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AUG 03 1994

Remedial Project Manager
VA/WV Superfund Federal Facilities Section
Attn: Mr. Robert G. Thomson, P.E.
Region III, U. S. Environmental Protection Agency
841 Chestnut Building
Philadelphia, Pennsylvania 19107

Re: CLP Method Contract Required Quantitation Limits (CRQLs) vs SW846 Method Detection Limits (MDLs), Naval Weapons Station, Yorktown, Virginia

Dear Mr. Thomson:

During a meeting at your office on May 5, 1994, Mr. Bob Davis asked the Navy to evaluate the use of USEPA SW846 3rd Edition analytical methods in place of Contract Laboratory Program (CLP) methods to lower the limits of detection and therefore provide more usable data for use in the Phase I ecological risk assessment (ERA) process. These two methods have been evaluated and the attached formal response is provided for the record.

To summarize the document, the Navy believes the use of CLP procedures is the overall best method for the ERA analyses. Use of CLP will ensure the data remains consistent with the Data Quality Objectives proposed in the master Quality Assurance Project Plans for WPNSTA Yorktown.

If you have any questions, please contact Mrs. Brenda R. Norton, P.E., at (804) 322-4778.

Sincerely,

N. M. JOHNSON, P.E.
Head, Installation Restoration
Section (North)
Environmental Programs Branch
Environmental Quality Division
By direction of the Commander

Enclosure

Copy to:
VDEQ (Mr. Stephen Mihalko)
NOAA (Mr. Peter Knight)
Baker Environmental, Inc. (Mr. Rich Hoff)
WPNSTA Yorktown (Code 09E3)

Blind copy to:
1822 (BRN)
1822 (Admin Record)
18S
SW846MDL.BRN

**Response to Comment from Bob Davis,**
**U.S. Environmental Protection Agency (USEPA)**
**Region III Biological Technical Assistance Group (BTAG) Coordinator**

RE: CLP Method Contract Required Quantitation Limits (CRQLs) vs. SW846 Method Detection Limits (MDLs): The use of more sensitive analytical methods for the ecological risk assessment.

## BACKGROUND

Mr. Bob Davis, USEPA Region III BTAG Coordinator, was present at the May 5, 1994 meeting between LANTDIV, USEPA Region III, Naval Weapons Station Yorktown (WPNSTA Yorktown), Naval Environmental Health Center (NEHC) and Baker Environmental, Inc. (Baker) personnel, where the final comments to the Draft Master Project Plans and the Site-Specific Project Plans were discussed. Mr. Davis asked LANTDIV to evaluate the use of USEPA SW846 3rd. Edition analytical methods (SW846) in place of Contract Laboratory Program (CLP) methods to lower the limits of detection and therefore provide more usable data for use in the Phase I ecological risk assessment (ERA) process. The Phase I ecological risk assessment consists of a comparison of soil, surface water, and sediment data to appropriate environmental standards and criteria, such as Ambient Water Quality Criteria (AWQC). Because of the manner in which certain criteria and standards are derived, Contract Required Quantitation Limits (CRQLs) from CLP methods are sometimes higher than the corresponding criteria and standards.

In order to better understand how the selection of alternate analytical methods could possibly produce lower detection limits, the types of detection limits commonly used by laboratories is discussed below. Limits of detection reported by analytical laboratories include the CRQL, the Method Detection Limit (MDL), and the Instrument Detection Limit (IDL).

CRQLs are contract required quantitation limits specific to CLP, which consider a CLP laboratory's ability to reproduce these limits of detection on a consistent, contract-wide basis. MDLs are limits of detection that should be attainable by nearly every laboratory capable of performing the SW 846 analyses. MDLs are generally (but not always) lower than CRQLs and are reported when SW846 methods of analysis are specified. IDLs are limits of detection specific to a given analytical instrument and are usually lower than MDLs and CRQLs. However, they are seldom reproducible unless the same piece of analytical equipment is used throughout the process or project. IDLs are not reported by the laboratory; however, constituents detected above the IDL but below the CRQL or the MDL are usually reported with an estimated qualifier (a "J" qualifier). CRQLs, MDLs, and IDLs are all affected by sample matrices and variables such as percent moisture of sediment and soil samples.

## CLP

The CLP methods, for which alternate methods were suggested, were the Target Compound List (TCL) semivolatile organics, TCL pesticides/PCBs and the Target Analyte List (TAL) inorganics. The TCL semivolatile analytical method employs the use of gas chromatography (GC) and mass spectrometry (MS). The GC separates chemical constituents according to their chemical properties and identifies each chemical by retention time. The MS serves as the detector and further identifies each chemical emanating from the GC by compiling a unique mass profile of the chemical and comparing the mass profile to a library or reference profile. Therefore, the CLP TCL semivolatile method of analysis is very specific in the identification of compounds. The method is also very sensitive, but sensitivity is moderated in the reporting of the analytical data and the use of the CRQL. The CRQL takes into consideration the inter and intra-laboratory variability associated with the CLP program. The CRQL is typically higher than the method detection limit, but provides a margin of error for labs that could not achieve the MDL on a daily basis. It also provides for uniformity throughout the CLP program with respect to reporting. It should be emphasized that in the CLP program, compounds detected above the IDL but less than the CRQL are reported and quantified as estimated values.

