REGISTRATION REPORT

**Part B Section 8**

**Environmental Fate**

Detailed summary of the risk assessment

Product code: ADM.09250.H.1.A

Product name(s): **2,4-D 95 SP**

Chemical active substance:

2,4-dichlorophenoxy acetic acid**,** 80.4% or 804 g/kg

Central

Zonal Rapporteur Member State: Poland

CORE ASSESSMENT

(authorization)

Applicant: XXXX

Sponsor: XXXX

Submission date: ~~March~~ October 2023

Evaluation date: December 2023

MS Finalisation date: March 2024

Version history

|  |  |
| --- | --- |
| **When** | **What** |
| March 2023 | 1st applicant version |
| May 2023 | dRR submitted by applicant to the Polish Ministry of Agriculture and Rural Development |
| July 2023 | Submission to the evaluation unit |
| October 2023 | Amended to include additional surface water modelling for the R1 scenario. |
| December 2023 | zRMS finalised dRR evaluation |

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# Fate and behaviour in the environment (KCP 9)

|  |
| --- |
| **Review Comments:**  This document describes the acceptable use conditions required for registration of ADM.0950.H.1.A, a soluble powder containing 2,4-D 950 g/kg as sodium salt monohydrate (804 g/kg as acetic acid), for use as a herbicide in spring wheat.  This Part B document only reviews data and additional information that has not previously been considered within the EU review process.  Since this document is based on the information provided by the applicant, all review comments, additions and corrections have been made using commenting boxes or highlighted in grey. |

This document reviews the environmental fate studies and modelling for the plant protection product 2,4- D 95 SP formulation containing the active substance 2,4-dichlorophenoxy acetic acid (2,4-D) (804 g/kg ~~750 g/L~~). 2,4-D was reviewed as part of the renewal of approval procedure by the Member States and the Commission under Commission Implementing Regulation, (EU) 2015/2033 for 2,4-D in accordance with Regulation (EC) No. 1107/2009.

The renewal assessment report for 2,4-D (SANCO/11961/2014) as well as the EFSA conclusion for 2,4-D (2014;12(9):3812, revised 21 March 2017) are considered to provide the relevant review information or act as a reference to where such information can be found. New studies which have not been reviewed at the EU level have also been presented in this document to address any data gaps raised during the EU review.

Maximum soil, groundwater and surface water predicted environmental concentrations (PEC) associated with the supported uses of the 2,4-D 95 SP formulation following application to spring cereal in the EU Central Zone are presented in this document.

## 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 situ- ation  (crop destination  / purpose of crop) | F, Fn,  Fpn G,  Gn, Gpn or  I \*\* | Pests or Group of pests controlled  (additionally: develop- mental stages of the pest or pest group) | Application | | | | Application rate | | | PHI  (days) | Remarks:  e.g. g saf- ener/ syn- ergist per ha | Conclusion |
| Method / Kind | Timing / Growth stage of crop & season | Max. number   1. per use 2. per crop/ season | Min. interval between ap- plications (days) | kg product/ha   1. max. rate per appl. 2. max. total rate per crop/season | kg a.s./ha   1. max. rate per appl. 2. max. total rate per crop/season | Water L/ha min/max | Groundwater |
| **Zonal uses (field or outdoor uses, certain types of protected crops)** | | | | | | | | | | | | | | |
| 1 | Poland | Spring Wheat | F | Broadleaf Weeds  CENCY, VERPE, BRSNW, THLAR, CAPBP | Overall, Broad- cast foliar spray | BBCH 15-25 | 1. 1 2. 1 | - | a) 0.9328  b) 0.9328 | a) 0.75  b) 0.75  (as acetic acid) | 200-300 | - | - | A |

\* 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 |

**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 | Crop and/or situ- ation  (crop destination  / purpose of crop) | F, Fn,  Fpn G,  Gn, Gpn or  I \*\* | Pests or Group of pests controlled  (additionally: develop- mental 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   1. per use 2. per crop/ season | Min. interval between ap- plications (days) | kg product/ha   1. max. rate per appl. 2. max. total rate per crop/season | kg a.s./ha   1. max. rate per appl. 2. max. total rate per crop/season | Water L/ha min/max |
| 1 | EU | Spring wheat, spring barley, spring oats &  spring rye | F | Dicotyled onous weeds | Broadcast | 11-32 | 1 | - | a) 0.75  b) 0.75 | a) 0.75  b) 0.75 | 100-400 | - |  |
| 2 | EU | Winterwheat, winter barley, winter oats, winter rye &  triticale | F | Dicotyled onous weeds | Broadcast | 21-32 | 1 | - | a) 0.75  b) 0.75 | a) 0.75  b) 0.75 | 100-400 | - |  |
| 3 | EU | Maize | F | Dicotyled onous weeds | Broadcast | 11-16 | 1 | - | a) 0.75  b) 0.75 | a) 0.75  b) 0.75 | 100-400 | - |  |

