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BAY AREA CLEAN WATER AGENCIES

POTW PCBs Sampling, Analysis & Reporting Protocols Using EPA Method 1668C

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SUMMARY

On December 14, 2022, the San Francisco Bay Regional Water Quality Control Board (Regional Water Board) adopted Order R2-2022-0038, *Waste Discharge Requirements for Mercury and PCBs From Municipal and Industrial Wastewater Discharges to San Francisco Bay, NPDES Permit CA0038849*. The order supersedes Order R2-2017-0041 and continues to implement the waste load allocations (WLAs) and implementation requirements of the polychlorinated biphenyls Total Maximum Daily Load (PCBs TMDL) that was adopted February 13, 2008. The Order includes requirements for monitoring and reporting of PCBs using both the approved EPA Method 608, and proposed EPA Method 1668C by publicly owned treatment works (POTWs). The following Sampling, Analysis & Reporting Protocols (Protocols) were prepared to provide a guidance document for POTWs and laboratories when generating data using EPA Method 1668C. They are intended to serve as a supplement to the official EPA Method 1668C instructions (USEPA, 2010), which, at this time, have not been confirmed as final nor promulgated as a rule by the USEPA. Protocols for analysis and reporting using EPA Method 608 are not discussed in this document.

This guidance document was originally issued on December 9, 2013. It was updated in 2024 to update references to reissued NPDES permits and reflect contemporary laboratory practices, particularly those implementing the 2016 TNI-2 Standard .

BACKGROUND

The February 2008 San Francisco Bay Basin Plan Amendment for the PCBs TMDL included a WLA for municipal wastewater dischargers of 2.0 kg/yr (kilograms per year). The estimated aggregate loading from municipal dischargers based on 2003 flow data was 2.3 kg/yr, but the final load for municipal wastewater dischargers was promulgated at 2.0 kg/yr by the Regional Water Board to incorporate expected reductions. The TMDL also splits the 2.0 kg/yr into individual POTW waste load allocations by dividing each POTW's flow rate by a group flow rate (grouped according to secondary and advanced-secondary treatment) and multiplying that value by the total POTW aggregate waste load allocation. The allocations in Order R2-2022-0038 were originally developed from available PCB effluent concentration data for nine POTWs as presented in the PCBs TMDL Project Report (RWQCB, 2004). The data were collected using EPA Method 1668A from five POTWs with secondary treatment and four POTWs with advanced secondary treatment. A total of nine samples were collected over a three-month period in 2000-2001 to characterize PCB effluent levels for secondary treatment and a total of fourteen samples were collected over a nine-month period to characterize PCB effluent levels for advanced secondary treatment in 1999- 2000. These data are included in Appendix F-4 of Order R2-2022-0038. No data was available to characterize effluent quality from the remaining 30 facilities that received WLAs in the February 2008 TMDL.

OrderR2-2022-0038 includes the same performance-based limits for PCBs as previous orders. The limits are based on data for 40 congeners that are representative surrogates for PCBs that are causing impairment (**Table 1**). These 40 congeners are the same ones that formed the basis for the impairment and were monitored in the Regional Monitoring program using USEPA method 1668A.

OBJECTIVE

The objective of these Protocols is to produce and report data that represent as closely as possible actual concentrations of PCBs in POTW effluent. This objective will be achieved, in part, by using established methods for sample collection and laboratory analysis, accepted QA/QC procedures, and consistent reporting practices. The ability to meet this objective will be accomplished by evaluating the resulting laboratory measurements in terms of reporting limits, precision, accuracy, representativeness, comparability, and completeness.

