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IN REPLY REFER TO:

NATIONAL WATER QUALITY LABORATORY TECHNICAL MEMORANDUM 2005.03

February 3, 2005

Distribution:	E
Subject:	Changes in Reporting Levels and Data Qualifiers for Selected Pesticides and Degradation Products in Schedule 2060
Effective date of changes:	October 1, 2004
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Revision:	N/A

SUMMARY

An evaluation of quality-control data has shown that the absolute recoveries and variability of recoveries for many compounds in Schedule 2060 have changed temporally after the method was officially approved; most notably, a substantial change occurred after July 31, 2002. This technical memorandum describes the data analysis at the NWQL to (1) quantify the effects of this change, (2) provide guidance for interpreting results from environmental samples produced during this period of diminished method performance, (3) describe corrections made to restore method performance to conditions equal or better than conditions occurring prior to July 31, 2002, and (4) provide a quality control data summary that documents restoration of method performance.

These data are part of a multiyear Schedule 2060 data set, and this technical memorandum provides the time history of changes to Schedule 2060 to the present (December 2004). Also described are the recoding procedures that the NWQL will apply to ensure consistency within the Schedule 2060 data set. The recoding to produce this consistency was undertaken to provide the National Water-Quality Assessment Program and District customers with the ability to interpret Schedule 2060 data produced by the NWQL between July 31, 2002, and September 30, 2004. This recoding also will ensure that these data are properly remarked and qualified for use by the USGS and the public.

Finally, this technical memorandum describes the method audits used to identify sensitive components in the method procedure, where subtle changes may have resulted in the observed performance changes. Evaluation of these components resulted in corrective actions that have been implemented to restore method performance, which also is described. Quality-control sample results

collected after these corrective actions were implemented demonstrate restoration or improvement of method performance and are included in this document.

PURPOSE

This technical memorandum describes procedures and guidance for changing remark codes and adding supplemental data-quality indicators to data produced using Schedule 2060 during a period of diminished method performance. The procedures and guidance apply only to data reported to customers who submitted environmental samples for analysis using lab Schedule 2060 from June 1, 2002, to September 30, 2004. These data qualifications were made because the quality-control data collected during this period indicated reduced or variable recoveries. Data from environmental samples received during this period require qualification in light of this documented method performance change. The data are qualified by the NWQL and are implemented for the affected Schedule 2060 data through the National Water Information System (NWIS). These changes, expected to be completed about 1 month after issuance of this technical memorandum, will be made to the national NWIS database by the NWQL. The following NWIS code types will be used to qualify the data in the NWIS database:

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, control the ability of a batch input program to overwrite a value, and affect 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.

Comment

While not a code, the comment field will be used to indicate the corrective action type and will refer the data user to this technical memorandum for additional information.

The specific implementation of these codes is described in the body of this Technical Memorandum. This NWQL Technical Memorandum, related figures and tables are available on the NWQL website.

SCOPE

In June 1999, the National Water Quality Laboratory began analyzing polar pesticides using solid-phase extraction (SPE) and high-performance liquid chromatography (HPLC) with mass spectrometry (MS)(Schedule 2060), as described by Furlong and others, 2001. The NWQL routinely analyzes a reagent water blank sample and a reagent water spiked sample along with every set of 10 environmental (field) samples. Periodically these quality-control data are evaluated and new schedule control limits are determined. An evaluation of reagent water blanks and spikes was completed in 2004, and it was determined that there was a statistically significant change (either decrease or increase in compound mean recovery or variance) for several compounds. Evaluation of the reagent water blank data identified four compounds that demonstrated blank contamination in more than 10 percent of the environmental samples, the internal NWQL threshold defining chronic blank contamination, thus requiring adjustments to the data-reporting protocols for these compounds. Evaluation of the reagent water spike and matrix spike data indicated a general decrease in the recovery of most compounds. The decrease apparently occurred in a short period near or after July 31, 2002. This decrease caused concern because the method performance for nine previously well-behaved compounds decreased sufficiently to require routine qualification as estimated concentrations (E-coding).

Conversely, four compounds requiring E coding before July 31, 2002, caused by poor recovery (25 percent), were found to have sufficient improvements in method performance so that they could be reported without routine qualification.

