

Analytical Feasibility Support Document for the Third Six-Year Review of Existing National Primary Drinking Water Regulations: Chemical Phase Rules and Radionuclides Rules

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Abbreviations and Acronyms

ASTM	American Society for Testing and Materials
CCGC	Capillary Column Gas Chromatography
CBI	Confidential Business Information
CASRN	Chemical Abstract Services Registry Number
DAI	Direct Aqueous Injection
DL	Detection Limit
DW	Drinking Water
ECD	Electron Capture Detector
ECGC	Electron Capture Gas Chromatography
ELCD	Electrolytic Conductivity Detector
EPA	Environmental Protection Agency
FR	Federal Register
GC	Gas Chromatography
HPLC	High Performance Liquid Chromatography
HRGC	High Resolution Gas Chromatography
HRMS	High Resolution Mass Spectrometry
ICP	Inductively Coupled Plasma
LLE	Liquid-Liquid Extraction
LSE	Liquid-Solid Extraction
MCL	Maximum Contaminant Level
MCLG	Maximum Contaminant Level Goal
MDL	Method Detection Limit
ME	Microextraction
MS	Mass Spectrometry
N/A	Not Available
NELAC	National Environmental Laboratory Accreditation Conference
NPDWR	National Primary Drinking Water Regulation
OIA	OI Analytical
PE	Performance Evaluation
PQL	Practical Quantitation Level
PT	Proficiency Testing
PTRL	Proficiency Testing Reporting Limit
SDWA	Safe Drinking Water Act
SM	Standard Methods
SPE	Solid-Phase Extraction
TCR	Total Coliform Rule
WS	Water Supply
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Executive Summary

The Safe Drinking Water Act (SDWA), as amended in 1996, requires the Environmental Protection Agency (EPA) to review and revise, if appropriate, existing National Primary Drinking Water Regulations (NPDWRs). The review involves consideration of five key elements, as appropriate: health effects, analytical and treatment feasibility, implementation-related issues, occurrence and exposure, and economic impact. This report addresses the analytical feasibility aspect of the review which has been based on the laboratories' analytical performance data generated as part of EPA's certification program for drinking water laboratories. This analytical feasibility assessment is based on the recent analytical performance data collected during the third six-year review (period of 2008-2014). Efforts are also made to determine if the analytical performance assessments based on the laboratory data are supported by the adoption of improved methods or revision of existing methods since the last review. The goal is to create a comprehensive document to address all regulated chemical analytes for which data is available.

Analytical Performance Assessment Based on the Laboratories' Analytical Performance Data

The Practical Quantitation Level (PQL) assessments are presented by way of linear regressions that plot laboratory passing rate versus true concentration of the analyte. The PQL is defined as "the lowest achievable level of analytical quantitation during routine laboratory operating conditions within specified limits of precision and accuracy" (USEPA, 1985a). The PQL is set at a concentration where 75 percent of laboratories achieve results within a specific range around the spike value or acceptance criteria. PQL determination can be a useful tool in assessing whether promulgated PQLs can be reduced as a result of improved laboratory performance over time. The PQL incorporates quantitation, precision and bias, normal operations of a laboratory and the fundamental need to have a sufficient number of laboratories available to conduct compliance monitoring analyses (USEPA, 1985b; USEPA, 1987; USEPA, 1989).

The current report includes PQL assessments for available Performance Evaluation (PE) data generated under The NELAC Institute (TNI) Proficiency Testing (PT) program. Out of the seven TNI-accredited PT providers that were approached to provide PT data, only two PT providers, i.e., Environmental Resource Associates, Inc. (ERA) and Phenova were able to provide the requested information. After an initial review and analysis conducted under the Six-Year Review 3 Protocol, PQL analysis was performed on 16 analytes. The results for the 16 regulated analytes are categorized into two subsets based on the limitation of the PQL for setting the Maximum Contaminant Level (MCL) at the time of promulgation: 1) analytes with MCL equal to the current PQL and thus the PQL is limiting and 2) analytes with MCL greater than the current PQL and thus it is technically feasible to reduce an MCL.

The recommendations for the PQL assessment for the 16 analytes are as follows:

• For eight analytes, the PQL is equal to the MCL and hence the PQL is limiting (refer to Exhibit ES.1 for results of the PQL analyses).

For all eight analytes (chlordane, 1,2-dibromo-3-chloropropane, dioxin, heptachlor, heptachlor epoxide, pentachlorophenol, thallium and toxaphene), the PT data does not support reduction of the current PQL.

• Out of these eight analytes, new or improved analytical methods are available for three analytes (chlordane, 1,2-dibromo-3-chloropropane and pentachlorophenol).

Exhibit ES.1: Analytical Feasibility Assessment Summary for Analytes with MCL Equal to Current PQL

Analyte	Current PQL (µg/L)	MCL (µg/L)	New or Updated Methods?	Qualitative Recommendation
Chlordane	2	2	Yes	No change to current PQL
1,2-Dibromo-3-chloropropane (DBCP)	0.2	0.2	Yes	No change to current PQL
Dioxin	0.00003	0.00003	No	No change to current PQL
Heptachlor	0.4	0.4	No	No change to current PQL
Heptachlor Epoxide	0.2	0.2	No	No change to current PQL
Pentachlorophenol	1	1	Yes	No change to current PQL
Thallium	2	2	No	No change to current PQL
Toxaphene	3	3	No	No change to current PQL

- For the remaining eight analytes (carbofuran, cis-1,2-dichloroethylene, cyanide, hexachlorocyclopentadiene, oxamyl, selenium, toluene and xylenes), the PQL is lower than the MCL and hence, the MCL may be reduced (refer to Exhibit ES.2 for results of the PQL analyses).
 - Of the eight analytes, two analytes (cis-1, 2-dichloroethylene and toluene) have PT data that support further reduction of the PQL.
 - For these two analytes (cis-1,2-dichloroethylene and toluene), new or improved analytical methods are available. However, it is not known if these new method(s) are expected to improve analytical performance below the current PQL.
 - For the remaining six analytes (carbofuran, cyanide, hexachlorocyclopentadiene, oxamyl, selenium and xylenes), PT data does not support the reduction of the current PQL.
 - Out of these six analytes, new or improved analytical methods are available for three analytes (cyanide, hexachlorocyclopentadiene and xylenes).

Analyte	Current PQL (µg/L)	MCL (µg/L)	New or Updated Methods?	Qualitative Recommendation
Carbofuran	7	40	No	No change to current PQL
Cis-1,2-dichloroethylene	5	70	Yes	Reduction of current PQL is supported
Cyanide	100	200	Yes, MDLs lower	No change to current PQL
Hexachlorocyclopentadiene	1	50	Yes	No change to current PQL
Oxamyl (vydate)	20	200	No	No change to current PQL
Selenium	10	50	No	No change to current PQL
Toluene	5	1,000	Yes	Reduction of current PQL is supported
Xylenes	5	10,000	Yes	No change to current PQL

Exhibit ES.2: Analytical Feasibility Assessment Summary for Analytes with MCL Greater than the Current PQL

For those analytes with improved laboratory methods, the existence of new methods may not directly translate to improved analytical performance, even with improved detection limits. It is possible that only a small number of laboratories will use a new method, or it may take time for the method to be utilized to its full effectiveness, i.e. if 75 percent or more laboratories cannot meet the acceptance criteria using a certain analytical method, then the PQL cannot be lowered any further.

Overall, the results show that for only two of the 16 analytes evaluated in this report, laboratory performance data was sufficient to qualitatively conclude that the PQL can be lowered. For the others, there was either no correlation or a correlation could not be made due to insufficient data.

1 Introduction

The Safe Drinking Water Act (SDWA), as amended in 1996, requires the Environmental Protection Agency (EPA) to review and revise, if appropriate, existing National Primary Drinking Water Regulations (NPDWRs). Under the 1996 SDWA Amendments, EPA has completed two comprehensive reviews of the existing NPDWRs: Six-Year Review 1 (completed in July 2003) and Six-Year Review 2 (completed in March 2010). Under Six-Year Review 2, EPA reviewed 71 NPDWRs and identified four chemical NPDWRs for revision.

As part of the second Six-Year Review, EPA developed a protocol document (USEPA, 2009a) that describes the process and strategy EPA uses to review existing NPDWRs in order to meet its statutory requirement. The protocol was based on the recommendations from the National Drinking Water Advisory Council (NDWAC), internal Agency deliberations and discussions with the diverse stakeholders involved in drinking water and its protection. As part of the review, EPA reviewed the following key technical elements to make decisions regarding regulatory changes: health effects assessments; technology assessments (analytical feasibility and treatment technology); other regulatory revisions (e.g. monitoring and reporting); occurrence and exposure analyses; and available economic information. This document specifically addresses the analytical feasibility aspect of the Six-Year Review 3. Analytical feasibility assessment is one of the key components of regulations review because the analytical feasibility may have been the limiting factor in setting the Maximum Contaminant Level (MCL) for some of the existing NPDWRs or because the health effects reviews may indicate a potential change in the Maximum Contaminant Level Goal (MCLG). This document examines analytical method performance over time by determining if the Practical Quantitation Levels (PQLs) may have changed since promulgation. The PQL is defined as "the lowest achievable level of analytical quantitation during routine laboratory operating conditions within specified limits of precision and accuracy" (USEPA, 1985b) and is derived from the laboratory accreditation studies performed as part of the drinking water laboratory certification program. Data from these studies was referred to as Performance Evaluation (PE) data while the program was under EPA oversight until 1999 and as Proficiency Testing (PT) data when the program was privatized with The NELAC Institute (TNI) providing oversight.

Analytical method performance is also assessed by comparing the Method Detection Limits (MDLs) of the analytical methods which were available at the time of promulgation to those of the currently approved methods. The purpose was to determine if PQL changes based on the PT data were also supported by the approval and availability of new/improved methods to the testing laboratories. This analytical feasibility assessment is based on the recent analytical performance data collected after Six-Year Review 2, where applicable. Efforts were also made to determine if the analytical performance assessments based on the laboratory data are supported by improved methods or revision of existing methods since the last review. The goal was to create a comprehensive document that addresses all regulated chemical analytes for which data is available.

In this document, PQL assessments are presented for 16 regulated contaminants for which data was available based on an initial review and analysis conducted under the Six-Year Review 3 Protocol. The results for the 16 regulated analytes are categorized into two subsets based on the limitation of the PQL for setting the Maximum Contaminant Level (MCL) at the time of promulgation: 1) analytes with MCL equal to the current PQL and thus the PQL is limiting and 2) analytes with MCL greater than the current PQL and thus it is technically feasible to reduce an MCL.

2 Background

2.1 SDWA Requirements for Analytical Methods

Section 1401(1)(C)(i) of SDWA (as amended in 1996); 42 U.S.C. § 300f(1)(C)(i), states that an MCL for a national primary drinking water regulation is set "if, in the judgment of the Administrator, it is economically and technologically feasible to ascertain the level of such contaminant in water in public water systems." According to SDWA, NPDWRs include "criteria and procedures to assure a supply of drinking water which dependably complies with such maximum contaminant levels; including accepted methods of quality control and testing procedures to insure compliance with such levels" [§1401(1)(D) of SDWA; 42 U.S.C. § 300f(1)(D)]. Except in certain circumstances, EPA is to set the MCL as close to the MCLG as is feasible with the best available technologies (Section 1412 (b)(4)(B)) of SDWA. The MCLs for several SDWA contaminants were set at levels higher than MCLGs due to the limits of the analytical feasibility at that time. Since the promulgation of pre-1996 SDWA NPDWRs, newer analytical methods and updated methods for measuring SDWA contaminants have been approved. The approval of newer analytical techniques may have provided laboratories with the analytical capability to measure some contaminants at lower levels. In addition, some laboratories may have improved in their ability to measure at lower levels using the same methods that were originally promulgated.

EPA evaluated the overall sensitivity of analytical methods when considering analytical methods for the contaminants of interest. EPA has used two measures of analytical capability, the MDL and the PQL.

- The MDL is a measure of method sensitivity. The MDL is defined at 40 CFR Part 136 Appendix B as "the minimum concentration of a substance that can be reported with 99 percent confidence that the analyte concentration is greater than zero." MDLs can be operator, method, laboratory and matrix-specific. Due to normal day-to-day and run-torun analytical variability, MDLs may not be reproducible within a laboratory or between laboratories. The regulatory significance of the MDL is that EPA uses the MDL to determine when a contaminant is considered to be detected and it can be used to calculate a PQL for that contaminant.
- The PQL is defined as "the lowest achievable level of analytical quantitation during routine laboratory operating conditions within specified limits of precision and accuracy (USEPA, 1985b)". The Agency has used the PQL to estimate or evaluate the minimum concentration at which most laboratories can be expected to reliably measure a specific chemical contaminant during day-to-day analyses of drinking water samples. The PQL is a means of integrating information on the performance of the approved analytical methods into the development of a drinking water regulation (USEPA, 1987). The PQL incorporates the following (USEPA, 1985a; USEPA, 1987; 54 USEPA, 1989):
 - o Quantitation,
 - Precision and bias,
 - o Normal operations of a laboratory, and

• The fundamental need to have a sufficient number of laboratories available to conduct compliance monitoring analyses.

In some cases, the quantitation level for a particular analyte may have been the limiting factor in the determination of the MCL for that analyte. This could be especially true for contaminants with MCLGs of zero. In addition, there are several SDWA contaminants with non-zero MCLGs that have their MCL set at the PQL.

