Guidance for the Selection of Analytical Methods and the Evaluation of MDLs and PQLs List Referenced in Chapter 62-4.246(4), F.A.C.

Prepared by
Division of Environmental Assessment and Restoration

November 10, 2020

Intended Use of This Document

This guidance is published to assist DEP staff and other data reviewers with the evaluation of appropriate analytical methodologies used to generate water quality data. Subsection 62-4.246(4), Florida Administrative Code (F.A.C.), requires DEP to establish and publish a list of target Method Detection Limits (MDLs) and Practical Quantitation Limits (PQLs) for published analytical methods that may be used for the analysis of wastewater, surface water and groundwater. Data reviewers must compare MDLs and PQLs reported for permit compliance data with the listed MDLs and PQLs to ensure that adequately sensitive analytical techniques were utilized to meet permit requirements or other data quality objectives.

If the target MDL or PQL was not achieved for a given report, there may be valid reasons why this occurred, and the reviewer should refer to justification provided by the laboratory. Situations that may prevent achievement of target limits include, but are not limited to, environmental samples that contain constituents that cause analytical interferences or other quality control problems and sample collection anomalies (e.g., the collection of less than ideal sample volumes). In some cases, DEP may approve alternative MDLs and PQLs for the duration of a specific permit if sufficient justification is provided. Alternative MDLs and PQLs may be approved if alternative target limits remain below compliance limits or if matrix-specific MDLs and PQLs are developed.

Sources of Listed Target MDLs

The listed target MDLs were obtained from the following sources:

1) MDLs published in approved methods. The EPA and the APHA (“Standard Methods”) were the primary sources used.

2) MDLs published in the Environmental Monitoring Methods Index (historical); and, the National Environmental Monitoring Index (NEMI).

3) Consultations from laboratories in Florida, including the DEP laboratory in Tallahassee.

MDLs from the sources above may differ for the same analyte-technique combination. In these cases, the MDL included in the 62-4.246(4) list was judged to be the most appropriate target value for the listed method.

Calculation of Target PQLs

1) Except as noted below, many of the listed PQLs were calculated as 4 X MDL, per the default calculation of the PQL indicated at subsection 62-160.120(23), F.A.C. For some listings, the PQL is taken from the information in the method about minimum levels applicable to quantitation.

2) PQLs are listed as equivalent to the MDL or as some other factor of the MDL for certain analytes, where the detection or quantitation value is affected by practical considerations associated with the analytical technique or where the concept of a statistically derived MDL may not be appropriate. The analytical techniques for these analytes are specifically designated in the MDL/PQL list as described in the next section. Examples of these analytes include:

Biochemical Oxygen Demand (BOD)
Carbonaceous Biochemical Oxygen Demand (CBOD)
Chlorine, Total
Chlorophyll
Coliforms, Fecal and Total
Color
Dissolved Oxygen (DO)
E. Coli
Enterococci
Hardness (by calculation)
Hydrogen ion (pH)
Hydrogen sulfide
Nitrate (by calculation)
Nitrogen, Total (by calculation)
Odor
Radiochemistry analytes
Residues (TDS, TSS)
Specific conductance
Temperature
Titrimetric methods
Turbidity
Un-ionized ammonia

MDL/PQL Listings Where MDL May Not Be Applicable

An “X” in the column titled “MDL Not Required” indicates an analytical technique for which the EPA procedure for MDL determination may not be appropriate (see 40 CFR, Part 136, Appendix B). The laboratory may instead indicate the PQL or laboratory Reporting Limit as an equivalent detection level for a specified analyte, as determined by alternative procedures. Field organizations may report field test results as a minimum increment based on the field sensor specifications. Per paragraph 62-160.340(3)(c), F.A.C., analytical results below the laboratory reporting limit shall be indicated as the reporting limit value followed by the data qualifier code "U" (see Table 1, Rule 62-160.700, F.A.C.).

