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厌氧条件水稻土铁对砷释放的影响

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摘要: 水稻土无定型铁矿物是砷的重要吸附载体, 水稻种植需要经历的淹水厌氧阶段能促进铁矿物还原溶解并使其吸附的砷释放进入水稻土溶液。本研究重点考察了厌氧环境中水稻土在培养液的富集培养下不同形态砷对砷释放的贡献作用, 并探究淹水缺氧环境下水稻土无定型铁矿物对砷迁移转化的影响。结果表明, 相比于第一阶段, 第二阶段培养液中 Fe(II) 和总砷浓度均显著提高 ($P < 0.05$), 其中两个阶段的土壤溶液均主要来源于可交换态砷 (F1) 和专属吸附态砷 (F2), 且两个阶段的培养液砷与 F1 + F2 均呈显著正相关关系, 分别为 $r = 0.73$, $P < 0.05$ 和 $r = 0.657$, $P < 0.05$, 无定型铁结合态砷 (F3) 与砷浓度呈不显著正相关。两阶段的水稻土不同形态铁与培养液砷浓度均存在一定关系, 水稻土盐酸提取 Fe(II) 浓度与砷浓度呈显著正相关 ($r = 0.577$, $P < 0.05$; $r = 0.613$, $P < 0.05$), 无定型铁矿物与砷存在负相关关系 ($r = -0.428$, $P = 0.126$; $r = -0.564$, $P < 0.05$)。因此, 厌氧环境下水稻土中处于亚稳态的无定型铁矿物在总体上能有效地吸持固定砷从而抑制砷的移动和迁移。

关键词: 水稻土; 淹水缺氧; 土壤微环境; 砷; 铁

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Effect of Iron on the Release of Arsenic in Flooded Paddy Soils

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Abstract: Amorphous iron oxides in paddy soil are critical adsorbents of arsenic. The flooding period during rice cultivation contributes to the reductive dissolution of these amorphous iron oxides, which releases sorbed arsenic into the paddy soil solution. However, more detailed work should be conducted to evaluate quantitatively arsenic immobilization, release, and transformation regulated by metastable amorphous iron oxides. In previous studies, arsenic in the soil solution phase and solid phase were classified into F1 (exchangeable arsenic), F2 (specifically sorbed arsenic), F3 (amorphous iron oxide bound arsenic), and F4 (crystalline iron oxide bound arsenic), according to a sequential extraction procedure using reagents of increasing dissolution strength. In this study, soil samples were collected from the vicinity of a silver smelting plant in Chenzhou, Hunan Province, and the contribution of different arsenic speciation (F1, F2, F3, and F4) to arsenic release during anaerobic enrichment incubation of paddy soil was investigated. Sample analysis was conducted at the end of the first phase (day 15) and the second phase (day 30). The effects of amorphous iron oxides in paddy soil on migration and transformation of arsenic were discussed. Results showed significant elevation of dissolved Fe(II) and arsenic concentration ($P < 0.05$) in enrichment solutions in the second phase compared with that in the first phase. Arsenic released in the soil solution in both phases originated from exchangeable arsenic and specifically sorbed arsenic, as indicated by its significantly positive correlation with F1 and F2 ($r = 0.73$, $P < 0.05$; $r = 0.657$, $P < 0.05$). However, an insignificant positive correlation was found between the arsenic released and F3. Moreover, HCl-extractable Fe(II) was significantly and positively correlated with arsenic ($r = 0.577$, $P < 0.05$; $r = 0.613$, $P < 0.05$), while amorphous iron oxides were significantly and negatively correlated with arsenic ($r = -0.428$, $P = 0.126$; $r = -0.564$, $P < 0.05$). In conclusion, arsenic in the F1 and F2 fractions acted as the major source of released arsenic. Despite elevated levels of HCl-extractable Fe(II) that might result from the slight reductive dissolution of amorphous iron oxide, the significant negative correlation between dissolved arsenic and amorphous iron oxides indicated that metastable amorphous iron oxides in anaerobic paddy soil can generally sorb dissolved arsenic effectively, resulting in lower mobility of arsenic. Increasing the level of amorphous iron oxides in paddy soil is conducive to inactivation of arsenic.

