

Test Material: Telone

MRID: 44536511
Title: Method Validation Report for GRM 94.11 and GRM 94.13: Determination of Residues of 1,2-Dichloropropane and *cis*- and *trans*-1,3-Dichloropropene in Water and Soil and Residues of Chloropicrin in Water by Purge and Trap Extraction, Capillary Gas Chromatography and Mass Selective Detection

MRID: 44536509
Title: Independent Laboratory Validation of Method GRM 94.11 - Determination of Residues of 1,2-Dichloropropane and *cis*- and *trans*-1,3-Dichloropropene, and Trichloronitromethane in Water by Purge and Trap Extraction, Capillary Gas Chromatography and Mass Selective Detection

MRID: 44536508
Title: Independent Laboratory Validation of Method GRM 94.13 - Determination of Residues of 1,2-Dichloropropane and *cis*- and *trans*-1,3-Dichloropropene in Soil by Purge and Trap Extraction, Capillary Gas Chromatography and Mass Selective Detection


EPA PC Code: 029001

OCSPP Guideline: 850.6100

For CDM Smith

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Analytical methods for telone (1,3-dichloropropene), 1,2-dichloropropane, and trichloronitromethane (chloropicrin) in water, and telone and 1,2-dichloropropane in soil

- Reports:** ECM: EPA MRID No.: 44536511. Dolder, S.C. 1998. Method Validation Report for GRM 94.11 and GRM 94.13: Determination of Residues of 1,2-Dichloropropane and *cis*- and *trans*-1,3-Dichloropropene in Water and Soil and Residues of Chloropicrin in Water by Purge and Trap Extraction, Capillary Gas Chromatography and Mass Selective Detection. Report prepared, sponsored, and submitted by Global Environmental Chemistry Laboratory - Indianapolis Lab, DowElanco, Indianapolis, Indiana; 118 pages. DowElanco Study ID: RES94060. Final report issued March 27, 1998.
- ILV: EPA MRID No. 44536509. Eckert, J., and S.C. Dolder. 1997. Independent Laboratory Validation of Method GRM 94.11 - Determination of Residues of 1,2-Dichloropropane and *cis*- and *trans*-1,3-Dichloropropene, and Trichloronitromethane in Water by Purge and Trap Extraction, Capillary Gas Chromatography and Mass Selective Detection. Report prepared by Enviro-Bio-Tech, Ltd., Bernville, Pennsylvania, and Global Environmental Chemistry Laboratory - Indianapolis Lab, DowElanco, Indianapolis, Indiana, sponsored and submitted by Global Environmental Chemistry Laboratory - Indianapolis Lab, DowElanco, Indianapolis, Indiana; 37 pages. DowElanco Study No.: RES95174. Final report issued December 17, 1997.
- ILV: EPA MRID No. 44536508. Eckert, J., and S.C. Dolder. 1997. Independent Laboratory Validation of Method GRM 94.13 - Determination of Residues of 1,2-Dichloropropane and *cis*- and *trans*-1,3-Dichloropropene in Soil by Purge and Trap Extraction, Capillary Gas Chromatography and Mass Selective Detection. Report prepared by Enviro-Bio-Tech, Ltd., Bernville, Pennsylvania, and Global Environmental Chemistry Laboratory - Indianapolis Lab, DowElanco, Indianapolis, Indiana, sponsored and submitted by Global Environmental Chemistry Laboratory - Indianapolis Lab, DowElanco, Indianapolis, Indiana; 32 pages. DowElanco Study No.: RES95173. Final report issued December 17, 1997.
- Document No.:** MRIDs 44536511, 44536509 & 44536508
- Guideline:** 850.6100
- Statements:** ECM: The study was conducted in compliance with USEPA Good Laboratory Practice (GLP) standards, with minor exceptions (p. 3 of MRID 44536511). Signed and dated Data Confidentiality, GLP, and Quality Assurance statements were provided (pp. 2-4). The certification of the authenticity of the study report is included in the Quality Assurance Statement (p. 4).
- ILV (MRID 44536509): The study was conducted in compliance with USEPA GLP standards (p. 3). Signed and dated Data Confidentiality, GLP, and Quality Assurance statements were provided (pp. 2-4). The certification of the authenticity of the study report is included in the Quality Assurance Statement (p. 4).
- ILV (MRID 44536508): The study was conducted in compliance with USEPA GLP standards (p. 3). Signed and dated Data Confidentiality, GLP, and Quality Assurance statements were provided (pp. 2-4). The certification of the authenticity of the study report is included in the Quality Assurance Statement (p. 4).

Classification: Analytical method GRM 94.11 (water) is classified as unacceptable. Analytical method GRM 94.13 (soil) is classified as unacceptable. The ILVs were not conducted independently of the ECM originating laboratory. The author of the ECMs is also the study director of the ILVs. The experimental design of the ILVs was inadequate to produce a successful validation of the respective ECM, with insufficient performance data at the LOQ (n = 2) and no performance data at 10x LOQ. The registrant failed to verify that the independent laboratories performed the ILV with a matrix (water/soil) of the most difficult analytical sample condition to analyze to demonstrate how well the method performs. For Method GRM 94.11, the water matrices used in the ECM validation and ILV were not characterized. For the ILV of Method GRM 94.13, the soil matrix was not characterized. The ILVs did not verify the LODs for the analytes. For both ILVs, the chromatograms were illegible. For both ECM validations, performance data at 10x LOQ were not reported.

PC Code: 029001

Reviewer:

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Date: May 10, 2016

For all three MRIDs, page citations in this review refer to the uppermost set of page numbers located in the top right corner of each page of the MRID.

