

LABORATORY DETECTION AND REPORTING LIMIT ISSUES RELATED TO RISK ASSESSMENTS

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Abstract

"I expected low parts-per-billion reporting limits and got high parts per million, what's wrong with the lab?" This is a statement often heard when the Laboratory Measurement Quality Objectives (MQO) for either a Human Health Risk Assessment (HHRA) or an Ecological Risk Assessment (ERA) are not met, even though the selected analytical method indicated that the compounds should have had reporting limits that were low enough to permit risk assessment. The difference between what the analytical procedure can report for a prepared standard and what is reported for the environmental sample is the difference between ideal and real-world samples. Does this mean it is never possible to achieve MQOs? Not necessarily. However, to do so, it is important to (1) establish specific reporting limit goals, (2) communicate and contractually negotiate those goals with the analytical laboratory, (3) make the laboratory aware that if goals are not being met, actions are to be taken immediately to identify what needs to be done to obtain the required data, and (4) if analytical constraints do preclude achieving the MQOs, be prepared to negotiate alternative screening options with the regulatory agency.

Issue Paper Objective

The objective of this issue paper is to provide an overview of what may be required to achieve data quality objectives. It is not intended to transform its readers into analytical chemists nor to be a definitive set of guidelines that will always get the reporting limits required from the laboratory. Rather, this paper presents a brief discussion of how environmental samples are processed and analyzed, of the terminology typically used during analysis and data reporting, and ways to improve the reporting limits. It also stresses the importance of maintaining close communications with the laboratory so that the lab understands the necessity for achieving data reporting goals and the need to notify the prime contractor/remedial project manager (RPM) as soon as the lab realizes that goals will not be met (rather than waiting until the data report is delivered).

Presented are examples of how reporting limits can be lowered. Although the examples used here are typically for organic compounds in aqueous environmental samples, the rationale is also applicable for other compounds (i.e., inorganics) and matrices (i.e., soils, sediments, and tissue).

In addition, the methods presented in the text generally reflect the most recent U.S. Environmental Protection Agency (U.S. EPA) methods. The use of these methods in no way implies that older versions are no longer appropriate. A high degree of flexibility for method-modification is possible and actually encouraged by the U.S. EPA to achieve detection/reporting goals, as long as valid quality control/quality assurance (QA/QC) policies are applied and documented.

Issue Discussion

1.0 Introduction and Background

Generally, some variance will exist between the lowest concentration that an analytical instrument can detect and the concentration that is reported for an environmental sample. This variance reflects the difference between analyzing a relatively simple laboratory-prepared standard and a complex environmental sample that may contain a substantial difference in concentrations between a standard and the sample.

The laboratory standard normally contains only the compound or compounds of interest, in an optimal calibration range, and in a medium that does not interfere with and can even enhance the performance of the analytical instrument. Under these ideal conditions, the analytical system provides the lowest concentration that can be reported, while minimizing uncertainty due to matrix effects. This concentration is the method detection limit (MDL). On the other hand, an environmental sample may not only contain the compounds of interest in relatively smaller concentrations, but also many nontargeted compounds and other constituents that can interfere with the sample analysis. Any deviation from the ideal laboratory sample results in a method reporting limit (MRL), which is the corrected concentration reportable for that sample under those conditions. The MRL is always equal to or greater than the MDL.

Once the targeted compounds and MQO reporting limits are established by the project team, the appropriate analytical methods are selected that would best address the compounds and the environmental sample matrix (i.e., water, soil, sediment, or tissue). Communicating with the laboratory during the method selection process is advisable so it can be confirmed that they can perform the analysis and meet MQOs. The method that is selected will provide guidance on how to prepare the sample, analyze the sample, and report the concentration of the compounds in the samples within appropriate QA/QC guidelines. It should be emphasized that the commonly used SW-846 methods: (1) are not the only source of methods that can be used, (2) do NOT have to be implemented exactly as written, and (3) performance presented in those methods should NOT be used as a regulatory default or absolute "QC requirements" (Crumbling and Lesnik, 2001).

To understand what causes MRLs to be higher than the MDLs, it is important to have some knowledge of what is involved in processing an environmental sample. Generally, three steps are associated with the analytical process: (1) sample preparation (which can include an extraction and additional preparation of the extract), (2) sample analysis, and (3) raw data reporting (see Figure 1).

