

REGISTRATION REPORT

Part B

Section 8

Environmental Fate

Detailed summary of the risk assessment

Product code: ADM.3304.H.1.A

(old code AG-CDF1-480 EC)

Product name(s): Tricera

Chemical active substance(s):

2,4-D, 375 g/L (562.5 g/L as 2,4-D EHE)

Clopyralid, 30 g/L

Fluroxypyr, 75 g/L

Central Zone

Zonal Rapporteur Member State: Poland

CORE ASSESSMENT

(authorization)

Sponsor: ADAMA Agan Ltd.

Applicant: Country organisation / representative of ADAMA,
as given in Part A

Submission date: September 2021

MS Finalisation date: May 2022 (initial Core Assessment)

November 2022, updated February 2023 (final Core Assessment)

Version history

When	What
September 2019	dRR Part B Section 8, version 1 submitted by Applicant
September 2021	dRR Part B Section 8, version 2 submitted by Applicant – Update of clopyralid endpoints according to the new EU-agreed endpoints found in the EFSA conclusion LoEP (EFSA, 2018). New PEC modelling with corresponding modelling reports are provided. The previous results included in the Appendix 2 are cross-out.
May 2021	Initial zRMS assessment The report in the dRR format has been prepared by the Applicant, therefore all comments, additional evaluations and conclusions of the zRMS are presented in grey commenting boxes. Minor changes are introduced directly in the text and highlighted in grey . Not agreed or not relevant information are struck through and shaded for transparency .
November 2022	Final report (Core Assessment updated following the commenting period). No additional information or assessments after the commenting period.
February 2023	Final report (Core Assessment updated following the Applicant's comments). Additional information/assessments included by the zRMS in the report in response to comments received from the Applicant are highlighted in green . Information no longer relevant is struck through and shaded .

DATA PROTECTION CLAIM

Under Article 59, Regulation 1107/2009/EC, on behalf of the Sponsor Company the applicant claims data protection for these studies. The data protection status and corresponding justification as valid for the respective country will be confirmed in the respective PART A

STATEMENT FOR OWNERSHIP

The summaries and evaluations contained in this document may be based on unpublished proprietary data submitted for the purpose of the assessment undertaken by the regulatory authority that prepared it. Other registration authorities should not grant, amend, or renew a registration on the basis of the summaries and evaluation of unpublished proprietary data contained in this document unless they have received the data on which the summaries and evaluation are based, either –

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8 Fate and behaviour in the environment (KCP 9)

General remark:

The product with product code ADM.3304.H.1.A (old code AG-CDF1-480 EC) is a herbicide containing the active substance 2,4-D (as the ester variant 2,4-D EHE).

In the dossier below information is presented for the acid form –that will be referred as 2,4-D- as well as for the ester form (that will be referred as 2,4-D EHE).

This document reviews the environmental fate studies and modelling for the product ADM.3304.H.1.A (old code AG-CDF1-480 EC) containing the active substances 2,4-D, Clopyralid and Fluroxypyr.

2,4-D was reviewed as part of the renewal of approval procedure by the Member States and the Commission and the Commission review report finalised on 13.11.2015 approved 2,4-D in accordance with Regulation (EC) No. 1107/2009.

Clopyralid was included into Annex I of Directive 91/414/EEC according to Commission Regulation (EC) No 451/2000 (renewal of inclusion of the second and third group of active substances in Annex I, see Commission Directive 2006/64/EC of 18 July 2006, Commission Implementing Regulation (EU) No 540/2011 of 25 May 2011 that replace the Directive 2006/64/EC after the application of Regulation 1107/2009, and Commission Implementing Regulation (EU) 2021/566 of 30 March 2021 that sets out the new expiry date of approval to 30/04/2022..

Fluroxypyr was included into Annex I of Directive 91/414/EEC according to Commission Regulation (EC) No 736/2011 (renewal of inclusion of the first group of active substances in Annex I). However, all the relevant information about this last approval are indicated in Review Report for active substance Fluroxypyr (SANCO/111019/201, 17 June 2011), as was evaluated within the assessment of active substance Fluroxypyr.

Where appropriate this document refers to the conclusions of the EU review or the Draft Assessment Report (DAR) of the active substances. This will be where:

- the active substance data is relied upon in the risk assessment of the formulation; *or when*
- the EU review or DAR concluded that additional data/information should be considered at national re-registration.

Note: this Part B document only reviews data (Annex II or Annex III) and additional information that has not previously been considered within the EU review process, as part of the Annex I inclusion decision. New annex II data have only be included if they were considered essential for the evaluation and in this case a full study summary was be provided. In the case where the formulation has been previously evaluated, at European level, detailed summaries have not been provided.

This product was not the representative formulation. The product has not been previously evaluated according to Uniform Principles.

The EFSA Report of 2,4-D (EFSA Journal 2014;12(9):3812), of clopyralid (EFSA Conclusion (2018) 16(7):5389) and the EFSA Report of fluroxypyr (EFSA Journal 2011;9(3):2091) are considered to provide the relevant review information or a reference to where such information can be found. For the information on 2,4-D EHE, please refer to the Bridging dossier (2018) prepared by the RMS for the a.i. (Greece).

For the implementation of the uniform principles of Regulation (EC) 546/2011, the conclusions of the review report on **2,4-D**, and in particular Appendices I and II thereof, as finalised in the Standing Committee on the Food Chain and Animal Health on 28. May 2015 shall be taken into account. In this overall assessment:

Member States must pay particular attention to the:

- Risk to aquatic organisms, terrestrial organisms and consumers in cases of uses above 750 g/ha.

The renewal Regulation for the active substance **clopyralid** (Commission Implementing Regulation (EU) 2021/1191 of 19 July 2021) gives specific provisions under Part B which need to be considered by the applicant in the preparation of their submission prior to granting an authorisation.

In order to facilitate Member States, in granting or reviewing authorisations, to apply adequately the provisions of Article 29(1) of Regulation (EC) No 1107/2009 and the uniform principles laid down in Regulation (EU) No 546/2011, the most important endpoints were identified during the re-evaluation process. These endpoints are listed in the conclusion of the EFSA.

- the specification of the technical material as commercially manufactured;
- the protection of operators, ensuring that conditions of use for operators include the application of adequate personal protective equipment;
- possible presence of clopyralid residues in rotational crops;
- the possible transfer of clopyralid residues via compost or manure of animals whose feed originates from treated areas, to avoid damage to susceptible crops;
- the protection of groundwater under vulnerable conditions.

Fluroxypyr (Commission Implementing Regulation (EU) No 736/2011) gives specific provisions under Part B which need to be considered by the applicant in the preparation of their submission prior to granting an authorisation.

For the implementation of the uniform principles, as referred to in Article 29(6) of Regulation (EC) No 1107/2009, the conclusions of the review report on **fluroxypyr**, and in particular Appendices I and II thereof, as finalised in the Standing Committee on the Food Chain and Animal Health on 17 June 2011 shall be taken into account.

- Only uses as herbicides may be authorised.

In this overall assessment Member States shall pay particular attention to:

- The potential contamination of groundwater by metabolite fluroxypyr pyridinol, when the active substance is applied in regions with alkaline or vulnerable soil and/or with vulnerable climatic condition.
- The risk to aquatic organisms.

These concerns have, where relevant, been addressed within the current submission.

8.1 Critical GAP and overall conclusions

Table 8.1-1: Critical use pattern of the formulated product

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Use- No. *	Member state(s)	Crop and/or situation (crop destination / purpose of crop)	F, Fn, Fpn G, Gn, Gpn or I **	Pests or Group of pests controlled (additionally: developmental stages of the pest or pest group)	Application				Application rate			PHI (days)	Remarks: e.g. g safener/ synergist per ha	Conclusion Groundwater
					Method / Kind	Timing / Growth stage of crop & season	Max. number a) per use b) per crop/ season	Min. interval between applications (days)	kg or L product/ha a) max. rate per appl. b) max. total rate per crop/season	g or kg as/ha a) max. rate per appl. b) max. total rate per crop/season	Water L/ha min/max			
Zonal uses (field or outdoor uses, certain types of protected crops)														
1	PL	Established grassland (NNNFW)	F	broadleaved weeds (TTTDD)	foliar spraying, overall	Mar-Aug/ BBCH 21-39	a) 1 (-) b) 1 (-)	-	a) 2 L/ha b) 2 L/ha	a) 750 ¹ / 60 / 150 ² b) 750 ¹ / 60 / 150 ² (2,4-D / clopyralid / fluroxypyr)	200-400	n.a.	The BBCH stages were removed since for the established grass the time of the season will be more indicative for application timing than the growth stage	A R Biennial application
2	PL	Spring cereals (umbrella GAP)	F	broadleaved weeds (TTTDD)	foliar spraying, overall	Mar-Jun/ BBCH 21-39	a) 1 (-) b) 1 (-)	-	a) 2 L/ha b) 2 L/ha	a) 750 ¹ / 60 / 150 ² b) 750 ¹ / 60 / 150 ² (2,4-D / clopyralid / fluroxypyr)	200-400	n.a.		R Triennial application
3	PL	Winter cereals (umbrella GAP)	F	broadleaved weeds (TTTDD)	foliar spraying, overall	Mar-May/ BBCH 21-39	a) 1 (-) b) 1 (-)	-	a) 2 L/ha b) 2 L/ha	a) 750 ¹ / 60 / 150 ² b) 750 ¹ / 60 / 150 ² (2,4-D / clopyralid / fluroxypyr)	200-400	n.a.		R Biennial application
4	PL	Winter cereals	F	broadleaved weeds (TTTDD)	foliar spraying, overall	Mar-May/ BBCH 21-39	a) 1 (-) b) 1 (-)	-	a) 1.5 L/ha b) 1.5 L/ha	a) 563 ³ / 45 / 113 ⁴ b) 563 ³ / 45 / 113 ⁴ (2,4-D / clopyralid / fluroxypyr)	200-400	n.a.		A

¹ equal to 1125 g/ha of 2,4-D EHE

² equal to 216 g/ha Fluroxypyr-meptyl

³ equal to 849 g/ha of 2,4-D EHE

⁴ equal to 163 g/ha Fluroxypyr-meptyl

* Use number(s) in accordance with the list of all intended GAPs in Part B, Section 0 should be given in column 1

** F: professional field use, Fn: non-professional field use, Fpn: professional and non-professional field use, G: professional greenhouse use, Gn: non-professional greenhouse use, Gpn: professional and non-professional greenhouse use, I: indoor application

Explanation for column 15 “Conclusion”

A	Safe use
R	Further refinement and/or risk mitigation measures required
C	To be confirmed by cMS
N	No safe use

zRMS comments:

It is noted that initially in the GAP table above the additional 2 uses intended in Poland were indicated. One included application to winter cereals at BBCH 21-39 at application rate 1.5 L product/ha (indicated as “fallback scenario 1”) and at BBCH 30-39 at 2.0 L product/ha (indicated as “fallback scenario 2”), which both fall into the use pattern No 3, which covers all intended BBCH stages. Displaying the different stages on the label could be confusing for the end-user, since single application is possible over the BBCH 21-39, regardless of the rate. Taking this into account, the fallback scenarios were removed from the Table 8.1-1 and additional use No 4 has been added for the lower application rate (1.5 L/ha) due to the different risk mitigation measures required for the lower and higher rate. Please note, however, that application to winter cereals at the reduced rate of 1.5 L/ha was not evaluated in area of efficacy and conclusions presented in the Core Assessment, Part B, Section 3 clearly indicate that the minimum effective rate of ADM.3304.H.1.A was determined to be 2.0 L/ha. Taking this into account the lower rate has been considered in area of efate only for informative purposes. The Applicant is kindly reminded that in case any changes of the intended uses are being proposed, dRR in area of all sections and particularly in area of Section 3 must be also updated so respective evaluation is performed by the efficacy experts.

During the commenting period the Applicant requested to reinstate the fallback scenario 2 (winter cereals at BBCH 30-39) in case use in winter cereals is restricted to BBCH 30-39. However, intention for removal of BBCH 20-29 was not communicated by the Applicant and on the label the BBCH stages of 20-39 were still indicated with no proposal for the change of the label entry. Taking this into account, the information in the GAP table remains unchanged and in case the Applicant would like to remove application to winter cereals at BBCH 20-29 and leave only application at BBCH 30-39 every year, this may be done in the separate procedure with Applicants’ intentions in this area clearly communicated.

The first version of the GAP included also intended uses in UK. However, the Applicant informed that uses of ADM.3304.H.1.A in UK are no longer supported and PL is the only cMS listed in the GAP. United Kingdom has been removed as cMS from the Table 8.1-1 above for transparency.

Detailed GAP for ADM.3304.H.1.A may be found in the Core Assessment, Part B, Section 0.

Table 8.1-2: Assessed (critical) uses during approval of 2,4-D concerning the Section Environmental Fate

1	2	3	4	5	6	7	8	9	10	11	12	13	14
Use- No.	Member state(s)	Crop and/or situation (crop destination / purpose of crop)	F, Fn, Fpn G, Gn, Gpn or I *	Pests or Group of pests controlled (additionally: developmental stages of the pest or pest group)	Application				Application rate			PHI (days)	Remarks: e.g. g safener/ synergist per ha
					Method / Kind	Timing / Growth stage of crop & season	Max. number a) per use b) per crop/ season	Min. interval between applications (days)	kg or L product/ha a) max. rate per appl. b) max. total rate per crop/season	g or kg as/ha a) max. rate per appl. b) max. total rate per crop/season	Water L/ha min/max		
		Winter cereals	F	Dicotyledonous weeds	Broadcast	BBCH 21- 32 Feb to May	1	-		187.5-750	100-400		
		Spring cereals	F	Dicotyledonous weeds	Broadcast	BBCH 11- 32 Mar to May	1	-		187.5-750	100-400		
		Maize	F	Dicotyledonous weeds	Broadcast	BBCH 11- 16 Apr to Jun	1	-		187.5-750	100-400		

* F: professional field use, Fn: non-professional field use, Fpn: professional and non-professional field use, G: professional greenhouse use, Gn: non-professional greenhouse use, Gpn: professional and non-professional greenhouse use, I: indoor application

Table 8.1-3: Assessed (critical) uses during approval of clopyralid concerning the Section Environmental Fate

1	2	3	4	5	6	7	8	9	10	11	12	13	14
Use- No.	Member state(s)	Crop and/or situation (crop destination / purpose of crop)	F, Fn, Fpn G, Gn, Gpn or I*	Pests or Group of pests controlled (additionally: developmental stages of the pest or pest group)	Application				Application rate			PHI (days)	Remarks: e.g. g safener/ synergist per ha
					Method / Kind	Timing / Growth stage of crop & season	Max. number a) per use b) per crop/ season	Min. interval between applications (days)	kg or L product/ha a) max. rate per appl. b) max. total rate per crop/season	g or kg as/ha a) max. rate per appl. b) max. total rate per crop/season	Water L/ha min/max		
	C-EU	Winter cereal (wheat, barley, oat, rye, triticale, spelt)	F	Broad leaved weeds	Overall broadcast foliar spray	BBCH 13-39 (1st Feb to 30 th June)	1	-	-	80 g/ha	80-400	None	Dose: 1L GF-1374/ha Due to clopyralid content, straw treated with GF- 1374 must not be used for compost production (for cultivating susceptible vegetables).
	S-EU	Winter cereal (wheat, barley, oat, rye, triticale, spelt)	F	Broad leaved weeds	Overall broadcast foliar spray	BBCH 13-39 (1st Feb to 30 th June)	1	-	-	80 g/ha	80-400	None	
	C-EU	Established permanent pasture	F	Broad leaved weeds	Overall broadcast foliar spray	1 st Feb to 30 th September	1	-	-	120 g/ha	100-400	7	Dose: 1.5L GF-1374/ha. PHI: Interval before any crop cutting or grazing. Clopyralid residues in plant tissue (including manure) which has not completely decayed may affect succeeding susceptible crops. Do not use any plant material treated with GF-1374 for composting. Do not use manure from animals fed on crops treated with GF- 1374 for composting or mulching. Manure produced from animals fed on grass or forage treated with clopyralid can be used on or before the planting of crops such as grass, cereals and maize.
	S-EU	Established permanent pasture	F	Broad leaved weeds	Overall broadcast foliar spray	1 st Feb to 30 th September	1	-	-	120 g/ha	100-400	14	

* F: professional field use, Fn: non-professional field use, Fpn: professional and non-professional field use, G: professional greenhouse use, Gn: non-professional greenhouse use, Gpn: professional and non-professional greenhouse use, I: indoor application

^a The risk assessment has revealed data gaps in section 4

Table 8.1-4: Assessed (critical) uses during approval of fluroxypyr concerning the Section Environmental Fate

1	2	3	4	5	6	7	8	9	10	11	12	13	14
Use- No.	Member state(s)	Crop and/or situation (crop destination / purpose of crop)	F, Fn, Fpn G, Gn, Gpn or I *	Pests or Group of pests controlled (additionally: developmental stages of the pest or pest group)	Application				Application rate			PHI (days)	Remarks: e.g. g safener/ synergist per ha
					Method / Kind	Timing / Growth stage of crop & season	Max. number a) per use b) per crop/ season	Min. interval between applications (days)	kg or L product/ha a) max. rate per appl. b) max. total rate per crop/season	g or kg as/ha a) max. rate per appl. b) max. total rate per crop/season	Water L/ha min/max		
	North Europe	Cereals (winter and spring)	F	Broadleaved weeds	Volume spraying	GS12-39	1	-	-	200 g/ha	200-400	n.a.	All concentrations in formulations and application details are reported as acid equivalents. n.a. = not applicable a, b, c
	South Europe	Cereals (winter and spring)	F	Broadleaved weeds	Volume spraying	GS12-39	1	-	-	200 g/ha	200-400	n.a.	
	Germany	Cereals (winter and spring)	F	Broadleaved weeds	Volume spraying	Winter cereals: GS13-39 Spring cereals: GS13-29	1	-	-	180 g/ha	200-400	n.a.	
	North Europe	Pasture/Amenity	F	Broadleaved weeds	Medium volume	GS20-25	1	-	-	200 g/ha	200-400	7	
	South Europe	Pasture/Amenity	F	Broadleaved weeds	Medium volume	GS20-25	1	-	-	200 g/ha	200-400	14	
	North Europe	Maize	F	Broadleaved weeds	Medium volume	GS12-16	1	-	-	200 g/ha	200-400	n.a.	
	South Europe	Maize	F	Broadleaved weeds	Medium volume	GS12-16	1	-	-	200 g/ha	200-400	n.a.	

* F: professional field use, Fn: non-professional field use, Fpn: professional and non-professional field use, G: professional greenhouse use, Gn: non-professional greenhouse use, Gpn: professional and non-professional greenhouse use, I: indoor application

^a The proposed minimum purity of the active substance and the specification of the impurities for the reference source are not supported by available data and no conclusion could be reached whether the batches used in the toxicological studies cover the current proposed technical specification.

^b The toxicological relevance of the ground water metabolites fluroxypyr pyridinol and fluroxypyr methoxypyridine needs to be addressed.

^c The long-term risk assessment to earthworms and soil macro-organisms for the metabolite fluroxypyr methoxypyridine could not be finalised. The risk to soil micro-organisms (nitrogen turnover) for the formulation EF-1502 and the metabolite fluroxypyr pyridinol could not be finalised.

8.2 Metabolites considered in the assessment

Table 8.2-1: Metabolites of 2,4-D potentially relevant for exposure assessment

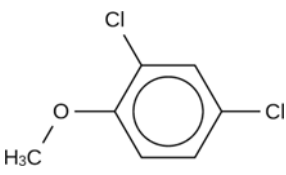
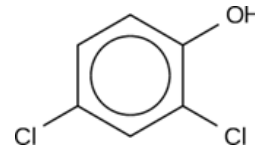
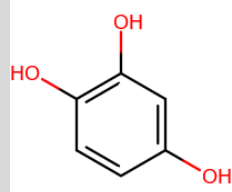
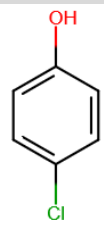
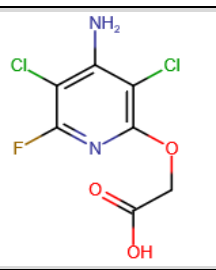
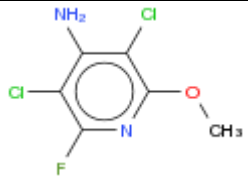
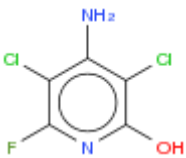
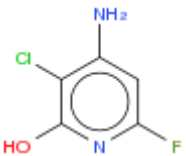
Metabolite	Molar mass	Chemical structure	Maximum observed occurrence in compartments	Exposure assessment required in
2,4-DCA (2,4-dichloro-1-methoxybenzene)	177		Soil: 15% 8.7% Water/sediment: 5.3% 32.1%	Soil, groundwater, surface water, sediment
2,4-DCP (2,4-dichlorophenol)	163		Soil aerobic: 8.7% 15% Soil anaerobic: 38.0% Water/sediment: 32.1% 5.3%	Soil, groundwater, surface water, sediment
1,2,4-Benzenetriol (photolysis metabolite)	126.11		Water: 31.7%	Surface water, sediment
4-Chlorophenol (4-CP)	128.56		Soil anaerobic: 33.0%	Soil

Table 8.2-2: Metabolites of clopyralid potentially relevant for exposure assessment

Metabolite	Molar mass	Chemical structure	Maximum observed occurrence in compartments	Exposure assessment required in
-	-	-	-	-

Table 8.2-3: Metabolites of fluroxypyr potentially relevant for exposure assessment

Metabolite	Molar mass	Chemical structure	Maximum observed occurrence in compartments	Exposure assessment required in
Fluroxypyr acid	255.03		Soil: 100% Water/sediment: 100% (calculations performed as parent)	Soil, surface water, sediment, ground water
Methoxypyridine (DMP, 4-amino-3,5-dichloro-6-fluoro-methoxypyridine)	211		Soil: 38.2% Water/sediment: -	Soil, surface water, sediment, ground water

Metabolite	Molar mass	Chemical structure	Maximum observed occurrence in compartments	Exposure assessment required in
Pyridinol (DCP, 4-amino-3,5-dichloro-6-fluoro-2-pyridinol)	197		Soil: 23.9% Water: 44% Sediment: 11.5%	Soil, surface water, sediment, ground water
3-CP	162		Soil: - Water: 17.9% Sediment: 6.5%	Surface water

zRMS comments:

Information regarding metabolites of 2,4-D, clopyralid and fluroxypyr provided in Tables 8.2-1 to 8.2-3 above is in general in line with EU agreed data reported in:

- EFSA Journal 2014;12(9):3812 for 2,4-D,
- EFSA Journal 2018;16(7):5389 for clopyralid,
- EFSA Journal 2011;9(3):2091 for fluroxypyr.

It was noted that information regarding 2,4-D metabolites 2,4-DCA and 2,4-DCP was switched so respective corrections were introduced by the zRMS. Furthermore, two metabolites of 2,-D were missing and Table 8.2-1 was completed by the zRMS.

With regard to fluroxypyr it is noted that although fluroxypyr acid is an active substance itself, in case of products containing fluroxypyr in an ester form, fluroxypyr acid should be treated as a primary metabolite. For this reason respective information has been added by the zRMS in Table 8.2-3 above.

8.3 Rate of degradation in soil (KCP 9.1.1)

Studies on degradation in soil with the formulation were not performed, since it is possible to extrapolate from data obtained with the active substance.

The rate of degradation of 2,4-D (and 2,4-D EHE), clopyralid and fluroxypyr in soil was evaluated during Annex I Inclusion.

8.3.1 Aerobic degradation in soil (KCP 9.1.1.1)

8.3.1.1 2,4-D and its metabolites

The product ADM.3304.H.1.A (old code AG-CDF1-480 EC) contains the ester derivative 2,4-D EHE.

2,4-D EHE

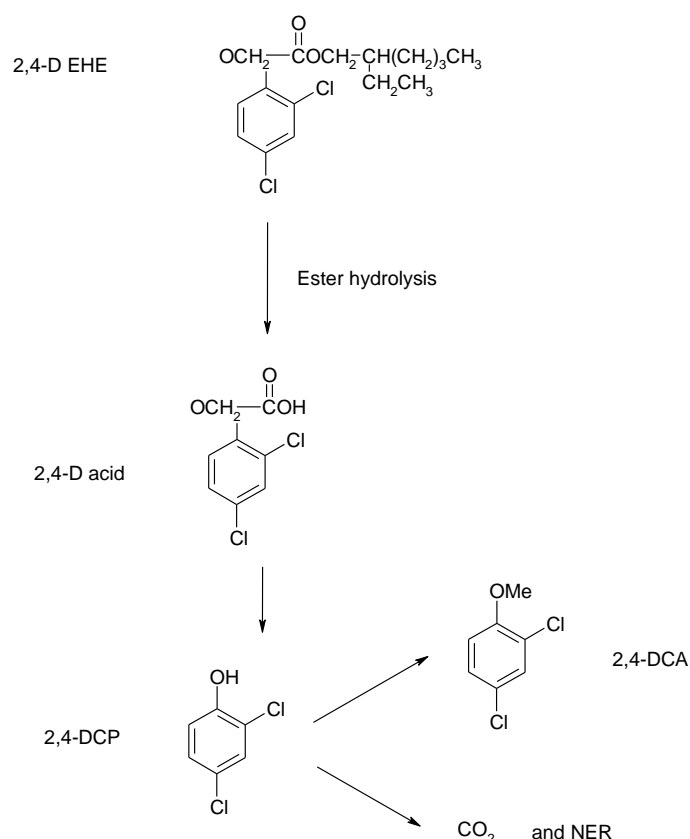
Environmental fate studies with 2,4-D EHE were evaluated as part of the Annex I review of 2,4-D in 2001; the subsequent Annex I Renewal (AIR) predominantly focused on 2,4-D since the ester is considered to be a derivative of 2,4-D acid, however summaries of relevant studies on 2,4-D EHE previously reviewed were reported for completeness. Additionally, two new studies with 2,4-D EHE were performed and are summarised in the final addendum to the Renewal Assessment Report (RAR Addendum, 2014)¹, study summaries are presented in Section A.2 of the bridging report regarding 2,4-D acid and 2,4-D EHE (prepared by RMS Greece (2018)²), as well as a complete list of old and new studies on 2,4-D EHE as considered relevant for the current assessment (Appendix I of bridging report, 2018).

As a conclusion, the ester of the 2,4-D is transformed in soil into the acid form almost instantaneously within few hours.

The degradation pathway of 2,4-D EHE in soil under aerobic conditions is presented in the figure below.

¹ Final Addendum to the Renewal Assessment Report. Risk assessment provided by the rapporteur Member State Hellas and co-rapporteur Member State Poland for the active substance 2,4-D (March 2014)

² Bridging Report. Environmental fate. 2,4-dichlorophenoxy acetic acid (2,4-D Acid) and 2,4-dichlorophenoxy 2-ethylhexyl ester (2,4-D 2-EHE) (Herbicide). Rapporteur Member State: Greece (September 2018).



Data on soil degradation is presented below.

Table 8.3-1: Summary of aerobic degradation half-lives of 2,4-D EHE in laboratory soils (Bridging Report regarding 2,4-D acid and 2,4-D 2-EHE, 2018)

2,4-D 2-EHE	Aerobic conditions						
Soil type	X ³	pH	t. °C / % MWHC	DT ₅₀ /DT ₉₀ (days)	DT ₅₀ (d) 20 °C pF2/10kPa	St. (r ²) X ²	Method of calculation
Silt Loam Chelmorton		6.2	20 °C / pF2	<0.1/0.8	<0.1	3.31	FOMC
Clay loam South Witham		6.9	20 °C / pF2	<0.1/0.5	<0.1	0.69	FOMC
Loamy sand Speyer 2.2		5.5	20 °C / pF2	0.1/3.3	0.1	2.37	FOMC
Sandy loam Speyer 5M		7.3	20 °C / pF2	0.1/1.2	0.1	2.16	DFOP
Geometric mean/median					0.1		

2,4- D

The route and rate of degradation under aerobic conditions was investigated in four soils (pH [H₂O]: 6.2 - 7.8) at 20°C and in one soil (pH [H₂O]: 7.4) at 25°C (submitted for the first EU approval). 2,4-D exhibited low to moderate persistence in these studies. The degradation of 2,4-D resulted in the formation of a major metabolite, 2,4-DCA (max 15 % AR), and a minor non-transient metabolite, 2,4-DCP, that need to be addressed for potential groundwater contamination. These metabolites exhibited moderate or low to moderate persistence in soil (FOCUS, 2006). Non-extractable residues amounted to 58 % AR and the amount of volatiles collected in alkaline trap (presumed to be CO₂) accounted for a maximum of 49 % AR.

³ X This column is reserved for any other property that is considered to have a particular impact on the degradation rate.

Summary of the route of degradation of 2,4-D (EFSA Journal 2014;12(9):3812):

Mineralization after 100 days:

Non-extractable residues after 100 days:

Metabolites requiring further consideration:

28-49 % after 26 d, ¹⁴ C-label (n = 4)
33-58 % after 26 d, ¹⁴ C-label (n = 4)
2,4-DCP – 8.7 % at 10 d (n = 4)
2,4-DCA – 15 % at 17 d (n = 4)

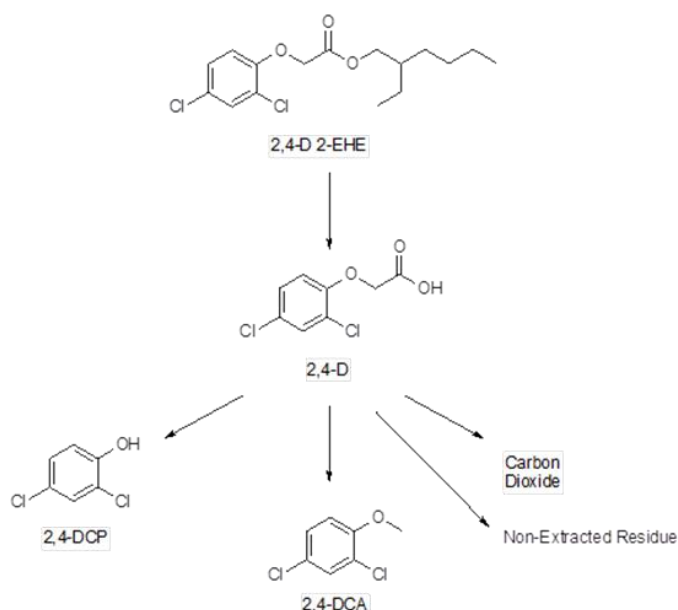


Figure 8.3-1: Proposed pathway of 2,4-D in soil under aerobic conditions

Table 8.3-2: Summary of aerobic degradation half-lives of 2,4-D in laboratory soils

Soil	pH (H ₂ O)	Temp. / Moisture	DT ₅₀ /DT ₉₀ [d]	Model	DT ₅₀ [d]	DT ₅₀ [d] 20°C pF2/10kPa	St. (r ²) X ²	Model
			Best-fit endpoints ^a		Modelling endpoints ^b			
Silt loam (Mississippi)**	7.4	25°C / 75% 1/3 bar ^c	ND	ND	58.9	94.6 ^d (66.6 ^e)	7.4	SFO
Clay loam (Fayette)	6.2	20°C / 50% MWHC	7.5 / 24.8	SFO	7.5	5.3	6.3	SFO
Clay loam (RefSol 03-G)	6.2	20°C / 50% MWHC	1.4 / 6.2	DFOP	1.6	1.2	6.3	SFO
Clay loam (RefSol 03-G)	6.2	10°C / 50% MWHC	4.9 / 16.3	SFO	–	–	–	–
Sandy loam (Site E1)	6.7	20°C / 50% MWHC	2.0 / 6.9	DFOP	2.2	1.6	4.5	SFO
Sandy loam (Site I2)	7.8	20°C / 50% MWHC	1.9 ^f / 6.2 ^f	SFO ^f	2.0	1.8	7.8	SFO
Geometric mean					2.66	4.4 (EU agreed) 4.14 (using normalised DT ₅₀ in Mississippi soil)		

^a as presented in RAR Addendum (2014), Vol. 3, Annex B.8

^b as presented in EFSA Journal 2014; 12(9): 3812

^c moisture content not reported in EFSA Journal (2014); presented value as per Cohen (1991)

^d normalised only for temperature

^e newly calculated value normalised for temperature and moisture (20°C, pF2) provided by the applicant; used in order to determine the modelling endpoint of 4.14 d

^f use of uncorrected data set: all data points included, ignoring that day 3 to day 26 samples display recovery levels

Moisture normalization of lab soil deg DT₅₀ for Mississippi soil

Studies presented in the EU renewal review were considered acceptable. However, the DT₅₀ resulting from soil Mississippi (Cohen, 1991) presented in the EFSA Journal (2014) was only normalised for soil temperature, not for soil moisture. A summary of the recalculated DT₅₀ normalised to soil temperature and moisture (20°C, pF2) performed by the applicant is presented below.

The soil moisture at study conditions for the “Mississippi” soil is given as 75% of the moisture content at 0.33 (p. 22, Cohen, 1991). No further irrigation had been applied during the study. The soil texture was determined as “Silt loam” according to USDA. Using FOCUS defaults for USDA Silt Loam texture the following moisture normalisation should be considered:

USDA Silt loam water content at 0.33 bar	21 %
USDA Silt loam water content at study conditions (e.g. 75% of water content at 0.33 bar)	= 0.75 x 21% = 15.75 %
USDA Silt loam water content at field capacity	26%
Factor for moisture normalisation	
$fw = (\text{water content in study} / \text{water content at field capacity})^{0.7}$	$fw = (15.75 / 26)^{0.7}$
DT ₅₀ (20°C) presented in EFSA Conclusion Report	94.6 d
DT ₅₀ (20°C, pF2)	= 94.6 x fw = 66.6 d

The applicant considers it more appropriate to use the fully normalised laboratory soil degradation DT₅₀ (66.6 days) for modelling purposes. The newly calculated endpoint used in PEC_{GW} and PEC_{SW} simulations is presented in the table above.

The data gap regarding potential pH-dependence of the degradation process of 2,4-D in soil identified during the renewal review has been addressed by the applicant: A new study has been performed (Crabtree, 2015) and a summary is presented in Appendix 4. The outcome of this study confirms that degradation of 2,4-D in soil is not pH-dependent.

Table 8.3-3: Summary of the rate of degradation of 2,4-DCP (laboratory studies) (EFSA Journal 2014;12(9):3812):

2,4-DCP	Aerobic conditions						
Soil type	pH	t. °C / % MWHC	DT ₅₀ / DT ₉₀ [d]	f. f. k _{dp} /k _f	DT ₅₀ [d] 20 °C pF2/10kPa	St. (r ²) X ²	Method of calculation
Clay loam (Fayette)	6.2	20 °C / 50 % MWHC	-		-		
Clay loam (RefSol 03-G)	6.2	20 °C / 50 % MWHC	15.5	1	11.1	6.3	HS
Sandy loam (Site E1)	6.7	20 °C / 50 % MWHC	6.2	1	4.4	9.2	SFO
Sandy loam (Site I2)	7.8	20 °C / 50 % MWHC	7.7	1	6.9	12.8	FOMC
Geometric mean/median			9.0		7.0 ^a		

a) According to FOCUS (2006) the DT₅₀ was back-calculated from DT₉₀/3.32 of the FOMC kinetic model and should be used for modelling.

Table 8.3-4: Summary of the rate of degradation of 2,4-DCA (laboratory studies) (EFSA Journal 2014;12(9):3812):

2,4-DCA	Aerobic conditions						
Soil type	pH	t. °C / % MWHC	DT ₅₀ /DT ₉₀ [d]	f. f. k _{dp} /k _f	DT ₅₀ [d] 20° C pF2/10kPa	St. (r ²) X ²	Method of calculation
Clay loam (Fayette)	6.2	20 °C / 50 % MWHC	-		-		
Clay loam (RefSol 03-G)	6.2	20 °C / 50 % MWHC	16.3		11.7	3.7	SFO
Sandy loam (Site E1)	6.7	20 °C / 50 % MWHC	13.7		9.8	6.3	SFO
Sandy loam (Site I2)	7.8	20 °C / 50 % MWHC	10.9		9.8	8.5	SFO
Geometric mean/median			13.4		10.4		

zRMS comments:

Soil degradation data for 2,4-D presented in Tables 8.3-2 to 8.3-4 are in general line with EU agreed endpoints reported in EFSA Journal 2014;12(9):3812. It is noted that in Table 8.3-2 the Applicant provided information on moisture of Mississippi soil taken from the study report. Degradation at 10°C reported in Table 8.3-2 is not reported in the LoEP and was thus struck through.

The Applicant normalised the DT₅₀ value in soil Mississippi for soil moisture since value reported in the EFSA Journal 2014;12(9):3812 was normalised for temperature only (an explanation was given that the soil moisture was not reported in the RAR, but it is not clear why this was not clarified in the course of the peer-review based on the data from the study report). Although additional normalisation generates endpoint deviating from the EU agreed value, it is noted that recalculation had only marginal impact on mean DT₅₀ value, since mean soil DT₅₀ of 4.4 days is reported in the LoEP, while recalculation resulted with DT₅₀ of 4.14 days. For this reason consideration of normalised DT₅₀ for Mississippi soil is accepted by the zRMS.

In order to address the data gap regarding the dependence between the degradation of 2,4-D and soil pH identified in the EFSA Journal 2014;12(9):3812, the Applicant provided study on degradation of 2,4-D in acidic soils (Crabtree, 2015). The study has been already evaluated in the course of several zonal evaluations of formulations containing 2,4-D, including products owned by ADAMA. Following conclusion has been provided by the zRMS (NL) in the Core Assessment, Part B, Section 5 for AG-D2-600 SL (September 2017):

The data gap regarding potential pH-dependence of the degradation process of 2,4-D in soil identified during the renewal review has been addressed by the applicant: A new study has been performed (Crabtree, 2015) and a summary is presented in Appendix 3. The outcome of this study confirms that degradation of 2,4-D in soil is not pH-dependent.

The evaluation of the study (Crabtree, 2015) by zRMS is presented in Appendix 3. ZRMS considers that the study followed current guidance (OECD guideline 307) and is acceptable .

Since the study was already agreed in the Central Zone, there was no need for its re-evaluation and conclusions of evaluation performed by the zRMS (NL) for AG-D2-600 SL are also applicable for this assessment in order to maintain consistent approach within the zone. Overall, results of the study by Crabtree (2015) confirm that degradation of 2,4-D does not depend on the soil pH and currently EU agreed DT₅₀ values are relevant for purposes of the exposure assessment.

The degradation data for 2,4-D EHE presented in Table 8.3-1 are in line with endpoints presented in the 2,4-D 2-EHE Bridging Report in area of efate (October 2018).

8.3.1.2 Clopyralid

Clopyralid metabolism in soil under dark aerobic conditions was investigated in three studies with a total of ten different soils. The ten soils covered a range of pH (5.6 – 8.3), clay contents (3% - 37%) and organic matter content (1.28% – 27.6%). Nine of the soils were incubated at 20°C, while one soil was incubated at 25°C. Additionally, three of the soils were tested at 10°C and at various moisture levels.

No degradation products of clopyralid that accounted for more than 10% AR were identified in soil under aerobic conditions.

Summary of the route of degradation of clopyralid (EFSA Conclusion (2018) 16(7):5389):

Mineralization after 100 days:	CO ₂ : 47.5 – 70.3% of AR after 90-92 days at 20°C, [2,6-pyridinyl- ¹⁴ C]-label (n=9)
Non-extractable residues after 100 days:	11.2 – 35.1% of AR after 90-92 days at 20°C, [2,6-pyridinyl- ¹⁴ C]-label (n=9)
Metabolites requiring further consideration:	None

Table 8.3-3: Summary of laboratory aerobic rates of degradation studies for clopyralid – (EFSA Conclusion (2018) 16(7):5389)

Soil type	Biomass mg C/100g	pH (H ₂ O)	t. °C / % MWHC	DT ₅₀ / DT ₉₀ [d]	DT ₅₀ [d] 20°C (Q ₁₀ =2.58) pF2/10kPa	St. [χ ²]	Method of calculation
Parabraunerde (silt loam)	47	7.7	20 / 18.63 ^a	44.4 / 147.3	34.2	6.796	SFO
Marcham (sandy clay loam)	170	8.3	20 / 20.19 ^a	34.5 / 114.7	32.4	5.478	SFO
Castle Rising (sandy loam)	313	8.0	20 / 65.13 ^a	26.3 / 87.3	26.3	8.284	SFO
Speyer 2.1 (sand)	NA	6.5	20 / 12.58 ^a	64.6 / 214.6	64.6	5.466	SFO
Speyer 2.2 (sand)	110	6.3	20 / 18.56 ^a	16.2 / 53.8	16.2	7.78	SFO
Marshall county (silt loam)	11.92	6.0	25 / 23.42 ^b	8.6 / 28.5	11.6	6.49	SFO
A (sandy loam)	33.2	6.2	20 / 24.28 ^c	16.5 / 54.8	16.5	4.856	SFO
B (clay loam)	78.2	7.6	20 / 28.05 ^c	23 / 76.4	23.0	6.767	SFO
C (clay loam)	48.5	5.6	20 / 48.17 ^c	4.9 / 16.2	4.9	12.73	SFO
D (loam)	70.9	7.5	20 / 35.30 ^c	9.8 / 32.4	9.8	10.17	SFO
Geomean/median			-	-	19.1	-	-
pH dependence			No				

- a) Reported soil moisture: 40% of maximum WHC
b) Reported soil moisture: 75% of 1/3 bar WHC
c) Reported soil moisture: 45% WHC

zRMS comments:

Soil degradation data for clopyralid presented in Table 8.3-3 are in line with the EU agreed endpoint reported in EFSA Journal 2018;16(7):5389.

8.3.1.3 Fluroxypyr and its metabolites

Fluroxypyr-meptyl exhibits very low persistence in soil under laboratory dark aerobic conditions at 20°C and quickly transforms to the active substance Fluroxypyr acid. Fluroxypyr acid is low to moderate persistent in soil under these conditions and degrades into two major metabolites: Pyridinol (max. 23.9 % after 28 d) and Methoxypyridine (max 38.2 % after 56 d). Unextractable residues were formed up to a maximum of 41 % AR and mineralization to CO₂ reached 65 % AR.

Summary of the route of degradation (aerobic) of Fluroxypyr and its metabolites (EFSA Journal 2011;9(3):2091) and confirmatory information, December 2014)

Mineralization after 100 days:

65 % after 101 days at 20°C, [¹⁴C-2,6 pyridine ring]-label (n=4)
 Up to 77 % after 365 days at 20°C, [¹⁴C-2,6 pyridine ring]-label (n=12)

Non-extractable residues after 100 days:

Up to 41 % after 14-28 days at 20°C, [¹⁴C-2,6 pyridine ring]-label (n=12; max. value)
 13-42.6 % at the end of the studies at 20°C, [¹⁴C-2,6 pyridine ring]-label (n=12)

Relevant metabolites above 10 % of a.i.: name and/or code
 % of applies rate (range and maximum)

Pyridinol (4-amino-3,5-dichloro-6-fluoro-2-pyridinol) – max. 23.9% at DAT 28, 20°C, [¹⁴C-2,6 pyridine ring]-label (n=12)
 Second maximum, at about 19% (for the Pyridinol formed from Methoxypyridine and remaining of Pyridinol formed from Fluroxypyr) expected to occur around DAT 63 (confirmatory information)

Methoxypyridine (4-amino-3,5-dichloro-6-fluoro-methoxypyridine) – max. 38.2 % at DAT 56, 20°C, [¹⁴C-2,6 pyridine ring]-label (n=12)

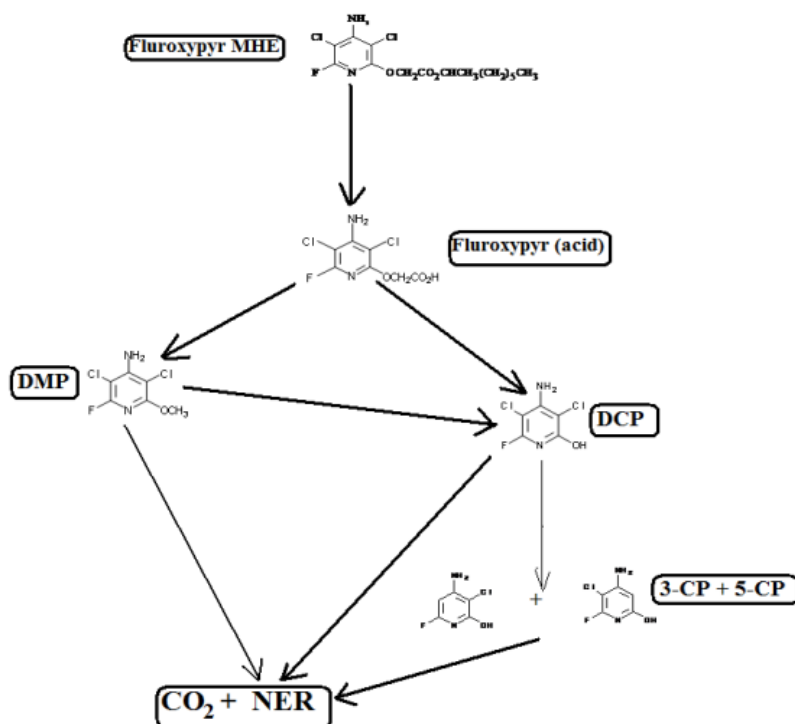


Figure 8.3-2: Degradation pathway for Fluroxypyr-meptyl in soil under aerobic conditions (confirmatory information, December 2014)

The rate of degradation was investigated in 12 – 14 laboratory soils for Fluroxypyr-meptyl, Fluroxypyr-meptyl + acid and its metabolites Methoxypyridine and Pyridine. The geomean values (in case of Fluroxypyr acid the median value) were used for the PEC_{SW} and PEC_{GW} calculations. For detailed information please refer to the following tables.

Table 8.3-4: Summary of aerobic degradation rates for Fluroxypyr-meptyl - laboratory studies (EFSA Journal 2011;9(3):2091)

Soil type	pH	Temp. [°C] / actual soil moisture [%]	DT ₅₀ / DT ₉₀ [d]	DT ₅₀ [d] 20°C (Q ₁₀ =2.58) pF2/10kPa	χ ²	Method of calculation
Sandy loam	7.7	20/33.4	1.8/6.0	1.8	23.6	SFO
Clay loam	7.7	20/23.8	0.8/2.7	0.8	18.5	SFO
Silty clay loam	8.1	20/19.2	1.5/5.0	1.5	36.6	SFO
Loamy sand	6.7	20/23.4	1.3/4.3	1.3	24.7	SFO
Silty clay loam	5.9	26/20.0	0.3/1.0	0.5	7.4	SFO
Sandy loam	7.5	26/6.4	0.3/1.0	0.5	3.1	SFO
Clay loam	6.8	26/21.0	0.4/1.3	0.7	8.4	SFO
Clay	7.0	26/19.1	0.5/1.7	0.9	16.6	SFO
Clay loam	6.1	25/15.8	0.7/2.3	1.1	10.3	SFO
Clay loam	7.7	25/12.8	0.9/3.0	1.4	10.9	SFO
Silty clay loam	7.9	25/13.6	0.7/2.3	1.1	0.9	SFO
Loamy sand	5.7	25/9.6	0.9/3.0	1.4	2.6	SFO
Geomean/median			0.7/2.8**	1.0	13.6**	

* Values normalised only for the temperature using Q₁₀ = 2.58

** Arithmetic mean

Table 8.3-5: Summary of aerobic degradation rates for fluroxypyr-meptyl + acid - laboratory studies (EFSA Journal 2011;9(3):2091)

Soil type	pH	Temp. [°C] / actual soil moisture [%]	DT ₅₀ / DT ₉₀ [d]	DT ₅₀ [d] 20°C (Q ₁₀ =2.58) pF2/10kPa	χ ²	Method of calculation
Sandy loam	7.7	20/33.4	10.8/35.9	10.8	10.7	SFO
Clay loam	7.7	20/23.8	7.2/23.9	6.4	7.7	SFO
Silty clay loam	8.1	20/19.2	12.7/41.2	9.3	15.8	SFO
Loamy sand	6.7	20/23.4	7.8/25.9	7.8	8.5	SFO
Silty clay loam	5.9	26/20.0	12.8/42.5	17.0	2.5	SFO
Sandy loam	7.5	26/6.4	30.2/100.3	25.1	4.1	SFO
Clay loam	6.8	26/21.0	14.4/47.8	20.9	9.5	SFO
Clay	7.0	26/19.1	8.8/29.2	8.1	5.8	SFO
Clay loam	6.1	25/15.8	20.3/67.4	21.8	8.0	SFO
Clay loam	7.7	25/12.8	2.9/9.6	2.7	10.2	SFO
Silty clay loam	7.9	25/13.6	6.90/22.91	6.3	6.52	SFO
Loamy sand	5.7	25/9.6	17.1/56.8	21.1	13.1	SFO
Loamy sand	n.d. ¹⁾	25/9.6	41.8/138.8 ²⁾	38.4 ²⁾	6.80	SFO
Sandy loam	n.d. ¹⁾	25/10.8	49.4/163.2 ²⁾	39.6 ²⁾	6.38	SFO
Geomean/median			13.3/44.0	13.1/13.9	8.26	

¹⁾ Not determined, only range of pH -5.5 – 7.5, given in the study report

²⁾ Kinetic endpoint for Fluroxypyr acid only

Table 8.3-6: Summary of aerobic degradation rates for pyridinol- laboratory studies (EFSA Journal 2011;9(3):2091 and confirmatory information, December 2014)

Soil type	pH	Temp. [°C] / actual soil moisture [%]	DT ₅₀ / DT ₉₀ [d]	f.f. k _{dp} /k _f	DT ₅₀ [d] 20°C (Q ₁₀ =2.58) pF2/10kPa	χ ²	Method of calculation
Sandy loam	7.7	20/33.4	16.3/54.2	0.184 ¹⁾	16.3	28.9	SFO
Clay loam	7.7	20/23.8	15.7/52.1	0.089 ¹⁾	14.0	26.6	SFO
Silty clay loam	8.1	20/19.2	17.2/57.1	0.152 ¹⁾	12.6	22.7	SFO
Loamy sand	6.7	20/23.4	4.1/13.6	0.427 ¹⁾	4.1	10.1	SFO
Silty clay loam	5.9	26/20.0	43.8/145.5	0.358 ¹⁾	58.0	17.1	SFO
Sandy loam	7.5	26/6.4	13.8/45.8	0.250 ¹⁾	11.5	20.6	SFO
Clay loam	6.8	26/21.0	17/56.5	0.299 ¹⁾	24.6	18.7	SFO
Clay	7.0	26/19.1	9.2/30.6	0.360 ¹⁾	8.4	13.6	SFO
Clay loam	6.1	25/15.8	54.5/181.0	0.666 ¹⁾	58.7	7.1	SFO
Clay loam	7.7	25/12.8	12/39.8	0.280 ¹⁾	11.2	18.4	SFO
Silty clay loam	7.9	25/13.6	14.7/48.8	0.117 ¹⁾	13.5	11.2	SFO
Loamy sand	5.7	25/9.6	85.2/283.0	0.254 ¹⁾	105.4	26.8	SFO
Sandy loam	5.9	20/50	14.72/48.91	0.664 ²⁾	14.72	10.98	SFO
Loamy sand	7.8	20/50	11.84/39.34	0.760 ²⁾	11.84	10.52	SFO
Silt loam	6.3	20/50	29.06/95.53	0.727 ²⁾	29.06	11.31	SFO
Loam	5.8	20/50	10.84/36.00	0.740 ²⁾	10.84	21.48	SFO
Geomean/median		--	17.6/58.0 (geomean)	0.286 ¹⁾ 0.723 ²⁾	17.6 (geomean) 13.8 (median)	--	--

¹⁾ from Fluroxypyr acid, an arithmetic mean

²⁾ from Methoxy pyridine, an arithmetic mean

Table 8.3-7: Summary of aerobic degradation rates for methoxypyridine- laboratory studies (EFSA Journal 2011;9(3):2091 and confirmatory information, December 2014)

Soil type	pH	Temp. [°C] / actual soil moisture [%]	DT ₅₀ / DT ₉₀ [d]	f.f. k _{dp} /k _r	DT ₅₀ [d] 20°C (Q ₁₀ =2.58) pF2/10kPa	χ ²	Method of calculation
Sandy loam	7.7	20/33.4	64.5/214.2	0.183	65.4	57.0	SFO
Clay loam	7.7	20/23.8	208.9/692.3	0.160	185.5	27.0	SFO
Silty clay loam	8.1	20/19.2	743.1/2468.5	0.119	542.5	30.3	SFO
Loamy sand	6.7	20/23.4	16.7/55.5	0.118	16.7	16.2	SFO
Silty clay loam	5.9	26/20.0	110.5/367.1	0.149	146.4	10.5	SFO
Sandy loam	7.5	26/6.4	142.2/472.4	0.115	118.0	11.9	SFO
Clay loam	6.8	26/21.0	801.7/2663.2	0.420	1160.9	12.8	SFO
Clay	7.0	26/19.1	295.9/983.0	0.286	271.7	17.5	SFO
Clay loam	6.1	25/15.8	>1000/>3322 ¹⁾	0.221	1000 ²⁾	--	SFO
Clay loam	7.7	25/12.8	47.8/158.8	0.317	44.5	9.7	SFO
Silty clay loam	7.9	25/13.6	101.0/335.5	0.201	92.7	14.9	SFO
Loamy sand	5.7	25/9.6	196.7/653.4	0.126	243.3	6.4	SFO
Sandy loam	5.9	20/50	4.63/37.91	--	17.86	8.81	DFOP/ slow phase DFOP
Loamy sand	7.8	20/50	6.72/61.40	--	30.40	5.21	DFOP/ slow phase DFOP
Silt loam	6.3	20/50	12.23/11787	--	49.16	8.29	DFOP/ slow phase DFOP
Loam	5.8	20/50	24.72/10292	--	33.65	2.48	DFOP/ slow phase DFOP
Geomean/median	--	--	70.8/291.0 (geomean)	0.201 ³⁾	111.11 (geomean) 105.35 (median)	--	--

¹⁾ Values excluded from calculating the mean values

²⁾ FOCUS default value

³⁾ Arithmetic mean

zRMS comments:

Soil degradation data for fluroxypyr presented in Tables 8.3-4 to 8.3-7 are in line with the EU agreed endpoints reported in in EFSA Journal 2011;9(3):2091 and additional data evaluated in Fluroxypyr Addendum to Vol 3: Confirmatory Information (December 2014).

