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植被生态系统汞的生物地球化学循环研究进展与挑战

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摘 要: 汞是联合国环境规划署重点管控的全球性污染物.植被是联结大气圈与土壤圈的关键纽带,在全球汞生物地球化学循环中扮演着举足轻重的角色.植被生态系统是全球大气重要的汞汇,但由于大气-植被-土壤的汞界面交换过程及植物组织中汞的分布、来源与迁移转化规律及驱动机制认识不清,致使当前的全球汞生物地球化学循环模型缺失植被过程模块,无法厘定全球植被的大气汞汇通量.近年来迅速发展的汞同位素地球化学、同步辐射和微气象汞通量观测等新方法,为多层次解析不同类型植被与土壤及大气界面汞交换过程,阐明植物组织中汞的分布、来源与迁移规律提升了可能,能为进一步解决当前森林生态系统汞的生物地球化学循环的研究难点提供独辟蹊径的视角.

关键词: 汞;植被;生物地球化学循环;通量;地球化学.

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Research Progresses and Challenges of Mercury Biogeochemical Cycling in Global Vegetation Ecosystem

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Abstract: Mercury (Hg) is a global pollutant which has been listed by the United Nations Environment Programme focusing on control. Vegetation is a foundational link between atmosphere and pedosphere, and plays an important role in global Hg cycles. Currently, vegetation has been regarded as the important global sink of atmospheric Hg. However, the distinct knowledge gaps in Hg cycling among interface of air-vegetation-soil, and Hg distribution, sources, transformation and their biogeochemical mechanisms in vegetation components, lead to the current global Hg models with the poor parameterization schemes of vegetation related Hg processes. These largely restrain the comprehensive quantification of the vegetation sink for atmospheric Hg across the globe. Recently, the quickly developing Hg isotopic chemistry, HR-XANES/micro-XANES, and micro meteorological mercury flux observation technology provides a new insight in understanding the interface Hg biogeochemical processes among vegetation-soil-air surfaces, and assessing Hg sources and transformation and translocation in vegetations, specifically in forest ecosystems.

Key words: mercury; vegetation; biogeochemical cycling; flux; geochemistry.

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1　汞是国际关注的全球性污染物

汞是一种毒性很强的环境污染物,尤其以甲基汞毒性最强,甲基汞在食物链可富集放大千万倍,因而即使环境中微量甲基汞存在也能造成显著的汞污染(Clarkson, 1993; Stein *et al.*, 1996; Lucotte *et al.*, 1999).自然状态下,汞主要通过火山、地热和地质构造活动等从地球深部储库迁移到地球表层生态系统,以及随岩石风化、土壤/水体排放、大气沉降,进而在表生环境进行全球生物地球化学循环(Pirrone *et al.*, 2010;冯新斌等, 2011, 2013; Streets *et al.*, 2011; Agnan *et al.*, 2016).但工业革命以来急剧增加的人为活动大气汞排放,扰乱了自然状态下的全球汞质量平衡.举世震惊的日本"水俣病事件",就是因为当地富含甲基汞的工业废水直接排放至海洋环境,经生物放大富集至海产品中,最终造成 1 780 人死亡与 3 000 多人患病.最新的研究表明,孕妇长期低剂量甲基汞暴露会对新生儿智力发育产生影响(Zhang *et al.*, 2021),以美国为例,每年有 316 500~637 200 名新生儿受影响,造成的经济损失约 87 亿美元(Grandjean *et al.*, 2012).

