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Stability of selenide in reducing waters - insights from chromatographic analyses

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Selenium (Se) is a contaminant of high environmental relevance in North America, due to its bioaccumulation potential in freshwater food chains impacted by industrial Se discharges. Bioreduction processes, both in ambient sediments and in industrial treatment processes, remove the Se oxyanions selenate Se(VI) and selenite Se(IV) from impacted waters, and convert them into reduced Se species, namely elemental Se(0) and selenite Se(-II). While Se(0) is considered to be not bioavailable, because it is not soluble in water, Se(-II) is of potential ecotoxicological concern, due to the possibility of it forming both volatile and organic Se species with high bioavailability.

While the existence of Se(-II) in ambient waters has often been postulated, there is to date no analytical evidence of its existence or environmental relevance. In this study, we provide the first chromatographic evidence that Se(-II) does indeed exist in certain industrially-impacted waters. However, we also show that it is not stable in anoxic waters, and undergoes reactions leading to the formation of other dissolved reduced, but currently unidentified, Se species.

Selenide in the form of H_2Se was determined by GC-ICP-MS in reducing waters impacted by mining activities. Waters were collected and kept unpreserved and without a headspace, before volatile Se species were determined by GC-ICP-MS after purge-and-trap preconcentration. Although H_2Se was found in lower concentrations than volatile organic Se species, this approach proves conclusively for the first time that free selenide existed in the tested waters.

In controlled laboratory experiments, we investigated by IC-ICP-MS whether Se(-II) is stable in reducing waters in anionic form. Sodium selenide was dissolved in degassed deionized water in a glove box at pH values that prevent the formation and loss of H_2Se, and analyzed in a glove box. Despite these precautions, the AEC-ICP-MS results show that only a very small fraction of the total Se in solution elutes from the chromatographic column, and even that Se fraction appears to undergo oxidation on the chromatographic column, indicating that Se(-II) easily converts to Se(0) in anoxic waters. Additionally, however, several unidentified soluble Se species were encountered, which are presumably secondary products formed from Se(-II) and Se(0).