NJ Drinking Water Quality Institute
Testing Subcommittee

Report on the Development of a Practical Quantitation Level for Perfluorooctanoic Acid (PFOA) in Drinking Water

8/29/2016

Testing Subcommittee Members:
Bahman Parsa, Ph.D., Chair
Sandra Krietzman
Daniel Salvito, Ph.D.
Sheng-Lu Soong, Ph.D.

Technical Support:
Linda Bonnette
Tina Fan, Ph.D.
Robert Lee Lippincott, Ph.D.
Collin D. Riker

Testing Subcommittee Report on PQL Development for Perfluorooctanoic Acid in Drinking Water

Background:

In February 2006 the New Jersey Department of Environmental Protection (NJDEP) first became aware of the presence of perfluorinated compounds (PFC) in New Jersey drinking waters. This finding was a result of the Penns Grove Water Supply Company of Salem County, NJ sharing their perfluorooctanoic acid (PFOA) water test results with the NJDEP. A concentration of 64 nanograms per liter (ng/L or parts per trillion) of PFOA was found in the Penns Grove Water Supply Company's finished drinking water. These concentrations of PFOA prompted the NJDEP to conduct a study for determining the occurrence and levels of PFOA and perfluorooctane sulfonic acid (PFOS) in NJ water systems' raw and finished drinking water. Of the 23 New Jersey drinking water systems monitored in the NJDEP 2006 PFC study, 65% had concentrations of PFOA and 30% had concentrations of PFOS in their finished drinking water or drinking water sources. A PFC follow-up study conducted in 2009 determined the occurrence of PFOA, PFOS and eight additional PFCs in drinking water sources of 30 public water systems throughout New Jersey. In contrast to the 2006 PFC study which included samples from both raw (untreated) and treated water sources, the 2009 PFC study included only *untreated* water samples. In the 2009 study, between one and eight PFCs were detected in 21 of 30 NJ public water systems sampled, with total PFC concentrations ranging between 5 ng/L and 174 ng/L.

In 2014, the Drinking Water Quality Institute (DWQI) was tasked with recommending a Maximum Contaminant Level (MCL) for PFOA to the Commissioner of the New Jersey Department of Environmental Protection (NJDEP). This advisory panel comprised of 15 members from academia, regulated water systems, governmental agencies, and public health experts is responsible for providing MCL recommendations as part of the regulatory process in setting an MCL specific to New Jersey. The DWQI recommendations are a result of the collaboration of three DWQI Subcommittees: the Health Effects Subcommittee, the Treatment Subcommittee and the Testing Subcommittee. The Health Effects Subcommittee is responsible for recommending "health-based MCL[1]" levels for contaminants. The Treatment Subcommittee is responsible for evaluating the best available treatment technologies for removal of the contaminant from drinking water supplies. The Testing Subcommittee is responsible for developing Practical Quantitation Levels (PQL) for the contaminants. (A PQL is the minimum concentration for which the contaminant under review can be reliably quantitated within acceptable limits of uncertainty.)

Developing a PQL involves researching analytical methods that are reliable and have the sensitivity to detect the contaminant at or as close as possible to the health-based MCL developed by the

[1] Health-based MCLs are goals, not enforceable standards, similar to USEPA Maximum Contaminant Level Goals (MCLG). For carcinogens, health-based MCLS are set at levels that are not expected to result in cancer in more than one in one million persons ingesting the contaminant for a lifetime, and for non-carcinogens, at levels not expected to result in "any adverse physiological effects from ingestion" for a lifetime. The enforceable MCLs consider other factors such as analytical quantitation limits and availability of treatment removal technology and may be set higher than the MCLGs.

Health Effects Subcommittee. When developing a PQL, the Testing Subcommittee considers available analytical methods and laboratory performance. In 2009, the EPA published Method 537, a solid-phase extraction and liquid chromatography/ tandem mass spectrometry (LC/MS/MS) method for perfluorinated alkyl acids (which includes PFOA). Although published and required for the analysis of UCMR3 samples by the USEPA (2013-2015), this method has not been promulgated in federal regulation, as PFOA does not yet have an MCL. In response to the lack of a promulgated method, some laboratories developed their own proprietary methods or modified EPA 537 to enhance performance of the method. The PQL for PFOA recommended by the Testing Subcommittee in this document was developed solely on the performance data of a group of drinking water laboratories that meet certain criteria established by the Testing Subcommittee.

If the health-based MCL for a contaminant is known, the Testing Subcommittee will attempt to establish a PQL at a level less than that health-based MCL. This is not always feasible and ultimately it is the performance data from robust analytical methods and accredited laboratories that determine the PQL. In the current process of developing a PFOA MCL recommendation, the health-based MCL and the PQL were being developed simultaneously.

In 2007, in response to a request by the Penns Grove Water Supply Company, a health-based guidance for PFOA was developed by the NJDEP Office of Science and Research to provide guidance in assessing the public health implications of the PFOA concentrations detected in their drinking water. This health-based value was determined to be 40 ng/L and was developed "to provide preliminary guidance to the system within a reasonable timeframe and does not represent a comprehensive review of the toxicological literature on PFOA which will be needed as additional information becomes available." Since 2007, laboratories have demonstrated that lower reporting limits are achievable. Therefore, when requesting that water systems conduct additional sampling for PFOA, the NJDEP recommends a reporting limit (or MRL) of 10 ng/L or lower.

In the absence of an EPA developed MCL, as other states have discovered PFCs in their drinking water sources many have developed their own health advisories or guidance levels. For instance, in March 2016, Vermont's Agency of Natural Resources and Department of Health set a health advisory of 20 ng/L for PFOA in groundwater. The New York Department of Environmental Conservation (NYDEC) has been using 100 ng/L as a health advisory level which was developed by EPA Region 2 for the Hoosick Falls area. EPA-issued health advisories provide non-cancer health effects information on contaminants that may be found in drinking water, and are non-enforceable. New Hampshire Department of Environmental Services (NHDES) used 100 ng/L as their action level. In many cases the states use these health derived guidance or advisory values to establish the reporting limits for the analysis of those PFCs in their state. Vermont uses laboratories that offer detection limits or reporting limits lower than their health advisory of 20 ng/L for their investigative studies. Because NYDEC had considered the possibility that the EPA would set a PFOA health advisory lower than the EPA Region 2 Hoosick Falls health advisory of 100 ng/L, they contracted the services of a laboratory capable of providing a PFOA reporting limit of 2 ng/L, thereby ensuring the usefulness of all or most of their previously acquired data.