Key words: paddy soil; flooded and anaerobic; soil micro-environment; arsenic; iron

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矿山开采、金属冶炼、施肥和农药等是导致农田砷污染的主要原因^[1]。湖南石门雄黄矿区和湖南株洲冶炼厂周边农田土壤平均砷含量分别达到 $79.0 \text{ mg} \cdot \text{kg}^{-1}$ ($n=39$) 和 $36.8 \text{ mg} \cdot \text{kg}^{-1}$ ($n=34$)，均超过《土壤环境质量标准》(GB 15618-1995) III 级标准^[1,2]。水稻是东南亚重要的粮食作物，也是我国主要粮食作物，据研究报道，我国水稻面积占全世界水稻面积的 23%^[3]。我国热带亚热带红壤区是水稻的主产区，涉及 14 个省区 203 万 km^2 ，占全国土地总面积 21%^[4]。有研究表明，中国人均砷摄入量达到 $42 \text{ } \mu\text{g} \cdot \text{d}^{-1}$ ，其中大米的砷占总砷日摄入量的 60%^[5]。砷可导致肺损伤、外周神经损伤、皮肤病或心血管病等疾病，其中无机砷(III)毒性最大，因而无机砷被国际癌症研究机构归类为第一类致癌物。因此稻田土壤砷污染使得以稻米为主食的居民健康受到严重威胁^[6,7]。

据研究表明，淹水管理过程是导致水稻对砷吸收量增加的关键环节^[8]；相反，间歇式淹水管理则能有效地降低水稻土砷的释放^[9]，这与水稻土铁的氧化还原密切相关^[10]。水稻土铁矿物是砷的贮存器并主要以无定型铁矿物结合态砷和结晶型铁结合态砷形态存在^[10-12]。同样，水稻根表铁膜(水铁矿和针铁矿为主)可作为水稻土孔隙水与水稻之间的屏障，抑制或降低土壤溶液砷进入根部^[13]。此外，淹水缺氧条件下砷污染水稻土在外源添加不同铁矿物(水铁矿、针铁矿和赤铁矿)时，均可促进水稻土可交换态和专属吸附态砷向无定型铁和结晶型铁结合态砷转化^[11]。相反，大量研究报道淹水厌氧环境驱动下水稻土铁矿物的还原溶解是引起砷释放的主要原因^[14]。水稻土无定型铁氧化物与砷的关系即存在两种关系，一方面无定型铁氧化物可充当砷的储存器^[15]，另一方面可能是砷释放最主要的源头^[16]。这与水稻土无定型铁在淹水缺氧条件下处于亚稳状态以及水稻土颗粒物微界面环境密切相关，因而铁的成矿或者还原溶解直接影响砷的环境化学行为^[10, 17, 18]。其中，淹水缺氧条件是考察水稻土无定型铁氧化物稳定性，放大微生物作用下水稻土颗粒物界面微环境改变以及驱动铁砷环境化学行为和归趋的重要控制因素。

为此，本文采用砷污染水稻土于富集培养液中厌氧条件下富集培养，探讨淹水缺氧条件微生物驱动作用下水稻土不同形态砷与培养液砷浓度以及水稻土无定型铁矿物与培养液砷浓度之间的关系，以期水稻土砷污染防治提供科学依据和理论指导。

1 材料与方法

1.1 供试土壤

供试水稻土采自湖南郴州市炼银厂周边砷污染农田，经自然风干，研磨过 100 目筛后冷藏备用，具体采样点分布图见图 1，采样点经纬度，各采集的水稻土理化性质和不同砷形态见表 1。

