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NATIONAL WATER QUALITY LABORATORY TECHNICAL MEMORANDUM 1994.06

January 24, 1994

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From: Peter F. Rogerson, Chief
National Water Quality Laboratory
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Subject: Limitation in the determination of selected carbamate pesticides in water

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Revision: No

SCOPE

National Water Quality Laboratory (NWQL) Schedule 1359 determines select carbamate pesticides and some related degradation products in water. This memorandum details the removal of four analytes from Schedule 1359 on the basis of nonoptimum methodological performance and recommends new Schedule 2050 as an alternative method for projects requiring environmental data for these four compounds.

BACKGROUND

The (NWQL) has been analyzing water samples for carbamate pesticides and some related degradation products since 1985 using reverse-phase high-performance liquid chromatography (HPLC). Beginning in October 1985 and until June 24, 1987, USGS Method O-3107-83 was used (Wershaw and others, 1987). Samples were extracted with methylene chloride and the extract concentrated and analyzed by HPLC using fixed-wavelength measurements. The determined pesticides and related degradation products included aldicarb, carbaryl, carbofuran, 3-hydroxy-carbofuran, methomyl, 1-naphthol, and propham.

Beginning on June 25, 1987, Schedule 1359--a more comprehensive, but comparable, HPLC method which includes multiple wavelengths--was used to determine carbamate pesticides. This schedule included 12 pesticides and related degradation products. In addition to the seven aforementioned compounds, Schedule 1359 included aldicarb sulfone, aldicarb sulfoxide, methiocarb, oxamyl, and propoxur. These five compounds were included as unvalidated add-ons because of intense district interest.

METHOD DOCUMENTATION

Schedule 1359 was validated using three types of water for precision and recovery studies: (1) organic-free distilled water; (2) ground water from the Arvada, Colorado, Well 14; and (3) surface water from the South Platte River at Englewood, Colorado. These samples were spiked with the 12 analytes and extracted on the same day. All samples were instrumentally analyzed by a single operator within 2 days. Table 1 lists the single-operator precision recoveries for aldicarb sulfone, aldicarb sulfoxide, 3-hydroxycarbofuran, and oxamyl. The recoveries for the first 3 compounds were less than 50 percent. For oxamyl, some single-operator mean recoveries were greater than 50 percent; however, mean recoveries on spiked environmental samples have been less than 50 percent. On the basis of the method validation study and historical recovery data, the NWQL decided (beginning on October 1, 1993) to no longer report results for these four compounds. The data previously reported for each compound should not be used in any quantitative manner. Instead, the data should only be used to determine the presence of each compound in the environmental samples.

An Open-file Report (OFR) entitled "Determination of selected carbamate pesticides in water by high-performance liquid chromatography" will be available shortly. The OFR provides complete details of the analytical method and discusses results for the 12 analytes. This includes both the acceptable precision and bias of the eight included analytes for Schedule 1359 and the unacceptable precision and bias of the four excluded analytes. The discussion includes: (1) identification and confirmation, (2) retention-time stability, (3) detector sensitivity, (4) detection specificity, (5) duration of application, (6) precision and recovery, and (7) use of method data. If you are not on the distribution list for the OFR and wish to receive a copy, please contact Karlin Allen (KIALLEN), (303) 467-8006, in the Office of the Chief, NWQL.

SCHEDULES 2050 AND 2051

As an improved alternative to Schedule 1359, the NWQL recently developed a new solid-phase extraction cartridge method (Schedules 2050 and 2051) for the determination of 12 carbamate pesticides and related degradation products (including the four analytes now removed from Schedule 1359) in filtered-water samples. This new method also determines 29 other pesticides and provides the option of pesticide isolation onto the cartridge either at the NWQL (Schedule 2050) or in the field by the customer (Schedule 2051). Limited reagent-water spike recovery data for the 12

carbamate pesticides and products from Schedule 2050 are shown in table 2. Project Chiefs requiring environmental data for the four analytes deleted from Schedule 1359 could request Schedule 2050 or 2051 although those schedules are not yet documented and approved as official USGS methods. They were developed and implemented because of an urgent need of the National Water Quality Assessment (NAWQA) Program; publication of the methods and approval as an official USGS method are expected in 1994.

Enclosures

Reference: Wershaw, R.L., Fishman, M.J., Grabbe, R.R., and Lowe, L.E., Eds., 1987, Methods of the determination of organic substances in water and fluvial sediments: U.S. Geological Survey Techniques of Water-Resources Investigations, Book 5, Chapter A3.

Supersedes: None

Key Words: Carbamate pesticides, Schedule 1359

Distribution: See above plus LABNEWS & QWTALK

Table 1.- Single-operator precision recoveries for selected carbamate pesticides and degradation products

[$\mu\text{g/L}$, micrograms per liter; RSD, relative standard deviation; <, less than]

Pesticide and degradation product	Matrix water	Concentration level ($\mu\text{g/L}$)	Replicates	Mean recovery (%)	Standard deviation ($\mu\text{g/L}$)	RSD (%)
Selected carbamate pesticides						
Aldicarb sulfone	Organic free	0.5	7	49.4	0.120	25
		2.0	7	45.3	.041	9
	Ground	.5	7	46.7	.014	3
		2.0	7	50.6	.034	7
	Surface	.5	7	79.0	.097	12
		2.0	7	46.2	.037	8
Aldicarb sulfoxide	Organic free	.5	7	6.9	.092	133
		2.0	7	4.3	.023	52
	Ground	.5	7	.7	<.001	3
		2.0	7	4.6	.008	18
	Surface	.5	7	5.3	.011	21
		2.0	7	5.2	.008	15

3-Hydroxy-carbofuran	Organic free	.5	7	30.3	.038	13
		2.0	7	33.1	.036	11
	Ground	.5	7	34.3	.021	6
		2.0	7	42.3	.030	7
	Surface	.5	7	17.2	.086	50
		2.0	7	24.9	.022	9
Oxamyl	Organic free	.5	7	48.5	.099	20
		2.0	7	60.1	.094	16
	Ground	.5	7	51.9	.044	8
		2.0	7	75.5	.065	9
	Surface	.5	7	76.3	.073	10
		2.0	7	50.2	.045	9

Table 2.- Spike recoveries from organic-free distilled water for the carbamate pesticides and related degradation products included in Schedule 2050 from September 21 to October 19, 1993

[RSD, relative standard deviation]

Pesticide & degradation product	Mean Recovery (%)	Number of Replicates	RSD (%)
Aldicarb	95	9	9
Aldicarb sulfone*	65	8	29
Aldicarb sulfoxide*	86	9	9
Carbaryl	78	9	26
Carbofuran	100	9	18
3-Hydroxycarbofuran*	90	7	14
Methiocarb	92	3	16
Methomyl	91	9	11
1-Naphthol	62	8	34
Oxamyl*	62	8	31
Propham	82	7	14
Propoxur	92	7	4

*Analytes removed from Schedule 1359