2.2 PQL Determination Methods for the SDWA Contaminants

EPA used two main approaches to determine PQLs for SDWA analytes. One approach (and the preferred approach) used data from laboratory Performance Evaluaiton (PE studies, now called PT or Proficiency Testing studies). Although the primary use of the PE/PT data was for EPA's laboratory certification, the data was also used as a secondary data source for many years to develop PQLs when the spike concentrations were in the appropriate concentration range.

In deriving a PQL from the laboratory performance data (contaminants spiked in reagent grade water), EPA typically sets a fixed percentage, or 2 Sigma (two standard deviations), acceptance criteria around the known concentration (or spike value) of the samples. While the acceptance limits for inorganics typically range from 15 to 30 percent (40 CFR§141.23(k)(3)(ii)), the acceptance limits for organics generally range from 20 to 50 percent (40 CFR §141.24(f)(17)(i) and 40 CFR§141.24(h)(19)(i). Several SDWA analytes have acceptance limits of 2 Sigma (two standard deviations). The derivation of the PQL using PE/PT data involved determining the concentration of an analyte at which 75 percent of the participating laboratories achieved results within a specified range around the spike value or acceptance criteria.

In the absence of PE/PT data, the other approach that EPA used was the MDL multiplier method. In this approach, the PQL was calculated by multiplying the EPA-derived MDL by a factor of 5 or 10. The MDL multiplier method was mostly used in the early years of rule development for NPDWRs when sufficient WS data was not available. Once sufficient WS data became available, most of the PQLs developed using the MDL multiplier were validated using WS data.

2.3 Operational Details of the PE/PT Programs

Performance Evaluation studies are no longer performed by EPA. In December 1999, the PT program became privatized under the direction of the National Environmental Laboratory Accreditation Conference (NELAC, or now, TheNELAC Institute [TNI]). PT data services under TNI's program are provided by private companies that prepare and provide PT samples (spiked at concentrations in accordance with TNI policies) to analytical laboratories as part of maintaining laboratory accreditation. Approximately 10-12 such PT providers (e.g., Environmental Resource Associates (ERA)) exist nationwide. PT providers also compile the results of the PT analyses for use by TNI.

A laboratory either passes or fails for each analyte based upon the Acceptance Limits (referred to as Acceptance Criteria by TNI). The acceptance criteria adopted by TNI could be:

1. Percentage based (20 percent of the spiked, or true value),

- 2. Standard deviation-based (± 2 standard deviations), or
- 3. Based on average and range of replicate analyses (radionuclides only).

The acceptance criteria for a contaminant may also change based on its concentration. While more laboratories and more spiking concentrations were represented in the TNI PT data, fewer analytes had data at, or below, their PQL. Further, TNI data was not separated by any analytical methods.

Similar to the previous six-year reviews, the data was categorized into two subsets: 1) analytes with an MCL equal to the current PQL, and thus the PQL is limiting; or 2) analytes with MCL greater than the current PQL and thus it is technically feasible to reduce an MCL.

It is noted that the PT data obtained from the PT providers did not include a PQL, however, the results reported from the laboratories was based on a TNI Proficiency Testing Reporting Limit (PTRL). A PTRL is the lowest level acceptable result that could be obtained from the lowest spike level for each analyte. Laboratories report any positive result down to the PTRL. It is possible that in some cases (especially for analytes that exhibit low recovery), the PTRL may be below the standard laboratory reporting limit. TNI PTRLs are provided as guidance to laboratories analyzing TNI PT samples. At a minimum, the laboratory should use a method that is sensitive enough to generate quantitative results at the PTRLs shown.

2.4 Efforts Made to Obtain PT Data

The following is a summary of the efforts made by EPA to obtain nationally representative PT data from private firms that now provide PT services and/or directly from TNI. EPA contacted seven PT providers to find out if they were willing to provide data for the Six-Year Review 3 along with a data request. Only basic information was requested as listed below:

- Contaminant name being tested,
- Analytical method being used (including EPA Methods and any newer methods),
- Current MDL or MDL range,
- PQL,
- Concentration of PE sample,
- Acceptance criteria, and
- Pass/fail rates at different concentrations.

In the communication with all the PT providers, it was made very clear that EPA needed only basic information and would not require the identity of any individual lab, etc. and would not require the disclosure of what would be considered confidential business information (CBI).

Several attempts were made to contact and obtain data from seven PT providers. Out of the seven PT providers, only two PT providers, Environmental Resources Associates, Inc. (ERA) and Phenova responded and provided the information requested. The remaining five PT providers either did not respond back to any communication from EPA, or responded that although they were willing to provide data, time and budget constraints did not allow them to do so; or responded that the information requested was CBI, and therefore, could not be released.

3 Representativeness of Available PT Data

As of July 2014, there were seven TNI-accredited companies that provided PT services. Two of these PT providers agreed to provide pass/fail rate data to EPA, while the other five were unable or unwilling to provide the requested information. The Six-Year Review 2 report relied on data from one PT provider. The additional data source in the current analysis removes some of the uncertainties associated with using only one data source.

The following contaminant assessments are based on the available PT data from two sources but obviously do not reflect all of the PT data generated throughout the country. There is no reason to expect that the two sources of data are not representative of the larger pool of data, however, since it is not known, it does provide an element of uncertainty. It is unknown if the data from those PT providers who were not able to participate differs from data from those providers who were able to participate. Also, because the pass/fail rates of the available data are reported anonymously, it is not known how many labs or locations are represented or whether failure rates tend to be influenced by certain labs. A qualitative comparison of the two data sources was performed to analyze if the available data was adequate for analysis and if there was any bias in the results between the two sources. The qualitative comparison between the two data sources is presented in Exhibit 3.1.

SNo.	Contaminant	PT Provider 1 No. of data points	PT Provider 1 % Data Acceptable	PT Provider 2 No. of Data Points	PT Provider 2 % Data Acceptable
1	1,2-Dibromo-3-chloropropane	442	96%	NA	NA
2	Carbofuran	24	100%	718	97%
3	Chlordane	12	100%	858	96%
4	cis-1,2-Dichloroethylene	355	95%	2580	85%
5	Cyanide	468	89%	1066	92%
6	Dioxin	3	100%	NA	NA
7	Heptachlor	111	97%	1111	95%
8	Heptachlor Epoxide	112	96%	NA	NA
9	Hexachlorocyclopentadiene	141	94%	1030	95%
10	Oxamyl (vydate)	25	96%	708	95%
11	Pentachlorophenol	75	95%	837	95%
12	Selenium	958	93%	4523	95%
13	Thallium	814	91%	3725	95%
14	Toluene	355	97%	2636	97%
15	Toxaphene	13	100%	853	91%
16	Xylenes	354	93%	2644	93%

Exhibit 3.1: Qualitative Comparison of Two Data Sources

As shown in Exhibit 3.1, for most of the contaminants except 1,2-dibromo-3-chloropropane, dioxin and heptachlor epoxide, the amount of data provided by PT Provider 1 is more than PT Provider 2. However, a comparison of the percentage of data acceptable, i.e., the percent passing rates for both the data sets shows that these values are very similar for both the data sets. Based on this comparison, the data provided by the two PT providers was considered adequate for performing the analysis per the Six-Year Review 3 protocol.

4 Identification of Regulated Analytes for PQL Assessment

The Six-Year Review 1 analytical feasibility assessed whether the PQL value changed for 40 of the 68 chemical NPDWRs. The Six-Year Review 2 analytical feasibility evaluated all regulated analytes for which PT data were available. For the Six-Year Review 3, EPA prioritized 24 of the 68 analytes for review to determine if concentrations below the PTRL or PQL were routinely measured. Based on an initial analysis of the PT data obtained from the PT providers, the number of analytes for which PQL analysis would be performed was narrowed down to only 16 analytes. Exhibit 4.1 summarizes the 16 analytes evaluated in the Six-Year Review 3, their range of MDLs, current PTRL value, MCL and current PT acceptance criteria.

Analyte CASRN	EPA MDL or Range (µg/L)	PTRL (µg/L)	PQL (µg/L)	MCL (µg/L)	Acceptance Criteria
Benzo[a]pyrene 50-32-8	0.043 - 0.52	0.02	0.2	0.2	Mean ± 2 Std Dev
Carbofuran 1563-66-2	0.01 - 0.12	8.3	7	40	± 45%
cis-1,2-Dichloroethylene 156-59-2	0.0015 - 0.14	1.2	5	70	± 40% at < 10 ± 20% ≥ 10
Cyanide 57-12-5	0.5 - 50	75	100	200	± 25%
1,2-Dibromo-3-chloropropane (DBCP) 96-12-8	0.0016 - 0.063	0.06	0.2	0.2	± 40%
Dioxin 1746-01-6	0.0000044	0.000011	0.00003	0.00003	Mean ± 2 Std Dev
Heptachlor 76-44-8	0.0015 - 0.34	0.11	0.4	0.4	± 45%
Heptachlor Epoxide 1024-57-3	0.0001 - 0.202	0.11	0.2	0.2	± 45%
Hexachlorocyclopentadiene 77-47-4	0.004 - 0.16	0.49	1	50	Mean ± 2 Std Dev
Oxamyl (vydate) 23135-22-0	0.045 - 0.86	11	20	200	Mean ± 2 Std Dev
Pentachlorophenol 87-86-5	0.021 - 1.6	0.5	1	1	± 50%
Selenium 7782-49-2	1.0 - 2.0	8	10	50	± 20%
Thallium 7440-28-0	0.7 - 1.0	1.4	2	2	± 30%
Toluene 108-88-3	0.01 - 0.11	1.2	5	1000	± 40% at < 10 ± 20% ≥ 10

Exhibit 4.1: US EPA National Primary Drinking Water Standards and Analytical Information

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Analyte CASRN	EPA MDL or Range (μg/L)	PTRL (µg/L)	PQL (µg/L)	MCL (µg/L)	Acceptance Criteria
Toxaphene 8001-35-2	0.13 - 1.0	1.1	3	3	± 45%
Xylenes 1330-20-7	0.01 - 0.13	1.2	5	10000	± 40% at < 10 ± 20% ≥ 10

5 Six-Year Review 3 Assessment Methodology

5.1 Data Available for PQL Assessments

The quantitative PTRL assessments are based on data from the two TNI-accredited PT providers who were willing to share pass/fail testing data results with EPA. Exhibit 5.1 summarizes the availability of Six-Year Review 1 PE data, Six-Year Review 2, Six-Year Review 3 PT data and whether data is available at or below the PQL or PTRL for each analyte. Data available below the PQL or PTRL indicates that technology or methodology improvements allow for an increased range of chemical measurements. Improved measurement ability is an important consideration to determine whether an analytical or regulatory value for a particular analyte may be lowered. In comparison to the first and second Six-Year Reviews, where a total of 68 analytes were evaluated, Six-Year Review3 evaluated 24 analytes, out of which the final PQL analysis was performed for 16 analytes. The remaining eight analytes did not require further analysis based on the Six-Year Review 3 protocol.

A review of new or revised EPA-approved drinking water methods was performed to evaluate the analytical methods available between 2007 and 2014. The approval of new methods might reflect an improvement in analytical performance and thus potential rationale for lowering analytical or regulatory values for a particular compound. Section 6 contains a summary of findings for each analyte including the currently applicable analytical methods.

Analyte CASRN	In Six-Year Review 1 Data 1996-2000	In Six-Year Review 2 Data (ERA) 2000-2007	In Six-Year Review 3 Data (Phenova and ERA) 2008-2014
Acrylamide 79-06-1	No	No	Not reviewed
Alachlor 15972-60-8	Yes, some data <u><</u> PQL	Yes, no data <u><</u> PQL	Not reviewed
Antimony 7440-36-0	Yes, some data <u><</u> PQL ¹	Yes, no data <u><</u> PQL	Not reviewed
Arsenic 7440-38-2	Yes, some data <u><</u> PQL ¹	Yes, no data <u><</u> PQL	Not reviewed
Atrazine 1912-24-9	Yes, some data <u><</u> PQL ¹	Yes, no data <u><</u> PQL	Not reviewed
Barium 7440-39-3	Yes, some data <u><</u> PQL ¹	Yes, no data <u><</u> PQL	Not reviewed
Benzene 71-43-2	Yes, some data <u><</u> PQL	Yes, some data <u><</u> PQL	Not reviewed
Benzo[a]pyrene 50-32-8	Yes, no data <u><</u> PQL	Yes, no data <u><</u> PQL	Yes ³

Exhibit 5.1: Availability of Six-Year Review 1 PE Data and Six-Year Review 2 and Six-Year Review 3 PT Data for Regulated Analytes

