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Field Fluxes and Speciation of Arsines Emanating from Soils

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S Supporting Information

ABSTRACT: The biogeochemical cycle of arsenic (As) has been extensively studied over the past decades because As is an environmentally ubiquitous, nonthreshold carcinogen, which is often elevated in drinking water and food. It has been known for over a century that micro-organisms can volatilize inorganic As salts to arsines (arsine AsH₃, mono-, di-, and trimethylarsines, MeAsH₂, Me₂AsH, and TMAs, respectively), but this part of the As cycle, with the exception of geothermal environs, has been almost entirely neglected because of a lack of suited field measurement approaches. Here, a validated, robust, and low-level field-deployable method employing arsine chemotrapping was used to quantify and qualify arsines emanating from soil surfaces in the field. Up to 240 mg/ha/y arsines was released from low-level polluted paddy soils (11.3 ± 0.9 mg/kg As), primarily as TMAs, whereas arsine flux below method detection limit was measured from a highly contaminated mine spoil (1359 ± 212 mg/kg As), indicating that soil chemistry is vital in understanding this phenomenon. In microcosm studies, we could show that under reducing conditions, induced by organic matter (OM) amendment, a range of soils varied in their properties, from natural upland peats to highly impacted mine-spoils, could all volatilize arsines. Volatilization rates from 0.5 to 70 μg/kg/y were measured, and AsH₃, MeAsH₂, Me₂AsH, and TMAs were all identified. Addition of methylated oxidized pentavalent As, namely monomethylarsonic acid (MMAA) and dimethylarsinic acid (DMAA), to soil resulted in elevated yearly rates of volatilization with up to 3.5% of the total As volatilized, suggesting that the initial conversion of inorganic As to MMAA limits the rate of arsine and methylarsines production by soils. The nature of OM amendment altered volatilization quantitatively and qualitatively, and total arsines release from soil showed correlation between the quantity of As and the concentration of dissolved organic carbon (DOC) in the soil porewater. The global flux of arsines emanating from soils was estimated and placed in the context of As atmospheric inputs, with arsines contributing from 0.9 to 2.6% of the global budget.



INTRODUCTION

Arsines (arsine AsH₃, mono-, di-, and trimethylarsines, MeAsH₂, Me₂AsH, and TMAs, respectively) can be synthesized from inorganic arsenic (As) by fungi, yeast, and bacteria through successive reduction/methylation steps leading to TMAs as an end product.^{1,2} Arsines, which are highly toxic,^{3,4} have been consistently found to emanate from soils in laboratory microcosm studies^{5–9} and have been measured in geothermal environs such as hot springs and volcanic fumes.^{10,11} Yet their environmental role and subsequent consequences for human exposure are poorly understood because of a lack of robust and low-level field measurement techniques. The contribution of soil arsines to global inputs of As into the atmosphere is ill-defined with very few previous studies, all lacking field validation.^{12–14} Mestrot and

co-workers⁹ developed a highly sensitive, quantitative and qualitative, robust field deployable arsines trap based on silver nitrate impregnated silica gel, enabling low-level measurements of arsines to be made, as well as greatly enhancing confidence in the results produced from laboratory microcosm studies. Here we deployed the device in the field for the first time to monitor arsine efflux from both As impacted and nonimpacted soils and conducted thorough laboratory mass balances to investigate soil factors regulating emission of arsines.

Received: October 13, 2010

Accepted: January 6, 2011

Revised: December 9, 2010

Published: February 01, 2011

MATERIALS AND METHODS

Field Measurements. Plastic flow boxes of known surface area of the open face were used (0.184 m² for the Spanish sampling campaign and 0.102 m² for the Bangladesh one). The boxes had a hole drilled in the center of one vertical face (the open face being placed into the soil) to enable the attachment of an inlet port, and on the opposite face, an outlet port. The inlet port was connected directly to the silver nitrate trap with platinum-cured silicon tubing which was itself then connected to a 1 μ m pore size Teflon filter in a cassette for particulate matter trapping. The outlet port was fitted with the silver nitrate trap. The open face of the flux box was pushed 2 cm into the soil surface, and the box had a weight (brick) placed on top to secure it in position. The flux box was then pumped from the outlet, to maintain a negative pressure in the chamber, at a rate of 200 mL/min by a Pocket Pump (SKC, Dorset, UK). Rhizon samplers (Eijkelkamp, Giesbeek, Netherlands) were inserted 5 cm below the soil surface around the area to be covered by the flux chamber to allow for porewater sampling during the trapping period, which lasted from 2 to 5 d. On termination of the sampling, soils were sampled to a depth of 10 cm from under the chamber.

