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水环境中铁-汞耦合对汞生物地球化学循环的影响研究进展*

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摘 要 汞及其化合物是一类重要的全球污染物. 水环境是汞重要的汇,也是汞发生形态转化与生物富集的重要场所. 水环境中铁-汞相互作用对汞的生物地球化学循环有重要的影响. 本文围绕水环境中铁-汞生物地球化学循环的耦合,讨论并总结了含铁矿物对汞的吸附、硫铁矿物对汞的硫化、溶解性铁与含铁矿物对二价汞的还原、铁对汞微生物甲基化的影响、铁参与的甲基汞降解、铁硫矿物介导二甲基汞生成以及水稻根系铁膜对汞吸收的影响,并进一步对铁-汞耦合对汞的生物地球化学循环影响的未来研究重点进行了展望.

关键词 汞, 甲基汞, 铁, 生物地球化学循环,水环境.

Influence of iron-mercury coupling on biogeochemical cycle of mercury in aquatic environment: A review of recent studies

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Abstract: Mercury and its compounds are a class of important global pollutants. Aquatic environment is an important sink for mercury and also crucial sites for its transformation and bioaccumulation. The interaction of iron and mercury in aquatic environment has important impacts on the biogeochemical cycle of mercury. This review focused on the coupling of biogeochemical cycles of iron and mercury in aquatic environment, and discussed and summarized the adsorption of mercury to iron minerals, sulfidation of mercury by iron sulfide, reduction of mercury by dissolved iron and iron minerals, effect of iron on the microbial methylation of mercury, degradation of

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methylmercury by iron, formation of dimethylmercury induced by iron sulfide, as well as effect of iron plaque on the uptake of mercury. The future trends in iron-mercury coupling on biogeochemical cycle of mercury in aquatic environment was also proposed.

Keywords: mercury, methylmercury, iron, biogeochemical cycle, aquatic environment.

由于大气长距离传输、食物链累积以及高毒等特性,汞及其化合物被视为一类重要的全球污染物[1]. 据估计,每年人为因素向大气排放的汞约为 2320 t[2]. 这些人为源主要包括化石燃料火电站、手工小规模金矿开采、有色金属制造、水泥生产、废物处置、烧碱生产等[2]. 而从地表环境经一次或二次释放(即沉降汞的再释放)至大气中的汞约为 5207 t[2]. 这些自然或人为来源的汞可在不同生态系统的土壤、水、大气及生物体各介质中进行再分配. 研究表明,由于汞减排措施的实施,近些年来大气中汞浓度呈一定下降趋势[3-5],但由于地表汞的再释放与全球再分布,全球汞污染问题仍将长期存在[6].

在环境与生物体中,无机汞可以零价、一价以及二价形式存在. 通常,一价汞被认为不稳定,多以二聚体(Hg_2^{2+})形式存在,并易于歧化为相对稳定的二价汞与零价汞[7]. 因此,除氯化亚汞外,一般认为一价汞在实际环境中较少存在. 通常,大气中汞主要以零价汞形态存在,而在水、土壤、底泥等介质中汞主要以二价汞形式存在. 在生物体中,除了无机二价汞之外,甲基汞是汞存在的最主要形态. 此外,在海洋环境中,汞也可以较低浓度的二甲基汞形式存在[8]. 在以上汞形态中,甲基汞因其高的神经毒性与生物积累性备受关注[9].

1 水环境与汞的生物地球化学循环(Aquatic environments and biogeochemical cycle of mercury)

水环境是汞迁移重要的汇. 据 2013 年发布的全球汞评估报告估计,每年通过大气沉降向陆地及淡水系统输入汞达 3200 t;向海洋输入汞 3700 t[10]. 点源如有色金属制造业、消费品废弃物、氯碱生产、炼油等每年向水中直接释放汞约 185 t,污染地点如汞矿区、贵金属生产区、有色金属生产区、氯碱生产区等每年向水中释放汞约 8.3—33.5 t[10]. 此外,森林砍伐可导致土壤侵蚀,进而释放之前积累在土壤中的汞. 根据 2010 年全球森林砍伐情况及土壤汞浓度估算,全球范围内的森林砍伐导致的水土流失每年向河流输送的汞高达 260 t[10]. 除了以上来源,含汞农药使用也可能是环境水体中汞的重要来源[10].

水环境是汞形态转化的重要场所,对汞的迁移及生物累积有重要影响. 如图 1 所示,进入水环境中的汞可经受一系列化学与物理转化,如还原、氧化、甲基化、去甲基化、吸附、硫化等过程. 零价汞在水中溶解度较低且具有较高亨利定律常数,因此二价汞还原后易于从水中逸散出来,进入大气. 水中溶解性气态汞占总汞的比例通常小于 30%[10]. 模型估计显示,沉降至海洋中的汞约 70%还原后再次释放至大气中[10]. 在水中也存在溶解性气态汞的再氧化[11]. 二价汞或零价汞可吸附在颗粒物表面,从而影响汞的沉降、甲基化、水气交换等过程[12-13]. 底泥及上覆水中的汞可被微生物甲基化为高毒性的甲基汞,并进一步生物富集与生物放大[14]. 与此同时,底泥或水中的甲基汞可被化学或生物途径降解[14]. 水体或底泥中的无机汞可被一系列化学及生物过程转化为低反应活性的硫化汞;而硫化汞也可经过溶解等过程,再次进入汞的生物地球化学循环[15].

2 水环境中铁-汞生物地球化学循环的耦合(Coupling of biogeochemical cycles of iron and mercury in aquatic environment)

铁在地壳元素中含量位于第四位,是地球上分布最广、最重要的金属元素之一. 已有研究表明,微生物介导的铁循环及其与碳、氮、氧、硫的耦合驱动了全球的生物地球化学循环,并对多种有毒金属的生物地球化学循环产生重要影响[16-18]. 环境中的铁通常以二价或三价存在. 其中,还原态二价铁可以以可溶性离子或不溶铁矿物形式存在,而氧化态三价铁通常以不溶的矿物颗粒形式存在. 环境中常见的铁矿物包括:磁铁矿(Fe_3O_4)、赤铁矿(Fe_2O_3)、磁赤铁矿(γ-Fe_2O_3)、针铁矿(α-FeO(OH))、纤铁矿(γ-FeOOH)和菱铁矿($FeCO_3$)、四方硫铁矿(FeS)、黄铁矿(FeS_2)等. 如图 2 所示,微生物在底泥与水体铁氧化还原中起着决定性的作用. 在缺氧区,三价铁氧化物可被铁还原微生物直接或间接(经由电子穿梭体进行电子传递)还原,同时微生物氧化有机碳与氢气等;而在缺氧或有氧条件下,铁氧化微生物可利用二价铁

作为电子供体将碳同化为生物质,铁的微生物氧化也可耦合硝酸盐、高氯酸盐、氯酸盐等的还原过程. 此外,在厌氧底泥中微生物铁-硫循环耦合可促进硫铁矿物如四方硫铁矿、黄铁矿的生成.

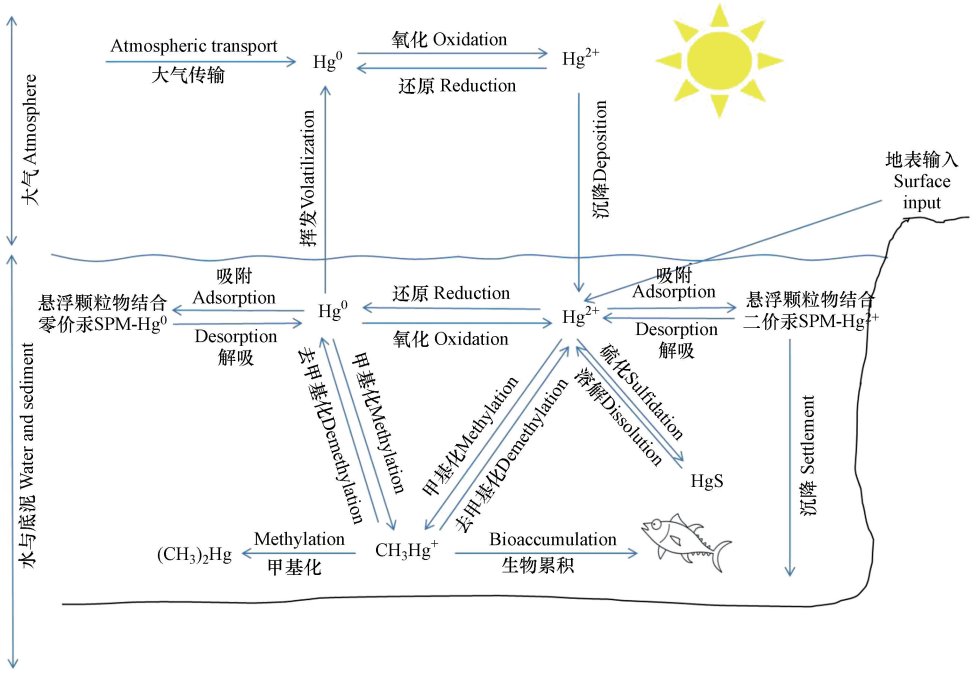

图 1　环境水体汞的生物地球化学循环

Fig.1　Biogeochemical cycle of mercury in environmental waters

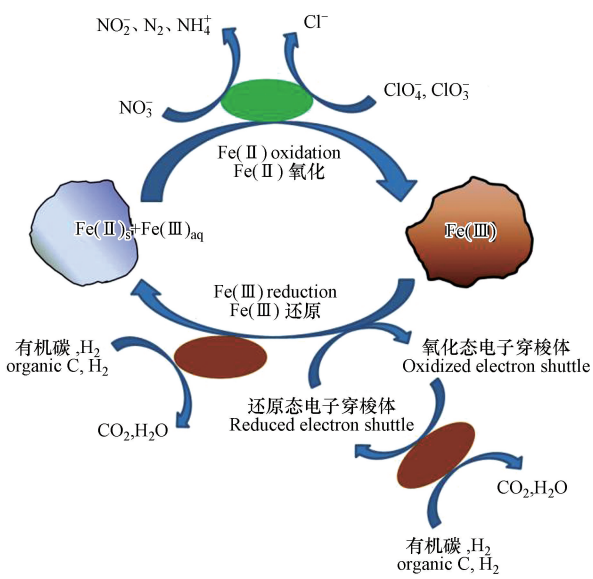

图 2　微生物介导铁的氧化还原循环(根据文献[16]重绘)

Fig.2　Redox cycle of iron mediated by microorganisms (modified from reference [16])

水环境中的铁循环对汞的迁移、转化等过程具有显著的影响[19]. 含铁矿物可吸附二价汞,从而影响二价汞的迁移与生物可给性. 溶解性铁或含铁矿物可引发汞的化学转化,如二价汞的还原、硫化、甲基汞的光降解、二甲基汞的生成等. 溶解性二价铁或二价铁矿物在氧化过程中可生成大量羟基自由基,强氧化性的羟基自由基可能在硫化汞溶解、甲基汞降解、零价汞氧化中起着重要的作用. 此外,铁可显著影响水环境中微生物群落组成与活性,从而间接影响微生物对汞的转化过程,如铁还原菌对汞的生物甲基化.