8.3.2 Anaerobic degradation in soil (KCP 9.1.1.1)

Refer to the respective published information available from the EU evaluations for the 3 actives. No further metabolites than those cited for aerobic conditions need to be considered for the risk assessment from anaerobic soil degradation.

Studies on anaerobic degradation in soil with the formulation were not performed, since it is possible to extrapolate from data obtained with the active substances.

zRMS comments:

Respective information on anaerobic degradation of particular active compounds in soil as provided in the EFSA peer-review reports is presented by the zRMS below:

2,4-D

The degradation of 2,4-D under anaerobic conditions (pH 5.8 – 8.1) was investigated in four soils. Under these conditions 2,4-D exhibited moderate persistence ($DT_{50} = 22 - 38$ days) and two major metabolites were formed: 2,4-DCP (max. 38 % AR) and 4-CP (max. 33 % AR). According to information available in EFSA Journal 2014;12(9):3812, some MS may consider metabolite 4-CP as relevant for the exposure assessment.

Clopyralid

Anaerobic soil degradation data for clopyralid according to the EU agreed endpoints as reported in EFSA Journal 2018;16(7):5389 is longer than a year and no major metabolites were detected.

Fluroxypyr

In anaerobic soil degradation data for fluroxypyr according to EFSA Journal 2011;9(3):2091, the two metabolites 3-CP and 5-CP (the two mono dechlorinated fluroxypyr pyridinols) were identified at overall levels above 5%. The separation of these two metabolites was not possible. It is assumed that the level for each of these separated metabolites would be below 5% AR and therefore would not need further assessment.

8.4 Field studies (KCP 9.1.1.2)

The field dissipation rates of the active substances were evaluated for Annex I Inclusion. Additional data was not required as a result of the review. No additional studies have been performed.

8.4.1 Soil dissipation testing on a range of representative soils (KCP 9.1.1.2.1)

8.4.1.1 2,4-D and its metabolites

Field studies are not triggered in the EU unless the DT_{50} values derived under laboratory conditions at 20°C are more than 60 days. The results of aerobic laboratory degradation studies of 2,4-D showed DT_{50} values predominantly below this threshold value. Only the DT_{50} derived from the “Mississippi” soil that was excluded from the application for renewal of the active substance (2,4-D) by the applicant resulted in a value slightly above 60 days (66.6 d).

A field dissipation study was reported and assessed to be acceptable during the 2001 evaluation, with 2,4-D having a field DT_{50} of 4.6-17.2 days (average of 10.7 days; RAR (2013), Vol. 3, Annex B, Part B8).

Field data were not used in the assessment presented below; as a conservative approach, laboratory data (DT_{50} soil = 66.6 d) were used for PEC_S calculations of the parent as this value is higher than the actually measured DT_{50} (58.9 d), and hence represents a more conservative approach for the PEC_S calculations.

zRMS comments:

According to EFSA Journal 2014;12(9):3812, there are no reliable field degradation data for 2,4-D and its metabolites.

8.4.1.2 Clopyralid

Table 8.4-1: Field soil dissipation studies for clopyralid – (EFSA Conclusion (2018); 16(7):5389)

Soil type	Location	pH (H ₂ O)	Depth [cm]	DT ₅₀ actual [d]	DT ₉₀ actual[d]	St. [χ ²]	DT ₅₀ [d] Norm.	Method of calculation
Loamy sand (bare)	Bargstedt, DE	4.3	0-100	21	69.6	23.9	13	SFO
Loam (bare)	Wilson, UK	6.2	0-100	16.7	55.6	22.6	13.5	SFO
Silty clay loam (bare)	Sermaises, FR	7.0	0-100	16.3	54	19.3	7.5	SFO
Silty clay loam (bare)	Ansonville, FR	8.2	0-20	0.16	12.1	5.36	2.07	DFOP / SFO Norm
Clay loam (bare)	Mainbervilliers, FR	7.1	0-20	6.04	28.3	7.22	2.7	DFOP / SFO Norm
Silty clay loam (bare)	Oederquart, DE	7.5	0-20	16.2	53.9	12	5.69	SFO
Sandy clay loam (bare)	Middlefart, DK	7.5	0-20	23.7	78.7	13.1	8.46	SFO
Clay loam (bare)	Canals, ES	8.0	0-100	13.7	45.5	19.2	12.3	SFO
Silty clay loam (bare)	B. Württemberg, DE	7.4 ^b	0-100	10.2	33.9	7.94	9.34	SFO
Silt loam (bare)	B. d'Islemade, FR	7.3 ^b	0-100	9.11	30.3	17.6	7.41	SFO
Geomean/median							7.05	
pH dependence			No					

- a) Normalised using a Q10 of 2.58 and Walker equation coefficient of 0.7, values are DegT₅₀matrix
b) 0-30 cm

zRMS comments:

Field degradation data for clopyralid presented in Table 8.4-1 are in line with EU agreed endpoints reported in EFSA Journal 2018;16(7):5389.

8.4.1.3 Fluroxypyr MHE

Summary of the rate of degradation of Fluroxypyr-meptyl, Fluroxypyr acid, and Fluroxypyr-meptyl + acid (EFSA Journal 2011;9(3):2091):

DT₅₀ [d]:

Fluroxypyr acid

34-68 (Canada: 4 locations, UK: 3 locations)

Fluroxypyr-meptyl

< 3 (Canada: 4 locations, UK: 3 locations)

Fluroxypyr MHE + acid

11-38 (Canada: 4 locations, UK: 3 locations)

zRMS comments:

Field degradation data for fluroxypyr presented above are in line with EU agreed endpoints reported in EFSA Journal 2018;16(7):5379.

8.4.2 Soil accumulation testing (KCP 9.1.1.2.2)

Based on the results obtained with the active substances in the field residue trials, soil accumulation testing with the formulation is not required.

zRMS comments:

According to conclusions from the EU review of particular active compounds, soil accumulation testing for 2,4-D, clopyralid and fluroxypyr is not required.

8.5 Mobility in soil (KCP 9.1.2)

Studies on mobility in soil with the formulation were not performed, since it is possible to extrapolate from data obtained with the active substance.

8.5.1 Batch adsorption/desorption

8.5.1.1 2,4-D and its metabolites

Table 8.5-1: Agreed EU endpoints used in the evaluation (2,4-D; EFSA Journal 2014; 12(9): 3812)

Endpoint	2,4-D EHE	2,4-D ^a	2,4-DCP	2,4-DCA
K _{FOC} [L/kg]	n.a.*	58.6 ^b (EU agreed for surface water modelling) 24.0 (EU agreed for groundwater modelling)	512	1028
1/n	n.a.*	0.87 (EU agreed for surface water modelling) 0.83 (EU agreed for groundwater modelling)	0.88	0.92

* No values are available for 2,4-D EHE since it is transformed into the acid form in soil in few hours (DT₅₀ < 0.1 d)

^a incorrect values presented in the EFSA Journal (EFSA, 2014); only seven soils instead of 42 soils considered (RAR Addendum (2014), Vol. 3, Annex B.8)

^b median

The mobility in soil of 2,4-D and its metabolites was evaluated during the EU renewal review based on data requirements according to Commission Regulation (EU) No. 544/2011. No additional studies were performed. Summaries of available data for 2,4-D, 2,4-DCP and 2,4-DCA are provided in the following tables.

According to these studies 2,4-D may be expected to exhibit very high mobility in soil, while its metabolites 2,4-DCA and 2,4-DCP may be expected to exhibit low and low to medium mobility in soil, respectively.

Table 8.5-2: Adsorption parameters for 2,4-D (RAR Addendum (2014), Vol. 3, Annex B.8)

Study	Soil type	OC [%]	pH ^a [-]	K _d [L/kg]	K _F [L/kg]	K _{FOC} [L/kg]	1/n [-]
Yoder & Adusumilli (2011)	Clay loam (M800)	1.3	7.1	0.89	0.55	42	0.83
	Loamy sand (M801)	1.1	5.2	0.72	0.45	41	0.83
	Loam (M802)	2.5	5.0	0.69	0.42	17	0.82
	Silt loam (M803)	3.6	5.9	1.22	0.83	23	0.87
	Sandy loam (M804)	1.4	7.5	0.32	0.19	14	0.81
	Silt loam (M816)	0.9	5.9	0.37	0.21	23	0.78
	Clay loam (M822)	4.4	7.2	0.68	0.51	12	0.90
Swoboda (2006)	Loamy sand (Soil I)	6.1	6.18	3.45	4.5	56.62	0.85
	Silt loam ^b (Soil II)	1.7	5.56	0.76	2.42	44.85	0.59
	Loamy sand ^b (Soil III)	1.4	4.04	1.78	4.18	126.79	0.63
	Silt ^b (Soil VI)	1.5	5.65	0.76	3.21	50.38	0.56
	Silt loam (Soil V)	1.6	5.33	0.84	1.25	52.6	0.83
Fathulla (1996)	Sand (Plainfield)	0.46 ^d	5.6	- ^e	0.357	76	0.882
	Sandy loam ^b (California)	0.58 ^d	6.7	- ^e	0.167	70	0.677
	Loam (Mississippi)	0.23 ^d	7.0	- ^e	0.281	117	0.803
	Silty clay loam (Arizona)	0.87 ^d	7.9	- ^e	0.517	59	0.816
Barrusio &	Rendzina ^c (Lorraine)	6.8-9.5	7.0	2.5	3.09	30.67	0.78

Study	Soil type	OC [%]	pH ^a [-]	K _d [L/kg]	K _F [L/kg]	K _{FOC} [L/kg]	1/n [-]
	Humic Cambisols ^c (Jura I)	10.0 - 14.1	6.5 - 7.0	3.1	5.03	25.73	0.80
	Mollic Cambisols ^c (Jura II)	4.5 - 9.2	6.8 - 7.8	2.7	4.99	39.42	0.72
	Calcic Cambisols ^c (Ile de France)	0.9 - 1.4	7.0 - 7.5	0.3	0.54	26.09	0.78
	Dystric Cambisols ^c (Lorraine/Jura)	1.4 - 2.6	4.5 - 5.4	0.8	1.19	40	0.73
	Gleyic Cambisols ^{b,c} (Lorraine)	1.3 - 1.5	6.2 - 6.5	0.8	1.27	57.14	0.68
	Vertisols ^{b,c} (Martinique)	2.0 - 2.9	5.9 - 6.3	1.3	2.44	53.06	0.61
	Ferralsols ^c (Brazil)	1.2 - 4.7	4.2 - 5.5	9.2	16.81	311.86	0.75
	Andosols ^c (Martinique)	9.2 - 10.7	4.3 - 4.4	26.6	32.55	267.33	0.80
Cohen (1991)	Clay (Louisiana)	2.09 ^d	7.3	1.33	- ^e	58.1	0.83
Hermosin & Cornejo (1991)	Silty Clay Chromoxerert (0-10cm)	2.57 ^d	7.9	- ^e	0.82	31.91 ^{g,h}	0.91
	Clay Chromoxerert (10-20cm)	1.40 ^d	7.8	- ^e	0.37	26.46 ^{g,h}	0.99
	Clay ^b Chromoxerert (35-40cm)	1.10 ^d	7.7	- ^e	0.16	14.85 ^{g,h}	1.16
	Clay Pelloxerert I (0-20cm)	0.97 ^d	7.6	- ^e	0.62	68.79 ^{g,h}	0.90
	Clay Pelloxerert I (20-40cm)	0.60 ^d	7.6	- ^e	0.53	88.61 ^{g,h}	0.87
	Clay Pelloxerert I (120-150cm)	0.51 ^d	7.8	- ^e	0.18	35.26 ^{g,h}	0.95
	Clay Pelloxerert II (0-10cm)	0.98 ^d	7.7	- ^e	0.77	78.54 ^{g,h}	0.90
	Clay Pelloxerert II (90-100cm)	0.84 ^d	8.3	- ^e	0.30	35.65 ^{g,h}	1.02
	Clay loam Xerofluvent I (0-10 cm)	1.29 ^d	7.7	- ^e	0.77	59.79 ^{g,h}	0.96
	Sandy loam Xerofluvent II (0-10 cm)	0.71 ^d	7.2	- ^e	0.93	131.42 ^{g,h}	0.90
	Sandy loam Xerofluvent II (10-20 cm)	0.37 ^d	6.9	- ^e	0.78	382.42 ^{g,h}	0.97
	Sandy clay loam Xerofluvent III (0-20 cm)	2.73 ^d	6.3	- ^e	3.08	112.97 ^{g,h}	0.88
	Loam Eutrochrepts I (0-25 cm)	1.86 ^d	6.5	- ^e	1.43	77.03 ^{g,h}	0.90
	Loam Eutrochrepts I (50-100 cm)	0.68 ^d	6.8	- ^e	1.14	167.97 ^{g,h}	0.94
	Loam Haploxeralf (0-10 cm)	2.41 ^d	6.5	- ^e	1.64	68.11 ^{g,h}	0.93
	Clay loam Haploxeralf (10-40 cm)	0.47 ^d	6.5	- ^e	0.43	91.51 ^{g,h}	0.96
	Silty loam Haploxeralf (70-100 cm)	0.28 ^d	6.5	- ^e	0.41	147.25 ^{g,h}	0.82
	Silty loam Eutrochrepts II (0-25 cm)	2.52 ^d	7.8	- ^e	2.20	87.39 ^{g,h}	0.92
	Clay loam Eutrochrepts II (50-85 cm)	0.49 ^d	7.7	- ^e	0.68	139.56 ^{g,h}	0.96
	soil no. 20 ^f	-	-	-	2.23	116.85 ^h	0.95

Study	Soil type	OC [%]	pH ^a [-]	K _d [L/kg]	K _F [L/kg]	K _{FOC} [L/kg]	1/n [-]
Mc Coy & Lehmann (1988)	Silt loam (Illinois)	2.23	5.9	0.91	- ^e	41	0.896
	Silt loam ^b (California)	0.22	7.5	0.067	- ^e	31	0.632
	Loam (North Dakota)	3.08	6.8	1.1	- ^e	35	0.930
	Clay (Mississippi)	1.26	7	0.93	- ^e	74	0.795
Median					0.77	58.6	-
Arithmetic mean					-	-	0.87
pH dependence (yes or no)					No		

^a buffer solution = CaCl₂

^b soil excluded from selection of modelling input parameters since 1/n is out of acceptable range (0.7-1.1)

^c FAO classification

^d calculated; %OC = %OM / 1.724

^e not given in study report

^f no soil property data given in study report

^g corrected K_{FOC} values given in Massey (2006); Hermosin & Cornejo (1991) originally divided K_{OM} by 1.724 instead of multiplying

^h calculated; K_{FOC} = K_{FOM} × 1.724

Table 8.5-3: Soil adsorption / desorption data for 2,4-DCP taken from the EFSA Journal 2014;12(9):3812:

Soil Type	OC %	Soil pH (CaCl ₂)	K _d [mL/g]	K _{oc} [mL/g]	K _f [mL/g]	K _{foc} [mL/g]	1/n
Clay loam (M800)	1.3	7.1	18	1395	10	765	0.85
Loamy sand (M801)	1.1	5.2	9	799	4	405	0.80
Loam (M802)	2.5	5.0	21	823	16	655	0.94
Silt loam (M803)	3.6	5.9	33	906	25	690	0.94
Sandy loam (M804)	1.4	7.5	5	351	3	244	0.88
Silt loam (M816)	0.9	5.9	9	1043	5	574	0.83
Clay loam (M822)	4.4	7.2	14	318	11	250	0.93
Sand (Plainfield)	0.46	5.6				368	0.906
Silty clay loam (Arizona)	0.87	7.9				374	0.739
Median						405	
Geometric mean						444	
Arithmetic mean					44	512	0.868 0.88
pH dependence (yes or no)				No			

Table 8.5-4: Soil adsorption / desorption data for 2,4-DCA taken from the EFSA Journal 2014;12(9):3812:

Soil Type	OC %	Soil pH (CaCl ₂)	K _d [mL/g]	K _{oc} [mL/g]	K _f [mL/g]	K _{foc} [mL/g]	1/n
Clay loam (M800)	1.3	7.1	32	2465	18	1386	0.85
Loamy sand (M801)	1.1	5.2	23	2122	18	1630	0.93
Loam (M802)	2.5	5.0	28	1104	21	841	0.93
Silt loam (M803)	3.6	5.9	37	1017	27	746	0.93
Sandy loam (M804)	1.4	7.5	14	1004	12	836	0.95
Silt loam (M816)	0.9	5.9	13	1496	10	1137	0.92
Clay loam (M822)	4.4	7.2	47	1077	27	622	0.92
Sand (Plainfield)	0.46	5.6				436	0.955
Sandy loam (California)	0.58	6.7				667	0.987
Silty clay loam (Arizona)	0.87	7.9				616	0.809
Median						791	
Geometric mean						827	
Arithmetic mean					49	1028	0.917 0.92
pH dependence (yes or no)				No			

zRMS comments:

Soil mobility data for 2,4-D and its metabolites presented in Table 8.5-2 to 8.5-4 are in general in line with EFSA Journal 2014;12(9):3812.

It is noted that endpoints for 2,4-DCA and 2,4-DCP reported in Table 8.5-1 were agreed at the EU level for modelling purposes. However, values provided by the Applicant for 2,4-D were agreed only for surface water modelling, while for groundwater modelling lower K_{foc} (24 L/kg) has been agreed at the EU level together with 1/n of 0.83. Respective information has been added in Table 8.5-1.

It is noted that results reported in Table 8.5-2 for some soils are not presented in the LoEP, but all these data are provided in the revised Vol. 3, B.8 (January 2014) resulting with median K_{foc} agreed at the EU level for purposes of the surface water modelling.

In Tables 8.5-3 and 8.5-4 only soil sorption data for metabolites 2,4-DCA and 2,4-DCP resulting with mean K_{foc} values agreed at the EU level for modelling purposes are presented. However, in the LoEP results for additional soils are reported and these were included by the zRMS for completeness. The mean/median values were also corrected to comply with the LoEP, although these values were not used for exposure assessment at the EU level.

According to the Bridging Report for 2,4-D EHE (October 2018), no adsorption/desorption coefficients could be derived for the ester form of 2,4-D due to extremely rapid degradation.

8.5.1.2 Clopyralid

The batch soil adsorption/desorption studies indicate that clopyralid is very high mobile in soil.

Table 8.5-5: Soil adsorption/desorption for clopyralid – (EFSA Conclusion (2018); 16(7):5389)

Soil type	OC [%]	pH (CaCl)	K _d [mL/g]	K _{d,oc} [mL/g]	K _F [mL/g]	K _{F,OC} [mL/g]	1/n [-]
Merzenhausen	1.00	7.19	0.051	Not calculated	0.0057	0.57 ^a	0.9 ^b
Kaldenkirchen	0.98	5.34	0.048		0.0267	2.72 ^a	0.9 ^b
Lanna	2.06	6.62	0.151		0.0054	0.26 ^a	0.9 ^b
Overhetfeld	0.93	6.49	0.032		0.0125	1.34 ^a	0.9 ^b
Calke sandy loam	3.15	5.7	0.139 ^a	Not calculated	0.01	0.5	0.489
Longwoods sandy loam	3.13	7.4	0.069 ^a		0.08	2.5	0.9 ^b
LUFA 2.1 loamy sand	0.68	4.9	0.040 ^a		0.03	4.1	0.9 ^b
Quilen loam	4.02	6.9	0.356 ^a		0.16	3.9	0.804
DU-L-PF clay loam	6.47	6.3	0.282 ^a		0.14	2.1	0.829
Geometric mean (if not pH dependent)					0.026	1.41	
Arithmetic mean (if not pH dependent)							0.836
pH dependence					No		

a) Calculated and reported in M-CA, not in the study report

b) For modelling each soil was checked against OECD 106 reliability criterion (K_d > 0.1 for direct method and K_d > 0.3 for indirect method). Freundlich coefficient of soils not meeting the criteria was set to 0.9.

zRMS comments:

Soil mobility data for clopyralid presented in Table 8.5-5 are in line with the EU agreed endpoints reported in EFSA Journal 2018;16(7):5389

8.5.1.3 Fluroxypyr and its metabolites

Soil batch adsorption/desorption experiments indicate that Fluroxypyr-meptyl may be classified as immobile in soil, Fluroxypyr acid as high to very high mobile, Methoxypyridine as medium mobile. For Pyridinol adsorption to soil was found to be pH dependent. Pyridinol was found to be medium to high mobile in neutral and acidic soils and high to very high mobile in alkaline soils.

Table 8.5-6: Summary of soil adsorption/desorption for fluroxypyr-meptyl

Table 8.5-7: Summary of soil adsorption/desorption for fluroxypyr acid

Table 8.5-8: Summary of soil adsorption/desorption for pyridinol (including confirmatory information, December 2014)

[illegible]

Table 8.5-9: Summary of soil adsorption/desorption for methoxyppyridine

Soil type	OC %	Soil pH	Kd [mL/g]	Kdoc [mL/g]	Kf [mL/g]	Kfoc [mL/g]	1/n
Sandy clay loam	2.6	7.0	--	--	7.14	274.6	0.81
Loamy sand	2.0	5.8	--	--	9.28	464.0	0.96
Silty clay loam	3.8	7.4	--	--	8.93	235.0	0.84
Clay soil	1.9	7.1	--	--	5.93	312.0	0.75
Arithmetic mean					7.8	321.4	0.84
pH dependence			No				

In the course of matching the dataset of the original notifier of Fluroxypyr, new soil sorption data for the metabolite Pyridinol and Methoxyppyridine have been generated (Flörchinger 2010 a,b). Including these new data provides additional information, mainly on the nonlinearity of the sorption of the Pyridinol metabolite at basic soil pH ($\text{pH} \geq 7$), where no information was available from the EU pesticide risk assessment peer review process previously. Refined modelling endpoints for these metabolites, based on the combination of the data reviewed at EU level and the new data are given below.

Table 8.5-10: Pyridinol ($\text{pH} \geq 7$)

Soil type	OC %	Soil pH	Kfoc [mL/g]	1/n
Sandy clay loam	1.9	7.4	41.4	1
Silty clay loam	3.8	7.7	36.5	1
Clay loam	1.9	7.7	55.1	1
LUFA 2.3 sandy loam*	1.08	7.48	124.02	0.714
LUFA 6S*	1.75	7.75	68.50	0.562
Arithmetic mean			65	0.86

* Data matching study not reviewed on EU level (Flörchinger 2010a, Report No. S09-02569)

The adsorption/desorption studies of Flörchinger 2010a and b performed with the Fluroxypyr metabolites Pyridinol and Methoxyppyridine were provided in support of the assessment. Please refer to Appendix 2 and 3 for details.

zRMS comments:

Soil mobility data for fluroxypyr (meptyl and acid) and methoxyppyridine presented in Tables 8.5-6, 8.5-7 and 8.5-9 are in line with the EU agreed endpoints reported in EFSA Journal 2011;9(3):2091.

Soil mobility data for pyridinol reported in Table 8.5-8 are in line with the EU agreed endpoints reported in in EFSA Journal 2011;9(3):2091 and additional data evaluated in Fluroxypyr Addendum to Vol 3: Confirmatory Information (December 2014).

It is noted that for purposes of data matching the Applicant performed additional study on soil sorption of pyridinol in soil. Results of this study derived for $\text{pH} \geq 7$ were merged with EU agreed data in Table 8.5-10 above. First of all it should be noted that data matching studies are included in the evaluation only when they are considered adverse, which is not the case for pyridinol. Furthermore, generation of new active substance data should be avoided at the zonal level, unless critical for the exposure assessment, which is also not the case for pyridinol since sufficient data for the exposure assessment for pyridinol are available from the EU review and for this reason derivation of endpoints deviating from EU agreed values is not necessary, especially ADAMA has access to these data via the LoA from the authorisation holder. Furthermore, in Table 8.5-10 for LUFA 2.3 and LUFA 6S soil Kfoc values were considered, while EU agreed values indicated in Table 8.5-10 as Kfoc for sandy clay loam, silty clay loam and clay loam are actually the Kdoc values (see EFSA Journal 2011;9(3):2091 because no Kfoc values were obtained in these soils at the EU level. Since Kdoc and Kfoc values refer to different parameters (Kd is a distribution coefficient for adsorption, while Kf is a Freundlich adsorption coefficient), they should not be merged in order to calculate the mean value. For this reason values indicated by the Applicant as “refined modelling endpoints” are not correctly calculated and are thus struck through in Table 8.5-10 above.

8.5.2 Column leaching (KCP 9.1.2.1)

Not required for 2,4-D and clopyralid.

For Fluroxypyr column leaching study is available and presented in the EFSA Journal 2011;9(3):2091:

Elution (mm): 393 mL of distilled water
Time period (d): 2 d (48 hours)
Leachate: < 2 % of Fluroxypyr-meptyl, 18 - 74 % Fluroxypyr (acid) (a.s. equivalents)

zRMS comments:

Column leaching studies for 2,4-D and clopyralid were not required, information on column leaching studies for fluroxypyr is in line with conclusions derived at the EU level and presented in EFSA Journal 2011;9(3):2091.

8.5.3 Lysimeter studies (KCP 9.1.2.2)

As it is possible to extrapolate from data provided for the active substances, no further data are provided on the preparation.

2,4-D

A lysimeter study with 2,4-D was submitted for the first Annex I inclusion (Burgener, A., 1993). During two growing seasons, neither the parent compound nor its metabolites 2-CP, 4-CP or 2,4-DCP could be detected in any of the analysed leachates. No further studies have been conducted.

zRMS comments:

According conclusions from the EU review presented in EFSA Journal 2014;12(9):3812, the concentration of 2,4-D in leachate was lower than 0.1 µg/L and 2,4-D metabolites were not detected in the leachates.

Clopyralid

For clopyralid four lysimeter studies are performed in Germany and presented in the EFSA Conclusion (2018); 16(7):5389:

1) Germany, spring application of 150 or 200 g clopyralid/ha on oilseed rape + partly a second application of 125 g a.s./ha on winter wheat 1 year later. A total of 935 mm of precipitation was received in year 1 and 895.5 mm in year 2. 438 – 478 L of leachate was collected in year 1 and 411-437 L in year 2. In the first year of application the annual average concentration in leachate was < 0.050 µg/L a.s. equivalent, however occasional exceedances of 0.10 µg/L were detected. In the second year the annual average concentration in leachate was < 0.055 µg/L. In the soil cores the majority of radioactivity remained in the top layers of 0 – 40 cm. 11.49 – 12.38% of AR was found in soil 2 years after the single application. In the third year the annual average concentration in leachate was 0.001 – 0.019 µg/L. Maximum concentration of a.s. equivalents in leachate of the third year was 0.043 µg/L in the lysimeter, which received two applications. In the soil cores 9.82 – 10.11% of RA was found 2 years after the second application. The total recovery of RA in the three year monitoring period was 12.81 – 17.53% of the applied RA, considering the both applications.

2) Germany, winter oilseed rape, 120 or 141 g clopyralid/ha, 847 and 1011 mm rain in years 1 and 204 – 417 mm of leachate was collected in two lysimeters in years 1 and 2. In the lysimeter with higher application rate the annual average concentration of unidentified radioactivity was 0.127 µg/L equivalent in year 1, but taken over the whole study period of two years, the average concentration was 0.064 – 0.078 µg/L equivalent. Occasional exceedances of 0.1 µg/L were detected soon after the application in both lysimeters.

3) Germany, sugar beet, spring application of 118 g clopyralid/ha, 754 and 871 mm rainfall in years 1 and 2: 113 and 196 mm of leachate was collected in years 1 and 2. Annual average concentrations of clopyralid were 0.010 and 0.002 µg/L in years 1 and 2. Non-extractable radioactivity was also present in the leachate at annual average concentrations of 0.113 and 0.031 µg/L equivalent in years 1 and 2, respectively. Dissolved CO₂ was the major metabolite observed in the leachate. 24.6% of AR was measured in soil after 111 days, and after 2 years 13.2% of AR was recovered. (It was considered very unlikely that a single unknown substance would exceed an annual concentration of 0.1 µg/L.).

4) Germany, sugar beet, spring application of 99 or 185 g clopyralid/ha, ca 700 mm rainfall/year: In year 1 the leachate volume was 180 and 248 mm, and in year 2 70 to 79 mm. Annual average concentrations in the leachate were not calculated, but in individual samples the clopyralid concentrations up to 0.135 µg/L were detected occasionally. 26 months after application 20% of AR was recovered from the soil, majority of it in tillage layer (0 – 30 cm).

zRMS comments:

Information on lysimeter studies for clopyralid is in line with conclusions derived at the EU level.

Fluroxypyr

Two lysimeter studies for Fluroxypyr-meptyl were evaluated during the Annex I Inclusion. Fluroxypyr acid, Pyridinol and Methoxypyridine were detected in the leachate but at low levels. No leaching above 0.1 µg/L was observed in this study. No additional studies have been performed.

zRMS comments:

Information on lysimeter studies for fluroxypyr-meptyl is in line with conclusions derived at the EU level.

8.5.4 Field leaching studies (KCP 9.1.2.3)

No such studies are required. The groundwater assessment is considered to be addressed fully by the FOCUS groundwater modelling.

zRMS comments:

Information on field leaching studies for all active compounds is in line with conclusions derived at the EU level.

8.6 Degradation in the water/sediment systems (KCP 9.2, KCP 9.2.1, KCP 9.2.2, KCP 9.2.3)

Studies on degradation in water/sediment systems with the formulation were not performed, since it is possible to extrapolate from data obtained with the active substances.

8.6.1 2,4-D and its metabolites

A brief summary of the relevant water/sediment data of 2,4-D / 2,4-D EHE is given hereafter. The metabolism of 2,4-D EHE in the aquatic environment is described in the Bridging report (2018) prepared by the RMS Greece for the ester form of the 2,4-D.

In aquatic environment, 2,4-D EHE is rapidly hydrolysed to 2,4-D. Due to this quick transformation, photolysis does not play a major role on the degradation. Photolytic degradation in natural aqueous systems is negligible, with only 2,4-D acid and 2,4-DCA identified as major products in the irradiated sample of the photodegradation study.

A newly conducted water sediment study with 2,4-D 2-EHE confirms the rapid transformation to 2,4-D in

water and sediment. Thus, even if 2,4-D EHE reaches sediment in natural systems it will be transformed quickly to the acid. In conclusion, RMS agrees that the rapid dissipation of the ester, from the two tested water/sediment systems, is clearly demonstrated (DT₅₀: 2.3 and 2.5 hours).

The behaviour of 2,4-D (acid) in the aquatic environment is summarised in the EFSA Journal 2014;12 (9): 3812. The endpoints presented in this document are shown in the following table:

Table 8.6-1: Summary of degradation in water/sediment of 2,4-D and 2,4-D EHE

2,4-D	Distribution (e.g. max in water 100 % after 0 d. Max. sed 24.7 % after 7 d)									
Water/sediment system	pH water phase	pH sed	t. °C	DT50 DT90 whole system	St. (r ²) X ²	DT50- DT90 water	St. (r ²) X ²	DT50- DT90 sed	St. (r ²) X ²	Method of calculation
Pond system (loamy sand)	6.5	6.4	20	18/60	2.6	12.6/41.9	4.0	9.8/32.6	8.6	SFO
Pond system (silt loam)	8.3	7.8	20	6.4/21.1	8.8	4.7/15.7	9.9	-	-	SFO
Pond system (silty clay loam)	6.9	7.8	25	(29/96.3) DT50 Norm 20 C = 52 d	-	-	-	-	-	SFO
Geometric mean/median				18.16		7.7		9.8		
2,4-D EHE	Distribution (e.g. max in water 66.8% at 0 d. Max. sed 48.6% at 0 d)									
Calwich Abbey (sandy silt loam)	7.4	7.4	20	2.5/8.2	11.4	3.1/10.2	19.4	1.9/6.3	5.7	SFO
Swiss lake (loamy sand)	6.1	6.6	20	2.3/7.5	17.1	2.4/8.0	21.4	1.8/6.1	3.0	SFO
Geometric mean/median				2.4		2.7		1.85		

*DT50/90 in hours

Table 8.6-2: Summary of degradation in water/sediment of 2,4-DCP

2,4-DCP	Distribution (e.g. max in water 2.6 % after 26 d. Max. sed 31.8 % after 13 d)									
Water/sediment system	pH water phase	pH sed	t. °C	DT50- DT90 whole system	St. (r ²) X ²	DT50- DT90 water	St. (r ²) X ²	DT50-DT90 sed	St. (r ²) X ²	Method of calculation
Pond system (loamy sand)	6.5	6.4	20	1000 ^{a b}		-	-	197.2/654.7	5.8	SFO
Pond system (silt loam)	8.3	7.8	20	10.8 ^c		-	-	11/36.6		FOMC
Geometric mean/median				103.9		-		46.6		

^a No acceptable fit could be derived.

^b Default value

^c According to FOCUS (2006) the DT₅₀ was back-calculated from DT₉₀/3.32 of the FOMC kinetic model and should be used for modelling.

Table 8.6-3: Summary of observed metabolites

2,4-DCA Water/sediment system	Max. in water/sediment: 5.3% 32.1%	Evaluated on EU level: yes
2,4-DCP Water/sediment system	Max. in water/sediment: 32.1% 5.3%	Evaluated on EU level: yes

Table 8.6-4: Mineralization and non-extractable residues (2,4-D and 2,4-D EHE)

Water / sediment system	pH water phase	pH sed	Mineralization x % after n d. (end of the study).	Non-extractable residues in sed. max x % after n d	Non-extractable residues in sed. max x % after n d (end of the study)
2,4-D					
Pond system (loamy sand)	6.5	6.4	57.3 % after 105 days	26.2 % after 105 days	26.2 % after 105 days
Pond system (silt loam)	8.3	7.8	60.8 % after 105 days	27.9 % after 70 days	17 % after 105 days
Pond system (silty clay loam)	6.9	7.8	63.9 % after 46 days	15.6 % after 46 days	15.6 % after 46 days
2,4-D EHE					
Calwich Abbey (sandy silt loam)	7.4	7.4	<1 % after 120 days	1.5 % after 6 days	
Swiss lake (loamy sand)	6.1	6.6	<1 % after 120 days	1.6 % after 6 days	

zRMS comments:

Information on degradation of 2,4-D and its metabolites in water/sediment systems presented in Tables 8.6-1 to 8.6-2 is in line with EU agreed endpoints reported in EFSA Journal 2014;12(9):3812.

It is noted that information on maximum occurrence for metabolites in water/sediment system presented in Table 8.6-4 was switched between metabolites, so respective corrections were made by the zRMS.

The degradation data for 2,4-D EHE presented in Tables 8.6-1 and 8.6-4 are in line with endpoints presented in the 2,4-D 2-EHE Bridging Report in area of efate (October 2018).

8.6.2 Clopyralid

The behaviour of clopyralid in the aquatic environment is summarised in the EFSA Conclusion (2018); 16(7):5389. The endpoints presented in this document are shown in the following table:

Table 8.6-5: Summary of degradation in water/sediment of clopyralid

Parent Clopyralid	Distribution: max in water 100.13 % at 0d, max. sediment 19 % at 100 d (Loamy sand) Distribution: max in water 99.0 % at 0 d, max sediment 26 % at 100 d (Sandy silt loam)									
Water / sediment system	pH water phase	pH sed ^{a)}	t. °C	DT ₅₀ /DT ₉₀ whole sys.	St. (χ^2)	DT ₅₀ /DT ₉₀ water	St. (χ^2)	DT ₅₀ /DT ₉₀ sed	St. (χ^2)	Method of calculation
Loamy sand	6.5	5.5	20	>500 days	n/a	128	n/a	>500 days	n/a	First-order
Sandy silt loam	8.16	7.7	20	>500 days	n/a	167	n/a	>500 days	n/a	First-order
Geometric mean at 20°C ^{b)}						148				

^{a)} Measured in [medium to be stated, usually calcium chloride solution or water]

^{b)} Normalised using a Q10 of 2.58

Water / sediment system	pH water phase	pH sed	Mineralisation x % after n d. (end of the study).	Non-extractable residues in sed. max x % after n d
Loamy sand	6.5	5.5	2% after 100 d	5% at 100 d
Sandy silt loam	8.1	7.7	5% after 100 d	5% at 100 d

zRMS comments:

Information on degradation of clopyralid in water/sediment systems presented in Tables 8.6-5 is in line with EU agreed endpoints reported in EFSA Journal 2018;16(7):5389.

8.6.3 Fluroxypyr

The fate/behaviour in water/sediment of fluroxypyr was evaluated during the Annex I Inclusion. No additional studies have been performed. The EU-agreed endpoints (EFSA Journal 2011;9(3):2091) used in the evaluation for the risk assessments are listed in the table below and in Appendix 3 of this document.

For fluroxypyr (ester + acid) a DT₅₀ of 31.3 and 38.1 days was measured for the water system and 103.9 and 126.5 days for the sediment system. For pyridinol DT₅₀ of 27.8 and 35.5 days was measured for the water system and 92.3 and 118 days for the sediment system.

	Fluroxypyr MHE	Fluroxypyr acid
Hydrolytic degradation of the active substance and metabolites > 10 %	pH 5: DT ₅₀ > 454 days at 25°C pH 7: DT ₅₀ = 454 days at 25°C pH 9: DT ₅₀ = 3.2 days at 25°C	Stable (during study period of 30 days)
Photolytic degradation of active substance and metabolites above 10 %	DT ₅₀ not determined	$\lambda < 10 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ for $\lambda \geq 290\text{nm}$
Quantum yield of direct phototransformation in water at $\sum > 290 \text{ nm}$	Not applicable, the compound does not absorb the light at $\lambda \geq 290 \text{ nm}$	
Readily biodegradable (yes/no)	Study I (closed bottle test): no Study II (modified sturm test): no (22-39 % mineralisation after 28 days)	Study I (closed bottle test): no Study II (modified sturm test): no (7 % ThCO ₂)

Table 8.6-6: Summary of degradation in water/sediment of fluroxypyr MHE

Summary of degradation in water/sediment of fluroxypyr MHE										
Fluroxypyr MHE*	Distribution: in the system 25-50 % after 1 day, almost totally disappearing from the system after 7 days; max. in sediment: 50 % of the applied after 2 hours									
Water/sediment system	pH		t. °C	DT ₅₀ /DT ₉₀						Method of calculation
	water	sed.		w/s	χ ²	water	χ ²	sed.	χ ²	
Thornham ditch	7.5	--	18-23	38.1/126.5	10.04	--	--	--	--	SFO
Crimplesham ditch	3.1-3.8	--	18-23	31.3/103.9	9.55	--	--	--	--	SFO

* DT₅₀/DT₉₀ values for the whole system calculated for the sum of Fluroxypyr MHE and Fluroxypyr acid

Table 8.6-7: Summary of degradation in water/sediment of fluroxypyr acid

Table 6.6-7: Summary of degradation in water/sediment of fluroxypyr acid										
Fluroxypyr acid*	Distribution: in the system 88-93 % after 1-2 weeks, < 10 % after 13 weeks; up to 80 % in water phase, up to 20 % in sediment phase									
Water/sediment system	pH		t.°C	DT ₅₀ /DT ₉₀						Method of calculation
	water	sed.		w/s	χ ²	water	χ ²	sed.	χ ²	
Thornham ditch	7.5	--	18-23	38.1/126.5	10.04	--	--	--	--	SFO
Crimplesham ditch	3.1-3.8	--	18-23	31.3/103.9	9.55	--	--	--	--	SFO

* DT₅₀/DT₉₀ values for the whole system calculated for the sum of Fluroxypyr MHE and Fluroxypyr acid

Table 8.6-8: Summary of degradation in water/sediment of pyridinol

Pyridinol	Distribution: max. in the system 46 % after 8 weeks, mainly in water phase; max. observed in water/sediment system: 55.5 % (44 % in water phase, 11.5 % in sediment phase)									
Water/sediment system	pH		t.°C	DT ₅₀ /DT ₉₀						Method of calculation
	water	sed.		w/s	χ ²	water	χ ²	sed.	χ ²	
Thornham ditch	7.5	--	18-23	27.8/92.3	6.11	--	--	--	--	SFO
Crimplesham ditch	3.1-3.8	--	18-23	35.5 /118.0	2.86	--	--	--	--	SFO

Table 8.6-9: Summary of degradation in water/sediment of methoxypyridine

3-CP	Distribution: max. in the system 25.2 % after 4 weeks, mainly in water phase									
Water/sediment system	pH		t. °C	DT ₅₀ /DT ₉₀						Method of calculation
	water	sed.		w/s	χ ²	water	χ ²	sed.	χ ²	
Brewer Lake/ND/USA	8.2	8.1	25	--	--	--	--	--	--	--

zRMS comments:

Information on degradation of fluroxypyr and its metabolites in water/sediment systems presented in Tables 8.6-6 to 8.6-9 is in line with EU agreed endpoints reported in EFSA Journal 2011;9(3):2091.

8.7 Predicted Environmental Concentrations in soil (PEC_{SOIL}) (KCP 9.1.3)

The PEC_{soil} of 2,4-D, clopyralid and fluroxypyr in soil has been assessed with the software **ESCAPE ver. 2.0** (Estimation of Soil Concentration After Pesticide applications) taking into account the EFSA groundwater interception values and the DT₅₀ values agreed in the EU review. The following tables provide the input parameters that were used in the calculations. For a more detailed list of endpoints including the respective sources, please refer to Appendix 3.

For clopyralid, PEC_{SOIL} modelling is reported in Fortin-McCuaig (2021a) (KCP 9.1.3/01).

PEC_{soil} calculations using “ESCAPE v2.0”

The calculation is based on a realistic worst case modelling with specific information on soil cores and daily weather series. The predicted concentration of a plant protection product or its active ingredients in soil is calculated by assuming homogenous distribution of the maximal application rate over a soil horizon of 5 cm, respectively and a standard soil dry weight of 1.5 g/cm³.

$$PEC_i = \text{Application rate} \cdot \frac{1 - \text{interception}}{\text{soil dept } h \cdot \text{soil density}} \quad [\text{mg a.s./kg dw soil}]$$

Calculation of degradation

The degradation of the active ingredient is calculated using a 1st order decay function. The long-term PECs is calculated according to the formula

$$PEC_{LT} = PEC_i \cdot e^{\left(-t_{LT} \frac{\ln(2)}{DT_{50}}\right)}$$

with PEC_{i/LT} = initial/long-term concentration, DT₅₀ = half-life of dissipation and t = considered time period.

The maximum (‘moving window’) time weighted average (TWA) PEC values are found by calculating a set of TWA PECs over a time window that is moved along the time axis. The TWA over the moving window is calculated from the simple numerical average of the respective daily values.

In case of multiple applications, the maximal PEC is calculated according to the formula

$$PEC_{max} = PEC_s \cdot MAF \quad \text{and}$$

$$MAF = (1 - e^{(-nki)}) / (1 - e^{(-ki)})$$

With MAF the multiple application factor, n the number of applications, i the interval (in days), and k the first order dissipation constant derived from the DT₅₀.

8.7.1 Justification for new endpoints

Table 8.7-1: Justification for new endpoints for 2,4-D and metabolites

Endpoint	EU agreed endpoints	Endpoints used in risk assessment	Justification for deviation ^a
2,4-D EHE			
Molecular mass [g/mol]	333.26	333.26	
DT ₅₀ soil [days]	0.1	0.1	Endpoint from Bridging report from the ester prepared by RMS Greece
K _{oc} [mL/g]	Not applicable-	Not applicable	Not available due to very fast degradation in soil
Kinetic	SFO	SFO	
Max. occurrence in soil [%]	Not applicable	Not applicable	
2,4-D			
Molecular mass [g/mol]	221	221	
DT ₅₀ soil [days]	7.5	66.6	Highest normalised (20°C, pF2, SFO) EU lab value (i.e. Mississippi) ^b
K _{oc} [mL/g]	24	58.6	Median of 42 soils (in the LoE (EFSA, 2014) K _{FOC} and 1/n was incorrectly reported for only seven soils instead of 42; presented PEC _{sw} were however base on the correct data (RAR Addendum (2014), Part 4))
Kinetic	SFO	SFO	
Max. occurrence in soil [%]	Not applicable	Not applicable	
2,4-DCP			
Molecular mass [g/mol]	163	163	
DT ₅₀ soil [days]	14	14	Worst case persistence end-point (best-fit, DFOP) determined according to FOCUS kinetics (FOCUS 2006)
K _{oc} [mL/g]	512	512	Arithmetic mean
Kinetic	SFO	SFO	
Max. occurrence in soil [%]	8.7	8.7	(38% under anaerobic conditions)
Formation fraction [%]	--	100	Worst case default
2,4-DCA			
Molecular mass [g/mol]	177	177	
DT ₅₀ soil [days]	15.4	15.4	Worst case persistence end-point (best-fit, DFOP) determined according to FOCUS kinetics (FOCUS 2006)
K _{oc} [mL/g]	1028	1028	Arithmetic mean
Kinetic	SFO	SFO	
Max. occurrence in soil [%]	15	15	
Formation fraction [%]	--	100	Worst case default

^a Since Annex I inclusion new studies and/or information on the active substance have been generated and as a result there are new endpoints which are used in the risk assessment.

^b conservative approach; normalised data resulted in a longer max. DT₅₀ soil than the measured values (max. DT₅₀ soil = 58.9 d)

Table 8.7-2: Justification for new endpoints for clopyralid

Endpoint	EU-agreed endpoints	Endpoints used in risk assessment	Justification for deviation ^a
Molecular mass [g/mol]	191.96	192	
DT ₅₀ soil [days]	23.7	23.7	Highest, non-normalized field value (Denmark)
Koc [mL/g]	1.41	1.41	Geometric mean (n = 9)
Kinetic	--	SFO	
Max. occurrence in soil [%]	Not applicable	Not applicable	

^a Since Annex I inclusion new studies and/or information on the active substance have been generated and as a result there are new endpoints which are used in the risk assessment.

Table 8.7-3: Justification for new endpoints for fluroxypyr

Endpoint	EU agreed endpoints	Endpoints used in risk assessment	Justification for deviation ^a
Fluroxypyr-meptyl			
Molecular mass [g/mol]			
DT ₅₀ soil [days]	1.8	1.8	Highest normalised lab value
Koc [mL/g]	19550	19550	Arithmetic mean
Kinetic	SFO	SFO	
Max. occurrence in soil [%]	Not applicable	Not applicable	
Fluroxypyr acid ("parent compound")			
Molecular mass [g/mol]	255	255	
DT ₅₀ soil [days]	39.6	39.6	Highest normalised lab value
Koc [mL/g]	68	68	Arithmetic mean
Kinetic	SFO	SFO	
Max. occurrence in soil [%]	Not applicable	Not applicable	
Pyridinol			
Molecular mass [g/mol]	197	197	
DT ₅₀ soil [days]	105.4	105.4	Highest normalised lab value
Koc [mL/g]	44.3	44.3	Arithmetic mean at pH ≥ 7 (worst case)
Kinetic	SFO	SFO	
Max. occurrence in soil [%]	23.9	23.9	
Formation fraction [%]	28.6	28.6	
Methoxypyridine			
Molecular mass [g/mol]	211	211	
DT ₅₀ soil [days]	1160.9	1160.9	Highest normalised lab value
Koc [mL/g]	321	321	Arithmetic mean
Kinetic	SFO	SFO	
Max. occurrence in soil [%]	38.2	38.2	
Formation fraction [%]	20.1	20.1	

^a Since Annex I inclusion new studies and/or information on the active substance have been generated and as a result there are new endpoints which are used in the risk assessment.

zRMS comments:

Endpoints presented in Tables 8.7-1 to 8.7-3 are in general in line with EU endpoints reported in respective EFSA conclusions for particular active compounds, with exception of soil DT₅₀ of 66.6 days considered in soil exposure assessment performed by the Applicant for 2,4-D acid, while 7.5 days was used at the EU level, however, the rationale behind selection of the DT₅₀ of 7.5 days at the EU level is not fully clear to the zRMS since for purposes of the soil exposure assessment the longest un-normalised value should be used, which means that the DT₅₀ of 58.9 days derived for Mississippi soil should have been used.

The value used by the Applicant is the longest DT₅₀ obtained in Mississippi soil after normalisation for soil temperature and moisture. As already indicated in the zRMS comment in point 8.3.1.3 above, the DT₅₀ in Mississippi soil normalised only for temperature is reported in the EFSA Journal 2014;12(9):3812, since the moisture content was not given in the summary presented in the RAR. For purposes of zonal evaluation of ADM.3304.H.1.A the Applicant performed also normalisation for moisture based on information available in the study report and it is not clear why this was not done by the RMS in the course of the EU renewal process. Although this additional normalisation resulted with endpoint deviating from the EU agreed value, it was agreed by the zRMS as having only marginal impact on the geometric mean normalised DT₅₀ used for modelling purposes.

