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National Water Quality Laboratory Technical Memorandum 2003.01

February 28, 2003

Distribution: E

Subject: Data-reporting conventions and implications for interpreting results from custom method 9060 for samples collected from March 1, 1999, to December 31, 1999

Effective date of Change: February 28, 2003

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Revision: N/A

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SUMMARY

Most samples analyzed using custom laboratory code 9060 (LC9060) between March 1999 and March 18, 2000 were subject to extended holding times. This technical memorandum describes the holding time studies undertaken at the NWQL to evaluate the effects of these extended holding times and guidance for the interpretation of these results. Data recoding procedures that the NWQL will implement also are described. This recoding is undertaken so that these results are properly remarked and qualified for USGS and public use.

These results are part of a multiyear LC9060 data set, and this technical memorandum provides the time history of changes to LC9060 up until the approval of the official method SH2060. Also described are the recoding procedures that the NWQL will apply to ensure (1) consistency within the LC9060 dataset and (2) compatibility with SH2060 results. The recoding to produce this consistency and compatibility was undertaken to provide the National Water-Quality Assessment Program with the ability to interpret these LC9060 and SH2060 data over the multiple years in which data were collected.

PURPOSE

This technical memorandum describes procedures and guidance for adding supplemental data-quality indicators to results produced using custom method 9060. The procedures and guidance apply only to results reported to National Water Quality Assessment (NAWQA) study units that submitted samples for custom analysis lab code (LC) 9060 from March 1, 1999, to December 31, 1999. These data qualifications were made because many samples received during this period were held for extended periods beyond the normal sample-holding times. The data qualifications are made by the NWQL and are implemented for the affected LC9060 data through the National Water Information System (NWIS). These changes, expected to be completed approximately one month after issuance of this technical memorandum, will be made to the national NWIS data base by the NWQL to consistently make the required changes for all the affected data.

Remark Code

Remark codes provide additional information about the magnitude (or absence) of a value. The remark code is almost always viewed with the value in the software to avoid misinterpretation of the value.

Value Qualifier Codes

Value Qualifier Codes provide information about the process used to determine an analytical value and, often, the remark code associated with the value. Up to three value qualifiers can be stored with any single result.

Data Quality Indicator Code

Data Quality Indicator Codes indicate the review status of a result, controls the ability of a batch input program to overwrite a value, and affects the inclusion of a result in output.

Method Code

Method codes identify the analytical method used to determine a value. In QWDATA 4.2, a table containing parameter codes and associated method codes was established and used to validate a data entry.

The specific implementation of these codes is described in the body of this text. This NWQL Technical Memorandum, related figures and tables are available at <http://nwql.cr.usgs.gov/usgs/lc9060/index.html>.

SCOPE

In December 1998, the National Water Quality Laboratory (NWQL) and the NAWQA leadership agreed to begin development of a new method for analyzing pesticides in water as a replacement and upgrade for schedule (SH) 2050. This method had been used to identify and quantify polar pesticides using solid-phase extraction, high-performance liquid chromatography, and UV-diode array

detection. The purpose of developing the new method LC9060 was to improve specificity and sensitivity and to include additional polar organic compounds. The NWQL and NAWQA agreed that solid-phase extraction followed by high-performance liquid chromatography/mass spectrometry (LC/MS) would be used for the new method. This analytical approach was chosen to improve method specificity in the presence of dissolved organic carbon and to resolve several important co-eluting compounds, two factors that limited the application of SH2050.

NWQL and NAWQA leadership mutually understood that the short lead time for method development (January-March 1999) might be insufficient to achieve a smooth startup of analysis of environmental samples from NAWQA, which would begin arriving in March 1999. This risk was explicitly acknowledged and accepted by NWQL and NAWQA as acceptable because LC9060 potentially would provide substantial gains in sensitivity and analyte coverage with LC9060. The implementation of LC9060 as a custom method demonstrated that the primary impact of the fast-track implementation was a substantial startup period, including longer-than-recommended holding times prior to sample extraction. In this technical memorandum, holding time is defined as the time interval, in days from the time a submitted sample is logged into the NWQL laboratory information management system until the sample is extracted. This definition was chosen because the sample tracking information available was indexed to the laboratory identification number, or laboratory ID, which is based on sample login date. Actual sampling-to extraction holding times could be 1-4 days longer, depending on when the sample was shipped. This memorandum (1) describes the extent of these holding-time delays, (2) provides the results of experiments conducted to evaluate the impact of extended holding times and estimate analyte half lives, and (3) reports data-reporting conventions and basic considerations for data interpretation for samples with extended holding times. A Water-Resources Investigations Report (WRIR), providing additional interpretive guidelines for data analysis, will be published after this memorandum.