Analytical Feasibility Support Document for the Third Six-Year Review

Analyte CASRN	In Six-Year Review 1 Data 1996-2000	In Six-Year Review 2 Data (ERA) 2000-2007	In Six-Year Review 3 Data (Phenova and ERA) 2008-2014
Beryllium 7440-41-7	Yes, some data <u><</u> PQL	Yes, no data <u><</u> PQL	Not reviewed
Bromate 15541-45-4	Yes, some data <u><</u> PQL	Yes, some data <u><</u> PQL	Not reviewed
Cadmium 7440-43-9	Yes, no data <u><</u> PQL	Yes, no data <u><</u> PQL	Not reviewed
Carbofuran 1563-66-2	Yes, some data <u><</u> PQL	Yes, no data <u><</u> PQL	Yes, no data <u><</u> PQL
Carbon tetrachloride 56-23-5	Yes, some data <u><</u> PQL	Yes, some data <u><</u> PQL	Not reviewed
Chlordane 57-74-9	Yes, some data <u><</u> PQL	Yes, no data <u><</u> PQL	Yes, no data <u><</u> PQL
Chlorite 7758-19-2	Yes, but no PQL	Yes, but no PQL	Not reviewed
Chromium (total) Cr III: 6065-83-1 Cr VI: 18540-29-9	Yes, no data <u><</u> PQL	Yes, no data <u><</u> PQL	Not reviewed
Copper 7440-50-8	Yes, some data <u><</u> PQL ¹	Yes, no data <u><</u> PQL	Not reviewed
Cyanide (as free cyanide) 57-12-5	Yes, only one datum = PQL; no data < PQL	Yes, no data <u><</u> PQL	Yes, no data <u><</u> PQL
Dalapon 75-99-0	Yes, some data <u><</u> PQL; passing rates below PQL could not be calculated ²	Yes, no data <u><</u> PQL	Not reviewed
1,2-Dibromo-3-chloropropane (DBCP) 96-12-8	Yes, some data <u><</u> PQL	Yes, some data <u><</u> PQL	Yes, no data <u><</u> PQL
1,2-Dichlorobenzene (<i>o</i> -Dichlorobenzene) 95-50-1	Yes, no data < PQL	Yes, no data <u><</u> PQL	Not reviewed
1,4-Dichlorobenzene (<i>p</i> -Dichlorobenzene) 106-46-7	Yes, some data <u><</u> PQL	Yes, some data <u><</u> PQL	Not reviewed
1,2-Dichloroethane (Ethylene dichloride) 107-06-2	Yes, some data <u><</u> PQL ¹	Yes, some data <u><</u> PQL	Not reviewed
1,1-Dichloroethylene 75-35-4	Yes, no data <u><</u> PQL	Yes, some data <u><</u> PQL	Not reviewed

Analyte CASRN	In Six-Year Review 1 Data 1996-2000	In Six-Year Review 2 Data (ERA) 2000-2007	In Six-Year Review 3 Data (Phenova and ERA) 2008-2014
<i>cis</i> -1,2-Dichloroethylene 156-59-2	Yes, no data <u><</u> PQL	Yes, some data <u><</u> PQL	Yes, some data <u><</u> PQL
<i>trans</i> -1,2-Dichloroethylene 156-60-5	Yes, no data <u><</u> PQL	Yes, some data <u><</u> PQL	Yes ³
Dichloromethane (Methylene chloride) 75-09-2	Yes, no data <u><</u> PQL	Yes, no data <u><</u> PQL	Not reviewed
2,4-Dichlorophenoxyacetic acid (2,4-D) 94-75-7	Yes, some data <u><</u> PQL	Yes, no data <u><</u> PQL	Not reviewed
1,2-Dichloropropane 78-87-5	Yes, no data <u><</u> PQL	Yes, some data <u><</u> PQL	Not reviewed
Di(2-ethylhexyl)adipate (DEHA) 103-23-1	Yes, some data <u><</u> PQL; passing rates below PQL could not be calculated ²	Yes, no data <u><</u> PQL	Not reviewed
Di(2-ethylhexyl) phthalate (DEHP) 117-81-7	Yes, some data <u><</u> PQL	Yes, no data <u><</u> PQL	Yes ³
Dinoseb 88-85-7	Yes, no data <u><</u> PQL	Yes, no data <u><</u> PQL	Not reviewed
Diquat 85-00-7	Yes, no data <u><</u> PQL	Yes, no data <u><</u> PQL	Not reviewed
Endothall 145-73-3	Yes, some data <u><</u> PQL; passing rates below PQL could not be calculated ²	Yes, no data <u><</u> PQL	Yes ³
Endrin 72-20-8	Yes, no data <u><</u> PQL ¹	Yes, no data <u><</u> PQL	Not reviewed
Epichlorohydrin 106-89-8	No	No	Not reviewed
Ethylbenzene 100-41-4	Yes, no data <u><</u> PQL	Yes, some data <u><</u> PQL	Not reviewed
Ethylene dibromide (EDB) 106-93-4	Yes, no data <u><</u> PQL	Yes, no data <u><</u> PQL	Yes ³
Fluoride 16984-48-8	Yes, some data <u><</u> PQL	Yes, no data <u><</u> PQL	Not reviewed
Glyphosate 1071-83-6	Yes, no data <u><</u> PQL	Yes, no data <u><</u> PQL	Not reviewed

Analyte CASRN	In Six-Year Review 1 Data 1996-2000	In Six-Year Review 2 Data (ERA) 2000-2007	In Six-Year Review 3 Data (Phenova and ERA) 2008-2014
Heptachlor 76-44-8	Yes, some data <u><</u> PQL	Yes, no data <u><</u> PQL	Yes, some data <u><</u> PQL
Heptachlor epoxide 1024-57-3	Yes, some data <u><</u> PQL	Yes, no data <u><</u> PQL	Yes, no data <u><</u> PQL
Hexachlorobenzene 118-74-1	Yes, some data <u><</u> PQL	Yes, some data <u><</u> PQL	Yes ³
Hexachlorocyclopentadiene 77-47-4	Yes, some data <u><</u> PQL	Yes, no data <u><</u> PQL	Yes, some data <u><</u> PQL
Lead 7439-92-1	Yes, some data <u><</u> PQL¹	Yes, no data <u><</u> PQL	Not reviewed
Lindane 58-89-9	Yes, some data <u><</u> PQL ¹	Yes, no data <u><</u> PQL	Not reviewed
Mercury (Inorganic) 7439-97-6	Yes, no data <u><</u> PQL	Yes, no data <u><</u> PQL	Not reviewed
Methoxychlor 72-43-5	Yes, some data <u><</u> PQL	Yes, no data <u><</u> PQL	Not reviewed
Monochlorobenzene (Chlorobenzene) 108-90-7	Yes, no data <u><</u> PQL	Yes, some data <u><</u> PQL	Not reviewed
Nitrate (as N) 14797-55-8	Yes, no data <u><</u> PQL	Yes, no data <u><</u> PQL	Not reviewed
Nitrite (as N) 14797-65-0	Yes, some data <u><</u> PQL	Yes, no data <u><</u> PQL	Not reviewed
Oxamyl (Vydate) 23135-22-0	Yes, some data <u><</u> PQL	Yes, no data <u><</u> PQL	Yes, some data <u><</u> PQL
Pentachlorophenol 87-86-5	Yes, some data <u><</u> PQL	Yes, no data <u><</u> PQL	Yes, no data <u><</u> PQL
Picloram 1918-02-1	Yes, no data <u><</u> PQL	Yes, no data <u><</u> PQL	Not reviewed
Polychlorinated biphenyls (PCBs) as Decachlorobiphenyl (DCBP) 1336-36-3	Yes, some data <u><</u> PQL	Yes, no data <u><</u> PQL	Yes ³
Selenium 7782-49-2	Yes, some data <u><</u> PQL ¹	Yes, no data <u><</u> PQL	Yes, no data <u><</u> PQL
Simazine 122-34-9	Yes, some data <u><</u> PQL; passing rates below PQL could not be calculated ²	Yes, no data <u><</u> PQL	Not reviewed

Analyte CASRN	In Six-Year Review 1 Data 1996-2000	In Six-Year Review 2 Data (ERA) 2000-2007	In Six-Year Review 3 Data (Phenova and ERA) 2008-2014
Styrene 100-42-5	Yes, no data <u><</u> PQL	Yes, some data <u><</u> PQL	Not reviewed
2,3,7,8-TCDD (Dioxin) 1746-01-6	No	Yes, no data <u><</u> PQL; only one spike level	Yes (data limited)
Tetrachloroethylene 127-18-4	Yes, no data <u><</u> PQL	Yes, some data <u><</u> PQL	Not reviewed
Thallium 7440-28-0	Yes, some data <u><</u> PQL	Yes, no data <u><</u> PQL	Yes, no data <u><</u> PQL
Toluene 108-88-3	Yes, no data <u><</u> PQL	Yes, some data <u><</u> PQL	Yes, some data <u><</u> PQL
Toxaphene 8001-35-2	Yes, some data <u><</u> PQL	Yes, no data <u><</u> PQL	Yes, some data <u><</u> PQL
2,4,5-TP (Silvex) 93-72-1	Yes, some data <u><</u> PQL ¹	Yes, no data <u><</u> PQL	Not reviewed
1,2,4-Trichlorobenzene 120-82-1	Yes, no data <u><</u> PQL	Yes, some data <u><</u> PQL	Not reviewed
1,1,1-Trichloroethane 71-55-6	Yes, some data <u><</u> PQL	Yes, some data <u><</u> PQL	Not reviewed
1,1,2-Trichloroethane 79-00-5	Yes, no data <u><</u> PQL	Yes, some data <u><</u> PQL	Yes ³
Trichloroethylene 79-01-6	Yes, no data <u><</u> PQL	Yes, some data <u><</u> PQL	Not reviewed
Vinyl chloride 75-01-4	Yes, no data <u><</u> PQL	Yes, some data <u><</u> PQL	Not reviewed
Xylenes (total) 1330-20-7	Yes, no data <u><</u> PQL	Yes, some data <u><</u> PQL	Yes, no data <u><</u> PQL

Notes:

¹ Means passing rates for Six-Year 1 data were calculated as these analytes were not evaluated in the March 2003 report, and acceptance criteria are percentage-based, not ± 2 Std Dev.

² Passing rates for Six-Year 1 data at or below the PQL could not be calculated as these analytes were not evaluated in the March 2003 report, acceptance criteria are \pm Std Dev and available regression coefficients are not valid at or below the PQL.

³ Initial data evaluation was performed for PQL analysis suitability and were not further considered for final PQL analysis and summary.

5.2 Data Assessment Methodology

The data obtained from the two PT providers was combined into one data set. A preliminary data review was performed to assess the methods used for analysis and verify if the methods correspond to the EPA approved analytical methods listed in the Federal Register (FR). Data outliers including EPA Methods used for analyzing wastewater samples, etc., non-EPA approved methods, etc., were eliminated. If the true concentration of the samples reported by the laboratories met the acceptance criteria set forth in the FR, the samples were reported as "acceptable". If the true concentration of the samples did not meet the acceptance criteria, the samples were reported as "not acceptable". The acceptable data points were converted into laboratory passing rates. A linear regression was plotted for each contaminant with laboratory passing rates versus the true concentration of the sample. The PQL is set at the concentration where 75 percent of the laboratories are predicted to meet acceptance criteria.

6 Results of PQL Assessment

EPA used two very different approaches to assess improvements in laboratory analytical performance over time: 1) evaluating data from the laboratory accreditation studies performed as part of the drinking water laboratory certification program (PT data) and 2) comparing information of the analytical methods available for compliance monitoring at the time of promulgation to those available currently. For analytes with no new methods, analytical performance was measured solely by PT data. For those analytes with new methods, analytical performance was measured by PT data, but may be supported by lower detection limits (DLs) from new methods. However, the existence of new methods with lower detection limits may not directly translate to improved analytical performance. It is possible that only a small number of laboratories will use a new method, or it may take time for the method to be utilized to its full effectiveness. A passing rate of 75 percent was used as a basis for evaluation of the results of the PQL assessment.

For each analyte, MDLs from EPA-approved methods were compared and a PQL/PTRL assessment was presented by means of linear regression of the data obtained from the combined PT data from both PT providers. Note that MDLs from proprietary methods (i.e., analytical methods not developed by EPA) are not included in the MDL comparison, as they are not readily available. Based on the data evaluation, a qualitative conclusion is drawn by presenting a recommendation of whether a PQL might be reduced. The discussion includes an indication of how the true concentrations relate to the PQL/PTRL and how the PT data may or may not suggest potential changes to the PQL.

The results for the regulated analytes are broken down into two categories based on the limitation of the PQL for setting MCL at the time of promulgation: 1) analytes with MCL equal to the current PQL, and thus the PQL is limiting; or 2) analytes with MCL greater than the current PQL and therefore it is technically feasible to reduce an MCL. PQL assessments for these analytes can indicate the potential for MCL reduction beyond the current PQL. The PQL assessments were made and are presented in this report for a total of 16 analytes.

Using this framework, the following sub-categories are used to summarize the results of PQL analysis. These categorizations were made based on a visual inspection of the regressions. In some cases, even though the regression line was above the 75 percent passing rate, several factors, including poor performance above the PQL or lack of data below the PQL led to a conclusion that perhaps the PQL should not be reduced. In addition, consideration was given to recent laboratory performance as indicated by the data provided by the PT providers. For example, if the older Six-Year Review 1 data indicated that the PQL should not be reduced, and if the more recent data indicated better performance, this was a factor in making the overall determination as to whether or not a PQL could be reduced.

- 1. Analytes with an MCL equal to the current PQL, and therefore the PQL is limiting The outcome of this categorization would be summarized as one of the following:
 - a. PQL assessment supports reduction of the current PQL,
 - b. PQL assessment may support reduction of the current PQL, or

- c. PQL assessment does not support reduction of the current PQL, or data is inconclusive or insufficient to reach a conclusion.
- 2. Analytes with an MCL greater than the current PQL and thus it is technically feasible to reduce an MCL the outcome of this categorization would be summarized as one of the following:
 - a. PQL assessment supports reduction of the current PQL,
 - b. PQL assessment may support reduction of the current PQL, or
 - c. PQL assessment does not support reduction of the current PQL, or data is inconclusive or insufficient to reach a conclusion.

