NJ Drinking Water Quality Institute
Testing Subcommittee

Report on the Development of a Practical Quantitation Level for Perfluorononanoic Acid in Drinking Water

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Testing Subcommittee Members:
Bahman Parsa, Ph.D., Chair
Sandra Krietzman
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
Perfluorononanoic Acid in Drinking Water

Background

The New Jersey Department of Environmental Protection (NJDEP) became aware of perfluorinated
compounds (PFC) in New Jersey drinking waters in 2006, when the NJDEP conducted a study of
New Jersey water systems to determine the occurrence of perfluorooctanoic acid (PFOA) and
perfluorooctane sulfonic acid (PFOS) in wells and surface waters that are sources of drinking water.
PFOA and PFOS were detected in 65% and 30%, respectively, of 23 New Jersey public drinking
water systems sampled in 2006. A PFC follow-up study was conducted in 2009 to determine the
occurrence of PFOA, PFOS and eight additional PFCs in drinking water sources throughout New
Jersey and included only untreated water samples, in contrast to the 2006 study which included
samples from both raw (untreated) and treated water sources. Between one and eight PFCs were
detected in 21 of 30 public water system samples at total PFC concentrations of 5-174 nanograms
per liter (ng/L, or parts per trillion). Perfluoronanoic acid (PFNA) was detected more frequently
and at higher concentrations than in raw or finished drinking water elsewhere, and it was found at
several sites as the sole or predominant PFC (Post et al., 2013).

In 2014, the Drinking Water Quality Institute (DWQI) was charged with recommending a Maximum
Contaminant Level (MCL) for perfluoronanoic acid (PFNA) in drinking water to the Commissioner
of the New Jersey Department of Environmental Protection (NJDEP). The DWQI is an advisory
panel comprised of 15 members from academia, regulated water systems, governmental agencies,
and public health experts that make recommendations concerning the regulation of contaminants
in drinking water. 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
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. This 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 Health Effects Subcommittee. The Testing
Subcommittee’s role in the recommendation of a PFNA MCL was to identify acceptable methods for
PFNA analysis and to develop a PQL for PFNA.

In determining the availability of analytical methods with adequate sensitivity, the Testing
Subcommittee queried the existing NJDEP drinking water PFC database for PFNA data from water
samples collected from September 2009 through August 2014. The NJDEP PFC database had been
established to house PFC laboratory results obtained through the NJDEP Bureau of Safe Drinking
Water’s investigation of PFOA and PFOS and other PFCs, and follow up monitoring performed by
those water systems with detectable PFCs resulting from the PFC studies. The body of PFNA data
obtained through the query provided information pertinent to the PQL development such as 1) the laboratories that generated the PFNA data, 2) the analytical method(s) used by the laboratories and 3) the reporting limit (the minimum concentration by which PFNA is reliably quantitated by the individual laboratory) for each laboratory and method combination.

The NJDEP PFC database contains 313 PFNA results, 99% of which were generated by MWH Laboratories (which became Eurofins Eaton Analytical in June 2012), and less than 1% that were analyzed by Test America-Denver. Both laboratories are certified by the NJDEP Office of Quality Assurance (OQA). For the initial PFOA study in 2006, the NJDEP contracted with Severn Trent Laboratory since their proprietary method for PFOA and PFOS analysis was reviewed and approved by the NJDEP Office of Quality Assurance as a Department Sanctioned Analytical Method (DSAM) and met the reporting limits required by the NJDEP Bureau of Safe Drinking Water (BSDW) at that time (10 ng/L). The Severn Trent method did not include PFNA, among other PFCs, as target analytes within the method. The MWH Laboratories proprietary method, MWH SOP-HPLC 12 (also referred to as MWH PFC Extra), was used for samples analyzed for the 2009 NJDEP study. This method was approved by OQA and offered lower reporting limits for the PFCs of concern. The MWH PFC Extra method included the following PFCs: perfluorobutanoic acid (PFBA), perfluorobutane sulfonate (PFBS), perfluoropentanoic acid (PFPA), perfluorohexanoic acid (PFHxA), perfluorohexane sulfonate (PFHxS), perfluorooctanoic acid (PFOA), perfluorooctane sulfonate (PFOS), perfluorononanoic acid (PFNA), and perfluorodecanoic acid (PFDA). The proprietary method DV-LC-0012 developed by Test America-Denver also includes the analytes perfluorobutane sulfonate (PFBS), perfluorodecane sulfonate (PFDS), perfluoroundecanoic acid (PFUnA), perfluorotridecanoic acid (PFTriA) and perfluorotetradecanoic acid (PFTeA). The reporting limits for the Test America-Denver method are higher than those for MWH PFC Extra, which is presented in Table 1. Because the initial study conducted by NJDEP focused primarily on PFOA and PFOS and there were few PFC methods available at that time, there is less PFNA data compared to that for PFOA and PFOS.