Fluxes of arsines emanating from soil were ascertained at four field sites: two sites in Spain (a low-level As-contaminated rice paddy and an As-contaminated pyrite mine tailing), and two sites in Bangladesh (an As-elevated groundwater irrigated rice paddy and an uncontaminated mangrove forest soil). The four sites are periodically flooded and were permanently under water during sampling, apart from the tidal mangrove site which was diurnally flooded. Flooded sites were chosen, as they present reducing conditions which are optimal for arsine and methylarsine production from soil.^{9,15}

Microcosm Experiments. The first microcosm experiment utilized nine soils of diverse origin, replicated in triplicate, with 50 g of 1 mm sieved dry soil, 2.5 g of milled dry cattle manure, and 120 mL of ultrapure water placed in the microcosms, and chemotraps were analyzed for total As and As speciation as described in Mestrot et al.⁹ Arsines were trapped over an optimal period of 69 d.⁹ Rhizon samplers (5 cm) were placed into the soil of each microcosm with a sampling valve outside the microcosm to enable sampling of porewater without having to stop or open the microcosms. The microcosms were incubated at 26 °C in Sanyo growth cabinets with a 14/10 h light/dark cycle. Soils ranged from uncontaminated (1.2 \pm 0.1 mg/kg As) to highly contaminated (15199 \pm 117 mg/kg As) and from highly organic peats to low organic matter (OM) mine-spoils (Table S3, Supporting Information). Since manuring and flooding optimizes arsine and methylarsine production,^{9,16} most soils were amended with dried and milled 5% cow dung (As content 1 \pm 0.1 mg/kg) on a soil dry weight basis and kept under a standing head of water. The Bangladeshi mangrove soils were amended with dried and milled 5% Sundari leaves (the dominant flora of the ecosystem samples), while the peat microcosms were not amended because of their already high OM content.

For the second microcosm experiment, 18 microcosms were prepared with 15 g of Bangladeshi paddy soil and amended with 1.5 g of dried and milled cow dung or with 1.5 g of dried and milled rice straw. The experiment had a factorial design of either no treatment, \pm 150 μ g of monomethylarsonic acid (MMAA), or \pm 150 μ g of dimethylarsinic acid (DMAA). Ultrapure water (40 mL) was added initially and a further 10 mL added every 2 wk. Microcosms were setup, incubated, and sampled as

described above but for a slightly longer period of 80 d in this case.

Porewater and Soil Sampling. In both field and microcosm experiments, the porewater was collected using Rhizon samplers and vacuum tubes. For As speciation analysis, the porewater was immediately diluted 10-times in a 5 mM EDTA solution in order to preserve the integrity of the sample and immediately frozen or placed in a cool box. For total As determination, the porewater was diluted 10-times in a 1% HNO₃ solution while the porewater for dissolved organic carbon (DOC) analysis was diluted 10-times in ultrapure water. In the second experiment, 2 mL of porewater was also used to measure oxidoreduction potential and pH (HI 9126N Hanna Instruments). Soils from the microcosms and the field sites were digested by microwave together with blanks and CRM for quality control.

Instrumentation. C, N, and S analysis were made using a CNS analyzer (NA 1500 Series 2, Fisons Instruments, UK). DOC measured using LabTOC (PPM Ltd., UK). As total concentration in soil, porewater, and traps was determined by an inductively coupled plasma mass spectrometry, ICP-MS (Agilent 7500c, Japan), and an octopole reaction cell with H₂ as a reaction gas was used for soil and porewater analysis to help prevent interferences. As speciation analysis in porewater and traps was carried out using an anion exchange HPLC (PRP X-100, Hamilton, Switzerland) with a 6.6 mM phosphate buffer (pH = 6.2) coupled to an ICP-MS Agilent 7500c. The ICP-MS was tuned for the monitoring of *m/z* 75 (arsenic) and *m/z* 77 and 82 (or *m/z* 77 and 78 when using the collision cell) to verify that no ArCl interferences were present. *m/z* 73 (germanium) and *m/z* 103 (rhodium) were also monitored, as they were used as internal standards for total and speciation analysis respectively.