Executive Summary

DowElanco Analytical Method GRM 94.11 is designed for the quantitative determination of cis- and trans-1,3-dichloropropene (1,3-D, telone), 1,2-dichloropropane (1,2-D), and trichloronitromethane (TCNM) in water and Analytical Method GRM 94.13 is designed for the quantitative determination of cis- and trans-1,3-D and 1,2-D in soil using purge and trap methodology with GC/MS. 1,3-D and TCNM are active ingredients in Telone brand soil fumigants, while 1,2-D is a process contaminant found at low levels in formulations containing 1,3-D. The methods are quantitative for the analytes at the stated LOQ of 0.05 ng/mL in water and 0.20 µg/kg in soil. The respective LOQ is less than the lowest toxicological level of concern in water and soil. No major modifications were made by the independent laboratories. The independent laboratories failed to validate the methods for analysis of cis- and trans-1,3-D, 1,2-D, and TCNM in water (uncharacterized) and cis- and trans-1,3-D and 1,2-D soil (uncharacterized) because insufficient performance data were reported at the LOQ (n = 2) and no performance data were reported at 10x LOQ. The ILVs did not verify the LODs for the analytes. For both ILVs, the chromatograms were illegible. The registrant failed to verify that the independent laboratories performed the ILVs with a matrix (water/soil) of the most difficult analytical sample condition to analyze to demonstrate how well the method performs. For Method GRM 94.11, the water matrices used in the ECM validation and ILV were not characterized. For the ILV of Method GRM 94.13, the soil matrix was not characterized. The ILVs were not conducted independently of the ECM originating laboratory.

Table 1. Analytical Method Summary

Analyte(s) by Pesticide ¹	MRID		EPA Review	Matrix	Method Date (dd/mm/yyyy)	Registrant	Analysis	Limit of Quantitation (LOQ)
	Environmental Chemistry Method	Independent Laboratory Validation						
cis-1,3-D	44536511: GRM 94.11	44536509		Water ²	14/04/1995 ³	DowElanco	Purge & Trap with GC/MS	0.05 ng/mL (µg/L)
trans-1,3-D								
1,2-D								
TCNM								
cis-1,3-D	44536511: GRM 94.13	44536508		Soil ⁴	26/07/1995 ⁵			0.20 µg/kg
trans-1,3-D								
1,2-D								

1 1,3-Dichloropropene (1,3-D, telone) and trichloronitromethane (TCNM, chloropicrin) are active ingredients in Telone brand soil fumigants, while 1,2-dichloropropane (1,2-D) is a process contaminant found at low levels in formulations containing 1,3-D (p. 9 of MRID 44536511).

2 Uncharacterized surface water obtained near Immokalee, Florida, was used for the ECM validation (pp. 8, 10 of MRID 44536511). Source location and characterization for water used in ILV were not reported.

3 Appendix A, p. 19 of MRID 44536511.

4 Sand soil (M465A, M465B, M465E) obtained near Immokalee, Florida, was used for the ECM validation (pp. 8, 10; Tables I-VI, pp. 88-92; Appendix C, pp. 117-118 of MRID 44536511). Source location and characterization for soil used in ILV were not reported.

5 Appendix B, p. 65 of MRID 44536511.

I. Principle of the Method

1,3-Dichloropropene (1,3-D, telone) and trichloronitromethane (TCNM, chloropicrin) are active ingredients in Telone brand soil fumigants, while 1,2-dichloropropane (1,2-D) is a process contaminant found at low levels in formulations containing 1,3-D (p. 9 of MRID 44536511).

The test compounds are volatile organic analytes (VOAs), and aqueous solutions of VOAs are not stable in any container with headspace (Appendix A, pp. 19, 22; Appendix B, pp. 65, 69-70). Calibration standards should be prepared just prior to the purge and trap analysis described below.

Water: This method is based on USEPA purge and trap methodology for volatile organic analytes, similar to Method 524.2 (see section **V. References** below; Appendix A, pp. 19, 34 of MRID 44536511). Water (100 mL) was fortified with 1,2-dichloropropane (1,2-D), cis- and trans-1,3-dichloropropene (cis- and trans-1,3-D, telone), and trichloronitromethane (TCNM, chloropicrin) in methanol for procedural recoveries (p. 8; Appendix A, pp. 21-23, 28). For TCNM, natural water matrices may need to be acidified to *ca.* pH 2 prior to fortification to prevent microbial degradation of the analyte (pp. 11-12; Appendix A, p. 33). Uncharacterized surface water from a site near Immokalee, Florida, was used for the validation (pp. 8, 10). A Tekmar 3000 purge and trap concentrator, equipped with a Tenax trap and frit sparge glassware, was connected to an Hewlett-Packard 5971 Mass Selective Detector (MSD) equipped with an Hewlett-Packard 5890 (II) GC system (Appendix A, pp. 20-21, 23-25). An aliquot (25.0 mL) of water is fortified with 2-bromo-1-chloropropane in methanol as an internal standard (Appendix A, pp. 21-22, 28). The analytes are purged from the 25.0 mL water sample by sparging with helium and captured on the sorbent-containing trap (Appendix A, pp. 19-21, 28). After purging, the trap is heated, back-flushed with helium, and the analytes are directly transferred to the GC injection port.

Soil: This method is based on USEPA purge and trap methodology for volatile organic analytes, similar to Method 8260 (see section **V. References** below; Appendix B, pp. 65, 86 of MRID

44536511). Soil (5.0 ± 0.05 g) was fortified with 1,2-dichloropropane (1,2-D) and cis- and trans-1,3-dichloropropene (cis- and trans-1,3-D, telone) in methanol for procedural recoveries (p. 8; Appendix B, pp. 67-68, 77-78 of MRID 44536511). Sand soil (M465A, M465B, M465E) from a site near Immokalee, Florida, was used for the validation (p. 10; Tables I-VI, pp. 88-92; Appendix C, pp. 117-118). For low level (0.20-200 $\mu\text{g}/\text{kg}$) fortifications, a Dynatrap purge and trap concentrator, equipped with a Tenax trap and frit sparge glassware, was connected to the GC/MSD described above (Appendix B, pp. 66-67, 71, 73-74, 77, 79-81). Soil (5.0 ± 0.05 g) is placed in an amber volatile analysis vial with 10 mL distilled, deionized water, a magnetic stir bar, and 2-bromo-1-chloropropane in methanol as an internal standard (Appendix B, pp. 69, 77, 79-80). The Dynatrap heats the soil:water slurry with stirring, then the analytes are purged from the sample by sparging with helium and captured on the sorbent-containing trap (Appendix B, pp. 65-66, 80). After purging, the trap is heated, back-flushed with helium, and the analytes are directly transferred to the GC injection port.