汞不仅具有极强的生物毒性,还能在大气中进行长距离迁移传输造成全球性的污染.由于特殊的物理化学性质,汞在大气中主要以气态单质形式存在,大气居留时间可达 0.5~1.5 年(Shah *et al.*, 2021).21 世纪 80 年代在北欧与北美的调查研究发现,即使在没有人为污染源的北欧和北美偏远地区湖泊中,部分鱼体汞含量远超出世界卫生组织建议的水产品食用标准,严重威胁生态安全和人体健康;人为活动排放的汞经大气长距离迁移后沉降在这些水体中,是造成鱼体汞污染的主要原因(Khalizov *et al.*, 2003; Selin *et al.*, 2008; UNEP, 2013).相比于工业革命前,当前全球大气汞平均沉降速率已升高 3~4 倍(Khalizov *et al.*, 2003; Selin *et al.*, 2008; UNEP, 2013; Streets *et al.*, 2017);截止到 2010 年,人类活动向大气排放了 33.6 万吨,其中 12.3~15.6 万吨的汞沉积到陆地生态系统,其余汞沉降进入海洋(Streets *et al.*, 2017),全球面临着严峻的汞污染形势.

对于当前汞在地表各圈层的交换通量与储库,联合国环境规划署主导的《2018 年全球汞评估报告》中对此进行了最新的梳理(图 1).当前全球大气、土壤与海洋各圈层汞的储量以土壤汞库最大(约 95 万吨),海洋汞库次之(约 31.3 万吨),大气汞库最小(约 4 400 吨);全球向大气汞总排放约 8 000 吨/年,而总沉降约为 7 400 吨/年;其中,全球海洋排放约 3 400 吨/年而接受大气沉降约 3 800 吨/年,人为活动汞排放约 2 500 吨/年,地质过程和自然界面排放约 2 100 吨/年,整个陆地大

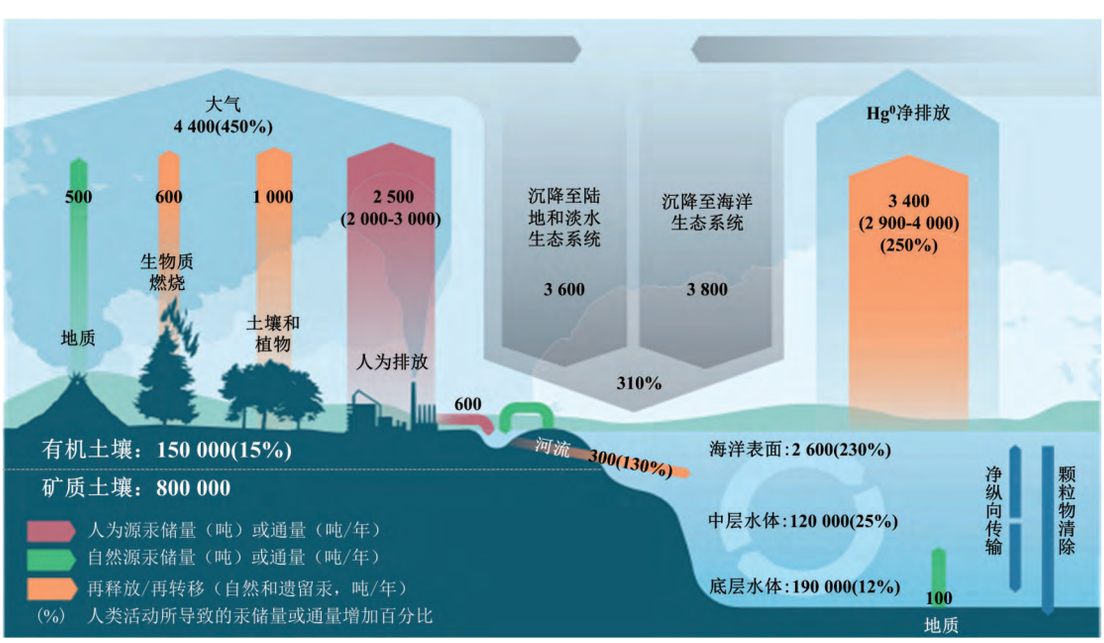

图 1　当前全球汞的分布与各圈层交换通量(据 Outridge *et al.*, 2018 修改)

Fig.1　Modified by updated global Hg budget showing the anthropogenic impact on the Hg cycle since the preanthropogenic period (prior to 1450 AD) (Outridge *et al.*, 2018)

气沉降约3 600吨/年;工业革命以来急剧增加人为活动的影响,大气汞的排放和沉降与工业革命前比均升高了2~4倍,海洋和陆地汞的储量显著上升(UNEP, 2018).然而,目前对植被生态系统汞的大气源汇关系认识还存在很大不确定性.

