



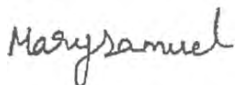
## **Analytical method for 2,4-DP-p, 2,4-D, 2,4-DB, MCPA, MCPB, Mecoprop-p and their 2-EHs in soil**

- Reports:** ECM: EPA MRID No. 49775206. Allen, L. 2014. Validation of Draft Residue Method CAM-0004/003 for the Determination of Phenoxy Acids and Their Corresponding 2 Ethyl-Hexyl Esters in Surface Water, Soil and Air. Study No. CEMS-6230. Report No. CEMR-6230. Report prepared by CEM Analytical Services Limited (CEMAS), Berkshire, United Kingdom; sponsored by Nufarm UK Limited, Bradford, West Yorkshire, United Kingdom; and submitted by Nufarm Americas, Alsip, Illinois; 364 pages. Final report issued August 5, 2014.
- ILV: EPA MRID No. 50768601. Wabbel, C. 2019. Independent Laboratory Validation of Analytical Method for the Determination of Six Phenoxy Acids and Their Corresponding 2-Ethyl-hexyl Esters in Soil. EAS Study No. S18-07036. Report prepared by Eurofins Agrosience Services EcoChem GmbH, Niefern-Öschelbronn, Germany; sponsored by Nufarm UK Limited, Bradford, West Yorkshire, United Kingdom; and submitted by Nufarm Americas, Alsip, Illinois; 137 pages. Final report issued January 22, 2019.
- Document No.:** MRIDs 49775206 & 50768601
- Guideline:** 850.6100
- Statements:** ECM: The study was conducted compliance with OECD, UK and The Department of Health of the Government of the United Kingdom Principles of Good Laboratory Practice (GLP; p. 3; Appendix 2, pp. 363-364 of MRID 49775206). Signed and dated No Data Confidentiality, GLP and Quality Assurance statements were provided (pp. 2-4; Appendix 2, pp. 363-364). Authenticity statements were included with the GLP and Quality Assurance statements.
- ILV: The study was conducted compliance with German and OECD Principles of Good Laboratory Practice which are accepted by regulatory authorities throughout the European Community, the United States of America (FDA and EPA) and Japan (MHW, MAFF and METI; p. 3; Appendix G, p. 137 of MRID 50768601). Signed and dated No Data Confidentiality, GLP and Quality Assurance statements were provided (pp. 2-4; Appendix G, p. 137). Authenticity statements were included with the GLP and Quality Assurance statements.
- Classification:** This analytical method is classified as **supplemental**. The limit of quantitation (LOQ) is one to four orders of magnitude higher than the lowest toxicological levels of concern and inadequate to address risk concerns. The CEMAS CAM-0004/003 method was not provided in the ECM report (MRID, 49775206) or ILV report (MRID 50768601). However, the CEMAS CAM-0004/003 method can be obtained from an appendix of the recently submitted ILV report for a water method (MRID 49986901). The specificity of the soil method was not supported by ILV representative chromatograms of 2,4-D, 2,4-D 2-EH, MCPA, and MCPA 2-EH. The number of ILV trials required to validate the ECM was not specified.

**PC Code:** 031402 (2,4-DP-p) ; 019201 (MCPB); 030001 (2,4-D) ; 030501 (MCPA) ; 030801 (2,4-DB) ; 129046 (Mecoprop-p)

**EFED Final Reviewer:** Faruque Khan Signature:   
Senior Fate Scientist Date: 06-04-2019

Lisa Muto, M.S., Signature:   
Environmental Scientist Date: 04/29/2019

**CDM/CSS-Dynamac JV Reviewers:** Mary Samuel, M.S., Signature:   
Environmental Scientist Date: 04/29/2019

*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.*

**All cited page numbers refer to those written in the bottom, right-hand corner of the pages of the MRIDs.**

## Executive Summary

This analytical method, CEMAS CAM-0004/003 and CEMAS Study No. CEMS-6230, is designed for the quantitative determination of 2,4-DP-p, 2,4-DP-p 2-EH, 2,4-D, 2,4-D 2-EH, 2,4-DB, 2,4-DB 2-EH, MCPA, MCPA 2-EH, MCPB, MCPB 2-EH, Mecoprop-p, and Mecoprop-p 2-EH at the LOQ of 0.01 mg/kg in soil using LC/MS/MS. The LOQ is one to four orders of magnitude higher than the lowest toxicological levels of concern<sup>1</sup> in soil for each analyte. Analytes were identified using two ion pair transitions, one quantification and one confirmation. The 2 ethyl-hexyl ester analytes (2-EH analytes) were intended to be fully hydrolysed back to the corresponding esters during sample processing, so 2-EH analytes were monitored with the same ion transitions as the corresponding acids. The ECM validated the method using characterized sandy loam and clay soil matrices; the ILV validated the method using a different characterized sandy loam soil matrix. It could not be determined if the ILV was provided with the most difficult matrix with which to validate the method and to cover the range of soils used in the terrestrial field dissipation studies. The number of ILV trials required to validate the ECM was not specified; however, the reviewer assumed that the ILV validated the ECM in the first trial with only insignificant modifications to the analytical equipment and parameters. All ILV and ECM data regarding repeatability, accuracy, and precision were satisfactory for all analytes in all matrices. All ILV data regarding linearity and specificity were acceptable for 2,4-DP-p, 2,4-DP-p 2-EH, Mecoprop-p, and Mecoprop-p 2-EH. ILV specificity was acceptable for 2,4-DB, 2,4-DB 2-EH, MCPB, and MCPB 2-EH, but linearity was marginally acceptable. ILV linearity was

<sup>1</sup> The lowest toxicological levels of concern: 2,4-DP-p: 0.0042 mg/Kg & 2,4-DP-p EH: 0.0007 mg/Kg (USEPA, 2019a); 2,4-DB: 0.008 mg/Kg (USEPA, 2018a); 2,4-D (acid): 0.0019 mg/Kg & 2,4-D-EH: 0.00041 mg/Kg (USEPA, 2016); MCPA 0.0015 mg/Kg (USEPA, 2018b); MCPB: 0.000058 mg/Kg (USEPA, 2019b); and Mecoprop-p: 0.00095 mg/Kg (USEPA, 2014).

acceptable for MCPA and MCPA 2-EH, but specificity was unacceptable. ILV linearity was marginally acceptable but specificity was unacceptable for 2,4-D and 2,4-D 2-EH. The specificity of the method was not supported by ILV representative chromatograms of 2,4-D, 2,4-D 2-EH, MCPA, and MCPA 2-EH because matrix interferences were *ca.* 20-21% of the LOQ (>50% of the LOD). All ECM data regarding linearity and specificity were acceptable for all analytes in both matrices. The one-sided nature of multiple unacceptable results for this method, especially since it is the ILV data, indicated that this method may not be very rugged or analytically reproducible. A detailed description of method CEMAS CAM-0004/003 was missing in the ECM report (MRID, 49775206) and the ILV report (MRID 50768601). However, the CEMAS CAM-0004/003 method was obtained from an appendix of the recently submitted ILV report for an analytical method in water (MRID 49986901).

