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秸秆还田影响汞污染地区“稻田汞”环境行为的研究进展

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摘要 秸秆还田是一项正大力推广的农业措施, 既可避免秸秆焚烧导致的空气污染, 又可通过提升土壤肥力、改善土壤性质而促进作物生长. 与此同时, 秸秆还田对农田重金属生态风险的影响值得关注. 已有不少研究报道了秸秆还田导致铜、镉、锌等重金属生物有效性下降, 然而秸秆还田对土壤中汞环境行为与风险的影响却鲜有报道. 本文综述了近年来秸秆还田影响汞污染地区“稻田汞”行为与风险的研究进展. 近期研究揭示秸秆还田可显著提升“稻田汞”的生态风险: 秸秆还田可影响“稻田汞”的地球化学相态分布、汞的微生物甲基化、汞的生物有效性, 以及汞的植物累积, 并讨论了这些影响可能的内在机制(如微生物活性上升、秸秆产生溶解性有机质导致汞活性上升等). 本文所阐述的信息, 有助于从机理层面理解陆生系统中汞的行为与风险, 并有助于汞污染地区有关秸秆处理方式的决策.

关键词 秸秆还田, 土壤, 汞, 水稻, 有机质

汞是一种持久性、高毒性、易生物富集(尤其是甲基汞形态)的常见污染物. 甲基汞作为汞形态中毒性较强的一种形态, 即使在低浓度下也可能对人类和哺乳类动物的中枢神经系统造成不可逆的损伤[1]. 相比于旱地系统, 在水生生态系统和湿地环境中, 无机汞(Hg^{2+})转化为甲基汞(CH_3Hg^+)的环境过程更易发生[2]. 水稻田作为一个典型的湿地系统, 其土壤的氧化还原状况、有机质含量和微生物群落等对于汞的甲基化过程具较强的调控作用[3~6]. 近年来的研究表明, 在中国内陆的一些汞污染地区, 食用大米而非水产品已经成为人体甲基汞暴露的主要途径[7], 其原因可能是汞污染稻田在淹水条件下土壤甲基汞含量提高, 进而使稻米中甲基汞浓度提升[8].

秸秆还田是一种典型的农业措施, 既能增加土壤肥力又能减少秸秆焚烧带来的大气污染. 农作物残体(crop residues, 如秸秆和根)及其降解产物是土壤有机质的重要来源[9], 作物的根一般是在作物收获之后残留在土壤中, 而秸秆则是为了提升土壤肥力而被施入土壤[10~12]. 中国的秸秆资源十分丰富, 每年产生约有6~8亿吨秸秆[13], 其中水稻秸秆的产量最多, 而且这个数字正逐年增加[14]. 秸秆还田能显著提高土壤肥力[10,11], 被厌氧微生物分解的秸秆是稻田土壤中有机碳的主要来源[15,16]. 并且秸秆的施入可以增加土壤养分含量、改善土壤理化性质进而促进作物生长[17,18]. 此外, 秸秆的降解产物可通过与金属反应从而降低金属的活性, 如秸秆还田显著影响Cu, Cd, Zn的植物有效性进而影响其在植物体内的积累[19~21], 因此秸秆还田也被用于修复重金属污染土壤[22,23].

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同时, 由于秸秆燃烧可能是造成空气污染的重要污染源, 而研究表明作物秸秆还田在提高土壤肥力的同时还能减少空气污染[24,25], 因此政府正大力推广作物秸秆还田.

已有的研究表明有机质很大程度上影响着土壤中汞的环境行为[26,27], 并且土壤有机质对于汞的植物有效性以及生物积累的抑制效应早有报道[28], 因此作物秸秆及其降解产物(糖类、醇类、低分子量有机酸、酚醛[29,30])可能会对土壤中汞的环境行为产生影响. 本文旨在总结近年来学术界在秸秆还田影响“稻田汞”环境行为这一领域的最新进展, 以期为掌握乃至预测“稻田汞”的风险提供参考.