For high level (200-160,000 $\mu\text{g}/\text{kg}$) fortifications, a Tekmar 3000 purge and trap concentrator, equipped with a Tenax trap and fritted U-shaped sparge tubes, was connected to the GC/MSD described above (Appendix B, pp. 65-67, 72-73, 75, 77-78, 81-82). Soil (5.0 g) is extracted with 10.0 mL of methanol by vortexing for 15 seconds (Appendix B, p. 82). Soil and extract are separated by centrifugation (2,500 rpm, 3 minutes). A 25.0- μL aliquot of the extract is diluted with 25.0 mL of water and fortified with 2-bromo-1-chloropropane in methanol as an internal standard. The analytes are then purged, trapped, and transferred to the GC injection port as described above for water samples.

GC/MS: Samples are analyzed using an Hewlett-Packard 5971 Mass Selective Detector (MSD) equipped with an Hewlett-Packard 5890 (II) GC system (Appendix A, p. 25; Appendix B, p. 73 of MRID 44536511). The following GC conditions were used: J&W Scientific fused silica capillary, DB-VRX liquid phase column (0.25 mm x 30 m, 1.4 μm film thickness, injector temperature 200°C), temperature program [35°C (hold for 1.0 min.), 9°C/min. to 140°C (hold for 0.10 min.), 20°C/min. to 210°C (hold for 2.0 min.)]. The following MSD conditions were used: electron impact ionization and selected ion monitoring (SIM). Analytes were identified using two ions; one for quantitation (Q) and one for confirmation (C). The following ion were monitored: m/z 63 (Q) and m/z 76 (C) for 1,2-D, m/z 75 (Q) and m/z 112 (C) for both cis- and trans-1,3-D, m/z 119 (Q) and m/z 82 (C) for TCNM, and m/z 77 (Q) for the 2-bromo-1-chloropropane internal standard (IS). Identification is considered positive when the confirmation ion ratio [(peak area of the quantitation ion)/(peak area of the confirmation ion)] of the sample is $\pm 15\%$ of the average confirmation ion ratio found for the calibration standards (Appendix A, pp. 28-29; Appendix B, p. 78). Retention times were 7.38-7.44, 8.33-8.35, 8.89-8.92, 9.56-9.58, and 9.34-9.37 minutes for 1,2-D, cis-1,3-D, trans-1,3-D, TCNM, and the IS, respectively (Appendix A, Figures 6-17, pp. 48-59; Appendix B, Figures 5-13, pp. 101-109).

ILV - water: Sources of the test compounds (1,2-D, cis- and trans-1,3-D, TCNM) and water matrix used for the ILV were not reported (pp. 8-9; Appendix A, p. 35 of MRID 44536509). The water matrix was not characterized. The independent laboratory performed the method as written, except a Tekmar LSC 2000 with needle sparge/Supelco Vocarb 3000 (K) Purge/Trap, Hewlett-Packard 5970B MSD, and Supelco Vocol Capillary column (0.25 mm x 30 m, 1.4 μm film thickness were used, and the temperature program was modified to [35°C (hold for 1.0 min.), 11°C/min. to 140°C, set manually to 210°C at end of run for 5.0 min., then reset to 35°C] (pp. 8-10, 30; Appendix A, pp. 36-37). Approximate retention times were 7.8, 8.7, 9.3, 9.5, and 9.6 minutes for 1,2-D, cis-1,3-D, trans-1,3-D, TCNM, and the IS, respectively (p. 30).

ILV - soil: Sources of the test compounds (1,2-D, cis- and trans-1,3-D) and soil matrix used for the ILV were not reported (pp. 8-9; Appendix A, p. 30 of MRID 44536508). The soil matrix was not characterized. The independent laboratory performed the method as written, except using the same modifications as the ILV - water: above (pp. 8-10, 25; Appendix A, p. 31). Approximate retention times were 7.79, 8.73, 9.34, and 9.60 minutes for 1,2-D, cis-1,3-D, trans-1,3-D, and the IS, respectively (p. 25).

LOQ and LOD - water: In the ECM and ILV, the LOQ for 1,2-D, cis- and trans-1,3-D, and TCNM in water was 0.05 ng/mL ($\mu\text{g/L}$; Appendix A, p. 19 of MRID 44536511; p. 8; Appendix A, p. 34 of MRID 44536509). In the ECM, the LODs for 1,2-D, cis-1,3-D, trans-1,3-D, and TCNM were calculated as 0.0072, 0.0015, 0.0036, and 0.0060 ng/mL, respectively (Appendix A, p. 31; Tables V-VIII, pp. 39-42 of MRID 44536511). In the ILV, the LODs were not specified.

LOQ and LOD - soil: In the ECM and ILV, the LOQ for 1,2-D and cis- and trans-1,3-D in soil was 0.20 $\mu\text{g/kg}$ (Appendix B, p. 65 of MRID 44536511; p. 8; Appendix A, p. 29 of MRID 44536508). In the ECM, the LODs for 1,2-D, cis-1,3-D, and trans-1,3-D were calculated as 0.039, 0.020, and 0.023 $\mu\text{g/kg}$, respectively (p. 14; Appendix B, p. 85; Tables VII-IX, pp. 94-96 of MRID 44536508). In the ILV, the LODs were not specified.

