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## 1. Thioarsenates discovered in planted paddy fields in Italy and France

**Methods.** For an initial field survey, we sampled 23 different paddy fields in Italy (17 fields) and France (6 fields) (all located in the Mediterranean climate zone, for coordinates see Table S1) during the cropping season in August 2016 when the rice plants were in the flowering to grain filling stage. Sampling in Italy covered most of the rice cropping areas of the river Po plain, where the majority of the Italian rice is produced. The paddy fields were located in the alluvial plain, the river valley, and the lower river plain. All Italian soils developed on recent clastic deposits with mixed lithology (e.g., noncalcareous gravels, silty sands), and are mostly classified as luvisols, gleysols, and a few fluvisols and cambisols (Soil Atlas of Europe, https://esdac.jrc.ec.europa.eu/content/soil-atlas-europe). Paddy fields in France covered the whole extent of the only rice cultivation area in France which is located in the coastal plain of the Camargue region, in the delta of the river Rhone. The soils there developed on recent deposits of the Rhone river and are classified as gleyic fluvisols. In total, 35 pore-water samples were collected. At most paddy fields only one pore water sample was taken, at five paddy soils we took replicates. Pore-water was extracted by micro rhizon samplers (Rhizon MOM, Rhizosphere Research Products, The Netherlands) inserted about 3-4 cm deep into the paddy soil and connected to evacuated 100 mL glass bottles. The bottles were first sealed with a butyl rubber septum in an anoxic glovebox ($N_2/H_2$ 95/5% (v/v)), then evacuated to negative atmospheric pressure of ~900 mbar. During sampling, glass bottles were shielded with aluminum foil to avoid potential photooxidation [1]. To retrieve enough volume (minimum 10 mL) for all analyses, minimum sampling time was 4 hours, maximum sampling time up to 24 hours. After retrieving the pore water samples, one soil sample from the plow layer was collected at each site.

After collection, pore-water samples were filtered through 0.2 µm cellulose-acetate filters. Samples for As speciation analysis were immediately flash-frozen on dry ice, and stored at -20 °C before being analyzed by ion chromatography (IC, Dionex ICS-3000) coupled to inductively coupled plasma-mass spectrometry (ICP-MS, XSeries2, Thermo-Fisher) at Bayreuth University following a previously established method for analysis of inorganic and methylated thioarsenates [2].

Retention times of the As species were verified by comparison with commercial standards (arsenite ($NaAsO_2$, Fluka), arsenate ($Na_2HAsO_4 \times 7H_2O$, Fluka), MMA ($CH_3AsNa_2O_3 \times 6H_2O$, Supelco), DMA ($C_2H_6AsNaO_2 \times 3H_2O$, Sigma-Aldrich)), standards synthesized according to previously published methods (DMMTA (purity 67%; 28% DMDTA, 5% DMA) and MMMTA (purity 96%; 1% MMA, 3% MMDTA) [3], MTA (purity of 98.5%; 0.5% arsenite, 1% arsenate)) [4]

or by comparison with previously published [5] retention times (MMDTA, DMDTA, DTA, TTA). Calibration standard solutions were made from arsenate dibasic-heptahydrate, sodium (meta)arsenite, disodium methyl arsonate hexahydrate, and dimethylarsinic acid. All other As species were quantified by peak area comparison to the standard closest in retention time. Validity of this method has been proven previously [2].

An example of the chromatographic separation of the different As species is reported in Fig. S1. Samples for total As and Fe were acidified in 0.5% $H_2O_2$ and 0.8% $HNO_3$ and kept at 4°C until analysis by ICP-MS. Samples for zero-valent S were stabilized with zinc acetate (25 µL of 200 g/L ZnAc +725 µL sample), kept at 4°C until extraction by chloroform in the laboratory, then measured with high performance liquid chromatography (HPLC) (Merck Hitachi L-2130 pump, L-2200 autosampler, and L-2420 UV-VIS detector; C18 column, 100% methanol eluent at 0.2 mL/min) as described before [6]. Sulfide was measured photometrically on-site using the methylene blue method (HACH procedure No. 8131). Redox potential, pH, and conductivity were measured directly on-site by a WinLab redox micro-electrode, a WinLab 423 combination pH electrode, and a Mettler Toledo TetraCon 325 electrode.

Soil samples were analyzed for soil pH (measured in 2.5 mL 0.1 M $CaCl_2$ solution with 1 g soil), 0.5 M HCl-extractable Fe, total C and N (CHN analyzer), and total As and S (determination by ICP-MS after microwave digestion in aqua regia).

**Results.** Soil pH ranged from 5.0-6.1 and 7.5-7.6, total soil As contents from 5.2-16 and 10.4-20.2 mg/kg, HCl-extractable Soil Fe contents from 50-198 and 105-181 mmol/kg, and total C from 0.8-4.7 and 4.5-6.0 %, for the Italian and French paddy soils, respectively (Table S1a). Thioarsenates were determined in 23 out of 35 pore-water samples and in 14 out of 23 different fields (Table S1b). The contribution of total thiolation to total As concentrations was 8.3% at maximum and 2.1% on average. These numbers are comparable to those observed for the much more-commonly-investigated methylated oxyarsenates which we detected in 31 samples from 20 fields (max. 10.4%, on average 1.3%). Inorganic thioarsenates (monothioarsenate (MTA) and dithioarsenate (DTA)) were detected in 11 samples (max. 7.4%, on average 3.2%) and methylated thioarsenates (monomethylmonothioarsenate (MMMTA), DMMTA, dimethyldithioarsenate (DMDTA)) in 18 samples (max. 2.9%, on average 0.7%). Seven samples taken within the same paddy field (Veronica, Table S1b) showed large heterogeneity in the proportion of thioarsenates (2.9-8.3%) without any obvious relation to pore-water chemistry, such as dissolved sulfide concentrations (Table S1b). Inorganic thioarsenates were observed in large quantities only at pore-water Fe concentrations < 0.5 mmol/L suggesting that Fe concentrations above a threshold value could limit their formation

(Fig. S2a). Methylated thioarsenates, in contrast, occurred over a wider range of dissolved Fe concentrations (Fig. S2b) and Spearman´s correlation test showed positive correlation with methylated oxyarsenates ($r = 0.60$, $P<10^{-4}$; Fig. S2b, S2c, S3). There was no correlation between inorganic and methylated thioarsenates.

For these first field surveys, we used relatively long pore-water sampling times (4-24 hours) to obtain enough volume for analyses (minimum 10 mL) and, for species preservation, we used just flash-freezing, without adding stabilizing agents. Even though all As chromatographic peaks were clearly distinguishable (Fig. S1), high Fe concentrations (up to 2.3 mmol/L) caused Fe precipitation and, by co-precipitation and sorption, low As recoveries (calculated as the sum of all detected As species in flash-frozen samples versus total As measured in oxidized and acid-stabilized samples; Fig. S4).

All species proportions are reported with respect to total As (not the sum of species). As such, a partial precipitation or sorption of thiolated As species on any Fe (hydr)oxides [7] formed during sample storage could have contributed to an underestimation of the true proportions reported here.

For all later analyses, short sampling times (0.5-1 hour) and an optimized DTPA-sample stabilization and analysis were chosen. For details on the DTPA method development and evaluation see main manuscript and Fig. S15-S18.

**Table S1a |** Coordinates and basic soil chemistry from 17 Italian paddy fields (IT) and 6 French paddy fields (FR)

| Paddy fields | Longitude | Latitude | Soil pH | HCl extract-able soil Fe | total soil As | total soil S | total soil C |
|---|---|---|---|---|---|---|---|
| | | | | mmol/kg | mg/kg | g/kg | % |
| **ITALY** | | | | | | | |
| IT_Vignarello | 8°44′42.82″ | 45°20′39.77″ | 5.5 | 62.6 | 8.9 | 3.4 | 2.0 |
| IT_Barbavara | 8°47′09.49″ | 45°21′19.41″ | 5.5 | 67.6 | 10.5 | 3.2 | 2.7 |
| IT_Gambarana | 8°46′30.88″ | 45°01′38.88″ | 5.8 | 197.7 | 16.0 | 6.0 | 1.4 |
| IT_Breme | 8°37′06.19″ | 45°08′38.34″ | 5.8 | 177.0 | 13.8 | 5.4 | 1.3 |
| IT_Langosco | 8°32′43.84″ | 45°12′34.24″ | 5.7 | 165.5 | 12.9 | 8.4 | 1.3 |
| IT_Vercelli | 8°15′12.88″ | 45°18′36.59″ | 5.7 | 75.9 | 11.4 | 9.5 | 1.1 |
| IT_Cascina Oschiena | 8°45′03.84″ | 45°18′36.58″ | 5.7 | 109.9 | 6.1 | 4.2 | 1.3 |
| IT_Fontanetto Po | 8°11′59.46″ | 45°12′15.50″ | 6.0 | 144.9 | 9.1 | 4.8 | 3.4 |
| IT_Terranova | 8°30′02.95″ | 45°11′53.56″ | 6.1 | 125.3 | 11.8 | 5.3 | 1.4 |
| IT_Rovasenda | 8°16′40.00″ | 45°32′34.05″ | 5.8 | 97.2 | 14.3 | 4.3 | 1.0 |
| IT_Cascina Albera | 8°56′48.18″ | 45°10′49.49″ | 5.8 | 52.0 | 5.9 | 2.7 | 1.4 |
| IT_Lomello | 8°47′55.87″ | 45°07′26.71″ | 5.0 | 120.6 | 8.9 | 4.1 | 1.4 |
| | | | 5.6 | 90.2 | 7.3 | 3.9 | 1.5 |
| IT_Cascina Fornazzo | 8°57′49.97″ | 45°13′53.76″ | 5.8 | 71.7 | 5.6 | 3.2 | 4.7 |
| IT_Cascina Veronica | 8°53′47.60″ | 45°10′39.30″ | 5.6 | 50.0 | 5.2 | 2.2 | 2.1 |
| IT_Castello d´Agogna (ENR) field 1 | 8°41′56.50″ | 45°14′51.30″ | 5.5 | 53.0 | 5.8 | 2.6 | 2.0 |
| | | | 5.4 | 50.6 | 5.8 | 2.4 | 1.9 |
| | | | 5.5 | 145.9 | 16.0 | 4.3 | 0.9 |
| | | | 5.5 | 152.3 | 15.6 | 4.3 | 0.8 |
| IT_Castello d´Agogna (ENR) field 2 | | | 5.5 | 146.7 | 15.2 | 4.4 | 0.8 |
| | | | 5.5 | 144.1 | 15.6 | 4.2 | 0.8 |
| IT_Castello d´Agogna (ENR) field 3 | | | 5.6 | 181.0 | 15.8 | 4.2 | 0.9 |
| | | | 5.5 | 159.3 | 14.9 | 4.2 | 0.9 |
| **FRANCE** | | | | | | | |
| FR_Seyne | 4°42′57.24″ | 43°34′23.63″ | 7.5 | 166.0 | 18.2 | 22.1 | 5.4 |
| FR_Vedeau | 4°42′24.53″ | 43°26′04.63″ | 7.6 | 143.0 | 14.7 | 23.1 | 6.0 |
| FR_Adrien | 4°33'40.93" | 43°42'07.42" | 7.5 | 109.5 | 10.4 | 18.0 | 4.9 |
| FR_Furane | 4°31′06.35″ | 43°41′11.58″ | 7.5 | 134.1 | 20.2 | 19.8 | 4.9 |
| FR_Boismeaux | 4°28′14.10″ | 43°35′54.44″ | 7.5 | 138.9 | 13.1 | 18.8 | 4.5 |
| FR_Signore | 4°29′46.35″ | 43°37′10.51″ | 7.6 | 104.7 | 10.6 | 22.6 | 5.2 |

**Table S1b |** Pore water chemistry including As speciation for samples from 17 Italian paddy fields (IT) and 6 French paddy fields (FR)

| Paddy fields | pore water pH | $E_H$ | Conductivity | Sulfide | Zerovalent sulfur | Fe | DMA | DMMTAa | Arsenite | DMDTA[b] | MMA | MMMTA[c] | Arsenate | MTA[d] | DTA[e] | Total Thiolated As | Sum As species | Total As |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | mV | µS/cm | µmol/L | | mmol/L | µg/L | | | | | | | | | | | |
| **ITALY** | | | | | | | | | | | | | | | | | | |
| **IT_Vignarello** | 6.1 | 194 | 310 | <0.3 | 4.6 | 0.3 | 0.2 | | 2.8 | | | | 1.0 | | | | 3.9 | 38.1 |
| **IT_Barbavara** | 6.6 | 184 | 305 | <0.3 | 2.4 | 0.2 | 0.04 | | 0.5 | | | | 0.2 | | | | 0.7 | 10.6 |
| **IT_Gambarana** | 6.9 | 71 | 1154 | <0.3 | <1 | 0.3 | 0.1 | | 3.1 | | 0.3 | | 2.5 | | | | 6.1 | 86.2 |
| **IT_Breme** | 6.6 | -21 | 1340 | <0.3 | 4.3 | 2.6 | 0.4 | | 1.1 | | 0.4 | 0.2 | 0.3 | | | 0.2 | 2.4 | 82.0 |
| **IT_Langosco** | 6.4 | 145 | 575 | <0.3 | 5.4 | 0.9 | 0.2 | 0.2 | 0.5 | | 0.1 | 0.1 | 0.2 | | | 0.3 | 1.3 | 37.3 |
| **IT_Vercelli** | 6.3 | 339 | 209 | <0.3 | <1 | 0.0 | | | 1.9 | | | | 1.6 | | | | 3.4 | 7.8 |
| **IT_Cascina Oschiena** | 6.5 | 72 | 1092 | 1.2 | <1 | 1.5 | | 0.1 | 0.5 | | | | 0.2 | | | 0.1 | 0.9 | 68.2 |
| **IT_Fontanetto Po** | 7.0 | 377 | 1831 | 1.2 | <1 | <0.1 | 0.1 | | 2.7 | | 0.1 | | 1.0 | | | | 3.9 | 9.0 |
| **IT_Terranova** | 7.0 | 68 | 2490 | 1.3 | 5.8 | 0.2 | 1.5 | 0.1 | 11.8 | | | | 2.3 | | | 0.1 | 15.8 | 84.2 |
| **IT_Rovasenda** | 6.6 | 116 | 370 | 1.2 | <1 | 0.1 | 0.6 | 0.1 | 0.3 | | | | 0.4 | | | 0.1 | 1.4 | 6.0 |
| **IT_Cascina Albera** | 6.7 | 93 | 315 | 1.8 | 1.2 | 0.6 | 0.1 | | 1.4 | | | 0.04 | 0.3 | | | 0.04 | 1.8 | 31.3 |
| **IT_Lomello** | 6.8 | 92 | 280 | 0.9 | 2.7 | 0.1 | | | 1.4 | | | | 0.4 | | | | 1.8 | 25.9 |
| | 7.0 | 97 | 362 | <0.3 | 5.2 | 0.0 | 0.2 | | 2.6 | | 0.1 | | 2.3 | 0.2 | | 0.2 | 5.5 | 15.2 |
| **IT_Cascina Fornazzo** | 7.1 | 98 | 673 | <0.3 | 5.2 | 0.3 | 0.5 | 0.1 | 1.3 | | 0.2 | 0.3 | 0.5 | 0.1 | 0.2 | 0.8 | 3.3 | 14.9 |
| **IT_Cascina Veronica** | 6.4 | 90 | 541 | <0.3 | <1 | 0.5 | 0.6 | 0.4 | 1.8 | 0.1 | 0.1 | 0.03 | 0.6 | 0.2 | 0.4 | 1.2 | 4.4 | 28.2 |
| | 6.2 | 122 | 341 | <0.3 | <1 | 0.3 | | 0.1 | 0.9 | | | 0.1 | 0.7 | 0.2 | 0.2 | 0.5 | 2.1 | 9.1 |
| | 6.4 | 83 | n.a | 3.0 | <1 | 0.3 | | | 1.6 | | 0.04 | 0.0 | 3.8 | 0.4 | 0.3 | 0.8 | 6.2 | 17.7 |

| Paddy fields | pore water pH | $E_H$ | Conductivity | Sulfide | Zerovalent sulfur | Fe | DMA | DMMTAa | Arsenite | DMDTA[b] | MMA | MMMTA[c] | Arsenate | MTA[d] | DTA[e] | Total Thiolated As | Sum As species | Total As |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | mV | µS/cm | µmol/L | | mmol/L | µg/L | | | | | | | | | | | |
| IT_Cascina Veronica | 6.3 | 117 | 285 | 1.1 | <1 | 0.3 | | | 2.8 | | 0.2 | 0.1 | 1.8 | 0.3 | 0.6 | 1.0 | 5.8 | 11.9 |
| | n.a. | n.a. | n.a. | <0.3 | <1 | 0.3 | | | 2.3 | | 0.1 | | 6.9 | 0.5 | 0.2 | 0.8 | 10.1 | 20.6 |
| | 6.5 | 169 | n.a. | <0.3 | 1.8 | 0.3 | | | 0.7 | | 0.05 | | 1.2 | 0.2 | 0.3 | 0.5 | 2.4 | 8.0 |
| | 6.2 | 105 | 400 | <0.3 | <1 | 0.3 | 0.03 | | 0.4 | | 0.1 | | 0.7 | 0.1 | 0.1 | 0.2 | 1.5 | 7.1 |
| IT_Castello d´Agogna (ENR) field 1 | 6.8 | -13 | 1183 | 1.0 | 1.5 | 1.8 | 0.1 | 0.3 | 0.6 | | 0.5 | | 0.1 | | | 0.3 | 1.6 | 105 |
| | 6.6 | 85 | 723 | <0.3 | <1 | 0.8 | 0.1 | | 0.6 | | | | 0.3 | | | | 1.0 | 44.4 |
| IT_Castello d´Agogna (ENR) field 2 | 6.7 | 83 | n.a. | 1.1 | 2.4 | 0.6 | 0.1 | 0.03 | 0.7 | | | | 0.2 | | | 0.03 | 1.0 | 30.0 |
| | 6.8 | 1 | 1346 | 1.0 | <1 | 1.8 | 0.1 | 0.1 | 0.5 | | 0.3 | 0.1 | 0.1 | | | 0.2 | 1.2 | 58.5 |
| | 6.8 | 44 | 1181 | <0.3 | <1 | 0.8 | 0.2 | 0.1 | 0.5 | | 0.5 | 0.2 | 0.1 | | | 0.3 | 1.6 | 24.8 |
| | 6.7 | 70 | 890 | <0.3 | <1 | 1.2 | 0.1 | 0.1 | 0.4 | | 0.2 | | 0.1 | | | 0.1 | 0.9 | 36.7 |
| IT_Castello d´Agogna (ENR) field 3 | 6.7 | 83 | 792 | <0.3 | 3.8 | 0.7 | 0.1 | | 1.2 | | 0.1 | | 0.2 | | | | 1.6 | 45.4 |
| | 6.8 | 117 | 364 | <0.3 | 2.8 | 0.3 | 0.1 | | 2.0 | | | | 0.6 | | | | 2.6 | 47.1 |
| **FRANCE** | | | | | | | | | | | | | | | | | | |
| FR_Seyne | 7.2 | 37 | 1030 | <0.3 | | 0.5 | | | 1.9 | | | | 0.2 | | | | 2.1 | 72.8 |
| FR_Vedeau | 6.8 | 32 | 2200 | <0.3 | | 0.7 | 1.4 | | 6.7 | | | | 0.5 | | | | 8.6 | 165 |
| FR_Adrien | 7.3 | 91 | 1340 | <0.3 | | 0.2 | 0.2 | 0.1 | 21.9 | | 0.04 | | 2.8 | 0.2 | 0.1 | 0.4 | 25.3 | 86.7 |
| FR_Furane | 7.2 | -16 | 1854 | <0.3 | | 1.4 | 1.0 | 0.1 | 11.7 | | | | 2.5 | | | 0.1 | 15.3 | 335 |
| FR_Boismeaux | 7.3 | 16 | 2010 | <0.3 | | 1.2 | 1.1 | 0.4 | 16.8 | 0.1 | 0.9 | 0.2 | 2.5 | 0.1 | | 0.8 | 22.2 | 268 |
| FR_Signore | 7.5 | 37 | 1509 | <0.3 | | 0.6 | 0.3 | | 4.4 | | 0.1 | | 0.4 | | | | 5.3 | 69.5 |

