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NATIONAL WATER QUALITY LABORATORY TECHNICAL MEMORANDUM 1998.03A

August 28, 1998

Subject: Changes in Reporting Levels and Data Qualifiers for Selected Pesticides and Degradation Products in Schedules 2050 and 2051

Effective date of changes: December 15, 1997

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Revision: This memorandum replaces NWQL Technical Memorandum 98.03 and portions of 96.06A.

Supplemental

Material: Further information regarding schedule 2050 reporting changes and the procedure used to establish the new reporting levels is available as a supplement to the web page version of this technical memorandum, which is accessible under "Technical Memoranda" on the National Water Quality Laboratory's home page at <http://wwwnwql.cr.usgs.gov/USGS>.

SCOPE

This technical memorandum announces changes, effective December 15, 1997, in the following data reporting practices for NWQL schedules 2050 and 2051 (Werner and others, 1996):

- (1) Reporting levels for nondetections will be raised for 14 constituents.
- (2) An "E" code (estimated value) data qualifier will be added for all values of aldicarb, aldicarb sulfoxide, and aldicarb sulfone.
- (3) Esfenvalerate and 1-naphthol are deleted from the method.

These changes are based on analysis of performance data for schedule 2050 from the Organic Blind Sample Program by the NWQL's Quality Assurance Unit and from routine laboratory reagent spike recovery data. This memorandum also clarifies approaches previously used to derive reporting levels for all constituents in schedules 2050 and 2051.

BACKGROUND ON REPORTING LEVELS

Reporting levels for all constituents in schedules 2050 and 2051 previously were announced in NWQL Technical Memorandum 96.06A issued April 15, 1996, and were defined as equivalent to the method detection limit (MDL), as determined by the U.S. Environmental Protection Agency's (USEPA, 1994) MDL procedure. However, as noted in USGS Open-File Report 96-216 (Werner and others, 1996) documenting the schedule 2050 method, reporting levels (mistakenly listed as MDLs in table 12 of the OFR) for a number of the constituents were set higher than MDL values determined by the USEPA procedure (table 4 in the OFR). These higher reporting levels were based on in-house experiments, which showed that the calculated MDLs could not be achieved in practice (based on producing an ultraviolet spectra of sufficient sensitivity for matching with a spectral library).

MDL values provided in memo 96.06A were obtained using the USEPA's MDL procedure for 20 method constituents (see table A at the end of this memo). For the remaining 21 method constituents listed in memo 96.06A (see table B at the end of this memo), the reporting level was set at a value greater than the MDL, because the MDL could not be achieved.

SUMMARY OF CHANGES IN DATA REPORTING

Reporting changes are required for the schedule 2050 and 2051 constituents listed in table 1. These changes were based on method performance data for schedule 2050 acquired from the Quality Assurance Unit's Organic Blind Sample Program, which revealed a substantial number of false negatives and several serious method recovery performance problems, and from routine laboratory reagent spike recovery samples. No reporting changes were deemed necessary for any of the remaining constituents in schedules 2050 and 2051.

Changes in reporting levels for nondetections are required for 14 method constituents (table 1). The 14 constituents include 5 for which MDL values have been used to date as the reporting level (table A), and 9 for which reporting levels greater than the MDL have been used to date (table B).

An "E" code is added to all values for aldicarb, aldicarb sulfoxide, and aldicarb sulfone because of: (1) low and variable recoveries of aldicarb and aldicarb sulfone and (2) post-collection conversion of aldicarb to aldicarb sulfoxide, resulting in variable high bias in aldicarb sulfoxide. As reported in Werner and others (1996, p.34), chlorothalonil, dichlobenil, and DNOC continue to be "E" coded because of variable recovery performance during solid-phase extraction and HPLC analysis.

The NWQL will no longer report esfenvalerate and 1-naphthol in schedules 2050 and 2051 because of unacceptable performance (mean recoveries of <16% for both constituents from 165 laboratory reagent spike samples).

Table 1. Changes in data reporting for selected constituents in schedules 2050 and 2051 at the NWQL

[WATSTORE, Water Data Storage and Retrieval System]

Constituent	Parameter (WATSTORE) code*	NWQL lab code 2050/2051	Reporting level (microgram/liter)	
			Current	Effective Dec.15,1997
Constituents with Increased Reporting Levels				
Carbofuran	49309A/B	5418/5618	0.028	0.12
Chloramben	49307A/B	5419/5619	0.011	0.42
Clopyralid	49305A/B	5423/5623	0.050	0.23
2,4-D	39732B/C	5408/5608	0.035	0.15
2,4-DB	38746A/B	5407/5607	0.035	0.24
MCPA	38482A/B	5433/5633	0.050	0.17
MCPB	38487A/B	5434/5634	0.035	0.14
Oryzalin	49292A/B	5440/5640	0.019	0.31
Triclopyr	49235A/B	5446/5646	0.050	0.25
Current "E" Coded Constituents with Increased Reporting Levels				
DNOC	49299A/B	5402/5602	0.035	0.42
Dichlobenil	49303A/B	5404/5604	0.020	1.20
Chlorothalonil	49306A/B	5421/5621	0.035	0.48
New "E" Coded Constituents with Increased Reporting Levels				
Adicarb	49312A/B	5411/5611	0.016	0.55
Adicarb sulfone	49313A/B	5413/5613	0.016	0.10
New "E" Coded Constituent with No Reporting Level Change				
Aldicarb sulfoxide	49314A/B	5412/5612	0.021	no change
Constituents Deleted from Schedules				
Esfenvalerate	49298A/B	5429/5629	0.019	deleted
1-Naphthol	49295A/B	5438/5638	0.007	deleted

*Letter following 5 digits represents method code for schedule 2050/2051.

