Appendix A-11: Practical Quantitation Limits

INTRODUCTION

During the risk evaluation process when collecting media-specific chemical concentration data and establishing remediation standards situations may arise where practical quantitation limits (PQL) for specific chemicals and samples may exceed screening levels or site-specific, risk based concentrations. Section 500 of IDAPA 58.01.24, Application of Risk Based Corrective Action at Petroleum Release Sites delineates factors which may be used to allow the use of PQLs as remediation standards, as follows:

- Analytical Method
- Method Detection Limit
- Sampling Procedures
- Estimated Risk Levels
- Other

This appendix provides guidance on how to apply these factors when making this determination.

PRACTICAL QUANTITATION LIMITS AND METHOD DETECTION LIMITS

A PQL is defined in part in 58.01.24.010 as "The lowest concentration of a chemical that can be reliably quantified among laboratories within specified limits of precision and accuracy for a specific laboratory analytical method during routine laboratory operating conditions". The Method Detection Limit (MDL) is defined as "The minimum concentration of a substance that can be reported with 99% confidence is greater than zero".

PQL values are derived in a number of ways and there is no consensus as to the process used to develop them. In some cases they are derived as a fixed multiplier applied to the MDL value or the standard deviation of samples used to develop the MDL. The multiplier commonly ranges from 3 to 5 and may be as great as 10. In other cases PQL may be derived by analysis of data from actual laboratory performance studies. In these cases, PQL values are a function of analytical methods, a given laboratory's equipment, operating protocols, operating conditions, QA/QC procedures, and sampling and media considerations. Values are sometimes reported by laboratories at levels between the MDL and the PQL and are commonly qualified as estimated quantities. The closer the estimated value is to the PQL the more confidence in the estimated value.

For the petroleum chemicals of interest (COI) listed in the rule the common analytical methods employed at petroleum release sites are established by the U.S. Environmental Protection Agency (EPA) in SW-846 (EPA, 2011). Table A-11-1 lists methods commonly employed in the analysis of the petroleum COI along with typically achieved detection and quantitation limits.

These values were obtained from sample laboratory reports for site investigations done for DEQ at a number of sites where petroleum COI were suspected. In their method descriptions EPA lists examples of lower limits of quantitation for individual analytes but indicates that they are instrument dependent and influenced by sample preparation/introduction technique (EPA, 2006) or highly matrix-dependent and are provided for guidance only (EPA, 2007).

For a given media, sampling considerations may have an impact on achievable detection limits. For example, when sampling soil vapor or ambient air with certain methods, the achievable quantitation limit can be a function of the amount of vapor or air sampled. Quantitation limits are commonly reduced as the amount of air sampled increases.

Specialized analytical techniques can sometimes provide lower MDL and PQL values. Table A-11-1 illustrates this with a comparison of values between the use of standard method 8270 for semivolatile compounds vs. employing 8270 using selective ion monitoring (SIM). PQL values are 6X lower for soils and 20X lower for water samples.

Depending on the petroleum product released, the levels of contamination, chemicals present and the media in question (soil, water, and vapor) interferences to analytical detection and quantitation may be present. This may require procedures such as sample dilution in order to quantify COI concentrations in a sample but that result in elevated detection and quantitation limits.

REMEDIATION STANDARD

A remediation standard is defined in IDAPA 58.01.24 as a “media specific concentration which, when attained, is considered to provide adequate protection of human health and the environment”.

Remediation standards are established at petroleum release sites where corrective action has been determined to be required. The need for corrective action is commonly determined after completion of a risk evaluation. Remediation standards are commonly established as part of a risk evaluation or an approved corrective action plan (CAP).

The magnitude of a remediation standard that is established for a given chemical and the potential that it may be exceeded by a PQL is dependent on a number of factors. These factors include, but are not limited to:

- assumptions regarding current and future site land use, both on and off site,
- what petroleum products were released and the relative distribution of chemicals detected,
- the magnitude and distribution of contamination (which media are impacted) and
- the routes of exposure determined to pose the greatest threats.

The two risk evaluation scenarios where elevated PQL values may require the reevaluation of initially selected remediation standards include:

1) Screening Level Evaluation
The screening level evaluation described in IDAPA 58.01.24 employs the simplest and most straightforward use of remediation standards, in the form of the residential use screening levels. The screening levels are conservative, calculated, risk-based concentrations determined to be protective of unrestricted use exposures.
These media-specific chemical concentrations are established without consideration of the ability of standard laboratory methods to detect and quantify these values.