Reported Versus Target MDLs and PQLs

The listed MDLs and PQLs are targets that should be achievable ***under optimal conditions of quality control*** by most environmental laboratories***.*** However, the laboratory cannot always be expected to meet the MDLs or PQLs listed in the table. Often, environmental samples may contain constituents that cause analytical interferences or other quality control problems that can prevent achieving the target limits (e.g., cyanide, semi-volatiles, and phenols). Even sample collection anomalies (e.g., the collection of less than ideal sample volumes) can affect the MDL or PQL reported by the laboratory. Laboratory representatives should be able to explain the rationale behind the MDLs and PQLs reported with the analytical results, *especially if the reported MDLs and PQLs are above the required compliance limits*. If necessary, data reviewers should request documentation that demonstrates how the reported MDLs and PQLs were derived or adjusted. In general, laboratories are required to calculate or determine MDLs and PQLs using established procedures that are required by rules (e.g. 40 CFR, Part 136, Appendix B), certification standards (e.g. TNI, 2016), and the laboratories’ internal Standard Operating Procedures. *Note that some laboratories may use allowable modifications or optimizations of approved analytical methods or use improved*

instrumentation that provide MDLs and PQLs lower than those found in the 62-4.246(4) list.

Reporting Data Below the MDL or PQL

Chapter 62-160, F.A.C., addresses reporting requirements for data submitted to the FDEP programs. Laboratory analytical reports should present the sample data in accordance with these requirements. Additionally, *data reporting instructions specific to DEP-required forms must be followed for regulatory compliance.*

"Non-detect" results
Whenever an analyte is not detected *at or above* the MDL, the MDL for the measurement must be reported along with the qualifier code "U" indicating that the analyte was not detected at the reported detection limit.

Results reported below the MDL
Alternately, laboratories have the option of reporting the analytical value from the sample analysis followed by the qualifier code "T" indicating the reported value was below the MDL.

Results between the MDL and PQL
If an analyte was detected *at or above* the MDL but was below the PQL, the result may be reported in one of two ways:

1) the *value from the sample analysis* can be reported with the qualifier code "I," indicating that the analyte was detected but could not be quantified with certainty.

2) the *PQL associated with the sample analysis* can be reported followed by the qualifier code "M," indicating that the analyte was detected but was below the reported PQL.

Refer to Table 1 in Rule 62-160.700, F.A.C., for a complete list of appropriate data qualifier codes.

If the analyte is not detected *at or above* the MDL or is detected at a level below the PQL, the reviewer should compare the reported MDL and PQL with the 62-4.246(4) list to determine if an appropriately sensitive method was utilized for the permit or other project objective. If the target MDL or PQL was not achieved, there may be valid reasons why this occurred, and the reviewer should refer to justification provided by the laboratory.

MDLs and PQLs for "Calculated" Quantities

Some analytes are not tested by direct analysis but are calculated from the results of other analyses; for example:

Hardness (by calculation)
Hydrogen sulfide
Nitrate (by calculation)
Total nitrogen (by calculation)
Un-ionized ammonia

MDLs and PQLs for calculated results are therefore not directly determinable. Limits reported for these analytical quantities are dependent on the limits for the component analyses and the

number of significant figures carried in the calculations. The “MDLs” and “PQLs” in the 62-4.246(4) list for these calculated analytes were selected based on the above considerations.

Laboratory Certification Requirements

Laboratories must be certified by the DOH Environmental Laboratory Certification Program (ELCP) for all reported matrix-analyte-method combinations. Per Rule 62-160.300, F.A.C., DEP may temporarily waive this requirement while the laboratory pursues certification with the DOH ELCP.

Revisions to Analytical Methods

All citations of analytical methods in the 62-4.246(4) list refer to the edition of the method listed in 40 CFR Part 136.3. If the method is not listed in this federal rule, the most current, published edition of the method should be used.

Letter suffixes associated with EPA SW-846 method revisions have been omitted from the applicable entries in the 62-4.246(4) method list. The most current published edition of the SW- 846 method should be used.

