

Analytical method for propanil and 3,4-dichloroaniline in water

Reports: ECM: EPA MRID No.: 50487601. Ahmad, S., and A.D. Budgeon, Jr. 2017. Method Validation of Propanil and 3, 4-Dichloroaniline Analysis in Surface and Drinking Waters. Analytical Method No.: AU-287R0. Laboratory Project ID: AU-2017-40. Report prepared by JRF America, Inc., Audubon, Pennsylvania, and sponsored and submitted by Propanil Task Force II, c/o McDermott, Will and Emery, Washington, D.C.; 239 pages. Final report issued December 27, 2017.

ILV: EPA MRID No. 50597801. Upadhyay, G. 2018. INDEPENDENT LABORATORY VALIDATION OF AN ANALYTICAL METHOD FOR THE DETERMINATION OF PROPANIL AND 3,4-DICHLOROANILINE IN SURFACE AND DRINKING WATERS BY LC-MS/MS ANALYSIS. JRF Study No.: 228-2-14-19546 (Final Report). Report prepared by Jai Research Foundation, Gujarat, India, sponsored and submitted by Propanil Task Force II, c/o McDermott, Will and Emery, Washington, D.C.; 67 pages. Final report issued May 21, 2018.

Document No.: MRIDs 50487601 & 50597801

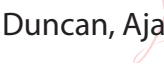
Guideline: 850.6100

Statements: ECM: The study was conducted in accordance with USEPA FIFRA Good Laboratory Practice (GLP) standards (40 CFR Part 160; p. 3 of MRID 50487601). Signed and dated No Data Confidentiality, GLP, and Quality Assurance statements were provided (pp. 2-4). The authenticity statement was included with the Quality Assurance statement (p. 4).
ILV: The study was conducted in accordance with OECD and Indian GLP standards, which is considered to be comparable to EPA FIFRA GLP standards (p. 3; Appendix 5, pp. 66-67 of MRID 50597801). Signed and dated No Data Confidentiality, GLP, and Quality Assurance statements were provided (pp. 2-4; Appendix 5, pp. 66-67). The authenticity statement was included with the Quality Assurance statement (p. 4).


Classification: This analytical method is classified as Unacceptable. Insufficient chromatographic support was provided in the ILV. The specificity of the method for propanil was not supported in the ECM. Communications between the ILV and ECM/Study Monitor were not detailed in the ILV. The number of trials required to validate the method was not reported. The LOD was not reported in the ILV.

PC Code: 028201

EFED Final Reviewer: A'ja Duncan, M.S., Ph.D.
Chemist

Signature:  Duncan, Aja
Date: 11/20/18
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CDM/CSS-Dynamac JV Reviewers: Lisa Muto, M.S.,
Environmental Scientist

Signature: 
Date: 10/04/2018

Reviewers: Mary Samuel, M.S.,
Environmental Scientist

Signature: 

Date: 10/24/2018

This Data Evaluation Record may have been altered by the Environmental Fate and Effects Division subsequent to signing by CDM/CSS-Dynamac JV personnel. The CDM/CSS-Dynamac Joint Venture role does not include establishing Agency policies.

Executive Summary

The analytical method, Analytical Method No.: AU-287R0, is designed for the quantitative determination of propanil and 3,4-dichloroaniline in water at the LOQ of 0.10 µg/L using LC/MS/MS. The LOQ is less than the lowest toxicological level of concern in water for propanil and 3,4-dichloroaniline (9.1 µg/L; USEPA, 2015). The ECM and ILV validated the method using characterized surface and drinking water. The number of trials required to validate the method was not reported; however, the reviewer assumed that the method was validated for drinking and surface water matrices in the first trial with minor modifications to the analytical instrumentation and parameters. The filtration of the water samples prior to analysis was not reported in the ILV. Communications between the ILV (JRFI) and ECM (JRFA) were not detailed. All ILV and ECM data regarding repeatability, accuracy, precision, and linearity were satisfactory for propanil and 3,4-dichloroaniline in both matrices, except for the ILV linearity for 3,4-dichloroaniline in surface water. The specificity of the method was not supported in the ILV because no LOQ and 10×LOQ representative chromatograms were provided. The specificity of the method for propanil was not supported in the ECM because matrix interferences were *ca.* 60% of the LOQ (based on peak area) in both matrices. The LOD was not reported in the ILV.