2.1 含铁矿物对汞的吸附

底泥与上覆水中存在的铁矿物对多种金属污染物具有较强的吸附能力,对金属的分配、反应活性与生物地球化学循环有重要影响[20]. 悬浮颗粒物中,除了有机颗粒物,天然有机质包裹的铁氧化物等颗粒物也可吸附汞[21],水中总汞与富铁的悬浮颗粒物浓度呈正相关[22]. 多项现场研究发现,除了有机质外,底泥中的汞与铁氧化物、铁硫化物也呈正相关,这可能与汞在铁矿物表面的吸附有关[22-26]. 例如,在葡萄牙一污染区的底泥中,固相中汞与铁氧化物的相关性 r 可达 0.919[24];美国南卡罗来纳州一处湿地底泥中汞浓度与铁氧化物浓度也呈显著相关($r=0.94$)[26];美国缅因州一处河口底泥的 FeS 沉淀区往往伴随着汞的消耗,这与 FeS 对二价汞的吸附有关[25]. 盐酸提取实验也显示,6 mol·L^{-1}盐酸可将底泥中50%—60%的汞提取出来,说明大部分汞可能与酸挥发性硫组分(如 FeS)相结合,剩余的汞可能在提取过程中与酸生成的硫化氢反应生成硫化汞,从而保留在固相[27]. 另一些研究也发现,孔隙水中溶解态总汞与溶解态 Fe^{2+}浓度正相关($r=0.61$),而与溶解性有机碳浓度相关性稍弱($r=0.54$)[28-29],提示铁还原一定程度促进汞的溶解与移动[24,30]. 一方面,铁氧化物的还原溶解可能释放自身吸附的汞;另一方面,其还原溶解可导致所吸附有机质的再释放,从而促进汞的移动[30]. 铁还原菌与硫还原菌在底泥汞迁移中的作用存在一定差异. 柱实验表明,铁还原菌可导致铁氧化物直接还原,这一过程伴随着汞的释放与甲基化;而硫还原菌可通过生成的 S(-Ⅱ)间接还原铁氧化物,生成 FeS,并吸附汞或生成硫化汞,可过滤汞可以 FeS 胶体吸附汞形式进行迁移[31].

室内模拟实验显示,Hg LIII 边 X 射线吸收精细结构谱(EXAFS)分析显示,二价汞在针铁矿表面的吸附以单齿(≡Fe-O Hg^+)与双齿络合(≡Fe-OHgOH)形式为主,其吸附模式在 pH 4.3—7.4 范围内相近[32-33]. 同位素示踪二价汞在针铁矿上的交换动力学发现,游离二价汞可与吸附在针铁矿上的二价汞发生交换,交换动力学在初期较快,而后交换速率下降;约 29%吸附在针铁矿上的汞是不可交换的,这部分不可交换汞形态的存在可能与汞扩散至针铁矿孔内有关[34]. 此外,二价汞在针铁矿表面吸附存在同位素质量分馏,汞轻同位素更易吸附在针铁矿表面($\varepsilon^{202}Hg=-0.30‰$—$-0.44‰$)[35],这为理解水环境中铁-汞耦合提供新的视角. 除了二价无机汞,铁氧化物也可吸附甲基汞[36-37]. 针铁矿对甲基汞的吸附可较快发生,这一吸附服从一级反应模型,吸附过程可能涉及不同的机制(如表面络合与表面沉淀);在饱和吸附位点被占据后,甲基汞仍可进一步吸附,这可能与甲基汞之间的疏水作用有关[37]. X 射线衍射(XRD)与 X 射线光电子能谱分析显示,FeS 对二价汞的吸附过程包含沉淀(式 1—2)、离子交换(式 3)和表面络合(式 4—5)等[38].

$$FeS(s)+H^+\longrightarrow Fe^{2+}+HS^- \quad (1)$$

$$Hg^{2+}+HS^-\longrightarrow HgS(s)+H^+ \quad (2)$$

$$FeS(s)+xHg^{2+}\longrightarrow [Fe_{1-x}Hg_x]S(s)+x\ Fe^{2+}\ (x\leqslant 1) \quad (3)$$

$$\equiv FeS(s)+Hg^{2+}\longrightarrow \equiv FeS-Hg^{2+} \quad (4)$$

$$\equiv FeS(s)+Hg\ OH^-\longrightarrow FeS—Hg—OH \quad (5)$$

相较于游离二价汞,羟基汞离子更易在 FeS 表面吸附(如式 5),因此随着 Hg^{2+}/FeS 浓度比的增加,溶液 pH 相应降低[39]. 而低 pH 可造成铁矿物的溶解,从而降低 Hg^{2+}的吸附[39-42]. 黄铁矿对汞的吸附亦随 pH 降低而降低,EXAFS 分析显示经过 2 周的老化,二价汞主要以 Hg-Cl 单齿单层的形式吸附于黄铁矿表面[43],而溶解氧可抑制二价汞在黄铁矿上的吸附[43].

共存离子与有机质可抑制或促进铁矿物对汞的吸附. 10^{-5}—10^{-2} mol·L^{-1}氯离子可与汞形成 $HgCl_2$,降低二价汞在针铁矿表面的吸附,而 10^{-5}—0.9 mol·L^{-1}硫酸根在针铁矿表面的吸附可改变其表面电荷,促进二价汞在表面的吸附[32-33]. 另一研究也显示,共存氯离子可显著抑制二价汞在水合氧化铁表面的吸附,^{36}Cl 示踪表明水合氧化铁并不吸附 Hg(Ⅱ)-Cl 络合物[44]. 天然有机质在铁矿物吸附二价汞与甲基汞中的作用则较为复杂. 一方面,天然有机质在针铁矿等表面的吸附可提供额外的吸附位点(如巯基),从而促进了汞的吸附[36, 45];另一方面,溶液中的天然有机质中的巯基也可与铁矿物(如 FeS)竞争结合汞,形成 $Hg(SR)_2$,从而抑制二价汞在铁矿物表面的吸附与反应[46].

最近研究表明,环境水体中的悬浮颗粒物亦可吸附零价汞[13]. 采用稳定同位素示踪结合同位素稀释技术,发现加入环境水样中的零价汞可转化为颗粒结合态零价汞(4 h 转化率可达 70%),且这部分颗

粒结合态零价汞不能被吹扫出来[13]. 考虑到颗粒结合态零价汞的赋存可能降低零价汞的水气交换,其可能对汞的全球循环具有较大影响. 在后续研究中,需进一步考察不同颗粒物组分对颗粒结合态零价汞形态的影响[47],识别铁矿物组分吸附对颗粒结合态零价汞的贡献.

FeS 对汞的吸附可能降低汞的生物可给性[48],从而进一步降低汞的微生物甲基化效率[49-51]. 由于含铁矿物对汞的吸附及对甲基化的抑制作用,其在汞污染区域的修复治理上有很大应用空间[41].

2.2　硫铁矿物对汞的硫化

硫铁矿物对汞吸附的同时,往往伴随着汞的硫化过程. XRD 显示,在有氧条件下,FeS 可在湿润条件下将氧化汞与零价汞部分转化为硫化汞,转化率为 5%—50%;而在 FeS_2 存在下未观测到硫化现象[52]. 在缺氧条件下,FeS 可将氧化汞转化为硫化汞,转化率为 10%—20%,零价汞未见转化;FeS_2 对 HgO 的硫化可在湿润碱性条件下发生,转化率为 15%[52]. 类似地,XRD 分析发现二价汞快速吸附在 FeS 表面之后,逐步转化为 α-HgS 与 β-HgS,其中 HgS 比例可达 77%,其余 23%的汞以吸附二价汞的形式存在[39]. 另一项采用 XRD、高角度环形暗场扫描透射电镜对二价汞在 FeS 上吸附的研究则认为,β-HgS 是主要的转化产物[53]. Hg LIII 边 EXAFS 分析揭示,二价汞与 FeS 作用后,除了表面吸附的二价汞外,主要在 FeS 表面形成 β-HgS 团簇[54].

伴随着 β-HgS 的生成,水相中溶解铁的浓度相应增加,表明存在 Hg^{2+} 与 FeS 矿物中 Fe^{2+} 的置换(式 6)[55]:

$$Hg^{2+}+FeS \longrightarrow HgS+Fe^{2+} \tag{6}$$

环境中的其它配体也可和 S^{2-} 竞争结合 Hg^{2+},从而抑制 HgS 生成. 在氯离子与高 $[Hg^{2+}]_0/[FeS]_0$ (>1)摩尔比条件下,β-HgS 的生成得到抑制,Hg_2Cl_2(酸性条件)与 $HgCl_2 \cdot 3HgO$(碱性条件)生成量相应增加[55]. 类似地,溶解有机质中高亲和的巯基的存在可部分抑制 FeS 表面 β-HgS 的生成[46].