Table 1. List of 40 PCB Congeners Causing Impairment in the Bay

PCB 008	PCB 066	PCB 118	PCB 170
PCB 018	PCB 070	PCB 128	PCB 174
PCB 028	PCB 074	PCB 132	PCB 177
PCB 031	PCB 087	PCB 138	PCB 180
PCB 033	PCB 095	PCB 141	PCB 183
PCB 044	PCB 097	PCB 149	PCB 187
PCB 049	PCB 099	PCB 151	PCB 194
PCB 052	PCB 101	PCB 153	PCB 195
PCB 056	PCB 105	PCB 156	PCB 201
PCB 060	PCB 110	PCB 158	PCB 203

SOURCE: Table F-14 in Order R2-2012-0096

IMPORTANCE OF COLLECTING DATA

Data obtained from EPA Method 1668C analyses from all POTWs allows the Regional Water Board to compare the actual POTW load to the WLA, and to assess variability in PCB monitoring data due to different treatment processes, diurnal patterns, flow changes (dry weather versus wet weather), and other factors. This data set may eventually be useful in recalculating WLAs and/or incorporating uncertainty factors when translating WLAs into future NPDES permit limits.

SAMPLING PROTOCOLS

The following protocols must be followed when collecting, holding, and transporting PCBs samples for analysis using EPA Method 1668C.

Sample protocols are as specified in Order R2-2022-0038, with additional markup removing references to EPA Method 1669 in red underline ~~strikeout~~. Method 1669 is applicable to low-level metals such as mercury (EPA Method 1631). Method 1669 is not applicable to PCBs. The specific reason for the change is Method 1669 specifies collection of a field blank, but Method 1668C does not require use of a field blank.

Samples shall be collected at the locations indicated as compliance monitoring points in the individual POTW NPDES permits (often, but not always, EFF-001).

Sample Collection

Samples shall be collected as 1-liter (L) grab samples in appropriate pre-cleaned amber glass containers ~~following clean sampling techniques from EPA Method 1669 (U.S. EPA, 1996)~~.

The following procedures should be used to reduce the likelihood of sample contamination:

- Wear clean, powder-free gloves
- Minimize time bottle is open
- Don't set lid down
- Don't allow rainwater to drip into bottle
- Don't touch inside of bottle/lid

Care shall also be taken to keep bottles dust-free prior to sample collection. At a minimum, three (3) 1-L grab samples shall be collected at each sampling location. One of the grab samples should be sent to the analytical laboratory and two (2) should be refrigerated and retained at the POTW until the analysis is completed and the data are accepted for reporting to the Regional Water Board. The extra sample retained at the POTW will be sent to the laboratory, analyzed and reported in the event of a batch QC failure or the first grab sample being lost.

Sample Handling

If residual chlorine is present, add 80 mg of sodium thiosulfate to each 1-L sample. Samples must be kept in the dark at less than or equal to 6ºC from the time of collection until receipt at the laboratory. Sample bottles, shipping instructions, chain of custody templates, and billing information will be provided by the analytical laboratory. If the sample will be frozen, allow room for expansion. EPA Method 1668C allows samples to be held for up to 1 year prior to extraction if stored in the dark at less than or equal to 6ºC.

Sampling Frequency

The effluent monitoring requirements for POTWs using proposed EPA Method 1668C are shown in **Table 2** (excerpted from Table E-3 in Order R2-2022-0038). The largest dischargers (those with design flows exceeding 50 MGD) are required to sample more than once per year to ensure collection of samples during the wet and dry seasons. All dischargers must follow Attachment G requirements to collect effluent samples on days that are coincident with influent sampling and during periods of daytime maximum peak effluent flows.

Table 2. PCBs Monitoring Requirements for POTWs

Parameter	Units	Sample Type	Minimum Sampling Frequency
PCBs, Total (as Aroclors) [5]	µg/L or pg/L	Grab	Once per permit term
PCBs (as congeners) [6]	µg/L or pg/L	Grab	2/Year for Dischargers with design flows [7] ≥ 50 MGD
			1/Year for Dischargers with design flows [7] 5.0 MGD ≤ Q < 50 MGD [8]
			Once per permit term for Major Dischargers with design flows [7] < 5.0 MGD, and for Minor Dischargers

Unit: µg/L = micrograms per liter; pg/L = picograms per liter

Grab Samples: If allowed in the Pretreatment and Biosolids Monitoring Requirements of the Dischargers' individual NPDES permits, grab samples shall be collected coincident with composite samples collected for the analysis of other regulated parameters.

