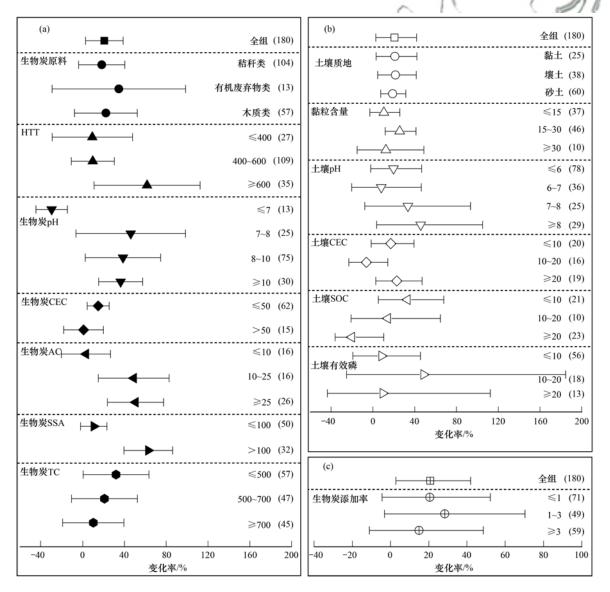
#### 2.2.1 生物炭特性对土壤磷酸盐固持响应的影响

土壤磷酸盐固持对生物炭添加的总体响应及其在不同因素分组中的变化见图 2. 与对照相比,生物炭添加可显著提高磷酸盐固持量为 20. 8% (全组均值,不考虑任何影响因素),表明生物炭对磷酸盐的固持具有积极的提高潜力. 但对于单个生物炭指标而言,不同考察指标对生物炭介导的磷酸盐固持响应的影响具有明显的差异. 从具体结果来看,磷酸盐固持最大的正响应值出现在 SSA >  $100 \text{ m}^2 \cdot \text{g}^{-1}$  (62. 8%)和 HTT $\geq 600 \, \text{℃}$  (61. 7%)组中;而在生物炭 pH $\leq 7$  组中,生物炭的添加显著降低了磷酸盐固

持,响应值为 - 29.7%. 从各指标的不同组之间的磷酸盐固持响应值变化规律来看,随着 HTT、pH、AC或 SSA 升高,生物炭提高磷酸盐固持的潜力升高.这些规律说明生物炭的 HTT 越高、AC和 SSA 越大以及 pH 呈较强碱性时,越有利于提高磷酸盐固持.相反,随着生物炭 CEC和 TC升高,生物炭越不利于磷酸盐固持的提高.

# **2.2.2** 土壤特性和生物炭添加率对土壤磷酸盐固持响应的影响

根据图 2(b) 和表 2 中组间异质性检验的结果显示:除 SOC 外( $Q_b = 11.350$ , P = 0.018),其他所有土壤特性指标对磷酸盐固持响应均无显著性影响. 值得注意的是, 虽然在土壤 CEC 为  $10 \sim 20$  cmol·kg<sup>-1</sup>和 SOC  $\geq 20$  g·kg<sup>-1</sup>的组中观测到负响应值,但是与对照相比没有显著性差异. 上述结果表



(a)生物炭特性组,(b)土壤特性组,(c)实验条件组(各因素分组及其标准的详细信息见表1);括号内的数值为该分组的样本数量 图2 土壤磷酸盐固持对生物炭添加结果

Fig. 2 Results of the response of soil phosphate retention to biochar application

明,土壤特性对生物炭介导的磷酸盐固持的变化影响很小.总体上来看,生物炭添加到高黏粒、高 pH、高 CEC 或低 SOC 的土壤中,更加有利于其提高磷酸盐固持.此外,磷酸盐固持响应在不同生物炭添加率下无显著性差异[图 2(c)],表明生物炭添加规模效应对磷酸盐固持的影响很小.

