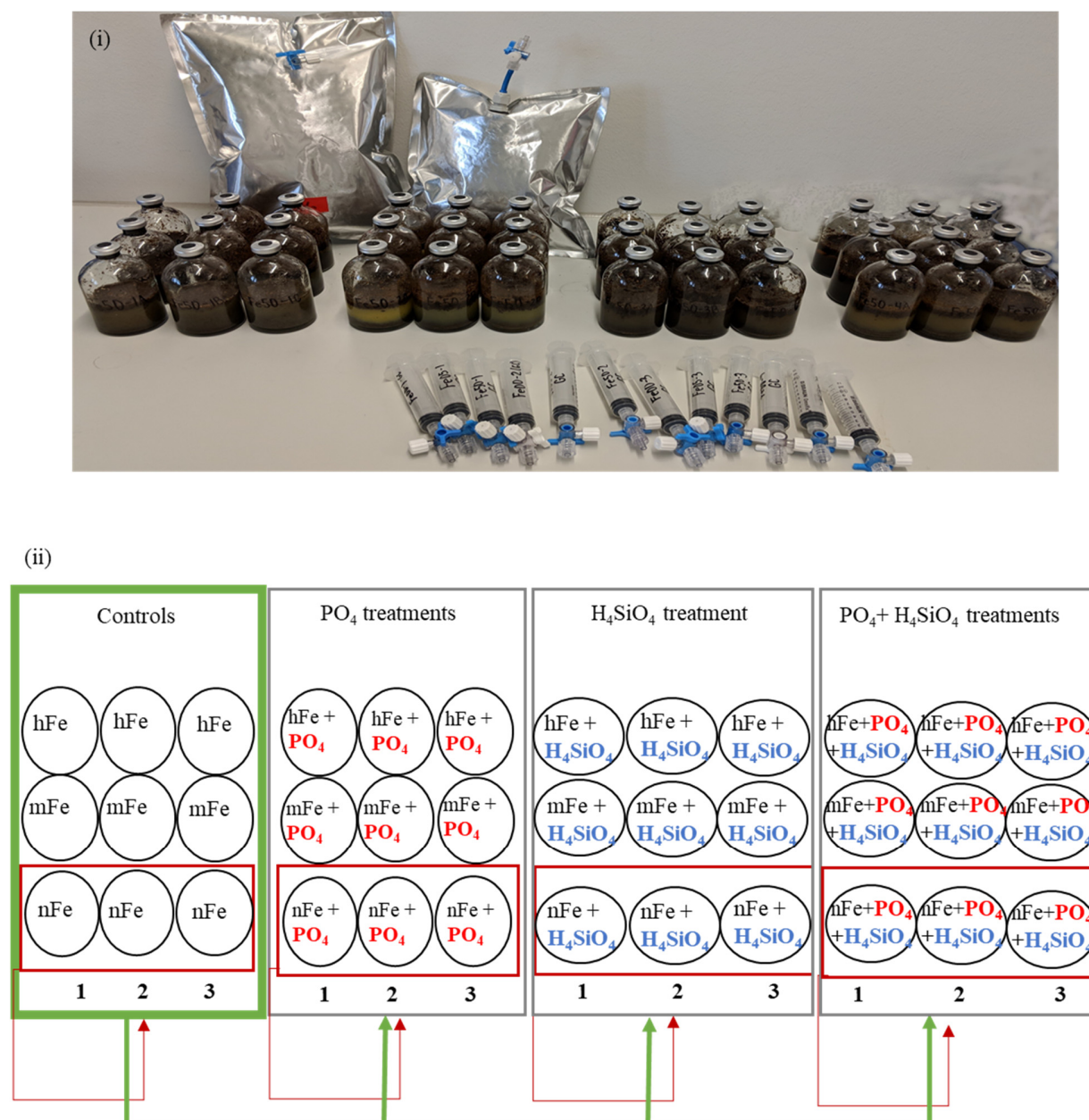


Sketch of treatments for arsenic mobilization from goethite and analysis of gaseous samples

Supplementary Material 1 (S1)



Note: Red boxes mark the controls for each grouped treatment.

Green box and arrows show the grouped the control for other treatment groups (PO_4 , H_4SiO_4 and $\text{PO}_4 + \text{H}_4\text{SiO}_4$) with different levels of Fe. All batch experiments were as triplicate ($n=3$).