In May 2016, the EPA released a lifetime health advisory for a combined PFOA and PFOS concentration of 70 ng/L.[2] Prior to this, the EPA had developed a provisional short-term health advisory of 400 ng/L for PFOA in January 2009, due to a contamination event in Alabama. Provisional health advisory values are developed to provide information in response to an urgent or rapidly developing situation. They reflect reasonable, health-based hazard concentrations above which action should be taken to reduce exposure to unregulated contaminants in drinking water and are developed with the intention that they will be updated as additional information becomes available for reevaluation. The short-term provisional drinking water health advisory is usually developed to be protective of a one-day or 10-day exposure timeframe. The EPA was not clear for which timeframe their value was developed

It had already been established through the USEPA Unregulated Monitoring Rule 3 (UCMR3), which will be discussed later in this document, that laboratories participating in this rule and performing the PFC analysis could detect, and reliably quantitate PFOA at and over 20 ng/L. Through conversations with these UCMR3 participating laboratories, 65% were already reporting PFOA lower than 20 ng/L or, if requested, were confident that they would be able to provide a client with a lower reporting limit. The above information further corroborates that the PFOA reporting limits for PFOA are generally client driven.

Data Sources for PQL Determination:

As a first step in the PQL development process, data from drinking water laboratories with adequate sensitivity for reliably analyzing PFOA were compiled from the following sources:

1) Laboratories that analyzed water samples for PFOA for NJDEP PFC studies (2006 and 2009) and as requested by water systems;
2) Laboratories that are certified for the analysis of PFOA in drinking water by the NJDEP Office of Quality Assurance (OQA); and
3) National laboratories that have obtained US Environmental Protection Agency (EPA) approval to analyze six PFCs under the Unregulated Contaminant Monitoring Rule 3 (UCMR3) program using EPA Method 537 and that have demonstrated that they are capable of reporting PFOA lower than the required UCMR3 minimum reporting level (MRL) of 20 ng/L.

The PQL for PFOA has been determined as a result of performance data compiled from these three data sources.

1) The NJDEP PFC Database:

The NJDEP PFC Database was originally set up to house the results of the NJDEP 2006 and 2009 PFC studies. The laboratories and methods which generated the study data were reviewed and sanctioned by both the NJDEP OQA and the NJDEP Bureau of Safe Drinking Water (BSDW). Subsequently, PFC results from public water systems conducting their own PFC monitoring were

[2] https://www.epa.gov/ground-water-and-drinking-water/drinking-water-health-advisories-pfoa-and-pfos

added to this database. Public water system data includes follow up testing results based on recommendations made by the NJDEP, as a result of findings of the 2006 and 2009 studies, and data from water systems that voluntarily initiated PFC testing.

The NJDEP PFC database contains 911 PFOA results, 4% of which were generated by STL-Denver, 20% by MWH Laboratories, 35% by Eurofins Eaton Analytical, 34% by Test America-Denver and 7% by Underwriters Laboratories. Severn Trent Laboratory (STL-Denver) became Test America-Denver in 2007. Similarly, MWH Laboratories became Eurofins Eaton Analytical (California) in 2012, and in 2014, part of the Underwriters Laboratory in South Bend, Indiana became Eurofins Eaton Analytical, Inc. (Indiana). Using the current names of the laboratories, the above information would breakdown to the following: 38% Test America-Denver (Colorado), 55 % Eurofins Eaton Analytical (California), and 7% Eurofins Eaton Analytical (Indiana).

In 2006, PFCs were considered emerging contaminants and few laboratories had developed analytical methods capable of analyzing PFOA. The federal safe drinking water regulations required the use of EPA approved drinking water methods for the analyses of regulated contaminants, and although preferred, it was not required that emerging contaminants be analyzed with EPA approved methods. In the absence of an EPA published analytical method for PFOA, the OQA reviewed and approved as a Department Sanctioned Analytical Method (DSAM) an acceptable method for the 2006 PFC study. In addition to reviewing and approving an analytical method, the BSDW requested that the OQA determine the lowest reporting limit (or minimum reporting limit) for PFOA that could be achieved with sufficient precision and accuracy. As a result of the research performed by OQA, the value of 10 ng/L was determined to be a reliable minimum reporting limit for PFOA based on the proprietary methods of Axys Laboratory, STL-Denver (Test America-Denver) and Exygen Laboratory.[3] By 2009, EPA Method 537 was available, although any of the NJDEP OQA sanctioned PFC laboratory methods were acceptable to NJDEP at that time.

Test America-Denver

The NJDEP selected STL-Denver (Test America-Denver) for the 2006 PFC study. STL-Denver's proprietary method, SOP DEN-LC-0012 Revision 4, had been reviewed and approved by OQA as a DSAM for PFOA analysis. They used a Reporting Limit (RL) of 10 ng/L for PFOA and the lowest PFOA calibration standard was 4 ng/L. Any result between 4 ng/L and 10 ng/L was considered a reportable and quantifiable value. (Although the laboratory reports stated 10 ng/L as the RL, 4 ng/L was used as the RL for the 2006 study results). In addition to PFOA, the STL-Denver method was capable of reporting PFOS to 10 ng/L. STL-Denver's certification with NJDEP OQA was specifically for PFOA, however the PFOS concentrations were also reported with the 2006 NJDEP PFC study results.

In February 2009, Revision 7 of the Test America-Denver SOP, DEN-LC-0012, included 14 additional PFC compounds to the analyte target list. Although Revision 7 of SOP DEN-LC-0012 expanded the capability of Test America-Denver to analyze and report 16 PFCs, in

[3] OQA referred to this reporting limit as the "practical quantitation limit."

many cases only PFOA and PFOS results were reported based upon instructions provided to the laboratory by the water system (client).