This technical memorandum describes the assessment of reagent water blank, reagent water spike, and laboratory matrix spike data undertaken to document changes in the percent recovery and variation (as indicated by the standard deviation) for all compounds determined using Schedule 2060. This assessment is specific to those environmental samples collected and submitted for Schedule 2060 from June 2002, to September 30, 2004. Corrections applied to Schedule 2060 to restore or improve performance are described and a quantitative assessment of the efficacy of these corrections, based on laboratory quality control data is described. The interpretation and guidance based on the corrective action assessment is specific to those environmental samples collected and submitted for Schedule 2060 after September 30, 2004.

A statistical definition summary used to evaluate the Schedule 2060 data is included at the end of this technical memorandum.

Laboratory Reagent Water Blank Study (LRWB or set blank)

In the Schedule 2060 analysis, laboratory reagent water blank (LRWB) is prepared with each set of 10 environmental samples. Data from June 1, 2002, to January 1, 2004, for all compounds determined in Schedule 2060 LRWB, were retrieved from the NWQL laboratory information system (LIMS) by laboratory identification number. This time period was chosen because of an observed drop in compound recovery and increase in compound standard deviation for some compounds around July 31, 2002. The collated data were reviewed for inconsistencies. These inconsistencies included data-transcription errors, analysis errors, and human errors. QC sample data in the blank data aggregation that were not specifically identified as a set blank sample (i.e., set spike, data transmittal error) were removed from the statistical analysis. Table 1 (attached Excel spreadsheet) lists the statistical analysis of the LRWB data.

The LRWB data analysis shows that there are four compounds that exceed the NWQL chronic blank contamination criteria between July 31, 2002 and January 1, 2004. These criteria, defined as detection of the compound in >10 percent of the LRWBs, require that the minimum reporting level (MRL) of that compound must be raised by calculating the 95th percentile concentration from the blank data, and then multiplying this calculated value by ten.

The four compounds meeting this criterion in the data interval evaluated are desethyl deisopropyl atrazine, diuron, fenuron, and tebuthiuron. All other compounds did not meet the 10 percent or greater presence criteria. The MRLs for diuron and fenuron do not change based on the 95th percentile level multiplied by 10 requirements; the long-term method detection level (LT-MDL; Childress and others, 1999) calculated from low-level spiking data is the same. For the time period between July 31, 2002, and September 30, 2004, the reporting levels for desethyl deisopropyl atrazine and tebuthiuron will be raised according to the NWQL blank-contamination criteria of using the 95th percentile concentration multiplied by 10. Desethyl deisopropyl atrazine's MRL will be raised from 0.010 to 0.022 ug/L. The new MRLs and the resulting data updates will be implemented in NWIS by the NWQL using a data reload about one month after approval of this technical memorandum.

Table 1. Schedule 2060 LRWB Summary. Statistical abbreviations and tests defined at end of document.

Laboratory Reagent Water Spike Study (LRWS or set spike)

Data, from June 1, 2002, to January 1, 2004, for all compounds in Schedule 2606 LRWS study, were retrieved from the NWQL laboratory information management system (LIMS) by laboratory identification number. This time period was chosen because of a drop in compound recovery and increase in compound standard deviation noticed for some compounds around July 31, 2002. Data were statistically analyzed and divided into two periods based on the statistical review. Data from June 1, 2002, to July 31, 2002, were determined to be unaffected by the drop in recovery. A drop in recovery affected data from July 31, 2002, to September 30, 2004. These two time periods were used throughout this document as the dividing points for the data analysis and resulting suggestions.

The collated LRWS data were reviewed for data inconsistencies. These inconsistencies included data transcription errors, analysis errors, and human errors. Data determined to be from a sample other than a LRWS were removed from the statistical analysis. Table 2 (attached Excel spreadsheet) lists the statistical analysis of the LRWS data gathered. Figures 1 and 2 show the statistical analysis of the aggregated LRWS data for each compound. Compounds are segregated into either figure based on whether the compounds are determined by either positive or negative ionization during mass spectrometric analysis. The data from the statistical analysis show method performance for 19 out of the 23 compounds that were routinely reported as estimates (E-coded) before July 31, 2002, had not improved sufficiently, and will continue to be E-coded. These criteria for E coding are based on median recoveries 25 percent.