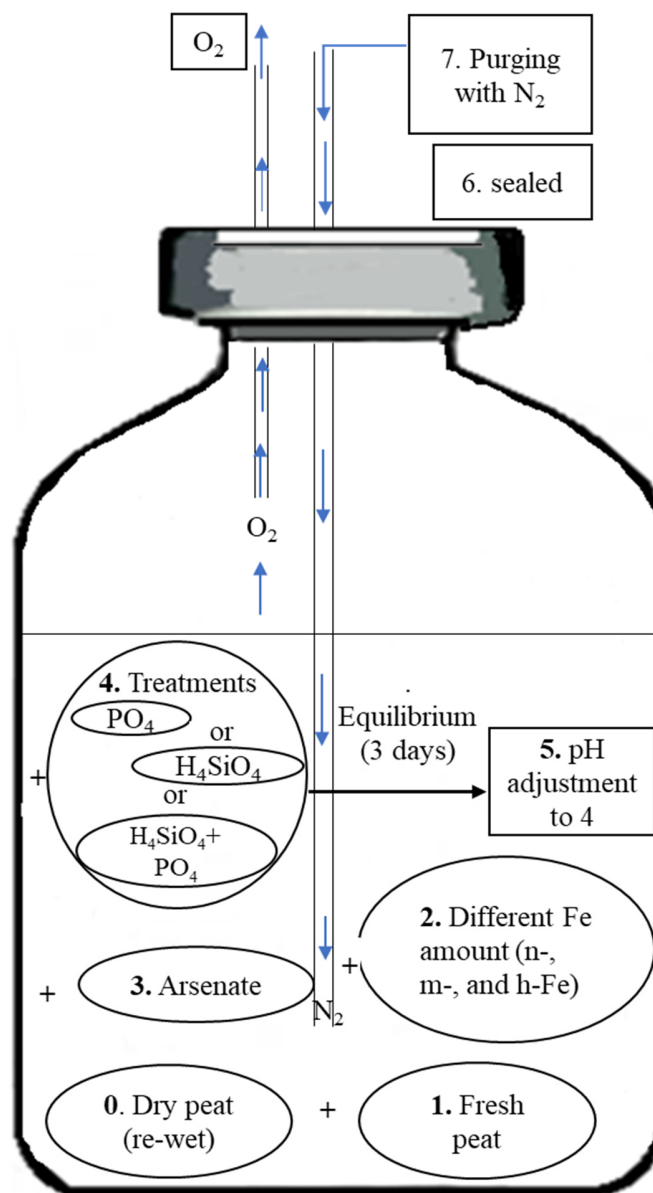


Figure S2. Schematic of the incubation batch preparation and the respective treatments with phosphate: PO_4 ; silicic acid: H_4SiO_4 ; goethite: Fe; no goethite: nFe; medium goethite: mFe; high goethite: hFe.

Supplementary Material (S2)

Methods: analysis of gaseous samples

The potential of CO₂ and CH₄ productions rates were measured to quantify microbial respiratory activity during the course of the experiment. The concentrations of CO₂ and CH₄ in the incubation bottles were measured over time using a gas chromatograph (SRI Instrument 8610C, Torrance, USA) equipped with a flame ionization detector (FID) and methanizer to simultaneously measure CO₂ and CH₄. Before each sampling, the pressure inside the incubation bottles was measured with a pressure sensor (GMH 3110, Greisinger, Regenstauf, Germany). The headspace of incubation bottles was sampled using syringes, and samples were injected into the GC directly. Concentrations were obtained by analyzing the headspace at the beginning (t₀: 24 h) and after 72, 168 and 336 h (t₁–t₃). The measured concentrations (in ppmV) were corrected for pressure and converted using the ideal gas law:

$$n = (p \cdot V) / (R \cdot T) \quad (1)$$

where n is the amount of substance in mol, p is the partial pressure in atm, V is the headspace volume in L, R is the ideal gas constant (0.082 L atm mol⁻¹ K⁻¹) and T is the laboratory temperature in K.

Total concentration of CO₂ and CH₄ in gas and water phase in the incubation bottles were calculated using the ideal gas with constants corrected for 20 °C (K_H, CO₂= 3.8x10⁻² mol L⁻¹ atm⁻¹ and K_H, CH₄= 3.8x10⁻² mol L⁻¹ atm⁻¹, from Sander. R [1].

Results and discussion:

Redox conditions and production of CO₂ and CH₄

Under oxic conditions, microbial respiration is dominated by the reduction of molecular O₂ due to its abundance and thermodynamic favorability as an electron acceptor, while anaerobic respiration pathways using alternative terminal electron acceptors (TEAs) such as Fe(III), sulfate or organic matter (OM) are suppressed until depletion of O₂. Thereafter, respiration using other TEAs sets in, according to their thermodynamic energy yields [2]. The reduction of O₂ or alternative TEAs through microbial respiration can be quantified by monitoring CO₂ production from oxidation of labile OM [3]. Upon depletion of TEAs, reduction of CO₂ via hydrogenotrophic methanogenesis or cleavage of acetate via acetoclastic methanogenesis leads to an equal production of CH₄ and CO₂ under strictly methanogenic conditions [4].