During the seven years in which Test America-Denver analyzed NJ water system drinking water samples, several different revisions of the method were used. Revision 4 was used for the 2006 PFC study while the latest version currently being used is Revision 12.[4] Table 1 shows that over the course of seven years Test America-Denver reported PFOA data using different RLs with the most frequently occurring RL in the PFC database being 15 ng/L. This RL in addition to the lowest calibration standard of 4 ng/L used in the 2006 PFC study (where the actual laboratory reporting limit was 10 ng/L) will be the values selected from the NJDEP database to represent Test America-Denver's performance data in the consideration of a PQL value (see Table 2). The lowest Test America-Denver Method Detection Limit (MDL)[5] reported, 1.1 ng/L.

Table 1.
Test America PFOA Data from the NJDEP Historical Database
using their Proprietary Method, SOP DEN-LC 0012
June 2006 to April 2016

Reporting Limit (ng/L)	Method Detection Limit (ng/L)	# of Results
4	NP	32
9	NP, 2.1	30
10	NP, 1.1,1.9, 2.1	112
12	1.2	3
15	NP, 1.1, 2.1, 2.6, 3.1, 3.6	123
19	1.2, 4.4, 9.3,	7
20	NP, 1.2, 4.1, 4.4, 4.5, 4.6, 9.7, 9.8, 12	35

NP =Information not provided in the PFC database.

MWH Laboratory

The MWH Laboratories proprietary method, MWH SOP-HPLC 12 (also referred to as MWH PFC Extra), was the analytical method used in the 2009 NJDEP PFC Study. This method was approved by OQA and offered lower reporting limits for the PFCs of concern. The MWH PFC Extra method includes PFOA and nine other PFCs. The MWH-PFC Extra reporting limit for

[4] The revision number of the method was not noted in the PFC database. However, if needed, this could be determined based on the date of the analysis. The solid phase extraction method used to prepare the water samples for analysis exists as a stand-alone extraction method (DV-OP-0019).

[5] An MDL is a measurement used by a laboratory to determine specific minimum detection capabilities for a particular method. It is the minimum concentration of a substance that can be measured and reported with 99% confidence that the true value is greater than zero (See 40 CFR 136 Appendix B for procedure).

PFOA is 5 ng/L. Eurofins Eaton Analytical (formally MWH Labs) also offers the method MWH PFC which analyzes PFOA, PFOS and PFBA using the same reporting limits as in MWH PFC Extra.

Underwriters Laboratory

Several water systems used Underwriters Laboratory for their follow up testing. PFC proprietary method L400 was developed by Underwriters Laboratory and was capable of reporting both PFOA and PFOS to 10 ng/L. (The official name for L400 was UL-SBN-LCMS-013-03 and subsequently, 06-LO-S0442). Underwriters Laboratory was certified by NJDEP OQA for analysis of PFOA and PFOS by L400 until 2014 when Eurofins purchased the South Bend, Indiana Underwriters Laboratory. Eurofins Eaton Indiana no longer utilizes the Underwriter's L400 method.

As a result of the of the NJDEP 2006 and 2009 PFC studies, those water systems found to have PFOA and/or PFOS in their drinking water were requested by the NJDEP to conduct follow-up testing within each quarter of the calendar (or every three months). Letters from NJDEP to water systems following the 2006 PFC study included a recommendation to use a method approved by the NJDEP OQA (DSAM), a PFOA RL of 10 ng/L or lower and a low PFOA calibration standard of 4 ng/L. Letters sent to water systems following the 2009 PFC study did not specify reporting limits however, the NJDEP's PFOA health-based level of 40 ng/L developed by the NJDEP Office of Science in 2007 was provided as guidance.

Table 2 provides a summary of PFOA laboratory information obtained from the NJDEP PFC database for samples collected between June 2006 and April 2016. It includes analytical methods, RLs, MDLs, and the number of analyses performed with those RLs/MDLs by three laboratories.

Table 2.
Laboratories/Methods with Reporting Limits and MDLs from the NJDEP PFC Database
PFOA Data from the NJDEP Historical Database[6] June 2006 to April 2016

Laboratory	Method	Reporting Limit (ng/L)	MDL (ng/L)	# of Analyses
Test America Denver	SOP DEN-LC-0012	10	NP, 1.1, 1.9, 2.1	112
		15*	NP, 1.1, 2.1, 2.6, 3.1, 3.6	123
Underwriters Laboratories	L400	10	NP	66
MWH Laboratories/Eurofins Eaton Analytical CA	EPA 537 PFAA	2.5	NP	205
	MWH PFC EXTRA	5	NP	266
	MWH PFC	5	NP	2

NP =Information not provided in the PFC database.
* The most frequent reporting limit from Test America Denver (see Table 1).

[6] The laboratories presented in this table are those that analyzed samples for the NJDEP PFC occurrence studies and those that analyzed follow up samples for those water systems that had detections of PFCs in the NJDEP occurrence studies. This does not include all laboratories capable of performing PFC analysis, only those that analyzed New Jersey public water systems samples during June 2006-April 2016.

2) OQA Sanctioned Methods and Laboratories Certified to Report PFOA in Drinking Water

There are currently three drinking water analytical methods that have been approved by NJDEP OQA as DSAMs for the analysis of PFOA. These consist of EPA 537 and two proprietary methods: DV-LC-0012 Rev 12 developed by Test America-Denver and MWH SOP-HPLC12 Rev 4.0 developed by Eurofins Eaton Analytical (California). The three DSAMs are similar in that they utilize solid phase extraction, isotope dilution and electrospray ionization with LC/MS/MS. Eurofins Eaton Analytical (California), Eurofins Lancaster Laboratories Environmental, Eurofins Eaton Analytical (Indiana), SGS Accutest-Orlando and Test America- Sacramento are certified for analysis of PFOA in drinking water using EPA 537.