[5] Aroclor Monitoring: Dischargers shall use U.S. EPA Method 608.3 or 625.1 for Aroclor monitoring. These data will be used to assess compliance with the limits in Tables 3B and 4B of the Order. Non-detected and estimated values shall be treated as zeros in the calculation of Total PCBs .

[6] Congener Monitoring: PCBs congeners monitoring is for informational purposes. Dischargers shall use U.S. EPA Proposed Method 1668C and report the results for each of the 40 congeners that contribute to San Francisco Bay's impairment and congeners that co-elute with the 40 congeners (see Fact Sheet Tables F-7 and F-8). For congeners that co-elute with the 40 congeners, Dischargers shall report the sum of these co-eluting congeners. A summation for total PCBs as congeners is not required. When the Regional Water Board estimates sums, non-detected values are treated as zeros and estimated values are counted .

[7] Design Flow: The design flows for each facility are included in Tables F-1A and F-1B of the Fact Sheet.

[8] For the Cities of San Jose and Santa Clara and the Treasure Island Development Authority, the minimum monitoring frequency for PCBs (as congeners) shall be 1/Year.

ANALYTICAL LABORATORIES

All samples shall be analyzed using proposed EPA Method 1668C (April 2010 version) to provide consistent concentration information for the 40 PCB congeners and their co-elutions. Each laboratory must demonstrate annually its capability to analyze the required 40 congeners and co-elutions at the method-specified minimum levels (MLs, Table 2 of EPA 1668C) by following the procedure described in USEPA 1668C Section 17.6.1.4.1.

Between 2011 and 2013, method blanks which otherwise met criteria listed in EPA 1668C and the 2011 PCB Reporting Guideline contained background levels that affected the sum of PCBs reported by POTWs. In an effort to ensure quality data is reported for all POTW's, the following guidelines are adopted to prevent laboratory contamination from skewing analytical results. Any analytical laboratory that wishes to analyze and report PCB congener data for Region 2 must demonstrate that their laboratory background levels do not adversely affect the analytical results. This shall be done by documenting and statistically determining if laboratory background levels that are found in laboratory method blanks are acceptable. In order to achieve this, for each congener, the value of two standard deviations above the average (mean) level in minimum of 10 blanks must be at or below 75% of the corresponding method-specified ML. The estimated detection limit (also called a sample-specific detection limit) of the corresponding congener shall be used as numerical value in the following calculations when the congener is not detected as specified by the method.

$$MEAN_{MB,10} + 2*SD_{MB,\ 10} < 0.75 * ML$$

$MEAN_{MB,10}$ = The mean of 10 or more method blanks.
$SD_{MB,\ 10}$ = Standard deviation of 10 or more method blanks.
ML = Corresponding ML for the congener

Quality Assurance/Quality Control

Quality assurance and quality control (QA/QC) samples are required in conjunction with POTW samples to verify data quality. With each batch of 20 or fewer samples, the laboratory will analyze method-required QA/QC samples of method blanks and spike blanks. Matrix spikes may be analyzed based on sample availability.

Method required batch controls are as follows:

- Method Blank—as batch contamination monitoring
- Spike Blank—as sample preparation recovery assessment
- Mid-Calibration Range Standards performed at the start and every 12 hours of instrument operation—as calibration verification

Additional required batch controls are as follows:

- Method Blank—If any of the 40 congeners of interest are present in the method blank at greater than 20 pg/L, the batch is invalidated.
- Mid-Calibration Range calibration verification performed at the end of the run.

