TITLE: **Sampling and Analysis of Fraction Organic Carbon (f_{oc}) in Soils**

DATE EFFECTIVE: January 2014

HISTORY: Update of VA30007.09.024 - Revisions made to clarify the technical content within this TGC.

KEYWORDS: Organic carbon (OC), property-specific soil standards, sampling

RULE/ AUTHORITY: OAC 3745-300-07(F)(3), 3745-300-07(G)(4), 3745-300-08(C)(3)(e), 3745-300-09(D)(3)(b)(iv) and 3745-300-09(H)(5)

QUESTION: If a property-specific $\mathbf{f_{oc}}$ for soils is measured at a property, what considerations are necessary for sampling and analysis?

BACKGROUND: Fraction organic carbon ($\mathbf{f_{oc}}$) is a dimensionless (mass $_{(carbon)}$/mass $_{(soil)}$), mass measure of soil organic carbon (OC) relative to soil. The measurement is used to estimate the capacity of a soil to adsorb or bind certain contaminants. The $\mathbf{f_{oc}}$ is needed when calculating property-specific soil standards for various exposure pathways, including but not limited to: direct contact with soil, determination of soil saturation limits; OAC 3745-300-08(C)(3)(e) and 3745-300-09(H)(5)), leaching to ground water (OAC 3745-300-07(F)(3)), and volatilization to indoor air (OAC 3745-300-07(G)(4) and 3745-300-09(D)(3)(b)(iv)). Due to its important role in binding contaminants in soil media, the $\mathbf{f_{oc}}$ can affect the analysis of exposure pathways and migration of the contaminants to other environmental media. In order to accurately determine $\mathbf{f_{oc}}$ of soil at a property, it is important to consider the geologic setting of the property, the heterogeneity of the soil profile, the presence of hydrocarbons or other sources of organic carbon in the soil, and the purpose for which the determination is being made.

ANSWER: Sampling Considerations

The determination of $\mathbf{f_{oc}}$ must be based on sampling locations that are not impacted by releases of petroleum or other organic chemicals of concern.

Sampling depth and location may be dependent on the geologic features of the property, such as topography, soil type and the possible incorporation of non-native fill material. It is very important that the reason $\mathbf{f_{oc}}$ is being determined is taken into consideration when choosing a sample location(s) - it must be representative of the

pathway of concern.

The surface organic layer (typically the top 6 inches/ 15 cm) should not be used to represent the OC composition of soils at the property. The number of samples and the horizontal and vertical distribution of sampling are dependant on the heterogeneity of the subsurface and the purpose for which the determination is being made. If the property-specific $\mathbf{f_{oc}}$ is measured to determine a property-specific soil saturation concentration (as described in OAC 3745-300-08(C)(3)(e)), an $\mathbf{f_{oc}}$ value representative of the vadose zone as described in OAC 3745-300-07(I)(1)(a)(ii) should be used. **For leaching and vapor intrusion assessments, a set of samples should be collected at varying depths to adequately represent the vadose zone.** The minimum number of samples (8, per US EPA's ProUCL software: http://www.epa.gov/osp/hstl/tsc/software.htm) should adequately describe the distribution of values. The final input value for $\mathbf{f_{oc}}$ should be the lower 95% confidence interval of the mean. US EPA has several methods and guidance documents that can be consulted for this determination, including US EPA (1989), *Methods for the Attainment of Cleanup Standards* (EPA 230/01-89-042), RCRA Waste Sampling Draft Technical Guidance (EPA530-D-02-002; http://www.epa.gov/osw/hazard/testmethods/sw846/pdfs/rwsdtg.pdf) and within the assessment criteria in USEPA's ProUCL software (http://www.epa.gov/osp/hstl/tsc/software.htm). Ohio EPA (OEPA) recommends that additional samples be taken during field operations to prevent unnecessary costs for remobilization of sampling equipment.

Studies have shown that differences in soil bulk density (ρ) can skew final calculation of $\mathbf{f_{oc}}$ within the soil profile, and lead to overestimation of this parameter. For this reason, it is recommended that a method to normalize $\mathbf{f_{oc}}$ values based on ρ at depth be employed. Calculation of a depth weighted average or a composite sampling regime, such as described in OEPA TGC 300007.09.002 can be utilized.