This technical memorandum describes extraction holding-time studies undertaken to determine the effect of extended (3 to 4 months) sample storage prior to extraction on the recovery of the polar pesticides determined using LC9060. Findings are specific to those samples collected and submitted for LC9060 prior to January 1, 2000, after which extraction holding-times did not exceed NWQL holding-time guidelines for this procedure (four days from time of sample receipt, with between one and four days for sample shipment). However, it is important to note that the procedure described in Furlong and others (2001) is exactly the same for all samples processed since June 1999, whether the procedure used to process the sample is referred to as LC9060 or SH2060. The sole difference between the samples processed before and after January 1, 2000, is that most of the samples extracted before that date were held for longer than four days from receipt.

Historical Synopsis: Between December 1998 and June 1999, the Methods Research and Development (MRDP) and Analytical Services programs of the NWQL developed LC9060, a custom method based on a modified version of the extraction procedure used for SH2050, coupled with a quadrupole LC/MS procedure. After initial method validation on reagent, surface and ground-water matrices at a single concentration, LC9060 was put into limited custom use for the NAWQA program.

The first samples were received in March 1999. By July 22, 1999, more than 1,000 samples had been submitted, many more than previously predicted. NWQL sample preparation capacity was overwhelmed. As a result, samples were received and refrigerated at beyond the initial recommended sampling-to-extraction holding time of 4 days (Furlong and others, 2001). All

samples, which were received in amber glass bottles, were held continuously at 4°C until extraction. Sample extraction was made a priority from July 22, 1999, onward. In September 1999, one of the NWQL staff performing instrumental analysis was moved to sample preparation to further expedite extraction of samples. This was considered an acceptable compromise to reduce the number of unextracted samples, although this reassignment delayed the instrumental analysis of extracts. By the end of October 1999, 78 percent of samples on hand had been extracted and by the end of calendar year 1999, all samples to date had been extracted. The time from sample receipt to extraction for LC9060/SH2060 has been less than 4 days since January 1, 2000. Samples submitted prior to January 1, 2000, and their individual holding times prior to extraction are listed in Table 1 (see separate Microsoft Excel file attached). Between January 1, 2000, and March 18, 2000, samples were extracted within recommended sampling-to-extraction holding time of 4 days, but extracts were held longer than 30 days, the NWQL extract holding time limit, because of the substantial instrumental analysis backlog resulting from the focus on sample extraction. Accordingly, samples collected between March 1999, and March 18, 2000, are considered as a single dataset in this Technical Memorandum.

[Table 1.](http://nwql.usgs.gov/Public/tech_memos/lc9060-tbl1.pdf) Calculated holding time intervals for all LC9060 samples processed in calendar year 1999: http://nwql.usgs.gov/Public/tech_memos/lc9060-tbl1.pdf.

Concurrent with the LC9060 custom sample analysis, MRDP continued to validate the method at multiple concentrations. These data were combined with the initial validation data and submitted to the Office of Water Quality for approval as an official analytical method. LC9060 was approved as an official method (SH2060) on April 30, 2001. See Furlong and others (2001) for the approved method report, available electronically at: <http://nwql.usgs.gov/Public/pubs/WRIR01-4134.pdf>.