II. Recovery Findings

ECM - water (MRID 44536511): Mean recoveries and relative standard deviations (RSDs) were within guidelines (mean 70-120%; $\text{RSD} \leq 20\%$) for analysis of cis- and trans-1,3-D, 1,2-D, and TCNM in Florida surface water (uncharacterized) at a fortification level of 0.05 ng/mL ($\mu\text{g/L}$, LOQ, $n = 8$; Appendix A, Tables I-IV, pp. 35-38 and DER Attachment 2). At fortification levels of 5x LOQ (0.25 ng/mL), 20x LOQ (1.00 ng/mL), 100x LOQ (5.00 ng/mL), 200x LOQ (10.0 ng/mL), and 800x LOQ (40.0 ng/mL), only two recoveries were reported for each fortification level; therefore, meaningful statistics (mean, standard deviation, RSD) for the recovery results per analyte/fortification level/water matrix could not be generated. At the fortification levels of 5x to 800x LOQ, individual recovery results were within 70-120%. Performance data at 10x LOQ were not reported. Confirmation ion ratio results were only provided for one LOQ (0.050 ng/mL) fortified sample for each analyte and were $\pm 10\%$ of the average standard confirmation ratio (Appendix A, Figures 14-17, pp. 56-59).

ECM - soil (MRID 44536511): Mean recoveries and relative standard deviations (RSDs) were within guidelines (mean 70-120%; $\text{RSD} \leq 20\%$) for analysis of cis- and trans-1,3-D and 1,2-D in sand soil at fortification levels of 0.20 $\mu\text{g/kg}$ (LOQ, $n = 8$), 25x LOQ (4.95-500 $\mu\text{g/kg}$, $n = 4$), and *ca.* 1,000x LOQ (198-200 $\mu\text{g/kg}$, $n = 8$, high level method; p. 11; Appendix B, Tables I-VI, pp. 88-93 and DER Attachment 2). At fortification levels of *ca.* 5x LOQ (1.00 $\mu\text{g/kg}$), 100x (19.8-20.0 $\mu\text{g/kg}$), 400x (79.2-79.4 $\mu\text{g/kg}$), 1,000x (198-199 $\mu\text{g/kg}$, low level method), 5,000x (988-998 $\mu\text{g/kg}$), 100,000x (19,841-19,920 $\mu\text{g/kg}$), 400,000x (79,208-79,523 $\mu\text{g/kg}$), and 800,000x (159,046-160,000 $\mu\text{g/kg}$), only two recoveries were reported for each fortification level; therefore, meaningful statistics (mean, standard deviation, RSD) for the recovery results per analyte/fortification level/soil matrix could not be generated. Individual recovery results were within 70-120% for all analytes and fortification levels, except one 1.00 $\mu\text{g/kg}$ fortification of 1,2-D (125%). Performance data at 10x LOQ were not reported. Confirmation ion ratio results were only provided for one LOQ (0.20 $\mu\text{g/kg}$) fortified sample for each analyte and were $\pm 8\%$ of the average

standard confirmation ratio (Appendix B, Figures 11-13, pp. 107-109). Three sand soil matrices (M465A, M465B, M465E) used for this validation were characterized by A & L Great Lakes Laboratories, Inc., Fort Wayne, Indiana (Tables I-VI, pp. 88-92; Appendix C, pp. 117-118).

ILV - water (MRID 44536509): Only two recoveries were reported for each fortification level; therefore, meaningful statistics (mean, standard deviation, RSD) for the recovery results per analyte/fortification level/water matrix could not be generated. Individual recovery results were within 70-120% for cis- and trans-1,3-D, 1,2-D, and TCNM in water (uncharacterized) at fortification levels of 0.05 ng/mL (LOQ) and 0.25 ng/mL (5x LOQ; Tables I-IV, pp. 11-12). Performance data at 10x LOQ were not reported. Confirmation ion ratio results for all fortification analyses were $\pm 15.0\%$ of the average standard confirmation ratio (Tables V-VIII, pp. 13-16). One validation run was conducted and considered successful (p. 31). The method modifications and equipment substitutions implemented during the ILV (see **I. Principle of the Method, ILV - water**: above) are not considered substantial changes to the ECM.

ILV - soil (MRID 44536508): Only two recoveries were reported for each fortification level; therefore, meaningful statistics (mean, standard deviation, RSD) for the recovery results per analyte/fortification level/soil matrix could not be generated. Individual recovery results were within 70-120% for both cis- and trans-1,3-D and 1,2-D in soil (uncharacterized) at fortification levels of 0.20 $\mu\text{g}/\text{kg}$ (LOQ) and 1.0 $\mu\text{g}/\text{kg}$ (5x LOQ; Tables I-III, pp. 11-12). Performance data at 10x LOQ were not reported. Confirmation ion ratio results for all fortification analyses were $\pm 15\%$ of the average standard confirmation ratio (Tables IV-VI, pp. 13-15). One validation run was conducted and considered successful (p. 26). The method modifications and equipment substitutions implemented during the ILV (see **I. Principle of the Method, ILV - soil**: above) are not considered substantial changes to the ECM.

Table 2a. Initial Validation Method Recoveries for cis- and trans-1,3-Dichloropropene (cis- and trans-1,3-D, Telone), 1,2-Dichloropropane (1,2-D), and Trichloronitromethane (TCNM) in Surface Water¹

Analyte	Fortification Level (ng/mL)	Number of Tests	Recovery Range (%)	Mean Recovery (%)	Standard Deviation (%)	Relative Standard Deviation (%)
cis-1,3-D	0.050 (LOQ)	8	100-104	103	1	1
	0.25	2	100, 100	-- ²	--	--
	1.00	2	111, 110	--	--	--
	5.00	2	93, 98	--	--	--
	10.0	2	99, 101	--	--	--
	40.0	2	98, 98	--	--	--
trans-1,3-D	0.050 (LOQ)	8	94-101	97	2	3
	0.25	2	102, 103	--	--	--
	1.00	2	112, 113	--	--	--
	5.00	2	92, 97	--	--	--
	10.0	2	99, 104	--	--	--
	40.0	2	99, 100	--	--	--
1,2-D	0.050 (LOQ)	8	99-111	105	5	4
	0.25	2	101, 99	--	--	--
	1.00	2	108, 107	--	--	--
	5.00	2	96, 103	--	--	--
	10.0	2	101, 102	--	--	--
	40.0	2	96, 99	--	--	--
TCNM	0.050 (LOQ)	8	101-113	108	4	4
	0.25	2	96, 99	--	--	--
	1.00	2	108, 108	--	--	--
	5.00	2	95, 99	--	--	--
	10.0	2	102, 103	--	--	--
	40.0	2	96, 97	--	--	--

Data (uncorrected recovery results) were obtained from Appendix A, Tables I-IV, pp. 35-38 of MRID 44536511 and DER Attachment 2 (mean, SD, RSD).