Table 3 below lists the six laboratories that are currently certified by the NJDEP OQA to analyze and report PFOA in drinking water with their corresponding NJDEP approved analytical methods (DSAM), RLs and MDLs. Eurofins Lancaster Laboratories Environmental (Pennsylvania), Eurofins Eaton Analytical (Indiana), Test America Sacramento (California) and SGS Accutest-Orlando (Florida) were contacted for their MDLs and RLs. MDLs were not always provided since it is not required with EPA 537.

While PFOA was still an emerging contaminant of concern and EPA 537 was in development, the NJDEP OQA reviewed various proprietary analytical methods and approved them as DSAMs. The vetting and certification by the OQA of a PFC method was necessary in order for NJDEP to initiate the sampling for the 2006 PFC study. Since 2006, various laboratories have obtained OQA approval of their proprietary methods as DSAMS for the analysis of PFOA and other PFCs in New Jersey drinking water samples. After EPA 537 was published, a number of laboratories obtained OQA certification for EPA 537. Should the EPA regulate PFOA, only those PFOA analytical methods approved by the EPA would be allowed for the analysis of regulatory drinking water samples. Laboratories preferring to use their proprietary PFC method for regulatory purposes would then be required obtain EPA approval for their proprietary method as an alternate test method (ATP).

3) UCMR3 EPA Approved Laboratories for PFC Analysis

The Unregulated Contaminant Monitoring Rule (UCMR) is a national monitoring program administered every five years by the EPA in which community water systems serving 10,000 and over throughout the country are required to test their drinking water for a specific set of 30 unregulated contaminants. The UCMR analytes are usually chosen from the corresponding EPA Candidate Contaminant List (CCL) as was the case with the selection of most of the UCMR3 analytes from the CCL3. Besides PFOA and PFOS, the UCMR3 (third list of UCMR contaminants) includes perfluorononanoic acid (PFNA), perfluorohexane sulfonate (PFHxS), perfluoroheptanoic acid (PFHpA), and perfluorobutane sulfonate (PFBS) in the List 1 Assessment Monitoring part of the required monitoring. These four additional PFCs were not selected from the CCL3.

Table 3.
Laboratories Certified by NJDEP Office of Quality Assurance for Analysis of PFOA in Drinking Water with their NJDEP Department Sanctioned Analytical Method (DSAM) Reporting limits and MDLs

OQA Certified Lab	Location (State)	DSAM	Reporting Limit (ng/L)	MDL (ng/L)
Eurofins Eaton Analytical, Inc.	CA	EPA 537	2.5	0.23
		User Defined MWH SOP-HPLC 12, Rev 4.0 (MWH PFC EXTRA)	5	0.327
Eurofins Eaton Analytical, Inc.	IN	EPA 537	20	NR
Eurofins Lancaster Laboratories Environmental	PA	EPA 537	2	1
SGS Accutest Inc. - Orlando	FL	EPA 537	20	8
Test America-Denver	CO	User Defined DV-LC-0012 Rev 12	20	9.79
Test America-Sacramento	CA	EPA 537	20	NR

NR=Not Required.

The Testing Subcommittee identified the UCMR3 participating laboratories as potential sources of data to consider in the PFOA PQL determination, as long as these laboratories were able to provide better performance data than was required for UCMR3. As part of the UCMR3 rule, laboratories performing analyses for any of the UCMR3 contaminants were required to obtain approval from the EPA. Among other requirements, this approval included proficiency testing and on-site audits. The laboratories that applied for UCMR3 analyses were not required to have NELAP or state certification for the analytical methods used for the UCMR3. The EPA established the specific analytical methods to be used for analyzing the UCMR3 contaminants. The PFOA analysis, which also included the analysis of the other five PFCs mentioned above, was performed exclusively with EPA Method 537 version 1.1 for the UCMR3.

EPA 537 version 1.1, "Determination of Selected Perfluorinated Alkyl Acids in Drinking Water by Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS)" was developed by the EPA. The quantitation level term, Minimum Reporting Level (MRL) used in EPA 537, was defined as "the minimum concentration that can be reported as a quantitated value for a method analyte in a sample following analysis." The MRL could be no lower than the concentration

of the lowest calibration standard for that analyte and could only be used if acceptable quality control (QC) criteria for this standard were met. The MRL used in EPA 537 is a term that is more specific than a RL due to the additional requirement of meeting the verification criteria with a one-time demonstration of capability step in Section 9.2.5 of EPA 537. Laboratories using EPA 537 could not report results to a specific MRL unless it was verified with this procedure. Although the EPA required an MRL of 20 ng/L for UCMR3 reporting, a laboratory running EPA 537 had the option of using a different MRL provided that they met the QC requirements for reporting at that MRL. For example, Eurofins Eaton Analytical in Monrovia, California could report PFOA either at 2.5 ng/L or 20 ng/L depending on client requests.

The EPA's MRL of 20 ng/L for PFOA was statistically determined from three laboratories' Lowest Concentration MRLs (LCMRL) which were generated using the procedure described in the Environmental Science Technology article, *Statistical Procedures for Determination and Verification of MRLs for Drinking Water Methods* (Winslow et. al., 2006). The LCMRL is defined as the lowest spiking concentration at which recovery of between 50 and 150% is expected 99% of the time by a single analyst. The EPA determines an MRL using a Bayesian bootstrap of the LCMRL estimator using the LCMRL study data from each of several experienced drinking water laboratories. The Bayesian bootstrap replicates that were generated from each laboratory's data, serve to estimate the distribution of estimated LCMRL values that each laboratory might generate on repeated performance of the LCMRL study. The distribution of pooled Bayesian bootstrap replicates, generated from the LCMRL study data from a sample of experienced drinking water laboratories, approximates the distribution of estimated LCMRL values which might be generated from the *population* of experienced drinking water laboratories. The EPA statistical software, the LCMRL Calculator, performing this process was designed such that the MRL would be an estimate of the LCMRL that is achievable with 95% confidence by a capable analyst/laboratory at least 75% of the time.[7] For PFOA, three laboratory LCMRLs of 18 ng/L, 5.4 ng/L and 0.54 ng/L were integrated into the EPA statistical software resulting in the MRL of 20 ng/L.

