Biogeochemical redox transformations of pertechnetate ($^{99}TcO_4^-$)

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Technetium-99 is an important risk-driving radioactive subsurface contaminant at the U.S. Department of Energy (DOE)'s Hanford Site in southeastern Washington State. The monovalent anion $Tc(VII)O_4^-$ (pertechnetate) is subject to subsurface migration but Tc is considerably less soluble in its most reduced form, $Tc(IV)O_2$. Reduction can be catalyzed directly by a range of anaerobic microorganisms but also indirectly by products of microbial metabolism including ferrous iron and sulfide. We have investigated Tc(VII) reduction reactions in Hanford subsurface sediments and in well-defined model systems that include metal-reducing microorganisms and Fe-bearing minerals to explore speciation effects on reaction rates and Tc endproducts. In Hanford sediments collected from anoxic regions of the subsurface or oxic sediments subjected to microbial reduction, 2×10^{-5} M (20 μM) aqueous Tc(VII) was reduced to below the detection limit (3.98×10^{-9} M) over times ranging from days to months. The rate and extent of reduction was dependent on sediment source, Fe(II) speciation, and sulfide concentration. X-ray microprobe analyses, including fluorescence mapping, elemental multichannel analysis, and micro-diffraction, were used to deduce Tc speciation and mineralogic association in the various sediments. In bioreduced Hanford formation sediments Tc(IV) was associated with phyllosilicates (mica), as indicated by associated Fe and Rb (analogous to K) signals. X-ray absorption spectroscopy (XAS) revealed the presence of $Tc(IV)O_2$ and Fe(III)- associated Tc(IV). Tc(VII) was also reduced by sediment-associated biogenic sulfide; Tc-S bonding at the nearest coordination environment around absorber Tc atom was revealed by XAS. These results indicate that Fe(II) associated with Hanford subsurface sediments can be a facile reductant of $Tc(VII)O_4^-$ and that the rate of reduction and nature of Tc end product is a function of Fe(II) speciation. These results have implications for far-field ^{99}Tc migration at Hanford where groundwater flow paths traverse Fe(II)-bearing sediments that can reduce Tc(VII) to relatively insoluble Tc(IV) phases.

High CO_2 concentrations negatively affect methanogenesis and sulphate reduction in gas fields of the North German Plain

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In consequence of their global warming potential, large-scale solutions are needed to reduce the emissions of greenhouse gases like CO_2 or CH_4. The carbon capture and storage offers one option to reduce CO_2 emissions. Favorable CO_2 storage sites are depleted gas and oil fields. Our study is focusing on the direct influence of high CO_2 concentrations on the autochthonous microbial population and environmental parameters at such sites. The studied reservoir formation is operated by Gaz de France Suez E&P DEUTSCHLAND GmbH. The conditions in the reservoir around two production wells differ in various geochemical and microbiological parameters (Ehinger *et al.* 2009). Based on these results our study included cultivation and molecular-biological approaches. The two wells differed in the indigenous and inducible (with substrate addition) microbial activity. The addition of methanol to fluids of both wells induced biogenic methane production only in well A. Fluids of well B showed induced sulphide production after addition of hydrogen and CO_2. Results from molecular biological analysis of original fluids supported the activity profile for both sites. The abundance of archaeal 16S rDNA and *mrcA* was several magnitudes higher in fluids of site A whereas site B was dominated by *Bacteria*. Incubations with high carbon dioxide concentrations showed a significant decrease of methane and sulphide production with increasing CO_2 levels. In a second step actively growing methanogenic and sulphate-reducing enrichments from the reservoir fluids were incubated under in situ pressure and temperature with high CO_2 levels. First experiments indicated that the microorganisms survived short termed incubation although the respiratory activity was not detectable. From this experiment viability rates of micro-organisms together with molecular analysis of community changes were investigated. At the end, these experiments will provide information about biogeochemical and micro-biological changes during and after the storage of CO_2 and their potential impacts on reservoir geology, storage capacity, and long-term stability.