Note that the qualitative conclusions presented in this report are not necessarily identical to the conclusions that were documented in the previous six-year reviews' reports. Rather, a new assessment is made herein considering the advantages and disadvantages of the PQL concept, the availability of PT data in the vicinity of and/or below the PQL, and outliers. The qualitative conclusions are based primarily on data that are in the vicinity of and/or below the PQL.

6.1 Category 1: Analytes with MCL Equal to the Current PQL and Thus the PQL is Limiting

A total of eight analytes have an MCL that is set at the PQL. As a result, a PQL assessment is required to determine whether an MCL might be lowered in the future. These eight analytes can be further categorized into the three groups mentioned in Section 6 depending on whether or not the PT assessments support the reduction of the current PQL.

6.1.1 PQL Assessment Supports Reduction of the Current PQL

None of the analytes under consideration fall under this category.

6.1.2 PQL Assessment May Supports Reduction of the Current PQL

None of the analytes under consideration fall under this category.

6.1.3 PQL Assessment Does Not Support Reduction of the Current PQL or Data is Insufficient to Reach a Conclusion

All the eight analytes as mentioned in Section 6.1 have an existing PQL equal to the MCL and their PE/PT data indicate that the PQL should not be lowered or their PE/PT data are insufficient to reach a conclusion.

6.1.3.1 Chlordane

6.1.3.1.1 Results of the Method Comparison

Exhibit 6.1 summarizes the MDLs for chlordane as documented in EPA-developed analytical methods. One new analytical method, EPA 525.3 (USEPA, 2012), was approved for the analysis of chlordane in drinking water samples during the years 2008-2014. The MDL for chlordane by EPA 525.3 is similar to the MDL of EPA 508 and 508.1, but lower than the MDL of EPA 505 and 525.2.

EPA Methods Approved For Analysis of Drinking Water	EPA Methods Approved for the Analysis of Drinking Water - Technique	EPA Methods Approved for the Analysis of Drinking Water - MDL (μg/L)
EPA 505	Microextraction (ME) and Gas Chromatography (GC)	0.14 ¹
EPA 508	GC with Electron Capture Detector (ECD)	0.0015 ¹
EPA 508.1	Liquid-Solid Extraction (LSE) and Electron Capture Gas Chromatography (ECGC)	0.001 - 0.004
EPA 525.2	LSE and Capillary Column Gas Chromatography (CCGC)/Mass Spectroscopy (MS)	0.05 - 0.22 ²
EPA 525.3*	Solid-Phase Extraction (SPE)/GC/MS	0.002

Exhibit 6.1: Analytical Methods for Chlordane

Notes:

* New approved analytical methods since last Six-Year Review.

¹ MDL range for chlordane includes α -chlordane and γ -chlordane.

 $^2\,\text{MDL}$ range for chlordane includes $\alpha\text{-chlordane}$, $\gamma\text{-chlordane}$ and trans-nonachlor.

Regulatory DLs for organic compounds are listed at 40 CFR 141.24(h)(18).

Acceptance Criteria for organic compounds are listed at 40 CFR 141.24(h)(19)(i)(B).

 $MCL = 2.0 \ \mu g/L$

Current PQL = $2.0 \mu g/L$

 $DL = 0.2 \ \mu g/L$ Acceptance Criteria = ± 45%

6.1.3.1.2 Results of the PQL Analysis

The current PQL for chlordane is 2.0 μ g/L while the PTRL is 1.1 μ g/L. The data obtained from the PT providers is summarized in Exhibit 6.2, along with a regression analysis. The entire data obtained from the PT providers is based on using EPA Methods 505, 508, 508.1 and 525.2, as listed in Exhibit 6.1. As shown in Exhibit 6.2, none of the data is below the current PQL of 2.0 μ g/L or below the PTRL of 1.1 μ g/L. The passing rate for all the data is above 75 percent.

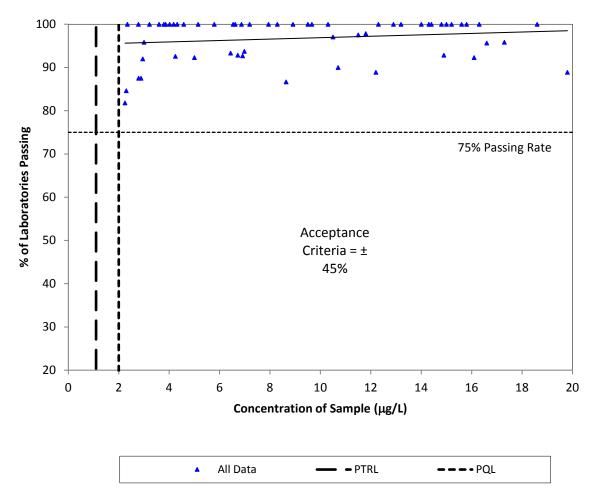


Exhibit 6.2: Evaluation of PT Data – Chlordane

6.1.3.1.3 Conclusions for Chlordane

Based on plotting the sample concentrations and the percent passing rate, it was observed that the regression does not show much correlation between the two. Given the variable laboratory passing rates for the data sets and the lack of data below the current PQL of 2.0 μ g/L, it may not be appropriate to recommend lowering of the PQL. Compared to the previous six-year analysis, one new method, i.e., EPA 525.3 was approved in February 2012. However, the data obtained from the PT providers does not include results from this new method. Therefore, it is unknown whether this method is expected to improve analytical performance below the current PQL (and hence suggest possible reduction of the PQL).

6.1.3.2 1,2-Dibromo-3-Chloropropane (DBCP)

6.1.3.2.1 Results of the Method Comparison

Exhibit 6.3 summarizes the MDLs for 1,2-dibromo-3-chloropropane (DBCP) as documented in EPA-developed analytical methods. One new analytical method, EPA Method 524.3 (USEPA, 2009b), was approved for the analysis of DBCP in drinking water samples during the years

2008-2014. The low end of the MDL range for DBCP by EPA Method 524.3 is lower than the MDL of EPA Methods 508 and 508.1, but higher than the MDL of EPA Method 551.1.

Exhibit 6.3: Analytical Methods for DBCP	
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EPA Methods Approved for the Analysis of Drinking Water	EPA Methods Approved for the Analysis of Drinking Water - Technique	EPA Methods Approved for the Analysis of Drinking Water - MDL (µg/L)
504.1	ME and GC	0.01
524.2	CCGC/MS	0.05 - 0.26
524.3*	Purge & Trap/CCGC/MS	0.0010 - 0.063
551.1	LLE and GC with ECD	0.006 - 0.009

Notes:

* New approved analytical methods since last Six-Year Review. Regulatory DLs for organic compounds are listed at 40 CFR 141.23(a) 4(l). Acceptance Criteria for organic compounds are listed at 40 CFR 141.23(k)(3)(ii). MCL = $0.2 \mu g/L$ Current PQL = $0.2 \mu g/L$ DL = $0.02 \mu g/L$ Acceptance Criteria = $\pm 40\%$

6.1.3.2.2 Results of the PQL Analysis

The current PQL for DBCP is 0.2 μ g/L while the PTRL is 0.06 μ g/L. The data obtained from the PT providers is summarized in Exhibit 6.4, along with a regression analysis. Approximately 2 percent data obtained from the PT providers is based on the new EPA Method 524.3 while the remaining 98 percent data is based on the existing EPA Methods 504.1, 524.2 and 551.1, as listed in Exhibit 6.3. None of the data are below the current PQL of 0.2 μ g/L or below the PTRL of 0.06 μ g/L. The passing rate for all the available data is at or above 75 percent.

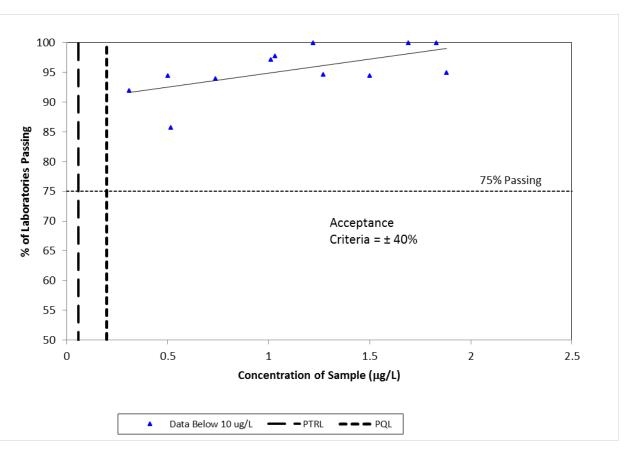


Exhibit 6.4: Evaluation of PT Data – DBCP

6.1.3.2.3 Conclusions for DBCP

Given lack of data below the current PQL of $0.2 \mu g/L$, it may not be appropriate to recommend lowering of the PQL. One new analytical method, EPA Method 524.3, has been approved since 2007, but since adequate data is not available using the new method, it is unknown whether this is expected to improve analytical performance below the current PQL (and hence suggest possible reduction of the PQL).

6.1.3.3 Dioxin

6.1.3.3.1 Results of the Method Comparison

Exhibit 6.5 summarizes the MDL for dioxin as documented in EPA-developed analytical methods. No updated or new analytical methods have been approved for the analysis of dioxin in drinking water samples during the years 2008-2014.

EPA Methods Approved for the Analysis of Drinking Water	EPA Methods Approved for the Analysis of Drinking Water - Technique	EPA Methods Approved for the Analysis of Drinking Water - MDL (μg/L)
1613	Isotope Dilution High Resolution GC (HRGC)/High Resolution MS (HRMS)	0.0000044

Exhibit 6.5: Analytical Methods for Dioxin

Notes:

Regulatory DLs for organic compounds are listed at 40 CFR 141.24(h)(18). Acceptance Criteria for organic compounds are listed at 40 CFR 141.24(h)(19)(i)(B). MCL = $0.00003 \mu g/L$ Current PQL = $0.00003 \mu g/L$ DL = $0.00005 \mu g/L$ Acceptance Criteria = Mean ± 2 Std Dev

6.1.3.3.2 Results of the PQL Analysis

The current PQL for dioxin is $0.00003 \ \mu g/L$ while the PTRL is $0.000011 \ \mu g/L$. The data obtained from the PT providers is summarized in Exhibit 6.6, along with a regression analysis. Not enough data was available to produce a regression that could be used for PQL analysis.

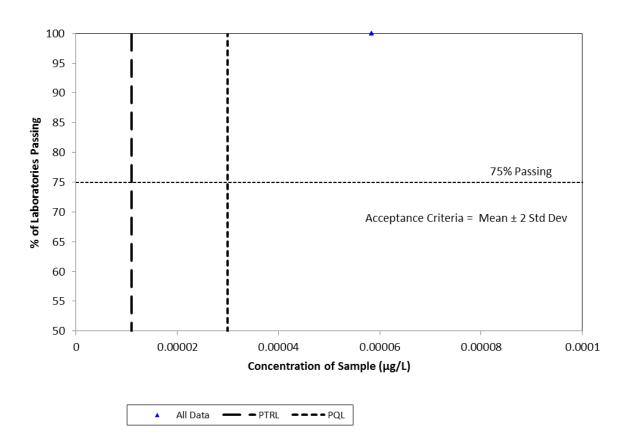


Exhibit 6.6: Evaluation of PT Data – Dioxin

6.1.3.3.3 Conclusions for Dioxin

Given the lack of data for dioxin, it is not appropriate to make any recommendations regarding the PQL. No new or revised methods that may be expected to improve analytical performance below the current PQL (and hence suggest possible reduction of the PQL).

6.1.3.4 Heptachlor

6.1.3.4.1 Results of the Method Comparison

Exhibit 6.7 summarizes the MDLs for heptachlor as documented in EPA-developed analytical methods. One new analytical method, EPA Method 525.3 (USEPA, 2012), was approved for the analysis of heptachlor in drinking water samples during the years 2008-2014. The MDL for the new EPA Method 525.3 is similar to the MDLs for other existing EPA Methods.

EPA Methods Approved for the Analysis of Drinking Water	EPA Methods Approved for the Analysis of Drinking Water - Technique	EPA Methods Approved for the Analysis of Drinking Water - MDL (μg/L)
505	ME and GC	0.003
508	GC/ECD	0.0015
508.1	LSE and ECGC	0.005
525.2	LSE and CCGC/MS	0.059 - 0.15
525.3*	SPE and CCGC/MS	0.0032 - 0.34
551.1	LLE/GC w/ ECD	0.002 - 0.081

Exhibit 6.7: Analytical Methods for Heptachlor

Notes:

* New approved analytical methods since last Six-Year Review.

Regulatory DLs for organic compounds are listed at 40 CFR 141.24(h)(18).

Acceptance Criteria for organic compounds are listed at 40 CFR 141.24(h)(19)(i)(B).

