# APPENDIX 9 – Laboratory Methods

Unless alternative methods are approved by Ecology in the Permittees' QAPP the following analytical methods shall be used by Permittees when analyzing stormwater as required by section S8 – *Monitoring* of this permit. Any alternative method proposed by the Permittee must have a similar reporting limit, or must be justified as adequate for the likely range of concentrations. Permittees are not guaranteed approval of their alternative methods or reporting limits.

**Table 9-1 Analytical Procedures in Stormwater**

| Analyte (or Surrogate) | Method in Water | Reporting Limit Target[a] |
|---|---|---|
| **Conventional Parameters** | | |
| Total suspended solids | SM 2540B[b] or SM 2540D | 1.0 mg/L |
| Turbidity | EPA Method 180.1 or SM2130B | ± 0.2 NTU |
| Conductivity | SM 2510 or EPA Method 120.1 | ± 1 umho/cm |
| Chloride | EPA Method 300.0, EPA Method 325.2, or SM4110B | 0.2 mg/L |
| $BOD_5$ | SM5210B | 2.0 mg/L |
| Particle Size Distribution | Coulter Counter, Laser diffraction, or comparable method - *see attached method* | NA |
| Grain Size | Ecology method sieve and pipette (ASTM 1997), PSEP 1986/2003, or comparable method | NA |
| pH | EPA Method 150.2 or SM 4500$H^+$ | 0.2 units |
| Hardness as $CaCO_3$ | EPA Method 200.7, SM2340B(ICP), SM2340C (titration) or SM 3120B | 1.0 mg/L |
| Methylene Blue Activated Substances (MBAS) | SM 2340B (ICP) or 2340C (Titration)CHEMetrics Colorimetric or SM5540C | 0.025 mg/L |
| | | |
| **Bacteria** | | |
| Fecal Coliform | SM 9221E | 2 min., 2E6 max. |
| | | |
| **Nutrients** | | |
| Total phosphorus | EPA Method 365.3, EPA Method 365.4, SM 4500-P E or SM4500-P F | 0.01 mg P/L |
| Orthophosphate | EPA Method 365.3, EPA Method 365.1, SM 4500-P E or SM4500-P F | 0.01 mg P/L |
| Total kjeldahl nitrogen | EPA Method 351.2, EPA Method 351.1, SM 4500 Norg-B, SM 4500 Norg-C, SM 4500 NH3-D, SM 4500 NH3-G, SM 4500 NH3-E or SM4500 NH3-F | 0.5 mg/L |
| Nitrate-Nitrite | EPA Method 353.2 or SM 4500 -$NO3^-$ E | 0.01 mg/L |
| | | |
| **Metals** | | |
| Total recoverable zinc | EPA Method 200.8 (ICP/MS), EPA Method 200.7 (ICP/MS) or SM 3125 (ICP/MS) | 5.0 µg/l |
| Dissolved zinc | EPA Method 200.8 (ICP/MS), or SM 3125 (ICP/MS) | 1.0 µg/l |

| Analyte (or Surrogate) | Method in Water | Reporting Limit Target[a] |
|---|---|---|
| Total recoverable lead | EPA Method 200.8 (ICP/MS), or SM 3125 (ICP/MS) | 0.1 µg/l |
| Dissolved lead | EPA Method 200.8 (ICP/MS), or SM 3125 (ICP/MS) | 0.1 µg/l |
| Total recoverable copper | EPA Method 200.8 (ICP/MS), or SM 3125 (ICP/MS) | 0.1 µg/l |
| Dissolved copper | EPA Method 200.8 (ICP/MS), or SM 3125 (ICP/MS) | 0.1 µg/l |
| Total recoverable cadmium | EPA Method 200.8 (ICP/MS), or SM 3125 (ICP/MS) | 0.2 µg/l |
| Dissolved cadmium | EPA Method 200.8 (ICP/MS), or SM 3125 (ICP/MS) | 0.1 µg/l |
| Total Mercury | EPA Method 7470 (CVAA), EPA Method 245.7, or EPA Method 1631E | 0.1 µg/l |
| Dissolved Mercury | EPA Method 7470 (CVAA), EPA Method 245.7, or EPA 1631E | 0.1 µg/l |
| | | |
| **Organics** | | |
| PAH Compounds | EPA Method 8310 or 8270D SIM | 0.1 µg/l |
| Phthalates | EPA Method 8270D | 1.0 µg/l |
| Herbicides (2,4-D, MCPP, Triclopyr, Dichlobenil, Pentachlorophenol) | EPA Method 8270D SIM or 8151 | 0.01 – 1.0 µg/l |
| Pesticides, Nitrogen (Prometon) | EPA Method 8270D SIM | 0.01 – 1.0 µg/l |
| Pesticides, Organophosphates (Diazinon) | EPA Method 8270D SIM or 8141 | 0.01 – 1.0 µg/l |
| | | |
| **Petroleum Hydrocarbons** | | |
| NWTPH-Dx | Ecology, 1997, (Publication No. 97-602) or EPA SW-846 method 8015B | 0.25-0.50 mg/L |
| NWTPH-Gx | Ecology, 1997, (Publication No. 97-602) | 0.25 mg/L |
| | | |
| **Toxicity** | | |
| Environment Canada Trout Embryo Viability | E-test in Env. Canada EPS 1/RM/28. See also Ecology publication no. WQ-R-95-80. | NA |

a. All results below reporting limits should also be reported and identified as such. These results may be used in the statistical evaluations.