**Table 1. Analytical Method Summary**

Analyte(s) by Pesticide <sup>1</sup>	MRID		EPA Review	Matrix	Method Date (dd/mm/yyyy)	Registrant	Analysis	Limit of Quantitation (LOQ)
	Environmental Chemistry Method	Independent Laboratory Validation						
2,4-DP-p	49775206	50768601		Soil <sup>2,3</sup>	05/08/2014	Nufarm UK LTD (Nufarm Americas)	LC/MS/MS	0.01 mg/kg
2,4-DP-p 2-EH								
2,4-D								
2,4-D 2-EH								
2,4-DB								
2,4-DB 2-EH								
MCPA								
MCPA 2-EH								
MCPB								
MCPB 2-EH								
Mecoprop-p								
Mecoprop-p 2-EH								

1 2,4-DP-p = Dichloroprop-p; (R+)-2-(2,4-dichlorophenoxy)propionic acid. 2,4-DP-p 2-EH = (R+)-2-(2,4-dichlorophenoxy)propionic acid 2-ethylhexyl ester. 2,4-D = (2,4-Dichlorophenoxy)acetic acid; 2,4-D 2-EH = 2,4-Dichlorophenoxyacetic acid, 2-ethylhexyl ester. 2,4-DB = 4-(2,4-Dichlorophenoxy)butyric acid; 2,4-DB 2-EH = 4-(2,4-Dichlorophenoxy)butyric acid, 2-ethylhexyl ester. MCPA = 4-Chloro-2-methylphenoxyacetic acid; MCPA 2-EH; 4-Chloro-2-methylphenoxyacetic acid, 2-ethylhexyl ester. MCPB = 4-(4-Chloro-2-methylphenoxy)butyric acid. MCPB 2-EH = 4-(4-Chloro-2-methylphenoxy)butyric acid, 2-ethylhexyl ester. Mecoprop-p = CMPP-p; (R+)- 2-(4-chloro-2-methylphenoxy)propionic acid. Mecoprop-p 2-EH = (R+)-2-(4-chloro-2-methylphenoxy)propionic acid, 2-ethylhexyl ester (Appendix 1, pp. 347-358 of MRID 49775206; and Appendix E, pp. 122-133 of MRID 50768601).

2 In the ECM, sandy loam soil [CEMAS Specimen Reference: CCON/073/002; particle distribution not reported; pH 6.8 ± 0.1 (0.01M CaCl<sub>2</sub>), 1.0 ± 0.13% organic carbon] and clay soil [CEMAS Specimen Reference: CCON/073/008; particle distribution not reported; pH 7.1 ± 0.1 (0.01M CaCl<sub>2</sub>), 1.66 ± 0.12% organic carbon] were characterized and used in the study (USDA soil texture classification; p. 23; Table 47, p. 72 of MRID 49775206). The specific sources of the soil matrices were not reported

3 In the ILV, sandy loam soil [63.90% sand, 18.97% silt, 17.13% clay; pH 7.41 (0.01M CaCl<sub>2</sub>), 1.35% organic carbon] was characterized and used in the study (USDA soil texture classification; p. 28; Appendix F, p. 135 of MRID 50768601). The soil matrix was obtained in Northwood, North Dakota, and characterized by Eurofins Agrosience Services EcoChem GmbH.

## I. Principle of the Method

Soil samples (5.0 g) were measured into 40-mL glass vials with PTFE lids and fortified, as necessary (0.01 and 0.1 mg/kg; p. 26 of MRID 49775206; p. 29; Appendix A, pp. 40-51 of MRID 50768601; see Reviewer's Comment #1). The samples were mixed with 10 mL of sodium hydroxide hydrolysis solution [47% sodium hydroxide:deionized water (15:85, v:v)] and 1 mL of methanol. The samples were placed in an oven set to 85°C overnight ( $\geq 16$  h) to hydrolyze. After cooling, the samples were acidified by mixing gently by hand with 2.5 mL of chilled 15N sulphuric acid to lower pH value to *ca.* 3. The extract was transferred to a 50-mL centrifuge tube; the flask was rinsed with 2 mL 1M chloroacetic acid and added to the extract. After adding 9 mL of acetonitrile, the contents of QuEChERS Bekolut Citrat-Kit-01 was added. After vigorous shaking, 10 mL hexane was added, and the sample was shaken vigorously again. The sample was shaken for 30 minutes on a flatbed shaker, then transferred to a centrifuge tube. After centrifugation (3500 rpm at 4°C for 15 minutes), 1.8 mL of the middle layer (acetonitrile/methanol) was transferred to a 2 mL Eppendorf tube. The extract was dried with 100 mg anhydrous magnesium sulphate, 50 mg graphitized carbon black, and 100 mg aluminium oxide. After vortexing then shaking for 10 minutes on a reciprocating shaker, the mixture was separated via microcentrifuge for 10 minutes at 13,000 rpm. And aliquot (0.4 mL) of the extract was added to an HPLC vial with 0.6 mL of water with 0.2% formic acid and 10  $\mu$ L of 5  $\mu$ g/mL internal standard solution.

Samples are analyzed using an Agilent 1290 Infinity HPLC coupled to a Sciex TripleQuad 6500 mass spectrometer (Appendix A, pp. 47-48 of MRID 50768601). The following LC conditions were used: Phenomenex Onyx C18 Monolithic column (3.0 mm x 100 mm, 0  $\mu$ m; column temperature 20°C), Phenomenex KJ0-4282 C18 guard column (4 mm), mobile phase of (A) water containing 0.1% formic acid and (B) methanol containing 0.1% formic acid [percent A:B (v:v) at 0.01-0.03 min. 55:45, 6.00 min. 25:75, 6.01-7.15 min. 5:95, 7.16-9.00 min. 55:45], split flow 1-7 min. to the mass spectrometer, and injection volume of 40  $\mu$ L. The MRM parameters were ESI (TurboIon Spray) in negative mode for all analytes. Two ion pair transitions were monitored for each analyte (quantitation and confirmation, respectively):  $m/z$  233 $\rightarrow$ 161 and  $m/z$  235 $\rightarrow$ 163 for 2,4-DP-p and 2,4-DP-p 2-EH,  $m/z$  219 $\rightarrow$ 161 and  $m/z$  221 $\rightarrow$ 163 for 2,4-D and 2,4-D 2-EH,  $m/z$  247 $\rightarrow$ 161 and  $m/z$  249 $\rightarrow$ 163 for 2,4-DB and 2,4-DB 2-EH,  $m/z$  199 $\rightarrow$ 141 and  $m/z$  201 $\rightarrow$ 143 for MCPA and MCPA 2-EH,  $m/z$  227 $\rightarrow$ 141 and  $m/z$  229 $\rightarrow$ 143 for MCPB and MCPB 2-EH, and  $m/z$  213 $\rightarrow$ 141 and  $m/z$  215 $\rightarrow$ 143 for Mecoprop-p and Mecoprop-p 2-EH. One ion transition was monitored for each internal standard:  $m/z$  193 $\rightarrow$ 135 for 2,4,6-TMAA, and  $m/z$  213 $\rightarrow$ 155 for 4-CDMAA. Expected retention times were minutes for 4.2 min. for 2,4-DP-p and 2,4-DP-p 2-EH, 3.3 min. for 2,4-D and 2,4-D 2-EH, 4.9 min. for 2,4-DB and 2,4-DB 2-EH, 4.5 min. for MCPA and MCPA 2-EH, 5.0 min. for MCPB and MCPB 2-EH, and 4.4 min. for Mecoprop-p and Mecoprop-p 2-EH.