Table 1 provides a summary of the laboratory performance data from the NJDEP PFC database from the three laboratories that analyzed PFNA in drinking water between September 2009 and August 2014. The number of analyses performed, the analytical method, the Reporting Limit(s) and the Method Detection Limit(s) (MDL) are listed.

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1 For purposes of this document the MWH Laboratories and Eurofins Eaton Analytical in Monrovia, California will be considered as the same laboratory.

2 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).
When developing a PQL, the Testing Subcommittee considers analytical methods and laboratory performance. In addition, the Testing Subcommittee considers the Health-based MCL, if available, as the goal of the Testing Subcommittee is to establish the PQL at a level less than the Health-based MCL. However, for PFNA, the Testing Subcommittee did not have access to the Health-based MCL during the development of the PQL. In the absence of a Health-based MCL, the Testing Subcommittee considered the NJDEP’s March 2014 proposed Interim Specific Ground Water Criterion (ISGWC) of 20 ng/L as a target, and throughout the PQL development process, excluded those laboratories with minimum reporting limits greater than 20 ng/L.

As can be seen in Table 1, only three laboratories submitted data to New Jersey for PFNA 2009-2014. The Testing Subcommittee needed to review analytical information from other laboratories performing PFC analyses. In considering other sources, it was necessary to adhere to the following criteria established by the Testing Subcommittee. These criteria were:

1) Laboratories must be drinking water laboratories certified by NJDEP OQA, NELAP, or EPA.

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Table 1
PFNA Data from the NJDEP Historical Database*3
September 2009 to August 2014

<table>
<thead>
<tr>
<th>Laboratory</th>
<th># of Results</th>
<th>Method</th>
<th>Reporting Limit (ng/L)</th>
<th>MDL (ng/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Test America Denver</td>
<td>2</td>
<td>DEN-LC-0012</td>
<td>40</td>
<td>17</td>
</tr>
<tr>
<td>Test America Denver</td>
<td>2</td>
<td>DEN-LC-0012</td>
<td>38</td>
<td>17</td>
</tr>
<tr>
<td>MWH Laboratories</td>
<td>5</td>
<td>EPA METHOD 537</td>
<td>2.5</td>
<td>Not reported</td>
</tr>
<tr>
<td>MWH Laboratories</td>
<td>160</td>
<td>MWH PFC EXTRA</td>
<td>5</td>
<td>Not reported</td>
</tr>
<tr>
<td>Eurofins Eaton Analytical</td>
<td>53</td>
<td>EPA METHOD 537</td>
<td>2.5</td>
<td>0.35</td>
</tr>
<tr>
<td>Eurofins Eaton Analytical</td>
<td>12</td>
<td>EPA METHOD 537</td>
<td>3</td>
<td>0.4</td>
</tr>
<tr>
<td>Eurofins Eaton Analytical</td>
<td>12</td>
<td>EPA METHOD 537</td>
<td>2.54</td>
<td>0.4</td>
</tr>
<tr>
<td>Eurofins Eaton Analytical</td>
<td>54</td>
<td>MWH PFC EXTRA</td>
<td>5</td>
<td>0.327</td>
</tr>
</tbody>
</table>

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3 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 reported results to the NJDEP during September 2009-August 2014.

4 Upon contacting Eurofins Eaton Analytical, they stated their true MRL and MDL as 2.5 ng/L and 0.35 ng/L, respectively. On various Eurofins EPA Method 537 laboratory reports one or both of these values had been rounded to one significant digit (See Table 1). Therefore, when considering the Eurofins Eaton Analytical (California) MDL and RL for the PQL derivation, only 2.5 ng/L will be used as their MRL and 0.35 ng/L as their MDL.
2) The laboratories must use methods that have been vetted by NJDEP OQA, EPA or analogous certifying body.

3) Only those laboratories using methods with minimum reporting limits lower than the 2014 draft NJDEP Interim Specific Ground Water Criterion (ISGWC) of 20 ng/L for PFNA would be considered.