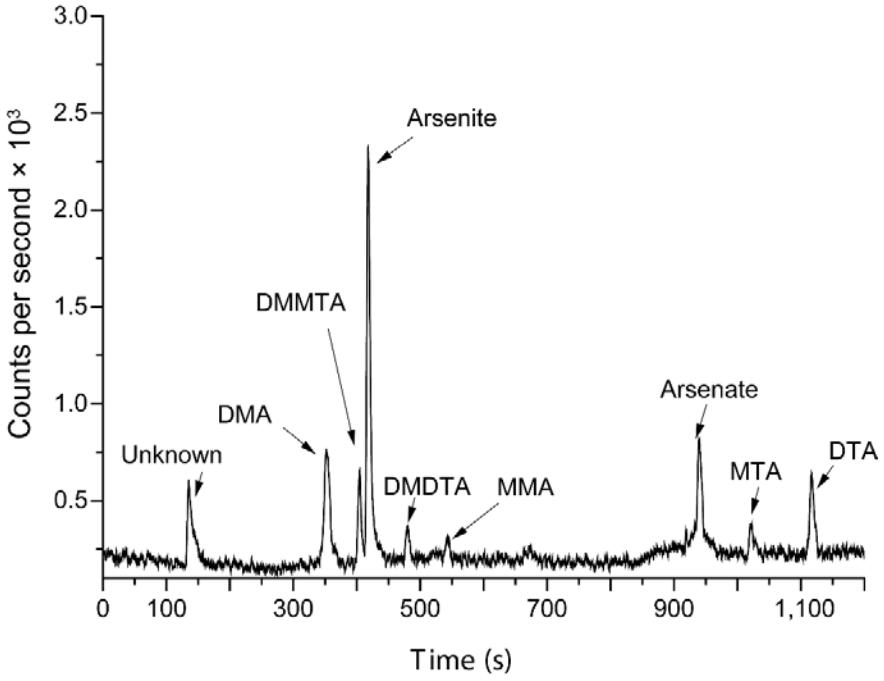


**Figure S1 | Example chromatogram for determination of inorganic and methylated thio and oxy As species in paddy field pore-water by IC-ICP-MS**. The presented sample is IT_Cascina Veronica (pH 6.36, Table S1).

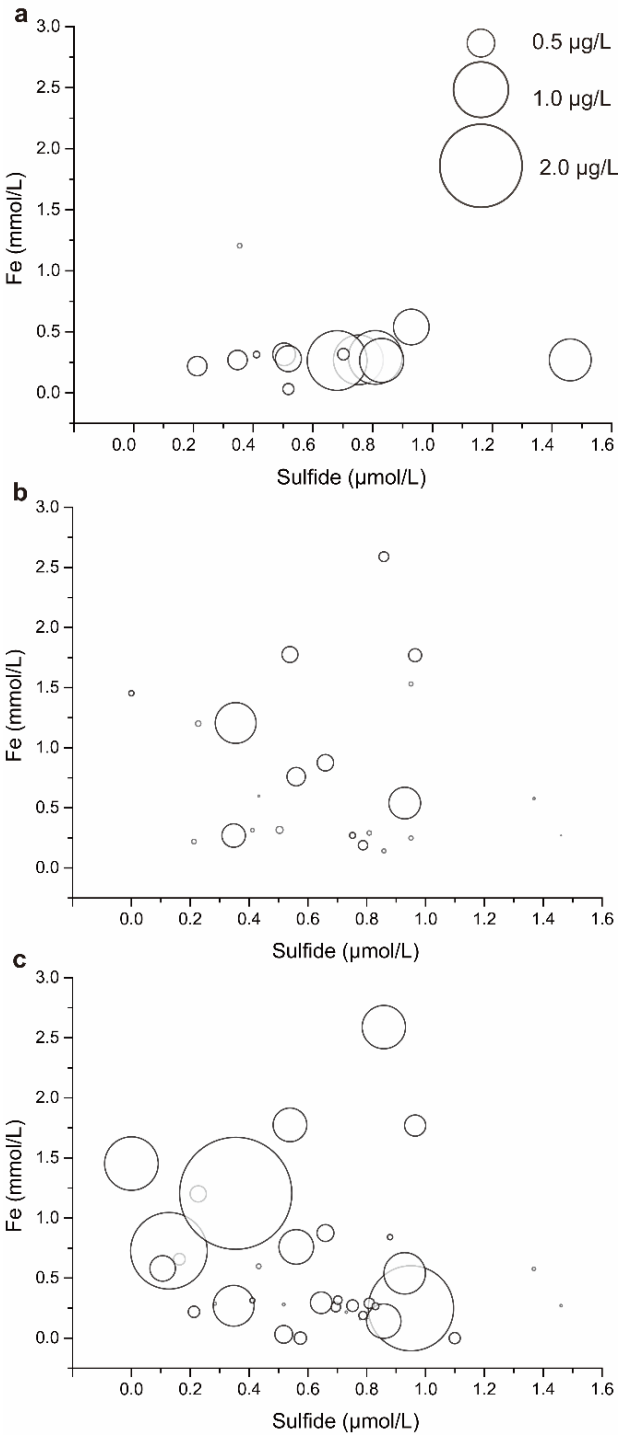


**Figure S2 | Arsenic speciation in paddy field pore-waters from Italy and France in relation to aqueous Fe and sulfide.** Contribution of a) inorganic thioarsenates, b) methylated thioarsenates and c) methylated oxyarsenates to total As; bubble size represents concentration of As species; bubbles are only displayed where concentrations of As species were above detection limit.

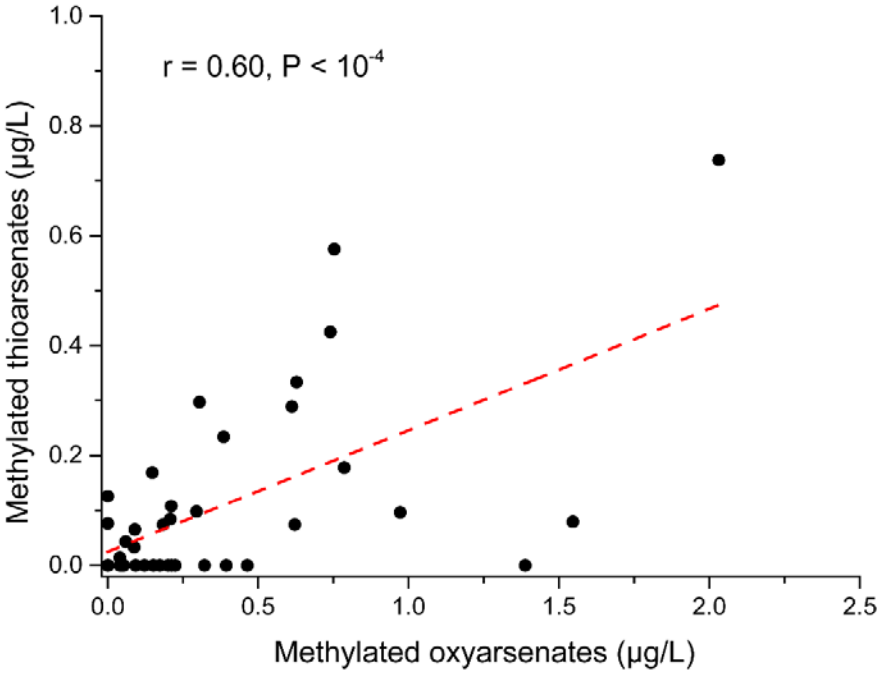


**Figure S3 | Correlation of methylated thioarsenates with methylated oxyarsenates in paddy field pore-waters from Italy and France.**

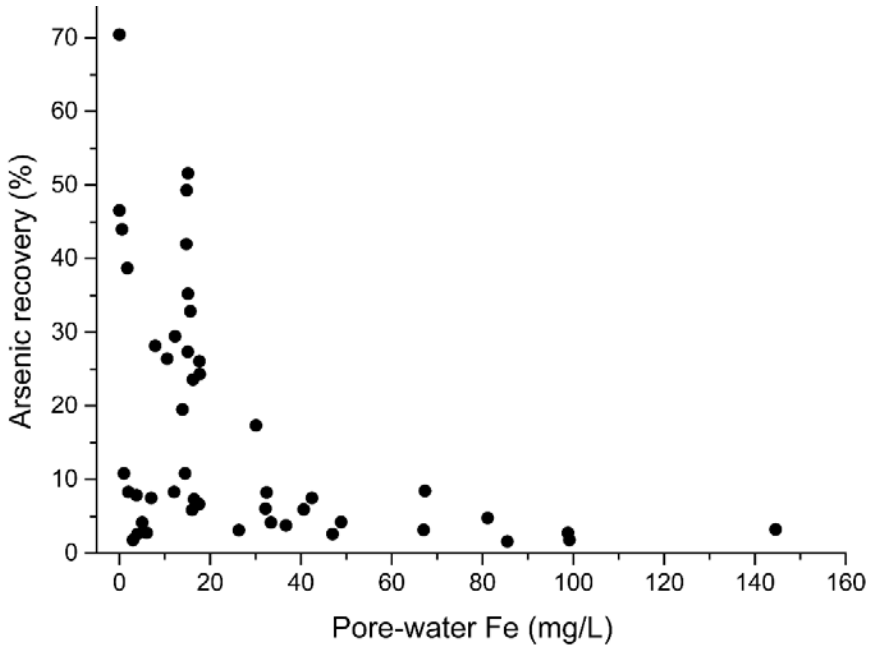


**Figure S4 | Effect of Fe on As recovery for samples from paddy fields in Italy and France.** Arsenic recovery is calculated as sum of As species from flash-frozen samples versus total As in $H_2O_2$-$HNO_3$-stabilized samples.

## 2. Mesocosm rice cultivation experiments – effects of sulfate-fertilization, seeding-practice, and soil type on thioarsenate formation

Looking at the pore-water total As concentrations during rice cultivation in the mesocosm experiments (Fig 2), one can see that over time, pore-water total As concentrations in control treatments decreased from approximately 100 and 50 µg/L at tillering stage in the dry and water seeded mesocosms, respectively, to <20 µg/L around flowering stage (except for the dry seeded Veronica soil where concentrations only dropped after the dough stage, Fig. 2e, f). Highest pore-water As concentrations occurred within days after flooding due to rapid As mobilization by reductive dissolution of Fe(III)-(oxy)hydroxides, and then decreased due to As re-adsorption on or precipitation with newly formed Fe minerals in line with previous reports [8, 9]. The higher As concentrations in dry vs. water seeded treatments at the same sampling date could be explained by an overall less As mobilization in water seeded treatments because they are flooded in May when microbially catalyzed As mobilization is still partially limited by lower temperatures while flooding of dry seeded treatments in June leads to higher As mobilization due to enhanced microbial activity. In addition, the difference could reflect the time it takes for As concentrations after flooding and initial mobilization to drop again due to re-adsorption and precipitation reactions (4 weeks later in dry than in water seeded treatments). No clear trend in the proportion of inorganic or methylated thioarsenates was observed over time (Fig. 2a-d).

**Table S2 |** Soil classification and basic chemical parameters for Veronica and Fornazzo soil

| Parameters | Veronica | Fornazzo |
|---|---|---|
| Geology/geomorphology | Lower river plain | Valley of the Ticino river |
| Parent material | Pleistocene alluvium | Olocene alluvium |
| Soil classification | | |
| USDA | Aeric Endoacquepts coarse-loamy over sandy, mixed, mesic | Histic Humaquepts coarse-loamy, mixed, mesic |
| FAO | Eutric Gleysoil | Umbric Gleysoil |
| Texture | | |
| gravel (%weight) | nd | 23.9 |
| clay % | 2.1 | 1.4 |
| fine silt % | 11.5 | 6.2 |
| coarse silt % | 8.8 | 6.8 |
| fine sand % | 18.2 | 23.7 |
| coarse sand % | 59.3 | 61.8 |
| Cation exchange capacity (cmol /kg) | 9.52 | 14.39 |
| Base saturation (%) | 0.24 | 0.24 |
| Effective base saturation (%) | 0.84 | 0.91 |
| soil pH | 5.6 | 5.8 |
| 0.5 M HCl-extractable Fe (mmol/kg) | 52 | 71 |
| Oxalate-extracted Fe (mmol/kg) | 9.9 | 19.2 |
| C (%) | 2.0 | 4.7 |
| N (%) | 0.6 | 0.5 |
| Total As (mg/kg) | 5.8 | 5.6 |
| Oxalate-extracted As (mg/kg) | 1.4 | 1.5 |
| S (g/kg) | 2.6 | 3.2 |

**Table S3 |** Pore water chemistry at different rice growing stages in the mesocosm experiments (2017) separated by soil type, fertilization (non-sulfate/sulfate), and seeding practice (dry-seeding/wet-seeding) (n=3)