¹ Uncharacterized surface water was collected from a site near Immokalee, Florida (pp. 8, 10).

² Not applicable; meaningful statistics could not be generated because n = 2.

Table 2b. Initial Validation Method Recoveries for cis- and trans-1,3-Dichloropropene (cis- and trans-1,3-D, Telone) and 1,2-Dichloropropane (1,2-D) in Sand Soil¹

Analyte	Fortification Level (µg/kg)	Number of Tests	Recovery Range (%)	Mean Recovery (%)	Standard Deviation (%)	Relative Standard Deviation (%)
cis-1,3-D	0.20 (LOQ) ²	8	93-102	99	3	3
	1.00	2	113, 112	-- ³	--	--
	4.95-5.00	4	88-105	94	7	8
	19.8-20.0	2	113, 101	--	--	--
	79.2-79.4	2	93, 104	--	--	--
	198-199 ⁴	2	99, 88	--	--	--
	198-200 ⁵	8	71-96	79	10	13
	988-998	2	94, 79	--	--	--
	4,970-5,000	2	71, 76	--	--	--
	19,841-19,920	2	70, 74	--	--	--
	79,208-79,523	2	77, 77	--	--	--
	159,046-160,000	2	74, 79	--	--	--
trans-1,3-D	0.20 (LOQ) ²	8	77-90	84	4	5
	1.00	2	106, 98	--	--	--
	4.95-5.00	4	78-97	84	9	11
	19.8-20.0	2	105, 93	--	--	--
	79.2-79.4	2	84, 103	--	--	--
	198-199 ⁴	2	93, 81	--	--	--
	198-200 ⁵	8	70-113	81	16	20
	988-998	2	96, 79	--	--	--
	4,970-5,000	2	71, 77	--	--	--
	19,841-19,920	2	71, 75	--	--	--
	79,208-79,523	2	80, 82	--	--	--
	159,046-160,000	2	76, 81	--	--	--
1,2-D	0.20 (LOQ) ²	8	101-119	112	6	6
	1.00	2	117, 125	--	--	--
	4.95-5.00	4	95-120	107	12	12
	19.8-20.0	2	119, 108	--	--	--
	79.2-79.4	2	104, 108	--	--	--
	198-199 ⁴	2	111, 98	--	--	--
	198-200 ⁵	8	74-105	84	10	12
	988-998	2	100, 85	--	--	--
	4,970-5,000	2	76, 82	--	--	--
	19,841-19,920	2	76, 80	--	--	--
	79,208-79,523	2	82, 81	--	--	--
	159,046-160,000	2	77, 85	--	--	--

Data (uncorrected recovery results) were obtained from Appendix B, Tables I-VI, pp. 88-93 of MRID 44536511 and DER Attachment 2 (mean, SD, RSD).

1 Sand soil matrices (M465A, M465B, M465E) were obtained from a site near Immokalee, Florida (p. 10; Tables I-VI, pp. 88-92; Appendix C, pp. 117-118).

2 Fortification levels were 0.199-0.202 µg/kg (Appendix B, Table I, p. 88; Table III, p. 90; Table V, p. 92). For each analyte, three fortifications were made at 0.099-0.100 µg/kg (50% of LOQ), but the results were only reported as <0.20 µg/kg.

3 Not applicable; meaningful statistics could not be generated because n = 2.

4 Using low level fortification method.

5 Using high level fortification method.

Table 3a. Independent Validation Method Recoveries for cis- and trans-1,3-Dichloropropene (cis- and trans-1,3-D, Telone), 1,2-Dichloropropene (1,2-D), and Trichloronitromethane (TCNM) in Water¹

Analyte	Fortification Level (ng/mL)	Number of Tests	Recovery Range (%)	Mean Recovery (%)	Standard Deviation (%)	Relative Standard Deviation (%)
cis-1,3-D	0.05 (LOQ)	2	96.6, 105	-- ²	--	--
	0.25	2	93.0, 97.1	--	--	--
trans-1,3-D	0.05 (LOQ)	2	98.6, 96.0	--	--	--
	0.25	2	87.8, 96.0	--	--	--
1,2-D	0.05 (LOQ)	2	111, 109	--	--	--
	0.25	2	98.0, 101	--	--	--
TCNM	0.05 (LOQ)	2	103, 96.3	--	--	--
	0.25	2	93.2, 93.8	--	--	--

Data (uncorrected recovery results) were obtained from Tables I-IV, pp. 11-12 of MRID 44536509.

1 Uncharacterized; source location was not reported (p. 8).

2 Not applicable; meaningful statistics could not be generated because n = 2.

Table 3b. Independent Validation Method Recoveries for cis- and trans-1,3-Dichloropropene (cis- and trans-1,3-D, Telone) and 1,2-Dichloropropene (1,2-D) in Soil¹

Analyte	Fortification Level (µg/kg)	Number of Tests	Recovery Range (%)	Mean Recovery (%)	Standard Deviation (%)	Relative Standard Deviation (%)
cis-1,3-D	0.2 (LOQ)	2	95.3, 93.5	-- ²	--	--
	1.0	2	103, 96.0	--	--	--
trans-1,3-D	0.2 (LOQ)	2	106, 93.1	--	--	--
	1.0	2	99.2, 90.5	--	--	--
1,2-D	0.2 (LOQ)	2	80.2, 83.1	--	--	--
	1.0	2	103, 97.1	--	--	--

Data (uncorrected recovery results) were obtained from Tables I-III, pp. 11-12 of MRID 44536508.