Since the DT₅₀ of 66.6 days considered in the Applicants' soil exposure calculations is longer than both, EU agreed DT₅₀ of 7.5 days and longest un-normalised DT₅₀ of 58.9 days, it is considered acceptable as representing worst case.

The input parameters considered in soil exposure assessment for 2,4-D EHE are in line with endpoints presented in the 2,4-D 2-EHE Bridging Report in area of efate (October 2018).

8.7.2 Active substance(s) and relevant metabolite(s)

Table 8.7-4: Summary of the PEC_{soil} calculations for single and multiple year application

Substance	PEC initial		21 day TWA	
	Single application	Persistence	Single application	Persistence
2,4-D EHE	1.2000	-	0.0082	-
2,4-D	0.8000	--	0.7186	--
2,4-DCP	0.0839	--	0.0832	--
2,4-DCA	0.0876	--	0.0870	--
Clopyralid	0.0640	--	0.0480	--
Fluroxypyr-meptyl	0.2304	--	0.0288	--
Fluroxypyr acid	0.1600	--	0.1339	--
Pyridinol	0.0197	0.0211	0.0196	0.0211
Methoxypyridine	0.0236	0.090 0.0664	0.0236	0.090 0.0664

Persistence in soil

Persistence in soil evaluation was performed in accordance with the recommendations of the “Guidance Document on persistence in soil”, from the Commission Services (9188/VI/97 rev. 8, July 12, 2000).

Persistence is defined as the residence time of an active substance, its metabolites, breakdown or reaction products in a defined compartment of the environment as outlined in Commission Regulation (EU) No. 546/2011 [EC, 2011] (provided for the implementation of Regulation 1107/2009 [EC, 2009]). Substances persistent in soil are those which exceed the limits defined in EU 546/2011, point 2.5.1.1 (part C). The limits are exceeded if the active substance, relevant metabolites, breakdown or reaction products

- (i) during tests in the field, persist in soil for more than one year (i.e. DT₉₀ > 1 year, and DT₅₀ > 3 month), or
- (ii) during laboratory tests, form non-extractable residues in amounts exceeding 70% of the initial rate after 100 days with a mineralisation rate of less than 5% in 100 days.

If these triggers are exceeded, it is to be scientifically demonstrated that under field conditions there is no accumulation in soil at such levels that unacceptable residues in succeeding crops and/or unacceptable phytotoxic effects on succeeding crops occur and/or that there is an unacceptable impact on the environment (EU 546/2011, part C, 2.5.1.1).

The active substances **2,4-D, clopyralid and fluroxypyr** do not exceed the trigger values set above. Accordingly, persistence in soil does not have to be taken into account.

For metabolite **pyridinol**, the worst case DT₅₀ > 90 days from laboratory studies (i.e. 105.4 days),

accordingly persistence needs to be taken into account and the PEC after multiple year applications was calculated with a $DT_{50} = 105.4$ days. For **methoxyppyridine**, the worst case DT_{50} would be 1160.9 days in laboratory studies. Therefore, persistence in soil was taken into account and the long-term PEC_{soil} was calculated.

Table 8.7-5: Long-term PEC_{soil} for fluroxypyr metabolites (single application + plateau)

Substance	Long-term maximum [mg/kg soil dry weight]
Pyridinol	0.0408 (0.0197 + 0.0211)
Methoxyppyridine	0.0900 (0.0236 + 0.0664)

zRMS comments:

Soil exposure reported in Table 8.7-4 above was corrected with consideration of the outcome of evaluation of calculations presented in points 8.7.2.1 to 8.7.2.3 below.

It is noted that PEC_{SOIL} values reported in Table 8.7-12 for fluroxypyr metabolites pyridinol and methoxyppyridine were $PEC_{SOIL,ACCU}$ and not $PEC_{SOIL,PLATEAU}$. Taking this into account, values reported in Table 8.7-5 were incorrectly calculated by summing up the $PEC_{SOIL,INI}$ with $PEC_{SOIL,ACCU}$. For this reason Table 8.7-5 was struck through and the risk assessment should be based on PEC_{SOIL} reported in Table 8.7-4.

8.7.2.1 2,4-D and its metabolites

For the **PEC_{soil} calculations** the applications with the highest rate reaching soil was chosen as representative worst case scenario. For the present calculations **cereals** was the application with the highest rate reaching soil (1125 g 2,4-D EHE and 750 g 2,4-D/ha) with 20 % crop interception.

Table 8.7-6: Input parameters related to application for PEC_{soil} calculations of 2,4-D

Use No.	1 (risk envelope)	2 (risk envelope)
Crop	Grassland	Cereals
Application rate (g as/ha)	2,4-D acid: 750 [§]	2,4-D acid: 750 [§]
Number of applications/interval	1	1
Crop interception (%)	60	20
Application timing (BBCH code)	Mar-Aug (BBCH 21-39)	Mar-June (BBCH 21-39)

§ The application rate of active substance 2,4-D is referring to 2,4-D-acid. The application rate in terms of 2,4-D-ethylhexylester (2,4-D-EHE) is 1.5 times the rate in terms of 2,4-D acid (i.e. 1125 g 2,4-D-EHE /ha)

Method of calculation

Application rate

Simulation

Date of application

DT_{50} soil

Single 1 st order kinetics (SFO)	
750 g 2,4-D/ha or 1125 g 2,4-D EHE/ha and 20 % interception (i.e. 2.0 L AG-CDF1-480 /ha)	
Parent and 2 metabolites in sequence	
01. March (worst case date)	
2,4-D EHE	$DT_{50} = 0.1$ days
2,4-D:	$DT_{50} = 66.6$ days
2,4-DCP:	$DT_{50} = 14.0$ days
2,4-DCA:	$DT_{50} = 15.4$ days

Table 8.7-7: PEC_{soil} for 2,4-D and its metabolites

Days after treatment		Predicted environmental concentration in soil (PEC _s) [mg a.i./kg soil at 5 cm]							
		2,4-D EHE		2,4-D		2,4-DCP		2,4-DCA	
		PEC	TWA	PEC	TWA	PEC	TWA	PEC	TWA
Initial		1.2000	--	0.8000	--	0.0839	--	0.0876	--
Short-term	1 d	0.0012	0.1730	0.7917	0.7959	0.0839	0.0839	0.0876	0.0876
	2 d	0.0000	0.0866	0.7835	0.7917	0.0838	0.0839	0.0875	0.0876
	4 d	0.0000	0.0433	0.7674	0.7836	0.0836	0.0839	0.0874	0.0876
Long-term	7 d	0.0000	0.0247	0.7438	0.7716	0.0830	0.0838	0.0869	0.0875
	14 d	0.0000	0.0124	0.6915	0.7445	0.0807	0.0836	0.0851	0.0873
	21 d	0.0000	0.0082	0.6429	0.7186	0.0775	0.0832	0.0826	0.0870
	28 d	0.0000	0.0062	0.5978	0.6940	0.0738	0.0826	0.0794	0.0866
	42 d	0.0000	0.0041	0.5167	0.6481	0.0658	0.0809	0.0721	0.0855
	50 d	0.0000	0.0035	0.4754	0.6237	0.0612	0.0798	0.0677	0.0846
	100 d	0.0000	0.0017	0.2825	0.4972	0.0373	0.0705	0.0426	0.0772

zRMS comments:

All endpoints considered by the Applicant in the soil exposure assessment for 2,4-D were agreed by the zRMS. For discussion on input parameters please refer to point 8.7.1 above.

Since in calculations for metabolites the worst case kinetic formation fractions of 1 were used, performed calculations cover also the exposure from formation of metabolite 2-DCP under anaerobic conditions with peak occurrence of 38% AR.

Due to DT₉₀ <365 days for all considered compound and single application during the season, accumulation of 2,4-D or its metabolites in soil is not expected and was thus not taken into account in performed evaluation.

Calculations were performed using risk envelope approach and cover both intended uses of ADM.3304.H.1.A in cereals and grassland.

The soil exposure for 2,4-D and its metabolites has been independently validated by the zRMS also using ESCAPE ver. 2. The same results were obtained and for this reason PEC_{soil} values reported in Table 8.7-7 are considered relevant for the soil risk assessment.

It is noted that in Appendix 4 soil exposure for anaerobic soil metabolite 4-chlorophenol was calculated with consideration of endpoints derived from the new studies submitted in order to address the data gap identified in EFSA Journal 2014;12(9):3812. Performed calculations were agreed by the zRMS and **PEC_{soil} of 0.192 mg pm/kg dws** may be used in the soil risk assessment for 4-CP.

For future evaluations the Applicant is kindly asked to provide soil exposure calculations for all relevant compounds in point 8.7 in order to facilitate the assessment by the zRMS and make the report more transparent..

8.7.2.1 Clopyralid

For the **PEC_{soil} calculations** the applications with the highest rate reaching soil was chosen as representative worst case scenario. For the present calculations **cereals** had the highest rate reaching soil (60 g Clopyralid/ha) with 20 % crop interception.

Table 8.7-8: Input parameters related to application for PEC_{soil} calculations of clopyralid

Use No.	2 (risk envelope)
Crop [-]	Cereals
Application rate [g a.s./ha]	60
Number of applications [-] / interval [d]	1 / –
Application date / BBCH growth stage [-]	01-May / BBCH 21-39
Frequency of application [-]	Annual
Crop interception [%]	20
Depth of soil layer [cm]	5
Models used for calculation	ESCAPE v2.0

Method of calculation
 Simulation
 DT₅₀ soil

Single 1st order kinetics (SFO)
 Parent only
 DT₅₀ = 23.7 days

Table 8.7-9: PEC_{soil} of clopyralid from the worst case application in cereals

Days after treatment		Predicted environmental concentration in soil (PEC _s) [mg a.i./kg soil at 5 cm]	
		Clopyralid	
		PEC	TWA
Initial		0.064	-
Short-term	1 d	0.062	0.063
	2 d	0.060	0.062
	4 d	0.057	0.060
Long-term	7 d	0.052	0.058
	14 d	0.043	0.053
	21 d	0.035	0.048
	28 d	0.028	0.044
	50 d	0.015	0.034
	100 d	0.003	0.021

zRMS comments:

Endpoints considered by the Applicant in the soil exposure assessment for clopyralid were agreed by the zRMS. For discussion on input parameters please refer to point 8.7.1 above.

Due to DT₉₀ <365 days and single application during the season, accumulation of clopyralid in soil is not expected and was thus not taken into account in performed evaluation.

Calculations were performed using risk envelope approach and cover both intended uses of ADM.3304.H.1.A in cereals and grassland.

The soil exposure for clopyralid has been independently validated by the zRMS using ESCAPE ver. 2. The same PEC_{SOIL} values were obtained and results provided in Table 8.7-9 may be used for the soil risk assessment purposes.

8.7.2.2 Fluroxypyr and its metabolites

For the **PEC_{soil} calculations** the applications with the highest rate reaching soil was chosen as representative worst case scenario. For the present calculations **cereals** had the highest rate reaching soil (150 g fluroxypyr/ha and 216 g fluroxypyr-meptyl/ha) with 20 % crop interception.

Table 8.7-10: Input parameters related to application for PEC_{soil} calculations of fluroxypyr and fluroxypyr-meptyl

Use No.	1 (risk envelope)	2 (risk envelope)
Crop	Grassland	Cereals
Application rate (g as/ha)	Fluroxypyr acid: 150 [#]	Fluroxypyr acid: 150 [#]
Number of applications/interval	1	1
Crop interception (%)	60	20
Application timing (BBCH code)	Mar-Aug (BBCH 21-39)	Mar-June (BBCH 21-39)

[#] The application rate of active substance fluroxypyr is referring to fluroxypyr acid. The application rate in terms of fluroxypyr-MHE is 1.44 times the rate in terms of Fluroxypyr acid (i.e. 216 g Fluroxypyr-MHE/ha)

Method of calculation

Application rate

Simulation

Date of application

DT₅₀ soil

Single 1 st order kinetics (SFO)	
216 g Fluroxypyr-meptyl/ha and 20 % interception (i.e. 2.0 L AG-CDF1-480 /ha)	
150 g Fluroxypyr acid/ha and 20 % interception (i.e. 2.0 L AG-CDF1-480 /ha)	
Fluroxypyr-meptyl: Parent only	
Fluroxypyr acid: parent and 2 metabolites in parallel	
01. March (worst case date)	
Fluroxypyr-meptyl:	DT ₅₀ = 1.8 days
Fluroxypyr acid:	DT ₅₀ = 39.6 days
Pyridinol:	DT ₅₀ = 105.4 days
Methoxyypyridine:	DT ₅₀ = 1160.9 days

Table 8.7-11: PEC_{soil} of Fluroxypyr and its metabolites from the worst case application in cereals

Days after treatment		Predicted environmental concentration in soil (PEC _s) [mg a.i./kg soil at 5 cm]							
		Fluroxypyr-meptyl		Fluroxypyr acid		Pyridinol		Methoxyypyridine	
		PEC	TWA	PEC	TWA	PEC	TWA	PEC	TWA
Initial		0.2304	--	0.1600	--	0.0197	--	0.0236	--
Short-term	1 d	0.1568	0.1936	0.1572	0.1586	0.0197	0.0197	0.0236	0.0236
	2 d	0.1067	0.1626	0.1545	0.1572	0.0197	0.0197	0.0236	0.0236
	4 d	0.0494	0.1190	0.1492	0.1545	0.0197	0.0197	0.0236	0.0236
Long-term	7 d	0.0156	0.0807	0.1415	0.1506	0.0196	0.0197	0.0236	0.0236
	14 d	0.0010	0.0431	0.1252	0.1419	0.0195	0.0197	0.0236	0.0236
	21 d	0.0001	0.0288	0.1108	0.1339	0.0192	0.0196	0.0236	0.0236
	28 d	<0.0001	0.0216	0.0980	0.1265	0.0189	0.0196	0.0235	0.0236
	42 d	<0.0001	0.0144	0.0767	0.1133	0.0182	0.0195	0.0235	0.0236
	50 d	<0.0001	0.0121	0.0667	0.1066	0.0177	0.0194	0.0234	0.0236
	100 d	<0.0001	0.0061	0.0278	0.0755	0.0142	0.0188	0.0229	0.0235

Table 8.7-12: Persistence PEC_{soil} for the Fluroxypyr metabolites Pyridinol and Methoxypyridine from the worst case application in cereals (assuming a tillage depth of 20 cm)

Days after treatment		Predicted environmental concentration in soil (PEC_s) [mg a.i./kg soil at 5 cm]			
		Pyridinol		Methoxypyridine	
		PEC	TWA	PEC	TWA
Initial		0.0211	--	0.0664	--
Short-term	1 d	0.0211	0.0211	0.0664	0.0664
	2 d	0.0211	0.0211	0.0664	0.0664
	4 d	0.0211	0.0211	0.0664	0.0664
Long-term	7 d	0.0211	0.0211	0.0664	0.0664
	14 d	0.0209	0.0211	0.0663	0.0664
	21 d	0.0207	0.0211	0.0663	0.0664
	28 d	0.0204	0.0211	0.0663	0.0664
	42 d	0.0197	0.0210	0.0662	0.0663
	50 d	0.0192	0.0209	0.0661	0.0663
	100 d	0.0157	0.0202	0.0656	0.0663

zRMS comments:

All endpoints considered by the Applicant in the soil exposure assessment for fluroxypyr and its metabolites were agreed by the zRMS. For discussion on input parameters please refer to point 8.7.1 above.

Due to $DT_{90} < 365$ days for fluroxypyr (acid and ester) and pyridinol as well as single application during the season, accumulation of these compounds in soil is not expected. However, the Applicant performed additional calculation in order to obtain $PEC_{SOIL, ACCU}$ for pyridinol.

Consideration of accumulation was required for methoxypyridine, which with $DT_{90} > 365$ days is considered to be persistent in soil.

Calculations were performed using risk envelope approach and cover both intended uses of ADM.3304.H.1.A in cereals and grassland.

The soil exposure for fluroxypyr and its metabolites has been independently validated by the zRMS also using ESCAPE ver. 2. The same initial PEC_{SOIL} values were obtained for all considered compounds. The $PEC_{SOIL, ACCU}$ for pyridinol were slightly lower comparing to these obtained by the Applicant and reported in Table 8.7-12. The accumulation PEC_{SOIL} for methoxypyridine derived by the zRMS (0.0474 mg pm/kg dws) was nearly 1.5 times lower comparing to $PEC_{SOIL, ACCU}$ of 0.0664 mg pm/kg dws presented in Table 8.7-12. Nevertheless, it is noted that the kinetic formation fraction of 0.201 considered in calculations for methoxypyridine is clearly lower than the peak occurrence of 38.2% observed in soil metabolism studies. Taking this into account, for precautionary reasons additional calculations were performed by the zRMS for methoxypyridine with assumption of the peak occurrence instead of kinetic formation fraction resulting with higher PEC_{SOIL} values:

- $PEC_{SOIL, INI}$: 0.0449 mg pm/kg dws
- $PEC_{SOIL, ACCU}$: 0.090 mg pm/kg dws,
- 21 d TWA $PEC_{SOIL, ACCU}$: 0.090 mg pm/kg dws.

Since consideration of the peak occurrence gives higher soil exposure for methoxypyridine, results obtained by the Applicant in Table 8.7-12 are struck through and results of the zRMS calculations should be used in the soil risk assessment. For fluroxypyr (acid and ester) and pyridinol PEC_{SOIL} values reported in Table 8.7-11 and 8.7-12 are relevant for the risk assessment purposes.

8.7.2.3 PEC_{soil} of AG-CDF1-480 EC

Table 8.7-13: PEC_{soil} for plant protection product AG-CDF1-480 EC (worst case scenario)

Application rate:	2.0 L AG-CDF1-480 EC/ha (20 % crop interception) in cereals
Density of the formulation [g/mL]:	1.095
Initial PEC_{soil} [mg/kg]:	2.336

zRMS comments:

PEC_{SOIL} value for the formulated product is agreed by the zRMS and may be used in the risk assessment for soil organisms.

8.8 Predicted Environmental Concentrations in groundwater (PEC_{GW}) (KCP 9.2.4)

The PEC in groundwater of the active substances 2,4-D, fluroxypyr and their metabolites has been assessed with standard FOCUS scenarios to obtain outputs from FOCUS PELMO 5.5.3, FOCUS PEARL 4.4.4 and MACRO 5.5.4. The PEC_{GW} for clopyralid was assessed for the standard FOCUS scenarios using the FOCUS models PELMO 6.6.4, PEARL 5.5.5 and MACRO 5.5.4.

PEC_{GW} results are presented below. FOCUS PELMO and PEARL modelling is reported in Ritzenthaler (2015a,b) for 2,4-D and fluroxypyr (KCP 9.2.4.1/01 and 02) and in Fortin-McCuaig (2021b) for clopyralid (KCP 9.2.4.1/03), which is presented in Appendix 2, while for the FOCUS MACRO model, exemplarily output files are given in Appendix 4.

In conclusion the calculated PEC_{GW} are well below the trigger value of 0.1 µg/L for 2,4-D, fluroxypyr and for their metabolites. No unacceptable leaching of 2,4-D, fluroxypyr and their metabolites is to be expected from the intended GAP use.

For clopyralid, the obtained results (Tables 8.8-12) show that there will be no substantial contamination of groundwater with the active substance following FOCUS PELMO, PEARL and MACRO calculations for established grassland. ~~In the case of cereals, all scenarios are below the trigger when a plant uptake factor of 0.5 is considered except for Hamburg and Jokioinen in PEARL for spring cereals~~

For winter cereals, if a plant uptake factor of 0 is considered, then, the scenario of Jokioinen remains above 0.1 µg/L in PELMO and Hamburg plus Okehampton in PEARL. However, all scenarios are below the trigger if biennial application is considered **or** annual applications either with a BBCH starting on 30 or with a reduced application rate of 1.5 L/ha.

For spring cereals, if a PUF of 0 is considered, the scenario of Jokioinen remains above 0.1 µg/L in PELMO and Hamburg as well as Jokioinen and Kremsmünster in PEARL. All scenarios are below the trigger in spring cereals if biennial application is considered (except Hamburg in PEARL) or a triennial application is respected.

~~A study was performed with clopyralid demonstrating that the substance is taken up by the roots and translocated into the plant tissues (see Gourlay (2021), KCP 9.2.4.1/04).~~

For 2,4-D EHE no PEC calculations were performed following the approach of the Bridging report (2018) prepared by the RMS Greece. The ester form of 2,4-D is transformed immediately in soil into the acid form (DT₅₀ of < 0.1 d). Therefore, the risk of groundwater contamination is negligible and can be extrapolated from the calculations performed for the acid form which are presented below.

zRMS comments:

Since the study on uptake of clopyralid by plants was not agreed for determination of the TSCF value, information on this refined parameter has been struck through in the text above. For discussion on TSCF for clopyralid, please refer to zRMS comments in point 8.8.1 below.

It is also noted that groundwater modelling for clopyralid was performed using the most recent versions of the modelling programs, required for submissions made from 1st of January 2022 and thus not applicable for exposure assessment for ADM.3304.H.1.A, for which dossier was submitted before that date. For discussion on this issue, please refer to point 8.8.2.2 below.

8.8.1 Justification for new endpoints

The following table provides the EU endpoints to be used for the PEC groundwater calculations. For a more detailed list of endpoints including the respective sources, please refer to Appendix 3.

Table 8.8-1: 2,4-D: Input parameters for PEC_{GW} calculation

Endpoint	EU agreed endpoints	Endpoints used in risk assessment	Justification for deviation
2,4-D			
Molecular Mass [g/mol]	221	221	
Water solubility [mg/L] (25°C)	24300	24300	
Saturated vapour pressure [Pa] (20°C)	9.9×10^{-6}	9.9×10^{-6}	
K _{OC} [mL/g]	24	58.6	Median of 42 soils (in the LoEP (EFSA, 2014) K _{FOC} and 1/n was incorrectly reported for only seven soils instead of 42; presented PEC _{SW} were however base on the correct data (RAR Addendum (2014), Part 4))
K _{OM} [mL/g]	--	34.0	K _{OM} = K _{OC} / 1.724
Freundlich sorption exponent (1/n)	0.83	0.87	Arithmetic mean of 42 soils (in the LoE (EFSA, 2014) K _{FOC} and 1/n was incorrectly reported for only seven soils instead of 42; presented PEC _{SW} were however base on the correct data (RAR Addendum (2014), Part 4))
pH-dependence	No	No	
DT ₅₀ soil [days]	4.4	4.14	Geometric mean, normalised lab (20°C, pF2); with “Mississippi” soil
Formation fraction	--	--	
Plant uptake	--	0	Worst case default
2,4-DCP			
Molecular Mass [g/mol]	163	163	
Water solubility [mg/L] (20°C)	4870	4870	
Saturated vapour pressure [Pa]	--	9.9×10^{-6}	Value from the parent
K _{OC} [mL/g]	512	512	Arithmetic mean
K _{OM} [mL/g]	--	297	K _{OM} = K _{OC} / 1.724
Freundlich sorption exponent (1/n)	0.88	0.88	Arithmetic mean
DT ₅₀ soil [days]	7.0	7.0	Geometric mean laboratory values, (normalised to pF2, 20°C with Q10 of 2.58)
Formation fraction	--	1 (from parent)	Worst case default
Plant uptake	--	0	Worst case default
2,4-DCA			
Molecular Mass [g/mol]	177	177	
Water solubility [mg/L] (20°C)	96.3	96.3	
Saturated vapour pressure [Pa]	--	9.9×10^{-6}	Value from the parent
K _{OC} [mL/g]	1028	1028	Arithmetic mean
K _{OM} [mL/g]	--	595	K _{OM} = K _{OC} / 1.724
Freundlich sorption exponent (1/n)	0.92	0.92	Arithmetic mean
DT ₅₀ soil [days]	10.4	10.4	Geometric mean laboratory values, (normalised to pF2, 20°C with Q10 of 2.58)
Formation fraction	--	1 (from parent)	Worst case default
Plant uptake	--	0	Worst case default

Table 8.8-2: Clopyralid: Input parameters for PEC_{GW} calculation

Endpoint	EU-agreed endpoints	Endpoints used in risk assessment	Justification for deviation
Molecular Mass [g/mol]	191.96	192	
Water solubility (20°C) [mg/L]	143 g/L	143 000 mg/L	
Saturated vapour pressure (25°C) [Pa]	1.36 x 10 ⁻³	0	Worst-case value
K _{oc} [mL/g]	1.41	1.41	Geometric mean (n = 9)
K _{OM} [mL/g]	--	0.818	K _{OM} = K _{OC} / 1.724
Freundlich sorption exponent (1/n) [-]	0.836	0.836	Arithmetic mean (n = 9)
pH-dependence [-]	No	No	
DT ₅₀ soil [days]	7.05	7.05	Geometric mean, field studies (n = 10, normalised to pF2, 20°C with Q10 of 2.58)
Formation fraction [-]	--	--	
Plant uptake [-]	--	Tier 1: 0	FOCUS recommendation, Worst case default
		Tier 2: 0.5	FOCUS recommendation for systemic compounds (see below)

With respect to the endpoint for the plant uptake factor, in the original renewal dossier of clopyralid, the notifier provided a specific plant uptake factor study for clopyralid (CA 6.2.1/4 — Gourlay, 2015) but its use to support the FOCUS default PUF for systemic substances of 0.5 was not accepted by the RMS due, in part, to the lack of any commonly agreed guideline for such an experiment at the time of submission. Since that time there has still been no finalisation of a commonly agreed (OECD guideline) approach, however there have been significant ongoing developments in the form of draft guidance and ring tests with the aim of finalising this guidance.

On this basis, ADAMA have therefore conducted a supplementary plant uptake study considering the draft guidance in place at the time of study conduct (draft guidance dated 21 December 2018). This study (Gourlay, 2019) is summarised in this dossier as KCP 9.2.4.1/04.

The results of this study clearly confirm the plant uptake demonstrated in the study performed by the original submitter for clopyralid and support the inclusion of the FOCUS default PUF of 0.5 for systemic substances as Tier 2 of the risk assessment.

Table 8.8-3: Fluroxypyr: Input parameters for PEC_{GW} calculation

Endpoint	EU agreed endpoints	Endpoints used in risk assessment	Justification for deviation
Fluroxypyr acid			
Molecular Mass [g/mol]	255	255	
Water solubility [mg/L] (20°C)	91	91	
Saturated vapour pressure [Pa] (20°C)	3.8×10^{-9}	3.8×10^{-9}	
K _{OC} [mL/g]	68	68	Arithmetic mean
K _{OM} [mL/g]	--	39	$K_{OM} = K_{OC} / 1.724$
Freundlich sorption exponent (1/n)	0.92	0.92	Arithmetic mean
pH-dependence	No	No	
DT ₅₀ soil [days]	13.9	13.9	Median laboratory values, (normalised to pF2, 20°C with Q10 of 2.58)
Formation fraction	0.513 (parent → sink)	0.513 (parent → sink)	
Plant uptake	--	0 0.5	FOCUS recommendation for systemic compounds
Pyridinol			
Molecular Mass [g/mol]	197	197	
Water solubility [mg/L] (20°C)	91	91	Value from the parent
Saturated vapour pressure [Pa]	3.8×10^{-9}	3.8×10^{-9}	Value from the parent
K _{OC} [mL/g]	1288 (pH < 7) 44.3 (pH ≥ 7) acid & neutral soils / alkaline soils	708 (pH < 7) 68.5* (pH ≥ 7)	Confirmatory information Arithmetic mean
K _{OM} [mL/g]	--	410.7 (pH < 7) 39.6 (pH ≥ 7)	$K_{OM} = K_{OC} / 1.724$
Freundlich sorption exponent (1/n)	0.84 (pH < 7) 1.00 (pH ≥ 7)	0.81 (pH < 7) 0.72 (pH ≥ 7)	Confirmatory information Arithmetic mean
DT ₅₀ soil [days]	18.4	17.6	Confirmatory information Geomean lab. values, (normalised to pF2, 20°C with Q10 of 2.58)
Formation fraction	0.286 (from parent)	0.286 (from parent) 0.723 (from methoxyppyridine)	Confirmatory information
Plant uptake	--	0	Worst case default
Methoxyppyridine			
Molecular Mass [g/mol]	211	211	
Water solubility [mg/L] (20°C)	91	91	Value from the parent
Saturated vapour pressure [Pa]	3.8×10^{-9}	3.8×10^{-9}	Value from the parent
K _{OC} [mL/g]	321	321	Arithmetic mean
K _{OM} [mL/g]	--	185	$K_{OM} = K_{OC} / 1.724$
Freundlich sorption exponent (1/n)	0.84	0.84	Arithmetic mean
DT ₅₀ soil [days]	170.4	111.11 (actually 111.14)	Confirmatory information Geomean lab. values, (normalised to pF2, 20°C with Q10 of 2.58)
Formation fraction	0.201 (from parent)	0.201 (from parent)	
Plant uptake	--	0	Worst case default

Please note:

- The calculations were performed for **Fluroxypyr acid** regarded as “parent” compound (recommendation of the EFSA Journal 2011;9(3):2091, p.68). There were no separate calculations for Fluroxypyr-meptyl. This was based on the assumption that in moist soil the ester

would rapidly and totally hydrolyse to the acid. Taking this into account, together with the high K_{OC} values for Fluroxypyr-meptyl (6200 – 43000) it was concluded that the probability of leaching of the ester to groundwater is minimal (the available results of lysimeter studies, where the ester was not detected, support this statement).

- According to the degradation scheme, Pyridinol is formed from the parent ($ff = 0.286$) and the metabolite Methoxypyridine ($ff = 0.723$). Because this was not calculable in FOCUS MACRO, two pathways were calculated and the concentrations added: Concentration Pyridinol resulted from Fluroxypyr + concentration Pyridinol resulted from Methoxypyridine (Methoxypyridine as parent with an application amount of: application amount Fluroxypyr * 0.201 (ff Fluroxypyr to Methoxypyridine)).

zRMS comments:

2,4-D

The input parameters for 2,4-D and its metabolites presented in Table 8.8-1 and considered by the Applicant for groundwater modelling are in general in line with EU agreed endpoints, with following exceptions:

- In the LoEP part reporting groundwater modelling K_{FOC} of 24 mL/g is indicated (being the arithmetic mean for 7 soils), while the Applicant considered K_{FOC} of 58.6 mL/g for PEC_{GW} calculation (being the median for 42 soils). It is, however, noted that at the EU level K_{FOC} of 24 mL/g was used for PELMO simulations performed by the Applicant for 2,4-D, while PEARL modelling was performed using the K_{FOC} of 58.6 mL/g. The median for 42 soils was also used for EU surface water modelling. It seems therefore that consideration of arithmetic mean for 7 soils was a mistake made by the Applicant for 2,4-D, not corrected or at least commented during the peer-review. Taking this into account, the K_{FOC} of 58.6 mL/g used by the Applicant is not considered to be deviation from the EU agreed endpoints and is accepted by the zRMS.
- The soil DT_{50} of 4.14 days was considered instead of the EU agreed of 4.4 days for 2,4-D, which is a result of consideration of the DT_{50} for Mississippi soil normalised for both, temperature and moisture (at the EU level value corrected for moisture only was used). As there is only marginal deviation from the EU agreed DT_{50} , it is not expected that it would have any impact on obtained results. For details of the normalisation procedure, please refer to point 8.3.1.1 of this report.

Clopyralid

The input parameters considered in Tier 1 groundwater modelling for clopyralid and presented in Table 8.8-2 are in line with EU agreed endpoints, with exception of vapour pressure set to 0, which is agreed by the zRMS as representing worst case. presented in EFSA Journal 2018;16(7):5389. For Tier 2 modelling the Applicant used refined TSCF of 0.5, indicating that results of the new study by Gourlay (2019) confirm that clopyralid is a systemic compound which is taken up by roots of wheat and barley. It should be, however, noted that a similar study by the same author was already evaluated at the EU level (Gourlay, 2015) and several uncertainties were noted, one of which was that due to the conditions, hydroponic systems promote uptake of the substance by plants which would be lower if plants were cultivated in soil, since adsorption of the substance to soil particles would reduce its availability. Taking this into account, the TSCF value should be refined based on results of experiments performed in plants cultivated in soil and not in the nutrient solutions. Detailed discussion on the study by Gourley (2015) may be found in clopyralid RAR (Vol. 3CP, B.8 of March 2018). It should be also noted that the uptake of the substance by plants would also depend on other factors, such as the size of soil particles (higher uptake would be expected in sandy soils comparing to clay soils), soil pH, temperature, humidity and the plant itself. This may be seen in results of the study by Gourlay (2019) submitted in support of authorisation of ADM.3304.H.1.A, where wheat and barley were used (both being cereals), but the average TSCF of 0.2 calculated for wheat was two times lower comparing to barley with mean TSCF of 0.47. The impact of variety on the uptake of the substance from soil is not known. Taking all this into account, the currently performed experiments to refine TSCF are highly uncertain and may lead to overestimation of TSCF and in consequence - underestimation of the groundwater exposure.

Since design of both studies by Gourley was similar, conclusions taken during the EU evaluation of study by Gourley (2015) are equally applicable to study by Gourley (2019), which was thus not validated by the zRMS, since obtained results are uncertain due to the test design. Taking this into account, the refined TSCF of 0.5 was not agreed by the zRMS to be used at Tier 2 modelling for clopyralid and only results of the Tier 1 simulations will be taken into account in the overall conclusion regarding the groundwater exposure.

Fluroxypyr

The input parameters for fluroxypyr and its metabolites presented in Table 8.8-3 and considered by the Applicant for groundwater modelling are in line with EU agreed endpoints. It should be pointed out that for pyridinol and

methoxypyridine endpoints as agreed during the evaluation of confirmatory data were taken into account (for details, see Fluroxypyr, Volume 3, Confirmatory Information of December 2014).

Consideration of TSCF of 0.5 for fluroxypyr is not accepted by the zRMS, since at Tier 1 TSCF of 0 should be used for all compounds, regardless if they are systemic or not. Respective correction was thus made by the zRMS in Table 8.8-3.

The additional explanations provided by the Applicant under Table 8.8-3 are agreed by the zRMS.

8.8.2 Active substance(s) and relevant metabolite(s) (KCP 9.2.4.1)

For registration of plant protection products in Europe, the exposure assessments in groundwater was carried out according to the data requirements set forth in Commission Regulation (EU) No 545/2011 implementing Regulation (EC) No 1107/2009.

The present document summarizes the FOCUS groundwater calculations for the application of the product ADM.3304.H.1.A (old code AG-CDF1-480 EC). The behaviour of a substance can be predicted using calculation models with soil degradation data (DT₅₀ values), adsorption data (K_{OC} values) and the product's use.

Table 8.8-4: Summary of default input parameters according to FOCUS⁴

Parameter	Value	Remarks
Physico-chemical parameters		
Molar enthalpy of dissolution [kJ/mol]	27	FOCUS recommendation
Molar enthalpy of vaporization [kJ/mol]	95	FOCUS recommendation
Diffusion coefficient in water	4.3 x 10 ⁻⁵ m ² d ⁻¹ (20 °C) (Pearl) 5.0 x 10 ⁻¹⁰ m ² s ⁻¹ (20 °C) (Macro)	FOCUS recommendation
Diffusion coefficient in gas [m ² /d]	0.43 (20 °C)	FOCUS recommendation
Degradation in soil		
Temperature correction function		
Reference temperature [°C]	20	FOCUS recommendation
MACRO: [1/K]	0.0948	FOCUS recommendation
PRZM / PELMO: Q ₁₀	2.58 / 1 for field values	FOCUS recommendation
Moisture correction function		
Reference moisture	pF 2	FOCUS recommendation
MACRO: moisture exponent	0.7 / 0 for field values	

zRMS comments:

The default input parameters provided in Table 8.8-4 above are in line with FOCUS recommendations and are thus agreed by the zRMS.

8.8.2.1 2,4-D and its metabolites

The models FOCUS PELMO 5.5.3, FOCUS PEARL 4.4.4 and FOCUS MACRO 5.5.4 were used for the calculation of potential groundwater contamination by the active substance 2,4-D.

⁴ Generic guidance for FOCUS groundwater scenarios (2014) surface water scenarios. Version: 1.0. January 2011

Table 8.8-5: Input parameters related to application for PEC_{gw} calculations

Crop or crop group	FOCUS scenario	BBCH, timing	Application rate [g a.i./ha]	Crop interception	Rate reaching soil [g a.i./ha]	Worst case application date
Grassland	Grass/alfalfa	BBCH 21-39	750 [§]	60	300	20 days after emergence
Winter cereals	Winter cereals	BBCH 21-39	750 [§]	20	600	100 days before harvest
Spring cereals	Spring cereals	BBCH 21-39	750 [§]	20	600	70 days before harvest

§ The application rate of active substance 2,4-D is referring to 2,4-D-acid. The application rate in terms of 2,4-D-ethylhexylester (2,4-D-EHE) is 1.5 times the rate in terms of 2,4-D acid (i.e. 1125 g 2,4-D-EHE /ha)

For the **PEC_{GW} calculations** the application with the highest rate reaching soil was chosen as representative worst case scenario. For the present calculations the application of 2 L/ha assuming 60 % crop interception for the application in grassland and 20 % crop interception for the use in winter and spring cereals was chosen as worst case.

The following endpoints are used for the PEC_{GW} calculations. Data were taken from the EFSA Report of 2,4-D (EFSA Journal 2014;12(9):3812).

Table 8.8-6: Input parameters related to active substance 2,4-D and metabolites for PEC_{gw} calculations

Parameter	2,4-D	2,4-DCP	2,4-DCA
Molecular Mass [g/mol]	221	163	177
Water solubility [mg/L]	24300 (25°C)*	4870 (20°C)	96.3 (20°C)
Saturated vapour pressure [Pa]	9.9 x 10 ⁻⁶ (20°C)	9.9 x 10 ⁻⁶ (20°C)	9.9 x 10 ⁻⁶ (20°C)
K _{oc} [mL/g]	58.6	512	1028
K _{OM} [mL/g]	34.0	297	595
Freudlich sorption exponent (1/n)	0.87	0.88	0.92
DT ₅₀ soil [days]	4.14	7.0	10.4
Formation fraction	--	1	1
Plant uptake factor	0	0	0

* Calculated for 20°C: 22684

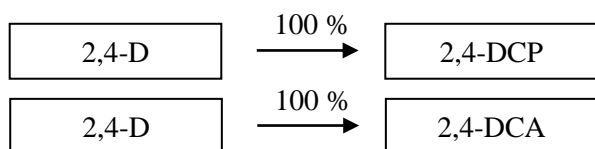


Figure 8.8-1: Degradation pathway of 2,4-D

Table 8.8-7: PEC_{gw} of 2,4-D and its metabolites using PELMO 5.5.3

Substance	2,4-D		
Weather/Soil scenario	Annual concentration in groundwater [µg/L] (80 th %ile value in the percolate at 1 m soil depth)		
	2,4-D	2,4-DCP	2,4-DCA
Winter cereals			
Châteaudun	0.000	0.000	0.000
Hamburg	0.000	0.000	0.000
Jokioinen	0.000	0.000	0.000
Kremsmünster	0.000	0.000	0.000
Okehampton	0.000	0.000	0.000
Piacenza	0.000	0.000	0.000
Porto	0.000	0.000	0.000
Sevilla	0.000	0.000	0.000
Thiva	0.000	0.000	0.000
Spring cereals			
Châteaudun	0.000	0.000	0.000
Hamburg	0.000	0.000	0.000
Jokioinen	0.000	0.000	0.000
Kremsmünster	0.000	0.000	0.000
Okehampton	0.000	0.000	0.000
Porto	0.000	0.000	0.000
Grassland			
Châteaudun	0.000	0.000	0.000
Hamburg	0.000	0.000	0.000
Jokioinen	0.000	0.000	0.000
Kremsmünster	0.000	0.000	0.000
Okehampton	0.000	0.000	0.000
Piacenza	0.000	0.000	0.000
Porto	0.000	0.000	0.000
Sevilla	0.000	0.000	0.000
Thiva	0.000	0.000	0.000

Table 8.8-8: PEC_{gw} of 2,4-D and its metabolites using PEARL 4.4.4

Substance	2,4-D		
Weather/Soil scenario	Annual concentration in groundwater [µg/L] (80 th %ile value in the percolate at 1 m soil depth)		
	2,4-D	2,4-DCP	2,4-DCA
Winter cereals			
Châteaudun	0.000000	0.000000	0.000000
Hamburg	0.000000	0.000000	0.000000
Jokioinen	0.000000	0.000000	0.000000
Kremsmünster	0.000000	0.000000	0.000000
Okehampton	0.000000	0.000000	0.000000
Piacenza	0.000000	0.000000	0.000000
Porto	0.000000	0.000000	0.000000
Sevilla	0.000000	0.000000	0.000000
Thiva	0.000000	0.000000	0.000000
Spring cereals			
Châteaudun	0.000000	0.000000	0.000000
Hamburg	0.000000	0.000000	0.000000
Jokioinen	0.000000	0.000000	0.000000
Kremsmünster	0.000000	0.000000	0.000000
Okehampton	0.000000	0.000000	0.000000
Porto	0.000000	0.000000	0.000000
Grassland			
Châteaudun	0.000000	0.000000	0.000000
Hamburg	0.000000	0.000000	0.000000
Jokioinen	0.000000	0.000000	0.000000
Kremsmünster	0.000000	0.000000	0.000000
Okehampton	0.000000	0.000000	0.000000
Piacenza	0.000000	0.000000	0.000000
Porto	0.000000	0.000000	0.000000
Sevilla	0.000000	0.000000	0.000000
Thiva	0.000000	0.000000	0.000000

Table 8.8-9: PEC_{gw} of 2,4-D and its metabolites using MACRO 5.4.4.

Substance	2,4-D		
Weather/Soil scenario	Annual concentration in groundwater [µg/L] (80 th %ile value in the percolate at 1 m soil depth)		
	2,4-D	2,4-DCP	2,4-DCA
Winter cereals			
Châteaudun	< 0.001	< 0.001	< 0.001
Spring cereals			
Châteaudun	< 0.001	< 0.001	< 0.001
Grassland			
Châteaudun	< 0.001	< 0.001	< 0.001

zRMS comments:

The application pattern presented in Table 8.8-5 is in line with the critical Central Zone GAP and is thus agreed by the zRMS. The selected application dates were in line with these suggested by the AppDate v. 3.06. Correct crop interception for the intended winter and spring cereals ~~crop~~ stages was selected for the modelling purposes. For established grassland crop interception of 60%, relevant for new grass at BBCH 21-39 was assumed as the risk envelope since for the established grass 90% crop interception is relevant in line with the FOCUS groundwater guidance.

For discussion on input parameters please refer to point 8.8.1 above. Values provided in Table 8.8-6 are confirmed to be agreed by the zRMS.

The performed calculations were independently validated by the zRMS in additional modelling using the same models and input parameters. Obtained PEC_{GW} values were the same as these derived by the Applicant and reported in Tables 8.8-7 to 8.8-9.

Overall, no unacceptable leaching of 2,4-D and its metabolites is expected following application of ADM 3304.H.1.A according to the intended use pattern.

No calculations for 2,4-D EHE were performed, since K_{FOC} value is not available from the EU review. Nevertheless, given the extremely rapid degradation of the ester form with soil DT₅₀ of 0.1 d and expected high K_{FOC} (or at least higher than for the acid form, which is typical in case of such compounds), no unacceptable leaching of 2,4-D EHE is expected.

It is noted that in Appendix 4 groundwater exposure for anaerobic soil metabolite 4-chlorophenol was calculated with consideration of endpoints derived from the new studies submitted in order to address the data gap identified in EFSA Journal 2014;12(9):3812. Performed calculations were agreed by the zRMS and PEC_{GW} <0.001 µg/L were obtained in all scenarios for the intended use pattern indicating that 4-CP has no leaching potential.

For future evaluations the Applicant is kindly asked to provide groundwater exposure calculations for all relevant compounds in point 8.8 in order to facilitate the assessment by the zRMS and make the report more transparent.

In case of mutual recognition process additional simulations may be requested by Member States considering other scenarios as representative or not accepting FOCUS modelling at all.

8.8.2.2 Clopyralid

For PEC_{GW} calculations with clopyralid, additional uses were considered as potential options of refinements.

Modelling was performed with a plant uptake factor (PUF) of 0 (Tier 1) ~~or 0.5 (Tier 2)~~. Calculations were performed with annual applications at the maximum rate of 2 L/ha. Since some scenarios are above the trigger of 0.1 µg/L with an annual application and the maximum application rate, these additional uses were considered:

- Winter cereals: Biennial application at a rate of 2 L/ha;
- Winter cereals: Annual application at a rate of 2 L/ha, starting only at BBCH 30;
- Winter cereals: Annual application at a rate of 1.5 L/ha;
- Spring cereals: Biennial or triennial application at a rate of 2 L/ha.

Table 8.8-10: Input parameters related to application for PEC_{gw} calculations

Crop or crop group	FOCUS scenario	BBCH, timing	Frequency [-]	Application rate [g a.i./ha]	Crop interception	Rate reaching soil [g a.i./ha]	Worst case application date
Established grassland	Grass/alfalfa	Not relevant for established grass; the earliest application is set to 20 days after the start of the vegetative season, referenced here as emergence BBCH 21-39	Annual	60	90 60	6 24	20 days after emergence
Winter cereals	Winter cereals	BBCH 21-39	Annual	60	20	48	100 days before harvest
Winter cereals	Winter cereals	BBCH 21-39	Biennial	60	20	48	100 days before harvest
Winter cereals	Winter cereals	BBCH 30-39	Annual	60	80	12	100 days before harvest
Winter cereals	Winter cereals	BBCH 21-39	Annual	45	20	36	100 days before harvest
Spring cereals	Spring cereals	BBCH 21-39	Annual	60	20	48	70 days before harvest
Spring cereals	Spring cereals	BBCH 21-39	Biennial	60	20	48	70 days before harvest
Spring cereals	Spring cereals	BBCH 21-39	Triennial	60	20	48	70 days before harvest

Table 8.8-11: Input parameters related to active substance clopyralid for PEC_{gw} calculations

Parameter	Clopyralid
Molecular Mass [g/mol]	192
Water solubility [mg/L]	143 000 (20°C)
Saturated vapour pressure [Pa]	0 (25°C)
K _{oc} [mL/g]	1.41
K _{OM} [mL/g]	0.818
Freudlich sorption exponent (1/n) [-]	0.836
DT ₅₀ soil [days]	7.05
Formation fraction [-]	--
Plant uptake factor [-]	Tier 1: 0 Tier 2: 0.5

Table 8.8-12: PEC_{gw} of clopyralid using PELMO 6.6.4

Substance	Clopyralid	
Weather/Soil scenario	Annual concentration in groundwater [µg/L] (80 th percentile value in the percolate at 1 m soil depth)	
	Tier 1	Tier 2
Established grassland (1 × 60 g/ha, BBCH 21-39, annual)		
Châteaudun	0.001	0.001
Hamburg	0.002	0.001
Jokioinen	0.016	0.008
Kremsmünster	0.003	0.002
Okehampton	0.008	0.004
Piacenza	0.002	0.001
Porto	<0.001	<0.001
Sevilla	<0.001	<0.001
Thiva	<0.001	<0.001
Winter cereals (1 × 60 g/ha, BBCH 21-39, annual)		
Châteaudun	0.002	0.001
Hamburg	0.020	0.006
Jokioinen	0.116	0.052

Substance	Clopyralid	
Weather/Soil scenario	Annual concentration in groundwater [µg/L] (80 th percentile value in the percolate at 1 m soil depth)	
	Tier 1	Tier 2
Kremsmünster	0.050	0.027
Okehampton	0.092	0.052
Piacenza	0.060	0.045
Porto	0.053	0.044
Sevilla	<0.001	<0.001
Thiva	<0.001	<0.001
Winter cereals (1 × 60 g/ha, BBCH 21-39, biennial)		
Châteaudun	0.001	0.001
Hamburg	0.013	0.004
Jokioinen	0.075	0.034
Kremsmünster	0.028	0.014
Okehampton	0.044	0.023
Piacenza	0.038	0.028
Porto	0.030	0.024
Sevilla	<0.001	<0.001
Thiva	<0.001	<0.001
Winter cereals (1 × 60 g/ha, BBCH 30-39, annual)		
Châteaudun	<0.001	<0.001
Hamburg	0.006	0.003
Jokioinen	0.028	0.014
Kremsmünster	0.013	0.008
Okehampton	0.019	0.010
Piacenza	0.009	0.007
Porto	0.001	0.001
Sevilla	<0.001	<0.001
Thiva	<0.001	<0.001
Winter cereals (1 × 45 g/ha, BBCH 21-39, annual)		
Châteaudun	0.001	0.001
Hamburg	0.015	0.005
Jokioinen	0.083	0.038
Kremsmünster	0.036	0.020
Okehampton	0.068	0.038
Piacenza	0.044	0.033
Porto	0.038	0.032
Sevilla	<0.001	<0.001
Thiva	<0.001	<0.001
Spring cereals (1 × 60 g/ha, BBCH 21-39, annual)		
Châteaudun	0.001	0.001
Hamburg	0.050	0.025
Jokioinen	0.133	0.074
Kremsmünster	0.074	0.046
Okehampton	0.074	0.047
Porto	0.002	0.001
Spring cereals (1 × 60 g/ha, BBCH 21-39, biennial)		
Châteaudun	0.001	<0.001
Hamburg	0.032	0.016
Jokioinen	0.076	0.042
Kremsmünster	0.052	0.031
Okehampton	0.048	0.032
Porto	0.001	<0.001
Spring cereals (1 × 60 g/ha, BBCH 21-39, triennial)		
Châteaudun	<0.001	<0.001
Hamburg	0.022	0.011
Jokioinen	0.043	0.024
Kremsmünster	0.042	0.025
Okehampton	0.033	0.022
Porto	0.001	<0.001

Table 8.8-13: PEC_{gw} of clopyralid using PEARL 5.5.5

Substance	Clopyralid	
Weather/Soil-scenario	Annual concentration in groundwater [µg/L] (80 th percentile value in the percolate at 1 m soil depth)	
	Tier-1	Tier-2
Established grassland (1 × 60 g/ha, BBCH 21-39, annual)		
Châteaudun	0.001	<0.001
Hamburg	0.010	0.006
Jokioinen	0.014	0.009
Kremsmünster	0.003	0.002
Okehampton	0.007	0.005
Piacenza	<0.001	<0.001
Porto	<0.001	<0.001
Sevilla	<0.001	<0.001
Thiva	<0.001	<0.001
Winter cereals (1 × 60 g/ha, BBCH 21-39, annual)		
Châteaudun	0.003	0.002
Hamburg	0.121	0.078
Jokioinen	0.089	0.050
Kremsmünster	0.073	0.050
Okehampton	0.117	0.068
Piacenza	0.047	0.030
Porto	0.017	0.011
Sevilla	<0.001	<0.001
Thiva	<0.001	<0.001
Winter cereals (1 × 60 g/ha, BBCH 21-39, biennial)		
Châteaudun	0.001	<0.001
Hamburg	0.070	0.046
Jokioinen	0.056	0.031
Kremsmünster	0.041	0.028
Okehampton	0.052	0.030
Piacenza	0.026	0.016
Porto	0.008	0.006
Sevilla	<0.001	<0.001
Thiva	<0.001	<0.001
Winter cereals (1 × 60 g/ha, BBCH 30-39, annual)		
Châteaudun	<0.001	<0.001
Hamburg	0.036	0.024
Jokioinen	0.023	0.015
Kremsmünster	0.019	0.014
Okehampton	0.019	0.012
Piacenza	0.009	0.006
Porto	0.002	0.001
Sevilla	<0.001	<0.001
Thiva	<0.001	<0.001
Winter cereals (1 × 45 g/ha, BBCH 21-39, annual)		
Châteaudun	0.002	0.001
Hamburg	0.088	0.057
Jokioinen	0.063	0.036
Kremsmünster	0.053	0.037
Okehampton	0.086	0.050
Piacenza	0.035	0.022
Porto	0.012	0.008
Sevilla	<0.001	<0.001
Thiva	<0.001	<0.001
Spring cereals (1 × 60 g/ha, BBCH 21-39, annual)		
Châteaudun	0.004	0.002
Hamburg	0.274	0.178
Jokioinen	0.156	0.102
Kremsmünster	0.113	0.087
Okehampton	0.082	0.053
Porto	0.002	0.001
Spring cereals (1 × 60 g/ha, BBCH 21-39, biennial)		
Châteaudun	0.002	0.001
Hamburg	0.138	0.089

Substance	Clopyralid	
Weather/Soil scenario	Annual concentration in groundwater [µg/L] (80 th percentile value in the percolate at 1 m soil depth)	
	Tier 1	Tier 2
Jokioinen	0.092	0.062
Kremsmünster	0.073	0.057
Okehampton	0.042	0.027
Porto	<0.001	<0.001
Spring cereals (1 × 60 g/ha, BBCH 21-39, triennial)		
Châteaudun	0.001	<0.001
Hamburg	0.098	0.069
Jokioinen	0.065	0.044
Kremsmünster	0.056	0.043
Okehampton	0.033	0.021
Porto	<0.001	<0.001

Table 8.8-14: PEC_{gw} of clopyralid using MACRO 5.4.4.