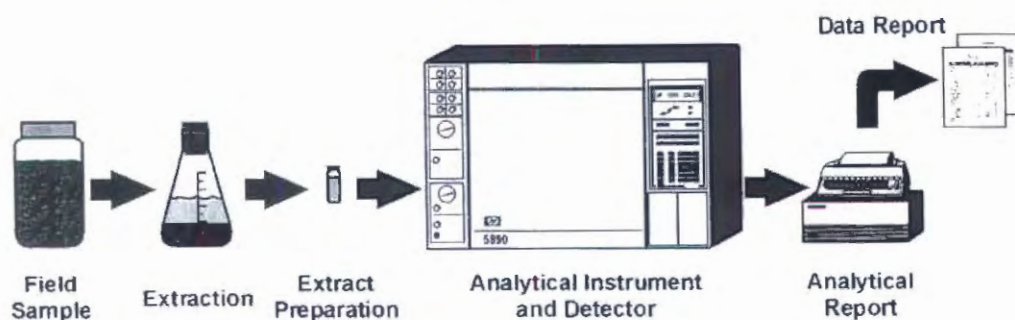


Figure 1. Sample Preparation and Analysis Process

Normally, it is not possible to introduce the environmental sample directly into the analytical instrument. The sample must undergo an extraction step during which the targeted compounds are removed from the environmental matrix (i.e., water, soil, sediments, tissue) and transferred to a secondary matrix (i.e., extraction solvent) that can be introduced into the analytical system. However, one drawback with most extraction processes is that both targeted and nontargeted compounds may be extracted. These extraneous compounds can cause interferences and make it impossible to report concentrations at the originally specified MDL.

When the extract is introduced into the analytical instrument, ideally, all of the compounds associated with that sample need to be separated into discrete bands for optimum detection limit applications. These bands then pass through a detector, which produces an electrical signal that is proportional to the amount of each compound in the sample. All of the detector responses for the sample are compiled in an analytical report that is used to generate the data report.

2.0 Analytical Method Terminology

The following terms are associated with the analytical method and should be understood in order to evaluate analytical and data reports. It is possible that different laboratories may use different terms to describe these same concepts. If the data report contains terminology you do not recognize or understand, contact the laboratory for an explanation and request that information be included in the case narrative.

- **Method Blank (MB):** The MB contains only the reagents/solvents being used to prepare the sample. The method blank confirms that the analytical instrument is “clean” and that the reagents/solvents are of good quality. If MB data indicate concentrations for any of the compounds associated with the sample, then the laboratory must explain why they were present, and must correct the problem before analyzing the environmental samples.
- **Method Detection Limit:** The MDL is the sample concentration of each compound that can be detected above zero and with a 99% confidence, when a particular analytical method is employed properly. As an example, in SW-846 Method 8260B (a gas chromatography [GC] analytical method with a mass spectrophotometer detector), the

stated MDL for benzene is 0.03 µg/L for a 25-mL groundwater sample processed with a purge and trap sample preparation by SW-846 Method 5030.

- **Practical Quantitation Limit (PQL)/Estimated Quantitation Limit (EQL):** PQLs and EQLs are synonymous terms in SW-846 and are the reporting limit provided in the method. They are a guide for the “expected” concentration that can be reliably achieved within specified limits of precision and accuracy during routine sample analyses. The PQL (or EQL) is generally 5 to 10 times the MDL, but highly matrix dependent. As an example, SW-846 Method 8260B provides PQLs for benzene of 1 µg/L for a 25-mL groundwater sample and 5 µg/kg for soils/sediments with low-level contamination. The method also indicates that PQLs are 50 times the MDL for water miscible samples, 125 times the MDL for high concentration soils and sludges, and 500 times the MDL for non-water-miscible waste. These multipliers are typically associated with dilution factors.
- **Method Reporting Limit:** The MRL is the lowest reported concentration, provided on the sample-analysis data report, after corrections have been made for sample dilution, sample weight, and (for soils and sediments) amount of moisture in the sample. MRLs can be as low as the MDL or exceed the PQL, depending on the matrix effects encountered during the analysis. **The MRL is the value that indicates whether the analytical MQOs have been achieved for that sample.**
- **Precision:** A QA/QC function that quantifies a laboratory’s ability to generate reproducible data, for multiple analyses of the same sample. It does not assume knowing the true concentration in the sample. Precision is expressed as a relative standard deviation (RSD) and is compared to the RSD provided in the analytical method. If the reported precision deviates from the laboratory’s specified acceptable range, then validity of the data may be compromised. In SW-846 Method 8260B, benzene’s RSD is ~3%, depending on the sample matrix.
- **Accuracy:** A QA/QC function that quantifies a laboratory’s ability to generate data that is in agreement with the true concentration or a reference value. In this case the true concentration is known. Accuracy of 100% indicates that the reported value is equal to the true concentration. The range of acceptable accuracy and precision is provided in the method or established through statistical procedures by the laboratory for each matrix. If accuracy and precision do not meet the guidelines, then the usefulness of the data is questionable. For example, in SW-846 Method 8260B, a measure of acceptable accuracy for benzene in water is a spike recovery of 80% to 120%.

