



Methylated arsenic species throughout a 4-m deep core from a free-floating peat island

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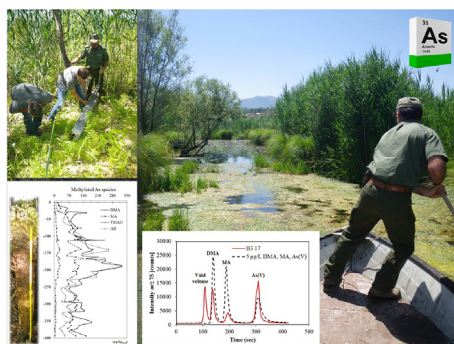
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HIGHLIGHTS

- Total As and its organic species in peat were determined by HPLC-ICPMS.
- An average extraction efficiency around 80% was obtained using trifluoroacetic acid.
- Organic As species accounted, on average, for $28 \pm 10\%$ of total As.
- The relative abundance of organoarsenicals followed the order DMA > TMAO ~ MA \gg AB.
- Significant proportions of methylated As species may occur in floating mires.

GRAPHICAL ABSTRACT



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ABSTRACT

Arsenic (As) occurs in soils mostly in inorganic forms, whereas the organic forms usually occur only in trace amounts. Peatlands are waterlogged, generally anoxic, organic soils representing the first step in coal formation; the contribution of organic vs. inorganic As species in this environment has received little research attention. Here, 57 peat samples collected throughout a 4-m deep, free-floating mire were analysed for total As and for its organic species, including dimethylarsinic acid (DMA), methylarsonic acid (MA), trimethylarsine oxide (TMAO) and arsenobetaine (AB), by HPLC-ICPMS. Aqueous trifluoroacetic acid was used as extractant, resulting in an average extraction efficiency of almost 80%. Total As concentration throughout the profile ranged between 0.2 and 9.8 mg/kg_{peat} (mean: 1.4 ± 1.2 mg/kg_{peat}). Organic As species (DMA + MA + TMAO + AB) accounted, on average, for $28 \pm 10\%$ of total As (range: 6–51%), and for $37 \pm 13\%$ of the extracted As (range: 7–64%). The relative abundance of organoarsenicals generally followed the order DMA > TMAO ~ MA \gg AB. A positive correlation ($p < 0.001$) was found among all organic As compounds, whereas their concentrations were negatively correlated with total sulfur content. The submerged zone (bottom 300 cm) showed average and maximum concentrations of organoarsenic compounds that were almost twice those found in the top 100 cm. This study shows that significant proportions of methylated As species occur even in peat samples characterized by low total As

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concentration (mostly <2 mg/kg). Finally, this work provides the first evidence of organoarsenic species in free-floating mires, i.e., a globally distributed but scarcely investigated ecosystem.

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1. Introduction

Arsenic (As) is recognized as a serious health risk worldwide (Nordstrom, 2002; Stoeppler, 2004). It is widely distributed in a large number of minerals (e.g., sulfidic ores arsenopyrite, realgar and orpiment, as well as arsenides of copper, lead, silver, or gold), but its presence in soils may also be the result of anthropogenic activities, including the use of pesticides, mining activities, or industrial processes (Frank et al., 2005). The fate of this metalloid in the environment is strongly affected by processes such as precipitation, dissolution, adsorption/desorption from the surface of oxides (especially Fe) (Smedley and Kinniburgh, 2002; Bostick and Fendorf, 2003) and natural organic matter (Bauer and Blodau, 2006; Hoffmann et al., 2012; Langner et al., 2013), as well as biological transformations (Braman and Foreback, 1973; Brown et al., 2000; Oremland and Stoltz, 2003).

Arsenic may occur in nature as inorganic or organic forms, and has four oxidation states in aqueous solution (Pourbaix, 1966), depending on pH, redox potential, occurrence of other ionic species, and biological activity (Smedley and Kinniburgh, 2002; Blute et al., 2004; Zhao et al., 2013). In the solid phase of mineral soils, As occurs mainly as inorganic species (As_{inorg}): under oxic conditions, the arsenate oxyanion ($As(V)$) is the predominant inorganic form in solution and can easily be sequestered by Fe(III) oxyhydroxide; in reducing conditions, the more toxic and mobile arsenite ($As(III)$) prevails, often precipitating as sulfur-containing minerals (Smedley and Kinniburgh, 2002).

