Appendix E-2

Chemical Analyses and EPA Methods Performed for the Puget Sound Sediment Monitoring Program

Analyses

Metals (except Mercury)

EPA Method 3050B is a strong acid (aqua regia) digest, which is used by Ecology for the characterization of sediments for trace metal contamination. **EPA Method 3050B** is also the recommended technique for digestion of sediments in the PSEP protocols (PSEP, 1997a). This digestion does not yield geologic (total) recoveries for most analytes, including silicon, iron, aluminum and manganese; it does, however, recover quantitatively most anthropogenic metals contamination and deposition. Determination of metals values will be made via Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) (**EPA Method 6020B**).

Mercury

Mercury will be determined by **EPA Method 245.5**, mercury in sediment by cold vapor atomic absorption (CVAA). The method consists of a strong acid sediment digestion, followed by reduction of ionic mercury to Hg^0, and analysis of mercury by cold vapor atomic absorption. This method is recommended by the PSEP protocols (PSEP, 1997a) for the determination of mercury in Puget Sound sediment.

Polynuclear Aromatic Hydrocarbons (PAH) and Phthalates

EPA Method 8270DSIM/SCAN, with isotopic dilution for the PAHs, a modification of the recommended PSEP method (PSEP, 1997b), will be used for analysis of PAHs and phthalates. Automated Soxhlet (Soxtherm) Extraction with methylene chloride, a modification of **EPA Method 3541**, is followed by cleanup with florisil (**EPA Method 3620C**). Analysis with **EPA Method 8270DSIM/SCAN** is by capillary GC/MS. The PAHs are analyzed with selected ion mode (SIM) used to enhance detection capability while the phthalates are analyzed with full scan mode.

Polychlorinated Biphenyl (PCB) Aroclors and Congeners

EPA Method 8082A for PCB will be used for the analysis of the PCB Aroclors. The method for analysis of PCB congeners will be based on the NOAA congener methods detailed in Volume IV of the NS&T Sampling and Analytical Methods documents (NOAA, 1993). Both of these methods are GC methods with dual dissimilar column confirmation. Electron capture detectors are used. Extraction is by **EPA Method 3541**, Soxtherm Extraction. Cleanup follows a modification of EPA Methods **3620C**, **3660B**, and **3665A**, and involves extraction with

tetrabutylammonium hydrogen sulfate (TBA) to remove sulfur, then eluting through a micro Florisil® column, followed by treatment with concentrated sulfuric acid.

Polybrominated Diphenyl Ether (PBDE) Congeners

For PBDEs, Soxtherm Extraction, **EPA Method 3541,** is followed by cleanup with silica gel (**EPA Method 3620C and 3660B**). Analysis with **EPA Method 8270DSIM** is by capillary GC/MS with selected ion mode (SIM) used to enhance detection capability.

EPA Methods

245.5 Mercury analysis

With the Cetac M-7600 cold vapor mercury analyzer, stannous chloride solution and sample solution are pumped simultaneously into a mixing tee. The reaction of stannous chloride ($SnCl_2$) with Hg^{++} results in the reduction of Hg^{++} to elemental mercury. The mixture is pumped through a gas liquid separator and drying tube into the sample absorbance cell. The amount of light absorbed at 253.7 nm is proportional to the mercury level in the sample.

3050B Metals extraction

Samples aliquots are transferred to digestion vessels. Appropriate spiked samples and blanks are also prepared. Samples are digested in nitric acid, hydrogen peroxide, and/or hydrochloric acid (for ICP analysis) on a hot plate or hot block. The samples are brought to a final volume and stored for analysis.

3541 Automated Soxhlet (Soxtherm) Extraction (method change from Soxhlet Extraction, EPA 3540, starting in 2007)

This method uses a commercially available, three stage extraction system to achieve analyte recovery from soil, sediment, sludges, and waste solids, comparable to Method 3540, but in a much shorter time. In the initial extraction stage of Method 3541, the sample-loaded, muffled, glass fiber extraction thimble is immersed into the boiling solvent. This ensures very rapid intimate contact between the specimen and solvent and rapid extraction of the organic analytes. In the second stage the thimble is elevated above the solvent, and is rinse-extracted as in Method 3540. In the third stage, the solvent is evaporated, as would occur in the Kuderna-Danish (K-D) concentration step in Method 3540. The concentrated extract is then ready for cleanup followed by measurement of the organic analytes.

3620C Florisil® Cleanup – PCB, PBDE, PAHs, Phthalates

Sample extracts are solvent exchanged to hexane, and transferred to the top of the Florisil® column. The Florisil® column is then eluted with a mixture of diethyl ether (preserved with 2% ethanol) and hexane. The percentage of preserved diethyl ether may be changed according to the analytes of interest.

3660B Sulfur cleanup - PCB

The sample to undergo cleanup is mixed with either copper or tetrabutylammonium (TBA) sulfite. The mixture is shaken and the extract is removed from the sulfur cleanup reagent.

3665A Sulfuric acid - Permanganate cleanup – PCB, PBDE

An extract for PCB analysis is treated with concentrated sulfuric acid. Sulfuric acid will destroy most organic chemicals including the pesticides Aldrin, Dieldrin, Endrin, Endosulfan (I and II), and Endosulfan sulfate.

6020B Inductively Coupled Plasma/Mass Spectrometry metals analysis (change from EPA Method 200.8 starting in 2017)

Sample material in solution is introduced into a radiofrequency plasma by pneumatic nebulization where energy transfer processes cause desolvation, atomization, and ionization. The ions are extracted from the plasma, through a vacuum interface, and separated on the basis of their mass-to-charge ratio by a quadrupole mass spectrometer. The ions passing through the mass spectrometer are counted by a dual stage discrete dynode electron multiplier detector and the resulting information processed by a Windows NT® based data handling system. Interferences, including isobaric, polyatomic, and matrix effects must be recognized and compensated for. Instrumental drift and sample matrix effects must be corrected by the use of internal standards.

8082A PCB Aroclor and congener analysis

The sample extract is analyzed by automatically injecting an aliquot of sample into a gas chromatograph, equipped with dual electron capture detectors (ECD).

8270DSIM/SCAN Semivolatile organic compounds by Gas Chromatography/Mass Spectrometry – PAH, PBDE, Phthalates analysis

This method uses a GC/MS system set up with a capillary column that separates the compounds in the sample extract and a mass spectrometer in full scan mode is used for their qualitative and quantitative analysis (BNAs). PAH and PBDE analysis is conducted in SIM (Selective Ion Mode) while phthalates is in full scan mode.

References

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