For risk assessments, the data being reported and subsequently used must be of the highest quality and certainty. The relationship between the method blank, MDL, limit of quantification (further discussed in Section 3.2), and the certainty associated with the measured concentration of the analyte is presented in Figure 2. The laboratory should be reporting data where the analytical concentration of the compound is in the region of high certainty.

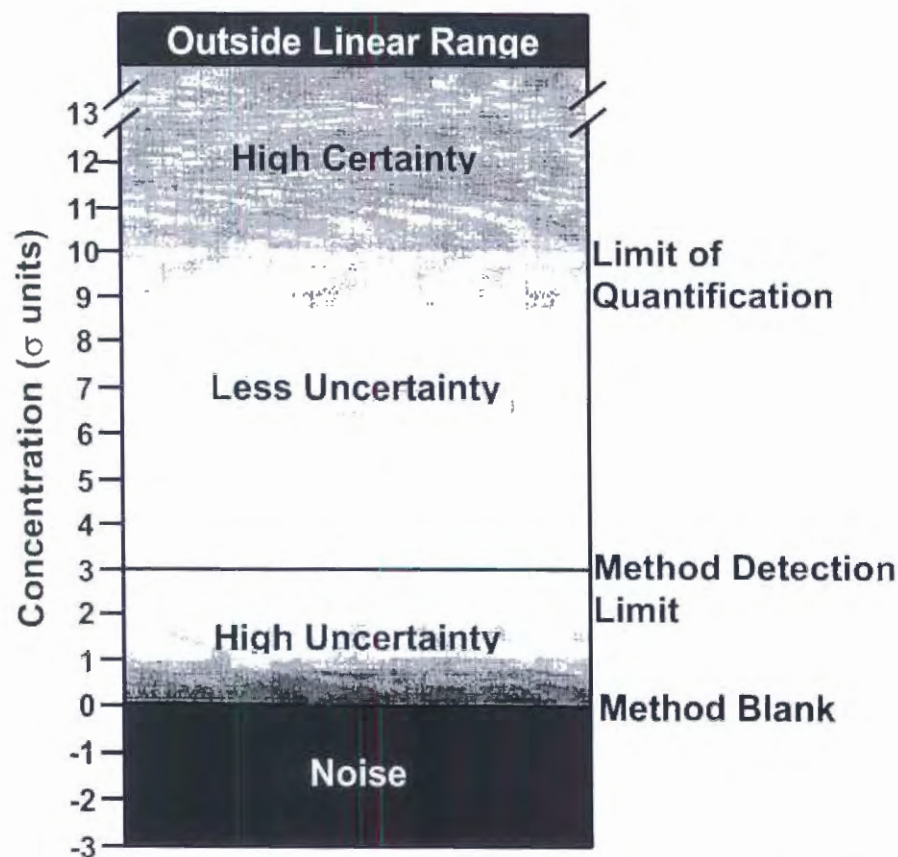


Figure 2. Analyte Concentration vs. Reporting Certainty. (The y axis represents signal strength, in units of the standard deviation (σ) used to determine the MDL.) Adapted from Keith, 1991 by Johnson, 2001.

3.0 Factors Affecting Method Reporting Limits

What prohibits achieving reporting limits at the MDL for all samples? Two factors that can significantly increase the reporting limit are matrix effects (i.e., bulk effects and coextractants) and the dilution of samples.

3.1 Matrix Effects

If the sample matrix possesses properties that affect the detection of a particular analyte, then it is said to be causing interference. A matrix spike is the QA/QC activity used to determine if a sample is providing any interference. When a sample is spiked, a known concentration of a targeted compound is carefully added to the sample, similar to a QA/QC accuracy analysis. The spiked sample is analyzed and the recovery percentage is calculated by comparing the reported

concentration of the compound before and after the spike. If the recovery is higher than the acceptable upper limit, then the matrix may be providing an additive effect and reported values could be higher than what is in the sample (Type I Error). If recovery is below the acceptable lower limit, then the sample matrix may be masking that compound and the reported data could be lower than what is actually present in the sample (Type II Error). Additional sample extract preparations can be performed that may negate matrix effects by removing the interfering compounds. However, extreme care must be taken during extract preparations since extraction efficiencies are never quantitative, and extraction effects can increase the uncertainty of the analytical measurement.