DATA DEFINITIONS

Estimated Detection Limit (EDL) is a theoretical maximum concentration that would meet signal-to-noise criteria for a target analyte. The term “Estimated Detection Limit” is a functional replacement for the term “Sample-Specific Detection Limit (SSDL)” used in Order R2-2022-0038 and is preferable because it includes the word “Estimated.” The sample-specific Estimated Detection Limit is calculated for each PCB that is either not present, or PCBs that are less than 2.5 times (<2.5x) the background level, and therefore do not meet the identification criteria. If there is a peak that meets signal to noise criteria, the Estimated Detection Limit cannot be calculated.

The following equation is used to calculate the sample-specific Estimated Detection Limit:

$$\text{Estimated Detection Limit} = \frac{(2.5)(H_N)(Q_{IS})}{(H_{IS})(W)(RRF)}$$

Where:

H_N = Noise height (peak to peak)
H_{IS} = Peak height of the internal standard
Q_{IS} = Quantity, in pg, of the internal standard added to the sample before extraction
W = Weight of the sample (solid or liquid), and
RRF = Calculated relative response factor for the analyte

Estimated Maximum Possible Concentration (EMPC) is calculated for a PCB congener that meets all selection criteria but does not meet the ion abundance ratio criteria. The instrument software calculates an estimated concentration using the theoretical chlorine isotope ratio of the target PCB to correct for the interference of the target ions. When an EMPC is generated, the concentration will be reported as ND (non-detect), and there will be no Estimated Detection Limit. The calculated EMPC may be provided on the laboratory report. The following equation is used:

$$\text{Estimated Maximum Possible Concentration (EMPC)} = \frac{(A_X)(Q_{IS})}{(A_{IS})(W)(RF_N)}$$

Where:

A_X = Sum of the area of the smaller peak and of the other peak area calculated using the theoretical chlorine isotope ratio
A_{IS} = Sum of the integrated ion abundances of the quantitation ions for the labeled internal standards
Q_{IS} = Quantity, in pg, of the internal standard added to the sample before extraction
W = Weight of the sample or volume of the aqueous sample
RF_N = Calculated mean relative response factor for the analyte

REPORTING

As specified in Order R2-2022-0038, with additional markup in red underline ~~strikeout~~ vetted by Regional Water Board staff in August 2024:

5.2.6. **PCBs Congeners Reporting.** General requirements for reporting U.S. EPA Method 1668C data are as follows:

5.2.6.1. **Minimum Levels.** The ML for each congener shall be published Method MLs (Table 2 of EPA1668C). The laboratory analyzing the samples shall have on file data demonstrating a lower calibration level that is equal to or less than the published Method ML. Laboratories may revise the lower calibration level based on final published values if and when U.S. EPA Method 1668C is fully approved or promulgated.

5.2.6.2. **Method Detection Limits**. The MDLs reported by the laboratory shall meet the criteria set in U.S. EPA Method 1668C. The laboratory shall demonstrate capability by achieving MDLs below method-specified MDLs. The MDL is based on analysis of low-level replicates of clean matrices (e.g., deionized water). ~~SSDLs~~ Estimated Detection Limits for each congener shall be reported when there is a ND result. The ~~SSDLs~~ Estimated Detection Limit is calculated by using the instrument processing method based on the noise level in the vicinity of the largest peak in sample extracts containing the real

matrix. If there is a peak that meets signal-to-noise criteria, the Estimated Detection Limit cannot be calculated.

5.2.6.3. **Co-elution**. Congeners in a co-elution shall be reported as a combination of the congeners, with the lowest numerically designated congener reported first and separated by a slash (/) from numerically higher designated congeners.

For example, if PCB congeners 020, 021, and 033 are co-eluted, the Discharger shall report the co elution as PCB 020/021/033.

For co-eluted congeners, report the largest of the MLs for the individual compounds.