2.3　溶解性铁与含铁矿物对二价汞的还原

如前所述,水环境中由于氧化还原梯度的存在,铁可以各种不同的氧化还原形态存在. 这些水相或底泥中存在的铁可介导汞的化学还原. 环境水样中三价铁的光反应可促进汞的还原. 向湖水中加入 5 μmol·L^{-1}或 10 μmol·L^{-1}硫酸铁,暗反应条件下溶解气态汞浓度无显著变化;但在日光光照下,加铁组溶解气态汞浓度较不加铁组提高约 1 倍[56]. 增加光照时间相应增加溶解气态汞生成量,之后到达一稳态浓度;而进一步增加三价铁浓度溶解气态汞生成量基本不变或降低[56]. 据推测,三价铁-有机酸配位化合物(organic acid coordination compounds,OACC)光解可生成二价铁以及高还原活性的有机自由基(organic free radicals,OFR),其可进一步将二价汞还原为零价汞(式 7—10);与此同时,有机自由基与溶解性有机碳(dissolved organic carbon,DOC)氧化过程中生成的羟基自由基也可导致零价汞的再氧化(式 11—14).

$$Fe^{3+}+OACC \longrightarrow Fe^{3+}-OACC \tag{7}$$

$$Fe^{3+}-OACC \xrightarrow{h\nu} Fe^{2+}+OFR \tag{8}$$

$$2Fe^{2+}+Hg^{2+} \longrightarrow Hg^0+2Fe^{3+} \tag{9}$$

$$OFR+Hg^{2+} \longrightarrow Hg^0+CO_2 \tag{10}$$

$$OFR+O_2 \longrightarrow CO_2+O_2^{\cdot-} \tag{11}$$

$$DOC+O_2 \longrightarrow DOC^{\cdot+}+O_2^{\cdot-} \tag{12}$$

$$O_2^{\cdot-}+O_2^{\cdot-}+2H^+ \longrightarrow H_2O_2+O_2 \tag{13}$$

$$H_2O_2+Fe^{2+} \longrightarrow \cdot OH+OH^-+Fe^{3+} \tag{14}$$

在 pH 1—4 与 UVA 光照条件下,草酸铁可将氯化汞部分还原为零价汞,准一级反应速率常数与 pH 相关[57]. 这一反应依赖于光照及其波长:在黑暗条件下未观测到还原,而可见光照下速率较 UVA 低 10 倍[57]. 这一还原反应可能涉及草酸光解生成的二氧化碳自由基($CO_2^{\cdot-}$). 溶解氧可与二价汞竞争 $CO_2^{\cdot-}$,从而可抑制还原;氯离子可显著降低还原速率[57].

类似地,水相中的三价铁矿物如针铁矿、赤铁矿、磁赤铁矿等均可促进草酸对二价汞的光还原,其中针铁矿与磁赤铁矿的促进作用最为显著[58]. 对赤铁矿而言,光反应初期,其可促进草酸对汞的还原;但

在反应后期,生成的羟基自由基进一步导致零价汞的再氧化,从而抑制汞的还原. 三价铁矿物对光还原的促进作用可能涉及矿物表面生成的草酸自由基与氢过氧自由基(如式 15—21 所示),同时光反应过程中还原的二价铁也可能在汞的还原中起着重要作用.

$$\equiv Fe^{\text{Ⅲ}}-OH+C_2O_4^{2-}+H^+ \longleftrightarrow \equiv Fe^{\text{Ⅲ}}-C_2O_4^-+H_2O \quad (15)$$

$$Fe^{3+}-C_2O_4^- + h\nu \longrightarrow Fe^{2+}+C_2O_4^{\cdot -} \quad (16)$$

$$\equiv Fe^{\text{Ⅱ}} \longrightarrow Fe^{2+} \quad (17)$$

$$C_2O_4^{\cdot -}+O_2 \longrightarrow O_2^{\cdot -}+2\,CO_2 \quad (18)$$

$$O_2^{\cdot -}+H^+ \longleftrightarrow HO_2^{\cdot} \quad (19)$$

$$HO_2^{\cdot}+Hg^{2+} \longrightarrow Hg^+ + O_2 + H^+ \quad (20)$$

$$HO_2^{\cdot}+Hg^+ \longrightarrow Hg^0 + O_2 + H^+ \quad (21)$$

需要特别指出的是,超氧阴离子($O_2^{\cdot -}$)与氢过氧自由基($HO_2^{\cdot}$)对汞的还原作用尚存在争议. 一些研究认为超氧阴离子与氢过氧自由基可还原二价汞[58-59],但也有研究认为其不能还原二价汞[57].

二价铁可直接将二价汞还原为零价汞. 模拟实验显示,零价汞的生成速率随 pH(5.5—8.1)与水相溶解性二价铁浓度(0.1—1 mmol·L^{-1})的增加而增加,反应速率 $r=k[FeOH^+][Hg(OH)_2]$,其中 $k=7.19\times10^3$ L·(mol·min)$^{-1}$[60]. 而二价铁在铁矿物上的吸附可进一步提高其对汞的还原[60]. 零价汞的这一非均相生成过程与二价铁/二价汞的吸附、吸附二价铁对汞的还原等步骤有关[60].

自然界中,多种铁矿物中均含有二价铁. 这些固相二价铁可引发二价汞的还原. 碱式绿锈可将氯化汞还原为零价汞,同时伴随着绿锈向磁铁矿的氧化转化(式 22—23)[61].

$$\equiv Fe^{\text{Ⅱ}}+Hg^{2+} \longrightarrow \equiv Fe^{\text{Ⅲ}}+Hg^+ \quad (22)$$

$$\equiv Fe^{\text{Ⅱ}}+Hg^+ \longrightarrow \equiv Fe^{\text{Ⅲ}}+Hg^0 \quad (23)$$

类似地,菱铁矿可在数分钟内将二价汞还原为零价汞,其还原速率随菱铁矿表面积增加而增加[62]. 汞 LIII 边 X 射线吸收近边结构(XANES)分析表明电子转移反应直接发生在菱铁矿-水界面,反应产物零价汞亦主要吸附在菱铁矿表面[62]. 磁铁矿亦可将二价汞快速还原为零价汞,反应速率随表面积及溶液 pH 增加而加快[63]. X-射线光电子能谱分析显示,还原过程可能涉及二价汞在磁铁矿表面的吸附;穆斯堡尔谱分析也表明在汞还原过程中磁铁矿中部分二价铁被氧化为三价铁[63]. Hg LIII 边 XANES 以及零价汞分析显示,在无氯离子情况下,$Fe^{\text{Ⅱ}}/Fe^{\text{Ⅲ}}$为 0.29—0.50 的磁铁矿均可还原二价汞为零价汞[64];但在氯离子存在下,二价汞的还原产物(零价汞、氯化亚汞)占比受磁铁矿中二价铁丰度的影响[64]. 磁铁矿中 $Fe^{\text{Ⅱ}}/Fe^{\text{Ⅲ}}$比例对二价汞还原速率亦有一定影响[64].

由于以上还原过程涉及二价汞在铁矿物表面的吸附,因此天然有机质与汞的结合对铁矿物介导的汞还原有重要影响. 在较高的汞:生物质比例条件下,汞主要通过羧基与生物质结合,可观测到磁铁矿对二价汞的还原;但在较低的汞:生物质比例条件下,生物质中巯基与汞的络合可完全抑制了磁铁矿对二价汞的还原[65],而还原性较强的绿锈仍可将 20%的二价汞还原为零价汞[65].

此外,硫铁矿物如黄铁矿、四方硫铁矿除了可将二价汞转化为硫化汞外,亦可将部分二价汞还原为零价汞[52]. Hg LIII 边 EXAFS 进一步揭示,在二价汞与四方硫铁矿反应过程中,除汞的硫化外,部分二价汞被还原为零价汞[54],这与吹扫捕集-原子荧光光谱联用对体系中零价汞的测定结果相符[54].

2.4 铁对微生物汞甲基化的影响

环境中的甲基汞主要来自于微生物对汞的甲基化过程. 近期研究表明,微生物中的 *hgcA* 与 *hgcB* 基因簇是生物甲基化所必需的[66]. 目前,发现的汞甲基化微生物主要为硫还原菌[67-69]、铁还原菌[70-71]以及产甲烷菌[72-73],也包括一些产乙酸发酵厚壁菌[74]. 2006 年,Fleming 等报道了美国加州一个湖泊底泥中硫还原菌抑制剂钼酸盐的加入基本可抑制全部硫酸盐还原活性,但汞甲基化活性仅抑制不到 1/2,这意味着底泥中存在硫还原菌以外的其它汞甲基化微生物[70]. 进一步首次从底泥中分离了铁还原菌 *Geobacter* sp. strain CLFeRB,发现实验室纯菌培养条件下该铁还原菌与硫还原菌 *Desulfobulbus propionicus* strain 1pr3 相近的汞甲基化能力[70]. 研究表明,脱硫单孢菌科、杆菌科以及希瓦氏菌科的 *Desulfuromonas palmitatas*[71]、*Geobacter sulfureducens* PCA[71]、*Geobacter bemidjiensis* Bem[75]、*Geobacter daltonii* FRC-32[74]、*Geobacter metallireducens* GS-15[71]、*Geobacter* sp. strain CLFeRB[70]、*Geobacter hydrogenophilus* H2[71]等铁还

原菌均有甲基化汞的能力. 需要指出的是,铁还原菌 *Shewanella* 能否甲基化汞还存在一定争议:Kerin 等认为其不能甲基化汞[71],但 Si 等发现 *Shewanella oneidensis* MR-1 具有较高的汞甲基化能力[76].