Substance	Clopyralid	
Weather/Soil scenario	Annual concentration in groundwater [µg/L] (80 th percentile in the percolate at 1 m soil depth)	
	Tier 1	Tier 2
Established grassland (1 × 60 g/ha, BBCH 21-39, annual)		
Châteaudun	< 0.001	<0.001
Winter cereals (1 × 60 g/ha, BBCH 21-39, annual)		
Châteaudun	0.002	0.001
Winter cereals (1 × 60 g/ha, BBCH 21-39, biennial)		
Châteaudun	< 0.001	<0.001
Winter cereals (1 × 60 g/ha, BBCH 30-39, annual)		
Châteaudun	< 0.001	<0.001
Winter cereals (1 × 45 g/ha, BBCH 21-39, annual)		
Châteaudun	0.001	<0.001
Spring cereals (1 × 60 g/ha, BBCH 21-39, annual)		
Châteaudun	0.001	<0.001
Spring cereals (1 × 60 g/ha, BBCH 21-39, biennial)		
Châteaudun	< 0.001	<0.001
Spring cereals (1 × 60 g/ha, BBCH 21-39, triennial)		
Châteaudun	< 0.001	<0.001

zRMS comments:

The application pattern presented in Table 8.8-10 is in line with the critical Central Zone GAP and is thus agreed by the zRMS. The selected application dates were in line with these suggested by the AppDate v. 3.06. Correct crop interception for the intended crop stages of cereals was selected for the modelling purposes. Although initially the zRMS indicated that for grassland the crop interception of 60% should have been assumed (BBCH 21-39) However, for application to grassland the Applicant considered crop interception of 90%, while for grass BBCH stages CI of 60% is relevant, resulting with higher rate reaching the soil (24 g a.s./ha). Respective corrections were thus made in Table 8.8-10.

For discussion on input parameters please refer to point 8.8.1 above. Values provided in Table 8.8-11 for Tier 1 modelling are confirmed to be agreed by the zRMS. Refinement of the TSCF was not accepted and is thus struck through.

It is noted that simulations were performed by the Applicant using most recent version of the modelling programs (PELMO 6.6.4 and PEARL 5.5.5). However, for dossiers submitted before 1st of January 2022, older versions are applicable (i.e. PELMO 5.5.3 and PEARL 4.4.4). Furthermore, modelling for 2,4-D and fluroxypyr was performed using older versions of models (PELMO 5.5.3 and PEARL 4.4.4) and in opinion of the zRMS the same models should be used for clopyralid in order to take the same assumptions for all compounds.

The performed calculations were independently validated by the zRMS in additional modelling using PELMO 5.5.3

and PEARL 4.4.4 5.5.5 and input parameters indicated in Table 8.8.-11. For winter and spring cereals the absolute application dates suggested by AppDate ver. 3.06 for BBCH 21 of the intended crops were selected, as presented in the table below. For grassland the relative application dates were set to 20 days after emergence.

FOCUS scenario	Crop	
	Winter cereals BBCH 21-39	Spring cereals BBCH 21-39
Châteaudun	06-Apr	31-Mar
Hamburg	25-Apr	16-Apr
Kremsmünster	15-Apr	16-Apr

In order to avoid confusion of the end-user, the whole period of intended application in cereals was considered (i.e. BBCH 21-39) without distinguishing between BBCH 21-29 and 30-39. Since Poland is the only cMS indicated in the GAP table, only scenarios required in Poland were considered (i.e. Châteaudun, Hamburg and Kremsmünster). Since there were some differences in results obtained by the zRMS (some PEC_{GW} were higher, some lower), the Applicants' results were struck through in Tables 8.8-12 and 8.8-13 and relevant PEC_{GW} values are presented in tables below. Results of MACRO simulations were the same as these presented in Table 8.8-14.

PEC_{gw} of clopyralid for annual application to intended crops

Substance	Clopyralid	
Weather/Soil scenario	Annual concentration in groundwater [µg/L] (80 th percentile value in the percolate at 1 m soil depth)	
	PELMO 5.5.3	PEARL 4.4.4 5.5.5
Established grassland (1 × 60 g/ha, earliest possible application date: 20 days after emergence)		
Châteaudun	0.001	0.006
Hamburg	0.002	0.030
Kremsmünster	0.004	0.014
Established grassland (1 × 60 g/ha, BBCH 21-39)		
Châteaudun	0.004	0.032
Hamburg	0.010	0.140
Kremsmünster	0.018	0.066

Winter cereals (1 × 60 g/ha, BBCH 21-39)		
Châteaudun	0.002	0.003
Hamburg	0.024	0.120
Kremsmünster	0.059	0.073
Winter cereals (1 × 45 g/ha, BBCH 21-39)		
Châteaudun	0.002	0.002
Hamburg	0.017	0.088
Kremsmünster	0.043	0.053
Spring cereals (1 × 60 g/ha, BBCH 21-39)		
Châteaudun	0.002	0.004
Hamburg	0.051	0.274
Kremsmünster	0.075	0.106

PEC_{gw} of clopyralid for biennial application to intended crops

Substance	Clopyralid	
Weather/Soil scenario	Annual concentration in groundwater [µg/L] (80 th percentile value in the percolate at 1 m soil depth)	
	PELMO 5.5.3	PEARL 4.4.4 5.5.5
Established grassland (1 × 60 g/ha, BBCH 21-39)		
Châteaudun	Not required	Not required 0.019
Hamburg		Not required 0.080
Kremsmünster		Not required 0.043
Winter cereals (1 × 60 g/ha, BBCH 21-39)		
Châteaudun	Not required	0.001

Hamburg		0.070
Kremsmünster		0.041
Winter cereals (1 × 45 g/ha, BBCH 21-39)		
Châteaudun	Not required	Not required
Hamburg		
Kremsmünster		
Spring cereals (1 × 60 g/ha, BBCH 21-39)		
Châteaudun	Not required	0.002
Hamburg		0.138
Kremsmünster		0.073

PEC_{gw} of clopyralid for triennial application to intended crops

Substance	Clopyralid	
Weather/Soil scenario	Annual concentration in groundwater [µg/L] (80 th percentile value in the percolate at 1 m soil depth)	
	PELMO 5.5.3	PEARL 4.4.4 5.5.5
Established grassland (1 × 60 g/ha, BBCH 21-39)		
Châteaudun	Not required	Not required
Hamburg		
Kremsmünster		
Winter cereals (1 × 60 g/ha, BBCH 21-39)		
Châteaudun	Not required	Not required
Hamburg		
Kremsmünster		
Winter cereals (1 × 45 g/ha, BBCH 21-39)		
Châteaudun	Not required	Not required
Hamburg		
Kremsmünster		
Spring cereals (1 × 60 g/ha, BBCH 21-39)		
Châteaudun	Not required	0.001
Hamburg		0.098
Kremsmünster		0.056

Based on the obtained results, no unacceptable leaching of clopyralid in scenarios relevant in Poland is expected after following application pattern of ADM 3304.H.1.A:

- **annual** ~~biennial~~ application to grassland at the rate of 60 g/ha at BBCH 21-39,
- biennial application to winter cereals at the rate of 60 g/ha at BBCH 21-39,
- annual application to winter cereals at the rate of 45 g/ha at BBCH 30-39,
- triennial application to spring cereals at the rate of 60 g/ha at BBCH 21-39.

In case of mutual recognition process additional simulations may be requested by Member States considering other scenarios as representative or not accepting FOCUS modelling at all.

During the commenting period the Applicant pointed out that in case of the grassland the application will be made to the established grass, so the 90% crop interception assumed initially by the Applicant was correct. The zRMS modelling presented above has been thus amended accordingly with results of the new modelling performed with assumption of the 90% crop interception. Information on BBCH stages in Table 8.8-10 above has been changed to make it clear that the product will not be applied to the new grass at BBCH 21-39, as the previously given information was misleading.

8.8.2.3 Fluroxypyr and its metabolites

For the present report, the models FOCUS PELMO 5.5.3, FOCUS PEARL 4.4.4 and FOCUS MACRO 5.5.4 were used for the calculation of potential groundwater contamination by the active substance fluroxypyr and its metabolites.

Table 8.8-15: Input parameters related to application for PEC_{gw} calculations

Crop or crop group	FOCUS scenario	BBCH, timing	Application rate [g a.i./ha]	Crop interception	Rate reaching soil [g a.i./ha]	Worst case application date
Grassland	Grass/alfalfa	BBCH 21-39	150 [#]	60	60	20 days after emergence
Winter cereals	Winter cereals	BBCH 21-39	150 [#]	20	120	100 days before harvest
Spring cereals	Spring cereals	BBCH 21-39	150 [#]	20	120	70 days before harvest

[#] The application rate of active substance Fluroxypyr is referring to Fluroxypyr acid. The application rate in terms of Fluroxypyr-MHE is 1.44 times the rate in terms of Fluroxypyr acid (i.e. 216 g Fluroxypyr-MHE/ha)

For the **PEC_{GW} calculations** the application with the highest rate reaching soil was chosen as representative worst case scenario. For the present calculations the application of 2 L/ha assuming 60 % crop interception for the application in grassland and 20 % crop interception for the use in winter and spring cereals was chosen as worst case.

The following endpoints are used for the PEC_{GW} calculations. Data were taken from the EFSA Report of fluroxypyr (EFSA Journal 2011;9(3):2091).

Table 8.8-16: Input parameters related to active substance fluroxypyr and its metabolites for PEC_{gw} calculations

Parameter	Fluroxypyr acid	Pyridinol	Methoxypyridine
Molecular Mass [g/mol]	255	197	211
Water solubility [mg/L]	91 (20°C)	91 (20°C)	91 (20°C)
Saturated vapour pressure [Pa]	3.8 x 10 ⁻⁹ (20°C)	3.8 x 10 ⁻⁹ (20°C)	3.8 x 10 ⁻⁹ (20°C)
K _{OC} [mL/g]	68	708 (pH < 7) 68.5* (pH ≥ 7)	321
K _{OM} [mL/g]	39	410.7 (pH < 7) 39.6 (pH ≥ 7)	185
Freudlich sorption exponent (1/n)	0.92	0.81 (pH < 7) 0.72 (pH ≥ 7)	0.84
DT ₅₀ soil [days]	13.9	17.6	111.11
Formation fraction	0.513 (to sink)	0.286 (from parent) 0.723 (from Methoxypyridine)	0.201 (from parent)
Plant uptake factor	0 0.5	0	0

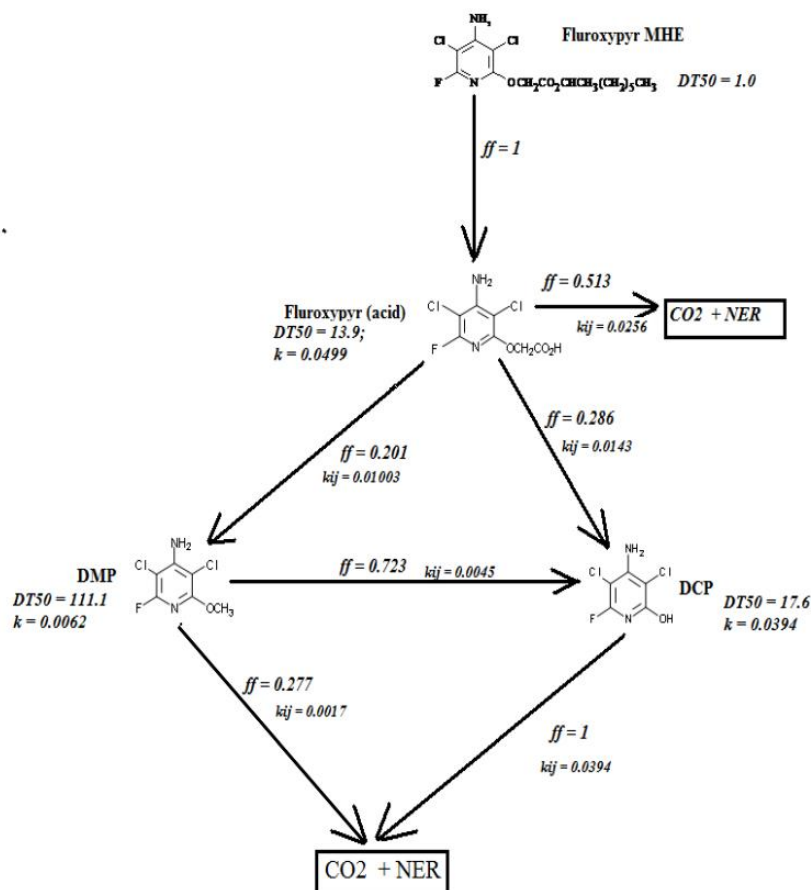


Figure 8.8-2: Degradation pathway for fluroxypyr (confirmatory information, 2014)

Table 8.8-17: PEC_{gw} of fluroxypyr and its metabolites using PELMO 5.5.3

Substance	Fluroxypyr			
Weather/Soil scenario	Annual concentration in groundwater [µg/L] (80 th %ile value in the percolate at 1 m soil depth)			
	Fluroxypyr	Pyridinol		Methoxy-pyridine
		pH < 7	pH ≥ 7	
Winter cereals				
Châteaudun	0.000	0.000	0.000	0.000
Hamburg	0.002	0.000	0.000	0.001
Jokioinen	0.000	0.000	0.000	0.000
Kremsmünster	0.002	0.000	0.000	0.001
Okehampton	0.004	0.000	0.000	0.002
Piacenza	0.002	0.000	0.000	0.001
Porto	0.001	0.000	0.000	0.000
Sevilla	0.000	0.000	0.000	0.000
Thiva	0.000	0.000	0.000	0.000
Spring cereals				
Châteaudun	0.000	0.000	0.000	0.000
Hamburg	0.004	0.000	0.000	0.001
Jokioinen	0.000	0.000	0.000	0.000
Kremsmünster	0.002	0.000	0.000	0.001
Okehampton	0.004	0.000	0.000	0.001
Porto	0.000	0.000	0.000	0.000
Grassland				
Châteaudun	0.000	0.000	0.000	0.000
Hamburg	0.000	0.000	0.000	0.000
Jokioinen	0.000	0.000	0.000	0.000
Kremsmünster	0.000	0.000	0.000	0.000
Okehampton	0.002	0.000	0.000	0.001
Piacenza	0.003	0.000	0.000	0.002
Porto	0.001	0.000	0.000	0.000
Sevilla	0.000	0.000	0.000	0.000
Thiva	0.000	0.000	0.000	0.000

Table 8.8-18: PEC_{gw} of fluroxypyr and its metabolites using PEARL 4.4.4

Substance	Fluroxypyr			
Weather/Soil scenario	Annual concentration in groundwater [µg/L] (80 th %ile value in the percolate at 1 m soil depth)			
	Fluroxypyr	Pyridinol		Methoxy- pyridine
		pH < 7	pH ≥ 7	
Winter cereals				
Châteaudun	0.000014	0.000000	0.000000	0.000002
Hamburg	0.002025	0.000109	0.000141	0.000791
Jokioinen	0.000126	0.000000	0.000001	0.000008
Kremsmünster	0.001711	0.000013	0.000035	0.000411
Okehampton	0.004887	0.000071	0.000230	0.001944
Piacenza	0.001775	0.000061	0.000079	0.000803
Porto	0.000350	0.000001	0.000002	0.000034
Sevilla	0.000000	0.000000	0.000000	0.000000
Thiva	0.000000	0.000000	0.000000	0.000000
Spring cereals				
Châteaudun	0.000005	0.000000	0.000000	0.000000
Hamburg	0.002912	0.000235	0.000361	0.001914
Jokioinen	0.000293	0.000001	0.000001	0.000015
Kremsmünster	0.002276	0.000015	0.000042	0.000471
Okehampton	0.004197	0.000038	0.000119	0.000928
Porto	0.000115	0.000001	0.000002	0.000047
Grassland				
Châteaudun	0.001843	0.000000	0.000083	0.000463
Hamburg	0.000126	0.000109	0.000001	0.000006
Jokioinen	0.000303	0.000000	0.000007	0.000114
Kremsmünster	0.002288	0.000013	0.000043	0.000621
Okehampton	0.002333	0.000071	0.000233	0.001964
Piacenza	0.001081	0.000061	0.000014	0.000257
Porto	0.000005	0.000001	0.000000	0.000001
Sevilla	0.000011	0.000000	0.000000	0.000000
Thiva	0.000238	0.000000	0.000002	0.000034

For MACRO calculations on Pyridinol, only pH >7 was considered since it is the only Koc above the trigger of 100 mL/g.

Table 8.8-19: PEC_{gw} of fluroxypyr and its metabolites using MACRO 5.4.4.

Substance	Fluroxypyr		
Weather/Soil scenario	Annual concentration in groundwater [µg/L] (80 th %ile value in the percolate at 1 m soil depth)		
	Fluroxypyr	Pyridinol	Methoxy- pyridine
Winter cereals			
Châteaudun	< 0.001	< 0.001	< 0.001
Spring cereals			
Châteaudun	< 0.001	< 0.001	< 0.001
Grassland			
Châteaudun	< 0.001	< 0.001	< 0.001

Conclusion

In all model calculations for the product AG-CDF1-480-EC demonstrate that no unacceptable leaching (concentrations > 0.1 µg/L) of the active ingredients 2,4-D, Clopyralid and Fluroxypyr and their metabolites into groundwater is to be expected from the intended GAP use of the product.

zRMS comments:

The application pattern presented in Table 8.8-15 is in line with the critical Central Zone GAP and is thus agreed by the zRMS. The selected application dates were in line with these suggested by the AppDate v. 3.06. Correct crop interception for the intended winter and spring cereals crop stages was selected for the modelling purposes. For established grassland crop interception of 60%, relevant for new grass at BBCH 21-39 was assumed as the risk envelope since for the established grass 90% crop interception is relevant in line with the FOCUS groundwater guidance.

For discussion on input parameters please refer to point 8.8.1 above. Values provided in Table 8.8-16 are confirmed to be agreed by the zRMS with exception of the PUF value (PUF of 0 should have been considered).

The performed calculations were independently validated by the zRMS in additional modelling using the same models and input parameters, with exception of PUF value (PUF of 0 was considered for all compounds). Obtained PEC_{Gw} values were the same as these derived by the Applicant and reported in Tables 8.8-17 to 8.8-19.

Overall, no unacceptable leaching of fluroxypyr and its metabolites is expected following application of ADM 3304.H.1.A according to the intended use pattern.

It is noted that no groundwater modelling was performed for fluroxypyr-meptyl, but it was considered not necessary in the course of the EU review due to properties of the ester form indicating that no unacceptable leaching is expected (rapid degradation with mean soil DT₅₀ of 1.0 d and high Koc).

In case of mutual recognition process additional simulations may be requested by Member States considering other scenarios as representative or not accepting FOCUS modelling at all.

8.9 Predicted Environmental Concentrations in surface water (PEC_{sw}) (KCP 9.2.5)

PEC_{sw} presented below are based on the results obtained from Ritzenthaler (2015d) and Fortin-McCuaig (2021c), which are presented in Appendix 2. The highest global maximum concentrations in surface water and sediment for each FOCUS Step of each active substance and its metabolites are summarised in the tables below.

8.9.1 Justifications for new endpoints

The following table provides the EU endpoints to be used for the PEC surface water calculations. For a more detailed list of endpoints including the respective sources, please refer to Appendix 3.

Table 8.9-1: 2,4-D: Input parameters for PEC_{sw} calculation

Parameter	EU agreed endpoints	Endpoints used in risk assessment	Justification for deviation
2,4.D EHE			
The ester form of the 2,4-D degrades very quickly in soil (DT ₅₀ < 0.1 d) therefore, spray drift is the only potential route of contamination of surface water. For drift entries phys-chem parameters are not applicable.			
2,4-D			
Molecular Mass [g/mol]	221	221	
Water solubility [mg/L]	24300 (25°C)	24300 (25°C)	
Saturated vapour pressure [Pa]	9.9 x 10 ⁻⁶ (20°C)	9.9 x 10 ⁻⁶ (20°C)	
K _{oc} [mL/g]	58.6 24	58.6	Median of 42 soils (in the LoE (EFSA, 2014) K _{FOC} and 1/n was incorrectly reported for only seven soils instead of 42; presented PEC _{sw} were however base on the correct data (RAR Addendum (2014), Part 4))
Freundlich sorption exponent (1/n)	0.83	0.87	Arithmetic mean of 42 soils (in the LoE (EFSA, 2014) K _{FOC} and 1/n was incorrectly reported for only seven soils instead of 42; presented PEC _{sw} were however base on the correct data (RAR Addendum (2014), Part 4))
DT ₅₀ soil [days]	4.4	4.14	Geometric mean, normalised (20°C, pF ₂), laboratory; including “Mississippi” soil
DT ₅₀ w/s system [days]	18.16	18.16	
DT ₅₀ water (degradation) [days]	18.16	18.16	
DT ₅₀ sediment (degradation) [days]	18.16 (Step 1&2) 1000 (Step 3)	18.16 (Step 1&2) 1000 (Step 3)	
DT ₅₀ plant [days]	--	10	Default value
Plant uptake	--	0	Default value
Max occurrence in soil/water/sediment	--	Not required	
2,4-DCP			
Molecular Mass [g/mol]	163	163	
Water solubility [mg/L]	4870 (20°C)	4870 (20°C)	
K _{oc} [mL/g]	512	512	Arithmetic mean
Freundlich sorption exponent (1/n)	--	Not required	
DT ₅₀ soil [days]	7.0	7.0	
DT ₅₀ w/s system [days]	103.9	103.9	
DT ₅₀ water (degradation) [days]	103.9	103.9	Value from w/s system
DT ₅₀ sediment (degradation) [days]	103.9	1000	Default value

Parameter		EU agreed endpoints	Endpoints used in risk assessment	Justification for deviation
Plant uptake		--	Not required	
Max occurrence [%] in	soil water/sediment	8.7 32.1	8.7 32.1	
2,4-DCA				
Molecular Mass	[g/mol]	177	177	
Water solubility	[mg/L]	96.3 (20°C)	96.3 (20°C)	
K _{oc}	[mL/g]	1028	1028	Arithmetic mean
Freundlich sorption exponent (1/n)		--	Not required	
DT ₅₀ soil	[days]	10.4	10.4	
DT ₅₀ w/s system	[days]	1000	1000	Default value
DT ₅₀ water (degradation)	[days]	1000	1000	Default value
DT ₅₀ sediment (degradation)	[days]	1000	1000	Default value
Plant uptake		--	Not required	
Max occurrence [%] in	soil water/sediment	15 5.3	15 5.3	

Table 8.9-2: Clopyralid: Input parameters for PEC_{sw} calculation

Parameter	EU-agreed endpoints	Endpoints used in risk assessment	Justification for deviation
Molecular Mass [g/mol]	191.96	192	
Water solubility [mg/L]	143 g/L (20°C)	143 000 (20°C)	
Saturated vapour pressure [Pa]	1.36 x 10 ⁻³ (25°C)	Not required	
K _{oc} [mL/g]	1.41	1.41	Geometric mean (n = 9)
Freundlich exponent (1/n) [-]	0.836	Not required	
DT ₅₀ soil [days]	7.05	7.05	Geometric mean field studies (n = 9, normalised to pF2, 20°C with Q10 of 2.58)
DT ₅₀ whole system [days]	--	1000	FOCUS default value
DT ₅₀ water (degradation) [days]	148	148	Geometric mean (n = 2)
DT ₅₀ sediment (degradation) [days]	--	1000	FOCUS default value
DT ₅₀ plant [days]	--	Not required	
Plant uptake [-]	--	Not required	
Max occurrence in soil/water/sediment [%]	--	Not required	

Table 8.9-3: Fluroxypyr: Input parameters for PEC_{sw} calculation

Parameter		EU agreed endpoints	Endpoints used in risk assessment	Justification for deviation
Fluroxypyr-meptyl				
Molecular Mass	[g/mol]	367.3	367.3	
Water solubility	[mg/L]	0.009	0.009	
Saturated vapour pressure [Pa]		1.349 x 10 ⁻⁶	1.349 x 10 ⁻⁶	
K _{oc}	[mL/g]	19950	19950	Arithmetic mean
Freundlich sorption exponent (1/n)		0.9	1	Default value
DT ₅₀ soil	[days]	1.0	1.0	Geometric mean laboratory values, (normalised to pF2, 20°C with Q10 of 2.58)
DT ₅₀ w/s system	[days]	38.1	38.1	
DT ₅₀ water (degradation)	[days]	38.1 (step 1&2)	38.1 (step 1&2)	Value from w/s system
DT ₅₀ sediment (degradation) [days]		38.1 (step 1&2)	38.1 (step 1&2) 1000 (step 3)	Value from w/s system Default value
DT ₅₀ plant [days]		--	10	Default value
Plant uptake		--	0 0.5	FOCUS recommendation for systemic compounds
Max occurrence in soil/water/sediment		--	Not required	
Fluroxypyr acid				
Molecular Mass	[g/mol]	255	255	
Water solubility	[mg/L]	91	91	
Saturated vapour pressure [Pa]		3.8 x 10 ⁻⁹ (20°C)	Not required	
K _{oc}	[mL/g]	68	68	Arithmetic mean
Freundlich sorption exponent (1/n)		0.92	Not required	
DT ₅₀ soil	[days]	13.9	13.9	Median laboratory values, (normalised to pF2, 20°C with Q10 of 2.58)
DT ₅₀ w/s system	[days]	38.1	38.1	
DT ₅₀ water (degradation)	[days]	38.1	38.1	Value from w/s system
DT ₅₀ sediment (degradation) [days]		1000	1000	Default value
Plant uptake		--	Not required	
Max occurrence in soil/water/sediment		--	Not required	
Pyridinol				
Molecular Mass	[g/mol]	197	197	
Water solubility	[mg/L]	91	91	Value from the parent
K _{oc}	[mL/g]	1288 (pH < 7) 44.3 (pH ≥ 7) acid & neutral soils / alkaline soils	708 (pH < 7), median 68.5 (pH ≥ 7) acid & neutral soils / alkaline soils	Confirmatory information Arithmetic mean
Freundlich sorption exponent (1/n)		0.84 (pH < 7) 1.00 (pH ≥ 7)	Not required	
DT ₅₀ soil	[days]	18.4	17.6	Confirmatory information Geometric mean laboratory values, (normalised to pF2, 20°C with Q10 of 2.58)
DT ₅₀ w/s system	[days]	35.5	35.5	
DT ₅₀ water (degradation)	[days]	35.5	35.5	Value from w/s system
DT ₅₀ sediment (degradation) [days]		1000	1000	Default value
Plant uptake		--	Not required	
Max occurrence [%] in	soil water/sediment	23.9 water: 44 sediment: 11.5	23.9 55.5	
Methoxy pyridine				
Molecular Mass	[g/mol]	211	211	
Water solubility	[mg/L]	91	91	Value from the parent
K _{oc}	[mL/g]	321	321	Arithmetic mean
Freundlich sorption exponent (1/n)		0.84	Not required	

Parameter		EU agreed endpoints	Endpoints used in risk assessment	Justification for deviation
DT ₅₀ soil	[days]	170.4	111.11	Confirmatory information Geometric mean laboratory values, (normalised to pF2, 20°C with Q10 of 2.58)
DT ₅₀ w/s system	[days]	1000	1000	Default value
DT ₅₀ water (degradation)	[days]	1000	1000	Default value
DT ₅₀ sediment (degradation)	[days]	1000	1000	Default value
Plant uptake		--	Not required	
Max occurrence [%] in	soil water/sediment	38.2 0	38.2 0	
3-CP				
Molecular Mass	[g/mol]	162	162	
Water solubility	[mg/L]	91	91	Value from the acid
K _{oc}	[mL/g]	--	1	Default value
Freundlich sorption exponent (1/n)		--	Not required	
DT ₅₀ soil	[days]	--	1000	Default value
DT ₅₀ w/s system	[days]	--	1000	Default value
DT ₅₀ water (degradation)	[days]	--	1000	Default value
DT ₅₀ sediment (degradation)	[days]	--	1000	Default value
Plant uptake		--	Not required	
Max occurrence [%] in	soil water/sediment	0 water: 17.9 sediment: 6.5	0 17.9	

Please note:

For **Fluroxypyr** the calculations were performed regarded Fluroxypyr-meptyl and Fluroxypyr acid as parent compound. For the metabolites Pyridinol, Methoxypyridine and 3-CP, Fluroxypyr acid was regarded as parent.

Table 8.9-4: Summary of highest PEC_{sw} values [µg/L] for 2,4-D, clopyralid and fluroxypyr and their metabolites from FOCUS calculations

Test substance	PEC _{sw} [µg/L]	Source of the PEC _{sw}
2,4-D EHE	10.35 40.388 (1 m distance)	Step 2, North-EU Spray drift
2,4-D	4.782 (spray, D3)	Step 3, grassland
2,4-DCP	13.31	Step 2, North-EU
2,4-DCA	6.15	Step 2, North-EU
4-CP	5.23	Step 2, North-EU
1,2,4-benzenetriol	11.7	Step 2, North-EU
Clopyralid	20.5	Step 1
Fluroxypyr-meptyl	1.356 (spray, D3)	Step 3, grassland
Fluroxypyr acid	47.22	Step 1
Pyridinol	28.69	Step 1
Methoxypyridine	11.17	Step 1
3-CP	5.84	Step 1
AG-CDF1-480 EC	20.22 (1 m distance)	Spray drift

zRMS comments:

2,4-D

The input parameters for 2,4-D and its metabolites presented in Table 8.9-1 and considered by the Applicant for surface water modelling are in general in line with EU agreed endpoints, with following exceptions:

- The soil DT₅₀ of 4.14 days was considered instead of the EU agreed of 4.4 days for 2,4-D, which is a result of consideration of the DT₅₀ for Mississippi soil normalised for both, temperature and moisture (at the EU level value corrected for moisture only was used). This deviation is considered to have marginal impact on

the calculated surface water exposure and is thus agreed by the zRMS. For details of the normalisation procedure, please refer to point 8.3.1.1 of this report.

The EU agreed K_{foc} for 2,4-D (24 mL/g) was corrected in Table 8.9-1 to 58.6 mL/g, as reported in EFSA Journal 2014;12(9):3812.

Clopyralid

The input parameters for clopyralid presented in Table 8.9-2 and considered by the Applicant for surface water modelling are in line with EU agreed endpoints.

Fluroxypyr

The input parameters for fluroxypyr and its metabolites presented in Table 8.9-3 and considered by the Applicant for surface water modelling are in line with EU agreed endpoints. It should be pointed out that for pyridinol and methoxypyridine endpoints as agreed during the evaluation of confirmatory data were taken into account (for details, see Fluroxypyr, Volume 3, Confirmatory Information of December 2014).

It is noted that although in the surface water modelling performed for fluroxypyr-meptyl the soil DT₅₀ of 0.7 days was considered, the correct normalised value reported in the LoEP (page 37) is 1.0 days and is considered relevant for the modelling purposes.

Consideration of TSCF of 0.5 for fluroxypyr is not accepted by the zRMS, since at Tier 1 TSCF of 0 should be used for all compounds, regardless if they are systemic or not. Respective correction was thus made by the zRMS in Table 8.9-3.

The additional explanations provided by the Applicant under Table 8.9-3 are agreed by the zRMS.

8.9.2 Active substance(s), relevant metabolite(s) and the formulation (KCP 9.2.5)

The PEC of 2,4-D, clopyralid, fluroxypyr and their metabolites in surface water has been assessed with FOCUS Step 1+2, FOCUS SWASH (Step 3) and the DT₅₀ water/sediment values established in the EU reviews of the active substances.

Table 8.9-5: Worst case use pattern/risk envelope of ADM.3304.H.1.A (old code AG-CDF1-480 EC) for PEC_{sw} calculations

Crop	Application rate		No. of appl.	Minimum application interval [days]	Application timing (BBCH code)
	[L product/ha]	[g a.i./ha]			
Grassland	2	2,4-D acid: 750 [§] Clopyralid: 60 Fluroxypyr acid: 150 [#]	1	--	BBCH 21-39 (Mar-Aug)
Winter cereals	2	2,4-D acid: 750 [§] Clopyralid: 60 Fluroxypyr acid: 150 [#]	1	--	BBCH 21-39 (Mar-May)
Spring cereals	2	2,4-D acid: 750 [§] Clopyralid: 60 Fluroxypyr acid: 150 [#]	1	--	BBCH 21-39 (Mar-June)

§ The application rate of active substance 2,4-D is referring to 2,4-D-acid. The application rate in terms of 2,4-D-ethylhexylester (2,4-D-EHE) is 1.5 times the rate in terms of 2,4-D acid (i.e. 1125 g 2,4-D-EHE/ha)

The application rate of active substance Fluroxypyr is referring to Fluroxypyr acid. The application rate in terms of Fluroxypyr-MHE is 1.44 times the rate in terms of Fluroxypyr acid (i.e. 216 g Fluroxypyr-MHE/ha)

Calculations were performed for the highest rates of application for which authorisation is sought. The following table gives the relevant intended uses for the FOCUS calculations.

Table 8.9-6: Application settings for FOCUS Step 1 – 3

Crop or crop group	FOCUS sw scenario	Application setting			
		BBCH, timing	Settings for Step 2**	Date for first possible application for Step 3*	Application rate [g a.i./ha]
Grassland	Grass / alfalfa	BBCH 21-39	Average crop cover (60%) North EU Oct. – Feb. Mar. – May June – Sep.	As worst case application dates an spring (01. March) and an autumn (01. August) application was chosen for the calculations	2,4-D acid: 750 Clopyralid: 60 Fluroxypyr acid: 150 [#]
Winter cereals	Winter cereals	BBCH 21-39	Average crop cover (20%) North EU Oct. – Feb. Mar. – May	100 days before harvest	2,4-D acid: 750 Clopyralid: 60 Fluroxypyr acid: 150 [#]
Spring cereals	Spring cereals	BBCH 21-39	Average crop cover (20%) North EU Mar. – May	70 days before harvest	2,4-D acid: 750 Clopyralid: 60 Fluroxypyr acid: 150 [#]

* For the application window set in FOCUS SWASH please refer to Table 8.9-7 below

[#] The application rate of active substance Fluroxypyr is referring to Fluroxypyr acid. The application rate in terms of Fluroxypyr-MHE is 1.44 times the rate in terms of Fluroxypyr acid (i.e. 216 g Fluroxypyr-MHE/ha)

** Risk envelope approach “winter cereals” assuming 0 % crop interception

Table 8.9-7: Application window chosen for FOCUS SWASH Step 3

Application window chosen for FOCUS SWIMM Step 1				
Scenario	Application window			
	Beginning		End	
Location	Date	Julian day	Date	Julian day
	Grassland BBCH 21-39 As worst case application dates an spring (01. March) and an autumn (01. August) application was chosen for the calculations			
D3 - Vreedepeel (NL)	01. Mar 01. Aug	60 213	01.Apr 01.Aug	91 244
D4 - Skousbo (DK)				
D5 - La Jalliere (N-FR)				
R3 - Bologna (IT)				
	Winter cereals BBCH 21-39 (beginning 100 days before harvest)			
D3 - Vreedepeel (NL)	07.May	127	06.June	157
D4 - Skousbo (DK)	13.May	133	12.June	163
D5 - La Jalliere (N-FR)	07.Apr	97	07.May	127
R1 - Weiherbach (DE)	22.Apr	112	22.May	142
R3 - Bologna (IT)	23.Mar	82	22.Apr	112
	Spring cereals BBCH 21-39 (beginning 70 days before harvest)			
D3 - Vreedepeel (NL)	11.Jun	162	11.Jul	192
D4 - Skousbo (DK)	17.Jun	168	17.Jul	198
D5 - La Jalliere (N-FR)	11.May	131	10.Jun	161

Table 8.9-8 lists the default parameters used in the PEC_{SW}-models. Following guidance from the EFSA opinion on the temperature dependence of chemical reactions⁵, a Q₁₀ of 2.58 (PRZM), an Arrhenius activation energy of 65400 J mol⁻¹ (TOXSWA) and an alpha factor of 0.0948 K⁻¹ (MACRO) were used as transformation factors.

⁵ Scientific Opinion of the Panel on Plant Protection Products and their Residues on a request from EFSA related to the default Q10 value used to describe the temperature effect on transformation rates of pesticides in soil. The EFSA Journal (2007) 622, 1-32 (<http://www.efsa.europa.eu/en/efsajournal/doc/622.pdf>)

Table 8.9-8: Summary of default input parameters for PEC_{SW} and PEC_{Sed} calculations according to FOCUS⁶

Parameter	Value	Remarks
Entry routes into surface water	Spray drift Runoff Drainage	-
Degradation in soil		
Temperature correction function Reference temperature [°C] MACRO: [1/K] PRZM: Q ₁₀ [-]	20 0.0948 2.58	FOCUS recommendation FOCUS recommendation FOCUS recommendation ⁷
Moisture correction function Reference moisture [-] PRZM/MACRO moisture exponent [-]	pF 2 0.7	FOCUS recommendation
Degradation in aquatic systems		
Temperature correction function Reference temperature [°C] TOXSWA: activation energy [J/mol]	20 65 400	FOCUS recommendation EFSA recommendation
Wash off coefficient PRZM: [1/cm] MACRO: [1/mm]	0.5 0.05	FOCUS recommendation

Table 8.9-9: Application settings for FOCUS Step 3

Application method:	Ground spray
Chemical application method:	CAM 2 (Foliar applied, linear application)
Incorporation depth [cm]:	4 (Default)

Table 8.9-10: Modelling software used

SWASH (Step 1 & 2)	Version 3.2
SWASH (Step 3)	Version 5.3 incorporating:
MACRO	Version 5.5.4
PRZM	Version 4.3.1
TOXWA	Version 4.4.3

zRMS comments:

The application pattern assumed in surface water simulations is in line with Central Zone GAP as presented in Table 8.1-1.

For Step 1&2 simulation a risk envelope approach has been taken by the Applicant and simulations were performed for calculations for winter cereals with assumption of 0% crop interception, which covers all intended uses of ADM.3304.H.1.A and is agreed by the zRMS as representing worst case.

It is noted that in the Step 3 modelling performed for uses in cereals the Applicant considered the relative application dates used in groundwater modelling (i.e. 100 and 70 days before harvest for winter and spring cereals, respectively) to determine the first day of the application window. However, in case of surface water scenarios, the AppDate provides the exact dates for start and end of the application windows for each scenario and does provide any information on the correct relative application dates to set the beginning of the application windows. The application windows suggested by the AppDate for uses in winter and spring cereals at BBCH 21-39 are presented in the table below. In line with the internal Polish agreements, winter cereals were considered as the surrogate crop for grassland. Since Poland is a single CMS indicated in the GAP table, only scenarios representative for Poland were considered (i.e. D3, D4 and R1).

⁶ Generic guidance for FOCUS surface water scenarios. Version: 1.0. January 2011

FOCUS scenario	Application windows relevant for surface water modelling according to AppDate ver. 3.06			
	Date		Julian Days	
	First Day	Last Day	First Day	Last Day
Grassland BBCH 21-39				
D3	7-Apr	7-May	97	127
D4	9-Mar	8-Apr	68	98
D5	6-Mar	5-Apr	65	95
R3	10-Mar	9-Apr	69	99
Winter cereals BBCH 21-39				
D3	7-Apr	7-May	97	127
D4	9-Mar	8-Apr	68	98
D5	6-Mar	5-Apr	65	95
R1	15-Apr	15-May	105	135
R3	10-Mar	9-Apr	69	99
Spring cereals BBCH 21-39				
D3	16-Apr	16-May	106	136
D4	9-May	8-Jun	129	159
D5	29-Mar	28-Apr	88	118

Comparison of the dates suggested by AppDate and these proposed by the Applicant shows that for majority scenarios the application windows used by the Applicant do not fall into dates suggested by the AppDate. Partial overlap could be seen in D4 scenario for grassland, D5 scenario for grassland and winter cereals as well as R3 and R1 scenarios for winter cereals. Since application dates will vary among different regions, the Applicants' assumptions are not regarded as not correct. Nevertheless, as impact of the different application windows on the results of surface water modelling cannot be easily predicted, additional set of simulations has been performed by the zRMS for each compound with consideration of the application windows suggested by AppDate. For details, see respective points below.

8.9.2.1 2,4-D and its metabolites

As **risk envelope approach for FOCUS Step 1 & 2** “winter cereals” was calculated assuming 0 % crop interception as default value (750 g 2,4-D/ha). This calculated worst case scenario also covers the application in winter and spring cereals assuming average crop interception as well as the application in grassland assuming average crop interception.

Table 8.9-11: Input parameters related to 2,4-D and its metabolites for PEC_{sw/sed} calculations

Parameter	2,4-D	2,4-DCP	2,4-DCA
Molecular Mass [g/mol]	221	163	177
Water solubility [mg/L]	24300 (25°C) Calculated for 20°C: 22684	4870 (20°C)	96.3 (20°C)
Saturated vapour pressure [Pa]	9.9 x 10 ⁻⁶ (20°C)	Not required	Not required
K _{OC} / K _{OM} [mL/g]	58.6 / 34.0	512	1028
Freundlich sorption exponent (1/n)	0.87	Not required	Not required
DT ₅₀ soil [days]	4.14	7.0	10.4
DT ₅₀ w/s system[days]	18.16	103.9	1000
DT ₅₀ water (degradation)[days]	18.16	103.9	1000
DT ₅₀ sediment (degradation) [days]	18.16 (Step 1&2) 1000 (Step 3)	1000	1000
DT ₅₀ on plants [days]	10	Not required	Not required
Plant uptake	0	Not required	Not required
Max occurrence [%] in soil	--	8.7	15.0
water/sediment	--	32.1	5.3

Table 8.9-12: FOCUS Step 1,2 PEC_{sw} and PEC_{sed} for 2,4-D and its metabolites – North EU

Scenario	Substance	Step 1		Step 2 [µg/L]	
		PEC _{sw} [µg/L]	PEC _{sed} [µg/kg]	PEC _{sw} [µg/L]	PEC _{sed} [µg/kg]
Winter cereals 750 g a.i./ha No crop interception North EU, Oct. – Feb.*	2,4-D	238.78	135.88	64.97	36.97
	2,4-DCP	46.34	232.33	13.31	67.34
	2,4-DCA	17.44	177.40	6.15	62.88
Winter cereals 750 g a.i./ha No crop interception South EU, Oct. – Feb.*	2,4-D	238.78	135.88	55.02 53.10	31.14 30.02
	2,4-DCP	46.34	232.33	10.87	54.85
	2,4-DCA	17.44	177.40	4.95	50.56

* Worst case application date autumn and winter, covers the application in spring and summer

Table 8.9-13: Step 3 - Maximum PEC_{sw} and PEC_{sed} values for 2,4-D in grassland – application 01.March

Scenario	PEC _{sw} [µg/L]	Event	Date of global max. PEC _{sw}	PEC _{sed} [µg/kg]
D3_Ditch	4.748	Spray	29-Feb-1992	0.8613
D4_Pond	0.164	Spray	01-Mar-1985	0.2324
D4_Stream	3.831	Spray	01-Mar-1985	0.1659
D5_Pond	0.164	Spray	07-Mar-1978	0.2138
D5_Stream	3.89	Spray	07-Mar-1978	0.107
R3_Stream	4.407	Spray	01-Mar-1980	0.4722

Table 8.9-14: Step 3 - Maximum PEC_{sw} and PEC_{sed} values for 2,4-D in grassland – application 01.August

Scenario	PEC _{sw} [µg/L]	Event	Date of global max. PEC _{sw}	PEC _{sed} [µg/kg]
D3_Ditch	4.782	Spray	31-Jul-1992	1.384
D4_Pond	0.1641	Spray	27-Aug-1985	0.1837
D4_Stream	4.111	Spray	27-Aug-1985	0.4336
D5_Pond	0.1642	Spray	04-Aug-1978	0.1637
D5_Stream	4.435	Spray	04-Aug-1978	0.5424
R3_Stream	4.433	Spray	01-Aug-1975	0.5714

Table 8.9-15: Step 3 - Maximum PEC_{sw} and PEC_{sed} values for 2,4-D in winter cereals

Scenario	PEC _{sw} [µg/L]	Event	Date of global max. PEC _{sw}	PEC _{sed} [µg/kg]
D3_Ditch	4.756	Spray	06-May-1992	0.9391
D4_Pond	0.164	Spray	30-May-1985	0.1771
D4_Stream	3.965	Spray	30-May-1985	0.2435
D5_Pond	0.164	Spray	08-Apr-1978	0.2033
D5_Stream	3.793	Spray	08-Apr-1978	0.09078
R1_Pond	0.1751	Runoff	20-May-1984	0.2763
R1_Stream	4.288	Runoff	07-May-1984	0.6655
R3_Stream	8.400 (zRMS modelling with dates in line with AppDate)	Runoff	22-Mar-1980	1.39
	4.398 (Applicants' initial modelling with dates not fully overlapping with Appdate suggestions)	Spray	28-Mar-1980	0.764

Table 8.9-16: Step 3 - Maximum PEC_{SW} and PEC_{SED} values for 2,4-D in spring cereals

Scenario	PEC _{SW} [µg/L]	Event	Date of global max. PEC _{SW}	PEC _{SED} [µg/kg]
D3_Ditch	4.766	Spray	15-Jun-1992	1.062
D4_Pond	0.1641	Spray	04-Jul-1985	0.1603
D4_Stream	4.099	Spray	04-Jul-1985	0.4111
D5_Pond	0.1642	Spray	11-May-1978	0.1795
D5_Stream	4.149	Spray	11-May-1978	0.1912

zRMS comments:

For discussion on input parameters and the assumed application pattern, please refer to points 8.9.1 and 8.9.2 above. Endpoints provided in Table 8.9-11 are confirmed to be agreed by the zRMS.

The surface water modelling was independently validated by the zRMS in additional modelling using endpoints as reported in Table 8.9-11 with exception of the soil DT₅₀ (EU agreed soil DT₅₀ of 4.4 days has been used by the zRMS). The application windows as suggested by AppDate were used (see commenting box in point 8.9.2 for details). Obtained PEC_{SW/SED} values were in good agreement with these obtained by the Applicant with exception of R3 scenario in winter cereals, for which PEC_{SW} obtained by the zRMS was much higher comparing to the Applicants' value. Nevertheless, as application windows may vary among Member States, the zRMS result is presented in Table 8.9-15 additionally to the Applicants' result for this scenario. Surface water exposure presented in Tables 8.9-13 to 8.9-16 may be thus used for purposes of the aquatic risk assessment. In case of R3 scenario in winter cereals, Member States may choose which value is most relevant depending on the application window relevant in their countries.

~~Since Poland is the only cMS indicated in the GAP table, results for scenarios not representative for Poland are displayed in grey font.~~

Results for R1 scenario in winter cereals may be used to address the risk in this scenario following uses in grassland and spring cereals, for which scenario R1 is not defined in FOCUS models.

Since Step 4 PEC_{SW} values were deemed necessary to address the risk from the mixture, additional simulations were performed by the zRMS with assumption of the unsprayed buffer zones using EU agreed data. Application dates suggested by AppDate ver. 3.06 were taken into account (see commenting box in point 8.9.2 for details). Results are presented below. Taking into account that only PEC_{SW} values were used for the mixture risk assessment, PEC_{SED} are not presented. Since scenario R1 is not defined for grassland, calculation for winter cereals are considered as surrogate, in line with Polish national agreements.

Substance	Application pattern	Step / mitigation	Scenario	PEC _{SW} [µg/L]
2,4-D	Winter cereals and grassland BBCH 21-39 750 g a.s./ha	4 10 m buffer	D3 ditch	0.683
			D4 pond	0.102
			D4 stream	0.681
			D5 pond	0.102
			D5 stream	0.727
			R1 pond	0.144
			R1 stream	4.367
			R3 stream	8.400
		4 10 m VFS (including 10 m buffer)	D3 ditch	0.683
			D4 pond	0.102
			D4 stream	0.681
	Spring cereals BBCH 21-39 750 g a.s./ha	4 10 m buffer	D5 pond	0.102
			D5 stream	0.727
			R1 pond	0.102
			R1 stream	0.607
			R3 stream	3.783

It is noted that in Appendix 4 surface water exposure for anaerobic soil metabolite 4-chlorophenol was calculated with consideration of endpoints derived from the new studies submitted in order to address the data gap identified in EFSA Journal 2014;12(9):3812. For details of calculations and zRMS evaluation, please refer to Appendix 4, point A 4.2 of this document. The following PEC_{SW/SED} values are relevant for the aquatic risk assessment purposes:

Crop	Period	Step	Scenario	4-CP	
				PEC _{SW} [µg/L]	PEC _{SED} [µg/kg]
Winter cereals ¹⁾	March-May	1	-	49.43	76.21
		2	N-Europe	5.23	8.0

¹⁾ Application to winter cereals at 750 g a.s./ha with 0% crop interception as representing worst case and covering all intended uses

Additional calculations were also performed for hydrolytic metabolite 1,2,4-benzenetriol, however due to lack of substantial data required for modelling, the PEC_{SW} for the metabolite was derived by the Applicant by correction of the parent (2,4-D acid) PEC_{SW} for the maximum occurrence and molar ratio. Additional Step 1&2 calculations performed by the zRMS using worst case default values were in good agreement with exposure obtained by the Applicant. For the aquatic risk assessment **PEC_{SW} of 43.2 µg/L (Step 1) and 11.7 µg/L (Step 2)** are considered relevant. For details of calculations and zRMS evaluation, please refer to Appendix 4, point A 4.2 of this document.

For future evaluations the Applicant is kindly asked to provide surface water exposure calculations for all relevant compounds in point 8.9 in order to facilitate the assessment by the zRMS and make the report more transparent.

Surface water exposure for 2,4-D EHE is presented below, in point 8.9.2.4. For clarity the Applicant is kindly asked to provide calculations for various forms of the same active compound in one point in future evaluations.