In the ILV, no modifications were reported; the ECM was performed as written in CEMAS CAM-0004/003, which was included in Appendix A of the ILV (pp. 29, 38; Appendix A, pp. 40-51 of MRID 50768601). The analytical instrument, equipment and parameters were not reported, but the ILV reported that modifications only included optimization of the instrumental parameters. The monitored ion transitions were the same as those in the ECM (pp. 33-36). Expected retention times were minutes for 4.3 min. for 2,4-DP-p and 2,4-DP-p 2-EH, 3.3 min.

for 2,4-D and 2,4-D 2-EH, 4.9 min. for 2,4-DB and 2,4-DB 2-EH, 3.5 min. for MCPA and MCPA 2-EH, 5.0 min. for MCPB and MCPB 2-EH, and 4.4 min. for Mecoprop-p and Mecoprop-p 2-EH (Appendix D, Figures 25-168, pp. 73-120).

In the ECM and ILV, the LOQ in soil was 0.01 mg/kg for 2,4-DP-p, 2,4-D, 2,4-DB, MCPA, MCPB, and Mecoprop-p, as well as their respective esters (pp. 23, 27, 29; Table 38, p. 65 of MRID 49775206; pp. 29, 36-37 of MRID 50768601). The calculated LODs in soil (clay type) were 0.000333-0.000335 mg/kg for 2,4-DP-p, 0.000338-0.000441 mg/kg for 2,4-D, 0.000659-0.000890 mg/kg for 2,4-DB, 0.000466-0.000480 mg/kg for MCPA, 0.000318-0.000913 mg/kg for MCPB, and 0.000222-0.000334 mg/kg for Mecoprop-p, as well as their respective esters, in the ECM. The LOD was reported in the ILV as equivalent to the 0.6 ng/mL standard, which equated to 30% of the LOQ for 2,4-DP-p, 2,4-D, 2,4-DB, MCPA, MCPB, and Mecoprop-p, as well as their respective esters. The calculated LODs in soil (clay type) were 0.000474-0.000552 mg/kg for 2,4-DP-p, 0.0000306-0.0000921 mg/kg for 2,4-D, 0.000126-0.000131 mg/kg for 2,4-DB, 0.0000375-0.0000871 mg/kg for MCPA, 0.0000806-0.000179 mg/kg for MCPB, and 0.000139-0.000212 mg/kg for Mecoprop-p, as well as their respective esters, in the ILV.

## II. Recovery Findings

ECM (MRID 49775206): Mean recoveries and relative standard deviations (RSD) were within guideline requirements (mean 70-120%; RSD  $\leq$ 20%) for analysis of 2,4-DP-p, 2,4-DP-p 2-EH, 2,4-D, 2,4-D 2-EH, 2,4-DB, 2,4-DB 2-EH, MCPA, MCPA 2-EH, MCPB, MCPB 2-EH, Mecoprop-p and Mecoprop-p 2-EH at the LOQ (0.01 mg/kg) and 10 $\times$ LOQ (0.1 mg/kg) in two soil matrices (Tables 7-18, pp. 37-48; DER Attachment 2). Analytes were identified using two ion pair transitions, one quantification and one confirmation; results were comparable or fairly comparable between quantification and confirmation ions. Standard deviations were reviewer-calculated because the study author did not provide these values. The 2 ethyl-hexyl ester analytes (2-EH analytes) were intended to be fully hydrolysed back to the corresponding esters during sample processing, so 2-EH analytes were monitored with the same ion transitions as the corresponding acids. In the ECM, sandy loam soil [CEMAS Specimen Reference: CCON/073/002; particle distribution not reported; pH  $6.8 \pm 0.1$  (0.01M CaCl<sub>2</sub>),  $1.0 \pm 0.13\%$  organic carbon] and clay soil [CEMAS Specimen Reference: CCON/073/008; particle distribution not reported; pH  $7.1 \pm 0.1$  (0.01M CaCl<sub>2</sub>),  $1.66 \pm 0.12\%$  organic carbon] were characterized and used in the study (USDA soil texture classification; p. 23; Table 47, p. 72 of MRID 49775206). The specific sources of the soil matrices were not reported.

ILV (MRID 50768601): Mean recoveries and RSDs were within guideline for analysis of 2,4-DP-p, 2,4-DP-p 2-EH, 2,4-D, 2,4-D 2-EH, 2,4-DB, 2,4-DB 2-EH, MCPA, MCPA 2-EH, MCPB, MCPB 2-EH, Mecoprop-p and Mecoprop-p 2-EH at the LOQ (0.01 mg/kg) and 10 $\times$ LOQ (0.1 mg/kg) in one soil matrix (pp. 33-36; DER Attachment 2). Analytes were identified using two ion pair transitions, one quantification and one confirmation; results were comparable or fairly comparable between quantification and confirmation ions. Analytes were identified using the same two ion pair transitions as the ECM. Standard deviations were reviewer-calculated because the study author did not provide these values. The sandy loam soil [63.90% sand, 18.97% silt, 17.13% clay; pH 7.41 (0.01M CaCl<sub>2</sub>), 1.35% organic carbon] was characterized and used in the study (USDA soil texture classification; p. 28; Appendix F, p. 135 of MRID 50768601). The soil matrix was obtained in Northwood, North Dakota, and characterized by Eurofins Agrosience Services EcoChem GmbH. Although the number of trials was not specified, the reviewer assumed that the ILV validated the ECM in the first trial with only insignificant modifications to the analytical parameters (pp. 29, 38).

**Table 2. Initial Validation Method Recoveries for 2,4-DP-p, 2,4-D, 2,4-DB, MCPA, MCPB, Mecoprop-p and their 2-EHs in Soil<sup>1</sup>**

