UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

OFFICE OF
PREVENTION, PESTICIDES
AND TOXIC SUBSTANCES

9/15/1995

057701

MEMORANDUM

SUBJECT: Malathion Method Evaluation - Report Nos. ECM0051S1-S2 and ECM0051W1-W2. Methods Validated by BEAD/ACB/ECS.

TO: Susan Jennings, PM Team #
Special Review and Reregistration Division (7508W)

FROM: Richard J. Mahler, Hydrologist
Environmental Chemistry Review Section I
Environmental Fate and Ground Water Branch
Environmental Fate and Effects Division (7507C)

THROUGH: Henry M. Jacoby, Chief
Environmental Fate and Ground Water Branch
Environmental Fate and Effects Division (7507C)

Paul J. Mastradone, Chief
Environmental Chemistry Review Section I
Environmental Fate and Ground Water Branch
Environmental Fate and Effects Division (7507C)

The Environmental Chemistry Section (ECS) of BEAD/ACB has completed the validation of the analytical methods taken from studies entitled "Terrestrial field dissipation for malathion in cotton (California) (MRID 41727701)" and Combined aquatic sediment field dissipation and irrigated crop accumulation study with malathion (California) (MRID 42058401)." The Ecological Effects Branch/EFED has requested an Environmental Chemistry Methods Validation for water and soil.

In summary, it was found that the method can be used to monitor soil and water for the presence of malathion and its degradate, malaoxon, at the levels claimed by the registrant.

Method performance met recovery (70-120%) and precision (Relative Standard Deviation, RSD, $\leq$20%) objectives at all spiking levels (10.0-300.0 ppb). The results obtained were comparable to those reported by the registrant.

It was stated by ECS that the registrant, American Cyanamid, reported that the validated sensitivity of the method is approximately 10.0 ppb (Minimum Detection Limit, MDL). The ECS estimated the Limit of Detection (LOD) to be 10.0 ppb and the estimated Limit of Quantitation (LOQ) to be 30.0 ppb using a 5 ul

injection for water extracts and a 3 ul injection for soil extracts.

Please request that the registrant send a copy of the non-confidential method to the following address for inclusion in the new ECM manual:

Laboratory Chief
U.S. Environmental Protection Agency
Environmental Chemistry Laboratory
Building No. 1105
Stennis Space Center, MS 39529

If you have questions, please call me at (703) 305-7991.

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

ENVIRONMENTAL CHEMISTRY SECTION
BUILDING 1105—JOHN C. STENNIS SPACE CENTER
STENNIS SPACE CENTER, MISSISSIPPI 39529-6000
TELEPHONE (601) 688-3216

MEMORANDUM

SUBJECT: Malathion Method Evaluation-Report No. ECM0051S1-S2 and Report No. ECM0051W1-W2.

FROM: Aubry E. Dupuy, Jr., Chief
BEAD/ACB/Environmental Chemistry Section

TO: Henry M. Jacoby
EFED/Environmental Fate and Groundwater (7507C)

THRU: Donald A. Marlow, Chief
BEAD/Analytical Chemistry Branch (7503W)

The EFED/Ecological Effects Branch has requested an Environmental Chemistry Method Validation for water and soil. The methods were taken from studies entitled "Terrestrial Field Dissipation For Malathion in Cotton (California)"(MRID 417277-01) and "Combined Aquatic Sediment Field Dissipation and Irrigated Crop Accumulation Study with Malathion (California)" (MRID 420584-01), performed by the registrant, American Cyanamid. The method evaluation was perfomed at three levels on soil, water and reagent blanks at fortification levels of 0.01, 0.03 and 0.3 parts per million(ppm).

The attached method evaluation reports include three parts:

Part I: Summary and Conclusions

In this section any problems encountered with the method and how they were handled are discussed. ECS's opinion of how well the method performed is also presented.

Part II: Analytical Results

In this section the individual results of each sample at each spiking level of each analyte is listed. The arithmetical means and descriptive statistics for each spiking level are also presented here.

Part III: Experimental Details

In this section any modification(s) that were made to the method, along with instrument parameters, spiking levels, example calculations, representative samples and standard chromatograms and standard curves are listed and/or discussed.

If you have questions concerning this report, please contact Charles Kennedy at (601) 688-2443 or Aubry Dupuy at (601) 688-3212.

cc: Christian Byrne, QA Officer
BEAD/ACB/ECS

Charles Kennedy
BEAD/ACB/ECS

Environmental Chemistry Method Evaluation Report

Malathion & Malaoxon

Report Number ECM0051W1-W2

Final Report

Environmental Chemistry Section
Analytical Chemistry Section
Biological and Economic Analysis Division

Prepared by: Charles Kennedy Charles Kennedy 9/18/95
ECS Chemists Signature Date

Reviewed by: Christian Byrne Christian Byrne 10/11/95
ECS/QA Coordinator Signature Date

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Part I

Summary and Conclusions

We have completed the Environmental Chemistry Method Evaluation (ECME) "Combined Aquatic Sediment Field Dissipation and Irrigated Crop Accumulation Study with Malathion (Ca)". The method used to accomplish the analyses was sponsored by American Cyanamid in support of registration. (MRID No. 420584-01) The method worked well for Malathion and Malaoxon and no major modifications were necessary for this ECME. Samples of soil were fortified at three concentrations for each of the compounds Malathion and Malaoxon and carried through the analysis method. From these results, the method provided satisfactory measurement for the residues of Malathion and Malaoxon between 10.0 ppb and 300.0 ppb.

Residues of Malathion and Malaoxon are extracted from water by partitioning twice with methylene chloride and then passing the samples through NaSO4. After taking to dryness on a rotary evaporator the extracts are reconstituted with acetone and transferred to a screw cap test tube. The samples are blown to dryness with a gentle stream of nitrogen and then diluted to a appropriate volumes with acetone/PEG for GC analysis. The malathion and malaoxon concentrations are determined by gas chromatography using an instrument equipped with a flame photometric detector operating in the phosphorus mode. Results are calculated using linear regression from external standards. The validated sensitivity of the method, which was determined by American Cyanamid's performing lab, ABC Laoratories, is approximately 10.0 ppb(MDL) for both Malathion and Malaoxon.

ECS's estimated Limit Of Detection (LOD) was 10.0 ppb and the estimated Limit of Quantitation (LOQ) was 30.0 ppb using a 5 ul injection for Malathion and Malaoxon.

Part II

EPA Analytical Results

Results:

1. Malathion

Recovery Values for Water Fortified at 10, 30, and 300.00 ppb in four replicates on Flame Photometric Detector.

(3) Fortified (ppb)	(4) Recovery (ppb)	(5) Recovery %	(7) SD	(8) RSD
Matrix Blk (1)	--	--	--	--
Run#1 10.00	10.7	107.2	10.64	11.41
Run#2 10.00	8.9	89.5	--	--
Run#3 10.00	9.5	94.5	--	--
Run#4 10.00	8.2	81.9	--	--
(2) Mean(6) Recovery	9.3	93.3	--	--
Run#1 30.0	30.9	103.2	5.00	5.01
Run#2 30.0	28.4	94.8	--	--
Run#3 30.0	28.9	96.3	--	--
Run#4 30.0	31.5	104.9	--	--
Mean Recovery	29.9	99.8	--	--
Run#1 300.0	317.8	105.9	5.79	5.24
Run#2 300.0	345.9	115.3	--	--
Run#3 300.0	316.5	105.5	--	--
Run#4 300.0	348.5	116.2	--	--
Mean Recovery	332.2	110.7	--	--

Results:

2. Malaoxon

Recovery Values for Water Fortified at 10, 30 and 300.0 ppb in four replicates on Flame Photometric Detector.

(3) Fortified (ppb)	(4) Recovery (ppb)	(5) Recovery %	(7) SD	(8) RSD
Matrix Blk (1)	--	--	--	--
Run#1 10.0	11.6	115.5	1.66	1.42
Run#2 10.0	11.6	115.5	--	--
Run#3 10.0	11.6	115.5	--	--
Run#4 10.0	11.9	118.9	--	--
(2) Mean(6) Recovery	11.7	116.4	--	--
Run#1 30.0	34.7	115.7	6.36	5.78
Run#2 30.0	31.4	104.7	--	--
Run#3 30.0	31.4	104.6	--	--
Run#4 30.0	34.7	115.7	--	--
Mean Recovery	33.1	110.2	--	--
Run#1 300.0	325.7	108.6	6.77	5.99
Run#2 300.0	362.0	120.7	--	--
Run#3 300.0	319.0	106.3	--	--
Run#4 300.0	350.5	116.8	--	--
Mean Recovery	339.2	113.1	--	--

Notes:

(1) Limit of Detection (LOD), equivalent to 10.0 ppb in water sample.

Limit of Quantitation (LOQ), equivalent to 30.0 ppb in water sample.

The LOD and LOQ were determined by 3:1 signal to noise ratio and 10:1 signal-to-noise ratio, respectively.

(2) The four values (Run#1, Run#2, Run#3, Run#4) are replicate water analyses at each of three concentration levels of 10.0, 30.0 and 300 ppb.

(3) Fortified(ppb) = Malathion and Malaoxon Fortification Levels.

(4) Recovery(ppb) = Malathion and Malaoxon Recovery Levels in Terms of Concentration.

(5) Recovery % = Percent Recovery of Malathion and Malaoxon as referred to in the Calculation Section.

(6) Mean Recovery = Average Percent Recovery of Run#1, Run#2, Run#3 and Run#4.

(7) SD = Standard Deviation of Four Replicate Runs Of Malathion and Malaoxon.

(8) RSD = Relative Standard Deviation of Four Replicate Runs Of Malathion and Malaoxon.

Part III

Experimental Details

General description of method:

One hundred mL of water were added to a 500 mL separatory funnel. Seventy-five mL of MeCl2 were added and the mixture was shaken by hand for 2 minutes. The organic extract was drained through rinsed NaSO4 in a powder funnel into a 500 mL flat bottom flask. The water was extracted again with 75 mL of MeCl2. The mixture was shaken for 2 minutes and drained over the same NaSO4 into the same 500 mL flask. The combined MeCl2 was taken to dryness on a rotary evaporator under partial vacuum with a water bath temperature of 40 degrees Centigrade. The residue was reconstituted with acetone and quantitatively transferred to a 15 mL screw cap test tube. The samples are taken to dryness under a gentle stream of nitrogen and brought back to appropriate volumes of 0.02% polyethylene glycol in acetone for GC analysis.
The fortification levels were at 0.0 (sample matrix blank), 10.0, 30.0, and 300.0 ppb. with four replicates at each level.

Table 1 (page 8) summarizes the retention times observed for the HP 5880A gas chromatograph in the Flame Photometric Detector mode.

The structural formula of Malathion and of Malaoxon is shown in Appendix A.

Modification to method:

1. Two minor modification to the ECMV "Combined Aquatic Sediment Field Dissipation and Irrigated Crop Accumulation Study with Malathion" was necessary for GC FPD analysis. The instrumentation suggested in the method was a Hewlett Packard 5890 series Flame Photometric with 2ul injection. ECS used a Hewlett Packard 5880A series equipped with a Flame Photometric Detector system and 5ul injections.