1 秸秆还田对汞的影响

1.1 秸秆还田对“稻田汞”地球化学相态分布的影响

土壤/沉积物中汞的地球化学相态(geochemical fractionation)可分为水溶态(water soluble fraction)、胃酸溶解态(stomach acid soluble fraction)、有机及其他结合态(organo-complexed fraction)、强结合态(strongly complexed fraction)、残渣态(residue fraction) 5种, 其中水溶态、胃酸溶解态的汞较易生物利用, 残渣态汞最难生物利用, 有机及其他结合态(与汞的甲基化能力呈正相关关系)和强结合态汞的生物可利用性介于其间[31]. Zhu等人[23]以万山汞矿区污染稻田的耕层土壤为研究对象, 发现土壤中汞主要是以惰性形态(refractory phases)存在, 90%以上分布在残渣态, 其次是强结合态, 而较易生物利用的水溶态和胃酸溶解态汞占比小于0.2%. 秸秆还田后, 强结合态汞的含量降低了22.2%~38.3%, 残渣态汞的含量也显著下降, 而有机及其他结合态的汞含量则有所增加, 表明汞从惰性形态向生物可利用性较高的形态发生转化. 与之类似, Zhu等人[32]将经过腐解生成的秸秆有机肥施入土壤研究其对土壤中汞环境行为的影响, 结果表明, 施加了秸秆有机肥的土壤中水溶态、胃酸溶解态、有机及其他结合态和强结合态汞的含量均显著提高, 而残渣态汞含量则显著降低.

秸秆还田导致“稻田汞”地球化学相态分布发生变化, 其主要原因是由于有机质对汞的作用. 秸秆还田后固体有机碳(POC)提高了0.1%~0.5%[33,34], 固体有机质由纤维素、半纤维素、木质素以及粗蛋白等组成[34,35], 包含了大量汞结合位点, 如羰基、羧基、酰胺、烷氧基等[35,36], 易与无机汞结合, 固体有机质对汞有“固定效应”. 但Zhu等人[23,32]的实验发现在秸秆还田或秸秆有机肥还田30天后, 随着时间推移, 土壤中固体有机碳被微生物分解为CO_2或转化为溶解性有机质, 其含量逐渐降低, 而溶解性有机碳(DOC)的含量却相应提高. 残渣态汞(主要是HgS)与溶解性有机质形成Hg-S-DOM[37,38]结合物, 其可能与土壤中有机质或铁锰氧化物结合, 从而迁移到有机及其他结合态和强结合态[32].

1.2 秸秆还田对“稻田汞”甲基化的影响

众所周知, 稻田土壤中甲基汞含量较高[8], 且在汞污染地区的水稻田中, 甲基汞的含量和土壤有机质的含量呈正相关[3]. Windham-Myers等人[9,39]对于湿地环境的研究表明, 将植物残体覆盖于受到汞污染的农业湿地表面, 其分解物进入土壤会提高土壤中甲基汞的含量. Marvin-DiPasquale等人[40]对比农田土壤和非农田土壤中汞的生物地球化学行为, 发现农田表层土壤(1~2 cm)比非农田表层土壤中的甲基汞浓度更高, 尤其是冬季水稻收获后的时间段(秸秆和根残留在土壤), 因而秸秆管理可能对于控制汞的甲基化具有重要意义. Zhu等人[23]研究表明水稻秸秆和根施入万山汞矿区污染的稻田土壤后, 土壤中甲基汞的浓度提高了2~8倍. Liu等人[41]对万山汞矿区两种汞含量不同的稻田土壤的研究表明, 秸秆还田促进了高汞土壤(汞含量5.53 mg kg^{-1})中汞的甲基化, 即提高了甲基汞的含量, 但对于汞含量相对较低的土壤(汞含量0.52 mg kg^{-1})则没有明显促进效应, 原因可能是由于两种土壤中微生物群落特征不同. 不同的土壤微生物群落组成影响秸秆的降解、溶解性有机碳含量及其与汞结合形态, 从而影响汞的微生物甲基化.