1 Uncharacterized; source location was not reported (p. 8).

2 Not applicable; meaningful statistics could not be generated because n = 2.

III. Method Characteristics

Water: In the ECM and ILV, the LOQ for cis- and trans-1,3-D, 1,2-D, and TCNM was 0.05 ng/mL (µg/L; Appendix A, p. 19 of MRID 44536511; p. 8; Appendix A, p. 34 of MRID 44536509). In the ECM, the LODs for 1,2-D, cis-1,3-D, trans-1,3-D, and TCNM were calculated as 0.0072, 0.0015, 0.0036, and 0.0060 ng/mL, respectively (p. 14; Appendix A, p. 31; Tables V-VIII, pp. 39-42 of MRID 44536511). In the ILV, the LODs were not specified. Following the method of Keith, L.H., *et al.* (see section V. **References** below), the LOD and LOQ for determination of cis- and trans-1,3-D, 1,2-D, and TCNM in water were calculated using the standard deviation from the 0.05 ng/mL (LOQ) recovery results (Appendix A, p. 31; Tables V-VIII, pp. 39-42 of MRID 44536511). The LOD was calculated as three times the standard deviation (3s), and the LOQ was calculated as ten times the standard deviation (10s) of the recovery results. Matrix blank values (n = 3) were 0.0000 ng/mL for all four analytes (Appendix A, Tables I-IV, pp. 35-38 of MRID 44536511). Calculated LOQ values were 0.024, 0.0049, 0.012, and 0.020 ng/mL for 1,2-D, cis-1,3-D, trans-1,3-D, and TCNM, respectively.

Soil: In the ECM and ILV, the LOQ for cis- and trans-1,3-D and 1,2-D was 0.20 µg/kg (Appendix B, p. 65 of MRID 44536511; p. 8; Appendix A, p. 29 of MRID 44536508). In the ECM, the LODs for 1,2-D, cis-1,3-D, and trans-1,3-D were calculated as 0.039, 0.020, and 0.023 µg/kg, respectively (p. 14; Appendix B, p. 85; Tables VII-IX, pp. 94-96 of MRID 44536511). In the ILV, the LODs were not specified. Following the method of Keith, L.H., *et al.*, as described above, the LOD and LOQ for determination cis- and trans-1,3-D and 1,2-D in soil were calculated using the standard deviation from the 0.20 µg/kg (LOQ) recovery results (Appendix B, p. 85; Tables VII-IX, pp. 94-96 of MRID 44536511). Matrix blank values (n = 6 for low level method, n = 3 for high level method) were 0.00 µg/kg for all analytes (Appendix B, Tables I-VI, pp. 88-93 of MRID 44536511). Calculated LOQ values were 0.13, 0.068, and 0.077 µg/kg for 1,2-D, cis-1,3-D, and trans-1,3-D, respectively.

Table 4a. Method Characteristics for cis- and trans-1,3-Dichloropropene (cis- and trans-1,3-D, Telone), 1,2-Dichloropropane (1,2-D), and Trichloronitromethane (TCNM) in Water¹

		cis-1,3-D	trans-1,3-D	1,2-D	TCNM
Limit of Quantitation (LOQ)		0.05 ng/mL (µg/L)			
Limit of Detection (LOD)		0.0015 ng/mL	0.0036 ng/mL	0.0072 ng/mL	0.0060 ng/mL
Linearity (calibration curve r^2 and concentration range) ²	ECM:	$r^2 = 0.9996$	$r^2 = 0.9976$	$r^2 = 0.9998$	$r^2 = 0.9998$
		Range: 0.025-1.00 ng/mL			
	ILV: ³	$r^2 = 0.9995$	$r^2 = 0.9998$	$r^2 = 0.9992$	$r^2 = 0.9988$
		Range: 0.025-0.5 mg/mL			
Repeatable	ECM:	Yes at LOQ (n = 8). Fortifications at 5x, 20x, 100x, 200x, and 800x LOQ performed at n = 2. No performance data at 10x LOQ.			
	ILV:	Undetermined. Fortifications at LOQ and 5x LOQ performed at n = 2. No performance data at 10x LOQ.			
Reproducible		Undetermined. ILV performed at n = 2 at LOQ and 5x LOQ.			
Specific ⁴	ECM:	Interferences were $\leq 10\%$ of LOQ, based on peak height, at analyte retention times. Matrix was uncharacterized Florida surface water.			
	ILV:	No interferences were detected at analyte retention times. Matrix was uncharacterized water; source location was not reported.			

Data were obtained from pp. 8, 10; Appendix A, p. 19; Tables I-VIII, pp. 35-42; Figures 10-17, pp. 52-59 of MRID 44536511; Tables I-VIII, pp. 11-16; Figures 4-6, pp. 21-23 of MRID 44536509.

Linearity is satisfactory when $r^2 \geq 0.995$.

1 1,3-Dichloropropene (1,3-D) and trichloronitromethane (TCNM, chloropicrin) are active ingredients in Telone soil fumigants, while 1,2-dichloropropane (1,2-D) is a process contaminant (p. 9 of MRID 44536511).

2 Calibration curve r^2 values determined using power regression equation where x = ng/mL, y = quantitation ratio (Appendix A, Figures 18-21, pp. 60-63 of MRID 44536511).

3 Coefficients of determination (r^2) were not reported by study authors. The r^2 values were determined by the reviewer using the same power regression equation, where x = ng/mL and y = quantitation ratio, as used in the ECM validation (DER Attachment 2).

4 For the ECM validation, confirmation ion ratio results were only provided for one LOQ (0.05 ng/mL) fortified sample for each analyte and were $\pm 10\%$ of the average standard confirmation ratio (Appendix A, Figures 14-17, pp. 56-59 of MRID 44536511). For the ILV, confirmation ion ratio results for all fortification analyses were $\pm 15.0\%$ of the average standard confirmation ratio (Tables V-VIII, pp. 13-16 of MRID 44536509). A confirmatory method is typically not required where GC/MS and LC/MS methods are used as the primary method.

