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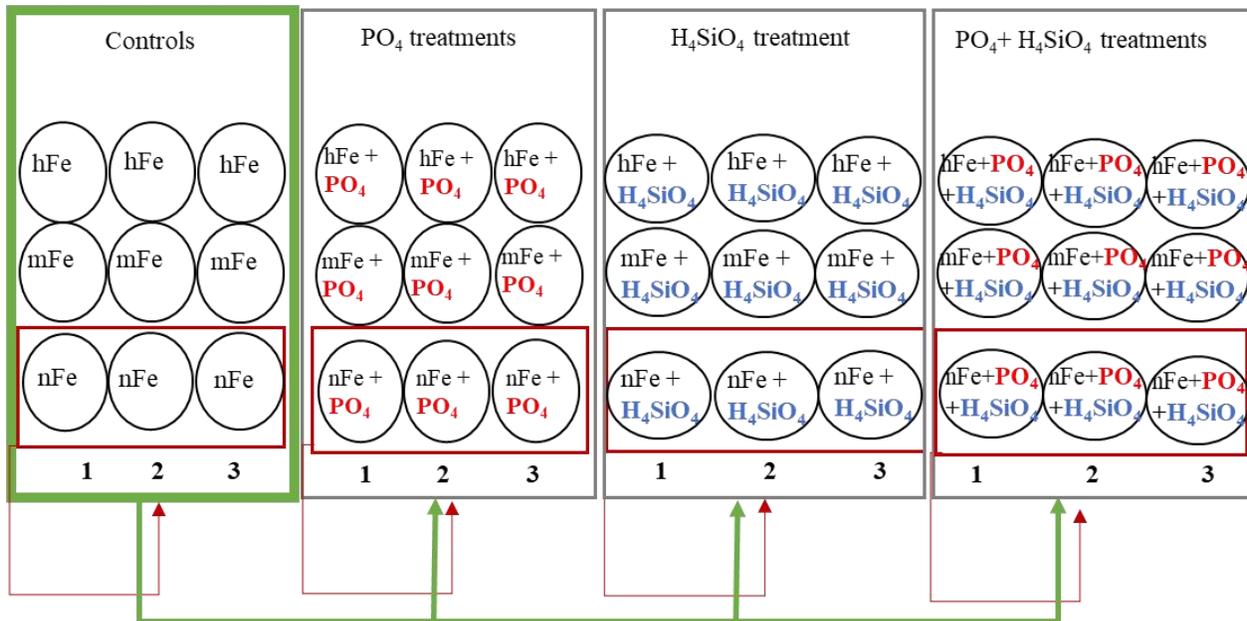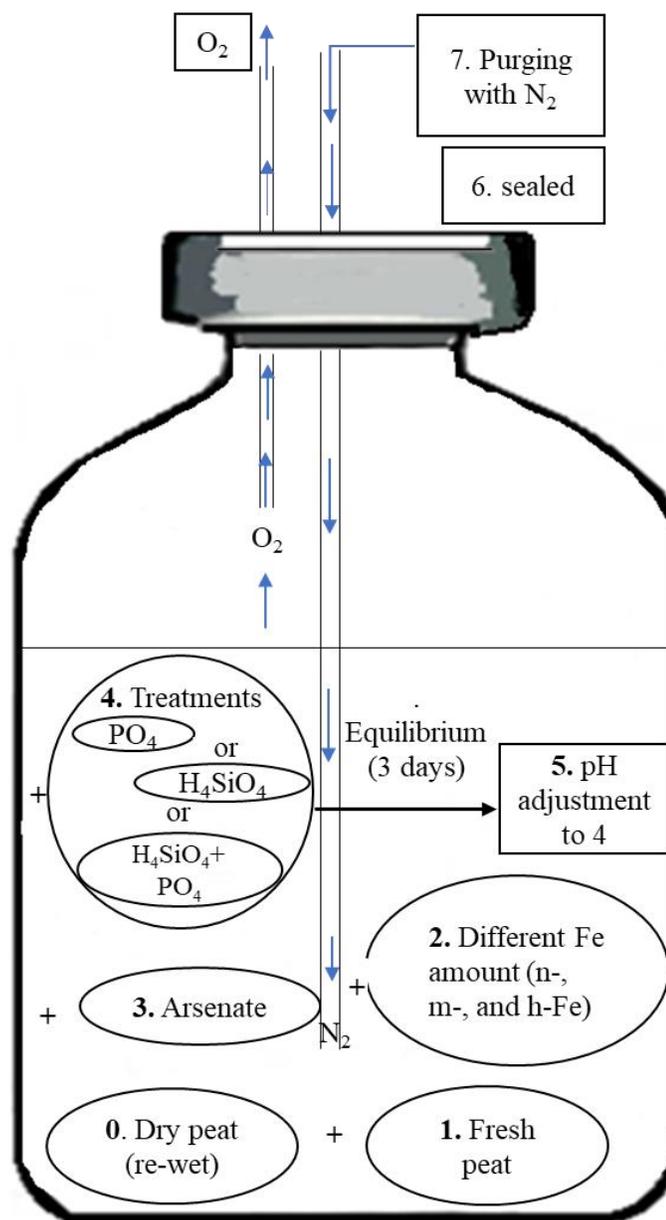## 2 of gaseous samples