In case of mutual recognition process additional simulations may be requested by Member States considering other scenarios as representative or not accepting FOCUS modelling at all.

8.9.2.2 Clopyralid

Table 8.9-17: Input parameters related to clopyralid for PEC_{sw/SED} calculations

Parameter		Clopyralid
Molecular Mass [g/mol]		192
Water solubility [mg/L]		143 000 (20°C)
Saturated vapour pressure [Pa]		Not required
K _{oc} [mL/g]		1.41
Freundlich sorption exponent (1/n) [-]		Not required
DT ₅₀ soil [days]		7.05
DT ₅₀ w/s system[days]		1000
DT ₅₀ water (degradation)[days]		148
DT ₅₀ sediment (degradation) [days]		1000
DT ₅₀ on plants [days]		Not required
Plant uptake [-]		Not required
Max occurrence [%] in	soil	--
	water/sediment	--

Table 8.9-18: PEC_{SW} and PEC_{SED} at FOCUS Step 1 for active substance clopyralid

Use No.	Crop	Application rate [g a.s./ha]	Max PEC _{SW} [µg/L]	21-day TWA PEC _{SW} [µg/L]	Max PEC _{SED} [µg/kg]
1	Grass (BBCH 21-39)	1 × 60 g a.s./ha	20.5	20.4	0.282
2	Winter cereals (BBCH 21-39)	1 × 60 g a.s./ha	20.5	20.4	0.282
3	Spring cereals (BBCH 21-39)	1 × 60 g a.s./ha	20.5	20.4	0.282

zRMS comments:

For discussion on input parameters and the assumed application pattern, please refer to points 8.9.1 and 8.9.2 above. Endpoints provided in Table 8.9-17 are confirmed to be agreed by the zRMS.

The surface water modelling was independently validated by the zRMS in additional modelling using endpoints as reported in Table 8.9-17. Obtained PEC_{SW/SED} values were in good agreement with these obtained by the Applicant. Surface water exposure presented in Table 8.9-18 may be thus used for purposes of the aquatic risk assessment.

Since Step 3 and 4 PEC_{SW} values were deemed necessary to address the risk from the mixture, additional simulations were performed by the zRMS using EU agreed data. Application dates suggested by AppDate ver. 3.06 were taken into account (see commenting box in point 8.9.2 for details). Results are presented below. Taking into account that only PEC_{SW} values were used for the mixture risk assessment, PEC_{SED} are not presented. Since scenario R1 is not defined for grassland, calculation for winter cereals are considered as surrogate, in line with Polish national agreements.

Substance	Application pattern	Step / mitigation	Scenario	PEC _{SW} [µg/L]
Clopyralid	Winter cereals and grassland BBCH 21-39 60 750 g a.s./ha	3	D3 ditch	0.381
			D4 pond	0.014
			D4 stream	0.282
			D5 pond	0.013
			D5 stream	0.300
			R1 pond	0.016
			R1 stream	0.517
			R3 stream	0.444
	Spring cereals BBCH 21-39 60 750 g a.s./ha	3	D3 ditch	0.382
			D4 pond	0.013
			D4 stream	0.311
			D5 pond	0.013
			D5 stream	0.302
Clopyralid	Winter cereals and grassland BBCH 21-39 60 750 g a.s./ha	4 10 m buffer	D3 ditch	0.056
			D4 pond	0.009
			D4 stream	0.055
			D5 pond	0.008
			D5 stream	0.058
			R1 pond	0.012
			R1 stream	0.517
			R3 stream	0.444
	Spring cereals BBCH 21-39 60 750 g a.s./ha	4 10 m buffer	D3 ditch	0.057
			D4 pond	0.008
			D4 stream	0.060
			D5 pond	0.008
			D5 stream	0.058

In case of mutual recognition process additional simulations may be requested by Member States not accepting FOCUS modelling.

8.9.2.3 Fluroxypyr

As **risk envelope approach for FOCUS Step 1 & 2** “winter cereals” was calculated assuming 0 % crop interception as default value (150 g fluroxypyr acid/ha and 216 Fluroxypyr-MHE/ha). This calculated worst case scenario also covers the application in winter and spring cereals assuming average crop interception as well as the application in grassland assuming average crop interception.

Table 8.9-19: Input parameters related to fluroxypyr and its metabolites for PEC_{sw/sed} calculations

Parameter	Fluroxypyr-meptyl	Fluroxypyr acid	Pyridinol	Methoxy-pyridine	3-CP
Molecular Mass [g/mol]	367.3	255	197	211	162
Water solubility [mg/L]	0.009	91	91	91	91
Saturated vapour pressure [Pa]	1.349 x 10 ⁻⁶	Not required	Not required	Not required	Not required
Koc [mL/g]	19950	68	708 (pH < 7) 68.5* (pH ≥ 7)	321	1
Freundlich sorption exponent (1/n)	0.9 ±	Not required	Not required	Not required	Not required
DT ₅₀ soil [days]	1.0	13.9	17.6	111.11	1000
DT ₅₀ w/s system [days]	38.1	38.1	35.5	1000	1000
DT ₅₀ water (degradation) [days]	38.1	38.1	35.5	1000	1000
DT ₅₀ sediment (degradation) [days]	38.1 (Step 1&2) 1000 (Step 3)	1000	1000	1000	1000
DT ₅₀ on plants [days]	10	Not required	Not required	Not required	Not required
Plant uptake	0 0.5	Not required	Not required	Not required	Not required
Max occurrence [%] in soil	--	--	23.9	38.2	0
water/ sediment	--	--	55.5	0	17.9

* Calculations are performed with the worst case Koc of 68.5 mL/g

Fluroxypyr as well as Fluroxypyr-MHE are calculated as parent compound. For the metabolites Pyridinol, Methoxypyridine and 3-CP, Fluroxypyr acid was assumed as parent compound.

Table 8.9-20: FOCUS Step 1-2 PEC_{sw} and PEC_{sed} for fluroxypyr and its metabolites

Scenario	Substance	Step 1		Step 2 [µg/L]	
		PEC _{sw} [µg/L]	PEC _{sed} [µg/kg]	PEC _{sw} [µg/L]	PEC _{sed} [µg/kg]
Winter cereals 150 g Fluroxypyr acid/ha 216 g Fluroxypyr-MHE/ha No crop interception North EU, Oct. – Feb.*	Fluroxypyr-meptyl	4.60	525.15	1.99	29.24
	Fluroxypyr acid	47.22	31.46	19.99	13.56
	Pyridinol	28.69	19.25	12.18	8.33
	Methoxypyridine	11.17	34.74	5.45	16.94
	3-CP	5.84	0.06	2.48	0.02
Winter cereals 150 g Fluroxypyr acid/ha 216 g Fluroxypyr-MHE/ha No crop interception South EU, Oct. – Feb.*	Fluroxypyr-meptyl	4.60	525.15	1.99	25.98
	Fluroxypyr acid	47.22	31.46	16.23	11.01
	Pyridinol	28.69	19.25	9.84	6.73
	Methoxypyridine	11.17	34.74	4.36	13.56
	3-CP	5.84	0.06	2.02	0.002

* Worst case application date autumn and winter, covers the application in spring and summer

Table 8.9-21: Step 3 - Maximum PEC_{SW} and PEC_{SED} for fluroxypyr-meptyl in grassland – application 01.March

Scenario	PEC _{SW} [µg/L]	Event	Date of global max. PEC _{SW}	PEC _{SED} [µg/kg]
D3_Ditch	1.346	Spray	29-Feb-1992	0.8807
D4_Pond	0.0465	Spray	01-Mar-1985	0.4682
D4_Stream	1.086	Spray	01-Mar-1985	0.06321
D5_Pond	0.04649	Spray	07-Mar-1978	0.4551
D5_Stream	1.103	Spray	07-Mar-1978	0.03816
R3_Stream	1.25	Spray	01-Mar-1980	0.2831

Table 8.9-22: Step 3 - Maximum PEC_{SW} and PEC_{SED} for fluroxypyr-meptyl in grassland – application 01.August

Scenario	PEC _{SW} [µg/L]	Event	Date of global max. PEC _{SW}	PEC _{SED} [µg/kg]
D3_Ditch	1.356	Spray	31-Jul-1992	2.052
D4_Pond	0.04652	Spray	27-Aug-1985	0.4235
D4_Stream	1.166	Spray	27-Aug-1985	0.2544
D5_Pond	0.04653	Spray	04-Aug-1978	0.3904
D5_Stream	1.258	Spray	04-Aug-1978	0.0988
R3_Stream	1.257	Spray	01-Aug-1975	0.3484

Table 8.9-23: Step 3 - Maximum PEC_{SW} and PEC_{SED} for fluroxypyr-meptyl in winter cereals

Scenario	PEC _{SW} [µg/L]	Event	Date of global max. PEC _{SW}	PEC _{SED} [µg/kg]
D3_Ditch	1.348	Spray	06-May-1992	1.035
D4_Pond	0.04651	Spray	30-May-1985	0.4066
D4_Stream	1.124	Spray	30-May-1985	0.1054
D5_Pond	0.04648	Spray	08-Apr-1978	0.4427
D5_Stream	1.076	Spray	08-Apr-1978	0.03131
R1_Pond	0.04648	Spray	26-Apr-1984	0.4115
R1_Stream	0.8879	Spray	26-Apr-1984	0.1255
R3_Stream	1.247	Spray	28-Mar-1980	0.2631

Table 8.9-24: Step 3 - Maximum PEC_{SW} and PEC_{SED} for fluroxypyr-meptyl in spring cereals

Scenario	PEC _{SW} [µg/L]	Event	Date of global max. PEC _{SW}	PEC _{SED} [µg/kg]
D3_Ditch	1.351	Spray	15-Jun-1992	1.292
D4_Pond	0.04651	Spray	04-Jul-1985	0.3842
D4_Stream	1.162	Spray	04-Jul-1985	0.2297
D5_Pond	0.04651	Spray	11-May-1978	0.4129
D5_Stream	1.177	Spray	11-May-1978	0.07643

zRMS comments:

For discussion on input parameters and the assumed application pattern, please refer to points 8.9.1 and 8.9.2 above. Endpoints provided in Table 8.9-19 are confirmed to be agreed by the zRMS.

The surface water modelling was independently validated by the zRMS in additional modelling using endpoints as reported in Table 8.9-19 with exception of the PUF and 1/n for fluroxypyr-meptyl (1/n of 0.9 was used, as agreed at the EU level, while PUF was set to 0 at Step 3 modelling as being in line with indications of the current FOCUS surface water guidance). The application windows as suggested by AppDate were used (see commenting box in point 8.9.2 for details). Obtained PEC_{SW/SED} values were in good agreement with these obtained by the Applicant. Surface water exposure presented in Tables 8.9-20 to 8.9-24 may be used for purposes of the aquatic risk assessment.

Since Step 4 PEC_{SW} values were deemed necessary to address the risk from the mixture, additional simulations were performed by the zRMS with assumption of the unsprayed buffer zones and vegetated filter strips using EU agreed data. To mitigate run-off, VFSmod in SWAN was used as being applicable in Poland. Application dates suggested by AppDate ver. 3.06 were taken into account (see commenting box in point 8.9.2 for details). Results are presented below. Taking into account that only PEC_{SW} values were used for the mixture risk assessment, PEC_{SED} are not presented. Since scenario R1 is not defined for grassland, calculation for winter cereals are considered as surrogate, in line with Polish national agreements.

Substance	Application pattern	Step / mitigation	Scenario	PEC _{SW} [µg/L] ¹⁾
Fluroxypyr-meptyl	Winter cereals and grassland BBCH 21-39 216 750 g a.s./ha	4 10 m buffer	D3 ditch	0.190 0.197
			D4 pond	0.028 0.029
			D4 stream	0.189 0.196
			D5 pond	0.028
			D5 stream	0.202
			R1 pond	0.028 0.029
			R1 stream	0.168 0.175
			R3 stream	0.237
	Spring cereals BBCH 21-39 216 750 g a.s./ha	4 10 m buffer	D3 ditch	0.190 0.196
			D4 pond	0.028 0.029
			D4 stream	0.209 0.202
			D5 pond	0.028
			D5 stream	0.203

¹⁾ Initially total PEC_{SW} values including suspended solids were presented, but in line with EFSA aquatic guidance (2013) PEC_{SW} for freely dissolved chemical is more relevant for the aquatic risk assessment, therefore results including suspended solids were struck through

Since Poland is the only eMS indicated in the GAP table, results for scenarios not representative for Poland are displayed in grey font.

Results for R1 scenario in winter cereals may be used to address the risk in this scenario following uses in grassland and spring cereals, for which scenario R1 is not defined in FOCUS models.

In case of mutual recognition process additional simulations may be requested by Member States considering other scenarios as representative or not accepting FOCUS modelling at all.

8.9.2.4 2,4-D EHE

PEC_{SW} calculations has been performed for the 2,4-D EHE (not included in the report above).

2,4-D EHE degrades almost instantaneously in soil with a DT₅₀ soil < 0.1 days. Therefore for the PEC_{SW} calculations only drift entries in surface water bodies are to be considered. This follows the approach used by the RMS Greece on the Bridging report (2018) prepared for the ester form.

The PEC_{SW} was calculated using the following equation:

$$PEC_{SW} (\mu g/L) = \frac{\% \text{ Drift}_{90th\ percentile} \times \text{Application rate (g/ha)}}{\text{Water depth (cm)} \times 10}$$

The drift rate used was the 90th percentile for cereals and grassland at 1 m from the application site at an application of 1125 g 2,4-D EHE /ha. The depth of the water body was assumed to be 30 cm.

Table 8.9-25: Use pattern of 2,4-D 2-EHE considered for PEC_{SW} calculations from spray drift

App. rate & frequency	1 × 1125 g a.s./ha
Scenario / Drift percentile	Arable crops / 90th percentile
Entry pathways considered	Drift: yes Volatilisation: no

Table 8.9-26: PEC_{SW} of 2,4-D EHE due to spray drift

Spray drift buffer [m]	Drift [%]	Initial PEC _{SW} [µg/L]			
		0% Drift Red.	50% Drift Red.	75% Drift Red.	90% Drift Red.
1	2.77	10.388	5.194	2.720	1.039
5	0.57	2.138	1.069	0.535	0.214
10	0.29	1.088	-	-	-

zRMS comments:

Although the approach taken by the Applicant with regard to calculation of the surface water exposure assessment for 2,4-D EHE are not described in respective FOCUS guidance documents, in opinion of the zRMS it is relevant for such rapidly degrading substances for which neither drainage, nor run-off will be the relevant route of migration to surface water bodies since the substance will degrade in soil before reaching the water body.

This could be potentially captured in Step 3 modelling, however due to extremely rapid degradation it was not possible to determine the soil adsorption coefficients (K_{foc}) which are necessary to perform reliable surface water modelling. Nevertheless, based on the available data for 2,4-D EHE the zRMS is of the opinion that spray drift would be identified as the main route of migration to surface water bodies and Step 4 simulation would be necessary to reduce the exposure using either unsprayed buffer zones or the drift reduction.

In order to check how the Applicants' approach falls into the FOCUS modelling Step 3 simulations were performed by the zRMS using the EU agreed data for 2,4-D 2-EHE as reported in the Bridging Report (2018) and K_{foc} of 10 and 10000 mL/g in order to simulate situations with low and high sorption of the substance to soil, but no impact on the exposure predicted for the water column was observed. Winter cereals were chosen as the modelled crop since all scenarios relevant for Poland are defined for this crop. Results are displayed in table below. Since no endpoints for sediment dwelling organisms are available for 2,4-D 2-EHE, only PEC_{SW} values are presented.

Substance	Application pattern	Step	Scenario	PEC _{SW} [µg/L]
2,4-D 2-EHE	Winter cereals BBCH 21-39 1125 g a.s./ha	3	D3 ditch	7.123
			D4 pond	0.246
			D4 stream	5.269
			D5 pond	0.246
			D5 stream	5.632
			R1 pond	0.246
			R1 stream	4.696
			R3 stream	6.597

Additional set of Step 4 simulations was performed with assumption of 5 m unsprayed buffer zone and 50% drift reduction. Results are displayed in table below. Since no endpoints for sediment dwelling organisms are available for 2,4-D 2-EHE, only PEC_{SW} values are presented.

Substance	Application pattern	Step / mitigation	Scenario	PEC _{SW} [µg/L]
2,4-D 2-EHE	Winter cereals BBCH 21-39 1125 g a.s./ha	4 5 m buffer	D3 ditch	1.931
			D4 pond	0.213
			D4 stream	1.925
			D5 pond	0.213
			D5 stream	2.060
			R1 pond	0.213
			R1 stream	1.716
			R3 stream	2.410
		4 50% drift reduction	D3 ditch	3.562
			D4 pond	0.123 0.184
			D4 stream	2.635 3.551
			D5 pond	0.123
			D5 stream	2.816
			R1 pond	0.123 0.184
			R1 stream	2.348 3.165
			R3 stream	3.299
		4 10 m buffer	R3 stream	1.278 ¹⁾

¹⁾ Additionally required by ecotox

As may be seen above, calculation of the surface water exposure using the Applicants' approach resulted with considerably higher PEC_{SW} values comparing to Step 3 and Step 4 modelling with exception of R3 scenario at Step 4 when 5 m buffer was assumed – the PEC_{SW} calculated using FOCUS models was slightly higher comparing to the spray drift value reported in Table 8.9-26 (2.410 vs. 2.138 µg/L, respectively). Nevertheless, since in other Steps No significant differences are expected for other crops due to the same rates, developmental stages and the fact that all crops belong to the same botanical group (monocots). Taking this into account, results reported in Table 8.9-26 may be used for the risk assessment purposes as representing worst case. Nevertheless, additional calculations for buffer zone of 10 m were added by the zRMS.

8.9.2.5 PEC_{sw}/sed of AG-CDF1-480 EC

The PEC_{sw} for the formulation was used in Section 9, the aquatic risk assessment (KCP 9.5.2). Due to the differing and unknown dissipation times of the constituents of AG-CDF1-480 EC in aquatic systems, it was only possible to calculate the maximum instantaneous PEC_{sw} value from entry through spray-drift that occurred immediately after a single application. The PEC_{sw} was calculated using the following equation:

$$\text{PEC}_{\text{sw}} (\mu\text{g/L}) = \frac{\% \text{ Drift}_{\text{xth \%ile}} \times \text{Application rate (g/ha)}}{\text{Water depth (cm)} \times 10}$$

Table 8.9-25: Use pattern of ADM.3304.H.1.A (old code AG-CDF1-480 EC) considered for PEC_{sw} calculations from spray drift

App. rate & frequency	1 × 2190 g/ha ^a
Scenario / Drift percentile	Arable crops / 90 th percentile
Entry pathways considered	Drift: yes Volatilisation: no

^a Assuming a density of 1.095 g/mL and an application rate of 2 L product/ha.

Table 8.9-26: PEC_{sw} of ADM.3304.H.1.A (old code AG-CDF1-480 EC) due to spray drift

Spray drift buffer [m]	Drift [%]	Initial PEC _{sw} [µg/L]			
		0 % drift red.	50 % drift red.	75 % drift red.	90 % drift red.
1	2.77	20.22	10.11	5.055	0.202
5	0.57	4.161	2.081	1.040	0.416
10	0.28	2.04	1.02	0.51	0.20

zRMS comments:

The surface water exposure to formulation was validated by the zRMS using Spray Drift Calculator. Obtained results were lower comparing to Applicants' results and for this reason PEC_{sw} reported in Table 8.9-26 represent worst case and may be thus used in the aquatic risk assessment.

8.10 Fate and behaviour in air (KCP 9.3, KCP 9.3.1)

Studies on volatility with the formulation were not performed, since it is possible to extrapolate from data obtained with the active substances.

All substances have a low vapour pressure at 20°C (i.e. 2,4-D: 9.9×10^{-6} Pa, 2,4-D EHE: 4.80×10^{-4} Pa (25°C), Clopyralid: 1.36×10^{-3} Pa (25°C), Fluroxypyr-meptyl: 1.0×10^{-5} Pa (pure), Fluroxypyr acid: 3.8×10^{-9} Pa) and are therefore characterised as being semi- or non-volatile from plant or soil surfaces.

The 2,4-D metabolites 2,4-DCP and 2,4-DCA have to be considered as volatile due to vapour pressures of 8.7 Pa (20°C) and 13.4 Pa (25°C), respectively.

Table 8.10-1 Summary of atmospheric degradation and behaviour

End-Point		2,4-D EFSA Journal 2014; 12(9): 3812	2,4-D 2-EHE Review Report for the initial Annex I inclusion of the a.s. 2,4-D acid (7599/V1/97-final, 1 October 2001), and –the original Monograph (1996) (DAR) as referred to in the Bridging report (2018)	Clopyralid EFSA Conclusion (2018); 16(7):5389	Fluroxypyr-meptyl EFSA Journal 2011;9(3):2091
Vapour pressure		9.9×10^{-6} (20°C)	4.80×10^{-4} Pa (25°C)	1.36×10^{-3} Pa (25°C)	Meptyl: 1.0×10^{-5} Pa (20°C) Acid: 3.8×10^{-9} Pa (20°C) 1.349×10^{-6} (20°C)
Volatilization	from soil	negligible (after 15 days)	negligible (after 15 days)	<2 % in 24 hours	Not examined due to low volatility of Fluroxypyr
	from plants	no data	no data	<4 % in 24 hours	
Photochemical oxidative degradation		DT ₅₀ of 1.6 d 71 hours (2.96 d)	-	DT ₅₀ = 19.5 days Atkinson calculation using AOPWIN v.1.90	Meptyl: 9.82 h (Atkinson model) Acid: 13.35 h (Atkinson model)

2,4-D / 2,4-D EHE

Based on the vapour pressure of 9.9×10^{-6} Pa (20°C) for 2,4-D and of 4.80×10^{-4} Pa (25°C) for 2,4-D EHE, the substances are non-volatile. Therefore, the short-range transport is negligible and needs not to be addressed further. The photochemical oxidative degradation of 2,4-D acid in air was estimated to be 1.6 days ~~2.96 days~~ and therefore long-range transport is not considered to be of relevance.

Clopyralid

Based on the vapour pressure of 1.36×10^{-3} Pa (25°C) for clopyralid, the substance is semi-volatile. According to the EFSA Conclusion (2018) 16(7):5389, the calculation of PEC_{air} for clopyralid is not anticipated to be present in air in significant quantities.

Fluroxypyr

Based on the vapour pressure of 3.8×10^{-9} Pa and 1.0×10^{-5} Pa ~~1.349×10^{-6} Pa~~ (20°C) for the acid and the ester, respectively, any significant volatilization resp. accumulation in air of Fluroxypyr acid and Fluroxypyr meptyl is highly unlikely. According to the FOCUS Air Guidance (SANCO/10553/2006), short-range transport in air can be considered negligible and does not need to be evaluated further.

As a conclusion no PECair were calculated.

zRMS comments:

Information provided in Table 8.10-1 was amended by the zRMS in order to comply with:

- EFSA Journal 2014;12(9):3812 for 2,4-D,
- EFSA Journal 2018;16(7):5389 for clopyralid,
- EFSA Journal 2011;9(3):2091 for fluroxypyr.

For 2,4-D EHE the endpoints presented in Table 8.10-1 are in line with endpoints presented in the 2,4-D 2-EHE Bridging Report in area of efate (October 2018). Since the SANCO 7599/VI/97 final is not applicable anymore, reference to this document has been struck through and the Bridging Report has been referenced as being the relevant document where the currently agreed EU data for 2,4-D 2-EHE may be found.

2,4-D

For the acid form of 2,4-D the vapour pressure is $<10^{-5}$ Pa and the DT₅₀ in the air is <2 days, so no unacceptable contamination of the atmosphere is expected following application of ADM.3304.H.1.A according to the intended Central Zone GAP.

The vapour pressure of the ester form of 2,4-D is greater than the trigger of 10^{-5} Pa, but the DT₅₀ in the air is <2 days, so the short- or long-range transport are not expected to occur. Taking this into account, the contamination of the atmosphere from the intended uses of ADM.3304.H.1.A is considered to be negligible.

Clopyralid

Although the vapour pressure and air DT₅₀ for clopyralid are above the triggers of 10^{-5} PA and 2 days, respectively, the volatilisation from soil and plant surfaces was investigated in the course of the renewal process and indicated low volatilisation potential of this compound ($<2\%$ and $<4\%$ from soil and plant surfaces, respectively). Taking this into account, the contamination of the atmosphere from the intended uses of ADM.3304.H.1.A is considered to be negligible.

Fluroxypyr

For both forms of fluroxypyr the vapour pressure is $<10^{-5}$ Pa and the DT₅₀ in the air is <2 days, so no unacceptable contamination of the atmosphere is expected following application of ADM.3304.H.1.A according to the intended Central Zone GAP.

Appendix 1 Lists of data considered in support of the evaluation

List of data submitted by the applicant and relied on

Data point	Author(s)	Year	Title Company Report No. Source (where different from company) GLP or GEP status Published or not	Vertebrate study Y/N	Data protection claimed Y/N	Justification if data protection is claimed	Owner
KCP 9.1.1/01	Crabtree, G.A	2015	[¹⁴ C] 2,4-D: Aerobic soil metabolism and transformation in acidic soils Smithers Viscient (ESG) Ltd, UK Report No. 3200898, 10 August 2015 Dow AgroSciences No. 141222 PCTR No. 10001705-004-70101-0002 GLP: Yes Unpublished Summarised in Appendix 2	N	Y	New study	2,4-D Task Force
KCP 9.1.1/02	Swales, S.E. & Crabtree, G.A.	2015a	4-Chlorophenol: Aerobic soil degradation in three EU soils and one US soil Smithers Viscient (ESG) Ltd, UK Report No. 3200919, 28 August 2015 Dow AgroSciences No. 141220 PCTR No. 10001705-004-70101-0001 GLP: Yes Unpublished Summarised in Appendix 2	N	Y	New study	2,4-D Task Force
KCP 9.1.2/03	Swales, S.E. & Crabtree, G.A.	2015b	4-Chlorophenol: Adsorption in four EU soils and one US soil Smithers Viscient (ESG) Ltd, UK Report No. 3200920, 28 August 2015 Dow AgroSciences No. 141221 PCTR No. 10001705-004-70601-0001 GLP: Yes Unpublished Summarised in Appendix 2	N	Y	New study	2,4-D Task Force
KCP 9.1.3/01	Fortin-McCuaig, M.	2021a	Clopyralid – Calculation of Predicted Environmental Concentrations in Soil for parent following spray application to established grassland, winter cereals and spring cereals in Europe Eurofins Agroscience Services Regulatory GmbH, Germany Report No.: S21-05839-01-002-C No GLP, not published	N	N		Adama Agan Ltd.

Data point	Author(s)	Year	Title Company Report No. Source (where different from company) GLP or GEP status Published or not	Vertebrate study Y/N	Data protection claimed Y/N	Justification if data protection is claimed	Owner
KCP 9.2.4.1/01	Ritzenthaler, J.	2015a	Predicted environmental concentrations (PEC) of AG-CDF1-480 EC (375 g 2,4-D/L, 30 g Clopyralid/L and 75 g Fluroxypyr/L) in groundwater using FOCUS PELMO 5.5.3. DHD-Consulting GmbH, Germany Report No. ADM-2015-02 No GLP, not published	N	N		Adama Agan Ltd.
KCP 9.2.4.1/02	Ritzenthaler, J.	2015b	Predicted environmental concentrations (PEC) of AG-CDF1-480 EC (375 g 2,4-D/L, 30 g Clopyralid/L and 75 g Fluroxypyr/L) in groundwater using FOCUS PEARL 4.4.4. DHD-Consulting GmbH, Germany Report No. ADM-2015-09 No GLP, not published	N	N		Adama Agan Ltd.
KCP 9.2.4.1/03	Fortin-McCuaig, M.	2021b	Clopyralid – A leaching assessment for clopyralid an using the FOCUS PEARL 5.5.5, PELMO 6.6.4 and MACRO 5.5.4 groundwater models following spray application to established grassland, winter cereals and spring cereals in Europe Eurofins Agrosience Services Regulatory GmbH, Germany Report No.: S21-05839-01-002-A No GLP, not published	N	N		Adama Agan Ltd.
KCP 9.2.5.1/01	Ritzenthaler, J.	2015d	Predicted environmental concentrations (PEC) of AG-CDF1-480 EC (375 g 2,4-D/L, 30 g Clopyralid/L and 75 g Fluroxypyr/L) and their degradation products in Surface Water (PEC _{SW}) and Sediment (PEC _{SED}) DHD-Consulting GmbH, Germany Report No. ADM-2015-04 No GLP, not published	N	N		Adama Agan Ltd.
KCP 9.2.5.1/02	Fortin-McCuaig, M.	2021c	Clopyralid – A European Environmental Fate Assessment for Clopyralid Using the FOCUS Surface Water Models at Step 1 Following Spray Application to Established Grassland, Winter Cereals and Spring Cereals in Europe Eurofins Agrosience Services Regulatory GmbH, Germany Report No.: S21-05839-01-002-B No GLP, not published	N	N		Adama Agan Ltd.

List of data submitted by the applicant and not relied on

Data point	Author(s)	Year	Title Company Report No. Source (where different from company) GLP or GEP status Published or not	Vertebrate study Y/N	Data protection claimed Y/N	Justification if data protection is claimed	Owner	Reason for rejection
KCP 9.1.2/01	Flörchinger, M.	2010a	Determination of the adsorption/desorption behaviour of Pyridinol (metabolite II of Fluroxypyr) in three soils eurofins-GAB GmbH, Germany Report no.: S09-02569 Document no.: 90012248 GLP, unpublished Summarised in Appendix 2	N	Y	New study	Adama Agan Ltd.	Study not necessary to finalise the exposure assessment, ADAMA has access to EU agreed data via the LoA
KCP 9.1.2/02	Flörchinger, M.	2010b	Determination of the adsorption/desorption behaviour of Methoxy (metabolite III of Fluroxypyr) in three soils eurofins-GAB GmbH, Germany Report no.: S09-02570 Document no.: 90012249 GLP, unpublished Summarised in Appendix 2	N	Y	New study	Adama Agan Ltd.	Study not necessary to finalise the exposure assessment, ADAMA has access to EU agreed data via the LoA
KCP 9.1.2/04	Swales, S.E. & Crabtree, G.A.	2015c	1,2,4-Benzenetriol: Adsorption in four EU soils and one US Soil Smithers Viscient (ESG) Ltd, UK Report No. 3200921, 28 August 2015 Dow AgroSciences No. 141224 PCTR No. 10001705-004-70601-0002 GLP: Yes Unpublished Summarised in Appendix 2	N	Y	New study	2,4-D Task Force	Study not required since 1,2,4-benzenetriol i an aquatic metaoblite
KCP 9.2.4.1/04	Gourlay, V.	2019	Clopyralid (14C-labelled): Quantification of plant uptake with wheat and barley plants, incubated in a hydroponic system under controlled greenhouse conditions RLP AgroScience GmbH, Neustadt a.d. Weinstraße, Germany Report number: 000102834 GLP: yes, not published	N	Y	New study not submitted before	Adama Agan Ltd.	Study not accepted due to incorrect test design

List of data relied on not submitted by the applicant but necessary for evaluation

Data point	Author(s)	Year	Title Company Report No. Source (where different from company) GLP or GEP status Published or not	Vertebrate study Y/N	Data protection claimed Y/N	Justification if data protection is claimed	Owner
There were no data relied on and not submitted by the Applicant.							

Appendix 2 Detailed evaluation of Annex III studies

A 2.1 KCP 9.1.3 Predicted Environmental Concentrations in soil (PEC_{SOIL})

Comments of zRMS:	Detailed zRMS assessment of the soil exposure calculations is presented in point 8.7 of this report. Information below was not verified by the zRMS for compliance with data available in point 8.7 and it thus struck through.
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A 2.1.1 PEC_{SOIL} report

Reference	KCP-9.1.3/01
Report:	Clopyralid – Calculation of Predicted Environmental Concentrations in Soil for parent following spray application to established grassland, winter cereals and spring cereals in Europe. Fortin-McCuaig, M. (2021a). Report No.: S21-05839-01-002-C
Guidelines	FOCUS (1997) <i>Soil persistence models and EU registration</i> Guidance Document
Deviations	No
GLP	No

Methods

The formulated product is an herbicide containing the active substances 2,4 D, clopyralid and fluroxypyr. The product is to be applied once per year on cereals and established grassland at a maximum application rate of 2 L product/ha.

Predicted environmental concentrations in soil (PEC_{SOIL}) were calculated using the ESCAPE model (v2.0). The substance input parameters used for the modelling are summarised in **Błąd! Nie można odnaleźć źródła odwołania.**, while the application data is included in **Błąd! Nie można odnaleźć źródła odwołania.** of the present dossier.

Findings

PEC_{SOIL} values show a safe use for clopyralid. The summary of the maximum PEC values obtained is included below.

Table 2.2-11: Summary of highest PEC_{SOIL} values [mg clopyralid /kg soil at 5 cm] from FOCUS calculations

Substance	PEC initial		21-day TWA	
	Single application	Persistence	Single application	Persistence
Clopyralid	0.0640	–	0.0480	–

Conclusions

The results of PEC_{SOIL} calculations for the active substance clopyralid show that unacceptable contamination of the soil compartments can be excluded following use of the product AG-CDF1-480-EC in established grassland and cereals according to GAP and considering realistic worst case scenarios and country representative scenarios.

Fortin-McCuaig (2021a)

A 2.1 KCP 9.2.4 Predicted Environmental Concentrations in groundwater (PEC_{GW})

Comments of zRMS:	Detailed zRMS assessment of the groundwater modelling is presented in point 8.8 of this report. Information below was not verified by the zRMS for compliance with data available in point 8.8 and it thus struck through.
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A 2.1.1 PEC_{GW} report

Reference	KCP-9.2.4.1/01
Report:	Predicted environmental concentrations (PEC) of AG-CDF1-480 EC (375 g 2,4-D/L, 30 g Clopyralid/L and 75 g Fluroxypyr/L) in groundwater using FOCUS PELMO 5.5.3. Ritzenthaler, J. (2015). Report No.: ADM-2015-02
Guidelines	FOCUS (2011): Generic guidance for Tier 1 FOCUS ground water assessments, version 2.0. FOCUS groundwater scenarios working group. EFSA Journal 2013;11(2):3114: Scientific Opinion on the report of the FOCUS groundwater working group (FOCUS, 2009): assessment of lower tiers EFSA Journal 2013;11(6):3291: Scientific Opinion on the report of the FOCUS groundwater working group (FOCUS, 2009): assessment of higher tiers
Deviations	No
GLP	No

Reference	KCP-9.2.4.1/02
Report:	Predicted environmental concentrations (PEC) of AG-CDF1-480 EC (375 g 2,4-D/L, 30 g Clopyralid/L and 75 g Fluroxypyr/L) in groundwater using FOCUS PEARL 4.4.4. Ritzenthaler, J. (2015b). Report No.: ADM-2015-09
Guidelines	FOCUS (2011): Generic guidance for Tier 1 FOCUS ground water assessments, version 2.0. FOCUS groundwater scenarios working group. EFSA Journal 2013;11(2):3114: Scientific Opinion on the report of the FOCUS groundwater working group (FOCUS, 2009): assessment of lower tiers EFSA Journal 2013;11(6):3291: Scientific Opinion on the report of the FOCUS groundwater working group (FOCUS, 2009): assessment of higher tiers
Deviations	No
GLP	No

Methods

The simulation models FOCUS PELMO 5.5.3 and FOCUS PEARL 4.4.4 were used to estimate the concentrations of active substances and metabolites in the leachate at 1 meter soil depth following application of AG-CDF1 480 EC. AG-CDF1 480 EC is an herbicide containing the active substances 2,4-D (ester form), fluroxypyr methyl and clopyralid. The product is to be applied twice per season on cereals and grassland at a maximum application rate of 2 L product/ha.

For this risk assessment, single application was considered using maximum application rate of 2 L product/ha (equivalent to 750 g of 2,4 D acid, 60 g of clopyralid and 150 of fluroxypyr acid) with 60% crop interception for grassland and 20% for cereals. The application data is included in Table 8.8-4 of the present dossier while the input parameters used for the modelling are summarised in Table 8.8-5, 8.8-6, 8.8-9 and 8.8-12.

Results and discussion

The obtained results (Tables 8.8-7 and 8, Tables 8.8-10 and 11, Tables 8.8-13 and 14) show that there will be no substantial contamination of ground water with the active substances or metabolites following FOCUS PELMO and PEARL calculations. For clopyralid, the PEC_{GW} values were above the trigger of 0.1 µg/L for some of the scenarios. However, a refinement with the DT_{50} obtained in field studies lead to concentrations below 0.01 µg/L in all scenarios and models.

The PEC_{GW} for the remaining active substances and metabolites were in all cases below 0.01 µg/L.

Conclusions

The results of PEC_{GW} water calculations for active substances included in the product and their major metabolites show that contamination of ground water compartment can be excluded following use of the product AG-CDF1-480-EC on grassland and cereals according to GAP and considering realistic worst case scenarios and country representative scenarios.

Ritzenthaler (2015)

Reference	KCP-9.2.4.1/03
Report:	Clopyralid – A leaching assessment for clopyralid using the FOCUS PEARL 5.5.5, PELMO 6.6.4 and MACRO 5.5.4 groundwater models following spray application to established grassland, winter cereals and spring cereals in Europe. Fortin-McCuaig, M. (2021b). Report No.: S21-05839-01-002-A
Guidelines	FOCUS (2014): Generic guidance for Tier 1 FOCUS ground water assessments, version 2.2. FOCUS groundwater scenarios working group.
Deviations	No
GLP	No

Methods

The simulation models FOCUS PELMO 6.6.4, FOCUS PEARL 5.5.5 and MACRO 5.5.4. were used to estimate the concentrations of clopyralid in the leachate at a 1-meter soil depth.

The application data is included in **Błąd! Nie można odnaleźć źródła odwołania.** of the present dossier while the input parameters used for the modelling are summarised in **Błąd! Nie można odnaleźć źródła odwołania.**

Results

The results are included in Table 8.8-12 to 8.8-14

Fortin-McCuaig (2021b)

Comments of zRMS:	<p>The results of the study below were used by the Applicant to confirm that clopyralid is taken up by the plant roots and translocated to the upper parts of the plant. It should be, however, noted that a similar study by the same author was already evaluated at the EU level (Gourlay, 2015) and several uncertainties were noted, one of which was that due to the conditions, hydroponic systems promote uptake of the substance by plants which would be lower if plants were cultivated in soil, since adsorption of the substance to soil particles would reduce its availability. Taking this into account, the TSCF value should be refined based on results of experiments performed in plants cultivated in soil and not in the nutrient solutions. Detailed discussion on the study by Gourley (2015) may be found in clopyralid RAR (Vol. 3CP, B.8 of March 2018). It should be also noted that the uptake of the substance by plants would also depend on other factors, such as the size of soil particles (higher uptake would be expected in sandy soils comparing to clay soils), soil pH, temperature, humidity and the plant itself. This may be seen in results of the below study by Gourlay (2019), where wheat and barley were used (both being cereals), but the average TSCF of 0.2 calculated for wheat was two times lower comparing to barley with mean TSCF of 0.47. The impact of variety on the uptake of the substance from soil is not known. Taking all this into account, the currently performed experiments to refine TSCF are highly uncertain and may lead to overestimation of TSCF and in consequence - underestimation of the groundwater exposure.</p> <p>Since design of both studies by Gourley was similar, conclusions taken during the EU evaluation of study by Gourley (2015) are equally applicable to study by Gourley (2019), which was thus not validated by the zRMS, since obtained results are uncertain due to the test design.</p> <p>Summary below is struck through as being not validated by the zRMS.</p>
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Reference	KCP-9.2.4.1/04
Report:	Clopyralid (¹⁴ C-labelled): Quantification of plant uptake with wheat and barley plants, incubated in a hydroponic system under controlled greenhouse conditions. Gourlay, V. (2019). Report No.: 000102834 (Laboratory study AS588)
Guidelines	Interim study design to determine uptake of chemicals by plant roots” ECPA/IVA Working Group “Plant Uptake Factor” (21.12.2018)
Deviations	No
GLP	Yes

Executive Summary

The purpose of this study was to quantify the plant uptake of Clopyralid. The plant uptake was determined in terms of transpiration stream concentration factor (TSCF), which could be used in the parameterization of leaching models.

Wheat and barley plants were investigated individually under the target pH level range of 5.5–6.5. Plants were kept 2, 4 or 6 days in the test solutions with a known concentration of the test item and volume of the solution (i.e. 1 L). The variation of these two parameters, together with the equivalent recovered in the plant material, allowed calculating the transpiration stream concentration factor.

Over the course of the experiment the pH level in solution with plants remained in the target range, with values between 5.52 and 6.40 for both crop types. The regular aeration ensured a minimum 40.8 % of oxygen saturation in solution. Plants remained healthy, with a clear increase of biomass up to (227.0 & 246.4) %_{DAT 0} (CV ≤ 16.0%) for treated and control wheat plants respectively, and up to (328.4 & 396.6) %_{DAT 0} (CV ≤ 21.1%) for treated and control barley plants respectively. The volume of solution remaining on termination corresponded to at least 77 %_{initial} for both crop types. Part of the volume diminution was attributed to transpiration alone, with an average cumulative water uptake of at least (15.5 & 30.2) mL on DAT 2 for wheat and barley respectively. There was no influence of the test item on the plant behaviour.

The radiochemical purity of the test item was confirmed and no glass adsorption or volatilisation was detected during the course of the experiment.

The radioactivity measurements of the final compartments showed that the test protocol allows the recovery of most of the test item given to the system on application. The test item was actively transferred to the shoots and leaves of wheat plant, with average translocation ratio between (93.9 & 94.9) %_{plant} for both crop types and all incubation periods (CV ≤ 1.5%).

The average TSCF was found to be between 0.57 for barley (range 0.40 and 0.54 (CV ≤ 17.9%) and 0.2 for wheat (range 0.18 & 0.22 (CV ≤ 14.7%) for wheat. The TSCF was relatively independent from the incubation period.

I. MATERIALS AND METHODS

A. MATERIALS

1. Test Material	Clopyralid, [pyridyl-2,6-14C]
Code	CC754
Specific Activity	5.640 MBq·mg ⁻¹
Radiochemical Purity	98.34 % (HPLC)
Chemical Purity	98.09 % (HPLC)
Specific Activity	5.640 MBq·mg ⁻¹
Batch number	2643598
Expiry date (re-test)	31.03.2023
2. System	
Species	Wheat “Tybalt” (W) and barley “Beckie” (B)
Solution	BBCH 10: Hakaphos® solution BBCH 11: Ferty® 9 Hydro

B. STUDY DESIGN

1. Experimental conditions

Each test system consisted of a gas washing glass bottle filled with buffered nutrient solution. “1000 mL” vessels filled with 1000 mL of buffered nutrient solution were used. Single plants were incubated in each vessel. In order to avoid contamination of the seed and to ensure the transpiration as exclusive plant uptake process, the contact with the solution was limited to the roots. Furthermore, the shape of the vessels allowed transferring the plants without damaging the roots.

After application and plant insertion, the opening around the plant stems was sealed with a piece of foam (included in vessel's tare) in order to reduce evaporation losses. Dark plastic foil cover was used to avoid algal bloom and to exclude any photolytic transformation processes. A Teflon® capillary linked to a peristaltic pump was fixed to the test system for aeration. An external rod with a clamp was adapted to the vessel in order to maintain the plants during the incubation period.

The entire setup was placed in a similar greenhouse chamber as used for cultivation (i.e. comparable

temperature and air humidity conditions) in order to reduce eventual stress for the test plants.

The target application concentration for the test item was $192 \mu\text{g}\cdot\text{L}^{-1}$ (i.e. $1 \mu\text{mol}\cdot\text{L}^{-1}$). The stock solution was used directly for application. On application date, each test vessel (tared with magnetic stir bar and PU foam) was filled with the nutrient solution to the target 1000 mL volume. The test item was then given via pipetting a volume of stock solution into the nutrient solution.

For each experimental run, the daily cultivation conditions in the greenhouse were controlled, and an average daily temperature of $(22 \pm 2) ^\circ\text{C}$ during day and $(18 \pm 2) ^\circ\text{C}$ during night was targeted, as well as a minimum air humidity of 50% of saturation. The light regime corresponded to 16 h light / 8 h dark. Additional artificial light was supplied when natural daylight was less than 10 klux.

2. Sampling and analytics

Intermediate and final samplings were performed on DAT 2, 4 and 6. The volume of the remaining solutions was determined gravimetrically by difference between the full test system and the vessel tare, the biomass, the aeration system and the fixation system. It was assumed that the density of the test solution is equivalent to water ($1000 \text{ g}\cdot\text{L}^{-1}$) and that the biomass had a linear variation over time.

The amount of test item potentially present on the root system in contact with the solution was removed and measured by gently agitating the roots in 150 mL acetonitrile/water (4:1, v/v) solution. In order to prepare a radioactive mass balance, the plant material was fractionated into roots and shoots (i.e. stem/leaves) parts. Fresh weights were determined for each plant fraction and the separated roots and stem/leaves were deep frozen ($\leq -18 ^\circ\text{C}$) and lyophilised. The dry plant material was fully combusted in a sample oxidizer and was analysed for radioactivity via LSC.

The radioactive mass balance was calculated as the sum of the radioactivity recovered from the test solution, the root and test vessel rinsing solution and the plant material.

Liquid specimens were measured using a liquid scintillation counter (TRI CARB 2800 TR/L; Canberra Packard Corp.) employing Ultima GoldTM as scintillator. Liquid Scintillation Counting (LSC) was used to determine overall radioactivity in the stock solution, application solution and test solutions, and in combination with combustion in the plant material. The HPLC method provided by the sponsor was used for co-chromatography with the reference items. The radiochemical purity of the test item in the stock solution and in the treated vessels after application and incubation was determined.

A statistical evaluation was performed on the volume uptake values and the biomass on termination in order to investigate potential influences of the test items. All statistical tests were obtained by using “R” statistical system, version 3.6.1 (05.07.2019; Non GLP) and Excel[®] functions (GLP).

II. — RESULTS AND DISCUSSION

A. CONDITIONS

For wheat plants the daily average temperature was between $(24.6 \text{ \& } 27.4) ^\circ\text{C}$ during day and $(17.0 \text{ \& } 17.5) ^\circ\text{C}$ during night. Overall the average temperature was $(22.8 \pm 2.0) ^\circ\text{C}$. The daily average air humidity was between $(32.6 \text{ \& } 44.2) \%$ of saturation (i.e. %sat) during day and $(66.8 \text{ \& } 74.0) \%$ sat. Overall, the average air humidity was $(48.1 \pm 4.5) \%$ sat. The daily average illuminance was between $(8.8 \text{ \& } 19.9) ^\circ\text{C}$ during day period.

For barley plants the daily average temperature was between $(23.0 \text{ \& } 26.8) ^\circ\text{C}$ during day and $(17.0 \text{ \& } 19.6) ^\circ\text{C}$ during night. Overall the average temperature was $(22.4 \pm 1.2) ^\circ\text{C}$. The daily average air humidity was between $(32.6 \text{ \& } 43.7) \%$ sat during day and $(60.1 \text{ \& } 79.9) \%$ sat. Overall, the average air humidity was $(48.0 \pm 6.4) \%$ sat. The daily average illuminance was between $(12.2 \text{ \& } 17.1) ^\circ\text{C}$ during day period.

Regarding the pH, for wheat plants the initial pH level ranged between (6.19 and 6.25). Without plants, the pH level slightly increased with values between (6.43 and 6.61) on DAT 6. With plants, independently from the treatment, the pH level showed relatively steady behaviour, with values between (5.96 and 6.40) over the incubation. For barley plants, the initial pH level ranged between (6.21 and 6.25). Without plants, the pH level slightly increased with values between (6.37 and 6.41) on DAT 6. With plants, independently from the treatment, the pH level showed a slight decrease over time, with values between (5.52 and 5.78) on DAT 6. The pH level in solution with plants remained within the range of the target pH level for the whole incubation.

The oxygen saturation in water exceeded 84% in wheat and 40% in barley granting aerobic conditions

B. DATA

Overall, treated and non-treated plants, the biomass clearly increased. For wheat, on DAT 2, the values were (150.5 & 145.2) % of the initial biomass (i.e. %DAT 0) [CV ≤ 6.9%]. On DAT 4, the values were (190.1 & 187.9) %DAT 0 [CV ≤ 3.9%]. On DAT 6, the values were (227.0 & 246.4) %DAT 0 [CV ≤ 16.0%]. For barley, on DAT 2, the values were (131.4 & 195.2) % of the initial biomass (i.e. %DAT 0) [CV ≤ 11.3%]. On DAT 4, the values were (194.8 & 250.1) %DAT 0 [CV ≤ 25.0%]. On DAT 6, the values were (291.6 & 326.6) %DAT 0 [CV ≤ 24.0%].

Water consumption was 79 and 73% for wheat and barley. The VUP for wheat was [treated and non-treated] as follows: on DAT 2, values were 36.6 & 35.8 mL [CV ≤ 30.2%] while on DAT 4, values were 84.5 & 72.4 mL [CV ≤ 15.4%] and on DAT 6, values were (136.9 & 128.0) mL [CV ≤ 38.2%]. The VUP for barley was [treated and non-treated] as follows: on DAT 2 43.5 & 45.6 mL [CV ≤ 20.1%] while on DAT 4, values were (114.6 & 128.8) mL [CV ≤ 13.5%] and on DAT 6, values were (208.4 & 236.9) mL [CV ≤ 17.2%].

Regarding the fate of test item, the concentration on application was between 211.29 and 215.35 $\mu\text{g}\cdot\text{L}^{-1}$ for wheat and 191.08 and 196.82 $\mu\text{g}\cdot\text{L}^{-1}$ for barley. The concentration without plants remained relatively constant over time while in systems with plants, the concentration increased over time. In terminated vessels, the average concentration on wheat was 218.44, 226.87 & 235.70 $\mu\text{g}\cdot\text{L}^{-1}$ [CV ≤ 3.4 %] for DAT 2, 4 and 6 respectively while for barley it was 196.82, 206.38 & 211.42 $\mu\text{g}\cdot\text{L}^{-1}$ [CV ≤ 2.1 %] for DAT 2, 4 and 6 respectively.

The constant concentration of the stability control indicated no sample losses caused by volatilisation or glass adsorption. Whereas, the increasing concentration in the treated systems with plants was linked to a selectivity of the roots toward the test item.

The amount of test item found in the root and glass rinsing solutions corresponded to (average values) 0.4, 0.6 and 1.0 % of applied radioactivity on DAT 2, 4 & 6 respectively on both crops. Glass rinsing solution corresponded to a maximum of 0.2 %AR, independently from the termination date.

The radioactive analysis of the separate roots and shoots material showed a good transfer of the taken radioactive equivalents from the roots to the shoots, with an average translocation to shoots corresponding to 93.7, 93.9 & 94.6 %plant on DAT 2, 4 & 6 respectively (CV ≤ 1.4%) for wheat and 94.9, 94.8 & 94.8 for barley (CV ≤ 1.6%)

In wheat, the sum of all processed fractions and solutions yielded in mean radioactive mass recoveries of (99.6, 99.9 & 98.7) %AR on DAT 2, 4 & 6 respectively (CV ≤ 0.7 %), and 99.1 %AR for stability control. In barley, the sum of all processed fractions and solutions yielded in mean radioactive mass recoveries of (99.8, 100.3 & 98.8) %AR on DAT 2, 4 & 6 respectively (CV ≤ 0.3 %), and 100.1 %AR for stability control.

