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2000~2018年我国大气重金属沉降通量时空变化特征

陈其永, 郜允兵, 倪润祥, 潘瑜春, 阎跃观, 杨晶, 刘孝阳, 顾晓鹤



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生物炭施用对黄壤土壤养分及酶活性的影响

袁访, 李开钰, 杨慧, 邓承佳, 梁红, 宋理洪*

(贵州大学农学院, 贵阳 550025)

摘要: 生物炭因其具有特殊的理化性质, 作为土壤改良剂或调理剂被广泛应用于改善土壤质量; 土壤养分与土壤酶活性是表征土壤质量化学性质和生物学性质的重要指标. 采用大田试验, 研究生物炭不同施水平: 0 (CK)、5 (B5)、10 (B10)、20 (B20) 和 50 (B50) $\text{t} \cdot \text{hm}^{-2}$ 对黄壤养分和土壤酶活性的影响, 运用结构方程模型 (SEM) 定量分析生物炭处理对土壤养分和酶活性的直接或间接影响及其作用大小. 结果表明, 生物炭显著增加土壤 pH 值、电导率、有机碳、碱解氮、有效磷和速效钾 ($P < 0.05$); 随生物炭施用量的增加, 土壤过氧化氢酶和脲酶活性先增加后降低, 磷酸酶和蔗糖酶活性增加 ($P < 0.05$); B10 处理下, 土壤过氧化氢酶、脲酶和磷酸酶的活性均达到最大值, 蔗糖酶活性也相对较高. 随生物炭作用时间增加, 土壤 pH 值、碱解氮、有效磷和速效钾含量均增加, 而电导率和有机碳与之相反; 过氧化氢酶活性降低, 脲酶和磷酸酶活性升高, 蔗糖酶活性无明显变化规律. SEM 结果显示, 生物炭施用对过氧化氢酶具有直接的负效应; 通过提升 pH、电导率、有机碳和碱解氮含量间接影响过氧化氢酶活性, 通过提升 pH 和电导率间接促进蔗糖酶活性, 通过提高电导率以及碱解氮和有效磷含量间接增加磷酸酶活性. 综上, 生物炭施用量及作用时间显著影响土壤养分含量, 进而间接作用于土壤酶活性; 酸性黄壤施用 10 $\text{t} \cdot \text{hm}^{-2}$ 的生物炭较为适宜.

关键词: 生物炭; 黄壤; 土壤养分; 酶活性; 结构方程模型

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Effects of Biochar Application on Yellow Soil Nutrients and Enzyme Activities

YUAN Fang, LI Kai-yu, YANG Hui, DENG Cheng-jia, LIANG Hong, SONG Li-hong*

(College of Agriculture, Guizhou University, Guiyang 550025, China)

Abstract: Due to its special physical and chemical properties, biochar is widely used as a multi-beneficial amendment to improve soil quality. Soil nutrient content and enzyme activities are important chemical and biological factors indicating soil quality. Despite increased interest and studies, a knowledge gap remains regarding the ability of biochar to assess soil nutrient content and enzyme activities due to differences in biochar application amount and soil texture. In the present study, the effects of different amounts of biochar application (CK: 0 $\text{t} \cdot \text{hm}^{-2}$, B5: 5 $\text{t} \cdot \text{hm}^{-2}$, B10: 10 $\text{t} \cdot \text{hm}^{-2}$, B20: 20 $\text{t} \cdot \text{hm}^{-2}$, and B50: 50 $\text{t} \cdot \text{hm}^{-2}$) on soil nutrient content and enzyme activities were studied based on a field experiment on typical yellow soil in Guizhou province, southwest China. Structural equation models (SEM) were used to quantitatively evaluate the direct or indirect effects of biochar application on soil nutrient content and enzyme activities. The results showed that soil pH, electrical conductivity (EC), soil organic carbon (SOC), alkaline hydrolysis nitrogen (AHN), available phosphorus (AP), and available potassium (AK) increased with the applied amount of biochar. With the increase in biochar application amount, the activities of soil catalase and urease showed first an increasing and then a decreasing trend, and the activities of soil sucrase and phosphatase showed an almost constant increasing trend ($P < 0.05$). The highest activities of soil catalase, urease, and phosphatase were recorded under treatment B10. A relatively high activity of soil sucrase was also observed under treatment B10. With the same amount of biochar application, soil pH and the content of soil AHN, AP, and AK in treatments after four months of biochar application were greater than those after 12 months. After 12 months of biochar application treatment, the contents of SOC and EC were greater than those at four months. Compared to those in treatments after four months of biochar application, activities of soil urease and phosphatase increased, activities of soil catalase decreased, and activities of soil sucrase did not obviously change after 12 months of biochar application. The results of SEM showed that biochar application directly decreased activities of soil catalase and indirectly promoted activities of soil sucrase and phosphatase by increasing soil pH, EC, AHN, AK, and AP. In conclusion, the amount and duration of biochar application significantly increased soil nutrient content, directly and indirectly affecting soil enzyme activities. Based on the results of the presents study, biochar application at 10 $\text{t} \cdot \text{hm}^{-2}$ was recommended for acidic yellow soil.