The EPA's goal in developing this MRL was to establish a reporting concentration where laboratories across the nation would be able to reliably analyze PFCs for the UCMR3. When discussing the MRLs for the six UCMR3 PFCs, the EPA states in the May 2, 2012 Federal Register, "While particular laboratories may be able to meet MRLs lower than those proposed, the selected MRLs reflect those achievable by the national array of laboratories that support the program."

On behalf of the Testing Subcommittee, the NJDEP conducted a phone inquiry of those EPA laboratories approved for PFC analysis for the UCMR3. The intention of this inquiry was to determine if any of these laboratories with experience analyzing PFCs are also reporting PFOA lower than 20 ng/L for purposes other than the UCMR3. Of the 20 UCMR3 participating laboratories that were solicited for information, five stated that they are reporting PFOA lower than 20 ng/L and five stated that they do not report lower than 20 ng/L. Two labs did not respond. Of the remaining eight labs, five stated either that they were in the process of lowering the reporting

[7] Technical Basis for the Lowest Concentration Minimum Reporting Level (LCMRL) Calculator (EPA 815-R-11-001). http://water.epa.gov/scitech/drinkingwater/labcert/analyticalmethods_ogwdw.cfm

limit or were confident that they could achieve lower reporting limits if client requested and three actually conducted low level calibrations or MRL confirmations in response to our inquiry.

Those UCMR3 participating laboratories reporting PFOA less than 20 ng/L are listed in Table 4. Although these laboratories use EPA 537 for the UCMR3, they may use a modified EPA 537 method or a proprietary method for reporting PFOA to lower concentrations.

Table 4.
UCMR3 Laboratories using PFC Analytical Methods with Reporting Limit or Lowest Calibration Standard Lower than 20 ng/L

UCMR3 Participating Laboratory	State	Analytical Method	Reporting Limit (ng/L)	Lowest Calibration Standard	MDL (ng/L)
American Water Central Laboratory	IL	EPA 537	10	NA[8]	0.382
Columbia Analytical Services ALS	WA	Modified EPA 537	2	2	0.27
Eurofins Eaton Analytical	CA	EPA 537	2.5	2.5	0.23
Eurofins Eaton Analytical	CA	MWH-PFC Extra	5	5	0.550
Orange County Water District Advanced Water Quality Assurance Lab	CA	EPA 537	20	10	NR
Pace Analytical Services-Ormond Beach	FL	S-Fl-O-045 Rev.00	2	2	0.67
State Hygienic Laboratory-Coralville	IA	EPA 537	15	6	NR
Test America- Sacramento	CA	WS-LC-0025	2	1	0.748
Weck Laboratories	CA	Modified EPA 537	5	5	1.81

NA=Not Applicable; NR=Not Required.

This information supports the conclusion that the current reporting limits being used for PFOA are mostly client driven and that if needed, many of these laboratories would be able to accommodate a lower reporting limit than the MRL required by the UCMR3.

[8] American Water Central laboratory conducted an MRL Confirmation Study found in Section 9.2.5 of EPA 537 to prove that they can use an MRL of 10 ng/L. Since that reporting limit had not been requested by any clients, they had not pursued changing their calibration curve and other QAQC requirements for reporting to 10 ng/L.

PQL Determination

In developing the PQL for PFOA, the DWQI Testing Subcommittee considered the RLs, lowest calibration standards and MDLs from laboratories that meet at least one of the criteria below:

1) The laboratories that analyzed water samples for PFOA during the NJDEP 2006 and 2009 studies.;
2) The laboratories must use PFOA methods that have been vetted by the NJDEP OQA, NELAP or EPA; and
3) The laboratories must be EPA UCMR3 approved and demonstrated capability of reporting PFOA lower than the UCMR3 MRL of 20 mg/L using EPA 537 or modifications of EPA 537.

Table 5 consolidates the RL, the lowest calibration standard and MDL data from Tables 2, 3 and 4. Table 2 consists of laboratories that have generated PFOA data that had been entered into the NJDEP's PFC Database. Table 3 consists of laboratories certified by NJDEP OQA for PFOA in drinking water and Table 4 consists of EPA UCMR3 approved laboratories for EPA 537 that are capable of reporting to a lower MRL or RL with either EPA 537, a modification of EPA 537 or a proprietary method. Eurofins Eaton Analytical (Indiana) and Test America-Denver which report to 20 ng/L are included in Table 5. They are included in the consideration of the PQL because water systems that are monitoring for PFCs are directed to the list of OQA certified laboratories which include these laboratories. The NJDEP has been recommending a reporting limit of 10 ng/L for PFOA, however, this was not a requirement.

Determination of the PQL using MDLs

The determination of the PQL using MDLs requires a sample size of at least five MDLs from which to obtain an inter-laboratory MDL value. The individual MDL value from each laboratory for a given method is used to obtain a median MDL value as a representative inter-laboratory MDL. This inter-laboratory MDL is then multiplied by a factor of five. In 1993, a research project was conducted by NJDEP to determine if the MDL multiplied by a certain factor could yield a supportable PQL value. The outcome of this research concluded that a factor of 4, 5 or 6 could be used to derive a PQL (Eaton, et. al., 1993). In 1994, the Testing Subcommittee chose to use a multiplier of five to determine the PQLs generated as part of the NJ DWQI MCL contaminant recommendations. This multiplier approach for determination of a PQL is also consistent with that outlined in the Ground Water Quality Standards (N.J.A.C. 7:9-6).

For PFOA, the Testing Subcommittee was able to derive a PQL from a sample size of 13 MDLs, from ten laboratories and eight different methods. As seen in Table 6 the median MDL value of these 13 MDLs is 1 ng/L. This median value 1 when multiplied by 5 is 5 ng/L.