Holding-Time Variances

The affected samples listed in Table 1 (Excel File; included as an attachment) are ordered by the Julian date encoded in the Laboratory ID. The median holding-time interval was 97 days. The total numbers of samples per holding time interval are plotted in Figure 1 (included as an Adobe Acrobat pdf file, attached). This figure shows a bimodal distribution of holding times, with a narrow peak of samples with holding times of zero to seven days and a broad peak of samples with holding times between 96 and 117 days. Many samples were held for 3 to 4 months, caused in part by the difference between when NAWQA samples began to be routinely submitted during March 1999 (Julian day 64), and when the method was first put into routine production on June 24, 1999 (Julian day 175). Figure 2 (included as an Adobe Acrobat pdf file, attached) shows the holding-time interval for each sample, plotted by Julian date of sample arrival at the NWQL. Note that each point may represent multiple samples. The red circle in figure 2 indicates the date when sample extraction and analysis began; at that time, more than 780 samples had been submitted. Sample-holding times decreased steadily from June 24, 1999 (Julian day 175) to 31 December 1999 (Julian day 365). Figure 2 also contains a scattered population of samples whose holding-time intervals are lower than the observed trend. This population resulted from the NWQL decision to extract concurrently the oldest and newest samples. Overall, for the 2,306 samples submitted in 1999, 499 samples had holding time intervals of 30 days or less, 702 samples had holding-time intervals of 60 days or less, 1,019 samples had holding times of 90 days or less, and 2,253 samples had holding times of 120 days or less. More than half (55.8%) of the samples collected in 1999 had holding-time intervals greater than 90 days.

[Figures 1 & 2](#) Number of Samples per Holding Time Interval and Holding Time Interval by Date of Sample Arrival (Laboratory ID).

Assessment of Holding-Time Effects

Owing to the large number of samples with holding times in excess of the recommended four-day limit established by the NWQL, studies were conducted to determine effects of length of holding time on analyte recovery. These results can be used to report and qualify analytical results and to estimate the potential effects of extended holding times on the reported concentrations of individual samples.

Laboratory Holding-Time Study (LHTS)

The NWQL performed a holding-time study for the same sample matrices used to validate LC9060 as an official method, SH2060. These matrices are domestic ground water, surface water from the South Platte River, and pesticide-free, organic blank water. The laboratory holding-time study lasted 90 days. All samples were spiked at a time = 0, and triplicate samples of each matrix, taken from a single bulk sample, were extracted at 1, 2, 4, 7, 10, 15, 21, 30, 45, 60, and 90 days. The volume of spike solution added resulted in a final concentration of 0.5 ug/L in the 1-L samples. This concentration was used for all samples and compounds. The samples were held continuously at 4°C in 1-liter amber glass bottles until extraction. Possible problems with the spiking solution used for compounds analyzed by negative ionization (a possible spiking volume error or an instrument sensitivity loss) resulted in a decision to use only the laboratory holding time study results for compounds analyzed by positive ionization. A laboratory reagent water blank sample, analyzed concurrently with the spiked samples, contained no detectable concentrations of any of the compounds.

Field Holding-Time Studies (FHTS1 and FHTS2)

After initial review of LHTS results, the NWQL and NAWQA decided to conduct additional holding-time studies using environmental water samples provided by five NAWQA study units. The purpose of these additional holding-time studies was to assess whether dissolved organic carbon content or other characteristics of environmental samples was affecting the stability of LC9060 analytes. Since these holding-time samples were to be collected during regular NAWQA sample collection, samples were processed in duplicate rather than in triplicate, and the samples were processed at 0, 3, 7, 15, 30, and 60 days. As in the original holding-time study, all samples were spiked at Time =0 and samples were held continuously at 4°C in amber 1-liter glass bottles until extraction. However, because NAWQA-provided samples were collected over several weeks, it was necessary to start the field holding-time studies in two batches. In addition, an unspiked sample was analyzed to determine ambient pesticide concentrations so that results could be corrected for these contributions.

The first field holding-time study (FHTS1) focused on three surface-water sources with a wide range of dissolved organic carbon (DOC). Previous experience had suggested that DOC might be a controlling variable for pesticide degradation, so source waters, covering the likely range of DOC concentrations, were identified and collected. The source waters used in FHTS1 are described in table 2.

Table 2. Source waters for the first field holding-time study (FHTS1).
[LRL, laboratory reporting level; <, less than]

Station ID	Site Description	NAWQA Study Unit	DOC Concentration (mg/L)
393944084120700	Holes Creek at Huffman Park Near Kettering, Ohio	White River/Miami	4.5
07379960	Dawson Creek at Bluebonnet Blvd., Baton Rouge, Louisiana	Acadian-Pontchartrain	10.3
02281200	Hillsboro Canal at S-6 Near Shawano, Florida	South Florida	30.1
--	Residential Ground-Water Sample, Evergreen, Colorado	Obtained by NWQL employee	< LRL (1.5 mg/L; from a commercial laboratory)

A second set of field holding-time samples (FHTS2) was collected from sources described in table 3. However, the unprocessed data for FHTS2 were lost because of a computer-drive failure and data are available only from day 0 to day 15. As a result, FHTS2 is considered no further in this analysis of holding-time effects. FHTS2 results will be provided, however, as part of data interpretation guidelines in the Water-Resources Investigations Report that will be published following this technical memorandum.