\* 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

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## 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 oc- currence in compart- ments | Exposure assessment required due to |
| 2,4-DCP | 163 |  | OH |  | Soil (aerobic): 8.7% | PECGW: not covered by |
|  |  |  |  |  |  | EU assessment |
|  |  | Cl | Cl |  | Water/Sediment: 32.1% | PECSOIL: not covered by EU assessment  PECSW/SED: not covered |
|  |  |  |  |  |  | by EU assessment |
| 2,4-DCA | 177 |  | O | CH3 | Soil (aerobic): 15% | PECGW: not covered by EU assessment |
|  |  | Cl | Cl |  | Water/Sediment: 5.3% | PECSOIL: not covered by EU assessment |
|  |  |  |  |  |  | PECSW/SED: not covered |
|  |  |  |  |  |  | by EU assessment |
| 4-CP | 128.6 |  | | | Soil (anaerobic): 33% | PECGW: not covered by |
|  |  |  | EU assessment |
|  |  | Water/Sediment: 6.9% | PECSOIL: not covered by EU assessment |
|  |  |  | PECSW/SED: not covered |
|  |  |  | by EU assessment |
| 1,2,4-benzene- triol | 126.1 |  | | | Soil (aerobic): 0.1%  Water/Sediment: 31.7% | PECSW/SED: not covered by EU assessment |

## 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 extrapo- late from data obtained with the active substance.

## 8.3.1 Aerobic degradation in soil (KCP 9.1.1.1)

The aerobic degradation of 2,4-dichlorophenoxy acetic acid (2,4-D) in soil was evaluated during the EU review and is summarised in the EFSA Conclusion (2014;12(9):3812, revised 21 March 2017). All studies presented in the EU renewal review were considered acceptable.

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 for- mation 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 an alkaline trap (presumed to be CO2) accounted for a maximum of 49 % AR. Figure 8.3-1 shows the proposed degradation pathway of 2,4-D.

**Figure 8.3-1: Proposed pathway of 2,4-D in soil**

O

O OH

Cl Cl

2,4-D



OH

Cl

4-CP

anaerobic

OH

Cl Cl

2,4-DCP



Cl

2,4-DCA

O

Cl

CO2 + NER

However, the DT50 resulting from soil Mississippi (Cohen, 1991a) presented in the EFSA Conclusion (2014;12(9):3812, revised 21 March 2017) was only normalised for soil temperature, not for soil mois- ture. 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 was 75% of the moisture content at

0.33 (p. 22, Cohen, 1991a). No further irrigation was applied during the study. The soil texture was determined as “silt loam” (according to the USDA classification system). 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 (75% of water content at 0.33 bar) | = 0.75 × 21%  = 15.75% |
| USDA Silt loam water content at field capacity | 26% |

|  |  |
| --- | --- |
| Factor for moisture normalisation  water content in study 0.7  𝑓𝑓𝑓𝑓 = � �  water content at field capacity | 15.75 0.7  𝑓𝑓𝑓𝑓 = � �  26 |
| DT50 (20°C) presented in EFSA Conclusion Report | 94.6 d |
| DT50 (20°C, pF2) | = 94.6 × 𝑓𝑓𝑓𝑓  **= 66.6 d** |

The newly calculated modelling endpoints for the rate of degradation of parent 2,4-D used in PECGW and PECSW simulations is presented in [Table 8.3-1.](#_bookmark5)