Analyte	Fortification Level (mg/kg)	Number of Tests	Recovery Range (%)	Mean Recovery (%)	Standard Deviation (%)	Relative Standard Deviation (%)
<b>Sandy Loam Soil<sup>2</sup></b>						
Quantification ion transition <sup>3</sup>						
2,4-DP-p	0.01 (LOQ)	5	98-104	101	3	2.6
	0.1	5	100-109	103	4	3.7
2,4-DP-p 2-EH	0.01 (LOQ)	5	89-98	95	4	3.9
	0.1	5	91-105	98	5	5.1
2,4-D	0.01 (LOQ)	5	84-94	89	4	4.4
	0.1	5	97-106	104	4	3.8
2,4-D 2-EH	0.01 (LOQ)	5	88-101	94	5	5.0
	0.1	5	84-107	94	9	9.5
2,4-DB	0.01 (LOQ)	5	91-100	95	4	3.9
	0.1	5	92-100	96	4	3.7
2,4-DB 2-EH	0.01 (LOQ)	5	90-98	94	3	3.7
	0.1	5	90-98	93	3	3.7
MCPA	0.01 (LOQ)	5	96-112	106	6	6.1
	0.1	5	101-113	107	4	4.1
MCPA 2-EH	0.01 (LOQ)	5	101-111	107	5	4.7
	0.1	5	103-109	106	3	2.4
MCPB	0.01 (LOQ)	5	91-108	97	7	6.8
	0.1	5	97-107	103	4	3.7
MCPB 2-EH	0.01 (LOQ)	5	88-100	91	5	5.3
	0.1	5	89-111	100	8	8.1
Mecoprop-p	0.01 (LOQ)	5	99-108	103	4	4.0
	0.1	5	103-112	108	3	3.1
Mecoprop-p 2-EH	0.01 (LOQ)	5	102-112	106	4	3.9
	0.1	5	101-110	106	4	3.9
Confirmation ion transition <sup>3</sup>						
2,4-DP-p	0.01 (LOQ)	5	93-104	99	4	4.2
	0.1	5	92-101	95	4	3.7
2,4-DP-p 2-EH	0.01 (LOQ)	5	93-108	98	6	6.0
	0.1	5	96-104	100	3	3.3
2,4-D	0.01 (LOQ)	5	79-94	87	5	6.3
	0.1	5	99-113	105	5	5.0
2,4-D 2-EH	0.01 (LOQ)	5	84-98	93	6	6.2
	0.1	5	81-105	95	9	9.7
2,4-DB	0.01 (LOQ)	5	94-107	103	5	5.3
	0.1	5	88-100	94	5	5.1
2,4-DB 2-EH	0.01 (LOQ)	5	77-96	86	7	8.2
	0.1	5	86-96	90	4	4.4
MCPA	0.01 (LOQ)	5	99-114	107	6	5.6
	0.1	5	102-107	104	2	2.0
MCPA 2-EH	0.01 (LOQ)	5	106-113	109	3	2.8
	0.1	5	100-109	105	4	4.4

Analyte	Fortification Level (mg/kg)	Number of Tests	Recovery Range (%)	Mean Recovery (%)	Standard Deviation (%)	Relative Standard Deviation (%)
MCPB	0.01 (LOQ)	5	85-106	92	9	9.6
	0.1	5	95-102	99	3	2.6
MCPB 2-EH	0.01 (LOQ)	5	99-115	108	6	5.9
	0.1	5	90-120	103	11	10.5
Mecoprop-p	0.01 (LOQ)	5	99-111	104	5	4.5
	0.1	5	99-110	105	4	4.1
Mecoprop-p 2-EH	0.01 (LOQ)	5	100-106	102	2	2.4
	0.1	5	97-107	102	4	4.3
<b>Clay Soil<sup>2</sup></b>						
Quantification ion transition <sup>3</sup>						
2,4-DP-p	0.01 (LOQ)	5	91-94	93	1	1.4
	0.1	5	92-95	94	1	1.2
2,4-DP-p 2-EH	0.01 (LOQ)	5	88-101	94	6	5.9
	0.1	5	89-97	94	3	3.4
2,4-D	0.01 (LOQ)	5	84-98	90	6	6.2
	0.1	5	87-93	91	2	2.7
2,4-D 2-EH	0.01 (LOQ)	5	76-83	80	3	3.6
	0.1	5	74-84	79	4	4.9
2,4-DB	0.01 (LOQ)	5	81-92	87	5	5.8
	0.1	5	88-96	91	3	3.3
2,4-DB 2-EH	0.01 (LOQ)	5	78-91	83	5	6.0
	0.1	5	73-84	81	4	5.5
MCPA	0.01 (LOQ)	5	92-96	95	2	1.6
	0.1	5	93-99	98	3	2.7
MCPA 2-EH	0.01 (LOQ)	5	87-101	96	6	5.8
	0.1	5	95-108	102	5	5.1
MCPB	0.01 (LOQ)	5	86-100	92	6	6.6
	0.1	5	89-103	96	6	6.3
MCPB 2-EH	0.01 (LOQ)	5	82-94	87	5	5.8
	0.1	5	90-109	98	8	7.8
Mecoprop-p	0.01 (LOQ)	5	95-103	100	3	3.1
	0.1	5	98-109	104	4	3.9
Mecoprop-p 2-EH	0.01 (LOQ)	5	99-105	102	3	2.5
	0.1	5	95-107	100	4	4.4
Confirmation ion transition <sup>3</sup>						
2,4-DP-p	0.01 (LOQ)	5	85-90	88	2	2.4
	0.1	5	90-94	92	2	2.0
2,4-DP-p 2-EH	0.01 (LOQ)	5	96-100	98	2	2.1
	0.1	5	89-100	94	5	5.5
2,4-D	0.01 (LOQ)	5	78-89	84	5	5.5
	0.1	5	89-91	90	1	0.9
2,4-D 2-EH	0.01 (LOQ)	5	81-88	85	3	3.6
	0.1	5	78-92	84	6	6.8
2,4-DB	0.01 (LOQ)	5	76-88	81	4	5.4
	0.1	5	85-93	87	3	3.8



Analyte	Fortification Level (mg/kg)	Number of Tests	Recovery Range (%)	Mean Recovery (%)	Standard Deviation (%)	Relative Standard Deviation (%)
2,4-DB 2-EH	0.01 (LOQ)	5	87-112	98	9	9.6
	0.1	5	77-91	90	7	8.2
MCPA	0.01 (LOQ)	5	89-108	100	7	7.1
	0.1	5	93-99	97	3	2.9
MCPA 2-EH	0.01 (LOQ)	5	85-117	96	12	12.7
	0.1	5	82-105	94	8	9.0
MCPB	0.01 (LOQ)	5	92-109	99	6	6.2
	0.1	5	94-101	97	3	3.1
MCPB 2-EH	0.01 (LOQ)	5	82-104	93	8	8.8
	0.1	5	85-95	88	4	4.8
Mecoprop-p	0.01 (LOQ)	5	99-102	101	2	1.5
	0.1	5	96-104	100	3	3.2
Mecoprop-p 2-EH	0.01 (LOQ)	5	96-105	101	4	3.7
	0.1	5	91-104	100	5	5.2

1 Data (corrected results, Appendix A, pp. 49-50 of MRID 50768601) were obtained from Tables 7-18, pp. 37-48 of MRID 49775206. Reported values for standard deviation were reviewer-calculated because the study author did not provide these values (see DER Attachment 2). Rules of significant figures were followed.

2 The sandy loam soil [CEMAS Specimen Reference: CCON/073/002; particle distribution not reported; pH  $6.8 \pm 0.1$  (0.01M CaCl<sub>2</sub>),  $1.0 \pm 0.13\%$  organic carbon] and clay soil [CEMAS Specimen Reference: CCON/073/008; particle distribution not reported; pH  $7.1 \pm 0.1$  (0.01M CaCl<sub>2</sub>),  $1.66 \pm 0.12\%$  organic carbon] were characterized and used in the study (USDA soil texture classification; p. 23; Table 47, p. 72 of MRID 49775206). The specific sources of the soil matrices were not reported.