C. TSCF Calculation

The transpiration stream concentration factor is reported over the incubation periods DAT 0-2, 0-4 and 0-6. The average TSCF was found to be:

	Wheat	Barley
DAT-2	0.20 (CV 13.5%)	0.54 (CV 17.9%)
DAT-4	0.18 (CV 14.7%)	0.40 (CV 9.8%)
DAT-6	0.22 (CV 14.7%)	0.46 (CV 8.3%)
Average	0.20	0.47
Overall average	0.34	

Conclusion

Simple standardized test systems with intact plants were used to provide an experimental set of data required for the calculation of the transpiration stream concentration factor for Clopyralid. There was a clear translocation of Clopyralid from roots to shoots, with average translocation ratio between (93.7 & 94.9) %plant for both crop types and all incubation periods ($CV \leq 1.6\%$). The average TSCF was found to be between 0.57 for barley (range 0.40 and 0.54 ($CV \leq 17.9\%$)) and 0.2 for wheat (range 0.18 & 0.22 ($CV \leq 14.7\%$)) for wheat. The TSCF was relatively independent from the incubation period.

A 2.2 KCP 9.2.5 Predicted Environmental Concentrations in surface water (PEC_{sw})

Comments of zRMS:	Detailed zRMS assessment of the surface water modelling is presented in point 8.9 of this report. Information below was not verified by the zRMS for compliance with data available in point 8.9 and it thus struck through.
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A 2.2.1 PEC_{sw} report

Reference	KCP-9.2.5.1/01
Report:	Predicted environmental concentrations (PEC) of AG-CDF1-480 EC (375 g 2,4-D/L, 30 g Clopyralid/L and 75 g Fluroxypyr/L) in surface water (PEC _{sw}) and sediment (PEC _{sed}). Ritzenthaler, J. (2015). Report No.: ADM-2015-04
Guidelines	SANCO/4802/2001 rev. 2, version 1.3, December 2014 (Generic guidance for FOCUS surface water Scenarios)
Deviations	No
GLP	No

Methods

The formulated product is a herbicide containing the active substances 2,4 D, Clopyralid and Fluroxypyr. The product is to be applied twice per season on cereals and grassland at a maximum application rate of 2 L product/ha.

Predicted environmental concentrations in surface water (PEC_{sw}) and in sediment (PEC_{sed}) were calculated using the FOCUS Step 1-2 calculator. Additionally, FOCUS step 3 calculations were conducted for 2,4 D (acid) as well as Fluroxypyr.

The substance input parameters used for the modelling are summarised in Tables 8.9-1, 8.9-2 and 8.9-3, while the application data is included in Tables 8.9-6 and 8.9-7 of the present dossier.

Findings

Step 1-2 results lead to PEC values low enough to grant a safe use for 2,4-D metabolites as well as for Clopyralid and all the metabolites of Fluroxypyr meptyl.

For 2,4-D as well as Fluroxypyr meptyl Step 3 calculations were needed. However, mitigation measures (Step 4) were not needed in any case.

The summary of the maximum PEC values obtained is included below.

Table 2.2-11: Summary of highest PEC_{sw} values [µg/L] for 2,4-D, Clopyralid and Fluroxypyr and their metabolites from FOCUS calculations

Test substance	PEC _{sw} [µg/L]	Source of the PEC _{sw}
2,4-D	4.782 (spray, D3)	Step 3, grassland
2,4 DCP	13.31	Step 2, North-EU
2,4-DCA	6.15	Step 2, North-EU
Clopyralid	20.42	Step 1, North-EU
Fluroxypyr meptyl	1.356 (spray, D3)	Step 3, grassland
Fluroxypyr acid	47.22	Step 1
Pyridinol	28.69	Step 1
Methoxypyridine	11.17	Step 1
3-CP	5.84	Step 1

Conclusions

The results of PEC_{sw} calculations for active substances and their major metabolites show that unacceptable contamination of surface water compartment can be excluded following use of the product AG-CDF1-480-EC in grassland and cereals according to GAP and considering realistic worst case scenarios and country representative scenarios.

Ritzenthaler (2015)

Reference	KCP-9.2.5.1/02
Report:	Clopyralid – A European Environmental Fate Assessment for Clopyralid Using the FOCUS Surface Water Models at Step 1 Following Spray Application to Established Grassland, Winter Cereals and Spring Cereals in Europe. Fortin-McCuaig, M. (2021c). Report No.: S21-05839-01-002-B
Guidelines	SANCO/4802/2001 rev. 2, version 1.3, December 2014 (Generic guidance for FOCUS surface water Scenarios)
Deviations	No
GLP	No

Methods

The formulated product is an herbicide containing the active substances 2,4-D, clopyralid and fluroxypyr. The product is to be applied once per year on cereals and established grassland at a maximum application rate of 2 L product/ha.

Predicted environmental concentrations in surface water (PEC_{sw}) and in sediment (PEC_{sed}) were calculated using the FOCUS Steps 1-2 calculator (v3.2). The substance input parameters used for the modelling are summarised in **Błąd! Nie można odnaleźć źródła odwołania.** and **Błąd! Nie można odnaleźć źródła odwołania.**, while the application data is included in **Błąd! Nie można odnaleźć źródła odwołania.** and **Błąd! Nie można odnaleźć źródła odwołania.** of the present dossier.

Findings

Step 1-2 results lead to PEC values low enough to grant a safe use for clopyralid. The summary of the maximum PEC values obtained is included below.

Table 2.2-12: Summary of highest PEC_{sw} values [µg/L] for clopyralid from FOCUS calculations

Test substance	PEC _{sw} [µg/L]	Source of the PEC _{sw}
Clopyralid	20.5	Step 1

Fortin-McCuaig (2021c)

Appendix 3 Detailed evaluation of the new Annex II studies

A 3.1 Matching study on pyridinol sorption to soil

Comments of zRMS:	The Applicant for ADM.3304.H.1.A has access to fluroxypyr EU agreed data via the LoA and for this reason the matching study on pyridinol sorption to soil was not required for purposes of the exposure assessment and was thus not validated by the zRMS. The study summary below is struck through.
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Reference:	KCP- 9.1.2/01
Report	Flörchinger, M. (2010a) Determination of the adsorption/desorption behaviour of Pyridinol (metabolite II of Fluroxypyr) in three soils
Owner:	Makhteshim Agan Agro Poland S.A.
Document No.:	90012248
Report date:	14.01.2010
Published:	No
Test facility:	Eurofins-GAB GmbH, Niefern-Öschelbronn, Germany
Report No.:	S09-02569
Dates of work:	17.08. – 18.11.2009 (Experimental phase)
Test substance:	Pyridinol (purity: 99.2 %)
Guideline:	OECD guideline No. 106
Deviations:	None
GLP:	Yes – Certified laboratory (Umweltministerium Baden-Württemberg, Stuttgart, 23.05.2007)

Executive Summary

The adsorption/desorption property of Pyridinol was determined in three different soils (LUF 2.2, 2.3 and 6S), according to OECD guideline 106 and SETAC requirements. Tier 1 testing was performed at a concentration of 1 mg/L Pyridinol in 0.01 M CaCl₂ solution with the soils LUF 2.2 and 6S at a soil solution ratio of 1/1, 1/5 and 1/25. Tier 2 testing was only performed with the soil LUF 2.3 at a soil solution ratio of 1/1.

I. MATERIALS AND METHODS

A. MATERIALS

1. Test Material	Pyridinol
GAB Code	20091306
Lot No.	FXPYR (2) BP9-1992
Concentration/Purity	99.2 %
Stability of test compound	Expiry date: 04.2010

Table A 1: Soil characteristics

Soil description	LUFA 2.2 F2.23708	LUFA 2.3 F2.32508	LUFA 6S F6S0209
pH (CaCl ₂)	5.74	6.96	7.24
Organic carbon [%]	1.72	1.08	1.75
Maximum water holding capacity [%]	42.6	35.8	38.7
Cation exchange capacity [meq/100 g]	9.4	12.1	26.6
Soil density [g/L]	1271	1268	1459
Particle size according to German DIN [%]			
Soil type	Silty sand	Loamy sand	Clayey loam
Particle size			
<0.002 mm	3.8	10.3	44.0
0.002-0.006 mm	3.1	4.1	9.2
0.006-0.020 mm	3.6	10.4	12.9
0.020-0.063 mm	7.4	20.6	12.3
0.063-0.200 mm	34.9	24.4	8.8
0.200-0.630 mm	45.9	25.8	9.2
0.630-2.0 mm	1.3	4.4	3.6
Particle size according to USDA [%]			
Soil type (USDA)	Loamy sand	Sandy loam	Clay
Particle size			
<0.002 mm	4.7	10.3	44.0
0.002-0.05 mm	11.1	33.8	31.9
0.05-2.00 mm	84.2	55.9	24.1

B. STUDY DESIGN

A. Scope of the test

The test was designed to evaluate the adsorption/desorption of a chemical on three soils. It comprises three tiers for adsorption and desorption, which are:

- *Tier 1:* Preliminary study (using 2 soils) in order to determine:
 - the soil/solution ratio
 - the equilibration time for adsorption and the amount of test item adsorbed at equilibrium
 - the adsorption of the test item on the surface of the test vessel and the stability of the test item during the test period
- *Tier 2:* Screening test: the adsorption was studied in the remaining third soil by means of adsorption kinetics at a single concentration and single soil/solution ratio by determination of distribution coefficient K_d and organic carbon normalized adsorption coefficient K_{oc}.
- *Tier 3:* Determination of Freundlich adsorption/desorption isotherms was performed to determine the influence of concentration on the extent of adsorption/desorption on the tested soils.

B. Principle of the method

Different volumes of solutions of the test item, at known concentrations in 0.01 M CaCl₂ were added to soil samples of known dry weight which had been pre-equilibrated in 0.01 M CaCl₂. The mixture was agitated for an appropriate time. The soil suspensions were then separated by centrifugation and the aqueous phase was analysed. The amount of test item adsorbed on the soil sample was calculated as the difference between the amount of test item initially present in solution and the amount remaining at the end of the experiment (indirect method). For the desorption study the treated 0.01 M CaCl₂ solution was drained after equilibrium and adjusted to the volume before with untreated 0.01 M CaCl₂ solution. The amount of test item desorbed on the soil sample was calculated as the difference between the amount of test item at the equilibrium of adsorption and the amount remaining at the end of the experiment (indirect method).

C. Validation of the analytical method

The key parameters that can influence the accuracy of sorption measurements include the accuracy of the analytical method in analysis of both the solution and adsorbed phases, the stability and purity of the test item, the attainment of sorption equilibrium, the magnitude of the solution concentration change, the soil/solution ratio and changes in the soil structure during the equilibration process.

For the results of the validation please refer to the original report.

II. RESULTS AND DISCUSSION

The pH value of test item solution in 0.1 M CaCl₂ was 5.7–6.0. During the test conditions the pH value of the water phase are shown the following table:

Table A 2: pH values for a soil/solution ratio of 1/1

Soil	pH
LUFA 2.2	6.2–6.4
LUFA 2.3	6.9–7.2
LUFA 6S	7.5–7.6

The following table shows the adsorption coefficients (K_d) and organic carbon partition coefficients (K_{oc}) after 48 hours of adsorption.

Table A 3: Adsorption coefficients after 48 hours for soil LUFA 2.2, 2.3 and 6S

	Parameters	1/1	1/5	1/25
LUFA 2.2	A-%	79.3	37.0	7.3
	K_d	3.80	2.91	1.95
	K_{oc}	220.9	169.2	113.4
	Log K_{oc}	2.34	2.23	2.05
	% OC	1.72		
LUFA 2.3	A-%	70.2	n.d.	n.d.
	K_d	2.34	n.d.	n.d.
	K_{oc}	216.7	n.d.	n.d.
	Log K_{oc}	2.34	n.d.	n.d.
	% OC	1.08		
LUFA 6S	A-%	65.3	25.8	8.0
	K_d	1.87	1.72	2.16
	K_{oc}	106.9	98.3	123.4
	Log K_{oc}	2.03	1.99	2.09
	% OC	1.75		

n.d.: not detected

In order to meet the requirements of the OECD 106 guideline (adsorption above 20 % and preferably > 50 %) the soil/solution ratio of 1/1 was used for the further studies. Control samples revealed that no test item adhered to the test vessel and that the test item was stable during the 48 hours incubation period. The mass balance was performed after the end of the Tier 1 and 2 testing for the soil/solution ratio of 1/1. For soils LUFA 2.2, 2.3 and 6S 84, 71 and 53 % were recovered, respectively. It is assumed that the rest of the test item was bound non extractable onto soil since no adsorption to the glass surface of the test vessels was observed. Since Pyridinol was stable the indirect method could be used in the advanced test in accordance to the OECD 106 guideline. The adsorption isotherms (Tier 3) were estimated at a soil/solution ratio of 1/1 and at five test item concentration (0.01 to 1.00 mg/L). The results are shown in the table below.

Table A 4: Adsorption isotherm results at equilibrium (48 hours)

Soil	LUFA 2.2	LUFA 2.3	LUFA 6S
Slope (1/n)	0.7429	0.7137	0.56
Intercept ($\log K_{ads,F}$)	0.2979	0.1269	0.0787
$K_{ads,F}$	1.99	1.34	1.20
R-squared	0.9921	0.9806	0.9988
% OC	1.72	1.08	1.75
$K_{ads,F,OC}$	115.44	124.02	68.50

The desorption study (Tier 1 and 2) was performed at a concentration of 1 mg/L Pyridinol in 0.01 M $CaCl_2$ solution at a soil/solution ratio of 1/1. The results are shown in the table below.

Table A 5: Desorption coefficients after 48 hours for soil LUFA 2.2, 2.3 and 6S

Parameters	LUFA 2.2	LUFA 2.3	LUFA 6S
D-%	13.8	22.3	12.3
Kd	6.26	17.47	35.84
Koc	978.1	1617.1	2048.0
Log Koc	2.99	3.21	3.31
% OC	1.72	1.08	1.75

The amount of desorption was < 75 % of the amount adsorbed, so the adsorption is considered to be non-reversible.

The desorption isotherms (Tier 3) were estimated at a soil/solution ratio of 1/1 and at the same amount of test item as used for the adsorption isotherms. The results are shown in the table below.

Table A 6: Desorption isotherm results at equilibrium (48 hours)

Soil	LUFA 2.2	LUFA 2.3	LUFA 6S
Slope (1/n)	0.6647	0.6968	0.4452
Intercept ($\log K_{des,F}$)	0.3673	0.3724	0.3134
$K_{des,F}$	2.33	2.36	2.06
R-squared	0.9990	0.9816	0.9829
% OC	1.72	1.08	1.75
$K_{des,F,OC}$	135.45	218.26	117.59

Flörchinger, M. (2010a)

A 3.2 Matching study on methoxy pyridine sorption to soil

Comments of zRMS:	The Applicant for ADM.3304.H.1.A has access to fluroxypyr EU agreed data via the LoA and for this reason the matching study on methoxy pyridine sorption to soil was not required for purposes of the exposure assessment and was thus not validated by the zRMS. The study summary below is struck through.
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Reference:	KCP-9.1.2/02
Report	Flörchinger, M. (2010b) Determination of the adsorption/desorption behaviour of Methoxy (metabolite III of Fluroxypyr) in three soils
Owner:	Makhteshim Agan Agro Poland S.A.
Document No.:	90012249
Report date:	14.01.2010
Published:	No
Test facility:	eurofins-GAB GmbH, Niefern-Öschelbronn, Germany
Report No.:	S09-02570
Dates of work:	17.08. – 17.11.2009 (Experimental phase)
Test substance:	Methoxy (purity: 98.4 %)
Guideline:	OECD guideline No. 106

Deviations:	None
GLP:	Yes – Certified laboratory (Umweltministerium Baden-Württemberg, Stuttgart, 23.05.2007)
Acceptability:	Yes

Executive Summary

The adsorption/desorption property of Methoxy was determined in three different soils (LUF 2.2, 2.3 and 6S), according to OECD guideline 106 and SETAC requirements. Tier 1 testing was performed at a concentration of 10 mg/L Methoxy in 0.01 M CaCl₂ solution with the soils LUF 2.2 and 6S at a soil solution ratio of 1/1, 1/5 and 1/25. Tier 2 testing was only performed with the soil LUF 2.3 at a soil solution ratio of 1/5.

I. MATERIALS AND METHODS

A. MATERIALS

1. Test Material	Methoxy
GAB Code	20091304
Lot No.	FXPYR (3) BP6 1991
Concentration/Purity	98.4 %
Stability of test compound	Expiry date: 04.2010

Table A 7: Soil characteristics

Soil description	LUF 2.2 F2.23708	LUF 2.3 F2.32508	LUF 6S F6S0209
pH (CaCl ₂)	5.74	6.96	7.24
Organic carbon [%]	1.72	1.08	1.75
Maximum water holding capacity [%]	42.6	35.8	38.7
Cation exchange capacity [meq/100 g]	9.4	12.1	26.6
Soil density [g/L]	1271	1268	1459
Particle size according to German DIN [%]			
Soil type	Silty sand	Loamy sand	Clayey loam
Particle size			
< 0.002 mm	3.8	10.3	44.0
0.002-0.006 mm	3.1	4.1	9.2
0.006-0.020 mm	3.6	10.4	12.9
0.020-0.063 mm	7.4	20.6	12.3
0.063-0.200 mm	34.9	24.4	8.8
0.200-0.630 mm	45.9	25.8	9.2
0.630-2.0 mm	1.3	4.4	3.6
Particle size according to USDA [%]			
Soil type (USDA)	Loamy sand	Sandy loam	Clay
Particle size			
< 0.002 mm	4.7	10.3	44.0
0.002-0.05 mm	11.1	33.8	31.9
0.05-2.00 mm	84.2	55.9	24.1

B. STUDY DESIGN

A. Scope of the test

The test was designed to evaluate the adsorption/desorption of a chemical on three soils. It comprises three tiers for adsorption and desorption, which are:

- *Tier 1:* Preliminary study (using 2 soils) in order to determine:
 - the soil/solution ratio
 - the equilibration time for adsorption and the amount of test item adsorbed at equilibrium
 - the adsorption of the test item on the surface of the test vessel and the stability of the test item during the test period

- *Tier 2:* Screening test: the adsorption was studied in the remaining third soil by means of adsorption kinetics at a single concentration and single soil/solution ratio by determination of distribution coefficient K_d and organic carbon normalized adsorption coefficient K_{oc} .
- *Tier 3:* Determination of Freundlich adsorption/desorption isotherms was performed to determine the influence of concentration on the extent of adsorption/desorption on the tested soils

B. Principle of the method

Different volumes of solutions of the test item, at known concentrations in 0.01 M CaCl_2 were added to soil samples of known dry weight which had been pre-equilibrated in 0.01 M CaCl_2 . The mixture was agitated for an appropriate time. The soil suspensions were then separated by centrifugation and the aqueous phase was analysed. The amount of test item adsorbed on the soil sample was calculated as the difference between the amount of test item initially present in solution and the amount remaining at the end of the experiment (indirect method). For the desorption study the treated 0.01 M CaCl_2 solution was drained after equilibrium and adjusted to the volume before with untreated 0.01 M CaCl_2 solution. The amount of test item desorbed on the soil sample was calculated as the difference between the amount of test item at the equilibrium of adsorption and the amount remaining at the end of the experiment (indirect method).

C. Validation of the analytical method

The key parameters that can influence the accuracy of sorption measurements include the accuracy of the analytical method in analysis of both the solution and adsorbed phases, the stability and purity of the test item, the attainment of sorption equilibrium, the magnitude of the solution concentration change, the soil/solution ratio and changes in the soil structure during the equilibration process. For the results of the validation please refer to the original report.

II. RESULTS AND DISCUSSION

The pH value of test item solution in 0.01 M CaCl_2 was 5.7–6.2. During the test conditions the pH value of the water phase are shown the following table.

Table A 8: pH values for a soil/solution ratio of 1/5

Soil	pH
LUFA 2.2	5.9–6.5
LUFA 2.3	7.0–7.3
LUFA 6S	7.3–7.5

The following table shows the adsorption coefficients (K_d) and organic carbon partition coefficients (K_{oc}) after 48 hours of adsorption.

Table A 9: Adsorption coefficients after 48 hours for soil LUFA 2.2, 2.3 and 6S

	Parameters	1/1	1/5	1/25
LUFA 2.2	A-%	91.9	57.4	9.3
	K_d	11.26	6.68	2.54
	K_{oc}	654.7	388.4	147.7
	Log- K_{oc}	2.82	2.59	2.17
	% OC	1.72		
LUFA 2.3	A-%	n.d.	45.9	n.d.
	K_d	n.d.	4.21	n.d.
	K_{oc}	n.d.	389.8	n.d.
	Log- K_{oc}	n.d.	2.59	n.d.
	% OC	1.08		
LUFA 6S	A-%	88.2	61.3	12.4
	K_d	7.42	7.86	3.51
	K_{oc}	424	449.1	200.6
	Log- K_{oc}	2.63	2.65	2.3
	% OC	1.75		

n.d. not detected

In order to meet the requirements of the OECD 106 guideline (adsorption above 20 % and preferably > 50 %) the soil/solution ratio of 1/5 was used for the further studies. Control samples revealed that no test item adhered to the test vessel and that the test item was stable during the 48 hours incubation period. The mass balance was performed after the end of the Tier1 and 2 testing for the soil/solution ratio of 1/5. For soils LUFA 2.2, 2.3 and 6S 104, 92 and 96% were recovered, respectively. Since Methoxy was stable the indirect method could be used in the advanced test in accordance to the OECD 106 guideline. The adsorption isotherms (Tier 3) were estimated at a soil/solution ratio of 1/5 and at five test item concentration (0.1 to 7.0 mg/L). The results are shown in the table below.

Table A 10: Adsorption isotherm results at equilibrium (48 hours)

Soil	LUFA 2.2	LUFA 2.3	LUFA 6S
Slope (1/n)	0.7600	0.6864	0.7153
Intercept ($\log K^{\text{ads}}_{\text{F}}$)	0.8546	0.7614	0.7374
$K^{\text{ads}}_{\text{F}}$	7.15	5.77	5.46
R-squared	0.9987	0.9988	0.9963
% OC	1.72	1.08	1.75
$K^{\text{ads}}_{\text{FOC}}$	415.98	534.54	312.15

The desorption study (Tier 1 and 2) was performed at a concentration of 10 mg/L Methoxy in 0.01 M CaCl_2 solution at a soil/solution ratio of 1/5. The results are shown in the table below.

Table A 11: Desorption coefficients after 48 hours for soil LUFA 2.2, 2.3 and 6S

Parameters	LUFA 2.2	LUFA 2.3	LUFA 6S
D %	25.4	35.1	28.5
K _d	14.77	9.47	12.55
K _{oe}	858.7	876.4	717.2
Log K _{oe}	2.94	2.94	2.86
% OC	1.72	1.08	1.75

The amount of desorption was < 75 % of the amount adsorbed, so the adsorption is considered to be non-reversible.

The desorption isotherms (Tier 3) were estimated at a soil/solution ratio of 1/5 and at the same amount of test item as used for the adsorption isotherms. The results are shown in the table below.

Table A 12: Desorption isotherm results at equilibrium (48 hours)

Soil	LUFA 2.2	LUFA 2.3	LUFA 6S
Slope (1/n)	0.7191	0.6804	0.7270
Intercept ($\log K^{\text{des}}_{\text{F}}$)	0.9248	0.8687	0.8356
$K^{\text{des}}_{\text{F}}$	8.41	7.39	6.85
R-squared	0.9983	0.9974	0.9947
% OC	1.72	1.08	1.75
$K^{\text{des}}_{\text{FOC}}$	488.96	684.35	391.35

Flörchinger, M. (2010b)

A 3.3 Aerobic soil metabolism of 2,4-D in acidic soils

Comments of zRMS:	<p>The study was evaluated and agreed by the zRMS (NL) in the course of the zonal evaluation of ADAMA formulation AG-D2-600 SL finalised in September 2017. Following conclusions may be found in the Core Assessment for this product:</p> <p><i>The data gap regarding potential pH-dependence of the degradation process of 2,4-D in soil identified during the renewal review has been addressed by the applicant: A new study has been performed (Crabtree, 2015) and a summary is presented in Appendix 3. The outcome of this study confirms that degradation of 2,4-D in soil is not pH-dependent. The evaluation of the study (Crabtree, 2015) by zRMS is presented in Appendix 3. ZRMS considers that the study followed current guidance (OECD guideline 307) and is acceptable .</i></p> <p>Since the study was already agreed in the Central Zone, there was no need for its re-evaluation and conclusions taken by the zRMS for AG-D2-600 SL are also applicable for assessment performed for ADM.3304.H.1.A in order to maintain consistent approach within the zone. Overall, results of the study by Crabtree (2015) confirm that degradation of 2,4-D does not depend on the soil pH and currently EU agreed DT₅₀ values are relevant for purposes of the exposure assessment.</p> <p>Since the study was not re-evaluated, the summary below is displayed in grey font.</p>
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Report:	KCP-9.1.1/01, Crabtree, G.A. (2015)
Title:	[¹⁴ C] 2,4-D: Aerobic soil metabolism and transformation in acidic soils
Document No:	Lab Study No. 3200898 Dow AgroSciences No. 141222; PCTR No. 10001705-004-70101-0002
Guidelines:	OECD 307 OSCPP 835.4100, OPPTS 835.4100
Deviations:	The organic carbon content (as a % of microbial biomass) was <1% in Kenslow Wood soil throughout the incubation which deviates from the study guideline. The aim of the test was to use acidic soils and with the high microbial biomass it was deemed acceptable to use this soil.
Dates of work:	28 November 2015 to 23 April 2015
GLP:	Yes

STUDY SUMMARY

The route and rate of degradation of 2,4-D-Ph-UL-[¹⁴C] was studied in two acidic soils under aerobic conditions at 20 ± 2°C over a period of 37 to 50 days after treatment (DAT) in the dark. The nominal application rate was 50 µg per unit (1.0 mg/kg soil), equivalent to a field application rate of 750 g a.i./ha. Warsop soil is either a UK loamy sand or sand (pH 6.0 in water) from Nottinghamshire, UK and Kenslow Wood is a UK sandy silt loam (pH 4.7 in water) from Derbyshire, UK.

Samples, along with the associated traps, were removed for analysis immediately after application of 2,4-D-Ph-UL-[¹⁴C] and on eight further sampling occasions. Soil samples were extracted three times with acetonitrile: 1N HCl (9:1 v/v, 100 mL) and the 2,4-D residues were analysed by HPLC with RAM detection.

Mass balance (mean) was 96 to 101% AR. The amount extracted from soil decreased throughout the incubation period from 101% to 12% AR in Warsop and from 98% to 7% AR in Kenslow Wood. The level of unextracted radioactivity in each soil increased throughout the incubation period to a maximum of 30% (Warsop) and 36% AR (Kenslow Wood) at 22 DAT before decreasing to 24% (Warsop) and 32% (Kenslow Wood) at the end of the incubation period.

Additional extractions (acetonitrile: 1N HCl 7:3 v/v, room temperature followed by reflux) were conducted on the residues from the final sampling interval. The total additional radioactivity extracted from these solvents accounted for a maximum of 12% AR. Bound residue fractionation was performed on the 22 DAT samples. Radioactivity was recovered in humin, humic acid, and fulvic acid fractions.

At the end of the study a maximum of 57% to 60% AR was present as CO₂.
 Residues of 2,4-D declined from a range of 97% to 98% AR at 0 DAT to 2 to 4% at the last sampling interval. 2,4-D degraded to three known metabolites, 2,4-DCP (major), 2,4-DCA (minor), 4-CP (minor) and a polar unknown (minor). 2,4-DCP, 2,4 DCA and 4-CP were confirmed by TLC.
 2,4-D degraded with a DT₅₀ value in the range 4 to 5 days in acidic soil under aerobic conditions. DT₅₀ values for 2,4-DCP were in the range 0.5 to 0.6 days.

Table A 13: Results Synopsis

Soil type	2,4-D		2,4-DCP	
	DT ₅₀ [days]	DT ₉₀ [days]	DT ₅₀ [days]	DT ₉₀ [days]
Warsop	4.8	15.8	0.45	1.5
Kenslow Wood	4.4	14.7	0.64	2.1

Major transformation products: 2,4-DCP, CO₂.
 Minor transformation products: 2,4-DCA, 4-CP.

EXECUTIVE SUMMARY

MATERIALS AND METHODS

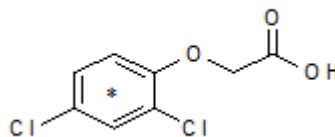
Test Item(s)

Non-radiolabelled test item

ISO Common name:	2,4-D (2,4-Dichlorophenoxyacetic acid)
Test item (chemical/other name):	2,4-Dichlorophenoxyacetic acid
Purity:	Not applicable
Description (physical state):	Not applicable
Lot/batch no.:	Not applicable
CAS no.:	Not applicable
SMILES string:	Not applicable

Radiolabelled test item #1

Name:	2,4-D-Ph-UL-[¹⁴ C]
Test item (chemical/other name):	(2,4-dichlorophenoxy)acetic acid-Ph-UL- ¹⁴ C
Structural Formula:	
Position of labelling (*)	



Lot/batch no.:	INV306796, Lot DE3-142118-49
Radiochemical purity:	99.7%
Specific radioactivity:	42.6 mCi/mmol

Methods

Soil Characteristics

Table A 14: Description of soil collection and storage

Description	Warsop	Kenslow Wood
Geographic location	Warsop, Nottinghamshire, UK	Middleton, Derbyshire, UK
Soil series	Not stated	Not stated
Latitude and longitude	53° 13' 14.2 N, 1° 9' 4.0 W	53° 9' 9.6 N, 1° 43' 52.1 W
Pesticide use history at the collection site	No pesticides used in last 5 years	No pesticides used in last 5 years
Collection procedures	ISO 10381-6	ISO 10381-6
Sampling depth	12-20 cm	5-20 cm
Storage conditions	4 ± 2 °C	4 ± 2 °C
Storage length	50 days	63 days
Soil preparation (e.g., 2 mm sieved; air dried, etc.)	2 mm sieved, air-dried	2 mm sieved, air-dried

Table A 15: Properties of the soil

Property	Warsop	Kenslow Wood
Soil texture (USDA)	Loamy sand or sand	Loam
% sand	88	44
% silt	6	45
% clay	6	11
Soil texture (UK)	Loamy sand or sand	Sandy silt loam
% sand	88	43
% silt	6	46
% clay	6	11
pH (water) ^a	6.0	4.7
pH (calcium chloride) ^a	4.0	3.8
Organic carbon [%]	1.0	7.5
CEC [meq/100 g]	12.8	51.0
Moisture holding capacity	20.4	73.9
Bulk density [g/cm ³]	1.1	0.6
Soil taxonomic classification	Entisol	Inceptisol

^a ISO 103900, 1:5 ratio of soil to solution

Preliminary Study

A preliminary test was conducted to develop/investigate extraction methods and estimate the half-life (DT₅₀) of 2,4-D in each soil, in order to determine sampling intervals for the definitive test. Results were not reported.

Definitive Study Experimental Conditions

Table A 16: Experimental parameters

Parameter	Description
Duration of test	Up to 50 days after treatment
Soil conditions (Air dried/fresh)	Fresh soils (stored <3 months at test facility)
Soil sample weight [g/replicate]	50 g/replicate (oven-dry weight)
Test concentrations	mg a.i./kg soil
	0.50
Test concentrations	g a.i./ha
	0.1
Control conditions, if used	
Number of replicates	Controls, if used
	6/soil
Number of replicates	Treatments
	None
Test apparatus (Type/material/volume)	Glass vessels (250 mL volume, 6 cm diameter), flow-through system
Traps for CO ₂ and organic volatiles, if any	Two sodium hydroxide traps
If no traps were used, is the system closed/open	Not applicable

Parameter		Description
Identity and concentration of co-solvent		Acetonitrile (<0.05%)
Test item application	Identity of solvent	Acetonitrile
	Volume of solution used/treatment	48 µL
	Application method	Surface of soil followed by thorough mixing
	Evaporation of solvent	Yes
Initial microbial biomass/microbial population of control soil		286.5 µg C/g (Warsop); 557.5 µg C/g (Kenslow Wood);
Final microbial biomass/microbial population of control soil		127.6 µg C/g (Warsop); 571.6 µg C/g (Kenslow Wood);
Initial microbial biomass/microbial population of treated soil, if provided		Not measured in treated soil
Final microbial biomass/microbial population of treated soil, if provided		Not measured in treated soil
Any indication of the test item adsorbing to the walls of the test apparatus		None
Experimental conditions	Temperature	20 ± 2°C
	Moisture content	pF 2
	Moisture maintenance method	Soil units weighed weekly and weight loss adjusted by addition of water.
	Continuous darkness	Yes
Other details, if any		None

Aerobic Conditions

Each test vessel was connected to two sodium hydroxide traps for the collection of CO₂. Moistened air was pulled through the connected vessel and traps by vacuum.

Supplementary Experiments

None

Sampling

Table A 17: Sampling details

Parameters	Details
Sampling intervals	Warsop; 0, 0.17, 1, 2, 3, 6, 13, 22, 50 DAT Kenslow Wood, 0, 0.17, 1, 2, 3, 6, 13, 22, 37 DAT.
Sampling method for soil samples	Soils transferred from incubation unit using extraction solvent
Method of collection of CO ₂ and volatile organic compounds	NaOH traps, 2 connected in series to each incubation unit
Sampling intervals/times for:	
sterility check, if sterile controls are used:	None
moisture content	Adjusted by addition of water every 8 days
Redox potential/Other	None
Sample storage before analysis	Analysis started on the day the units were removed
Other observations, if any	None

Analytical Methodology

Determination of physico-chemical parameters

No measurements made on the test system.

Extraction

Soil samples were extracted three times with acetonitrile:1N HCl (9:1 v/v, 200 mL) by shaking (20 minutes) and centrifugation (10 minutes). The three extracts were pooled prior to quantification of radioactivity by LSC and analysis by HPLC.

Non-extractable residue determination

Following initial extraction, air-dried sediment was ground to homogenise and sub-sampled in triplicate (0.02 g) prior to combustion using a Harvey Biological Sample Oxidiser.

Further investigation into the non-extractable residue was performed on the soils from the last sampling interval, by using increasing the acid strength followed by increasing the temperature. Soils were sequentially extracted with acetonitrile:1 N HCl (7:3 v:v) followed by acetonitrile:1 N HCl (7:3 v:v) and acetone (to facilitate drying).

Bound residue fractionation was performed on residues of each soil from the 22 DAT sampling interval (highest unextracted residue). Samples were initially extracted with NaOH (0.5M, 100 mL, bound residue extract), by shaking (24 hours) and centrifugation. The post extracted pellet was then further extracted with NaOH (0.5M, 2 x 25 mL) followed by centrifugation. The supernatants were combined with the bound residue extract and quantified by LSC. The post-extracted pellet was left to air dry. The pH of the caustic extracts was adjusted to *ca* pH 1 using HCl (5M) to cause the humic acids to precipitate out of solution. The precipitate was separated from the supernatant by centrifugation (fulvic acid extract). The resulting precipitate was re-suspended sequentially with hydrochloric acid (0.1M, 25 mL) and the precipitate separated from the supernatant by centrifugation. The supernatant was combined with the fulvic acids extract and quantified by LSC. Humic acids were re-dissolved by sonication, using sodium hydroxide (0.5M, 100 mL) and quantified by LSC.

Total ¹⁴C measurement

LSC of weighed aliquots.

High performance liquid chromatography (HPLC) for quantitation

HPLC analyses of all sample extracts were accomplished using an ACE 5 C18 column (250 x 4.6 mm i.d., 5.0 µm; 1.0 mL/min; UV detection at 280 nm) and gradient elution. A binary gradient system was used consisting of 0.1% acetic acid in water and 0.1% acetic acid in acetonitrile.

Whenever possible, initial metabolite identification was accomplished by co-chromatography with available reference standards using HPLC and confirmed using TLC (Merck Silica Gel 60F₂₅₄ plate; toluene:ethyl acetate:acetic acid 86:10:4 v/v/v).

Table A 18: Detection limits (LOD, LOQ) for the parent and transformation products

Matrix	LOD [%AR]	LOD [dpm]	LOQ [%AR]	LOQ [dpm]
Warsop soil - HPLC	0.42	29.1	0.42	29.1
Kenslow wood soil - HPLC	0.15	27.8	0.15	27.8

Kinetics calculations

The degradation rate of the test item was calculated using CAKE software (version 2.0) according to FOCUS Kinetics Guidance (2006) on estimating persistence and degradation kinetics from Environmental Fate Studies. In order to estimate DT₅₀ and DT₉₀ values, two different kinetic models were fitted to the degradation data:

- 1 Single First-Order (SFO)
- 2 First-Order Multi Compartment (FOMC)

Input data sets for modelling were derived from individual data for each time-point. Sample values were unweighted

DT₅₀ and DT₉₀, chi-square and r² values were calculated directly by the software.

Storage stability

Sample analysis started on the day of sacrifice. Soil extracts were stored frozen (<-10°C) during work-up prior to analysis by HPLC. HPLC analysis for % AR determination was completed within 22 days. As a result no formal storage stability was performed.

RESULTS AND DISCUSSION

A. Route of Degradation

Test conditions

Aerobic conditions were maintained throughout the study. Soil biomass was determined at study initiation and termination. In Warsop soil the final biomass declined, from 286.5 µg/g to 127.6 µg/g, over the course of the study. In Kenslow soil there was no decline in biomass over the duration of the study.

Test Item Balance

Total recovery of radiolabelled material ranged from 100 to 101% of the applied amount at 0 DAT. Overall mass balance was ≥96% for both systems throughout the incubation period.

Table A 19: Biotransformation of 2,4-D, expressed as percentage of the applied radioactivity, in Warsop soil under aerobic conditions

DAT	Rep	Trap	Extract	2,4-D	2,4-DCP	2,4-DCA	4-CP	Polar	Other	NER	Total
0	1	NA	102.8	100.5	1.3	ND	ND	ND	ND	0.3	103.1
0	2	NA	98.2	96.2	1.1	ND	ND	ND	0.7	0.2	98.4
Ave		NA	100.5	98.3	1.2	ND	ND	ND	0.4	0.3	100.8
0.17	1	0.1	99.6	96.3	2.0	ND	ND	ND	0.6	0.6	100.3
0.17	2	ND	97.5	95.3	1.4	ND	ND	ND	0.5	0.5	98.0
Ave		0.1	98.6	95.8	1.7	ND	ND	ND	0.5	0.6	99.2
1	1	1.3	93.5	84.9	6.9	ND	ND	ND	ND	3.9	98.7
1	2	1.4	94.0	85.4	7.8	ND	ND	ND	ND	4.2	99.6
Ave		1.4	93.8	85.2	7.3	ND	ND	ND	ND	4.1	99.2
2	1	2.4	92.4	85.1	5.9	ND	ND	ND	ND	5.1	99.9
2	2	3.2	90.2	82.8	7.4	ND	ND	ND	ND	6.4	99.8
Ave		2.8	91.3	83.9	6.6	ND	ND	ND	ND	5.8	99.9
3	1	6.5	82.5	69.1	6.5	1.1	ND	1.3	2.6	9.3	98.3
3	2	5.5	84.1	75.1	5.3	1.1	ND	1.2	ND	8.1	97.7
Ave		6.0	83.3	72.1	5.9	1.1	ND	1.2	1.3	8.7	98.0
6	1	22.7	53.5	42.5	5.2	1.5	ND	2.4	1.1	19.2	95.4
6	2	25.1	46.9	34.0	4.9	1.3	0.8	2.5	2.4	23.5	95.5
Ave		23.9	50.2	38.2	5.0	1.4	0.4	2.4	1.7	21.4	95.5
13	1	51.0	20.7	7.8	2.7	2.9	0.5	3.6	2.7	24.9	96.6
13	2	43.6	23.5	11.2	1.9	ND	0.5	6.5	3.2	30.4	97.5
Ave		47.3	22.1	9.5	2.3	1.5	0.5	5.1	2.9	27.7	97.1
22	1	51.5	16.0	5.2	1.5	2.4	0.5	0.9	5.4	29.0	96.5
22	2	49.7	16.4	5.7	1.5	1.1	0.3	0.4	7.1	30.6	96.7
Ave		50.6	16.2	5.4	1.5	1.8	0.4	0.6	6.2	29.8	96.6
50	1	62.7	11.5	4.4	0.9	0.3	0.6	3.0	2.4	22.6	96.8
50	2	57.7	12.7	3.0	1.2	0.5	1.1	3.0	3.8	24.8	95.2
Ave		60.2	12.1	3.7	1.0	0.4	0.9	3.0	3.1	23.7	96.0

ND = Not detected, NA = Not applicable

Table A 20: Biotransformation of 2,4-D, expressed as percentage of the applied radioactivity, in Kenslow Wood soil under aerobic conditions

DAT	Rep	Trap	Extract	2,4-D	2,4-DCP	2,4-DCA	4-CP	Polar	Other	NER	Total
0	1	NA	98.9	97.1	1.1	ND	ND	ND	ND	1.7	100.6
0	2	NA	97.5	96.1	1.0	ND	ND	ND	ND	1.8	99.3
Ave		NA	98.2	96.6	1.1	ND	ND	ND	ND	1.8	100.0
0.17	1	ND	96.4	94.7	1.4	ND	ND	ND	ND	1.5	97.9
0.17	2	ND	99.0	95.8	1.9	ND	ND	ND	ND	1.5	100.5
Ave		ND	97.7	95.2	1.6	ND	ND	ND	ND	1.5	99.2
1	1	1.3	90.3	81.8	7.4	ND	ND	ND	ND	5.5	97.1
1	2	ND	92.1	81.2	8.3	1.2	ND	ND	0.7	5.1	97.2
Ave		0.7	91.2	81.5	7.8	0.6	ND	ND	0.4	5.3	97.2
2	1	7.1	74.8	57.2	14.8	2.1	ND	ND	ND	15.6	97.5
2	2	4.1	80.1	66.8	10.4	1.5	ND	ND	ND	12.6	96.8
Ave		5.6	77.5	62.0	12.6	1.8	ND	ND	ND	14.1	97.2
3	1	9.2	70.8	56.6	10.8	1.5	ND	1.5	ND	17.4	97.4
3	2	6.5	80.4	64.8	9.1	2.3	ND	4.2	ND	13.1	100.0
Ave		7.9	75.6	60.7	10.0	1.9	ND	2.8	ND	15.3	98.7
6	1	14.4	64.9	58.6	4.2	1.4	ND	ND	ND	20.5	99.8
6	2	23.4	47.4	37.3	6.1	2.5	ND	1.3	ND	23.1	93.9
Ave		18.9	56.2	47.9	5.1	1.9	ND	0.6	ND	21.8	96.9
13	1	43.5	17.1	3.8	1.4	ND	ND	6.0	5.8	34.8	95.4
13	2	44.0	17.4	4.8	1.0	ND	ND	5.6	6.0	35.1	96.5
Ave		43.8	17.3	4.3	1.2	ND	ND	5.8	5.9	35.0	96.0
22	1	53.0	9.9	4.1	1.8	0.9	ND	0.7	2.3	35.6	98.5
22	2	50.5	10.3	4.7	1.2	ND	ND	1.0	3.3	36.8	97.6
Ave		51.8	10.1	4.4	1.5	0.5	ND	0.8	2.8	36.2	98.1
37	1	56.8	7.1	1.9	1.3	0.2	0.5	2.0	1.1	32.2	96.1
37	2	56.4	7.1	2.0	0.9	0.2	0.2	2.3	1.6	31.3	94.8
Ave		56.6	7.1	1.9	1.1	0.2	0.3	2.1	1.3	31.8	95.5

ND = Not detected, NA = Not applicable

Non-extractable and extractable residues

The extractable [¹⁴C]-residues declined from 98 to 101% AR initially to 12% AR (Warsop) and 7% AR (Kenslow Wood) at the end of the incubation period. In Warsop soil, unextracted residues increased to 30% AR at 22 DAT before decreasing at the last sampling interval (24% AR). In Kenslow Wood soil, unextracted residues increased to 36% AR at 22 DAT before decreasing at the last sampling interval (32% AR).

Additional extractions using an increased acid strength and increased temperature were conducted on the unextracted residue from the last sampling interval. Additional radioactivity extracted accounted for up to 12% AR though the majority was only extracted when the temperature was elevated (reflux conditions). Bound residue fractionation was performed on the residues from the 22 DAT sampling interval (max % AR). Radioactivity was recovered in all three fractions, indicating progressive assimilation and metabolism of the test compound within the soil organic matter fraction.

Volatilisation

At study termination evolved ¹⁴CO₂ accounted for 57 to 60% AR. The evolved volatile radioactivity trapped in the sodium hydroxide traps was confirmed to be carbon dioxide by precipitation with barium chloride.

Transformation of Parent Compound

Residues of 2,4-D declined from a range of 97% to 98% AR at 0 DAT to a range of 2% to 4% AR at the end of the incubation period.

Transformation Products

The decline of 2,4-D was followed by an increase in the formation of three metabolites, (which were known) during the course of the study. These included the major metabolite 2,4-DCP and minor metabolites 2,4-DCA and 4-CP (each <5% AR).

The maximum levels of 2,4-DCP ranged from 7% (Warsop, 1 DAT) to 13% AR (Kenslow Wood, 2 DAT). The level of 2,4-DCP declined to 1% AR at the end of the incubation period for both soils. The maximum level of 2,4-DCA was 2% AR at 22 DAT (Warsop) and 3 and 6 DAT (Kenslow Wood). The maximum level of 4-CP was <1% AR in both soils at the end of the test.

A polar unknown increased to a maximum of 5 to 6% AR at 13 DAT before decreasing to 2 to 3% at the end of the test. As >5% AR was only seen at one sampling interval, no identification or separation of the polar material was conducted. A number of minor unknowns were observed during the test but as the maximum level of any individual metabolite did not exceed 5% AR no further work was done.

Pathway

With the exception of carbon dioxide, the main metabolites that formed were 2,4-DCP, 2,4-DCA and 4-CP. The probable route to 4-CP is removal of the side chain from 2,4-D to form 2,4-DCP, followed by dechlorination. 2,4-DCA was also formed from 2,4-D by the removal of the hydroxyl group. 2,4-DCA could also degrade to 2,4-DCP by removal of the side chain. None of the major degradates were persistent, 2,4-DCP and 2,4-DCA were observed to decline with time, and 4-CP was at a maximum <1% at the end of the incubation period.

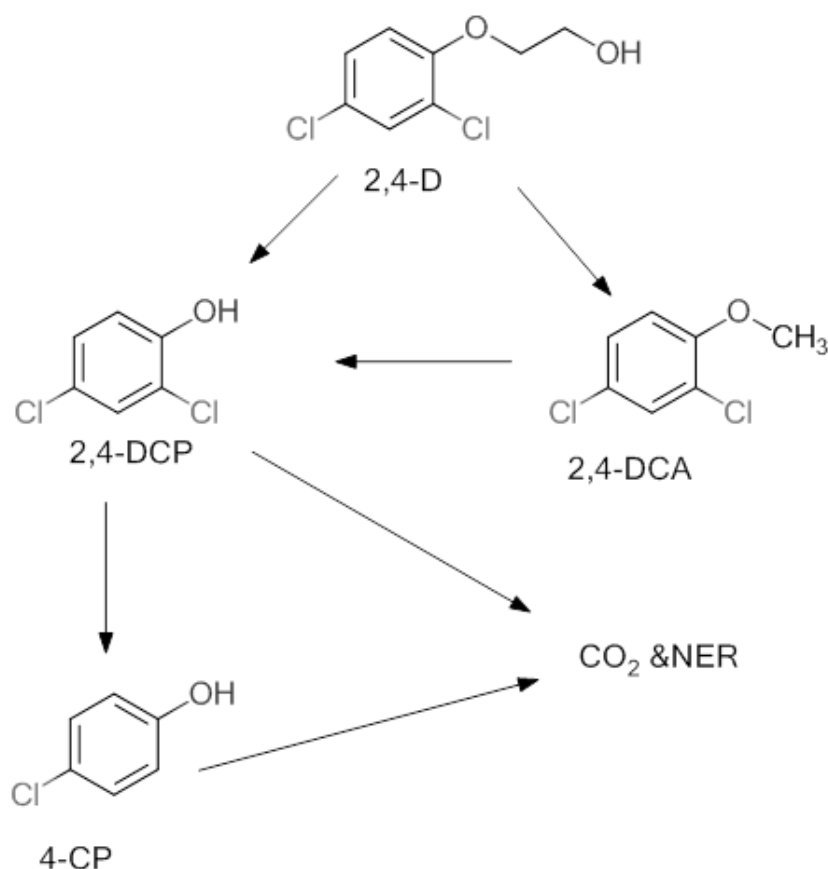


Figure A 1: Aerobic biotransformation pathway of 2,4-D in acidic soil

Table A 21: Chemical names and CAS numbers for the transformation products of test item

Code name	CAS number	CAS and/or IUPAC chemical name(s)	Chemical formula	Molecular weight	SMILES string	Maximum % formed
2,4-DCP	120-83-2	2,4-Dichlorophenol	C ₆ H ₄ Cl ₂ O	163.0	Clc1cc(Cl)c(O)cc1	14.8
2,4- DCA	553-82-2	2,4- Dichloroanisole	C ₇ H ₆ Cl ₂ O	177.03	COc1ccc(cc1Cl)Cl	2.9
4-CP	106-48-9	4-Chlorophenol	C ₆ H ₅ ClO	128.56	Clc1ccc(O)cc1	1.1

B. Rate of Degradation

Half-life

The best fit endpoints for the DT₅₀ (50% decline time) of 2,4-D using SFO kinetics, are shown in the following table:

Table A 22: Degradation rate of 2,4-D

Test item	Soil type	DT ₅₀ [days]	DT ₉₀ [days]	Model used	χ ² error %	Parameters
2,4-D	Warsop	4.8	15.8	SFO	6.7	visual fit good; t-test prob <0.05; confidence intervals >0
2,4-D	Kenslow Wood	4.4	14.7	SFO	8.4	visual fit good; t-test prob <0.05; confidence intervals >0

Supplementary Experiment - Results

None

C. Rate of Degradation at 10°C

A study was not conducted, since the degradation rate at different temperatures may be calculated.

D. Rate of Degradation of Metabolites

The best fit endpoints for the DT₅₀ (50% decline time) of 2,4-DCP using SFO kinetics, are shown in the following table:

Table A 23: Degradation rate of metabolites formed

Test item	Soil type	DT ₅₀ [days]	DT ₉₀ [days]	Model used	Formation fraction	χ ² error %	Parameters
2,4-DCP	Warsop	0.45	1.5	SFO	0.9	16.0	visual fit good; t-test prob <0.05; confidence intervals >0
2,4-DCP	Kenslow Wood	0.64	2.1	SFO	1	19.0	visual fit good; t-test prob <0.05; confidence intervals >0

CONCLUSION

2,4-D degraded in acidic soil under aerobic conditions with DT₅₀ values in the range 4 to 5 days. 2,4-D degraded to two major transformation products 2,4-DCP (7 to 13% AR) and carbon dioxide (57 to 60% AR). DT₅₀ of the transformation product 2,4-DCP was < 1 day.

Minor transformation products, 2,4-DCA, 4-CP, a polar unknown and multiple minor unknowns were formed (individually < 5% AR).

