An Overview of Techniques for Mercury Speciation of Contaminated Sediments
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Introduction
Mercury is often considered an environmental pollutant of interest because of its potential toxic effects on humans and the environment. Mercury contamination can occur through a variety of natural and anthropogenic processes. The fate and transport of mercury in the environment (Figure 1) can vary greatly depending on the environmental substances to which it is exposed or its chemical form (2). Performing total mercury analysis is now commonplace; it is often useful to determine the dominant form of mercury in order to successfully remediate or better characterize the environmental hazards of a specific site. In soils and sediments, often only a very small portion of the total mercury is bioavailable (2). Though there is no universally- accepted method for measuring mobility, the total mobility of mercury in the environment, a variety of methods exist in the literature to determine operationally-defined mercury fractions in a sample (4–6,8,9). This analysis is particularly useful for contaminated mine wastes that may contain high levels of mercury, as it has been known that mercury is primarily in a stable form such as mercury sulfide (4–6,10). A fraction refers to a group of similar characteristics, such as bioavailability or environmental mobility, but cannot be distinguished from one another.

Thermal Volatilization
Thermal volatilization, or thermodesorption, coupled to an atomic absorption detector (TDAAS) is a technique that has been employed for the determination of mercury species. TDAAS works by heating a sample at a specific rate and temperature. As the sample is heated, the different mercury compounds are released at different temperatures (11,12). As the mercury is released, it is swept into an atomic absorption spectrophotometer and the absorbance is recorded on a chromatogram. The species of mercury is determined by comparing the thermodesorption profile to that of a known, pure source (12). This technique may produce peaks that do not fit well with any of the known models due to the complex interactions and oxidation states of mercury compounds (6). Though it is a good method for determining elemental mercury and gaining information about mercury oxidation states, thermal volatilization does not provide much information about mercury mobility (6).

Table 1 compares some of the advantages and disadvantages of the SSE procedure and Method 3200. They are both operationally-defined procedures that provide information on the distribution of mercury in the different fractions that can help determine what remediation methods may be the most useful. Depending on what the requirements are for a certain project, one method may be more applicable than the other.

Comparison of 5-Step SSE and Method 3200
Method 3200 is an accepted EPA method for the determination of mercury fractions. As with the SSE, it is an operationally-defined procedure and does not provide specific mercury species information but rather provides information values for a group of species. For Method 3200, there is an initial preparation procedure that yields a supernatant and a pellet (Figure 2). The supernatant is further analyzed to extract organic and non-mobile fractions. This technique may provide peaks that do not fit well with any of the known models due to the complex interactions and oxidation states of mercury compounds (6). Though it is a good method for determining elemental mercury and gaining information about mercury oxidation states, thermal volatilization does not provide much information about mercury mobility (6).

X-Ray Absorption Fine Structure Spectroscopy (XAFS)
X-Ray Absorption Fine Structure Spectroscopy (XAFS) uses high energy X-rays from a synchrotron source to determine information such as the number and type of shells around an atom or the oxidation state of the atom. It is useful to determine Mercury inorganic and organic compounds in sediments. XAFS has been used to develop standards for mercury speciation methods (14–16). XAFS successfully determines the number of shells around the atom, the oxidation state of the atom, and the crystal structure of the atom. XAFS is a useful tool for determining mercury speciation in soils and sediments. (Brooks Rand Labs, 2010).

XAFS can be used to determine the elemental and organic mercury in a sample. It can also be used to determine the oxidation state of the mercury. XAFS has been used to determine the number of shells around the atom, the oxidation state of the atom, and the crystal structure of the atom. XAFS is a useful tool for determining mercury speciation in soils and sediments. (Brooks Rand Labs, 2010).

Reference Materials
No certified reference materials are commercially available for the mercury fractionation methods. However, SSE results and Method 3200 results were developed by Nicolas S. Bloom, formerly of Studio Environmental (SGC). For the purpose of method validation, these reference materials (Hg\textsubscript{0}, HgCl\textsubscript{2}, and HgS) were made by depositing elemental mercury in an oven, dissolving the elemental mercury in acid, and reacting the acid solution with sulfuric acid to form mercury sulfide. The standards were distributed to labs that participated in a round robin study in 2005 to validate different analysis methods for the speciation of mercury in solid samples. The results were presented at Bloom’s International Conference on Mercury as a Global Pollutant in Madison, Wisconsin, in 2005. Though these reference materials are not officially certified for any analyte, SGC provided additional certified reference materials for the fraction of the SSE procedure, as well as for total mercury. National Institute of Standards and Technology (NIST) Standard Reference Material 2710 is available that has a total mercury concentration of 22.6 mg/kg, and the SGC reference materials (Hg\textsubscript{0}, HgCl\textsubscript{2}, and HgS) were prepared by EPA Method 3200 and by the 5-Step SSE.

Figure 5 shows the result of each fraction of the SSE procedure as a percentage of the sum of the mercury fractions. The sum of all fractions then shows the recovery of the reference material as a percentage of the certified or reference value. Figure 6 shows the percent of each reference material that would be considered bioavailable by each method. For the SSE, fractions 1-3 were summed. For Method 3200, the Extractable Inorganic and Extractable Organic fractions were summed (there was no contribution from the semi-mobile or non-mobile fraction in this case). Figure 7 compares the Semi-mobile fraction from Method 3200 in Fraction 4 of the SSE. Figure 8 compares the Non-mobile fraction from Method 3200 to Fraction 5 of the SSE. The semi-mobile and non-mobile fractions generally do not compare well with fractions 4 and 5 from the SSE. According to the method, elemental mercury should be extracted in the semi-mobile fraction, but when the SSE was applied to material for Hg\textsubscript{0}, a material made by depositing elemental mercury in an oven, was analyzed, a significant portion (49%) was extracted in the non-mobile fraction. For the SSGE procedure, 88% of mercury in the SGC Hg\textsubscript{0} reference material was extracted in Fraction 4, as would be expected (12). Similarly, for the SGC HgS reference material, 77% of the mercury was extracted in Fraction 5 of the SSE, while 76% was recovered in Fraction 4 for SSE. Hg\textsubscript{0} is primarily associated to be recovered in the semi-mobile fraction, though there may be some more mobile forms.

For both the SSE procedure and Method 3200 analyses, analyzing total mercury in the sample provides an important quality assurance check. This allows for a comparison of the sum of the fractions to the total mercury concentration. In this way, sample loss, contamination, or other errors can be assessed if the sum of the fractions significantly differs from the total mercury concentrations. It also allows for a more accurate representation of the data because the fractions are operationally-defined, having a known concentration of mercury. The sum of the fractions is not necessarily meaningful by itself, rather it is needed to take into the context of the sample as a whole (2,11).

Table 2 shows the relative similarities in speciation between Method 3200 and the SSE procedure. Fractions 1 and 2 of the SSE procedure are expected to be roughly equivalent to the extractable inorganic mercury portion of Method 3200. Fraction 3 of the SSE is equivalent to the extractable organic portion of Method 3200 except Hg\textsubscript{0}, which is recovered in Fraction 3 for the SSE compared to being recovered in the semi-mobile and non-mobile fractions for Method 3200. Fraction 4 of the SSE is expected to be equivalent to the semi-mobile fraction. Fraction 5 of the SSE is expected to be equivalent to non-mobile for Method 3200.