USE OF PRACTICAL QUANTITATION LIMITS (PQLs) TO ESTABLISH CLEANUP STANDARDS FOR CONTAMINATED SEDIMENT SITES UNDER THE SEDIMENT MANAGEMENT STANDARDS (SMS)

SMS ISSUE PAPER
Sediment Management Annual Review Meeting, May 2, 2012

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INTRODUCTION

This issue paper describes challenges associated with developing cleanup standards based on practical quantitation limits (PQLs), existing rules and guidance, a proposed approach for developing cleanup standards based on PQLs, and analytical considerations for remedial investigations at sediment sites.

Human health risk-based cleanup standards based on the seafood ingestion pathway are frequently below both natural background concentrations as defined in the Model Toxics Control Act (MTCA) Cleanup Regulation (Chapter 173-340 WAC) and PQLs. This is particularly true for carcinogenic chemicals detected even in nonanthropogenically impacted areas of Puget Sound and other parts of the state, including dioxins/furans, PCB congeners, carcinogenic PAHs, mercury, and arsenic. With increasing emphasis on protection of human health for sediment cleanup, it is likely this will be an issue at the majority of sediment cleanup sites contaminated with bioaccumulative chemicals.

The MTCA rule requires that cleanup standards be established at concentrations that are the highest of 1) the risk-based concentration (this would be the lowest risk based concentration for protection of both ecological and human health), 2) natural background, and 3) the PQL. The Sediment Management Standards (SMS) rule (Chapter 173-204 WAC) is silent on the use of cleanup standards based on PQLs. Therefore, the MTCA requirements apply because it is the more specific rule on this issue. Under the MTCA rule, the PQL is defined as follows (WAC 173-340-200):

> *… the lowest concentration that can be reliably measured within specified limits of precision, accuracy, representativeness, completeness, and comparability during routine laboratory operating conditions, using department approved methods.*

The SMS rule is currently under revision to address the issues of human and ecological risk from bioaccumulatives and how to incorporate natural background concentrations and PQLs when establishing cleanup standards. Supporting guidance is being developed on assessing human health risk and calculating background for sediment cleanup to support these rule revisions. This issue paper provides guidance on using the third element, PQLs, to develop cleanup standards.

Nothing in this guidance is intended to limit the selection of individual laboratories or PQLs during remedial investigations for purposes of analysis, quality assurance, and data interpretation based on site-specific conditions. The following guidance applies only to the development of cleanup standards based on PQLs. Analytical PQLs used during the RI/FS or for monitoring may differ from the PQL-based cleanup standards.

PROBLEM STATEMENT

The following issues have arisen in using PQLs to develop cleanup standards at sediment sites:

- **Terminology.** Various laboratories, programs, guidance documents, and methods have different terminology for similar concepts. Conversely, the same term may not be used for the same thing in all contexts. Notwithstanding the MTCA rule definition above, this continues to be a challenge when working with PQLs. In general, there is a lower limit at which a chemical may be detected, and a higher limit at which a chemical concentration may be quantified. This higher limit may be termed the PQL or Limit of Quantitation (LOQ). There may also be method-specified reporting limits (MRLs), which may or may not be similar in concept to a PQL. Finally, these values may be 1) sample-specific, 2) "typical" values for the method that can be achieved by a specific laboratory, or 3) contract-required limits such under EPA's Contract Laboratory Program (CLP). Thus, identifying the specific value closest to that defined by rule can be a challenge.

- **Selecting PQLs for Use in Establishing Cleanup Standards.** Ecology maintains a list of accredited laboratories for each analytical procedure. However, these laboratories may not all have the same PQLs, even if they are all using the same terminology, for a given analyte. Ecology must select among this range of available PQLs in developing a cleanup standard, and that selection may affect 1) the protectiveness of the cleanup standard for that site, and 2) how many laboratories will have PQLs below that standard and thus can participate in future monitoring at that site. Ecology will also consider the capacity and potential cost of the few laboratories that can meet very low PQLs, as well as marketplace impacts, should low PQL-based standards be selected.