3.2 Dilution Factors

No laboratory activity can have a more dramatic effect on MRLs than the dilution of a sample. The more a sample is diluted, the higher the reporting limit automatically becomes. As an example, if the laboratory dilutes a sample tenfold (meaning one volume of the sample is added to nine volumes of a solvent), and the target MDL for the analyte is 1 part per million (ppm), then the reporting limit automatically increases by a factor of 10 and becomes 10 parts per million.

Why is it necessary to dilute a sample? An analytical detector is limited not only by the smallest amount of material it can respond to, but also by a maximum amount of signal per unit concentration of the sample. The lowest concentration, reported with high certainty, is the limit of quantification, and the highest concentration is called "full-scale response". Acceptable performance for a detector falls between this low- and full-scale-response loading. Optimal performance occurs when there is a linear increase in detector response versus a compound's concentration. That is, if a compound's concentration is doubled, the signal from the detector also would double. It is within this range of linearity-of-response that a detector is typically calibrated and operated.

Therefore, sample dilution is required when the concentration of a compound exceeds the amount that produces a full-scale response. At that point the detector becomes saturated and fails to respond to any additional material. During saturated conditions, the detector also can become contaminated and require extensive cleaning and conditioning in order to recover its linearity-of-response for later analyses. This results in downtime for the instrument and loss of sample throughput for the laboratory.

Normally, if a target compound has a very high concentration and it requires dilution, there should be little concern about the MDL because the concentration is well above its detection limit. In this case dilution is necessary to bring the measured concentration within the optimal calibration (measurement) range. Dilution impacts screening values when the compound's concentration in a sample is close to or at the MQO level, but there are several other nontarget analytes at very high concentrations. Any dilution of the sample to accommodate the high concentration of nontarget analytes may reduce the concentration of the target analyte to a level where it can no longer be detected.

It is a common practice for the analytical laboratory to screen the sample extracts on an instrument that is not used for data generation. Based on the results of that injection, the decision is made by the laboratory as to whether a sample requires dilution.

3.3 Data Flags

The laboratory must flag any data associated with low or high matrix-spike-recovery issues or other abnormal analytical conditions that deviate from stated method procedures. QA/QC deviations must be communicated to the RPM/Comprehensive Long-Term Environmental Action Navy (CLEAN) contractor as soon as they are observed so that data quality can be immediately assessed. Table 1 provides a list of commonly used data flags and their effects on data quality.

Table 1. Data Qualifier Flags*

Flag	Description	Does it Compromise the Utility of the Data?"		
		Yes	No	Maybe
B	Compound was detected in the method blank. Indicates possible/probable blank or system contamination and warns the data user to take appropriate action.			X
C	Pesticide results where the identification has been confirmed with gas chromatography-mass spectrometry (GC-MS).		X	
D	Compound was detected in an analysis performed at a secondary dilution.		X	
E	Reported value is either an estimate or it exceeded the linear range of calibration. An explanatory note must be provided by the laboratory.	X		
F	Analyte was positively identified, but the reported value is below the PQL.			X
J	Compound was detected, but below the specified reporting quantification limit. Any such reported amount should be considered an estimate.			X
M	Duplicate injection precision not met. Can also mean matrix effect was present.	X		
N	Spiked sample recovery not within control limits.	X		
Q	No analytical result.	X		
R	Quality control indicates that the data are not usable (compound may or may not be present). Resampling and reanalysis are necessary for verification.	X		
S	Reported value was determined by the Method of Standard Addition.			X
	Can also mean it was a saturated peak.	X		
T	Tentatively identified compound (using GC-MS).			X
U	Compound was analyzed for but not detected at or above the specified reporting limit.			X
X,Y,Z	Other specific flags (laboratory defined) required to properly define the results.			X

* Note: flag descriptions may vary between laboratories; therefore, the use of qualifiers should be well defined on each data report.

**Final designations are dependent upon the specific cause of the qualifier.

4.0 Options for Lowering Reporting Limits

The U.S. EPA not only allows but encourages method modifications in order to meet reporting requirements. As stated by Crumblin and Lesnik (2001), "EPA policy in the waste programs is that analyses are required to 'get the right answer' as demonstrated by the quality assurance mechanisms. If an accepted method cannot 'get the right answer' due to analytical difficulties

with the matrix, etc., selection of a different method, or modification of a method is required". It should be remembered that modifications to existing methods must be done with the approval of the regulator and should be addressed in the Quality Assurance Project Plan (QAPP). Additionally, any extra efforts to lower reporting limits will likely result in higher analytical costs.