2 植被可能是被遗忘的全球重要大气汞汇

植被是联结大气圈与土壤圈的关键纽带,在全球汞生物地球化学循环中扮演着举足轻重的角色.20世纪70年代末以来,植被生态系统汞的生物地球化学过程研究一直是陆地生态系统汞循环研究的重点与前沿方向之一,先后经历了基于总汞含量分析阶段、汞形态分析的研究阶段与近十多年来汞同位素示踪等新技术应用下的快速发展阶段.

早期的研究认为,与大多数微量元素类似,土壤中的汞被植被根吸收,然后迁移转运至地上部分的组织中(Lindberg *et al.*, 1979; Bishop *et al.*, 1998; Leonard *et al.*, 1998).因此,早期的汞生物地球化学模型仅把植被作为大气零价汞(Hg^0)的源,认为植被通过根吸收土壤溶液的汞,在蒸腾作用驱动下,经导管传输至地上部分组织,最终在叶片中将其还原为Hg^0进而释放到大气环境中(Hanson *et al.*, 1995; Gbor *et al.*, 2006; Shetty *et al.*, 2008).近十年来,随着非传统稳定同位素分析技术在汞研究领域的快速发展与应用,学界逐渐认识到植被地上部分组织中的汞主要来自于叶片吸收大气中的Hg^0(Obrist *et al.*, 2018; Wang *et al.*, 2021; Zhou and Obrist, 2021).大气汞的组分95%以上为Hg^0;植被叶片在呼吸和光合作用的过程中,可通过叶片气孔途径或者表皮角质层的非气孔途径,摄取大气中的Hg^0(Stamenkovic and Gustin, 2009; Arnold *et al.*, 2018; Wang *et al.*, 2021).因此,大气中的汞可通过植被吸收与凋落物沉降,进入陆地生态系统,进而影响全球汞的生物地球化学循环.

基于局域尺度的研究,本文作者领导的团队与法国Sonke教授研究团队均发现:植被吸收大气Hg^0不仅是北半球背景地区大气汞动态变化的重要驱动力之一,而且还是造成敏感生态系统汞污染风险持续升高的关键因素(Fu *et al.*, 2016a, 2019; Jiskra *et al.*, 2018).最近的研究还表明,全球海洋性冰川退缩后的植被演替,使得冰川退缩区大气Hg^0来源新近累积的汞库相比冰川未退缩前的冰中汞库增加了一个数量级(Wang *et al.*, 2020b).此外,Obrist *et al.*(2017)发表于Nature的研究也证实,苔原植被对大气Hg^0的吸收是北极地区汞污染的主因.

从全球尺度而言,森林每年以凋落物汞沉降的形式从大气中转运1 000~1 200吨汞至林下土壤(Wang *et al.*, 2016; Zhou and Obrist, 2021),这相当于全球人为源大气汞年均排放量的50%~60%(UNEP, 2018).全球陆地表层土壤60%的汞来源于植被叶片吸收大气Hg^0后的沉降,换言之,植被是驱动全球背景区域表层土壤汞空间分布的核心因素(Wang *et al.*, 2019; Srivastava *et al.*, 2020;毛欣等, 2021;韦一等,2021).传统的基于含量和通量观测的研究认为湿沉降是土壤汞的重要来源(Lindberg *et al.*, 1995, 2007; Blackwell and Driscoll, 2015),但近十多年结合模型及汞同位素的研究将植被吸收大气Hg^0的重要性提升到新的高度,这极大提高了全球汞生物地球化学循环规律的认识水平.综上所述,植被叶片是陆地生态系统大气Hg^0沉降的"生物泵",因此,植被可能是全球大气Hg^0的重要汇,然而目前全球汞质量平衡的估算中还没有考虑这一重要汞汇.