3 Two ion pair transitions were monitored for each analyte (quantitation and confirmation, respectively): *m/z* 233→161 and *m/z* 235→163 for 2,4-DP-p and 2,4-DP-p 2-EH, *m/z* 219→161 and *m/z* 221→163 for 2,4-D and 2,4-D 2-EH, *m/z* 247→161 and *m/z* 249→163 for 2,4-DB and 2,4-DB 2-EH, *m/z* 199→141 and *m/z* 201→143 for MCPA and MCPA 2-EH, *m/z* 227→141 and *m/z* 229→143 for MCPB and MCPB 2-EH, and *m/z* 213→141 and *m/z* 215→143 for Mecoprop-p and Mecoprop-p 2-EH.

**Table 3. Independent Validation Method Recoveries for 2,4-DP-p, 2,4-D, 2,4-DB, MCPA, MCPB, Mecoprop-p and their 2-EHs in Soil<sup>1</sup>**

Analyte	Fortification Level (mg/kg)	Number of Tests	Recovery Range (%)	Mean Recovery (%)	Standard Deviation (%)	Relative Standard Deviation (%)
<b>Sandy Loam Soil<sup>2</sup></b>						
Quantification ion transition <sup>3</sup>						
2,4-DP-p	0.01 (LOQ)	6	91-112	103	8	8
	0.1	6	93-118	105	9	9
2,4-DP-p 2-EH	0.01 (LOQ)	6	84-109	97	11	11
	0.1	6	84-113	98	11	12
2,4-D	0.01 (LOQ)	6	83-127	107	15	14
	0.1	6	84-113	100	12	12
2,4-D 2-EH	0.01 (LOQ)	6	91-122	109	14	13
	0.1	6	80-101	87	8	9
2,4-DB	0.01 (LOQ)	6	81-110	94	10	10
	0.1	6	89-109	97	7	7
2,4-DB 2-EH	0.01 (LOQ)	6	78-90	84	5	6
	0.1	6	71-101	86	12	14
MCPA	0.01 (LOQ)	6	97-129	109	12	11
	0.1	6	96-113	107	6	6
MCPA 2-EH	0.01 (LOQ)	6	91-121	105	10	9
	0.1	6	85-108	100	9	8
MCPB	0.01 (LOQ)	6	78-102	88	8	9
	0.1	6	91-101	96	4	4
MCPB 2-EH	0.01 (LOQ)	6	76-107	91	12	14
	0.1	6	87-112	98	10	10
Mecoprop-p	0.01 (LOQ)	6	90-124	108	13	12
	0.1	6	91-124	108	12	11
Mecoprop-p 2-EH	0.01 (LOQ)	6	90-129	108	13	13
	0.1	6	83-116	101	12	12
Confirmation ion transition <sup>3</sup>						
2,4-DP-p	0.01 (LOQ)	6	95-111	104	6	6
	0.1	6	98-109	103	5	5
2,4-DP-p 2-EH	0.01 (LOQ)	6	83-107	96	10	10
	0.1	6	91-112	99	9	9
2,4-D	0.01 (LOQ)	6	91-119	105	11	10
	0.1	6	86-114	101	11	11
2,4-D 2-EH	0.01 (LOQ)	6	92-119	106	10	9
	0.1	6	84-104	92	8	9
2,4-DB	0.01 (LOQ)	6	80-100	92	8	9
	0.1	6	84-105	93	8	9
2,4-DB 2-EH	0.01 (LOQ)	6	82-98	89	6	6
	0.1	6	70-99	85	11	13
MCPA	0.01 (LOQ)	6	90-110	99	10	10
	0.1	6	92-115	104	8	7
MCPA 2-EH	0.01 (LOQ)	6	84-126	103	14	14
	0.1	6	88-112	101	8	8

Analyte	Fortification Level (mg/kg)	Number of Tests	Recovery Range (%)	Mean Recovery (%)	Standard Deviation (%)	Relative Standard Deviation (%)
MCPB	0.01 (LOQ)	6	72-108	87	12	14
	0.1	6	89-100	94	4	5
MCPB 2-EH	0.01 (LOQ)	6	70-107	89	14	16
	0.1	6	88-107	98	8	8
Mecoprop-p	0.01 (LOQ)	6	83-124	106	15	14
	0.1	6	92-123	106	13	12
Mecoprop-p 2-EH	0.01 (LOQ)	6	92-129	105	15	14
	0.1	6	80-122	103	14	14

- 1 Data (uncorrected results, p. 33; Appendix A, pp. 49-50) were obtained from pp. 33-36 of MRID 50768601. Reported values for standard deviation were reviewer-calculated because the study author did not provide these values (see DER Attachment 2). Rules of significant figures were followed.
- 2 The sandy loam soil [63.90% sand, 18.97% silt, 17.13% clay; pH 7.41 (0.01M CaCl<sub>2</sub>), 1.35% organic carbon] was characterized and used in the study (USDA soil texture classification; p. 28; Appendix F, p. 135 of MRID 50768601). The soil matrix was obtained in Northwood, North Dakota, and characterized by Eurofins Agrosience Services EcoChem GmbH.
- 3 Two ion pair transitions were monitored for each analyte (quantitation and confirmation, respectively): *m/z* 233→161 and *m/z* 235→163 for 2,4-DP-p and 2,4-DP-p 2-EH, *m/z* 219→161 and *m/z* 221→163 for 2,4-D and 2,4-D 2-EH, *m/z* 247→161 and *m/z* 249→163 for 2,4-DB and 2,4-DB 2-EH, *m/z* 199→141 and *m/z* 201→143 for MCPA and MCPA 2-EH, *m/z* 227→141 and *m/z* 229→143 for MCPB and MCPB 2-EH, and *m/z* 213→141 and *m/z* 215→143 for Mecoprop-p and Mecoprop-p 2-EH. delete extra period

### III. Method Characteristics

In the ECM and ILV, LOQ in soil was 0.01 mg/kg for 2,4-DP-p, 2,4-D, 2,4-DB, MCPA, MCPB, and Mecoprop-p, as well as their respective esters (pp. 23, 27, 29; Table 38, p. 65 of MRID 49775206; pp. 29, 36-37 of MRID 50768601). The LOQ was defined in the ECM as the lowest fortification level where an acceptable mean recovery is obtained (70-120%). No comparison to baseline noise, other justification or calculation was provided. The ECM study author reported that the LOD was calculated as the estimated “baseline noise in the control sample multiplied by 3 and then “compared to the intensity of the 3 ng/mL standard for...soil (clay type)” (p. 25 of MRID 49775206). In the ILV and ECM, the LOD was calculated using the following equation:

$$\text{LOD} = C_{\text{standard}} \times [(3 \times \text{Noise})/h_{\text{peak}}]$$

Where  $C_{\text{standard}}$  is the concentration of the lowest standard (0.6 ng/mL = 0.003 mg/kg), Noise is the estimate of the background noise at the retention time of the peak of interest, and  $h_{\text{peak}}$  is the peak height (pp. 26-27; Table 38, p. 65 of MRID 49775206; pp. 36-37 of MRID 50768601). The calculated LODs in soil (clay type) were 0.000333-0.000335 mg/kg for 2,4-DP-p, 0.000338-0.000441 mg/kg for 2,4-D, 0.000659-0.000890 mg/kg for 2,4-DB, 0.000466-0.000480 mg/kg for MCPA, 0.000318-0.000913 mg/kg for MCPB, and 0.000222-0.000334 mg/kg for Mecoprop-p, as well as their respective esters, in the ECM. The LOD was reported in the ILV as equivalent to the 0.6 ng/mL standard, which equated to 30% of the LOQ for 2,4-DP-p, 2,4-D, 2,4-DB, MCPA, MCPB, and Mecoprop-p, as well as their respective esters. The calculated LODs in soil (clay type) were 0.000474-0.000552 mg/kg for 2,4-DP-p, 0.0000306-0.0000921 mg/kg for 2,4-D, 0.000126-0.000131 mg/kg for 2,4-DB, 0.0000375-0.0000871 mg/kg for MCPA, 0.0000806-0.000179 mg/kg for MCPB, and 0.000139-0.000212 mg/kg for Mecoprop-p, as well as their respective esters, in the ILV.