RESULTS AND DISCUSSION

Field Measurements. There is much interest in As cycling in paddy soil environments,^{17,18} as well as in seminatural systems, for instance wetland ecosystems such as mangrove swamps.^{19,20} There is also considerable concern regarding As cycling in highly contaminated mine spoils as As is often associated with precious and base metal ores.²¹

For air sampling, a flux box was embedded into the surface of the soils and arsines released trapped up to 5 d (Table S1, Supporting Information). The highest levels of arsines measured emanated from paddy soils with fluxes significantly elevated above background concentration, and the As impacted soil having a higher flux than the nonimpacted paddy (Figure 1). The arsine flux recorded for the Bangladeshi paddy soil (240 \pm 90 mg/ha/year) was 5-fold higher than for the Spanish paddy (44 \pm 15 mg/ha/year). In addition, the As soil porewater concentration was 14-times higher in the contaminated paddy compared to the nonimpacted site, and the mangrove swamp was poor at volatilizing arsines, as was the mine spoil, even though the mine spoil contained over 120-times more total As than the other soils (Table S2, Supporting Information). The mangrove and mine sediment both had low porewater As concentration, indicating poor bioavailability of this element (Figure 1). Speciation analysis of the trapped arsines from the Bangladeshi paddy soil (Figure 2) found that TMAs dominated the efflux from soils, TMAs being the dominant species found in anaerobic microcosm studies.^{5,9,22}

Microcosm Studies. A microcosm experiment using nine different soils and sediments was conducted to investigate the

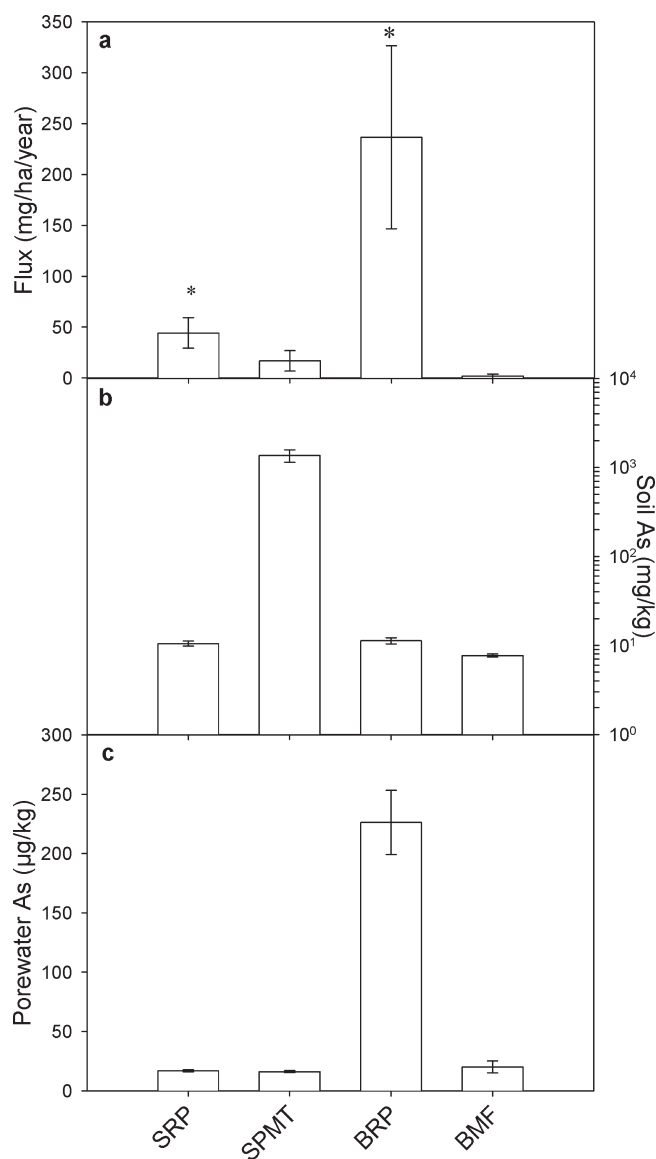


Figure 1. Field measurement results obtained by ICP-MS. Flow boxes linked to pumps were fitted with traps on the inlet and the outlet and continuously purged for several days. Arsenic fluxes are calculated by subtracting the inlet value to the outlet one and by dividing this value by the time and area covered by the flow box. * indicates that for those sites the flux is significantly >0 ($p < 0.05$). Error bars represent the standard error. For the Spanish field sites $\text{LOD}_{\text{flux}} = 4.26 \text{ mg/ha/year}$ and for the Bangladeshi field sites $\text{LOD}_{\text{flux}} = 51.5 \text{ mg/ha/year}$ under normal trapping conditions. SRP: Spanish rice paddy; SPMT: Spanish pyrite mine tailing; BRP: Bangladesh rice paddy; BMF: Bangladesh mangrove forest. (a) Flux of arsenic volatilized during the whole sampling period ($n = 6$ boxes). (b) Arsenic concentration in the monitored fields ($n = 3$). (c) Arsenic concentration in the pore water ($n = 3$ for Spanish sites, $n = 5$ for Bangladeshi sites).

factors regulating As volatilization. Microcosms allowed for a more rigorous control of soil conditions than possible in the field, as well as enabled mass balances to be calculated. The soils tested included the Spanish soils (pyrite tailing and paddy) as well as the Bangladeshi mangrove soil originated from the sites investigated in the field campaign.

