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玉米根际土壤中铜形态的动态变化

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摘要:采用根垫法研究玉米根际土壤铜形态动态变化。结果表明:玉米生长过程中根际土壤铜形态发生显著变化。植物生长前期交换态和碳酸盐结合态铜含量逐渐增加,随后增加量减少。植物生长后期根际交换态和碳酸盐结合态铜含量低于非根际土壤。这种变化主要由根际环境变化与植物吸收引起。与根际土壤中铜形态变化,特别是交换态铜含量变化关系密切的因素包括土壤溶解性有机碳、pH 和土壤微生物。随着植物生物量的增加,对铜的吸收速率不断增加,导致根际土壤中有效态铜的先增后减。

关键词:铜;根际土壤;形态;吸收

Transformation of Copper Speciation in Maize Rhizosphere

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Abstract: Rhizobox was used to study the distribution of copper species in maize rhizosphere and transformation kinetics of copper speciation under controlled condition. Copper speciation was characterized using Tessier's procedure. Exchangeable, carbonate bound, Fe-Mn oxide bound, organic bound, and residuals in maize rhizosphere and control (as bulk soil) were extracted sequentially after various growth period from 20 to 100 days. pH, Eh, dissolved organic carbon, and microbial mass were detected at the same time. The copper accumulated in the maize was also measured for the plant grew for various days.

The results of the experiment revealed that transformation among copper species occurred during the growth period. The exchangeable copper in the rhizosphere increased at the beginning and reached its climax after 20 days or so, after which the exchangeable copper decreased gradually and hit its original lever around the 40th day. The trend of decrease continued for rest of time to a very low level. For the carbonate bound copper, the level of the species showed a very similar pattern of the transformation but much slower than that of the exchangeable copper. It did not reach the maximum value till about 40 days and dropped to the starting value at the 80th day or so.

As for Fe-Mn oxides, it also followed a similar pattern of the exchangeable and the carbonate bound copper and increased in the early period and decreased late. However, Fe-Mn oxides bound copper in the rhizosphere remained elevated in comparing to the bulk soil.

Organic bound copper, however, varied in an opposite direction. It decreased at the beginning and increased slightly during the later stage.

If the change in fractionation after certain days were examined, the change in various species are similar to those reported in the literature. For instance, after 30 days of incubation, the exchangeable, the

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万方数据

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carbonate bound, and the Fe-Mn oxide bound copper increased to 0.21, 0.48 and 1.57mg/kg, respectively. Significant differences in the exchangeable and the carbonate bound copper between the rhizosphere and the bulk soil were confirmed by the results of *t*-test at this time.

By average, amount of the exchangeable, the carbonate bound, the Fe-Mn oxides bound, and the organic bound copper transformed in the rhizosphere were 0.4, 1.0, 1.4, and 2.4 mg/kg respectively, which approximately accounted for 50%, 10%, 6.0%, and 4.0% of the corresponding copper species in the rhizosphere. In other words, the intensity of copper species transformation in the rhizosphere decreased in following order, the exchangeable > the carbonate bound > the Fe-Mn oxides bound > the organic bound. Results of the measurement of other parameters including pH, Eh, DOC, and microbial mass indicate that rhizosphere pH steadily increased about 0.25 pH unit while Eh decreased about 60mV during the incubation. DOC in the rhizosphere remained higher than that in non-rhizosphere soil during the entire experimental period. DOC reached its climax, e.g. 29.2 mg/kg, after 15 days of incubation and decreased afterwards. After 100 days, the difference in DOC between the rhizosphere and the non-rhizosphere was only 2.5 mg/kg. Microbial mass in rhizosphere rapidly increased in the late period. The difference in the microbial mass carbon between the rhizosphere and the non-rhizosphere reached 220.6 mg/kg after 100 days. The results of correlation analysis suggested that variation in the exchangeable copper negatively correlated with the change in rhizosphere pH significantly. And there was a significantly positive correlation between the changes in the exchangeable copper and Eh. It is clear that the change in the exchangeable copper in the rhizosphere was markedly influenced by pH and Eh. On the other hand, the increase in DOC in the rhizosphere increased the level of the exchangeable copper. Since changes in both pH and DOC in the rhizosphere are at least partially the results of root exudation. It is believe that root exudates from the plant affected the transformation of copper species in the rhizosphere. The significantly negative correlation between Eh and the Fe-Mn oxides bound copper suggested that reduced Eh caused the increase in the Fe-Mn oxides bound copper in the rhizosphere. There was also a negative correlation between the exchangeable and the carbonate bound copper. A direct transformation from the later to the former is expected.

