TECHNICAL INFORMATION MEMORANDUM

ORGANIC CARBON NORMALIZATION OF SEDIMENT DATA

Prepared by:

Teresa C Michelsen, Ph.D.
Washington Department of Ecology
Sediment Management Unit

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1. INTRODUCTION

All sediment data collected in Washington State are evaluated using the Sediment Management Standards (SMS), Chapter 173-204 WAC. Under the SMS rule, the numerical sediment standards for most organic chemicals are organic carbon normalized. Consequently, all sediment samples that are analyzed for organic chemicals must also be analyzed for organic carbon to facilitate comparisons with the numerical standards.

This technical information memorandum describes why some sediment data are organic carbon normalized, how organic carbon data are collected and analyzed, provides an equation for organic carbon normalizing data, and explains how to evaluate historical data for which organic carbon data are not available. Finally, guidelines are presented for determining when it may not be appropriate to organic carbon normalize data.

For questions on the enclosed information or for further information, please contact the Sediment Management Unit at (SCAN 585)206/459-6824, or contact the NWRO or SWRO Sediment Technical Specialist.

2. WHY SEDIMENT DATA ARE ORGANIC-CARBON NORMALIZED

Concentrations of organic contaminants (particularly nonpolar, nonionizable chemicals) and the toxicity of these contaminants in sediments have been observed to correlate well with the organic carbon content of sediments (DiToro et al., 1991; Lyman, 1982; Roy and Griffin, 1985). Nonpolar contaminants in sediments or water preferentially partition into the organic material in sediments because of the similar chemical nature of the organic material to the nonpolar organic contaminants. Contaminants that form ions, such as acids, bases, phenols, and metals, do not partition as strongly into the organic fraction in sediments.

DiToro et al. (1991) and others have reported that the toxicity of nonionic organic chemicals in sediments appears to be correlated to the concentration of those chemicals in the organic carbon fraction of sediments, but is not well-correlated with the overall (dry weight) concentration of the chemicals in sediments. Therefore, the concentrations of contaminants in the organic fraction of sediments may be more relevant than dry weight concentrations for setting standards that are intended to prevent adverse biological effects.

In addition, because nonpolar organic contaminants are primarily associated with the organic matter in sediments, these contaminants move in the environment along with the organic fraction in sediments and may also move along with suspended organic matter in water. Therefore, gradients of chemical concentration associated with a source may be more easily observed when the data are OC-normalized than when they are presented in dry weight.

The Sediment Management Standards criteria for nonionizable organic chemicals have been set on an OC-normalized basis. Because the bioavailability of acids, bases, other ionizable organic chemicals, and metals are generally not controlled by organic matter in sediments, standards for these contaminants are set on a dry weight basis.

3. COLLECTING AND ANALYZING ORGANIC CARBON DATA

The organic carbon content of sediments is measured and referred to as *total organic carbon* (TOC). TOC refers to the total amount of organic carbon in the sediment, and does not include mineralized carbon present as carbonates or bicarbonates. These inorganic forms of carbon do not substantially affect the partitioning of organic chemicals, and are removed from the sample by the laboratory.

TOC samples may be collected in glass or plastic containers. A minimum sample size of 25 grams (wet weight) is recommended. Because a special bottle is not required, sediments for TOC analysis may be combined with sediments for other analyses that will be performed at the same laboratory. Samples should be stored frozen and can be held for up to six months if frozen.

Detailed methods for analyzing TOC samples may be found in the 18th Edition of *Standard Methods for the Examination of Water and Wastewater* (Franson, 1992). Method 5310B is recommended, slightly modified for sediment samples. A description of the method is attached as an addendum (*Clarification: Recommended Methods for Measuring TOC in Sediments*, K. Bragdon-Cook). The laboratory calculates the amount of carbon that was present in the sample from the amount of CO_2 released during combustion. TOC values are reported as percentage of the dry weight sample.