**Table 8.3-1: Summary of aerobic degradation rates for 2,4-D- laboratory studies**

|  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| 2,4-D, Laboratory studies, aerobic conditions | | | | | | | | | | |
| Soil name | Soil type (USDA) | pH (H2O) | Temp  ℃ | MWHC  % | DT50 (d) | DT90  (d) | DT50 (d) 20°C  pF2/10k Pa | Chi2 (%) | Kinetic model | Evalu- ated on EU  level  Refer- ence |
| Silt | Silt | 7.4 | 25 | 75 (at | 58.9 | 195.6 | 66.62 | 7.4 | SFO | Yes |
| Loam (Missis- sippi) | Loam |  |  | 1/3 bar)1 |  |  |  |  |  | Cohen, S.P. (1991a) |
| Clay | Clay | 6.2 | 20 | 50 | 7.5 | 24.8 | 5.3 | 6.3 | SFO | Yes |
| loam | loam |  |  |  |  |  |  |  |  | Liu, D. |
| (Fayette |  |  |  |  |  |  |  |  |  | (2011) |
| ) |  |  |  |  |  |  |  |  |  |  |
| Clay loam (RefSol 03-G) | Clay loam | 6.2 | 20 | 50 | 1.6 | 5.4 | 1.2 | 6.3 | SFO |  |
| Clay loam (RefSol 03-G) | Clay loam | 6.2 | 10 | 50 | 4.9 | 16.3 | - | - | SFO |  |
| Sandy loam (Site E1) | Sandy loam | 6.7 | 20 | 50 | 2.2 | 7.4 | 1.6 | 4.5 | SFO |  |
| Sandy loam (Site I2) | Sandy loam | 7.8 | 20 | 50 | 2.0 | 6.5 | 1.8 | 7.8 | SFO |  |
| Geometric mean (n=5) | | | | | | | 4.14 |  | | |
| pH-dependency: | | | | | | | No |  | | |

1 Moisture content not reported in EFSA Conclusion (2014;12(9):3812, revised 21 March 2017); value given

as per Cohen, S.P. (1991a).

2 Calculated value normalised for temperature and moisture (20ºC, pF2) used in order to determine the model- ling endpoint of 4.14 d.

|  |
| --- |
| **Review Comments:**  The normalised DT50 for Mississippi soil and recalculated mean DT50 of 4.14 days were accepted by the zRMS-PL/NL during evaluation of other XXXX products containing 2,4-D (e.g. Tricera). Thus, further assessment is not required. |

The data gap regarding potential pH-dependence of the degradation process of 2,4-D in soil identi- fied during the renewal review has been addressed by the applicant: A new study has been performed which has not undergone EU approval; (Crabtree, 2015), a summary is presented in Appendix 2.1.

The outcome of this study confirms that degradation of 2,4-D in soil is not pH-dependent.

**Table 8.3-2: Summary of aerobic degradation rates for 2,4-DCP - laboratory studies**

|  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| 2,4-DCP Laboratory studies, aerobic conditions | | | | | | | | | | |
| Soil name | Soil type (USDA) | pH (H2O) | Temp  ℃ | MWHC  % | DT50  (d) | DT90  (d) | DT50 (d) 20°C  pF2/10kPa | Chi2 (%) | Kinetic model | Evaluated on EU level  Reference |
| Clay loam (Fayette) | Clay loam | 6.2 | 20 | 50 | -1 | -1 | -1 | -1 | -1 | Yes, Liu, D.  (2011) |
| Clay loam (RefSol 03-G) | Clay loam | 6.2 | 20 | 50 | 15.52,3 | - | 11.12,3 | 6.32 | HS2 |
| Clay loam (RefSol 03-G) | Clay loam | 6.2 | 10 | 50 | -5 | -5 | -5 | -5 | -5 |
| Sandy loam (Site E1) | Sandy loam | 6.7 | 20 | 50 | 6.26 | - | 4.46 | 9.26 | SFO6 |
| Sandy loam (Site I2) | Sandy loam | 7.8 | 20 | 50 | 7.72,7 | - | 6.92,7,8 | 12.82 | FOMC2 |
| Geometric mean (n=3) | | | | | | | 7.0 |  | | |
| pH-dependency: | | | | | | | No |  | | |

1 Pathway fit not acceptable; decline fit not possible due to limited number of data points

2 Decline fit

3 Slow phase

5 Pathway and decline fit not acceptable

6 Decline fit with only 4 data points

7 Use of uncorrected data set: all data points included, ignoring that day 3 to day 26 samples display recovery levels <90%