Key words: biochar; yellow soil; soil nutrients; enzyme activity; structural equation model

黄壤广泛分布在贵州的高原地带, 是喀斯特地区分布面积最广泛的地带性土壤, 占喀斯特地区总土壤面积的 37.26%^[1], 土壤厚度范围为 33 ~ 60 cm, 是贵州主要的农业土壤类型^[2]. 喀斯特黄壤质地黏、酸度大、保肥持水能力弱、生产力低下. 且喀斯特地区水土流失严重, 造成该地区土壤肥力下降, 大量流失的 N、P 进一步扩散导致农业面源污染和水体富营养化等环境问题^[3]. 目前, 众多学者对黄壤的研究主要集中在黄壤的理化性质和持水性能变化特征及影响机制等方面^[4~7].

生物炭 (biochar) 是在低氧或缺氧环境下, 通常在 300 ~ 1 000 °C 的温度下热裂解有机物质而产生的富碳的固态产物^[8]. 生物炭具有孔隙结构丰富、比表面积巨大、吸附性能强、富含有机碳和 pH 值高等特性^[9,10], 能够提高土壤肥力和调节气候变化等^[11,12], 作为土壤改良剂被广泛应用. 低碳循环和

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作者简介: 袁访 (1997 ~), 女, 硕士研究生, 主要研究方向为生物炭土壤改良, E-mail: 1809316074@qq.com

* 通信作者, E-mail: lihong_song@qq.com

可持续发展是当今社会经济发展的迫切需求,尤其发展低碳农业对于国家粮食安全、环境安全和可持续发展意义重大.采用生物炭还田改土能够有效促进作物生长及产量,并能在固碳减排等方面发挥重要作用,因而在低碳发展方面具有十分广阔的应用前景^[13].目前研究普遍认为,施加生物炭可改善土壤结构、中和土壤酸性和增加养分保持能力等.生物炭改良土壤理化性质的效果受到生物炭性质、施加量、施用时间长短和土壤环境条件等诸多因素的影响.生物炭多孔性和表面积改变土壤容重、孔隙度和持水能力,生物炭固有元素改善土壤的化学特性,其活性表面将长期持续地影响土壤理化性质^[14,15].同时生物炭可通过改善土壤理化性质,间接增加微生物活性.生物炭施入农田后对土壤微生物生物量、微生物群落结构和酶活性等土壤微生物性质产生调控作用,从而影响微生物驱动的养分循环和养分形态转化过程,最终改变土壤肥力质量和功能^[16,17].