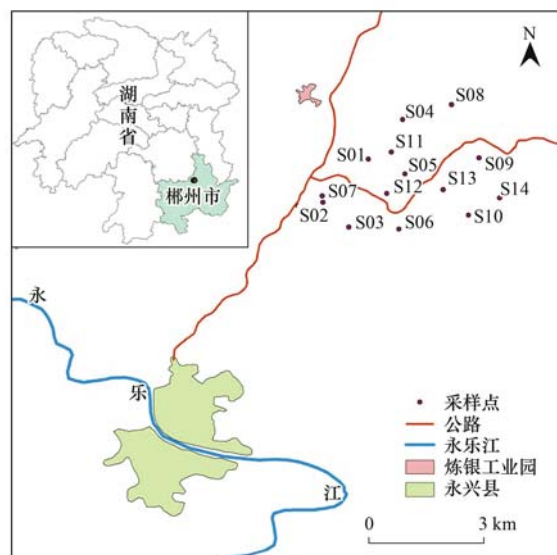


图 1 研究区域和采样地点示意

Fig. 1 Map of the study area and sampling sites

1.2 富集培养

水稻土采用灭菌处理的富集培养液[固(g):液(mL)比=1:5,下同]富集培养,经 100% 高纯氮气排氧 25 min 后,用橡胶塞压紧瓶子,立即用压铝盖密封,然后将样品置于厌氧手套箱(25 ± 2) $^{\circ}\text{C}$ (混合气成分:氮气 85%,二氧化碳 10% 和氢气 5%)中进行避光培养 1 个月。富集培养液主要成分为:10 $\text{mmol} \cdot \text{L}^{-1}$ PIPES (pH=7.0)的生物缓冲溶液,含有 10 $\text{mmol} \cdot \text{L}^{-1}$ NH_4Cl 、1.0 $\text{mmol} \cdot \text{L}^{-1}$ KH_2PO_4 、1.0 $\text{mmol} \cdot \text{L}^{-1}$ $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ 、1.0 $\text{mmol} \cdot \text{L}^{-1}$ $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ 、30 $\text{mmol} \cdot \text{L}^{-1}$ NaHCO_3 , 1 mL 微量矿物元素以及 1 mL 维他命,主要目的是富集培养微生物,以便促进水稻土铁砷还原^[19]。富集培养 1 个月,第一阶段采样时间为第 15 d,第二阶段为第 30 d。

1.3 分析方法

土壤砷的形态提取采用改进的 Wenzel 提取法^[20, 21],具体提取步骤为:可交换态砷(F1)采用 0.05 $\text{mol} \cdot \text{L}^{-1}$ $(\text{NH}_4)_2\text{SO}_4$ 溶液(土壤与提取液比为 1:30)室温下振荡 2 h,提取两次;专属吸附态砷(F2)采用土壤与提取液(0.05 $\text{mol} \cdot \text{L}^{-1}$ $\text{NH}_4\text{H}_2\text{PO}_4$)比为 1:25 (g:mL)于室温下振荡 12 h;无定型铁结

表 1 各农田土壤采样点以及对应的不同形态砷浓度和理化性质¹⁾

Table 1 Concentration of different arsenic species and physicochemical properties of paddy soil sampling sites

采样点	经纬度	采样个数	F1 /mg·kg ⁻¹	F2 /mg·kg ⁻¹	F3 /mg·kg ⁻¹	F4 /mg·kg ⁻¹	总砷 /mg·kg ⁻¹	总铁 /g·kg ⁻¹	pH	CEC /cmol·kg ⁻¹	有效 Si /mg·kg ⁻¹	有效 P /mg·kg ⁻¹	SOM /%
S01	N26°11'34.80", E113°09'11.84"	1	0.873	1.05	16.16	15.02	77.91	10.43	6.26	4.77	379.29	3.99	1.20
S02	N26°10'58.05", E113°08'33.37"	1	0.848	2.87	52.23	25.78	119.37	10.18	5.99	5.10	355.57	2.24	6.92
S03	N26°10'37.25", E113°08'55.24"	1	0.948	4.22	23.19	24.13	139.32	11.28	6.25	5.20	413.54	2.71	8.43
S04	N26°12'08.43", E113°09'40.83"	1	0.346	2.33	56.28	21.78	156.12	11.59	6.87	28.90	352.94	11.04	7.41
S05	N26°11'22.17", E113°09'42.89"	1	1.422	6.16	53.79	20.19	131.27	12.13	6.70	9.89	675.74	5.67	5.82
S06	N26°10'35.46", E113°09'37.73"	1	1.062	3.84	30.15	44.14	186.51	10.76	5.66	7.46	323.95	4.03	2.89
S07	N26°11'03.65", E113°08'32.78"	1	0.609	5.59	26.89	14.22	69.53	9.32	5.37	5.53	204.05	2.70	2.51
S08	N26°12'20.97", E113°10'22.22"	1	0.744	5.59	27.84	15.80	88.46	10.12	4.61	4.77	48.05	2.07	1.51
S09	N26°11'35.82", E113°10'45.42"	1	1.591	6.03	31.26	17.54	106.42	9.66	4.30	4.84	57.77	2.29	3.34
S10	N26°10'47.23", E113°10'36.64"	1	0.549	1.11	17.90	14.57	72.63	12.37	4.33	3.31	48.71	1.91	0.33
S11	N26°11'40.75", E113°09'31.31"	1	1.502	4.88	30.85	10.28	87.58	9.52	3.99	3.84	53.32	3.28	2.78
S12	N26°11'05.60", E113°09'27.43"	1	0.411	1.51	16.86	17.01	67.47	13.29	5.23	4.89	117.06	2.20	3.01
S13	N26°11'08.92", E113°10'15.15"	1	0.552	1.36	15.52	11.37	54.39	14.12	5.30	1.54	68.64	2.44	7.48
S14	N26°11'01.95", E113°11'02.94"	1	0.369	0.92	12.81	15.41	40.47	12.18	4.67	1.43	52.17	2.05	4.72