Unextracted residues in the soil increased to a maximum (30 to 36% AR) before decreasing. Characterisation of the PES from the final time point indicated that minimal additional 2,4-D or known degradates remained in the soil, while significant portions of the residue were associated with humin, humic, and fulvic acids indicating breakdown of the ring into small carbon chains that have been incorporated into soil.

A 3.4 4-CP aerobic degradation

Comments of zRMS:	<p>The study was evaluated and agreed by the zRMS (PL) in the course of the zonal Art. 43 evaluation of ADAMA formulation Camaro 306 SE (AG-FD1-306 SE) finalised in March 2017. Following conclusions may be found in the Core Assessment for this product:</p> <p><i>The study was provided by the Applicant in order to address a data gap identified in EFSA Journal 2014;12(9):3812.</i></p> <p><i>In general, in opinion of the zRMS such studies should be evaluated at the EU level by the RMS (as a confirmatory data) in order to provide uniform and consistent endpoints for all Member States.</i></p> <p><i>4-chlorophenol is metabolite of 2,4-D formed under anaerobic conditions. In general, anaerobic conditions are not expected at the time of application of the formulation, however they cannot be fully excluded (especially during early spring). Taking this into account, the study was evaluated by the zRMS for purposes of the zonal authorisation.</i></p> <p><i>The study was well performed and is general in line with recommendations of OECD 307. It was performed with non-labelled material and initial recoveries in range 91-102% were well within range provided by the guideline (i.e. 700-110% for non-labelled chemicals). The test was terminated after 168 hours after treatment, when more than 90% of 4-chlorophenol was transformed.</i></p> <p><i>It was, however, noted that mass balance for each sampling interval was not given, while according to recommendations of the test guideline it should be provided. Nevertheless, the study was performed in order to determine rate and not route of degradation of 4-chlorophenol and for this reason lack of this information is not considered as serious drawback of the study.</i></p> <p><i>The study was performed in the dark, at 20°C and soil moisture content maintained at pF 2.</i></p> <p><i>The study is considered acceptable.</i></p> <p><i>Worst case soil DT₅₀ of 4-chlorophenol was determined to be 0.69 days (16.6 hours) and mean DT₅₀ was 0.22 days.</i></p> <p>Since the study was already agreed in the Central Zone, there was no need for its re-evaluation and conclusions taken by the zRMS for Camaro 306 SE (AG-FD1-306 SE) are also applicable for assessment performed for ADM.3304.H.1.A in order to maintain consistent approach within the zone. The worst case soil DT₅₀ of 0.69 d is relevant for the soil exposure assessment, while for the groundwater and surface water modelling the mean DT₅₀ of 0.22 d is considered relevant.</p> <p>Since the study is considered acceptable, its summary is retained below. However, as no new evaluation has been performed by the zRMS specifically for purposes of authorisation of ADM.3304.H.1.A, the font colour has been changed to grey.</p>
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Report:	KCP-9.1.1/02, Swales, S.E. & Crabtree, G.A. (2015a)
Title:	4-Chlorophenol: Aerobic soil degradation in three EU soils and one US soil
Document No:	Lab Study No. 3200919 Dow AgroSciences No. 141220; PCTR No. 10001705-004-70101-0001
Guidelines:	OECD 307 OSCPP 835.4100, OPPTS 835.4100
Deviations:	None
Dates of work:	11 December 2014 to 27 February 2015
GLP:	Yes

STUDY SUMMARY

The rate of degradation of 4-chlorophenol was studied in three EU soils and one US soil under aerobic conditions at 20 ± 2°C over a period of up to 168 hours after treatment (HAT) in the dark. The nominal

application rate was 50 µg per unit (1.0 mg/kg soil), equivalent to a field application rate of 750 g a.i./ha. Brierlow soil is a UK sandy silt loam (pH 7.4 in water) from Derbyshire, UK, Speyer 5M is a UK sandy loam (pH 8.4 in water) from Rheinland-Pfalz, Germany, Warsop soil is either a UK loamy sand or sand (pH 6.0 in water) from Nottinghamshire, UK and LAD-SCL-PF soil is a UK clay (pH 9.0 in water) from Wyoming, USA.

Samples were removed for analysis immediately after application of 4-chlorophenol and on six further sampling occasions for Brierlow, Speyer 5M and Warsop soils and seven further sampling occasions for LAD-SCL-PF soil. Samples were removed for analysis up to 24 hours (Brierlow and Speyer 5M soils), 96 hours (Warsop soil) and 168 hours (LAD-SCL-PF soil). Soils were extracted with 0.1M HCl : acetonitrile (1:9 v/v, 2 x 150 mL), pooled extracts were subjected to solid phase extraction (SPE) and the residues of 4-chlorophenol determined by LC-MS/MS.

At 0 HAT, mean recoveries of 4-chlorophenol were 91 to 102% for each soil. The amount of 4-chlorophenol declined throughout the incubation period from 94 to 4% in Brierlow soil, 96 to 2% in Speyer 5M, 102 to 3% in Warsop soil and 91 to 1% in LAD-SCL-PF soil.

4-Chlorophenol degraded with a DT₅₀ value in the range 1.9 to 17 hours in soil under aerobic conditions.

Results Synopsis

Soil type	4-Chlorophenol	
	DT ₅₀ [hours]	DT ₉₀ [hours]
Brierlow	1.9	6.4
Speyer 5M	3.2	10.7
Warsop	16.6	55.0
LAD-SCL-PF	7.4	24.5

EXECUTIVE SUMMARY

MATERIALS AND METHODS

Test Item(s)

Non-radiolabelled test item

ISO Common name:	4-Chlorophenol
Test item (chemical/other name):	4-Chlorophenol
Purity:	100%
Description (physical state):	White Crystalline Solid
Lot/batch no.:	TSN304318, Lot MKBJ7452V
CAS no.:	106-48-9
SMILES string:	<chem>c1cc(ccc1O)Cl</chem>

Methods

Soil Characteristics

Table A-24 Description of soil collection and storage

Description	Brierlow	Speyer 5M	Warsop	LAD-SCL-PF
Geographic location	Brierlow, Derbyshire, UK	In der Speyerer Hohl, Nr 977, Mechttersheim, Rheinland-Pfalz, Germany	Warsop, Nottinghamshire, UK	Wyoming, USA
Soil series	Not Stated	Not Stated	Not Stated	Not Stated
Latitude and longitude	53° 13' 9.4 N, 1° 50' 32.4 W	not provided	53° 13' 14.2 N, 1° 9' 4.0 W	43° 15.486 N, 108° 33.973 W
Pesticide use history at the collection site	No pesticides used in last 5 years	No pesticides used in last 5 years	No pesticides used in last 5 years	No pesticides used in last 5 years
Collection Date	09 October 2014	22 October 2014	22 October 2014	18 October 2014
Collection procedures	ISO 10381-6	ISO 10381-6	ISO 10381-6	ISO 10381-6
Sampling depth	12-23 cm	20 cm	12-20 cm	0-6 inches
Storage conditions	4 ± 2°C	4 ± 2°C	4 ± 2°C	4 ± 2°C
Storage length	91 Days	78 Days	78 Days	82 Days
Soil preparation	2 mm sieved, air-dried	2 mm sieved, air-dried	2 mm sieved, air-dried	2 mm sieved, air-dried

Table A-25 Properties of the soil

Property	Brierlow	Speyer 5M	Warsop	LAD-SCL-PF
Soil texture (USDA)	Silt loam	Sandy loam	Loamy sand or sand	Clay or clay loam
% sand	32	58	88	35
% silt	52	31	6	25
% clay	16	11	6	40
Soil texture (UK)	Sandy silt loam	Sandy loam	Loamy sand or sand	Clay
% sand	31	53	88	32
% silt	53	36	6	28
% clay	16	11	6	40
pH (water) ^a	7.4	8.4	6.0	9.0
pH (calcium chloride) ^a	6.2	7.3	4.0	8.1
Organic carbon [%]	2.3	1.0	1.0	0.9
CEC [meq/100 g]	22.1	16.1	12.8	30.2
Moisture holding capacity	73.6	39.8	20.4	60.3
Bulk density [g/cm ³]	0.9	1.3	1.1	1.0
Soil taxonomic classification	Inceptisol	Entisol	Entisol	Not stated

^a ISO 103900, 1:5 ratio of soil to solution

Preliminary Study

A preliminary test was conducted to develop/investigate extraction methods and estimate the half-life (DT₅₀) of 4-chlorophenol in each soil, in order to determine sampling intervals for the definitive test. Results were not reported.

Definitive Study Experimental Conditions

Table A-25 Experimental parameters

Parameter		Description
Duration of test		Up to 7 days after treatment
Soil conditions (Air dried/fresh)		Fresh soils (stored <3 months at test facility)
Soil sample weight [g/replicate]		50 g/replicate (oven-dry weight)
Test concentrations	mg a.i./kg soil	1.0
	g a.i./ha	750
Control conditions, if used		
Number of replicates	Controls, if used	6/soil
	Treatments	None
Test apparatus (Type/material/volume)		Glass vessels (500 mL volume), adapted lids to allow continuous air exchange
Traps for CO ₂ and organic volatiles, if any		None
If no traps were used, is the system closed/open		Open
Identity and concentration of co-solvent		Details below
Test item application	Identity of solvent	Water
	Volume of solution used/treatment	500 µL
	Application method	Surface of soil followed by thorough mixing
	Evaporation of solvent	Yes
Initial microbial biomass/microbial population of control soil		793.4 µg C/g (Brierlow), 265.6 µg C/g (Speyer 5M), 146.1 µg C/g (Warsop); 415.9 µg C/g (LAD-SCL-PF)
Final microbial biomass/microbial population of control soil		512.7 µg C/g (Brierlow), 199.8 µg C/g (Speyer 5M), 179.7 µg C/g (Warsop); 301.4 µg C/g (LAD-SCL-PF)
Initial microbial biomass/microbial population of treated soil, if provided		Not measured in treated soil
Final microbial biomass/microbial population of treated soil, if provided		Not measured in treated soil
Any indication of the test item adsorbing to the walls of the test apparatus		None
Experimental conditions	Temperature	20 ± 2°C
	Moisture content	pF 2
	Moisture maintenance method	Soil units weighed weekly and weight loss adjusted by addition of water.
	Continuous darkness	Yes
Other details, if any		None

Aerobic Conditions

Each test vessel had a perforated lid allowing continuous air exchange.

Supplementary Experiments

None.

Sampling

Table A-26 **Sampling details**

Parameters	Details
Sampling intervals	Brierlow: 0, 0.5, 1, 1.5, 2, 4, 24 HAT Speyer 5M: 0, 1, 1.5, 2, 4, 6, 24 HAT Warsop: 0, 2, 4, 8, 24, 72, 168 HAT LAD-SCL-PF: 0, 1, 2, 4, 8, 24, 48, 96 HAT.
Sampling method for soil samples	Soils transferred from incubation unit using extraction solvent
Method of collection of CO ₂ and volatile organic compounds	None
Sampling intervals/times for:	
sterility check, if sterile controls are used:	None
moisture content	Adjusted by addition of water every 8 days (weight loss)
Redox potential/Other	None
Sample storage before analysis	Analysis started on the day the units were removed
Other observations, if any	None

HAT = hours after treatment

Analytical Methodology

Determination of physico-chemical parameters

No measurements made on the test system.

Extraction

Soil samples were extracted two times with acetonitrile:0.1N HCl (9:1 v/v, 150 mL) by shaking (30 minutes) and centrifugation (5 minutes). The extracts were pooled and the volume adjusted to 300 mL by addition of acetonitrile:0.1N HCl (9:1 v/v). An aliquot (1 mL) was diluted to 20 mL (using water) and HCl (1 mL, 2M) added prior to SPE (Oasis MCX, 60 mg, 3 mL). The cartridge was eluted using 0.1% acetic acid in acetonitrile:methanol (80:20 v/v, 2 x 500 µL), further diluted with 0.1% acetic acid (1 mL) and analysed by LC-MS/MS.

Non-extractable residue determination

Not applicable.

Method Validation

The analytical procedure for this study was validated by fortifying untreated control samples (50 g dry weight) of each soil at the limit of quantitation (0.05 mg/kg), at half the test concentration (0.5 mg/kg), and at the test concentration (1.0 mg/kg). There was a total of 8 replicates at each concentration. Validation included consideration of the following criteria; linearity, specificity, precision, recovery, LOQ and LOD.

Method Extraction Efficiency

Mean recovery of 4-chlorophenol at 0 DAT was 91 to 102% of the applied amount demonstrating that the extraction solvent was suitable for removing residues of 4-chlorophenol.

HPLC with mass spectral analysis (LC-MS/MS) for Quantitation

HPLC analyses of all sample extracts following SPE clean-up were accomplished using a Synergi Hydro-RP column (50 x 2.0 mm i.d., 4.0 µm; 0.5 mL/min).

The calibration samples and soil samples were analysed by liquid chromatography with negative-ion electrospray ionization mass spectrometry. To demonstrate confirmation, two distinct MS/MS ion transitions were monitored and illustrated in the raw data. A single transition for (126.9 to 90.9) was used for results calculation.

Analyst 1.6.2 software was used to calculate correlation coefficients, regression equations, and sample concentrations.

Detection limits (LOD, LOQ)

Matrix	LOD [mg/kg]	LOQ [mg/kg]
Soil Extract	0.004 – 0.005	0.05

Kinetics calculations

The degradation rate of the test item was calculated using CAKE software (version 2.0) according to FOCUS Kinetics Guidance (2006) on estimating persistence and degradation kinetics from Environmental Fate Studies. In order to estimate DT₅₀ and DT₉₀ values, two different kinetic models were fitted to the degradation data:

- 1 Single First-Order (SFO)
- 2 First-Order Multi Compartment (FOMC)

Input data sets for modelling were derived from individual data for each time-point. Sample values were unweighted

DT₅₀ and DT₉₀, chi-square and r² values were calculated directly by the software.

Storage stability

Sample analysis started on the day of sacrifice and all soil extracts were analysed within 3 days of sample collection. Soils and extracts were stored frozen (<-10°C) during work-up and analysis. As a result no formal storage stability was performed.

RESULTS AND DISCUSSION

A. Recovery of 4-Chlorophenol

Test conditions

Soil biomass was determined at study initiation and termination. In Brierlow soil, the final biomass declined from 793.4 µg C/g to 512.7 µg/g, over the course of the study. In Speyer 5M soil, the final biomass declined from 265.6 µg C/g to 199.8 µg C/g, over the course of the study. There was a slight increase in the final biomass for Warsop soil from 146.1 µg C/g to 179.7 µg C/g. In LAD-SCL-PF soil the final biomass declined from 415.9 µg C/g to 301.4 µg C/g. All soils had a viable biomass throughout the incubation period.

Extracted Residues

Mean recovery of 4-chlorophenol from soil immediately after treatment was in the range 91 to 102% of the applied. Residues of 4-chlorophenol rapidly declined in all soils, from 94 to 4% in 24 hours (Brierlow), 96 to 2% in 24 hours (Speyer 5M), 102 to 3% in 96 hours (Warsop) and 91 to 1% in 168 hours (LAD-SCL-PF).

Procedural recoveries from control soils were in the range 76 to 111% thereby demonstrating that the method was suitable. With the exception of Warsop soil at the middle concentration (0.5 mg/kg), precision of the analytical procedure was acceptable (<20% RSD). Precision (% RSD) ranged from 3.03 to 10.5% for Brierlow, 0.338 to 7.71% for Speyer 5M, 3.57 to 23.8% for Warsop and 1.30 to 6.15% for LAD-SCL-PF soil. As none of the control soils showed any detectable 4-chlorophenol or interferences, the specificity of the method was demonstrated.

Table A-27 **Degradation of 4-chlorophenol, expressed as concentration in soils extracts and percentage of the test substance, in Brierlow soil under aerobic conditions**

HAT	Replicate	Concentration [mg/kg]	% of Applied
0	1	0.913	91.3
0	2	0.957	95.7
Mean		0.935	93.5
0.5	1	0.718	71.8
0.5	2	0.745	74.5
Mean		0.732	73.2
1	1	0.592	59.2
1	2	0.679	67.9
Mean		0.636	63.6
1.5	1	0.574	57.4
1.5	2	0.491	49.1
Mean		0.533	53.3
2	1	0.453	45.3
2	2	0.446	44.6
Mean		0.450	45.0
4	1	0.225	22.5
4	2	0.225	22.5
Mean		0.225	22.5
24	1	0.0369	3.69
24	2	0.0342	3.42
Mean		0.0356	3.56

Table A-28 **Degradation of 4-chlorophenol, expressed as concentration in soils extracts and percentage of the test substance, in Speyer 5M soil under aerobic conditions**

HAT	Replicate	Concentration [mg/kg]	% of Applied
0	1	0.981	98.1
0	2	0.947	94.7
Mean		0.964	96.4
1	1	0.791	79.1
1	2	0.847	84.7
Mean		0.819	81.9
1.5	1	0.670	67.0
1.5	2	0.708	70.8
Mean		0.689	68.9
2	1	0.581	58.1
2	2	0.561	56.1
Mean		0.571	57.1
4	1	0.409	40.9
4	2	0.404	40.4
Mean		0.407	40.7
6	1	0.273	27.3
6	2	0.310	31.0
Mean		0.292	29.2
24	1	0.0170	1.70
24	2	0.0188	1.88
Mean		0.0179	1.79

Table A-29 Degradation of 4-chlorophenol, expressed as concentration in soils extracts and percentage of the test substance, in Warsop soil under aerobic conditions

HAT	Replicate	Concentration [mg/kg]	% of Applied
0	1	1.060	106
0	2	0.975	97.5
Mean		1.018	101.8
2	1	0.881	88.1
2	2	0.829	82.9
Mean		0.855	85.5
4	1	0.799	79.9
4	2	0.789	78.9
Mean		0.794	79.4
8	1	0.720	72.0
8	2	0.686	68.6
Mean		0.703	70.3
24	1	0.345	34.5
24	2	0.376	37.6
Mean		0.361	36.1
96	1	0.0481	4.81
96	2	0.0515	5.15
Mean		0.0498	4.98
168	1	0.0266	2.66
168	2	0.0268	2.68
Mean		0.0267	2.67

Table A-30 Degradation of 4-chlorophenol, expressed as concentration in soils extracts and percentage of the test substance, in LAD-SCL-PF soil under aerobic conditions

HAT	Replicate	Concentration [mg/kg]	% of Applied
0	1	0.898	89.8
0	2	0.916	91.6
Mean		0.907	90.7
1	1	0.890	89.0
1	2	0.924	92.4
Mean		0.907	90.7
2	1	0.776	77.6
2	2	0.792	79.2
Mean		0.784	78.4
4	1	0.688	68.8
4	2	0.577	57.7
Mean		0.633	63.3
8	1	0.470	47.0
8	2	0.482	48.2
Mean		0.476	47.6
24	1	0.0696	6.96
24	2	0.0450	4.50
Mean		0.0573	5.73
48	1	0.00787	0.787
48	2	0.00820	0.820
Mean		0.00804	0.804
96	1	0.00649	0.649
96	2	0.00659	0.659
Mean		0.00654	0.654

Non-extractable and extractable residues

Not applicable.

Volatilisation

Not applicable.

Transformation of Parent Compound

Not applicable.

Transformation Products

Not applicable.

B. Rate of Degradation

Half-life

The best fit endpoints for the DT₅₀ (50% decline time) of 4-chlorophenol are shown in the following table:

Table A-31 Degradation rate of 4-chlorophenol

Test item	Soil type	DT ₅₀ [hours]	DT ₉₀ [hours]	Model used	χ ² error %	Parameters
4-CP	Brierlow	1.93	6.40	SFO	3.15	visual fit good; t-test prob <0.05; confidence intervals >0
4-CP	Speyer 5M	3.21	10.7	SFO	4.26	visual fit good; t-test prob <0.05; confidence intervals >0
4-CP	Warsop	16.6	55.0	SFO	4.34	visual fit good; t-test prob <0.05; confidence intervals >0
4-CP	LAD-SCL-PF	7.38	24.5	SFO	4.85	visual fit good; t-test prob <0.05; confidence intervals >0

Supplementary Experiment - Results

None.

C. Rate of Degradation at 10°C

A study was not conducted, since the degradation rate at different temperatures may be calculated.

D. Rate of Degradation of Metabolites

Not applicable.

CONCLUSION

4-Chlorophenol was rapidly degraded under aerobic conditions at 20 ± 2°C in three EU soils and a US soil, with DT₅₀ values in the range 1.9 to 17 hours.

A 3.5 4-CP sorption to soil

Comments of zRMS:	<p>The study was evaluated and agreed by the zRMS (PL) in the course of the zonal Art. 43 evaluation of ADAMA formulation Camaro 306 SE (AG-FD1-306 SE) finalised in March 2017. Following conclusions may be found in the Core Assessment for this product:</p> <p><i>The study was provided by the Applicant in order to address a data gap identified in EFSA Journal 2014;12(9):3812.</i></p> <p><i>In general, in opinion of the zRMS such studies should be evaluated at the EU level by the RMS (as a confirmatory data) in order to provide uniform and consistent endpoints for all Member States.</i></p> <p><i>4-chlorophenol is metabolite of 2,4-D formed under anaerobic conditions. In general, anaerobic conditions are not expected at the time of application of the formulation, however they cannot be fully excluded (especially during early spring). Taking this into account, the study was evaluated by the zRMS for purposes of the zonal authorisation.</i></p> <p><i>The study was well performed and is general in line with recommendations of OECD 106. During the study the test substance turned out to be unstable at time intervals longer than 3 hours (recovery <70%) and for this reason equilibrium time could not be determined. For sampling intervals up to 3 hours the recovery was >70%. On this basis 3 hours equilibrium</i></p>
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	<p><i>time has been selected.</i></p> <p><i>Due to instability of 4-chlorophenol, adsorption coefficients were based on actual measured concentrations in both, aqueous and soil phases, which is in line with recommendations of the test guideline for recoveries <90%.</i></p> <p><i>The study is considered acceptable.</i></p> <p><i>Kfoc values for 4-chlorophenol in 5 soils were in range 155-254 L/kg.</i></p> <p>Since the study was already agreed in the Central Zone, there was no need for its re-evaluation and conclusions taken by the zRMS for Camaro 306 SE (AG-FD1-306 SE) are also applicable for assessment performed for ADM.3304.H.1.A in order to maintain consistent approach within the zone. The Kfoc values for 4-chlorophenol were in range of 155-254 mL/g with arithmetic mean of 182.4 mL/g and geometric mean of 179.0 mL/g. The Freundlich exponents ranged from 0.7564 to 0.8481 with arithmetic mean of 0.792.</p> <p>It is noted that in the study summary below it is indicated that no correlation between sorption of 4-chlorophenol and the soil pH could be found, but it is not clear on what basis this was concluded, since no specific analyses has been presented by the Applicant and none was performed in the study report.</p> <p>The issue of potential impact of pH on sorption of 4-chlorophenol in soil was also not considered in the course of the zonal evaluation of Camaro 306 SE (AG-FD1-306 SE), while it seems that there is some dependency between soil pH and Kfoc. This is confirmed by the correlation coefficient of -0.85 calculated by the zRMS, indicating clear negative correlation between soil pH and sorption of 4-chlorophenol, i.e. lower sorption at higher pH. It is, however, noted that sorption at pH 6.1 (weakly acidic) was the same as at 8.1 (alkaline). Nevertheless, in other soils there was clear trend and for precautionary reasons the lowest Kfoc should be considered for modelling purposes (i.e. 155 mL/g) together with 1/n of 0.81, relevant for alkaline soil LAD-SCL-PF.</p> <p>Since the study is considered acceptable, its summary is retained below. However, as no new evaluation has been performed by the zRMS specifically for purposes of authorisation of ADM.3304.H.1.A, the font colour has been changed to grey.</p>
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Report:	KCP-9.1.2/03, Swales, S.E. & Crabtree, G.A. (2015b)
Title:	4-Chlorophenol: Adsorption in four EU soils and one US soil
Document No:	Lab Study No. 3200920 Dow AgroSciences No. 141221; PCTR No. 10001705-004-70601-0001
Guidelines:	OECD 106 OSCPP 835.1230, OPPTS 835.1230
Deviations:	None
Dates of work:	11 March 2015 to 28 July 2015
GLP:	Yes

STUDY SUMMARY

The adsorption characteristics of 4-chlorophenol were determined in four EU soils and one US soil. Empingham soil is a UK clay loam (organic carbon 3.6%; pH 7.6 in CaCl₂) from Rutland, UK, Warsop soil is a UK loamy sand (organic carbon 0.7%; pH 4.1 in CaCl₂) from Nottinghamshire, UK, Kenslow soil is a UK sandy silt loam (organic carbon 3.8%; pH 5.5 in CaCl₂) from Derbyshire, UK, Brierlow soil is a UK sandy silt loam (organic carbon 2.4%; pH 6.1 in CaCl₂) from Derbyshire, UK and LAD-SCL-PF soil is a UK clay (organic carbon 0.9%; pH 8.1 in CaCl₂) from Wyoming, USA.

The definitive adsorption assessment was carried out by equilibrating sterile air-dried soil, 1 g (Empingham and Kenslow soils) or 5 g (Warsop, Brierlow and LAD-SCL-PF soils) with sterile 0.01M CaCl₂ (22.5 mL) overnight in Teflon® tubes. Samples were treated with 4-chlorophenol (2.5 mL 0.01M CaCl₂) to give final test concentrations of 0.5, 1, 5, 10 and 50 µg/mL (soil : solution ratio 1:5 w/v or 1:25 w/v). The test solutions were shaken in the dark at 20 °C for 3 hours.

The adsorption supernatant was separated by centrifugation. Soils were extracted with 0.1M HCl : acetonitrile (1:9 v/v, 2 x 10 mL) and the pooled extracts subjected to solid phase extraction (SPE). Residues of 4-chlorophenol were determined by LC-MS/MS in both supernatant and soil extracts using a validated method (SMV 3200920-03V). Due to the instability of 4-chlorophenol over the duration of the test, the mass balance was in the range 69 to 101%. As a result, the adsorption coefficients were calculated based on actual measured concentrations of 4 chlorophenol in both aqueous and soil phases. Freundlich coefficients (K_{FOC}) were in the range 155 to 254 L/kg. The range of $1/n$ values was 0.7564 to 0.8481. Using the McCall Classification scale to assess the potential mobility of a chemical in soil (based on K_{FOC}), 4-Chlorophenol can be classified as having ‘medium mobility’ in all five soils.

Results Synopsis

Table A 32: 4-Chlorophenol

Soil	Adsorption			
	K_F	K_{FOC}	$1/n$	r^2
Empingham	5.8	162	0.7564	0.9796
Warsop	1.8	254	0.7888	0.9931
Kenslow	7.1	186	0.8481	0.9333
Brierlow	3.7	155	0.7581	0.9771
LAD-SCL-PF	1.4	155	0.8108	0.9423

K_F - Freundlich adsorption coefficient

K_{oc} - Coefficient adsorption per organic carbon ($K_F \times 100/\%$ organic carbon)

$1/n$ -Slope of Freundlich adsorption isotherm

r^2 - Correlation coefficient of Freundlich equation

EXECUTIVE SUMMARY

MATERIALS AND METHODS

Test Item(s)

Non-radiolabelled test item

ISO Common name:	4-Chlorophenol
Test item (chemical/other name):	4-Chlorophenol
Purity:	100%
Description (physical state):	White Crystalline Solid
Lot/batch no.:	TSN304318, Lot MKBJ7452V
CAS no.:	106-48-9
SMILES string:	c1cc(ccc1O)Cl

Methods

Soil Characteristics

Table A 33: Description of soil collection and storage

Description	Empingham	Warsop	Kenslow	Brierlow	LAD-SCL-PF
Geographic location	Empingham, Rutland, UK	Warsop, Nottingham, UK	Kenslow, Middleton, Derbyshire, UK	Brierlow, Derbyshire, UK	Fremont, Wyoming, USA
Pesticide use history at the collection site	No pesticides used in last 5 years	No pesticides used in last 5 years	No pesticides used in last 5 years	No pesticides used in last 5 years	No pesticides used in last 5 years
Collection procedures	ISO 10381-6	ISO 10381-6	ISO 10381-6	ISO 10381-6	ISO 10381-6
Sampling depth	8-15 cm	10-20 cm	10-20 cm	12-23 cm	0-6 inches
Date of collection	28 May 2014	30 May 2014	9 October 2014	5 June 2014	18 October 2014
Storage conditions	RT, dark	RT, dark	RT, dark	RT, dark	RT, dark
Soil preparation	2 mm sieved, air-dried	2 mm sieved, air-dried	2 mm sieved, air-dried	2 mm sieved, air-dried	2 mm sieved, air-dried

RT = Room Temperature

Table A 34: Properties of the soil

Property	Empingham	Warsop	Kenslow	Brierlow	LAD-SCL-PF
Soil texture (USDA)	Clay Loam	Loamy sand	Loam	Silt Loam	Clay or Clay loam
% sand	39	87	42	29	35
% silt	33	6	44	55	25
% clay	28	7	14	16	40
Soil texture (UK)	Clay Loam	Loamy sand	Sandy silt loam	Sandy silt loam	Clay
% sand	37	87	40	30	32
% silt	35	6	46	54	28
% clay	28	7	14	16	40
pH (water) ^a	7.9	5.4	6.3	7.2	9.0
pH (calcium chloride) ^a	7.6	4.1	5.5	6.1	8.1
Organic carbon [%]	3.6	0.7	3.8	2.4	0.9
CEC [meq/100 g]	26.6	10.24	20.2	20.5	30.2
Moisture holding capacity (pF 2)	35.7	10.1	42.3	35.8	36.2
Bulk density [g/cm ³]	1.1	1.3	Not Stated	1.0	1.0
Soil taxonomic classification	Inceptisol	Entisol	Inceptisol	Inceptisol	Not stated

^a ISO 103900, 1:5 ratio of soil to solution

Experimental Conditions

Preliminary Study

Preliminary (Tier 1 and Tier 2) studies were conducted to determine the appropriate solubility, soil/solution ratio, the adsorption equilibration time and the amount of test material absorbed at equilibrium, the sorption of the test material to the test vessel and the stability of the test materials during the tests.

Solubility of 4-chlorophenol in 0.01M CaCl₂ was assessed at 500 µg/mL. Adsorption of the test material to test vessels was assessed at a concentration of 0.5 µg/mL. The soil:solution ratio and equilibrium time tests were conducted in duplicate with 4-chlorophenol at a concentration of 1.0 µg/mL. All soils were sterilised by gamma irradiation prior to sample treatment to minimize degradation of the test material during the tests.

Definitive Study Experimental Conditions

Table A 35: Experimental parameters

Parameters		Empingham	Warsop	Kenslow	Brierlow	LAD-SCL-PF
Condition of soil (air dried/fresh)		Air-dried	Air-dried	Air-dried	Air-dried	Air-dried
Have these soils been used for other laboratory studies? (specify which)		No	4-CP soil degradation 141220	No	4-CP soil degradation 141220	4-CP soil degradation 141220
Soil (g/replicate, oven-dry weight)		1 g	5 g	1 g	5 g	5 g
Equilibrium solution used		0.01M CaCl ₂				
Control used (with salt solution only) (Yes/No)		Yes	Yes	Yes	Yes	Yes
Test material concentrations (mg/L)	Nominal application	0.5, 1.0, 5.0, 10.0 and 50.0 mg/L				
	Analytically measured concentrations	0.5, 1.0, 5.0, 10.0 and 50.0 mg/L				
Identity and concentration of co-solvent, if any		None	None	None	None	None
Soil:solution ratio (w:v)		1:25	1:5	1:25	1:5	1:5
Initial pH of the equilibration solution, if provided		NA	NA	NA	NA	NA
No. of replications	Controls	2	2	2	2	2
	Treatments	2	2	2	2	2
Equilibration	Time	3 h	3 h	3 h	3 h	3 h
	Temperature	20 ± 2°C				
	Darkness (Yes/No)	Yes				
	Shaking method	Reciprocating Shaker				
	Shaking time	3 h				
Method of separation of supernatant		Centrifugation				
Centrifugation	Speed (rpm or g)	5054 g	5054 g	5054 g	5054 g	5054 g
	Duration (min)	34 min	34 min	34 min	34 min	34 min
	Method of separation of soil and solution	Supernatant decanted				

Tier 3 samples were sterilised by gamma irradiation prior to sample treatment to minimize degradation of the test material during the tests.
 No desorption step was conducted.

Supplementary Experiments

None.

Method Validation

The analytical procedure was validated by fortifying untreated control soil (1 or 5 g), pre-equilibrated overnight with 0.01M calcium chloride (25 mL), at the limit of quantitation (0.001 mg/kg), at an intermediate concentration (0.1 mg/kg), and at the highest expected concentration (1.25 mg/kg). The calcium chloride supernatant used for pre-equilibration of soils was fortified at the limit of quantification (0.05 mg/L), at an intermediate concentration (2.0 mg/L) and at the highest expected concentration (40 mg/L).

For each matrix (soil and CaCl₂) there were a total of 8 replicates at each concentration. Validation included consideration of the following criteria; linearity, specificity, precision, recovery, LOQ and LOD.

Analytical Methodology

Extraction

Calcium chloride (0.01M) extracts were diluted with 0.1% acetic acid and analysed by LC-MS/MS.

Soil samples were extracted twice with acetonitrile:0.1N HCl (9:1 v/v, 10 mL) by shaking (30 minutes) and centrifugation (5 minutes). The extracts were pooled and the volume adjusted to 20 mL by addition of acetonitrile:0.1N HCl (9:1 v/v). An aliquot (1 mL) was diluted to 20 mL (using water) and HCl (1 mL, 2M) added prior to SPE (Oasis MCX, 60 mg, 3 mL). The cartridge was eluted using 0.1% acetic acid in acetonitrile:methanol (80:20 v/v, 2 x 500 µL), further diluted with 0.1% acetic acid (1 mL) and analysed by LC-MS/MS.

HPLC with mass spectral analysis (LC-MS/MS) for Quantitation

HPLC analyses of all sample extracts following SPE clean-up were accomplished using a Synergi Hydro-RP column (50 x 2.0 mm i.d., 4.0 µm; 0.5 mL/min).

The calibration samples and soil samples were analysed by liquid chromatography with negative-ion electrospray ionization mass spectrometry. To demonstrate confirmation, two distinct MS/MS ion transitions were monitored and illustrated in the raw data. A single transition for 4-chlorophenol (126.9 to 90.9) was used for calculation of the results.

Analyst 1.6.2 software was used to calculate correlation coefficients, regression equations, and sample concentrations.

Table A 36: Detection limits (LOD, LOQ) for the parent compound

Matrix	LOD [µg/mL]	LOQ [µg/mL]
CaCl ₂ supernatant	0.0004-0.0006	0.05
Soil Extract	0.0004-0.0006	1.0

Storage stability

Sample analysis started on the day of sacrifice therefore no storage stability was conducted.

RESULTS AND DISCUSSION

Test Conditions

Preliminary tests were conducted to determine the conditions to be used in the definitive isotherms test. 4-Chlorophenol was determined to be soluble at 0.5 mg/mL and at a concentration of 0.5 µg/mL did not adsorb to the test vessels. A soil : solution ratio of 1:5 w/v were considered appropriate for Empingham and Kenslow soils, whilst a ratio of 1:25 w/v was more appropriate for Warsop, Brierlow and LAD-SCL-PF soils.

For the determination of equilibrium time, recovery of 4 chlorophenol was >70% at sampling intervals up to 3 hours in all soils tested, but was <70% at the longer sampling intervals (6, 24 and 48 hours). This indicated that 4-chlorophenol was not stable, even under sterile conditions and, as a result, an equilibrium time could not be obtained. A 3 hour equilibrium time was selected for the definitive isotherms test to ensure sufficient time for adsorption but to minimise degradation. Furthermore, both the aqueous and soil phases were analysed for 4-chlorophenol.

Mass Balance

The recovery of 4-chlorophenol was calculated for each definitive sample as the sum of the amount of 4-chlorophenol recovered from the adsorption supernatant and the soil extract.

Overall recoveries from the soils analysed were in the range 69-101%. Since both the aqueous and soil phases were directly measured, these values are acceptable.

For all five soils, the mean procedural recovery values from the control soil extracts per fortification level were in the range 70 to 110% with RSD < 20%, thereby demonstrating that the method was suitable.

The values obtained for calcium chloride were generally higher, than those obtained for soil with individual recoveries across all soils and fortification levels in the range 98.5 to 125%. For two of the soils (Empingham and Warsop), the mean recovery was acceptable at all three fortification levels, and therefore the overall mean was acceptable for both soils. For Kenslow and LAD-SCL-PF soils, mean recoveries were acceptable at fortification levels of 0.05 and 2.0 µg/mL, but were high (121 to 122%) at the highest fortification level (40 µg/mL). The overall mean recoveries for these two soil were <110% and as the precision was also good (RSD <10%), the method was considered acceptable for these two soils.

The calcium chloride from Brierlow soil had mean procedural recoveries >110% at all fortification levels and an overall mean recovery of 120%. Despite the high values, the precision was good (RSD = 3.1%) across the fortification levels. Since the method was acceptable for four of the soils, the slightly elevated recovery values were considered acceptable for Brierlow, based on the precision data and taking into account that the recoveries were not high enough to affect the overall results of the study.

Table A 37: Recovery of 4-chlorophenol, expressed as percentage of the applied amount, in soil after adsorption

Soil	Rep	% Adsorb Solution	% soil Extract	% NER	% Total
Empingham					
50 µg/mL	1	85.7	7.4	NA	93.1
50 µg/mL	2	88.3	4.9	NA	93.3
10 µg/mL	1	84.3	8.7	NA	93.0
10 µg/mL	2	83.9	8.7	NA	92.6
5 µg/mL	1	76.6	6.7	NA	83.3
5 µg/mL	2	85.1	5.4	NA	90.6
1.0 µg/mL	1	76.4	5.0	NA	81.5
1.0 µg/mL	2	80.4	5.9	NA	86.4
0.5 µg/mL	1	71.7	5.8	NA	77.5
0.5 µg/mL	2	72.0	5.6	NA	77.6
Warsop					
50 µg/mL	1	79.0	19.2	NA	98.2
50 µg/mL	2	77.1	20.8	NA	97.9
10 µg/mL	1	75.4	27.1	NA	102.5
10 µg/mL	2	75.4	24.7	NA	100.1
5 µg/mL	1	69.0	22.4	NA	91.4
5 µg/mL	2	70.6	24.2	NA	94.8
1.0 µg/mL	1	68.7	23.2	NA	91.9
1.0 µg/mL	2	67.8	24.0	NA	91.8
0.5 µg/mL	1	60.7	25.0	NA	85.8
0.5 µg/mL	2	61.5	25.1	NA	86.8
Kenslow					
50 µg/mL	1	88.1	9.8	NA	97.9
50 µg/mL	2	70.1	9.8	NA	79.9
10 µg/mL	1	84.8	10.7	NA	95.5
10 µg/mL	2	80.6	10.5	NA	91.1
5 µg/mL	1	76.4	7.7	NA	84.1
5 µg/mL	2	75.8	8.5	NA	84.3
1.0 µg/mL	1	67.1	6.7	NA	73.8
1.0 µg/mL	2	68.7	6.7	NA	75.5
0.5 µg/mL	1	75.7	6.9	NA	82.6
0.5 µg/mL	2	75.9	7.1	NA	83.0
Brierlow					
50 µg/mL	1	57.3	32.1	NA	89.4
50 µg/mL	2	71.0	28.5	NA	99.5
10 µg/mL	1	63.4	37.8	NA	101.2
10 µg/mL	2	63.0	36.4	NA	99.4
5 µg/mL	1	54.6	30.0	NA	84.5
5 µg/mL	2	55.6	28.5	NA	84.1
1.0 µg/mL	1	45.6	27.9	NA	73.5
1.0 µg/mL	2	46.1	27.9	NA	74.0
0.5 µg/mL	1	41.4	27.2	NA	68.6
0.5 µg/mL	2	42.5	26.7	NA	69.2
LAD-SCL-PF					
50 µg/mL	1	219.0	17.6	NA	89.7
50 µg/mL	2	210.0	16.9	NA	89.7
10 µg/mL	1	43.0	17.8	NA	96.8
10 µg/mL	2	43.6	17.9	NA	97.9
5 µg/mL	1	21.4	17.3	NA	85.2
5 µg/mL	2	22.5	18.4	NA	86.6
1.0 µg/mL	1	3.3	13.6	NA	79.3
1.0 µg/mL	2	3.0	12.1	NA	77.4
0.5 µg/mL	1	1.5	12.2	NA	74.1
0.5 µg/mL	2	1.9	15.3	NA	80.7
				average	87.2
				SD	8.8
				Maximum	102.5
				Minimum	68.6

Table A 38: Concentration of 4-chlorophenol, in the solid and liquid phases at the end of adsorption equilibration period

Conc [µg/mL]	Rep	Sorbed [µg/g]	In soln [µg/mL]	% Sorbed
		Empingham		
50	1	120.8960	44.3000	9.9
50	2	99.6030	46.3000	8.2
10	1	26.6446	8.6600	11.2
10	2	28.2332	8.6300	11.9
5	1	23.6164	3.9700	19.9
5	2	13.6645	4.3700	11.2
1	1	5.0844	0.7950	20.5
1	2	3.8431	0.8380	15.9
0.5	1	3.1141	0.3820	24.9
0.5	2	3.1121	0.3830	24.6
		Warsop		
50	1	32.7642	44.1000	13.0
50	2	39.3950	42.9000	15.7
10	1	8.3501	7.9600	17.7
10	2	8.1954	8.1900	17.0
5	1	5.9879	3.7700	24.5
5	2	5.5162	3.8300	22.8
1	1	1.2201	0.7510	24.9
1	2	1.2692	0.7400	25.8
0.5	1	0.8330	0.3430	33.1
0.5	2	0.8286	0.3460	32.6
		Kenslow		
50	1	100.6343	46.2000	8.1
50	2	335.1640	37.0000	26.9
10	1	29.4568	8.5200	12.4
10	2	37.8578	8.3400	15.7
5	1	24.7924	4.0000	20.0
5	2	25.5246	3.9600	20.8
1	1	7.2832	0.7170	29.8
1	2	6.9435	0.7190	28.2
0.5	1	2.6327	0.4050	20.9
0.5	2	2.5721	0.4020	20.4
		Brierlow		
50	1	87.3638	32.8000	34.9
50	2	50.0399	40.4000	20.0
10	1	12.6770	7.1900	26.3
10	2	13.1520	7.1500	27.0
5	1	9.3808	3.0900	38.0
5	2	8.9349	3.0800	36.9
1	1	2.3419	0.5120	47.8
1	2	2.2655	0.5290	46.3
0.5	1	1.3304	0.2400	52.8
0.5	2	1.3108	0.2440	51.9
		LAD-SCL-PF		
50	1	38.0424	42.2000	15.4
50	2	40.3624	41.8000	16.3
10	1	4.4465	8.8700	9.2
10	2	4.2468	8.9200	8.7
5	1	5.3487	3.8700	21.7
5	2	5.1798	3.8600	21.3
1	1	1.1566	0.7460	23.8
1	2	1.2337	0.7460	25.1
0.5	1	0.7200	0.3620	28.6
0.5	2	0.5797	0.3890	23.1

Table A 39: Adsorption constants of 4-chlorophenol, in the soils

Soil	Adsorption			
	K _F	K _{FOC}	1/n	r ²
Empingham	5.82	162	0.7564	0.9796
Warsop	1.78	254	0.7888	0.9931
Kenslow	7.07	186	0.8481	0.9333
Brierlow	3.72	155	0.7581	0.9771
LAD-SCL-PF	1.40	155	0.8108	0.9423

K_F - Freundlich adsorption coefficient

K_{FOC} - Coefficient adsorption per organic carbon (K_F x 100/% organic carbon)

1/n -Slope of Freundlich adsorption/desorption isotherm

r² - Correlation coefficient of Freundlich equation

Adsorption

Adsorption decreased with increasing concentration. After a 3 hour of equilibration time, the amount of 4-chlorophenol residues adsorbed to soil were in the range 9 to 25% (Empingham), 14 to 33% (Warsop), 14 to 29% (Kenslow), 27 to 52% (Brierlow) and 9 to 26% (LAD-SCL-PF).

K_d values were 4.76, 1.49, 6.46, 3.32 and 1.23 in Empingham, Warsop, Kenslow, Brierlow and LAD-SCL-PF soils, respectively.

K_{oc} values were 132, 213, 170, 138 and 136 in Empingham, Warsop, Kenslow, Brierlow and LAD-SCL-PF soils, respectively.

Correlation to Soil pH

There was no correlation between the soil pH and the K_d or K_{FOC}.

CONCLUSION

Freundlich coefficients K_{FOC} were in the range 155 to 254 L/kg. Using the McCall Classification scale to assess the potential mobility of a chemical in soil (based on K_{FOC}), 4-chlorophenol can be classified as having ‘medium mobility’ in all five soils.

A 3.6 1,2,4-Benzenetriol: Adsorption in soil

Comments of zRMS:	The purpose of submission of this study is unclear to the zRMS. Metabolite 1,2,4-benzenetriol is an aquatic metabolite of 2,4-D and was not found during soil metabolism studies. Moreover, investigation of mobility of this compound in soil was not indicated as a data gap in EFSA Journal 2014;12(9):3812. For this reason the study was not validated by the zRMS and its summary is struck through.
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Report:	KCP-9.1.2/04, Swales, S.E., Crabtree, G.A. (2015c)
Title:	1,2,4-Benzenetriol: Adsorption in four EU soils and one US soil
Document No:	Lab Study No. 3200921 Dow AgroSciences No. 141224; PCTR No. 10001705-004-70601-0002
Guidelines:	OECD 106 OSCPP 835.1230, OPPTS 835.1230
Deviations:	None
Dates of work:	11 March 2015 to 29 June 2015
GLP:	Yes

STUDY SUMMARY

The study was designed to assess the adsorption of 1,2,4 benzenetriol in soils. However, the results of the preliminary test (solubility, adsorption to containers and stability) indicated that the 1,2,4 benzenetriol may not be stable in aqueous media. As a result of the preliminary investigations, the study design was

changed to assess the stability in aqueous solution at different pH in order to determine whether it was technically feasible to perform an adsorption test.

The stability of 1,2,4 benzenetriol (0.5 µg/mL) in calcium chloride (0.01M) under sterile and non-sterile conditions was determined. 1,2,4 Benzenetriol was analysed immediately after application (2 minutes) and after 90 minutes by LC-MS/MS. Recovery of 1,2,4 benzenetriol from all solutions (sterile and non-sterile) was in the range 12 to 14% of applied, indicating that it is not hydrolytically stable in calcium chloride.

A solution of 1,2,4 benzenetriol prepared in calcium chloride (0.01M) at 100 µg/L was compared to a stock solution of 1,2,4 benzenetriol prepared in acetonitrile at 100 µg/L. Results indicated that 1,2,4 benzenetriol was stable in acetonitrile but was unstable in calcium chloride (0.01M).

The stability of 1,2,4 benzenetriol was determined in 0.01 M buffer solutions at pH 4, 7 and 9. Buffer samples were analysed for 1,2,4 benzenetriol at 0, 20, 40, 60, 90, 120, 180 and 360 minutes after treatment and additionally at 1 day after treatment (DAT). A further sampling interval at 4 DAT was included for the buffer solutions at pH 4.

At pH 4, recovery of 1,2,4 benzenetriol accounted for 68 to 116% of the applied amount over the first 6 hours (360 minutes), thereafter the level declined with < 30% recovered at 4 DAT.

At pH 7, recovery of 1,2,4 benzenetriol was in the range 4 to 17% of the applied amount across all sampling times (0 to 1 DAT).

At pH 9, recovery of 1,2,4 benzenetriol was 95% immediately after treatment but declined rapidly, with only 50% of the applied amount present after 60 minutes.

The results demonstrated that 1,2,4 benzenetriol was hydrolytically unstable in pH 4, 7 and 9 buffers. It is most stable at pH 4 (with a $DT_{50} > 6$ h), but at environmentally relevant pH the 1,2,4 benzenetriol is rapidly hydrolysed.

Adsorption characteristics in soil could not be conducted, as it is not sufficiently stable to perform the test by analysing both aqueous and soil phases. In addition, 1,2,4 benzenetriol cannot be perceived to be an environmental hazard in aqueous solution due to the rapid hydrolysis.

EXECUTIVE SUMMARY

MATERIALS AND METHODS

Test Item(s)

Non-radiolabelled test item

ISO Common name:	1,2,4 Benzenetriol
Test item (chemical/other name):	1,2,4 Benzenetriol
Purity:	98%
Description (physical state):	Brown powder
Lot/batch no.:	TSN300766, Lot DE3-11913-29
CAS no.:	533-73-3
SMILES string:	<chem>Oc1cc(c(O)O)O</chem>

Methods

Soil Characteristics

No soils were used as it was determined during the preliminary tests that 1,2,4 benzenetriol was hydrolytically unstable.

Experimental Conditions

Preliminary Study

Preliminary (Tier 1) studies were conducted to determine the appropriate solubility, the amount of test material absorbed to the test vessel and the stability of the test material during the tests.

Solubility was assessed as follows:

Duplicate solutions (SS1r and SS2r) were prepared at 500 µg/L by dissolving 1,2,4 benzenetriol (ca 50 mg) in 0.01M calcium chloride (ca 100 mL). Immediately following preparation, aliquots (0.1 mL) of

~~SS1r and SS2r were removed, diluted (using the dilution solution) to give solutions at a concentration 0.05 µg/mL and analysed by LC MS/MS.~~

~~Adsorption to Containers was assessed as follows:~~

~~Aliquots (125 µL) of stock solution 2 were added to duplicate plastic and Teflon™ tubes containing ca 24.875 mL of 0.01M calcium chloride for a final concentration of 0.5 µg/mL (lowest test concentration). The samples were mixed and aliquots (100 µL) removed for analysis (pre-shake). The remaining samples were placed on a reciprocating shaker in the dark at 20 ± 2°C. After shaking for 24 hours, the samples were removed from the shaker and aliquots (100 µL) were removed for analysis (post shake). The pre- and post-shake aliquots were diluted (using the dilution solution, 900 µL) and analysed for 1,2,4-benzenetriol by LC MS/MS.~~

~~Low recoveries were observed from the solubility test and no peaks associated with 1,2,4 benzenetriol were observed by LC MS/MS in this adsorption to containers test.~~

~~As a result of the low recoveries observed during the solubility and adsorption to containers test, further preliminary tests were conducted. The stability of 1,2,4 benzenetriol (0.5 µg/mL) in calcium chloride (0.01M) under sterile and non-sterile conditions was determined. 1,2,4 Benzenetriol was analysed immediately after application (2 minutes) and after 90 minutes by LC MS/MS. Recovery of 1,2,4 benzenetriol from all solutions (sterile and non-sterile) was in the range 12 to 14% of applied, indicating that it is not hydrolytically stable in calcium chloride.~~

~~A solution of 1,2,4 benzenetriol prepared in calcium chloride (0.01M) at 100 µg/L was compared to a stock solution of 1,2,4 benzenetriol prepared in acetonitrile at 100 µg/L. Results indicated that 1,2,4 benzenetriol was stable in acetonitrile but was unstable in calcium chloride (0.01M).~~

~~Preliminary tests to assess the soil:solution ratio and equilibrium time determination were not conducted.~~

Definitive Study Experimental Conditions

~~No definitive test was conducted.~~

Supplementary Experiments

~~Due to the instability of 1,2,4 benzenetriol in 0.01M calcium chloride, the hydrolytic stability was assessed in buffers (pH 4,7 and 9) at room temperature.~~

~~Buffers solutions were prepared at pH 4 (0.01M acetate buffer), pH 7 (0.01M phosphate buffer) and pH 9 (0.01M borate buffer). A subsample (20 mL) of each buffer was treated with 1,2,4 benzenetriol (10 µg/mL in acetonitrile) mixed briefly and allowed to stand at room temperature. Aliquots of each buffer were taken at 0, 20, 40, 60, 90, 120, 180, 360 minutes and 1 day for analysis by LC MS/MS.~~

~~Due to high initial concentrations of 1,2,4 benzenetriol in pH 4 buffer, the test was repeated at pH 4 with the same initial sampling interval but with a 4 DAT sampling interval, rather than 1 DAT.~~

Method Validation

~~Due to the nature of the study a validated analytical method was not required.~~

Analytical Methodology

Extraction

~~Calcium chloride (0.01M) or buffer samples were diluted with water: acetonitrile: methanol: acetic acid, 50:40:10:0.1 v/v/v/v and analysed by LC MS/MS.~~

HPLC with mass spectral analysis (LC MS/MS) for Quantitation

~~HPLC analyses of all samples were accomplished using an ACE C18 column (4.6 x 250 mm, i.d., 4.6 µm; 1.0 mL/min).~~

~~The calibration standards and sample were analysed by liquid chromatography with negative ion electrospray ionization mass spectrometry. A single transition for 1,2,4 benzenetriol (125.3 to 40.9) was used for calculation of the results.~~

~~Analyst 1.6.2 software was used to calculate correlation coefficients, regression equations, and sample concentrations.~~

Detection limits (LOD, LOQ) for the parent compound

An LOD and LOQ was not established in the study.