 $MCL = 0.4 \mu g/L$

Current PQL = $0.4 \mu g/L$ DL = $0.04 \mu g/L$

Acceptance Criteria = $\pm 45\%$

6.1.3.4.2 Results of the PQL Analysis

The current PQL for heptachlor is 0.4 μ g/L while the PTRL is 0.11 μ g/L. The data obtained from the PT providers is summarized in Exhibit 6.8, along with a regression analysis. The entire data obtained from the PT providers is based on using EPA Methods 505, 508, 508.1, 525.2 and 551.1, as listed in Exhibit 6.7. Two of the data points are below the current PQL of 0.4 μ g/L and of those two, both are at or below the PTRL of 0.11 μ g/L. Except for one point, the passing rate for all the data is at or above 75 percent.

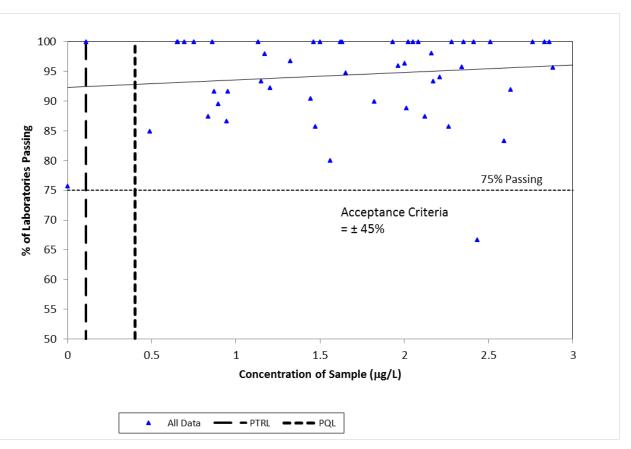


Exhibit 6.8: Evaluation of PT Data – Heptachlor

6.1.3.4.3 Conclusions for Heptachlor

Given limited data below the current PQL of $0.4 \mu g/L$, it may not be appropriate to recommend lowering of the PQL for heptachlor. One new analytical method has been approved since 2007, but since the data provided by the PT providers does not include results from the new method, it is unknown whether this is expected to improve analytical performance below the current PQL (and hence suggest possible reduction of the PQL).

6.1.3.5 Heptachlor Epoxide

6.1.3.5.1 Results of the Method Comparison

Exhibit 6.9 summarizes the MDLs for heptachlor epoxide as documented in EPA-developed analytical methods. One new analytical method, EPA Method 525.3 (USEPA, 2012), was approved for the analysis of heptachlor epoxide in drinking water samples during the years 2008-2014. The MDL for the new EPA Method 525.3 is similar to the MDLs for other existing EPA Methods listed in Exhibit 6.9.

EPA Methods Approved for the Analysis of Drinking Water	EPA Methods Approved for the Analysis of Drinking Water - Technique	EPA Methods Approved for the Analysis of Drinking Water - MDL (µg/L)
EPA 505	ME and GC	0.004
EPA 508	GC with ECD	0.015
EPA 508.1	LSE and ECGC	0.0001
EPA 525.2	LSE and CCGC/MS	0.048 - 0.13
EPA 525.3*	SPE and CCGC/MS	0.0026
EPA 551.1	LLE and GC with ECD	0.002 - 0.202

Exhibit 6.9: Analytical Methods for Heptachlor Epoxide

Notes:

* New approved analytical methods since last Six-Year Review (USEPA, 2012). Regulatory DLs for semi-volatile organic compounds are listed at 40 CFR 141.24(h)(18). Acceptance Criteria for organic compounds are listed at 40 CFR 141.24(h)(19)(i)(B). MCL = $0.2 \mu g/L$ Current PQL = $0.2 \mu g/L$ DL = $0.02 \mu g/L$ Acceptance Criteria = $\pm 45\%$

6.1.3.5.2 Results of the PQL Analysis

The current PQL for heptachlor epoxide is $0.2 \mu g/L$ while the PTRL is $0.11 \mu g/L$. The data obtained from the PT providers is limited and is summarized in Exhibit 6.10, along with a regression analysis. The entire data obtained from the PT providers is based on using EPA Methods 505, 508, 508.1, 525.2 and 551.1, as listed in Exhibit 6.9, except the new EPA Method 525.3. As shown in Exhibit 6.10, none of the data is below the current PQL of $0.2 \mu g/L$ or below the PTRL of $0.11 \mu g/L$. Except one data point, the passing rate for the entire data set is above 75 percent.

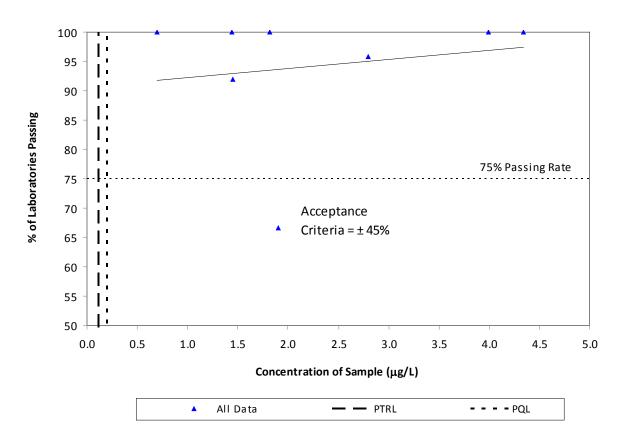


Exhibit 6.10: Evaluation of PT Data – Heptachlor Epoxide

6.1.3.5.3 Conclusions for Heptachlor Epoxide

Given the limited data available for analysis and the lack of data below the current PQL of 0.2 μ g/L, it may not be appropriate to recommend lowering the PQL. One new analytical method has been approved since 2007, but since the data provided by the PT providers does not include results from the new method, it is unknown whether this method is expected to improve analytical performance below the current PQL (and hence suggest possible reduction of the PQL).

6.1.3.6 Pentachlorophenol

6.1.3.6.1 Results of the Method Comparison

Exhibit 6.11 summarizes the MDLs for pentachlorophenol as documented in EPA-developed analytical methods. One new analytical method, EPA Method 525.3 (USEPA, 2012), was approved for the analysis of pentachlorophenol in drinking water samples during the years 2008-2014. The MDL for the new EPA Method 525.3 is the range of MDLs for other existing EPA Methods listed in Exhibit 6.11.

EPA Methods Approved for the Analysis of Drinking Water	EPA Methods Approved for the Analysis of Drinking Water - Technique	EPA Methods Approved for the Analysis of Drinking Water - MDL (μg/L)
515.1	GC with ECD	0.032
515.2	LSE and GC with ECD	0.16
515.3	LLE, Derivatization and GC with ECD	0.021 - 0.085
515.4	Liquid-Liquid ME, Derivatization and Fast GC with ECD	0.014 - 0.084
525.2	LSE and CCGC/MS	0.72 - 1.0
525.3*	SPE and CCGC/MS	0.047 - 0.069
528	SPE and CCGC/MS	0.081 - 0.25
555	High Pressure Liquid Chromatography (HPLC) with Photodiode Array Ultraviolet Detector	0.15 - 1.6

Exhibit 6.11: Analytical Methods for Pentachlorophenol

Notes:

* New approved analytical methods since last Six-Year Review (USEPA, 2012).

Regulatory DLs for organic compounds are listed at 40 CFR 141.24(h)(18).

Acceptance Criteria for organic compounds are listed at 141.24(h)(19)(i)(B).

MCL = 1.0 µg/L

Current PQL = $1.0 \mu g/L$

 $DL = 0.04 \ \mu g/L$ Acceptance Criteria = ± 50%

6.1.3.6.2 Results of the PQL Analysis

The current PQL for pentachlorophenol is 1.0 μ g/L while the PTRL is 0.5 μ g/L. The data obtained from the PT providers is summarized in Exhibit 6.12, along with a regression analysis. The entire data obtained from the PT providers is based on using EPA Methods listed in Exhibit 6.11, except the new EPA Method 525.3. None of the data is below the current PQL of 1.0 μ g/L or below the PTRL of 0.5 μ g/L. Except for four points, the passing rate for all the data is at or above 75 percent.

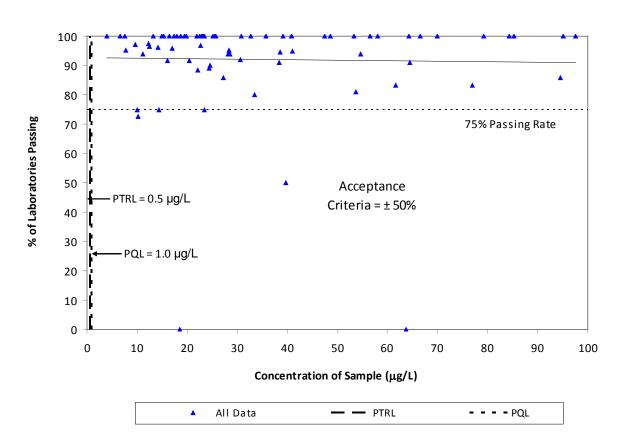


Exhibit 6.12: Evaluation of PT Data – Pentachlorophenol

6.1.3.6.3 Conclusions for Pentachlorophenol

Given lack of data below the current PQL of $1.0 \ \mu g/L$, it may not be appropriate to recommend lowering of the PQL. One new analytical method has been approved since 2007, but since the data provided by the PT providers does not include results from the new method, it is unknown whether this is expected to improve analytical performance below the current PQL (and hence suggest possible reduction of the PQL).

6.1.3.7 Thallium

6.1.3.7.1 Results of the Method Comparison

Exhibit 6.13 summarizes the MDLs for thallium as documented in EPA-developed analytical methods. No updated or new analytical methods have been approved for the analysis of dioxin in drinking water samples during the years 2008-2014. The MDLs for some of the approved EPA methods are not known.

EPA Methods Approved for the Analysis of Drinking Water	EPA Methods Approved for the Analysis of Drinking Water - Technique	EPA Methods Approved for the Analysis of Drinking Water - MDL (µg/L)
EPA 200.7	Inductively Coupled Plasma (ICP)-Atomic Emission Spectrometry	No MDL
EPA 200.8	ICP with MS	0.3
EPA 200.9	Stabilized Temperature Graphite Furnace Atomic Absorption	1.0

Exhibit 6.13: Analytical Methods for Thallium

Notes:

Regulatory DLs for inorganic compounds are listed at 40 CFR 141.23(a)(4)(i). Acceptance Criteria for inorganic compounds are listed at 40 CFR 141.23(k)(3)(ii). MCL = $2.0 \mu g/L$ Current PQL = $2.0 \mu g/L$ DL = $0.3-1.0 \mu g/L$ Acceptance Criteria = $\pm 30\%$

6.1.3.7.2 Results of the PQL Analysis

The current PQL for thallium is 2.0 μ g/L while the PTRL is 1.4 μ g/L. The data obtained from the PT providers is summarized in Exhibit 6.14, along with a regression analysis. Approximately 95 percent data obtained from the PT providers is based on EPA Methods 200.7 (14 percent), 200.8 (61 percent) and 200.9 (20 percent) while the remaining 5 percent data is based on Standard Methods SM 3113 B, SM 3120, SM 3125, as listed in Exhibit 6.13. As shown in Exhibit 6.14, none of the data is below the current PQL of 2.0 μ g/L or below the PTRL of 1.4 μ g/L. Except one point, the passing rate for all the data is above 75 percent.

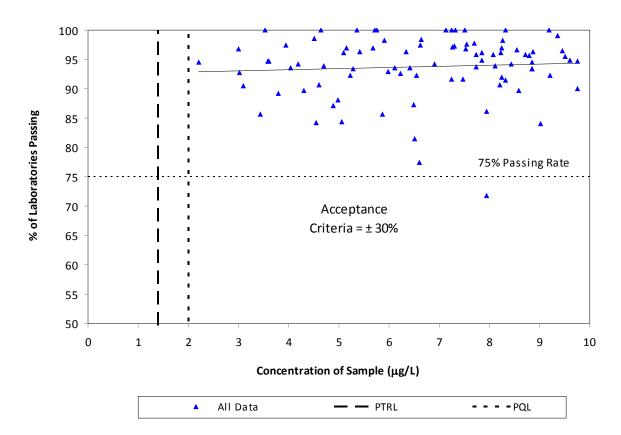


Exhibit 6.14: Evaluation of PT Data – Thallium

6.1.3.7.3 Conclusions for Thallium

Given the lack of data below the current PQL of $2.0 \,\mu$ g/L, it may not be appropriate to recommend lowering of the PQL. No new or revised methods that may be expected to improve analytical performance below the current PQL (and hence suggest possible reduction of the PQL) have been approved since 2007.

6.1.3.8 Toxaphene

6.1.3.8.1 Results of the Method Comparison

Exhibit 6.15 summarizes the MDLs for toxaphene as documented in EPA-developed analytical methods. One new analytical method, EPA Method 525.3 (USEPA, 2012), was approved for the analysis of toxaphene in drinking water samples during the years 2008-2014. The MDLs for some of the methods are not known. The MDL for the new EPA Method 525.3 is in between the range of the MDLs for the other existing EPA Methods.

EPA Methods Approved for the Analysis of Drinking Water	EPA Methods Approved for the Analysis of Drinking Water - Technique	EPA Methods Approved for the Analysis of Drinking Water - MDL (μg/L)
EPA 505	ME and GC	1.0
EPA 508	GC with ECD	Not given
EPA 508.1	LSE and ECGC	0.13
EPA 525.2	LSE and CCGC/MS	1.0 - 1.7
EPA 525.3*	SPE and CCGC/MS	0.32

Exhibit 6.15: Analytical Methods for Toxaphene

Notes:

* New approved analytical methods since last Six-Year Review (USEPA, 2012).