5.2.6.4. **Qualifiers.** Qualifiers allowed in reporting U.S. EPA 1668C data are as follows:

Table E-5. U.S. EPA Method 1668C Qualifiers in CIWQS

Qualifiers	CIWQS Field	Qualifier Description
ND	Qualifier	The analyte was not detected in the sample at the ~~SSDL~~ MDL or the Estimated Detection Limit, whichever is greater.
DNQ	Qualifier	The reported result is an estimate. The concentration is greater than the ~~SSDL~~ MDL but less than the method-specified ML.
~~M~~	~~QA Code~~	~~Estimated maximum possible concentration.~~
D	QA Code	Result obtained from the analysis of a diluted sample.
B	QA Code	Congener is present in the method blank at or above the MDL.

5.2.6.5. **Method Blank Correction.** Results shall be reported without method blank correction.

5.2.6.6. **Units.** Concentrations shall be reported in micrograms per liter (µg/L) or picograms per liter (pg/L).

The following additional guidance was not included in Order R2-2022-003:

- The Estimated Detection Limit must be reported when the analyte is not detected. In this situation, report the Estimated Detection Limit in lieu of the MDL. If there is a positive detection or an Estimated Maximum Possible Concentration (EMPC), the Estimated Detection Limit cannot be reported.

- ND must be reported when a value is less than the MDL, even if the result was considered a “positive detection”.

- DNQ must be reported when a congener is detected above the MDL, but is less than the method-specified ML.

- If there is an Estimated Maximum Possible Concentration (EMPC), report the result as ND<MDL. For samples with an EMPC, it is optional (not required) to report the results with the 'M' QA code and to report the EMPC in the comment section of the eSMR.

- Consistent with Attachment G of NPDES permits, data should not be reported by an agency if data have been invalidated based on QA/QC results and analysis. If data are invalidated, it is recommended that documentation be prepared and filed internally to explain the process and reasons for invalidation. If data quality is discovered to be insufficient after the data have been reported to the Regional Water Board, the data invalidation procedure indicated in Attachment G should be followed.

PCBs Concentrations and Use of Qualified Data

PCB congeners shall be reported as individual congener concentrations with assigned qualifiers. A summation of individual congeners to produce a "Total PCBs" value is not required by Order R2-2022-0038. When the Regional Water Board estimates sums:

- Data qualified with ND will be set to "0" for the purpose of performing summation.

  Data reported with the optional QA Code "M" should also include the qualifier ND and should also be set to "0" for the purposes of reporting.