IMPLICATIONS OF CHANGES IN REPORTING LEVELS

These changes in reporting levels for nondetections (the value that accompanies the "<" code) result in a much more realistic assessment of what actual concentration of a pesticide could likely be detected if it were present. For example, many nondetections of carbofuran may have been reported when the actual concentration was greater than 0.028 ug/L (false negatives), but a very small percent of actual concentrations greater than 0.12 ug/L will not be detected (see table 1).

Each constituent has a set of qualitative identification criteria that must be met before it is quantified. If these criteria are not met, a "less than" concentration at the reporting level listed in table 1 will be reported. However, if identification criteria are met, the concentration will be reported, even if less than the new reporting level. This is consistent with the previous reporting conventions for schedules 2050 and 2051, which use an "E" data qualifier to denote estimated low-level concentrations.

EFFECT ON DATA BASE

The National Pesticide Synthesis Team of the NAWQA Program and NWQL recommend that Districts delete all historic values of esfenvalerate and 1-naphthol produced using schedules 2050 and 2051 from their data base.

There will be no change in historical results reported for detections of constituents listed in table 1, since all reported detections and concentrations have been and still are considered reliable (except for esfenvalerate and 1-naphthol).

Reporting level changes for the constituents in table 1 will cause a shift in reporting levels, and thus nondetection (less than) concentrations, in the data base. Historical reporting levels are not being changed in the data base at this time. During FY 1998, the Office of Water Quality, the NAWQA Program, the NWQL, and other Water Resources Division representatives will develop policy on changes in historical data and further guidance on interpreting analytical results, both new and historical, for these schedules. Data users should 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.

CLARIFICATION OF REPORTING LEVELS LISTED IN NWQL TECHNICAL MEMORADUM 96.06A

Table A. Constituents with reporting levels listed in NWQL Technical Memorandum 96.06A that were set equivalent to the Method Detection Limit (MDL)

Constituent	Parameter (WATSTORE) code*	NWQL lab code 2050/2051	Reporting level set in 96.06A at the MDL (microgram/liter)
Aldicarb	49312A/B	5411/5611	0.016**
Aldicarb sulfone	49313A/B	5413/5613	0.016**
Aldicarb sulfoxide	49314A/B	5412/5612	0.021
Bentazon	38711A/B	5414/5614	0.014
Carbaryl	49310A/B	5417/5617	0.008
Carbofuran	49309A/B	5418/5618	0.028**
Chloramben	49307A/B	5419/5619	0.011**
Dacthal monoacid	49304A/B	5447/5647	0.017
Dichlorprop	49302A/B	5401/5601	0.032
Esfenvalerate	49298A/B	5429/5629	0.019**
Fenuron	49297A/B	5405/5605	0.013
3-Hydroxycarbofuran	49308A/B	5449/5649	0.014
Methiocarb	38501A/B	5436/5636	0.026
Methomyl	49296A/B	5437/5637	0.017
Neburon	49294A/B	5403/5603	0.015
Norflurazon	49293A/B	5439/5639	0.024
1-Naphthol	49295A/B	5438/5638	0.007**
Oryzalin	49292A/B	5440/5640	0.019**
Oxamyl	38866A/B	5441/5641	0.018
Silvex	39762B/C	5444/5644	0.021

*Letter following 5 digits represents method code for schedule 2050/2051.

**Reporting level for constituent being changed effective December 15, 1997 (see table 1).

Table B. Constituents with reporting levels listed in NWQL Technical Memorandum 96.06A as being equivalent to the MDL but that were actually set in 96.06A at a concentration greater than the MDL

Constituent	Parameter (WATSTORE) code*	NWQL lab code 2050/2051	Reporting level set in 96.06A at a concentration greater than the MDL (microgram/liter)
Acifluorfen	49315A/B	5410/5610	0.035
Bromacil	04029A/B	5415/5615	0.035
Bromoxini	49311A/B	5416/5616	0.035
Chlorthalonil	49306A/B	5421/5621	0.035**
Clopyralid	49305A/B	5423/5623	0.050**
2,4-D	39732B/C	5408/5608	0.035**
2,4-DB	38746A/B	5407/5607	0.035**
Dicamba	38442A/B	5426/5626	0.035
Dichlobenil	49303A/B	5404/5604	0.020**
Dinoseb	49301A/B	5400/5600	0.035
Diuron	49300A/B	5427/5627	0.020
DNOC	49299A/B	5402/5602	0.035**
Fluometuron	38811A/B	5430/5630	0.035
Linuron	38478A/B	5432/5632	0.018
MCPA	38482A/B	5433/5633	0.050**
MCPB	38487A/B	5434/5634	0.035**
Picloram	49291A/B	5442/5642	0.050
Propham	49236A/B	5443/5643	0.035
Propoxur	38538A/B	5450/5650	0.035
2,4,5-T	39742B/C	5409/5609	0.035
Trichlopyr	49235A/B	5446/5646	0.050**

*Letter following 5 digits represents method code for schedule 2050/2051.

**Reporting level for constituent being changed effective December 15, 1997 (see table 1).

REFERENCES

U.S. Environmental Protection Agency, 1994, Guidelines establishing test procedures for the analysis of pollutants (App. B, Part 136, Definition and procedures for the determination of the method detection limit): U.S. Code of Federal Regulations, Title 40, revised July 1, 1994, p. 635-637.

Werner, S.L., Burkhardt, M.R., and DeRusseau, S.N., 1996, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory--Determination of pesticides in water by Carbopak-B solid-phase extraction and high-performance liquid chromatography: U.S. Geological Survey Open-File Report 96-216.

/s/

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Supersedes: This memorandum replaces NWQL Technical Memorandum 98.03 and portions of 96.06A.

Key Words: Schedule 2050, Reporting levels, Pesticides, Deletions

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