Regulatory DLs for organic compounds are listed at 40 CFR 141.24(h)(18).

Acceptance Criteria for organic compounds are listed at 40 CFR 141.24(h)(19)(i)(B).

 $MCL = 3.0 \ \mu g/L$

Current PQL = $3.0 \mu g/L$ DL = $1.0 \mu g/L$

Acceptance Criteria = $\pm 45\%$

6.1.3.8.2 Results of the PQL Analysis

The current PQL for toxaphene is 3.0 μ g/L while the PTRL is 1.1 μ g/L. The data obtained from the PT providers is summarized in Exhibit 6.16, along with a regression analysis. The entire data obtained from the PT providers is based on using EPA Methods 505, 508, 508.1 and 525.2, as listed in Exhibit 6.15. As shown in Exhibit 6.16, except for one data point which is below the current PQL of 3.0 μ g/L and above the PTRL of 1.1 μ g/L, the rest of the data is above the current PQL of 3.0 μ g/L and PTRL of 1.1 μ g/L. Except for a few data points, the passing rate for all the data is above 75 percent.

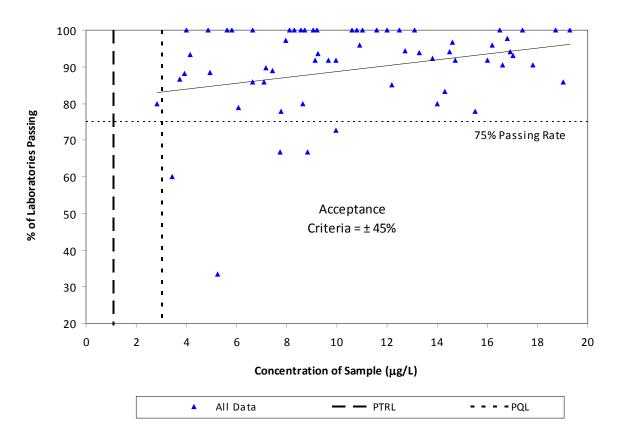


Exhibit 6.16: Evaluation of PT Data – Toxaphene

6.1.3.8.3 Conclusions for Toxaphene

As shown in Exhibit 6.16, only one data point is below the current PQL of $3.0 \ \mu g/L$ with a passing rate of greater than 75 percent. Although most of the data is above the PQL with high laboratory passing rates (above 75 percent), five data points failed the acceptance criteria. Given the lack of adequate data points below the PQL and some failure rates at the current PQL, it may not be appropriate to recommend lowering the PQL. One new analytical method has been approved since 2007, but since adequate data is not available using the new method, it is unknown whether this is expected to improve analytical performance below the current PQL (and hence suggest possible reduction of the PQL).

6.2 Analytes with MCL Greater Than the Current PQL and Thus It is Technically Feasible to Reduce an MCL

The analytes in this category have an existing PQL that is less than the MCL. If new health information were to become available for any of these analytes, causing EPA to consider reducing the MCL, the existing PQL would not hinder reduction of the MCL (to the level of the current PQL). Eight analytes fit into this category. These eight analytes can be further categorized into the two groups mentioned in Section 6.0 depending on whether or not the PE/PT assessments support the further reduction of the current PQL.

6.2.1 PQL Assessment Supports Reduction of the Current PQL

Of the eight analytes mentioned above, two analytes have an existing PQL that is less than the MCL and their PE/PT data suggest that the PQL could be lower.

6.2.1.1 cis-1,2-Dichloroethylene

6.2.1.1.1 Results of the Method Comparison

Exhibit 6.17 summarizes the MDLs for cis-1,2-dichloroethlyene as documented in EPAdeveloped analytical methods. Two new analytical methods, EPA Method 524.3 USEPA, 2009b) and EPA Method 524.4 (USEPA, 2013), were approved for the analysis of cis-1,2dichloroethylene in drinking water samples during the years 2008-2014. The MDLs for the two new methods are within the range of MDLs for the other existing EPA Methods and are lower than the current PQL.

EPA Methods Approved for the Analysis of Drinking Water	EPA Methods Approved for the Analysis of Drinking Water - Technique	EPA Methods Approved for the Analysis of Drinking Water - MDL (μg/L)
EPA 502.2	CCGC with Photoionization and Electrolytic Conductivity Detectors (ELCD)	0.01 - 0.05
EPA 524.2	CCGC/Mass Spectrometry (MS)	0.06 - 0.12
EPA 524.3*	CCGC/MS	0.042
EPA 524.4*	GC/MS Using Nitrogen Purge Gas	0.083
EPA 524.4* Notes:	GC/MS Using Nitrogen Purge Gas	0.083

Notes:

* New approved analytical methods since the last Six-Year Review (USEPA, 2009b and USEPA, 2013).

Regulatory DLs for organic compounds are listed at 40 CFR 141.24(k)(17)(ii)(C).

Acceptance Criteria for organic compounds are listed at 141.24(f)(17)(i) and also available at http://www.nelac-institute.org/docs/pt/DW_FOPT_2012_01_03.pdf.

Current PQL = $5.0 \mu g/L$ DL = N/A

Acceptance Criteria = $\pm 40\%$ at <10 µg/L or $\pm 20\%$ at >10 µg/L

6.2.1.1.2 Results of the PQL Analysis

The current PQL for cis-1,2-dichloroethylene is 5.0 μ g/L while the PTRL is 1.2 μ g/L. The data obtained from the PT providers is summarized in Exhibit 6.18, along with a regression analysis. Approximately 96 percent data obtained from the PT providers is based on EPA Methods 502.2 and 524.2, while the remaining 4 percent data is based on the new EPA Method 524.3, as listed in Exhibit 6.17. Since the acceptance criteria is ±40 percent at spike concentrations below 10 μ g/L and ±20 percent at or above 10 μ g/L, the data is regressed as two independent populations. As shown in Exhibit 6.18, several data points are below the current PQL of 5.0 μ g/L. However, none of the data is below the PTRL of 1.2 μ g/L. Except for two points, all the passing rates are above 75 percent.

 $MCL = 70 \mu g/L$

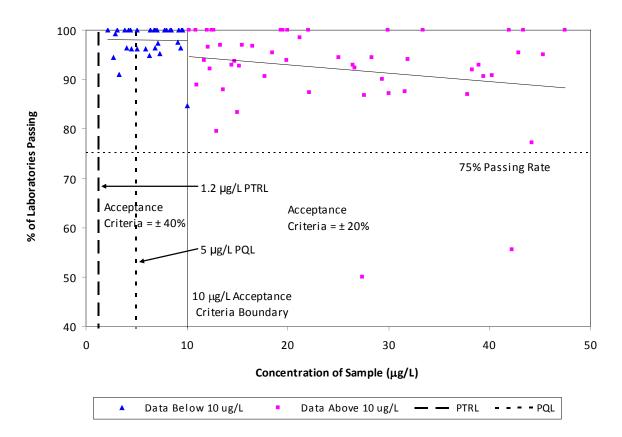


Exhibit 6.18: Evaluation of PT Data - cis-1,2-Dichloroethylene

6.2.1.1.3 Conclusions for cis-1,2-dichloroethylene

The high laboratory passing rates (above 75%) at concentrations below the current PQL of 5.0 μ g/L suggest that the PQL could be lowered using the current methods. Two new analytical methods have been approved since 2007. However, only 4 percent of the data provided by the PT providers represents data from one new method EPA 524.3, out of which only three data points are below the current PQL. Due to lack of sufficient data from the new method, it is unknown whether this method is expected to improve analytical performance below the current PQL.

6.2.1.2 Toluene

6.2.1.2.1 Results of the Method Comparison

Exhibit 6.19 summarizes the MDLs for toluene as documented in EPA-developed analytical methods. Two new analytical methods, EPA Method 524.3 (USEPA, 2009b) and EPA Method 524.4 (USEPA, 2013), were approved for the analysis of toluene in drinking water samples during the years 2008-2014. The MDL for the new EPA Method 524.4 is not known. The MDL for the new EPA Method 524.2 and slightly higher than the MDL for EPA Method 502.2.

EPA Methods Approved for the Analysis of Drinking Water	EPA Methods Approved for the Analysis of Drinking Water - Technique	EPA Methods Approved for the Analysis of Drinking Water - MDL (μg/L)
EPA 502.2	Purge and Trap CCGC with Photoionization and ECDs in Series	0.01 - 0.02
EPA 524.2	CCGC/MS	0.08 - 0.11
EPA 524.3*	CCGC/MS	0.024
EPA 524.4*	GC/MS using Nitrogen Purge Gas	No MDL

Exhibit 6.19: Analytical Methods for Toluene

Notes:

* New approved analytical methods since the last Six-Year Review (USEPA, 2009b, USEPA, 2013). Regulatory DLs for volatile organic compounds are listed at 141.24(k)(17)(ii)(C). Acceptance Criteria for toluene is listed at 40 CFR 141.24(f)(17)(i).

http://www.nelac-institute.org/docs/pt/DW_FOPT_2012_01_03.pdf.

MCL = 1,000 µg/L

Current PQL = $5.0 \mu g/L$

DL = N/A

Acceptance Criteria = $\pm 40\%$ at < 10 µg/L or $\pm 20\% \ge 10$ µg/L

6.2.1.2.2 Results of the PQL Analysis

The current PQL for toluene is 5.0 μ g/L while the PTRL is 1.2 μ g/L. The data obtained from the PT providers is summarized in Exhibit 6.20, along with a regression analysis. Approximately 96 percent data obtained from the PT providers is based on EPA Methods listed in Exhibit 6.19 and excluding the new EPA Methods while the remaining 4 percent data is based on the new EPA Methods 524.3 and 524.4, as listed in Exhibit 22. Since the acceptance criteria is ±40 percent at spike concentrations below 10 μ g/L and ± 20 percent at or above 10 μ g/L, the data is regressed as two independent populations. As shown in Exhibit 6.20, several data points are below the current PQL of 5.0 μ g/L. However, none of the data is below the PTRL of 1.2 μ g/L. Except for one point, all the passing rates are above 75 percent.

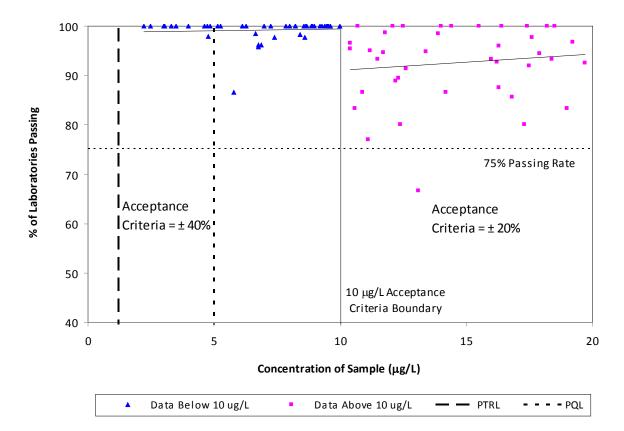


Exhibit 6.20: Evaluation of PT Data - Toluene

6.2.1.2.3 Conclusions for Toluene

The high laboratory passing rates (above 75 percent) at concentrations below the current PQL of $5.0 \ \mu g/L$ suggest that the PQL could be lowered. Two new analytical methods have been approved since 2007. However, only 4 percent of the data provided by the PT providers represents data from the two new methods EPA 524.3 and EPA 524.4, out of which only two data points are below the current PQL. Due to lack of sufficient data from the two new methods, it is unknown whether these methods are expected to improve analytical performance below the current PQL.

6.2.2 PQL Assessment May Support Reduction of the Current PQL

None of the analytes under consideration fall under this category.

6.2.3 PQL Assessment Does Not Support Reduction of the Current PQL or Data is Insufficient to Reach a Conclusion

Of the eight analytes mentioned in Section 6.2, six analytes have an existing PQL that is less than the MCL and their PT data either indicate that the PQL should not be lower or their PE/PT data are insufficient to reach a conclusion.

6.2.3.1 Carbofuran

6.2.3.1.1 Results of the Method Comparison

Exhibit 6.21 summarizes the MDLs for carbofuran as documented in EPA-developed analytical methods. No updated or new analytical methods have been approved for the analysis of carbofuran in drinking water samples during the years 2008-2014.

EPA Methods Approved for the Analysis of Drinking Water	EPA Methods Approved for the Analysis of Drinking Water - Technique	EPA Methods Approved for the Analysis of Drinking Water - MDL (µg/L)
531.1	DAI/ HPLC with Post Column Derivatization	0.52
531.2	DAI/ HPLC with Post Column Derivatization	0.043 - 0.058

Exhibit 6.21: Analytical Methods for Carbofuran

Notes:

Regulatory DLs for organic compounds are listed at 40 CFR 141.24(h)(18). Acceptance Criteria for organic compounds are listed at 40 CFR 141.24(h)(19)(i)(B). MCL = 40 μ g/L Current PQL = 7.0 μ g/L DL = 0.9 μ g/L Acceptance Criteria = ± 45%

6.2.3.1.2 Results of the PQL Analysis

The current PQL for carbofuran is 7.0 μ g/L while the PTRL is 8.3 μ g/L. The data obtained from the PT providers is summarized in Exhibit 6.22, along with a regression analysis. The entire data obtained from the PT providers is based on using EPA Methods listed in Exhibit 6.21. None of the data is below the current PQL of 7.0 μ g/L or below the PTRL of 8.3 μ g/L. Except for one point, the passing rate for all the data is at or above 75 percent.