The federal safe drinking water regulations require that the analysis of regulated contaminants must be performed with EPA approved drinking water methods. The EPA approved methods are subsequently adopted by the NJDEP OQA as DSAM. In studies involving unregulated contaminants of concern, it is preferred, but not required, that the methods used for their analysis be EPA approved methods or NJDEP sanctioned methods. This is especially true for emerging contaminants when approved analytical methods are unavailable at the time when studies are initiated.

For PFNA there are currently four drinking water analytical methods that have been approved by NJDEP OQA as DSAMs. These consist of EPA Method 537 and three proprietary methods, DV-LC-0012 Rev B (Test America-Denver), MWH SOP-HPLC12 Rev 4.0 (Eurofins Eaton Analytical California), and AXYS SOP MLA-060 (Axys Analytical Services). Vista Analytical Laboratory, Eurofins Eaton Analytical (CA), Eurofins Lancaster Laboratories Environmental and Eurofins Eaton Analytical (IN) are certified by NJDEP for PFNA using EPA Method 537. All NJDEP sanctioned methods use the same technique of isotope dilution and electrospray ionization with LC/MS/MS.

Table 2 below lists the six certified laboratories with their corresponding NJDEP approved analytical methods (or DSAM), reporting limits and MDLs. Axys Analytical Services Ltd., Vista Analytical Laboratory, Eurofins Lancaster Laboratories Environmental and Eurofins Eaton Analytical (Indiana) were contacted by phone for their MDLs and reporting limits.

In the Testing Subcommittee’s pursuit to acquire as much data as is available for inclusion in the PFNA PQL determination, the UCMR3 (Unregulated Contaminant Monitoring Rule 3) participating laboratories were identified as a potential source of data. The UCMR3 is a national monitoring program administered by the EPA that requires community water systems (serving 10,000 and over) throughout the country to test their drinking water for a specific set of 30 unregulated contaminants every five years. The current UCMR3 list includes PFNA and five other PFCs in the List 1 Assessment Monitoring part of the required monitoring.

UCMR analytes are usually chosen from the corresponding EPA Candidate Contaminant List (CCL). The CCL is a list developed by EPA based on the adverse health effects and presumed prevalence and magnitude of occurrence data and currently includes over 100 chemical and microbiological contaminants. PFNA was not first listed on the CCL, but was included on the UCMR3 list based on other sources of information and the health-effect evaluation of the contaminant had not been fully developed by the EPA prior to it being included on the UCMR3. Therefore, EPA did not require laboratories participating in the UCMR3 to achieve results at or below a particular health goal.

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5 *Possible Contaminants for Inclusion on UCMR3 – Information Compendium*, EPA 815-B-10-002, December 2010.
Table 2
Laboratories Certified by NJDEP Office of Quality Assurance for Analysis of PFNA Reporting Limit and MDL Information Acquired by Phone or Email (2014)

<table>
<thead>
<tr>
<th>OQA Certified Lab</th>
<th>Location</th>
<th>DSAM</th>
<th>Reporting Limit (ng/L)</th>
<th>MDL (ng/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Test America Denver</td>
<td>CO</td>
<td>DEN-LC-0012</td>
<td>38</td>
<td>17</td>
</tr>
<tr>
<td>Eurofins Eaton Analytical</td>
<td>CA</td>
<td>EPA METHOD 537</td>
<td>2.5</td>
<td>0.35</td>
</tr>
<tr>
<td>Eurofins Eaton Analytical</td>
<td>CA</td>
<td>MWH PFC EXTRA</td>
<td>5</td>
<td>0.327</td>
</tr>
<tr>
<td>Áxys Analytical Services LTD</td>
<td>Canada</td>
<td>MLA-060</td>
<td>1</td>
<td>0.4</td>
</tr>
<tr>
<td>Vista Analytical Laboratory</td>
<td>CA</td>
<td>EPA METHOD 537</td>
<td>2</td>
<td>0.807</td>
</tr>
<tr>
<td>Eurofins Eaton Analytical</td>
<td>IN</td>
<td>EPA METHOD 537</td>
<td>20</td>
<td>2.3</td>
</tr>
<tr>
<td>Eurofins Lancaster Laboratories</td>
<td>PA</td>
<td>EPA METHOD 537</td>
<td>2</td>
<td>1</td>
</tr>
</tbody>
</table>

Laboratories performing analysis of any of the UCMR3 contaminants must obtain approval by the EPA for the analyses, but are not required to be NELAP or state certified. Proficiency testing and on-site audits are among the requirements for obtaining EPA approval for UCMR3 analyses. The EPA determines the methods by which each UCMR3 contaminant must be analyzed. The PFNA (PFC) analysis for the UCMR3 must be performed exclusively with EPA Method 537.

