United States Department of the Interior

U.S. GEOLOGICAL SURVEY
Box 25046 M.S. 407
Denver Federal Center
Denver, Colorado 80225

IN REPLY REFER TO:

NATIONAL WATER QUALITY LABORATORY TECHNICAL MEMORANDUM 2007.02

May 31, 2007

Subject: Removal of Selected Pesticides and Degradation Products from Schedule 2060
Effective: January 1, 2007
Authors: Bruce Anderson, National Water Quality Laboratory – Analytical Services, (303) 236-3214, bdanders@usgs.gov
Revision: N/A

PURPOSE

This technical memorandum outlines the results of the evaluation of quality control (QC) data for selected compounds determined by pesticide analysis laboratory schedule 2060 (Furlong, and others, 2001). The QC data for three of these compounds (chlorothalonil, 3-keto-carbofuran, and chlordiamino-s-triazine) indicate that method performance is below National Water Quality Laboratory (NWQL) standards, and therefore these compounds will no longer be reported as part of the analytical method.

BACKGROUND

The NWQL strives to produce the highest quality and most scientifically sound data in all the analytical methods it offers. To ensure continued excellence, quality control samples are systematically included in all of our analyses. The QC data are periodically compiled and analyzed for trends, problems and overall method performance. In addition to the NWQL's internal QC program the Water Resources Discipline (WRD) monitors select analytical methods, independently, through the Branch of Quality Systems (BQS) Organic Blind Sample Project (OBSP). This program assesses the operational performance of the organic analytical methods by means of blind samples submitted to the NWQL. The results from the blind sample analyses are compiled, discussed and reported quarterly. Time-series charts are produced to aid in the assessment of the organic method's performance over time. The charts and the reports located at the OBSP website (http://bqs.usgs.gov/obsp/) are provided to assist the users of NWQL data in their interpretation of the environmental data over time.

In February of 2005 the laboratory released Technical Memorandum 2005.03 (U.S. Geological Survey, 2005), outlining diminished method performance for many schedule 2060 compounds during the period from June 1, 2002 and September 30, 2004. Changes to the method procedure after September of 2004 were expected to improve method

performance dramatically. As expected, we did observe dramatic improvements for most analytes. The data provided below summarize the poor performance of three schedule 2060 analytes based on recent NWQL QC data and QC data provided by the BQS through their OBSP website.

SCOPE

The NWQL uses established criteria to evaluate whether individual compounds in QC samples demonstrate sufficiently poor performance to be removed from the method. These criteria are described in the NWQL standard operating procedure (SOP) MX0015.2, *Guidelines for Method Validation and Publication at the National Water Quality Laboratory*. This document describes specific criteria for acceptance of compounds based on the performance of laboratory reagent water spikes (LRWS). Two statistical tools, f-pseudosigma (RF_σ) and mean or median are used. F-pseudosigma, used to evaluate performance, is a non-parametric statistical measure of variance, similar to the standard deviation (σ), that is used to reduce the influence of statistical outliers relative to the more commonly used parametric version (σ).

Based on this evaluation, and supporting OBSP data, the method performance for three schedule 2060 analytes have been determined to be unacceptable. Chlorothalonil and 3-keto-carbofuran were removed as of January 1, 2006 (see NWQL Rapi-Note 06-001, at http://wwwnwql.cr.usgs.gov/USGS/rapi-note/06-001.html). Chlordiamino-s-triazine was removed as of January 1, 2007. The supporting data and explanation for these actions are outlined below for each compound.