b. To ensure accurate results, Ecology recommends modifying these methods to analyze (filter) the entire field sample. Research results indicate that errors may be introduced by decanting a subsample, although using a funnel splitter may help. The analyst may also consider analyzing several premixed subsamples from the same sample container to determine if significant variability occurred due to stratification. Reports shall indicate whether the entire field sample or a subsample was used.

NA – Not applicable

SM – Standard Methods

**Table 9-2 Analytical Procedures in Sediments**

| Analyte (or Surrogate) | Method in Sediment | Reporting Limit Target[a] |
|---|---|---|
| **Conventional Parameters** | | |
| Total Solids | or SM 2540B | NA |
| Total Organic Carbon | Puget Sound Estuary Protocols (PSEP 1997), SM 5310B, SM 5310C, SM 5310D or EPA Method 9060 | 0.1% |
| Grain-size | Ecology Method Sieve and Pipette (ASTM 1997), ASTM F312-97, ASTMD422 or PSEP 1986/2003 | NA |
| Total Phosphorus | EPA Method 365.3, EPA Method 365.4, SM 4500 P E or SM 4500 P F | 0.01 mg/kg |
| Total Volatile Solids | EPA Method 160.4 or SM 2540E | 0.1% |
| | | |
| **Metals** | | |
| Total Recoverable Zinc | EPA Method 200.8 (ICP/MS), EPA Method 6010, EPA Method 6020 or SM 3125 (ICP/MS), or EPA Method 200.7 (ICP) | 5.0 mg/kg |
| Total Recoverable Lead | EPA Method 200.8 (ICP/MS), EPA Method 6010, EPA Method 6020 or SM 3125 (ICP/MS) | 0.1 mg/kg |
| Total Recoverable Copper | EPA Method 200.8 (ICP/MS), EPA Method 6010, EPA Method 6020 or SM 3125 (ICP/MS) | 0.1 mg/kg |
| Total Recoverable Cadmium | EPA Method 200.8 (ICP/MS), EPA Method 6010, EPA Method 6020 or SM 3125 (ICP/MS) | 0.1 mg/kg |
| Total Recoverable Mercury | EPA Method 245.5 or EPA Method 7471B | 0.1 mg/kg |
| | | |
| **Organics** | | |
| PAH Compounds | EPA Method 8270D[b] | 70 µg/Kg dry |
| Phthalates | EPA Method 8270D[b] | 70 µg/Kg dry |
| Phenolics | EPA Method 8270D[b] or PSEP 1997 | 70 µg/Kg dry |
| PCB's | EPA Method 8082 | 80 µg/Kg dry |
| Pentachlorophenol | EPA Method 8270D SIM or EPA Method 8151 | 1.0 µg/kg |
| Diazinon | EPA Method 8270D SIM or EPA Method 8141 | 50 µg/kg |
| Chlorpyrifos and Malathion | EPA Method 8270D SIM or EPA Method 8141 | 25 µg/kg |
| | | |
| **Petroleum Hydrocarbons** | | |
| NWTPH-Dx | Ecology, 1997 (Publication No. 97-602) or EPA SW-846 method 8015B | 25.0-100.0 mg/Kg |
| | | |

a. All results below reporting limits shall also be reported and identified as such. These results may be used in the statistical evaluations.
b. Sample preparation procedures followed: 3550, 3640, 3660G, and 3620
NA – Not applicable
SM – Standard Methods

# WET SIEVING AND MASS MEASUREMENT FOR LASER DIFFRACTION ANALYSIS

## WET SIEVING

**Sample Collection/Handling**
Samples should be collected in HDPE or Teflon containers and held at 4 degrees C during the collection process. If organic compounds are being collected, the sample containers should be glass or Teflon.

**Preservation/Holding Time**
Samples should be stored at $4^{o}$ C and must be analyzed within 7 days (EPA, 1998). Samples may not be frozen or dried prior to analysis, as either process may change the particle size distribution.

**Sonication**
Do not sonicate samples prior to analysis to preserve particle integrity and representativeness. Laboratories using laser diffraction will have to be notified not to sonicate these samples at any time during the analysis. It is recommended that this request also be written on the chain-of-custody form that the analytical laboratory receives in order to assure that sonication is omitted.