EPA Method 537, “Determination of Selected Perfluorinated Alkyl Acids in Drinking Water by Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS)” was developed and approved by the EPA. The quantitation level term, minimum reporting level (MRL), used in EPA Method 537 is defined as “the minimum concentration that can be reported as a quantitated value for a method analyte in a sample following analysis. This defined concentration can be no lower than the concentration of the lowest calibration standard for that analyte and can only be used if acceptable quality control (QC) criteria for this standard are met.” The MRL used in EPA Method 537 is more than a reporting limit in that it requires a one-time demonstration of capability step that verifies the reporting limit used by the laboratory. This procedure is described in Section 9.2.5 of EPA Method 537.

Specifically for UCMR3 reporting, the EPA requires PFNA data to be reported to a 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. Statistical software was designed so that the MRL would be an estimate of the lowest concentration MRL (LCMRL) that is achievable with 95% confidence by a capable analyst/laboratory at least 75% of
the time. 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.

As part of the MRL development for PFNA, three laboratories each generated a LCMRL 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). These LCMRLs (12 ng/L, 6.7 ng/L and 0.8 ng/L) were integrated into the EPA statistical software resulting in the MRL of 20 ng/L. (The names of the three laboratories that determined the LCMRLs were requested from the EPA however, a response had not been obtained other than a confirmation by the EPA that Eurofins Eaton Analytical (CA) was one of the participating laboratories.) Again, without a PFNA health-based level target for comparison to the PFNA MRL, the UCMR3 laboratories reported the PFNA MRL as 20 ng/L to the EPA.

The Testing Subcommittee considered that among those laboratories with UCMR3 EPA approval, some laboratories may be able to report PFNA concentrations lower than 20 ng/L for purposes other than the UCMR3. Based on this premise, the NJDEP conducted a phone inquiry on behalf of the Testing Subcommittee in which twenty UCMR3 participating laboratories throughout the country were contacted. Four laboratories, Eurofins Eaton Analytical (California), American Water Central Laboratory (Illinois), BSK Associates (California) and Test America-Sacramento (California) are able to report PFNA at concentrations lower than 20 ng/L for purposes other than the UCMR3. In addition, one laboratory, State Hygienic Laboratory Coralville (Iowa) uses a low calibration standard of 6.27 ng/L for PFNA but does not report PFNA lower than 20 ng/L to its clients. Seven laboratories expressed confidence that without working through the method QC, PFNA could be reported in the 5-10 ng/L range and possibility lower. Six UCMR3 participating laboratories stated that they do not report PFNA lower than 20 ng/L. Two laboratories did not respond.

Those UCMR3 participating laboratories with reporting limits lower than 20 ng/L are listed in Table 3 below.

### Table 3

<table>
<thead>
<tr>
<th>UCMR3 Participating Laboratory</th>
<th>State</th>
<th>Analytical Method</th>
<th>Reporting Limit (ng/L)</th>
<th>MDL (ng/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eurofins Eaton Analytical</td>
<td>CA</td>
<td>EPA Method 537</td>
<td>2.5</td>
<td>0.35</td>
</tr>
<tr>
<td>Eurofins Eaton Analytical</td>
<td>CA</td>
<td>Proprietary MWH PFC EXTRA</td>
<td>5</td>
<td>0.327</td>
</tr>
<tr>
<td>Test America Sacramento</td>
<td>CA</td>
<td>Proprietary WS-LC-0025 Rev 1.2</td>
<td>2</td>
<td>0.65</td>
</tr>
<tr>
<td>American Water Central Laboratory</td>
<td>IL</td>
<td>EPA Method 537</td>
<td>1</td>
<td>0.13</td>
</tr>
<tr>
<td>State Hygienic Laboratory-Coralville</td>
<td>IA</td>
<td>EPA Method 537</td>
<td>16</td>
<td>1.39</td>
</tr>
<tr>
<td>BSK Associates</td>
<td>CA</td>
<td>EPA Method 537</td>
<td>10</td>
<td>0.476</td>
</tr>
</tbody>
</table>

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6 *Technical Basis for the Lowest Concentration Minimum Reporting Level (LCMRL) Calculator* (EPA 815-R-11-001).
Besides having EPA UCMR3 approval, Eurofins Eaton Analytical is NELAP accredited through New Jersey for the two methods in Table 3. The proprietary method (WS-LC-0025 Rev.1.2) by which Test America Sacramento can report PFNA lower than 20 ng/L is accredited by the Department of Defense.