Peatlands are waterlogged, generally anoxic, organic soils (<25% mineral matter) that represent the first step in coal formation (Shotyk, 1992). Because As is one of the chalcophile elements most commonly enriched in coal (Valkovic, 1983), it is possible that As enrichment in coal has its origin in the earliest phases of peat accumulation (Gonzalez et al., 2006). Arsenic concentrations in peatlands range from <1 mg/kg (e.g., Shotyk et al., 2002) to several hundreds of mg/kg; up to 350 mg/kg of As were found by Gonzalez et al. (2006) in the minerotrophic peatland of Gola di Lago, Switzerland. Most of the studies on As occurrence in peatlands focused mainly on the determination of its natural concentration in the solid vs. liquid phase (Gonzalez et al., 2006), on the impact of human activity on its geochemical cycle during centuries (Shotyk, 1996; Shotyk et al., 2002, 2003), on the emissions/fluxes of (methyl)arsines (Vriens et al., 2014), and on the interaction between As_{inorg} and organic matter (Gonzalez et al., 2006; Zaccone et al., 2008; Rothwell et al., 2009; Hoffmann et al., 2012, 2013; Langner et al., 2013). Few studies, however, have examined the occurrence and distribution of organoarsenic species in the solid phase of peat, probably because these species are present at low concentrations, which increases the analytical challenge of their reliable identification and quantification.

Organic As species (or organoarsenicals), defined as compounds containing a covalent bond between a carbon atom and arsenic, include dimethylarsinic acid (DMA), methylarsonic acid (MA), trimethylarsine oxide (TMAO) and arsenobetaine (AB). Although DMA and MA may have minor and highly localized anthropogenic sources, organic As compounds generally occur as a result of biotic methylation (Challenger, 1945; Bentley and Chasteen, 2002; Blodau et al., 2008; Yamaguchi et al., 2011). In fact, despite arsenic's toxicity, there are many microorganisms able to grow at high As concentrations and to facilitate its transformation by oxidation, reduction, methylation and demethylation processes (Braman and Foreback, 1973; Craig, 1989; Cullen and Reimer, 1989).

One of the first works on specific organic As compounds in peat was carried out by Frank (2005) using samples from Finnish bogs. In that

work, following a preliminary test where a few peat samples were subjected to different preparations (fresh vs. freeze- and oven-drying) and the As extracted using both high purity water and 2 M orthophosphoric acid, water was selected as extractant. Probably because of the low extraction efficiency obtained using water (0.7–23%), only MA and DMA were detected, with DMA being the dominant species. Analysing a 70-cm deep fen peat core, Huang and Matzner (2006) found the total concentration of organic As compounds (MA, DMA, TMAO, AB and two unknown organic As species) in methanol–water extracts to be greatest at the surface (0–10 cm depth), where they accounted for 24% of total extractable As; concentrations of those organic species dropped to zero below 40–50 cm of depth. Arsenobetaine was reported as the most abundant organic As species (up to 14 µg/kg), while concentrations of MA, DMA and TMAO were much lower (<2 µg/kg). The same authors observed a seasonal variation of the concentration of organic As species in porewaters, along with a depth-spatial variation of As species and other chemical parameters including pH and redox potential. In particular, the concentration of organic As species increased in summer (up to 1.2 µg/L, i.e., 70% of total As), while in spring (after the snowmelt) no organic As compounds were detected. Those results suggested that biotic methylation of As during the growing season is a major transformation pathway leading to the formation of organoarsenic species.

In a laboratory study, Huang et al. (2007) incubated DMA and AB in bulk soil and aqueous extracts from forest floor and fen peat samples at various redox conditions, and demonstrated that the demethylation of AB to DMA and of DMA to As_{inorg} was also possible. In a recent study, Mikutta and Rothwell (2016) found that organic As in peat accounted for 62 to 100% of the total, and concluded that organic As species (namely AB, DMA and MA) dominate the solid-phase As speciation in wetlands. This study was carried out on 5 bogs in England containing abundant As (9–92 mg/kg), but quite shallow (10–15 cm) peat profiles were considered.

Floating mires are unique peatlands consisting of emergent vegetation rooted in highly organic buoyant mats. Ranging from small, free-floating islands to extensive, stationary, vegetated mats which may cover hundreds of hectares of surface water (Mallison et al., 2001), floating mires are distributed world-wide, e.g., along rivers and lakes in Africa, the Danube delta in Romania, the Amazon River in South America, the Mississippi delta in USA, but also in The Netherlands, Australia and Canada (Swarzenski et al., 1991). O'Neil (1949) identified and mapped ca. 100,000 ha of floating marshes just in Louisiana, USA. At the same time, these ecosystems have received limited research attention. With 400 cm of peat accumulated in <700 yr, the free-floating island of Posta Fibreno, Italy, shows the thickest accumulation of peat reported for this ecosystem in the scientific literature, and an incredibly high average growth rate (0.5–0.6 cm/yr) (Zaccone et al., 2017).

The main goal of the present study was to investigate the speciation and distribution of methylated As compounds throughout a peat island profile characterized by floating conditions, differences in peat-forming plants and physical and chemical features, and low As concentrations. Fifty-seven samples were analysed for concentrations of DMA, MA, TMA and AB by HPLC-ICPMS.

2. Material and methods

2.1. Peat coring and sample preparation

A 400-cm peat profile was collected in July 2012 from the central domed area of the Posta Fibreno free-floating island, where the surface

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