3 精确评估植被汞汇通量是当前全球汞生物地球化学循环研究难点

目前学术界对植被汞生物地球化学过程的研究主要取得以下3点共识:

(1)植被地上部分的化学计量特征及来源贡献较为明晰.近年来,对典型生态系统植被地上部分汞的含量和储库的研究表明,汞在植物组织中的含量基本上遵循叶>皮>枝>干的分布趋势(Blackwell *et al.*, 2014; Yang *et al.*, 2017; Wang *et al.*, 2021; Zhou and Obrist, 2021; Zhou *et al.*, 2021).叶片汞含量受大气汞含量、环境气候因子、叶片类型及生理特征的综合影响(Liu *et al.*, 2021; Wang *et al.*, 2021; Zhou and Obrist, 2021; Zhou *et al.*, 2021).树皮中的汞一部分继承叶片向韧皮部的传输;另一部分汞来自疏松多孔结构的树皮对大气汞的吸附(Kang *et al.*, 2019; Wang *et al.*, 2021; Zhou *et al.*, 2021).对于木质部汞,当前的研究共识是其主要来自于叶片吸收大气Hg^0后沿筛管及木质部射线细胞的传输累积(Arnold *et al.*, 2018; Wang *et al.*, 2020c, 2021).由于树干的生物量远高于叶片,因此森林植被汞

储库会出现树干高于叶片的情况(Blackwell *et al.*, 2014; Yang *et al.*, 2017; Wang *et al.*, 2021; Zhou and Obrist, 2021; Zhou *et al.*, 2021).最新的研究表明,全球森林植被地上部分每年积累的汞库约为 1 200～1 950 吨(Wang *et al.*, 2021).

(2)植被叶片与大气汞交换通量规律认识取得重要进展.叶片-大气汞的交换通量主要受制于大气汞含量与叶片生理特性,因此凡是影响叶片表面结构、叶片气孔开合及大气汞含量变化的因子,都可能影响叶片与大气间汞的交换通量(Agnan *et al.*, 2016; Zhu *et al.*, 2016; Obrist *et al.*, 2018).当前多数观测结果显示,叶片-大气汞的交换通量整体上表现为叶片吸收大气 Hg^0,但在特定时间或季节会出现叶片向大气释放汞的过程,如中午或者叶片凋落前的秋冬季(Agnan *et al.*, 2016; Yuan *et al.*, 2019; Wang *et al.*, 2021).叶片向大气再释放的汞可能有两个主要来源:①先前沉降在叶片表皮层的汞在光还原作用下形成 Hg^0 后的再释放;②叶片组织细胞内先前固定的汞释放至细胞液后被还原成 Hg^0 后再释放(Wang *et al.*, 2017a, 2017b, 2021; Yuan *et al.*, 2019).整体而言,阔叶林叶片因具有较高的气孔密度和导度,其汞的交换通量往往显著高于针叶林叶片.从叶片汞的年净累计速率来看,针叶林叶片汞累积速率在 10～15 $ng \cdot g^{-1}a^{-1}$;落叶林在 30～50 $ng \cdot g^{-1}a^{-1}$;常绿阔叶林在 40～70 $ng \cdot g^{-1}a^{-1}$(Wohlgemuth *et al.*, 2022; Zeng *et al.*, 2022).