1) F1 是土壤可交换态砷, F2 为土壤专属吸附态砷, F3 是无定型铁结合态砷, F4 是结晶型铁结合态砷; 土壤 pH 值利用 0.01 mol·L⁻¹ CaCl₂ 溶液(土:液=1:2.5)提取; 阳离子交换量(CEC): 采用 BaCl₂ 置换法; 土壤有机质采用重铬酸钾外加热法; 总铁利用连二亚硫酸钠-柠檬酸钠-重碳酸钠联合提取

合态(F3) 利用 0.2 mol·L⁻¹ (NH₄)₂C₂O₄/H₂C₂O₄ (pH=3.0) 固液比为 1:25 于室温避光条件下振荡 4 h; 结晶型铁结合态(F4) 的提取利用 0.2 mol·L⁻¹ (NH₄)₂C₂O₄/H₂C₂O₄ 和 0.1 mol·L⁻¹ C₆H₈O₆ 混合液(pH=3.0), 在见光水浴 30 min, 温度为 96℃ 条件下提取. 其中, 每种砷形态提取后均采用 0.05 mol·L⁻¹ NaCl 溶液冲洗, 以避免每步提取过后残余砷. 各形态提取中, 提取液在 3 000 r·min⁻¹ 离心分离 15 min, 且上层液利用 0.45 μm 滤膜过滤以便砷浓度分析. 砷浓度测定利用 2% 硼氢化钾和 0.5% 氢氧化钾作为还原剂以及浓盐酸为载液, 且添加 5% 硫脲和 5% 抗坏血酸将提取砷(V) 还原, 并采用原子荧光(AFS-52) 进行测定.

土壤无定型铁采用 2.0 mol·L⁻¹ (NH₄)₂C₂O₄ 溶液(pH=3.0±0.02) 以土壤与提取液比为 1:50 在 20℃ 下避光振荡 2 h^[22]; 盐酸提取态铁(Ⅱ) 的分析采用 5 mmol·L⁻¹ HCl 提取, 将离心分离过滤后的提取液放入 HEPES 缓冲液以防止氧化^[12]. 每次提取后, 将泥浆混合液在 3 000 r·min⁻¹ 离心速度离心分离 15 min, 随即将上层液用 0.22 μm 滤膜过滤; 其中, 经过滤的上层液用于铁(Ⅱ) 的测定, 其方法参照菲洛嗟法^[12], 并采用紫外分光光度计(UV-1800, 岛津) 分析测定.

1.4 数据分析

本研究采用 SPSS19.0 统计分析软件分析进行单因素方差分析实验, 当 $P < 0.05$ 时, 为显著, 否则为不显著.

2 结果与分析

2.1 培养液中铁砷浓度

由图 2 可知, 水稻土经富集培养后, 土壤砷不断释放, 第二阶段各土壤溶液中总砷浓度相比于第一阶段均显著提高($P < 0.05$), 其中 S03、S04、S05、S08、S09、S10 和 S11 增幅最大, 分别提高 1.34、1.36、0.96、1.08、1.42、1.10 和 1.74 mg·L⁻¹; 同样, Fe²⁺ 出现与砷一致的变化现象, Fe²⁺ 浓度均显著提高($P < 0.05$), 且增幅相比于砷的变化均较大. 说明厌氧条件下有利于水稻土铁矿物的还原溶解和砷的释放, 这可能与先前大量研究表明淹水缺氧条件下水稻土界面微环境中存在铁矿物还原溶解驱动砷的释放的结果相一致^[19]. 同样, 这与进一步的研究证实厌氧淹水管理是导致水稻土砷释放和相继地水稻砷吸收累积的关键环节相符^[23].

2.2 水稻土不同形态砷对砷释放的贡献

由图 3 可知, F1 + F2 均与两个阶段土壤培养液中砷的浓度呈显著正相关关系, 第一阶段和第二阶段相关系数分别为 $r = 0.736$, $P < 0.05$ 和 $r = 0.630$, $P < 0.05$. 表明水稻土砷的释放主要来源于土壤可交换态砷(F1) 和专属吸附态砷(F2), 前者最不稳定, 后者在 PO₄³⁻ 的作用下与专属吸附态砷产生竞争吸附作用而促进砷的释放, 这与 PO₄³⁻ 与砷酸盐的性质有关, 可与砷酸盐竞争铁矿物等吸附