8 Back-calculated from DT90/3.32 according to FOCUS (2006)

|  |
| --- |
| **Review Comments:**  The study by Crabtree (2015) is already agreed in the Central Zone, thus further assessment is not required.  In conclusion, degradation of 2,4-D in soil is not pH-dependent. |

**Table 8.3-3: Summary of aerobic degradation rates for 2,4-DCA - laboratory studies**

|  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| 2,4-DCA Laboratory studies, aerobic conditions | | | | | | | | | | |
| Soil name | Soil type (USDA) | pH (H2O) | Temp  ℃ | MWHC  % | DT50  (d) | DT90  (d) | DT50 (d) 20°C  pF2/10kPa | Chi2 (%) | Kinetic model | Evaluated on EU level  Reference |
| Clay loam (Fayette) | Clay loam | 6.2 | 20 | 50 | -1 | -1 | -1 | -1 | -1 | Yes, Liu, D.  (2011) |
| Clay loam (RefSol 03-G) | Clay loam | 6.2 | 20 | 50 | 16.32 | - | 11.72 | 3.72 | SFO2 |
| Clay loam (RefSol 03-G) | Clay loam | 6.2 | 10 | 50 | -1 | -1 | -1 | -1 | -1 |
| Sandy loam (Site E1) | Sandy loam | 6.7 | 20 | 50 | 13.73 | - | 9.83 | 6.33 | SFO3 |
| Sandy loam (Site I2) | Sandy loam | 7.8 | 20 | 50 | 10.92,4 | - | 9.82,4 | 8.52,4 | SFO2,4 |
| Geometric mean (n=3) | | | | | | | 10.4 |  | | |
| pH-dependency: | | | | | | | No |  | | |

1 Pathway fit of preceding metabolite 2,4-DCP not acceptable; decline fit not possible due to limited number of data points

2 Decline fit with only 4 data points

3 Decline fit

4 Use of uncorrected data set: all data points included, ignoring that day 3 to day 26 samples display recovery levels <90%

## 8.3.2 Anaerobic degradation of 2,4-D in soil (KCP 9.1.1.1)

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

Studies on the degradation of 2,4-D under anaerobic conditions have been performed on four soils and were evaluated in the EU renewal review; degradation half-lives are presented in [Table 8.3-4](#_bookmark7) be- low.

**Table 8.3-4: Summary of aerobic degradation rates for 2,4-DCA - laboratory studies**

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Soil name | Soil type (USDA) | pH (H2O) | Temp ℃ | MWHC (%) | DT50 (d) | DT90 (d) | R2 | Kinetic model | Evaluated on EU level y/n/ Reference |
| Clay loam | Clay | 6.9 | 20 | pF2 | 32 | 107 | 0.9861 | SFO | Yes, |
| (RefeSol 03- G) | loam |  |  |  |  |  |  |  | Lewis, C.J. |
| Loam (Kenslow) | Loam | 5.8 | 20 | pF2 | 23 | 77 | 0.9778 | SFO | (2011) |
| Silt loam (Chelmorton) | Silt loam | 6.8 | 20 | pF2 | 38 | 127 | 0.9824 | SFO |  |
| Sandy loam (Longwoods) | Sandy loam | 8.1 | 20 | pF2 | 22 | 74 | 0.9031 | SFO |  |
| Arithmetic mean | | | | | 28.8 |  |  |  |  |
| Geometric mean | | | | | 28.0 |  |  |  |  |

In addition to 2,4-DCA (≤10% AR) and 2,4-DCP (38% AR), a third major metabolite was identified under anaerobic conditions, 4-CP, with a maximum occurrence of 33% AR (EFSA Conclusion (2014;12(9):3812, revised 21 March 2017). Anaerobic conditions would not be expected to oc- cur during or shortly after the application of 2,4-D to spring cereals according to the recom- mended GAP, therefore it is not necessary to consider the metabolite 4-CP. Nevertheless for the avoidance of any doubt a risk assessment for 4-CP has been considered for soil, surface water and ground water compartments. A new study has been performed which has not undergone EU approval; (Swales 2015a) to address the degradation of 4-CP in soil under aerobic conditions; a summary is presented in Appendix 2.2.