Storage stability

Not applicable. Samples were analysed immediately.

RESULTS AND DISCUSSION

Test Conditions

Preliminary tests were conducted to determine the conditions to be used in the definitive isotherms test.

Solubility

Solubility of 1,2,4 benzenetriol was assessed in 0.01M calcium chloride solution at a nominal concentration of 500 µg/mL (the highest proposed concentration of a treatment solution). Duplicate solutions (SS1r and SS2r) were analysed immediately after preparation and the concentrations of 1,2,4 benzenetriol were 115 and 278 µg/mL for SS1r and SS2r respectively. The water solubility of 1,2,4 benzenetriol is 486 mg/mL which is approximately 3 orders of magnitude higher than the solubility that was tested for use in the study (500 µg/L) and, therefore, the low recoveries observed from calcium chloride solution are unlikely to be due to poor solubility. The low recovery indicated that 1,2,4 benzenetriol is more likely unstable in calcium chloride.

Adsorption to Containers

In order to check that the low recoveries were not due to adsorption to the test vessels, a test was conducted in the absence of soil using plastic and Teflon® test vessels containing 0.01M calcium chloride and 1,2,4 benzenetriol at a concentration of 0.5 µg/mL, (the lowest test concentration). No peaks associated to 1,2,4 benzenetriol were observed pre shaking or post shaking for 24 hours in either Teflon® or plastic containers. These data also pointed to instability in 0.01M calcium chloride.

Additional investigations were conducted into the stability, including a comparison between sterile and non-sterile conditions.

Analysis of samples treated with 1,2,4 benzenetriol in sterile and non-sterile 0.01M calcium chloride (0.5 µg/mL) immediately after application and after 90 minutes is shown below.

Table A-41 — Concentrations of 1,2,4 benzenetriol in comparison of stability between sterile and non-sterile conditions

Sample	Time [minutes]	Concentration [µg/mL]	% Recovery
Sterile	2	0.0605	12.1
	90	0.0632	12.6
Non-sterile	2	0.0689	13.8
	90	0.0616	12.3

There was no difference in stability of 1,2,4 benzenetriol at 2 and 90 minutes between sterile and non-sterile but very low recoveries (ca 12 to 14%) were observed. This may have been due to use of stock solution 2 (calcium chloride) which had been degraded during the 15 days refrigerated storage (see below). Due to these low recoveries, additional work was performed using the acetonitrile stock solution, which had demonstrated stability of 1,2,4 benzenetriol during the same storage period. A check on the adsorption to test vessels and stability was repeated using 1,2,4 benzenetriol in acetonitrile (stock solution 1).

Stability of Stock Solution

Stock solution 2 (0.01M calcium chloride) had a peak area ca 47% of that from stock solution 1 (acetonitrile), indicating that the 1,2,4 benzenetriol prepared in 0.01M calcium chloride stock solution was not stable over 15 days refrigerated storage (2–8 °C), but it was stable in acetonitrile (94% of the original concentration recovered as 1,2,4 benzenetriol).

Concentrations in Glass and Plastic Vessels after Application from an Acetonitrile Stock Solution

Samples, treated with 1,2,4 benzenetriol (0.1 µg/mL) with stock solution 1 (acetonitrile), were analysed immediately after application and after 3 hours.

Table A-41 Concentrations of 1,2,4 benzenetriol in glass and plastic vessels following application of 1,2,4 benzenetriol from an acetonitrile stock solution

Vessel type	Time [hours]	Concentration [µg/mL]	% Recovery
Glass	0	0.0322	32.2
	3	0.0152	15.2
Plastic	0	0.0781	78.1
	3	0.0150	15.0

Despite immediate analysis, low recoveries of 1,2,4 benzenetriol were observed (32 to 78% of the applied amount) and these declined further to 15% of the applied amount after 3 hours. In order to check whether the low recoveries were due to degradation or adsorption to the vessel surfaces, an acetonitrile wash of each vessel was analysed. There were no detectable residues of 1,2,4 benzenetriol in any of the vessel washes indicating no additional 1,2,4 benzenetriol could be removed.

These results confirm that 1,2,4 benzenetriol was not stable in the 0.01M calcium chloride, which made the OECD 106 test technically unfeasible to conduct. For completeness, the hydrolytic stability of 1,2,4 benzenetriol in buffers (pH 4, 7 and 9 was assessed).

Hydrolytic Stability at pH 4, 7 and 9

Buffer samples (pH 4, 7 and 9) were treated with 1,2,4 benzenetriol (10 µg/mL) from an stock solution 1 (acetonitrile). Aliquots were removed for analysis from 0 to 1440 minutes (1 day) by LC MS/MS. The test was repeated at pH 4 due to the high recoveries obtained. Concentration and recovery results are shown below.

Table A-42 Recovery of 1,2,4 benzenetriol from buffer (pH 4)

Sampling interval [min]	Concentration [µg]	% recovery	Mean Recovery
0	0.125	125.0	139
0	0.153	153.0	
20	0.145	145.0	136.5
20	0.128	128.0	
40	0.116	116.0	133.0
40	0.150	150.0	
60	0.126	126.0	132.0
60	0.138	138.0	
90	0.0311	31.1	32.6
90	0.034	34.0	
120	0.0635	63.5	65.7
120	0.0678	67.8	
180	0.0926	92.6	86.9
180	0.0812	81.2	
360	0.101	101.0	94.9
360	0.0878	87.8	
1440	0.0380	38.0	38.5
1440	0.0389	38.9	

Inconclusive results; see next table for repeated experimental results.

Table A-43 Recovery of 1,2,4-benzenetriol from buffer (pH 4, repeat)

Sampling interval	Concentration [µg]	% recovery	Mean Recovery
0 min	0.0691	69.1 [‡]	68.4 [‡]
0 min	0.0677	67.7 [‡]	
20 min	0.0826	82.6 [‡]	80.1 [‡]
20 min	0.0775	77.5 [‡]	
40 min	0.1060	106.0	106.0
40 min	0.1060	106.0	
60 min	0.0966	96.6	99.8
60 min	0.103	103.0	
90 min	0.105	105.0	103.5
90 min	0.102	102.0	
120 min	0.0933	93.3	92.1
120 min	0.0908	90.8	
180 min	0.0896	89.6	92.8
180 min	0.0960	96.0	
360 min	0.1130	113.0	116.0
360 min	0.1190	119.0	
4 day	0.0238	23.8	27.2
4 day	0.0305	30.5	

[‡]Lower than expected recoveries obtained at the 0 and 20 minute sampling time, were attributed to insufficient mixing rather than poor analytical recoveries

Table A-44 Recovery of 1,2,4-benzenetriol from buffer (pH 7)

Sampling interval [min]	Concentration [µg]	% recovery	Mean Recovery
0	0.0116	11.6	10.7
0	0.0099	9.9	
20	0.0144	14.4	15.5
20	0.0166	16.6	
40	0.0161	16.1	17.2
40	0.0183	18.3	
60	0.0141	14.1	14.6
60	0.0150	15.0	
90	0.0018	1.8	3.6
90	0.0055	5.5	
120	0.0047	4.7	6.9
120	0.0091	9.1	
180	0.0112	11.2	11.6
180	0.0119	11.9	
360	0.0150	15.0	11.8
360	0.0085	8.5	
1440	0.0122	12.2	12.0
1440	0.1180	11.8	

Table A-45 Recovery of 1,2,4-benzenetriol from buffer (pH 9)

Sampling interval [min]	Concentration [µg]	% recovery	Mean Recovery
0	0.1040	104.0	94.5
0	0.0849	84.9	
20	0.0783	78.3	93.7
20	0.1090	109.0	
40	0.0646	64.6	76.7
40	0.0888	88.8	
60	0.0496	49.6	49.8
60	0.0500	50.0	
90	0.0355	35.5	32.7
90	0.0299	29.9	
120	0.0268	26.8	23.7
120	0.0206	20.6	
180	0.0139	13.9	22.8
180	0.0316	31.6	
360	0.0203	20.3	19.3
360	0.0183	18.3	
1440	0.0192	19.2	29.9
1440	0.0406	40.6	

At pH 4, the recovery was high 132 to 139% of applied amount (0 to 60 minutes) before declining with 39% of the applied amount remaining at 1 DAT. In the repeat test at pH 4, recovery of 1,2,4 benzenetriol typically accounted for 80 to 116% of the applied amount over the first 6 hours (360 minutes), thereafter the level declined with <30% recovered at 4 DAT. Lower than expected recoveries were obtained at the 0 and 20 minute sampling time, which was attributed to insufficient mixing rather than poor analytical recoveries. As the variation was substantially less than that observed in the first pH 4 test, these results are considered suitable to demonstrate that 1,2,4 benzenetriol was stable for up to 6 hours and thereafter, the concentration declined rapidly.

At pH 7, recovery of 1,2,4 benzenetriol was in the range 4 to 17% of the applied amount across all sampling times (0 to 1 DAT). These results indicated that an immediate hydrolytic degradation process was occurring at pH 7.

At pH 9, recovery of 1,2,4 benzenetriol was 95% immediately after treatment but declined rapidly, with only 50% of the applied amount present after 60 minutes. A general decline in 1,2,4 benzenetriol occurred over the remaining 1 day duration of the test.

The results demonstrated that 1,2,4 benzenetriol was hydrolytically unstable in pH 7 and 9 buffers. It was more stable at pH 4, but this is not an environmental relevant pH. At environmentally relevant pH, 1,2,4 benzenetriol is rapidly hydrolysed.

Adsorption

Adsorption characteristics in soil could not be conducted, as 1,2,4 benzenetriol is not sufficiently stable to perform the test, even by analysing both aqueous and soil phases. In addition, 1,2,4 benzenetriol cannot be perceived to be an environmental hazard in aqueous solution due to its instability, particularly at neutral pH.

CONCLUSION

Due to the hydrolytic instability in aqueous buffers and calcium chloride, adsorption characteristics in soil could not be performed and 1,2,4 benzenetriol cannot be perceived to be an environmental hazard in aqueous solution.

Appendix 4 Additional information provided by the applicant (e.g. detailed modelling data)

Detailed modelling data and example modelling input and output files could be found in the corresponding reports, listed under Appendix 1.

A 4.1 Detailed list of endpoints

zRMS comments:

All respective input parameters used in exposure assessment are already presented and discussed in detail in points 8.7 (soil), 8.8 (groundwater) and 8.9 (surface water) of this document. Taking this into account, information presented in tables below was not checked by the zRMS and is thus struck through.

Parameters for PEC_{soil} calculations

~~2,4-D~~

Parameter	Input Parameter	Comment
2,4-D		
Molecular mass [g/mol]	224	EFSA Journal 2014;12(9):3812
DT ₅₀ soil [days]	66.6	Longest normalised (20°C, pF2, SFO) EU lab value (i.e. Mississippi)
K _{oc} [mL/g]	58.6	Median of 42 soils (in the LoE (EFSA, 2014) K _{roc} and 1/n was incorrectly reported for only seven soils instead of 42; presented PEC _{sw} were however base on the correct data (RAR Addendum (2014), Part 4))
Kinetic	SFO	EFSA Journal 2014;12(9):3812
2,4-DCP		
Molecular mass [g/mol]	163	EFSA Journal 2014;12(9):3812
DT ₅₀ soil [days]	14.0	Worst case persistence end-point (best fit, DFOP) determined according to FOCUS kinetics (FOCUS 2006)
K _{oc} [mL/g]	512	Arithmetic mean
Kinetic	SFO	EFSA Journal 2014;12(9):3812
Max. occurrence in soil [%]	8.7	EFSA Journal 2014;12(9):3812
2,4-DCA		
Molecular mass [g/mol]	177	EFSA Journal 2014;12(9):3812
DT ₅₀ soil [days]	15.4	worst case persistence end-point (best fit, DFOP) determined according to FOCUS kinetics (FOCUS 2006)
K _{oc} [mL/g]	4028	Arithmetic mean
Kinetic	SFO	EFSA Journal 2014;12(9):3812
Max. occurrence in soil [%]	15	EFSA Journal 2014;12(9):3812

Clopyralid

Parameter	Input Parameter	Comment
Clopyralid		
Molecular mass [g/mol]	191.96	EFSA Conclusion (2018) 16(7):5389
DT ₅₀ soil [days]	23.7	EFSA Conclusion (2018) 16(7):5389 Longest field value (Denmark) (n = 10)
K _{oc} [mL/g]	1.41	EFSA Conclusion (2018) 16(7):5389 Geometric mean (n = 9)
Kinetic	SFO	—

Fluroxypyr

Parameter	Input Parameter	Comment
Fluroxypyr-meptyl		
Molecular mass [g/mol]	367.3	EFSA Journal 2011;9(3):2091
DT ₅₀ soil [days]	1.8	EFSA Journal 2011;9(3):2091 Longest normalised (only for temperature) lab value
K _{oc} [mL/g]	19550	Arithmetic mean
Kinetic	SFO	EFSA Journal 2011;9(3):2091
Fluroxypyr acid		
Molecular mass [g/mol]	255	EFSA Journal 2011;9(3):2091
DT ₅₀ soil [days]	39.6	EFSA Journal 2011;9(3):2091 Longest normalised lab value
K _{oc} [mL/g]	68	Arithmetic mean
Kinetic	SFO	EFSA Journal 2011;9(3):2091
Pyridinol		
Molecular mass [g/mol]	197	EFSA Journal 2011;9(3):2091
DT ₅₀ soil [days]	105.4	EFSA Journal 2011;9(3):2091 Longest normalised lab value
K _{oc} [mL/g]	44.3	Arithmetic mean at pH ≥ 7 (worst case)
Kinetic	SFO	EFSA Journal 2011;9(3):2091
Max. occurrence in soil [%]	23.9	EFSA Journal 2011;9(3):2091
Methoxypyridine		
Molecular mass [g/mol]	211	EFSA Journal 2011;9(3):2091
DT ₅₀ soil [days]	1160.9	EFSA Journal 2011;9(3):2091 Longest normalised lab value
K _{oc} [mL/g]	321	Arithmetic mean
Kinetic	SFO	EFSA Journal 2011;9(3):2091
Max. occurrence in soil [%]	38.2	EFSA Journal 2011;9(3):2091

Parameters for PEC_{CW}-calculations

2,4-D

Parameter	Input Parameter	Comment
2,4-D		
Molecular mass [g/mol]	221	EFSA Journal 2014;12(9):3812
Water solubility [mg/L]	24300 (25°C)	EFSA Journal 2014;12(9):3812
Vapour pressure [Pa]	9.9×10^{-6} (20°C)	EFSA Journal 2014;12(9):3812
K _{OC} [mL/g]	58.6	Median (n = 42) (in the LoEP (EFSA, 2014), K _{FOC} and 1/n were incorrectly reported for seven soils only instead of 42 (RAR Addendum (2014), Part 4))
K _{OM} [mL/g]	34.0	K _{OM} = K _{OC} / 1.724
1/n	0.87	Arithmetic mean (n = 42) (in the LoEP (EFSA, 2014) K _{FOC} and 1/n were incorrectly reported for seven soils only instead of 42 (RAR Addendum (2014), Part 4))
DT ₅₀ -soil [days]	4.14	Geometric mean, lab normalised (20°C, pF2) with "Mississippi" soil
Formation fraction	—	
Plant uptake	0	Worst case default
Q ₁₀ -value	2.58	EFSA recommendation
2,4-DCP		
Molecular mass [g/mol]	163	EFSA Journal 2014;12(9):3812
Water solubility [mg/L]	4870 (20°C)	EFSA Journal 2014;12(9):3812
Vapour pressure [Pa]	9.9×10^{-6} (20°C)	Value from the parent
K _{OC} [mL/g]	512	Arithmetic mean
K _{OM} [mL/g]	297	K _{OM} = K _{OC} / 1.724
1/n	0.88	EFSA Journal 2014;12(9):3812 Arithmetic mean
DT ₅₀ -soil [days]	7.0	EFSA Journal 2014;12(9):3812 Geometric mean lab, normalised (pF2, 20°C, Q10=2.58)
Formation fraction	1 (from parent)	Worst case default
Plant uptake	0	Worst case default
Q ₁₀ -value	2.58	EFSA recommendation
2,4-DCA		
Molecular mass [g/mol]	177	EFSA Journal 2014;12(9):3812
Water solubility [mg/L]	96.3 (20°C)	EFSA Journal 2014;12(9):3812
Vapour pressure [Pa]	9.9×10^{-6} (20°C)	Value from the parent
K _{OC} [mL/g]	1028	Arithmetic mean
K _{OM} [mL/g]	595	K _{OM} = K _{OC} / 1.724
1/n	0.92	EFSA Journal 2014;12(9):3812 Arithmetic mean
DT ₅₀ -soil [days]	10.4	EFSA Journal 2014;12(9):3812 Geometric mean lab, normalised (pF2, 20°C, Q10=2.58)
Formation fraction	1 (from parent)	Worst case default
Plant uptake	0	Worst case default
Q ₁₀ -value	2.58	EFSA recommendation

Clopyralid

Parameter	Input Parameter	Comment
Clopyralid		
Molecular mass [g/mol]	191.96	EFSA Conclusion (2018) 16(7):5389
Water solubility [mg/L]	143 000 (20°C)	EFSA Conclusion (2018) 16(7):5389 Value at pH 7
Vapour pressure [Pa]	1.36×10^{-3}	EFSA Conclusion (2018) 16(7):5389
K _{OC} [mL/g]	1.41	EFSA Conclusion (2018) 16(7):5389 Geometric mean (n = 9)
K _{OM} [mL/g]	0.818	K _{OM} = K _{OC} / 1.724
1/n	0.836	EFSA Conclusion (2018) 16(7):5389 Arithmetic mean (n = 9)
DT ₅₀ -soil [days]	7.05	EFSA Conclusion (2018) 16(7):5389 Geometric mean field values (n=10) (normalised to pF2, 20°C with Q10 of 2.58)
Formation fraction	—	

Parameter	Input Parameter	Comment
Plant uptake	Tier 1: 0	FOCUS recommendation
	Tier 2: 0.5	FOCUS recommendation for systemic compounds
Q ₁₀ -value	2.58	EFSA recommendation

Fluroxypyr

Parameter	Input Parameter	Comment
Fluroxypyr acid		
Molecular mass [g/mol]	255	EFSA Journal 2011;9(3):2091
Water solubility [mg/L]	91	EFSA Journal 2011;9(3):2091
Vapour pressure [Pa]	3.8×10^{-9} (20°C)	EFSA Journal 2011;9(3):2091
K _{OC} [mL/g]	68	Arithmetic mean
K _{OM} [mL/g]	39	$K_{OM} = K_{OC} / 1.724$
1/n [-]	0.92	EFSA Journal 2011;9(3):2091 Arithmetic mean
DT ₅₀ -soil [days]	13.9	EFSA Journal 2011;9(3):2091 Median, lab, normalised (pF2, 20°C, Q10=2.58)
Formation fraction	0.513 (parent → sink)	EFSA Journal 2011;9(3):2091
Plant uptake	0.5	FOCUS recommendation for systemic compounds
Q ₁₀ -value	2.58	EFSA recommendation
Pyridinol		
Molecular mass [g/mol]	197	EFSA Journal 2011;9(3):2091
Water solubility [mg/L]	91	Value from the parent
Vapour pressure [Pa]	3.8×10^{-9} (20°C)	Value from the parent
K _{OC} [mL/g]	708 (pH < 7), median 68.5 (pH ≥ 7) acid & neutral / alkaline soils	Confirmatory information Arithmetic mean
K _{OM} [mL/g]	410.7 (pH < 7) 39.6 (pH ≥ 7)	$K_{OM} = K_{OC} / 1.724$
1/n [-]	0.81 (pH < 7) 0.72 (pH ≥ 7)	Confirmatory information Arithmetic mean
DT ₅₀ -soil [days]	17.6	Confirmatory information Geometric mean lab, normalised (pF2, 20°C, Q10=2.58)
Formation fraction	0.286 (from parent) 0.723 (from methoxypyridine)	Confirmatory information
Plant uptake	0	Worst case default
Q ₁₀ -value	2.58	EFSA recommendation
Methoxypyridine		
Molecular mass [g/mol]	211	EFSA Journal 2011;9(3):2091
Water solubility [mg/L]	91	Value from the parent
Vapour pressure [Pa]	3.8×10^{-9} (20°C)	Value from the parent
K _{OC} [mL/g]	321	Arithmetic mean
K _{OM} [mL/g]	185	$K_{OM} = K_{OC} / 1.724$
1/n [-]	0.84	EFSA Journal 2011;9(3):2091 Arithmetic mean
DT ₅₀ -soil [days]	111.11	Confirmatory information Geometric mean lab, normalised (pF2, 20°C, Q10=2.58)
Formation fraction	0.201 (from parent)	EFSA Journal 2011;9(3):2091
Plant uptake	0	Worst case default
Q ₁₀ -value	2.58	EFSA recommendation

Parameters for PEC_{SW}-calculations

2,4-D

Parameter	Input Parameter	Comment
2,4-D		
Molecular mass [g/mol]	221	EFSA Journal 2014;12(9):3812
Water solubility [mg/L]	24300 (25°C)	EFSA Journal 2014;12(9):3812
Vapour pressure [Pa]	9.9×10^{-6} (20°C)	EFSA Journal 2014;12(9):3812
K _{oc} [mL/g]	58.6	Median (n = 42) (in the LoEP (EFSA, 2014), K _{FOC} and 1/n were incorrectly reported for seven soils only instead of 42 (RAR Addendum (2014), Part 4))
1/n [-]	0.87	Arithmetic mean (n = 42) (in the LoEP (EFSA, 2014), K _{FOC} and 1/n were incorrectly reported for seven soils only instead of 42 (RAR Addendum (2014), Part 4))
DT ₅₀ -soil [days]	4.14	Geometric mean, normalised (20°C, pF ₂), laboratory; including "Mississippi" soil
DT ₅₀ -w/s system [days]	18.16	EFSA Journal 2014;12(9):3812
DT ₅₀ -water (degradation) [days]	18.16	EFSA Journal 2014;12(9):3812 Value from w/s system
DT ₅₀ -sediment (degradation)[days]	18.16 (Step 1&2) 1000 (Step 3)	Value from w/s system Default value
DT ₅₀ -on plants[days]	10	Default value
Plant uptake	0	Default value
Max. occurrence in soil	—	
Max. occurrence in water/sediment	—	
2,4-DCP		
Molecular mass [g/mol]	163	EFSA Journal 2014;12(9):3812
Water solubility [mg/L]	4870 (20°C)	EFSA Journal 2014;12(9):3812
K _{oc} [mL/g]	512	Arithmetic mean
1/n [-]	Not required	
DT ₅₀ -soil [days]	7.0	EFSA Journal 2014;12(9):3812 Geometric mean lab, normalised (pF ₂ , 20°C, Q10=2.58)
DT ₅₀ -w/s system [days]	103.9	EFSA Journal 2014;12(9):3812
DT ₅₀ -water [days]	103.9	Value from w/s system
DT ₅₀ -sediment [days]	1000	Default value
Plant uptake	Not required	
Max. occurrence in soil	8.7	EFSA Journal 2014;12(9):3812
Max. occurrence in water/sediment	32.1	EFSA Journal 2014;12(9):3812
2,4-DCA		
Molecular mass [g/mol]	177	EFSA Journal 2014;12(9):3812
Water solubility [mg/L]	96.3 (20°C)	EFSA Journal 2014;12(9):3812
K _{oc} [mL/g]	1028	Arithmetic mean
1/n [-]	Not required	
DT ₅₀ -soil [days]	10.4	EFSA Journal 2014;12(9):3812 Geometric mean lab, normalised (pF ₂ , 20°C, Q10=2.58)
DT ₅₀ -w/s system [days]	1000	Default value
DT ₅₀ -water [days]	1000	Default value
DT ₅₀ -sediment [days]	1000	Default value
Plant uptake	Not required	
Max. occurrence in soil	15	EFSA Journal 2014;12(9):3812
Max. occurrence in water/sediment	5.3	EFSA Journal 2014;12(9):3812

Clopyralid

Parameter	Input Parameter	Comment
Clopyralid		
Molecular mass [g/mol]	191.96	EFSA Conclusion (2018) 16(7):5389
Water solubility [mg/L]	143 000 (20°C)	EFSA Conclusion (2018) 16(7):5389 Value at pH 7
Vapour pressure [Pa]	Not required	
K _{oc} [mL/g]	1.41	EFSA Conclusion (2018) 16(7):5389 Geometric mean (n = 9)
Freundlich exponent (1/n) [-]	Not required	

Parameter	Input Parameter	Comment
DT ₅₀ -soil [days]	7.05	EFSA Conclusion (2018) 16(7):5389 Geometric mean field values (n=10) (normalised to pF ₂ , 20°C with Q10 of 2.58)
DT ₅₀ -whole system [days]	1000	FOCUS default value
DT ₅₀ -water [days]	148	EFSA Conclusion (2018) 16(7):5389 Geometric mean (n = 2)
DT ₅₀ -sediment [days]	1000	FOCUS default value
DT ₅₀ -on plants[days]	Not required	
Plant uptake	Not required	
Max. occurrence in soil [%]	—	
water/sediment [%]	—	

Fluroxypyr

Parameter	Input Parameter	Comment
Fluroxypyr-methyl		
Molecular mass [g/mol]	367.3	EFSA Journal 2011;9(3):2091
Water solubility [mg/L]	0.009	EFSA Journal 2011;9(3):2091
Vapour pressure [Pa]	1.349×10^{-6}	EFSA Journal 2011;9(3):2091
K _{oc} [mL/g]	19950	Arithmetic mean
Freundlich sorption exponent (1/n)	4	Default value
DT ₅₀ -soil [days]	1.0	Geometric mean laboratory values, (normalised to pF ₂ , 20°C with Q10 of 2.58)
DT ₅₀ -w/s system [days]	38.1	EFSA Journal 2011;9(3):2091
DT ₅₀ -water (degradation) [days]	38.1 (step 1&2)	EFSA Journal 2011;9(3):2091 Value from w/s system
DT ₅₀ -sediment (degradation)[days]	38.1 (step 1&2) 1000 (step 3)	Value from w/s system Default value
DT ₅₀ -on plants[days]	10	Default value
Plant uptake	0.5	FOCUS recommendation for systemic compounds
Max. occurrence in soil	—	
water/sediment	—	
Fluroxypyr-acid		
Molecular mass [g/mol]	255	EFSA Journal 2011;9(3):2091
Water solubility [mg/L]	91	EFSA Journal 2011;9(3):2091
Vapour pressure [Pa]	Not required	
K _{oc} [mL/g]	68	Arithmetic mean
Freundlich sorption exponent (1/n)	Not required	
DT ₅₀ -soil [days]	13.9	EFSA Journal 2011;9(3):2091 Median laboratory values, (normalised to pF ₂ , 20°C with Q10 of 2.58)
DT ₅₀ -w/s system [days]	38.1	EFSA Journal 2011;9(3):2091
DT ₅₀ -water [days]	38.1	EFSA Journal 2011;9(3):2091 Value from w/s system
DT ₅₀ -sediment [days]	1000	Default value
Plant uptake	Not required	
Max. occurrence in soil	—	
water/sediment	—	
Pyridinol		
Molecular mass [g/mol]	197	EFSA Journal 2011;9(3):2091
Water solubility [mg/L]	91	Value from the parent
K _{oc} [mL/g]	708 (pH < 7), median 68.5 (pH ≥ 7) acid & neutral soils / alkaline soils	Confirmatory information Arithmetic mean
Freundlich sorption exponent (1/n)	Not required	
DT ₅₀ -soil [days]	17.6	Confirmatory information Geometric mean laboratory values, (normalised to pF ₂ , 20°C with Q10 of 2.58)
DT ₅₀ -w/s system [days]	35.5	EFSA Journal 2011;9(3):2091
DT ₅₀ -water [days]	35.5	EFSA Journal 2011;9(3):2091 Value from w/s system
DT ₅₀ -sediment [days]	1000	Default value
Plant uptake	Not required	

Parameter	Input Parameter	Comment
Max. occurrence in soil	23.9	EFSA Journal 2011;9(3):2091
water/sediment	44	Value from the water phase
Methoxy pyridine		
Molecular mass [g/mol]	211	EFSA Journal 2011;9(3):2091
Water solubility [mg/L]	91	Value from the parent
K _{oc} [mL/g]	321	Arithmetic mean
Freundlich sorption exponent (1/n)	Not required	
DT ₅₀ soil [days]	111.11	Confirmatory information Geometric mean laboratory values, (normalised to pF2, 20°C with Q10 of 2.58)
DT ₅₀ w/s system [days]	1000	Default value
DT ₅₀ water [days]	1000	Default value
DT ₅₀ sediment [days]	1000	Default value
Plant uptake	Not required	
Max. occurrence in soil	38.2	EFSA Journal 2011;9(3):2091
water/sediment	0	EFSA Journal 2011;9(3):2091
3-CP		
Molecular mass [g/mol]	162	EFSA Journal 2011;9(3):2091
Water solubility [mg/L]	91	Value from the acid
K _{oc} [mL/g]	1	Default value
Freundlich sorption exponent (1/n)	Not required	
DT ₅₀ soil [days]	1000	Default value
DT ₅₀ w/s system [days]	1000	Default value
DT ₅₀ water [days]	1000	Default value
DT ₅₀ sediment [days]	1000	Default value
Plant uptake	Not required	
Max. occurrence in soil	0	EFSA Journal 2011;9(3):2091
water/sediment	17.9	EFSA Journal 2011;9(3):2091 Value from the water phase

A 4.2 Exposure assessment for metabolites 4-CP and 1,2,4-Benzenetriole

Predicted Environmental Concentrations in Soil (PECs) for Relevant Metabolites

PEC_s of 4-CP was calculated based on worst case persistence endpoint. Results are presented in the table below.

Table A 46: Maximum initial PEC_s of metabolite 4-CP

Crop	Molar correction factor ^a [-]	Max. occurrence metabolite [%]	DT ₅₀ [days]	Application rate metabolite [g/ha]	Interception [%]	Max. PEC _s metabolite [mg/kg]
Cereals / grass	0.582	33.0	0.69	144	0	0.192

^a MM_{metabolite} = 128.6 g/mol
 MM_{parent} = 221 g/mol

Table A 47: Predicted Environmental Concentrations of 4-CP in soil (PEC_s) after application of 2,4-D to cereals / grass

Days from last application or TWA period	Actual PEC _s [mg/kg]	Maximum TWA PEC _s [mg/kg]
0	0.192	--
1	0.070	0.121
2	0.026	0.083
4	0.003	0.047
7	0.000	0.027
14	0.000	0.014
21	0.000	0.009
28	0.000	0.007
50	0.000	0.004
100	0.000	0.002

zRMS comments:

The study on degradation of 4-chlorophenol in soil was agreed by the zRMS with DT₅₀ of 0.69 days considered relevant for the soil exposure assessment. For details of the study evaluation, please refer to Appendix 3, KCP-9.1.1/02.

The input parameters considered by the Applicant in calculation of the soil exposure to 4-CP following application of ADM.3304.H.1.A are agreed by the zRMS.

Performed calculations were independently validated by the zRMS and regardless of the method used (ESCAPE ver. 2 with ff of 1 or calculations metabolite as parent using pseudo-application rate) obtained PEC_{SOIL} were lower comparing to these reported in Table A47 above. Taking this into account, the Applicants' results may be used in the soil risk assessment as representing worst case.

For future evaluations the Applicant is kindly asked to provide soil exposure calculations for all relevant compounds in point 8.7 in order to facilitate the assessment by the zRMS.

Predicted Environmental Concentrations in Ground Water (PEC_{GW})

It is highly unlikely that prolonged anaerobic conditions would occur during or shortly after the application of AG-CDF1-480 EC to cereals and grass/alfalfa to the recommended GAP. However, in order to demonstrate safe uses it is the unlikely event of anaerobic conditions, the PEC of the active substance 2,4-D and anaerobic metabolite 4-CP in groundwater has been assessed with the standard FOCUS scenarios using the FOCUS PEARL 4.4.4 and FOCUS PELMO 5.5.3 models. The same modelling approach as described under Section IIIA 9.6 was applied. The use patterns considered in the modelling are presented under Section IIIA 9.6, model input parameters for 4-CP are presented in the table below.

For detailed results please refer to **KCP-9.6.1/01**.

Table A 48: Summary of model input parameters for 2,4-D metabolite 4-CP used in the leaching simulation models FOCUS PEARL and FOCUS PELMO

Parameter	4-CP	Remarks/Reference
PHYSICO-CHEMICAL PARAMETERS		
Molecular weight [g/mol]	128.6	Euro Chlor (2002) ^a
Water solubility [mg/L]	27100 (20°C)	Euro Chlor (2002) ^a
Vapour pressure [Pa]	0	Worst case assumption
DEGRADATION IN SOIL		
Formation fraction [-]	1 (2,4-D → 4-CP)	Worst case assumption
DT ₅₀ soil [d]	0.22 (n = 4)	Swales & Crabtree (2015a), Geometric mean, laboratory (20°C, pF2)
SORPTION TO SOIL		
K _{FOC} [mL/g]	182 (n = 5)	Swales & Crabtree (2015b), Arithmetic mean (lowest K _{foc} of 155 mL/g with 1/n of 0.81 should have been used due to potential dependency between adsorption and soil pH)
K _{FOM} [mL/g]	105.6	Calculated, Arithmetic mean K _{FOC} /1.724
Freundlich exponent 1/n [-]	0.792 (n = 5)	Swales & Crabtree (2015b), Arithmetic mean
CROP/ MANAGEMENT RELATED PARAMETERS		
Crop uptake factor [-]	0	Worst case assumption

^a Euro Chlor (2002): Euro Chlor Risk Assessment for the Marine Environment. OSPARCOM Region – North Sea. Monochlorophenols. February 2002.

Table A 49: Overall maximum PEC_{GW} at 1 m soil depth for 2,4-D and metabolite 4-CP

Crop	FOCUS model	80 th percentile PEC _{GW} at 1 m soil depth [µg/L]	
		2,4-D	4-CP
Winter cereals	PELMO	0.000	0.000
	PEARL	0.000000	0.000000
Spring cereals	PELMO	0.000	0.000
	PEARL	0.000000	0.000000
Grassland	PELMO	0.000	0.000
	PEARL	0.000000	0.000000

The predicted environmental concentrations in groundwater (PEC_{GW}) of the active substance 2,4-D and its anaerobic metabolite 4-CP were calculated to be < 0.1 µg/L for all scenarios. Therefore, it can be concluded that the use of 2,4-D on winter cereals, spring cereals and grassland is unlikely to pose a risk to

shallow groundwater in Europe if the active substance is used in compliance with the label recommendations.

zRMS comments:

The studies on degradation of 4-chlorophenol and sorption in soil were agreed by the zRMS with DT₅₀ of 0.22 days and K_{foc} of 155 mL/g considered relevant for the groundwater exposure assessment. For details of the studies evaluation, please refer to Appendix 3, KCP-9.1.1/02 and KCP-9.1.1/03.

The input parameters considered by the Applicant in calculation of the groundwater exposure to 4-CP following application of ADM.3304.H.1.A are agreed by the zRMS with exception of K_{foc}, since due to potential dependency between adsorption and soil pH the lowest K_{foc} of 155 mL/g should have been considered.

Performed calculations were independently validated by the zRMS using the same inputs and K_{foc} of 155 mL/g with 1/n of 0.81. The 2,4-D input values and application scheme as agreed in point 8.8 of this document has been considered. Results reported in Table A 49 may be confirmed. Regardless of the K_{foc} used, no unacceptable leaching of metabolite 4-chlorophenol is expected following the intended Central Zone uses of ADM.3304.H.1.A.

For future evaluations the Applicant is kindly asked to provide soil exposure calculations for all relevant compounds in point 8.8 in order to facilitate the assessment by the zRMS.

Predicted Environmental Concentrations in Surface Water (PEC_{SW}) for Metabolites

PEC_{SW} and PEC_{SED} simulations for metabolite 4-CP were performed with the model FOCUS STEPS 1-2 v3.2. Input parameters used in the modelling are summarised in the table below; for details of the considered use patterns please refer to Section IIIA 9.7. The overall maximum PEC_{SW} and PEC_{SED} values are presented in the table below.

For detailed results please refer to **KCP-9.7.1/01**.

As it was not possible to determine input parameters for aquatic photolysis metabolite 1,2,4-Benzenetriol (see Swales & Crabtree, 2015c), PEC_{SW} were determined based on PEC_{SW, ini} of the parent 2,4-D according to the following equation:

$$PEC_{sw,ini,metabolite} = PEC_{sw,ini,parent} * \frac{P_{max,sw}}{100} * f_{mol}$$

Where:

PEC_{SW,ini,parent} = max. PEC_{SW, parent} [µg/L]

P_{max,SW} = maximum occurrence metabolite in surface water (31.7%; EFSA, 2014) [%]

f_{mol} = molecular correction factor (molecular mass metabolite (126.1 g/mol) / molecular mass parent (221 g/mol)) [-]

Table A 50: Summary of input parameters of 4-CP for PEC_{SW} and PEC_{SED} calculations according to FOCUS STEPS 1-2

Parameter	4-CP	Remarks/Reference
Entry routes into surface water	Spray drift Runoff Drainage	-
Molecular weight [g/mol]	128.6	Euro Chlor (2002) ^a
Water solubility [mg/L]	27100 (20°C)	Euro Chlor (2002) ^a
DEGRADATION IN SOIL		
DT ₅₀ soil [d] (Step 1, Step 2)	0.22 (n = 4)	Swales & Crabtree (2015a), Geometric mean, laboratory (20°C, pF2)
Max. occurrence in soil [%]	33.0	EFSA (2014)
SORPTION TO SOIL		
K _{FOC} [mL/g]	182 (n = 5)	Swales & Crabtree (2015b), Arithmetic mean (lowest K _{foc} of 155 mL/g with 1/n of 0.81 should have been used due to potential dependency between adsorption and soil pH)
DEGRADATION IN AQUATIC SYSTEMS		
DT ₅₀ total system [d] (Step 1)	1000	FOCUS default
DT ₅₀ water [d] (Step 2)	1000	FOCUS default
DT ₅₀ sediment [d] (Step 2)	1000	FOCUS default
Max. occurrence in water/sediment [%]	6.9	RAR Addendum (2014), Lewis & Fletcher (2011e)
Max. occurrence in water/sediment [%]	33	EU agreed

^a Euro Chlor (2002): Euro Chlor Risk Assessment for the Marine Environment. OSPARCOM Region – North Sea. Monochlorophenols. February 2002.

As **risk envelope approach for FOCUS Step 1 & 2** “winter cereals” was calculated assuming 0 % crop interception (750 g 2,4-D/ha). This calculated worst case scenario also covers the application in winter and spring cereals assuming average crop interception as well as the application in grassland assuming average crop interception.

Table A 51: Maximum PEC_{SW} and PEC_{SED} of 2,4-D and metabolites 4-CP and 1,2,4-Benzenetriol

Crop	Scenario	Period	2,4-D		4-CP		1,2,4-Benzenetriol
			PEC _{SW} [µg/L]	PEC _{SED} [µg/kg]	PEC _{SW} [µg/L]	PEC _{SED} [µg/kg]	PEC _{sw} ^a [µg/L]
FOCUS Step 1							
Winter cereals	–	–	238.78	135.88	46.99	85.36	43.2
FOCUS Step 2							
Winter cereals	N-Europe	Oct – Feb*	64.97	36.97	2.31	4.16	11.7
	S-Europe	Oct – Feb*	53.10	30.02	1.89	3.41	9.6

^a calculated based on PEC_{SW, parent}

* Worst case application date autumn and winter, covers the application in spring and summer

zRMS comments:

The studies on degradation of 4-chlorophenol and sorption in soil were agreed by the zRMS with DT₅₀ of 0.22 days and K_{foc} of 155 mL/g considered relevant for the surface water exposure assessment. For details of the studies evaluation, please refer to Appendix 3, KCP-9.1.1/02 and KCP-9.1.1/03.

The input parameters considered by the Applicant in calculation of the surface water exposure to 4-CP following application of ADM.3304.H.1.A are agreed by the zRMS with exception of K_{foc}, since due to potential dependency

between adsorption and soil pH the lowest K_{foc} of 155 mL/g should have been considered.

Calculations performed for 4-CP were independently validated by the zRMS using the same inputs and K_{foc} of 155 mL/g with 1/n of 0.81. As a worst case the application to winter cereals in March-May at 750 g a.s./ha with 0% crop interception was assumed as representing worst case and covering all intended uses of ADM.3304.H.1.A. For 2,4-D input parameters as agreed in point 8.9 of this document were used. Results obtained by the zRMS were higher (see table below) and for this reason they supersede these reported in Table A 51, which are struck through.

Crop	Period	Step	Scenario	4-CP	
				PEC _{SW} [µg/L]	PEC _{SED} [µg/kg]
Winter cereals ¹⁾	March-May	1	-	49.43	76.21
		2	N-Europe	5.23	8.0

¹⁾ Application to winter cereals at 750 g a.s./ha with 0% crop interception as representing worst case and covering all intended uses

With regard to hydrolytic metabolite 1,2,4-benzenetriol, the approach taken by the Applicant may be accepted as being one of the methods to derive exposure data when substantial information is missing. Nevertheless, the zRMS performed additional Step 1&2 calculations using worst case default values (i.e. DT₅₀ of 1000 days for aquatic systems and K_{foc} of 1.0 mL/g). Since metabolite 1,2,4-benzenetriol is not formed in soil, its peak occurrence in soil was set to 0.01% and soil DT₅₀ of 0.01 d was assumed. The application pattern was the same as in case of 4-chlorophenol. Results obtained by the zRMS were in good agreement with values reported in Table A 51 (with Step 2 PEC_{SW} actually lower) which may be thus used in the aquatic risk assessment.

For future evaluations the Applicant is kindly asked to provide soil exposure calculations for all relevant compounds in point 8.9 in order to facilitate the assessment by the zRMS.

A 4.3 References

General

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Specific

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- EC (2014): Revised Renewal report for the active substance 2,4-D finalised in the Standing Committee on Plants, Animals, Food and Feed at its meeting on 9 October 2015 in view of the approval of 2,4-D as active substance in accordance with Regulation (EC) No 1107/2009. SANCO/11961/2014 Rev 5 6 October 2017
- EFSA (2018): Conclusion on the peer review of the pesticide risk assessment of the active substance clopyralid. EFSA Journal 2018;16(7):5389, 28 pp.
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- EFSA (2014): Conclusion on the peer review of the pesticide risk assessment of the active substance 2,4-D. Update 21 March 2017. EFSA Journal 2014;12(9):3812
- Greece (2014): Final Addendum to the Renewal Assessment Report. Risk assessment provided by the rapporteur Member State Hellas and co-rapporteur Member State Poland for the active substance 2,4-D (March 2014)
- Greece (2018): Bridging Report. Environmental fate. 2,4-dichlorophenoxy acetic acid (2,4-D Acid) and 2,4-dichlorophenoxy 2-ethylhexyl ester (2,4-D 2-EHE) (Herbicide). Rapporteur Member State: Greece (September 2018).

Appendix 5 FOCUS MACRO 5.5.4 raw files - Chateaudun

2,4-D

MACRO in FOCUS Version 5.5.4
Output File = C:\SWASH\MACRO\macro384.bin
Type of compound = parent
Compound : 24DCZ
Scenario : Chateaudun
Groundwater

Simulation from 19010101 to 19270101, application every year
(6 year warm-up)

Crop : Grass/alfalfa, irrigated

Number of applications : 1

Application 1 : 300 g/ha of 24DCZ on day 74

Period	Av_FluxConc_at_reporting_depth
1	0
2	0
3	0
4	0
5	0
6	0
7	0
8	0
9	0
10	0
11	0
12	0
13	0
14	0
15	1.76386E-13
16	9.485624E-09
17	0
18	0
19	0
20	0
21	0
22	0
23	0
24	0
25	0
26	0

2,4-DCA

MACRO in FOCUS Version 5.5.4

Output File = C:\SWASH\MACRO\macro385.bin

Type of compound = metabolite

Compound : 24DCA

Scenario : Chateaudun

Groundwater

Simulation from 19010101 to 19270101, application every year
(6 year warm-up)

Crop : Grass/alfalfa, irrigated

Number of applications : 1

Application 1 : 300 g/ha of 24DCA on day 74

Period	Av_FluxConc_at_reporting_depth
1	0
2	0
3	0
4	0
5	0
6	0
7	0
8	0
9	0
10	0
11	1.345218E-40
12	3.28749E-38
13	6.98087E-37
14	2.177809E-36
15	4.426868E-14
16	1.093392E-08
17	8.616527E-09
18	0
19	0
20	0
21	0
22	0
23	0
24	0
25	0
26	0

2,4-DCP

MACRO in FOCUS Version 5.5.4

Output File = C:\SWASH\MACRO\macro387.bin

Type of compound = metabolite

Compound : 24DCP

Scenario : Chateaudun

Groundwater

Simulation from 19010101 to 19270101, application every year
(6 year warm-up)

Crop : Grass/alfalfa, irrigated

Number of applications : 1

Application 1 : 300 g/ha of 24DCP on day 74

Period	Av_FluxConc_at_reporting_depth
1	0
2	0
3	0
4	0
5	0
6	0
7	0
8	0
9	0
10	0
11	0
12	0
13	0
14	0
15	1.213497E-14
16	3.448372E-09
17	1.194987E-10
18	0
19	0
20	0
21	0
22	0
23	0
24	0
25	0
26	0

4-CP

MACRO in FOCUS Version 5.5.4

Output File = C:\SWASH\MACRO\macro415.bin

Type of compound = metabolite

Compound : 4CP

Scenario : Chateaudun

Groundwater

Simulation from 19010101 to 19270101, application every year
(6 year warm-up)

Crop : Grass/alfalfa, irrigated

Number of applications : 1

Application 1 : 300 g/ha of 4CP on day 74

Period	Av_FluxConc_at_reporting_depth
1	0
2	0
3	0
4	0
5	0
6	0
7	0
8	0
9	0
10	0
11	0
12	0
13	0
14	0
15	1.642428E-17
16	9.32511E-12
17	0
18	0
19	0
20	0
21	0
22	0
23	0
24	0
25	0
26	0

Fluroxypyr acid

MACRO in FOCUS Version 5.5.4

Output File = C:\SWASH\MACRO\macro396.bin

Type of compound = parent

Compound : Fluco

Scenario : Chateaudun

Groundwater

Simulation from 19010101 to 19270101, application every year
(6 year warm-up)

Crop : Grass/alfalfa, irrigated

Number of applications : 1

Application 1 : 60 g/ha of Fluco on day 74

Period	Av_FluxConc_at_reporting_depth
1	0
2	5.565152E-12
3	1.423421E-08
4	2.850603E-08
5	1.43865E-06
6	4.189531E-06
7	6.374066E-06
8	6.292094E-05
9	3.771268E-05
10	6.530884E-06
11	1.200153E-05
12	2.797723E-05
13	3.056621E-05
14	3.368145E-06
15	9.92585E-06
16	0.0008229205
17	0.0005366082
18	7.607639E-05
19	3.991855E-06
20	5.241151E-06
21	5.079543E-06
22	0
23	1.543143E-07
24	2.453291E-08
25	1.417989E-06
26	4.171362E-06

Methoxyypyridine (ff = 0.201)

MACRO in FOCUS Version 5.5.4

Output File = C:\SWASH\MACRO\macro397.bin

Type of compound = metabolite

Compound : Metco

Scenario : Chateaudun

Groundwater

Simulation from 19010101 to 19270101, application every year
(6 year warm-up)

Crop : Grass/alfalfa, irrigated

Number of applications : 1

Application 1 : 60 g/ha of Metco on day 74

Period	Av_FluxConc_at_reporting_depth
1	0
2	1.805574E-16
3	8.329961E-11
4	3.923227E-10
5	9.007255E-09
6	6.950371E-08
7	8.126924E-08
8	1.464821E-06
9	1.713468E-06
10	1.609021E-06
11	1.420611E-06
12	1.707389E-06
13	2.069773E-06
14	1.751961E-06
15	1.640148E-06
16	1.9973E-05
17	3.472878E-05
18	3.359196E-05
19	2.788671E-05
20	3.202511E-05
21	2.734455E-05
22	1.913661E-05
23	1.749132E-05
24	1.272423E-05
25	1.113556E-05
26	9.583582E-06

Pyridinol from Fluroxypyr acid (ff = 0.286)

MACRO in FOCUS Version 5.5.4

Output File = C:\SWASH\MACRO\macro403.bin

Type of compound = metabolite

Compound : Pyrco

Scenario : Chateaudun

Groundwater

Simulation from 19010101 to 19270101, application every year
(6 year warm-up)

Crop : Grass/alfalfa, irrigated

Number of applications : 1

Application 1 : 60 g/ha of Pyrco on day 74

Period	Av_FluxConc_at_reporting_depth
1	0
2	1.932952E-17
3	1.016723E-11
4	4.42364E-11
5	1.417141E-09
6	1.112293E-08
7	7.953012E-09
8	2.674209E-07
9	2.074373E-07
10	5.03914E-08
11	0
12	5.969683E-08
13	1.039408E-07
14	0
15	0
16	4.088824E-06
17	3.912608E-06
18	5.095671E-07
19	0
20	0
21	0
22	0
23	0
24	0
25	0
26	0

Pyridinol from Methoxypyridine (ff = 0.723)

MACRO in FOCUS Version 5.5.4

Output File = C:\SWASH\MACRO\macro409.bin

Type of compound = metabolite

Compound : Pyrco

Scenario : Chateaudun

Groundwater

Simulation from 19010101 to 19270101, application every year
(6 year warm-up)

Crop : Grass/alfalfa, irrigated

Number of applications : 1

Application 1 : 12.06 g/ha of Pyrco on day 74

Period	Av_FluxConc_at_reporting_depth
1	0
2	0
3	0
4	0
5	0
6	0
7	0
8	0
9	0
10	0
11	0
12	0
13	0
14	0
15	0
16	0
17	0
18	0
19	0
20	0
21	0
22	0
23	0
24	0
25	0
26	0