土壤酶是综合反映土壤肥力的指标^[18],主要来源于植物残体、根系分泌和土壤微生物^[19],对土壤生态系统中养分的转化和利用有着不可替代的作用^[20],同时受土壤物理、化学和生物学因子等综合因素影响.有研究表明,几乎所有土壤退化都伴随着不同程度土壤酶活性的丧失^[21].Oleszczuk等^[22]通过将生物炭添加到蔬菜地土壤中发现,生物炭能够保护土壤酶,且其对不同土壤酶活性的影响不同:随着生物炭施用量的增加,土壤酸性磷酸酶活性增加,过氧化氢酶和多酚氧化酶的活性则降低^[23].土壤酶活性与土壤养分存在一定相关关系,如脲酶和磷酸酶活性与C、N、P等养分循环密切相关.土壤酶活性也受到土壤结构、pH、微生物和微量元素等因子的影响.目前就土壤理化因子与土壤酶活性关系的研究方法中,如主成分提取等并不能同时处理多个因变量与自变量的联系^[24].这样在一定程度上就偏离了统计因果.近年来,结构方程模型(structural equation modeling, SEM)广泛应用于生态学领域,其不仅能同时处理多个自变量与因变量,还可直观描述潜变量,是探明因果关系的有力方法^[25~27].

目前,生物炭对土壤养分的研究主要集中在室内土柱模拟养分淋溶,尤其土壤氮和磷^[3,28],而田间条件下生物炭施用对黄壤养分含量和酶活性变化的研究较少.本文探讨生物炭不同施用量(0、5、10、20和50 t·hm⁻²)和不同作用时间(生物炭施用4个月后和12个月后)对黄壤养分含量及酶活性的影响,以期为黄壤的改良、农业可持续发展和生物炭资源合理利用提供理论参考.

1 材料与方法

1.1 研究区概况及试验处理

本试验地点位于贵州省贵阳市花溪区贵州大学试验农场(E 106°39'32", N 26°26'20").该区属于亚热带季风性湿润气候,年平均气温 14.9℃,年平均降雨量1 200 mm.试验地土壤类型为酸性黄壤(pH: 6.13,电导率: 47.39 μS·cm⁻¹,有机碳: 16.24 g·kg⁻¹,碱解氮: 127.85 mg·kg⁻¹,有效磷: 15.12 mg·kg⁻¹,速效钾: 23.15 mg·kg⁻¹).本试验采用完全随机区组设计:在试验区内,按5(B5)、10(B10)、20(B20)和50(B50) t·hm⁻²设置生物炭(原料:玉米秸秆,制备温度:500℃,热解时间:6 h, pH: 7.98,粒径: 0.3~0.35 cm,灰分: 29.53%)施用量,以不施生物炭为对照(CK).生物炭一次性施用,并翻耕使其与表层0~20 cm土壤充分混匀.每种处理重复5次,每个试验小区面积为15 m²,小区间设保护行.于2020年4月起进行玉米/油菜两熟轮作种植,其他处理同当地田间管理措施(复合肥施用600 kg·hm⁻²,人工除草,无灌溉).

1.2 土壤样品采集

于生物炭田间施用4个月后(2020-07)和12个月后(2021-03)采集土壤样品,每个试验小区随机采集土壤表层5²×π×10 cm³的土壤.将采集的土壤样品带回实验室,去除碎石、杂草等,风干后研磨,一部分过20目筛,用于土壤pH值、EC值、碱解氮、有效磷、速效钾和土壤酶的测定;另一部分过100目筛(0.149 mm),用于土壤有机炭的测定.

1.3 土壤养分及酶活性分析

土壤养分测定方法参照文献[29]:pH采用电位法,电导率使用电导率仪,有机碳采用重铬酸钾-浓硫酸外加热法,碱解氮采用碱解扩散法,有效磷测定采用0.5 mol·L⁻¹ NaHCO₃浸提-钼锑抗比色法,速效钾测定采用0.5 mol·L⁻¹ NH₄OAc浸提-火焰光度法.酶活性的测定方法参照文献[19]:过氧化氢酶(CAT)采用高锰酸钾滴定法,蔗糖酶(IVN)采用3,5-二硝基水杨酸比色法,脲酶(URE)采用苯酚钠-次氯酸钠比色法,磷酸酶(PHO)采用磷酸苯二钠比色法.

