



United States Department of the Interior

U.S. GEOLOGICAL SURVEY
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NATIONAL WATER QUALITY LABORATORY TECHNICAL MEMORANDUM 2014.01

September 29, 2014

Subject: Reduction in the use of sample-weight-based scaling of reporting levels for National Water Quality Laboratory methods for organics in solids and sediments

Effective: October 1, 2014

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Revision: N/A

PURPOSE

This memorandum describes changes to sample preparation procedures and resulting data reporting being implemented by the U.S. Geological Survey (USGS) National Water Quality Laboratory (NWQL) for five methods that determine organic compounds in solids and sediments (table 1). These changes will reduce the use of sample-specific adjustment (scaling) of the reporting-level concentrations for these methods, simplifying the comparison of analytical results among samples. These actions were prompted by concerns expressed by data users trying to interpret scaled results. These changes will be effective for solids samples collected on or after October 1, 2014.

BACKGROUND

Five NWQL methods (table 1) that determine organic compounds in solids samples (bed sediments, soils, biosolids, etc.) apply extraction to an aliquot of the typically wet sample material at elevated temperature and pressure using Accelerated Solvent ExtractionTM (ASE) procedures comparable to those described in Burkhardt and others (2006). Although each of these methods has a target (default) dry-weight amount of solid sample to use for the extraction, the amount of wet, solid material actually extracted and its moisture content can vary substantially sample-to-sample. The ASE procedures employed for NWQL laboratory schedules (LS) 5433 and 5506/5507 determine both the sample dry-weight extracted and the sample moisture content as a part of the extraction procedure, not prior to the extraction (Burkhardt and others, 2006; Zaugg and others, 2006). While this approach simplifies the extraction procedure, it does not facilitate the extraction of uniform dry-weight amounts. Thus, the dry-weight amounts of samples extracted for these (and newer) ASE solids methods were found to vary substantially. In addition, the NWQL might purposely extract amounts much less than the target (default) dry weight because of anticipated high matrix complexity and presence of co-extracted nontarget compounds for the sample (for example, biosolids and other matrices with relatively higher amounts of organic matter). Finally, amounts much less than the target (default) dry weight purposely might be extracted because insufficient sample was provided.

Table 1. National Water Quality Laboratory solids methods that have routinely applied sample-specific scaling of the reporting levels and that are affected by the changes described in this memorandum.

[USGS, U.S. Geological Survey; NWQL, National Water Quality Laboratory; LS, laboratory schedule; LC, laboratory code; g, gram; PAHs, polycyclic aromatic hydrocarbons]

Solids/sediment method NWQL LS or LC	Primary category of analytes determined by the method	Prior target (default) dry weight for extraction (g)	New target (default) dry weight beginning October 1, 2014 (g)	Default reporting levels increasing by a factor of 2 for method analytes on October 1, 2014	USGS method report
LS 5433	Waste-indicator compounds	10 ^b	5	Yes	Burkhardt and others (2006)
LS 5506/ 5507	PAHs/PAHs plus alkylated PAHs	10 ^b	5	Yes	Zaugg and others (2006)
LS 6434 ^c	Steroid hormones	10	5	Yes	—
LC 8093 ^c (LS 6438 ^d)	Organohalogens	5	5	No	—
LC 9019 ^c	Current-use Pesticides	10	5	Yes	—

^a The default reporting level (in micrograms per kilogram dry-weight extracted) is a value that is based on a specified target (default) sample dry weight. This reporting level is listed in the NWQL services catalog (internal USGS access only).

^b A target (default) dry weight of 25 grams (g) is stated in the method reports for LS 5433 and LS 5506/5507. However, this 25-g amount was relevant to the amount of reagent sand used for preparing the laboratory set blank and set spike samples, and is not practical for most solids matrices. The target (default) dry weight used for sample-specific scaling of the default reporting level for these methods has been 10 g since 2007.

^c Research (custom) method.

^d Laboratory code 8093 will become LS 6438 upon the forthcoming method approval by USGS.

The non-uniform dry-weight amounts extracted for samples determined by these ASE solids methods require adjustment of the reporting levels, especially for samples having extraction weights substantially below the target (default) weight on which the reporting levels are based. The NWQL currently scales sample-specific analyte reporting levels associated with sample results provided in the USGS National Water Information System (NWIS) database for these ASE methods.

Note: Analyte-specific increases in the reporting level may additionally be applied because of matrix interference or laboratory blank contamination issues; these are separate issues than the reporting-level scaling discussed in this memorandum.