Options exist that can enhance an analytical method and possibly permit lower reporting limits, and these tools should be employed to accomplish analytical goals. However, in order for the RPMs/CLEAN contractors to know that these or other options are needed, the laboratory must contact them when the screening process indicates MQOs are not going to be met. This requires good lines of communication to be established between lab/CLEAN/RPM prior to any samples being submitted for analysis.

During contractual negotiations with the laboratory, a request should be made for them to provide detailed information on how they intend to prepare and analyze the samples. Options that are available in the lab for sample cleanup, to enhance reporting limits, should also be identified. This should be established prior to any samples being sent to the lab.

4.1 Option 1: Adjust the Analytical Injection Volume or Reduce the Dilution Factor

One way of lowering the reporting limit is to deliver more of the targeted compound to the detector. This can be accomplished by either introducing a larger injection volume into the analytical instrument or by preconcentrating the sample before it is injected. However, the analyst must keep in mind that coextracted interferences may be present, and unless they are removed, the interfering signal response will increase as well, resulting in no net gain. Therefore, a balancing act exists when increasing the analytical injection volume or concentrating a sample. To make adjustments to the sample concentration, it may require a second extraction/preparation step for the environmental sample. Generally, a 500-g soil/sediment sample will provide more than enough material for multiple analyses. The CLEAN contractor should request information from the analytical laboratory on the volume and the number of bottles required to perform multiple aqueous analyses. Collecting additional material during the initial sampling effort, in case a second extraction/preparation step is required, could prevent the need for costly resampling.

4.2 Option 2: Sample Preparation Alternatives

Another option for lowering reporting limits is to separate the targeted compounds from nontargeted compounds. This procedure can substantially reduce problems associated with matrix interferences and the need for a dilution step. Sample preparation options also make it possible to preconcentrate a sample by reducing a large sample volume, which is too large to inject, down to a smaller volume (the opposite of dilution). The preconcentrated sample, which now contains a greater amount of the targeted compound per unit volume, is then injected. This may dramatically lower reporting limits, if matrix interferences are not present or if they can be subsequently removed. There are several sample preparation methods found in the EPA SW-846

3000 Series Methods. It should be emphasized that the performance of most cleanup procedures is not particularly complicated or expensive for the laboratory to perform. The key factor is working with an experienced chemist who is capable of determining what matrix effects are occurring and which cleanup procedure will be effective. Selected methods for organic cleanup/extraction are presented in Table 2. This table does not provide a complete summary of cleanup/extraction options, but provides examples of what types of options exist.

Enhancement by these and other sample preparation techniques has been investigated (NOAA, 1993 and 1998). During a Naval Facilities Engineering Activity Chesapeake (EFA Ches) investigation of sediment contamination at Mattawoman Creek, NSWC Dahlgren, standard methods were applied. However, to attain very low MRLs, larger than normal sample volumes were extracted, with extreme care being taken to maintain complete recoveries. Multiple cleanup steps then were applied to the extracts to exhaustively remove interferences and, whenever possible, the extracts were reduced in volume to concentrate the targeted compounds. With these extra steps, reporting limits that were close to the MDLs were achieved. Increased costs (i.e., ~50% higher) were associated with the laboratory work, but the costs were justifiable to obtain the required critical measurements. In this study, additional time was required to identify laboratories that could provide these types of custom service and negotiate costs. However, the ERA/MQO goals were met.

4.3 Option 3: Use an Alternate Detector

Just as additional sample preparation efforts can enhance reporting limits, it may be possible to achieve lower reporting limits by using a more sensitive or selective detector. However, the use of alternative detection methods will require consultation with an experienced chemist and the lab that will be doing the analysis.

In Table 3, examples of the characteristics of detectors commonly used during organic and inorganic analyses are presented. The selection of an alternate detector is within the guidelines of standard methods and can provide greater sensitivity while "ignoring" nontarget analytes and interferences. This change may make the difference in whether or not the MQOs are met.

As with other aspects of the analytical method, it is advisable to discuss detector options with the prime contractor/laboratory. For organic compounds, several detectors can be used. However, in most cases the GC-MS instrumentation will provide definitive analysis at the highest degree of sensitivity, with the lowest reporting limit, at a reasonable cost. Similarly, for inorganic compounds, several detector options exist. The inductively coupled plasma-mass spectrometry (ICP-MS) detector, however, permits the screening of multiple analytes in a single analysis, provides high sensitivity, low reporting limits, and the per-analyte cost is comparable to other detectors.