Use of Additional Methods in 40 CFR Part 136.3 Not Found in the 62-4.246(4) Method List

Laboratories may use additional analytical methods that are approved in 40 CFR part 136.3 but which are not found in the 62-4.246(4) list. The MDL and PQL for the alternative method must be at least as sensitive as the MDL and PQL for the equivalent analytical technique listed in the 62-4.246(4) list, if applicable.

Use of Methods Not Found in 40 CFR Part 136.3

If no analytical method is listed in 40 CFR Part 136.3 for the analyte, the laboratory may use any method specified for the analyte in the 62-4.246 list, in any applicable DEP rule, or as approved by the applicable DEP regulatory program. In some instances, approval for use of these alternative methods may be required by EPA, and approval must be obtained prior to analyzing samples for NPDES permits. The MDL and PQL for the alternative method must be at least as sensitive as the MDL and PQL for the equivalent analytical technique listed in the 62-4.246(4) list, if applicable.

Analysis of Samples for Gross Alpha Activity with High Total Dissolved Solids (TDS)

The co-precipitation methods for gross alpha analysis found in the 62-4.246 list may be used instead of 40 CFR Part 136.3 methods for high-TDS samples where the sample matrix is otherwise expected to raise the MDL. For compliance with NPDES permits, the laboratory should contact DEP with a request for approval of co-precipitation methods before analyzing compliance samples. The Department will forward the request to the EPA Regional coordinator for review as an alternative test procedure or method modification, per 40 CFR, Sections 136.4 and 136.6.

Reporting Total Nitrogen

Total Nitrogen is defined as the sum of the results of the sample analysis for total Kjeldahl nitrogen (TKN), nitrate (NO_3) and nitrite (NO_2), using approved testing methods to perform the calculation.

Direct-measurement techniques for the analysis of Total Nitrogen are described in some published methods and may be approved for specific uses of data by DEP programs, such as for the assessment of surface waters. The laboratory should contact DEP for approval prior to using direct-measurement methods for Total Nitrogen analysis. Approval by EPA of a direct-measurement test method for Total Nitrogen may be required for compliance monitoring for NPDES permits.

All concentrations for Total Nitrogen should be reported as nitrogen (N) in mg/L.

Reporting Nutrients for Ambient Samples and Compliance Monitoring

In permits with effluent limits for nutrients, the effluent limits will often be significantly higher than the nutrient criteria in Chapter 62-302, F.A.C. In these cases, the MDL selected should provide detectable results below the effluent limit instead of below the nutrient criteria, and all target MDLs on the 62-4.246 list likely meet that description. However, if the permit requires ambient monitoring of the receiving waters, the MDLs for that monitoring should be selected to provide detectable results below the applicable criteria, which for some waters (many estuaries, for example) would require selecting the method with the lowest MDL. If there are no permit limits for nutrients but nutrients are monitored for "report only," methods from the list with higher MDLs may be used.

Achieving Lower MDLs for Polycyclic Aromatic Hydrocarbon (PAH) Methods

Some methods for PAHs have an alternative prep method known as the Selected (Single) Ion Monitoring (SIM) method with which lower MDLs can be reached. Laboratories may use this prep method if DEP requires MDLs and PQLs lower than those found in this list for permit compliance or other objectives. Methods with the SIM option include: EPA 1625B, SM 6410 B, EPA 8270E, EPA 8260D, EPA 624.1, and EPA 625.1. Lower MDLs and PQLs achievable with the SIM option included in this list are EPA 1625B, SM 6410 B, and EPA 625.1.