Sources of analytical reference standards:

Malathion and Malaoxon analytical NEAT standards were received from US Environmental Protection Agency Pesticides Repository of Research Triangle Park, NC 27709. Fax Number: (919)541-2971.

1. Malathion, Code#P-054260-05-01, Lot#F16L, CAS#121-75-57, 98.4% purity.

2. Malaoxon, Code#F-003358-03-01, Lot#F06M, CAS1634-78-2, 92.9% purity.

Source of sample matrix:

The pond water used for samples in this ECMV were collected at Stennis Space Center, Ms. at a pond fed by artesian well water. This water was previously checked by ECS Analytical Unit and found be free of interfering peaks.

Instrumentation for quantitation (listed only if different from that listed in method)

Data Handling(GC-FPD): Hewlett Packard 5880A Series GC Terminal

Injection(GC-FPD): Manual 5ul

Instrumentation for confirmation: Not applicable.

Relative retention parameters for the present evaluation:

Table 1

Analyte	Chemical Abstracts Registry No.	Retention Time minutes(a)
Malathion	P-054260-05-01	16.40 (GC-FPD)
Malaoxon	F-003358-03-01	13.03 (GC-FPD)

Notes on analytical procedures:

ECS/EPA found the method to work well for both Malathion and Malaoxon. The only minor change concerned the injection volume which was increased from 2ul to 5ul.

Comments:

At least 1.5 working days (assuming 9-hr working day) would be needed to complete processing and to start GC FPD analysis for a set of six soil samples.

Calibration:

The HP 5880A gas chromatograph FPD was calibrated with Malathion and Malaoxon standards with concentrations, 10, 30, 100 and 300ppb. The correlation coefficient was 0.9998 for Malathion and 0.9998 for Malaoxon linear curve. A calibration standard was analyzed before each set of four fortified runs at a particular concentration level and peak height counts in millimeters was determined.

Calculation Formula

A standard curve was constructed by linear regression analysis of concentration of external standards (ppb) versus peak height counts (mm) for each analyte. The recovery concentration of the analyte (ppb) in fortified water was determined from the linear regression equation for the analyte:

$$\text{Recovery(ppb)} = \frac{\text{(Peak Height of Sample)} - \text{(y intercept)}}{\text{Slope}}$$

The recovery of each analyte from fortified water samples was calculated by the following equation:

$$\text{Recovery (\%)} = \frac{\text{ppb in Fortified Sample} \times 100\%}{\text{ppb Added}}$$

Actual Sample Calculation:

Sample: Run #2 @ 30.0 ppb for Malathion

Peak Height Count(Sample) = 13.0mm
y-intercept(Malathion) = 1.764542mm
Slope(Malathion) =.3950951

$$\text{Recovery(Sample @ 30.0 ppb)} = \frac{13.0 - 1.764542}{.3950951} = \frac{11.235458}{.3950951} = 28.44\text{ppb}$$

$$\text{Recovery (\%)} = \frac{28.44 \text{ ppb}}{30.0 \text{ ppb}} \times 100\% = 94.8\%$$

Chromatograms and Linear Regression Curves

A. Malathion and Malaoxon Calibration Standards Analyzed by GC-FPD at 10.0, 30.0, 100.0 and 300.0 ppb.

A-1: 10.0 ppb.

A-2: 30.0 ppb.

A-3: 100.0 ppb.

A-4: 300.0 ppb.

B. Linear Regression Curves for Malathion and Malaoxon

B-1: Linear Regression Curve for Malathion

B-2: Linear Regression Curve for Malathion

C. Malathion and Malaoxon Fortification Analyzed by GC-FPD at 10 ppb.

C-1: Matrix Blank

C-2: Water Fortified at 10.0 ppb.

D. Malathion and Malaoxon Fortification Analyzed by GC-FPD at 30.0 ppb.

D-1: Matrix Blank

D-2: Water Fortified at 30.0 ppb.

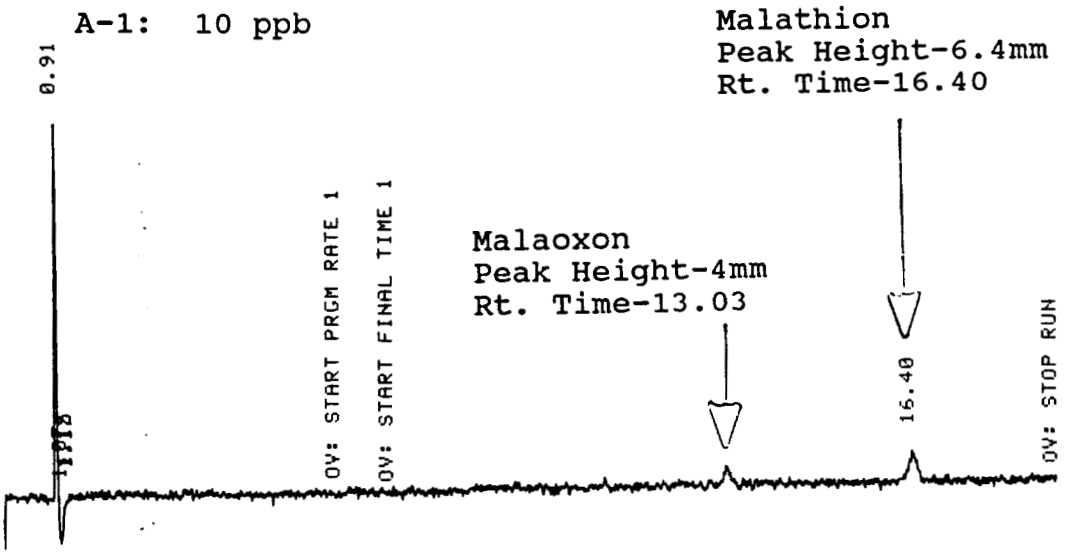
E. Malathion and Malaoxon Fortification Analyzed by GC-FPD at 300.0 ppb.

E-1: Matrix Blank

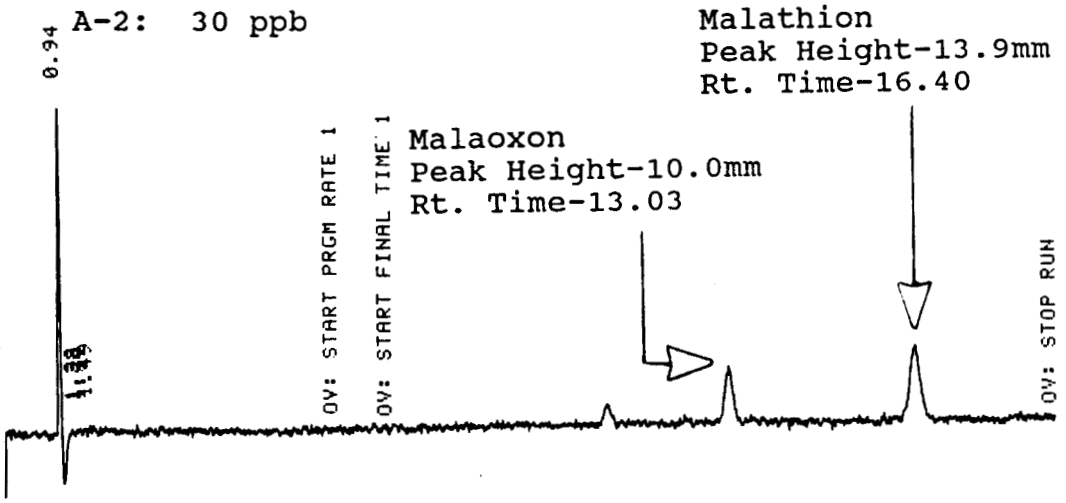
E-2: Water Fortified at 300.0 ppb.