#### 3 讨论

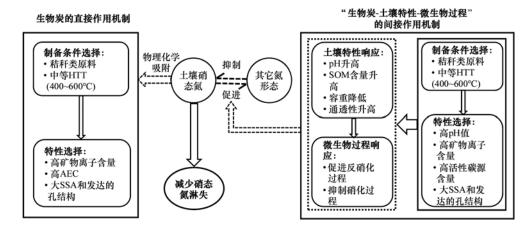
#### 3.1 生物炭对土壤硝态氮淋失影响的潜在机制

Borchard 等<sup>[19]</sup>的 MA 研究结果显示:生物炭添加能够减少硝态氮淋失量为 26%~32%. 该结论与本文所得到的 37. 1% 较为一致. 同时,在笔者先前的研究中发现,生物炭添加对土壤硝态氮含量无显著性影响<sup>[21]</sup>. 由此可推断,生物炭减少硝态氮淋失可能由两方面的机制同时发生作用(图 3):一是生物炭通过物理化学吸附直接固定硝态氮;二是通过促进硝态氮向其他氮形态的转化或抑制其他氮形态向硝态氮转化,减少土壤中可用于淋失的硝态氮含量.

有研究表明,生物炭通常含有较高的负表面电荷(如负电荷的官能团—COO<sup>-</sup>、—COH、—OH和CO<sup>2</sup>、等)<sup>[25]</sup>及较低的等电点<sup>[26]</sup>,导致其对硝态氮等阴离子具有较强的排斥力,因而具有较差的吸附性能<sup>[22]</sup>.因此,高CEC的生物炭将不利于硝态氮的吸附固持[图1(a)].然而,生物炭灰分中的金属氧化物,如MgO和CaO等物质具有较高的等电点,可通过静电吸引的方式增加对硝态氮的吸附,因而较高AC的生物炭有利于硝态氮的固持[图1(a)].生物炭的物理结构特性(如SSA、孔径分布和孔体积等)是影响生物炭对硝态氮吸附性能的关键因素<sup>[27]</sup>,且两者之间通常存在正相关的关系<sup>[22]</sup>.然而,本文MA的结果显示,最佳的减少硝态氮淋失潜

力出现在中等 SSA(50~100 m<sup>2</sup>·g<sup>-1</sup>)生物炭组,且 不同 SSA 生物炭组之间差异不显著,表明生物炭的 SSA 对其减少硝态氮淋失潜力的贡献有限. 制备原 料和HTT是影响生物炭特性的两个重要因 素[28~30].一般来说,污泥等有机废弃物制备的生物 炭营养物质和 AC 较高,但其 TC 很低,所制备的生 物炭 SSA 较小和孔隙不发达[31,32];同时,秸秆类生 物炭与木质类生物炭相比,其 AC 和 pH 值较高,因 而对硝态氮具有更强的吸附能力[33]. 由此推断, 秸 秆类生物炭具有更大的减少硝态氮淋失的潜力,这 一点在本次 MA 中得到了进一步证实[图 1(a)]. 从 HTT 方面来看,随着 HTT 的升高,在低 HTT 条件下 生成的酸性含氧官能团(如—COO<sup>-</sup>、—COH、 —OH和 CO2-)[25]逐渐分解并转化为中性或碱性的 融合芳香基团(包括色胺、酮和吡喃),导致 CEC 降 低[34,35],且生物炭的 AC、pH 和 SSA 逐渐升高[28]. 因此,相对于低 HTT,高 HTT 制备的生物炭有利于 阴离子(如硝态氮)的吸附<sup>[36]</sup>. 然而,本文的 MA 结 果发现,相对于高 HTT(≥600)组,中等 HTT(400~ 600℃)生物炭组表现出更大的减少硝态氮淋失的 潜力,说明 HTT 过高反而会削弱生物炭减少硝态氮 淋失的潜力. 这可能因为当温度升高超过某一阈值 时,生物炭的结构就会发生变化,而导致 SSA 减少. 例如, Chun 等[37] 报道了当 HTT 从 600℃ 升高到 700℃时,小麦秸秆生物炭的 SSA 从 438 m<sup>2</sup>·g<sup>-1</sup>下 降到363 m<sup>2</sup>·g<sup>-1</sup>. 此外,相关研究还提出生物炭对硝 态氮的吸附可能通过硝态氮与生物炭表面之间非常 规的氢键结合[22]. 然而,本研究的 MA 中因可收集 数据的限制,未涉及该方面内容,在未来研究中应值 得关注.