Because of the variability of the distribution of soil OC, only site samples should be used. In lieu of determining a property-specific $\mathbf{f_{oc}}$, the VAP will accept default values for various pathways. The defaults are 0.6% (0.006) for direct contact, 0.2% to 0.3% (0.002 to 0.003) for the leaching to ground water pathway, and 0.2% (0.002) for volatilization into indoor air. See OEPA's Support Documentation for the Development of Generic Numeric Standards (March 2009), OEPA's Derived Leach-Based Soil Values, Appendix Technical Support Document (October 2008), and Users Guide for the Johnson and Ettinger Model for Subsurface Vapor Intrusion into Buildings

(February 2004).

Sample Processing

After sampling, using the appropriate protocol, samples should be processed by removing roots, sticks, rocks and other debris that could influence the $\mathbf{f_{oc}}$ analysis, air dried, ground and sieved to a standard size (i.e.< 2 mm) prior to analysis (IDEM, Determining the Fraction of Organic Carbon, OLQ-General-ID-0119, September 2007; http://www.in.gov/idem/files/Foc_Guidance_070925_Final.pdf).

Method of Analysis

The method of analysis must be capable of measuring a $\mathbf{f_{oc}}$ value that is representative of the concentration of OC within the soil matrix. Care must be taken to differentiate between OC and total carbon (TC). Simple pyrolytic methods which do not quantitate the CO_2 that is produced, but simply record the loss on ignition (LOI) of the sample are not appropriate for environmental remediation purposes. **These methods should be avoided for determination of f_{oc} since it can lead to large overestimation of organic carbon content (Schumacher, 2002).** The second general category of soil organic matter analytical methods is wet chemical oxidation.

Additional analytical methods for determining TC and OC values by dry and wet combustion (acid digestion) are presented in “Total Carbon, Organic Carbon, and Organic Matter,” by D. W. Nelson and L. E. Sommers, from Methods of Soil Analysis, Part 3.Chemical Methods, SSSA Book Series No. 5. 1996.

Because soil analytical methods don’t distinguish between inorganic carbon (IC) and OC sources, the laboratory must provide assurances that IC does not bias the analytical results. Consequently, OEPA recommends that soil be pretreated to remove IC prior to analysis by pyrolitic methods, as an integral procedure to any analytical method. A detailed procedure of the pre-treatment procedure for wet chemical oxidation is found in Nelson and Sommers (1996). If the actual Walkley-Black method is used, it is recognized that incomplete oxidation of OC may occur without modification to the original method**. Because of this, the unmodified Walkley-Black Method is not recommended, due to uncertainty associated with unoxidized organic fractions.** Instead, a modification, such as described in Nelson and Sommer (1975; A rapid and Accurate Procedure for Estimation of Organic Carbon in soil, Proc. Indiana Acad. Sci., 84:456-462) is suggested. For pyrolytic methods, similar pretreatment procedures can be used, but HCl may be substituted for H_2SO_4 to remove inorganic carbon sources.

Reporting and Documentation

Ohio EPA recommends that data reports from the laboratory contain the following information in order to facilitate review and interpretation of the results:

- Laboratory SOP (should include a rationalization of the method and sampling procedures)
- Laboratory internal Chain of Custody
- Sample identification
- Laboratory reagents and standards (NIST)
- Sample pre-treatment and/or particle size reduction
- Date and time of analysis
- Lab sheets showing
  - Weight of sample
  - Volume and normality (or Molarity) of dichromate solution
  - Volume and normality (or Molarity) of titrant
  - Reaction time
  - Reaction temperature
  - Calibration results (appropriate for determinative method)
- Blank results determining concentration of titrant
- Laboratory control samples (NIST) and duplicate results
- Moisture content of soil samples
- Bulk density of soil samples
- Average of each $\mathbf{f_{oc}}$ sample (triplicate analyses) in dry weight
- Average $\mathbf{f_{oc}}$ of each soil strata

SUMMARY: Due to its important role in binding contaminants in soil media, the $\mathbf{f_{oc}}$ can affect the analysis of exposure pathways and migration of the contaminants to other environmental media. In order to accurately determine $\mathbf{f_{oc}}$ of soil at a property, it is important to consider the geologic setting of the property, the heterogeneity of the soil profile, the presence of hydrocarbons or other sources of organic carbon in the soil, and the purpose for which the determination is being made. To accurately determine the $\mathbf{f_{oc}}$ of soil at a property, VAP recommends use of a method which clearly delineates organic carbon concentration from inorganic carbon.

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