**Table 4. Method Characteristics**

Parameter		2,4-DP-p & 2,4-DP-p 2-EH	2,4-D & 2,4-D 2-EH	2,4-DB & 2,4-DB 2-EH	MCPA & MCPA 2-EH	MCPB & MCPB 2-EH	Mecoprop-p & Mecoprop-p 2-EH	
Limit of Quantitation (LOQ)		0.01 mg/kg						
Limit of Detection (LOD) <sup>1</sup>	ECM (calculated)	0.000335 mg/kg (Q)	0.000338 mg/kg (Q)	0.000659 mg/kg (Q)	0.000480 mg/kg (Q)	0.000318 mg/kg (Q)	0.000222 mg/kg (Q)	
		0.000333 mg/kg (C)	0.000441 mg/kg (C)	0.000890 mg/kg (C)	0.000466 mg/kg (C)	0.000913 mg/kg (C)	0.000334 mg/kg (C)	
	ILV (clay soil)	0.000474 mg/kg (Q)	0.0000306 mg/kg (Q)	0.000126 mg/kg (Q)	0.0000375 mg/kg (Q)	0.0000806 mg/kg (Q)	0.000139 mg/kg (Q)	
0.000552 mg/kg (C)		0.0000921 mg/kg (C)	0.000131 mg/kg (C)	0.0000871 mg/kg (C)	0.000179 mg/kg (C)	0.000212 mg/kg (C)		
method		30% of the LOQ (equivalent to 0.6 ng/mL standard)						
Linearity (calibration curve r <sup>2</sup> and concentration range) <sup>1</sup>	ECM	Sandy loam	r <sup>2</sup> = 0.9999 (Q & C)	r <sup>2</sup> = 0.9995 (Q) r <sup>2</sup> = 0.9997 (C)	r <sup>2</sup> = 0.9985 (Q) r <sup>2</sup> = 0.9998 (C)	r <sup>2</sup> = 0.9997 (Q) r <sup>2</sup> = 0.9985 (C)	r <sup>2</sup> = 0.9997 (Q) r <sup>2</sup> = 0.9999 (C)	r <sup>2</sup> = 0.9999 (Q & C)
		Clay	r <sup>2</sup> = 0.9997 (Q) r <sup>2</sup> = 0.9999 (C)	r <sup>2</sup> = 0.9999 (Q) r <sup>2</sup> = 0.9998 (C)	r <sup>2</sup> = 0.9996 (Q) r <sup>2</sup> = 0.9982 (C)	r <sup>2</sup> = 0.9996 (Q) r <sup>2</sup> = 0.9994 (C)	r <sup>2</sup> = 0.9999 (Q & C)	
	ILV <sup>2</sup> (sandy loam)	r <sup>2</sup> = 0.9962 (Q) r <sup>2</sup> = 0.9958 (C)	r <sup>2</sup> = 0.9912 (Q) r <sup>2</sup> = 0.9956 (C)	r <sup>2</sup> = 0.9942 (Q) r <sup>2</sup> = 0.9936 (C)	r <sup>2</sup> = 0.9966 (Q & C)	r <sup>2</sup> = 0.9926 (Q) r <sup>2</sup> = 0.9922 (C)	r <sup>2</sup> = 0.9958 (Q) r <sup>2</sup> = 0.9938 (C)	
	Concentration range	0.6-200 ng/mL (0.003-1 mg/kg)						
Repeatable	ECM <sup>3</sup>	Yes at the LOQ and 10×LOQ. (two characterized soil matrices)						
	ILV <sup>4,5</sup>	Yes at the LOQ and 10×LOQ. (one characterized soil matrix)						
Reproducible		Yes at the LOQ and 10×LOQ.						
Specific	ECM	Yes, no matrix interferences were observed. Minor baseline noise interfered with peak attenuation and integration.			Yes, matrix interferences were <3% of the LOQ (based on peak area). Minor baseline noise interfered with peak attenuation and integration.		Yes, no matrix interferences were observed. Minor baseline noise interfered with peak attenuation and integration.	

Parameter		2,4-DP-p & 2,4-DP-p 2-EH	2,4-D & 2,4-D 2-EH	2,4-DB & 2,4-DB 2-EH	MCPA & MCPA 2-EH	MCPB & MCPB 2-EH	Mecoprop-p & Mecoprop-p 2-EH
	ILV	Yes, matrix interferences were <2% of the LOQ (based on peak area).	<b>No</b> , matrix interferences were <i>ca.</i> 20% of the LOQ (based on peak area). <sup>6</sup>	Yes, matrix interferences were <2% of the LOQ (based on peak area).	<b>No</b> , matrix interferences were <i>ca.</i> 21% of the LOQ (based on peak area). <sup>7</sup>	Yes, matrix interferences were <2% of the LOQ (based on peak area).	

Data were obtained from pp. 23, 26-27, 29; Table 38, p. 65 (LOQ/LOD); Tables 7-18, pp. 37-48 (recovery results); Figures 13-36, pp. 85-108 (acid calibration curves); Figures 91-174, pp. 163-246 (acid and 2-EH chromatograms) of MRID 49775206; pp. 29, 36-37 (LOQ/LOD); pp. 33-36 (recovery results); Appendix C, pp. 60-71 (acid calibration curves); Appendix D, pp. 73-120 (acid and 2-EH chromatograms) of MRID 50768601; DER Attachment 2. Q = quantification ion; C = confirmation ion. Acid = 2,4-DP-p, 2,4-D, 2,4-DB, MCPA, MCPB and Mecoprop-p; 2-EH = 2,4-DP-p 2-EH, 2,4-D 2-EH, 2,4-DB 2-EH, MCPA 2-EH, MCPB 2-EH and Mecoprop-p 2-EH.

