Appendix J: Sampling and Analysis Procedures

This Appendix provides direction for field procedures and laboratory analytical methods. Other procedures and methods may be used if justification for them is provided in the sampling and analysis plan, and with written approval by the Executive Director of the State Water Board (or Executive Officer of the applicable Regional Water Board).

J.1 Clean Sample Handling Procedures

Mercury is ubiquitous in the environment, often at trace levels. As a result, much care must be taken in the sampling and handling of ambient samples collected for mercury analyses to prevent contamination. Monitoring for mercury should use USEPA Method 1669 clean sampling techniques.

J.2 Standard Methods for Mercury and Methylmercury Analysis

Sediment and Soil Procedures

For soil and sediment data comparisons with the mine site and downstream load allocations for particulate mercury, the fine-grained fraction (portion that passes through 62.5 micron sieve) of sediment or soil samples should be analyzed for mercury. Clean procedures should be followed by the laboratory during the sieving process.

If soil or sediment samples are collected for other reasons and are not sieved, it is preferable to also determine the fine-grained fraction in these samples.

Suspended Sediment Procedures

Particulate mercury concentration in water samples can be determined by either of two methods. The first method is to analyze water samples for total and dissolved mercury (THg, DHg) and either suspended sediment concentration (SSC) or total suspended solids (TSS), and then perform the following calculation and convert units as needed:

$$Particulate\ Hg\ \left(\frac{ng}{mg}\right) = \frac{THg\ \left(\frac{ng}{L}\right) - DHg\ \left(\frac{ng}{L}\right)}{SSC\ \left(\frac{mg}{L}\right) or\ TSS\ \left(\frac{mg}{L}\right)}$$

The TSS method is less common, and consists of filtering a water sample with a known volume and then analyzing the mercury mass of the solids collected on the filter, and then dividing the mercury mass by the water sample volume (unit is mg/L).

Fish Tissue Procedures

Mercury in fish samples can be quantified as total mercury, rather than methylmercury. As noted in section 1.3, mercury exists almost entirely in the methylated form in fish. Per sample cost is greater for methylmercury than mercury. Thus, most fish mercury data are reported as total mercury. There is a slight level of protection gained by assuming the entire concentration of mercury reported is methylmercury.

Fish tissue sampling and analysis procedures should follow USEPA's Standard Method 7473 (USEPA 2007) and the State Water Board's Surface Water Ambient Monitoring Program, Bioaccumulation Oversight Group (SWAMP/BOG) protocol (Bonnema 2014, SWAMP 2015). The method quantitation limit of 0.009 mg/kg wet weight for prey fish and 0.012 mg/kg wet weight for sport fish (see Table 10.1). Tissue mercury concentrations must always be clarified by either dry weight or wet weight basis, because the results can vary greatly. The water quality objectives specify that fish tissue data be reported as wet weight. Sample type (filet vs whole fish) and size ranges are specified in the water quality objectives (see Section 2.2). Fish samples should be collected and processed using the procedures above or by an alternative procedure only if approved in advance by staff of the State Water Board or a Regional Water Board. Table 10.1 provides a summary of quantitation and detection limits of standard methods.

Total Mercury Analysis (water, soil/sediment, and fish)

For total or dissolved mercury in water, water samples should be analyzed according to USEPA Method 1631 Revision E with a reporting limit of 0.2 ng/L or lower. If quality control objectives are not being met (for example, recoveries in matrix spike samples are outside of expected limits) and matrix interferences are suspected as the cause, responsible parties should consult with laboratory personnel and Water Board staff. The Water Boards could allow the use of USEPA Method 245.7 if detectable concentrations are within the range of the method's calibration and quality control criteria are met for that method.