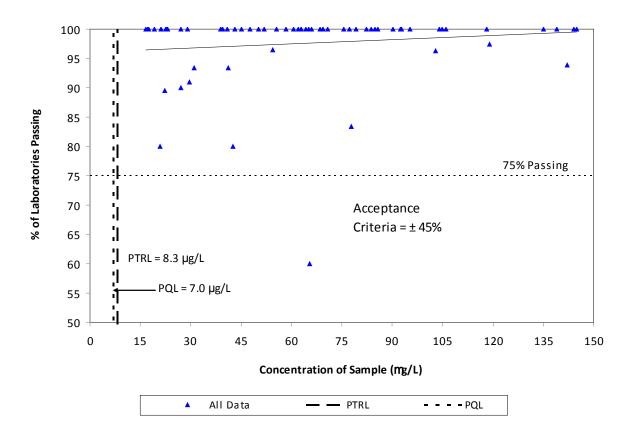


Exhibit 6.22: Evaluation of PT Data – Carbofuran

6.2.3.1.3 Conclusions for Carbofuran

Given lack of data below the current PQL of 7.0 μ g/L, it may not be appropriate to recommend lowering of the PQL. No new or revised methods that may be expected to improve analytical performance below the current PQL (and hence suggest possible reduction of the PQL) have been approved since 2007.

6.2.3.2 Cyanide

6.2.3.2.1 Results of the Method Comparison

Exhibit 6.23 summarizes the MDLs for cyanide as documented in EPA-developed analytical methods. The MDLs for some of the methods are not known. Two new analytical methods, Kelada-01 (USEPA, 2001), QuickChem-10-204-00-1-X (Lachat) (Lachat Instruments, 2000) and OIA-1677, DW (USEPA, 2004), were approved for the analysis of cyanide in drinking water samples during the years 2008-2014. The MDLs for the new methods are considerably lower than those of the existing EPA Methods.

EPA Methods Approved for the Analysis of Drinking Water	EPA Methods Approved for the Analysis of Drinking Water - Technique	EPA Methods Approved for the Analysis of Drinking Water - MDL (mg/L)
335.4	Semi-Automated Colorimetry	No MDL
SM 4500-CN C ¹	Manual Distillation	No MDL
SM 4500-CN E ¹	Colorimetry	No MDL
SM4500-CN F	Cyanide-Selective Electrode Method	50
SM4500-CN G ²	Cyanides Amenable to Chlorination after Distillation	20
Kelada-01*	UV, Distillation, Spectrophotometric	0.5
QuickChem-10-204-00-1- X (Lachat) *	Micro Distillation, Flow Injection, Spectrophotometric	0.6
OIA-1677, DW * ^{, 3}	Ligand Exchange and Amperometry	0.5

Exhibit 6.23: Analytical Methods for Cyanide

Notes:

* New EPA approved analytical methods since last Six-Year Review.

¹ This method is equivalent to American Society for Testing and Materials (ASTM)

2036-98 A as per 40 CFR 141.23(k)(1).

² This method is equivalent to ASTM 2036-98 B as per 40 CFR 141.23(k)(1).

³ This method is equivalent to ASTM D6668-04 as per 40 CFR 141.23(k)(1).

Regulatory DLs for inorganic compounds are listed at 40 CFR 141.23(a) 4(i).

Acceptance Criteria for inorganic compounds are listed at 40 CFR 141.23(k)(3)(ii).

MCL = 200 µg/L Current PQL = 100 µg/L

 $DL = 0.6 - 20 \mu g/L$

Acceptance Criteria = $\pm 25\%$

6.2.3.2.2 Results of the PQL Analysis

The current PQL for cyanide is 100 μ g/L while the PTRL is 75 μ g/L. The data obtained from the PT providers is summarized in Exhibit 6.24, along with a regression analysis. Approximately 39 percent data is based on using EPA Method 335.4, 51 percent data is based on using Standard Method 4500 and 10 percent data is based on using the three new methods shown in Exhibit 6.23. None of the data is below the current PQL of 100 μ g/L or below the PTRL of 75 μ g/L. Except for one point, the passing rate for the entire data set is above 75 percent.

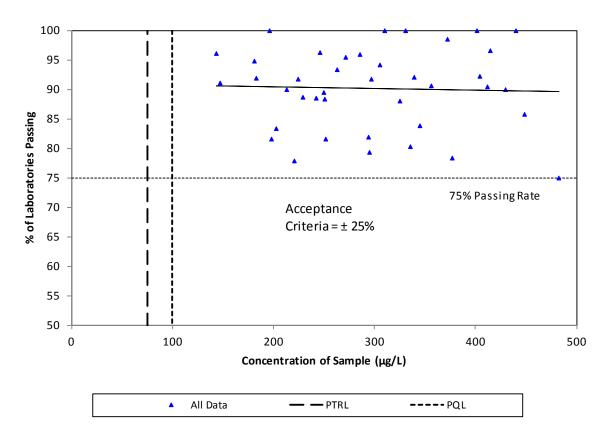


Exhibit 6.24: Evaluation of PT Data – Cyanide

6.2.3.2.3 Conclusions for Cyanide

Given the variable laboratory passing rates for the data sets and the lack of data below the current PQL of 100 μ g/L, it may not be appropriate to recommend lowering of the PQL. Compared to the previous 6-year analysis, other newer methods such as Lachat, Kelada-01, etc., are also being used for the analysis of cyanide. However, due to limited data available for the new methods, it is not known whether the MDLs from these methods could lead to an overall improvement in analytical performance below the current PQL and suggest possible reduction of the PQL.

6.2.3.3 Hexachlorocyclopentadiene

6.2.3.3.1 Results of the Method Comparison

Exhibit 6.25 summarizes the MDLs for hexachlorocyclopentadiene as documented in EPAdeveloped analytical methods. One new analytical method, EPA Method 525.3 (USEPA, 2012), was approved for the analysis of hexachlorocyclopentadiene in drinking water samples during the years 2008-2014. The MDLs for EPA Method 508 is not known. The MDL for the new EPA Method 525.3 is slightly higher than that of EPA Method 508.1 and is lower than the MDL of other approved EPA Methods listed in Exhibit 6.25, suggesting that laboratory performance at low concentrations may be improved through use of Method 525.3.

EPA Methods Approved for the Analysis of Drinking Water	EPA Methods Approved for the Analysis of Drinking Water - Technique	EPA Methods Approved for the Analysis of Drinking Water - MDL (μg/L)
505	ME and GC	0.13
508	GC/ECD	No MDL
508.1	LSE and ECGC	0.004
525.2	LSE and CCGC/MS	0.072 - 0.16
525.3*	SPE and CCGC/MS	0.0055 - 0.012
551.1	LLE/GC w/ECD	0.016 - 0.018

Exhibit 6.25: Analytical Methods for Hexachlorocyclopentadiene

Notes:

* New approved analytical methods since last Six-Year Review. Regulatory DLs for organic compounds are listed at 40 CFR 141.24(h)(18). Acceptance Criteria for organic compounds are listed at 40 CFR 141.24(h)(19)(i)(B). MCL = $50 \mu g/L$ Current PQL = $1.0 \mu g/L$ DL = $0.1 \mu g/L$ Acceptance Criteria = Mean ± 2 Std Dev

6.2.3.3.2 Results of the PQL Analysis

The current PQL for hexachlorocyclopentadiene is $1.0 \ \mu g/L$ while the PTRL is $0.5 \ \mu g/L$. The data obtained from the PT providers is summarized in Exhibit 6.26, along with a regression analysis. The entire data obtained from the PT providers is based on using EPA Methods listed in Exhibit 6.25 and does not include any data by the new EPA Method 525.3. Only two data points are below the current PQL of $1.0 \ \mu g/L$ or below the PTRL of $0.5 \ \mu g/L$ (and do not include the new Method 525.3). Except for one point, the passing rate for all the data is at or above 75 percent.

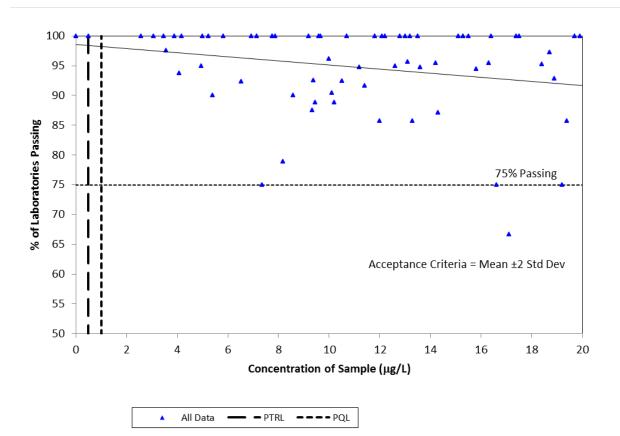


Exhibit 6.26: Evaluation of PT Data – Hexachlorocyclopentadiene

6.2.3.3.3 Conclusions for Hexachlorocyclopentadiene

Given that limited is below the current PQL of $1.0 \ \mu g/L$, it may not be appropriate to recommend lowering of the PQL. One new method has been approved since 2007 but since the data provided by the PT providers does not include this method, it is unknown whether it is expected to improve analytical performance below the current PQL (and hence suggest possible reduction of the PQL).

6.2.3.4 Oxamyl

6.2.3.4.1 Results of the Method Comparison

Exhibit 6.27 summarizes the MDLs for oxamyl as documented in EPA-developed analytical methods. No updated or new analytical methods have been approved for the analysis of oxamyl in drinking water samples during the years 2008-2014.

EPA Methods Approved for the Analysis of Drinking Water	EPA Methods Approved for the Analysis of Drinking Water - Technique	EPA Methods Approved for the Analysis of Drinking Water - MDL (μg/L)
531.1	Direct Aqueous Injection (DAI)/ HPLC with Post Column Derivatization	0.86
531.2	DAI/ HPLC with Post Column Derivatization	0.045 - 0.065

Exhibit 6.27: Analytical Methods for Oxamyl

Notes:

Regulatory DLs for organic compounds are listed at 40 CFR 141.24(h)(18).

Acceptance Criteria for organic compounds are listed at 40 CFR 141.24(h)(19)(i)(B).

MCL = $200 \mu g/L$ Current PQL = $20 \mu g/L$

DL = $2.0 \,\mu g/L$

Acceptance Criteria = Mean ± 2 Std Dev

6.2.3.4.2 Results of the PQL Analysis

The current PQL for oxamyl is 20 μ g/L while the PTRL is 11 μ g/L. The data obtained from the PT providers is summarized in Exhibit 6.28, along with a regression analysis. The entire data set provided by the PT providers is based on the two EPA Methods listed in Exhibit 6.27. Two data points are below the current PQL of 20 μ g/L and no points are below the PTRL of 11 μ g/L. Except for one point, the passing rate for all the data is at or above 75 percent.

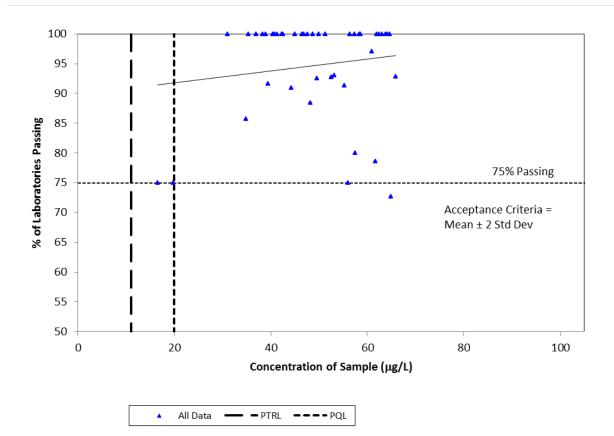


Exhibit 6.28: Evaluation of PT Data – Oxamyl

6.2.3.4.3 Conclusions for Oxamyl

Given the limited data below the current PQL of 20 μ g/L, it may not be appropriate to recommend lowering of the PQL. No new or revised methods that may be expected to improve analytical performance below the current PQL (and hence suggest possible reduction of the PQL) have been approved since 2007.

6.2.3.5 Selenium

6.2.3.5.1 Results of the Method Comparison

Exhibit 6.29 summarizes the MDLs for selenium as documented in EPA-developed analytical methods. No new analytical methods have been approved for the analysis of selenium in drinking water samples during the years 2008-2014. The MDLs for some of the methods are not known.

EPA Methods Approved for the Analysis of Drinking Water	EPA Methods Approved for the Analysis of Drinking Water - Technique	EPA Methods Approved for the Analysis of Drinking Water - MDL (μg/L)
EPA 200.5	Axially Viewed ICP-Atomic Emission Spectrometry	1.3
EPA 200.7	ICP – Atomic Emission Spectroscopy	2.0
EPA 200.8	ICP-MS	0.5
EPA 200.9	Stabilized Temperature Graphite Furnace Atomic Absorption	2.0
SM 3113B ¹	Electrothermal Atomic Absorption Spectrometry	No MDL
SM 3114B/ SM 3114B-97 ²	Hydride Generation/Atomic Absorption Spectrometry	2.0
SM 3114C	Continuous Hydride Generation/Atomic Absorption Spectrometry	No MDL
SM 3120A	ICP Emission Spectroscopy	No MDL
SM 3125	ICP/MS	1.0

Exhibit 6.29: Analytical Methods for Selenium

Notes:

¹ This method is equivalent to ASTM 3859-98 03A as per 40 CFR 141.23(k)(1).