生物炭添加通过改变土壤 pH、活性有机碳源 (如溶解有机碳)、氧环境和含水率等特性,改变土



虚线框内为土壤/微生物对特定生物炭添加的潜在响应,虚线箭头为生物炭直接的或间接的对硝态氮吸附/转化的潜在作用

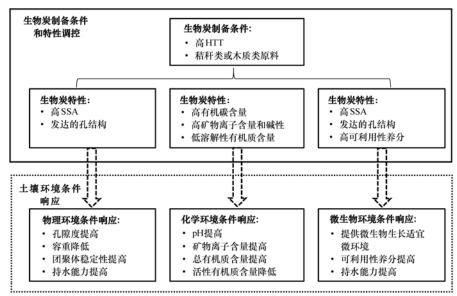
#### 图 3 生物炭降低土壤硝态氮淋失的潜在机制和适宜生物炭制备和特性条件

Fig. 3 Potential mechanisms of reducing soil nitrate leaching by biochar and the suitable production conditions and properties of biochar

壤氮转化相关微生物的活性和群落结构[38,39]. Wang 等[38] 发现花生壳生物炭能够显著提高土壤 pH 和 SOM 含量,而降低容重,导致显著降低氨氧化 细菌的丰度,进而抑制土壤硝化过程.在另外一项 MA 研究中发现:生物炭添加能够显著增加反硝化 功能基因丰度(如 narG、nirK 和 nirS),并且进一步 揭示这一增加结果与生物炭对土壤通透性和容重的 改善密切相关[13]. 此外,生物炭中活性有机碳源可 诱导微生物固定氮或通过在老化生物炭上的有机碳 层捕获硝态氮分子,也可提供维持微生物代谢所需 的能量和还原硝酸根所需的电子,促进反硝化作 用[40,41]. 综上,生物炭通过对土壤上述特性的改变, 抑制或促进硝化或反硝化过程,降低土壤中硝态氮 的总量,也就意味着土壤中可用于发生淋失的硝态 氮的量降低. 然而,生物炭对土壤特性的影响取决于 其初始特性,而原料和 HTT 是影响生物炭初始特性 的关键因素. 通常来讲, 相对于低 HTT( <500℃) 或 其他有机废弃物原料(如污水污泥和动物粪便),高 HTT(如 > 500℃)或木质纤维素含量高的原料(如 木质和秸秆类原料)条件下制备的生物炭具有更好 的物理结构、更高的 pH 和有机碳含量[28]. 这一类 生物炭对土壤反硝化过程具有更大的促进潜力. 这 与本研究 MA 得到的结论较为一致:中等或高 HTT 和木质或秸秆类原料的生物炭组表现出更大的减少 硝态氮淋失的潜力[图1(a)].

3.2 生物炭对土壤磷酸盐固持影响的过程和机制 磷酸盐在土壤中的动态变化过程主要受以下 3 个方面控制(图 4),包括:① 土壤化学环境,如 pH 和阴离子交换量(anion exchange capacity, AEC)等 条件调控的磷酸盐吸附/解吸、沉淀/溶解平衡和有机-矿物复合物等<sup>[18,42,43]</sup>;②土壤物理环境,如容重和孔隙度等<sup>[14]</sup>;③土壤微生物环境等<sup>[44,45]</sup>.

生物炭添加能够引起土壤化学环境(如 pH、离 子交换和 SOM 含量等)的显著变化,进而引起固磷 矿物的沉淀/溶解等平衡发生改变[14,46,47]. 土壤 pH 可调节固磷矿物在土壤中的吸附特征和各种含磷矿 物的溶解度. 在酸性土壤中, 磷主要被 Fe 和 Al 固 持,而在碱性土壤中,则主要被 Ca 和 Mg 固持,且环 境 pH > 7 时, 更有利于 Ca/Mg 磷酸盐沉淀的形 成<sup>[42]</sup>. 因此生物炭具备的"石灰效应(liming effect)"对增强土壤的磷酸盐固持具有积极作用. 本 研究的 MA 结果也证实高 pH 生物炭或生物炭在碱 性土壤中应用,表现出更好的磷酸盐固持提高效果 「图 2(a)和 2(b)]. 土壤的离子交换环境能直接影 响磷酸根的吸附/解吸过程. 当生物炭表面有大量氧 鎓基团、吡啶基团和质子化芳香结构时,其具有较 高的 AEC, 有利于增加对阴离子(如磷酸根)的吸 附<sup>[48,49]</sup>. 此外,生物炭灰分中含有的 Fe、Al、Ca 和 Mg等离子可通过沉淀或阳离子桥来捕获磷酸 根<sup>[49~51]</sup>. 因此,高 AC 或低 CEC 的生物炭更加有利 于磷酸盐的吸附固持,相反则不利于磷酸盐的吸附 固持[图 2(a)]. SOM 特征也是影响磷动态变化的 重要因素. 最新研究发现生物炭衍生的溶解有机质 (BDOM)可能参与(生物)地球化学过程:相比自然 溶解性有机质,BDOM 拥有更多的活性官能团(如— OH 和—COOH),这可能导致土壤矿物上已吸附的 磷与含氧阴离子对吸附位点的竞争[52],该竞争可随 土壤 pH 值的变化而变化[53]; BDOM 也可吸附金属