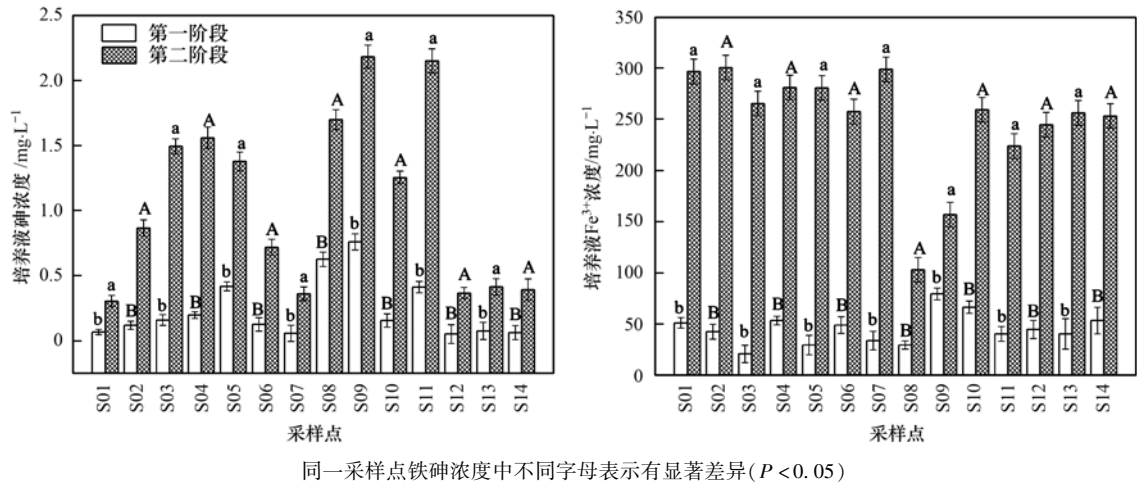


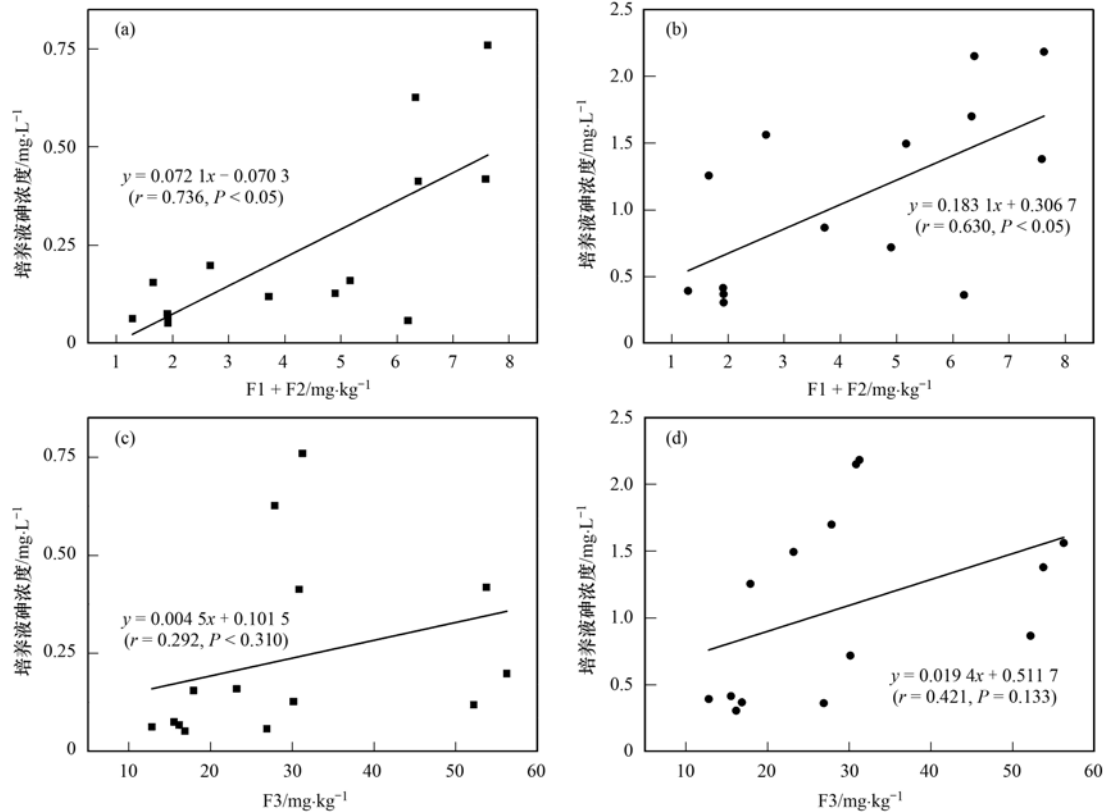
Fig. 2 Iron and arsenic concentration in enrichment solution of soil samples