Four E-coded compounds, 2,4-DB, MCPB, desisopropyl atrazine, and desethyl atrazine, showed improvement in either recovery or variation as reflected by the collated laboratory reagent spike data. Data for environmental samples analyzed after July 31, 2002, until September 30, 2004, will have the "E" remark code removed. Nine compounds that were not routinely reported, as estimates prior to July 2002, will be qualified with an "E" remark code for environmental samples analyzed between July 31, 2002, and September 30, 2004. The compounds that will be qualified are dinoseb, benomyl, bensulfuron methyl, chlorimuron ethyl, fenuron, methomyl, nicosulfuron, oryzalin, and

oxamyl. Thirty compounds showed acceptable recoveries and standard deviations before and after July 31, 2002. These compounds may have shown small increases/decreases in recovery or small increases/decreases in the standard deviations, but all the data meet NWQL acceptance criteria and so require no changes to remark coding or data-quality indicators.

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The collated LRWS data were reviewed for data inconsistencies. These inconsistencies included data transcription errors, analysis errors, and human errors. Data determined to be from a sample other than a LRWS were removed from the statistical analysis. Table 2 (attached Excel spreadsheet) lists the statistical analysis of the LRWS data gathered. Figures 1 and 2 show the statistical analysis of the aggregated LRWS data for each compound. Compounds are segregated into either figure based on whether the compounds are determined by either positive or negative ionization during mass spectrometric analysis. The data from the statistical analysis show method performance for 19 out of the 23 compounds that were routinely reported as estimates (E-coded) before July 31, 2002, had not improved sufficiently, and will continue to be E-coded. These criteria for E coding are based on median recoveries 25 percent.

Four E-coded compounds, 2,4-DB, MCPB, desisopropyl atrazine, and desethyl atrazine, showed improvement in either recovery or variation as reflected by the collated laboratory reagent spike data. Data for environmental samples analyzed after July 31, 2002, until September 30, 2004, will have the "E" remark code removed. Nine compounds that were not routinely reported, as estimates prior to July 2002, will be qualified with an "E" remark code for environmental samples analyzed between July 31, 2002, and September 30, 2004. The compounds that will be qualified are dinoseb, benomyl, bensulfuron methyl, chlorimuron ethyl, fenuron, methomyl, nicosulfuron, oryzalin, and oxamyl. Thirty compounds showed acceptable recoveries and standard deviations before and after July 31, 2002. These compounds may have shown small increases/decreases in recovery or small increases/decreases in the standard deviations, but all the data meet NWQL acceptance criteria and so require no changes to remark coding or data-quality indicators.

Table 2. SH 2060 LRWS Summary. Statistical abbreviations and tests defined at end of document.

Figure 1. LRWS Statistical Summary for individual Schedule 2060 compounds analyzed for in the negative fraction. Statistical Abbreviations and tests defined at end of document. Unless otherwise indicated, units in figure are recovery, in percent.

Figure 2. LRWS Statistical Summary for individual Schedule 2060 compounds analyzed for in the positive fraction. Statistical Abbreviations and tests defined at end of document. Unless otherwise indicated, units in figure are recovery, in percent.

Laboratory Matrix Spike Study (LMS)

Laboratory matrix spike samples were, and continue to be, collected and analyzed as a means for understanding how the complex sample matrix affects recovery of Schedule 2060 compounds. Data from June 1, 2002, to January 1, 2004, for all compounds in Schecule 2060 LMS's and the unspiked replicate environmental samples were retrieved from the NWQL LIMS by laboratory identification number. This period was chosen because it reflected the observed decrease compound recovery and an increase in compound variability in LRWS samples, as indicated by standard deviation noticed for some compounds around July 31, 2002. The reason for evaluating the LMS data, in addition to the LRWS samples, was to determine if sample matrixes had any systematic effect on compound recovery when compared to the matrix-free LRWS samples. Data were statistically analyzed and divided into the same two data periods used for the LRWS analyses, and the same statistical tests were applied as were used in the analysis of LRWS samples.

Ground-water and surface-water data were aggregated in the statistical analysis because of the low number of LMS samples for the period (62 samples). The collated data were reviewed for data inconsistencies. These inconsistencies included transcription errors, analysis errors, and human errors. Data identified as not being a LMS or associated environmental sample were removed from the statistical analysis. The corresponding ambient environmental sample concentrations, if detected, were subtracted from the LMS data to remove any background contribution. Table 3 (attached Excel spreadsheet) lists the statistical analysis for the LMS data gathered. Figures 3 and 4 show the statistical analyses of the data for each compound. The data are segregated between the two figures based on whether the compounds where determined by either positive or negative ionization mass spectrometry.