CHLOROTHALONIL

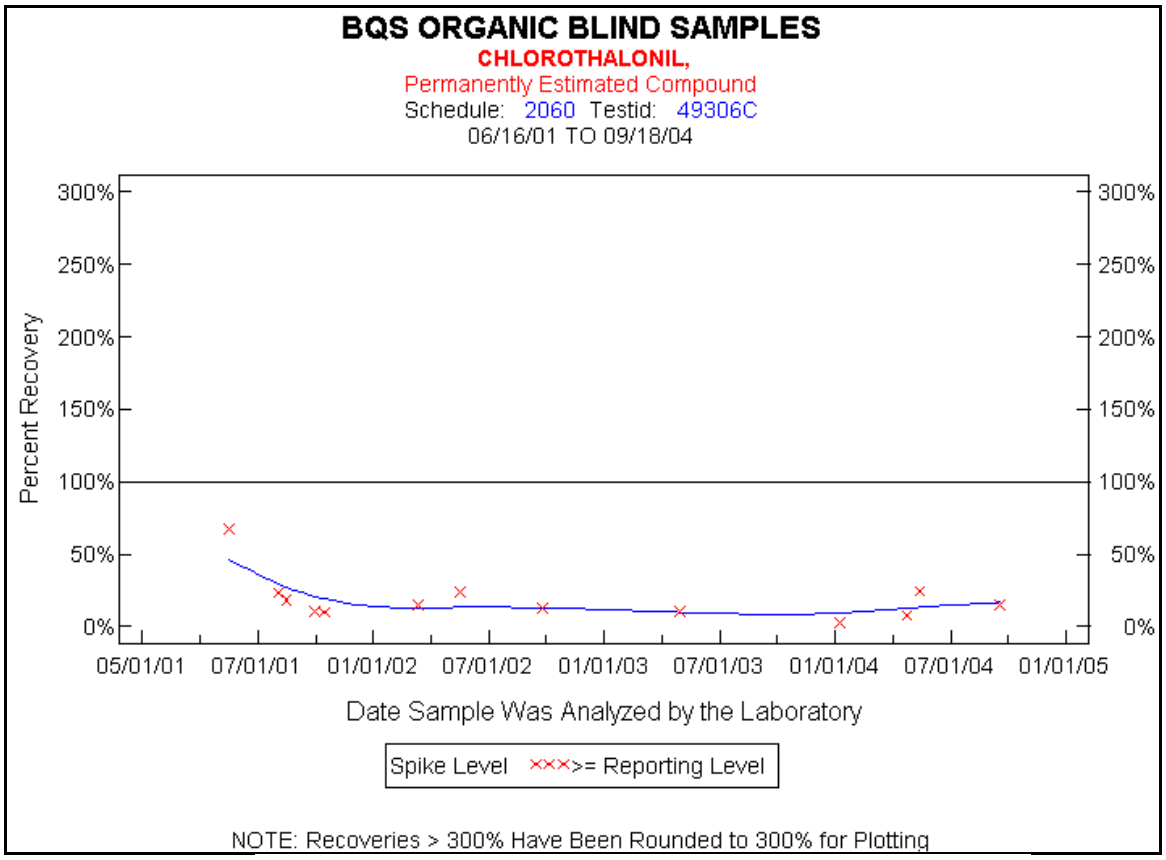
Parameter Code – 49306C

LRWS recoveries were evaluated during the period from October 1, 2004 through September 1, 2005. During this period, 136 spikes at a concentration of 0.25 micrograms per liter (µg/L) were analyzed. Of these 136 spikes, chlorothalonil was detected on only 2 occasions.

BQS Organic Blind Sample data from June 16, 2001 through September 18, 2004 (prior to method improvements) for chlorothalonil show mean recoveries of 19 percent, with 67 percent false negatives among the 67 samples tested with this analyte (Figure 1).

Analysis of continuing calibration verifications (CCV) standards, which provide an indication of the validity of instrument calibration and general instrument performance, for the period between October 1, 2004 and September 1, 2005 demonstrated a median recovery of 100.9 percent with an f-pseudosigma of 13.8 percent. The CCV data indicate that the instrument performance for chlorothalonil is acceptable; therefore the inadequate performance for this compound is a consequence of its poor extraction efficiency. LRWS and OBSP data demonstrated that the mean recovery of chlorothalonil by schedule 2060 is well below the 35 percent limit set by NWQL policy and that this compound should therefore not be included in the method.

Figure 1. BQS data for chlorothalonil; 6/16/01 through 9/18/04



Statistics for the Plotted Points
CHLOROTHALONIL

Spike Level	N	Mean	Std-Dev.	Median	F_Pseudo
>= Reporting Level	13	19%	16%	15%	10%
Total	13	19%	16%	15%	10%