Table 2. Examples of Organic Sample-Preparation Alternatives (not intended to be an all inclusive list)

Method Number	Method Title	Description	Advantages	Disadvantages
Method 3510C	Separatory Funnel Liquid-Liquid Extraction	Serial extraction of aqueous samples with methylene chloride in a separatory funnel.	Extract is suitable for cleanup steps to remove interferences and through preconcentration, possibly lower MRLs.	Moderately labor intensive, requires careful attention to ensure complete recoveries.
Method 3520C	Continuous Liquid-Liquid Extraction	Specialized glassware permits the automatic extraction of aqueous samples with an organic solvent for 18-24 hours.	Minimal manual effort, very effective extraction method, and it generates an extract that is suitable for cleanup and preconcentration.	Decomposition of some analytes (organochlorine pesticides, phalate esters, and phenols) may occur under high pH (basic) extraction conditions.
Method 3535	Solid-Phase Extraction (SPE)	Uses commercially available preparation columns/discs to remove interferences.	Fast, can be used to preconcentrate samples and possibly lower MRLs.	Additional analytical costs.
Method 3540C	Soxhlet Extraction	Specialized glassware permits the automatic extraction of soils and sediments over several hours.	Very thorough extraction and produces an extract suitable for cleanup and preconcentration.	Fritted glassware may be difficult to clean and cause contamination problems for later samples.
Method 3545	Pressurized Fluid Extraction (PFE)	Uses elevated temperature and pressure to accelerate the extraction of soils, clays, sediments, sludges and solid wastes.	Extraction completed in minutes instead of hours.	Method has been validated for pesticides, herbicides, and semivolatile organics at moderate to high parts per billion concentrations.
Method 3610B	Alumina Cleanup	Used to separate analytes from interfering compounds of different polarity.	By adjusting pH, interfering compounds can be selectively removed.	Can cause chemical reactions that may affect certain target compounds. Additional costs.
Method 3620B	Florisol Cleanup	Used to remove interferences from pesticide residues, chlorinated hydrocarbons, and PCB samples.	Can permit sample concentration and lower MRLs.	Requires more time and will result in additional costs.
Method 3630C	Silica Gel Cleanup	Column cleanup of sample extracts with polyaromatic hydrocarbon (PAH), organic pesticides, and polychlorinated biphenyls (PCBs).	Can permit sample concentration and lower MRLs.	Requires more time and will result in additional costs.
Method 3640A	Gel-Permeation Cleanup	Compounds are separated based on their molecular size.	Effective at eliminating matrix interferences from sulfur, humic/fulvic compounds, and petroleum organics.	Requires skilled analysts and special instrumentation. Results in a dilution of the sample, which may hinder achieving DQOs. Additional costs.
Method 3650B	Acid-Base Partition Cleanup	A liquid-liquid partitioning process, separates acid from base-neutral analytes.	Can reduce interferences associated with petroleum wastes.	Requires more time and will result in additional costs.
Method 3660B	Sulfur Cleanup	Removal of sulfur interferences from sediment samples.	Can enhance performance of selected detectors.	Requires more time and will result in additional costs.

