

[OP 1.1]

Use of Selective Extractions to Assess the Bioavailability of Inorganic Mercury in Sediments and Soils

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After review and cross-testing of previously published methods (Revis, et. al, 1989; Wallschlaeger, et. al, 1998), a novel sequence of selective extractions was developed specifically for inorganic Hg in solid media (Bloom, et. al, 1999). These extractions separate Hg into operationally defined fractions which 'make sense' biogeochemically, rather than striving for true compound-specific identification, which is impossible by wet extraction methods (Davis, et. al, 1997). Experiments were done to understand the effects of extraction time, solids:liquid ratio, and alternate aqueous phases (1N HCl, 1N HN₂OH), as well as relationships to independently measures of CH₃Hg, (CH₃)₂Hg, and Hg volatile at 150 °C in natural samples, reference materials, and pure compounds. Compounds tested included cinnabar (red HgS), metacinnabar (black HgS), freshly precipitated HgS, HgCl₂, Hg⁰, Hg-humate, Hg/Au amalgam, and HgO. Based on these preliminary findings a 5 step sequence of extractions was established which provided the best separation of the compounds into distinct biogeochemically meaningful categories.

Each extraction is performed sequentially on the same 0.4 g sample aliquot in 40 mL of extractant. Samples are extracted for 12-18 hours, centrifuged and filtered, and then extracted a second time for 5 minutes with the same extractant. The two extracts are then combined for each phase. All samples except the volatile Hg fraction are oxidized with BrCl, and analyzed for total Hg by dual amalgamation cold vapor atomic fluorescence spectrometry (CVAFS). Volatile Hg in the deionized water fraction was determined by direct purging of an aliquot of the initial supernatant, prior to filtration and oxidation.

Each of the extraction steps was evaluated in terms of method detection limits (MDLs) and analytical precision by the repeat analysis of blanks, homogeneous low level samples, and reference materials. The sum of species for the certified reference materials was used to assess the overall accuracy of the method, although no independent checks are possible for each operationally defined fraction. For fractions 1-a, 1-b, 2, and 5, method blanks and detection limits of 0.1-1 ng/g were easily obtained, while for fractions 3 and 4, MDLs were generally in the range of 1-5 ng/g, owing to the higher reagent concentrations used. These values are sufficiently low to allow the use of this extraction methodology for the speciation of almost all pristine as well as contaminated sediment and soil samples. Analytical precision as determined by the relative percent difference (RPD) of duplicate digestions of homogeneous samples was in the range of 2-8% for the major fractions in a given sample, but for fractions making up less than 5% of the total Hg concentration, RPDs varied from 2-40%. Recovery of total Hg by the sum of species in reference materials, and in other samples by comparison to an independent measure of total Hg (HF/HNO₃ or aqua regia digestion) showed that the overall accuracy of the method on homogeneous samples is in the range of 90-105% of the expected values.

To help understand the meaningfulness of the extraction scheme, comparisons were made both to EXAFS analysis (Kim, et. al, 1999) of true speciation in high level mine tailings, and to the methylation potential of the samples. Although the data set is limited, EXAFS generally confirmed the ability of the selective extraction scheme to separate HgS from non-HgS in high level samples. Methylation potential was determined by anoxic incubation of aliquots of the test samples with biologically active low Hg, high organic matter freshwater lake sediments. These incubation experiments showed that inorganic Hg extracted in the 1N KOH fraction is strongly correlated with methylation potential. The water fraction showed a weak positive correlation with methylation potential, while the 12N HNO₃ and aqua regia fractions showed weak negative correlations with methylation. In all natural and sediment incubation samples, most of the Hg present was found either in the 1N KOH (organic) or aqua regia (HgS) fractions.

References

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