Miscellaneous Statistics for the Samples
CHLOROTHALONIL

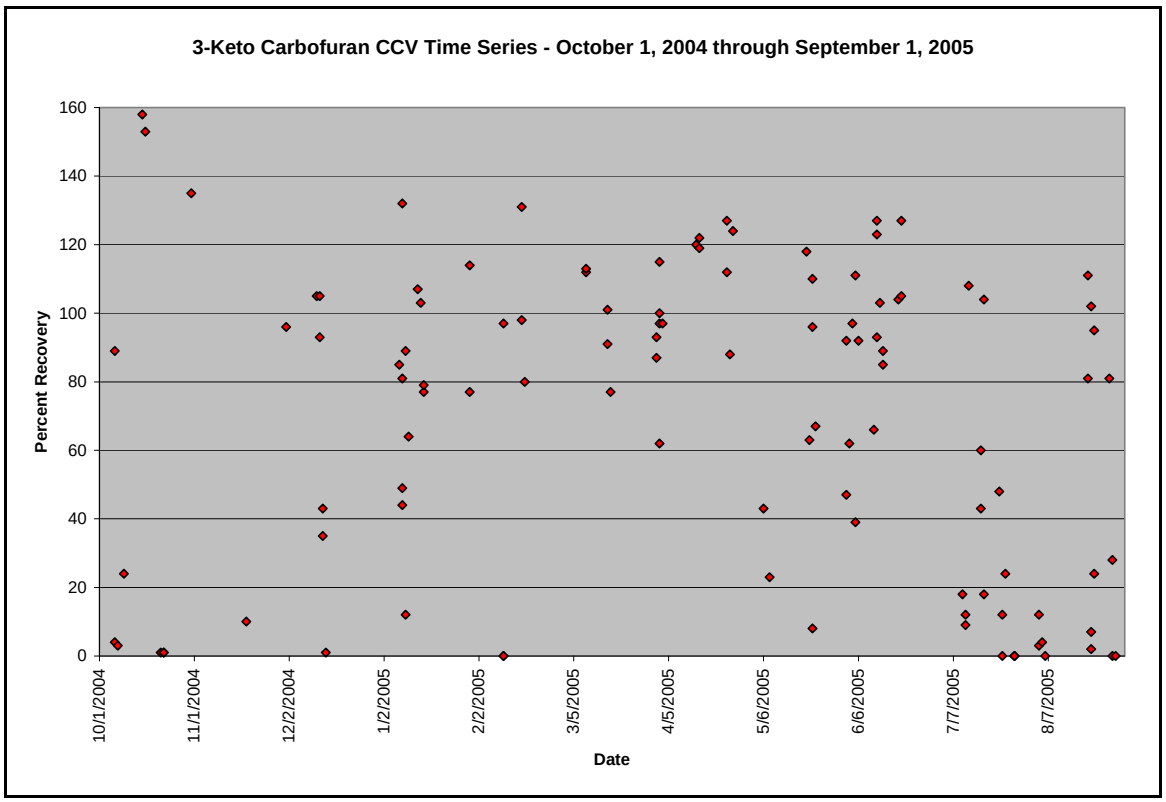
Characteristic	N	%	% Basis
Plotted	13	19%	Spiked
Estimated Values	13	19%	Spiked
Deleted Values	3	2%	Spiked + Not Spiked
Spiked, Censored	9	13%	Spiked
Spiked	68	.	
False Negatives	45	67%	45 out of 67
Not Spiked	95	.	
False Positives	0	0%	0 out of 93

3-KETO-CARBOFURAN
Parameter Code – 50295A

LRWS recoveries for 3-keto-carbofuran were also evaluated during the period from October 1, 2004 through September 1, 2005, including 136 spikes at a concentration of 0.25 µg/L. The median recovery was 78.1 percent for laboratory reagent water spikes and 81.4 percent for CCV standards.

Variability in compound recovery and CCV standards indicate very low reliability of quantitation, with f-pseudosigma values for the LRWS and CCVs of 32.7 percent and 45.5 percent, respectively. Figure 2 shows the plot of 88 CCV standards during the time period described.