- 1 Calculated LODs and linear regression curves were prepared for the acid test materials only since the 2-EH esters were identified and quantified in acid equivalents.
- 2 ILV correlation coefficients were reviewer-calculated  $r^2$  values from the reported  $r$  values (Appendix C, pp. 60-71 of MRID 50768601; see DER Attachment 2).
- 3 In the ECM, sandy loam soil [CEMAS Specimen Reference: CCON/073/002; particle distribution not reported; pH  $6.8 \pm 0.1$  (0.01M CaCl<sub>2</sub>),  $1.0 \pm 0.13\%$  organic carbon] and clay soil [CEMAS Specimen Reference: CCON/073/008; particle distribution not reported; pH  $7.1 \pm 0.1$  (0.01M CaCl<sub>2</sub>),  $1.66 \pm 0.12\%$  organic carbon] were characterized and used in the study (USDA soil texture classification; p. 23; Table 47, p. 72 of MRID 49775206). The specific sources of the soil matrices were not reported
- 4 in the ILV, sandy loam soil [63.90% sand, 18.97% silt, 17.13% clay; pH 7.41 (0.01M CaCl<sub>2</sub>), 1.35% organic carbon] was characterized and used in the study (USDA soil texture classification; p. 28; Appendix F, p. 135 of MRID 50768601). The soil matrix was obtained in Northwood, North Dakota, and characterized by Eurofins Agrosience Services EcoChem GmbH.
- 5 Although the number of trials was not specified, the reviewer assumed that the ILV validated the ECM in the first trial with only insignificant modifications to the analytical parameters (pp. 29, 38 of MRID 50768601).
- 6 Based on Appendix C, pp. 76-78 of MRID 49775206. The ECM study author reported the residues as <30% of the LOQ.
- 7 Based on Appendix C, pp. 100-102 of MRID 49775206. The ECM study author reported the residues as <30% of the LOQ. Linearity is satisfactory when  $r^2 \geq 0.995$ .

#### IV. Method Deficiencies and Reviewer's Comments

1. The only details of the method contained in the ECM report (MRID 49775206) was the "Principle of the method" (p. 24 of MRID 49775206). The ECM MRID 49775206 did not contain any specific information or details about the extraction procedure or analytical method, except the ion transitions for the analytes which was reported in the recovery data tables. ECM MRID 49775206 did contain procedural recovery results and chromatograms. An excerpt of the method for ECM MRID 49775206, not the full report, was contained in Appendix A of ILV MRID 50768601. The reviewer reported the ECM information for the DER using Appendix A of the ILV MRID 50768601 and ECM MRID 49775206. Also, the method CEMAS CAM-0004/003 was obtained from an appendix of the recently submitted ILV report for an analytical method in water (MRID 49986901).
2. The specificity of the method was not supported by ILV representative chromatograms of 2,4-D, 2,4-D 2-EH, MCPA, and MCPA 2-EH. Matrix interferences were *ca.* 20-21% of the LOQ (based on peak area) which was >50% of the LOD (Appendix D, Figures 34-41, pp. 76-78, Figures 106-113, pp. 100-102 of MRID 50768601).
3. Linear regression curves were prepared for the acid test materials only since the 2-EH esters were identified and quantified in acid equivalents. The reviewer noted that linearity deviations in the confirmation ion analyses do not affect the validity of the method since a confirmation method is not usually required when LC/MS or GC/MS is used as the primary method to generate study data.
4. It could not be determined that the ILV was provided with the most difficult soil matrix with which to validate the method since only one characterized soil matrix was tested. Even though a certain number of soil matrices is not specified in the OCSPP guidelines, more than one soil/soil matrix would need to be included in an ILV in order to cover the range of soils used in the terrestrial field dissipation studies. A terrestrial field dissipation study was not submitted along with the method validations (MRIDs 49775206/50768601) to determine if the ILV soil matrix was representative of terrestrial field dissipation soil matrices.
5. The number of trials was not specified; the reviewer assumed that the ILV validated the ECM in the first trial with only insignificant modifications to the analytical equipment and parameters (pp. 29, 38 of MRID 50768601). OCSPP guidelines state that the ILV should be able to validate the ECM within three trials.
6. The reviewer noted that the ILV yielded poor method results of specificity for several analytes, while the ECM validation yielded only exceptional results. In method validations, it is typical to see unacceptable data; however, usually the problems in recovery, linearity, or specificity are seen in both the ECM and ILV validations. Typically, an issue with the method or test material is apparent as the cause of the unacceptable results. However, the one-sided nature of the unacceptable results for this method, especially since it is the ILV data, indicated to the reviewer that this method may not be adequately rugged or analytically reproducible.

7. The estimations of the LOQ and LOD in the ECM were not based on scientifically acceptable procedures as defined in 40 CFR Part 136 (pp. 23, 26-27, 29; Table 38, p. 65 of MRID 49775206; pp. 29, 36-37 of MRID 50768601). No calculations were reported for the LOQ; no comparison was made to chromatogram background levels. Detection limits should not be based on the arbitrarily selected lowest concentration in the spiked samples. For the LOD, the explanation of the LOD calculation in the ECM was vague, i.e. the estimated “baseline noise in the control sample multiplied by 3 and then “compared to the intensity of the 3 ng/mL standard for surface soil” (p. 25 of MRID 49775206). An exact equation was provided in CEMAS CAM-0004/003 and the ILV { $LOD = C_{standard} \times [(3 \times \text{Noise})/h_{peak}]$ , where  $C_{standard}$  is the concentration of the lowest standard (0.6 ng/mL = 0.003 mg/kg), Noise is the estimate of the background noise at the retention time of the peak of interest, and  $h_{peak}$  is the peak height}.
8. Matrix interferences were studied in the ECM (pp. 25, 27; Table 40, pp. 67-68 of MRID 49775206). Significant (>20%) suppression of detector response was observed for all analytes in the sandy loam soil matrix. Matrix-matched calibration standards were used in the ECM and ILV (p. 29 of MRID 49775206; p. 37 of MRID 50768601).
9. Stability of the extracts and standards was studied in the ECM (pp. 27, 29; Tables 31-36, pp. 61-63; Tables 41-46, pp. 69-71 of MRID 49775206). Extracts were determined to be stable for at least 7 days when stored at 2-8°C. Standards were determined to be stable for up to 149 days when stored at 2-8°C.
10. The ILV reported that no communication between the ILV and ECM occurred and that the ECM and ILV were performed at different locations by different study personnel, using different instrumentation and stocks of chemicals (p. 38 of MRID 50768601).
11. No time requirement for the method was reported in the ECM or ILV.



## V. References

- 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.
- U.S. Environmental Protection Agency. 2016. DP Barcode 424054. Preliminary Ecological Risk Assessment for Registration Review of 2,4-D. U.S. Environmental Protection Agency, Office of Chemical Safety and Pollution Prevention, Environmental Fate and Effects Division. June 6, 2016.
- U.S. Environmental Protection Agency. 2014. DP Barcode 416759. Problem Formulation for the Environmental Fate and Ecological Risk, Endangered Species, and Drinking Water Assessments in Support of the Registration Review of Mecoprop-p (MCPB-p). U.S. Environmental Protection Agency, Office of Chemical Safety and Pollution Prevention, Environmental Fate and Effects Division. April 2, 2014.
- U.S. Environmental Protection Agency. 2018a. DP Barcode 445364. 2,4-DB & 2,4-DB DMAS: Draft Ecological Risk Assessment for Registration Review. U.S. Environmental Protection Agency, Office of Chemical Safety and Pollution Prevention, Environmental Fate and Effects Division. October 11, 2018a.
- U.S. Environmental Protection Agency. 2018b. DP Barcode 446320. MCPA and its sodium salt, amine salt and ester – EFED Registration Review Draft Risk Assessment: U.S. Environmental Protection Agency, Office of Chemical Safety and Pollution Prevention, Environmental Fate and Effects Division. September 13, 2018b.
- U.S. Environmental Protection Agency. 2019a. DP Barcode 446500. 2,4-DP-p: Draft Ecological Risk Assessment for Registration Review. U.S. Environmental Protection Agency, Office of Chemical Safety and Pollution Prevention, Environmental Fate and Effects Division. March 29, 2019a.
- U.S. Environmental Protection Agency. 2019b. DP Barcode 449348. MCPB: Draft Ecological Risk Assessment for Registration Review. U.S. Environmental Protection Agency, Office of Chemical Safety and Pollution Prevention, Environmental Fate and Effects Division. May 17, 2019b.
- 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