Nearly any full-service laboratory is equipped to perform this analysis, which costs approximately $60 per sample.

4. ORGANIC CARBON NORMALIZATION OF DRY WEIGHT DATA

As discussed in Section 5, organic carbon (OC) normalization is performed on a sample-by-sample basis, because TOC values vary from station to station. Because some site-specific evaluation is required (see Section 7), OC normalization should be performed by the project manager or consultant who receives data from the laboratory. Laboratories are generally not expected to perform the normalization.

To convert chemical concentration data expressed as mg/kg dry weight to mg/kg OC, divide the dry weight concentration by the percent TOC (expressed as a decimal), as shown in the following equation:

$$\text{mg/kg OC} = \frac{\text{mg/kg dry weight}}{\text{kg TOC/kg dry weight}}$$

where: mg/kg OC = milligrams of the chemical per kilogram of organic carbon

mg/kg dry weight = milligrams of the chemical per kilogram of dry weight sample

kg TOC/kg dry weight = percent total organic carbon in dry weight sample (expressed as a decimal; for example, 1% TOC = 0.01)

Although data are typically reported in mg/kg, data reported in ug/kg, ppb, or ppm can also be used in the above equation. For example:

$$\frac{\text{2 ug phenanthrene/kg dry sediment}}{\text{0.01 kg TOC/kg dry sediment}}$$

= 200 ug phenanthrene/kg TOC
= 200 ppb phenanthrene, OC-normalized.

Because this conversion is tedious to do by hand for large data sets, the data may either be entered into a spreadsheet or database that can be used to perform the conversion. **Contractors providing sediment data for permit applicants, cleanup proponents, or for Ecology should perform the normalization (for nonionic organic chemicals) and report the data for these chemicals both as dry weight and as OC-normalized data.**

5. TYPICAL TOC VALUES FOR SEDIMENTS

TOC values vary widely in the natural environment. A range of 0.5-3 percent is typical for Puget Sound marine sediments, particularly those in the main basin and in the central portions of urban bays. For example, the Puget Sound Ambient Monitoring Program reports a mean TOC value of 1 percent (PSAMP, 1990). TOC values less than 0.5 percent are commonly found in sandy or gravelly areas, erosional areas, or areas with fast-flowing currents (including rivers). In addition, the percent organic carbon in subsurface sediments usually decreases with depth, to as little as 0.01 percent.

Natural TOC values greater than 3 percent are common in nearshore environments. On occasion, natural TOC values of up to 12-15 percent have been observed in Puget Sound and other areas, particularly in depositional and/or quiescent areas where organic matter may collect. Natural TOC values may be much higher in marshy areas or other wetlands environments.

TOC values may also be artificially elevated in sediments that are heavily contaminated with organic substances (sewage, petroleum hydrocarbons, wood chips). Sewage and organic chemicals will typically raise TOC values by at most a few percent; in a majority of the cases, the effect will be negligible. However, organic debris such as wood chips can raise the TOC value by anywhere from several percent to 50 percent or more.

Because TOC values may vary widely within a single site, organic carbon normalization is preformed on a station-by-station basis. **Therefore, each sample that is analyzed for nonionizable organic contaminants must also be analyzed for TOC.**

6. EVALUATION OF HISTORICAL DATA SETS

Collection of TOC data is currently required for all sediment sampling to allow comparison to numerical sediment standards. However, many historical data sets are not OC-normalized and may not contain station-by-station TOC data. If any TOC data are available for the data set, it is recommended that a conservative value be chosen from the data available that represents the lowest percent TOC observed at the site. If different areas of the site appear to have widely varying levels of TOC, a different value may be chosen for each area that represents the lower end of the range of TOC values for that area. The professional judgment of the site/permit manager should be used to select an appropriate value in each case.