² This method is equivalent to ASTM 3859-98 03B as per 40 CFR 141.23(k)(1).

Regulatory DLs for inorganic compounds are listed at 40 CFR 141.23(a)(4)(i).

Acceptance Criteria for inorganic compounds are listed at 40 CFR 141.23(k)(3)(ii).

 $MCL = 50 \ \mu g/L$

Current $PQL = 10 \mu g/$ DL = 2.0 $\mu g/L$

Acceptance Criteria = $\pm 20\%$

6.2.3.5.2 Results of the PQL Analysis

The current PQL for selenium is 10 μ g/L while the PTRL is 8 μ g/L. The data obtained from the PT providers is summarized in Exhibit 6.30, along with a regression analysis. Approximately 82 percent data is based on using EPA Methods listed in Exhibit 6.29 while 18 percent data is based on using the Standard Methods listed in Exhibit 6.29. As shown in Exhibit 6.30, except for one data point, all the data is above the current PQL of 10 μ g/L and above the PTRL of 8 μ g/L. The passing rate for the entire data set is above 75 percent.

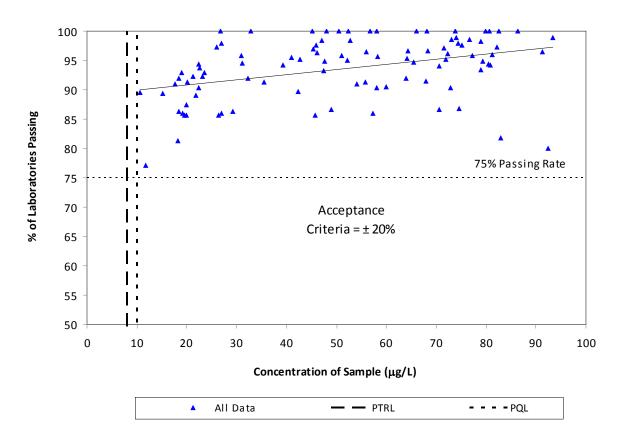


Exhibit 6.30: Evaluation of PT Data - Selenium

6.2.3.5.3 Conclusions for Selenium

Given the variable laboratory passing rates for the data set and the limited data (only one data point) below the current PQL of 10 μ g/L, it may not be appropriate to recommend lowering of the PQL. It is noted that in 2007, revisions were made to two methods, i.e. ASTM 3859-98A and ASTM 3859-98B were modified to ASTM 3859-93A and ASTM 3859-93B, respectively. These revisions were minor modifications associated with hazardous materials handling and safer techniques to conduct hazardous or complicated analytical procedures and are not related to changes in procedures or instrumentation. No new or revised methods that may be expected to improve analytical performance below the current PQL (and hence suggest possible reduction of the PQL) have been approved since 2007.

6.2.3.6 Xylenes

6.2.3.6.1 Results of the Method Comparison

Exhibit 6.31 summarizes the MDLs for xylenes as documented in EPA-developed analytical methods. Two new analytical methods, EPA Method 524.3 (USEPA, 2009b) and EPA Method 524.4 (USEPA, 2013), were approved for the analysis of xylenes in drinking water samples during the years 2008-2014. The MDL for the new EPA Method 524.4 is not known. The MDL for the new EPA Method 524.2 and slightly higher than the MDL for EPA Method 502.2.

EPA Methods Approved for the Analysis of Drinking Water	EPA Methods Approved for the Analysis of Drinking Water - Technique	EPA Methods Approved for the Analysis of Drinking Water - MDL (μg/L)
EPA 502.2	Purge and Trap CCGC with Photoionization and ECDs in Series	0.01
EPA 524.2	CCGC/MS	0.03 - 0.13
EPA 524.3*	CCGC/MS	0.05
EPA 524.4*	GC/MS using Nitrogen Purge Gas	No MDL

Exhibit 6.31: Analytical Methods for Xylenes

Notes:

* New approved analytical methods since the last Six-Year Review.

Regulatory DLs for volatile organic compounds are listed at 40 CFR 141.24(k)(17)(ii)(C).

Acceptance Criteria for volatile organic compounds are listed at 40 CFR 141.24(f)(17)(i): <u>http://www.nelac-institute.org/docs/pt/DW_FOPT_2012_01_03.pdf</u>. MCL = 10,000 µg/L Current PQL = 5.0 µg/L

DL = N/A

Acceptance Criteria = $\pm 40\%$ at < 10 µg/L or $\pm 20\% \ge 10$ µg/L

6.2.3.6.2 Results of the PQL Analysis

The current PQL for xylenes is 5.0 μ g/L while the PTRL is 1.2 μ g/L. The data obtained from the PT providers is summarized in Exhibit 6.32, along with a regression analysis. Approximately 96 percent data is based on using EPA Methods 502.2 and 524.2 as listed in Exhibit 6.31 while 4 percent data is based on using the new EPA Methods 524.3 and 524.4 listed in Exhibit 6.31. Since the acceptance criteria is ±40 percent at spike concentrations below 10 μ g/L and ±20 percent at or above 10 μ g/L, the data is regressed as two independent populations. As shown in Exhibit 6.32, none of the data is below the current PQL of 5.0 μ g/L or below the PTRL of 1.2 μ g/L. Except for two points, the passing rates for the rest of the data are at or above 75 percent.

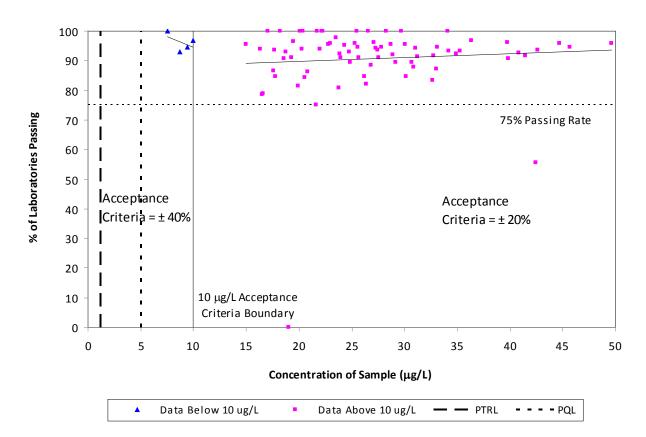


Exhibit 6.32: Evaluation of PT Data – Xylenes

6.2.3.6.3 Conclusions for Xylenes

Given the variable laboratory passing rates for the data set and the lack of data below the current PQL of $5.0 \mu g/L$, it may not be appropriate to recommend lowering of the PQL. Two new methods have been approved since 2007 but since this data does not fall below the current PQL, it may not be expected to improve analytical performance below the current PQL (and hence suggest possible reduction of the PQL).

6.3 Summary

This document examines analytical method performance over time by determining if the PQLs may have changed since promulgation. PQL assessments are presented by means of linear regression of available PE/PT data. A qualitative conclusion is drawn by presenting a recommendation of whether a PQL might be reduced. In addition, analytical method performance is also assessed by comparing the MDL of the analytical methods which were available at the time of promulgation to those of the currently approved methods.

Exhibit 6.33 and Exhibit 6.34 provide summary observations the PE/PT data review of the 16 analytes that were included in the Six-Year Review 3. The summary tables also include a notation as to whether any recently approved analytical methods or updates (i.e., 2007 to 2014) are available for these analytes that might indicate improved laboratory performance at low concentrations. Lastly, a recommendation as to whether a PQL can be reduced is provided (these analytes are italicized). The recommendations were made based on the availability of PE/PT data in the vicinity of and/or below the PQL, and outliers. The qualitative conclusions are based primarily on data that are in the vicinity of and/or below the PQL (for VOCs, this corresponds to concentrations <10 μ g/L).

The recommendations to not reduce the PQL/MCL could be related to many factors, since the PE/PT data sets may reflect one or more of the following traits:

- No PE/PT data or insufficient data is available at or below the PQL,
- Laboratory performance is poor as PE/PT data approaches the PQL, and/or
- Laboratory performance is highly variable over the range of concentrations analyzed.

The overall assessment decision presented in the final columns of Exhibit 6.33 consists of the following possible outcomes:

- Regulated contaminants for which the MCL is set at the PQL, and thus, the PQL is limiting
 - PQL assessment supports reduction of the current PQL;
 - PQL assessment may support reduction of the current PQL; and
 - PQL assessment does not support reduction of the current PQL, or data are inconclusive or insufficient to reach a conclusion.

Exhibit 6.33: Analytical Feasibility Assessment Summary for Analytes with MCL Equal to the Current PQL

Analyte	Units	Current PQL	MCL	New or Updated Methods?	PQL Assessment Results	Qualitative Recommendation
Chlordane	µg/L	2	2	Yes – not known if it improves analytical performance in vicinity of current PQL	No data ≤current PQL; variable passing rates	No change to current PQL
1,2-Dibromo-3- chloropropane (DBCP)	µg/L	0.2	0.2	Yes – not known if it improves analytical performance in vicinity of current PQL	No data ≤current PQL; variable passing rates	No change to current PQL
Dioxin	µg/L	0.00003	0.00003	No	Insufficient data for analysis	No change to current PQL
Heptachlor	µg/L	0.4	0.4	No	Two data points ≤current PQL; variable passing rates	No change to current PQL
Heptachlor Epoxide	µg/L	0.2	0.2	No	No data ≤current PQL; variable passing rates	No change to current PQL
Pentachlorophenol	µg/L	1	1	Yes – not known if it improves analytical performance in vicinity of current PQL	No data ≤current PQL; passing rates generally high in vicinity of current PQL	No change to current PQL
Thallium	µg/L	2	2	No	No data ≤current PQL; passing rates generally high in vicinity of current PQL	No change to current PQL
Toxaphene	µg/L	3	3	No	One data point ≤current PQL, variable passing rates	No change to current PQL

The overall assessment decision presented in the final columns of Exhibit 6.34 consists of the following possible outcomes:

- Regulated contaminants for which the MCL is greater than the PQL
 - PQL assessment supports reduction of the current PQL;
 - PQL assessment may support reduction of the current PQL; and
 - PQL assessment does not support reduction of the current PQL, or data are inconclusive or insufficient to reach a conclusion

Exhibit 6.34: Analytical Feasibility Assessment Summary for Analytes with MCL Greater than the Current PQL

Analyte	Units	Current PQL	MCL	New or Updated Methods?	PQL Assessment Results	Qualitative Recommendation
Carbofuran	µg/L	7	40	No	No data ≤current PQL; variable passing rates	No change to current PQL
Cis-1,2-dichloroethylene	µg/L	5	70	Yes – not known if it improves analytical performance in vicinity of current PQL	Several data points ≤current PQL	Reduction of current PQL is supported
Cyanide	µg/L	100	200	Yes, MDLs lower, however, not known if they improve analytical performance in vicinity of current PQL	No data ≤current PQL; variable passing rates	No change to current PQL
Hexachlorocyclopentadiene	µg/L	1	50	Yes – not known if it improves analytical performance in vicinity of current PQL	Two data points ≤current PQL; variable passing rates	No change to current PQL
Oxamyl (vydate)	µg/L	20	200	No	Two data points ≤current PQL; variable passing rates	No change to current PQL
Selenium	µg/L	10	50	No	No data ≤current PQL; passing rates generally high in vicinity of current PQL	No change to current PQL
Toluene	µg/L	5	1,000	Yes – not known if it improves analytical performance in vicinity of current PQL	Several data points ≤current PQL	Reduction of current PQL is supported
Xylenes	µg/L	5	10,000	Yes – not known if it improves analytical performance in vicinity of current PQL	No data ≤current PQL; variable passing rates	No change to current PQL

As shown in Exhibit 6.33 and Exhibit 6.34, of the 16 analytes that were analyzed as part of this report, the qualitative recommendations for PQL assessment are summarized as follows:

- For eight analytes, the PQL is equal to the MCL and hence the PQL is limiting. For all the eight analytes, the PE/PT data does not support reduction of the current PQL. Out of these eight analytes, new or improved analytical methods are available for three analytes (chlordane, 1,2-dibromo-3-chloropropane and pentachlorophenol). However, it is not known if the new method(s) are expected to improve analytical performance in the vicinity of the current PQL. For the remaining five analytes (dioxin, heptachlor, heptachlor epoxide, thallium and toxaphene), new or improved analytical methods are not available.
- For eight analytes, the PQL is lower than the MCL and hence, the MCL may be reduced. Of the eight analytes, two analytes have PE/PT data that support further reduction of the PQL. For these two analytes (cis-1,2-dichloroethylene and toluene), new or improved analytical methods are available. However, it is not known if these new method(s) are expected to improve analytical performance in the vicinity of the current PQL. For the remaining six analytes, PE/PT data does not support the reduction of the current PQL. Out of these six analytes, new or improved analytical methods are available for three analytes (cyanide, hexachlorocyclopentadiene and xylenes). However, it is not known if the new method(s) are expected to improve analytical performance in the vicinity of the current PQL.

It is noted that for the analytes with improved laboratory methods, the existence of new methods may not directly translate to improved analytical performance, even with improved detection limits. It is possible that only a small number of laboratories will use a new method, or it may take time for the method to be utilized to its full effectiveness.

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