**Table 8.3-5: Summary of aerobic degradation rates for 4-CP - laboratory studies**

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Soil name | Soil type (USDA) | pH (H2O) | Temp ℃ | MWHC (%) | DT50  (hours) | DT90  (hours) | **Chi2 (%)** | Kinetic model | Evaluated on EU level y/n/ Reference |
| Brierlow | Sandy silt loam | 7.4 | 20 | pF2 | 1.93 | 6.40 | 3.15 | SFO | No,  Swales, S.E. (2015a) |
| Speyer 5M | Sandy loam | 8.4 | 20 | pF2 | 3.21 | 10.7 | 4.26 | SFO |
| Warsop | Loamy sand/sand | 6.0 | 20 | pF2 | 16.6 | 55.0 | 4.34 | SFO |
| LAD-SCL- PF | Clay/Clay loam | 9.0 | 20 | pF2 | 7.38 | 24.5 | 4.85 | SFO |
| Geometric mean (hours) | | | | | 5.2 |  |  |  |  |
| Geometric mean (days) | | | | | 0.22 |  |  |  |  |
| Worst case (days) | | | | | 0.69 |  |  |  |  |

|  |
| --- |
| **Review Comments:**  The study by Swales 2015a is already agreed in the Central Zone (e.g. Camaro 306 SE), thus further assessment is not required.  In conclusion, the soil DT50 of 0.69 d is relevant for the soil exposure assessment, while the mean DT50 of 0.22 d is accepted for the groundwater and surface water modelling. |

## Field studies (KCP 9.1.1.2)

Field studies are not triggered in the EU unless the DT50 values derived under laboratory conditions at 20°C are more than 60 days (Commission Regulation (EU) No. 544/2011). The results of aerobic laboratory degradation studies of 2,4-D showed DT50 values below this threshold value. Only the DT50 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 when normalised for soil temperature and moisture (66.6 d; normalised to 20ºC and pF2).

A field dissipation study was reported and assessed to be acceptable during the 2001 evaluation, with 2,4-D having a field DT50 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; worst case normalised laboratory data (DT50 soil = 66.6 d) was used for PEC calculations of the parent as this value is higher than the actu- ally measured DT50 (58.9 d), hence representing a more conservative approach for the PECsoil calcu- lations.

## Soil accumulation testing (KCP 9.1.1.2.2)

Soil accumulation studies are not required.

## Mobility in soil (KCP 9.1.2)

The mobility of 2,4-D and its metabolites 2,4-DCP and 2,4-DCA in soil are presented in the corre- sponding document of the EU review dossier (EFSA Conclusion (2014;12(9):3812, revised 21 March 2017)) where the study references can be found. The endpoints are summarised in [Table 8.5-1](#_bookmark12) to [Table 8.5-3.](#_bookmark13) Two new studies which have not been previously reported at an EU level were conducted to investigate the mobility of the anaerobic metabolite 4-CP and photolysis metabolite 1,2,4-benzene- triol to fill a data gap identified during the previous EU review. The studies have been summarised in Appendix 2.3 (Swales, 2015b) and 2.4 (Swales, 2015c).

|  |
| --- |
| **Review Comments:**  The study by Swales 2015b is already agreed in the Central Zone (e.g. Camaro 306 SE), thus further assessment is not required.  In conclusion, 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.  The study by Swales 2015c was not evaluated by zRMS-PL. |

## 2,4-D and its metabolites

**Table 8.5-1: Summary of soil adsorption/desorption for 2,4-D**

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| 2,4-D | | | | | | | |
| Soil name | Soil type | OC (%) | pH (CaCl2) | KF  (mL/g) | KFOC  (mL/g) | 1/n (-) | Evaluated on EU level  Reference |
| Clay loam (M800) | Clay loam | 1.3 | 7.1 | 0.55 | 42 | 0.83 | Yes,  Yoder, R.N. (2011) |
| Loamy sand (M801) | Loamy sand | 1.1 | 5.2 | 0.45 | 41 | 0.83 |
| Loam (M802) | Loam | 2.5 | 5.0 | 0.42 | 17 | 0.82 |
| Silt loam (M803) | Silt loam | 3.6 | 5.9 | 0.83 | 23 | 0.87 |
| Sandy loam (M804) | Sandy loam | 1.4 | 7.5 | 0.19 | 14 | 0.81 |
| Silt loam (M816) | Silt loam | 0.9 | 5.9 | 0.21 | 23 | 0.78 |
| Clay loam (M822) | Clay loam | 4.4 | 7.2 | 0.51 | 12 | 0.90 |
| Loamy sand (soil I) | Loamy sand | 6.1 | 6.18 | 4.5 | 56.62 | 0.85 | Yes, Swoboda, T. (2006) |
| **Silt loam (Soil** | **Silt loam** | **1.7** | **5.56** | **2.42** | **44.85** | **0.59** |