载体的吸附点位. 在本研究中富集培养液存在 PO_4^{3-} , 一定程度上有利于水稻土砷的释放. 这与先前大量研究报道水稻土颗粒物微界面砷在 P 的交互作用下可以促进砷释放的研究报道相似^[24]. 而 F3 均与两个阶段的培养中砷不存在显著相关性, 但是相关系数 r 从 0.292 增长至 0.421, 相应地 P 也从 0.310 降低至 0.133, 说明水稻土无定型铁结

合态砷处于亚稳状态, 初始阶段无定型铁不易被还原而引起砷的释放, 后期则可能在微生物的驱动下发生铁矿物还原溶解而引起砷释放. 这也说明土壤可交换态砷和专属吸附态砷对土壤砷释放的贡献最大.

2.3 不同类型铁对砷释放的影响

由图 4 可知, 土壤盐酸提取态铁(Ⅱ)与土壤培



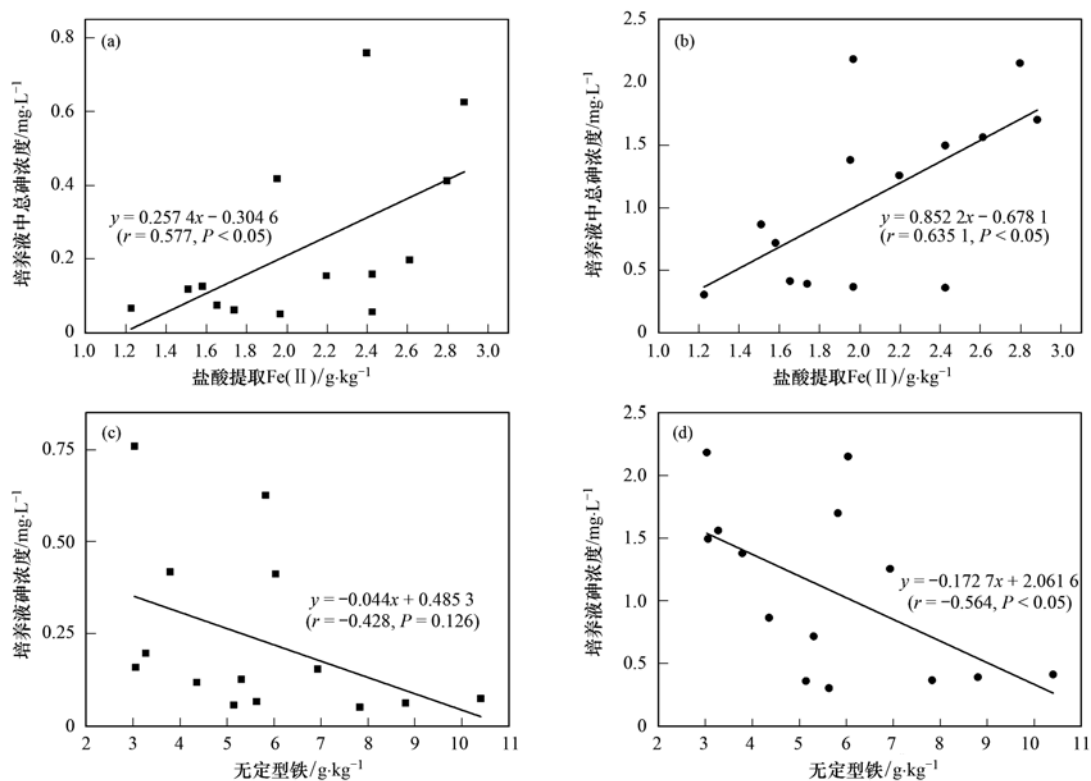
(a) 和 (c) 为第一阶段; (b) 和 (d) 为第二阶段

图 3 水稻土砷形态与土壤砷释放的相关性分析

Fig. 3 Correlation analysis of paddy soil arsenic species and soil arsenic release

培养液中总砷均存在显著正相关性, 相关系数分别为 $r = 0.577$ ($P < 0.05$) 和 $r = 0.635$ ($P < 0.05$), 表明盐酸提取态铁(II)与土壤砷存在耦合释放的现象。目前, 有研究证实盐酸提取态铁(II)占土壤无定型铁的5%, 且为无定型铁最为活跃的部分, 容易在淹水缺氧条件下释放^[25]。相反, 由图4(c)和4(d)可知, 土壤无定型铁与培养液砷存在负相关关系,