A. Malathion And Malaoxon Calibration Standards Analyzed By GC-FPD at 10.0, 30.0, 100.0 and 300.0 ppb.

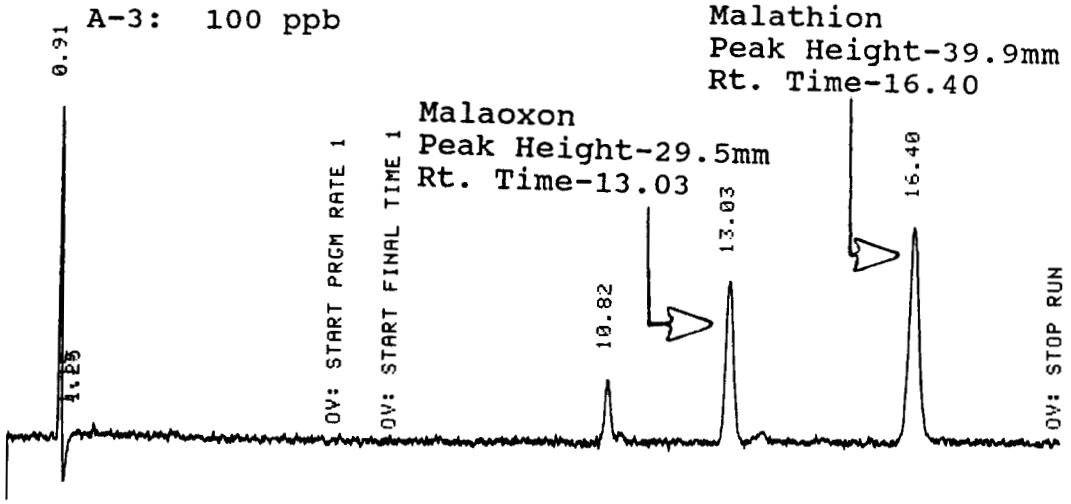
A-1: 10 ppb



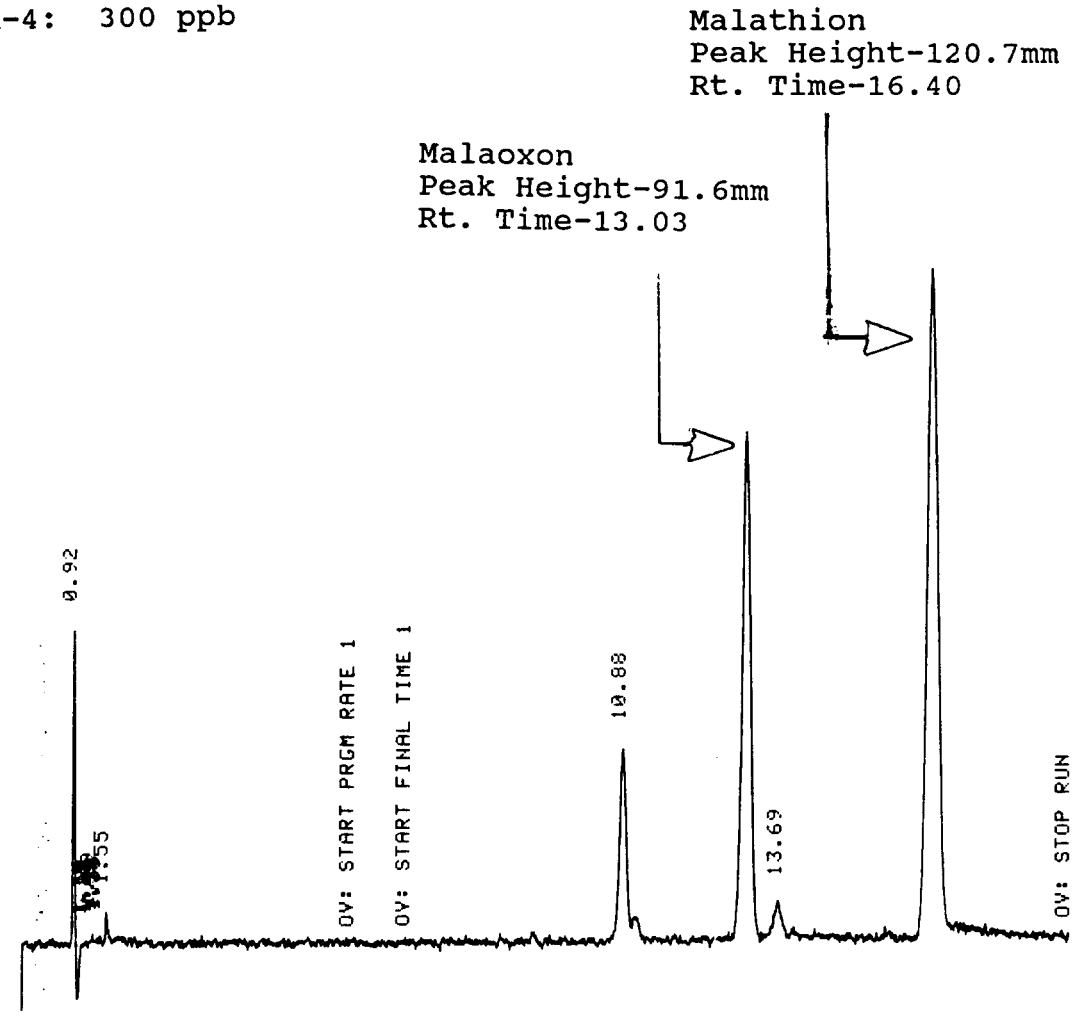
A-2: 30 ppb



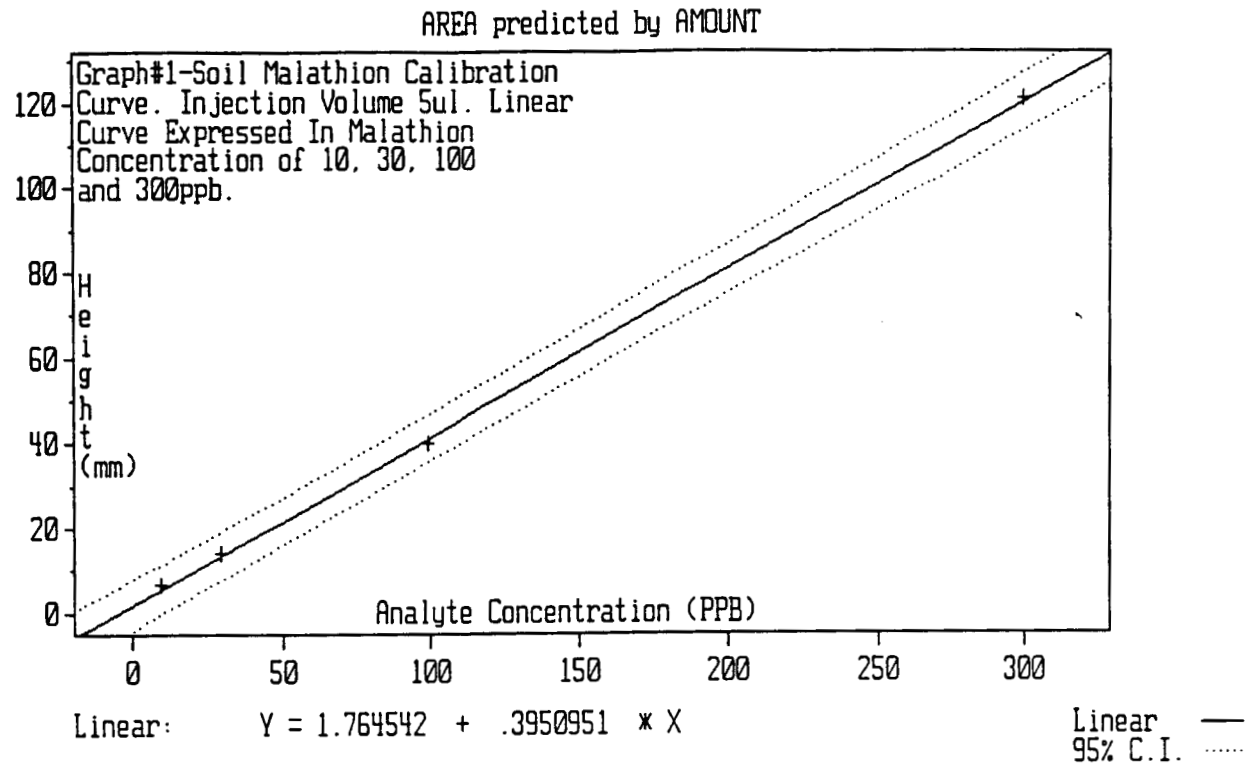
A-3: 100 ppb



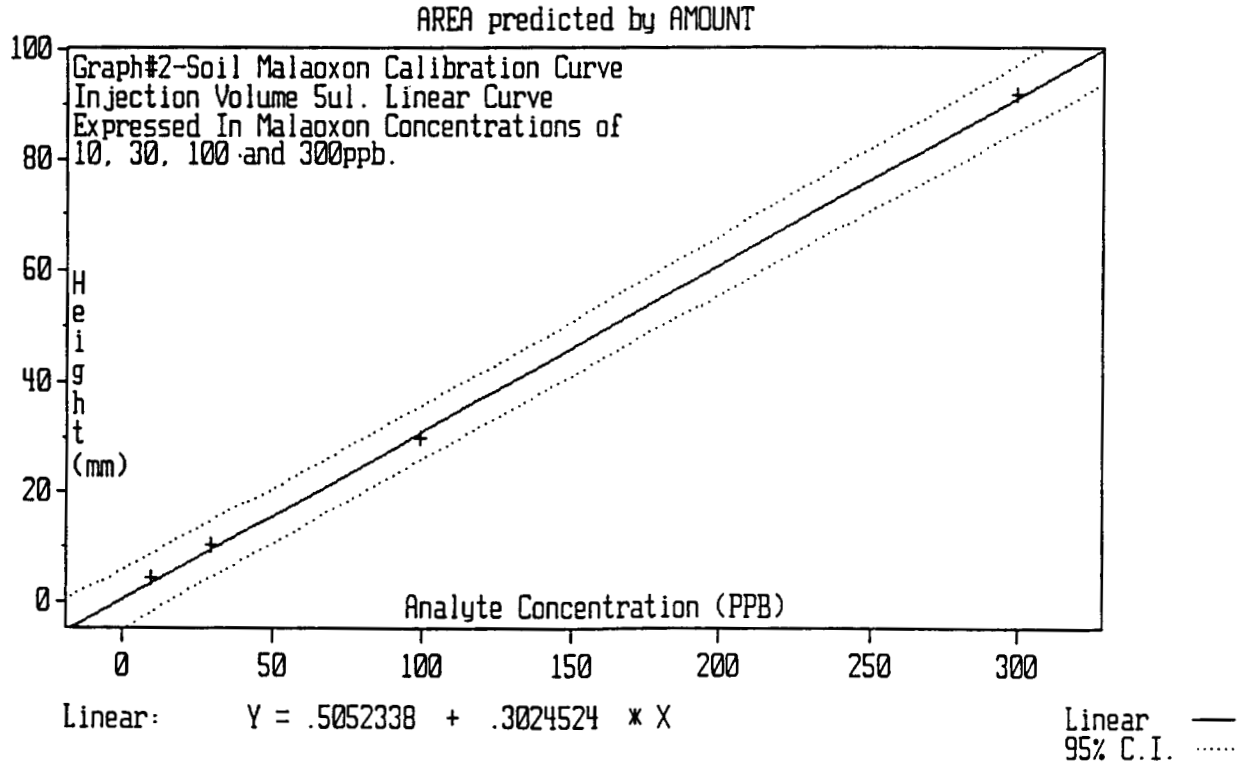
A-4: 300 ppb


Malathion
Peak Height-120.7mm
Rt. Time-16.40
Malaoxon
Peak Height-91.6mm
Rt. Time-13.03
0.92
1.55
OV: START PRGM RATE 1
OV: START FINAL TIME 1
10.88
13.69
OV: STOP RUN