Table 4b. Method Characteristics for cis- and trans-1,3-Dichloropropene (cis- and trans-1,3-D, Telone) and 1,2-Dichloropropane (1,2-D) in Soil¹

		cis-1,3-D	trans-1,3-D	1,2-D
Limit of Quantitation (LOQ)		0.20 µg/kg		
Limit of Detection (LOD)		0.020 µg/kg	0.023 µg/kg	0.039 µg/kg
Linearity (calibration curve r ² and concentration range) ²	ECM:	r ² = 0.9958	r ² = 0.9961	r ² = 0.9977
		Range: 0.05-2.5 µg/L (ng/mL, low level method)		
		r ² = 0.9999	r ² = 0.9999	r ² = 0.9999
	ILV: ³	Range: 0.05-100.0 µg/L (high level method)		
		r ² = 0.9980	r ² = 0.9967	r ² = 0.9983
		Range: 0.1-2.0 µg/kg (low level method)		
Repeatable	ECM:	Yes at LOQ (n = 8), 25x LOQ (n = 4), and 1,000x LOQ (n = 8, high level method). Fortifications at 5x, 100x, 400x, 1,000x (low level method), 5,000x, 25,000x, 100,000x, 400,000x, and 800,000x LOQ performed at n = 2. No performance data at 10x LOQ.		
	ILV:	Undetermined. Fortifications at LOQ and 5x LOQ performed at n = 2. No performance data at 10x LOQ.		
Reproducible		Undetermined. ILV performed at n = 2 at LOQ and 5x LOQ.		
Specific ⁴	ECM:	Interferences were <5% of LOQ, based on peak height, at analyte retention times. Matrix was sand soil (M465A, M465B, M465E).		
	ILV:	No interferences were detected at analyte retention times.		Interference apparent, but could not be quantified because chromatograms were illegible.
		Matrix was uncharacterized soil; source location was not reported.		

Data were obtained from p. 10; Appendix B, p. 65; Tables I-IX, pp. 88-96; Figures 8-19, pp. 104-115; Appendix C, pp. 117-118 of MRID 44536511; p. 8; Tables I-III, pp. 11-12; Figures 3-4, pp. 19-20; Appendix A, p. 29 of MRID 44536508.

Linearity is satisfactory when $r^2 \geq 0.995$.

1 1,3-Dichloropropene (1,3-D) is an active ingredients in Telone soil fumigants, while 1,2-dichloropropane (1,2-D) is a process contaminant (p. 9 of MRID 44536511).

2 Calibration curve r² values determined using power regression equation where x = µg/L (ng/mL), y = quantitation ratio (Appendix B, Figures 14-19, pp. 110-115 of MRID 44536511).

3 Coefficients of determination (r²) were not reported by study authors. The r² values were determined by the reviewer using the same power regression equation, where x = ng/mL and y = quantitation ratio, as used in the ECM validation (DER Attachment 2).

4 For the ECM validation, confirmation ion ratio results were only provided for one LOQ (0.20 µg/kg) fortified sample for each analyte and were ± 8% of the average standard confirmation ratio (Appendix B, Figures 11-13, pp. 107-109 of MRID 44536511). For the ILV, confirmation ion ratio results for all fortification analyses were ± 15% of the average standard confirmation ratio (Tables IV-VI, pp. 13-15 of MRID 44536508). A confirmatory method is typically not required where GC/MS and LC/MS methods are used as the primary method.

IV. Method Deficiencies and Reviewer's Comments

Methods GRM 94.11 (water) and GRM 94.13 (soil):

1. The ILVs were not conducted independently of the ECM originating laboratory. Global Environmental Chemistry Laboratory - Indianapolis Lab, DowElanco was the originating laboratory for the ECMs. Enviro-Bio-Tech, Ltd., performed both the ILV for GRM 94.11 (water) and the ILV for GRM 94.13 (soil). However, the study director of the ECM validations, and co-author/author of the methods and ECM validation study reports, S.C. Dolder, was also the study director of the ILVs and co-author of the ILV study reports (pp. 1, 3, 5; Appendix A, p. 19; Appendix B, p. 65 of MRID 44536511; pp. 1, 3, 5 of MRID 44536509; pp. 1, 3, 5 of MRID 44536508).
2. The experimental design of the ILVs was inadequate to produce a successful validation of the respective ECM. For the ILV, only two recoveries were reported for both the LOQ and 5x LOQ fortification levels, with no performance data at 10x LOQ (Tables I-IV, pp. 11-12 of MRID 44536509; Tables I-III, pp. 11-12 of MRID 44536508). A validation sample set should consist of, at a minimum, a reagent blank, two unspiked matrix control samples, five matrix control samples spike at the LOQ, and five matrix control samples spiked at 10x LOQ for each analyte and matrix.
3. The ILVs did not verify the LODs for the analytes as determined by the ECM validations.
4. For the GRM 94.11 (water) ECM validation the water matrix was described as surface water obtained from a site near Immokalee, Florida, but characterization was not provided, and for the ILV the source and characterization of the water matrix were not provided (pp. 8, 10 of MRID 44536511; p. 8; Appendix A, p. 35 of MRID 44536509). For the ILV of GRM 94.13 (soil), the source and characterization for the soil matrix were not provided (Soil Identification No. 17595101; pp. 8, 10; Appendix C, pp. 117-118 of MRID 44536511; p. 8; Appendix A, p. 30 of MRID 44536508).

The registrant failed to verify that the independent laboratory performed the ILV with a matrix (water/soil) of the most difficult analytical sample condition to analyze to demonstrate how well the method performs.