Change in the biomass and copper accumulation in maize were calculated and compared with the variation in copper speciation at various period of the experiment. The result suggested that uptake of copper by the plant increased with the biomass

Nevertheless, the amount of accumulation was far exceeded variation in the exchangeable copper, indicating that other species including the carbonate bound, the Fe-Mn oxide bound, as well as the organic bound copper were potential supplier to the plant accumulation, through speciation transformation of course.

Key words: copper; rhizosphere; fractionation; plant absorption

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由于植物吸收、分泌及其周围微生物活动等影响,根际土壤物理、化学和生物学性质与土体截然不同[1,2]。根际环境的改变可能引起土壤重金属形态的再分配,从而改变其植物有效性。因此,研究根际土壤重金属形态转化对于阐明重金属在土壤-植物系统的传递机制,尤其是重金属超富集植物抗逆机理都具有重要的理论意义[3,4]。

大量事实证明根际土壤重金属形态与土体的差异。Youssef 等采用根箱法研究镍在土壤植物系统迁移时发现,小麦根际土壤镍可迁移性与植物有效性大大高于非根际[5]。Mench 等发现燕麦根系分泌物可以溶解铁氧化物从而增加锌、镉和镍的植物有效性[6]。黄艺和陈有 等人也报道了相似结果[7,8]。由于研究条件

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的差异，有关结果并非完全一致。例如，McGrath 等人发现 *Thlaspi caerulescens* 根际土壤溶液锌含量远远高于非根际，并认为 pH 的变化是造成这种变化的主要原因[9]。而 Hutchinson 等人发现 *Thlaspi caerulescens* 在根系分泌物增加和根际 pH 降低的条件下也不能利用镉[10]。事实上，可能导致根际土壤金属形态变化的因素很多，不仅受根际理化条件和微生物、菌根菌存在的影响，而且与金属种类和植物种类有关[11,12]。

本研究采用根垫装置在相同实验条件下设置多组重复，并根据根系与土壤接触时间长短依次取样，以研究根际环境和根际土壤性质与铜形态的动态变化。

1 材料与方法

土壤样品采自天津徐庄子东 250m 左右菜地表土。该地块有 30a 以上污灌历史。土样风干后，过 1mm 尼龙筛备用。供试土壤有机质含量 37.4g/kg、CEC32.2 cmol/kg、pH8.12，土壤铜总量，有机碳和微生物量碳含量分别为 125.8、37.4 和 82.5mg/kg。供试玉米为常规品种，玉米发芽前用含 0.3%过氧化氢的饱和 $CaSO_4$ 溶液浸泡 30min，再把种子置于覆有湿润纱布培养皿发芽。待玉米长出第 3 片真叶后移植到根垫盒上层。

根垫盒由上下两部分组成，上盒(70 mm×70 mm×35mm)用 500 目孔径尼龙网封底与下盒(74 mm×74 mm×50 mm)分隔[13]。上下盒各盛 150g 土壤，先在上盒移栽已发芽露白玉米种子 8 颗，每天补充水分 2 次，保持土壤湿润(含水量 25%左右)，直至植物根系在盒底形成根垫。然后移开上盒，在下盒土壤表面加一层尼龙纱网，称取充分混匀的污染土壤 20.0g，平铺在纱网上(土层厚度约 2 mm)，将已经形成根垫的的上盒放置其上并用细绳固定，使根垫与根际土壤紧密接触。对照处理(非根际)除上盒不种植植物外，其余步骤相同。处理后每个装置加水 25 ml 后称重并记录，作为其后补充水分的参照。将装置置于强光照培养箱(HPG-280B，9000 Lx)内。光照和非光照时间分别为 14 和 10h，对应温度为 30℃和 26℃。同时布置 9 组实验，每个处理安排 3 个以上重复，根据玉米生长不同时期，按根垫与根际土壤接触时间分批取样(15、24、30、36、42、53、57 和 100d). 取样前 12h 停止加水，每个独立培养取两个混合土样。植物样品冲洗干净后沿根轴将根与茎叶分开，在 60℃下烘干，用玛瑙研钵研碎备用。

土壤铜形态分析采用 Tessier 连续浸提法[14]。与原方法相比，提取液体积和土壤样重均减半。重金属总量测定用 HF-$HClO_4$-HNO_3 体系消解，残渣态含量差减获得。植物样用微波消解炉(CEM-MDS-2000)消解。消解过程为：称取约 0.2000g 样品于聚四氟乙烯管中，加 10ml 70%HNO_3，在 PSI-120 条件下，用 50%能量(630W)消解 60min。消解液定容至 50ml 后待测。制备液铜含量用原子吸收分光光度计(日立 180-80)测定。分析过程使用去离子水，所有玻璃器皿使用前用 10% HNO_3 浸泡 24h。土壤水溶性有机碳用 TOC 测定仪(岛津-500A)测定。土壤微生物量测定采用熏蒸法[15]。土壤 pH 和 Eh 用常规方法测定。