Table 3. Source waters for the second field holding-time study (FHTS2).

Station ID	Site Description	NAWQA Study Unit	DOC Concentration (mg/L)
14200400	Little Abiqua Creek near Scotts Mills, Oregon	Willamette Basin	0.864
03575100	Flint River at Brownsboro, Alabama	Lower Tennessee River Basin	3.00
06719505	Clear Creek at Golden, Colorado	South Platte River*	1.60
--	Organic blank Water	NWQL-Provided	Less than the detection limit (0.33 mg/L)

*This sample collected by NWQL personnel.

The spiking levels and intervals for sample processing were identical for both FHTS1 and FHTS2 (500 ng/L = 0.5 ug/L), and a single operator processed all samples.

A first-order exponential decay model was fit to the results used from the LHTS, FHTS1, and FHTS2 studies for each analyte and sample matrix, and the half-life was determined from the model for each analyte/matrix combination.

Results

Half-lives, calculated by using the first-order decay model, are listed in table 4 (*see attached Table 4*). A mean half-life for each compound was determined from the replicate samples for each matrix. The median half-life for each compound is calculated from the median of all individual experiments and is not the median of the mean half-lives for each matrix. Note that in the LHTS study, nine compounds had initially low recoveries that varied unpredictably through the course of the LHTS experiment. This resulted in unexplainable half-life estimates for these compounds. In one case (atrazine in organic blank water) the estimated half-life was greater than 1,880 days. For the remaining eight compounds, the estimated half-life ranged between -20 and -5400 days, also highly improbable results. These highly improbable half-life estimations indicate that the exponential decay function used to model these data was inappropriate data. These improbable half-life estimations were replaced in table 4 with ">90 days." Table 4 provides the estimated half-life for each analyte/matrix combination, as well as the median half-life estimated for each analyte among all of the matrices tested. During the holding time study instrumental analyses, the concentrations of bentazon and acifluorfen in laboratory and field holding time studies could not be determined because of instrumental stability problems specific to these two compounds. An estimated half-life for acifluorfen and bentazon was calculated, using the median of the median half lives of the other similar pesticides determined using negative ionization. Those pesticides are 2,4-D, 2,4-DB, 2,4,5-T (Surrogate), Bromoxynil, Chlorothalonil, Clopyralid, Dacthal mono acid, Dicamba, Dichlorprop, Dinoseb, MCPA, MCPB, Picloram, and Triclopyr. This estimated half live is included in table 4.

Table 4. Estimated half-lives determined for sample matrices from the laboratory holding-time study (LHTS) and the first field holding-time study (FHTS1) for compounds included in provisional NWQL method LC9060. The samples were stored at 4°C in precleaned amber glass bottles for up to 60 days (FHTS1) or 90 days (LHTS).

Figure 3 shows the distribution of calculated half-lives for each compound, excluding acifluorfen and bentazon, for all matrixes, and plotted as a box plot. These box plots describe the range of calculated half-lives and reflect the cumulative variation resulting from multiple experiments for each matrix, and the diversity of matrixes represented in the data set.

Figure 3 Estimated Half-Lives from Field Holding Time Study.

Median half-lives ranged between 4 and 62 days. The mean of the median half-lives was 24 days, with a standard deviation of 12 days. The median of the median half-lives was 21 days, with an f-pseudosigma statistic of 11 days. The most readily degraded compound class were the carbamates, whose median half-lives ranged 4 and 20 days. It is important to note that most compounds showed substantial variability in estimated half-lives among matrixes. In general, ground water and organic blank water had the longest half-lives for most compounds, and surface water the shorter half-lives. There is some evidence that high DOC results in shorter half-lives, however, a quantitative relationship between DOC and compound half-life cannot be defined, given the limited data available.

