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NATIONAL WATER QUALITY LABORATORY TECHNICAL MEMORANDUM 1998.07

September 28, 1998

Subject: Reporting Level Changes for Volatile Organic Compounds (Schedules 2020/2021), Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES), Ammonia plus Organic Nitrogen and Phosphorus (micro-Kjeldahl) in Water Methods at the National Water Quality Laboratory

Effective date of changes: October 1, 1998

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Revision: None

Supplemental Material: None

PURPOSE

This memorandum provides long-term method detection levels (LT-MDLs) and sets reporting levels at the nondetection value (NDV) for four water methods at the National Water Quality Laboratory (NWQL), effective on October 1, 1998:

1. Low-level volatile organic compounds (VOCs) by gas chromatography/mass spectrometry (schedules 2020 and 2021),
2. Trace elements in filtered water by inductively coupled plasma-atomic emission spectrometry (ICP-AES),
3. Ammonia plus organic nitrogen (micro-Kjeldahl digestion), and
4. Phosphorus (micro-Kjeldahl digestion).

This memorandum also outlines new reporting conventions for these four methods. A forthcoming Office of Water Quality (OWQ) technical memorandum will describe the LT–MDL procedure for establishing detection and reporting levels, detail the new reporting conventions and the potential changes to the historic data record, and provide guidance on data interpretation using data reported with the new conventions. Distribution of this OWQ technical memorandum is planned for early FY99.

SCOPE

The new reporting conventions being implemented October 1, 1998, by the NWQL for VOC schedules 2020/2021, and ICP–AES, Ammonia/Organic Nitrogen and Phosphorus methods only are outlined below.

New Reporting Conventions

If the analyte is not qualitatively detected in the sample, **then** the reported value will be <NDV. (The nondetection value (NDV) is the default “less than” concentration provided when the analyte is not detected in the sample.)

If the analyte is detected at a concentration:

1. Equal to or greater than the NDV or the lowest calibration standard (for multipoint calibration methods), whichever is higher, **then** report the analyte concentration.
 2. Equal to or greater than the LT–MDL, but less than the NDV or lowest calibration standard (for multipoint calibration methods), whichever is higher, **then** report the analyte concentration with an “E” estimated remark code.
 3. Less than the LT–MDL, **then** report <NDV.
 4. Less than the LT–MDL for information-rich methods only, **then** report the analyte concentration with an “E” estimated remark code. (Situation 4 applies only to the VOC method (schedules 2020/2021) of the four methods discussed in this memorandum.)
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The long-term method detection level (LT–MDL) represents the lowest concentration of a detected analyte that will be provided for the ICP–AES and ammonia/organic nitrogen and phosphorus methods. Concentrations of detected analytes that are less than the LT–MDL are reported for VOC schedules 2020 and 2021.

In tables 1 through 4, the number of digits used for the LT–MDL and NDV concentrations were based on the decade unit of the standard deviation used to calculate the LT–MDL. For example, beryllium had a standard deviation of 0.13, so the LT–MDL and NDV are provided to the tenths (0.1) decimal place.

LT–MDLs and NDVs for Schedules 2020 and 2021—Volatile Organic Compounds in Water

Table 1 lists the current reporting levels that were set at the nondetection values (NDVs) published in Connor and others (1998) for 10 analytes from Schedules 2020 and 2021. Also listed are the new NDVs and LT–MDLs for these 10 analytes that will become effective October 1, 1998. The NDVs and LT–MDLs for all other analytes in these two schedules remain unchanged and previously were provided in Connor and others (1998).

Table 1. Current nondetection values (NDVs) and new NDVs and long-term method detection levels (LT–MDLs) for 10 analytes from volatile organic compounds in water schedules 2020 and 2021 at the NWQL
[µg/L, micrograms per liter; na, not available]