### *LABORATORY PROCEDURES*

### *Equipment*

__ 2 Liters of stormwater sample water (total sample required for analysis (ASTM D 3977))
__ Drying oven (90 degrees C $\pm$2 degrees)
__ Analytical balance (0.01 mg accuracy)
__ Desiccator (large enough diameter to accommodate sieve)
__ Standard sieves - larger than 2" diameter may be desirable
    __ 500 um (Tyler 32, US Standard 35)
    __ 250 um (Tyler 60, US Standard 60)
__ Beakers - plastic (HDPE)
__ Funnel (HDPE - Large enough diameter to accommodate sieve)
__ Wash bottle
__ Pre-measured reagent-grade water

***Sample Processing***

- Dry 250 um and 500 um mesh sieves in a drying oven to a constant weight at 90 ± 2° C.
- Cool the sieves to room temperature in a desiccator.
- Weigh each sieve to the nearest 0.01 mg.
- Record the initial weight of each dry sieve.
- Measure the volume of sample water and record.
- Pour the sample through a nested sieve stack (the 500 um sieve should be on the top and the sieve stack should be stabilized in a funnel and the funnel should be resting above/inside a collection beaker).
- Use some of the pre-measured reagent-grade water in wash bottle to thoroughly rinse all soil particles from sample container so that all soil particles are rinsed through the sieve.
- Thoroughly rinse the soil particles in the sieve using a pre-measured volume of reagent-grade water.
- The particles that pass through the sieve stack will be analyzed by laser diffraction Particle Size Distribution (PSD) analysis using the manufacturers recommended protocols (with the exception of no sonication).
- Particles retained on the sieve (>250 um) will not be analyzed with the laser diffraction PSD.
- Dry each sieve (500 um and 250 um) with the material it retained in a drying oven to a constant weight at 90 ± 2° C. The drying temperature should be less than 100° C to prevent boiling and potential loss of sample (PSEP, 1986).
- Cool the samples to room temperature in a desiccator.
- Weigh the cooled sample with each sieve to the nearest 0.01 mg.
- Subtract initial dry weight of each sieve from final dry weight of the sample and sieve together.
- Record weight of particles/debris separately for each size fraction (≥ 500 um and 499 - 250 um).
- Document the dominant types of particles/debris found in this each size fraction.

## Laser Diffraction (PSD)

PSD results are reported in ml/L for each particle size range. Particle size gradations should match the Wentworth grade scale (Wentworth, 1922).

## Mass Measurement

### *Equipment*

__ Glass filter - 0.45 um (pore size) glass fiber filter disk (Standard Method D 3977) (larger diameter sized filter is preferable)
__ Drying oven (90 degrees C ±2 degrees)
__ Analytical balance (0.01 mg accuracy)
__ Wash bottle
__ Reagent-grade water

### *Procedure*

- Dry glass filter in drying oven at 90 ± 2° C to a constant weight.
- Cool the glass filter to room temperature in a desiccator.
- Weigh the 0.45 um glass filter to the nearest 0.01mg.
- Record the initial weight of the glass filter.
- Slowly pour the laser diffraction sample water (after analysis) through the previously weighed 0.45 um glass filter and discard the water.
- Use reagent-grade water in wash bottle to rinse particles adhering to the analysis container onto glass filter
- Dry glass filter with particles in a drying oven at 90 ± 2° C to a constant weight.
- Cool the glass filter and dried particles to room temperature in a desiccator.
- Weigh the glass filter and particles to the nearest 0.01mg.
- Subtract the initial glass filter weight from the final glass filter and particle sample weight.
- Record the final sample weight for particles <250 um in size.

### *Quality Assurance*

Dried samples should be cooled in a desiccator and held there until they are weighed. If a desiccator is not used, the particles will accumulate ambient moisture and the sample weight will be overestimated. A color-indicating desiccant is recommended so that spent desiccant can be detected easily. Also, the seal on the desiccator should be checked periodically, and, if necessary, the ground glass rims should be greased or the "O" rings should be replaced.

Handle sieves with clean gloves to avoid adding oils or other products that could increase the weight. The weighing room should not have fluctuating temperatures or changing humidity. Any conditions that could affect results such as doors opening and closing should be minimized as much as possible.

After the initial weight of the sieve is measured, the sieve should be kept covered and dust free. Duplicate samples should be analyzed on 10% of the samples for both wet sieving and mass measurements.

**Reporting**

Visual observations should be made on all wet sieved fractions and recorded. For example if the very coarse sand fraction (2,000-1,000 um) is composed primarily of beauty bark, or cigarette butts, or other organic debris this should be noted. An option might also be for a professional geologist to record the geological composition of the sediment as well.

**REFERENCES**

ASTM. 1997. Standard test methods for determining sediment concentration in water samples. Method D 3977. American Society for Testing and Materials, Philadelphia, PA.

PSEP. 1986. Recommended Protocols for measuring conventional sediment variables in Puget Sound. Prepared by Tetra Tech, Inc. for U.S. Environmental Protection Agency and Puget Sound Water Quality Authority. Tetra Tech Inc., Bellevue, WA.

U. S. EPA. 1998. Analysis of total suspended solids by EPA Method 160.2. Region 9, Revision 1. SOP 462. 12 pp

Wentworth, C.K. 1922. A scale of grade and class terms for clastic sediments. *Journal of Geology*. 30:377-392