All soils tested volatilized quantifiable and qualifiable levels of As (Figure 3). An antimony mine spoil soil and the Spanish pyrite

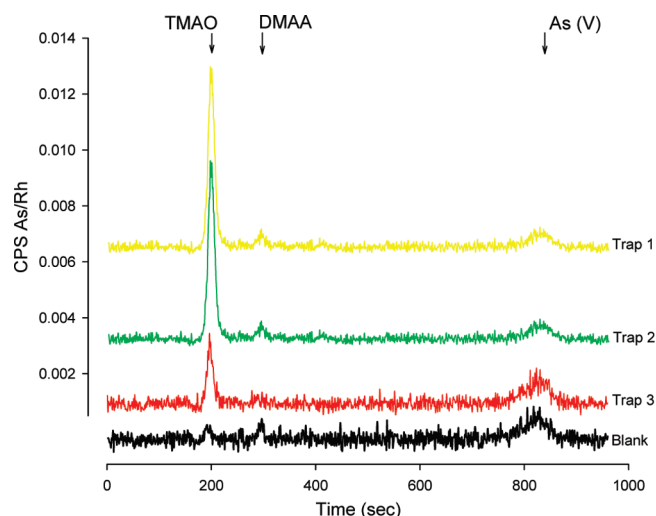


Figure 2. Eluate chromatogram of three traps from the Bangladeshi rice paddy and a blank obtained by HPLC-ICP-MS. Volatiles AsH_3 , MeAsH_2 , Me_2AsH , and TMAs are quantitatively converted to their oxy-anions equivalent during the trapping/eluting process, respectively As (V), MMAA, DMAA, and TMAO.

mine soil were the most As contaminated and produced the most arsines $\sim 70 \mu\text{g/kg/year}$ (Figure 3c). The Bangladeshi rice paddy and the Chinese mine-impacted rice paddy both produced 20-times less volatile As than that of mine spoils with a rate of $\sim 4 \mu\text{g/kg/year}$. Interestingly, even though the Chinese paddy soil had 10-times more total As concentration and 5-times more As in porewater than the Bangladeshi soil, both paddies produced similar rates for As volatilization. Soil factors, such as the size and activity of the volatilizing microbial biomass, may be responsible for the enhanced volatilization from the paddy soil. In particular As, and other cocontaminants present in the mine soil, may cause a toxicological impairment of biovolatilization.²³ The Bangladeshi mangrove forest soil, the Spanish rice paddy, and the U.K. upland peat generated approximately $2 \mu\text{g/kg/year}$ volatile As, although these soils and porewaters had very different As contents (Figure 3). Finally, the UK estuary sediment and the UK lead mine spoil produced similar small amounts of arsines ($0.5 \mu\text{g/kg/year}$). The lead mine spoil, which ranked second to last in terms of emissions, contained ~ 5000 -times more total As than that of the upland peat, but the peat produced 4-times more arsines even though there was no significant difference in the porewater As content between these two sites ($225 \pm 64 \mu\text{g/kg}$ and $191 \pm 13.6 \mu\text{g/kg}$, respectively). Again, toxicological impairment may be at play in the lead mine soil. The quantity of As volatilized from each soil was not directly driven by the total As content of the soil ($p = 0.07$), but there was a positive correlation ($p < 0.015$) between As concentration in the porewater and production of total arsine and methylarsines (Figure 3). Finally, the mangrove and pyrite mine tailing soils which had arsine fluxes below the field method's limits of detection were found to volatilize As under laboratory conditions (Figures 1 and 3). This is due in part to the longer time period for monitoring the microcosms, additional to the OM amendment known to stimulate volatilization.^{9,16}

The arsines produced by the soils in the microcosms were TMAs followed by Me_2AsH and AsH_3 (Figure 3; Table S4, Supporting Information). MeAsH_2 was only found in the mine impacted Chinese rice paddy. These findings confirm the fact