Table 1. Analytical Method Summary

Analyte(s) by Pesticide	MRID		EPA Review	Matrix	Method Date (dd/mm/yyyy)	Registrant	Analysis	Limit of Quantitation (LOQ)
	Environmental Chemistry Method	Independent Laboratory Validation						
Propanil	50487601 ¹	50597801 ²	Yes	Water	27/12/2017	Propanil Task Force II c/o McDermott, Will and Emery	LC/MS/MS	0.10 µg/L
3,4-Dichloroaniline								

1 In the ECM, the surface water (Sample ID 202854 0-3"; pH 8.1; 199 mg/L as CaCO₃ hardness; 984 ppm total dissolved solids) obtained from Skippack Creek in Collegetown, Pennsylvania (coordinates 40.150077, -75.447406) and drinking water (Sample ID 202301 Drinking Water; pH 6.1; <1 mg/L as CaCO₃ hardness; 0.3 ppm total organic carbon; 10 ppm total dissolved solids), Aquafina bottled water, were used in the study (pp. 18; Appendix VII, pp. 236-237 of MRID 50487601). The water samples were characterized by Agvise Laboratories, Northwood, North Dakota.

2 In the ILV, the surface water (pH 8.15; 122 mg/L as CaCO₃ hardness; 0.15 ppm total organic carbon) obtained from the Daman Ganga River, JRF, NH No. 8 (near Jai Research Foundation, Gujarat, India) and drinking water (pH 7.15; 12 mg/L as CaCO₃ hardness; 11.47 ppm total organic carbon) obtained from Jai Research Foundation, Gujarat, India were used in the study (p. 14; Appendix 3, p. 63 of MRID 50597801). The water samples were characterized by Jai Research Foundation, Gujarat, India.

I. Principle of the Method

Samples (10.00 - x mL, where x is the volume of fortification solution to be added) were fortified, as necessary, with 100 or 1000 µg/L propanil and 3,4-dichloroaniline mixed fortification solutions in 15-mL glass test tubes, filtered (0.45 µm), and analyzed directly or diluted with untreated test matrix, as needed, by LC/MS/MS (pp. 18-22 of MRID 50487601). Fortification solutions were prepared by serial dilutions of the stock solutions in test matrices.

Samples were analyzed for propanil and 3,4-dichloroaniline by Shimadzu UFLC XR system coupled with a Sciex API 4000 MS (Phenomenex Luna C18(2) column 100 Å, 2.0 mm x 100 mm, 3 µm column; column temperature ambient) using a gradient mobile phase of A) 0.1% acetic acid in LC/MS grade water and B) 0.1% acetic acid in LC/MS grade methanol [percent A:B; 0.00-2.00 min. 80:20, 5.00-9.00 min. 10:90, 10.00-12.01 min. 80:20] with MS/MS-ESI (electrospray ionization; temperature 550°C) detection in positive ion mode and multiple reaction monitoring (MRM; pp. 19, 23-24 of MRID 50487601). Injection volume was 40 µL. Propanil and 3,4-dichloroaniline was identified using two ion transitions; one for quantitation (Q) and one for confirmation (C). Ion transitions monitored were m/z 218.056→161.900 (Q) and m/z 218.056→126.900 (C) for propanil and m/z 162.014→127.000 (Q) and m/z 162.014→74.000 (C) for 3,4-dichloroaniline. Approximate retention times were 5.66 and 5.23 minutes for propanil and 3,4-dichloroaniline, respectively.

In the ILV, the ECM was performed as written, except filtration was not reported and minor modifications to the analytical instrumentation and parameters (pp. 8, 14, 16-19 of MRID 50597801). A Shimadzu Nexera X2 HPLC System was coupled to an AB Sciex API 6500 Q Trap MS with ESI for analyte identification. The following modifications of the ECM analytical method were made: injection volume was 20 µL; and MS temperature was 400°C. All other analytical parameters were the same as the ECM. Propanil and 3,4-dichloroaniline was identified using two ion transitions; one for quantitation (Q) and one for confirmation (C). Ion transitions monitored were m/z 218.1→162.1 (Q) and m/z 218.1→127.2 (C) for propanil and m/z 162.1→127.1 (Q) and m/z 162.1→74.0 (C) for 3,4-dichloroaniline. Approximate retention times were 5.20 and 4.65 minutes for propanil and 3,4-dichloroaniline, respectively (Appendix I, pp. 47-50).