For PQL development, the Testing Subcommittee considered NELAP and state accredited laboratories and those with EPA approval for UCMR3 analyzing PFNA using approved (or sanctioned) methods with reporting limits under 20 ng/L. Therefore, the Test America-Denver and Eurofins Eaton Analytical (IN) reporting limit and MDL data (Table 2) were eliminated from consideration because their respective reporting limits exceeded 20 ng/L. Table 4 consolidates the reporting limit and MDL data from Tables 2 and 3.

### Table 4
Consolidation of Laboratory Data Meeting Criteria for Determination of PQL Using MDLs

<table>
<thead>
<tr>
<th>Laboratory/Location</th>
<th>Method</th>
<th>Reporting Limit (ng/L)</th>
<th>MDL (ng/L)</th>
<th>Accreditation</th>
</tr>
</thead>
<tbody>
<tr>
<td>American Water Central Laboratory Illinois</td>
<td>EPA Method 537</td>
<td>1</td>
<td>0.13</td>
<td>UCMR3</td>
</tr>
<tr>
<td>Axys Analytical Services LTD Canada</td>
<td>Proprietary MLA -060</td>
<td>1</td>
<td>0.4</td>
<td>NELAP-FL</td>
</tr>
<tr>
<td>Vista Analytical Laboratory California</td>
<td>EPA Method 537</td>
<td>2</td>
<td>0.342</td>
<td>NELAP-OR Department of Defense</td>
</tr>
<tr>
<td>Test America Sacramento California</td>
<td>Proprietary WS-LC-0025 Rev 1.2</td>
<td>2</td>
<td>0.65</td>
<td>Department of Defense</td>
</tr>
<tr>
<td>Eurofins Lancaster Laboratories Environmental</td>
<td>EPA Method 537</td>
<td>2</td>
<td>1</td>
<td>NELAP-NJ</td>
</tr>
<tr>
<td>Eurofins Eaton Analytical California</td>
<td>EPA Method 537</td>
<td>2.5</td>
<td>0.35</td>
<td>NELAP-NJ</td>
</tr>
<tr>
<td>Eurofins Eaton Analytical California</td>
<td>Proprietary MWH PFC EXTRA</td>
<td>5</td>
<td>0.327</td>
<td>NELAP-NJ</td>
</tr>
<tr>
<td>State Hygienic Laboratory-Coralville Iowa</td>
<td>EPA Method 537</td>
<td>16*</td>
<td>1.39</td>
<td>UCMR3</td>
</tr>
<tr>
<td>BSK Associates California</td>
<td>EPA Method 537</td>
<td>10</td>
<td>0.476</td>
<td>UCMR3</td>
</tr>
</tbody>
</table>

7 Table 4 is a consolidation of Table 2: Laboratories Certified by NJDEP Office of Quality Assurance for Analysis of PFNA Reporting Limit and MDL Information Acquired by Phone or Email (2014) and Table 3: UCMR3 Laboratories with Reporting Limits Lower than 20 ng/L.

8 The State Hygienic Laboratory Coralville uses a low calibration standard of 6.27 ng/L and if needed, would report PFNA to an MRL of 16 ng/L.
Determination of the PQL using MDLs

Determination of the PQL 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 median MDL value as a representative inter-laboratory MDL. This inter-laboratory MDL is then multiplied by a factor of five. A research project was conducted by NJDEP in 1993 to determine if the MDL multiplied by a certain factor could yield a supportable PQL value. The outcome of this research found 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 PFNA, the Testing Subcommittee was able to derive the PQL from a sample size of nine MDLs, from six laboratories using four different methods. The median MDL value of these nine MDLs is 0.4 ng/L as seen in Table 5. This value multiplied by 5 is 2.0 ng/L.

### Table 5
Laboratories Used for PQL Calculation in order of Increasing MDL Values

<table>
<thead>
<tr>
<th>Laboratory</th>
<th>MDL (ng/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>American Water Central Laboratory</td>
<td>0.13</td>
</tr>
<tr>
<td>Eurofins Eaton Analytical CA</td>
<td>0.327</td>
</tr>
<tr>
<td>Vista Analytical Laboratory</td>
<td>0.342</td>
</tr>
<tr>
<td>Eurofins Eaton Analytical CA</td>
<td>0.35</td>
</tr>
<tr>
<td>Axys Analytical Services Ltd.</td>
<td>0.4 (median)</td>
</tr>
<tr>
<td>BSK Associates</td>
<td>0.476</td>
</tr>
<tr>
<td>Test America Sacramento</td>
<td>0.65</td>
</tr>
<tr>
<td>Eurofins Lancaster Laboratories Environmental</td>
<td>1</td>
</tr>
<tr>
<td>State Hygienic Laboratory Coralville</td>
<td>1.39</td>
</tr>
</tbody>
</table>