Required Addition of Data Qualifiers to NWIS, Reporting of Analytical Results, and Interpretive Guidelines

Most of the samples collected for LC9060 analysis in calendar year 1999 exceeded the initial recommended holding time of four days. However, useful interpretations of pesticide occurrence and distribution can be derived from the results of these sample analyses, if properly qualified. First, it is crucial to note that all reported detections have met the qualitative identification criteria used for positive identification by high-performance liquid chromatography/mass spectrometry [as outlined in Furlong and others (2001)], and these identifications are valid. However, data from LC9060 during 1999 should be carefully qualified with respect to the effects of extended laboratory holding times on the reported concentrations of many of the samples. Interpretation of individual compound concentrations for compounds with extended holding times (defined as greater than the median half-life) requires particular attention to the potential rate of compound decay. Reported concentrations for such cases generally should be viewed and discussed as minimums (i.e., the results are biased low), although confidence bounds on analytical results may still include the actual concentration.

LC9060 contains matched sets of parent pesticides and their degradates. The suite of atrazine and its related degradates (desethylatrazine, desisopropylatrazine, desethyldeisopropyl atrazine, and 2-hydroxyatrazine) are the most frequently detected examples. Samples containing high concentrations of atrazine relative to the product degradates could have elevated degradate concentrations after extending holding times. No increase in degradate concentrations, either transient or sustained, was apparent in either laboratory and field holding-time studies, but these samples were amended with equal concentrations of parent compounds and product degradates, and any transient increase in degradate concentrations could be hidden by the variation in recoveries observed. In the absence of documented transformations of parents pesticides to degradates in the holding-time studies, pesticide degradate concentrations in samples with extended holding-time violations should be carefully qualified and interpreted, particularly if there are known sources of parent pesticide that may contribute to the water sample.

Results for samples where a compound was not detected and whose holding times exceeded the median half-life requires additional qualification. For those samples where the four-day holding time

was exceeded, and the compound was not detected, there is an increase in the probability that the compound was present at the time of sample collection, but not detected because the compound degraded in the sample during storage to a concentration below the laboratory reporting level. This probability increases as the holding time of the sample increases. The possibility that a compound was not detected due to degradation in the sample during storage needs to be acknowledged in any discussion of reported data. However, no claim that the compound was ever present can be made in light of the actual analytical result.

Distributional analyses of groups of samples that include extended holding times must also account for potential decay. Frequencies of detections should be considered minimums because there may have been some loss of compounds during the extended holding period, resulting in undetectable concentrations. Descriptive statistics calculated for sets of data, such as maximum, median, and mean values also should be considered as a lower bound because of the potential for these undetectable concentrations. In cases where only a small percentage of the study unit's data set includes the samples with extended holding times, excluding those data when calculating aggregate statistics should be considered. Note that this exclusion must be done for individual compounds, which may result in different size sample populations for different compounds.

Table 5 provides coding criteria to qualify LC9060 results from March 1999 through March 18, 2000. These criteria will be implemented at the national level by the NWQL and distributed through reloads to local NWIS databases and the NAWQA Data Warehouse. Holding time violations and the effect of extended holding times are reflected in the use of value-qualifier codes. The value-qualifier codes used have been implemented in NWIS 4.1 (current) or are being implemented in NWIS 4.2 implemented in all Districts as of February 21, 2003). Up to three value qualifier codes (at the active result level) can be associated with each result (see http://ok.water.usgs.gov/nawqa/phoenix/www/release4_1.html and http://ok.water.usgs.gov/nawqa/phoenix/www/release4_2.html for more detailed information). For the 1999 LC9060 data, the "E" remark code, two value qualifier codes, and a 50 character comment (maximum number of characters display limit for text comments under NWIS 4.2) are used to (1) indicate the specific holding time for each sample and whether sample holding times exceeded the 4-day holding time recommendation of Furlong and others (2001), and (2) the potential of extended holding times and known high variability for specific compounds on sample pesticide concentrations, as reflected by the holding-time interval for each sample and the compound-specific median half life (table 4).