秸秆还田促进“稻田汞”的甲基化, 原因可能是秸秆还田后促使稻田土壤性质发生变化, 如氧化还原电位的变化、土壤中有机质含量的升高、高价S, Fe的还原、无机汞活性的变化、甲基化微生物数量和活性的变化. 在这诸多影响因素中, 溶解性有机质含量的升高, 对汞的甲基化行为影响较大. 溶解性有机质促进稻田土壤甲基汞浓度升高的主要原因归纳如下: (1) 秸秆分解产生的活性有机碳(如乙酸)直接作为速效碳源提高汞甲基化微生物的数量和活性, 促进微生物的代谢活动, 从而促进无机汞的甲基化[9,40]; (2)

溶解性有机质与HgS络合形成甲基化微生物可利用的复合物[37,38]; (3) 溶解性有机质通过与土壤有机质竞争甲基汞的结合位点, 促进甲基汞溶出[42]; (4) 孔隙水中的溶解性有机质在液相络合汞, 降低汞在土壤颗粒上的吸附量, 促进土壤中结合态汞的溶出, 从而提高可甲基化的原料的含量[43]. 针对这4种机制, 已有许多研究者进行了更深入的探讨. Windham-Myers等人[9]的研究认为土壤中的溶解性有机质, 尤其是乙酸可能对汞的甲基化起着重要作用. 其研究表明植物残体的腐解物可通过向汞甲基化微生物提供碳源, 提高其活性, 从而促进汞的甲基化, 更加深入的研究发现植物残体量与乙酸生成量成正比, 且甲基汞生成速率与乙酸含量之间成正比, 由此可以推测乙酸这种小分子活性有机质在很大程度上调控汞的甲基化作用. Marvin-DiPasquale等人[40]研究秸秆还田后土壤环境中有机质, S, Fe, Hg及甲基化微生物等对汞行为的影响, 结果表明相对于无机汞活性而言, 汞甲基化微生物对于汞的甲基化过程影响更大, 并且活性有机碳而非硫酸盐, 是限制汞甲基化微生物活性的关键因子. 在Marvin-DiPasquale等人[40]所研究湿地系统中, 乙酸的重要性不容忽视, 虽然乙酸只占溶解性有机碳的一小部分, 但其是异养微生物(包括硫酸盐还原菌(SRB)、铁还原菌(FeRB))的关键底物, 因而比DOC更适合指示小分子碳源供给. 乙酸是秸秆腐解后经发酵作用产生的, 其含量在淹水种植季升高, 乙酸含量的升高会促进汞的甲基化. 同时土壤孔隙水中的溶解有机质通过与以难溶态HgS形式存在的汞结合, 促进无机汞转化成微生物可利用的形式(如Hg-S-DOM[37,38]), 从而促进无机汞的甲基化. Zhu等人[23]认为植物残体的腐解物为微生物提供速效碳源, 使得甲基化微生物活性和数量升高, 促使土壤甲基汞浓度升高; 实验结束后(30 d), 土壤固体有机碳含量的下降与甲基汞浓度升高呈正相关, 间接证明了微生物在汞甲基化中发生的作用. 同时Zhu等人[23]认为秸秆还田后汞的地球化学相态的变化也是导致甲基汞浓度升高的一大原因, 其研究发现土壤甲基汞的浓度和残渣态汞在总汞中所占比例的下降量呈正相关, 表明水稻残体施入土壤中, 发生一系列反应促使惰性的残渣态汞(如HgS等)释放, 促进无机汞的甲基化. 还有报道称秸秆腐解产生的溶解性有机质能显著降低汞在土壤中的吸附量与吸附速率, 促进土壤中结合态汞的溶出[42], 将无机汞释放, 为微生物进行甲基化提供底物. 此外, 微生物分解水稻残体有机质的过程中会消耗氧气, 促进厌氧微区的形成[43], 可能会进一步促进汞的甲基化[2,44,45].