Median MDL : 0.4 ng/L

0.4 ng/L x 5 = 2.0 ng/L

Therefore, the PQL based on the interlaboratory MDL is 2 ng/L.
Determination of PQL Using Reporting Limits

Quantitation levels such as the MDL which are based on multiples of the standard deviation are a measure of precision. They do not account for non ideal instrumental and analytical occurrences of interference, analyte degradation, matrix enhancement, background contamination which can, particularly at low concentrations, contribute to false positive and false negative results. Laboratories following EPA Method 537 report results to a MRL which is a concentration equal to or greater than the lowest calibration standard but also a concentration which must meet the QC criteria at Section 9.2.5 of the method which verifies laboratory proficiency at a preset MRL. EPA Method 537 does not require laboratories to perform the LCMRL procedure that was previously discussed, 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.

The MRL can be established by the laboratory for a specific purpose or can be established by a regulatory agency (such as the PFNA MRL of 20 ng/L set by the EPA for the UCMR3). EPA Method 537 describes the MRL as the lowest analyte concentration that meets the Data Quality Objectives that are developed based on the intended use of this method and, as such, can be applicable to the determination of the PQL for PFNA. It would follow that in addition to using inter-laboratory MDLs, the PQL should be assessed by considering the MRLs used by these laboratories.

As seen in in Table 6 below, six laboratories use EPA Method 537 or a modified EPA Method 537 and of these six, four have performed the MRL confirmation procedure contained in the method. EPA Method 537 (as Version 1.0) was not available until 2008. In most cases, the proprietary methods such as the NJDEP sanctioned proprietary methods and the Department of Defense accredited Test America Sacramento proprietary method were developed prior to this and, as a result, they also do not include the MRL confirmation procedure. As much information as possible was obtained regarding the proprietary methods and in doing so it was determined that the reporting limits listed are verified prior to analysis of field samples at the beginning of an analysis batch and must meet recovery criteria of 50-150% (or 100±50%). (This is also a QC requirement within EPA Method 537.) In the absence of an MRL, the reporting limit will be considered in the PQL assessment provided the laboratory verifies the reporting limit by analyzing a continuing calibration standard at or lower than the reporting limit prior to analyzing field samples at the start of an analytical run. The exception to this is Test America Sacramento which does not verify the instrument sensitivity prior to any analyses with an initial calibration verification (ICV) standard at or below the reporting limit. With the exclusion of the Test America Sacramento reporting limit, the average of the remaining eight reporting limits is 4.9 ng/L. Because the 4.9 ng/L is based on actual reporting limits obtained from laboratories performing PFNA analysis, the Testing Subcommittee is recommending the PQL for PFNA be established at 5 ng/L.
Table 6
Reporting Limits and Verification Status and Lowest Calibration Standard for Each Laboratory/Method with PFNA Reporting Limits under 20 ng/L

<table>
<thead>
<tr>
<th>Laboratory</th>
<th>Reporting Limit (ng/L)</th>
<th>Minimum Reporting Level confirmation or verification of reporting limit</th>
<th>Method Detection Limit (ng/L)</th>
<th>Lowest Calibration Standard (ng/L)</th>
<th>Method Accreditation</th>
</tr>
</thead>
<tbody>
<tr>
<td>American Water Central Laboratory</td>
<td>1</td>
<td>Yes</td>
<td>0.13</td>
<td>1</td>
<td>EPA Method 537</td>
</tr>
<tr>
<td>Axys Analytical Services Ltd.</td>
<td>1</td>
<td>Yes</td>
<td>0.4</td>
<td>0.5</td>
<td>Axys SOP MLA-060</td>
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<tr>
<td>BSK Associates</td>
<td>10</td>
<td>Yes</td>
<td>0.476</td>
<td>2</td>
<td>EPA Method 537</td>
</tr>
<tr>
<td>Eurofins Eaton Analytical CA</td>
<td>2.5</td>
<td>Yes</td>
<td>0.35</td>
<td>2.5</td>
<td>NJ Certified</td>
</tr>
<tr>
<td>Eurofins Eaton Analytical CA</td>
<td>5</td>
<td>Yes</td>
<td>0.327</td>
<td>2.5</td>
<td>NJ Certified</td>
</tr>
<tr>
<td>Eurofins Lancaster Laboratories Environmental</td>
<td>2</td>
<td>Yes</td>
<td>1</td>
<td>2</td>
<td>EPA Method 537</td>
</tr>
<tr>
<td>State Hygienic Laboratory Coralville</td>
<td>16 ⁹</td>
<td>Yes</td>
<td>1.39</td>
<td>6.27</td>
<td>EPA Method 537</td>
</tr>
<tr>
<td>Test America Sacramento ¹⁰, ¹¹</td>
<td>2</td>
<td>No</td>
<td>0.65</td>
<td>1</td>
<td>WS-LC-0025 Rev 1.2</td>
</tr>
<tr>
<td>Vista Analytical Laboratory</td>
<td>2</td>
<td>Yes</td>
<td>0.342</td>
<td>2</td>
<td>EPA Method 537</td>
</tr>
<tr>
<td>Mean</td>
<td>4.9</td>
<td></td>
<td>0.6</td>
<td>2.3</td>
<td></td>
</tr>
<tr>
<td>Median</td>
<td>2.3</td>
<td></td>
<td>0.4</td>
<td>2.0</td>
<td></td>
</tr>
</tbody>
</table>