Table 5. Guidelines for adding value-qualifier codes to LC9060 results for samples collected between March, 1999 and March 18, 2000. [LRL, laboratory reporting level; >, greater than]		
	Compound Detected	Compound Not Detected
<i>Sample holding time less than four days</i>	Report concentration according to standard practice.	Report as less than the interim reporting level as per standard practice.
<i>Sample holding time greater than four days and compound routinely reported with an "E" remark code</i>	Report concentration with (a) an "E" remark code, (b) the value-qualifier code for "holding time violation" (symbol= @ in NWIS 4.2), (c) the value-qualifier code for "highly variable compound, using this	Report as less than interim reporting level with (a) the value-qualifier code for "holding time violation" (symbol= @ in NWIS 4.2), (b) the value-qualifier code for "highly variable compound, using this method"

	method" (symbol= m in NWIS 4_1 and NWIS 4_2), and (d) the comment "Hold Time XX days [note: specific for each sample]; WRIR 01-4134, NWQL TMem 2003.01"	(symbol= m in NWIS 4_1 and NWIS 4_2), and (c) the comment "Hold Time XX days [note: specific for each sample]; WRIR 01-4134, NWQL TMem 2003. 01"
<i>Sample holding time greater than four days and compound <u>not</u> routinely reported with an "E" remark code</i>	Report concentration with (a) an "E" remark code, (b) the value-qualifier code for "holding time violation" (symbol= @ in NWIS 4.2), (c) the value-qualifier code for "highly variable compound" (symbol= w in NWIS 4_1 and NWIS 4_2), and (d) the comment "Hold Time XX days [note: specific for each sample]; NWQL Tech Memo 2003. 01"	Report as less than interim reporting level with (a) the value-qualifier code for "holding time violation" (symbol= @ in NWIS 4.2), (b) the value-qualifier code for "highly variable compound" (symbol= w in NWIS 4_1 and NWIS 4_2), and (c) the comment "Hold Time XX days [note: specific for each sample]; NWQL Tech Memo 2003.01"

An example text description follows which can be used to describe the qualitative effects of holding time violations:

"Analytical results in this (report, data table, map, chart...) from March, 1999 through March 18, 2000, were produced with a custom analytical method. Because the number of samples submitted for analysis far exceeded the available laboratory capacity, some samples were held for extended periods. Analytical results for samples that exceeded the method-specified holding time of 4 days (Furlong and others, 2001) are qualified with value qualifier code "@" which indicates a holding time violation. Detections and concentrations of pesticides in samples with holding time violations may be biased low. The degree of bias for a particular pesticide is a function of the length of the holding time and the half-life of the pesticide in water. The half-lives of pesticides in environmental samples held for extended periods were determined using selected surface water, ground water and reagent waters. Pesticide recoveries were determined from water samples that had been amended with pesticides and held for known periods of time (up to 90days; Furlong and others, 2001) prior to extraction and analysis. Combining the results from all water types, a compound-specific median half-life was determined. Holding times for some samples exceeded the median half-life of some pesticides. Where this occurred, the concentrations measured are expected to be less than one half the concentration that would have been measured had the sample been held less than 4 days. As a result, holding times in excess of pesticide half-life increases the probability that (1) a pesticide reported as not detected was present at the time of sample collection, but not detected because of degradation during storage to a concentration below the reporting limit, (2) the reported concentration is less than the measured concentration, because of degradation during storage, or (3) in the case of compounds that are degradation products of pesticides, the concentration could increase due to degradation of the parent pesticide during storage. Measurements of pesticides in samples that exceeded holding time are qualified with "m" or "w" which indicates that the measurement has higher variability as a result of holding time effects on precision and accuracy. The "m" qualifies results that are routinely reported with an "E" remark code, while the "w" qualifies results that are not routinely remarked upon.

For the purposes of writing reports and releasing data publicly, it is critical to indicate that the LC9060 results from samples collected between March 1999 and March 18, 2000, were produced using a new custom method. Accordingly, these data will be given the Data Quality Indicator code "U", for unapproved method. This will prevent default public release of the data. Furthermore, as stated in OWQ Tech Memo 98.05: "Data produced using new, unapproved methods or using research methods may not be published in data reports or in district annual data reports. In addition,

the data may not be released to the public in publicly accessible databases. Data provided to the public from unapproved methods or research methods must be accompanied by a method description that documents the method and the quality of the data reported." Reports containing LC9060 data from between March 1999 and March 18, 2000, must cite (1) Furlong and others (2001), which describes the method used in detail, and (2) this technical memorandum, which describes the subsequent qualifications applied to this data.