针对Fe, S对汞的甲基化的影响而言, 由于还田后的秸秆腐解产生的有机质能够促进甲基化微生物(SRB, FeRB)的生长, 从而促使该微生物还原土壤中的高价S和Fe, 形成硫化亚铁(FeS). 研究表明, FeS对无机汞有抑制作用, 原因是FeS会吸附无机汞[46]或者通过S^{2-}与无机汞结合形成β-HgS(s)[47]. 此外Marvin-DiPasquale等人[40]研究发现影响汞的甲基化的因素中, 和铁相比, 沉积物中总还原性硫(TRS)对活性汞含量以及汞甲基化速率的影响更为显著, TRS与活性汞含量成反比. Alpers等人[48]的研究表明稻田土壤表层水中甲基汞浓度与DOC, Fe, Mn, 硫酸盐还原相关, 其研究结果和Marvin-DiPasquale等人[40]一致: 硫酸盐并非汞甲基化的限制性因子, 且还原性硫与活性无机汞呈负相关关系, 表明还原性硫抑制了汞的活性以及汞的甲基化. 综上所述, 秸秆还田后的稻田土壤中C, S, Fe, Hg等的生物地球化学行为共同影响着无机汞的甲基化过程, 该过程行为复杂、涉及众多生物化学反应, 还需要更深入的展开研究.

1.3 秸秆还田对“稻田汞”生物有效性与生物累积的影响

固体有机质或溶解有机质能够降低土壤-沉积物中的无机汞的生物可利用性, 如微生物[49,50]、植物[28]和无脊椎动物[51]. Zhu等人[23]2015年的研究通过$CaCl_2$或牛血清白蛋白(BSA)萃取法测定无机汞或甲基汞的提取率以估测无机汞或甲基汞的生物有效性, 结果表明秸秆还田后的土壤中无机汞的生物可利用性降低, 即秸秆还田导致无机汞对水稻和以底泥为食的土壤动物的暴露风险降低. 秸秆还田后, 甲基汞的萃取效率也有所降低, 但降低幅度较无机汞小, 由于土壤中的甲基汞的浓度大大提高, 综合效应下生物可利用态甲基汞浓度(以可萃取浓度表征, 单位ng/g)显著增加, 导致甲基汞暴露风险显著提高. Zhu等人[32]2016年的研究表明, 加入大量秸秆有机肥(POC 4.97%)的土壤中无机汞的提取率提高, 原因可能是秸秆有机肥分解产生溶解性有机质, 促进土壤无机汞的溶解, 称之为“溶出效应”; 但加入少量(POC 2.47%)或者中等量(POC 2.67%)的秸秆有机肥

的土壤中无机汞的提取率显著降低，这主要归因于固体有机质对无机汞的“固定效应”[35,36]，因此加入少量或者中等量的秸秆有机肥的土壤，无机汞的植物有效性降低．Zhu等人[52]2016年的研究表明，秸秆还田后土壤孔隙水中甲基汞含量提高，使得水稻更易于吸收和积累甲基汞，并且甲基汞更易于迁移到稻米中，导致稻米中甲基汞含量大幅提高，但同时秸秆施入土壤会促进水稻的生长，稻米生物量的增加会在一定程度上缓解稻米中甲基汞的影响．另一方面，葛立立等人[53]的研究表明玉米秸秆施入土壤能够提高稻米中蛋白质含量，考虑到汞和蛋白质的高结合力[46,54]，稻米蛋白质含量的升高也会促使更多的汞转移到稻米中，促进了汞的生物累积．

秸秆还田导致“稻田汞”生物有效性提高进而促进汞的生物累积，主要是由于土壤中生物可利用的汞含量提高．如上所述，秸秆分解产生的固体有机质和溶解性有机质促进汞由残渣态向生物可利用性更高的形态转化[23,32]，提高了生物可利用的汞的含量．同时，稻田土壤环境中的有机质，S, Fe, Mn以及Hg在秸秆还田后发生变化，通过向微生物提供活性有机碳(如乙酸[9,40])提高微生物的活性、将汞转化成微生物容易利用的形态(如Hg-S-DOM[37,38])等促进无机汞的甲基化，提高土壤中甲基汞的浓度，进而促进水稻吸收甲基汞，累积在稻米中，增加汞在食物链富集的风险．