For soil, sediment, and fish samples, total mercury analysis should be analyzed by USEPA Method 7473 or comparable method with a method detection limit (MDL) of 0.01 ng or lower, with one exception. An example of a comparable method is Marine Pollution Studies Laboratory (MPSL) use of method MPSL-107/ MPSL-103. The one exception pertains to high levels of mercury contamination from mine sites. Responsible parties should consult with laboratory personnel and Water Board staff for alternate methods for soil and sediment samples that may have extremely high mercury concentrations from mining waste.

Note that fish tissue is analyzed for total mercury, not methylmercury, for cost and accuracy. Methylmercury tissue analyses are more costly and more difficult than total mercury. Methylmercury comprises 80 – 100% of the total mercury measured in fish (Becker and Bigham 1995; Bloom 1992; Nichols et al. 1999; Slotton et al. 2004; Sveinsdottir and Mason 2005; Wiener et al. 2003). Therefore, total mercury may be analyzed and reported without adjustment. (See the following section regarding analysis of other biota for methylmercury.)

Methylmercury Analysis (water and soils/sediment)

For water samples, total or dissolved methylmercury analysis should be analyzed by USEPA Method 1630 modified to achieve a method detection limit of 0.009 ng/L or lower and reporting limit of 0.02 ng/L. For methylmercury in soil and sediment, USEPA Method 1630 can be modified to achieve a detection limit of 0.004 – 0.02 mg/kg dry weight and reporting limit of 0.04 mg/kg dry weight.

Aqueous methylmercury analysis for pilot studies may be a necessary component of the sampling and analysis plan. Currently, laboratories commonly use a Reporting Limit of 0.02 ng/L for aqueous methylmercury. USEPA Method 1630 describes that the technically feasible MDL for aqueous methylmercury is 0.009 ng/L.

J.3 Quality Assurance Project Plans, Quality Assurance, and Quality Control

Quality assurance project plans (QAPPs) will be required to ensure data are of high quality. If monitoring is partly or fully funded by the State Water Board, the QAPPs are required to ensure data are "SWAMP comparable". Therefore, if reservoir studies and pilot tests receive any funding from the State, including coordinating with SWAMP for some monitoring, the reservoir studies and pilot tests will be required to be "SWAMP comparable." Particularly relevant examples of QAPPs for reservoir mercury studies are the QAPPs developed for the SWAMP BOG lakes studies[1]. It is recommend that non-State funded monitoring programs and QAPPs also be SWAMP comparable to ensure quality data and to ensure data that is shared between entities conducting pilot studies is comparable.

The State Water Board has a quality system and numerous informative documents about QAPPs and SWAMP procedures on their website: www.waterboards.ca.gov/water_issues/programs/quality_assurance/index.shtml. The following definitions are from this website and are useful for developing a QAPP and sampling plan.

> Quality assurance (QA) is an integrated system of management activities that involves planning, implementation, documentation, assessment, reporting, and quality improvement to ensure that a process, item, or service is of the type and quality required for the project needs. A QA plan should include proper documentation of all project related procedures, training of staff and volunteers, study design, data management and analysis and specific quality control measures.
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> Quality control (QC) is an overall system of technical activities that measures the attributes and performance of a process, item, or service against defined standards to verify that they meet the stated requirements established by the customer. QC also involves analytical frequency requirements and control limits. Examples of quality control components are field blanks, field duplicates, lab duplicates, spike samples, calibration blanks, and calibration standards.

[1] SWAMP BOG 2014 (low concentrations of contaminants study) and 2007 (two-year screening study) sampling and analysis plans are available at: www.waterboards.ca.gov/water_issues/programs/swamp/lakes_study.shtml

> The QA/QC requirements for monitoring are documented in QAPPs. A QAPP contains 24 elements that describe a project's goals, data needs and assessment, responsible individuals, quality assurance plan, quality control measures, and reporting deadlines. A QAPP is project-specific and is designed to provide the type and quality of data required to answer questions posed by the project.

Guidelines, checklists, and example QAPPs are all provided on the previously-mentioned State Water Board’s quality system website.