现场研究显示底泥中溶解性铁浓度往往与甲基汞浓度正相关[62, 77-82],这提示在这些地区的底泥中以铁作为电子受体的铁还原菌可能在汞甲基化起着一定作用. 铁在汞的微生物甲基化中的作用较为复杂:多项底泥与纯菌培养研究表明,低浓度氯化铁、氢氧化铁或针铁矿的加入可促进底泥中汞的甲基化,而高浓度铁的加入则部分抑制汞甲基化[51, 83-84]. 例如,向弗吉尼亚南河底泥中加入氢氧化铁[85]及瑞士日内瓦湖底泥中加入无定型氧化铁[86]均可一定程度促进汞的甲基化. 向意大利威尼斯泻湖底泥中加入低浓度 $Fe(NO_3)_3$可促进甲基汞生成,但当 $Fe(NO_3)_3$浓度高于 1 mmol·L^{-1}时,甲基汞浓度显著下降[51]. 纯菌培养体系也显示,向铁还原菌 *Shewanella oneidensis* MR-1 加入 1、2、5 g·L^{-1}的针铁矿,可不同程度促进铁还原菌对汞的甲基化[76]. 其中投加 1 g·L^{-1}针铁矿时汞的甲基化率最高;但随着针铁矿的投加量的增加,甲基化率有所下降[76]. 也有研究表明铁的加入降低底泥中汞的甲基化. 向底泥中加入硫铁矿物(含有四方硫铁矿、四硫化三铁、磁黄铁矿、黄铁矿及元素硫等)降低了汞的甲基化[49]. 铁在汞微生物甲基化过程中的复杂作用可能与以下因素有关:(1)作为电子受体的低浓度铁的加入可促进铁还原菌的活性与生长,从而促进铁还原菌对汞的甲基化. 不同形态铁对甲基化的促进作用存在差异,其促进作用为 $Fe(OH)_3$> $FeCl_3$> 柠檬酸铁. 铁还原比例(Fe(Ⅱ)%)与甲基化比例呈现显著正相关(R^2>0.9),说明铁作为电子受体在汞甲基化中的关键作用. (2)铁矿物如羟基氧化铁[87-91]、硫化亚铁[87, 92-94]均可吸附无机汞,从而降低了无机汞对微生物的生物可给性,进一步抑制了其生物甲基化. 除了铁还原菌,铁也可影响硫还原菌对汞的甲基化. 向硫还原菌 *Desulfobulbus propionicus* (1pr3)培养瓶或湿地底泥中加入 $FeCl_2$,高铁组(10^{-2} mol·L^{-1})甲基汞产量分别为低铁组的 1/4 与 1/3[91]. 底泥的微宇宙实验进一步证实了这一结果:高铁组(360、720 g·m^{-2})将甲基汞的输出降低了 80%以上[95]. 高铁组较低的甲基汞产量也可能与铁的加入降低了 S(-Ⅱ)的活性并进一步降低了溶解态汞浓度有关[91]. 研究发现,铁浓度的选择至关重要,当二价铁浓度低于 S(-Ⅱ)浓度时,甲基汞产量反而可能增高[93]. 由于铁在汞甲基化中的作用较为复杂,应对污染治理中铁剂使用对甲基化的影响进行谨慎评估[81]. 此外,应加强对高铁环境如矿区、废水处理厂等区域汞甲基化及铁潜在作用的研究[86, 89, 96-97].

2.5　铁参与的甲基汞降解

1996 年,Sellers 等首次报道了环境水样中甲基汞的光降解[98]. 经计算,甲基汞的光降解速率约是通过湿沉降、地表径流引入的两倍,表明甲基汞的光降解过程在甲基汞的生物地球化学循环中扮演着重要的角色. 随后,多个研究组对甲基汞的光降解机制进行了研究. 研究显示,甲基汞的光降解可能存在多个途径[99]. 其中,天然有机质与甲基汞络合物的形成是甲基汞光降解的关键步骤[100],天然有机质与甲基汞络合物光解是甲基汞光降解的重要途径之一[99, 101-102]. 除了天然有机质与甲基汞络合物光解,羟基自由基也可导致甲基汞的快速降解[103-106]. 羟基自由基与氯化甲基汞的反应产物为 Hg^{2+}、Hg^0、$CHCl_3$和甲醛,pH 5 时二级速率常数为 9.83(±0.66)×10^9 L·mol^{-1}·s^{-1}[105]. 在光照条件下,溶解性铁可介导羟基自由基生成(式 24—25)[107].

$$Fe^{3+}+H_2O \longrightarrow Fe(OH)^{2+}+H^+ \quad (24)$$

$$Fe(OH)^{2+} \xrightarrow{h\nu} Fe^{2+}+{}^{\cdot}OH \quad (25)$$

因此在部分地区,溶解性铁在甲基汞的光降解中亦起着重要作用[108]. Hammerschmidt 等发现阿拉斯加 Toolik 湖水中甲基汞光降解是其主要去除途径[109]. 湖水过滤、灭菌与暗反应对照实验显示,Toolik 湖水中甲基汞光降解以由日光照射引发的非生物过程为主[109]. 研究表明,在去离子水中加入 40 μmol·L^{-1} $Fe_2(SO_4)_3$可有效降解甲基汞,而向湖水或含铁去离子水中加入三价铁络合剂去铁胺或羟基自由基清除剂甲酸、二甲基亚砜均可显著抑制甲基汞光降解,表明湖水中甲基汞的光降解与光照下铁生成的羟基自由基有关[108]. 采用不同遮光膜研究了日光波长组分对光降解的影响,发现光降解主要是由日光中 320—480 nm 波段引起的,而 UVB(280—320 nm)以及 480—800 nm 部分对光降解影响不大[108]. 自由基清除实验显示,羟基自由基在青岛地区地表水如老人头景区海水、崂山水库、墨水河水中甲基汞光降解中贡献比例约为 19%、16%与 33%,这可能与水中的溶解性铁及硝酸根有关[99]. 在模拟水样中,2.5 μmol·L^{-1}三价铁的加入可将甲基汞光降解(UVA, λ = 365 nm)速率提高 2 倍,而 50 μmol·L^{-1}

三价铁可将甲基汞光降解速率提高 7.5 倍[110]. 对于实际环境水样,20 μmol·L^{-1}三价铁的加入亦可一定程度增加表层水中甲基汞的光降解[111]. 研究发现,在模拟日光照射下,2 μmol·L^{-1}三价铁可引发甲基汞的快速降解;羟基自由基清除剂异丙醇的加入可显著抑制降解,表明羟基自由基是三价铁引发甲基汞降解的主要途径[112]. 但也有一些研究表明,实际水样中铁的浓度对甲基汞光降解影响较小. 如 Black 等发现向地表水中加入 10 μmol·L^{-1}的铁导致甲基汞光降解速率降低约 11%,这可能与铁对光量子的吸收致使甲基汞光降解的有效光量子数降低有关[113]. 25—100 μg·L^{-1}的 $FeCl_3$加入对三峡库区及嘉陵江地表水甲基汞光降解影响也不大[114-115]. 以上铁在甲基汞光降解作用上的差异可能由水化学组成的不同解释. 研究发现,虽然三价铁可导致甲基汞的光降解,但在溶解有机质存在下,三价铁对甲基汞的光降解受到显著抑制[112]. 这主要是由于溶解有机质可清除羟基自由基[116],部分抑制了甲基汞的光降解,且由于溶解有机质对甲基汞的络合作用,甲基汞的光降解途径由羟基自由基途径转变为溶解有机质-甲基汞络合物途径[112].

随着水深的增加,由于水中各组分对日光的吸收,日光照射强度逐渐下降[98]. 因此,在底泥及上覆水层,往往日光照射难以到达. 目前对于这一区域黑暗条件下甲基汞的降解还知之甚少. 最近的研究显示,高压蒸汽灭菌后 Alder 沼泽地区部分采样点底泥中甲基汞降解并无显著降低,表明除了生物降解外,底泥中甲基汞也存在显著的非生物降解[117]. 目前,对这一底泥中的甲基汞非生物降解过程的机制还不清楚. 还原性铁矿物介导的羟基自由基途径可能参与了黑暗条件下甲基汞的降解. 研究表明,底泥或厌氧上覆水曝氧可生成大量羟基自由基[118]. 底泥或水中的溶解性二价铁[119]或二价铁矿物(如绿脱石[120-121]、黄铁矿[122-123]、四方硫铁矿[124])的氧化可能在羟基自由基生成中起着主要作用. 这些黑暗条件下生成的羟基自由基可能进一步介导甲基汞的降解.

2.6 铁硫矿物介导二甲基汞生成

在海洋或陆地底泥、上覆水[125-128]以及垃圾填埋场[129-131]中,除甲基汞外,二甲基汞是另一种重要的有机汞形态. 跃温层之下低氧区微生物对汞的甲基化可能是海洋中二甲基汞的来源之一[132]. 在化学模拟体系中,甲基钴胺素可将二价汞部分甲基化为二甲基汞[133-135]. 细菌培养实验显示,脱硫弧菌属硫还原菌可将甲基汞转化为硫化甲基化汞($(CH_3Hg)_2S$)[136],并进一步将其转化为硫化汞与二甲基汞[136-137]. 除此之外,铁硫矿物如四方硫铁矿也可介导甲基汞向二甲基汞的转化[138](如图 3 所示).

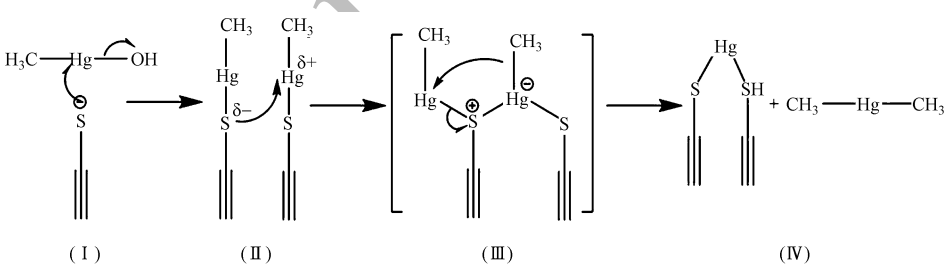

图 3 四方硫铁矿与甲基汞反应生成二甲基汞的可能机制(根据文献[138]重绘)

Fig.3 Possible reaction mechanism of mackinawite with methylmercury to produce dimethylmercury (modified from reference [138])

据推测,这一反应可能为双分子亲核取代反应(SN2):甲基汞通过 Hg-S 键吸附到矿物表面(Ⅰ)后,结合甲基汞的硫原子可进一步亲核进攻另一相邻甲基汞上的汞原子(Ⅱ),形成新的中间体(Ⅲ),并分解为二甲基汞与吸附与矿物表面的无机汞或硫化汞(Ⅳ)[138]. 这一转化的效率依赖于甲基汞/四方硫铁矿比例,其产率随甲基汞/四方硫铁矿比例的升高先升高后降低[138]. 在甲基汞/四方硫铁矿比例为 5×10^{-3}时,二甲基汞产率最高,约为 0.12%[138]. 相较而言,四方硫铁矿存在下二甲基汞的生成量显著高于 S(-Ⅱ)及巯基化合物(L-半胱氨酸、巯基丙酸、1, 3-丙二硫醇),这一转化率也高于海水中甲基汞向二甲基汞的转化[138]. 因此,据推测,铁硫矿物介导的二甲基汞生成可能是海洋中二甲基汞的来源.

