Memorandum

Florida Department of Environmental Protection

To: Petroleum Cleanup Program Staff
District Program Coordinators
Environmental Consultants
Laboratories
Interested Parties

Through: Michael E. Ashey 5/15/07
Bureau Chief
Bureau of Petroleum Storage Systems

Through: Thomas W. Conrardy, P.E. TC
Petroleum Cleanup Section 3
Bureau of Petroleum Storage Systems

From: Guillermo J. Wibmer, Ph.D. GW
Petroleum Cleanup Section 3
Bureau of Petroleum Storage Systems

Date: May 14, 2007

Subject: **Quality Assurance and Related Issues**

REMINDER OF NEW RULE REQUIREMENTS

The revisions to Chapter 62-770, Florida Administrative Code (F.A.C.) and the other cleanup rules became effective on April 17, 2005 and included several important changes, including changes in Cleanup Target Levels (CTLs). As described below, for four carcinogenic Polycyclic Aromatic Hydrocarbons (PAHs) in groundwater and for carcinogenic PAHs in soil, two of the changes require some up-front evaluation before comparing analytical results to CTL tables.

GENERAL CONSIDERATIONS

Except as described below for four carcinogenic PAHs in groundwater, laboratories are expected to achieve Practical Quantitation Limits (PQLs) as low as or lower than CTLs. However, samples may require dilution prior to analyses when high concentrations of one or more chemicals are present or because of matrix interference. In that case, all the Method Detection Limits (MDLs) and the PQLs will be raised based on the dilution factors used. This procedure should not be considered to be a problem when contaminants are present even though the PQLs for contaminants not detected may be higher than their respective CTLs (if matrix interference is a problem, the laboratory should find ways to overcome the interference). However, in order to achieve site rehabilitation completion it must be demonstrated that no CTLs are exceeded.

REPORTING REQUIREMENTS FOR LABORATORIES

Paragraph 62-770.400(2)(a), F.A.C., states that laboratory reports must include all information specified in Subsection 62-160.340(2), F.A.C., and must be in the format specified in Chapter 62-160, F.A.C. In general, laboratories have been slow in changing the format of their reports as applicable to comply in full with this requirement.

(1) Several of the items listed in Subsection 62-160.340(2), F.A.C., are always included in laboratory reports and some of the ones not always included are not as critical for review purposes; however, it is important that a column listing the MDLs and a column listing the PQLs always be included. Many laboratories use Reporting Limits (RLs), some of which are equivalent to MDLs, some of which are equivalent to PQLs, and some of which are adjusted MDLs or PQLs; this terminology is unacceptable and must not be used.

(2) Data qualifiers must be used.

(a) Non-detects must be reported at the MDL. The format required by Chapter 62-160, F.A.C., is to list the MDL utilized for the particular analyte followed by the data qualifier "U".

(b) If a contaminant is detected at a concentration between the MDL and the PQL, the laboratory has two options:

(i) The concentration can be estimated and the estimated value reported with the data qualifier "I", or

(ii) The concentration can be reported as the PQL with the data qualifier "M".

(c) If a contaminant is detected in the method blank, all environmental samples associated with that method blank must be clearly linked to the method blank and the results for that analyte in the samples must be reported by the laboratory with the data qualifier "V" (and the laboratory should make the effort to control the laboratory environment in order to avoid this problem in the future).

REPORTING REQUIREMENTS FOR CONSULTANTS

(1) Analytical results must be listed on summary tables with the same level of precision reported by the laboratory and not rounded off.

Examples:

Benzene was detected in a groundwater sample at 35 μg/L. This result should be summarized as "35", not "35.0".

Benzene was detected in a groundwater sample at 5.7 μg/L. This result should be summarized as "5.7", not "6" or "6.0".

(2) Analytes that were not detected (as indicated by the MDL followed by the data qualifier "U") should be summarized as "[MDL] U" or "ND ([MDL])", where "[MDL]" is the MDL value reported by the laboratory for each analyte.