Analyte	Parameter (WATSTORE) code ¹	NWQL lab code	Current NDV (µg/L)	Effective October 1, 1998	
				NDV (µg/L)	LT–MDL ² (µg/L)
Benzene	34030 E	2433	0.032	0.10	0.05
<i>tert</i> -Butyl methyl ether	78032 D	2418	0.112	0.17	0.08
Carbon disulfide	77041 B	2413	0.080	0.37	0.18
Dichlorodifluoromethane	34668 D	2400	0.096	0.14	0.07
Methyl acrylate	49991 A	2425	0.612	1.4	0.7
Methyl iodide	77424 A	2412	0.076	0.21	0.10
Tetrachloroethylene	34475 E	2447	0.038	0.10	0.05
Tetrahydrofuran ³	81607 A	2428	1.15	9 ³	na
Toluene	34010 E	2443	0.038	0.05	0.03
1,2,3-Trichloropropane	77443 D	2462	0.070	0.16	0.08

¹The letter following the 5-digit parameter code represents the method code for both schedules 2020 and 2021.

²LT–MDL determined using 50 samples.

³Tetrahydrofuran LT–MDL not available. The 9-µg/L concentration is a raised reporting level due to tetrahydrofuran blank interference in new method instrumentation.

The reporting level changes listed above resulted from a change in method instrumentation in October 1997 that produced a statistically significant change in detection capabilities for the 10 analytes. Other method analytes with improved sensitivity or that exhibited insignificant changes (new NDV comparable to current NDV) will remain at the current NDV reporting level. Analytes with improved sensitivity are not being adjusted to lower NDVs because of the planned acquisition of new method instrumentation in early FY99 for these schedules.

Interpretation of Historical Data for VOC Schedules 2020 and 2021

Data that have been transmitted for all detected VOCs are correct. Nondetection reporting levels that have been provide for 7 of the 10 analytes listed in table 1 also are correct. Some nondetections for methyl *tert*-butyl ether, 1,2,3-trichloropropane, and methyl acrylate in sample sets analyzed from October 15, 1997 through June 30, 1998, should be interpreted using the new NDVs listed in table 1 only if the analyte was not detected in the NDV check standard that was analyzed along with the sample. The NDV check standard result is included in the hardcopy report provided for each sample. After June 30, 1998, all samples were reported with raised reporting levels equivalent to the new NDVs for nondetections of the 10 VOCs listed in table 1.

LT–MDLs and NDVs for Inductively Coupled Plasma–Atomic Emission Spectrometry (ICP–AES) Filtered-Water Method

Table 2 lists current minimum reporting levels (MRLs) for trace elements in filtered water determined by the ICP–AES method, including the 18 elements that had MRL changes implemented on December 15, 1997, as announced in NWQL Technical Memorandum 98.05. Also listed are the new NDVs and LT–MDLs for all method elements that will become effective October 1, 1998. For most elements, the calculated NDV was not statistically different from the current MRL and, thus, was set equivalent to the current MRL concentration.

NOTE: Changes are for the USGS filtered-water method (I-1472-87), not EPA drinking-water methods, performed at the NWQL.

Table 2. Current minimum reporting levels (MRLs) and new nondetection values (NDVs) and long-term method detection levels (LT–MDLs) for the inductively coupled plasma–atomic emission spectrometry filtered-water method at the NWQL

[µg/L, micrograms per liter; na, not available]

Element	Parameter (WATSTORE) code ¹	NWQL lab code	Current MRL (µg/L)	Effective October 1, 1998		Number of LT– MDL samples
				NDV (µg/L)	LT–MDL (µg/L)	
Aluminum	01106 F	2111	10	10	6	38
Barium	01005 C	641	1	1.0	0.3	19
Beryllium	01010 B	655	1	1.6	0.8	19
Boron	01020 F	2110	16	16	7	38
Cadmium	01025 D	673	8	8	3	19
Calcium ²	00915 D	659	0.02	0.02	0.01	37
Chromium	01030 E	722	14	14	7	19
Cobalt	01035 C	644	12	7	4	19
Copper	01040 C	657	10	10	5	19
Iron	01046 D	645	10	10	5	37
Lead	01049 C	646	100	100	50	19
Lithium	01130 B	664	4	6	3	19
Magnesium ²	00925 C	663	0.004	0.004	0.002	37
Manganese	01056 C	648	4	3.0	1.5	37
Molybdenum ³	01060 A	649	60	50 ³	na	na
Nickel	01065 E	721	40	40	17	19
Silica ²	00955 D	667	0.1	0.05	0.03	37
Silver	01075 C	723	4	4.0	1.8	19
Sodium ²	00930 C	675	0.1	0.06	0.03	38
Strontium	01080 B	652	1	1.0	0.5	38
Vanadium	01085 B	653	10	10	5	19
Zinc	01090 B	671	20	20	7	38

¹The letter following the 5-digit parameter code represents the method.