(3)森林系统大气汞湿沉降与凋落物汞沉降规律较为确定.近 30 年国内外学者围绕森林生态系统大气汞沉降进行了大量的研究工作.在温带/北方森林,凋落物汞沉降通量是大气汞湿沉降的 2～4 倍,而在亚热带常绿阔叶林这一比例可达 5～10 倍;凋落物与穿透雨汞沉降通量的比例与冠层结构、植被类型相关,总体上二者通量相近或凋落物汞沉降通量略高;大部分(>70%)森林凋落物沉降汞输入生态系统后被保留在土壤中(Fu *et al.*, 2010, 2014, 2016b; Wang *et al.*, 2016, 2017b, 2021; Wright *et al.*, 2016; Zhou and Obrist, 2021).整个大气汞的沉降途径中,尤以凋落物汞沉降通量规律刻画最为透彻.本文作者领导的团队成果表明,从全球 1 km × 1 km 分辨率的凋落物汞沉降分布的空间格局上看,全球凋落物汞沉降通量约为 1 200 吨/年,且近 70% 的凋落物汞沉降发生在热带/亚热带森林中(Wang *et al.*, 2016).

虽然植被汞研究已取得了上述重要进展,但是对不同类型植被与土壤、大气间汞交换过程及植物组织中汞的来源、分布与相态转化机制等仍认识不清楚,精确评估植被对全球汞生物地球化学循环的影响仍存在如下 3 方面难点.

3.1　大气-植被汞交换过程中的相态转化机制不清

首先,大气 Hg^0 进入植物叶片会发生氧化反应,并以二价汞形态(Hg(II))稳定存在,然而这一关键反应背后的机制尚不明确.近期利用杨树匀浆开展实验表明,Hg^0 氧化生成 Hg(II)可通过两步单电子转移进行,并推测 Hg^0 到 Hg(I)的转化为非酶过程,而 Hg(I)向 Hg(II)的转化由酶和巯基生物分子共同介导(Liu *et al.*, 2022).此外,对于叶片 Hg^0 再释放过程中的相关机制认识更加不明确,目前只是粗略推测可能与光致还原过程相关(Yuan *et al.*, 2019).其次,氧化后的汞在叶片组织中的化学形态关乎叶片汞的再还原及迁移分配过程,但目前尚不清楚汞在叶片组织中主要以何种化学形态存在.学界猜测叶片中富含巯基的植物螯合肽或金属硫蛋白可能是络合汞的重要底物,能对汞在植物组织中的迁移分配及氧化还原产生重要影响(Laacouri *et al.*, 2013; Manceau *et al.*, 2015, 2018; Liu *et al.*, 2021).

3.2　植被地下部分汞库、来源及组织间迁移分配规律不明

目前对于植被根的汞来源与迁移转化规律的认识十分欠缺.目前对全球森林植被根中汞库年增加量的估算误差很大,从 2 100～3 200 吨/年不等(Wang *et al.*, 2021).造成上述估算误差的原因有两方面:一是,当前多数的研究只是简单测定浅层土壤混合根的汞含量,而事实上根系不同分级及不同土壤深度的根汞含量差异很大;二是,当前文献报道的根汞含量数据集的异质性过大,且代表性不够,主要集中在中国、北美与欧洲的温带与北方森林系统,而根生物量较大的热带和亚热带森林的数据较为匮乏(Frescholtz *et al.*, 2003; Wang *et al.*, 2012, 2020c, 2021; Zhou and Obrist, 2021).早期的研究认为根中汞来自于土壤溶液汞(Lindberg *et al.*, 1979; Bishop *et al.*, 1998; Leonard *et al.*, 1998; Pereira *et al.*, 2005; Cui *et al.*, 2014; Luo *et al.*,

2016),然而最近的研究认为根中汞可能有较高比例是来自叶片吸收并转运的汞,并估算有高达300吨/年大气Hg^0贮存在根中(Zhou *et al.*, 2021).总之,由于植被根的储库、来源及其迁移分配机制不清,上述评估仍存在较大的不确定性.