Example:

Benzene was reported by the laboratory in a groundwater sample as "0.5 U" (in μg/L). This result should be summarized as "0.5 U" or "ND (0.5)".

(3) When a value reported is followed by the data qualifier "I", meaning that the analyte was detected at a concentration between the MDL and the PQL and the reported value was estimated, the value should be listed on the table followed by "I" and the table should include a footnote to explain what the data qualifier "I" means.

Example:

Benzo(a)anthracene was reported by the laboratory in a groundwater sample as "0.16 I" (in μg/L). This result should be summarized as "0.16 I".

(4) When a value reported is followed by the data qualifier "M", meaning that the analyte was detected at a concentration between the MDL and the PQL and the reported value is the PQL (the concentration was not estimated), the value should be listed on the table followed by "M" and the table should include a footnote to explain what the data qualifier "M" means.

Example:

Benzo(a)anthracene was reported by the laboratory in a groundwater sample as "0.2 M" (in μg/L). This result should be summarized as "0.2 M".

(5) When a value reported is followed by the data qualifier "V", meaning that the analyte was detected in the method blank, the value should be listed on the table followed by "V", and the table should include a footnote to explain what the data qualifier "V" means and the concentration detected in the blank. The text of the report should include a discussion as to whether the result should be considered to be a false positive.

Example:

Benzo(a)anthracene was reported by the laboratory in a groundwater sample as "2.3 V" (in μg/L). This result should be summarized as "2.3 V".

CARCINOGENIC PAHS IN GROUNDWATER

Prior to April 17, 2005, the groundwater CTLs for four carcinogenic PAHs [Benzo(a)anthracene, Benzo(b)fluoranthene, Dibenz(a,h)anthracene, and Indeno(1,2,3-cd)pyrene] were based on the PQL, that is, "the lowest level that can be reliably measured during routine laboratory operating conditions within specified limits of precision and accuracy" [see Subsection 62-770.200(44), F.A.C.]. Since April 17, 2005, the groundwater CTLs for those four contaminants have been

based on their respective toxicities. While this change is consistent with the way other CTLs were calculated, it creates a little confusion because the risk-based groundwater CTLs for those four carcinogenic PAHs are lower than their respective PQLs. However, as specified in Chapter 62-770, F.A.C. and the other cleanup rules, when the risk-based CTL is lower than the PQL, the PQL becomes the alternative CTL as long as it is the best achievable detection limit. In order to provide assistance in determining whether PQLs reported in laboratory reports are actually the best achievable detection limit for each contaminant, the FDEP prepared the document "Guidance for the Selection of Analytical Methods and for the Evaluation of Practical Quantitation Limits", dated October 12, 2004, and referenced in the cleanup rules (the document can be accessed at www.dep.state.fl.us/waste/categories/wc/pages/LinksToGuidanceDocuments.htm). Table C of that document provides Target PQLs for the four carcinogenic PAHs in question as follows:

Contaminant	GCTL (µg/L)	Target PQL (µg/L)	EPA Method
Benzo(a)anthracene	0.05	0.2	8310
Benzo(b)fluoranthene	0.05	0.1	8310
Dibenz(a,h)anthracene	0.005	0.2	8310
Indeno(1,2,3-cd)pyrene	0.05	0.2	8310

Note: Although the guidance document references EPA Method 8310 (Liquid Chromatography), it should be possible to achieve those Target PQLs using EPA Method 8270 (Gas Chromatography/Mass Spectrometry).

In conclusion: If Benzo(a)anthracene, Benzo(b)fluoranthene, Dibenz(a,h)anthracene, and Indeno(1,2,3-cd)pyrene are not detected, or if one of more are detected but their concentrations do not exceed their respective PQLs, it is considered that the alternative groundwater CTLs are met even if the risk-based groundwater CTLs referenced in Table I of Chapter 62-777, F.A.C. are lower than the PQL.

Examples:

1) Benzo(a)anthracene was not detected in a groundwater sample. The result must be reported by the laboratory as a concentration equal to the MDL with the data qualifier "U". If the MDL is 0.1 µg/L, the laboratory report would list the analytical result as "0.1 U".