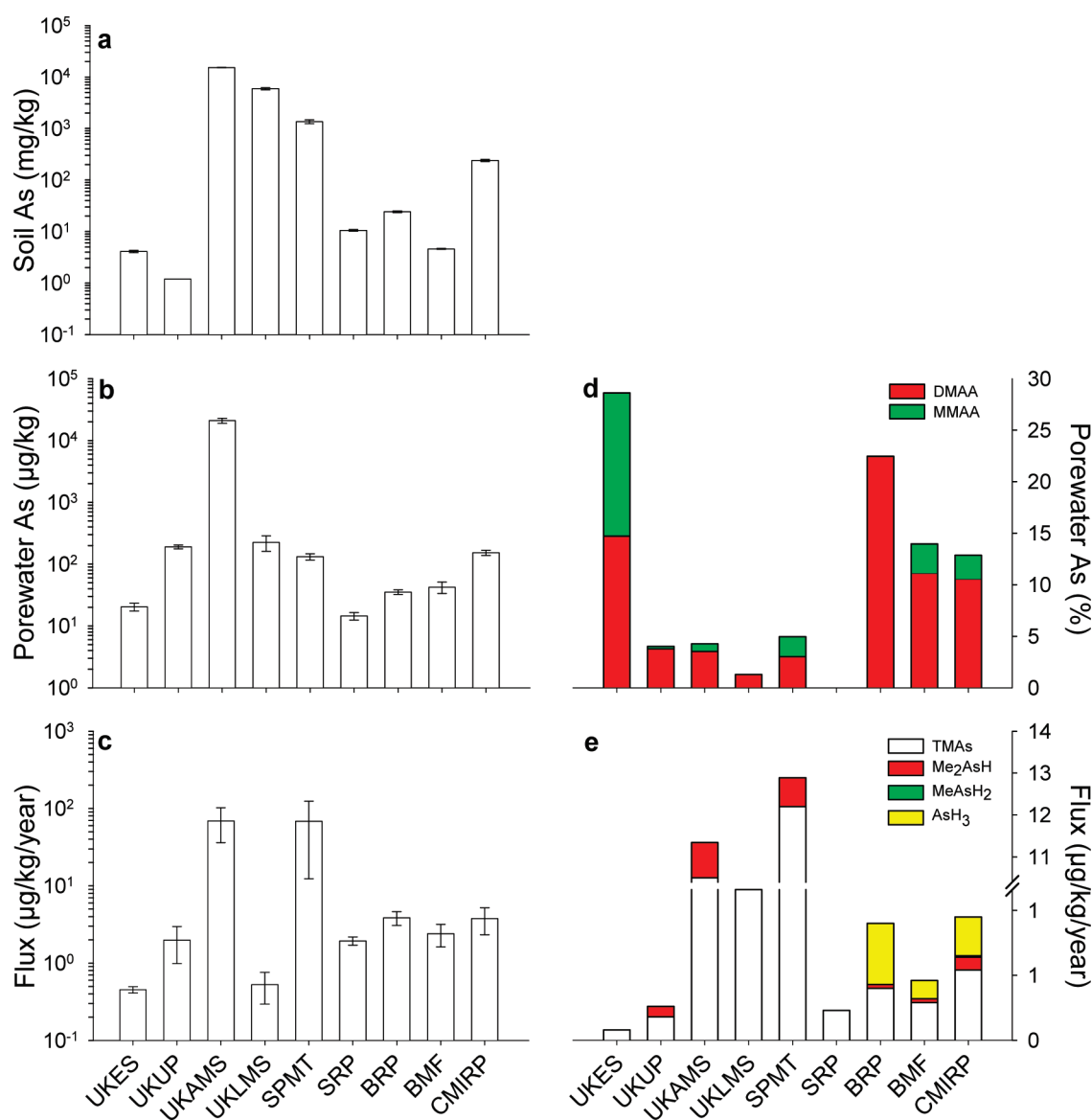


Figure 3. Microcosms experiment 1. (a) Arsenic concentration in the soils monitored ($n = 3$). (b) Arsenic concentration in the pore water ($n = 3$). (c) Flux of arsenic volatilized during the whole period ($n = 3$). (d) Speciation of arsenic in the pore water after the experiment ($n = 3$), expressed as the percentage of the sum of all species. (e) Speciation of the arsenic volatilized during the experiment ($n = 3$). Error bars represent the standard error based on three distinct samples and $\text{LOD}_{\text{flux}} = 0.3 \mu\text{g/kg/year}$ under normal trapping conditions. UKES: UK estuary sediment; UKUP: UK upland peat; UKAMS: UK antimony mine soil; UKLMS: UK lead mine spoil; SPMT: Spain pyrite mine tailing; SRP: Spain rice paddy; BRP: Bangladesh rice paddy; BMF: Bangladesh mangrove forest; CMIRP: China mine impacted rice paddy.