²MRL, NDV, and LT–MDL information for these analytes are in milligram per liter (mg/L).

³Molybdenum LT–MDL not available. The MRL is changed based on LT–MDL-related tests performed to date indicating a reliable MRL of 50 µg/L.

Interpretation of Historical ICP–AES Data

The minimum reporting levels (MRLs) provided in Technical Memorandum 98.05 that became effective on December 15, 1997, were established based on pilot LT–MDL data collected in 1997 for the ICP–AES method. ICP–AES data (actual detections) reported prior to December 15, 1997, that are equal to or greater than the LT–MDLs listed in table 2 can be used. The NWQL recommends that data (detections) reported prior to December 15, 1997, that are less than the LT–MDLs in table 2 not be used, especially for regulatory purposes. Use of data at concentrations less than the LT–MDL are subject to an increased risk beyond 1 percent of false positive occurrences (analyte reported present when not in sample).

Some of the MRLs used prior to December 15, 1997, are subject to a risk factor that might exceed 50 percent for false negative occurrences (analyte reported not present at the MRL concentration when present at that concentration) based on the LT–MDL and NDV concentrations provided in table 2. Two examples include 10 µg/L for lead and 1 µg/L for cadmium. The NWQL urges careful consideration of historic ICP–AES data in light of the NDVs and LT–MDLs listed in table 2. The NWQL recommends that the minimum reporting levels provided in 98.05 or the NDVs for analytes listed in table 2 be used as more appropriate reporting levels for nondetections in ICP–AES data produced prior to December 15, 1997.

As noted in NWQL Technical Memorandum 98.05, the reporting levels for selected analytes determined by ICP–AES might be too high for some environmental water-quality studies. The NWQL recommends use of the more sensitive inductively coupled plasma-mass spectrometry or graphite furnace atomic absorption spectrophotometry methods available at the NWQL as an alternative to the ICP–AES method.

LT–MDLs and NDVs for Ammonia Plus Organic Nitrogen Water Methods

Table 3 lists current minimum reporting levels for ammonia plus organic nitrogen in water methods that were implemented on December 15, 1997, as announced in NWQL Technical Memorandum 98.01. Also listed are the new NDVs and LT–MDLs for these methods that will become effective October 1, 1998. The calculated NDV was equivalent to the current MRL concentration.

Table 3. Current minimum reporting levels (MRLs) and new nondetection values (NDVs) and long-term method detection levels (LT–MDLs) for ammonia plus organic nitrogen in water methods at the NWQL

[ASF, automated segmented-flow spectrophotometry; FIL, 0.45 µm filtered; mg–N/L, milligram nitrogen per liter; N, nitrogen; WWR, whole water recoverable]

Ammonia + organic nitrogen as N, micro-Kjeldahl digestion, colorimetry, ASF	Parameter (WATSTORE) code ¹	NWQL lab code	Current MRL (mg–N/L)	Effective October 1, 1998	
				NDV (mg–N/L)	LT–MDL ² (mg–N/L)
FIL	00623 D	1985	0.1	0.10	0.05
WWR	00625 D	1986	0.1	0.10	0.05
FIL, acidified	00623 E	1994	0.1	0.10	0.05
WWR, acidified	00625 E	1995	0.1	0.10	0.05

¹The letter following the 5-digit parameter code represents the method.

²LT–MDL determined using 283 samples.

LT-MDLs and NDVs for Phosphorus in Water Micro-Kjeldahl Digestion Methods

Table 4 lists current minimum reporting levels and new NDVs and LT-MDLs for phosphorus in water micro-Kjeldahl digestion methods that will become effective October 1, 1998.