The data from the analysis show that there may be potential preservation effects caused by environmental sample matrix. Individual compound recoveries show a marked increase in environmental matrices as compared to the LRWS. For example, the median LRWS bentazon recovery after July 31, 2002, is 2.0 percent. The average median recovery in the LMS samples after July 31, 2002, is 56.8 percent. The Schedule 2060 compounds affected by this apparent matrix preservation effect are bentazon, bromoxynil, chlorothalonil, dinoseb, aldicarb sulfoxide, aldicarb, benomyl, bromacil, chloramben, cycloate, methiocarb, methomyl, metsulfuron, norflurazon, and terbacil. The average median recoveries for these compounds may be higher in environmental samples as compared to the median recovery in LRWS. It is critical to note that results should not be corrected for matrix effect on recovery because the results presented in table 3 and figures 3 and 4 are aggregate values, and the amount and type of sample matrix can vary substantially between samples collected in differing watersheds or at different times of the year in the same watershed. These LMS results reinforce the NWQL recommendation to collect and analyze multiple LMS spikes (if possible) to characterize individual compound recoveries in specific sample matrices. The additional information provided by site-specific or watershed-specific matrix samples markedly improves the interpretation of individual compound concentrations.

Table 3. SH 2060 Matrix Spike Summary. Statistical Abbreviations and tests defined at end of document.

Figure 3. Matrix Spike Statistical Summary for individual Schedule 2060 compounds analyzed for in the negative fraction. Statistical Abbreviations and tests defined at end of document. Unless otherwise indicated, units in figure are recovery, in percent. Recoveries in matrix spike samples are corrected for ambient environmental sample concentrations.

Figure 4. Matrix Spike Statistical Summary for individual Schedule 2060 compounds analyzed for in the positive fraction. Statistical Abbreviations and tests defined at end of document. Unless otherwise indicated, units in figure are recovery, in percent. Recoveries in matrix spike samples are corrected for ambient environmental sample concentrations.

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

It is important to understand that all reported detections for Schedule 2060 compounds during the discussed time periods have met the qualitative identification criteria used for positive identification by high-performance liquid chromatography/mass spectrometry (HPLC/MS) [as outlined in Furlong and others (2001)], and these identifications are valid. The issue of changing method performance documented in this technical memorandum only affects reported concentrations of Schedule 2060 compounds. The purpose of this memorandum is to provide an explanation and guidance for interpreting and qualifying affected data from Schedule 2060 for samples collected between July 31, 2002, and September 30, 2004, so that they are appropriately qualified and reflect the effects of lower recovery, greater variability (as expressed as standard deviations), or blank contamination, when appropriate. Interpretation of individual compound concentrations requires particular attention to the recovery in environmental matrixes. Reported concentrations for such cases generally need to be viewed and discussed as minima (i.e., the data are biased low), although confidence bounds on analytical data may still include the actual concentration.

The data from the LRWB analysis show that there are four compounds that exceed the NWQL chronic blank-contamination criteria. These criteria, defined as a compound present in >10 percent of the LRWBs, require that the MRL of a compound must be raised by calculating the 95th percentile concentration from the blank data, and then multiplying this calculated value by ten. The four compounds meeting this criterion are desethyl deisopropyl atrazine, diuron, fenuron, and tebuthiuron. All other compounds did not meet the 10 percent or greater presence criteria. Diuron (0.015 µg/L) and fenuron (0.032 µg/L) will not have a change in their MRLs based on the 95th percentile level multiplied by 10 requirements because their MRLs are the same as the LT-MDL calculated level. Desethyl deisopropyl atrazine and tebuthiuron will have raised reporting levels based on the 95-percent level multiplied by 10 requirements. Desethyl deisopropyl atrazine's MRL will be raised from 0.010 to 0.022 µg/L, with tebuthiuron's MRL being raised from 0.006 to 0.013 µg/L.

The data from the LRWS statistical analysis show that 19 out of the 23 compounds that were E-coded before July 31, 2002, need to continue to be E-coded. This result is based on median recoveries 25 percent. Four E-coded compounds, 2,4-DB, MCPB, desisopropyl atrazine, and desethyl atrazine, showed improvement in either recovery or standard deviation and so will have the E-code removed on all data between July 31, 2002, and September 30, 2004. Nine non-E-coded compounds need to be E-coded based on the statistical analysis. Dinoseb, benomyl, bensulfuron methyl, chlorimuron ethyl, fenuron, methomyl, nicosulfuron, oryzalin, and oxamyl will have "E" remark codes added to all data between July 31, 2002, and September 30, 2004. Thirty compounds showed acceptable recoveries and standard deviations before and after July 31, 2002. These compounds may have shown small increases/decreases in recovery or small increases/decreases in

the standard deviations, but all the data meet NWQL acceptance criteria and so require no additional remark coding or data qualification.