分别为 $r = -0.428$ ($P = 0.126$) 和 $r = -0.564$ ($P < 0.05$), 说明无定型铁在淹水缺氧条件下对砷具有截留贮存作用。这与 Hu 等^[13]研究报道水稻土无定型铁对砷具有截留和屏障作用的结果相一致。同样, 这也表明盐酸提取铁(II)与无定型铁二者性质的差异性, 主要集中表现在对水稻土砷的环境化学行为的影响。



(a) 和 (c) 为第一阶段; (b) 和 (d) 为第二阶段

图4 土壤不同形态铁与土壤砷释放的相关性分析

Fig. 4 Correlation analysis of different iron species and soil arsenic release

3 讨论

长期食用砷污染大米会给人类带来一系列健康问题, 如癌症、皮肤损害、神经障碍等^[26]。深入研究砷在水稻土铁氧化物微界面的环境化学行为对治理和缓解水稻土砷污染以至降低人类健康风险具有重要意义。水稻土中铁矿物是砷的主要吸附载体, 对砷的环境化学行为和归趋有重要影响。水稻种植经历的淹水厌氧阶段有助于铁还原微生物还原铁矿物, 从而导致吸持在铁矿物表面的砷释放到水稻土溶液中, 增大水稻土砷对水稻的可给性, 这是导致水稻对水稻土砷大量吸收累积的关键环节。

水稻土富集培养过程, 第二阶段各水稻土溶液中的砷浓度与 Fe^{2+} 浓度均远大于第一阶段时的浓度, 这与先前的研究中表明淹水缺氧条件是驱动水

稻土颗粒物界面微环境中砷不断释放, 提高厌氧水稻土溶液中的砷浓度的现象相符合^[18]。且与进一步研究证实水稻土长期厌氧处理的模式是导致水稻大量累积砷的关键因素相一致^[27]。相似地, Zecchin 等^[28]指出长期持续淹水是驱动水稻土中 *Geobacteraceae* 族铁还原菌属丰度显著提高的关键条件, 且砷(V)持续从铁矿物中释放。本研究中, (F1 + F2) 与两种水稻土培养液中砷的浓度均呈显著相关性 ($r = 0.730$, $P < 0.05$ 和 $r = 0.657$, $P < 0.05$), 这与 Liu 等^[12]的研究表明水稻土在 F1 与 F2 都与大米谷粒砷含量呈显著正相关 ($P < 0.001$) 相似。F3 与水稻土溶液中砷的浓度不呈显著相关性 ($r = 0.292$, $P = 0.310$; $r = 0.421$, $P = 0.133$), 这表明无定型铁处于亚稳状态, 初始阶段水稻土砷释放主要来源于有效态和专属吸附态砷的释放, 而

后一阶段则可能潜在无定形铁结合态砷释放的现象。同样地, Somenahally 等^[29]采用间歇式淹水处理水稻, 发现根际土孔隙水总砷浓度约比厌氧淹水处理时降低了 86%, 且在厌氧淹水处理的水稻土具有更高丰度的地杆菌、希瓦氏菌和厌氧黏细菌等异化铁还原菌。Wang 等^[30]则指出水稻土中 *Geobacter*、*Anaeromyxobacter*、*Desulfosporosinus* 和 *Pedobacter* 等铁还原菌丰度的上升与铁(Ⅱ)和砷释放量的增加紧密相关。Das 等^[31]进一步研究证实不同水管理模式中, 水稻土铁还原菌的丰度依次为: 淹水厌氧处理 > 干湿交替处理 > 不淹水处理(落干处理), 同时水稻土孔隙水总砷浓度的大小与水稻土铁还原菌丰度呈一致性, 依次为淹水处理 > 干湿交替处理 > 不淹水处理。相似地, Bennett 等^[32]指出淹水厌氧水稻土溶液中铁(Ⅱ)和 As(Ⅲ)的浓度呈极显著正相关, 而 As(Ⅲ)是厌氧水稻土中砷的主要形态; 本研究与之前的研究相似, 水稻土溶液中砷浓度与铁(Ⅱ)浓度同样呈显著相关性($r = 0.577$, $P < 0.05$; $r = 0.613$, $P < 0.05$)。Wang 等^[30]和 Chen 等^[33]一步指出生物炭可作为电子穿梭体促进水稻土铁砷耦合还原而提高砷释放量与铁(Ⅱ)浓度。Honma 等^[34]进一步指出厌氧水稻土溶液中溶解态铁(Ⅱ)与水稻土溶液中总溶解性砷浓度存在二次函数关系, 其关系式为 $[As] = -0.0024 [Fe(Ⅱ)]^2 + 0.3125 [Fe(Ⅱ)] + 3.5886$, 这说明了随着土壤溶液铁(Ⅱ)浓度提高, 土壤砷的释放量增大, 都进一步证实了土壤溶液砷浓度的不断提高可能和铁氧化物的还原溶解有关。基于本研究过程, 不能持续提供营养物质足以支持铁砷还原微生物的长期活动, 因而可能存在铁砷还原现象停滞的现象, 这也说明持续淹水厌氧过程才是主要驱动水稻土砷释放的关键因素。同样, 尽管移动性较小的 As(V)在铁矿物表面被微生物直接还原为移动性更强的 As(Ⅲ)而进入溶液也是溶液相砷浓度提高的一种途径, 但铁矿物还原溶解导致吸持的砷释放进入溶液是水稻土溶液砷浓度提高的最为重要机制^[35]。其中, 铁还原微生物在驱动处于亚稳状态的铁矿物的还原溶解扮演着重要角色。