B-2: Linear Regression Curve For Malaoxon

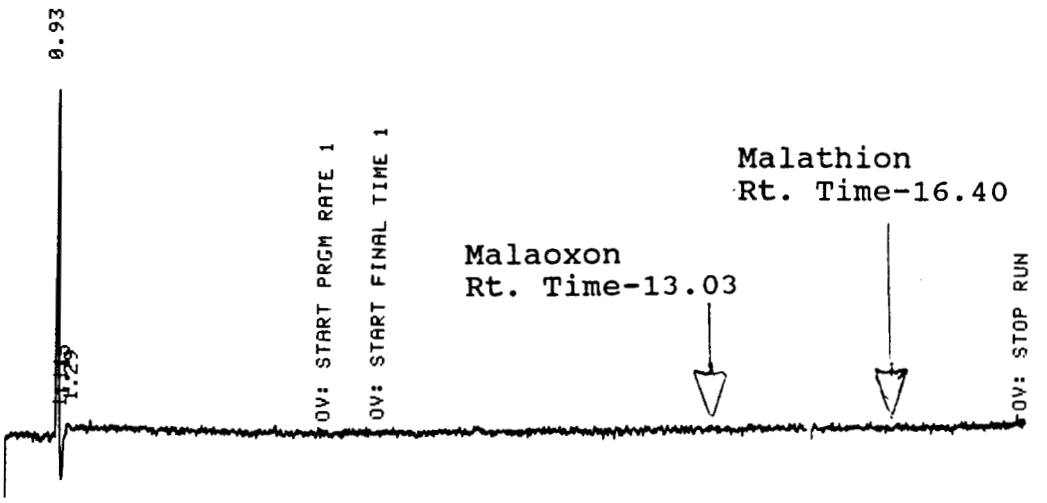


B-1: Linear Regression Curve for Malathion

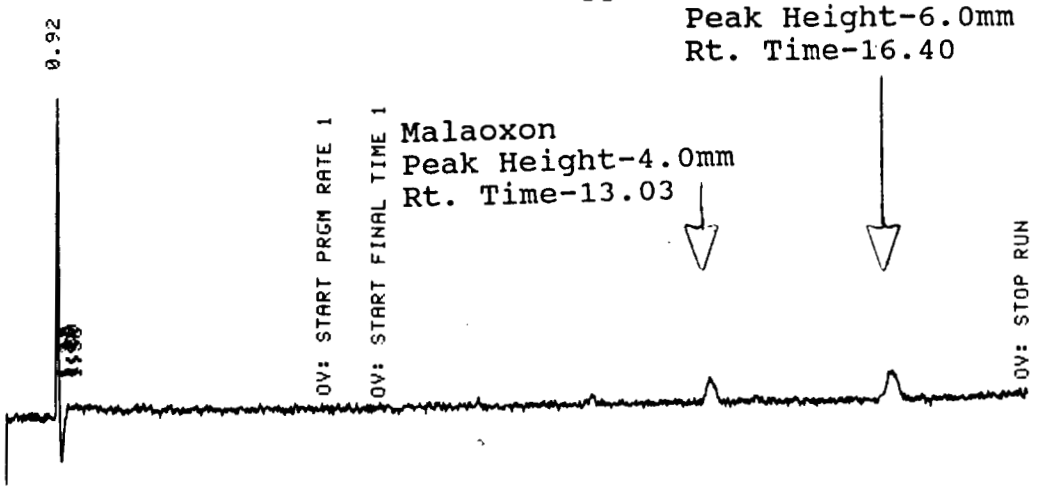


C. Malathion and Malaoxon Fortification Analyzed by GC-FPD at 10.0 ppb.

C-1: Matrix Blank

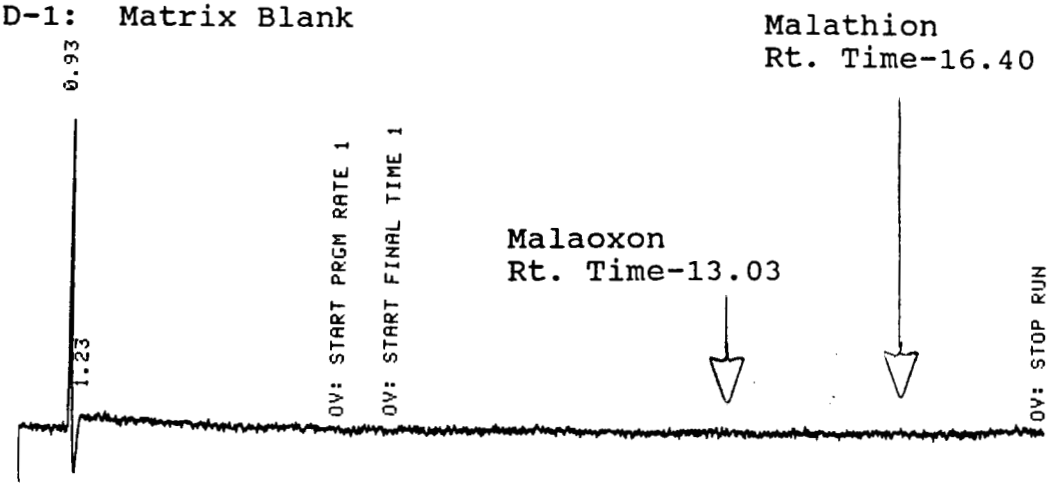


C-2: Water Fortified at 10.0 ppb.

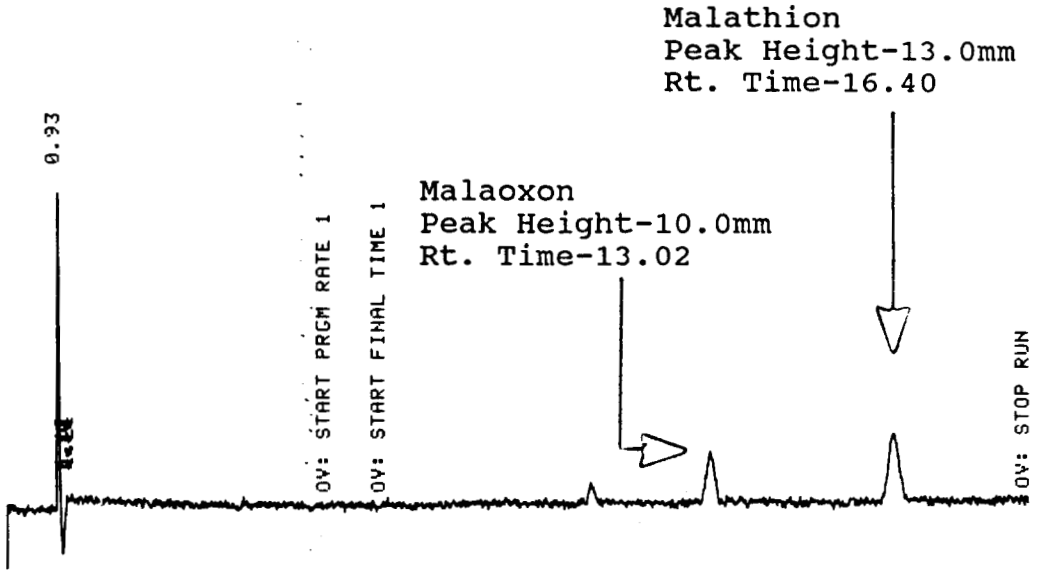


D. Malathion and Malaoxon Fortification Analyzed by GC-FPD at 30.0 ppb.

D-1: Matrix Blank

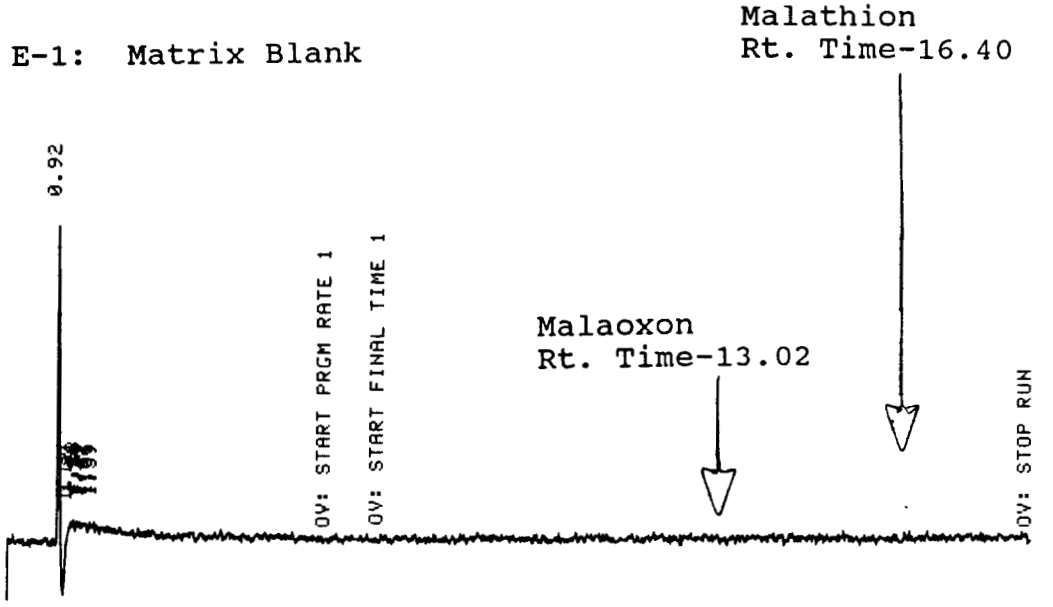


D-2: Water Fortified at 30.0 ppb.

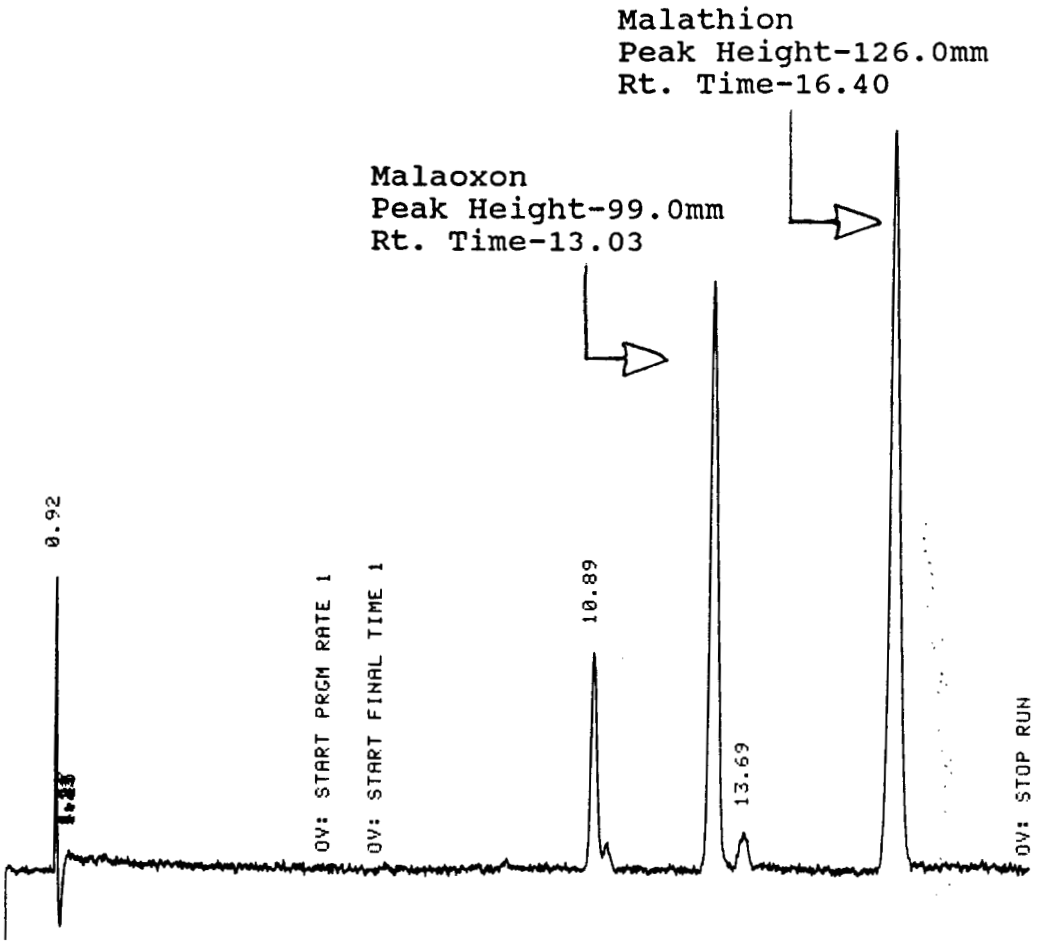


E. Malathion and Malaoxon Fortification Analyzed by GC-FPD at 300.0 ppb.

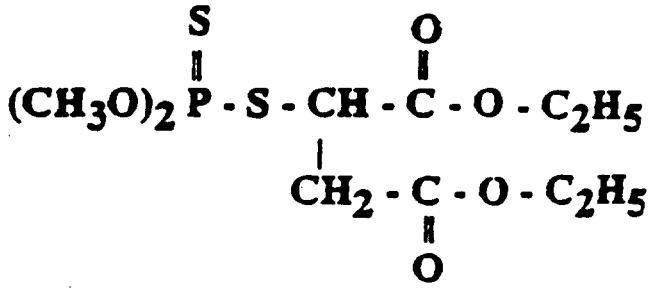
E-1: Matrix Blank



E-2: Water Fortified at 300.0 ppb.