| Pore water parameters | Soil type & Seeding practice | Fertili-zation | Jun 14th | Jul 4th | Jul 18th | Aug 1th | Aug 8th | Aug 22th | Sep 13th |
|---|---|---|---|---|---|---|---|---|---|
| | | | Tillering | Stem elongation | Booting | Flowering | Grain filling | Dough | Mature |
| **pH** | **Veronica** | | | | | | | | |
| | water-seeding | non-sulfate | 6.9 ± 0.1 | 6.8 ± 0.1 | 6.7 ± 0.2 | 6.5 ± 0.1 | 6.5 ± 0.1 | 6.8 ± 0.1 | 6.8 ± 0.1 |
| | | sulfate | 6.9 ± 0.1 | 6.9 ± 0.2 | 6.6 ± 0.1 | 6.8 ± 0.1 | 6.7 ± 0.1 | 7.1 ± 0.1 | 6.8 ± 0.2 |
| | dry-seeding | non-sulfate | 6.8 ± 0.3 | 6.5 ± 0.4 | 6.5 ± 0.1 | 6.4 ± 0.1 | 6.5 ± 0.1 | 6.8 ± 0.3 | 6.6 ± 0.1 |
| | | sulfate | 6.8 ± 0.2 | 6.9 ± 0.1 | 6.7 ± 0.1 | 6.7 ± 0.1 | 6.8 ± 0.2 | 7.0 ± 0.1 | 6.8 ± 0.1 |
| | **Fornazzo** | | | | | | | | |
| | water-seeding | non-sulfate | 7.2 ± 0.2 | 7.3 ± 0.1 | 7.2 ± 0.1 | 7.1 ± 0.1 | 7.2 ± 0.1 | 7.2 ± 0.2 | 7.3 ± 0.2 |
| | | sulfate | 7.0 ± 0.1 | 7.1 ± 0.1 | 6.9 ± 0.1 | 7.1 ± 0.1 | 7.1 ± 0.1 | 7.5 ± 0.1 | 7.1 ± 0.1 |
| | dry-seeding | non-sulfate | 7.0 ± 0.1 | 7.0 ± 0.3 | 7.2 ± 0.1 | 7.0 ± 0.1 | 7.1 ± 0.1 | 7.2 ± 0.1 | 7.4 ± 0.1 |
| | | sulfate | 7.2 ± 0.1 | 7.2 ± 0.2 | 7.3 ± 0.1 | 7.0 ± 0.04 | 7.1 ± 0.1 | 7.3 ± 0.1 | 7.4 ± 0.1 |
| | | | | | | | | | |
| **$E_H$ (mV)** | **Veronica** | | | | | | | | |
| | water-seeding | non-sulfate | 181 ± 85 | 168 ± 62 | 185 ± 56 | 122 ± 5 | 161 ± 9 | 179 ± 19 | 160 ± 26 |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | sulfate | 123 ± 25 | 131 ± 36 | 159 ± 24 | 92 ± 16 | 121 ± 11 | 149 ± 18 | 126 ± 16 |
| | dry-seeding | non-sulfate | 212 ± 44 | 163 ± 9 | 162 ± 11 | 180 ± 98 | 163 ± 5 | 165 ± 11 | 167 ± 24 |
| | | sulfate | 207 ± 59 | 135 ± 30 | 127 ± 47 | 89 ± 30 | 130 ± 17 | 131 ± 31 | 129 ± 16 |
| | **Fornazzo** | | | | | | | | |
| | water-seeding | non-sulfate | 181 ± 81 | 163 ± 15 | 148 ± 59 | 116 ± 19 | 103 ± 19 | 130 ± 36 | 118 ± 26 |
| | | sulfate | 96 ± 2 | 112 ± 50 | 87 ± 7 | 69 ± 10 | 77 ± 20 | 80 ± 11 | 84 ± 13 |
| | dry-seeding | non-sulfate | 287 ± 6 | 211 ± 4 | 132 ± 43 | 111 ± 37 | 126 ± 11 | 135 ± 5 | 130 ± 29 |
| | | sulfate | 163 ± 61 | 143 ± 37 | 193 ± 75 | 109 ± 75 | 119 ± 35 | 146 ± 20 | 143 ± 51 |
| | | | | | | | | | |
| **Conductivity (µS/cm)** | **Veronica** | | | | | | | | |
| | water-seeding | non-sulfate | 533 ± 92 | 325 ± 30 | 504 ± 83 | 580 ± 54 | 777 ± 13 | 667 ± 263 | 601 ± 170 |
| | | sulfate | 745 ± 374 | 382 ± 165 | 455 ± 51 | 412 ± 34 | 493 ± 111 | 386 ± 59 | 567 ± 21 |
| | dry-seeding | non-sulfate | 805 ± 184 | 324 ± 41 | 554 ± 153 | 630 ± 52 | 835 ± 89 | 693 ± 38 | 651 ± 76 |
| | | sulfate | 614 ± 52 | 335 ± 72 | 434 ± 59 | 631 ± 424 | 414 ± 64 | 345 ± 37 | 478 ± 66 |
| | **Fornazzo** | | | | | | | | |
| | water-seeding | non-sulfate | 956 ± 54 | 932 ± 94 | 1128 ± 95 | 1171 ± 118 | 1362 ± 120 | 1392 ± 211 | 1469 ± 223 |
| | | sulfate | 1026 ± 116 | 781 ± 32 | 922 ± 60 | 1038 ± 208 | 955 ± 64 | 1051 ± 147 | 1188 ± 10 |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | dry-seeding | non-sulfate | 723 ± 113 | 909 ± 63 | 1102 ± 24 | 1133 ± 49 | 1281 ± 37 | 1397 ± 125 | 1416 ± 130 |
| | | sulfate | 988 ± 124 | 846 ± 79 | 1483 ± 731 | 876 ± 119 | 841 ± 65 | 866 ± 69 | 1016 ± 102 |
| | | | | | | | | | |
| **TIC (mg/L)[a]** | **Veronica** | | | | | | | | |
| | water-seeding | non-sulfate | 14.2 ± 2.79 | 19.5 ± 1.75 | 15.7 ± 0.96 | 16.7 ± 2.62 | 10.4 ± 1.14 | 15.8 ± 5.37 | 20.4 ± 6.69 |
| | | sulfate | 15.8 ± 4.27 | 15.4 ± 4.62 | 20.3 ± 7.46 | 25.4 ± 5.94 | 33.6 ± 10.4 | 28.7 ± 3.37 | 31.5 ± 3.61 |
| | dry-seeding | non-sulfate | 21.9 ± 8.47 | 18.0 ± 0.8 | 14.1 ± 0.9 | 12.8 ± 1.39 | 13.3 ± 9.72 | 10.5 ± 1.57 | 15.1 ± 0.65 |
| | | sulfate | 19.2 ± 1.69 | 22.3 ± 7.27 | 23.8 ± 6.24 | 25.2 ± 5.07 | 23.5 ± 5.28 | 24.8 ± 3.58 | 25.7 ± 3.73 |
| | **Fornazzo** | | | | | | | | |
| | water-seeding | non-sulfate | 43.1 ± 12.9 | 88.9 ± 7.44 | 90.4 ± 8.63 | 101 ± 12.11 | 82.7 ± 7.89 | 97.0 ± 18.0 | 108 ± 22.4 |
| | | sulfate | 50.4 ± 10.5 | 76.1 ± 3.13 | 77.1 ± 0.79 | 89.3 ± 0.76 | 84.9 ± 9.04 | 99.8 ± 5.25 | 107 ± 5.75 |
| | dry-seeding | non-sulfate | 66.7 ± 24.6 | 79.0 ± 6.86 | 75.8 ± 6.10 | 81.6 ± 12.7 | 62.0 ± 38.6 | 77.9 ± 1.59 | 85.6 ± 1.77 |
| | | sulfate | 86.3 ± 10.8 | 85.1 ± 9.16 | 79.5 ± 6.38 | 83.9 ± 6.11 | 98.3 ± 14.6 | 85.6 ± 6.21 | 89.1 ± 7.56 |
| | | | | | | | | | |
| **TOC (mg/L)[b]** | **Veronica** | | | | | | | | |
| | water-seeding | non-sulfate | 23.0 ± 2.46 | 94.3 ± 25.9 | 102 ± 63.2 | 91.6 ± 60.9 | 73.4 ± 51.0 | 64.9 ± 41.3 | 59.9 ± 32.5 |
| | | sulfate | 30.6 ± 5.57 | 85.8 ± 33.0 | 93.5 ± 44.7 | 95.5 ± 47.8 | 91.6 ± 50.6 | 95.0 ± 53.4 | 92.0 ± 49.4 |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | dry-seeding | non-sulfate | 59.1 ± 21.0 | 58.7 ± 3.22 | 64.2 ± 6.93 | 61.3 ± 1.29 | 49.1 ± 5.30 | 46.0 ± 3.51 | 47.3 ± 3.09 |
| | | sulfate | 47.9 ± 6.44 | 57.3 ± 6.04 | 57.8 ± 6.06 | 57.9 ± 15.7 | 65.8 ± 12.2 | 57.3 ± 25.2 | 51.2 ± 25.6 |
| | **Fornazzo** | | | | | | | | |
| | water-seeding | non-sulfate | 73.9 ± 44.2 | 136 ± 21.0 | 147 ± 48.5 | 131 ± 49.7 | 103 ± 24.2 | 96.4 ± 35.5 | 94.2 ± 34.2 |
| | | sulfate | 56.5 ± 11.0 | 116 ± 26.0 | 111 ± 21.8 | 105 ± 10.8 | 95.8 ± 3.61 | 104 ± 10.1 | 99.9 ± 18.2 |
| | dry-seeding | non-sulfate | 96.5 ± 17.5 | 106 ± 6.54 | 122 ± 9.10 | 118 ± 17.3 | 104 ± 7.21 | 81.0 ± 5.29 | 81.2 ± 10.6 |
| | | sulfate | 96.7 ± 10.3 | 108 ± 2.00 | 113 ± 20.6 | 110 ± 28.6 | 134 ± 38.8 | 106 ± 36.4 | 108 ± 42.6 |
| | | | | | | | | | |
| **$Fe^{II}$(mmol/L)[c]** | **Veronica** | | | | | | | | |
| | water-seeding | non-sulfate | 0.23 ± 0.02 | 0.25 ± 0.01 | 0.29 ± 0.04 | 0.31 ± 0.07 | 0.45 ± 0.03 | 0.34 ± 0.14 | 0.28 ± 0.07 |
| | | sulfate | 0.22 ± 0.03 | 0.27 ± 0.02 | 0.25 ± 0.06 | 0.28 ± 0.07 | 0.34 ± 0.06 | 0.29 ± 0.07 | 0.25 ± 0.06 |
| | dry-seeding | non-sulfate | 0.07 ± 0.04 | 0.20 ± 0.01 | 0.29 ± 0.03 | 0.35 ± 0.03 | 0.48 ± 0.04 | 0.43 ± 0.01 | 0.33 ± 0.00 |
| | | sulfate | 0.08 ± 0.02 | 0.25 ± 0.02 | 0.26 ± 0.01 | 0.26 ± 0.04 | 0.31 ± 0.04 | 0.30 ± 0.04 | 0.24 ± 0.04 |
| | **Fornazzo** | | | | | | | | |
| | water-seeding | non-sulfate | 0.32 ± 0.07 | 0.43 ± 0.04 | 0.43 ± 0.03 | 0.43 ± 0.04 | 0.48 ± 0.03 | 0.41 ± 0.06 | 0.40 ± 0.03 |
| | | sulfate | 0.34 ± 0.05 | 0.40 ± 0.08 | 0.36 ± 0.05 | 0.37 ± 0.06 | 0.40 ± 0.03 | 0.39 ± 0.03 | 0.35 ± 0.04 |
| | dry-seeding | non-sulfate | 0.11 ± 0.04 | 0.34 ± 0.01 | 0.40 ± 0.01 | 0.42 ± 0.04 | 0.49 ± 0.04 | 0.47 ± 0.03 | 0.42 ± 0.04 |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | sulfate | 0.14 ± 0.09 | 0.37 ± 0.05 | 0.37 ± 0.04 | 0.37 ± 0.07 | 0.44 ± 0.08 | 0.40 ± 0.08 | 0.37 ± 0.05 |
| | | | | | | | | | |
| **Total As (µg/L)** | **Veronica** | | | | | | | | |
| | water-seeding | non-sulfate | 48.2 ± 19.5 | 41.2 ± 10.3 | 31.6 ± 10.1 | 17.8 ± 4.89 | 12.1 ± 2.7 | 7.67 ± 1.55 | 5.57 ± 1.30 |
| | | sulfate | 24.2 ± 11.8 | 11.2 ± 1.07 | 9.26 ± 1.73 | 10.2 ± 2.27 | 11.7 ± 2.98 | 9.69 ± 4.03 | 7.58 ± 2.62 |
| | dry-seeding | non-sulfate | 104 ± 9.1 | 83.3 ± 17.9 | 76.4 ± 12.0 | 46.9 ± 13.4 | 31.8 ± 8.53 | 18.4 ± 5.70 | 7.57 ± 1.73 |
| | | sulfate | 72.6 ± 15.2 | 8.04 ± 0.84 | 6.97 ± 0.86 | 7.69 ± 1.05 | 10.0 ± 1.10 | 8.71 ± 1.27 | 5.41 ± 1.25 |
| | **Fornazzo** | | | | | | | | |
| | water-seeding | non-sulfate | 48.0 ± 4.66 | 22.0 ± 2.44 | 19.8 ± 3.80 | 19.7 ± 4.60 | 18.6 ± 4.58 | 15.6 ± 3.34 | 13.3 ± 3.22 |
| | | sulfate | 27.6 ± 4.80 | 18.5 ± 1.07 | 16.0 ± 1.38 | 15.5 ± 0.75 | 15.2 ± 0.55 | 14.1 ± 0.41 | 12.2 ± 0.74 |
| | dry-seeding | non-sulfate | 97.3 ± 7.49 | 61.5 ± 13.5 | 25.3 ± 2.57 | 20.9 ± 0.66 | 19.7 ± 1.27 | 17.0 ± 1.62 | 14.9 ± 1.82 |
| | | sulfate | 76.5 ± 9.82 | 23.4 ± 1.56 | 19.3 ± 1.46 | 17.9 ± 2.19 | 17.0 ± 2.51 | 14.7 ± 2.69 | 12.7 ± 2.78 |

[a] Total inorganic carbon; [b] Total organic carbon;[c] $Fe^{II}$ was spectrophotometricaly determinated via 1,10-phenanthroline method.

**Table S4 |** Mean values for thiolation and methylation (integrated over the seven sampling times) for comparison of factors of increases by sulfate-addition (ratio S/no S) for the two different soil types (Veronica/Fornazzo) and water- vs. dry-seeding

| | **water-seeding** | | | **dry-seeding** | |
|---|---|---|---|---|---|
| **Inorganic thioarsenates** | Veronica | Fornazzo | | Veronica | Fornazzo |
| **contribution to As speciation - no S [%]** | 3.0 | 1.8 | | 0.6 | 1.3 |
| **contribution to As speciation - S [%]** | 4.7 | 5.5 | | 3.9 | 2.6 |
| **ratio S/noS** | 1.5 | 3.1 | | 6.4 | 2.1 |
| | | | | | |
| **Methylated thioarsenates** | Veronica | Fornazzo | | Veronica | Fornazzo |
| **contribution to As speciation - no S [%]** | 0.1 | 0.9 | | 0.2 | 1.0 |
| **contribution to As speciation - S [%]** | 2.1 | 1.4 | | 1.7 | 1.7 |
| **ratio S/noS** | 19.8 | 1.6 | | 11.6 | 1.8 |
| | | | | | |
| **Total Thiolation** | Veronica | Fornazzo | | Veronica | Fornazzo |
| **contribution to As speciation - no S [%]** | 3.1 | 2.7 | | 0.8 | 2.2 |
| **contribution to As speciation - S [%]** | 6.8 | 6.9 | | 5.6 | 4.3 |
| **ratio S/noS** | 2.2 | 2.5 | | 7.4 | 2 |
| | | | | | |
| **Methylated oxyarsenates** | Veronica | Fornazzo | | Veronica | Fornazzo |
| **contribution to As speciation - no S [%]** | 5.0 | 5.6 | | 2.1 | 4.4 |
| **contribution to As speciation - S [%]** | 12.7 | 5.2 | | 11.1 | 6.1 |
| **ratio S/noS** | 2.6 | 0.9 | | 5.3 | 1.4 |

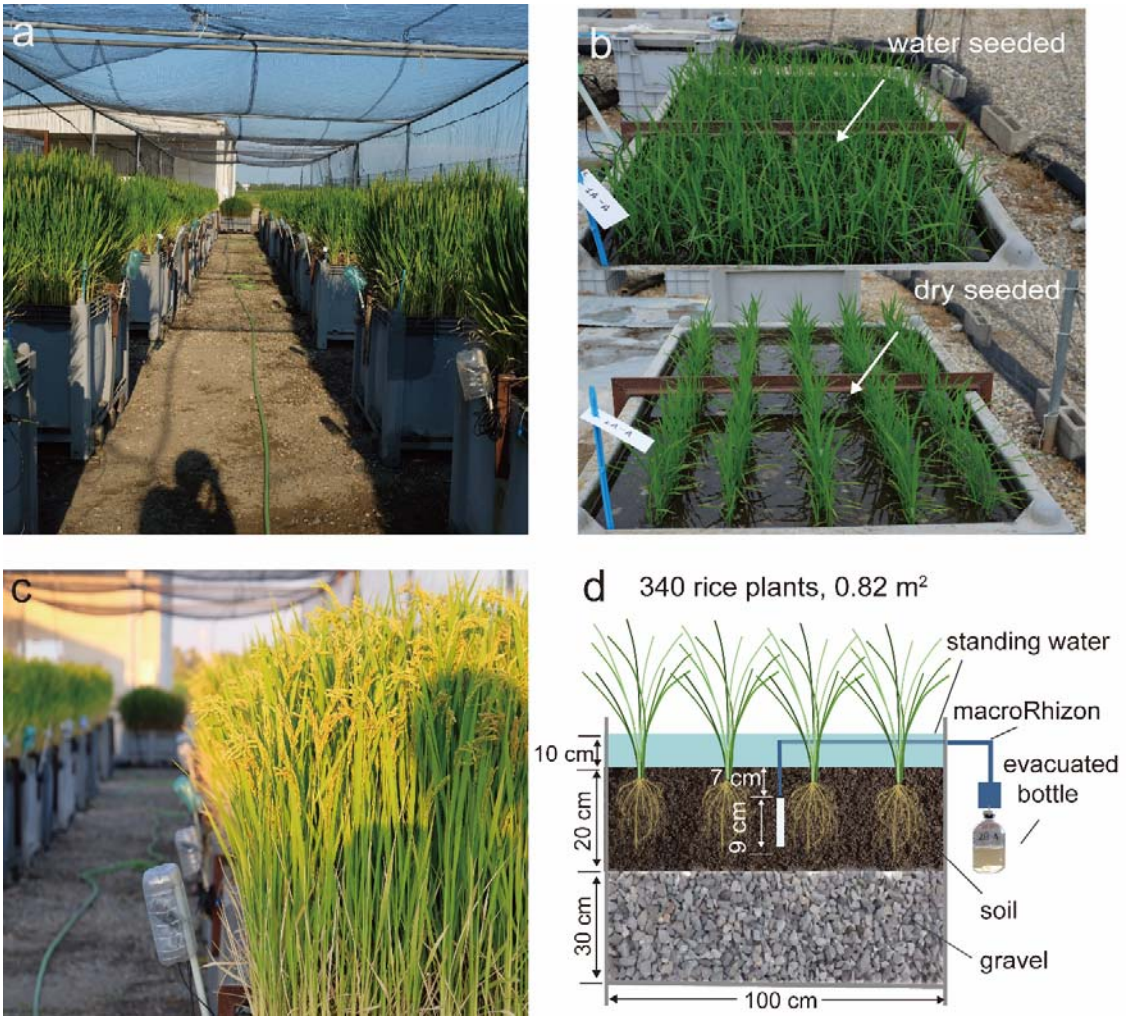


**Figure S5 | Photos and schematic design of the mesocosm rice cultivation experiments.** A total of 24 mesocosms with 2 different soil types, water and dry seeded, with and without sulfate fertilization (each setup conducted in triplicates) were installed at the Rice Research Centre Ente Nazionale Risi in Castello d'Agogna (Pavia, Italy); a) flowering stage; b) seeding practices; c) mature stage; d) scheme of the setup.

