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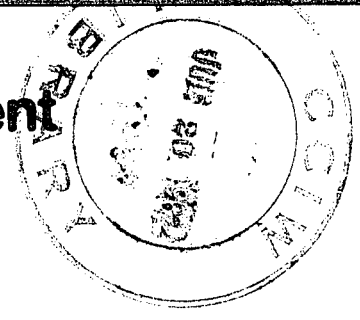
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Analysis of Fenitrothion in Water - An  
Interlaboratory Assessment

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## Executive Summary

In response to the urgent request of the WQB (Atlantic Region) a special Q.C. study in 2 parts was designed and conducted to provide information on the comparability of data for the analysis of fenitrothion in water among laboratories of different agencies in the Maritime provinces.

The results of this study indicated that the data are comparable at the concentration levels of this study.

**ANALYSIS OF FENITROTHION IN WATER -  
AN INTERLABORATORY ASSESSMENT**

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## ABSTRACT

In response to the urgent request of the WQB (Atlantic region), a special QC study in 2 parts was designed and conducted to provide information on the comparability of data for the analysis of fenitrothion in water among different laboratories in the Maritime Provinces.

Eight ampules of standard solutions and 6 water samples including two samples of high humic content were sent out. The results of these studies show that both the standard solutions in use and the analytical data generated by these laboratories are comparable.

## INTRODUCTION

Fenitrothion (Sumithion<sup>R</sup>) is an organophosphorus pesticide for the control of spruce budworm and Douglas fir tussock moth and has been widely used in Eastern Canada. To assess the environmental impact of the forest spray activity, there is a need to monitor the quality of the run-off waters and related aquatic substances in addition to foliage and soil of the target area. Several laboratories of different agencies in the maritime provinces were engaged in the analysis of fenitrothion in water. It was deemed necessary to determine the comparability of the data generated by these laboratories. Consequently, the WQB (Atlantic region) requested this section to design a QC study to assess laboratory performance and data quality before the field season started.

The design of our QC study was comprised of two parts. The first part was to assess comparability of the analytical reference standards currently used in these laboratories. The second part was designed to assess laboratory performance and comparability of data in the analysis of water samples. The design is simple but quite adequate for the purpose of the request.

This report describes the results of the fenitrothion QC study.

### Fenitrothion Stock Solutions

Two fenitrothion stock solutions in 1:9 benzene/isooctane were prepared for this QC study. One solution was prepared from a sample supplied by Canada Centre for Pesticide Analytical Standards (CCPAS) with a labelled purity of 99.7%. Another fenitrothion solution was prepared from a "pure" Sumithion sample obtained from Sumitomo Chemical Co. In-house GLC analysis of the two standard solutions on two different columns indicated that the fenitrothion sample from CCPAS was only 91% pure relative to the "pure" Sumithion. The Sumithion stock solution was used to prepare all the QC samples and the concentrations were calculated by assuming the pesticide used was 100% pure.

### Preparation of the Ampule Samples (Part I)

The solutions used to prepare the ampule samples were prepared by serial dilutions from the Sumithion stock solution using isooctane. In Part I of the study, each participant was supplied with ca 1½ mL of each solution in sealed glass ampule for analysis.

### Preparation of the Water Samples (Part II)

Water samples 1 and 2 were prepared from organic-free water while samples 3 and 4 were derived from a bulk sample from Hamilton

Bay. Each sample was adjusted to a volume of  $1000 \pm 10$  mL. In order to prevent possible microbial degradation of the samples, the natural water samples were boiled and cooled to room temperature before spiking. Each water sample was then fortified with  $100 \mu\text{L}$  of an appropriate solution on the shipping day in order to minimize any chemical degradation during transit. According to the returned reports, the samples arrived at their destinations within 2 to 3 days. The stability of the fortified water samples stored at  $4^\circ\text{C}$  in the dark was also briefly monitored. Under such conditions, no decomposition of fenitrothion was observed in a period of 2 weeks.

