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Biogenic arsenic volatilisation from an acidic wetland soil

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Biogenic arsenic (As) volatilisation was budgeted at 26000 t yr^{-1}as the largest input of the global As release into the atmosphere, thereby playing an important role in the biogeochemical cycle of As in the surface environment. In order to quantify As volatilisation from wetland soils and to elucidate the geochemical and microbiological factors governing As volatilisation, a series of incubations with an acidic wetland soil collected in NE-Bavaria in Germany were performed at 15^{o}C for 4 months with addition of NaN_3, arsenite (As(III)), $FeCl_3$, $NaSO_4$ and NaOAc with N_2 and air in the headspace. Speciation of gaseous As in the headspace using GC-ICP-MS/ ESI-MS coupling showed the predominance of either arsine (AsH_3) or trimethylarsine ($(CH_3)_3As$) in all treatments during the time course of incubation. Monomethylarsine ($(CH_3)AsH_2$) and dimethylarsine ($(CH_3)_2AsH$) could be only detected in trace amounts. Arsenic speciation in porewater with HPLC-ICP-MS revealed the predominance of As(III) and methylated As was never detectable. Arsenic volatilisation summed to 2.3 ng As (88% as AsH_3) in the control incubations, which accounted for $\sim$0.25 % of the total As storage in the wetland soil. Treatments with 10 mM NaN_3 resulted in emission of only 0.03 ng As. In contrast, addition of 10 mM NaOAc stimulated microbial activities in wetland soils and subsequently rose As volatilisation to 8.5 ng As. It could be therefore concluded that As volatilisation from the wetland soils was mainly biological. Spiking 67 μM As(III) increased 10 times of As volatilisation and the proportion of methylated arsines increased to 66%, which is supposed to be caused by the largely enhanced As availability in porewater for microbes (480 ppb, $\sim$65 times higher than those in the controls). Adding 10 mM $FeCl_3$ stimulated microbial Fe(III) reducing activities but suppressed other microbial activities by lowering soil pH from 5 to 3.6, decreasing consequently As volatilisation to 0.3 ng As. The much lower redox potential (-250 mV) than the other incubations (-50-50 mV) caused by microbial sulphidisation may benefit microbial As methylation. However, incubations manipulated with 10 mM $NaSO_4$ decreased As volatilisation to 0.8 ng As in accompany with the very low As concentrations in porewater ($\sim$1 ppb), since sulphidisation may trap solution As by forming AsS precipitates. In addition, the presence of O_2 in headspace had no significant influence on the amounts and speciation of As volatilisation. This study evidenced the strong linkage between the microorganism and As volatilisation from wetland soils and furthermore highlighted the potential utilising microbial As volatilisation to remediate As polluted soils. Further studies will focus on investigating the correlations between As volatilisation and microbial As methylation by quantifying the arsenite methyltransferase (*arsM*) gene-containing microbial communities in treatments mentioned above, using quantitative PCR assay with *arsM*-specific primer set.