that TMAs are the dominant end product of inorganic As methylation, as shown for the field measurements (Figure 2) and in previous studies.^{5,9,22} AsH_3 production, as observed for Bangladeshi and Chinese paddies as well as from upland peat (Figure 3e), has also been reported in previous anaerobic incubation experiments.^{6,8,22} Whether AsH_3 is produced biotically and/or abiotically is still unknown. There was no clear relationship between As speciation in soil porewaters and that of the arsines, except that methylated As oxyanions were observed in all porewaters, apart from the Spanish paddy (Figure 3d,e). Moreover, such a relationship is complicated to prove, as the rates of both methylation and volatilization are possibly very different; hence, if TMAs are present in quantity in the headspace, there will be fewer TMAOs in the porewater. However, we know that methylated oxyanions are the intermediates in the production of

methylated arsines² but could also be their oxidation product,^{24,25} as it is a possibility that arsines are both produced and consumed by soil micro-organisms, analogous to methane production and oxidation in soils.²⁶

A second microcosm study was conducted utilizing the Bangladesh paddy soil from the field experiment which showed high rates of volatilization compared to the other field sites (Figure 1). The soil was amended with 10% (w/w) of either rice straw ($1.8 \pm 0.1 \text{ mg/kg As}$) or cow dung ($0.7 \pm 0.1 \text{ mg/kg As}$) on a soil dry weight basis, with the OM originating from the field site location with the aim of imitating local agronomic practice. Further factorial treatments of either $150 \mu\text{g}$ of MMAA, $150 \mu\text{g}$ of DMAA, or nonspiked were applied. For all treatments, production of arsine and methylarsines was evidenced, with rice straw, a widely used paddy field amendment, being more effective at