3.3 全球植被大气汞汇定量化评估存在极大不确定性

目前研究认为森林凋落物汞沉降通量可近似代表森林植被的大气Hg^0沉降通量,其前提是叶片向枝干传递的汞量极少,叶片中汞主要来自于自由大气,森林其他组分对大气Hg^0的吸收可忽略不计.然而,近年来相关研究表明上述假设的前提条件可能并不完全成立.一是,叶片吸收的大气Hg^0不完全来自于冠层外的自由大气,且吸收后存在显著的迁移.土壤再排放的汞(森林系统内循环的汞)可扩散至冠层并被叶片吸收;叶片吸收大气汞后,还会向植被木质部迁移传输(St Louis *et al.*, 2001, 2019; Wang *et al.*, 2021).二是,森林系统中其他大气汞沉降也包含Hg^0的沉降.传统的汞质量平衡的研究认为森林穿透雨中的汞,主要来源于雨水洗刷沉降到冠层表面的大气中二价汞,但最近研究表明冠层附生植被能吸收大气中Hg^0,这些附生植物腐化形成腐殖质附着于树干与冠层,其中的汞被降水冲刷进入穿透雨(Wang *et al.*, 2020c).此外,最新研究表明森林附生植被大气Hg^0汇(630± 315吨/年)相当于全球凋落物汞沉降通量的50%左右(Wang *et al.*, 2020c),而当前的全球汞生物地球化学模型中尚没有考虑附生植被的汞汇.

植被汞循环理论的不完善,使得当前主流的全球汞循环模型如GEOS-Chem、GRAHM、CAM-Chem还停留在陆地生态系统因植被的存在仅改变了下垫面的粗糙度进而影响大气零价汞的干沉降速率的认识层面(Smith-Downey *et al.*, 2010; St Louis *et al.*, 2019).显然这与植被叶片吸收大气零价汞随凋落物进入地表或传递至木质部库存的生物地球化学过程是不相符合的.故而,目前几乎所有的全球汞生物地球化学循环模型均难以客观考虑到全球植被大气汞汇的贡献,不能量化不同植被类型、物候、生理参数的时空动态变化对全球汞循环的影响作用.

4 多学科交叉、多技术融合为攻克植被汞生物地球化学循环研究的难点提供了契机

传统植被汞生物地球化学循环研究主要侧重汞在植被中含量、储库及通量,无法追溯相关的生物地球化学过程,而近年来环境地球化学新技术新方法的涌现,为攻克当前相关研究难点提供了契机.

首先,同步辐射技术在环境科学领域的应用取得了长足的发展,为解析环境介质中汞的形态转化及迁移分布规律提供了新的手段.因具有无损检测、需样量少和指纹谱等特征,同步辐射技术成为解析复杂基质样品中汞形态的强有力工具.特别是近年来随着高能量分辨率X-射线近边吸收谱技术(HR-XANES)与micro-XANES的快速发展,使其甚至能够原位检测植被亚细胞结构中重金属的形态分布(Manceau *et al.*, 2018; Wang *et al.*, 2020a, 2022b, 2022c).近年有学者利用HR-XANES对于禾本科和蕨类植物叶片研究,发现植物叶片中大部分汞是以纳米硫化汞形式存在,其次是以巯基汞化合物形式存在(Manceau *et al.*, 2018; Wang *et al.*, 2022b).目前尚不清楚乔木组织的汞形态分布特征,但同步辐射技术为解决这一难题提供方法学支撑.