2.7 根系铁膜对水稻汞吸收的影响

由于水生植物根系泌氧导致铁的氧化,在其根表会形成一层结晶态和无定型态铁氧化物和氢氧化物组成的铁膜. 铁膜广泛存在于水生植物根表,是水生植物适应淹水和其它环境胁迫的重要机制之一.

根表铁膜往往对水生植物营养及有毒元素的根部吸收有重要影响. 水稻作为一种重要的半水生植物,其籽粒对无机汞与甲基汞具有较显著的累积[139-140]. 食用稻米是除食鱼外的另一人体汞重要暴露途径[141]. 研究发现,水稻根表铁膜可吸附甲基汞与二价汞,根表铁膜显著降低了汞暴露水稻根、茎叶中汞的含量以及从根部到茎叶部的转运[142]. 同时,铁膜未对水稻植株体内无机汞与甲基汞的络合形态(RS-Hg-SR或 CH_3-Hg-SR)产生影响[143]. 另一项研究也显示,水稻根系铁膜铁含量与铁膜总汞正相关,而与水稻植株与糙米总汞负相关,表明铁膜吸附汞抑制汞的吸收[144-145];但是,铁膜铁含量与铁膜、植株中甲基汞含量无显著相关[144]. 此外,毒性测试也显示,根表铁膜的生成可以在一定程度上减弱二价汞对水稻幼苗根系生长的危害[146].

稻田施硒是抑制水稻对汞吸收的有效手段[147]. 水培实验显示,施硒可增加铁膜对无机汞与甲基汞的吸附,降低水稻对无机汞与甲基汞的吸收和转运[142, 148]. 但另一项土-砂根际袋培养实验显示,施硒可抑制水稻根表铁膜对汞的吸附[149]. 但与前一研究相一致的是,施硒也可显著降低水稻茎、叶、稻壳与稻米中汞的含量[149]. 此外,施硫(硫酸盐或元素硫)不仅可促进土壤汞向硫化汞的转化,亦可促进根表铁膜形成,从而降低无机汞与甲基汞在水稻根、茎叶以及稻米中的累积[150]. 类似地,缺磷可促进水稻根表铁膜的形成,增加铁膜对甲基汞的固定,降低甲基汞的吸收与转运[151].

3　结论与展望(Conclusion and prospect)

综上所述,水环境中铁可通过多种物理(吸附)与化学(硫化、还原、甲基化、去甲基化)作用影响汞的迁移、转化与生物摄入,在汞的生物地球化学循环中起着至关重要的作用. 铁-汞生物地球化学循环的耦合为我们理解水环境中汞的生物地球化学循环、发展新的汞修复手段提供了新的视角. 然而, 目前关于水环境中铁-汞耦合对汞生物地球化学循环的影响研究仍不够深入, 以下几个方面的研究仍有待加强:

(1)实际水环境氧化还原梯度条件下不同形态铁矿物对汞的吸附与迁移:需进一步明确环境水化学条件与参数对铁矿物形态及其吸附汞的影响,识别这种吸附对汞迁移的作用,探寻铁矿物形态转化对汞吸附与迁移的潜在作用;

(2)研究暗反应条件及氧化还原梯度下铁矿物氧化过程中羟基自由基生成,识别这种羟基自由基生成途径对甲基汞降解、零价汞氧化、硫化汞溶解的贡献,评估这一过程在缺氧-有氧循环条件下对汞生物地球化学循环的影响;

(3)利用宏基因组学方法,研究铁对微生物群落组成的影响,识别铁作用下微生物群落变化对汞的微生物转化的影响;

(4)利用铁、汞的化学与生物转化过程的同位素分馏,识别与模拟天然环境中铁与汞的生物地球化学循环的耦合;

(5)在利用铁对汞污染场地的修复中,需增加长期条件下汞的溶出与甲基化的评估.

参考文献(References)

[1] DRISCOLL C T, MASON R P, CHAN H M, et al. Mercury as a global pollutant: Sources, pathways, and effects [J]. Environmental Science & Technology, 2013, 47(10): 4967-4983.

[2] PIRRONE N, CINNIRELLA S, FENG X, et al. Global mercury emissions to the atmosphere from anthropogenic and natural sources [J]. Atmospheric Chemistry and Physics, 2010, 10(13): 5951-5964.

[3] SLEMR F, BRUNKE E G, EBINGHAUS R, et al. Worldwide trend of atmospheric mercury since 1995 [J]. Atmospheric Chemistry and Physics, 2011, 11(10): 4779-4787.

[4] ZHANG Y, JACOB D J, HOROWITZ H M, et al. Observed decrease in atmospheric mercury explained by global decline in anthropogenic emissions [J]. Proceedings of the National Academy of Sciences of the United States of America, 2016, 113(3): 526-531.

[5] TONG Y, YIN X, LIN H, et al. Recent decline of atmospheric mercury recorded by *Androsace tapete* on the Tibetan plateau [J]. Environmental Science & Technology, 2016, 50(24): 13224-13231.

[6] ECKLEY C S, BLANCHARD P, MCLENNAN D, et al. Soil-air mercury flux near a large industrial emission source before and after closure (Flin Flon, Manitoba, Canada) [J]. Environmental Science & Technology, 2015, 49(16): 9750-9757.

[7] HAN Y, KINGSTON H M, BOYLAN H M, et al. Speciation of mercury in soil and sediment by selective solvent and acid extraction [J].

Analytical and Bioanalytical Chemistry, 2003, 375(5): 428-436.
[8] MASON R P, CHOI A L, FITZGERALD W F, et al. Mercury biogeochemical cycling in the ocean and policy implications [J]. Environmental Research, 2012, 119: 101-117.
[9] CLARKSON T W, MAGOS L. The toxicology of mercury and its chemical compounds [J]. Critical Reviews in Toxicology, 2006, 36(8): 609-662.
[10] UNEP. Global mercury assessment 2013: Sources, emissions, releases and environmental transport [R]. 2013.
[11] LALONDE J D, AMYOT M, KRAEPIEL A M L, et al. Photooxidation of Hg(0) in artificial and natural waters [J]. Environmental Science & Technology, 2001, 35(7): 1367-1372.
[12] DIEZ E G, LOIZEAU J-L, COSIO C, et al. Role of settling particles on mercury methylation in the oxic water column of freshwater systems [J]. Environmental Science & Technology, 2016, 50(21): 11672-11679.
[13] WANG Y, LI Y, LIU G, et al. Elemental mercury in natural waters: Occurrence and determination of particulate Hg(0) [J]. Environmental Science & Technology, 2015, 49(16): 9742-9749.
[14] LI Y B, CAI Y. Progress in the study of mercury methylation and demethylation in aquatic environments [J]. Chinese Science Bulletin, 2013, 58(2): 177-185.
[15] CHEN Y, YIN Y G, SHI J B, et al. Analytical methods, formation, and dissolution of cinnabar and its impact on environmental cycle of mercury [J]. Critical Reviews in Environmental Science and Technology, 2017, 47(24): 2415-2447.
[16] WEBER K A, ACHENBACH L A, COATES J D. Microorganisms pumping iron: Anaerobic microbial iron oxidation and reduction [J]. Nature Reviews Microbiology, 2006, 4(10): 752-764.
[17] 陈蕾, 张洪霞, 李莹, 等. 微生物在地球化学铁循环过程中的作用 [J]. 中国科学. 生命科学, 2016, 46(9): 1069-1078.
CHEN L, ZHANG H X, LI Y, et al. The role of microorganisms in the geochemical iron cycle [J]. Scientia Sinica Vitae, 2016, 46(9): 1069-1078 (in Chinese).
[18] COOPER D C, PICARDAL F F, COBY A J. Interactions between microbial iron reduction and metal geochemistry: Effect of redox cycling on transition metal speciation in iron bearing sediments [J]. Environmental Science & Technology, 2006, 40(6): 1884-1891.
[19] 钟顺清, 仇广乐, 冯新斌. 铁硫耦合影响甲基汞在土壤-水稻系统中迁移转化的研究进展 [J]. 生态学杂志, 2017, 36(8): 2351-2357.
ZHONG S Q, QIU G L, FENG X B. Coupling effects of iron and sulfur on the migration and transformation of methylmercury in soil-rice system: A review [J]. Chinese Journal of Ecology, 2017, 36(8): 2351-2357 (in Chinese).
[20] WAYCHUNAS G A, KIM C S, BANFIELD J F. Nanoparticulate iron oxide minerals in soils and sediments: Unique properties and contaminant scavenging mechanisms [J]. Journal of Nanoparticle Research, 2005, 7(4-5): 409-433.
[21] GU B H, MISHRA B, MILLER C, et al. X-ray fluorescence mapping of mercury on suspended mineral particles and diatoms in a contaminated freshwater system [J]. Biogeosciences, 2014, 11(18): 5259-5267.
[22] WARNER K A, BONZONGO J C J, RODEN E E, et al. Effect of watershed parameters on mercury distribution in different environmental compartments in the mobile Alabama river basin, USA [J]. Science of the Total Environment, 2005, 347(1-3): 187-207.
[23] THOMAS R L Distribution of mercury in surficial sediments of lake Huron [J]. Canadian Journal of Earth Sciences, 1973, 10(2): 194-204.
[24] RAMALHOSA E, SEGADE S R, PEREIRA E, et al. Mercury cycling between the water column and surface sediments in a contaminated area [J]. Water Research, 2006, 40(15): 2893-2900.
[25] MERRITT K A, AMIRBAHMAN A. Mercury dynamics in sulfide-rich sediments: Geochemical influence on contaminant mobilization within the Penobscot river estuary, Maine, USA [J]. Geochimica et Cosmochimica Acta, 2007, 71(4): 929-941.
[26] KAPLAN D I, KNOX A S, MYERS J. Mercury geochemistry in wetland and its implications for in situ remediation [J]. Journal of Environmental Engineering-ASCE, 2002, 128(8): 723-732.
[27] MIKAC N, NIESSEN S, OUDDANE B, et al. Effects of acid volatile sulfides on the use of hydrochloric acid for determining solid-phase associations of mercury in sediments [J]. Environmental Science & Technology, 2000, 34(9): 1871-1876.
[28] JOHANNESSON K H, NEUMANN K. Geochemical cycling of mercury in a deep, confined aquifer: Insights from biogeochemical reactive transport modeling [J]. Geochimica et Cosmochimica Acta, 2013, 106: 25-43.
[29] MATTY J M, LONG D T. Early diagenesis of mercury in the Laurentian great lakes [J]. Journal of Great Lakes Research, 1995, 21(4): 574-586.
[30] CHADWICK S P, BABIARZ C L, HURLEY J P, et al. Influences of iron, manganese, and dissolved organic carbon on the hypolimnetic cycling of amended mercury [J]. Science of the Total Environment, 2006, 368(1): 177-188.
[31] HELLAL J, GUEDRON S, HUGUET L, et al. Mercury mobilization and speciation linked to bacterial iron oxide and sulfate reduction: A column study to mimic reactive transfer in an anoxic aquifer [J]. Journal of Contaminant Hydrology, 2015, 180: 56-68.
[32] KIM C S, RYTUBA J J, BROWN G E. EXAFS study of mercury(Ⅱ) sorption to Fe- and Al-(hydr)oxides I. Effects of pH [J]. Journal of Colloid and Interface Science, 2004, 271(1): 1-15.
[33] KIM C S, RYTUBA J, BROWN G E. EXAFS study of mercury(Ⅱ) sorption to Fe- and Al-(hydr)oxides II. Effects of chloride and sulfate