2 结果与讨论

2.1 玉米生长 30d 根际铜形态变化

为与前期工作和文献资料比较，比较了第 30 天根际土壤中与非根际土壤中铜形态的差别。4 种形态的差别如图 1 所示。图中还给出了 T-检验的相伴概率(P)。

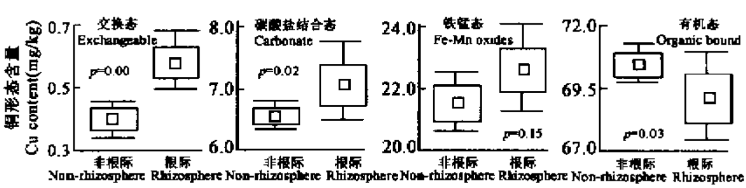

图 1 第 30d 玉米根际土壤与非根际土壤中铜形态的差异

Copper speciation changed in rhizosphere and non-rhizosphere of maize after 30 days of incubation

在第 30 天，多数形态在根际与非根际土壤中有明显差别。除铁锰氧化物态之外，T-检验的相伴概率都在 0.05 以下。铁锰氧化物态的检验结果不显著的主要原因是重复测定误差较大(图 1)。可见玉米生长 30d

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后根际土壤中铜的形态发生了很大变化。在测定的 4 种形态中,除有机结合态外,各形态铜在根际土壤中均在增加,可见形态转化向松结合方向进行。这与部分文献报道的结果一致[16,17]。

2.2　玉米生长不同时期根际土壤铜形态变化过程

考虑到植物生长是不间断的过程,其中根际环境也处于不断变化中,铜形态转化也必然是动态过程。在植物生长 100d 内不同时期测得 4 种形态铜含量变化趋势(根际-非根际)如图 2 所示。

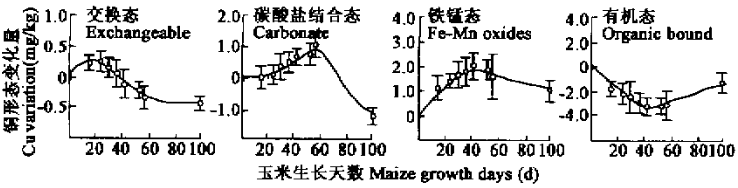

图 2　玉米生长不同时期根际土壤铜形态变化过程

Fig. 2　Copper speciation changed in rhizosphere of maize at various period of the experiment

图 2 显示,玉米生长不同时期根际铜形态变化幅度依提取顺序增加,即交换态 < 碳酸盐结合态 < 铁锰态 < 有机态。交换态铜最大变化量在 0.4mg/kg 以下,相当于交换态总量的 50%左右。碳酸盐态最大变化幅度达 1.0mg/kg,平均变化量相当于碳酸盐态总量的 10%左右。铁锰态平均变化量 1.4mg/kg,占铁锰态总量的 6.0%。有机态平均变化量 2.4mg/kg,相当于有机态总量的 4.0%。就相对变化量而言,根际环境对铜形态变化的影响依提取顺序降低,即交换态 > 碳酸盐态 > 铁锰态 > 有机态。

在玉米生长的不同时期,根际铜形态表现出规律性变化趋势。前 3 种形态均为先升后降,而有机结合态则表现为先降后升。虽然在根际土壤中交换态铜在前 40d 高于非根际土,但在 40d 后却低于根际土壤。碳酸盐态的转折点在 80d 左右。铁锰氧化物态虽然经历了相似的变化,但 100d 内其在根际土壤中的含量始终高于非根际土壤。这样的变化是两种作用,即活化和植物吸收共同作用的结果。紧结合态铜(如有机态)在根酸、根际微生物、pH 和 Eh 变化等作用下,向弱结合态方向活化,而植物吸收直接降低了交换态铜在根际土壤中的含量。

2.3　根际环境对铜形态变化的影响

为考察根际环境对铜形态变化的影响,在测定不同形态铜含量的同时测定了玉米生长不同时期根际土壤 pH、Eh、DOC 和微生物量碳,并计算根际变化量(根际-非根际),结果列于表 1。

表 1　玉米生长不同时期根际土壤 pH、Eh、DOC 和微生物量的相对变化

Table 1　Variation of pH、Eh、DOC and microbial mass in different maize growth period