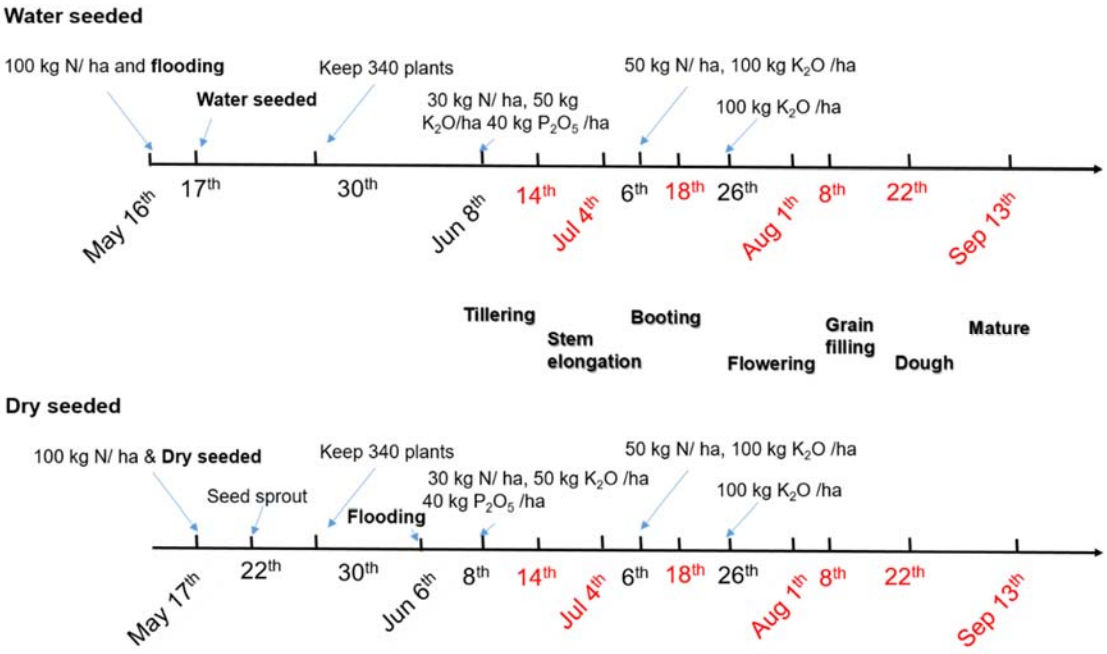


**Figure S6 | Agronomic management of water and dry seeded mesocosm rice cultivation experiments in 2017.** For sulfate treatments, ammonium sulfate and potassium sulfate were applied, while urea and potassium chloride were used equivalent in N and K for control treatments. Dates in red indicate pore-water sampling dates.

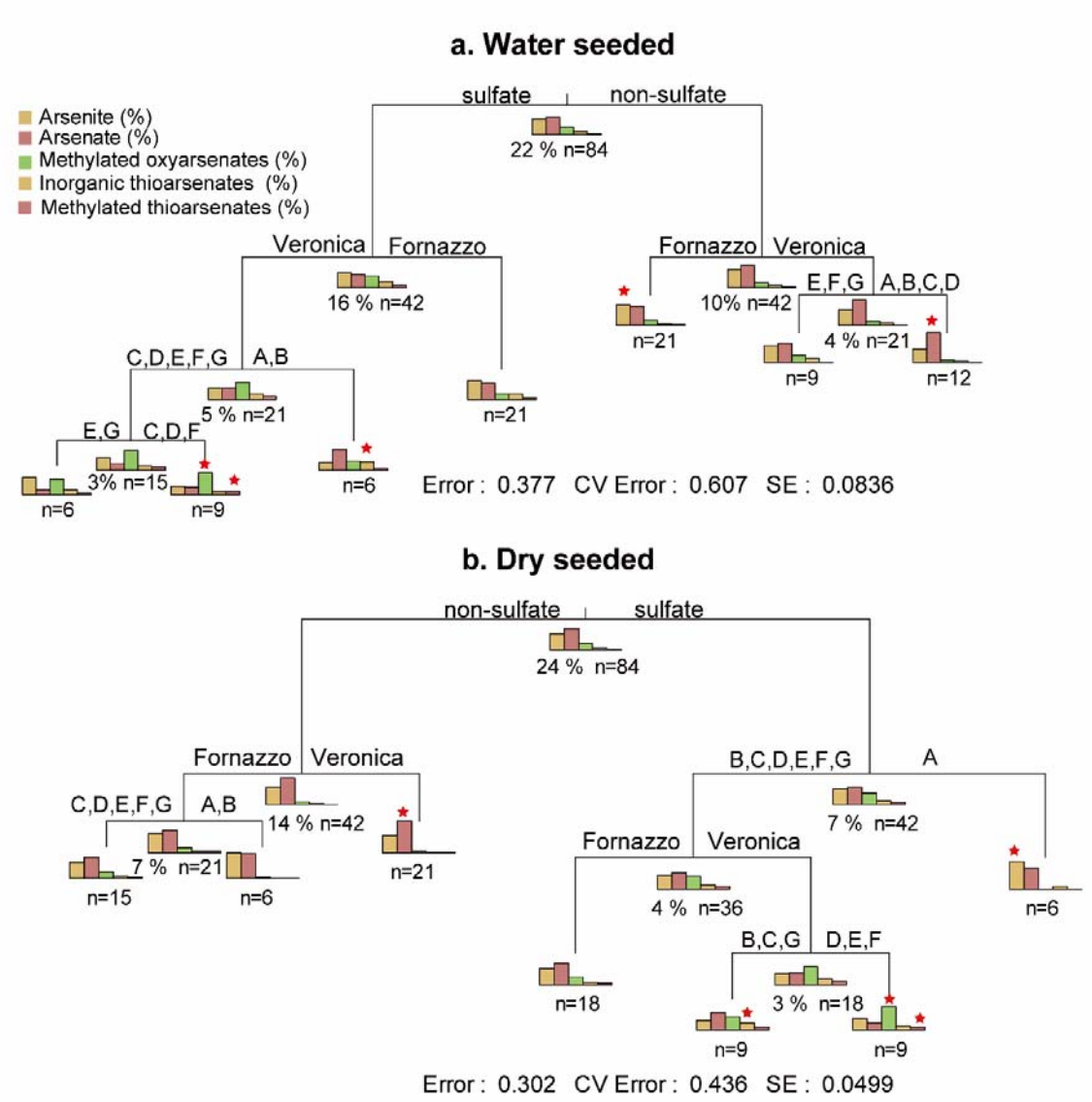


**Figure S7 | Multivariate regression tree for pore-water As speciation in the mesocosm experiments for a) water seeded and b) dry seeded treatments.** Multivariate regression tree analyses were done following previously published methods[10]. Capital letters A-G on the node represent the seven rice growth stages from tillering stage to maturity. Indicator species, based on relative abundance and relative frequency of occurrence of As species, are denoted by stars. Pre-separation in water and dry seeded was done because different redox regimes lead to an offset of growth stages in dry seeded compared to water seeded treatments by about 7-10 days.

## 3. Incubation experiments revealing soil properties that determine the potential for thioarsenate formation

**Table S5a |** Location, parent material, and soil classification of 31 paddy soils sampled in China.

| No. | Location | Longitude | Latitude | Parent material | Soil classification (within the suborder Stagnic Anthrosols[a] ) |
|---|---|---|---|---|---|
| CH1 | Jiangmen, Guangdong | 112º31′09.2″ | 22º30′33.9″ | river alluvium | Fe-accumuli- |
| CH2 | Nanning 2, Guangxi | 108º17′12.6″ | 23º06′22.4″ | limestone | Fe-accumuli- |
| CH3 | Nanning1, Guangxi | 108º16′52.0″ | 23º06′27.6″ | limestone | Fe-accumuli- |
| CH4 | Dehong, Yunnan | 98º25′55.1″ | 24º26′31.11″ | river alluvium | Fe-accumuli- |
| CH5 | Chuxiong, Yunnan | 102º03′5.71″ | 25º11′01.3″ | river alluvium (sandy) | Fe-leachi- |
| CH6 | Ganzhou, Jiangxi | 114º27′11.8″ | 25º26′31.8″ | river alluvium | Fe-accumuli- |
| CH7 | Guiyang, Guizhou | 106º40′17.6″ | 26º20′12.7″ | limestone | Fe-leachi- |
| CH8 | Qiandongnan, Guizhou | 108º03′43.19″ | 26º36′46.71″ | limestone | Fe-leachi- |
| CH9 | Sanming, Fujian | 117º10′30.44″ | 26º50′56.14″ | river alluvium | Fe-accumuli- |
| CH10 | Ji'an, Jiangxi | 114º54′36.0″ | 26º58′21.4″ | river alluvium | Fe-accumuli- |
| CH11 | Zunyi, Guizhou | 106º48′14.5″ | 27º30′13.15″ | limestone | Hapli- |
| CH12 | Yingtan, Jiangxi | 117º15′21.1″ | 28º20′31.1″ | river alluvium | Fe-accumuli- |
| CH13 | Yueyang, Hunan | 113°5'43.8" | 29°14'23.0" | lacustrine deposits | Fe-accumuli- |
| CH14 | Jinhua, Zhejiang | 119º20′34.1″ | 29º01′04.9″ | river alluvium | Hapli- |
| CH15 | Jingzhou, Hubei | 112º 31′49.03″ | 30º 5′53.10″ | river alluvium | Fe-accumuli- |
| CH16 | Hangzhou, Zhejiang | 120º05′13.3″ | 30º28′05.6″ | river alluvium | Fe-accumuli- |
| CH17 | Jiaxing, Zhejiang | 121º07′01.26″ | 30º48′06.3″ | marine sediment | Fe-leachi- |
| CH18 | Zhenjiang, Jiangsu | 119º18′15.47″ | 31º57′58.38″ | river alluvium | Fe-leachi- |
| CH19 | Xuancheng,Anhui | 118º29′55.7″ | 31º00′02.6″ | river alluvium | Hapli- |
| CH20 | Hefei, Anhui | 117º13′28.1″ | 31º35′54.1″ | lacustrine deposits | Fe-accumuli- |

| | | | | | |
|---|---|---|---|---|---|
| CH21 | Xinyang, Henan | 114º59′03″ | 31º54′13″ | river alluvium (loess) | Fe-accumuli- |
| CH22 | Hanzhong, Shaanxi | 106º54′36.15″ | 33º09′37.77″ | loess | Fe-leachi- |
| CH23 | Yancheng, Jingsu | 120º04′10.6″ | 33º16′12.5″ | marine sediment | Fe-accumuli- |
| CH24 | Xuzhou, Jiangsu | 117º24′38.49″ | 34º17′46.59″ | river alluvium | Fe-leachi- |
| CH25 | Lianyungang, Jiangsu | 119º20′06.1″ | 34º32′58.0″ | river alluvium | Fe-leachi- |
| CH26 | Jining, Shandong | 116º33′32.5″ | 35º18′47.7″ | river alluvium | Fe-accumuli- |
| CH27 | Yinchuan, Ningxia | 106º16′0.97″ | 38º10′04.78″ | river alluvium | Hapli- |
| CH28 | Panjin, Liaoning | 122º13′46.6″ | 40º58′26.09″ | marine sediment | Hapli- |
| CH29 | Siping, Jilin | 124º42′29.1″ | 43º28′47.8″ | river alluvium | Hapli- |
| CH30 | Wuchang, Heilongjiang | 127º02′12.9″ | 45º03′42.1″ | river alluvium | Hapli- |
| CH31 | Jiamusi, Heilongjiang | 131º36′34.2″ | 47º11′12.8″ | river alluvium | Hapli- |

[a] Based on the Chinese Soil Taxonomic Classification (adopted by WRB in 1998) all paddy soils used here are classified as Stagnic Anthrosols. Stagnic Anthrosols are anthrosols that have an anthrostagnic moisture regime, and both a hydragric epipedon (including a cultivated horizon and a plowpan) and a hydragric horizon.

**Table S5b |** Geology/geomorphology and climate zones of the 31 paddy fields sampled in China.

| No. | Geology/Geomorphology | Climate Zone |
|---|---|---|
| CH1 | The lower hilly and wide valley basin of Jiangmen | Sub-tropical Monsoon |
| CH2 | The valley plain area of Wuming Basin | Sub-tropical Monsoon |
| CH3 | The valley plain area of Wuming Basin | Sub-tropical Monsoon |
| CH4 | The lower hilly and wide valley basin of Dehong | Sub-tropical Monsoon |
| CH5 | The low mountain and hilly area in Lufeng Basin | Sub-tropical Monsoon |
| CH6 | The lower hilly and wide valley basin of Ganzhou | Sub-tropical Monsoon |
| CH7 | The lower hilly and wide valley basin of Guiyang | Sub-tropical Monsoon |
| CH8 | The lower hilly and wide valley basin of Qiandongnan | Sub-tropical Monsoon |
| CH9 | The lower hilly and wide valley basin of Sanming | Sub-tropical Monsoon |
| CH10 | The lower hilly and wide valley basin of Ji'an | Sub-tropical Monsoon |
| CH11 | The lower hilly and wide valley basin of Zunyi | Sub-tropical Monsoon |
| CH12 | The valley plain area of Xinjiang Basin | Sub-tropical Monsoon |
| CH13 | The low-lying land of lakeshore plain of Dongting Lake | Sub-tropical Monsoon |
| CH14 | The first grade terrace of Xinlixi River in the valley plain area of Jinqu Basin, Eastern China | Sub-tropical Monsoon |
| CH15 | The alluvial and lacustrine plain area of Jianghan Plain, Central China | Sub-tropical Monsoon |
| CH16 | The alluvial-marine plain area in North Zhejiang Plain, Eastern China | Sub-tropical Monsoon |
| CH17 | The alluvial-marine plain area of the Yangtze River Delt | Sub-tropical Monsoon |
| CH18 | The hilly and low-lying area of Zhenjiang in Jiangsu Province, Eastern China | Sub-tropical Monsoon |
| CH19 | The first grade terrace in the valley plain of QingYijiang River | Sub-tropical Monsoon |
| CH20 | The low-lying land of lakeshore plain of Chaohu Lake in Anhui Province, Eastern China | Sub-tropical Monsoon |
| CH21 | The low foothill area of Xinyang in southern margin of North China Plain | Sub-tropical Monsoon |

| | | |
|---|---|---|
| CH22 | The first grade terrace of Bao River in alluvial and lacustrine plain area of the Hanzhong Basin, in southern Shaanxi Province, China | Sub-tropical Monsoon |
| CH23 | The alluvial-marine plain area of Yancheng in North Jiangsu Plain, Eastern China | Sub-tropical Monsoon |
| CH24 | The alluvial and lacustrine plain area of Xuzhou in North China Plain | Temperate Monsoon |
| CH25 | The coastal plain area in North Jiangsu Plain, Eastern China | Temperate Monsoon |
| CH26 | The low-lying land of lakeshore plain of Weishan Lake in North China Plain | Temperate Monsoon |
| CH27 | The first grade terrace of the Yellow River in Yinchuan Plain, Northwest China | Temperate Continental |
| CH28 | The coastal plain area in Liaohe Plain, Northeast China | Temperate Monsoon |
| CH29 | The first grade terrace of East Liao River in Liaohe Plain, Northeast China | Temperate Monsoon |
| CH30 | The interchannel zone between Lalin River and Mangniu River in Song Nen Plain, Northeast China | Temperate Monsoon |
| CH31 | The first grade terrace of Songhua River in Sanjiang Plain, Northeast China | Temperate Monsoon |

**Table S5c |** Basic soil chemistry of the 31 paddy soils sampled in China.

| No. | soil pH | CEC[a] | Clay | SOC[b] | Total As | Chalcophile metals | | | | HCl-extractable Fe | Total zerovalent sulfur[c] | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | Cd | Pb | Cu | Zn | | control | 3 mmol/kg sulfate |
| | | cmol/kg | % | g/kg | mg/kg | | | | | mmol/kg | mmol/kg | |
| CH1 | 5.1 | 4.0 | 16.5 | 27.9 | 6.7 | 0.1 | 9.9 | 3.3 | 35.3 | 31.9 | 0.4 | 1.5 |
| CH2 | 5.6 | 9.2 | 20.3 | 56.5 | 34.2 | 0.3 | 33.3 | 15.7 | 82.3 | 74.7 | 0.9 | 1.9 |
| CH3 | 6.1 | 8.2 | 24.4 | 36.7 | 15.5 | 0.6 | 23.2 | 28.5 | 108.4 | 94.6 | 0.2 | 0.7 |
| CH4 | 6.2 | 9.2 | 33.0 | 25.9 | 5.9 | 0.1 | 24.6 | 11.7 | 87.3 | 84.1 | 2.2 | 2.2 |
| CH5 | 6.9 | 20.0 | 29.8 | 61.6 | 8.2 | 0.7 | 25.3 | 74.4 | 103.4 | 113.3 | 0.6 | 1.9 |
| CH6 | 4.9 | 5.5 | 14.7 | 20.7 | 38.8 | 0.4 | 53.9 | 36.7 | 111.3 | 78.1 | 0.0 | 0.7 |
| CH7 | 6.9 | 15.7 | 13.2 | 104.4 | 15.5 | 0.5 | 26.6 | 31.0 | 142.8 | 69.7 | 0.1 | 1.2 |
| CH8 | 5.8 | 8.2 | 37.5 | 39.7 | 10.3 | 0.2 | 21.1 | 17.5 | 83.7 | 30.0 | 0.2 | 1.3 |
| CH9 | 5.3 | 4.2 | 9.6 | 42.9 | 2.6 | 0.2 | 31.7 | 20.0 | 126.4 | 41.5 | 0.3 | 0.7 |
| CH10 | 4.9 | 5.6 | 17.0 | 25.5 | 8.4 | 0.1 | 19.1 | 14.0 | 63.8 | 106.3 | 0.2 | 0.9 |
| CH11 | 8.0 | 16.6 | 28.6 | 46.8 | 11.1 | 0.6 | 23.0 | 25.3 | 100.1 | 99.4 | 0.7 | 0.8 |
| CH12 | 4.5 | 4.2 | 18.5 | 39.3 | 7.5 | 0.6 | 19.7 | 74.3 | 52.8 | 60.4 | 0.1 | 1.2 |
| CH13 | 5.6 | 9.8 | 17.0 | 14.0 | 15.9 | 0.3 | 29.9 | 21.3 | 89.3 | 129.1 | 0.2 | 1.0 |
| CH14 | 5.5 | 10.9 | 16.9 | 21.4 | 8.0 | 0.2 | 23.2 | 7.9 | 57.4 | 57.2 | 0.3 | 0.9 |
| CH15 | 8.1 | 11.8 | 11.4 | 25.7 | 12.4 | 0.3 | 22.3 | 30.9 | 110.2 | 130.2 | 0.9 | 1.7 |
| CH16 | 6.4 | 16.6 | 43.2 | 35.8 | 6.1 | 0.2 | 24.6 | 24.4 | 79.7 | 98.1 | 0.2 | 1.8 |
| CH17 | 7.0 | 18.3 | 31.1 | 33.7 | 11.0 | 0.2 | 22.8 | 26.6 | 110.5 | 110.7 | 0.2 | 0.8 |
| CH18 | 7.2 | 9.7 | 16.6 | 28.2 | 7.9 | 0.1 | 18.7 | 16.9 | 58.9 | 110.3 | 0.6 | 1.5 |
| CH19 | 5.0 | 10.7 | 24.8 | 34.5 | 9.9 | 0.2 | 23.6 | 14.3 | 62.0 | 90.3 | 0.8 | 1.2 |
| CH20 | 5.7 | 15.7 | 20.6 | 27.6 | 7.0 | 0.1 | 14.8 | 12.5 | 44.1 | 99.5 | 0.4 | 1.3 |
| CH21 | 5.4 | 10.4 | 18.3 | 34.3 | 5.8 | 0.1 | 16.3 | 12.7 | 55.4 | 132.1 | 0.5 | 1.2 |
| CH22 | 5.5 | 12.9 | 21.0 | 38.8 | 9.5 | 0.3 | 20.4 | 19.5 | 77.6 | 142.3 | 0.6 | 1.8 |