How to Report Total Polycyclic Aromatic Hydrocarbons (PAHs) When One or More Were Non-detect

The water quality criterion for *total polycyclic aromatic hydrocarbons (PAHs)* in Chapter 62-302, F.A.C., is the total of the results for the following ten PAHs:

Acenaphthylene
Benzo(a)anthracene
Benzo(a)pyrene
Benzo(b)fluoranthene
Benzo(ghi)perylene
Benzo(k)fluoranthene
Chrysene
Dibenzo(a,h)anthracene
Indeno(1,2,3-cd)pyrene
Phenanthrene

When an individual PAH result is below the MDL, use a factor of 1/20th the MDL or 1/20th the water quality criterion (WQC), whichever is lower, when calculating the total PAHs. This modification from Rule 62-4.246(8), F.A.C., is necessary because it is possible that the sum of ten individual PAH values, each set to the lower ½ the WQC or ½ the respective MDL, could exceed the WQC even if all the component PAHs were not detected. The modified approach

applies 1/20th of the WQC or 1/20th of the MDL, whichever is lower, to replace all "U" qualified data. Data qualified with an "I" are handled consistent with the rule; the reported value is replaced with the MDL. An MDL for total PAHs is not determined as each individual PAH has its own MDL.

How to Report Total Chlorinated Phenols and Chlorinated Cresols When One or More Were Non-detect

The water quality criterion for *total chlorinated phenols and chlorinated cresols* in Chapter 62-302, F.A.C., is the total of the results for the following seventeen phenols and cresols.

- 4- Chloro-2-methylphenol
- 4- Chloro-3-methylphenol (4-chloro-*m*-cresol)
- 2- Chloro-5-methylphenol
- 3- Chlorophenol
- 4- Chlorophenol
- 2,3- Dichlorophenol
- 2,5- Dichlorophenol
- 2,6- Dichlorophenol
- 3,4- Dichlorophenol
- 3,5- Dichlorophenol
- 2,3,4,5- Tetrachlorophenol
- 2,3,4,6- Tetrachlorophenol
- 2,3,5,6- Tetrachlorophenol
- 2,3,4- Trichlorophenol
- 2,3,5- Trichlorophenol
- 2,3,6- Trichlorophenol
- 2,4,5- Trichlorophenol

When an individual result is below the MDL, use the formula WQC/(2*n), where WQC = water quality criterion and n = total number of congeners reported, or MDL/(2*n) if the MDL is lower than the WQC. For example, if the total consists of all the analytes above, a factor of 1/34th the MDL or 1/34th the water quality criterion (WQC) is used. This modification from Rule 62-4.246(8), F.A.C., is necessary because it is possible that the sum of individual phenol and cresol values, each set to the lower ½ the WQC or ½ the respective MDL, could exceed the WQC even if all the component phenol and cresols were not detected. The modified approach applies WQC/(2*n) or MDL/(2*n), whichever is lower, to replace all "U" qualified data. Data qualified with an "I" are handled consistent with the rule; the reported value is replaced with the MDL. An MDL for total chlorinated phenols and chlorinated cresols is not determined as each individual analyte has its own MDL.

How to Report Total Phthalates When One or More Were Non-detect

The water quality criterion for *phthalate esters* in Chapter 62-302, F.A.C., is the total of the results for the following six phthalates:

Butyl benzyl phthalate
bis (2-ethylhexyl) phthalate (DEHP)
Diethyl phthalate
Dimethyl phthalate

Di-n-butyl phthalate
Di-n-octyl phthalate

When an individual phthalate result is below the MDL, use a factor of 1/12th the MDL or 1/12th the water quality criterion (WQC), whichever is lower, when calculating the total phthalates. This modification from Rule 62-4.246(8), F.A.C., is necessary because it is possible that the sum of six individual phthalate values, each set to the lower ½ the WQC or ½ the respective MDL, could exceed the WQC even if all the component phthalates were not detected. The modified approach applies 1/12th of the WQC or 1/12th of the MDL, whichever is lower, to replace all "U" qualified data. Data qualified with an "I" are handled consistent with the rule; the reported value is replaced with the MDL. An MDL for total phthalate esters is not determined as each individual phthalate has its own MDL.