As shown in the Figure S3 below, under anoxic conditions as established in our incubations, high rates of anaerobic CO₂ production were indicative of active microbial respiration and the onset of increasingly reducing conditions over a timescale of hours (Figure S3, a-c). The availability of other TEAs, in our incubations mainly Fe(III) but presumably also OM [5], leads to the retardation of CH₄ production. Accordingly, in the system with the higher Fe content (hFe), the production of CH₄ is retarded longer and overall lower than in the nFe and mFe systems (Figure S3, d-f). Thus, the production of CO₂ and onset of CH₄ production served as a good indicator for redox conditions.

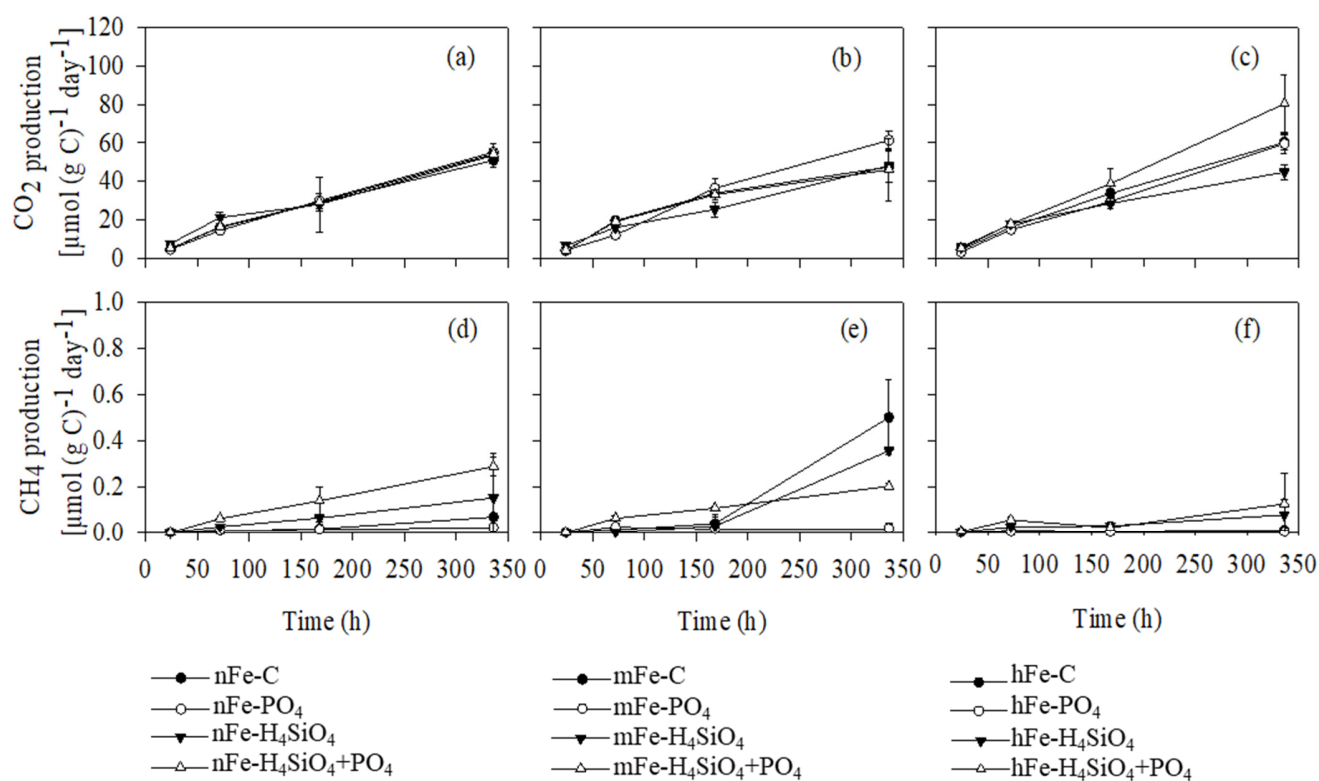


Figure S3. The rate of CO₂ (a–c) and CH₄ production (d–f) versus time during incubation under anoxic conditions. Data represent the mean; whiskers represent the standard deviation (n=3). Addition of goethite is indicated by Fe, where no Fe: nFe; medium Fe (4.4 mg g⁻¹): mFe; high Fe (44.6 mg g⁻¹): hFe; addition of phosphate is indicated by PO₄; addition of silicic acid indicated by H₄SiO₄.