Integration of calendar year 1999 LC9060 data with other LC9060/SH2060 data

The above guidance allows systematic qualification of LC9060 data from samples collected in between March 1999 and March 18, 2000. However, between 19 March 2000 and 30 April 2001, LC9060 results were produced until the approval of SH2060. The entire set of results from LC9060 analyses are likely to cover several years for many NAWQA study units, and also may require interpretation with results from SH2060. Thus, the combined LC9060/SH2060 data will need to be interpreted as consistently as possible across all changes to samples and the analytical method used to analyze them.

As of January 1, 2000, no sample holding time violations occurred, and after March 18, 2002, sample extracts were analyzed within 30 days. Also, after 1 January 2000, no changes were made in extraction, isolation, and instrumental analysis steps of the method. However, ongoing interpretation of method quality assurance/quality control data resulted in some changes to the interpretation of instrumental results. In order to simplify data interpretation across multiple years, any changes to the interpretation LC9060 results produced after 31 December 1999 were reviewed and the following recommended changes to data were implemented at the NWQL in order to make the LC9060 data produced after 1 January 2000 and the official SH2060 data compatible for interpretation. These changes were made to all LC9060 data and consisted of (1) adding "E" remark codes to some compounds and censoring detections below 0.003 µg/L for all LC9060 data. The result of these changes is that there is no systematic methodological or QA/QC difference that would prevent the LC9060 results generated after March 18, 2000, from being combined and interpreted with the SH2060 data. The specific recommended changes to the data are:

1. Data for samples submitted for LC9060 analysis prior to March 18, 2000 (Julian day 78 of calendar year 2000) are censored for any detections below 0.003 micrograms per liter AND by any detections of the 27 compounds routinely reported with E-codes [Table 32 of Furlong and others, 2001 See reference below)] are so qualified. **However**, these data are provisional (DQI=U) and must remain so because of extended holding times and lags in extract analysis. Individual results are qualified by the use of value qualifier codes as listed in Table 5. These data cannot be combined with later data for statistical interpretation and determination of aggregate measures such as means, medians, minimum and maximum concentrations, although these aggregate statistics can be applied within this dataset.
2. For purposes of interpretation, data for samples submitted for LC9060 analysis between March 19, 2000 (Julian day 79 of calendar year 2000) and 21 July 2000 (Julian day 203 of calendar year 2000) can be made comparable to data produced by SH2060 by censoring any detections below 0.003 micrograms per liter AND by ensuring that any detections of the 27 compounds routinely reported with E-codes [Table 32 of Furlong and others, 2001 See reference below)] are so qualified.
3. For purposes of interpretation, data for samples submitted for LC9060 analysis after 21 July 2000 (Julian day 203 of calendar year 2000) can be made comparable to data produced by SH2060 by ensuring that any detections of the 27 compounds routinely reported with E-codes [Table 32 of Furlong and others, 2001 See reference below)] are so qualified.

These recommendations were based on the following chronology of method changes that may affect data quality or the interpretation of reported data.

Chronology of shifts in LC9060 QA/QC:

March 1999 to December 31st 1999-Results for samples submitted during this period are to be considered provisional, because many of the samples had extended holding times and the method was still being implemented as a production analysis. By December 31, 1999, all submitted samples had been extracted and all samples subsequently submitted were extracted within 7 days.

January 1, 2000, to March 18, 2000-Results for samples submitted during this period met extraction holding time criteria; however, instrumental analysis of sample extracts lagged. Data generated during this time also are considered provisional, because the effect of lagging instrumental analysis on analyte stability in the extract is not known.

March 18, 2000, to July 21, 2000-From this point forward, there are no systematic differences between the analytical procedure used in LC9060 and SH2060. All results for samples submitted during this period met extraction and instrumental analysis holding-time criteria. However, installation of more sensitive mass spectrometers and close observation of set blank data indicated the potential for extremely low-level false positives due to carry over causing cross-contamination between samples. This problem was documented in a status report for methods 9002 and 9060 distributed by Bob Greene on 21 July 2000. In that report, guidance for interpreting low-level results was described. The most pertinent guidance was the establishment of a censoring level of 0.003 micrograms per liter for all detections. The guidance for data where low-level contamination was suspected was also clarified. The data collected during this time interval can be made comparable with the data produced using the SH2060 method, if all detections less than 0.003 micrograms per liter are censored to the appropriate detection level for that compound.