1.4 数据分析

使用单因素方差分析(ANOVA)进行生物炭对黄壤养分影响的分析,使用相关性热图进行生物炭与黄壤酶活性的相关分析.使用结构方程模型研究生物炭处理下各指标对土壤酶的间接和直接影响;将生物炭施用量设定为外生变量,土壤性质(pH、EC、有机碳、碱解氮、有效磷和速效钾)为内生变量,土壤酶活性(过氧化氢酶、蔗糖酶、脲酶和磷酸

酶)为内生解释变量;使用卡方自由度比(Chi/df)、拟合优度指数(GFI)和增进残差均方和平方根(RMESA)对模型进行适配性检验,RMESA<0.08,GFI>0.9,Chi/df<3,模型拟合结果较好^[30~32].所有数据统计分析及图形绘制均采用R语言(4.1.1)及其辅助包完成.

2 结果与分析

2.1 生物炭对黄壤养分的影响

随生物炭施用量的增加,土壤pH、电导率、有

机碳、碱解氮、有效磷和速效钾均显著增加,各指标在B50处理下显著高于其他处理($P<0.05$);B50处理下,各指标在生物炭施用4个月后和12个月后分别增加:pH(14.98%和8.88%)、电导率(32.69%和42.09%)、有机碳(39.10%和45.88%)、碱解氮(14.99%和19.01%)、有效磷(42.05%和31.79%)、速效钾(64.04%和43.65%).在生物炭同一施用量下,随生物炭作用时间的增加,土壤pH值、碱解氮、有效磷和速效钾均增加,而电导率和有机碳与之相反(表1).