The TCL pesticide/PCB analysis employs GC and an electron capture (EC) detector. The EC provides very good sensitivity and is highly specific to electron capturing chemical entities such as chlorine, which is a major element in the composition of pesticides and PCBs. As with the TCL semivolatiles, the sensitivity of the TCL pesticide/PCB method is moderated by the CRQL, and positive detected compounds at concentrations below the CRQL are quantified and reported as estimated values.

CLP TAL inorganic analyses are conducted using a combination of analytical methods which include inductively coupled plasma (ICP) cold vapor atomic absorption (CVAA) and graphite furnace atomic absorption (GFAA). Each analyte is identified and quantified by the amount of energy absorbed at a characteristic wavelength. CLP TAL inorganic analyses are also very specific methods of analysis and, as with the TCL semivolatiles, the CRQL may be higher than the MDLs. Again, positive concentrations below the CRQL are quantified and reported as estimated.

**SW-846**

For the semivolatile organic compounds (SVOCs), SW846 provides a number of analytical options. SW846 8270 is a comprehensive GC/MS semivolatile analytical method very similar to the CLP methods, but lists MDLs which are twice as high as the CLP TCL semivolatile CRQLs. Other more sensitive SW846 methods for semivolatiles exist, but these methods are limited by their specificity and the number of chemicals they encompass. For example, SW846 8100 is a GC/Flame ionization detector (FID) method which analyzes for only polynuclear aromatic hydrocarbons (PAHs). Using SW846 8100 does increase the sensitivity for some PAHs. For example, acenaphthylene has an MDL in water of 2.3 µg/L using Method 8100 while it has a CRQL of 10 µg/L using CLP methods. Using the SW846 method would provide for a more favorable comparison to some environmental standards and criteria. However, the FID is not a specific detector and will positively detect any chemical which can be ionized in the flame. Identification of chemicals is accomplished by an evaluation of GC retention time only and second column confirmation of all positive analytical results is required. When analyzing complex environmental samples, retention time identification on primary or confirmation column analyses is extremely difficult if not impossible. Any chemical that elutes during the retention time for a chemical of concern would be positively detected using SW846 8100.

In addition to a lack of specificity, four alternate GC analytical methods would be necessary to cover most of the chemicals analyzed by the CLP TCL semivolatiles method. These would include phenolic compounds (8240), phthalate esters (8060), chlorinated hydrocarbons (8120) and nitroaromatics (8090). This would greatly complicate and extend the field sampling effort because sample volumes would quadruple. Furthermore, the data management effort and sample tracking tasks would also quadruple. Also, these methods are not directly comparable to data previously collected at WPNSTA Yorktown, making data interpretation more difficult.

## CONCLUSION

Because no significant sensitivity increases will be realized and selectivity would be compromised, it is suggested that the more comprehensive CLP TCL semivolatiles analysis be conducted and not the SW846 alternative methods. As noted above, the laboratory will be required to report all positive results below the CRQL and above IDLs for all environmental samples.

For the pesticide/PCB fraction, SW846 8080 (pesticides/PCBs) is the same GC/EC analytical method as the TCL pesticides/PCBs analysis. 8080 MDLs are as much as 10 times lower than the specified CLP method CRQLs, but not as low as all of the environmental standards and criteria. Because the only real difference in these analytical methodologies is the more detailed deliverable, it is recommended that the CLP method be performed and the laboratory be required to report the MDL instead of the CRQL. Positive detections below the MDL should also be reported, if possible.

SW846 7000 methods for inorganic analytes are similar to the CLP TAL inorganic analyses, with the corresponding SW846 7000 MDLs that are lower than the respective CLP CRQLs depending on the selected means of analysis. However, it is recommended again that the CLP analysis be performed because the laboratory uses the most sensitive instrument, reports all positive results above the instrument detection limit (IDL), and the methods are consistent with previously performed analyses at WPNSTA Yorktown.

In summary, existing CLP procedures require that concentrations below CRQLs be reported. Laboratories under contract with Baker Environmental, Inc. have been notified that this will be the procedure. These results should provide the quality of data needed to perform the Phase I ERA. This will also ensure the data remains consistent with the Data Quality Objectives proposed in the Master Quality Assurance Project Plans for WPNSTA Yorktown.