How to Report Total Polychlorinated Biphenyls (PCBs) When One or More Were Non-detect

The water quality criteria for *Total Polychlorinated Biphenyls (PCBs)* in Chapter 62-302, F.A.C., are the total of the results of individual congeners tested. The actual number of congeners analyzed for PCBs will vary, but when an individual result is below the MDL, calculate the total by setting the value of any congener below detection limit as = WQC/(2*n), where WQC = water quality criterion and n = total number of congeners reported, or MDL/(2*n) if the MDL is lower than the WQC. This modification from Rule 62-4.246(8), F.A.C., is necessary because it is possible that the sum of individual values could exceed the WQC even if all the components were not detected. The modified approach applies the formula above, to replace all "U" qualified data. Data qualified with an "I" are handled consistent with the rule; the reported value is replaced with the MDL. An MDL for total PCBs is not determined as each individual PCB has its own MDL.

List of Acronyms and Abbreviations for Analytical Techniques

The following definitions apply to the analytical technique descriptions found in the 62-4.246(4) list.

A-GPC	Gas Flow Proportional Counter
AMP	Amperometric
A-SCINT	Scintillation Counter
Auto	Automated Analyzer
BAC-MF	Membrane Filter Technique
BAC-MPN	Most Probable Number (Multiple Tube/Multiple Well Plate)
CALC	Calculated by Indirect Analysis
Chelation-FLAAS	Flame Atomic Absorption Spectroscopy with Sample Chelation Preparation
CIE-UV	Capillary Electrophoresis-Ultraviolet Detector
COLOR	Colorimetric
COND	Conductivity
CO-PRECIP	Co-precipitation Sample Preparation
COUL	Coulometric Titration
CVAF	Cold Vapor Atomic Fluorescence
CVAAS	Cold Vapor Atomic Absorption Spectrophotometry
DCP-ES	Direct Current Plasma-Emission Spectrophotometry
DIFFUSION-Auto	Gas Diffusion – Automated Analyzer

FID	Flame Ionization Detector
FLAAS	Flame Atomic Absorption Spectroscopy
FLAAS-HYDRIDE	Flame Atomic Absorption Spectroscopy with Sample Hydride Preparation
FLUOR	Flourescence Spectrophotometry
GAS-FLOW-P	Gas Flow Proportional Counter
GC	Gas Chromatography
GC-ECD	Gas Chromatography - Electron Capture Detector
GC-ELCD	Gas Chromatography - Electrolytic Conductivity Detector
GC-ELCD-MCTD	Gas Chromatography- Electrolytic Conductivity or Microcoulometric Detector
GC-ELCD-PID	Electrolytic Conductivity and Photoionization Detector
GC-FID	Gas Chromatography-Flame Ionization Detector
GC-FPD	Gas Chromatography-Flame Photometric Detector
GC-MS	Gas Chromatography-Mass Spectrometry
GC-MS (SIM)	Gas Chromatography-Mass Spectrometry (Selected Ion Monitoring)
GC-NPD	Gas Chromatography-Nitrogen-Phosphorus Detector
GC-PID	Gas Chromatography-Photoionization Detector
GC-TBD	Gas Chromatography-Thermionic Bead Detector
GFAAS	Graphite Furnace - Atomic Absorption Spectrophotometry
GM	General Chemistry Method
GRAV	Gravimetry
HPLC	High Performance Liquid Chromatography
HPLC-UV	High Performance Liquid Chromatography-Ultraviolet Detector
HPLC-UV-FLUOR	High Performance Liquid Chromatography-Ultraviolet or Fluorescence Detector
Hydride	Flame Atomic Absorption Spectroscopy with Sample Hydride Preparation
IC	Ion Chromatography
ICP-ES	Inductively Coupled Argon Plasma Emission Spectrophotometry
ICP-MS	Inductively Coupled Argon Plasma Mass Spectrometry
IMS-FA	Immunomagnetic Separation-Immunofluorescent Assay
IR	Infrared Detector
IR-COUL	Infrared Detector or Coulometric Titration
IR-COUL-COND	Infrared Detector or Coulometric Titration or Conductivity Detector
IR-FID	Infrared Detector or Flame Ionization Detector
ISE	Ion-specific Electrode
ISE-Auto	Ion-specific Electrode-Automated
LC-ION	Ion Chromatography
LDO	Luminescence-Based Dissolved Oxygen Sensor
NESSLER	Nesslerization
POT	Potentiometry
SPEC	Spectrophotometry
SPEC-Auto	Spectrophotometry-Automated Analyzer
ST-GFAAS	Stabilized Temperature-Graphite Furnace Atomic Absorption Spectrophotometry
TEMP	Temperature
TITR	Titration
TITR-Auto	Titration-Automated Analyzer
TSGF	Thermally Stabilized Platform Graphite Furnace
TURBID	Turbidity/Turbidimetric
UV-VIS	Ultraviolet-Visible Detector