Table 5.
Consolidation of Laboratory Performance Data Meeting Established Criteria for Determining the PQL[9]

Laboratory	Method	Reporting Limit (ng/L)	Lowest Calibration Standard (ng/L)	MDL (ng/L)
American Water Central Laboratory	EPA 537	10	NA	0.382
Columbia Analytical Services Washington	Modified EPA 537	2	2	0.27
Eurofins Eaton Analytical California	Proprietary MWH PFC EXTRA	5	5	0.550
Eurofins Eaton Analytical California	EPA 537	2.5	2.5	0.23
Eurofins Eaton Analytical Indiana	EPA 537	20	20	NR
Eurofins Lancaster Laboratories Environmental	EPA 537	2	2	1
Orange County Water District Advanced Water Quality Assurance Laboratory	Modified EPA 537	10	10	NP
Pace Analytical Services Inc. Florida	Modified EPA 537	2	2	0.67
SGS Accutest – Orlando	EPA 537	20	20	8.0
State Hygienic Laboratory-Coralville	EPA 537	15	6	NR
Test America-Denver	DV-LC-0012 Rev 4	10	4	2
Test America-Denver	DV-LC-0012 Rev 8	15	4	1.1
Test America-Denver	DV-LC-0012 Rev 12	20	4	9.79
Test America-Sacramento	EPA 537	20	20	NR
Test America-Sacramento	Proprietary WS-LC-0025 Rev 1.2	2	1	0.748
Underwriters Laboratory	L400	10	5	2.9
Weck Labs	Modified EPA 537	5	5	1.81

NA=Not Applicable; NP=Not Provided; NR=Not Required.

[9] Table 5 is a consolidation of Table 2: PFOA Reporting Limits and MDLs from Laboratory Data in the NJDEP PFC Database, Table 3: Laboratories Certified by NJDEP Office of Quality Assurance for Analysis of PFOA Reporting Limit and MDL Information Acquired by Phone or Email (2015) and Table 4: UCMR3 Laboratories with Reporting Limits Lower than 20 ng/L.

Table 6.
Laboratories Used for PQL Calculation in order of Increasing MDL Values

Laboratory	Analytical Method	MDL (ng/L)
Eurofins Eaton Analytical CA	EPA 537	0.23
Columbia Analytical Services	Modified EPA 537	0.27
American Water Central Laboratory	EPA 537	0.382
Eurofins Eaton Analytical CA	Proprietary MWH PFC EXTRA	0.550
Pace Analytical Services, Inc.	S-FL-O-045 Rev.00	0.67
Test America-Sacramento	Proprietary WS-LC-0025 Rev 1.2	0.748
Eurofins Lancaster Laboratories Environmental	EPA 537	1
Test America-Denver	DV-LC-0012 Rev 8	1.1
Weck Laboratories	Modified EPA 537	1.81
Test America-Denver	DV-LC-0012 Rev 4	2
Underwriters Laboratory	L400	2.9
SGS Accutest – Orlando	EPA 537	8
Test America-Denver	DV-LC-0012 Rev 12	9.79
Median of the MDLs		**1**
PQL = Median of MDLs x 5		**5**

Determination of PQL Using Reporting Limits or Lowest Calibration Standards

Analytical terminology based on multiples of the standard deviation such as the MDL, does not account for non-ideal instrumental and analytical occurrences of interference, analyte degradation, matrix enhancement and background contamination which can, particularly at low concentrations, contribute to false positive and false negative results. The MRL in EPA 537 differs from an MDL in that it accounts for both accuracy and precision as a quantitation level. Laboratories using EPA 537 report results to a MRL which is a concentration equal to or greater than the lowest calibration standard, but must also meet the QC criteria at Section 9.2.5 of EPA 537. This criterion is a verification of laboratory proficiency at the laboratory's designated MRL. EPA 537 does not require laboratories to perform the previously discussed LCMRL procedure, but does require this less rigorous MRL confirmation. Both the LCMRL procedure and the confirmation MRL procedure account for the combined effect accuracy and precision have on these quantitation levels.

An MRL can be established either by the laboratory for their own specific purpose or by a regulatory agency as with the required MRL of 20 ng/L for the EPA UCMR3 program. Since EPA 537 describes the MRL as the lowest analyte concentration that meets the Data Quality Objectives developed for the intended use of this method, the MRL would be an important factor in determining the PQL for PFOA. It would follow that, in addition to using inter-laboratory MDLs, the PQL should be assessed by considering the MRLs used by these laboratories. Of the ten laboratories that use either EPA 537 or a modified EPA 537, eight have performed the method's MRL confirmation procedure.

In most cases proprietary methods such as those sanctioned by the NJDEP OQA were developed prior to the publication of EPA 537 and do not include the MRL confirmation procedure. It was helpful to the Testing Subcommittees that several laboratories not certified by the NJDEP OQA provided details on their proprietary methods even though they were not obligated to do so. Each of the proprietary methods required confirmation of the reporting limit within the analytical batch analysis.

If different than the MRL or reporting limit, the laboratories' lowest calibration standard was considered in the PQL assessment. As previously stated since the RLs are mostly client driven it is not obvious that greater sensitivity can be achieved. For this reason, in cases where the lowest calibration standard was lower than the reporting limit, the lowest calibration standard was used in lieu of the reporting limit when deriving the PQL. Three different reporting limits were considered for Test America-Denver since the data was generated using different versions of the original method. In Table 7 the lower of the RL or the lowest calibration standard was used to determine the median. This median was determined to be 5. Likewise, the calculated average (mean) was determined to be 7.2 ng/L.

The data in Table 7 indicates that reporting limits of 2 ng/L are achievable. In considering the PQL, the Testing Subcommittee was aware of background contamination issues with PFOA.

Bootstrap Estimate of a Confidence Interval of a Mean

Basic statistics were used in determining the median from the 13 MDL values in Table 6. The minimum criteria of five laboratories was met for the PQL calculation using the median of the MDLs and the value was determined to be 5 ng/L following the convention of multiplying the inter-laboratory MDL value of 1 ng/L by a factor of five (5).

Another approach that has been used most recently by the EPA for LCMRL range calculation is a statistical technique called "Bootstrap Estimate of a Confidence Interval of the Mean." This technique was applied to generate a normal distribution and associated 95 % upper and lower confidence intervals from the inter-laboratory MDL values from Table 6 and the RLs or the lowest calibration standard from Table 7.