If TOC data were not included in the data set, data may be available from other studies in the same area. The SEDQUAL database may be consulted to determine whether TOC values are available for the area of interest. Again, a value should be chosen that represents the lower end of TOC values for the area, to insure that the OC-normalized concentrations calculated using the general TOC value are protective. If no TOC data are available for the area of interest, the Sediment Management Unit or a regional sediment technical specialist should be consulted to determine an appropriate TOC value to use for the comparison.

7. WHEN ORGANIC-CARBON NORMALIZATION MAY NOT BE APPROPRIATE

There are several situations, including those described below, in which it may not be appropriate to OC normalize sediment data. For additional information or guidance on data evaluation and presentation for these situations, contact the Sediment Management Unit or a regional technical specialist. **Because of the variety of uses to which sediment data are put, sediment data for nonionic organic chemicals should be reported both as dry weight and as OC-normalized data.**

In areas where the TOC is very low or very high, biological testing or use of dry weight concentrations should be considered along with OC-normalized concentrations in evaluating the extent of contamination and potential biological effects.

For example, if TOC values are very low (e.g., 0.1-0.2), it is even possible for background concentrations of organic chemicals to exceed the Sediment Quality Standards when OC-normalized. In this situation, it may be appropriate, on a site-specific basis, to use Apparent Effects Thresholds (AETs) expressed as dry weight (see PSEP, 1988) to evaluate sediment toxicity. Please contact the Sediment Management Unit for assistance in evaluating such data.

Conversely, if TOC concentrations in sediments have been increased above normal concentrations by organic contamination (such as wood chips, sewage, or petroleum), the OC-normalized values may be inappropriately low. In these cases, although the OC-normalized chemical criteria would not be exceeded, the sediments may still cause adverse biological effects and may therefore exceed the narrative standards or biological criteria. To address this concern, if the organic chemicals or substances that are the primary contributors to the elevated TOC levels are known, the contribution of the organic contaminants to the percent TOC may be determined through analytical methods and subtracted from the TOC value before OC normalizing. Alternatively, as described above, biological testing or dry weight AETs may be used to evaluate sediment toxicity.

Bulk sediment concentrations expressed as dry weight are used to make decisions regarding treatment and disposal of sediments. Currently, the Puget Sound

Dredged Disposal Analysis (PSDDA) program uses dry weight data to determine whether sediments can be disposed of in open-water disposal areas. In addition, upland disposal options require evaluation of whether the sediment exceeds land disposal restrictions and dangerous/hazardous waste thresholds, based on dry weight concentrations. For treatment alternatives, the average dry weight concentrations of chemicals in sediment may be used to predict the effectiveness of processes such as bioremediation or chemical stabilization/solidification.

8. REFERENCES

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CLARIFICATION

RECOMMENDED METHODS FOR MEASURING TOC IN SEDIMENTS

Prepared by Kathryn Bragdon-Cook (Ecology, (206) 493-2931)

INTRODUCTION

Current PSEP protocols for measuring total organic carbon (TOC) in sediment call for drying a sediment sample at 70 degrees C in order to minimize the loss of volatile organic compounds. HCl is then added to the dried sample to remove inorganic carbon and dried again at 70 degrees C. The sample is then combusted using cupric oxide fines as a catalyst at 950 degrees C. A preweighed, ascarite-filled tube is used to capture the resulting CO_2 upon combustion. The tube is then weighed once more to determine the concentration of CO_2 which is used to calculate the TOC in percent dry weight based on total solids in the sample.

Ecology's Technical Information Memorandum, "Organic Carbon Normalization of Sediment Data", recommends Methods 5310A-D, slightly modified, from the 18th Edition of Standard Methods for the Examination of Water and Wastewater (Franson, 1992). These include a wet chemical oxidation method (5310D) and a combustion method (5310B), both using infrared detection (IR). The Department of Ecology Manchester Environmental Laboratory recommends Method 5310B for measuring TOC in wastewater or, with some modification, in sediments. Test Methods for Evaluating Solid Waste (EPA 1986) SW-846 Method 9060 also references Standard Methods for the Examination of Water and Wastewater for measuring TOC levels of solid and hazardous waste.