The Limit of Quantitation (LOQ) for propanil and 3,4-dichloroaniline in water was 0.10 µg/L in the ECM and ILV (pp. 15-17 of MRID 50487601; p. 8 of MRID 50597801). In the ECM, the Limit of Detection (LOD) for water was calculated as 0.0175 µg/L and 0.0238 µg/L for propanil in drinking water and surface water, respectively, and 0.0394 µg/L and 0.0374 µg/L for 3,4-dichloroaniline in drinking water and surface water, respectively. The LOD was not reported in the ILV.

II. Recovery Findings

ECM (MRID 50487601): Mean recoveries and relative standard deviations (RSDs) were within guideline requirements (mean 70-120%; RSD \leq 20%) for analysis of propanil and 3,4-dichloroaniline in two water matrices at fortification levels of 0.10 $\mu\text{g/L}$ (LOQ) and 1.0 $\mu\text{g/L}$ (10 \times LOQ; pp. 27-28). Propanil and 3,4-dichloroaniline were identified using two ion transitions; primary and confirmatory analyses were comparable, except in the case of the 10 \times LOQ analyses of 3,4-dichloroaniline. The surface water (Sample ID 202854 0-3"; pH 8.1; 199 mg/L as CaCO_3 hardness; 984 ppm total dissolved solids) obtained from Skippack Creek in Collegeville, Pennsylvania (coordinates 40.150077, -75.447406) and drinking water (Sample ID 202301 Drinking Water; pH 6.1; <1 mg/L as CaCO_3 hardness; 0.3 ppm total organic carbon; 10 ppm total dissolved solids), Aquafina bottled water, were used in the study (pp. 18; Appendix VII, pp. 236-237). The water samples were characterized by Agvise Laboratories, Northwood, North Dakota.

ILV (MRID 50597801): Mean recoveries and RSDs were within guideline requirements for analysis of propanil and 3,4-dichloroaniline in two water matrices at fortification levels of 0.10 $\mu\text{g/L}$ (LOQ) and 1.0 $\mu\text{g/L}$ (10 \times LOQ; Tables 9-16, pp. 31-34). Propanil and 3,4-dichloroaniline were identified using two ion transitions; performance data (recovery results) from primary and confirmatory analyses were comparable. The surface water (pH 8.15; 122 mg/L as CaCO_3 hardness; 0.15 ppm total organic carbon) obtained from the Daman Ganga River, JRF, NH No. 8 (near Jai Research Foundation, Gujarat, India) and drinking water (pH 7.15; 12 mg/L as CaCO_3 hardness; 11.47 ppm total organic carbon) obtained from Jai Research Foundation, Gujarat, India were used in the study (p. 14; Appendix 3, p. 63). The water samples were characterized by Jai Research Foundation, Gujarat, India and the number of trials required to validate the method was not reported. Therefore, it is assumed that the method was validated for drinking and surface water matrices in the first trial with minor modifications to the analytical instrumentation and parameters (pp. 8, 14, 16-19). In addition, the filtration of the water samples prior to analysis was not reported in the ILV.

Table 2. Initial Validation Method Recoveries for Propanil and 3,4-Dichloroaniline (3,4-DCA) in Water^{1,2}