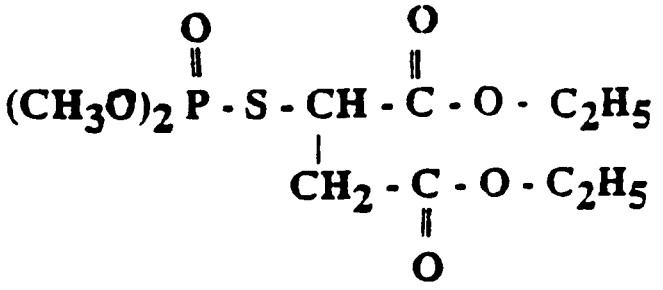


APPENDIX A: CHEMICAL STRUCTURES OF MALATHION AND MALAOXON



Malathion

Sucinic acid, mercapto-diethyl ester, S-ester with
O,O-dimethyl phosphorodithiate
$C_{10}H_{19}O_6PS_2$



Malaoxon

Butanedioic acid, (dimethoxyphosphinyl)thio)-diethyl ester
$C_{10}H_{19}C_6PS$

Environmental Chemistry Method Evaluation Report

Malathion & Malaoxon

Report Number ECM0051S1-S2

Final Report

Environmental Chemistry Section
Analytical Chemistry Section
Biological and Economic Analysis Division

Prepared by: Charles Kennedy Charles Kennedy 9/5/95
ECS Chemists Signature Date

Reviewed by: Christian Byrne Christian Byrne 9/8/95
ECS/QA Coordinator Signature Date

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Part I

Summary and Conclusions

We have completed the Environmental Chemistry Method Evaluation (ECME) "Terrestrial Field Dissipation For Malathion in Cotton (California)". The method used to accomplish the analyses was sponsored by American Cyanamid in support of registration (MRID No.417277-01). The method worked well for Malathion and Malaoxon and no major modifications were necessary for this ECME. Samples of soil were fortified at three concentrations for each of the compounds Malathion and Malaoxon and carried through the analysis method. From these results, the method provided satisfactory measurement for the residues of Malathion and Malaoxon between 10.0 ppb and 300.0 ppb.

Residues of Malathion and Malaoxon are extracted from soil with acetonitrile. The filtered extracts are subjected to cleanup procedures involving partitioning with hexane and then evaporating to dryness on a rotary evaporator. The extracts are then dissolved in acetone-methylene chloride solution and passed through a disposable silica-gel solid phase extraction cartridge. The samples are blown to dryness and diluted to appropriate volumes with acetone/PEG for GC analysis. The malathion and malaoxon concentrations are determined by gas chromatography using an instrument equipped with a flame photometric detector operating in the phosphorus mode. Results are calculated using linear regression from external standards. The validated sensitivity of the method, which was determined by American Cyanamid's performing lab, ABC Laboratories, is approximately 10.0 ppb(MDL) for both Malathion and Malaoxon.

ECS's estimated Limit Of Detection (LOD) was 10.0 ppb and the estimated Limit of Quantitation (LOQ) was 30.0 ppb using a 3 ul injection for Malathion and Malaoxon.

Part II

EPA Analytical Results

Results:

1. Malathion

Recovery Values for Soil Fortified at 10, 30, and 300.00 ppb in four replicates on Flame Photometric Detector.

(3) Fortified (ppb)	(4) Recovery (ppb)	(5) Recovery %	(7) SD	(8) RSD
Matrix Blk (1)	--	--	--	--
Run#1 10.00	9.98	99.9	6.11	5.82
Run#2 10.00	9.98	99.9	--	--
Run#3 10.00	11.2	112.0	--	--
Run#4 10.00	10.8	108.2	--	--
(2) Mean(6) Recovery	10.5	105.0	--	--
Run#1 30.0	32.8	109.5	9.94	10.3
Run#2 30.0	25.6	85.2	--	--
Run#3 30.0	28.7	95.6	--	--
Run#4 30.0	28.7	95.6	--	--
Mean Recovery	29.0	96.5	--	--
Run#1 300.0	233.4	77.8	6.83	7.84
Run#2 300.0	282.2	94.1	--	--
Run#3 300.0	261.5	87.2	--	--
Run#4 300.0	267.7	89.2	--	--
Mean Recovery	261.2	87.06	--	--

Results:

2. Malaoxon

Recovery Values for Soil Fortified at 10, 30 and 300.0 ppb in four replicates on Flame Photometric Detector.

(3) Fortified (ppb)	(4) Recovery (ppb)	(5) Recovery %	(7) SD	(8) RSD
Matrix Blk (1)	--	--	--	--
Run#1 10.0	9.96	99.6	13.3	13.7
Run#2 10.0	9.96	99.6	--	--
Run#3 10.0	7.85	78.5	--	--
Run#4 10.0	11.0	110.0	--	--
(2) Mean(6) Recovery	9.7	96.9	--	--
Run#1 30.0	31.1	103.7	6.53	6.62
Run#2 30.0	27.6	92.0	--	--
Run#3 30.0	28.3	94.3	--	--
Run#4 30.0	31.5	104.9	--	--
Mean Recovery	29.6	98.7	--	--
Run#1 300.0	258.5	86.2	7.04	7.47
Run#2 300.0	285.0	95.0	--	--
Run#3 300.0	278.0	92.6	--	--
Run#4 300.0	310.0	103.2	--	--
Mean Recovery	283.0	94.3	--	--

Notes:

(1) Limit of Detection (LOD), equivalent to 10.0 ppb in soil sample.

Limit of Quantitation (LOQ), equivalent to 30.0 ppb in soil sample.

The LOD and LOQ were determined by 3:1 signal to noise ratio and 10:1 signal-to-noise ratio, respectively.

(2) The four values (Run#1, Run#2, Run#3, Run#4) are replicate soil analyses at each of three concentration levels of 10.0, 30.0, and 300 ppb.

(3) Fortified(ppb) = Malathion and Malaoxon Fortification Levels.

(4) Recovery(ppb) = Malathion and Malaoxon Recovery Levels in Terms of Concentration.

(5) Recovery % = Percent Recovery of Malathion and Malaoxon as referred to in the Calculation Section.

(6) Mean Recovery = Average Percent Recovery of Run#1, Run#2, Run#3 and Run#4.

(7) SD = Standard Deviation of Four Replicate Runs Of Malathion and Malaoxon.

(8) RSD = Relative Standard Deviation of Four Replicate Runs Of Malathion and Malaoxon.

Part III

Experimental Details

General description of method:

Approximately twenty grams of homogeneous sample was weighed. Samples were then extracted by shaking on a platform shaker for 30 minutes with 250ml of pesticide-grade acetonitrile. The sample extract plus a 50ml rinse was filtered through filter paper into a 500ml flask. One hundred and fifty ml of the sample extract were transferred to a 250ml separator funnel with 50ml of hexane and shaken by hand for 1 minute. The acetonitrile was then drained through a NaSO4 powder funnel and collected in a 500ml flat bottom flask. The aliquot was taken to dryness on a rotary evaporator and reconstituted with 1-ml of acetone and then mixed well with 9ml of MeCl2. A disposable silica gel column was prepared and the sample passed through and collected in a screw cap test tube. The samples were then blown to dryness followed by a final dilution to 1ml with

acetone/PEG for analysis by FPD gas chromatography. The fortification levels were at 0.0 (sample matrix blank), 10.0, 30.0, and 300.0 ppb. with four replicates at each level.

Table 1 (page 8) summarizes the retention times observed for the HP 5880A gas chromatograph in the Flame Photometric Detector mode.

The structural formula of Malathion and Malaoxon is shown in Appendix A.

Modification to method:

1. Two minor modification to the ECMV "Terrestrial Field Dissipation for Malathion in Cotton" was necessary for GC FPD analysis. The instrumentation suggested in the method was a Hewlett Packard 5890 series Flame Photometric with 2ul injection. ECS used a Hewlett Packard 5880A series equipped with a Flame Photometric Detector system and 3ul injections.

Sources of analytical reference standards:

Malathion and Malaoxon analytical NEAT standards were received from US Environmental Protection Agency Pesticides Repository of Research Triangle Park, NC 27709. Fax Number: (919)541-2971.

1. Malathion, Code#P-054260-05-01, Lot#F16L, CAS#121-75-57, 98.4% purity.

2. Malaoxon, Code#F-003358-03-01, Lot#F06M, CAS1634-78-2, 92.9% purity.

Source of sample matrix:

The soil was part of a shipment from the Univ. of California received at ECS on 05/05/95. See Appendix B for a characterization of this soil.

Instrumentation for quantitation (listed only if different from that listed in method)

Data Handling(GC-FPD):	Hewlett Packard 5880A Series GC Terminal
Injection(GC-FPD):	Manual 3ul

Instrumentation for confirmation: Not applicable.

Relative retention parameters for the present evaluation:

Table 1

Analyte	Chemical Abstracts Registry No.	Retention Time minutes(a)
Malathion	P-054260-05-01	16.44 (GC-FPD)
Malaoxon	F-003358-03-01	12.89 (GC-FPD)

Notes on analytical procedures:

ECS/EPA found the method to work well for both Malathion and Malaoxon. The only minor change concerned the injection volume which was increased from 2ul to 3ul.

Comments:

At least 1.5 working days (assuming 9-hr working day) would be needed to complete processing and to start GC FPD analysis for a set of six soil samples.

Calibration:

The HP 5880A gas chromatograph FPD was calibrated with Malathion and Malaoxon standards with concentrations, 10, 30, 100 and 300ppb. The correlation coefficient was 0.9998 for Malathion and 0.9990 for Malaoxon linear curve. A calibration standard was analyzed before each set of four fortified runs at a particular concentration level and peak height counts in millimeters was determined.

Calculation Formula

A standard curve was constructed by linear regression analysis of concentration of external standards (ppb) versus peak height counts (mm) for each analyte. The recovery concentration of the analyte (ppb) in fortified soil was determined from the linear regression equation for the analyte:

$$\text{Recovery(ppb)} = \frac{\text{(Peak Height of Sample)} - \text{(y intercept)}}{\text{Slope}}$$

The recovery of each analyte from fortified soil samples was calculated by the following equation:

$$\text{Recovery (\%)} = \frac{\text{ppb in Fortified Sample x 100\%}}{\text{ppb Added}}$$

Actual Sample Calculation:

Sample: Run #3 @ 30.0 ppb for Malathion

Peak Height Count(Sample) = 13.0mm
y-intercept(Malathion) = -.804657mm
Slope(Malathion) =.4811787

$$\text{Recovery(Sample @ 30.0 ppb)} = \frac{13.0 + .8046575}{.4811787} = \frac{13.804657}{.4811787} = 28.69\text{ppb}$$

$$\text{Recovery (\%)} = \frac{28.7 \text{ ppb}}{30.0 \text{ ppb}} \times 100\% = 95.6\%$$

Chromatograms and Linear Regression Curves

A. Malathion and Malaoxon Calibration Standards Analyzed by GC-FPD at 10.0, 30.0, 100.0 and 300.0 ppb.

A-1: 10.0 ppb.