项目 Item	不同玉米生长时期 Different maize growth period (d)						
	0	15	36	42	53	57	100
pH	0.00	0.08	0.17	0.24	0.22	0.25	0.17
Eh (mV)	0.0	−30.0	−40.0	−40.0	−40.0	−43.0	−60.0
DOC (mg/kg)	0.0	29.2	14.1	8.6	6.1	4.0	2.5
微生物量碳 Microbial mass (mg/kg)	0.0	25.2	33.7	36.6	59.4	65.2	220.6

表 1 表明,玉米生长不同时期根际环境也有很大差异。其中根际土壤 pH、Eh 和微生物量随植物生长逐渐增加,土壤 DOC 则在植物生长前期变化最大,植物生长后期根际与非根际差别逐渐变小。计算了根际土壤 pH、Eh、DOC 和微生物变化量与不同形态铜变化量的相关系数,结果在表 2 中给出。

表 2 表明,根际土壤 pH 和 DOC 与交换态铜含量有显著相关关系。这两项参数均与根酸分泌有密切关系。根酸分泌应导致根际土壤中水溶性有机物含量(DOC)增加以及 pH 下降。两者均可能通过竞争(有机络合剂与质子)造成土壤中铜的活化。另外,虽然在 5%显著性水平微生物碳与交换态铜含量的相关关系不显著,但其相伴概率很接近 5%。尽管相关关系并不反映因果关系,但形态转化与这些因素之间显然存在某种重要联系。

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表 2 根际环境参数与不同形态铜相对变化量的相关系数

Table 2 Correlation between copper speciation variable and soil characterization

项目 Item	铜形态变化 Copper speciation variation(mg/kg)			
	交换态 Exchangeable	碳酸盐态 Carbonate	铁锰态 Fe-Mn oxides	有机态 Organic bound
pH	−0.77*	−0.03	0.63	−0.68
Eh (mV)	0.44	0.18	−0.76*	0.58
DOC (mg/kg)	0.84*	0.01	0.20	−0.13
微生物量碳 Microbial biomass (mg/kg)	−0.73	−0.69	0.09	0.05

* ($p < 0.05$)

2.4 植物吸收影响

为探讨植物吸收对根际土壤铜形态变化的影响，分别计算了植物生长不同时期根际铜交换态变化量和植物吸收量，以及植物平均吸收速率。结果列于表 3。

表 3 玉米生长不同时期植物生物量(干重 g)及植物铜吸收量(μg)

Table 3 Maize biomass and copper accumulation at various period of the experiment

项目 Item	时间 Time (d)					
	15	24	30	42	53	100
植物生物量 Dry weigh (g)	0.7	1.4	2.1	5.2	5.9	21.8
铜吸收量 Cu accumulation (μg)	9.6	19.0	20.3	70.9	76.5	296.8
铜交换态变化 Exchangeable Cu variation(μg)	1.2	12.4	3.0	−2.8	−5.8	−23.4
植物吸收速率 Average Cu uptake (μg/d)	0.6	0.8	0.7	1.7	1.4	3.0

表 3 表明，植物对铜的吸收随生物量增加而增加。与根际铜交换态变化量比较，植物吸收量远大于根际铜形态变化量，说明植物对铜的吸收主要来自其他形态的转化。植物生长前期根际铜交换态并没有因为植物吸收而减少，反而增加，说明根际存在其他铜形态向交换态转化机制，而且这种转化量大于植物吸收量，从而增加根际铜交换态含量；植物生长后期，随着植物生物量增加，铜吸收速率也增加，同期根际铜交换态低于非根际，说明植物生长后期根际铜交换态减少与植物吸收速率增加有关。

就根际土壤交换态铜变化量而言，其总量仅在 15μg 左右。考虑到植物对铜的吸收绝大部分来自根际土壤，加上本实验装置中非根际土壤交换态铜总量仅 100μg 左右，植物吸收的铜主要来自其他形态，特别是碳酸盐态向交换态的转化。

3 结论

玉米根际土壤中铜的形态发生显著变化，总体变化趋势为活化。变化的绝对量依提取顺序而增加，即交换态 < 碳酸盐结合态 < 铁锰态 < 有机态。而相对变化量与之相反。玉米生长不同时期根际土壤中铜的形态转化速率和方向并非恒定。根际土壤中交换态、碳酸盐态和铁锰氧化物态铜先增后减，而有机态恰恰相反。根酸分泌、根际微生物活动和植物吸收是影响根际土壤铜形态变化的主要因素。

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万方数据