#### Design of the QC Study

##### (a) Ampoule Samples

The fenitrothion concentrations in the ampoule samples (see Table 1) varied from 1 to  $1250 \text{ pg}/\mu\text{L}$ . This wide range of values corresponds to fenitrothion concentrations most commonly found in naturally contaminated water samples, namely, from 0.01 to  $12.5 \mu\text{g}/\text{L}$ . (An assumption is made here that 1 L of sample is extracted and the extract is concentrated to 10 mL for analysis).



(b) Water Samples

Water samples 1 and 3 were fortified with fenitrothion at 5 µg/L while samples 2 and 4 were fortified at 1 µg/L. As mentioned above, samples 1 and 2 were "pure" water samples while samples 3 and 4 came from a bulk samples from Hamilton Bay in the presence of humic substances and particulate matter. Participants were requested to prepare their own samples 5 (1.0 µg/L) and 6 (1.25 µg/L) with in-house reagent water and the ampoules provided. The Youden paired-sample design was adopted here as the concentrations of the samples were fortified to slightly different fenitrothion levels. This simple design enables us to detect any existing systematic and random errors.

**RESULTS AND DISCUSSIONS**

The data supplied by the participants are summarized in Tables 2 and 4 below.

The calculated % recoveries of the ampule samples of fenitrothion standard solutions (Table 3) were, except for a few random cases, all within a range of 80 to 120% for the entire concentration range used in the study. This indicates that the fenitrothion standard solutions used by the participants and our lab were generally comparable.

The quantitation techniques used by all participants were GLC with specific detectors such as FPD and TSD (or NPD). Results of this study indicated that both types of detectors were sensitive enough for the detection of fenitrothion at least to the 10 pg/ $\mu$ L concentration level, which is equivalent to 0.1 ppb of the pesticide in 1 L of water sample extracted and concentrated to 10 mL. However, lab E indicated in their report that they did not attempt to analyze fenitrothion below 70 pg/ $\mu$ L.

The mean intra-lab recoveries of the ampule samples for labs A and G were slightly over 110%, suggesting that their overall results were biased high. A possible cause for this could be that the purity of their fenitrothion standards used was lower than ours. Lab B provided two sets of results by using two different GLC columns (SE-30 and OV-17) and the two sets of data differed by over 20% with no apparent explanation. The results from the SE-30 column were very close to the design levels except that they became biased low in the high concentration range (500 to 1250 pg/ $\mu$ L). The results from the same lab using the OV-17 column were all biased high by over 20%. On the other hand lab F was biased high in the low concentration range (10 to 20 pg/ $\mu$ L) unless the high results for samples 3 and 5 were due to in-house cross-contamination. Except for the above cases, the results were generally close to the design levels.

The calculated % recoveries of fenitrothion in water samples are given in Table 5. The intra-lab mean calculated recoveries of all labs were close to quantitative (90 to 110%), indicating that the participants had no problems recovering fenitrothion from water samples of various quality. The results also confirmed our previous experience that these water samples were stable and there was little evaporative or adsorptive losses of the pesticide during transit and storage. Although it was not clear why the recoveries of the fortified natural water samples (samples 3 and 4) were slightly higher than those of pure water samples (samples 1 and 2) for some participants, it did not seem likely that humic substances and particulate matter present in the natural water samples posed any severe problems in the recovery and analysis of fenitrothion in this particular study.

Judging from the % recoveries of samples 5 and 6 (the Youden pair), all labs generated little or no random errors in the analysis of those water samples.

Labs A and G had calculated mean recovery of 96% and 90% respectively, on the water samples. Since these labs had results on the ampule samples which were biased high, the "adjusted" mean recovery of water samples could be lowered by approximately 10% assuming that the same fenitrothion standard solutions were used in both parts of the study. Lab B indicated in the report that a possible error could have occurred in the analysis of water sample No. 4 and thus the low result was rejected in the statistics.

It should be noted that, for Lab G, the water samples had been stored at 4°C for two months before extraction was performed. Compared with other labs, their results on water samples were slightly low. Nevertheless, the mean calculated recovery of water samples for Lab G was nearly 90% despite the lengthy storage.