July 22, 2000 to April 30, 2001-Results for samples submitted during this period met extraction and instrumental analysis holding-time criteria, and low-level detections were censored at the 0.003-microgram-per-liter level. However, upon implementation of LC9060 as an official USGS method (SH2060) on April 30, 2001, all results for an additional 17 compounds were routinely reported with an "E" remark code (also referred to as E-code; see table 6). Ten compounds initially were routinely E-coded during the use of LC9060 prior to approval. The criteria used to determine E-code status were based on the 285 laboratory set spikes processed in fiscal year 2000; the summary statistics for these lab spikes are listed in table 32 on p. 65 of Furlong and others (2001). These criteria were jointly agreed upon with representatives of the NAWQA Program (Jeff Martin, Bob Gilliom).

Note that the earliest sample processed as a SH2060 sample was submitted on Julian day 122 (May 2nd) of 2001. Between Julian day 122 and Julian day 141 (May 21), a mixture of SH2060 and LC9060 samples were submitted to the NWQL as method users made the transition to the approved method. However, these samples were extracted and analyzed identically and every effort was made to update the results to indicate that these were SH2060 samples. There are no differences between results for samples reported as SH2060 results and samples reported as LC9060 results during this time interval.

The two sets of compounds (after official method implementation and before and after official method implementation) routinely reported with "E" remark codes are listed below.

Table 6. Compounds routinely reported with "E" remark codes (E-codes) prior to and after conversion of custom method LC9060 to the approved method SH2060

Compound Name	Parameter Code	Method Code	E-coded Prior to Approval	E-coded After Approval
2,4-DB	38746	Z		X
2-Hydroxyatrazine	50355	Z	X	
3-Keto Carbofuran	50295	Z		"X
Aldicarb	49312	Z		X
Aldicarb Sulfone	49313	Z	X	
Aldicarb Sulfoxide	49314	Z		X
Bentazon	38711	Z	X	
Bromacil	04029	Z		X
Bromoxynil	49311	Z		X
Chloramben, methyl ester	61188	Z		X
Chlorothalonil	49306	Z	X	
Cycloate	04031	Z		X
Desethyl Atrazine	04040	Z		X
Desisopropyl Atrazine	04038	Z		X
Desethyl-desisopropyl Atrazine	04039	Z		X
Flumetsulam	61694	Z	X	
Imazaquin	50356	Z	X	
Imazethapyr	50407	Z	X	
MCPB	38487	Z		X
Methiocarb	38501	Z		X
Methomyl	49296	Z		X
Methomyl Oxime*	61696	Z	X	
Metsulfuron-methyl	61697	Z		X
Norflurazon	49293	Z		X
Oxamyl Oxime*	50410	Z	X	
Terbacil	04032	Z		X
Tribenuron-methyl	61159	Z	X	

* Compounds removed from the Schedule 2060 analyte list because of standard costs and poor recoveries. Documented in NWQL [Rapi-Note 02-007](#) (March 20, 2002).

In order to make all LC9060 data comparable with the data produced using the SH2060 method, all results for LC9060 for the 27 compounds routinely reported with an "E" remark code in SH2060 should also be remarked with an E-code.

Reference:

Furlong, E.T., Anderson, B.D., Werner, S.L., Soliven, P.P., Coffey, L.J., and Burkhardt, M.R., 2001, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory- Determination of pesticides in water by graphitized carbon-based solid-phase extraction and high-performance liquid chromatography/mass spectrometry: U.S. Geological Survey Water-Resources Investigations Report 01-4134, 73 p.

This WRIR is available at: <http://nwql.usgs.gov/Public/pubs/WRIR01-4134.html>

Effect on Data Base: The data-quality indicator qualifying procedure and guidance provided by this memorandum will be implemented at the NWQL level. The value qualifiers added (@ and m) will apply only to the historical data produced using LC9060 for samples submitted between March 1, 1999, and December 31, 1999. Data censoring at 0.003 ug/L and the addition of "E" remark codes will affect all LC9060 data in the database.

/signed/
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Key words: Custom method 9060, LC9060, Holding time, Method code, Remark code, Data quality indicator code, Value qualifier code, NAWQA

Distribution: E and <http://wwwnwql.cr.usgs.gov/USGS>