表1 不同生物炭用量对土壤主要养分的影响¹⁾

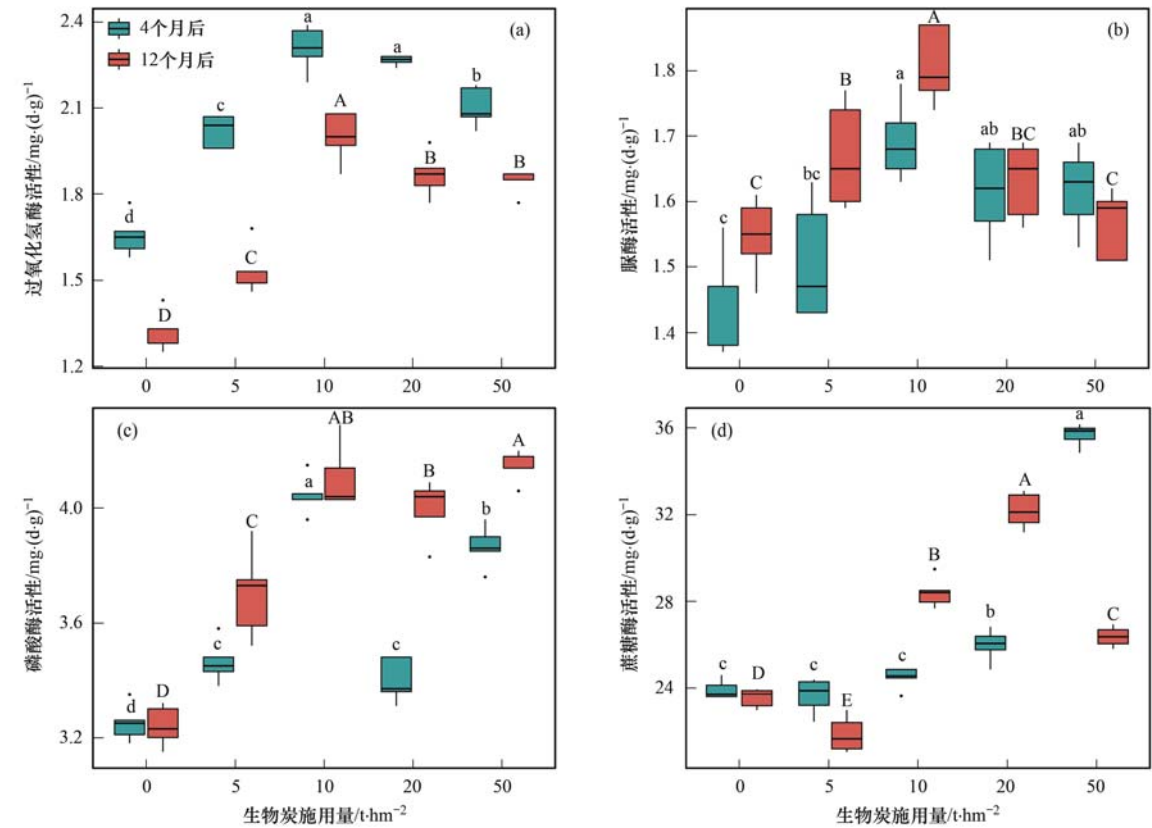
Table 1 Effect of biochar application on soil nutrient contents (Mean ± SD)							
作用时间	处理	pH	电导率 / $\mu\text{S}\cdot\text{cm}^{-1}$	ω (有机碳) / $\text{g}\cdot\text{kg}^{-1}$	ω (碱解氮) / $\text{mg}\cdot\text{kg}^{-1}$	ω (有效磷) / $\text{mg}\cdot\text{kg}^{-1}$	ω (速效钾) / $\text{mg}\cdot\text{kg}^{-1}$
4 个月后	CK	6.14 ± 0.2c	49.40 ± 1.4d	22.89 ± 1.6e	129.58 ± 6.6c	11.32 ± 1.9c	22.25 ± 1.5c
	B5	6.18 ± 0.1c	54.10 ± 1.2c	24.96 ± 1.1d	136.86 ± 9.2bc	13.12 ± 3.3b	22.75 ± 1.9c
	B10	6.32 ± 0.2c	54.93 ± 1.2c	26.34 ± 0.5c	138.96 ± 4.5abc	13.52 ± 2.4b	26.38 ± 3.1b
	B20	6.75 ± 0.1b	58.80 ± 1.5b	28.88 ± 1.3b	146.30 ± 7.8ab	14.18 ± 4.1b	35.38 ± 2.2a
	B50	7.06 ± 0.1a	65.55 ± 0.8a	31.84 ± 1.2a	149.01 ± 9.8a	16.08 ± 3.4a	36.50 ± 3.1a
12 个月后	CK	6.09 ± 0.1d	42.41 ± 0.8e	20.29 ± 1.0d	134.54 ± 5.9c	17.52 ± 2.3b	26.00 ± 2.1d
	B5	6.35 ± 0.2cd	45.72 ± 1.5d	20.45 ± 1.0d	143.20 ± 9.1b	20.65 ± 4.4ab	28.56 ± 0.3d
	B10	6.50 ± 0.1c	49.17 ± 0.3c	23.76 ± 1.2c	146.83 ± 8.2b	20.25 ± 3.8ab	32.56 ± 2.7c
	B20	6.92 ± 0.2b	56.92 ± 1.9b	25.36 ± 1.0b	149.71 ± 4.7b	22.32 ± 1.4a	37.35 ± 3.3b
	B50	7.24 ± 0.1a	60.26 ± 1.3a	29.60 ± 0.8a	160.12 ± 1.7a	23.09 ± 1.2a	42.00 ± 3.3a

1) 同列不同小写字母表示处理间差异显著($P<0.05$)

2.2 生物炭施用对黄壤酶活性的影响

生物炭显著影响土壤酶活性(图1):土壤过氧

化氢酶和脲酶的活性随生物炭施用量的增加先增加后降低,磷酸酶和蔗糖酶活性基本随生物炭施用量



不同小写和大写字母分别表示生物炭作用4个月后和12个月后处理间差异显著($P<0.05$)