The analytical methodologies used by the participating labs for the extraction and GLC analysis of fenitrothion in water are summarized in Table 6. The extraction, in general, involved stirring or shaking the sample with hexane two to three times. Because of the specificity of the detectors used, no cleanup of the sample extract was necessary. Most of the participants elected to add 100 g of anhydrous sodium sulfate prior to solvent extraction.

#### CONCLUSIONS

1. The fenitrothion standard solutions used by the participants are comparable. This is supported by the fact that the overall mean recovery of all ampule samples is 105.8% of the design value with a standard deviation of 7.8%. A likely possibility for high results of ampule sample is due to the purity of the primary standard used.

2. Recoveries of fenitrothion in fortified water samples of various quality are nearly quantitative.

The above findings suggested that results generated by the participants on water samples naturally contaminated with fenitrothion should be comparable, accurate and reliable at the concentration levels of this study.

**ACKNOWLEDGEMENTS**

The participants listed in the Appendix are gratefully acknowledged for their cooperation and patience.

Table 1. Samples distributed in the Fenitrothion QC study and design values

Part I		
Ampule sample	Fenitrothion concentration (pg/ $\mu$ L)	
1	50	
2	250	
3	20	
4	1250	
5	10	
6	100	
7	1	
8	500	
Part II		
Sample	Type of water	Fortification level ( $\mu$ g/L)
1	pure water	5.0
2	pure water	1.0
3	natural water	5.0
4	natural water	1.0
5	in-house pure water	1.0
6	in-house pure water	1.25

Table 2. Data submitted by participants for ampule samples (pg/ $\mu$ L)

Ampule	1	2	3	4	5	6	7	8
Lab	1	2	3	4	5	6	7	8
Design Value	50	250	20	1250	10	100	1	500
A	58	280	24	1300	12	120	N.D.	550
B-1	53	249	19	1040	11	90	N.D.	415
B-2	63	312	23	1640	13	126	N.D.	630
D	30	247	21	1060	10	100	Nil	519
E	<70	290	<70	1400	<70	96	<70	560
F-1	48.5	261	25	1240	17	94.3	N.D.	514
F-2	---	260	---	---	---	---	---	506
F-3	53	284	18.3	1488	---	108	N.D.	561
G	50	311	23	1479	12	116	N.D.	489

Notes

- B-1 = Results by TSD, SE-30 column
- B-2 = Results by TSD, OV-17 column
- F-1 = Results by FPD, manual peak height column
- F-2 = Results by FPD, integrator
- F-3 = Results by TSD, integrator



Table 3. % Recovery of Fenitrothion in Ampule Samples

Sample								
Lab	5	3	1	6	2	8	4	Mean $\pm$ S.D.
A	120	120	116	120	112	110	104	114.6 $\pm$ 6.2
B-1	110	95	106	90	100	83	83	95.3 $\pm$ 10.6
D	100	105	60R	100	99	104	85	98.7 $\pm$ 7.2
E	-	-	-	96	116	112	112	109.0 $\pm$ 8.9
F-1	170R	125	97	94	104	103	99	103.8 $\pm$ 11.0
G	120	115	100	116	124	98	118	113.1 $\pm$ 10.2
Design Level (pg/ $\mu$ L)	10	20	50	100	250	500	1250	Overall mean $\pm$ S.D. 105.8 $\pm$ 7.8

R = Outlier (according to US EPA "Fitness Test") - results not included in the statistics

Table 4. Data submitted by participants for water samples  
( $\mu\text{g/L}$ )

Sample						
Lab	1	2	3	4	5	6
Design Value	5.0	1.0	5.0	1.0	1.0	1.25
A	4.6	0.86	4.8	1.1	0.98	1.2
B	4.35	0.79	4.79	0.32	0.83	1.15
D	5.3	0.92	5.7	0.96	1.0	1.2
E	6.0	1.0	6.1	0.99	1.0	1.4
F-1	4.990	1.125	5.150	1.125	1.075	1.300
F-2	5.401	1.029	5.507	1.045	0.985	1.213
F-3	4.542	1.053	4.398	1.040	0.899	1.169
G	4.291	0.926	4.479	0.909	0.858	1.152