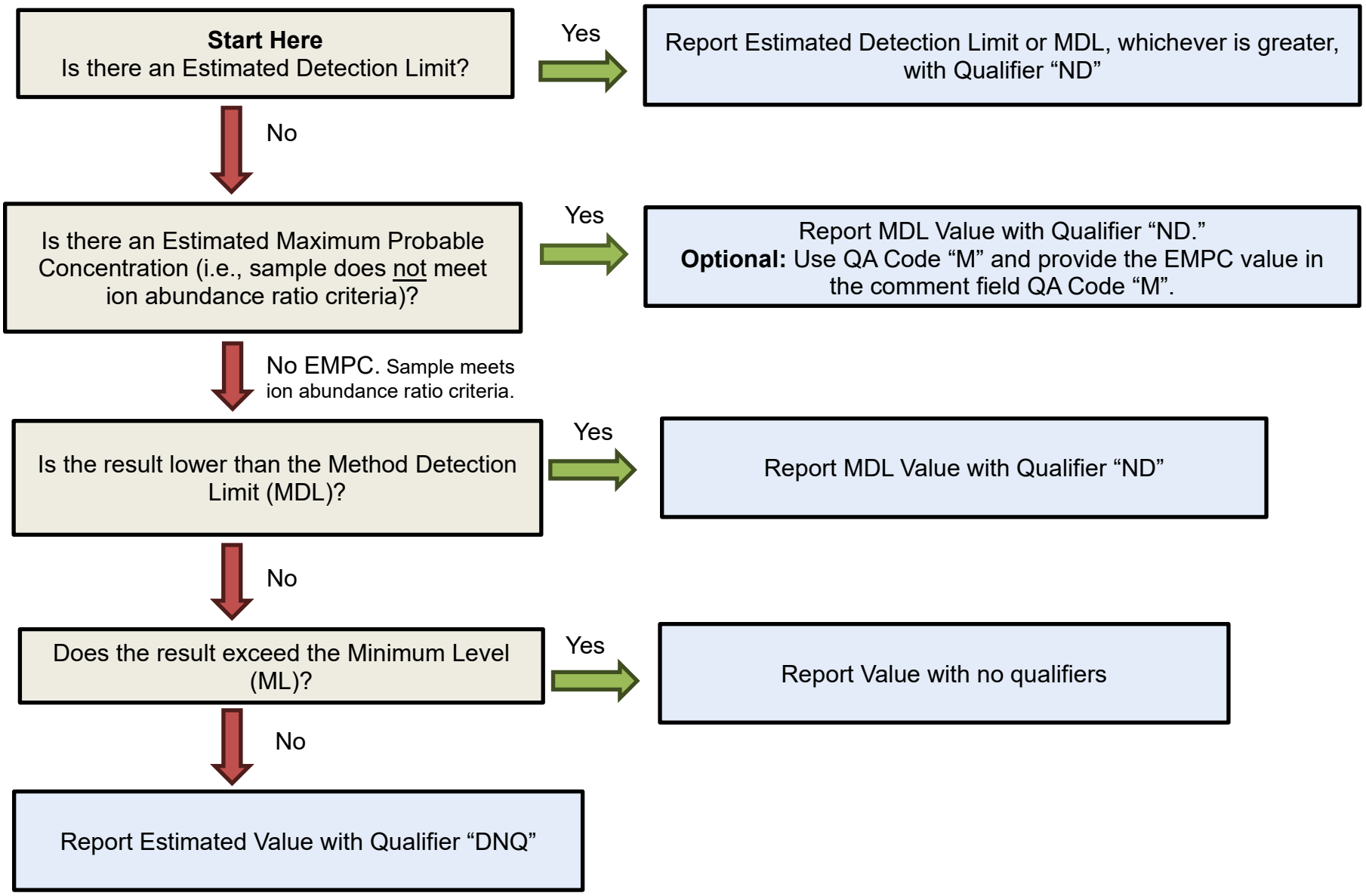
- Data qualified with DNQ, D, or B should be summed using the reported concentration.

Congener Naming Convention

Analytical laboratories and dischargers shall report PCBs congener results using the "Congener Number" (e.g., PCB 008) as specified in Table 1 of EPA Method 1668C, available online at: https://www.epa.gov/sites/default/files/2015-09/documents/method_1668c_2010.pdf

To ensure consistent recordkeeping and reporting formats, each congener shall be identified using the acronym "PCB" following by the three-digit congener number as in PCB XXX (e.g., PCB 008, PCB 028, PCB 118).

Flow Chart


Start Here
Is there an Estimated Detection Limit?
Yes
Report Estimated Detection Limit or MDL, whichever is greater, with Qualifier "ND"
No
Is there an Estimated Maximum Probable Concentration (i.e., sample does not meet ion abundance ratio criteria)?
Yes
Report MDL Value with Qualifier "ND."
Optional: Use QA Code "M" and provide the EMPC value in the comment field QA Code "M".
No EMPC. Sample meets ion abundance ratio criteria.
Is the result lower than the Method Detection Limit (MDL)?
Yes
Report MDL Value with Qualifier "ND"
No
Does the result exceed the Minimum Level (ML)?
Yes
Report Value with no qualifiers
No
Report Estimated Value with Qualifier "DNQ"

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