虚线框内为土壤环境条件对特定生物炭添加的潜在响应

图 4 生物炭提高土壤磷酸盐固持的潜在机制和适宜生物炭特性

Fig. 4 Potential mechanisms of enhancing soil phosphate retention by biochar and the suitable biochar properties

离子,改变土壤磷的吸附/解吸和沉淀/溶解过程,进一步与磷形成有机络合物组分<sup>[52,53]</sup>;另外,在富含 Fe/Al 氧化物的酸性土壤中,pH值的小幅增加可导致磷与土壤矿物质的相互作用大幅度减弱<sup>[46,54]</sup>,BDOM可作为电子穿梭体,在Fe(Ⅲ)矿物和微生物之间传递电子,推动Fe(Ⅲ)还原,从而释放矿物伴生的磷<sup>[55,56]</sup>.低 HTT 制备的生物炭,通常含有较高的 BDOM 含量,那么其是不是导致该类生物炭存在潜在的增加土壤磷酸盐淋失风险的原因[如图 2(a)中的低和中 HTT 生物炭组]?这一点值得在后期的研究中关注.

生物炭添加的土壤物理环境对磷固持的影响主要体现在对磷的存储和其流动性上. 研究表明,生物炭具有较大的 SSA 和大量的微孔,可通过孔隙填充机制增加对流动磷的吸附<sup>[57]</sup>. 因此生物炭 SSA 越大,对土壤磷酸盐固持提高潜力越大[图 2(a)]. 添加生物炭后,土壤孔隙度增加、容重降低和团聚体稳定性提高等有益效应也会间接提高土壤保水能力<sup>[14,58,59]</sup>,土壤持水能力的增加将减少营养物质的流失<sup>[60]</sup>,同时也可通过促进植物对磷的吸收来减少磷的损失<sup>[54]</sup>. 此外,土壤水分的入渗速率、渗透性和排水途径也会受生物炭的添加而有所改变,从而降低磷的淋失风险<sup>[61,62]</sup>.

生物炭添加可对土壤微生物磷循环产生复杂的影响<sup>[63]</sup>. 如生物炭的物理特征(如发达的孔隙结构和大 SSA)可改变土壤微气候和水分环境,从而有利于微生物的生长繁殖,使得微生物在干燥的气候条件下也能生存<sup>[64,65]</sup>;土壤 pH 值的变化可诱导酶活性及微生物种群(如溶磷菌溶解无机磷)的变化<sup>[66,67]</sup>;生物炭提供的营养物质及躲避捕食者的庇护场所,有利于真菌菌根的生长和溶磷菌的存活,从而使得微生物的生物量增加,这反过来可提高磷的可用性或在土壤中的固持,进一步影响内源磷在土壤中的溶解性<sup>[68]</sup>. 除上述有利于微生物磷循环的优点外,高 HTT 制备的生物炭也容易产生较多损害微生物生长繁殖的物质<sup>[57,69]</sup>,在今后的研究中有必要深入探讨毒性物质对土壤微生物磷循环的影响.

#### 4 结论

- (1)总体上,生物炭能够显著减少硝态氮淋失37.1%,显著提高磷酸盐固持20.8%.
- (2)生物炭 C/N、HTT 和添加率对硝态氮淋失响应具有显著影响,而其他考察因素则无显著性影响;生物炭 SSA、HTT 和 SOC 含量对磷酸盐固持响应具有显著影响,其他因素则无显著性影响.
  - (3) 秸秆和木质类原料、中高 HTT (400~

600℃)条件下制备的生物炭适宜于减少土壤硝态 氮的淋失;秸秆和木质类原料、高 HTT(>600℃) 条件下制备的生物炭适宜于提高土壤磷酸盐的 固持.

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