Table S1 Arsenite (As(III)) release rate (in % of total As in the system) during the course of the experiment. See methods section for analytical methods.

| Treatments | Time (h) | | | |
|---|----------|------|------|------|
| Fe Conc.– treatments | 24 | 72 | 168 | 336 |
| nFe-C | 21.5 | 80.0 | 68.0 | 51.0 |
| nFe-PO ₄ | 6.0 | 33.0 | 63.0 | 35.0 |
| nFe- H ₄ SiO ₄ | 11.0 | 60.0 | 55.0 | 61.0 |
| nFe-H ₄ SiO ₄ +PO ₄ | 15.2 | 46.4 | 52.0 | 61.3 |
| mFe-C | 28.0 | 80.0 | 73.0 | 67.0 |
| mFe-PO ₄ | 12.2 | 62.0 | 65.0 | 56.0 |
| mFe- H ₄ SiO ₄ | 8.0 | 39.0 | 62.0 | 81.0 |
| mFe- H ₄ SiO ₄ +PO ₄ | 15.6 | 59.0 | 64.0 | 71.0 |
| hFe-C | 47.0 | 77.0 | 65.0 | 50.0 |
| hFe-PO ₄ | 7.0 | 34.0 | 65.0 | 22.0 |
| hFe- H ₄ SiO ₄ | 23.0 | 75.0 | 70.0 | 71.0 |
| hFe-H ₄ SiO ₄ +PO ₄ | 11.5 | 66.0 | 76.0 | 53.0 |

Fe concentrations: Fe Conc.; no Fe: nFe; medium Fe: mFe; High Fe: hFe; control: C; phosphate: PO₄; silicic acid: H₄SiO₄.

Table S2 The significant effects of different treatments on arsenate (As(V)) mobilization in each sampling time, showing the significant effects of different treatments on arsenate release in the soil solution.

| Treatments | Time (h) | | | |
|---|----------|---------|--------|--------|
| | 24 | 72 | 168 | 336 |
| nFe-C | abc | abc | abc | abc |
| nFe-PO ₄ | b* | b* | abc | bc* |
| nFe- H ₄ SiO ₄ | bc*, ** | bc*, ** | b* | abc |
| nFe- H ₄ SiO ₄ +PO ₄ | abc | abc | cb** | abc |
| mFe-C | abc | abc | abc | abc |
| mFe-PO ₄ | abc | abc | abc | abc |
| mFe- H ₄ SiO ₄ | abc | abc | abc | abc |
| mFe- H ₄ SiO ₄ +PO ₄ | abc | abc | abc | abc |
| hFe-C | a* | a* | a*, ** | a*, ** |
| hFe-PO ₄ | abc | abc | abc | bc** |
| hFe- H ₄ SiO ₄ | ac** | ac** | abc | abc |
| hFe-H ₄ SiO ₄ +PO ₄ | abc | abc | abc | abc |

Treatments followed by the same letter are not significantly different ($p < 0.05$). Control: C; phosphate: PO₄; silicic acid: H₄SiO₄. The significant difference between treatments at each sampling time is distinguished by the same star and color.

Table 3 The significant effects of different treatments on arsenite (As(III)) mobilization in each sampling time, showing the significant effects of different treatments on arsenite release in the soil solution.

| Treatments | Time (h) | | | |
|---|---------------------------------|----------------|----------------|----------------|
| | 24 | 72 | 168 | 336 |
| nFe-C | bd [*] , ^{**} | a [*] | a [*] | ab |
| nFe-PO ₄ | ab ^{**} | ab | ab | ab |
| nFe- H ₄ SiO ₄ | abc | ab | ab | ab |
| nFe- H ₄ SiO ₄ +PO ₄ | abc | ab | ab | ab |
| mFe-C | cd [*] | a [*] | a [*] | ab |
| mFe-PO ₄ | a [*] | ab | a | ab |
| mFe- H ₄ SiO ₄ | abc | ab | ab | b [*] |
| mFe- H ₄ SiO ₄ +PO ₄ | abc | ab | ab | ab |
| hFe-C | abc | b [*] | b [*] | a [*] |
| hFe-PO ₄ | ab ^{**} | b [*] | ab | a [*] |
| hFe- H ₄ SiO ₄ | abc | ab | ab | ab |
| hFe-H ₄ SiO ₄ +PO ₄ | abc | ab | ab | ab |

Treatments followed by the same letter are not significantly different (p<0.05). Control: C; phosphate: PO₄; silicic acid: H₄SiO₄. The significant difference between treatments at each sampling time is distinguished by the same star and color.

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