图1 生物炭施用后土壤酶活性的变化

Fig. 1 Soil enzyme activities under biochar application

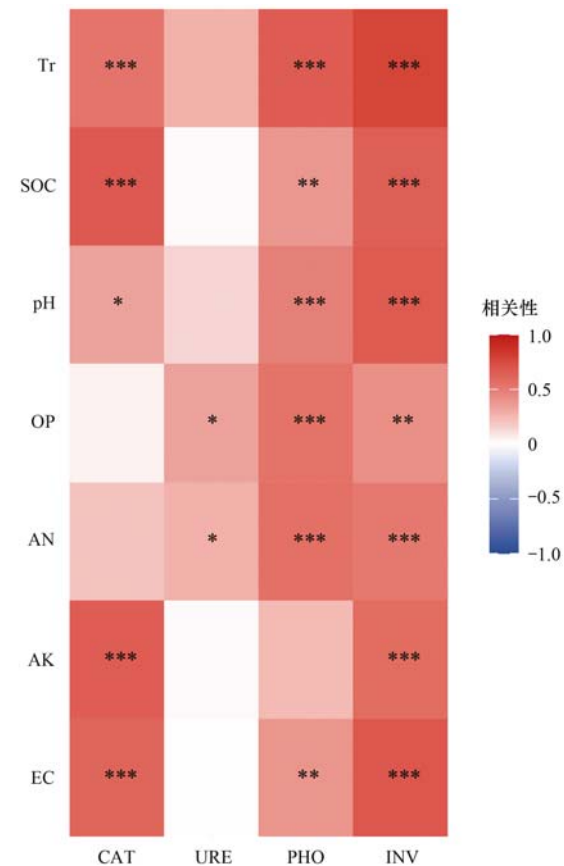
增加而升高($P < 0.05$). B10 处理下,土壤过氧化氢酶、脲酶和磷酸酶的活性均达到最大值,蔗糖酶活性也相对较高. 随着生物炭作用时间的增加,过氧化氢酶的活性降低,脲酶和磷酸酶活性升高,而蔗糖酶无明显变化规律.

2.3 土壤养分与土壤酶相关性分析

土壤酶与土壤养分之间存在较强的相关性(图2). 土壤过氧化氢酶与 pH、土壤有机碳、碱解氮、电导率和生物炭施用量显著正相关($P < 0.05$); 脲酶与有效磷、碱解氮显著正相关($P < 0.05$); 磷酸酶与有机碳、pH、有效磷、碱解氮、电导率和生物炭施用量显著正相关($P < 0.05$); 蔗糖酶与有机碳、pH、有效磷、碱解氮、速效钾、电导率和生物炭施用量显著正相关($P < 0.05$). 可见,土壤酶活性受生物炭施用导致的土壤多个理化因子改变的影响.

2.4 土壤酶活性调控因子

基于结构方程,构建生物炭处理-土壤养分-酶活性之间的驱动与耦合模型. 选取相关变量(生物炭施用量、pH、电导率、有机碳、碱解氮、有效磷和速效钾)整合到结构方程模型中,通过构建初始模型、检查模型、模型修改和对预测变量进行参数化,最终获得最佳结构方程模型(图3). 该模型对过氧化氢酶、蔗糖酶和磷酸酶的总解释度分别为 73.8%、51.4% 和 44.3%. 模型结果显示,生物炭施用的直接作用可对过氧化氢酶产生显著的负影响($\lambda = -1.15$, $P < 0.01$),对磷酸酶($\lambda = 0.05$, $P = 0.84$)和蔗糖酶($\lambda = 0.17$, $P = 0.47$)起一定程度的促进作用. 生物炭通过提升 pH 值、电导率值以及有机碳和碱解氮含量,从而间接影响过氧化氢酶的活