Table 4. Current minimum reporting levels (MRLs) and new nondetection values (NDVs) and long-term method detection levels (LT-MDLs) for phosphorus in water micro-Kjeldahl digestion methods at the NWQL

[ASF, automated segmented-flow spectrophotometry; FIL, 0.45 µm filtered; mg-P/L, milligram phosphorus per liter; WWR, whole water recoverable]

Phosphorus, micro-Kjeldahl digestion, colorimetry, ASF	Parameter (WATSTORE) code ¹	NWQL lab code	Current MRL (mg-P/L)	Effective October 1, 1998	
				NDV (mg-P/L)	LT-MDL ² (mg-P/L)
FIL	00666 D	1983	0.01	0.05	0.03
WWR	00665 D	1984	0.01	0.05	0.03
FIL, acidified	00666 E	1992	0.01	0.05	0.03
WWR, acidified	00665 E	1993	0.01	0.05	0.03

¹The letter following the 5-digit parameter code represents the method.

²LT-MDL determined using 392 samples.

Interpretation of Historical Phosphorus Data

The NWQL has assessed the results of blind blank QC samples submitted since the micro-Kjeldahl digestion method became operational in Water Year 1992 to determine if the variability of the method has changed over time. This assessment showed minimal change in variability. Further, the variability of the blind blank results confirms the level at which the LT-MDL has been set based on replicate data from a 0.05 mg-P/L standard. This standard was measured 392 times between May 2, 1998 and August 31, 1998 with a mean concentration of 0.05 mg-P/L and a standard deviation of 0.01 mg-P/L (22 percent relative standard deviation). The NWQL advises that phosphorus in water data by micro-Kjeldahl digestion released since the method became operational on October 1, 1991 (OWQ Technical Memorandum 92.10) be interpreted using the new reporting conventions provided in this Technical Memorandum. At the old 0.01 mg-P/L minimum reporting level, the risk of a false negative is well above 50 percent. The NWQL urges users to consider carefully their historic phosphorus data in light of the NDVs and LT-MDLs listed in table 4. It is recommended that the NDVs listed in the table be used as more appropriate reporting levels for nondetections in phosphorus data. Data originally reported below the 0.03 mg-P/L LT-MDL should be censored to the <0.05 mg-P/L NDV level.

The NWQL recognizes that the higher NDV and LT-MDL relative to the current MRL of 0.01 mg-P/L for the phosphorus methods might not be adequate for some environmental water-quality studies. A statistical assessment of phosphorus data in filtered samples released during water year 1997 showed that 50 percent of the samples were reported as nondetections at the 0.01 mg-P/L minimum reporting level and that nondetections increase to approximately 60 percent at the 0.03 mg-P/L LT-MDL level. Phosphorus in whole water samples had about 25 percent nondetections at the 0.01 mg-P/L minimum reporting level and nondetections increase to approximately 40 percent at the 0.03 mg-P/L LT-MDL level. The NWQL does offer a low-level phosphorus method that is based on an acid-persulfate digestion, but that method is recommended only for clean water matrices. The changes for data reporting described in this memo do not effect the results of data for the low-level acid-persulfate method.

The NWQL is validating the two-reagent variant of U.S. Environmental Protection Agency method 365.1, phosphorus by persulfate digestion, to replace the current low-level phosphorus method and as an alternative to the Kjeldahl digestion method. Method validation, proficiency testing, and collection of data necessary to estimate the LT–MDL will be performed over the next few months. This method will become available on January 1, 1999. Several state agencies that offer this method have set it up with an analytical range of 0.002 to 0.2 mg-P/L and the NWQL expects to offer this same analytical range. The current micro-Kjeldahl method will be used for samples with concentrations of phosphorus exceeding 0.2 mg/L, the upper analytical range of the EPA method.

REFERENCES

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/signed/

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Supersedes: NWQL technical memoranda 98.01 and 98.05 and portions of Open-File Report 97–829.

Key Words: Reporting level, Minimum reporting level, MRL, Method detection limit, MDL, Long-term method detection level, LT–MDL, Nondetection value, NDV, National Water Quality Laboratory, NWQL, Inductively coupled plasma–atomic emission spectrometry, ICP–AES, Trace elements, Volatile organic compounds, VOC, 2020, 2021, 9090, 9091, Ammonia + organic nitrogen, Kjeldahl nitrogen, Phosphorus, Kjeldahl phosphorus.

Distribution: E and http://wwwnwql.cr.usgs.gov/tech_memos/Public/nwql.98-07.html