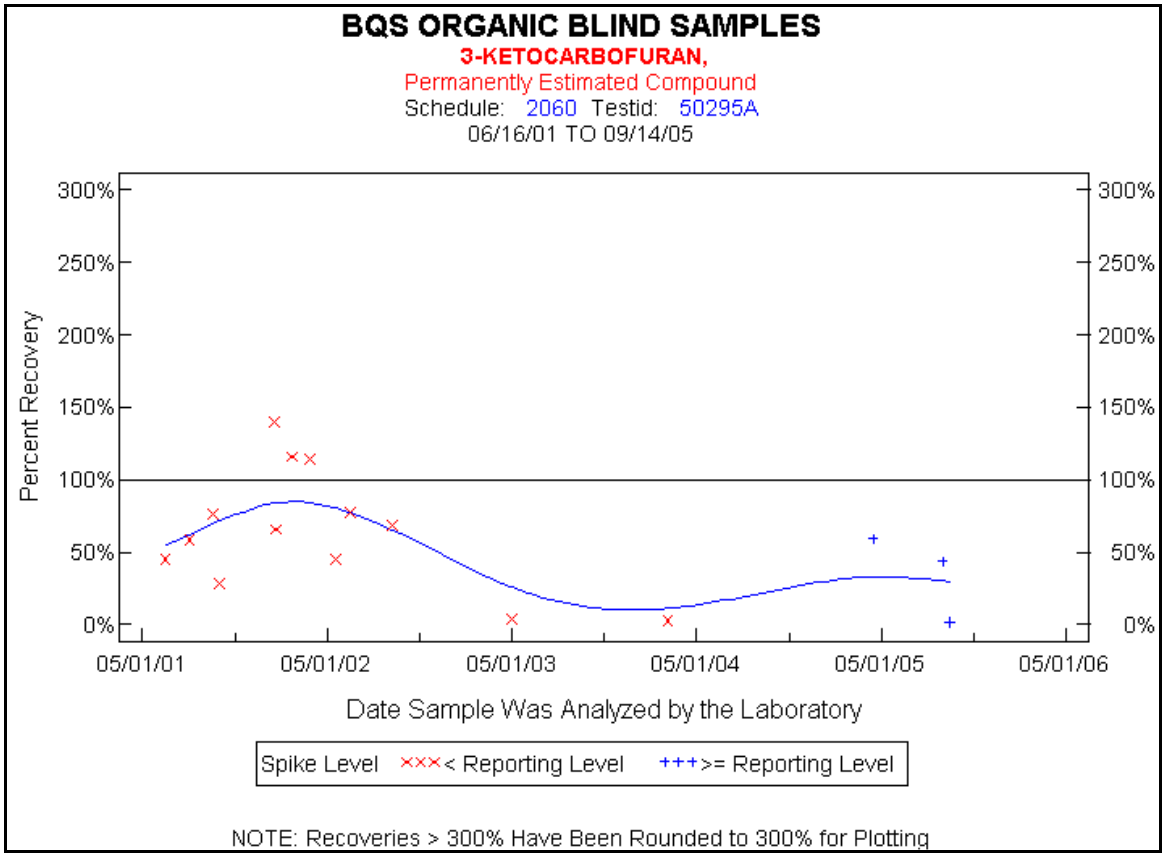
FIGURE 2. CCV standards for 3-keto-carbofuran, 10/1/04 through 9/1/05



While median recoveries are acceptable, inconsistent results are evident.

BQS Organic Blind Sample data from June 16, 2001 through September 14, 2005 show mean recovery of 59 percent with 26 percent false negatives among the 42 samples tested for this analyte (Figure 3).

Figure 3. BQS data for 3-keto-carbofuran; 6/16/01 through 9/14/05



Statistics for the Plotted Points
3-KETOCARBOFURAN

Spike Level	N	Mean	Std-Dev.	Median	F_Pseudo
< Reporting Level	13	65%	42%	66%	24%
>= Reporting Level	3	35%	30%	44%	43%
Total	16	59%	41%	59%	30%

Miscellaneous Statistics for the Samples
3-KETOCARBOFURAN

Characteristic	N	%	% Basis
Plotted	16	38%	Spiked
Estimated Values	16	38%	Spiked
Deleted Values	5	3%	Spiked + Not Spiked
Spiked, Censored	15	36%	Spiked
Spiked	44	.	
False Negatives	11	26%	11 out of 42
Not Spiked	119	.	
False Positives	0	0%	0 out of 116

LRWS, CCV and OBSP data demonstrate that results are highly unpredictable as evidenced by high variability in LRWS and CCV standards and the high incidence of false negative detections in the OBSP data.

CHLORDIAMINO-S-TRIAZINE
Parameter Code – 04039A

LRWS median recoveries between June 1, 2006 and October 1, 2006 for chlordiamino-s-triazine (deethyldeisopropyl atrazine) were 93.4 percent with an f-pseudosigma of 7.1 percent, indicating a compound exhibiting recovery values that are acceptable in relation to method performance criteria (Figure 4). However, discussion with the BQS OBSP section raised questions about the comparability of NWQL internal QC with external samples. Chlordiamino-s-triazine experiences transformation to one or more unknown products during acidification. Because the preparation steps in schedule 2060 include acidification, it was determined that the calibration standards would also need to be acidified to mimic the conditions of the samples. The fact that recoveries of this compound in the NWQL internal LRWS do not correlate with those from the OBSP samples indicates that our standards and spiking solution are not characterizing the acidification process adequately. OBSP data (Figure 5) show mean recoveries of 25 percent during the period from May 16, 2001 to July 28, 2006, much lower than the 93.4 percent found in the LRWS data. Furthermore, there were 27 percent false negatives among the 77 samples tested with this analyte, possibly due to low recovery issues or incomplete acidification.