The NWQL solids methods that apply ASE use a method-specific default dry weight (table 1) against which all analyte reporting levels are uniformly scaled, as needed, for a given sample based on the dry-weight amount of material extracted for that sample. For example, 10 grams (g) historically has been used as the default sample dry-weight for LS 5433. If the amount of material extracted for a given LS 5433 sample is only 2-g dry weight, then the associated reporting levels for all analytes for that sample are scaled higher by a factor of five (= 10-g default weight/2-g actual weight extracted). This scaling is done because detection and reporting levels are influenced, in part, by the dry-weight amount of material extracted (see further discussion in the “Detection and Reporting Level Considerations” section).

PROCEDURAL AND DATA REPORTING CHANGES

The NWQL is making the following procedural modifications to sample preparation and data reporting for the methods listed in table 1 to reduce the use of reporting-level scaling. These changes are being fully implemented for samples collected on or after October 1, 2014.

Procedural Changes

1. Sample moisture determinations will occur prior to the ASE extraction step, using a separate aliquot of the homogenized (mixed) sample by weighing the aliquot before (wet) and after drying overnight (≥ 16 hours) in an oven at 130 °C.
2. Sample aliquots of 5-g \pm 0.5-g dry weight will be used as the target weight for most ASE extractions.

Note: A 5-g target weight is being applied uniformly to all solids methods that use ASE because that amount has been found procedurally acceptable for many matrices. Some matrices will require extraction of smaller amounts (see below).

3. A target dry weight of 1 g will be extracted for samples with anticipated high matrix complexity or higher organic carbon content; lesser amounts might be extracted depending on anticipated or known complexity and analyte concentrations.
4. The default (assumed) sample weight of reagent sand extracted for the laboratory set blanks for all ASE-based methods will be 5 g to match the new target (default) weight in table 1. This change affects four of the five ASE-based methods (see further discussion in the “Laboratory Set Blank Data Considerations” section).

Data Reporting Changes

1. Default reporting levels for four of the five methods listed in table 1 will increase by a factor of two for samples collected on or after October 1, 2014 because the target (default) amount of sample extracted is decreasing from 10-g to 5-g dry weight for those methods.

Note: Increasing the default reporting levels coincides with the procedural change to extract 5-g \pm 0.5-g dry weight for most sample matrices for the ASE solids methods, which will provide uniform reporting levels for those samples and simplify sample-to-sample interpretation of results.

The default reporting level is unchanged for the organohalogenes in solids method (LC 8093; soon LS 6438) as its default weight will not change.

2. Reporting levels will no longer be scaled sample-specific for extracted sample amounts equal to or greater than 2.5-g dry weight, regardless of the amount of material extracted.

Note: Reporting level concentrations are at least twice as high as the estimated detection levels for the solids methods; thus, reporting-level scaling is not being applied if the sample amount is equal to or greater than one-half the 5-g default weight. Reporting levels also will no longer be scaled to lower concentrations if the extraction amount is greater than the 5-g target weight.

3. Reporting levels will be scaled sample-specific to higher concentrations for those samples having extracted dry weights less than 2.5 g.

LABORATORY SET BLANK DATA CONSIDERATIONS

All NWQL methods for organic compounds in solids/sediment (ASE and non-ASE type) use a method-specific sample weight as the uniform default weight of reagent sand for reporting concentrations of analytes determined in the laboratory reagent set blank (referred to hereinafter as the set blank). This default weight is the same as used for reporting-level scaling (table 1). A uniform weight of sand is used as a set blank sample's dry weight for determining blank sample concentrations regardless of actual weight of sand extracted, which typically is a much greater amount for ASE methods. This uniform weight is used to simplify comparison of multiple set blank results for a given method over time. The reagent sand is baked at 450 °C for at least 4 hours prior to use and typically has not been the source of contamination in the methods' set blanks. Instead, other aspects of sample preparation and analysis likely produce any analyte contamination in set blanks.

The decrease from 10 g to 5 g as the default dry-weight to be uniformly used for the set blank samples for four of the five methods shown in table 1 is expected to result in a shift in the distribution of concentrations (two-fold greater) for contaminants routinely reported present in set blanks. For example, if cholesterol (routinely detected in LS 6434 set blanks) was previously detected in a set blank at a total mass of 400 nanograms (ng), then the reported concentration in that blank would be 400 ng/10-g default sample weight = 40 ng/g = 40 micrograms per kilogram ($\mu\text{g}/\text{kg}$). After October 1, if cholesterol is detected in a set blank at the same total mass (400 ng), the reported concentration will then be 400 ng/5-g default weight = 80 $\mu\text{g}/\text{kg}$. The change in default weights used for set blanks will not result in more blank contamination nor the loss of data for environmental samples because of blank-based data censoring by the NWQL from this shift in set blank concentrations.

Note: Data users must be cognizant of this shift in set blank concentrations simply due to the change in the default sample weight being used for set blanks.