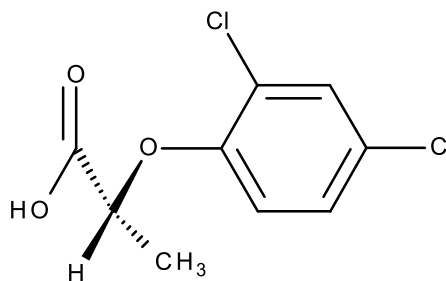
### 2,4-DP-p; Dichloroprop-p; Dichlorprop-p; 2,4-Dichlorprop-p

**IUPAC Name:** (2R)-2-(2,4-dichlorophenoxy)propanoic acid  
(+)-(R)-2-(2,4-dichlorophenoxy)propionic acid  
(R+)-2-(2,4-dichlorophenoxy)propionic acid

**CAS Name:** Not reported

**CAS Number:** 15165-67-0

**SMILES String:** O=C(O)C(Oc1ccc(Cl)cc1)C



### 2,4-DP-p 2-EH; Dichloroprop-p 2-EH

**IUPAC Name:** (R+)-2-(2,4-dichlorophenoxy)propionic acid 2-ethylhexyl ester

**CAS Name:** Not reported

**CAS Number:** 865363-39-9

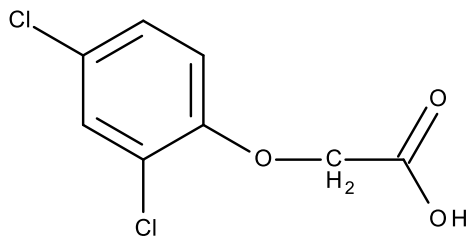
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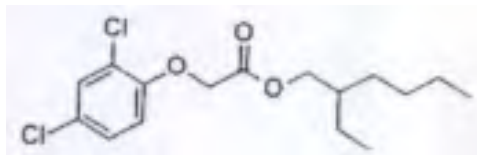
## 2,4-D

**IUPAC Name:** 2,4-Dichlorophenoxyacetic acid  
(2,4-Dichlorophenoxy)acetic acid  
**CAS Name:** 2-(2,4-Dichlorophenoxy)acetic acid  
**CAS Number:** 94-75-7  
**SMILES String:** O=C(O)COc(c(cc(c1)Cl)Cl)c1



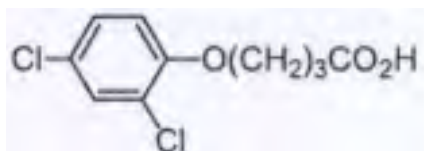
## 2,4-D 2-EH

**IUPAC Name:** 2,4-Dichlorophenoxyacetic acid, 2-ethylhexyl ester  
**CAS Name:** Not reported  
**CAS Number:** 1928-43-4  
**SMILES String:** Not found



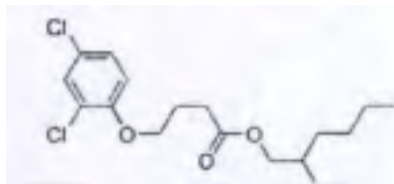
## 2,4-DB

**IUPAC Name:** 4-(2,4-Dichlorophenoxy)butyric acid  
**CAS Name:** Not reported  
**CAS Number:** 94-82-6  
**SMILES String:** Not found



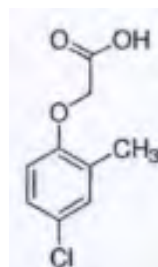
### 2,4-DB 2-EH

**IUPAC Name:** 4-(2,4-Dichlorophenoxy)butyric acid, 2-ethylhexyl ester  
**CAS Name:** Not reported  
**CAS Number:** 7720-36-7  
**SMILES String:** Not found



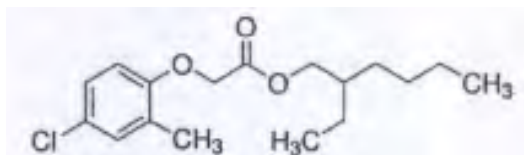
### MCPA

**IUPAC Name:** 4-Chloro-2-methylphenoxyacetic acid  
**CAS Name:** Not reported  
**CAS Number:** 94-74-6  
**SMILES String:** Not found



### MCPA 2-EH

**IUPAC Name:** 4-Chloro-2-methylphenoxyacetic acid, 2-ethylhexyl ester  
**CAS Name:** Not reported  
**CAS Number:** 29450-45-1  
**SMILES String:** Not found



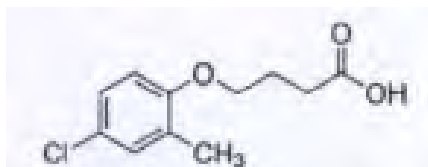
## MCPB

**IUPAC Name:** 4-(4-Chloro-2-methylphenoxy)butyric acid

**CAS Name:** Not reported

**CAS Number:** 94-81-5

**SMILES String:** Not found



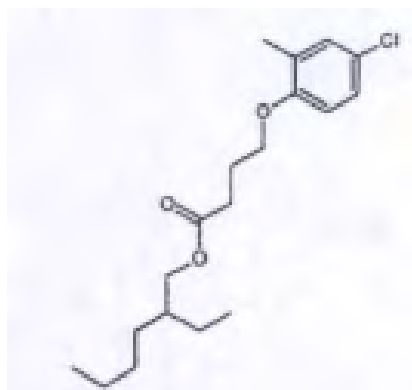
## MCPB 2-EH

**IUPAC Name:** 4-(4-Chloro-2-methylphenoxy)butyric acid, 2-ethylhexyl ester

**CAS Name:** Not reported

**CAS Number:** 94232-74-3

**SMILES String:** Not found



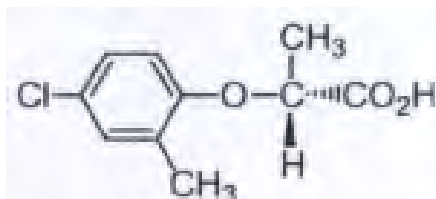
### Mecoprop-p (CMPP-p)

**IUPAC Name:** (R+)- 2-(4-chloro-2-methylphenoxy)propionic acid

**CAS Name:** Not reported

**CAS Number:** 16484-77-8

**SMILES String:** Not found



### Mecoprop-p 2-EH

**IUPAC Name:** (R+)-2-(4-chloro-2-methylphenoxy)propionic acid, 2-ethylhexyl ester

**CAS Name:** Not reported

**CAS Number:** 861229-15-4

**SMILES String:** Not found