[J]. Journal of Colloid and Interface Science, 2004, 270(1): 9-20.

[34] JISKRA M, SAILE D, WIEDERHOLD J G, et al. Kinetics of Hg(Ⅱ) exchange between organic ligands, goethite, and natural organic matter studied with an enriched stable isotope approach [J]. Environmental Science & Technology, 2014, 48(22): 13207-13217.

[35] JISKRA M, WIEDERHOLD J G, BOURDON B, et al. Solution speciation controls mercury isotope fractionation of Hg(Ⅱ) sorption to goethite [J]. Environmental Science & Technology, 2012, 46(12): 6654-6662.

[36] GAGNON C, FISHER N S. Bioavailability of sediment-bound methyl and inorganic mercury to a marine bivalve [J]. Environmental Science & Technology, 1997, 31(4): 993-998.

[37] DESAUZIERS V, CASTRE N, LECLOIREC P. Sorption of methylmercury by clays and mineral oxides [J]. Environmental Technology, 1997, 18(10): 1009-1018.

[38] SUN Y, LV D, ZHOU J S, et al. Adsorption of mercury (Ⅱ) from aqueous solutions using FeS and pyrite: A comparative study [J]. Chemosphere, 2017, 185: 452-461.

[39] LIU J R, VALSARAJ K T, DEVAI I, et al. Immobilization of aqueous Hg(Ⅱ) by mackinawite (FeS) [J]. Journal of Hazardous Materials, 2008, 157(2-3): 432-440.

[40] SUN M Y, CHENG G H, GE X L, et al. Aqueous Hg(Ⅱ) immobilization by chitosan stabilized magnetic iron sulfide nanoparticles [J]. Science of the Total Environment, 2018, 621: 1074-1083.

[41] DUAN Y, HAN D S, BATCHELOR B, et al. Application of a reactive adsorbent-coated support system for removal of mercury(Ⅱ) [J]. Colloids and Surfaces A-Physicochemical and Engineering Aspects, 2016, 509: 623-630.

[42] GONG Y Y, LIU Y Y, XIONG Z, et al. Immobilization of mercury by carboxymethyl cellulose stabilized iron sulfide nanoparticles: Reaction mechanisms and effects of stabilizer and water chemistry [J]. Environmental Science & Technology, 2014, 48(7): 3986-3994.

[43] BOWER J, SAVAGE K S, WEINMAN B, et al. Immobilization of mercury by pyrite (FeS_2) [J]. Environmental Pollution, 2008, 156(2): 504-514.

[44] KINNIBURGH D G, JACKSON M L. Adsorption of mercury (Ⅱ) by iron hydrous oxide gel [J]. Soil Science Society of America Journal, 1978, 42(1): 45-47.

[45] BACKSTROM M, DARIO M, KARLSSON S, et al. Effects of a fulvic acid on the adsorption of mercury and cadmium on goethite [J]. Science of the Total Environment, 2003, 304(1-3): 257-268.

[46] SKYLLBERG U, DROTT A. Competition between disordered iron sulfide and natural organic matter associated thiols for mercury(Ⅱ)-an EXAFS study [J]. Environmental Science & Technology, 2010, 44(4): 1254-1259.

[47] KLUSMAN R W, MATOSKE C P. Adsorption of mercury by soils from oil-shale development areas in the Piceance creek basin of northwestern Colorado [J]. Environmental Science & Technology, 1983, 17(5): 251-256.

[48] NDU U, CHRISTENSEN G A, RIVERA N A, et al. Quantification of mercury bioavailability for methylation using diffusive gradient in thin-film samplers [J]. Environmental Science & Technology, 2018, 52(15): 8521-8529.

[49] LIU J R, VALSARAJ K T, DELAUNE R D. Inhibition of mercury methylation by iron sulfides in an anoxic sediment [J]. Environmental Engineering Science, 2009, 26(4): 833-840.

[50] JONSSON S, SKYLLBERG U, NILSSON M B, et al. Mercury methylation rates for geochemically relevant Hg-II species in sediments [J]. Environmental Science & Technology, 2012, 46(21): 11653-11659.

[51] HAN S, OBRAZTSOVA A, PRETTO P, et al. Sulfide and iron control on mercury speciation in anoxic estuarine sediment slurries [J]. Marine Chemistry, 2008, 111(3-4): 214-220.

[52] SVENSSON M, ALLARD B, DUKER A. Formation of HgS- mixing HgO or elemental Hg with S, FeS or FeS_2 [J]. Science of the Total Environment, 2006, 368(1): 418-423.

[53] JEONG H Y, SUN K, HAYES K F. Microscopic and spectroscopic characterization of Hg(Ⅱ) immobilization by mackinawite (FeS) [J]. Environmental Science & Technology, 2010, 44(19): 7476-7483.

[54] BONE S E, BARGAR J R, SPOSITO G. Mackinawite (FeS) reduces mercury(Ⅱ) under sulfidic conditions [J]. Environmental Science & Technology, 2014, 48(18): 10681-10689.

[55] JEONG H Y, KLAUE B, BLUM J D, et al. Sorption of mercuric ion by synthetic nanocrystalline mackinawite (FeS) [J]. Environmental Science & Technology, 2007, 41(22): 7699-7705.

[56] ZHANG H, LINDBERG S E. Sunlight and iron(Ⅲ)-induced photochemical production of dissolved gaseous mercury in freshwater [J]. Environmental Science & Technology, 2001, 35(5): 928-935.

[57] ABABNEH F A, SCOTT S L, AL-REASI H A, et al. Photochemical reduction and reoxidation of aqueous mercuric chloride in the presence of ferrioxalate and air [J]. Science of the Total Environment, 2006, 367(2-3): 831-839.

[58] LIN C J, PEHKONEN S O. Aqueous free radical chemistry of mercury in the presence of iron oxides and ambient aerosol [J]. Atmospheric Environment, 1997, 31(24): 4125-4137.

[59] AIKOH H. Reduction of mercuric ion in vitro by superoxide anion [J]. Physiological Chemistry and Physics and Medical NMR, 2002, 34(2): 185-189.

[60] AMIRBAHMAN A, KENT D B, CURTIS G P, et al. Kinetics of homogeneous and surface-catalyzed mercury(Ⅱ) reduction by iron(Ⅱ)

[J]. Environmental Science & Technology, 2013, 47(13): 7204-7213.

[61] O'LOUGHLIN E J, KELLY S D, KEMNER K M, et al. Reduction of Ag-I, Au-III, Cu-II, and Hg-II by Fe-II/Fe-III hydroxysulfate green rust [J]. Chemosphere, 2003, 53(5): 437-446.

[62] CRESWELL J E, SHAFER M M, BABIARZ C L, et al. Biogeochemical controls on mercury methylation in the Allequash creek wetland [J]. Environmental Science and Pollution Research, 2017, 24(18): 15325-15339.

[63] WIATROWSKI H A, DAS S, KUKKADAPU R, et al. Reduction of Hg(Ⅱ) to Hg(0) by magnetite [J]. Geochimica et Cosmochimica Acta, 2009, 73(13): A1436-A1436.

[64] PASAKARNIS T S, BOYANOV M I, KEMNER K M, et al. Influence of chloride and Fe(Ⅱ) content on the reduction of Hg(Ⅱ) by magnetite [J]. Environmental Science & Technology, 2013, 47(13): 6987-6994.

[65] MISHRA B, O'LOUGHLIN E J, BOYANOV M I, et al. Binding of Hg-II to high-affinity sites on bacteria inhibits reduction to Hg-0 by mixed Fe-II/III phases [J]. Environmental Science & Technology, 2011, 45(22): 9597-9603.

[66] PARKS J M, JOHS A, PODAR M, et al. The genetic basis for bacterial mercury methylation [J]. Science, 2013, 339(6125): 1332-1335.

[67] COMPEAU G C, BARTHA R. Sulfate-reducing bacteria-principal methylators of mercury in anoxic estuarine sediment [J]. Applied and Environmental Microbiology, 1985, 50(2): 498-502.

[68] GILMOUR C C, ELIAS D A, KUCKEN A M, et al. Sulfate-reducing bacterium *Desulfovibrio desulfuricans* ND132 as a model for understanding bacterial mercury methylation [J]. Applied and Environmental Microbiology, 2011, 77(12): 3938-3951.