Table 4 lists the LRWB, LRWS, and matrix spike data along with the NWQL suggestions for data interpretation and coding criteria to qualify Schedule 2060 data from June 2002 through September 30, 2004. 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. Changing recoveries and standard deviations 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 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://wwwnwis.er.usgs.gov/nwisdocs4_4/qw/QW-AppxA.pdf for more detailed information). For Schedule 2060 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 blank contamination (>10 percent) for each compound detailed in the LRWB data, and (2) the low recovery (25 percent) for each compound detailed in the LRWS data. For the purposes of writing reports and releasing data publicly, it is critical to indicate the proper remark codes for Schedule 2060 data from environmental samples collected between July 31, 2002, and September 30, 2004.

Table 4. NWQL Recommendations Summary. Statistical Abbreviations and tests defined at end of document.

Integration of July 31, 2002—September 30, 2004 Data with Other Schedule 2060 Data

The guidance in Table 4 allows systematic qualification of Schedule 2060 data from samples collected from July 31, 2002 to September 30, 2004. However, the entire set of data from Schedule 2060 analyses are likely to cover several years for many NAWQA study units. Thus, the combined Schedule 2060 data will need to be interpreted as consistently as possible across all changes to environmental samples and the analytical method used to analyze them.

Initially Schedule 2060 was used in provisional status as custom labcode LC9060 to provide the NAWQA Program the opportunity to test this method as a replacement for Schedule 2050. Necessary changes in methodology and data reporting occurred and were documented in NWQL Technical Memorandum 03-01. In that technical memorandum, guidance was provided to qualify LC9060 sample data so that all samples analyzed after January 1, 2000, would be consistent with results produced after implementation of Schedule 2060 as an official method on April 30, 2001. After the data qualification recommendations in this technical memorandum are implemented, there will be no systematic methodological or QA/QC difference that prevents the Schedule 2060 data produced between July 31, 2002, and September 30, 2004, from being combined and interpreted with the data from Schedule 2060 between January 1, 2000, and July 31, 2002. Chronologically, the data qualifications required are as follows:

> Data for environmental samples submitted for Schedule 2060 analysis prior to July 31, 2002, are censored for any detections less than 0.003 microgram per liter AND detections of the 27 compounds routinely reported with E-codes (see table 32 in Furlong and others, 2001) are so qualified. These data can be combined with later data for statistical interpretation and determination of aggregate measures, such as means, medians, minimum and maximum concentrations.

For purposes of interpretation, data for environmental samples submitted for Schedule 2060 analysis between July 31, 2002, and September 30, 2004, can be compared to earlier Schedule 2060 data by 1) censoring any detection less than 0.003 microgram per liter AND 2) by ensuring that any detections of the 32 compounds routinely reported with E-codes during this time are so qualified. These data can be combined with later data for statistical interpretation and determination of aggregate measures, such as means, medians, minimum and maximum concentrations. These suggestions were based on the following chronology of method changes that may affect data quality or the interpretation of reported data.

Chronology of shifts in Schedule 2060 QA/QC

July 22, 2000, to July 31, 2002

Data for environmental 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 Schedule 2060 as an official USGS method on April 30, 2001, all data 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 Schedule 2060 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).

August 1, 2002, to September 30, 2004

Data for environmental 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 review of Schedule 2060 quality-assurance data (LRWB, LRWS, matrix spikes), an additional nine compounds needed to be routinely reported with an "E" remark code. Four compounds initially E-coded can have the E-code removed, resulting in a net increase from 27 to 33 compounds routinely E-coded during this period. The determination of E-code status in this period for these compounds was based on the data present herein and the E-code criteria developed in Furlong and others (2001).