A-2: 30.0 ppb.

A-3: 100.0 ppb.

A-4: 300.0 ppb.

B. Linear Regression Curves for Malathion and Malaoxon

B-1: Linear Regression Curve for Malathion

B-2: Linear Regression Curve for Malathion

C. Malathion and Malaoxon Fortification Analyzed by GC-FPD at 10 ppb.

C-1: Matrix Blank

C-2: Soil Fortified at 10.0 ppb.

D. Malathion and Malaoxon Fortification Analyzed by GC-FPD at 30.0 ppb.

D-1: Matrix Blank

D-2: Soil Fortified at 30.0 ppb.

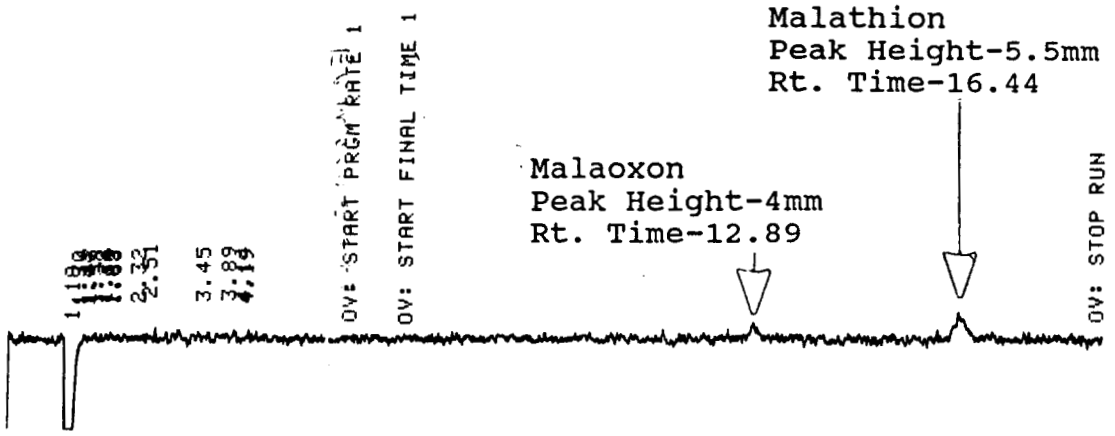
E. Malathion and Malaoxon Fortification Analyzed by GC-FPD at 300.0 ppb.

E-1: Matrix Blank

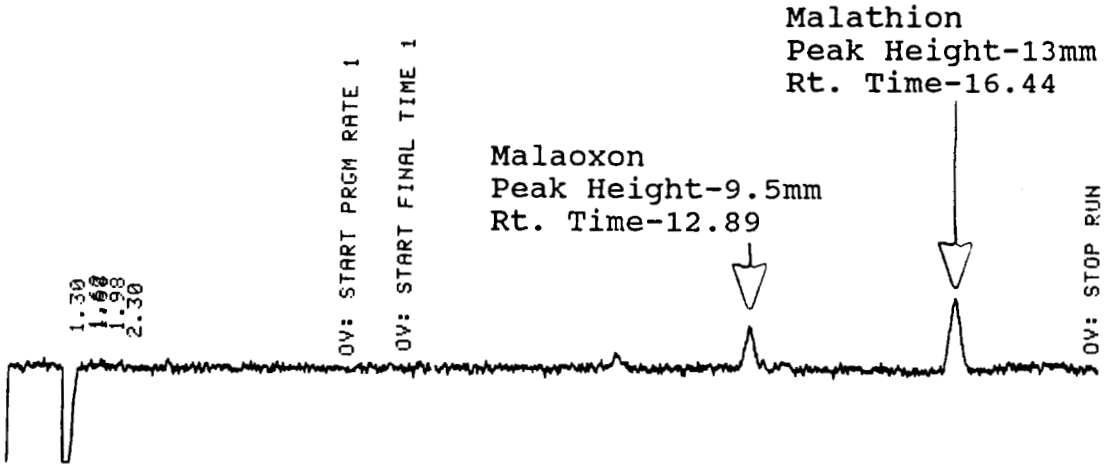
E-2: Soil Fortified at 300.0 ppb.

