

Ecophysiology of arsenic- and antimony-metabolizing microorganisms in peatlands treating mine wastewaters

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Large amounts of wastewater are produced in mining operations. Contaminants such as metals, sulfate and nitrogen compounds, and also the metalloids arsenic (As) and antimony (Sb) often occur in mining wastewaters and have to be removed before the water can be discharged into downstream water bodies. At our study site in Finnish Lapland, process and drainage wastewaters have been treated in two originally pristine peatlands (treatment peatlands (TP) A and B, respectively) for up to 10 years. Both water types contain elevated concentrations of As and Sb. As is more abundant in process water while Sb is more abundant in drainage water.

Microorganisms adapted to high As and Sb concentrations are likely to occur in these treatment peatlands, and those microorganisms play an important role in As and Sb turnover and removal. Thus, this study assessed (i) removal efficiencies and *in situ* speciation of As and Sb in the two treatment peatlands, (ii) potential of the peat microbial community to oxidize/reduce As and Sb under oxidizing/reducing conditions, and (iii) the effect of different variables on As and Sb turnover.

As retention has been good in both peatlands over the years, while Sb retention has decreased in TP B over the course of the years. In inflow waters, As and Sb occurred mainly as arsenate and antimonate. In the outflow waters total concentrations of As and Sb are lower. Here, arsenite was the main As species, while antimonite was not detected.

Arsenite/antimonite oxidation and arsenate/antimonate reduction potentials were assessed in oxic and anoxic microcosms, respectively. Sodium azide (NaN_3) was supplemented to part of the microcosms to inhibit microbial activity. Supplemental arsenite and antimonite were oxidized to arsenate/antimonate within 9 days of incubation. While arsenite oxidation occurred only in microcosms that did not receive NaN_3 , antimonite oxidation occurred also in NaN_3 -amended microcosms, indicating that (i) part of the antimonite was oxidized abiotically and/or (ii) NaN_3 did not completely inhibit antimonite oxidizers. Supplemental arsenate and antimonate were reduced within 9 days of incubation. Only minor reduction was observed in NaN_3 -amended microcosms, indicating that arsenate/antimonate reduction was biologically catalyzed. Sb was removed from the solution almost completely after 19 days of incubation, indicating that the produced antimonite was removed by precipitation or binding to the peat matrix.

Oxidation/reduction rates increased with increasing initial concentrations of supplied reactant, and maximum reaction rates (v_{max}) were 159, 54, and 30 $\text{nmol h}^{-1} \text{g}_{DW}^{-1}$ for arsenite oxidation, arsenate reduction, and antimonate reduction, respectively. Arsenite oxidation and antimonate reduction rates increased with increasing incubation temperature (5 to 30°C). On the contrary, arsenate reduction rates were higher at 20°C than at lower or higher temperatures, indicating that arsenate reducers are adapted to *in situ* near temperatures.

The collective data indicate that (i) As and Sb are removed in treatment peatlands, (ii) arsenate/antimonate are reduced within the peatland, (iii) peat soil microorganisms possess a high potential for oxidation/reduction of As and Sb species, (iv) oxidation/reduction processes occur at a range of *in situ* relevant temperatures.