



Sequestration of arsenic in ombrotrophic peatlands

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Peatlands can be important stores of arsenic but we are lacking spectroscopic evidence of the sequestration pathways of this toxic metalloid in peatland environments. This study reports on the solid-phase speciation of anthropogenically-derived arsenic in atmospherically contaminated peat from the Peak District National Park (UK). Surface and sub-surface peat samples were analysed by synchrotron X-ray absorption spectroscopy on B18 beamline at Diamond Light Source (UK). The results suggest that there are contrasting arsenic sequestration mechanisms in the peat. The bulk arsenic speciation results, in combination with strong arsenic-iron correlations at the surface, suggest that iron (hydr)oxides are key phases for the immobilisation of arsenic at the peat surface. In contrast, the deeper peat samples are dominated by arsenic sulphides (arsenopyrite, realgar and orpiment). Given that these peats receive inputs solely from the atmosphere, the presence of these sulphide phases suggests an in-situ authigenic formation. Redox oscillations in the peat due to a fluctuating water table and an abundant store of legacy sulphur from historic acid rain inputs may favour the precipitation of arsenic sequestering sulphides in sub-surface horizons. Oxidation-induced loss of these arsenic sequestering sulphur species by water table drawdown has important implications for the mobility of arsenic and the quality of waters draining peatlands.