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| CH23 | 6.2 | 6.4 | 25.1 | 33.3 | 5.9 | 0.1 | 15.0 | 13.5 | 67.4 | 105.7 | 0.2 | 1.3 |
| CH24 | 7.7 | 15.6 | 13.1 | 32.5 | 11.8 | 0.2 | 16.9 | 19.5 | 76.2 | 115.1 | 1.3 | 2.3 |
| CH25 | 8.9 | 16.3 | 28.3 | 27.2 | 16.5 | 0.2 | 27.9 | 27.1 | 119.6 | 120.4 | 1.4 | 1.6 |
| CH26 | 7.7 | 17.9 | 28.7 | 42.7 | 13.0 | 0.3 | 35.0 | 23.3 | 83.1 | 113.9 | 1.9 | 2.6 |
| CH27 | 8.5 | 4.7 | 10.6 | 17.9 | 11.3 | 0.2 | 12.4 | 15.8 | 61.9 | 79.2 | 2.4 | 3.1 |
| CH28 | 7.2 | 20.6 | 15.8 | 28.4 | 7.9 | 0.1 | 17.9 | 18.1 | 71.4 | 69.5 | 2.0 | 2.8 |
| CH29 | 6.7 | 16.6 | 13.8 | 30.4 | 8.6 | 0.1 | 15.4 | 16.9 | 67.2 | 130.5 | 2.0 | 2.3 |
| CH30 | 6.3 | 18.8 | 25.1 | 45.1 | 9.6 | 0.1 | 17.3 | 19.9 | 68.3 | 146.3 | 0.2 | 1.1 |
| CH31 | 5.9 | 19.0 | 25.3 | 39.5 | 10.0 | 0.1 | 14.9 | 14.0 | 44.8 | 184.7 | 0.3 | 1.0 |

[a] Cation exchange capacity; [b] Soil organic carbon; [c] Total zerovalent sulfur formation after 14 days of soil incubation as described in section 4, which was calculated as sum of aqueous and solid phase zerovalent sulfur for control treatments and 3 mmol/kg sulfate addition treatments, respectively.

**Table S6 |** Spearman's correlation analyses for soil and pore water parameters for anaerobic soil incubations of 31 paddy soils from China and 2 paddy soils from Italy; marked in green are R values with a P-value < 0.05

| **R (control, no S)** | methylated thioarsenates [%] | total thiolation [%] | soil pH | soil-bound zerovalent S [µmol/kg] | HCl-extractable Fe [g/kg] | soil total As [mg/kg] | soil organic carbon [g/kg] | CEC [cmol/kg] | Clay [%] | Total chalcophile metals [mmol/kg] | porewater pH | methylated oxyarsenates [%] | porewater zerovalent S [µmol/l] | porewater As [µg/L] | porewater Fe [mg/L] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| inorganic thioarsenates [%] | 0.22 | 0.85 | 0.58 | 0.46 | -0.10 | -0.18 | -0.10 | 0.17 | -0.25 | -0.04 | 0.44 | -0.01 | 0.25 | -0.48 | -0.89 |
| methylated thioarsenates [%] | | 0.54 | -0.31 | -0.21 | -0.36 | -0.63 | 0.19 | -0.01 | 0.00 | -0.17 | -0.46 | 0.69 | 0.03 | -0.63 | -0.04 |
| total thiolation [%] | | | 0.28 | 0.30 | -0.21 | -0.34 | 0.02 | 0.06 | -0.33 | -0.16 | 0.16 | 0.29 | 0.26 | -0.58 | -0.66 |
| soil pH | | | | 0.54 | 0.33 | 0.32 | 0.06 | 0.54 | 0.08 | 0.21 | 0.87 | -0.54 | -0.03 | -0.12 | -0.79 |
| soil-bound zerovalent S [µmol/kg] | | | | | 0.28 | 0.10 | -0.04 | 0.30 | -0.09 | -0.16 | 0.69 | -0.19 | 0.31 | -0.24 | -0.51 |
| HCl-extractable Fe [g/kg] | | | | | | 0.27 | 0.00 | 0.54 | 0.16 | -0.09 | 0.37 | -0.31 | -0.09 | 0.24 | 0.02 |
| soil total As [mg/kg] | | | | | | | 0.00 | 0.12 | -0.07 | 0.46 | 0.37 | -0.56 | -0.33 | 0.45 | 0.02 |
| soil organic carbon [g/kg] | | | | | | | | 0.30 | 0.36 | 0.32 | 0.04 | 0.12 | -0.02 | -0.24 | 0.06 |
| CEC [cmol/kg] | | | | | | | | | 0.37 | 0.08 | 0.57 | -0.17 | 0.08 | 0.00 | -0.33 |
| Clay [%] | | | | | | | | | | 0.10 | 0.05 | 0.22 | -0.16 | -0.09 | 0.13 |
| Total chalcophile metals [mmol/kg] | | | | | | | | | | | 0.23 | -0.27 | -0.26 | -0.15 | -0.16 |
| porewater pH | | | | | | | | | | | | -0.59 | 0.17 | -0.02 | -0.71 |
| methylated oxyarsenates [%] | | | | | | | | | | | | | 0.07 | -0.41 | 0.23 |
| porewater zerovalent S [µmol/L] | | | | | | | | | | | | | | 0.06 | -0.20 |
| porewater As [µg/L] | | | | | | | | | | | | | | | 0.33 |

| **P-Value (control, no S)** | methylated thioarsenates [%] | total thiolation [%] | soil pH | soil-bound zerovalent S [µmol/kg] | HCl-extractable Fe [g/kg] | soil total As [g/kg] | soil organic carbon [g/kg] | CEC [cmol/kg] | Clay [%] | Total chalcophile metals [mmol/kg] | porewater pH | methylated oxyarsenates [%] | porewater zerovalent S [µmol/l] | porewater As [µg/L] | porewater Fe [mg/L] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| inorganic thioarsenates [%] | 0.22 | 0.00 | 0.00 | 0.01 | 0.57 | 0.32 | 0.58 | 0.35 | 0.17 | 0.85 | 0.01 | 0.97 | 0.17 | 0.01 | 0.00 |
| methylated thioarsenates [%] | | 0.00 | 0.08 | 0.23 | 0.04 | 0.00 | 0.30 | 0.95 | 1.00 | 0.36 | 0.01 | 0.00 | 0.86 | 0.00 | 0.85 |
| total thiolation [%] | | | 0.11 | 0.09 | 0.24 | 0.05 | 0.93 | 0.75 | 0.07 | 0.39 | 0.38 | 0.10 | 0.15 | 0.00 | 0.00 |
| soil pH | | | | 0.00 | 0.06 | 0.07 | 0.74 | 0.00 | 0.69 | 0.26 | 0.00 | 0.00 | 0.89 | 0.52 | 0.00 |
| soil-bound zerovalent S [µmol/kg] | | | | | 0.12 | 0.56 | 0.82 | 0.10 | 0.64 | 0.38 | 0.00 | 0.29 | 0.08 | 0.20 | 0.00 |
| HCl-extractable Fe [g/kg] | | | | | | 0.14 | 0.98 | 0.00 | 0.40 | 0.64 | 0.04 | 0.07 | 0.62 | 0.19 | 0.91 |
| soil total As [mg/kg] | | | | | | | 1.00 | 0.52 | 0.72 | 0.01 | 0.04 | 0.00 | 0.06 | 0.01 | 0.90 |
| soil organic carbon [g/kg] | | | | | | | | 0.10 | 0.05 | 0.08 | 0.85 | 0.50 | 0.93 | 0.20 | 0.75 |
| CEC [cmol/kg] | | | | | | | | | 0.04 | 0.65 | 0.00 | 0.37 | 0.68 | 1.00 | 0.07 |
| Clay [%] | | | | | | | | | | 0.60 | 0.79 | 0.23 | 0.38 | 0.61 | 0.49 |
| Total chalcophile metals [mmol/kg] | | | | | | | | | | | 0.22 | 0.15 | 0.16 | 0.42 | 0.40 |
| porewater pH | | | | | | | | | | | | 0.00 | 0.36 | 0.92 | 0.00 |
| methylated oxyarsenates [%] | | | | | | | | | | | | | 0.69 | 0.02 | 0.19 |
| porewater zerovalent S [µmol/L] | | | | | | | | | | | | | | 0.74 | 0.25 |
| porewater As [µg/L] | | | | | | | | | | | | | | | 0.07 |

| **R (Sulfate Treatment)** | methylated thioarsenates [%] | total thiolation [%] | soil pH | soil-bound zerovalent S [µmol/kg] | HCl-extractable Fe [g/kg] | soil total As [mg/kg] | soil organic carbon [g/kg] | CEC [cmol/kg] | Clay [%] | Total chalcophile metals [mmol/kg] | porewater pH | methylated oxyarsenates [%] | porewater zerovalent S [µmol/l] | porewater As [µg/L] | porewater Fe [mg/L] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| inorganic thioarsenates [%] | 0.08 | 0.91 | 0.59 | 0.35 | -0.07 | -0.14 | -0.16 | 0.18 | -0.17 | -0.03 | 0.63 | -0.06 | -0.19 | -0.39 | -0.86 |
| methylated thioarsenates [%] | | 0.40 | -0.41 | -0.33 | -0.35 | -0.67 | 0.21 | -0.02 | 0.02 | -0.21 | -0.34 | 0.72 | -0.13 | -0.46 | 0.27 |
| total thiolation [%] | | | 0.38 | 0.21 | -0.22 | -0.34 | -0.06 | 0.11 | -0.20 | -0.11 | 0.52 | 0.18 | -0.23 | -0.50 | -0.73 |
| soil pH | | | | 0.49 | 0.33 | 0.32 | 0.06 | 0.54 | 0.08 | 0.21 | 0.66 | -0.47 | -0.07 | -0.05 | -0.90 |
| soil-bound zerovalent S [µmol/kg] | | | | | 0.21 | 0.12 | -0.04 | 0.25 | -0.04 | -0.15 | 0.44 | -0.30 | 0.25 | -0.26 | -0.54 |
| HCl-extractable Fe [g/kg] | | | | | | 0.26 | 0.00 | 0.54 | 0.15 | -0.09 | 0.39 | -0.38 | 0.07 | 0.29 | -0.07 |
| soil total As [mg/kg] | | | | | | | 0.00 | 0.12 | -0.07 | 0.46 | 0.09 | -0.67 | -0.17 | 0.47 | -0.08 |
| soil organic carbon [g/kg] | | | | | | | | 0.30 | 0.36 | 0.32 | -0.15 | 0.09 | 0.05 | -0.21 | -0.01 |
| CEC [cmol/kg] | | | | | | | | | 0.37 | 0.08 | 0.38 | -0.26 | 0.11 | 0.07 | -0.39 |
| Clay [%] | | | | | | | | | | 0.10 | -0.18 | 0.17 | 0.25 | -0.09 | 0.11 |
| Total chalcophile metals [mmol/kg] | | | | | | | | | | | -0.02 | -0.22 | -0.12 | -0.14 | -0.16 |
| porewater pH | | | | | | | | | | | | -0.36 | -0.03 | -0.04 | -0.69 |
| methylated oxyarsenates [%] | | | | | | | | | | | | | -0.14 | -0.46 | 0.34 |
| porewater zerovalent S [µmol/L] | | | | | | | | | | | | | | -0.04 | 0.03 |
| porewater As [µg/L] | | | | | | | | | | | | | | | 0.34 |

| **P-Value (Sulfate Treatment)** | methylated thioarsenates [%] | total thiolation [%] | soil pH | soil-bound zerovalent S [µmol/kg] | HCl-extractable Fe [g/kg] | soil total As [mg/kg] | [g/kg] | CEC [cmol/kg] | Clay [%] | Total chalcophile metals [mmol/kg] | porewater pH | methylated oxyarsenates [%] | porewater zerovalent S [µmol/l] | porewater As [µg/L] | porewater Fe [mg/L] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| inorganic thioarsenates [%] | 0.65 | 0.00 | 0.00 | 0.04 | 0.68 | 0.44 | 0.37 | 0.34 | 0.35 | 0.86 | 0.00 | 0.74 | 0.28 | 0.03 | 0.00 |
| methylated thioarsenates [%] | | 0.02 | 0.02 | 0.06 | 0.05 | 0.00 | 0.25 | 0.90 | 0.90 | 0.26 | 0.06 | 0.00 | 0.46 | 0.01 | 0.16 |
| total thiolation [%] | | | 0.03 | 0.23 | 0.22 | 0.05 | 0.73 | 0.56 | 0.27 | 0.56 | 0.00 | 0.32 | 0.20 | 0.00 | 0.00 |
| soil pH | | | | 0.00 | 0.06 | 0.07 | 0.74 | 0.00 | 0.69 | 0.26 | 0.00 | 0.01 | 0.68 | 0.79 | 0.00 |
| soil-bound zerovalent S [µmol/kg] | | | | | 0.25 | 0.49 | 0.81 | 0.18 | 0.82 | 0.41 | 0.01 | 0.09 | 0.16 | 0.15 | 0.00 |
| HCl-extractable Fe [g/kg] | | | | | | 0.14 | 0.99 | 0.00 | 0.41 | 0.62 | 0.03 | 0.03 | 0.71 | 0.12 | 0.72 |
| soil total As [mg/kg] | | | | | | | 1.00 | 0.52 | 0.72 | 0.01 | 0.65 | 0.00 | 0.33 | 0.01 | 0.69 |
| soil organic carbon [g/kg] | | | | | | | | 0.10 | 0.05 | 0.08 | 0.41 | 0.63 | 0.77 | 0.27 | 0.95 |
| CEC [cmol/kg] | | | | | | | | | 0.04 | 0.65 | 0.03 | 0.16 | 0.56 | 0.71 | 0.04 |
| Clay [%] | | | | | | | | | | 0.60 | 0.33 | 0.36 | 0.17 | 0.64 | 0.57 |
| Total chalcophile metals [mmol/kg] | | | | | | | | | | | 0.89 | 0.23 | 0.51 | 0.46 | 0.41 |
| porewater pH | | | | | | | | | | | | 0.05 | 0.87 | 0.82 | 0.00 |
| methylated oxyarsenates [%] | | | | | | | | | | | | | 0.42 | 0.01 | 0.08 |
| porewater zerovalent S [µmol/L] | | | | | | | | | | | | | | 0.81 | 0.88 |
| porewater As [µg/L] | | | | | | | | | | | | | | | 0.07 |