Chlordiamino-s-triazine has had the lowest detection frequency of the atrazine metabolites in schedule 2060. We now know that this low detection frequency could be due in part, or in whole, to poor analytical recoveries. This compound was removed based on the difficulties encountered with standardizing the acidification step employed by schedule 2060.

FIGURE 4. LRWS samples for Chlordiamino-s-triazine, June 1,2006 through October 1, 2006

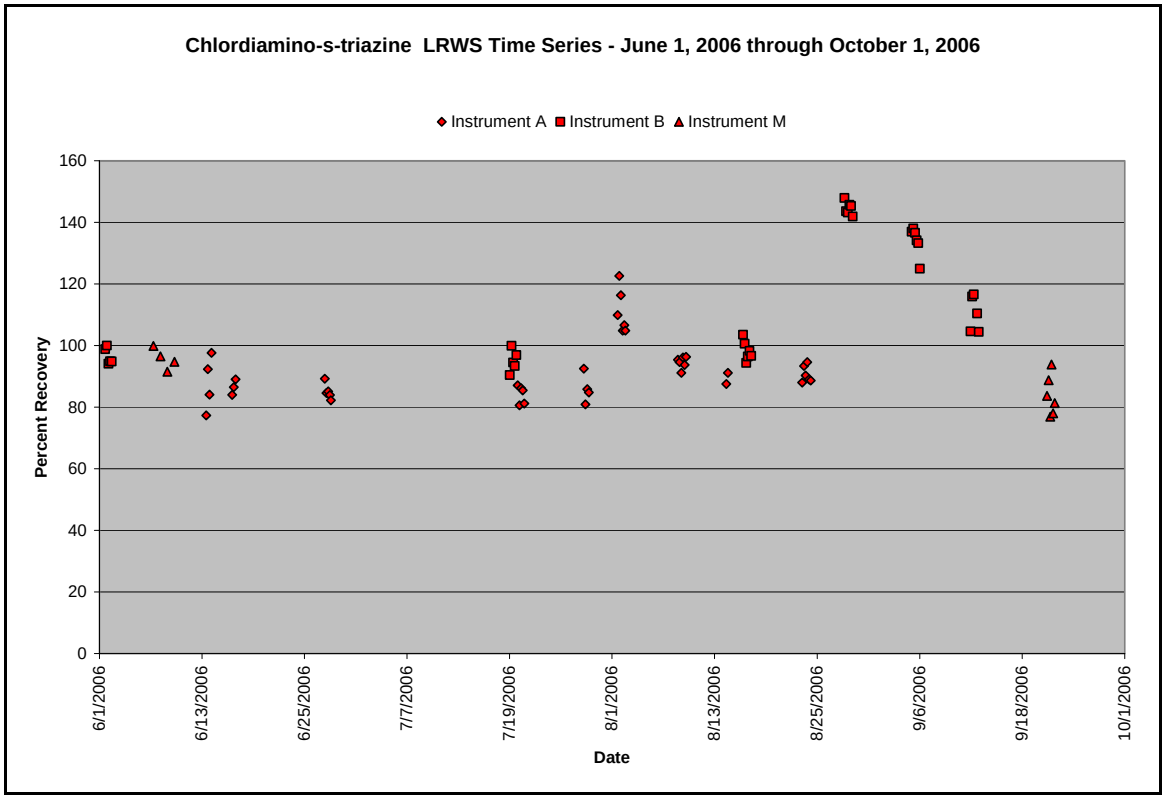
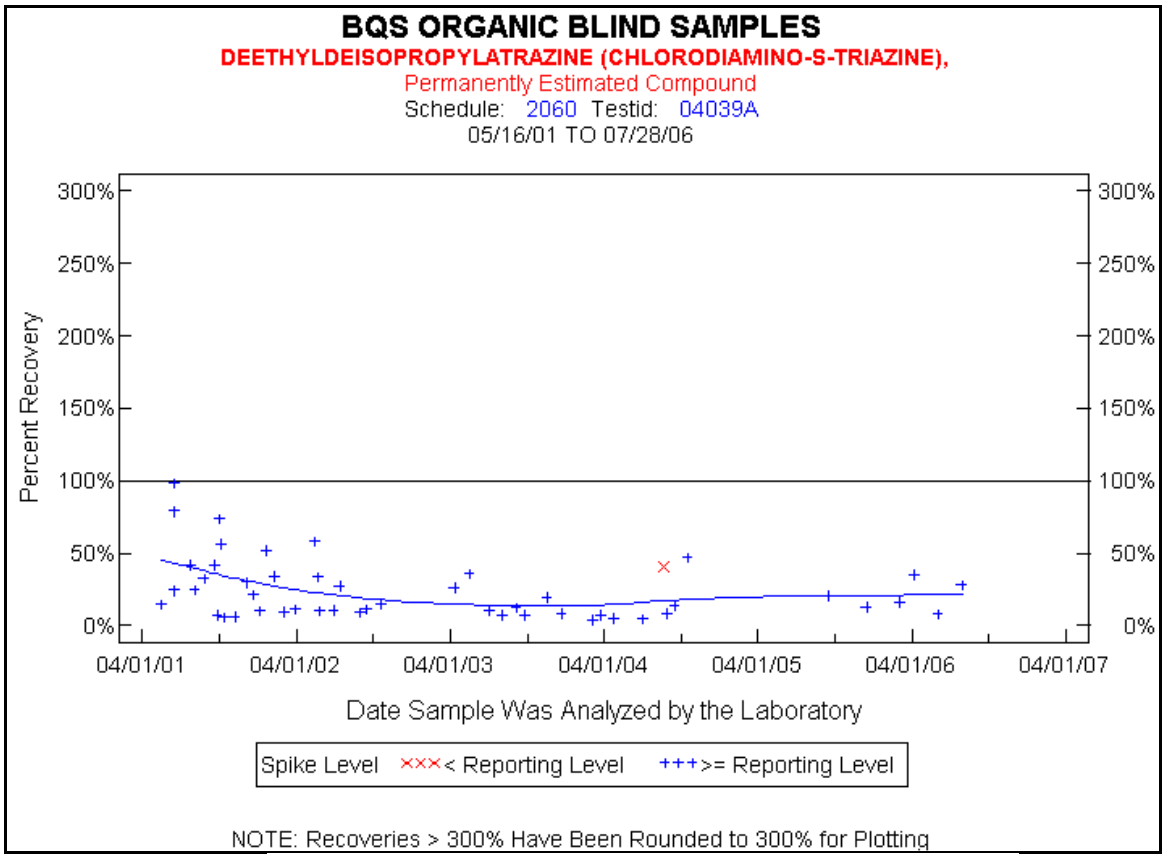