- **Recency.** Analytical methods change over time and PQLs may decline, which affects a number of aspects of the process. First, it is important that Ecology have recent information on PQLs prior to selecting a PQL-based cleanup standard for a sediment site. Second, because the PQL-based standard would in this case represent a risk level that is higher than that mandated by rule, the site manager must carefully consider what may happen if the PQL changes in the future and whether there is another alternative that could be chosen. Unlike most other cleanup standards, the permanence of the remedy could ultimately be called into question.

- **Remedial Investigation Data Reporting.** Despite the likely increased use of PQL-based cleanup standards for sediment sites in the future, Ecology wishes to re-emphasize its long-standing policy of requiring all remedial investigation data between the MDL and the PQL to be reported at face value and qualified appropriately. Ecology staff have noticed a recent trend in which many laboratories are reporting all data between the MDL and the PQL as undetected at the PQL. This limits the ability of site managers and contractors to perform needed evaluations of data that are frequently at these very low levels, including comparisons to natural background distributions, calculation of TEQs and human health risk evaluations, chemical fingerprinting, and trend analyses. As we deal more with natural background and human health evaluations for carcinogenic chemicals, concentrations of chemicals at these levels will become increasingly important to decision-making at sediment sites.

  Ecology believes that while these concentrations may be qualified and more uncertain than concentrations above the PQL, using the qualified data in these evaluations is preferable to substitution methods with even less statistical validity. In addition, simply knowing whether a

chemical is present at all (at the MDL) is valuable information that is lost when all concentrations are qualified as undetected at the PQL. This may inform us, for example, as to whether a more specialized analytical method is needed in a subsequent round of analyses. All of these uses are considered exploratory and deliberative in nature, as opposed to setting a cleanup standard, which necessitates use of a more accurate, precise, and achievable value such as the PQL.

EXISTING RULES AND GUIDANCE

Both the SMS and MTCA rules include provisions for situations where the calculated cleanup levels for protection of human health are below 1) natural background as defined in the MTCA rule or 2) non-anthropogenically affected background as defined in the SMS rule. Specifically:

- The SMS rule states that "…the existing sediment chemical and biological quality shall be identified on an area-wide basis as determined by the department, and used in place of the sediment quality standards of WAC 173-204-320(6).

- The MTCA rule specifies that "the cleanup level shall be established at a concentration equal to the practical quantitation limit or natural background concentration, whichever is higher" (WAC 173-340-700).

The SMS rule does not currently provide specific requirements or directives for addressing situations where human health risk-based or background levels are at concentrations that cannot be reliably quantified; therefore, the procedures set forth in MTCA are applicable to sediment sites.

The MTCA rule also requires that, where the PQL is used as a cleanup level, it must meet the more stringent of the following conditions (WAC 173-340-707(2)(a) and (b)):

- The PQL is no greater than ten times the method detection limit (MDL).

- The PQL is no greater than that established by the U.S. EPA and used to establish requirements in 40 CFR 136, 40 CFS 141-143, or 40 CFR 260-270.

The MTCA rule further requires that sites where the cleanup level was set at the PQL shall undergo periodic reviews, and that the availability of improved analytical techniques should be considered during the periodic review (WAC 173-340-707 (4)).

APPROACH

Ecology intends to take the following approach to identifying, selecting, and applying PQL-based cleanup standards at sediment cleanup sites under the SMS:

- **Definitions.** The PQL will continue to be defined as in the MTCA rule, which is not currently open for revision. When conducting surveys of laboratories, Ecology will take care to understand the various levels the laboratory may be using and how they relate to the rule definition. In general, Ecology is seeking to identify the lowest level at which each laboratory can reliably quantify the

chemical concentration on a method-specific basis, as distinguished from either a contract-required reporting limit or a sample-specific quantification limit.

- **Identifying PQLs in Current Use.** To identify the commercially available range of PQLs from which PQL based cleanup standards will be derived, Ecology will periodically survey Ecology-accredited laboratories for a chemical or chemicals of interest. Information on all available analytical methods will be requested. Ecology will specify that method-specific MDLs and PQLs should be provided that represent what the laboratory can actually and routinely achieve using each method that it runs for that chemical.