**Table S7 |** Relative importance of predictor values for the occurrence of inorganic and methylated thioarsenates (%) using multiple linear regression analysis with soil physical and chemical properties separated by control (no S) and sulfate-addition (S) incubations; for methylated thioarsenates two models were used, one including the share of methylated oxyarsenates in the pore water and one only using soil parameters; significance levels (sig. level) are indicated as *** (0-0.001), ** (0.001-0.01), * (0.01-0.05), and . (0.1-1)

| **Control (no S)** | **weight factor %** | **lower 95% range [%]** | **upper 95% range [%]** | **sig. level** |
|---|---|---|---|---|
| **inorganic thioarsenates** | | | | |
| CEC [cmol/kg] | 13.6 | 1.7 | 30.2 | ** |
| Clay [%] | -18.3 | -3.3 | -40.6 | ** |
| HCl-extractable Fe [g/kg] | -6 | -1.1 | -16.6 | * |
| {H+} [mol/L] | -4.4 | -2.8 | -14.5 | |
| zerovalent S [µmol/kg] | 50.8 | 17.8 | 74.9 | *** |
| SOC [g/kg] | -4.5 | -0.9 | -11.2 | |
| total soil As [mg/kg] | -1.3 | -0.4 | -8.1 | |
| Total chalcophile metals [mmol/kg] | -1.1 | -0.5 | -8.2 | |
| $r^2 = 0.7352$, $p = 7.1*10^{-5}$ | | | | |

| **methylated thioarsenates + oxyarsenates** | | | | |
|---|---|---|---|---|
| **CEC [cmol/kg]** | **3.2** | 1.6 | 24.5 | |
| Clay [%] | -9.8 | -1.1 | -21.6 | * |
| HCl-extractable Fe [g/kg] | -10.8 | -3.3 | -29.1 | |
| {H+} [mol/L] | -1.8 | -0.9 | -10.9 | |
| zerovalent S [µmol /kg] | -3.2 | -0.8 | -20.4 | |
| SOC [g/kg] | -0.8 | -0.7 | -9.4 | |
| total soil As [mg/kg] | -18.8 | -8.8 | -30.3 | * |
| Total chalcophile metals [mmol/kg] | 5.7 | 2.3 | 23 | * |
| methylated oxyarsenates [%] | 45.9 | 8.2 | 55.7 | ** |
| $r^2 = 0.6902$, $p = 8.9*10^{-4}$ | | | | |

| **methylated thioarsenates - oxyarsenates** | | | | |
|---|---|---|---|---|
| CEC [cmol/kg] | -6 | -1.6 | -25.7 | |
| Clay [%] | -10.1 | -1 | -23.8 | . |

| | | | | |
|---|---|---|---|---|
| HCl-extractable Fe [g/kg] | -26.9 | -3.9 | -45.4 | * |
| {H+} [mol/L] | -4 | -1.3 | -19.6 | |
| zerovalent S [µmol /kg] | -6.7 | -0.9 | -30.3 | |
| SOC [g/kg] | -1 | -0.8 | -15.6 | |
| total soil As [mg/kg] | -40.4 | -12.3 | -49.1 | ** |
| Total chalcophile metals [mmol/kg] | 4.9 | 2.6 | 37.1 | |
| $r^2 = 0.5022$, $p = 2.8*10^{-2}$ | | | | |

| **Sulfate treatment** | **weight factor %** | **lower 95% range [%]** | **upper 95% range [%]** | **sig. level** |
|---|---|---|---|---|
| **inorganic thioarsenates** | | | | |
| CEC [cmol/kg] | 20.6 | 3 | 30.6 | ** |
| Clay [%] | -12.6 | -1.6 | -31.5 | * |
| HCl-extractable Fe [g/kg] | -8.8 | -1.8 | -19.4 | * |
| {H+} [mol/L] | -4.2 | -2.7 | -17.3 | |
| zerovalent S [µmol /kg] | 46.1 | 21 | 68.6 | ** |
| SOC [g/kg] | -6.3 | -1.1 | -15.5 | * |
| total soil As [mg/kg] | -0.8 | -0.4 | -10.4 | |
| Total chalcophile metals [mmol/kg] | -0.8 | -0.5 | -7.7 | |
| $r^2 = 0.674$, $p = 5.6*10^{-4}$ | | | | |

| **methylated thioarsenates + oxyarsenates** | | | | |
|---|---|---|---|---|
| CEC [cmol/kg] | 4.3 | 1.5 | 14.6 | |
| Clay [%] | -1.5 | -0.5 | -17.5 | |
| HCl-extractable Fe [g/kg] | -12.9 | -3.2 | -21 | |
| {H+} [mol/L] | -0.8 | -0.5 | -15.4 | |
| zerovalent S [µmol /kg] | -3.7 | -0.6 | -13.6 | |
| SOC [g/kg] | -0.3 | -0.4 | -8.2 | |
| total soil As [mg/kg] | -11.2 | -4.7 | -23.6 | |
| Total chalcophile metals [mmol/kg] | 1.5 | 0.6 | 19.9 | |
| methylated oxyarsenates [%] | 63.8 | 21.2 | 65.8 | *** |
| $r^2 = 0.8304$, $p = 2.8*10^{-6}$ | | | | |

| **methylated thioarsenates - oxyarsenates** | | | | |
|---|---|---|---|---|
| CEC [cmol/kg] | -8.3 | -1.8 | -19.6 | |
| Clay [%] | -1.9 | -0.6 | -29.4 | |
| HCl-extractable Fe [g/kg] | -39.1 | -3.6 | -47.3 | * |
| {H+} [mol/L] | -1.7 | -1.2 | -27.5 | |
| zerovalent S [µmol /kg] | -10.9 | -0.9 | -28 | . |
| SOC [g/kg] | -0.8 | -0.8 | -14.9 | |
| total soil As [mg/kg] | -33.1 | -9.3 | -49.7 | * |
| Total chalcophile metals [mmol/kg] | 4.1 | 1.1 | 40.9 | |
| $r^2 = 0.5151$, $p = 2.2*10^{-2}$ | | | | |

Note: Implications of HCl-extractable Fe, pH, zerovalent S, total soil As, and methylated oxyarsenates are discussed in the main manuscript; the reasons for the sig. negative impact of clay on both inorganic and methylated thioarsenates and the sig. positive impact of CEC (Cation Exchange Capacity) on inorganic thioarsenates are currently unclear. The correlation with CEC might be in line with previous observations of high ionic strengths increasing the kinetics of inorganic thioarsenate formation from arsenite and reduced sulfur in solution. [11, 12]

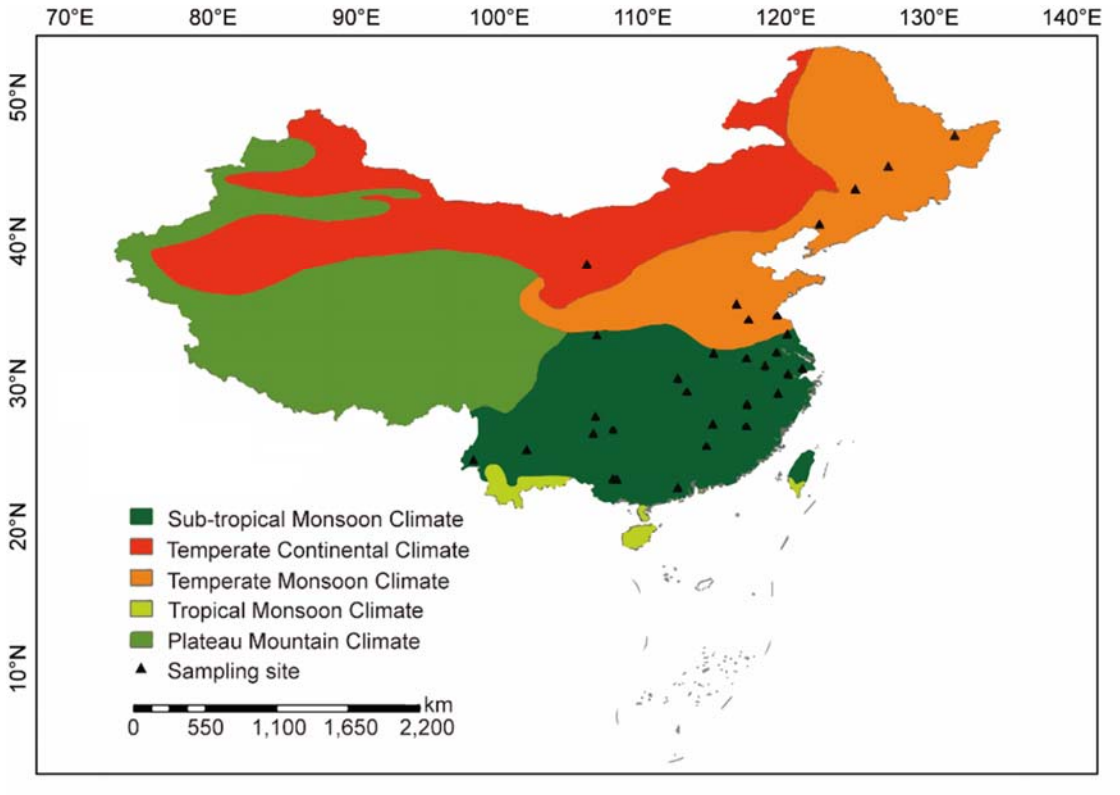


**Figure S8 | Sampling sites of 31 paddy fields in different climate zones over China.** The geographic origins covered an area from 22.5° to 47.2° N and 98.4° to 131.6° E, spanning climate zones from sub-tropical monsoon climate (23 fields) to temperate continental climate (1 fields) and temperate monsoon climate (7 fields).The base map used is from the National Fundamental Geographic Information System of China.

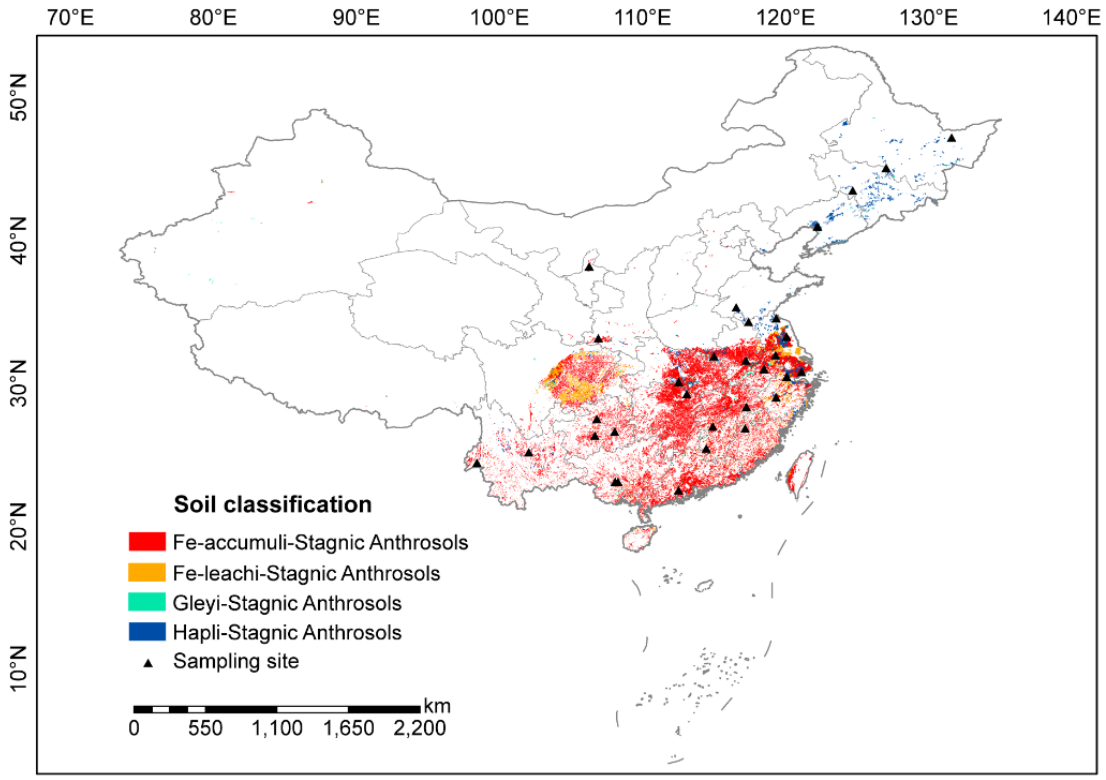


**Figure S9 | Sampling sites of 31 paddy fields based on soil classification over China.** The colored background indicates the distribution of Stagnic Anthrosols in China. Based on Chinese Soil Taxonomic Classification (adopted by WRB in 1998), all paddy soils used here are classified as Stagnic Anthrosols, including Fe-accumuli- (15 soils), Fe-leachi-(8 soils ), Hapli- (8 soils) Stagnic Anthrosols. Stagnic Anthrosols are anthrosols that have an anthrostagnic moisture regime and have both a hydragric epipedon (including a ultivated horizon and a plowpan) and a hydragric horizon. The base map used is from the National Fundamental Geographic Information System of China.

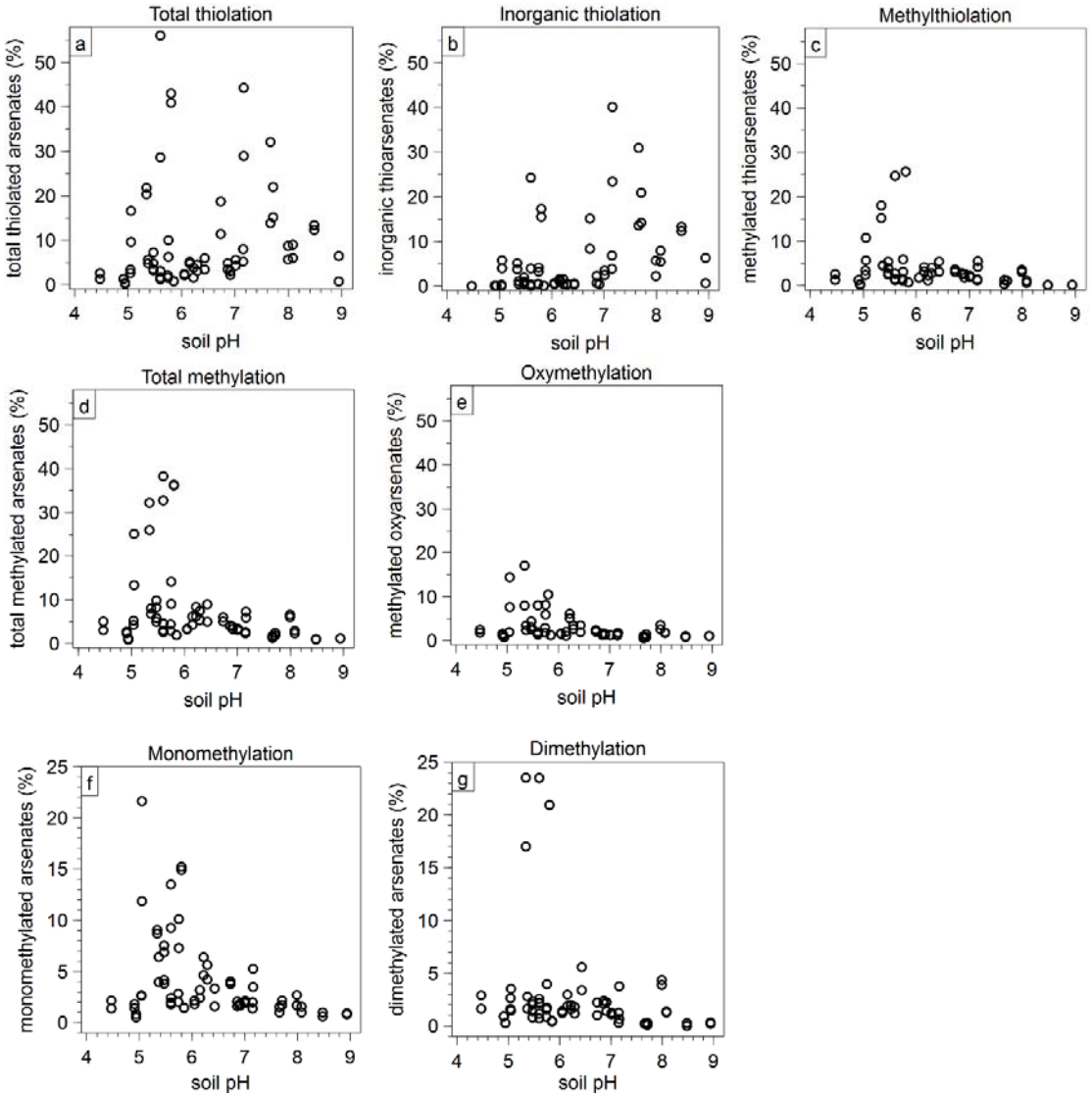


**Figure S10 | Summarized As speciation determined in anaerobic soil incubations in relation to soil pH.** Data from control and sulfate addition for 31 paddy soils from China and 2 paddy soils from Italy were combined. a) total thiolation which is the sum of b) inorganic thiolation and c) methylthiolation; d) total methylation which is the sum of e) oxymethylation and c) methylthiolation; f) all mono- and g) all dimethylated arsenates (integrating oxy and thio species).

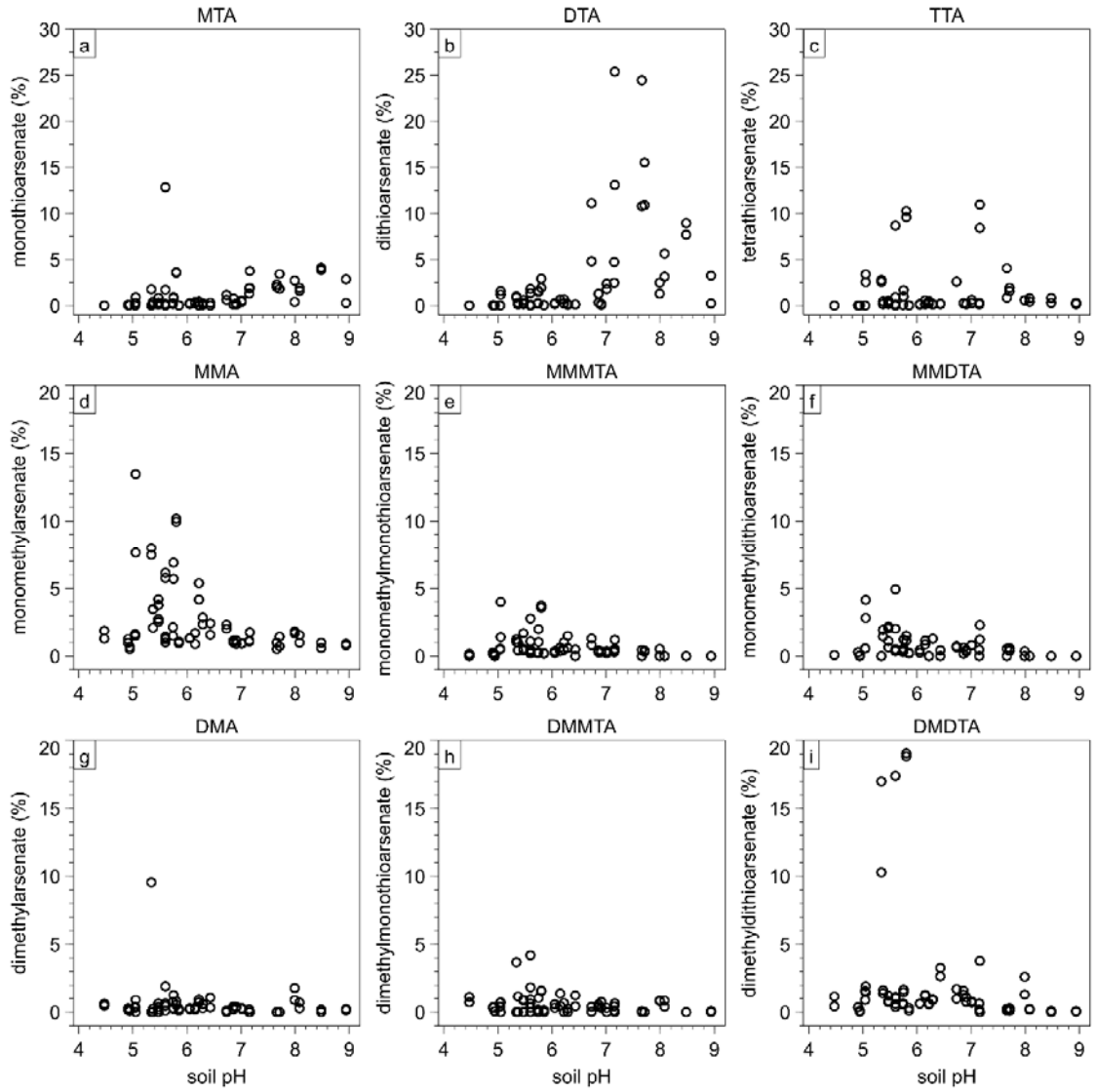


**Figure S11 | Individual As speciation of inorganic thioarsenates in anaerobic soil incubations in relation to soil pH**. a) MTA, b) DTA, c) TTA, d) monomethylated oxy- (MMA) and thioarsenates e) MMMTA, f) MMDTA) and g) dimethylated oxy- (DMA), and thioarsenates h) DMMTA, i) DMDTA .Data from control and sulfate addition for 31 paddy soils from China and 2 paddy soils from Italy were combined.