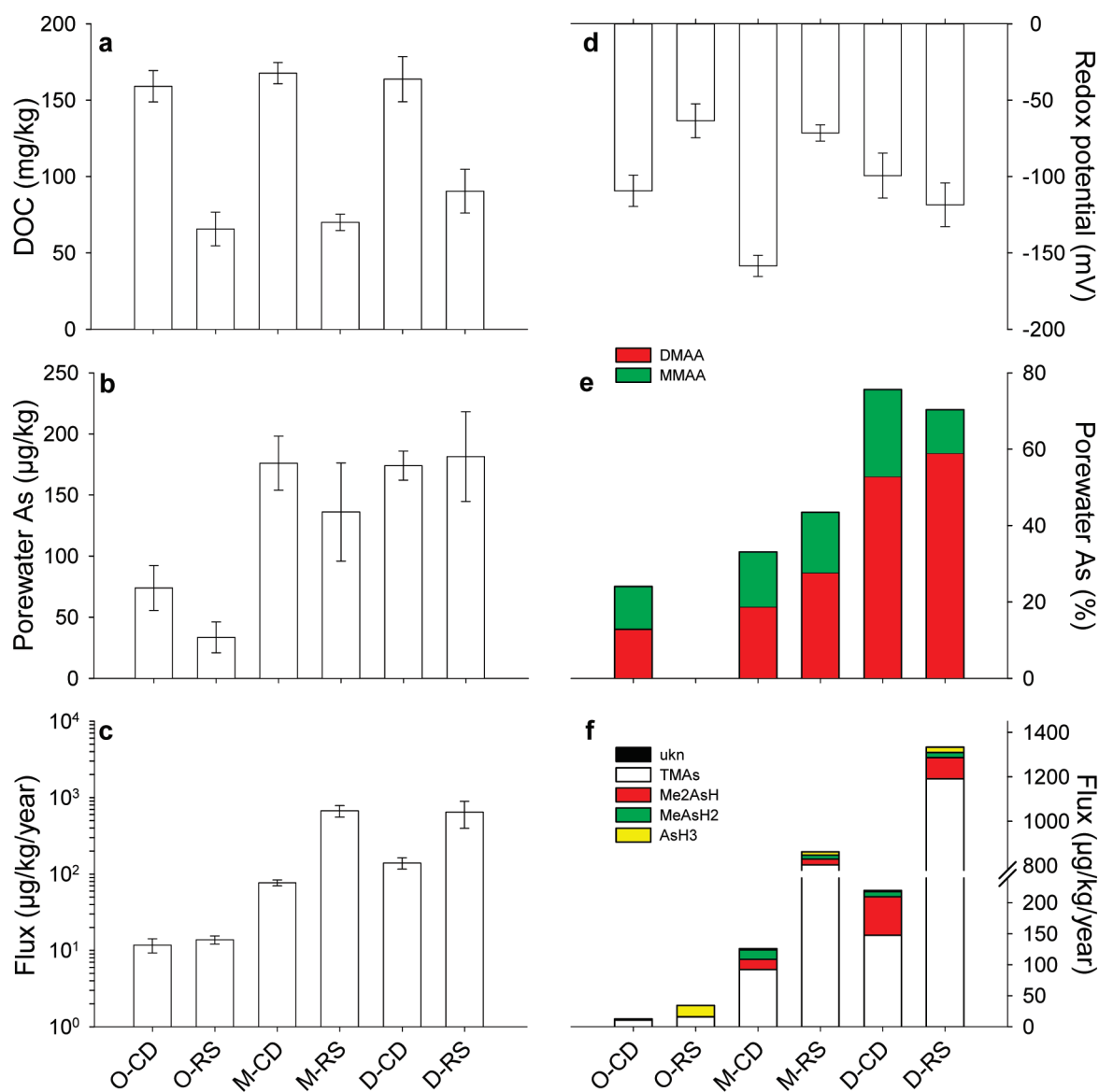


Figure 4. Microcosms experiment 2. (a) DOC concentration in the pore water ($n = 3$). (b) Arsenic concentration in the pore water ($n = 3$). (c) Flux of arsenic volatilized during the whole period ($n = 3$). (d) Redox potential of the porewater ($n = 3$). (e) Speciation of arsenic in the pore water ($n = 3$) expressed as a percentage of the sum of all species. (f) Speciation of the arsenic volatilized during the experiment ($n = 3$ reactors). Error bars represent the standard error based on three distinct samples and $\text{LOD}_{\text{flux}} = 0.5 \mu\text{g/kg/year}$ under normal trapping conditions. O: No As added, M: $150 \mu\text{g}$ of MMAA added, D: $150 \mu\text{g}$ of DMAA added, CD: 1.5 g of cow dung amendment, RS: 1.5 g of rice straw amendment.

eliciting volatilization compared with cow dung, and addition of methylated As species also enhancing emission rates (Figure 4). Addition of MMAA and DMAA led to enhanced production of MeAsH_2 and Me_2AsH , respectively, but only in cow dung amended microcosms, whereas only DMAA addition increased the DMAA percentage (Table S5, Supporting Information). Finally, AsH_3 production was greater when rice straw was used as amendment in the microcosms (Table S6, Supporting Information). There was no relationship between As speciation in the porewater and the volatile arsine species; however, arsines were trapped cumulatively over an 80 d period while porewater As was only measured upon termination of the experiment. No clear relationship could be measured between red-ox potential of the porewater and volatilization of As; however, this might be due to insufficient data, as the red-ox potential was only measured in the second set of microcosm experiments.

When total arsine fluxes were regressed against porewater As and dissolved organic carbon (DOC) concentrations for the two microcosm experiments, a significant ($p < 0.0005$) correlation was found (Figure 5). DOC seems to play a crucial role in As mobilization in soils and sediments; it drives microbial reduction, favoring the more mobile arsenite species in soil solution^{27,28} and may complex As and lead to increasing solubility. It can also compete with negatively charged As species, then leading to dissociation from mineral phases.²⁹

Implications for the As Biogeochemical Cycle. The upland peat was most efficient at biovolatilizing As as a percentage of total soil arsenic with 0.17% of total soil As evolved per year, while for paddy soil the volatilization rate was between 0.002% for a highly As-impacted Chinese paddy and 0.13% for a low contaminated As Bangladeshi paddy (Tables S4 and S6). Mine spoil soils with high total As contents only had a maximum