- **Programmatic Approach for Developing PQL-Based Cleanup Standards.** On a program-wide basis, Ecology will review the available PQLs and identify a representative value from the distribution of PQLs that is reasonably achievable and reliably attainable by most accredited laboratories using appropriate analytical methods. Ecology may choose not to include particularly high PQLs (e.g., that represent EPA CLP contract-required reporting limits) or particularly low PQLs (e.g., that only a few specialty or research labs can achieve) in the distribution. For chemicals that are identified program-wide to have high human health or ecological risks at natural background or PQL concentrations, a more sensitive commercially available method may be used to establish the distribution of PQLs.

  To select a specific PQL-based cleanup standard, a central tendency value such as a median or mean of the distribution will be used and rounded to one significant digit. For compound classes that are normally reported as TEQs (e.g., dioxins/furans/coplanar PCBs, carcinogenic PAHs), PQL-based cleanup standards will also be reported as TEQs by applying the appropriate TEFs to the PQLs for individual congeners and summing them. As required by MTCA, this value will be no more than 10 times the MDL and no higher than the EPA CLP. Ecology recognizes that it may not always be possible in practice for the PQL to be 10x the MDL, particularly given the evolving nature of these definitions in the industry. PQL-based cleanup standards for such chemicals would be developed on a case-by-case basis using the latest available science.

  Ecology will make each chemical-specific evaluation available through the Sampling and Analysis Plan Appendix or the Sediment Management Annual Review Meeting. In general, analytical PQLs should be reviewed every 3-5 years to ensure that they are still accurate and that cleanup standards derived from them are still appropriate.

- **Site-Specific Approach for Selecting a PQL-Based Cleanup Standard or a Cleanup Standard below the PQL.** PQL-based cleanup standards, as with other cleanup standards, are selected at the end of the RI process, and do not necessarily reflect the PQLs used during the RI for analytical purposes. Site managers may require site-specific PQLs during the remedial investigation for the purposes of laboratory selection, data analysis, quality assurance, and data evaluation. Such analytical PQLs may be higher or lower than the PQL-based cleanup standard, depending on the conceptual site model and other site-specific considerations.

  There may be circumstances in which a site manager needs to select a site-specific PQL-based cleanup standard that is different from the programmatic PQL-based standard, for example:

  - If a new method or improvement to a method comes into widespread commercial use.

- If the existing programmatic PQL-based cleanup standard for a chemical is more than 3-5 years old.
- If a PQL-based cleanup standard has not been developed for a chemical of concern at the site.
- If the sediment matrix at the site is sufficiently unusual to affect the achievable PQL.
- The conditions in WAC 173-340-830(2)(e) apply.

In these cases, the programmatic PQL-based cleanup standards may need to be updated or established and the site manager will work with the program to update the PQL-based cleanup standard needed for the site using the process above (or a simplified version of it for one or a few chemicals).

In addition, a site manager may wish to set a cleanup standard below the PQL on a site-specific basis if it would provide greater finality or protectiveness (e.g., based on human health risk, protection of ESA species, or natural background). This can be accomplished in one of two ways:

- Ecology and the liable party may negotiate a cleanup standard between the MDL and the PQL based on natural background or environmental/human health risk.

- A cleanup action may be selected that would achieve any reasonably foreseeable cleanup standard (e.g., dredging to native sediments).

Site managers should carefully consider the implications of selecting a PQL-based cleanup standard, including the possibility that the PQL may fall over time to below natural background or risk-based levels. An understanding of how decisions or actions could change if this occurs during the periodic reviews would be important to reach in cooperation with the PLP(s) prior to finalizing the Cleanup Action Plan.

- **Comparison of Natural Background or Risk-Based Concentration to PQLs.** In determining whether the cleanup standard should be based on PQLs under MTCA/SMS, the site manager will determine whether the risk-based concentration and/or natural background concentration is below the programmatic PQL. These comparisons will be based on bright-line values rather than distributions, e.g., the statistic representing natural background that would be selected as the cleanup standard is compared directly to the PQL-based cleanup standard to determine which is higher.

- **Remedial Investigation Data Reporting.** Ecology will continue to require that all data collected as part of the RI/FS process be reported at face value to the sample-specific detection limit, appropriately qualified. Data falling between the detection limit and the quantification limit (however defined) may not be U-qualified.