2) Benzo(a)anthracene was detected in a groundwater sample at a concentration which is between the MDL (say 0.1 µg/L) and the PQL (say 0.2 µg/L). If the laboratory estimated the concentration to be 0.14 µg/L, the laboratory report would list the analytical result as the estimated value with the data qualifier "I" ("0.14 I").

3) Benzo(a)anthracene was detected in a groundwater sample at a concentration which is between the MDL (say 0.1 µg/L) and the PQL (say 0.2 µg/L). If the laboratory did not estimate the concentration, the laboratory report would list the analytical result as the PQL with the data qualifier "M" ("0.2 M").

In all three examples, the concentration of Benzo(a)anthracene is considered to meet the alternative groundwater CTL even though the concentration may be higher than the risk-based groundwater CTL of 0.05 μg/L.

Note: The groundwater CTL for another carcinogen [Benzo(a)pyrene] also was based on the PQL, but it is a primary drinking water standard and cannot be changed in the cleanup rules until it is changed in Chapter 62-550, F.A.C.

CARCINOGENIC PAHS IN SOIL (DIRECT EXPOSURE ONLY)

Another concept introduced in the cleanup rules on April 17, 2005 is apportionment, which is the adjustment of CTLs to account for chemical interactions in their effects on human health. Currently, the only chemical interaction considered in the cleanup rules is additivity. Unless the 95% UCL approach is utilized, additivity is not considered in Risk Management Options Level I [Subsection 62-770.680(1), F.A.C.] with one exception, and that is the carcinogenic PAHs in the Direct Exposure (DE) scenarios (this procedure does not apply to Leachability-based soil CTLs). Table II of Chapter 62-777, F.A.C., provides DE soil CTLs for Benzo(a)pyrene but not for the other six carcinogenic PAHs [Benzo(a)anthracene, Benzo(b)fluoranthene, Benzo(k)fluoranthene, Chrysene, Dibenz(a,h)anthracene, and Indeno(1,2,3-cd)pyrene]. Apportionment is performed by adjusting the concentrations of the seven carcinogenic PAHs by multiplying each concentration by a Toxic Equivalency Factor which is based on the relative toxic potency of each carcinogenic PAH in relation to the toxic potency of Benzo(a)pyrene, adding the adjusted concentrations, and comparing the result to the DE Residential soil CTL for Benzo(a)pyrene [or to the DE Commercial/Industrial soil CTL for Benzo(a)pyrene if it has been indicated that the property owner will agree to the institutional controls that are necessary when Commercial/Industrial CTLs are used]. The FDEP has developed a conversion table with detailed instructions on when it is appropriate to perform the apportionment and how to list non-detects and estimated values, and which indicates whether the DE Residential and DE Commercial/Industrial soil CTLs for Benzo(a)pyrene are exceeded or not (the conversion table may be accessed at www.dep.state.fl.us/waste/categories/pcp/pages/pg_documents.htm under General Technical). [Note: Since the first footnote of Table II of Chapter 62-777, F.A.C., specifies that soil CTLs lower than 1 were rounded to one significant figure, the DE Residential soil CTL for Benzo(a)pyrene is not considered exceeded unless the total result exceeds 0.149 mg/kg and the DE Commercial/Industrial soil CTL for Benzo(a)pyrene is not considered exceeded unless the total result exceeds 0.749 mg/kg. These rounding considerations have been incorporated into the automated equivalency calculation table, which indicates whether the CTL is exceeded after rounding is applied to the calculated equivalency value.]

In conclusion: In order to evaluate the results of analyses for PAHs in soil as they relate to the DE scenarios, the B(a)P conversion table must be utilized according to the instructions. Consultants must fill out a conversion table for each sample (unless no carcinogenic PAHs are detected), must submit copies of the conversion table(s) in the reports for evaluation, and the total B(a)P equivalents result(s) must be summarized under Benzo(a)pyrene [if carcinogenic PAHs are not detected in a soil sample, the Benzo(a)pyrene result for that sample should be summarized as "ND"].