2 结论

中国的人口压力和经济发展需求导致土壤肥力逐年下降，同时农业生产中对于作物秸秆的不合理处置(如焚烧)等造成了大气污染，研究者认为生物质燃烧[55](如秸秆焚烧)是造成雾霾的一大诱因．因此，秸秆还田作为能够改善土壤营养状况同时减轻大气污染的一个重要举措，得到了政府的大力推广．但农田土壤是一个复杂的体系，其氧化还原状况、微生物群落的数量和活性等都可能由于秸秆还田而产生变化，导致土壤中的有害污染物(如汞)的存在形态发生变化而对作物产生影响，进而通过食物链对人体健康造成不良效应．本文通过综述秸秆还田对“稻田汞”地球化学相态分布、“稻田汞”的甲基化以及生物有效性与生物累积的影响，发现秸秆还田可能提高甲基汞的暴露风险，并对其可能原因进行总结．秸秆直接还田会使土壤中甲基汞浓度升高，导致水稻稻米中甲基汞浓度大幅提高，其中主要是溶解性有机质的作用，但其机理尚不完全明确，目前还需要更深入的进行研究．

此外，秸秆还田方式的不同对于汞的暴露风险的影响又有所不同．如上所述，秸秆直接还田会促进无机汞的甲基化，提高甲基汞的暴露风险[9,23,39~41,48]，秸秆有机肥还田对甲基汞的影响不明显，但会显著降低土壤中无机汞的含量[32]．同时，本文主要针对汞污染地区的水稻田，如贵州万山汞矿区[23,32,41,52]，土壤中总汞含量为330~790000 μg/kg，甲基汞含量为0.13~23 μg/kg[56~58]，秸秆还田显然会加重该地区的汞暴露风险．因此，对于秸秆还田这一举措，相关部门应根据不同地区的不同农田状况合理管理．

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Summary for “秸秆还田影响汞污染地区‘稻田汞’环境行为的研究进展”

Advances in understanding Hg dynamics in mercury contaminated paddy soils under straw amendment

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It is well-known that interactions between Hg and organic matter could greatly affect biogeochemistry of Hg in soils, and its subsequent uptake by plants. Crop straw is mainly composed of organic matter, and its incorporation into soils may have impacts on Hg dynamics in soil-plant systems. Straw return is being widely encouraged, in order to mitigate straw-burning induced air pollution, as well as to promote plant growth by increasing soil fertility and improving the soil. Meanwhile, potential impacts of straw return on the ecological risk of metals in agricultural soils warrant investigation. While much progresses have been made in understanding the reduced metal bioavailability (e.g., for Cu, Cd and Zn) under straw amendment, little is known about the potential effects of straw return on Hg dynamics in soils and the associated ecological risks. Here, we summarize recent advances in understanding Hg dynamics in soil-rice systems under straw amendment. Recent studies revealed evidently enhanced ecological risk of Hg in paddy soils under straw amendment. Especially, straw return was found to have positive effects on methylmercury (MeHg) concentrations in soils, as well as those in crops. The underlying mechanisms may include: (1) Straw amendment has evident effects on the geochemical fractionation of Hg in soils, by facilitating transformation of Hg from the refractory fractions (e.g., residual fractions, including HgS) to more mobile fractions (e.g., organic-complexed fraction), which may increase availability of inorganic Hg to microbial methylators. (2) Transformation of inorganic Hg to MeHg was facilitated under straw amendment, which could be mainly attributed to the increased availability of inorganic Hg as well as enhanced activities of microbial methylators (e.g., sulfate reducing bacteria). (3) Straw return was found to have positive effects on Hg accumulation in grains of crops. The observed effects could be explained by the increased soil MeHg levels, enhanced mobility of MeHg in the presence of dissolved straw-derived organic matter, as well as changes in plant physiology, e.g., increased uptake of MeHg by root and MeHg transformation from other tissues to grains. Information summarized in this manuscript would improve mechanistic understanding about dynamics and risk of Hg in soil-plant systems and ensure appropriate straw management in Hg-contaminated areas. Particularly, more attentions should be paid to the interactions between ‘fresh’ organic matter (e.g., those from crop straw), which may have great impacts on Hg speciation, methylation, mobility, and bioavailability in soils. Furthermore, results gained in those pioneering studies highlight the importance to re-consider the policy of straw return in farming soils, especially in Hg-contaminated areas.

straw return, soil, mercury, rice, organic matter

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