与含砷铁矿物的还原溶解引起砷释放的研究报道相反, 大量研究同样证实无定型铁氧化物可以对砷起截留和库存作用, 且能降低水稻对砷的吸收累积。在含砷水溶液中, 无定型水铁矿被证实可以吸附砷而大幅度降低砷在水环境中被直接还原的速率, 其中液相 As(V)和 $0.2 \text{ g} \cdot \text{L}^{-1}$ 水铁矿悬液中的

As(V)在 *Shewanella putrefaciens* strain CN-32 介导下的还原半衰期分别为 3 h 和 227 h^[36]。这说明铁矿物对砷的抑制和降低砷被直接还原的作用。相似地, 在水稻土环境中同样表明无定型铁矿物对砷具有吸附截留作用。钟松雄等^[11]通过不同铁矿物对砷的固定化作用研究, 发现水稻土无定型铁含量与水稻土溶液中砷的含量呈显著负相关($r = -0.895$, $P = 0.006$), 且无定型铁含量和 F3 呈显著正相关($r = 0.879$, $P = 0.009$)。Liu 等^[12]进一步研究表明, 无定型铁含量与大米谷粒和秸秆中的砷含量呈显著负相关, 分别为 $r = -0.838$, $P < 0.001$ 和 $r = -0.705$, $P < 0.001$, 说明水稻土无定型铁的存在能取得抑制水稻土砷被水稻吸收累积的关键作用, 而另一方面, 有研究表明, 耕种期间淹水水稻土中无定型铁矿物中只有少于 1% 的草酸铵提取铁被还原^[37]。本研究中, 土壤无定型铁与培养液砷存在负相关关系, 即第一阶段和第二阶段分别为 $r = -0.428$ ($P = 0.126$) 和 $r = -0.564$ ($P < 0.05$), 这与前人的研究报道相符, 证实在淹水缺氧条件下无定型铁矿物对砷具有截留贮存作用。这与无定型铁矿物具有巨大的比表面积, 砷可以在其表面形成外圈螯合物或直接与其表面未饱和的羟基进行配体交换形成稳定的内圈螯合物有关^[11, 38]。

本文的研究结果表明 F1 + F2 对溶液中砷浓度提高的贡献是主要的, 而 F3 主要是水稻土中砷的储藏库, 但 F3 处于亚稳状态, 其还原只占小部分。无定型铁矿物具有巨大的比表面积和表面未饱和的羟基功能团决定着无定型铁矿物对砷的贮存作用^[11]。铁还原微生物使铁氧化物还原是驱动砷释放的主要原因, 这种地球生物化学作用机制决定着砷的生物化学行为。通常, 无定型铁矿物的还原主要与厌氧淹水环境、时间和铁还原微生物所需的营养物质等有关。相比于间歇式淹水和落干处理, 处于亚稳状态的水稻土无定型铁矿物在长期持续淹水处理的条件下可能发生更为明显地还原溶解现象, 这可能在有氧环境条件下降低水稻土铁还原微生物丰度或者复氧过程促进亚铁氧化紧密相关。

4 结论

(1) 水稻土经富集培养后, 第二阶段培养液中 Fe(Ⅱ)、砷浓度相比于第一阶段均显著地提高($P < 0.05$), 且相关性分析表明富集培养液中砷主要来源于水稻土可交换态砷(F1)和专属吸附态砷(F2), 而短期内水稻土无定型铁结合态砷(F3)在

第一阶段没有出现释放的现象。

(2) 水稻土盐酸提取铁(Ⅱ)与砷释放在两个阶段均表现出显著正相关关系,而水稻土无定型铁与培养液砷浓度均呈负相关关系,表明水稻土无定型铁矿物能有效地截留和储存无定型铁结合态砷从而有效地降低砷释放。

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