Table 3. Examples of Analytical Detectors Options

Detector	EPA Methods	Sensitivity	Advantages	Disadvantages
Organic Analysis Detectors				
Flame Ionization Detector (FID)	Methods 8015, 8030, 8040, 8100. Volatile, semivolatile, and high molecular weight organic compounds.	Can report parts per billion concentrations for high molecular weight compounds.	Responds to many compounds and displays a very wide range of linear responses.	Lacks specificity, therefore it can provide false positives in complex samples.
Electron Capture Detector (ECD)	Methods 8060, 8080, 8090, and 8120. Chlorinated solvents and pesticides.	Extremely high sensitivity (parts per trillion) for halogenated compounds.	Does not respond well to hydrocarbons, so it can negate some interferences.	Narrow range of linear responses and easily contaminated.
Photoionization Detector (PID)	Methods 8020, 8021, 8021B. Responds to benzene, toluene, ethylbenzene (BTEX), PAHs, and some solvents.	Detection limits to parts per million levels.	Does not respond well to aliphatic hydrocarbons, so it can negate some interferences.	Fairly narrow range of linear responses, can become contaminated and require physical cleaning.
Flame Photometric Detector (FPD)	Methods 8140, 8150. Detects organo-phosphorous pesticides.	Detection limits to parts per billion levels.	Can be operated in a phosphorous mode, which negates interferences.	Relatively narrow range of linear responses, sulfur provides a severe interference.
Mass Spectrophotometer Detector (MSD)	Methods 8260, 8270, 8275, 8280, 8290. Volatile and semivolatile organic compounds.	Detection limits to parts per trillion levels for some organic compounds.	Provides definitive identification, good linearity of response, can identify "unknown" peaks.	Can be overloaded, requires high level of user expertise, typically more expensive analysis.
Inorganic Analysis Detectors				
Flame Atomic Absorption Spectrometry (FLAA)	7000 Series Methods Metals and elemental inorganics.	Detection limits in low parts per million for single element analyses.	Relatively free of spectral interferences, low cost.	High reporting limits and prone to chemical interferences.
Inductively Coupled Plasma (ICP) – Atomic Emission Spectrometry	Method 6010B. Metals and elemental inorganics.	Detection limits matrix dependent, typically lower than FLAA.	Permits simultaneous or rapid sequential analysis of many elements. Relatively free of chemical interferences.	Analyte cost may be slightly higher than FLAA.
Graphite Furnace Atomic Absorption (GFAA)	7000 Series Methods. Metals and elemental inorganics.	Typically, parts per billion detection limits. Can be reduced to sub-parts per billion through sample-preconcentration efforts.	Can provide high sensitivity for single elements.	May not be applicable for all Resource Conservation and Recovery Act (RCRA) and Priority Pollutant Metals, very sensitive to matrix effects, higher cost than FLAA or ICP. Single element sequential analysis.
Inductively Coupled Plasma-Mass Spectrometry (ICP-MS)	Method 6020. Metals and elemental inorganics.	Parts per trillion detection limits.	Monitor multiple analytes in a single analysis, higher sensitivity than FLAA, GFAA, or ICP.	Susceptible to interfering ions.
Ion Chromatography (IC) with a Conductivity Detector	Method 9056 for non-metallic inorganic compounds.	Parts per billion detection limits.	Monitor multiple anions in a single analysis.	Susceptible to interfering ions.

5.0 Using Nondetect Data in Risk Assessments

When an environmental sample is analyzed and a target compound is not detected or the detector signal is less than that required for definitive confirmation, the compound may be reported as “nondetect” (ND) or “U” flagged. There are decisions to be made when reporting ND data and the choice selected will have an impact on the MQOs.

5.1 Options for Reporting ND Data

If an analyte is indicated as a nondetect in the laboratory report, several quantitative values can be applied to that compound for screening purposes. It is recommended that the approach(s) to be used for ND data be negotiated with the regulators and documented as part of the MQO process and during the work plan development.

1. Nondetect = value for the MRL. This assumption is the most conservative for a risk assessment, because it will tend to bias data on the high side. When this approach is used, there is a high degree of confidence that the analyte is probably present, but at a level that is at or just below the MRL.
2. Nondetect = value of 0, indicating that the analyte is absent. This assumption is a nonconservative approach because it potentially will bias data on the low side. Assigning a value of 0 may be acceptable if it is highly unlikely that the analyte is present in the sample. An example would be the case for background samples where there is no history of the target analyte being detected.
3. Nondetect = “no value” given. This is different than providing a value of “0” in as much as a “0” value does have meaning if a statistical analysis of the data is performed. The “no value” approach is also a nonconservative approach.
4. Nondetect = value that is $\frac{1}{2}$ MRL. This is a “middle-of-the-road approach” where it is possible that the analyte would be detected in the sampling location and it “could be” as high as $\frac{1}{2}$ MRL.
5. Nondetect = value that is the percentage of NDs in a data set multiplied by the MRL. This is a statistical approach that takes into consideration the number of ND reports in relation to the overall number of data points in the data set. As an example, if there are 25 ND values in a data set of 100 samples, then 25% of the data were NDs. Therefore, 25% of the MRL would be the value given to ND data.

5.2 Decision Path for Assigning a Value to ND Data

How nondetects are treated will impact risk estimates. The following decision path can be used to assign a value to ND data.

- Does the substance pose a significant health or ecological risk at the MDL? If it does, then a more conservative reporting approach would be justified. If it does not pose a significant risk, then one of the less conservative reporting options could be used.
- Is it reasonable to think that the substance is present in the sample (is it in other site media, was it taken downgradient from detectable concentrations, are there chemical/physical considerations, and are other compounds typically associated with the targeted compound present)? If it is, then using $\frac{1}{2}$ MDL may be the appropriate value.

Interpretation of the ND data should be decided and negotiated when MQOs are established early in the HHRA and/or ERA process.

6.0 When Screening Levels are not Achieved

If MRLs are not low enough to perform the screening HHRA/ERA (i.e., when the MRL exceeds the HHRA/ERA screening concentration for a compound), then those compounds are usually carried forward to the baseline risk assessment. The goal should be to collect the proper data to eliminate as many compounds as possible during the screen. This can be done best by aggressively working with the analytical laboratory to achieve the MQO reporting limits. Detailed guidance for calculating site-specific screening values is presented in the HHRA and ERA web guidance.

