April 17, 2016

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Ms. Daniels:

I am providing these comments in response to the Disinfection Requirements Rule [46 Pa.B. 857], which was released for public comment [Saturday, February 20, 2016].

1. **In the section entitled "Amendments to disinfectant residual requirements in the distribution system", the document states that "The Department's existing treatment technique is not protective of public health because a residual of 0.02 mg/L does not represent a true detectable residual and the level is inadequate to protect against microbial growth within the distribution system." This should be revised.**

The term 'true detectable residual' is unclear. I would strongly urge the use of existing terms that are either defined in regulation or commonly accepted by the scientific community. What I believe is meant here is that 'a residual of 0.02mg/L does not represent the Minimum Level of Quantitation (ML), and thus the current standard is inadequate to meet the requirements of the Safe Drinking Water Act (SDWA)[1] for a detectable residual in the distribution system."

The issue of whether this level is inadequate to protect against microbial growth within the distribution system should be separated in this introductory remark as the analysis of the ML is distinct from the analysis of a level that is adequate to protect against microbial growth. The Pennsylvania Department of Environmental Protection (DEP) may decide to require a level that is higher than the ML for reasons that are not related to implementation of the requirement of 'detectable residual' in the SDWA. The DEP is not limited to requiring only the minimum detectable level, and a higher level may be required for reasons that are not associated with analytical detection issues. Further, future analytical advances may enable lower levels of quantitation, with the potential to change how the SDWA requirement is met.

2. **Later in the document in a section entitled "What is a true detectable residual?" this term is not adequately defined, and related terms that are introduced are incorrectly described.**

The value of introducing a term called "true detectable residual" is unclear, and the document further confuses things by introducing a term, Method Limit (ML), to replace several already existing terms with equivalent meaning.

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[1] 40 CFR Part 141.72 "The residual disinfectant concentration in the distribution system, measured as total chlorine, combined chlorine, or chlorine dioxide, as specified in 141.74(a)(2) and (b)(6), cannot be undetectable in more than 5 percent of the samples each month, for any two consecutive months that the system serves water to the public."

The document describes the Method Detection Limit (MDL) as a 'qualitative value that is determined in the lab," and states that it "does not represent a quantitative value." It is not clear what the document is trying to convey in these statements, since later in the document, a reference for a *quantitative* value is provided, and this value is used in subsequent calculations. It is unclear how a *qualitatively* reported MDL could have a numerical value with a specific precision as implied by the citation of the Hach value of 0.024mg/L.

Further, the MDL as routinely defined *does* represent a quantitative value. The MDL is defined as "the minimum concentration of an analyte that can be identified, measured and reported with 99% confidence that the analyte concentration is greater than zero."[2] The concentration is a quantitative value, representing the result of following a set of criteria for the laboratory analysis and the statistical interpretation of the data. The fact that the value is computed from a series of measurements does not make it any less a quantitative value. The MDL is routinely computed by the relevant laboratory rather than generically across all laboratories for all times. All standard methods for chlorine residual measurement require computing the MDL at the laboratory using prepared standards.

A related term, the *practical quantitation limit or level* (PQL) is the lowest level that can be reliably achieved within specified limits of precision and accuracy during routine laboratory operating conditions. The PQL is sometimes called the Minimum Level of Quantitation (ML), defined as "the lowest level at which the entire analytical system must give a recognizable signal and acceptable calibration point for the analyte."[3]

In the present document, the abbreviation ML is used for a term called the Method Limit (ML), which is defined as "also known as the practical quantitation limit." It is unclear why this different name for this term using the same abbreviation is introduced here. I strongly urge that this document not to add to the confusion over terms by using another term for this widely recognized value, unless the intent was to alter the definition.

The later conclusion that the "true detectable residual" is likely somewhere between 0.1 and 0.2 mg/L does not improve clarity. Many laboratories are conducting chlorine residual analyses regularly and could be requested to submit data for their MDL, which could then be used to compute ML values.

3. **The computation of the Minimum Level of Quantitation, called Method Limit in the rule, does not provide adequate justification for rounding steps.**

The minimum level of quantitation (referred to as ML by EPA) is "calculated by multiplying the MDL by 3.18 and rounding the result to the number nearest to (1, 2, or 5) x 10^n, where n is an integer."[4] This is not how the introduced term, Method Limit, was computed. It is not clear if this is an intentional change

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[2] 40 CFR Part 136, Appendix B to Part 136 – Definition and Procedure for the Determination of the Method Detection Limit – Revision 1.11   https://www.gpo.gov/fdsys/pkg/CFR-2011-title40-vol23/pdf/CFR-2011-title40-vol23-part136-appB.pdf

[3] *Ibid.*

[4] EPA (2004) Revised Assessment of Detection and Quantitation Approaches, Engineering and Analysis Division, Office of Science and Technology, Office of Water, U.S. Environmental Protection Agency. EPA-821-B-04-005. October, 2004. http://nepis.epa.gov/Exe/ZyPDF.cgi/901R0400.PDF?Dockey=901R0400.PDF
This definition is also found in EPA (2011) Supplement to Report Entitled, "A Laboratory Study of Procedures Evaluated by the Federal Advisory Committee on Detection and Quantitation Approaches and Uses in Clean Water Act Programs," Comparison of the EPA MDL and ML to the FACDQ DL and QL with Respect to Study Measurement Quality Objectives (MQOs). https://www.epa.gov/cwa-methods/procedures-detection-and-quantitation-documents

that creates a new meaning for Method Limit that is not equivalent to the Minimum Level of Quantitation or if this is an incorrect application of a presumed rounding method. A document, entitled "Primer on DPD Chlorine Method Limits and their Use in Compliance Reporting[5]," attributed to Hach Company, states that "the ML is often rounded to the nearest 10th of a mg/L." No citation in support of this statement is given in that document. If this is a standard practice for chlorine residual assessment, adequate references for this should be provided since it does not conform to methods for calculating ML published by EPA.