Table 7.
Reporting Limit and Lowest Calibration Standard for
Each PFOA Laboratory/Method Combination

Laboratory	State	Method	Reporting Limit (ng/L)	Lowest Calibration Standard (ng/L)
Eurofins Eaton Analytical	IN	EPA 537	20	20
SGS Accutest- Orlando	FL	EPA 537	20	20
Test America-Sacramento	CA	EPA 537	20	20
American Water Central Laboratory	IL	EPA 537	10	NA
Orange County Water District Advanced Water Quality Assurance Lab	CA	EPA 537	20	10
State Hygienic Laboratory Coralville	IO	EPA 537	15	6
Eurofins Eaton Analytical	CA	MWH-PFC	5	5
Weck Laboratories	CA	Modified EPA 537	5	5
Underwriters Laboratory	IN	L400	10	5
Test America-Denver	CO	DV-LC-0012 REV 12	20	4
Test America-Denver	CO	DV-LC-0012 REV 8	15	4
Test America-Denver	CO	DV-LC-0012 REV 4	10	4
Eurofins Eaton Analytical	CA	EPA 537	2.5	2.5
Columbia Analytical Services	WA	EPA 537	2	2
Eurofins Lancaster Laboratories Environmental	PA	EPA 537	2	2
Pace Analytical Services	FL	S-FL-O-045 Rev.00	2	2
Test America-Sacramento	CA	WS-LC-0025 Rev 1.2	2	1
Mean of underlined values[10]	**7.2**			
Median of underlined values	**5**			

NA=Not Applicable

[10] The underlined values are the lower of the reporting limit or MRL and the lowest calibration standard that was used in the 17 lab-method combinations to determine the mean and the median.

Bootstrap Analysis using Inter-laboratory MDLs

A bootstrap analysis of the MDL data presented in Table 6 resulted in a distribution where the upper confidence limit for MDL values reported by laboratories was 4.1 ng/L. The results of this data analysis are shown below in Table 8.

Table 8.
Bootstrap Estimate of Inter-laboratory MDLs

Lower Confidence Limit (ng/L)	Mean (ng/L)	Upper Confidence Limit (ng/L)	Confidence Level Range	Number of Randomly Selected Values[11]
0.9	2.3	4.1	95%	2000

Two laboratories reported MDL values above the upper confidence limit of 4.1 ng/L and were not included in a second iteration of the bootstrap analysis. The second iteration bootstrap analysis resulted in a distribution where the upper confidence limit was 1.6 ng/L. This data are presented in Table 9.

Table 9.
Second Iteration: Bootstrap Estimate of Inter-laboratory MDLs
(Excluding two laboratories with MDLs above the UCL of 4.1 ng/L)

Lower Confidence Limit (ng/L)	Mean (ng/L)	Upper Confidence Limit (ng/L)	Confidence Level Range	Number of Randomly Selected Values[11]
0.6	1.1	1.6	95%	2000

One laboratory reported an MDL above the upper confidence limit of 1.6 ng/L value and was not included in a third iteration of the bootstrap analysis. The third iteration bootstrap analysis resulted in a distribution where the upper confidence limit was 1.2 ng/L. These data are presented in Table 10.

Table 10.
Third Iteration: Bootstrap Estimate of Inter-laboratory MDLs
(Excluding one laboratory with an MDL above the UCL of 1.6 ng/L)

Lower Confidence Limit (ng/L)	Mean (ng/L)	Upper Confidence Limit (ng/L)	Confidence Level Range	Number of Randomly Selected Values[12]
0.5	0.9	1.3	95%	2000

[11] The Bootstrap Technique uses a default value of 2000 iterations to calculate the statistics presented.
[12] The Bootstrap Technique uses a default value of 2000 iterations to calculate the statistics presented.

Using the 95% upper confidence level from the bootstrap method, a PQL value (5 times the Upper Confidence Limit of the MDL) can be calculated following the regulatory convention that has been used by the NJDEP in the past. This value would be 1.3 ng/L x 5 which would be 6.5 ng/L. This MDL value and the PQL calculated from this value is achievable by 95% of the laboratory community that voluntarily provided the performance data presented in this recommendation.

Bootstrap Analysis using MRLs or Reporting Limits

To incorporate more recent techniques of calculating quantification levels, the bootstrap technique can also be applied to evaluate the consistency of the 17 laboratory reporting limits (RLs) or lowest calibration standards found in Table 7. This generated distribution of 2000 randomly selected values produced an upper confidence limit of 10.3 ng/L as a reporting level that 95% of the laboratory community should be able to achieve. The data generated by this bootstrap analysis is in Table 11.

Table 11.
Bootstrap Estimate of Reporting Levels or Lowest Calibration Standards

Lower Confidence Limit (ng/L)	Mean (ng/L)	Upper Confidence Limit (ng/L)	Confidence Level Range	Number of Randomly Selected Values
4.4	7.2	10.3	95%	2000

Three laboratories from Table 7 have RL values above the upper confidence level of 10.3 ng/L. These three laboratories reported RL values and lowest calibration standards information equivalent to the requirements of the UCMR3; the remaining 14 laboratories provided data to demonstrate performance better than that required of the UCMR3. Therefore, because these three laboratories have RL values outside of the 95% confidence interval and did not report their lowest calibration standard information as less than their RL, the RL values were excluded and the statistical analysis was rerun, producing the following information in Table 12.

Table 12.
Second Iteration: Bootstrap Estimate of Reporting Levels or Lowest Calibration Standards
(Excluding three laboratories with Reporting Levels above the Upper Confidence Level of 10.3 ng/L)

Lower Confidence Limit (ng/L)	Mean (ng/L)	Upper Confidence Limit (ng/L)	Confidence Level Range	Number of Randomly Selected Values
3.4	4.6	6.0	95%	2000

This bootstrap analysis generated an upper confidence limit of 6.0 ng/L. This distribution shows that 95% of the laboratory community can achieve a RL level of 6 ng/L. This value of 6 ng/L agrees closely with:

1) the PQL value of 5 ng/L derived from the median of the MDLs from 13 laboratories (Table 6),

2) the PQL value of 7.2 ng/L as the average (or mean) of the17 reporting limits or lowest calibration standards used by actual laboratories (Table 7),

3) the PQL value of 5 ng/L derived from the median of 17 reporting limits or lowest calibration standards used by actual laboratories (Table 7),

4) the PQL value of 6.5 ng/L derived from the bootstrap analysis of the MDLs multiplied by 5 (Table 10), and

5) the PQL value of 6.0 ng/L derived from the bootstrap analysis of the RLs (Table 12).