[69] GILMOUR C C, HENRY E A, MITCHELL R. Sulfate stimulation of mercury methylation in fresh-water sediments [J]. Environmental Science & Technology, 1992, 26(11): 2281-2287.

[70] FLEMING E J, MACK E E, GREEN P G, et al. Mercury methylation from unexpected sources: Molybdate-inhibited freshwater sediments and an iron-reducing bacterium [J]. Applied and Environmental Microbiology, 2006, 72(1): 457-464.

[71] KERIN E J, GILMOUR C C, RODEN E, et al. Mercury methylation by dissimilatory iron-reducing bacteria [J]. Applied and Environmental Microbiology, 2006, 72(12): 7919-7921.

[72] HAMELIN S, AMYOT M, BARKAY T, et al. Methanogens: Principal methylators of mercury in lake periphyton [J]. Environmental Science & Technology, 2011, 45(18): 7693-7700.

[73] YU R-Q, REINFELDER J R, HINES M E, et al. Mercury methylation by the methanogen *Methanospirillum hungatei* [J]. Applied and Environmental Microbiology, 2013, 79(20): 6325-6330.

[74] GILMOUR C C, PODAR M, BULLOCK A L, et al. Mercury methylation by novel microorganisms from new environments [J]. Environmental Science & Technology, 2013, 47(20): 11810-11820.

[75] LU X, LIU Y, JOHS A, et al. Anaerobic mercury methylation and demethylation by *Geobacter bemidjiensis* bem [J]. Environmental Science & Technology, 2016, 50(8): 4366-4373.

[76] 司友斌, 孙林, 王卉. *Shewanella oneidensis* MR-1 对针铁矿的还原与汞的生物甲基化 [J]. 环境科学, 2015, 36(6): 2252-2258.
SI Y, SUN L, WANG H. Effects of dissimilatory reduction of goethite on mercury methylation by *Shewanella oneidensis* MR-1 [J]. Environmental Science, 2015, 36(6): 2252-2258 (in Chinese).

[77] GUEDRON S, GRIMALDI M, GRIMALDI C, et al. Amazonian former gold mined soils as a source of methylmercury: Evidence from a small scale watershed in French Guiana [J]. Water Research, 2011, 45(8): 2659-2669.

[78] GABRIEL M C, KOLKA R, WICKMAN T, et al. Evaluating the spatial variation of total mercury in young-of-year yellow perch (*Perca flavescens*), surface water and upland soil for watershed-lake systems within the southern boreal shield [J]. Science of the Total Environment, 2009, 407(13): 4117-4126.

[79] ALPERS C N, FLECK J A, MARVIN-DIPASQUALE M, et al. Mercury cycling in agricultural and managed wetlands, Yolo Bypass, California: Spatial and seasonal variations in water quality [J]. Science of the Total Environment, 2014, 484: 276-287.

[80] ROTHENBERG S E, AMBROSE R F, JAY J A. Mercury cycling in surface water, pore water and sediments of Mugu lagoon, CA, USA [J]. Environmental Pollution, 2008, 154(1): 32-45.

[81] MITCHELL C P J, GILMOUR C C. Methylmercury production in a Chesapeake Bay salt marsh [J]. Journal of Geophysical Research-Biogeosciences, 2008, 113: G00C04.

[82] MARVIN-DIPASQUALE M, WINDHAM-MYERS L, AGEE J L, et al. Methylmercury production in sediment from agricultural and non-agricultural wetlands in the Yolo Bypass, California, USA [J]. Science of the Total Environment, 2014, 484: 288-299.

[83] CORREIA R R S, GUIMARAES J R D. Mercury methylation and sulfate reduction rates in mangrove sediments, Rio de Janeiro, Brazil: The role of different microorganism consortia [J]. Chemosphere, 2017, 167: 438-443.

[84] SI Y B, ZOU Y, LIU X H, et al. Mercury methylation coupled to iron reduction by dissimilatory iron-reducing bacteria [J]. Chemosphere, 2015, 122: 206-212.

[85] YU R Q, FLANDERS J R, MACK E E, et al. Contribution of coexisting sulfate and iron reducing bacteria to methylmercury production in freshwater river sediments [J]. Environmental Science & Technology, 2012, 46(5): 2684-2691.

[86] BRAVO A G, BOUCHET S, GUEDRON S, et al. High methylmercury production under ferruginous conditions in sediments impacted by

sewage treatment plant discharges [J]. Water Research, 2015, 80: 245-255.

[87] BAILEY L T, MITCHELL C P J, ENGSTROM D R, et al. Influence of porewater sulfide on methylmercury production and partitioning in sulfate-impacted lake sediments [J]. Science of the Total Environment, 2017, 580: 1197-1204.

[88] RYTUBA J J. Mercury mine drainage and processes that control its environmental impact [J]. Science of the Total Environment, 2000, 260 (1-3): 57-71.

[89] GANGULI P M, MASON R P, ABU-SABA K E, et al. Mercury speciation in drainage from the new Idria mercury mine, California [J]. Environmental Science & Technology, 2000, 34(22): 4773-4779.

[90] RAMALHOSA E, SEGADE S R, PEREIRA M E, et al. Monomethylmercury behaviour in sediments collected from a mercury-contaminated lagoon [J]. International Journal of Environmental Analytical Chemistry, 2011, 91(1): 49-61.

[91] MEHROTRA A S, HORNE A J, SEDLAK D L Reduction of net mercury methylation by iron in *Desulfobulbus propionicus* (1pr3) cultures: Implications for engineered wetlands [J]. Environmental Science & Technology, 2003, 37(13): 3018-3023.

[92] HAN S, OBRAZTSOVA A, PRETTO P, et al. Biogeochemical factors affecting mercury methylation in sediments of the Venice lagoon, Italy [J]. Environmental Toxicology and Chemistry, 2007, 26(4): 655-663.

[93] MEHROTRA A S, SEDLAK D L. Decrease in net mercury methylation rates following iron amendment to anoxic wetland sediment slurries [J]. Environmental Science & Technology, 2005, 39(8): 2564-2570.

[94] FEYTE S, GOBEIL C, TESSIER A, et al. Mercury dynamics in lake sediments [J]. Geochimica et Cosmochimica Acta, 2012, 82: 92-112.

[95] ULRICH P D, SEDLAK D L. Impact of iron amendment on net methylmercury export from tidal wetland microcosms [J]. Environmental Science & Technology, 2010, 44(19): 7659-7665.

[96] BRAVO A G, ZOPFI J, BUCK M, et al. *Geobacteraceae* are important members of mercury-methylating microbial communities of sediments impacted by waste water releases [J]. ISME Journal, 2018, 12(3): 802-812.

[97] ERICKSON P R, LIN V S. Research highlights: Elucidation of biogeochemical factors influencing methylmercury production [J]. Environmental Science-Processes & Impacts, 2015, 17(10): 1708-1711.

[98] SELLERS P, KELLY C A, RUDD J W M, et al. Photodegradation of methylmercury in lakes [J]. Nature, 1996, 380(6576): 694-697.

[99] HAN X X, LI Y B, LI D, et al. Role of free radicals/reactive oxygen species in MeHg photodegradation: Importance of utilizing appropriate scavengers [J]. Environmental Science & Technology, 2017, 51(7): 3784-3793.

[100] ZHANG T, HSU-KIM H. Photolytic degradation of methylmercury enhanced by binding to natural organic ligands [J]. Nature Geoscience, 2010, 3(7): 473-476.

[101] TAI C, LI Y B, YIN Y G, et al. Methylmercury photodegradation in surface water of the Florida Everglades: Importance of dissolved organic matter-methylmercury complexation [J]. Environmental Science & Technology, 2014, 48(13): 7333-7340.

[102] QIAN Y, YIN X, LIN H, et al. Why dissolved organic matter enhances photodegradation of methylmercury [J]. Environmental Science & Technology Letters, 2014, 1(10): 426-431.

[103] ZEPP R G, HOIGNE J, BADER H. Nitrate-induced photooxidation of trace organic-chemicals in water [J]. Environmental Science & Technology, 1987, 21(5): 443-450.

[104] GARDFELDT K, SOMMAR J, STROMBERG D, et al. Oxidation of atomic mercury by hydroxyl radicals and photoinduced decomposition of methylmercury in the aqueous phase [J]. Atmospheric Environment, 2001, 35(17): 3039-3047.

[105] CHEN J, PEHKONEN S O, LIN C J. Degradation of monomethylmercury chloride by hydroxyl radicals in simulated natural waters [J]. Water Research, 2003, 37(10): 2496-2504.

[106] SUDA I, TOTOKI S, TAKAHASHI H. Degradation of methyl and ethyl mercury into inorganic mercury by oxygen free radical-producing systems-involvement of hydroxyl radical [J]. Archives of Toxicology, 1991, 65(2): 129-134.

[107] FAUST B C, HOIGNE J. Photolysis of Fe(Ⅲ)-hydroxy complexes as sources of OH radicals in clouds, fog and rain [J]. Atmospheric Environment Part A-General Topics, 1990, 24(1): 79-89.

[108] HAMMERSCHMIDT C R, FITZGERALD W F. Iron-mediated photochemical decomposition of methylmercury in an Arctic Alaskan lake [J]. Environmental Science & Technology, 2010, 44(16): 6138-6143.

[109] HAMMERSCHMIDT C R, FITZGERALD W F. Photodecomposition of methylmercury in an Arctic Alaskan lake [J]. Environmental Science & Technology, 2006, 40(4): 1212-1216.

[110] KIM M K, ZOH K D. Effects of natural water constituents on the photo-decomposition of methylmercury and the role of hydroxyl radical [J]. Science of the Total Environment, 2013, 449: 95-101.

[111] PAN S H, FENG C C, LIN J L, et al. Occurrence and photodegradation of methylmercury in surface water of Wen-rui-tang river network, Wenzhou, China [J]. Environmental Science and Pollution Research, 2017, 24(12): 11289-11298.

[112] ZHANG D, YIN Y G, LI Y B, et al. Critical role of natural organic matter in photodegradation of methylmercury in water: Molecular weight and interactive effects with other environmental factors [J]. Science of the Total Environment, 2017, 578: 535-541.