3 Supplementary Material 1 (S1)

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5 Figure 1.i) Photograph of incubation bottles; ii) sketch of treatments and Fe addition in the form

6 of goethite: Fe; no Fe: nFe; medium Fe (4.4 mg g-1, the weight of Fe): mFe; high Fe (44.6 mg g-1,

7 the weight of Fe): hFe; addition of phosphate is indicated by PO₄; addition of silicic acid by H₄SiO₄.

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

9 Green box and arrows show the grouped the control for other treatment groups (PO4, H4SiO4 and

10 PO4+ H4SiO4) with different levels of Fe. All batch experiments were as triplicate (n=3).

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14 Figure 2. Schematic of the incubation batch preparation and the respective treatments with

15 phosphate: PO4; silicic acid: H4SiO4; goethite: Fe; no goethite: nFe; medium goethite: mFe; high

16 goethite: hFe.

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Supplementary Material (S2)

Methods: analysis of gaseous samples

The potential of CO_2 and CH_4 productions rates were measured to quantify microbial respiratory

activity during the course of the experiment. The concentrations of CO_2 and CH_4 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

CO_2 and CH_4. 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 (t_0:24 h) and after 72,

168 and 336 h (t_1–t_3). The measured concentrations (in ppmV) were corrected for pressure and

converted using the ideal gas law:

$$n= (p* V) / (R*T) \tag{1}$$

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 CO_2 and CH_4 in gas and water phase in the incubation bottles were

calculated using the ideal gas with constants corrected for 20 °C (K_H, CO_2= 3.8x10^{-2} mol L^{-1} atm^{-1}

and K_H, CH_4= 3.8x10^{-2} mol L^{-1} atm^{-1}, from Sander. R [1].
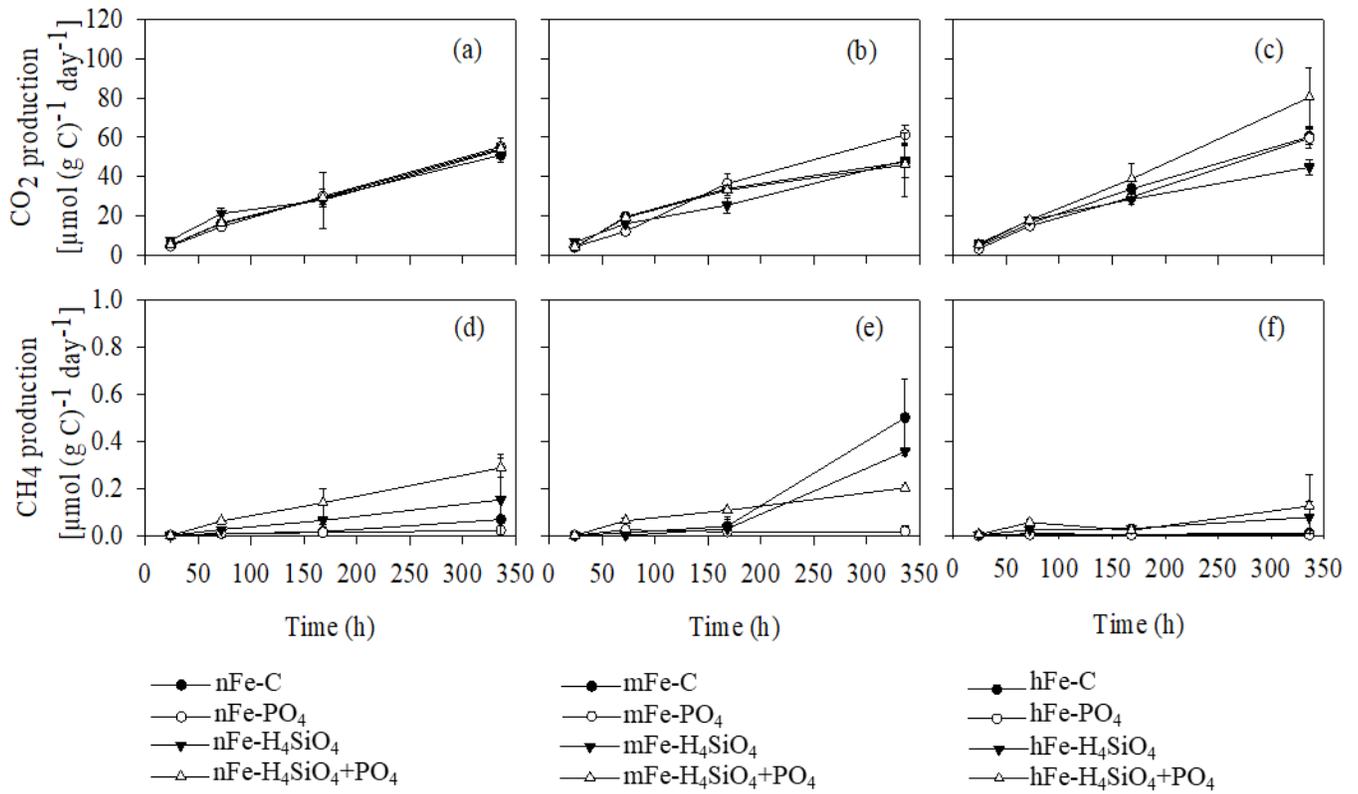
Results and discussion:

39 *Redox conditions and production of CO_2 and CH_4*

40 Under oxic conditions, microbial respiration is dominated by the reduction of molecular O_2 due

41 to its abundance and thermodynamic favorability as an electron acceptor, while anaerobic

42 respiration pathways using alternative terminal electron acceptors (TEAs) such as Fe(III), sulfate

43 or organic matter (OM) are suppressed until depletion of O_2. Thereafter, respiration using other

44 TEAs sets in, according to their thermodynamic energy yields [2]. The reduction of O_2 or

45 alternative TEAs through microbial respiration can be quantified by monitoring CO_2 production

46 from oxidation of labile OM [3]. Upon depletion of TEAs, reduction of CO_2 via hydrogenotrophic

47 methanogenesis or cleavage of acetate via acetoclastic methanogenesis leads to an equal

48 production of CH_4 and CO_2 under strictly methanogenic conditions [4].

49 As shown in the Figure 3 S2 below, under anoxic conditions as established in our

50 incubations, high rates of anaerobic CO_2 production were indicative of active microbial

51 respiration and the onset of increasingly reducing conditions over a timescale of hours (Figure 3,

52 a-c). The availability of other TEAs, in our incubations mainly Fe(III) but presumably also OM

53 [5], leads to the retardation of CH_4 production. Accordingly, in the system with the higher Fe

54 content (hFe), the production of CH_4 is retarded longer and overall lower than in the nFe and mFe

55 systems (Figure 3, d-f). Thus, the production of CO_2 and onset of CH_4 production served as a good

56 indicator for redox conditions.

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Figure 3. The rate of CO_2 (a–c) and CH_4 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 PO_4; addition of silicic acid indicated by H_4SiO_4.

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65   Table 1 Arsenite (As(III)) release rate (in % of total As in the system) during the course of the

66   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_4SiO_4	11.0	60.0	55.0	61.0
nFe-H_4SiO_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_4SiO_4	8.0	39.0	62.0	81.0
mFe- H_4SiO_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_4SiO_4	23.0	75.0	70.0	71.0
hFe-H_4SiO_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:

PO_4; silicic acid: H_4SiO_4.

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68 Table 2 The significant effects of different treatments on arsenate (As(V)) mobilization in each

69 sampling time, showing the significant effects of different treatments on arsenate release in the

70 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

71 Treatments followed by the same letter are not significantly different (p<0.05). Control: C;

72 phosphate: PO$_4$; silicic acid: H$_4$SiO$_4$. The significant difference between treatments at each

73 sampling time is distinguished by the same star and color.

74 Table 3 The significant effects of different treatments on arsenite (As(III)) mobilization in each

75 sampling time, showing the significant effects of different treatments on arsenite release in the

76 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

77 Treatments followed by the same letter are not significantly different ($p < 0.05$). Control: C;

78 phosphate: PO$_4$; silicic acid: H$_4$SiO$_4$. The significant difference between treatments at each

79 sampling time is distinguished by the same star and color.

80

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