⁹ The State Hygienic Laboratory Coralville uses a low calibration standard of 6.27 ng/L and if needed, would report PFNA to an MRL of 16 ng/L.

¹⁰ The Test America Sacramento MDL was used in the determination of an inter-laboratory MDL because it met the requirements of 40 CFR Part 136, Appendix B.

¹¹ The Test America Sacramento reporting limit was not included in the mean of the reporting limits because the initial calibration verification standard (ICV) analyzed at the beginning of a run is a midrange concentration standard. There is no requirement for verifying the lowest calibration standard prior to an analytical run in the method that was accredited by the Department of Defense.
Laboratories approved for analysis by EPA Method 537 must follow all QC requirements within the method and must use only those modifications allowable by the method. The Testing Subcommittee recommends that future proprietary methods should be evaluated by the NJDEP OQA based upon the initial demonstration of capability quality control requirements and the ongoing quality control requirements within EPA Method 537. In addition to meeting the PQL of 5 ng/L as a reporting limit for PFNA, requirements for existing and future proprietary methods should include but will not be limited to 1) verification of the reporting limit prior to the analysis batch in the analysis with the low level continuing calibration standard that must fall within a recovery range of 50-150% (or 100%±50%) and when this recovery criteria is not met, corrective action must be conducted according to EPA Method 537 and, 2) reporting of results according to EPA Method 537 when background contamination of PFNA is detected at greater than 1/3 of the reporting limit in the corresponding field blanks.

**Bootstrap Estimate of a Confidence Interval of a Mean**

Basic statistics were calculated using the nine data values in Table 6 to determine the homogeneity of the interlaboratory distribution. 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 2 ng/L following the convention of multiplying the interlaboratory MDL value (Table 5) by a factor of five (5). In addition, the median and mean values for the low calibration standards as well as the median MRL value were both 2 ng/L, as noted on Table 6.

Another approach that has been used most recently by the USEPA 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 interlaboratory MDL values from Table 6. The results of this data analysis are shown below in Table 7.

<table>
<thead>
<tr>
<th>Lower Confidence Limit (ng/L)</th>
<th>Mean (ng/L)</th>
<th>Upper Confidence Limit (ng/L)</th>
<th>Confidence Level Range</th>
<th>Number of Randomly Selected Values$^{12}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.36</td>
<td>0.61</td>
<td>0.91</td>
<td>95%</td>
<td>2000</td>
</tr>
</tbody>
</table>

Using the 95% upper confidence level from the bootstrap method of 0.91 ng/L, a PQL value (5 times the Upper Confidence Limit of the MDL) of 4.6 ng/L can be calculated which would be rounded to 5 ng/L following the regulatory convention that has been used by the NJDEP in the past. This value for the MDL 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. One laboratory, State Hygienic Laboratory Coralville, reported a method detection limit value of 1.39 ng/L, which is approximately 153% above the upper control limit (0.91 ng/L), but this value

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$^{12}$ The Bootstrap Technique uses a default value of 2000 iterations to calculate the statistics presented.
was not excluded from the statistical calculations because after rounding, the two reported values, method detection limit and upper confidence limit of the interlaboratory MDLs, are the same.