There undoubtedly will be cases when it is not possible to achieve all of the screening levels for an HHRA and/or ERA. If it can be communicated to regulators that analytical options were exhausted within the available funding, then it may be possible to obtain adjustments to the MQOs. One option is to use alternative screening values (for example, substituting plant values for invertebrates). By doing so, it then may be possible to perform the risk assessment with existing data.

Conclusions/Summary

In conclusion, options exist to enhance the utility of data relative to detection and reporting limits. Efforts must be made to ensure that the reporting limits meet the required MQOs and therefore allow the RPM to make risk-based decisions. At a minimum, the following items need to be addressed and considered by the RPM in conjunction with the CLEAN Contractor:

1. Clearly define the MQOs and contractually negotiate meeting these goals with the analytical laboratory before sampling activities begin.
2. Examine the methods that are being recommended. Bring the lab in early in the process and always ask the laboratory if the reporting limits can be lowered by

employing an alternative sample extraction technique, performing cleanup steps on the extract, or by using a different analytical detector. Identify what the cost will be for these additional efforts.

3. If possible, obtain historical chemical-analysis data for the site, or sites with similar characteristics, to determine if there have been problems achieving specific reporting levels for the targeted compounds.
4. Get involved in the establishment of the MQOs/QAPP to ensure that options are clearly identified up front if the screening MRLs cannot be achieved. Have these options well defined in the Final QAPP.
5. Have clear decision paths for how to report NDs and what to do when reporting limits are greater than the screening values.

Always be prepared to consult a chemist for specific options. Options are usually available, but they normally come at a cost, and it is the responsibility of the RPM to evaluate whether the extra efforts are worth the cost. Obtaining detection and reporting limits that achieve MQOs and meet risk-assessment needs are possible, but must be diligently pursued to prevent generating unusable data sets.

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Acronyms and Abbreviations

BTEX	benzene, toluene, ethylbenzene and xylenes
CLEAN	Comprehensive Long-Term Environmental Action Navy
ECD	electron capture detector
EQL	estimated quantitation limit
ERA	ecological risk assessment
FID	flame ionization detector
FLAA	flame atomic absorption spectrometry
FPD	flame photometric detector
GC	gas chromatography
GC-MS	gas chromatography-mass spectrometry

GFAA	graphite furnace atomic absorption
HHRA	human health risk assessment
IC	Ion Chromatography
ICP	inductively coupled plasma
ICP-MS	inductively coupled plasma-mass spectrometry
MB	method blank
MDL	method detection limit
MQO	measurement quality objectives
MRL	method reporting limit
MSD	mass spectrophotometer detector
ND	nondetect
NOAA	National Oceanic and Atmospheric Administration
PAH	polyaromatic hydrocarbon
PCB	polychlorinated biphenyl
PFE	pressurized fluid extraction
PID	photoionization detector
ppm	parts per million
PQL	practical quantitation limit
QAPP	quality assurance project plan
QA/QC	quality assurance/quality control
RCRA	Resource Conservation and Recovery Act
RPM	remedial project manager
RSD	relative standard deviation
U.S. EPA	U.S. Environmental Protection Agency

References, Sources of Information

Crumbling, D.M., and B. Lesnik. 2001. Current Perspectives in Site Remediation and Monitoring. *The Relationship Between SW-846, PBMS, and Innovative Analytical Technologies*. U.S. EPA 542-R-01-015. October 2001.

Johnson, R.K. 2001. *Specifying and Evaluating Analytical Chemistry Quality Requirements for Ecological Risk Assessments*. MESO-01-TM-01. February 2001.

National Oceanic and Atmospheric Administration. 1993. *Sampling and Analytical Methods of the National Status and Trends Program National Benthic Surveillance and Mussel Watch Project*. Elemental Analytical Methods (Volume III) and Analytical Procedures to Quantify Contaminants (Volume IV). NOAA Technical Memorandum NOS ORCA 71. National Oceanic and Atmospheric Administration, Silver Springs, MD.

National Oceanic and Atmospheric Administration. 1998. *Sampling and Analytical Methods of the National Status and Trends Mussel Watch Project: 1993-1998 Update*. NOAA Technical

Memorandum NOS/ORCA/CMBAD 130. National Oceanic and Atmospheric Administration, Silver Springs, MD.

NOAA. See National Oceanic and Atmospheric Administration.

U.S. EPA, SW-846 Web Site; www.epa.gov:80/epaoswer/hazwaste/test/sw846.htm