Although use of the same (5 g) default weight for the set blank samples as the target weight to be used for environmental samples helps to simplify comparison of set blank results with environmental results, data users are advised to convert blank and environmental sample concentrations to total mass of analyte to make comparisons between blank and environmental samples. This is especially important when comparing results from environmental samples where the sample amount extracted is substantially different from the default weight used for the set blank. Total mass of analyte is simply calculated by multiplying the analyte concentration in the sample (in $\mu\text{g}/\text{kg}$) by the dry weight of sample extracted (in kg).

EFFECT ON DATABASES

Effect on USGS National Water Information System (NWIS) database

1. No change to historical data in NWIS.
2. For samples submitted on or after October 1, 2014, reporting-level scaling will not be applied for many solids-sample matrices, providing more uniform analyte reporting levels and simplifying sample-to-sample comparisons.

Effect on NWQL Quality Control Database and Catalog (USGS internal access only)

1. No change to historical laboratory set blank data in the NWQL quality control database.
2. Concentrations for analytes detected in set blanks prepared on or after October 1, 2014, will be reported based on 5-g dry weight, instead of 10 g, for LS 5433, LS 5506/5507, LS 6434, and LC 9019. This change will likely result in higher contaminant concentrations in those set blank samples when compared to concentrations for set blanks prepared prior to October 1, 2014.

3. Beginning October 1, 2014, the default reporting levels displayed in the NWQL services catalog will change for LS 5433, LS 5506/5507, LS 6434, and LC 9019. The default reporting levels remain unchanged by the actions described herein for LC 8093 (soon to become LS 6438).

Data users need to be aware of the above changes with respect to interpreting historical data.

DETECTION AND REPORTING LEVEL CONSIDERATIONS

Detection levels (DLs) for the ASE solids methods typically were estimated using one of two approaches: (1) the U.S. Environmental Protection Agency's procedure for method detection level as described in Burkhardt and others (2006) and Zaugg and others (2006); or (2) based on the gas chromatography/mass spectrometry responses for the analytes in low-concentration calibration standards coupled with consideration of the procedural recoveries for the analytes in laboratory reagent-sand (set) spike samples (for example, LS 6434). For each method the DL estimate is based on a default weight of sand considered representative of the typical extraction weight. That default weight has been 10 g for four of the five ASE solids methods (table 1).

Actual analyte DLs for solid-sample matrices are influenced primarily by two factors. The most important is matrix complexity. High matrix complexity reduces the ability to detect analytes to the same low concentration compared to a cleaner matrix (particularly the spiked reagent sand used to estimate the DL) because complex matrices contain many co-extracted non-target compounds that can suppress analyte response signal and produce high noise levels or interference during gas chromatographic/mass spectrometric analysis. Substantial amounts of matrix co-extractants also can negatively affect analyte recovery because co-extractants reduce performance (by competitive sorption) of the sorbent materials used during the analyte isolation and extract cleanup steps for these ASE methods. Low recoveries increase DLs. Matrix complexity is a primary reason for the change in the target sample weight for the four ASE methods. Based on substantial experience with past sample analyses, the NWQL believes that use of a 5-g target weight will accommodate most sample matrices for the ASE method. This also meets a primary goal of substantially reducing the need to scale analyte reporting levels for most sample matrices unless an amount less than 2.5 g is extracted for sample matrices anticipated to have high complexity or analyte concentrations. This change also will make data reporting and interpretation more simple and consistent for data users.

The other factor affecting DLs is the amount of sample extracted. A greater number of analyte detections might be expected for an extraction weight of 10 g compared to 5 g, but only if the matrix is not complex. For more complex matrices, extracting only 5 g might actually provide lower DLs compared to 10 g for the reasons noted above.

Reporting levels for most analytes in the ASE solids methods are set at two times the DL. Because these ASE solids methods use mass spectrometry, analytes detected at concentrations below the reporting and detection levels are reported for most analytes (Childress and others, 1999). Concentrations for a few blank-limited analytes in several of these methods are not reported below a minimum reporting level concentration. Although the change in the target (default) weight from 10 g to 5 g for four of the ASE methods is increasing the methods' default reporting levels by a factor of two, note that the new default reporting level is equivalent to the scaled reporting level that would have been provided for a 5-g sample when the default sample weight was 10 g.

Sample weights extracted for many projects commonly have ranged over an order of magnitude, with resultant scaled reporting levels often varying over the range of concentrations reported as detections in samples. This condition complicates being able to discern meaningful patterns in the data. The changes described in this memorandum will allow for a greater consistency in reporting levels for many samples and help simplify interpretation of results for both non-detected and detected concentrations.

REFERENCES

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Supersedes: N/A

Key words: detection level, dry weight, reporting level, reporting-level scaling, sample weight, sediment methods, set blank, solids

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