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ADOPTED

SUBJECT: Solid Waste Policy: Practical Quantitation Limits Number: DDAGW-04-03-226
[OAC Rule 3745-27-10(C)(7)(e) and Issued: 07/25/95
OAC Rule 3745-27-10(C)(6)(e)] Revised:
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PURPOSE: To clarify the meaning of Practical Quantitation Limits (PQLs) and to provide information on how to interpret a PQL and apply it to the statistical analysis of ground water data.

BACKGROUND: The performance standards for a statistical method chosen to evaluate ground water monitoring data are outlined in Ohio Administrative Code (OAC) Rule 3745-27-10(C)(7). OAC Rule 3745-27-10(C)(7)(e) requires that "The statistical method shall account for data below the limit of detection with one or more statistical procedures that ensure protection of human health and the environment. Any PQL used in the statistical method shall be the lowest concentration level that can be reliably achieved within the specified limits of precision and accuracy during routine laboratory operating conditions that are available to the facility."

POLICY: U.S. EPA developed the PQL as an inter-laboratory concept (Federal Register, 1987) to define a measurement concentration that is time and laboratory independent for regulatory purposes. PQLs are used for data interpretation not in data generation and are a regulatory device rather than a standard that labs must specifically demonstrate (Federal Register, 1991). A PQL is the product of a factor times the Method Detection Limit (MDL) of an analytical method. The MDL is defined in the following paragraph. The factors are used to compensate for variances due to analytical methods and matrix type and are specified in SW-846 according to the analytical method chosen. After multiplying the MDL by this factor, analytical data from all labs can be evaluated on a consistent regulatory level.

The MDL is defined as the constituent concentration that, when processed through the complete analytical method, produces a signal with a 99% probability that it is different from the blank (Standard Methods, 1989). MDLs are a stringent target for laboratory measurements. The MDL is determined from analysis of a sample in a given matrix containing the analyte. The MDL for an analytical method may vary as a function of the sample type because of matrix interference and its effects (Anne, 1992). The procedure for determination of a MDL was designed for applicability to a broad range of physical and chemical methods. Because of this, the procedure is instrument or device-independent (U.S. EPA, 1986). But the MDL is sample and method dependent. Hence, PQLs can only be changed by using a different method for the determination of a lower MDL.

The acronym PQL was amended to Estimated Quantitation Limit (EQL) in Revision I, July 1992, of the U.S. EPA document SW-846, Test Methods for Evaluating Solid Waste: Physical/Chemical Methods, third edition, published in November 1986. The U.S. EPA definition of an EQL is verbatim to that used in previous editions of SW-846 for a PQL. The U.S. EPA was contacted for a clarification of this issue. EQL and PQL are equivalent. In order for this guidance document to be consistent with the wording used in OAC Rule 3745-27-10(C)(7)(e), we will continue to use the acronym PQL.

PQLs can be defined as the sum of seven times the standard deviation of the analytical measurements plus the MDL. When used in this context the MDL is defined as three

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times the standard deviation of the analytical measurements (again, producing a signal with a 99% probability that it is different from the blank) plus the smallest signal above background noise that the instrument used for the analytical measurements can detect. This signal is known as the Instrument Detection Limit (IDL). This equates the PQL to a total of 10 times the standard deviation of the analytical measurements plus the IDL.

PQLs are considered a surrogate for actual laboratory performance because they are determined from another measurement, the MDL. Therefore, PQLs do not actually represent the results of normal laboratory procedures, but are a model of what normal laboratory procedures might achieve.

Sample PQLs are also highly matrix-dependent. The PQLs in SW-846 are provided for guidance only and may not always be achievable. The PQLs published by U.S. EPA for its analytical methods are based on reagent water spiked with the compound of interest, so they do not represent limits achievable where matrix interferences exist, as with actual samples.

The single most important characteristic of any result obtained from one or more analytical measurements is an adequate statement of its uncertainty interval (Krochta, 1990). A measured value becomes believable when it is larger than the uncertainty associated with it. The point at which this occurs is the MDL. Even at the MDL, the measured value has a degree of uncertainty associated with it. Because of the uncertainty, the value may be believable but there is not enough confidence in the value to use the MDL as a decision point. This uncertainty may be contributed to by power fluctuations at the laboratory, electrical noise, contamination of the analytical apparatus, or other analytes detected in the sample with similar spectral wavelengths producing similar spectrograms to the analyte of interest (Minichillo, 1994). The level where measurements become quantitatively meaningful is the PQL (Taylor, 1987). Everything below the PQL is in a region of less-certain quantitation. The PQL computation assumes that the value is the lowest concentration of an analyte that can be quantified with a statistical degree of confidence. Because of the increased confidence in the value of the PQL, this level can be used as a decision point. The degree of both uncertainty and confidence must be clearly defined in cases involving litigation and/or enforcement proceedings.

Decisions or interpretations based on ground water quality data necessitate that the degree of both uncertainty and confidence of the data be considered. OEPA recognizes that analytical data at or near the MDL has considerably more uncertainty associated with it than when significant amounts of an analyte are present. If an analytical measurement falls below the MDL, the analyte should be reported as not or none detected using the data qualifier ND (Stanko, 1993). For analytical data between the MDL and the PQL there is a corresponding region of less-certain quantitation. This region may lead to a high degree of false positive (type I error) and/or false negative (type II error) contaminant identifications. Confidence in the apparent analyte concentration increases as the analytical signal increases above the MDL. If an analyte is detected but the analytical value is below the PQL, the analyte can be reported as detected but it should be stated that there is a degree of uncertainty associated with the analytical value.