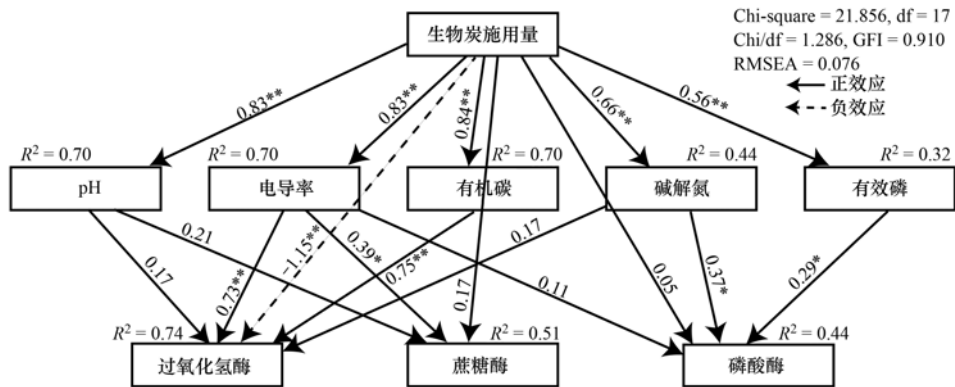


Tr:生物炭施用量; SOC:有机碳; pH:pH 值; OP:有效磷; AN:碱解氮; AK:速效钾; EC:电导率; CAT:过氧化氢酶; URE:脲酶; PHO:磷酸酶; INV:蔗糖酶; * 表示 $P < 0.05$, ** 表示 $P < 0.01$, *** 表示 $P < 0.001$

图2 土壤酶活性与土壤性质的相关性

Fig. 2 Correlation between soil enzyme activity and soil properties

性; 通过提升 pH 值和电导率值的方式间接促进蔗糖酶活性; 通过提高电导率值、碱解氮和有效磷含量,进而间接增加磷酸酶活性.



Chi-square: 卡方, df: 自由度, Chi/df: 卡方自由度比, GFI: 拟合优度指数, RMSEA: 增进残差均方和平方根;
线条上的数据为标准化路径系数(λ); * 表示显著($P < 0.05$), ** 表示极显著($P < 0.01$)

图3 生物炭施用对土壤酶活性的 SEM 分析结果

Fig. 3 Results of structural equation model about biochar application on enzyme activities

3 讨论

3.1 生物炭对黄壤养分的影响

生物炭因其具有特殊的理化性质,作为土壤改良剂或者外源碳被施用土壤后对土壤养分会产生影响. 本研究结果表明,生物炭施用土壤可以显著改变土壤养分,随生物炭施用量的增加,土壤 pH 值、电导率、有机碳、碱解氮、有效磷和速效钾均显著增加;在同一处理下,随生物炭作用时间的增加,土壤 pH 值、碱解氮、有效磷和速效钾均增加;而电导率和有机碳与之相反. 施用生物炭显著增加土壤 pH 值,可能是因为生物炭本身碱性,且其含有大量的 Ca^{2+} 、 K^{+} 和 Mg^{2+} ,降低土壤 Al^{3+} 水平使 pH 值升高. 随作用时间增长,生物炭逐渐老化也会释放碱性物质,提高土壤 pH^[33]. 生物炭含有大量的小颗粒和有机碳,因而电导率和有机碳随生物炭施用量增加显著升高. 但土壤有机碳含量随生物炭施用后时间的增加而降低. 本研究采样深度为表层 10 cm,可能是因为翻耕和作物作用导致生物炭向下转移,因而土壤有机碳和电导率含量降低. 本研究生物炭显著提升土壤速效养分含量,一是因为生物炭本身含有大量的矿物质,其灰分中携带大量的氮磷钾元素^[34],且易于释放到土壤中;二是因为生物炭具有较高的比表面积和较大的孔隙度,能够吸附土壤中的氮磷钾元素^[35],对肥料养分有延长释放的作用^[36],减少它们的淋失;三是因为生物炭能够提高土壤持水性^[37],提高土壤的持磷能力^[38]. 随生物炭作用时间增加,生物炭所含的矿物质持续被释放利用,同时对土壤的孔隙度及团聚体结构有所改良,导致速效氮磷钾含量持续增加.