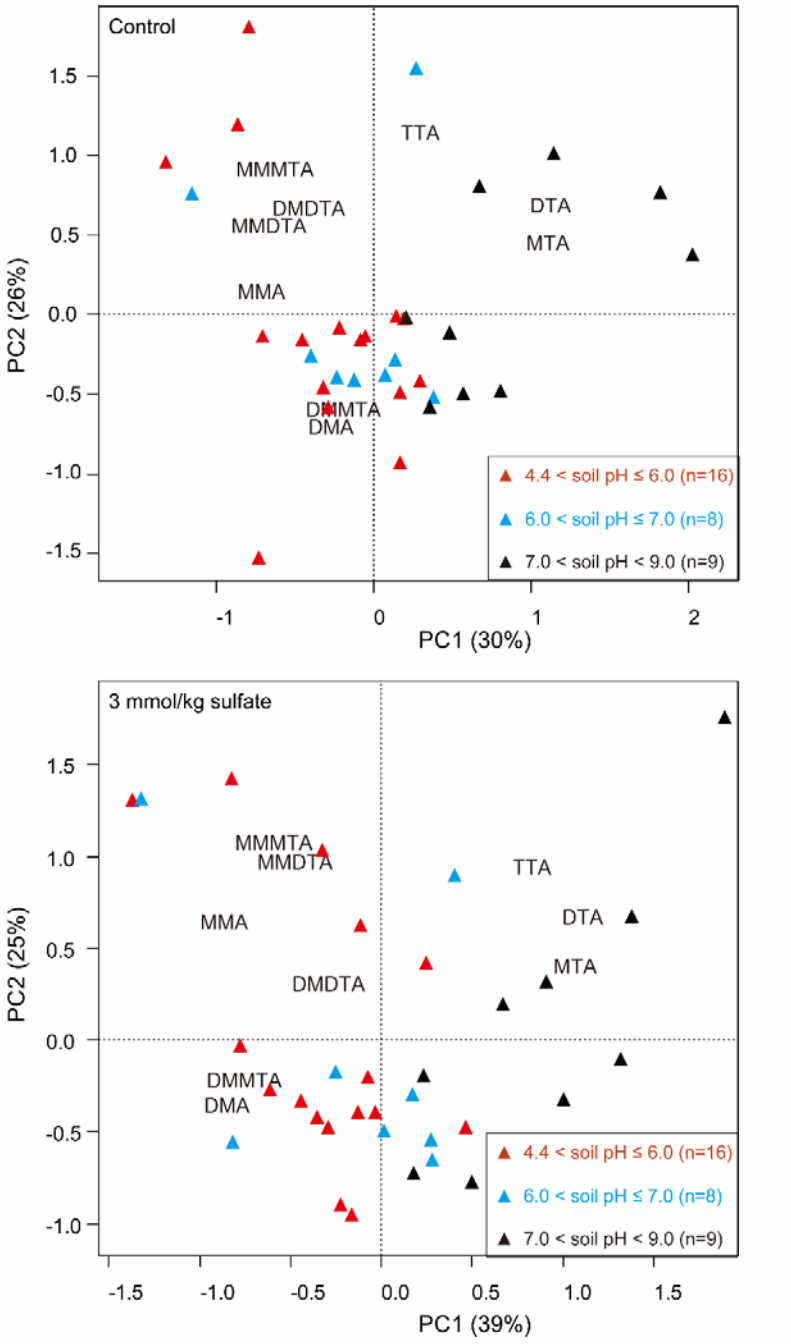


**Figure S12 | Principal component analysis of As speciation in anaerobic soil incubations.** Site distribution reveals clustering of methylated oxyarsenates (DMA and MMA) and methylated thioarsenates (DMDTA, MMDTA, MMMTA, DMMTA) with low pH soils and inorganic thioarsenates (MTA, DTA, and TTA) with high pH soils during anaerobic incubation of 31 paddy soils from China and 2 paddy soils from Italy; a) control treatment and b) sulfate addition.

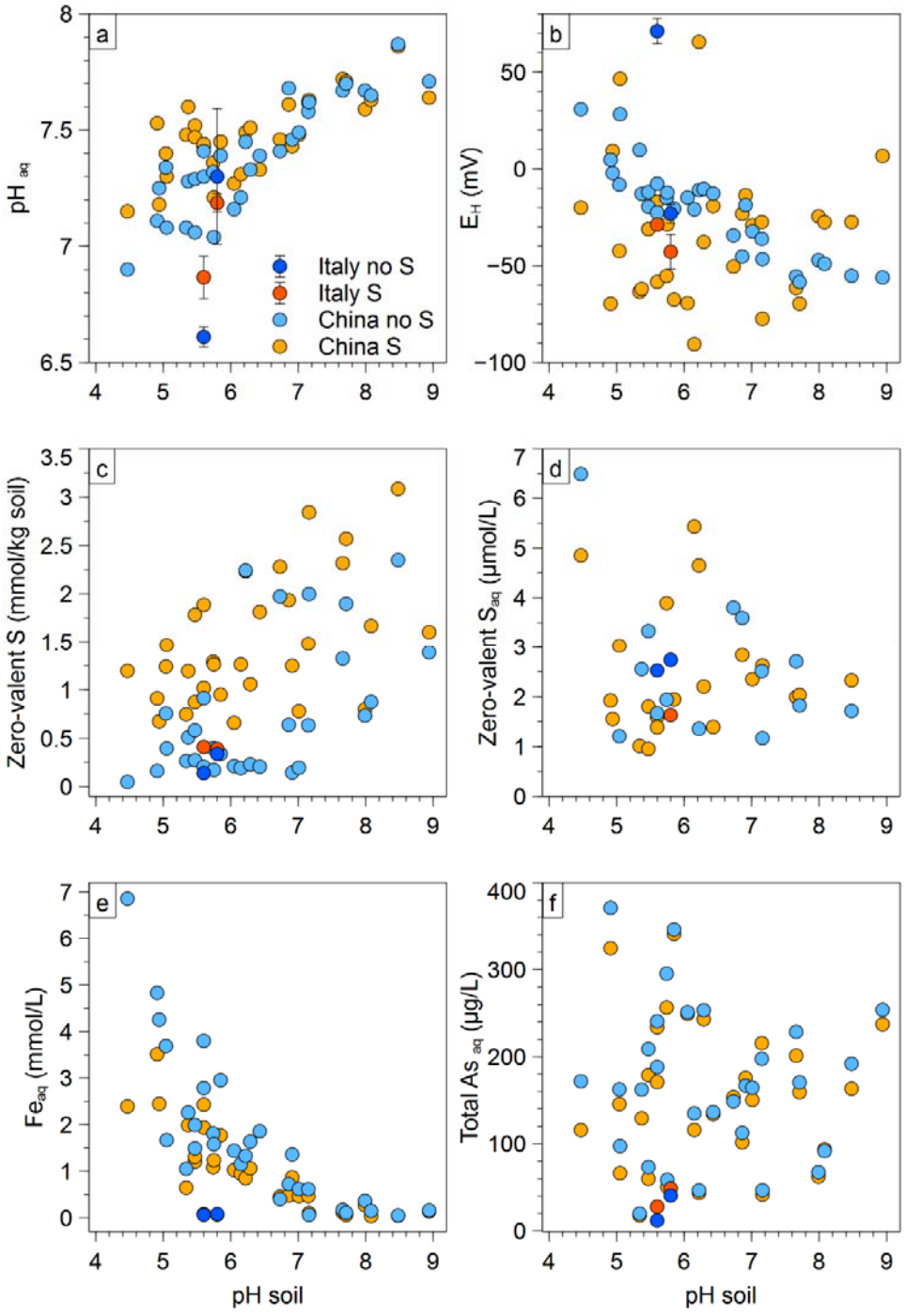


**Figure S13 | Pore-water chemistry for anaerobic soil incubations as a function of soil pH.** a) pore-water pH, b) $E_H$, c) solid phase zero-valent S, d) aqueous zero-valent S, e) total dissolved Fe, and f) total dissolved As for anaerobic soil incubations of 31 paddy soils from China and 2 paddy soils from Italy (experimental triplicates); blue colors refer to control treatments (no S), orange-red colors to sulfate addition (S).

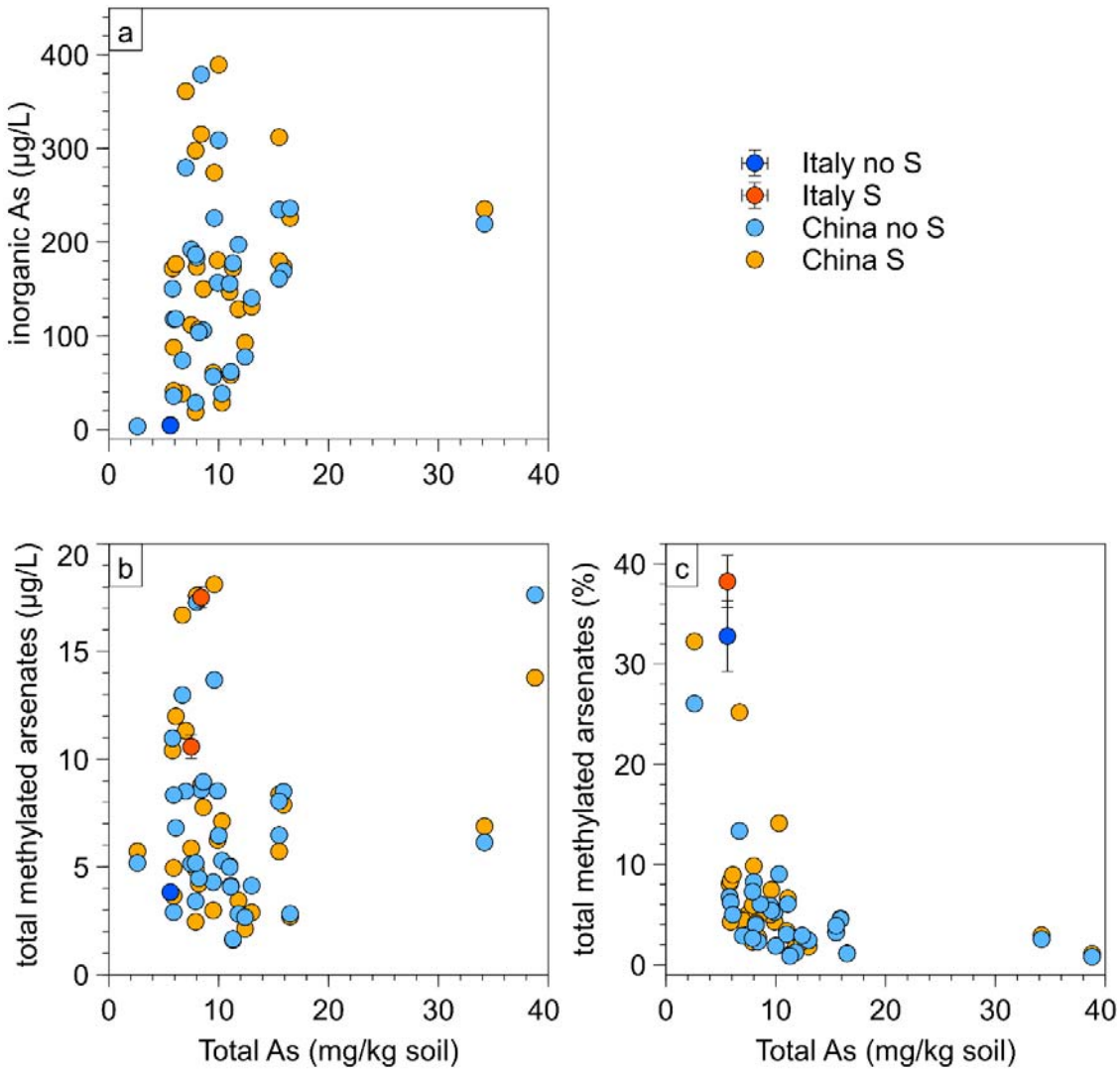


**Figure S14 | Absolute and relative concentrations of inorganic As (a, b) and methylated oxyarsenates (c, d) in relation to total soil As.** Anaerobic soil incubations were conducted with 31 paddy soils from China and 2 paddy soils from Italy (experimental triplicates); blue colors refer to control treatments (no S), orange-red colors to sulfate addition (S).

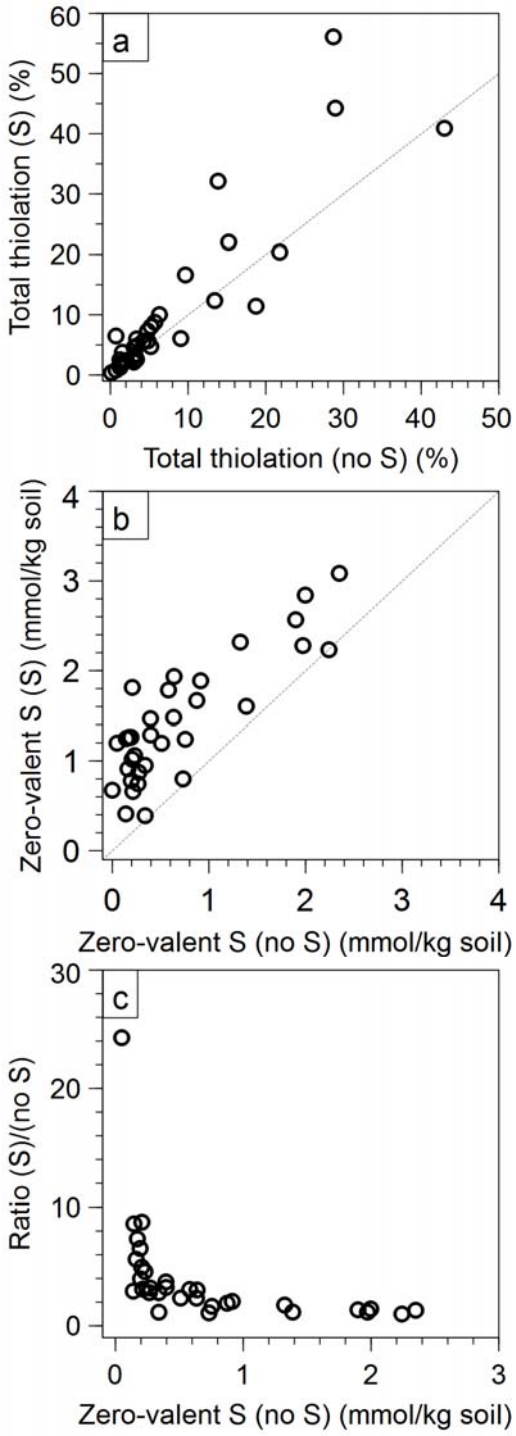


**Figure S15 | Effects of sulfate addition on arsenic thiolation and zero-valent S formation.** Comparison of a) total thiolation (%) and b) solid phase zero-valent S with and without sulfate addition; c) ratio of zero-valent S increase from control to sulfate-treatment versus original zero-valent S concentrations in control for anaerobic soil incubations of 31 paddy soils from China and 2 paddy soils from Italy.