Analyte	Fortification Level (µg/L)	Number of Tests	Recovery Range (%)	Mean Recovery (%)	Standard Deviation (%)	Relative Standard Deviation (%)
Drinking Water						
Quantitation ion						
Propanil	0.10 (LOQ)	7	98.4-114	103	5.56	5.41
	1.0	5	87.1-108	98.5	8.97	9.10
3,4-Dichloroaniline (3-DCA)	0.10 (LOQ)	7	85.4-114	103	12.5	12.2
	1.0	5	91.5-107	100	5.70	5.70
Confirmatory ion						
Propanil	0.10 (LOQ)	7	82.7-106	94.1	9.21	9.78
	1.0	5	88.0-109	96.7	9.46	9.78
3,4-Dichloroaniline (3-DCA)	0.10 (LOQ)	7	81.8-99.5	92.2	6.32	6.86
	1.0	5	79.6-92.9	87.0	6.07	6.98
Surface Water						
Quantitation ion						
Propanil	0.10 (LOQ)	7	90.9-115	102	7.58	7.46
	1.0	5	91.9-113	102	7.99	7.86
3,4-Dichloroaniline (3-DCA)	0.10 (LOQ)	7	92.4-125	100	11.9	11.8
	1.0	5	90.9-102	94.8	4.78	5.05
Confirmatory ion						
Propanil	0.10 (LOQ)	7	94.5-116	101	7.42	7.36
	1.0	5	83.2-107	96.7	10.6	11.0
3,4-Dichloroaniline (3-DCA)	0.10 (LOQ)	7	92.7-122	102	9.74	9.53
	1.0	5	82.0-89.3	85.9	2.76	3.22

Data (uncorrected recovery results, pp. 24-26) were obtained from pp. 27-28 of MRID 50487601.

1 The surface water (Sample ID 202854 0-3"; pH 8.1; 199 mg/L as CaCO₃ hardness; 984 ppm total dissolved solids) obtained from Skippack Creek in Collegeville, Pennsylvania (coordinates 40.150077, -75.447406) and drinking water (Sample ID 202301 Drinking Water; pH 6.1; <1 mg/L as CaCO₃ hardness; 0.3 ppm total organic carbon; 10 ppm total dissolved solids), Aquafina bottled water, were used in the study (pp. 18; Appendix VII, pp. 236-237). The water samples were characterized by Agvise Laboratories, Northwood, North Dakota.

2 Two ion transitions were monitored (quantitation and confirmatory, respectively) as follows: *m/z* 218.056→161.900 and *m/z* 218.056→126.900 for propanil and *m/z* 162.014→127.000 and *m/z* 162.014→74.000 for 3,4-dichloroaniline.

Table 3. Independent Validation Method Recoveries for Propanil and 3,4-Dichloroaniline (3,4-DCA) in Water^{1,2}

Analyte	Fortification Level (µg/L)	Number of Tests	Recovery Range (%)	Mean Recovery (%)	Standard Deviation (%)	Relative Standard Deviation (%)
Drinking Water						
Quantitation ion						
Propanil	0.10 (LOQ)	7	96.00-108.00	102.57	4	3.88
	1.0	5	97.71-101.29	98.94	1.5	1.51
3,4-Dichloroaniline (3-DCA)	0.10 (LOQ)	7	100.00-113.13	107.50	4	3.77
	1.0	5	100.20-113.77	104.77	5.7	5.43
Confirmatory ion						
Propanil	0.10 (LOQ)	7	98.00-105.00	101.43	3	2.97
	1.0	5	95.72-102.19	98.77	2.8	2.82
3,4-Dichloroaniline (3-DCA)	0.10 (LOQ)	7	101.01-121.21	109.67	7	6.42
	1.0	5	100.40-115.97	107.83	6.4	5.93
Surface Water						
Quantitation ion						
Propanil	0.10 (LOQ)	7	81.00-102.00	96.14	7	7.29
	1.0	5	95.32-100.00	97.59	2.2	2.24
3,4-Dichloroaniline (3-DCA)	0.10 (LOQ)	7	56.57-103.03	92.64	16	17.39
	1.0	5	84.33-96.41	91.72	5	5.44
Confirmatory ion						
Propanil	0.10 (LOQ)	7	84.00-101.00	97.14	6	6.19
	1.0	5	94.83-104.58	99.0	3.8	3.82
3,4-Dichloroaniline (3-DCA)	0.10 (LOQ)	7	62.63-105.05	92.35	14	15.38
	1.0	5	86.23-99.60	93.05	4.8	5.15

Data (uncorrected recovery results, Appendix 2 p. 57) were obtained from Tables 9-16, pp. 31-34 of MRID 50597801.