Corrective Actions Applied to Schedule 2060

As a consequence of this data review and the recognition by the NWQL that corrective action was required, two independent, bench-level reviews of the analytical procedures used in Schedule 2060 were conducted. The goals of these bench-level reviews were to determine (1) if Schedule 2060 data quality decreases resulted from small incremental changes in how extraction and analysis were performed, or if aspects of the 2060 extraction and analysis were not sufficiently in control under the existing standard operating procedure (SOP); and (2) how best to return Schedule 2060 to the pre-July 31, 2002, performance characteristics. NWQL Method Research and Development personnel, and NWQL Quality Assurance personnel independently reviewed Schedule 2060 bench-level operation. This process included reviewing SOPs, reviewing the associated method reports, interviewing all sample preparation and sample analysts, and following the current sample preparation and analysts through an entire Schedule 2060 analysis. These two reviews were conducted independently to maximize the potential for problem identification. Two major steps in the Schedule 2060 procedure were identified as possible sources of compound variable recovery or large variability. These two steps were the practice of using nitrogen to dry the solid-phase

extraction (SPE) cartridge before SPE elution (allowed as an option in the method SOP) and the reduction of the final sample extract to less than 300 microliters. Experiments were performed to validate that the elimination of the nitrogen drying step and keeping the final extract volume above 400 microliters returned Schedule 2060 data quality to pre-July 31, 2002, levels. The experiments demonstrated that the corrective actions to each of the steps were very likely to return Schedule 2060 data quality to pre-July 31, 2002, levels. These changes were documented in revisions to the method SOP, and all current and future analysts will be trained based on this updated procedure.

The NWQL is currently (2005) developing an automated, statistically–based, quality control chart review process for all compounds to minimize the chances of a similar quality shift situation developing in the future. This process will aggregate LRWS and LRWB data, process it using defined statistical tests, and deliver this data to the NWQL analysts and supervisors for review. This process will allow continuous review of the individual method and compound quality control data in a timely manner. This data is also planned to be made available to NWQL customers along with documentation detailing how the data was gathered, how to use, interpret, and report this summarized quality assurance data. Additional Rapi-Notes will follow when the process has been developed. Currently, analysts are reviewing the control charts for the LRWS and LRWB on a biweekly basis to minimize any change in quality.

LRWS Data Review Since Corrective Action

After implementation of corrective actions on May 1, 2004, LRWS data was collected and reviewed. From May 1, 2004, through September 30, 2004, 71 LRWS samples were analyzed. Table 5 lists the results of the LRWS study since May 1 showing mean, median, standard deviation and f-pseudo sigma for each compound. Based upon the criteria of median recovery from 60 to 120 percent and f-pseudo sigma less than 25 percent, only 9 of the 32 compounds routinely reported as estimates failed the remark criteria and should continue to be routinely reported as estimates (E-coded). Those nine compounds are desisopropyl atrazine, desethyl desisopropyl atrazine, aldicarb, chlorothalonil, 3-keto carbofuran, imazaquin, nicosulfuron, chlorimuron ethyl, and metsulfuron methyl. The data review suggested that the 23 compounds currently reported with E codes no longer require routine E codes. Based upon the data accumulated to date, the NWQL will routinely qualify only the aforementioned nine compounds after October 1, 2004.

Table 5. SH 2060 LRWS Summary for data after September 30, 2004. Statistical abbreviations and tests defined at end of document. Unless otherwise indicated, units in figure are recovery, in percent.

Removal of Tribenuron Methyl

Based upon the instability and quick deterioration of tribenuron methyl in calibration standards, the NWQL will delete tribenuron methyl (parameter code 61159) from schedule 2060. The NWQL has been routinely reporting tribenuron methyl as U-DELETED (remark code, unable to determine) because it cannot be calibrated accurately. Tribenuron methyl will continue to be reported as U-DELETED for samples collected through September 30, 2004, after which the compound will be removed from schedule 2060.

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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 will apply only to the data produced using Schedule 2060 for environmental samples submitted between July 31, 2002, and September 30, 2004. Reporting-level changes for the constituents in table 4 will cause a shift in reporting levels, and thus nondetection (less than) concentrations, in the database. Data users need to be cautious when interpreting historical data for these constituents in light of the new higher reporting levels. The new reporting levels for nondetections are more reliable indications of the actual concentrations that can be detected.

/signed/
Gregory B. Mohrman, Chief
National Water Quality Laboratory
Branch of Analytical Services

Key words: Schedule 2060, SH2060, Method code, Remark code, Data quality indicator code, Value qualifier code, NAWQA

Distribution: E and http://wwwnwql.cr.usgs.see Statistical Definition Summary

Summary