In the screening level evaluation, the user must compare maximum media-specific concentrations measured during site assessment activities to the screening levels. If the measured concentrations do not exceed the screening levels, the site may be eligible for site closure. If the measured concentrations do exceed screening levels, the user may select screening levels as the remediation standards upon which corrective action is based. Measured concentrations may exceed the screening levels either as a result of detected and quantified concentrations or by elevated PQLs. In the latter case, an unacceptable risk would be indicated and would require either additional investigation/evaluation or development of a cleanup plan.

2) Site-Specific Risk Evaluation
During the site-specific risk evaluation process media-specific chemical concentration data is collected and used, along with assumptions regarding exposure pathways and receptors, to calculate risk to expected receptors. If the calculated risk is unacceptable, media-specific risk-based chemical concentrations are established. These risk-based concentrations become the remediation standards for site corrective action. Samples are then taken during and after corrective action to demonstrate the standards have been attained.

PQLs for selected analytes in a given media sample may exceed one or more of the calculated risk based remediation standards, making the demonstration that the standard has been attained problematic. It is also problematic when samples with results below a PQL are included in the calculation of exposure point concentrations and risk.

Remediation standards are oftentimes the lowest at sites where:

- screening levels have been selected as the standards,
- unrestricted use is the desired corrective action land use goal,
- contamination has migrated offsite in ground water,
- onsite vapor intrusion risk is determined to exist, or
- diesel fuel contamination (and polynuclear aromatic hydrocarbon chemicals) are present in surface soil or in close proximity to surface water.

Accordingly, PQL-related issues often arise at such sites.

PROCESS FOR THE CONSIDERATION OF PQLs AS REMEDIATION STANDARDS

When a REM user proposes the use of PQLs as remediation standards, the user must develop and provide to DEQ as part of a proposed CAP a a proposal of PQLs as the remediation standards. . The proposal should include the results of any risk evaluation, the remediation standards developed from that process and the proposed PQL. The proposal should be completed so as to answer the questions below. The proposal should identify and discuss the site-specific issues, with supporting information, that justify the use of the proposed PQL(s) as a remediation standard(s).

Risk Evaluation

- What are the chemicals, media and pathway or route of exposure for which the issue exists?
- Is the PQL issue related to a Screening Evaluation and screening levels or a Site Specific Evaluation and risk based concentrations?
- If a Screening Level Evaluation, would performing a site specific evaluation address the PQL issue?
- If a Site Specific Evaluation, what is the impact on the estimated risk of assuming the specific COI at the proposed PQL? Is the risk still acceptable? If the risk was calculated for a residential receptor would the risk be acceptable for non-residential receptors? Does the chemical(s) with PQL issues contribute a significant portion of the cumulative risk?
- Would the implementation of activity and use limitations through an environmental covenant mitigate the risk presented by the chemical(s) at the PQL.
- If risk based concentrations (RATLs) are calculated for multiple chemicals can the risk be allocated in a different manner such that the allowable concentrations for chemical(s) without PQL issues be reduced to meet the cumulative risk criteria while maintaining the chemicals at issue at their respective PQL?

Analytical Methods

- What are the analytical methods being employed that are the basis of the PQL?
- Are there other analytical methods available with lower reporting limits?
- Are there special analytical techniques (such as Selective Ion Monitoring or SIM) which may be employed to achieve lower detection and quantitation limits?
- Are there other laboratories available which can achieve lower quantitation limits?
- Are there QA/QC issues that impact the stated PQL? Supporting lab QA information should be provided.

Method Detection Limit

- What is the stated method detection limit and what is the magnitude of the difference between it and the PQL?
- Is the method detection limit at or below the risk based remediation standard?

Sampling

- What sampling procedures are used for the media and chemical of interest?
- Are there alternative sampling procedures (such as increasing sample air volumes for soil vapor samples) which may result in lower detection and quantitation limits?
- Are there matrix interference issues with the samples being used in the proposal that prevent adequate quantitation limits from being attained? What is the supporting laboratory evidence that matrix interference issues exist? Are there specialized sample preparation methods which might reduce these interferences?
- Has resampling taken place to confirm the PQL issue?

DEQ will review the proposal for use of a specific PQL as a remediation standard as part of the overall CAP and approve or deny the request along with specifying any conditions of approval or reasons for denial.

REFERENCES

EPA, 2006. Method 8260C. Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS), Revision 3, August 2006 in *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods*. United States Environmental Protection Agency. SW-846.

EPA, 2007. Method 8270D. Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS).), Revision 4, February 2007 in *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods*. United States Environmental Protection Agency. SW-846.

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