Notes:

- F-1 = Results by FPD, manual calculations
- F-2 = Results by FPD, integrator
- F-3 = Results by TSD

Table 5. % Recovery of Fenitrothion in water samples

Sample	1	2	3	4	5	6	Mean $\pm$ S.D.
Lab A	92	86	96	110	98	96	96.3 $\pm$ 7.9
B	87	79	95.8	32R	83	92	87.4 $\pm$ 6.7
D	106	92	114	96	100	96	100.7 $\pm$ 8.1
E	120	100	122	99	100	112	108.8 $\pm$ 10.6
F-1	99.8	112.5	103	112.5	107.5	104	106.6 $\pm$ 5.2
G	85.8	92.6	89.6	90.9	85.8	92.2	89.5 $\pm$ 3.0
							Overall 98.2 $\pm$ 8.8

R = Outlier - results not included in the statistics

Table 6. Summary of Analytical Methodology

Lab	Extraction	GLC Analysis
A	<ul style="list-style-type: none"> <li>- add 100 g Na<sub>2</sub>SO<sub>4</sub></li> <li>- 3 x 50 mL hexane, sep. funnel and stirring</li> <li>- no cleanup</li> </ul>	<ul style="list-style-type: none"> <li>- Tracor MT 220 FPD</li> <li>- 4% OV-101 + 6% OV-210 column</li> <li>- standard curve</li> <li>- TSD results for confirmation</li> </ul>
B	<ul style="list-style-type: none"> <li>- add 100 g anhy. Na<sub>2</sub>SO<sub>4</sub></li> <li>- 3 x 100 mL hexane, sep. funnel</li> <li>- no cleanup</li> </ul>	<ul style="list-style-type: none"> <li>- Varian 3700, TSD</li> <li>- 3% SE-30 and 3% OV-17 columns</li> <li>- standard curve</li> </ul>
D	<ul style="list-style-type: none"> <li>- 3 x 30 mL hexanes stirring</li> <li>- no cleanup</li> </ul>	<ul style="list-style-type: none"> <li>- Tracor 560 NPD</li> <li>- 3% OV-17 column</li> <li>- individual standards</li> </ul>
F	<ul style="list-style-type: none"> <li>- add 100 g Na<sub>2</sub>SO<sub>4</sub></li> <li>- 3 x 50 mL hexane stirring</li> <li>- no cleanup</li> </ul>	<ul style="list-style-type: none"> <li>- PE 3920B FPD and Varian 3700 TSD</li> <li>- 5% OV-17 + 6% QF-1 and 3.6% OV-101 + 5.5% OV-210 columns</li> <li>- standard curve</li> </ul>
G	<ul style="list-style-type: none"> <li>- add 100 g Na<sub>2</sub>SO<sub>4</sub></li> <li>- 3 x 30 mL hexane sep. funnel and stirring</li> <li>- no cleanup</li> </ul>	<ul style="list-style-type: none"> <li>- PE 3920B FPD</li> <li>- 5% OV-210 + 3% OV-101</li> <li>- individual standards</li> </ul>
E	<ul style="list-style-type: none"> <li>- add Na<sub>2</sub>SO<sub>4</sub></li> <li>- 2 x 60 mL hexanes, sep. funnel</li> <li>- no cleanup</li> </ul>	<ul style="list-style-type: none"> <li>- Tracor 222 FPD</li> <li>- 3.6% OV-101 + 5.5% OV-210 column</li> <li>- individual standards</li> </ul>

**APPENDIX**

**List of Participants**

Atlantic Analytical Services Limited (St. John)

Environment Canada, Environmental Conservation Service, Water Quality  
Branch, Atlantic Region, Organic Analysis Laboratory (Moncton)

Environment Canada, Environmental Protection Service, Atlantic Region  
(Halifax)

Environment New Brunswick (Fredericton)

New Brunswick Research and Productivity Council, Department of  
Chemistry (Fredericton)

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