The median of the values above is 5.9 ng/L; when rounded to one significant figure, the value is 6 ng/L.

Summary and Recommendations

The decision by the Drinking Water Quality Institute to recommend an MCL for perfluorooctanoic acid (PFOA) required the Testing Subcommittee to develop a drinking water Practical Quantitation Limit (PQL) for PFOA. This PQL would then be used in conjunction with the information generated by the Health Effects Subcommittee and Treatment Subcommittee in recommending the PFOA MCL.

The three Drinking Water Quality Institute Subcommittees were tasked with developing values and researching treatment options for PFOA at the same time, therefore a drinking water Health-based MCL was unavailable to the Testing Subcommittee as guidance for determining analytical sensitivity requirements. As a result, several approaches were used to derive a PQL and the resulting PQLs from those approaches were considered in the final determination of the PQL. MDLs from 13 laboratories were used in the determination of the PFOA PQL and determine the PFOA PQL which included those laboratories that generated PFC data found in the NJ PFC database, the New Jersey Office of Quality Assurance certified laboratories and a subset of UCMR3 participating laboratories that analyze and report PFOA lower than the UCMR3 MRL of 20 ng/L. The median value of the MDL values (1 ng/L) multiplied by the factor of 5 resulted in a value of 5 ng/L and a calculated PQL of 5 ng/L. In addition to using the MDLs for determining the PQL, the median value of the lower of the MRLs or minimum reporting limits and lowest calibration standards for the 17 laboratory/method combination of performance data resulted in a PQL value of 5 ng/L. The "Bootstrap Estimate of a Confidence Interval of a Mean" was used to confirm that the calculated values were consistent with the statistically derived values for a PFOA PQL.

The Testing Subcommittee is basing the PQL recommendation to the DWQI on the MRL, using either the reporting limit or lowest calibration standard; whichever is lower. The Testing Subcommittee is not recommending a PQL based on the MDL because the MDL is a statistical value while the others are actual concentrations verified within the analysis. The RLs of the laboratories performing PFOA analysis, however, may be higher than what the laboratory is truly capable of achieving since performance data on emerging contaminants such as PFOA is largely client-driven.

For PFOA, the Testing Subcommittee recommends that the PQL be that derived using the bootstrap upper confidence limit of the RL to account for the lack of laboratory performance data.

Table 13.
Summary of approaches for calculating the PFOA PQL

PQL Approach	Value (ng/L)
Mean of RL (Table 7)	7.2
Median of RL (Table 7)	5.0
Bootstrap Upper Confidence Limit of RL or lowest calibration standard (Table 12)	6.0

The median of the values in Table 13 above that summarizes the approaches used for the PQL derivation and the PQL values derived from each is 6.1 ng/L; when rounded to one significant figure, the value is 6 ng/L. Therefore, the Testing Subcommittee recommends a PQL of 6 ng/L for PFOA to the Drinking Water Quality Institute.

Literature Cited

EPA 815-R-05-006. Statistical Protocol for the Determination of the Single Laboratory Lowest Concentration Minimum Reporting Level and Validation of laboratory Performance at or Below the Minimum Reporting Level, EPA Washington, D.C. November 2004.

EPA 600 R-08 092. Method 537 Determination of Selected Perfluorinated Alkyl Acids in Drinking Water by Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry (LC.MS.MS) Version 1.1, , Shoemaker, J.A.; Grimmett, P.E.; Boutin, B.K. September 2009.

EPA 815-R-11-001. Technical Basis for the Lowest Concentration Minimum Reporting Level (LCMRL) Calculator, EPA Washington, D.C. December 2010.

Eaton, Dr. Andrew, Principal Investigator, *Evaluation of PQL Determination Methodologies*, Division of Science and Research Final Report Contract P33501, 1993.

NJ Drinking Water Quality Institute, September 26, 1994, Maximum Contaminant Level Recommendations for Hazardous Contaminants in Drinking Water, NJ DWQI, 1994.

New Jersey Department of Environmental Protection, Determination of Perfluorooctanoic Acid (PFOA) in Aqueous Samples, Final Report. January 2007.

New Jersey Department of Environmental Protection, Occurrence of Perfluorinated Chemicals in Untreated Drinking Water Sources, Final Report. April 2014.

New Jersey Department of Environmental Protection, Office of Science. *Summary of the Basis for A Draft Interim Specific Ground Water Quality Criterion for Perfluorononanoic* Acid (*PFNA, C9)*, Gloria B. Post, Ph. D. March 14, 2014.

Oxenford, J.L.; McGeorge, L.J.; Jenniss, S.W. *Determination of Practical Quantitation Levels for Organic Compounds in Drinking Water* J. American Water Works Assoc. 1989, 149-153.

Post, G.B., Louis, J.B., Lippincott, R.L., and Procopio, N.A. *Occurrence of perfluorinated chemicals in raw water from New Jersey public drinking water systems*. Environ. Sci. Technol. 2013, 47, 13266-75.

Sanders, P.F.; Lippincott, R. L.; Eaton, A. *A Pragmatic Approach for Determining Quantitation Levels for Regulatory Purposes*, Proceedings of the Water Quality Technology Conference, American Water Works Association, Denver, Co. 1996 Vol 2.

Winslow, S.D; Martin J.J.; Hallberg, G.R.; Munch, D.J.; Frebis, C.P.; Hedrick, E.J.; Krop, R A.; *Statistical Procedures for Determination and Verification of Minimum Reporting Levels for Drinking Water Methods* Environ. Sci. Technol. 2006, 40, 281-288.