Based on the cited Hach Company Primer, a MDL for a set of seven replicates was reported as 0.024 mg/L, which is then rounded to 0.02mg/L. It is not clear why this rounding step is included, nor why this particular set of seven replicates is relevant to the broad question of MDL for the chlorine residual method. The document notes that 0.02mg/L was the MDL used by the EPA to approve Hach's methods. The Hach method and the EPA approval of that method should be cited in support of these values.

The Method Limit is then computed as: $ML = 0.02 \times 3.18 = 0.06mg/L = 6 \times 10^{-2}$ mg/L, which is then rounded to 1×10^{-1} mg/L, or 0.1 mg/L. This does not follow the method described by EPA to round "the result to the number nearest to $(1, 2, \text{ or } 5) \times 10^n$, where n is an integer." Following the EPA method would result in a value of 5×10^{-2} mg/L, or 0.05 mg/L. No reason for the application of an alternative rounding method at this final step is given in the document or in the Primer, beyond the assertion that the "ML is often rounded to the nearest 10th of a mg/L." As noted previously, there is no citation provided in support of this statement.

It is worth noting that if the EPA steps for determination of the practical quantitation limit (minimum level of quantitation, ML), were followed without the unexplained early rounding of the MDL, the computation would be:
$ML = 0.024 \times 3.18 = 0.076$ mg/L $= 7.6 \times 10^{-2}$mg/L. Following the specified rounding instructions, this would lead to a ML of 1×10^{-1} mg/L, or 0.1 mg/L.

I strongly urge the use of standard terminology for ML as meaning the Minimum Level of Quantitation, not Method Limit, and to follow the proscribed steps to compute this from the MDL. If there is sound reason for rounding the MDL to 0.02 mg/L, then the ML should be reported as 0.05mg/L not 0.1mg/L, following accepted practice for computation of the ML. If the early rounding of the MDL is not justified, then the ML should be reported at 0.1mg/L, again, computed using accepted practice.
If alternative practices are used in chlorine residual measurement, adequate supporting documents should be cited. Further, the Hach Company Primer is not the only source for MDL for this method, and additional information should be solicited on this value to improve the reliability of the ML value. As noted above, many laboratories within the Commonwealth measure chlorine residual regularly and would be required to assess MDL and ML values. These data could be used to provide more robust support for the ML to be adopted by Pennsylvania.

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[5] This document is associated with the rule-making and can be found at:
http://files.dep.state.pa.us/Water/BSDW/DrinkingWaterManagement/Regulations/Primer%20on%20DPD%20Chlo rine%20Method%20Detection%20Limits%20and%20their%20Use%20in%20Complian%20%20%20.pdf

4. **In the section entitled "Why is it important to maintain a disinfectant residual within the distribution system?" The document states: "There should be no change in the quality of treated water from the time it leaves the treatment plant until the time it is consumed."**

This is an impossible expectation, in direct opposition to well-known facts and long-accepted science regarding water chemistry and microbiology in distribution systems. As noted in the sentence directly following it "substantial changes can occur to finished water as a result of physical, chemical and biological reactions." Further, later the document states "water quality may degrade during water distribution" and lists a variety of reasons for these changes. Interestingly, the document does not note that water quality can improve during distribution (e.g., when water utilities install tank aeration). Several regulations are designed specifically with the knowledge that the water quality changes during distribution, including the Disinfectants/Disinfectant Byproducts Rule (D/DBPR) and the Lead and Copper Rule (LCR).

Thus, the broad statement is misleading and should be removed or significantly revised. Statements such as this that suggest the world is under greater engineering control than it actually can be do not add value to public discourse. Further, they undermine important attempts by many public and private entities to increase the scientific literacy of our citizens.

5. **The premise of the proposed rulemaking is to increase the public health protection by increasing the required disinfection residual in the distribution system. The document provides inadequate analysis of the benefits and drawbacks of this decision from a public health perspective, especially with respect to formation of disinfection by-products.**

Independent of updating the requirements for residual associated with having a 'detectable' residual, which is clearly required in 40 CR 40.141.72, the proposed rulemaking suggests that requiring chlorine residual above the ML (0.1mg/L or perhaps 0.05 mg/L as noted in calculations above) will improve public health.

Inadequate assessment of this assertion has been undertaken and insufficient justification is provided in the rule and associated supporting documents. When managing disinfection, we are always balancing the need for microbial control with the formation of disinfection by-products. This rule provides inadequate assessment of the changes in DBPs that might occur with a switch to higher residual concentrations, particularly in systems with long residence times.

Thank you for your consideration of these comments.

Sincerely,

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