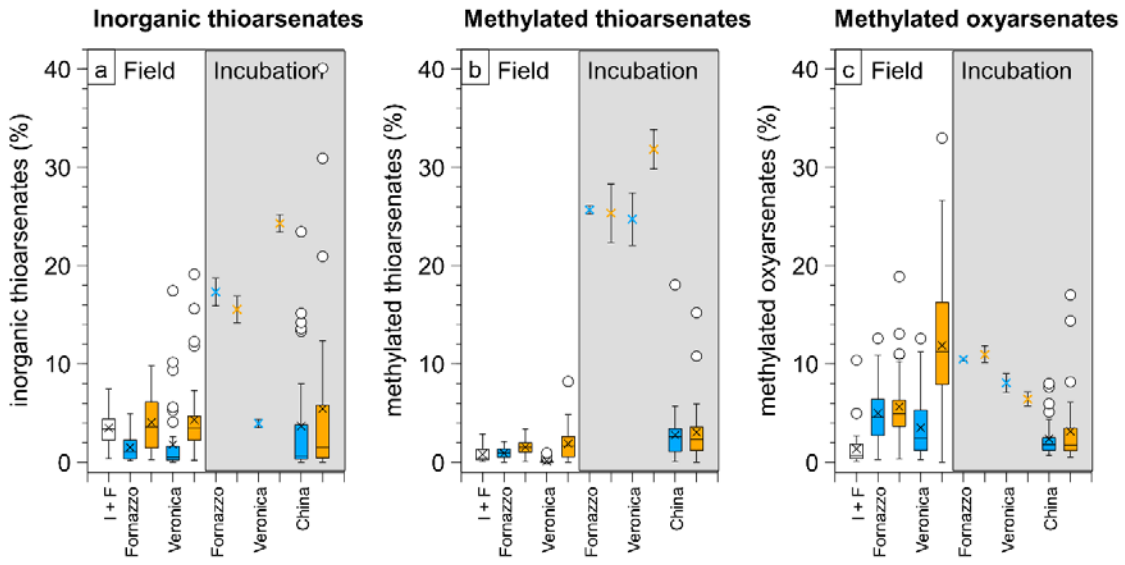


**Figure S16 | Comparison of arsenic speciation in anaerobic soil incubations to mesocosm experiments and field survey.** a) occurrence of inorganic thioarsenates, b) methylated thioarsenates, and c) methylated oxyarsenates in the field with plants (one-time survey Italy/France at late plant growth stage (I+F); n = 35; mesocosms with Veronica and Fornazzo soil integrated over whole rice cultivation period of 4 months; n = 42 each) and in anaerobic soil incubations (with Veronica and Fornazzo soils (n=3 each) and paddy soils over a pH-gradient in China (n=31 each); blue colors refer to control treatments (no S), orange colors to sulfate addition (S)

## 4. Methods

**Table S8 |** Quantitative Recovery of As species in a fresh model pore water sample spiked with 1 µg/L of DMA, DMMTA, arsenite, MMA, MMMTA, and arsenate, stabilized with 10 mM DTPA, and analyzed 1:5 and 1:10 diluted with deionized water using 2.4 % methanol in the eluent and either individual or averaged calibration

| | | DMA | DMMTA[a] | Arsenite | DMDTA[b] | MMA | MMMTA[c] | MMDTA[d] | Arsenate | MTA[e] | DTA[f] | Sum of As species |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Counts per sencond | DMA 1 µg/L Standard | 1001699 | | | | | | | | | | |
| | MMA 1 µg/L Standard | | | | | 815446 | | | | | | |
| | Arsenate 1 µg/L Standard | | | | | | | | 876310 | | | |
| | sample 1:10 dilution | 151318 | 164191 | 37415 | 14160 | 114871 | 62514 | 87301 | 252602 | 19856 | 13196 | |
| | sample 1:5 dilution | 309624 | 400192 | 104872 | 36697 | 247134 | 153063 | 185058 | 415801 | 23790 | 13544 | |
| | | | | | | | | | | | | |
| Concentration (µg/L) | sample 1:10 dilution (measured concentration) | 0.15 | 0.16 | 0.04 | 0.02 | 0.14 | 0.08 | 0.10 | 0.29 | 0.02 | 0.02 | |
| | sample 1:5 dilution (measured concentration) | 0.31 | 0.40 | 0.11 | 0.05 | 0.30 | 0.19 | 0.21 | 0.47 | 0.03 | 0.02 | |
| | | | | | | | | | | | | |
| | sample 1:10 dilution x 10 (final concentration by individual calibration) | 1.51 | 1.64 | 0.37 | 0.17 | 1.41 | 0.77 | 1.00 | 2.88 | 0.23 | 0.15 | 10.85[g] |

| | | DMA | DMMTA[a] | Arsenite | DMDTA[b] | MMA | MMMTA[c] | MMDTA[d] | Arsenate | MTA[e] | DTA[f] | Sum of As species |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | sample 1:5 dilution x 5 (final concentration by individual calibration) | 1.55 | 2.00 | 0.52 | 0.23 | 1.52 | 0.94 | 1.06 | 2.37 | 0.14 | 0.08 | 10.94[g] |
| | | | | | | | | | | | | |
| | sample 1:10 dilution x 10 (final concentration by averaged calibration) | 1.69 | 1.83 | 0.42 | 0.16 | 1.28 | 0.70 | 0.97 | 2.81 | 0.22 | 0.15 | 11.02[g] |
| | sample 1:5 dilution x 5 (final concentration by averaged calibration) | 1.72 | 2.23 | 0.58 | 0.20 | 1.38 | 0.85 | 1.03 | 2.32 | 0.13 | 0.08 | 11.14[g] |
| | | | | | | | | | | | | |
| (% ) of total As | sample 1:10 dilution | 13.9% | 15.1% | 3.4% | 1.6% | 13.0% | 7.1% | 9.2% | 26.6% | 2.1% | 1.4% | >2.5% well detectable |
| | sample 1:5 dilution | 14.1% | 18.3% | 4.8% | 2.1% | 13.9% | 8.6% | 9.7% | 21.7% | 1.2% | 0.7% | >1% well detectable |

**Table S9 |** Characteristics of irrigation water for mesocosm rice cultivation experiments.

| Parameters | Irrigation water |
|---|---|
| pH | 7.7 |
| Conductivity (μS/cm) | 508 |
| TIC (mg/L)[a] | 17.5 |
| TOC (mg/L)[b] | 1.2 |
| $Cl^-$ (mg/L) | 11.4 |
| $NO_3^-$ (mg/L) | 1.11 |
| $NO_2^-$ (mg/L) | 1.05 |
| $PO_4^{3-}$ (mg/L) | 1.01 |
| $SO_4^{2-}$ (mg/L) | 11.1 |
| Si (mg/L) | 8.9 |
| Mn (μg/L) | 1.5 |
| Cu (μg/L) | 2.6 |
| Zn (μg/L) | 16.5 |
| As (μg/L) | 6.4 |

[a] Total inorganic carbon; [b] Total organic carbon

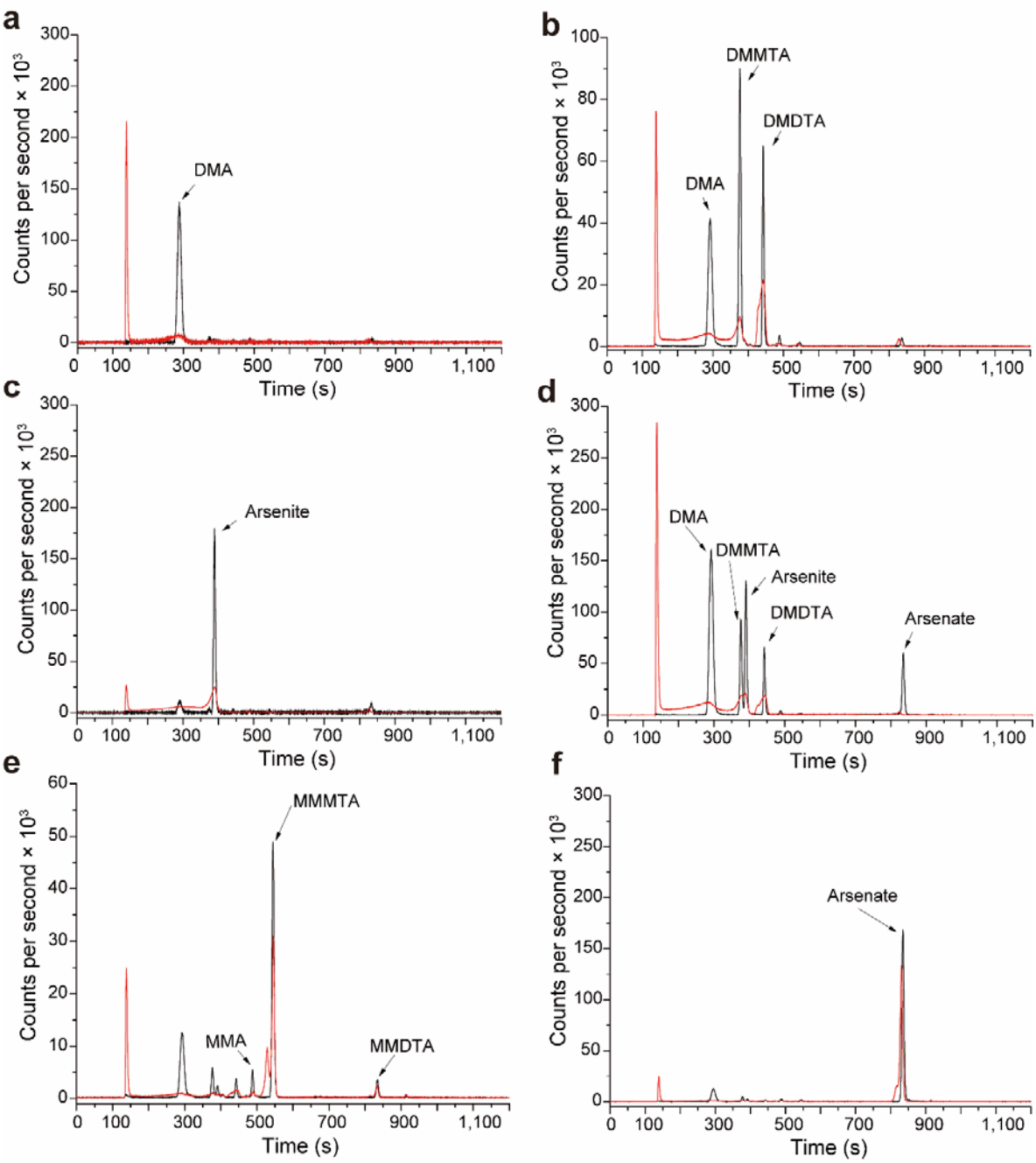


**Figure S17 | Effect of 10 mM DTPA on retention time, peak shape, and resolution of As speciation.** Tested model pore-water was spiked with 100 µg/L standards of a) DMA; b) DMMTA; c) arsenite; d) a mix of arsenite, DMA, DMMTA; e) MMMTA; f) arsenate; black lines = without DTPA, red lines = with 10 mM DTPA.

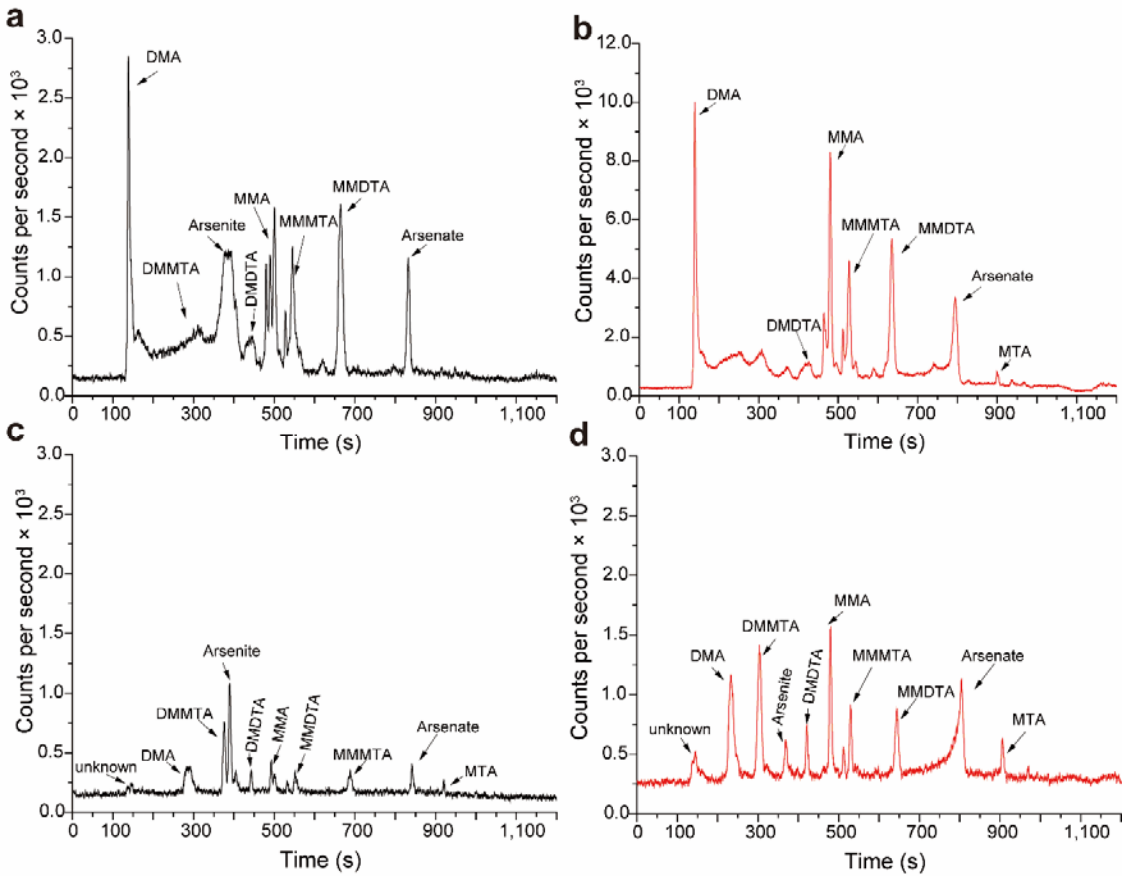


**Figure S18 | Effect of sample dilution and use of methanol in the eluent on retention time, peak shape, and resolution of As speciation.** Fresh, non-spiked model pore-water samples stabilized with 10 mM DTPAwere a) analyzed without dilution and without 2.4% methanol; b) analyzed without dilution with 2.4% methanol; c) diluted 1:10 with deionized water before analysis and analyzed without 2.4% methanol; d) diluted 1:10 with deionized water before analysis and analyzed with 2.4% methanol. All samples were analyzed with a 2.5-100 mM NaOH gradient eluent.

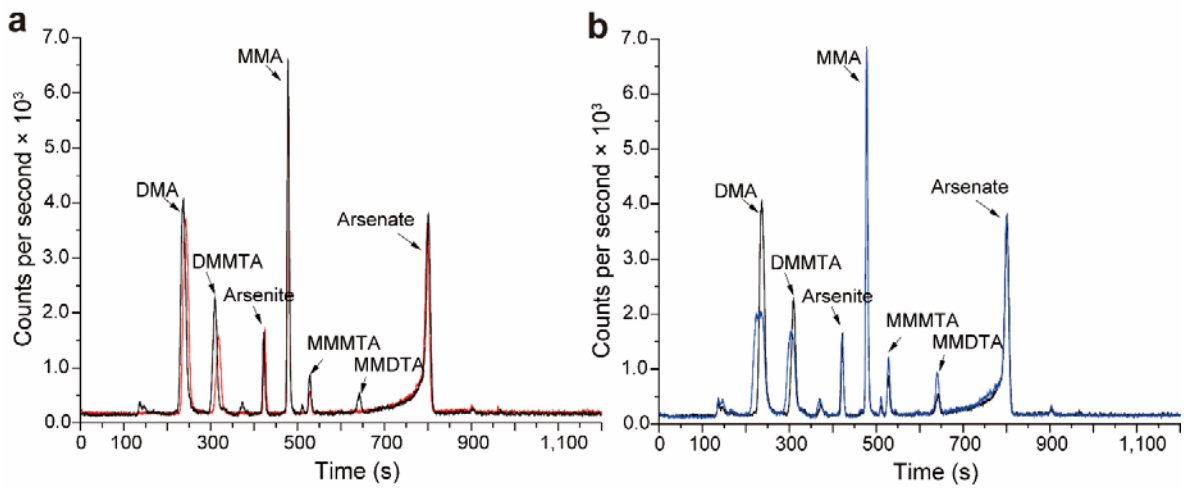


**Figure S19 | Effect of pore-water matrix and different DTPA dilution on retention time, peak shape, and resolution of As speciation.** Fresh model pore-water samples were spiked with 1 µg/L of DMA, DMMTA, arsenite, MMA, MMMTA, and arsenate,stabilized with 10 mM DTPA (all analyzed with 2.4% methanol in the eluent). a) comparison deionized water (red) and pore-water matrix 1:10 diluted (black), b) comparison 1:5 (blue) vs. 1:10 (black) dilution of pore-water matrix sample.

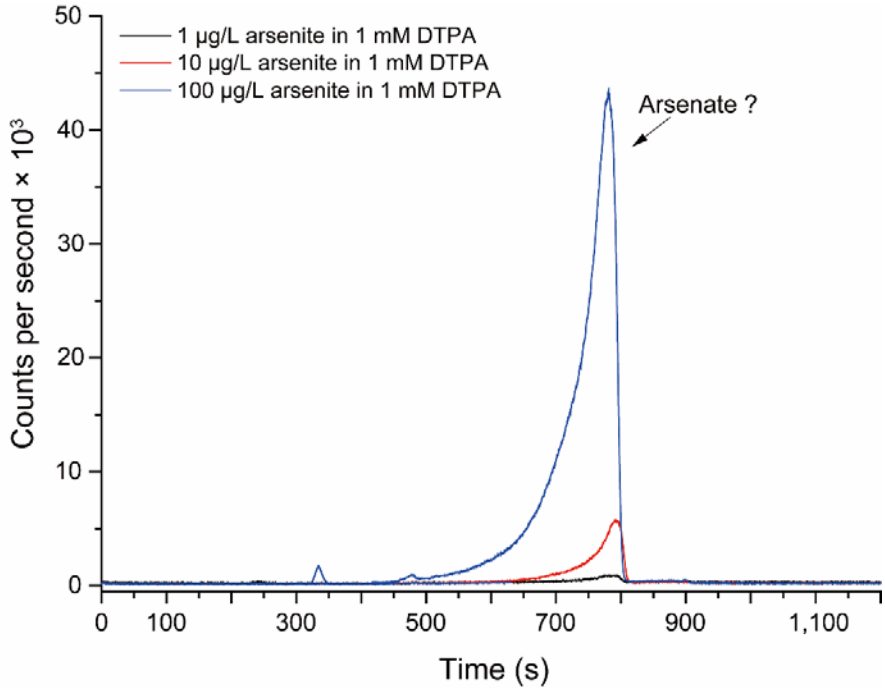


**Figure S20 | Effect of 1 mM DTPA on arsenite standards in deionized water.** The question mark behind the arsenate label indicates that the observed transformation product elutes at the retention time of arsenate but might also be an unidentified As-DTPA complex**.**

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