These methods require some modification for measuring TOC in sediment. Standard Method 5310B calls for the sample to be treated with HCl to convert inorganic carbon to CO_2 which is then purged using purified gas. The sample is homogenized and diluted as necessary. A portion is injected with a blunt-tipped syringe into a heated reaction chamber (packed with a catalyst) of a carbon analyzer using infrared detection. Needle size is selected to be consistent with particle size. Some accredited laboratories have adapted this technique to sediment by drying the sample at 70 degrees C and using an instrument attachment to the carbon analyzer designed specifically for sediment samples (Dohrman sludge/sediment boat sampler attachment, Model 183, for use with the Dohrman DC-80 TOC analyzer). The sample is then combusted and organic carbon in the sediment converted to CO_2 and transported in carrier gas streams to be measured by an infrared detector.

Method 5310D describes the wet-oxidation method where the sample is acidified and purged as above and oxidized with persulfate in an autoclave from 116 to 130 degrees C. Again, the resultant CO_2 is measured by infrared spectrometry. Adaptation of this method to sediments may be problematic. Reagents and analytical techniques may be adjusted by the laboratory, however, to increase oxidation of organic carbon in sediments.

The carbon analyzer/infrared detection used in these methods identifies characteristic spectral fingerprints as light in the infrared spectrum passes through various molecules. This instrument offers greater sensitivity than the ascarite-filled tube collector for measuring low levels of CO_2.

PROBLEM IDENTIFICATION

The combustion method dries the sediment sample at 70 degrees C to minimize the loss of organic compounds, but 70 degrees C is not enough to drive off all of the moisture in the sample. A minimum temperature of 104 degrees C is needed to ensure a truly dry sample for total solids calculations. At 104 degrees C, however, a significant loss of volatile organics occurs.

In addition, the ascarite-filled tube used to detect CO_2 in the PSEP method is less sensitive than the infrared detector of the standard methods, limiting accurate detection of low TOC concentrations. Comparative data between the two methods are not yet available.

PSDDA Reports, Development of Sediment Quality Values for Puget Sound, lists the 50%, 75%, and 90% TOC percentile concentrations for Puget Sound at 1.31%, 2.30%, and 4.50% respectively. TOC levels for individual test sites, however, vary greatly with some concentrations well below these averages. Low level detection of TOC in these areas is less accurate using the PSEP method.

Because the Ecology sediment clean up program and PSDDA program may overlap on projects, the need exists for consistency in the method used to measure TOC in sediments.

PROPOSED ACTION/MODIFICATION

Standard Method 5310B and SW-846 Method 9060 provide for more sensitive measurement of TOC concentrations in sediment. SW-846 Method 9060 (as modified by Laucks Laboratories for example) can detect TOC in sediments below 0.1%. Analytical precision for the PSEP method is not given in the protocols. For these reasons, utilization of Method 5310B or SW-846 Method 9060 using infrared detection is strongly recommended. Under conditions described below the PSEP method is acceptable.

Based on the lack of analytical error data for the PSEP method and greater instrument sensitivity of the combustion/IR method, the following guideline is given.

Prior to method selection, consideration should be given to the condition of the test site regarding probable TOC levels. When possible, historical data of particular sites should be reviewed to identify probable TOC concentration ranges.

When TOC concentrations are above 2% either method described could be used. Standard Method 5310B or SW-846 Method 9060 should be used for areas where TOC levels below 2% are likely. PSDDA applicants should state in their sampling and analysis plan which method for measuring TOC in sediment is proposed and provide detailed justification.

To correct for true dry weight with either method, the corresponding total solids analysis should be run twice, once at 70 degrees C and once at 104 degrees C, and the TOC calculation based on dry weight at 104 degrees C.

This document serves as an addendum to Ecology's Technical Information Memorandum noted above. An errata sheet to replace page 3 is included.

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