- The surface water (pH 8.15; 122 mg/L as CaCO₃ hardness; 0.15 ppm total organic carbon) obtained from the Daman Ganga River, JRF, NH No. 8 (near Jai Research Foundation, Gujarat, India) and drinking water (pH 7.15; 12 mg/L as CaCO₃ hardness; 11.47 ppm total organic carbon) obtained from Jai Research Foundation, Gujarat, India were used in the study (p. 14; Appendix 3, p. 63). The water samples were characterized by Jai Research Foundation, Gujarat, India.
- Two ion transitions were monitored (quantitation and confirmatory, respectively) as follows: m/z 218.1→162.1 (Q) and m/z 218.1→127.2 (C) for propanil and m/z 162.1→127.1 (Q) and m/z 162.1→74.0 (C) for 3,4-dichloroaniline.

III. Method Characteristics

The LOQ for propanil and 3,4-dichloroaniline in water was 0.10 µg/L in the ECM and ILV (pp. 15-17, 22 of MRID 50487601; p. 8 of MRID 50597801). In the ECM, the LOQ was justified as “per guideline for the method” (p. 22 of MRID 50487601). No justification was provided in the ILV. In the ECM, LOD was calculated from the data of the seven LOQ recovery samples, as described in "Assigning Values to Non-detected/Non-quantified Pesticide Residues in Human Health Food Exposure Assessments, Item 6047, U.S. EPA, March 23, 2000". The following equations were used (pp. 26-27 of MRID 50487601):

$$\text{LOD} = \text{Stdev}(\text{LOQ R1: LOQ R7}) \times t_{0.99} \times (1 \mu\text{g}/1000 \text{ ng})$$

The standard deviation is calculated using the following equation:

$$\text{Stdev}(\text{LOQ R1: LOQ R7}) = \sqrt{\frac{1}{n-1} \sum_{i=1}^n (x_i - \bar{x})^2}$$

Where, Stdev is the sample standard deviation of the calculated concentrations of the seven LOQ samples; n is number of samples, and \bar{x} is the average calculated concentration; and $t_{0.99}$ is the one-tailed t-statistic at the 99% confidence level for n-1 replicates and is equal to 3.143 for n = 7 samples.

The calculated LODs were 0.0175 µg/L and 0.0238 µg/L for propanil in drinking water and surface water, respectively, and 0.0394 µg/L and 0.0374 µg/L for 3,4-dichloroaniline in drinking water and surface water, respectively (pp. 15-17, 22 of MRID 50487601). The LOD was not reported in the ILV. No calculations were reported to justify the LOQ for the method in the ECM and ILV.

Table 4. Method Characteristics

Analyte ¹		Propanil	3,4-Dichloroaniline (3,4-DCA)	
Limit of Quantitation (LOQ)	ECM	0.10 µg/L		
	ILV			
Limit of Detection (LOD)	ECM (Calculated)	0.0175 µg/L (drinking) 0.0238 µg/L (surface)	0.0394 µg/L (drinking) 0.0374 µg/L (surface)	
	ILV	Not reported		
Linearity (calibration curve r^2 and concentration range) ¹	ECM	Drinking	$r^2 = 0.9979$ (Q) $r^2 = 0.9984$ (C)	$r^2 = 0.9983$ (Q) $r^2 = 0.9961$ (C)
		Surface	$r^2 = 0.9986$ (Q) $r^2 = 0.9988$ (C)	$r^2 = 0.9988$ (Q) $r^2 = 0.9964$ (C)
		Range	0.025-1.0 µg/L	
	ILV	Drinking	$r^2 = 0.9996$ (Q) $r^2 = 0.9994$ (C)	$r^2 = 0.9974$ (Q) $r^2 = 0.9972$ (C)
		Surface	$r^2 = 0.9996$ (Q) $r^2 = 0.9998$ (C)	$r^2 = 0.9946$ (Q) $r^2 = 0.9954$ (C)
		Range	0.025-0.782 µg/L	0.024-0.780 µg/L
Repeatable	ECM ²	Yes at LOQ and 10×LOQ (characterized surface and drinking water matrices)		
	ILV ^{3,4}			
Reproducible	Yes at LOQ and 10×LOQ			
Specific	ECM	No , matrix interferences were <i>ca.</i> 60% of the LOQ (based on peak area). ⁵ Some non-uniform peak integration was observed.	Yes, matrix interferences were <i>ca.</i> 9-13% of the LOQ (based on peak area). Some non-uniform peak integration was observed. A minor amount of propanil (RT 5.66 min.) was observed in the 3,4-DCA Q drinking water standard solution.	
	ILV	No , no LOQ and 10×LOQ representative chromatograms were provided. Only insignificant matrix interferences were observed in the controls; however, a minor amount of propanil (RT 5.19 min.) was observed in the 3,4-DCA Q drinking water standard solution.		