FIGURE 5. BQS data for chlordiamino-s-triazine; 5/16/01 through 7/28/06



Statistics for the Plotted Points
DEETHYLDEISOPROPYLATRAZINE (CHLORODIAMINO-S-TRIAZINE)

Spike Level	N	Mean	Std-Dev.	Median	F_Pseudo
< Reporting Level	1	41%	.	41%	0%
>= Reporting Level	49	24%	21%	15%	18%
Total	50	25%	21%	15%	19%

Miscellaneous Statistics for the Samples
DEETHYLDEISOPROPYLATRAZINE (CHLORODIAMINO-S-TRIAZINE)

Characteristic	N	%	% Basis
Plotted	50	65%	Spiked
Estimated Values	47	61%	Spiked
Deleted Values	1	1%	Spiked + Not Spiked
Spiked, Censored	6	8%	Spiked
Spiked	77	.	
False Negatives	21	27%	21 out of 77
Not Spiked	119	.	
False Positives	0	0%	0 out of 118

CONCLUSIONS

Three analytes have been removed from lab schedule 2060 because they do not meet NWQL criteria for retention in the method. Chlorothalonil was removed on January 1, 2006 because of its poor recovery. 3-keto-carbofuran was removed January 1, 2006 because of its high variability and unpredictability of its analytical results. Chlordiamino-s-triazine was removed January 1, 2007 because of a lack of adequate control over an acid-catalyzed transformation occurring during sample preparation.

Effect on Data Base: The National Water Quality Laboratory is taking no action to modify data in NWIS prior to the dates described above. All detections found where corresponding QC failed (either LRWS or CCVs) were qualified as estimated (E-qualifier). However, the poor performance issues described above were present throughout the method history. The performance issues described above will likely cause quantitative uncertainty and possibly a high number of false negative detections, but are not likely to cause false positive detections. It is the responsibility of each Water Science Center to determine the best course of action for their data based on project objectives.

REFERENCES

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

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