其次,近年来快速发展的汞稳定同位素示踪技术,能揭示生物地球化学过程中的汞同位素分馏规律,使精准识别环境汞的来源和生物地球化学过程成为可能.汞是自然界少数的拥有三维分馏体系的独特元素.汞同位素的三维分馏体系包括:同位素质量分馏(MDF)、奇数同位素非质量分馏(Odd-MIF)和偶数同位素非质量分馏(Even-MIF).在陆地生态系统中,叶片吸收大气Hg^0的过程中存在−2.8‰的汞同位素质量分馏(以$\delta^{202}Hg$为基准),远高于其他大多数汞生物地球化学过程的分馏(Demers *et al.*, 2013; Enrico *et al.*, 2016; Zheng *et al.*, 2016; Wang *et al.*, 2017a, 2019);因此植被能在汞含量和同位素组成特征的两个维度上揭示森林生态系统汞的生物地球化学循环规律(Fu *et al.*, 2016a, 2019).偶数同位素非质量分馏主要与高空大气的汞氧化过程相关,是示踪降水沉降来源汞的特征指纹;同样,环境中也只有少数的生物地球化学过程会引起奇数同位素非质量的分馏,如二价汞的光致还原过程(Bergquist and Blum, 2007; Zheng and Hintelmann, 2009, 2010; Chen *et al.*, 2012; Kri-

tee *et al.*, 2018;Yuan *et al.*, 2022).此外,在陆地生态系统中,大气汞湿沉降、凋落物汞沉降、土壤母质层岩石中汞、人为源排放汞等重要端元都具有独特的汞同位素组成指纹特征.正是由于其分馏体系的特异性,汞同位素组成已成为示踪陆地生态系统中汞的来源、迁移转化过程的重要工具.

此外,微气象学法的汞通量观测技术,为明确汞在生态系统尺度上的源汇通量提供了关键支撑.微气象学法是一类开放式的测量方法,可以进行汞通量观测的方法主要有波文比法(MBR)和弛豫涡旋积累法(REA).相比于传统通量箱/袋测定方法,它们的共同特点可归纳为:(1)基于生态系统尺度的测量,具有更大的空间尺度,测量范围可覆盖大至周边半径几百米的区域,能获得长时间尺度高时间分辨率的汞交换通量,显著提高了通量观测结果的代表性;(2)实验装置及观测活动基本不会干扰被测区域的自然环境状况,减少了传统通量箱密闭系统采样带来的原位扰动(Sommar *et al.*, 2013a, 2013b, 2020; Zhu *et al.*, 2015a, 2015b).基于微气象学法的汞通量观测表明,生态系统尺度的大气 Hg^0 沉降通量比凋落物汞沉降通量高 1~2 倍,这表明传统的森林汞沉降通量观测可能显著低估了森林生态系统汞的沉降通量(Obrist *et al.*, 2021;Wang *et al.*, 2022a).

此外,同步辐射、汞同位素及其微气象法通量测定等技术方法间的交叉融合,能为进一步解决当前森林生态系统汞的生物地球化学循环的研究难点提供独辟蹊径的崭新视角.同步辐射技术耦合汞同位素示踪技术,可以实现植被叶片和根中汞形态结构、氧化还原、迁移分配等多层次的解析,构建起微观-宏观的桥梁,实现深层次剖析根、叶中汞的氧化还原及其形态络合的机制,阐述乔木地上木质部中汞的迁移分配过程.微气象通量观测技术耦合汞同位素示踪技术,不仅可以获得生态系统尺度上的高时间分辨率汞通量交换规律,还能实现生态系统中汞同位素分馏过程的示踪.相比于当前汞同位素主要用于解析局部及单个生物地球化学过程,生态系统尺度的汞同位素组成变化特征,能够更加直接地反映植被对大气环境中汞循环的影响,拓展当前森林系统汞生物地球化学循环规律的认识.

5　总结

综上所述,植被是全球大气重要汞汇,但由于大气-植被-土壤的汞交换过程及植物组织中汞的分布、来源与迁移规律认识仍不清楚,因此无法厘定全球植被的大气汞汇通量.由于当前的全球汞生物地球化学循环模型均缺失植被过程模块的贡献,致使其难以全面解析全球汞生物地球化学循环的质量平衡.而近年来新兴的同步辐射、汞同位素示踪及其微气象法汞通量观测技术等新手段,为全面认识植被在全球汞生物地球化学循环中的作用,提供了崭新视角与系统解决方案.

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