Data were obtained from pp. 15-17, 22, 26-27 (LOQ/LOD); pp. 27-28 (recovery data); Appendix II, pp. 49, 70, 91, and 112 (calibration curves); Appendix II, pp. 55-69, 76-90, 97-111, and 118-132 (chromatograms) of MRID 50487601; pp. 8 (LOQ); Tables 9-16, pp. 31-34 (recovery data); Tables 1-8, pp. 23-30 (calibration curves); Appendix I, pp. 35-50 (chromatograms) of MRID 50597801; DER Attachment 2. Q = Quantitation ion transition; C = Confirmation ion transition.

1 Correlation coefficients (r^2) values were reviewer-calculated from r values provided in the study report (Appendix II, pp. 49, 70, 91, and 112 of MRID 50487601; Tables 1-8, pp. 23-30 of MRID 50597801; DER Attachment 2). Matrix-based calibration standards were used (p. 21 of MRID 50487601; pp. 8, 20 of MRID 50597801). For the ECM correlation coefficients, the reviewer limited the value to four significant figures, even though eleven significant figures were provided in the study report.

2 In the ECM, the surface water (Sample ID 202854 0-3"; pH 8.1; 199 mg/L as CaCO₃ hardness; 984 ppm total dissolved solids) obtained from Skippack Creek in Collegetown, Pennsylvania (coordinates 40.150077, -75.447406) and drinking water (Sample ID 202301 Drinking Water; pH 6.1; <1 mg/L as CaCO₃ hardness; 0.3 ppm total organic carbon; 10 ppm total dissolved solids), Aquafina bottled water, were used in the study (pp. 18; Appendix VII, pp. 236-237 of MRID 50487601). The water samples were characterized by Agvise Laboratories, Northwood, North Dakota.

- 3 In the ILV, the surface water (pH 8.15; 122 mg/L as CaCO₃ hardness; 0.15 ppm total organic carbon) obtained from the Daman Ganga River, JRF, NH No. 8 (near Jai Research Foundation, Gujarat, India) and drinking water (pH 7.15; 12 mg/L as CaCO₃ hardness; 11.47 ppm total organic carbon) obtained from Jai Research Foundation, Gujarat, India were used in the study (p. 14; Appendix 3, p. 63 of MRID 50597801). The water samples were characterized by Jai Research Foundation, Gujarat, India.
- 4 The number of trials required to validate the method was not reported. Therefore, it is assumed that the method was validated for drinking and surface water matrices in the first trial with minor modifications to the analytical instrumentation and parameters (pp. 8, 14, 16-19 of MRID 50597801). The filtration of the water samples prior to analysis was not reported in the ILV.
- 5 Appendix II, pp. 55-64, 99-100 of MRID 50487601.
Linearity is satisfactory when $r^2 \geq 0.995$.

IV. Method Deficiencies and Reviewer's Comments

1. The specificity of the method was not supported in the ILV because no LOQ and 10×LOQ representative chromatograms were provided (Appendix 1, pp. 35-50 of MRID 50597801). Only chromatograms of solvent blanks, matrix controls and standard mix solutions were provided for review. Only insignificant matrix interferences were observed in the controls; however, a minor nearby contaminant (RT 5.19 min.) was observed in the 3,4-DCA Q drinking water standard solution. Representative chromatograms of the LOQ and 10×LOQ fortifications should be provided to support the method by showing peak attenuation and magnitude compared to the baseline noise.

The specificity of the method for propanil was not supported in the ECM because matrix interferences were *ca.* 60% of the LOQ (based on peak area) in both matrices (Appendix II, pp. 55-64, 99-100 of MRID 50487601). Some non-uniform peak integration was also observed. In the ECM, the residues quantified in the controls was always reported as <LOD (Tables 3-10, pp. 33-40).

