Appendix D-1

Physical and Biogeochemical Analyses Performed for the Puget Sound Sediment Monitoring Program

Grain Size (PSEP, 1986)

The PSEP grain size method (PSEP, 1986) is a sieve-pipette method. In this method the sample is passed through a series of progressively smaller sieves, with each fraction being weighed. After this separation, the very fine material remaining is placed into a column of water, and allowed to settle. Aliquots are removed at measured intervals, and the amount of material in each settling fraction is measured.

The following parameters and grain size fractions will be reported:

- % Solids
- % Gravel (> 2000 μm)
- % Very Coarse Sand (1000 – 2000 μm)
- % Coarse Sand (500 – 1000 μm)
- % Medium Sand (250 – 500 μm)
- % Fine Sand (125 – 250 μm)
- % Very Fine Sand (62.5 – 125 μm)
- Total % Sand (calculated)
- % Silt (39 – 62.5 μm)
- % Clay (< 39 μm)
- % Fines (% Silt + % Clay; calculated)
- Total (calculated)

Total Organic Carbon (TOC) (PSEP, 1986)

Total organic carbon analysis will be performed according to PSEP methods for total organic carbon at 70°C and 104° C (PSEP, 1986). The method involves drying sediment material, pretreatment and subsequent oxidation of the dried sediment, and determination of CO_2 by infrared spectroscopy. Due to the non-homogeneous nature of organic carbon content in marine sediments, two to five analyses are run for each sample, the results of which are averaged.

Total Carbon, Total Organic Carbon, Total Inorganic Carbon, Total Nitrogen (TC, TOC, TIC, TN) (EPA, 440)

Elemental analysis is used to determine particulate carbon and nitrogen concentrations in Puget Sound sediments.

An accurately weighed dried sediment sample is combusted at 975°C using an elemental analyzer. The combustion products are passed over a copper reduction tube to convert the oxides of N into molecular N. Carbon dioxide, water vapor and N are homogeneously mixed at a known volume, temperature and pressure. The mixture is released to a series of thermal conductivity detectors/traps, measuring in turn by difference, hydrogen (as water vapor), C (as carbon dioxide), and N (as N_2).

Organic and inorganic carbon determination is made using a fuming HCl method. Samples are allowed to dry overnight at 103-105°C, then placed in a desiccator containing concentrated HCl and covered and fumed for 24 hrs. The fuming HCl converts inorganic carbonate in the samples to water vapor, carbon dioxide, and calcium chloride. Samples are analyzed for particulate C, and the resultant data are particulate organic carbon. Inorganic carbon concentrations are calculated from these values.

$\delta^{13}C$ and $\delta^{15}N$ stable isotopes (University of California, Santa Cruz)

Samples are freeze dried, homogenized and subsampled prior to analysis.

Solid materials are analyzed for $\delta^{15}N$ and $\delta^{13}C$ isotopes using either a Carlo Erba 1108 or a CE Instruments NC2500 elemental analyzer interfaced to a ThermoFinningan Delta Plus XP isotope ratio mass spectrometer (IRMS). Tin (or silver) encapsulated samples are flash (Dumas) combusted at 1020°C in a quartz column containing chromium oxide (acting as an oxygen source to aid combustion) and silvered colbatous/cobaltic oxide (acting as a scrubber to "clean" the combustion products of sulfur bearing compounds and halides). Following combustion, excess oxygen and oxides of nitrogen are reduced in a reduction column (reduced copper at 650°C). Helium carrier flows through a water trap containing magnesium perchlorate. N_2 and CO_2 are separated on a Carbosieve GC column (45°C, 100 mL/min) before introduction to the IRMS.

During analysis, calibrated in-house standards precede and are interspersed between samples to correct for linearity (size) effects and drift. A second calibrated laboratory standard is run "as-a-sample" to monitor quality control and long-term performance. These laboratory standards, which are selected to be compositionally similar to the samples being analyzed, have been previously calibrated against NIST Standard Reference Materials (IAEA-N2, IAEA-N3, IAEA-USGS25, and IAEA-USGS26 of $\delta^{15}N$ and IAEA-CH7, and NBS-22 and IAEA-USGS25 for $\delta^{13}C$).

Corrected delta values are expressed relative to international standards PDB (PeeDee Belemnite) for $\delta^{13}C$ and Air for $\delta^{15}N$.

Total Sulfides (PSEP, 1986; Plumb, 1981)

Total sulfide analysis will be performed according to methods detailed in PSEP, 1986. Sulfides are of concern because, depending on pH, they are potentially toxic to the benthos. The collection of samples for sulfide analysis is challenging because: 1) H2S is a gas, and sulfides may be lost by volatilization from the sample and, 2) sulfides are reducing agents and can be oxidized by dissolved oxygen. Bulk sediment samples to be analyzed for sulfides should be kept wet to reduce oxidation and may be treated with zinc acetate to precipitate zinc sulfide. They should be processed as soon as possible, preferably within 24 hours. Analysis procedures involve distillation, treatment with colorimetric reagents, and determination of the sulfide concentration of the sample distillate by comparing sample absorbance at 650nm with the standard curve.

Biogenic Silica (Opal) (BSi) (Mortlock and Froelich, 1989)

The percent of biogenic silica (BSi) in marine and freshwater surface sediments has been used as a chemical estimate of, and has been shown to be a valid proxy for, the abundance and productivity of diatoms and other siliceous microfossils. Spatial and temporal trends in these data reveal a close link to biosiliceous productivity patterns in the overlying surface waters, and provide information about nutrient enrichment, eutrophication, and acidification of surface waters, and about regional-scale hydrologic and climate change (Conley and Schelske, 2002).

In marine sediments, BSi is determined with a single extraction of silica into 2 M Na_2CO_3 solution at 85°C for 5 h. The wet chemical digestion techniques rely on the ability of the weak base solution to quantitatively dissolve all amorphous (non-crystalline, from biological sources, e.g. diatoms, sponges, etc.) Si components of the sediments while dissolving only a small fraction of the mineral silicates. Aliquots, withdrawn over time, are measured for the amount of Si extracted from amorphous vs. mineral silicates (Mortlock and Froelich, 1989).

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