A. Malathion and Malaoxon Calibration Standards Analyzed by GC-FPD at 10.0, 30.0, 100.0 and 300.0 ppb.

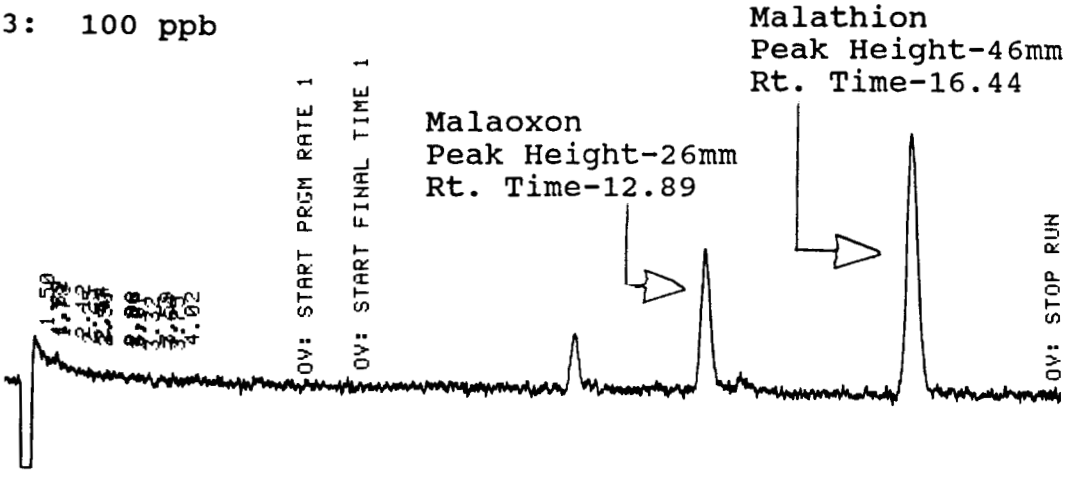
A-1: 10 ppb



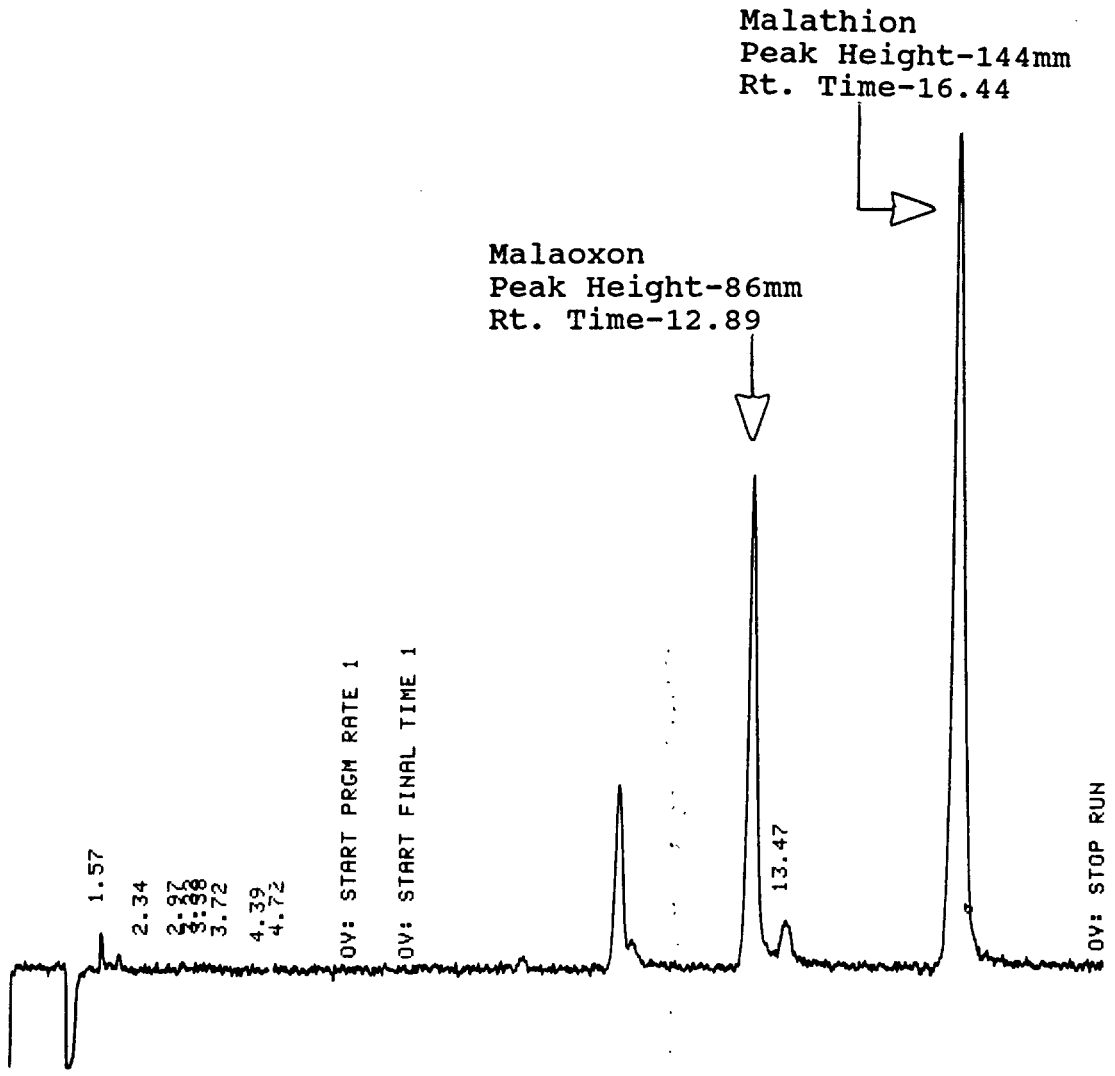
A-2: 30 ppb



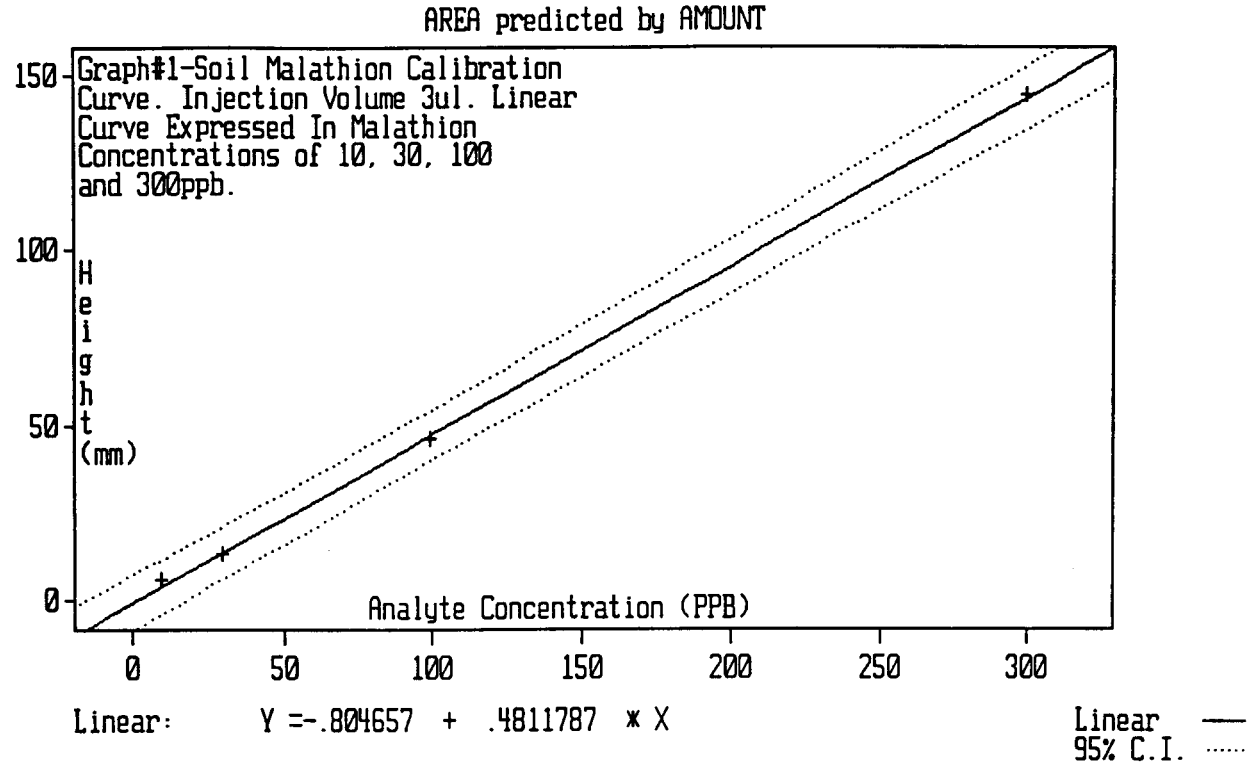
A-3: 100 ppb



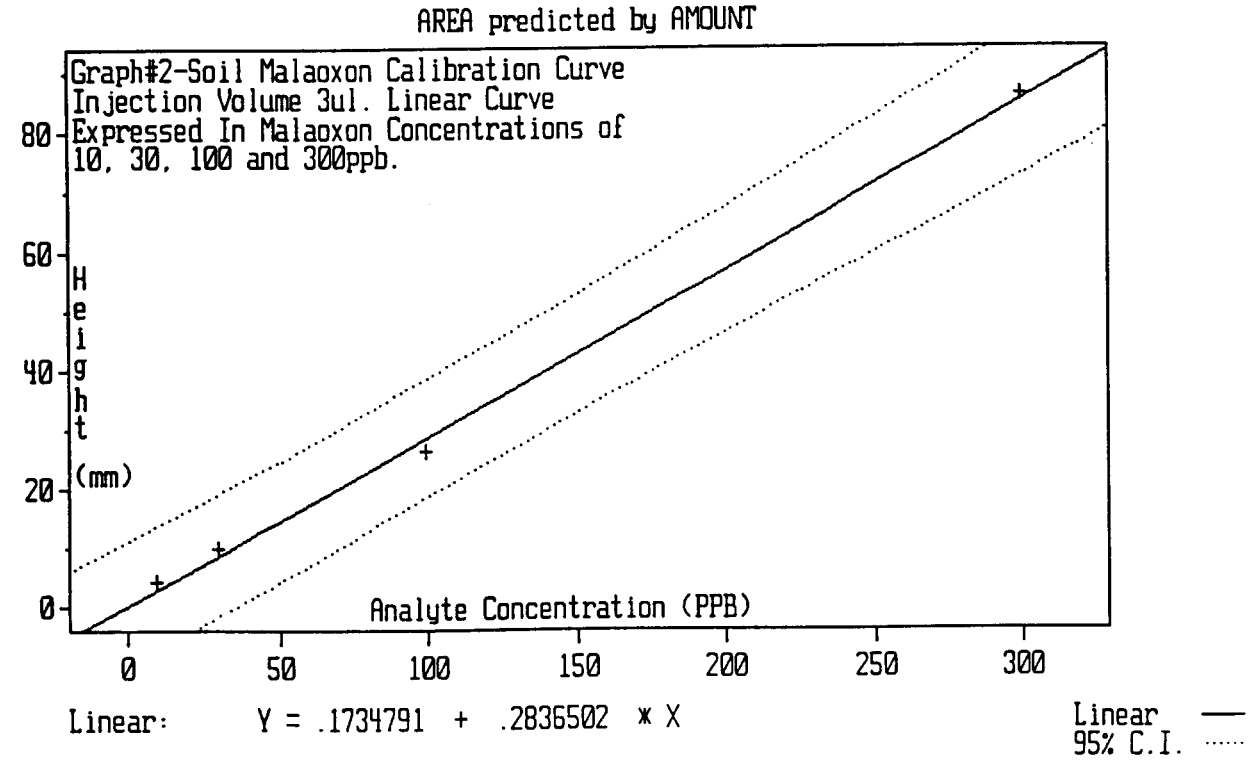
A-4: 300 ppb


Malathion
Peak Height-144mm
Rt. Time-16.44
Malaoxon
Peak Height-86mm
Rt. Time-12.89
1.57
2.34
2.97
3.98
3.72
4.39
4.72
OV: START PRGM RATE 1
OV: START FINAL TIME 1
13.47
OV: STOP RUN

B-1: Linear Regression Curve for Malathion

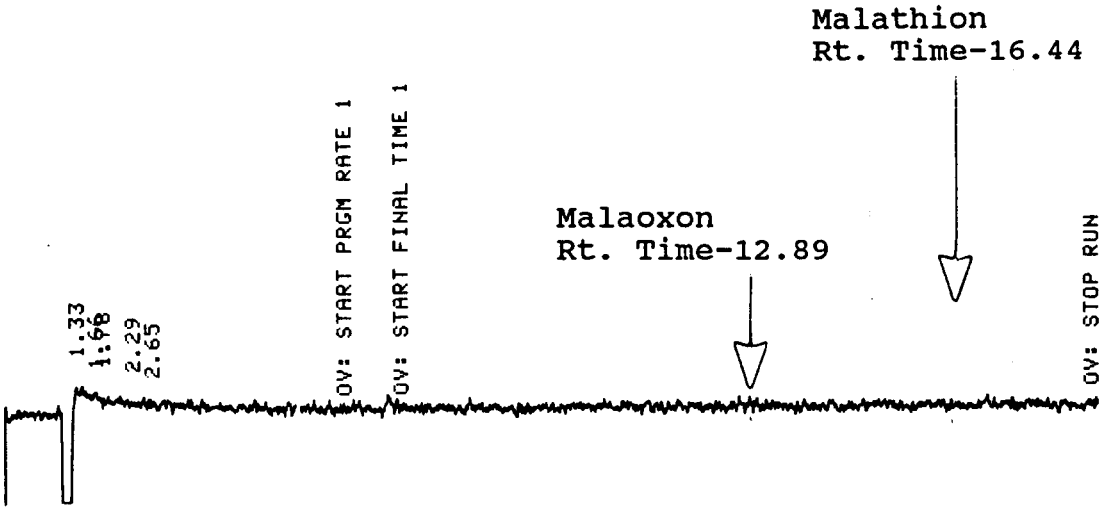


B-2: Linear Regression Curve For Malaoxon

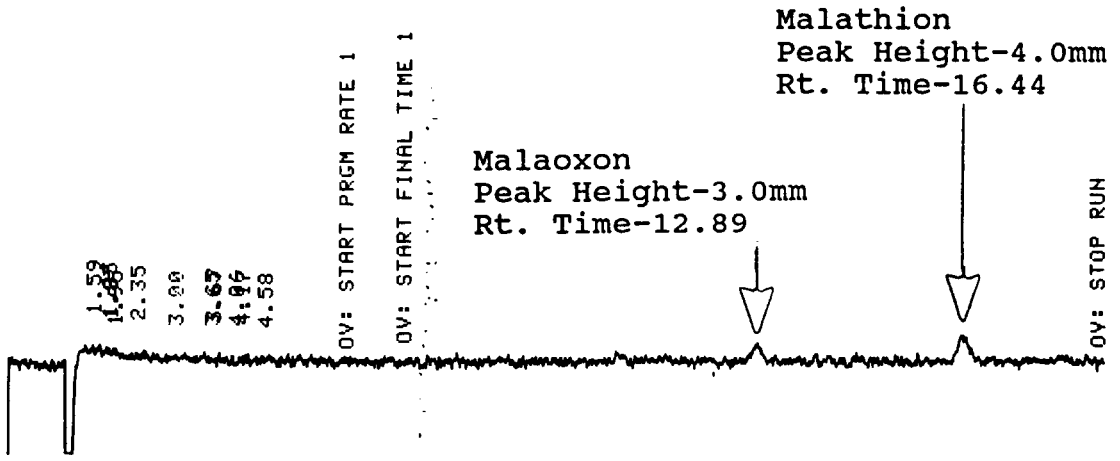


C. Malathion and Malaoxon Fortification Analyzed by GC-FPD at 10.0 ppb.

C-1: Matrix Blank

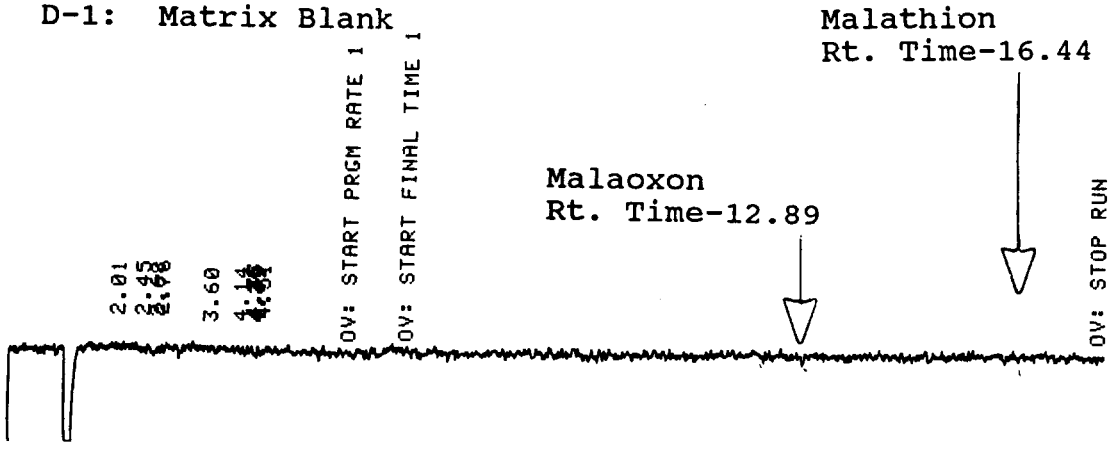


C-2: Soil Fortified at 10.0 ppb.