2. The communications between the ILV (Jai Research Foundation, Gujarat, India) and ECM (JRF America, Inc.) were not reported, summarized, or detailed in the ILV (pp. 8, 20-21 of MRID 50597801). Communication should be provided to demonstrate that no collusion occurred between the ECM and ILV. The communications between the Study Director and Sponsor Monitor during validation should have been provided since both laboratories are part of Jai Research Foundation (JRF).
3. The number of ILV trials required to validate the method was not reported. Therefore, it was assumed that the method was validated for drinking and surface water matrices with minor modifications to the analytical instrumentation and parameters (pp. 8, 14, 16-19 of MRID 50597801).
4. The reported limit of quantification (LOQ) was determined as the lowest level of method validation (LLMV) (pp. 15-17, 22 of MRID 50487601; p. 8 of MRID 50597801). In the ECM, the LOQ was justified as "per guideline for the method" (p. 22 of MRID 50487601). No justification was provided in the ILV. In the ECM, LOD was calculated from the data of the seven LOQ recovery samples, as described in "Assigning Values to Non-detected/Non-quantified Pesticide Residues in Human Health Food Exposure Assessments" (USEPA, 2000). The following equations were used (pp. 26-27 of MRID

50487601): $LOD = Stdev(LOQ R1: LOQ R7) \times t_{0.99} \times (1 \mu g/1000 ng)$. See above for equation definitions. The LOD was not reported in the ILV and further work could have been done to explore the LOD. No calculations were reported to justify the LOQ for the method in the ECM and ILV. There is uncertainty whether lower concentrations may also be reliably quantified.

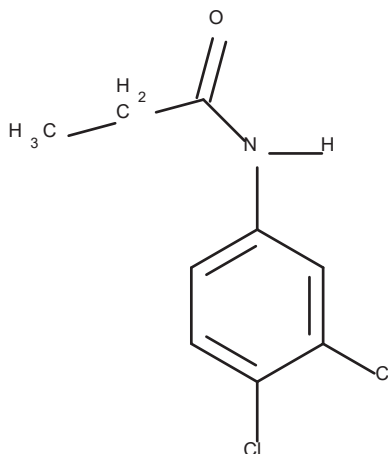
5. The reviewer assigned the minor nearby contaminant (RT 5.66 min.) observed in the ECM 3,4-DCA Q drinking water standard solution (Appendix II, pp. 71-79 of MRID 50487601) and minor nearby contaminant (RT 5.19 min.) observed in the ILV 3,4-DCA Q drinking water standard solution (Appendix 1, pp. 47-50 of MRID 50597801) as propanil based on the retention time of the contaminant.
6. In the ECM, the stability of the sample extracts was determined to be acceptable after 7 days (surface) and 10 days (drinking) of storage at -20°C (pp. 23, 29; Tables 11-18, pp. 41-48 of MRID 50487601). Stocks and fortification solutions in solvents stored at 4°C were not analyzed as both analytes were known to be stable under these storage conditions
7. The time required to complete the method for a validation set was not reported in the ECM or ILV.

V. References

- U.S. Environmental Protection Agency (USEPA). 2000. Assigning Values to Non-detected/Non-quantified Pesticide Residues in Human Health Food Exposure Assessments. Item 6047, U.S. EPA, Office of Pesticide Programs, March 23, 2000 (p. 30 of MRID 50487601).
- USEPA. 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.
- USEPA. 2015. Registration Review Problem Formulation for Propanil. DP barcode D424442. U.S. Environmental Protection Agency, Office of Chemical Safety and Pollution Prevention, Environmental Fate and Effects Division. Memorandum to the Pesticide Re-evaluation Division. April 28, 2015.
- 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**Propanil**

IUPAC Name: 3',4'-Dichloropropanilide
CAS Name: N-(3,4-Dichlorophenyl)propanamide
CAS Number: 709-98-8
SMILES String: CCC(=O)Nc1cc(c(c1)Cl)Cl

**3,4-Dichloroaniline (3,4-DCA)**

IUPAC Name: 3,4-Dichloroaniline
CAS Name: 3,4-Dichloroaniline
CAS Number: 95-76-1
SMILES String: c1cc(c(cc1N)Cl)Cl