[113] BLACK F J, POULIN B A, FLEGAL A R. Factors controlling the abiotic photo-degradation of monomethylmercury in surface waters [J]. Geochimica et Cosmochimica Acta, 2012, 84: 492-507.

[114] SUN R G, WANG D Y, MAO W, et al. Photodegradation of methylmercury in the water body of the Three Gorges Reservoir [J]. Science China-Chemistry, 2015, 58(6): 1073-1081.
[115] SUN R G, WANG D Y, MAO W, et al. Photodegradation of methylmercury in Jialing River of Chongqing, China [J]. Journal of Environmental Sciences, 2015, 32: 8-14.
[116] VIONE D, FALLETTI G, MAURINO V, et al. Sources and sinks of hydroxyl radicals upon irradiation of natural water samples [J]. Environmental Science & Technology, 2006, 40(12): 3775-3781.
[117] KRONBERG R M, SCHAEFER J K, BJORN E, et al. Mechanisms of methyl mercury net degradation in alder swamps: The role of methanogens and abiotic processes [J]. Environmental Science & Technology Letters, 2018, 5(4): 220-225.
[118] TONG M, YUAN S H, MA S C, et al. Production of abundant hydroxyl radicals from oxygenation of subsurface sediments [J]. Environmental Science & Technology, 2016, 50(1): 214-221.
[119] JIA M Q, BIAN X, YUAN S H. Production of hydroxyl radicals from Fe(Ⅱ) oxygenation induced by groundwater table fluctuations in a sand column [J]. Science of the Total Environment, 2017, 584: 41-47.
[120] YUAN S H, LIU X X, LIAO W J, et al. Mechanisms of electron transfer from structrual Fe(Ⅱ) in reduced nontronite to oxygen for production of hydroxyl radicals [J]. Geochimica et Cosmochimica Acta, 2018, 223: 422-436.
[121] LIU X X, YUAN S H, TONG M, et al. Oxidation of trichloroethylene by the hydroxyl radicals produced from oxygenation of reduced nontronite [J]. Water Research, 2017, 113: 72-79.
[122] ZHANG P, YUAN S H. Production of hydroxyl radicals from abiotic oxidation of pyrite by oxygen under circumneutral conditions in the presence of low-molecular-weight organic acids [J]. Geochimica et Cosmochimica Acta, 2017, 218: 153-166.
[123] ZHANG P, YUAN S H, LIAO P. Mechanisms of hydroxyl radical production from abiotic oxidation of pyrite under acidic conditions [J]. Geochimica et Cosmochimica Acta, 2016, 172: 444-457.
[124] CHENG D, YUAN S H, LIAO P, et al. Oxidizing impact induced by mackinawite (FeS) nanoparticles at oxic conditions due to production of hydroxyl radicals [J]. Environmental Science & Technology, 2016, 50(21): 11646-11653.
[125] MASON R P, FITZGERALD W F. Alkylmercury species in the equatorial Pacific [J]. Nature, 1990, 347(6292): 457-459.
[126] BAYA P A, GOSSELIN M, LEHNHERR I, et al. Determination of monomethylmercury and dimethylmercury in the Arctic marine boundary layer [J]. Environmental Science & Technology, 2015, 49(1): 223-232.
[127] CONAWAY C H, BLACK F J, GAULT-RINGOLD M, et al. Dimethylmercury in coastal upwelling waters, Monterey Bay, California [J]. Environmental Science & Technology, 2009, 43(5): 1305-1309.
[128] WALLSCHLAGER D, HINTELMANN H, EVANS R D, et al. Volatilization of dimethylmercury and elemental mercury from river Elbe floodplain soils [J]. Water Air and Soil Pollution, 1995, 80(1-4): 1325-1329.
[129] LINDBERG S E, SOUTHWORTH G, PRESTBO E M, et al. Gaseous methyl- and inorganic mercury in landfill gas from landfills in Florida, Minnesota, Delaware, and California [J]. Atmospheric Environment, 2005, 39(2): 249-258.
[130] FENG X B, TANG S L, LI Z G, et al. Landfill is an important atmospheric mercury emission source [J]. Chinese Science Bulletin, 2004, 49(19): 2068-2072.
[131] EARLE C D A, RHUE R D, CHYNOWETH D P. Partitioning of mercury among solid, liquid and gas phases following anaerobic decomposition of a simulated solid waste [J]. Water Air and Soil Pollution, 2000, 121(1-4): 189-203.
[132] COSSA D, MARTIN J M, SANJUAN J. Dimethylmercury formation in the Alboran Sea [J]. Marine Pollution Bulletin, 1994, 28(6): 381-384.
[133] FILIPPELLI M, BALDI F. Alkylation of ionic mercury to methylmercury and dimethylmercury by methylcobalamin-simultaneous determination by purge-and-trap GC in-line with FTIR [J]. Applied Organometallic Chemistry, 1993, 7(7): 487-493.
[134] PERROT V, JIMENEZ-MORENO M, BERAIL S, et al. Successive methylation and demethylation of methylated mercury species (MeHg and DMeHg) induce mass dependent fractionation of mercury isotopes [J]. Chemical Geology, 2013, 355: 153-162.
[135] 孙婷, 王章玮, 陈剑, 等. 气态二甲基汞的发生系统与产生速率 [J]. 环境化学, 2016, 35(9): 1792-1798.
SUN T, WANG Z W, CHEN J, et al. Efficient and stable gaseous dimethymercury generation system and generation rate [J]. Environmental Chemistry, 2016, 35(9): 1792-1798 (in Chinese).
[136] BALDI F, PARATI F, FILIPPELLI M. Dimethylmercury and dimethylmercury-sulfide of microbial origin in the biogeochemical cycle of Hg [J]. Water Air and Soil Pollution, 1995, 80(1-4): 805-815.
[137] BALDI F, PEPI M, FILIPPELLI M. Methylmercury resistance in *Desulfovibrio-desulfuricans* strains in relation to methylmercury degradation [J]. Applied Environmental Microbiology, 1993, 59: 2479-2485.
[138] JONSSON S, MAZRUI N M, MASON R P. Dimethylmercury formation mediated by inorganic and organic reduced sulfur surfaces [J]. Scientific Reports, 2016, 6: 27958.
[139] MENG B, FENG X, QIU G, et al. Distribution patterns of inorganic mercury and methylmercury in tissues of rice (*Oryza sativa L.*) plants and possible bioaccumulation pathways [J]. Journal of Agricultural and Food Chemistry, 2010, 58(8): 4951-4958.
[140] MENG B, FENG X, QIU G, et al. Localization and speciation of mercury in brown rice with implications for pan-Asian public health [J]. Environmental Science & Technology, 2014, 48(14): 7974-7981.

[141] ZHANG H, FENG X, LARSSEN T, et al. In inland China, rice, rather than fish, is the major pathway for methylmercury exposure [J]. Environmental Health Perspectives, 2010, 118(9): 1183-1188.

[142] 李云云, 赵甲亭, 高愈希, 等. 根表铁膜的形成和添加硒对水稻吸收转运无机汞和甲基汞的影响 [J]. 生态毒理学报, 2014, 9(5), 972-977.
LI Y Y, ZHAO J T, GAO Y X, et al. Effects of iron plaque and selenium on the absorption and translocation of inorganic mercury and methylmercury in rice (*Oryza sativa L.*) [J]. Asian Journal of Ecotoxicology, 2014, 9(5): 972-977 (in Chinese).

[143] LI Y, ZHAO J, ZHANG B, et al. The influence of iron plaque on the absorption, translocation and transformation of mercury in rice (*Oryza sativa L.*) seedlings exposed to different mercury species [J]. Plant and Soil, 2016, 398(1-2): 87-97.

[144] WANG X, LI B, TAM N F Y, et al. Radial oxygen loss has different effects on the accumulation of total mercury and methylmercury in rice [J]. Plant and Soil, 2014, 385(1-2): 343-355.

[145] WANG X, TAM N F-Y, HE H, et al. The role of root anatomy, organic acids and iron plaque on mercury accumulation in rice [J]. Plant and Soil, 2015, 394(1-2): 301-313.

[146] 黄天元, 邓泓. 汞胁迫下氮磷减施及铁膜形成对水稻幼苗根系生长的影响 [J]. 生态学杂志, 2016, 35(9): 2417-2421.
HUANG T Y, DENG H. Effects of reduced nitrogen and phosphorus applications and iron plaque formation on root growth of rice seedlings under mercury stress [J]. Chinese Journal of Ecology, 2016, 35(9): 2417-2421 (in Chinese).

[147] ZHANG H, FENG X, ZHU J, et al. Selenium in soil inhibits mercury uptake and trans location in rice (*Oryza sativa L.*) [J]. Environmental Science & Technology, 2012, 46(18): 10040-10046.

[148] 高阿祥, 周鑫斌, 张城铭. 硒(Ⅳ)预处理下根表铁膜对水稻幼苗吸收和转运汞的影响 [J]. 土壤学报, 2017, 54(4): 989-998.
GAO A X, ZHOU X B, ZHANG C M. Effect of iron plaque on root on uptake and translocation of mercury in rice seedlings treated with selenium(Ⅳ) [J]. Acta Pedologica Sinica, 2017, 54(4): 989-998 (in Chinese).

[149] 周鑫斌, 于淑慧, 王文华, 等. 土壤施硒对水稻根表铁膜形成和汞吸收的影响 [J]. 西南大学学报, 2014, 36(1): 91-95.
ZHOU X B, YU S H, WANG W H, et al. Effects of application of selenium in soil on the formation of root surface iron plaque and mercury uptake by rice plants [J]. Journal of Southwest University, 2014, 36(1): 91-95 (in Chinese).

[150] LI Y Y, ZHAO J T, GUO J X, et al. Influence of sulfur on the accumulation of mercury in rice plant (*Oryza sativa L.*) growing in mercury contaminated soils [J]. Chemosphere, 2017, 182: 293-300.

[151] GAO A X, ZHOU X B, ZHANG C M, et al. Effects of phosphorus on uptake and translocation of methylmercury in rice [J]. Toxicological and Environmental Chemistry, 2018, 100(1): 68-79.