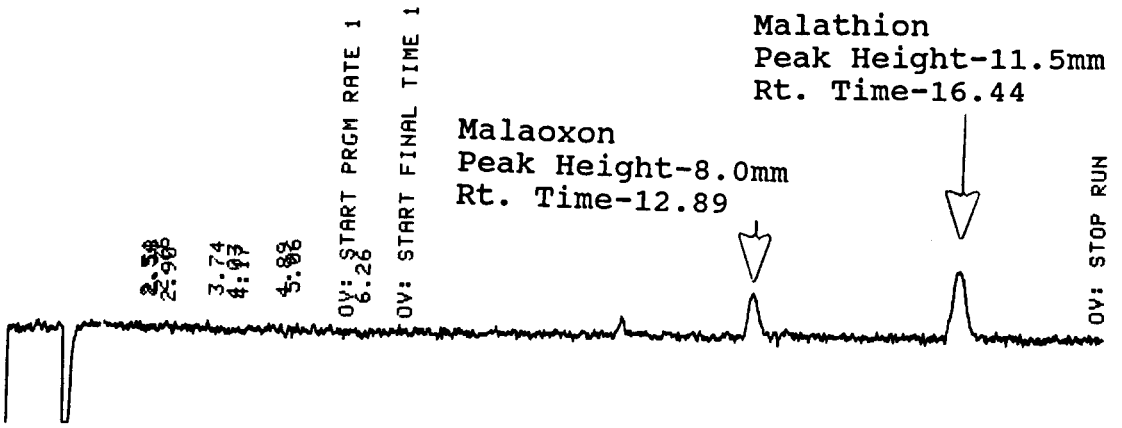


D. Malathion and Malaoxon Fortification Analyzed by GC-FPD at 30.0 ppb.

D-1: Matrix Blank

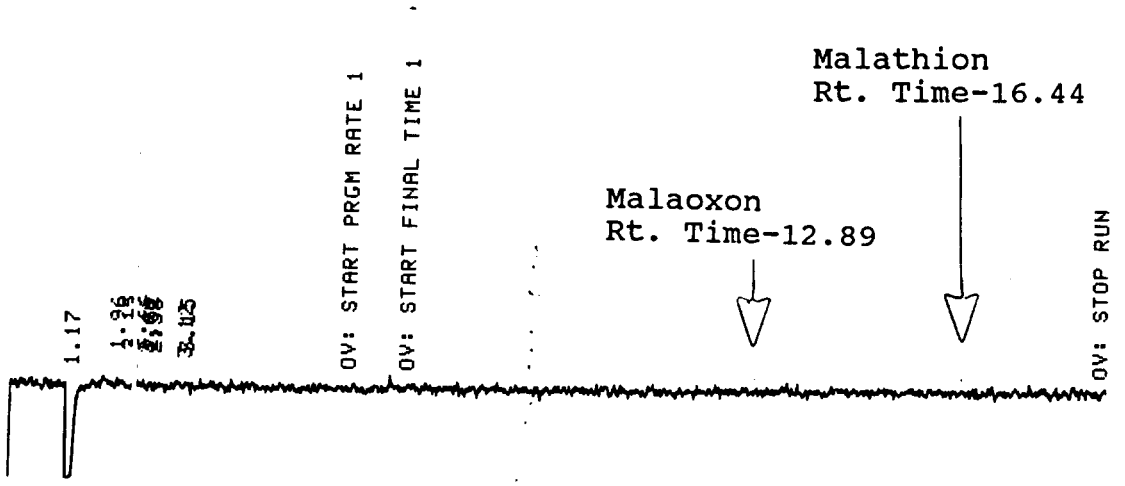


D-2: Soil Fortified at 30.0 ppb.

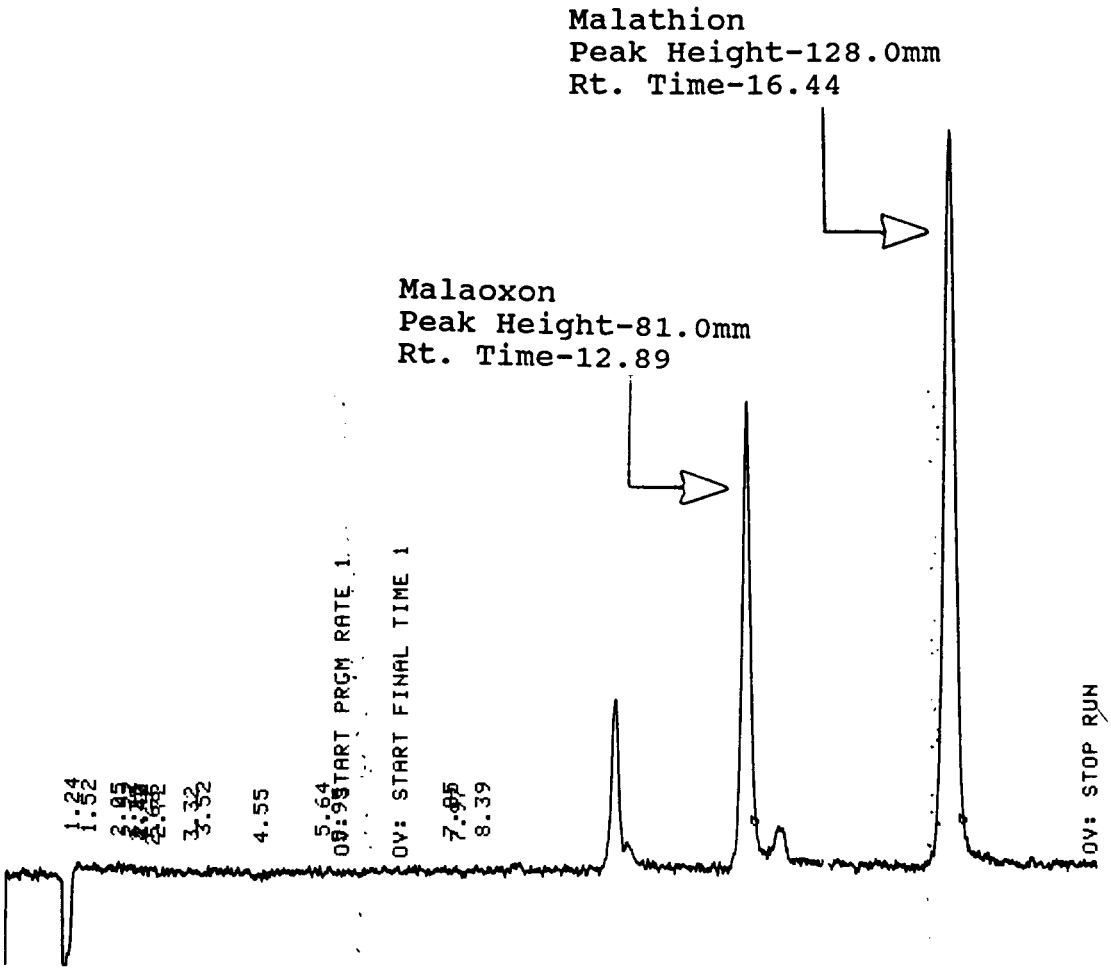


E. Malathion and Malaoxon Fortification Analyzed by GC-FPD at 300.0 ppb.

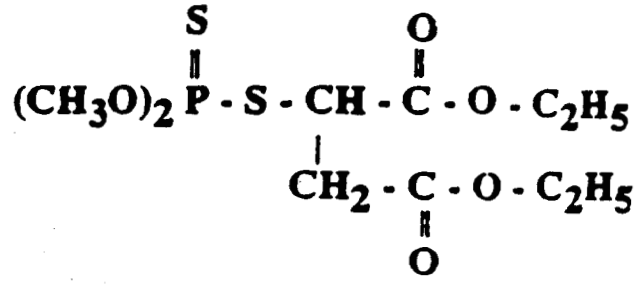
E-1: Matrix Blank



E-2: Soil Fortified at 300.0 ppb.

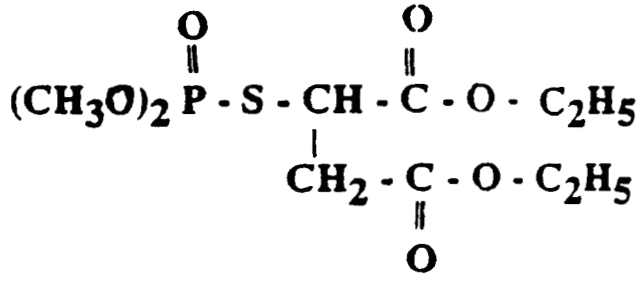


APPENDIX A: CHEMICAL STRUCTURES OF MALATHION AND MALAOXON



Malathion

Sucinic acid, mercapto-diethyl ester, S-ester with
O,O-dimethyl phosphorodithiate
$C_{10}H_{19}O_6PS_2$



Malaoxon

Butanedioic acid, (dimethoxyphosphinyl)thio)-diethyl ester
$C_{10}H_{19}C_6PS$

A&L Analytical Laboratories, Inc.
411 North Third Street • Memphis, TN 38105 • (901) 527-2780 • FAX (901) 526-1031

U.S. EPA/ECS
BLDG. 1105
STENNIS SPACE CNTR, MS 39529

CLIENT: GERALD G. GARDNER
U.S. EPA/ECS

REPORT OF ANALYSIS

REPORT DATE: 06/06/95
DATE RECEIVED: 06/01/95

LAB NO	SAMPLE IDENTIFICATION	PERCENT SAND	PERCENT SILT	PERCENT CLAY	TEXTURAL CLASSIFICATION
08780	CA1-B1	78	12	10	SANDY LOAM

A&L Analytical Laboratories, Inc.
411 North Third Street • Memphis, TN 38105 • (901) 527-2780 • FAX (901) 526-1031

SOIL ANALYSIS

CLIENT
U.S. EPA/ECS
BLDG. 1105
STENNIS SPACE CNTR, MS 3952

GROWER
GERALD G. GARDNER
U.S. EPA/ECS

DATE RECEIVED: 06/01/95

REPORT 153-0506
DATE 06/06/95
ACCOUNT 15028
PAGE 1
A & L AGRONOMIST
Richard Large

LAB NUMBER 08780 **SAMPLE ID** CA1-B1 **SIGNATURE** Richard Large

TEST	RESULTS	SOIL TEST RATINGS					CATION EXCHANGE CAPACITY
		Very Low	Low	Medium	High	Very High	
Soil pH	7.4						
Buffer pH							6.2 meq/100g
Phosphorus (P)	20 ppm						
Potassium (K)	138 ppm						CATION SATURATION
Calcium (Ca)	880 ppm						%K 5.7
Magnesium (Mg)	128 ppm						%Ca 71.0
Sulphur (S)							%Mg 17.2
Boron (B)							%H .0
Copper (Cu)							%Na 5.3
Iron (Fe)							
Manganese (Mn)							
Zinc (Zn)							SOIL TEST METHOD
Sodium (Na)	76 ppm						AMMONIUM ACETATE EXTRACTION
Soluble Salts	0.4 mmho/cm						
Organic Matter	1.4 % ENR 72						
NO_3-N							

SOIL FERTILITY GUIDELINES

CROP: **YIELD GOAL:**

LIME	N	P_2O_5	K_2O	Mg	S	B	Cu	Mn	Zn