To incorporate more recent techniques of calculating quantification levels, the bootstrap technique can also be applied to the reporting limit (RL) data that was provided to the state to evaluate the consistency of RLs used by the laboratories in Table 6. The results of the RL evaluation are presented in Table 8.

### Table 8
**Bootstrap Estimate of Reporting Levels**

<table>
<thead>
<tr>
<th>Lower Confidence Limit (ng/L)</th>
<th>Mean(^\text{13}) (ng/L)</th>
<th>Upper Confidence Limit (ng/L)</th>
<th>Confidence Level Range</th>
<th>Number of Randomly Selected Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.89</td>
<td>4.61</td>
<td>8.11</td>
<td>95%</td>
<td>2000</td>
</tr>
</tbody>
</table>

This generated distribution of 2000 randomly selected values produced an upper confidence limit of 8.11 ng/L as a reporting level that 95% of the laboratory community should be able to achieve. Two laboratories in Table 6 have RL values above the 95% confidence level threshold.

Because these two laboratories have RL values outside of the 95% confidence interval, the RL values were excluded and the statistical analysis was rerun, producing the following information in Table 9.

### Table 9
**Bootstrap Estimate of Reporting Levels**

**Excluding two laboratories with Reporting Levels above the Upper Confidence Level**

<table>
<thead>
<tr>
<th>Lower Confidence Limit (ng/L)</th>
<th>Mean (ng/L)</th>
<th>Upper Confidence Limit (ng/L)</th>
<th>Confidence Level Range</th>
<th>Number of Randomly Selected Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.33</td>
<td>2.25</td>
<td>3.42</td>
<td>96%</td>
<td>2000</td>
</tr>
</tbody>
</table>

This bootstrap analysis generates an upper confidence limit of 3.42 ng/L which agrees with the 4.6 ng/L level generated by the interlaboratory upper confidence limit of the MDL (0.91 ng/L from Table 7) times 5. The distribution shows that 96% of the laboratory community can achieve a RL level of 3.42 ng/L. The RL from one additional laboratory in Table 6 exceeded the upper confidence limit of the RL (3.42 ng/L). An additional bootstrap analysis was not performed as upper confidence limit of the RL (minus the two other labs) agreed with the PQL calculation using the traditional approach (MDL times 5).

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\(^{13}\) The calculation included the Test America Sacramento reporting limit.
Summary

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

Typically the PQL is developed by researching those analytical methods that are robust and possessing the sensitivity to reliably detect the analyte as close as possible to the recommended Health-based MCL derived by the Health Effects Subcommittee. From a sample size of at least five MDLs, a median MDL value is multiplied by a factor of five. This product, rounded to one significant figure, would be the proposed PQL. Since the three Drinking Water Quality Institute Subcommittees were tasked with developing values for PFNA, a drinking water Health-based MCL was unavailable to the Testing Subcommittee as guidance for determining analytical sensitivity requirements. For this reason, the draft Interim Specific Ground Water Criterion of 20 ng/L published in March 2014 was used as the upper limit in considering reporting limits and their respective MDLs. MDLs from nine laboratories were used to determine the PFNA PQL which included those of New Jersey Office of Quality Assurance certified laboratories and a subset of UCMR3 participating laboratories that analyze PFCs, including PFNA, for purposes other than the UCMR3. The median value of nine MDL values multiplied by the factor of 5 resulted in a PQL of 2 ng/L.

The MRL in EPA Method 537 is a quantitation level that differs from an MDL in that it accounts for both accuracy and precision. In addition to using the MDLs for determining the PQL, the mean of the MRLs or minimum reporting limits of eight laboratories resulted in a PQL value of 4.9 ng/L.

A “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 PFNA PQL.

Summary of approaches for calculating a PQL

<table>
<thead>
<tr>
<th>PQL Approach</th>
<th>Value (ng/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Median MDL x 5</td>
<td>2</td>
</tr>
<tr>
<td>Mean of RL</td>
<td>4.9</td>
</tr>
<tr>
<td>Bootstrap Upper Confidence Limit of MDL x 5</td>
<td>4.6</td>
</tr>
<tr>
<td>Bootstrap Upper Confidence Limit of RL</td>
<td>3.42</td>
</tr>
</tbody>
</table>

The Testing Subcommittee decided to use the method for deriving the PFNA PQL that takes into consideration both the precision and accuracy of the analytical method. Therefore the Testing Subcommittee relied on the actual reporting limits from laboratories currently performing PFNA analyses for determining its recommendation.

The Testing Subcommittee recommends a PQL of 5 ng/L for PFNA to the Drinking Water Quality Institute.
Literature cited:


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


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.