POLICY:

OAC Rule 3745-27-10(F)(7) requires that the corrective measures plan propose a concentration clean-up level for each leachate or leachate derived constituent which has been detected in the ground water at a statistically significant level and that this clean up level be "protective of human health and the environment." For those constituents for which Maximum Contaminant Levels (MCL) have been established, the clean-up level shall be the MCL for that constituent. This is due to the fact that MCLs are enforceable health-based risk standards. Anything above the MCL shall initially be considered not protective of human health and the environment.

OAC Rule 3745-27-10(C)(6) requires that any statistical method chosen to evaluate ground water quality data collected during the ground water detection monitoring program be "protective of human health and the environment." If an owner/operator decides to propose the use of a PQL or MDL for a constituent as a statistical concentration limit for that constituent, any concentration above which would be considered evidence of a statistically significant increase, then the PQL or MDL must be below the MCL for that constituent, if an MCL has been established, to be considered protective of human health and the environment and a valid statistical method under OAC Rule 3745-27-10(C)(6)(e).

Included with this guidance/policy document is Table 1 listing the OAC Rule 3745-27-10 Appendix I parameters which have MCLs. This table also includes the Chemical Abstracts Service registry number (CAS-RN) for that parameter, analytical methods from SW-846 which can be used for analyses of these parameters, the corresponding PQL for the method listed (for a ground water matrix), and the MCL for that parameter. The information on this Table should be referenced for selection of an analytical method which will provide a PQL less than a MCL.

SOURCES CONSULTED

American Public Health Association, Standard Methods for the Examination of Water and Wastewater, 17th Edition, 1989, Washington, D.C., p. 1-5.

Anne, Donald, Know Your Detection and Quantitation Limits, Pollution Engineering, May 1, 1992.

Federal Register, Vol. 52, No. 130, Wednesday, July 8, 1987, Rules and Regulations, p. 25699.

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Krochta, W.G., PPG Industries, et. al., U.S. EPA, Office of Water, Quantitation/Detection Limits for the Analysis of Environmental Samples, 13th EPA Conference on Analysis of Pollutants in the Environment, May 9-10, 1990 Norfolk, VA.

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SW-846, Test Methods for Evaluating Solid Waste; Physical/Chemical Methods, Revision 1, 3rd Edition, Nov. 1986, p. 1-24.

Taylor, John Keenan, Quality Assurance of Chemical Measurements, Lewis Publishers, 1987, p.79.

U.S. EPA, 40 CFR Chapter 1, Part 136 Appendix B, (7-1-86 Edition), p. 505

TABLE 1
RECOMMENDED ANALYTICAL METHOD(S) TO DETERMINE A PQL LESS THAN OR
EQUAL TO THE MCL¹ FOR OAC RULE 3745-27-10 APPENDIX I PARAMETERS WITH
MCLs

CAS RN ²	COMPOUND	Recommended Analytical Method	PQL($\mu\text{g/L}$) for a Ground Water Matrix	MCL ($\mu\text{g/L}$)
71-43-2	Benzene	8020	2	5
75-27-4	Bromodichloromethane	8010 8240	1 5	100 ⁴
75-25-2	Bromoform; Tribromomethane	8240 8010	5 2	100 ⁴
56-23-5	Carbon Tetrachloride	8010	1	5
108-90-7	Chlorobenzene	8010 8020 8240	2 2 5	100
67-66-3	Chloroform; Trichloromethane	8010 8240	0.5 5	100 ⁴
124-48-1	Dibromochloromethane; Chlorodibromomethane	8010 8240	1 5	100 ⁴
95-50-1	o-Dichlorobenzene; 1,2-Dichlorobenzene	8010 8020 8120 8270	2 5 10 10	600
106-46-7	p-Dichlorobenzene; 1,4-Dichlorobenzene	8010 8020 8120 8270	2 5 15 10	75
107-06-2	1,2-Dichloroethane; Ethylidene Dichloride	8010	0.5	5
75-35-4	1,1-Dichloroethylene; 1,1-Dichloroethene; Vinylidene Chloride	8010 8240	1 5	7
156-59-2	cis-1,2-Dichloroethylene; cis-1,2-Dichloroethene	8260	5	70
156-60-5	trans-1,2-Dichloroethylene; trans-1,2-Dichloroethene	8010 8240	1 5	100
78-87-5	1,2-Dichloropropane; Propylene Dichloride	8010	0.5	5

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CAS RN ²	COMPOUND	Recommended Analytical Method	PQL($\mu\text{g/L}$) for a Ground Water Matrix	MCL ($\mu\text{g/L}$)
100-41-4	Ethylbenzene	8020 8240	2 5	700
75-09-2	Methylene Chloride; Dichloromethane	8010 or 8240	5	5
100-42-5	Styrene	8240 8020	5 1	100
127-18-4	Tetrachloroethylene; Tetrachloroethene; Perchloroethylene	8010	0.5	5
108-88-3	Toluene	8020 8240	2 5	1000
71-55-6	1,1,1-Trichloroethane; Methylchloroform	8240	5	200
79-00-5	1,1,2-Trichloroethane	8010	0.2	5
79-01-6	Trichloroethylene; Trichloroethene	8010	1	5
75-01-4	Vinyl Chloride	8010	2	2
	³ Xylenes (Total)	8020 8240	5 5	10,000

¹ MCL standards effective January 1, 1993

² Chemical Abstracts Service registry number

³ This entry includes o, m, p-and unspecified xylenes

⁴ The MCL for trihalomethanes includes the sum of the concentrations for Bromodichloromethane, Dibromochloromethane, Bromoform and Chloroform