3.2 生物炭施用对黄壤酶活性的影响

生物炭施用影响土壤理化性质,而土壤酶活性与土壤性质密切相关,所以生物炭施用在一定程度上会引起土壤酶活性的变化. 本研究结果显示,随着生物炭施用量的增加土壤过氧化氢酶和脲酶活性均呈现先增加后降低的趋势,且均在施用量为 $10 \text{ t} \cdot \text{hm}^{-2}$ 达到峰值. 生物炭施用改善了土壤物理结构,增加土壤含水量^[39],从而促进过氧化氢酶活性^[40]. 脲酶活性可能受有机质含量的影响^[41],表现出随生物炭施用量增加而增加. 施炭量持续增加,土壤酶活性下降可能是因为生物炭施用量过高,吸附了土壤中的酶分子对酶促反应结合位点形成保护作用,同时产生一定毒性,从而抑制了土壤酶活性^[42~45]. 本研究中,随生物炭作用时间的增加磷酸酶活性增加. 可能由于生物炭促进土壤微生物的生长和繁殖^[46],加大了对磷素的需求,同时土壤 pH 持续增加,更适

宜磷酸酶活性的增长^[47]. 蔗糖酶活性随生物炭作用时间无显著变化,但是在施用 4 个月 after 随施用量的增加而增加,施用 12 个月 after 呈现先增加后降低的趋势. 土壤蔗糖酶与土壤有机质代谢及氮磷含量密切相关^[48]. 在生物炭作用 4 个月 after,由于外源碳的施入,土壤微生物活性提升,促进腐解,补充土壤养分,提高土壤蔗糖酶活性;而在生物炭作用 12 个月 after,生物炭施用量过高吸附作用及其毒性增大,蔗糖酶活性下降.

3.3 土壤酶活性的影响因子分析

施用生物炭对土壤酶活性的影响较复杂,与生物炭的类型、施用量、底物、酶种类和土壤性质等因素有关^[49]. 本研究通过土壤养分与土壤酶活性的相关性热图及构建结构方程模型,直接定量地得出生物炭处理及各指标对土壤酶活性的直接或间接作用及其影响大小. 模型对过氧化氢酶、蔗糖酶和磷酸酶的总解释度分别为 73.8%、51.4% 和 44.3%. 结果显示,土壤酶活性受多因子协同影响. 生物炭对过氧化氢酶产生显著抑制作用($P < 0.001$),对蔗糖酶($P = 0.47$)和磷酸酶($P = 0.84$)起促进作用. SEM 分析发现,生物炭可通过影响 pH、电导率、有机碳和碱解氮进而对过氧化氢酶产生间接影响,生物炭的施用显著增加土壤电导率和有机碳,从而显著促进过氧化氢酶的活性. 而生物炭对过氧化氢酶的负相关关系可能是因为,生物炭表面具有高电势,在酶与底物充足条件下,能吸附部分有机分子(酶和底物),阻止酶促反应的进行,从而抑制酶活性^[50],可以从其它未纳入的潜变量(温湿度等)或者残差来解释. 生物炭通过 pH、电导率间接作用于蔗糖酶,生物炭施用显著提升电导率,进而土壤微生物活性提升,土壤养分提高,促进了土壤蔗糖酶活性. 生物炭通过电导率、碱解氮和有效磷间接导致磷酸酶的变化,其中碱解氮和有效磷呈显著促进作用. 有效磷含量即磷的利用率提高,以及碱解氮含量提升进而促进微生物的生长和繁殖,从而促进磷酸酶活性.

4 结论

生物炭施用量及作用时间显著增加土壤养分含量,直接影响土壤酶活性. 同时,生物炭通过提升 pH、电导率、有机碳和碱解氮含量,间接影响过氧化氢酶活性;以提升 pH 值和电导率值的方式间接促进蔗糖酶活性;通过提高电导率值以及碱解氮和有效磷含量,间接增加磷酸酶活性. 综合施用生物炭对土壤养分含量和酶活性影响的研究结果,酸性黄壤施用 $10 \text{ t} \cdot \text{hm}^{-2}$ 的生物炭较为适宜.

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