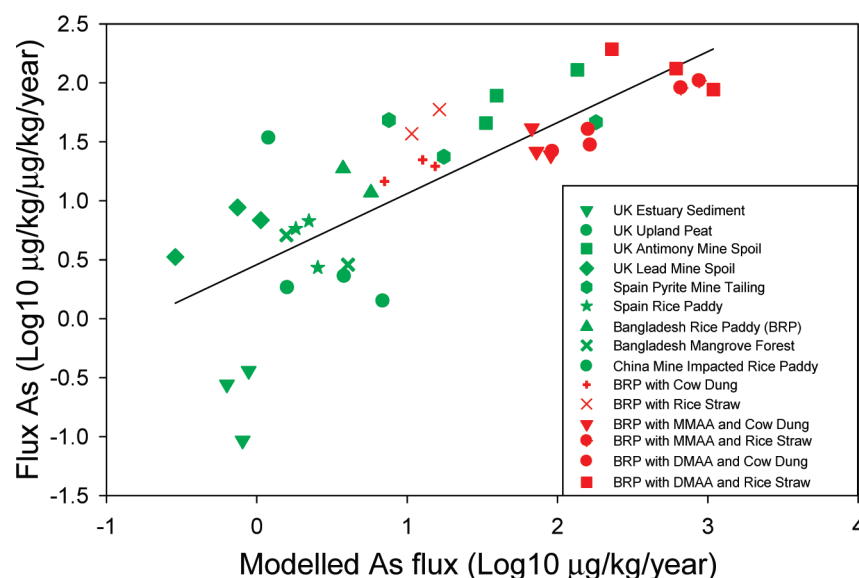


Figure 5. Flux modeled from DOC and As pore water concentration versus actual flux. The multiple regression formula used to predict the flux is $\log \text{flux} = 5.31 - 2.38 \log 10(\text{DOC}) + 0.650 \log 10(\text{pwAs})$; $r^2 = 0.602$; $p < 0.0005$.

Table 1. Estimates of Global Arsine Fluxes^a

	flux (mg/ha/y)	world coverage (ha)	global emissions (t/yr)
paddy Bangladesh	147–327	157×10^{-6}	23–51
paddy Spain	29–59	157×10^{-6}	4.5–9.2
peat UK	980–2980	300×10^{-6}	392–1192
total			419–1252

^a Paddy soil fluxes calculated from field data in Figure 1, peat fluxes from microcosm experiment 1, Figure 3. The peat data was scaled to a surface flux, assuming that the top 10 cm of peat responsible for arsine and methylarsine production. World coverage values from Holden (2005) and Kögel-Knabner et al. (2010). Ranges are average plus or minus standard error.

of 0.005% arsenic biovolatilization per annum, though this may equate to highly localized arsine release at such sites, if soil conditions are favorable, given the high total As content of the soil.

In an earlier paper by Chilvers and Peterson,¹³ the global As release into the atmosphere was compiled, and it was estimated that As emitted to the atmosphere is ~ 75000 t/y, 38% of it being of anthropogenic origin (mainly copper smelting and coal burning), the rest being of natural origin.¹³ As biovolatilization was budgeted as the largest input at 26000 t/y, accounting for 58% of natural emissions, while 17000 t/y was from volcanic origin. The biovolatilization figure was based on one microcosm study⁵ and not on actual field measurements. From that microcosm study, Chilvers and Peterson calculated that $\sim 0.1\%$ of As present in the soil worldwide was volatilized on average per annum, which is close to the values determined in this study for peat and paddy soil. However, based on the global surface area of peats (4×10^8 ha) and paddy soil (1.6×10^8 ha) from Holden³⁰ and Kögel-Knabner et al.,³¹ respectively, we can calculate from our actual field measurements as well as microcosm studies that between 419 and 1252 t/y As are emitted (Table 1). Compared to other natural sources, biovolatilization inputs calculated here are 15- to 45-times more important than sea spray (26.5 t/y),

3- to 10-times more important than forest fires (125 t/y), and represent 20 to 60% of wind erosion (2000 t/y) and 2 to 7% of volcanic emissions (17000 t/y). In conclusion, As biovolatilization estimated in this study represents 0.9 to 2.6% of global As emissions and thus represents 2 to 6% of total natural emissions,¹³ provided that Chilvers and Peterson's previous budget estimations are corrected for the lower estimates of biovolatilization that we evidenced here.

■ ASSOCIATED CONTENT

S Supporting Information. More detailed information about field and microcosm experiments, such as soil and pore-water characteristics as well as complete results provided as tables. This information is available free of charge via the Internet at <http://pubs.acs.org>.

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■ ACKNOWLEDGMENT

We thank C. Ayora, M. A. Rob, M. T. Arifin, R. Islam, and the people of Sonargaon for help with the field work and logistics. This publication is a contribution of the AquaTRAIN Marie Curie Research Training Network (Contract No. MRTN-CT-2006-035420) funded under the European Commission Sixth Framework Programme (2002–2006) Marie Curie Actions, Human Resources & Mobility Activity Area – Research Training Networks.

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