5. For the GRM 94.11 (water) ECM validation at all fortification levels >LOQ, only two recoveries were reported for each fortification level (Appendix A, Tables I-IV, pp. 35-38 of MRID 44536511). For the GRM 94.13 (soil) ECM validation at all fortification levels, except LOQ (n = 8), 25x LOQ (n = 4), and 1,000x LOQ (high level method, n = 8), only two recoveries were reported for each fortification level (Appendix B, Tables I-VI, pp. 88-93). For both ECM validations, no performance data at 10x LOQ were reported.
6. For both ILVs, the chromatograms were illegible (Figures 1-12, pp. 18-29 of MRID 44536509; Figures 1-8, pp. 17-24 of MRID 44536508). Chromatograms for reagent blank samples were not provided. For the calibration standards, only chromatograms of 0.05 ng/mL analyte standards (equivalent to 0.05 ng/mL in water matrix, 0.2 µg/kg in soil matrix) were provided (calibration standard ranges were 0.025-0.5 ng/mL for the GRM 94.11 ILV and 0.1-2.0 µg/kg for the GRM 94.13 ILV; Tables V-VIII, pp. 13-16 of MRID 44536509;

Tables IV-VI, pp. 13-15 of MRID 44536508). Standard curve plots with coefficients of determination (r^2) were not provided.

For both ILVs, confirmation ion (m/z 112) chromatograms of the lowest spiking for cis- and trans-1,3-D (telone) were barely attenuated above baseline (Figure 8, p. 25 of MRID 44536509; Figure 6, p. 22 of MRID 44536508). For the GRM 94.11 (water) ILV, both quantitation (m/z 119) and confirmation (m/z 82) ion chromatograms for TCNM were barely attenuated above baseline (Figure 9, p. 26 of MRID 44536509).

For the GRM 94.13 (soil) ILV, interferences were detected in both the quantitation (m/z 63) and confirmation (m/z 76) ion chromatograms of the matrix blank sample for 1,2-D, but could not be quantified because the chromatograms are illegible (Figure 3, p. 19 of MRID 44536508).

7. For the ECM validations, chromatograms for reagent blank and spiked samples, other than LOQ, were not provided (Appendix A, Figures 10-17, pp. 52-59; Appendix B, Figures 8-13, pp. 104-109 of MRID 44536511). For the calibration standards, only chromatograms of 0.050 ng/mL in water matrix (equivalent to 0.05 ng/mL standard) and 0.20 μ g/kg in soil matrix (equivalent to 1.0 ng/mL standard) analyte standards were provided (calibration standard ranges were 0.025-1.00 ng/mL for GRM 94.11 and 0.05-2.5 ng/mL and 0.05-100.0 ng/mL for GRM 94.13; Appendix A, Figures 6-9, pp. 48-51; Figures 18-21, pp. 60-63; Appendix B, Figures 5-7, pp. 101-103; Figures 14-19, pp. 110-115).

In the ECM study report, the study authors indicated correlation coefficients (r values) would be calculated for the power regression analyses, but in the method descriptions and validation results coefficients of determination (r^2 values) were calculated (p. 12; Appendix A, p. 31; Figures 18-21, pp. 60-63; Appendix B, p. 85; Figures 14-19, pp. 110-115).

8. For the GRM 94.11 (water) ILV, it was reported that a set of eight samples required *ca.* 8 person hours (1 calendar day) to complete (p. 31; Appendix A, p. 37 of MRID 44536509). "Eight" is probably a typographical error as the reported sample set consisted of seven samples (one reagent blank, two matrix controls, and four fortified samples; p. 32).
9. For the GRM 94.13 (soil) ILV, it was reported for the ILV that a set of eight samples (one reagent blank, three matrix controls, and four fortified samples) required *ca.* 8 person hours (1 calendar day) to complete (pp. 26-27; Appendix A, p. 32 of MRID 44536508).

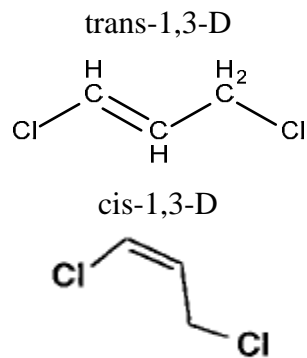
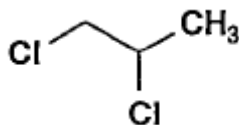
V. References

- Eichelberger, J.W.; Munch, J.W.; Bellar, T.A.; "Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry", Method 524.2, 1992, Environmental Monitoring Systems Laboratory, Office of Research and Development, U.S. Environmental Protection Agency (Appendix A, p. 34 of MRID 44536511).
- Keith, L.H.; Crummett, W.B.; Deegan, J.; Libby, R.A.; Taylor, J.T.; Wentler, G., "Principles of Environmental Analysis", *Anal. Chem.*, 1983, **55**, pp. 2210-2218 (Appendix A, p. 34; Appendix B, p. 87 of MRID 44536511).

United States Environmental Protection Agency, "Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS): Capillary Column Technique", Method 8260, Revision 0, July 1992 (Appendix B, p. 86 of MRID 44536511).

U.S. Environmental Protection Agency. 2012. Ecological Effects Test Guidelines, OCSPP 850.6100, Environmental Chemistry Methods and Associated Independent Laboratory Validation. Office of Chemical Safety and Pollution Prevention, Washington, DC. EPA 712-C-001.

40 CFR Part 136. Appendix B. Definition and Procedure for the Determination of the Method Detection Limit-Revision 1.11, pp. 317-319.

Attachment 1: Chemical Names and Structures**Telone (1,3-D)****IUPAC Name:** (E_Z)-1,3-dichloropropene**CAS Name:** 1,3-dichloro-1-propene
542-75-6**CAS Number:** cis- : 10061-01-5
trans- : 10061-02-6**SMILES String:** C(=CCl)CCl**1,2-Dichloropropane (1,2-D)****IUPAC Name:** 1,2-Dichloropropane
[2R_S]-1,2-dichloropropane**CAS Name:** 1,2-Dichloropropane**CAS Number:** 78-87-5**SMILES String:** Not found**Trichloronitromethane (TCNM, chloropicrin)****IUPAC Name:** Trichloronitromethane**CAS Name:** Trichloronitromethane**CAS Number:** 76-06-2**SMILES String:** Not found