UV-VIS-Auto	Ultraviolet-Visible Detector-Automated Analyzer
Voltammetry	Pulse Anodic Stripping Voltammetry

List of Acronyms for Organizations and Sources of Methods

The following definitions apply to the acronyms for organizations cited in the 62-4.246(4) list.

ANSI	American National Standard Institute
AOAC	AOAC International
ASTM	American Society for Testing and Materials
Bran Luebbe	Bran & Luebbe Analyzing Technologies, Inc. (Industrial Methods)
Brooks-Blanchard	"A Procedure for the Determination of ^{228}Ra," I.B. Brooks & R.L. Blanchard
CFR	Code of Federal Regulations (U.S.)
DEP	Florida Department of Environmental Protection
DOE	U.S. Dept. of Energy, Environmental Measurements Laboratory Procedures Manual
DOH	Florida Department of Health
EPA	United States Environmental Protection Agency
EPA, 1978	EPA Reference Method*
HACH	"Hach Handbook of Water Analysis," Hach Chemical Company
NCASI	National Council for Air and Stream Improvement, Inc.
OIA ALPKEM	OI Analytical/ALPKEM Corporation
OIC	Oceanography International Corporation
ORION	Orion Research, Inc. (Instruction Manual for 97-70 electrode)
SM	"Standard Methods for the Examination of Water and Wastewater" (APHA)
USGS	"Techniques of Water-Resources Investigation of the U.S. Geological Survey"

*Methods for Benzidine: Chlorinated Organic Compounds, Pentachlorophenol and Pesticides in Water and Wastewater. September 1978.

List of Acronyms and Abbreviations for Analytes, Units and Miscellaneous Terms

The following definitions apply to the acronyms and abbreviations for miscellaneous terms found in the 62-4.246(4) list.

ADMI	American Dye Manufacturers' Institute Color Value
BHC	Hexachlorocyclohexanes
COD	Chemical Oxygen Demand
Col/100 mL	Colonies per 100 mL of sample
D (2,4-)	2,4-Dichlorophenoxyacetic acid
DDE	1,1-Dichloro-2,2-di(p-chlorophenyl)ethylene
DDT	4,4'-Dichlorodiphenyltrichloroethane
degree C	Degrees Celsius
DEP-SOP	DEP Standard Operating Procedures for Field Activities (DEP-SOP-001/01, January 2017)
DEP-SOP (NH_3)	"Calculation of Un-Ionized Ammonia in Fresh Water" (DEP Chemistry Laboratory, 2/12/01)
FAC	Florida Administrative Code
mg/L	milligrams per liter
mL	milliliter(s)
MPN/100 mL	Most Probable Number per 100 mL
NTU	Nephelometric Turbidity Units

PCB	Polychlorinated biphenyl
pci/L	picocuries per liter
PCU	Platinum Cobalt Unit
pg/L	picograms per liter
SU	Standard Units (pH)
TCDD	Tetrachloro-dibenzo-p-dioxin
TDS	Total Dissolved Solids
TON	Threshold Odor Number
TP(2,4,5-)	2-(2,4,5-Trichlorophenoxy)propionic acid (*Silvex*)
TSS	Total Suspended Solids
µg/L	micrograms per liter
µmhos/cm	micromhos per centimeter; equivalent to microsiemens per centimeter (µS/cm)