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| 2,4-D | | | | | | | |
| Soil name | Soil type | OC (%) | pH (CaCl2) | KF  (mL/g) | KFOC  (mL/g) | 1/n (-) | Evaluated on EU level  Reference |
| **II)1** |  |  |  |  |  |  |  |
| **Loamy sand (Soil III)1** | **Loamy sand** | **1.4** | **4.04** | **4.18** | **126.79** | **0.63** |
| **Silt (Soil IV)1** | **Silt** | **1.5** | **5.65** | **3.21** | **50.38** | **0.56** |
| Silt loam (Soil V) | Silt loam | 1.6 | 5.33 | 1.25 | 52.6 | 0.83 |
| Sand (Plainfield) | Sand | 0.463 | 5.6 | 0.357 | 76 | 0.882 | Yes, Fathulla, R. (1996a) |
| **Sandy loam (Cal- ifornia)1** | **Sandy loam** | **0.58**3 | **6.7** | **0.167** | **70** | **0.677** |
| Loam (Missis- sippi) | Loam | 0.233 | 7.0 | 0.281 | 117 | 0.803 |
| Silty clay loam (Arizona) | Silty clay loam | 0.873 | 7.9 | 0.517 | 59 | 0.816 |
| Rendzina (Lor- raine) | Rendzina2 | 6.8-9.5 | 7.0 | 3.09 | 30.67 | 0.78 | Yes, Barrusio, E. (1991) |
| Humic Cambisol (Jura I) | Humic Cambisol2 | 10.0-14.1 | 6.5-7.0 | 5.03 | 25.73 | 0.80 |
| Mollic Cambisol (Jura II) | Mollic Cambisol2 | 4.5-9.2 | 6.8-7.8 | 4.99 | 39.42 | 0.72 |
| Calcic Cambisol (Ile de France) | Calcic Cambisol2 | 0.9-1.4 | 7.0-7.5 | 0.54 | 26.09 | 0.78 |
| Dystric Cambisol (Lorraine/Jura) | Dystric Cambisol2 | 1.4-2.6 | 4.5-5.4 | 1.19 | 40 | 0.73 |
| **Gleyic Cambisol (Lorraine)1** | **Gleyic Cambi- sol**2 | **1.3-1.5** | **6.2-6.5** | **1.27** | **57.14** | **0.68** |
| **Vertisols (Martinique)1** | **Vertisols**2 | **2.0-2.9** | **5.9-6.3** | **2.44** | **53.06** | **0.61** |
| Ferralsols (Brazil) | Fer- ralsols2 | 1.2-4.7 | 4.2-5.5 | 16.81 | 311.86 | 0.75 |
| Andosols (Martinique) | Andosols2 | 9.2-10.7 | 4.3-4.4 | 32.55 | 267.33 | 0.8 |
| Clay (Louisiana) | Clay | 2.093 | 7.3 | -4 | 58.1 | 0.83 | Yes, Cohen, S.P. |

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| 2,4-D | | | | | | | |
| Soil name | Soil type | OC (%) | pH (CaCl2) | KF  (mL/g) | KFOC  (mL/g) | 1/n (-) | Evaluated on EU level  Reference |
|  |  |  |  |  |  |  | (1991b) |
| Silty Clay Chro- moxerert (0-10cm) | Silty Clay | 2.573 | 7.9 | 0.82 | 31.916,7 | 0.91 | Yes, Hermosin,  M.C. (1991) |
| Clay Chromoxe- rert (10-20cm) | Clay | 1.403 | 7.8 | 0.37 | 26.466,7 | 0.99 |
| **Clay Chromoxe- rert (35-40cm)1** | **Clay** | **1.10**3 | **7.7** | **0.16** | **14.85**6,7 | **1.16** |
| Clay Pelloxerert I (0-20cm) | Clay | 0.973 | 7.6 | 0.62 | 68.796,7 | 0.90 |
| Clay Pelloxerert I (20-40cm) | Clay | 0.603 | 7.6 | 0.53 | 88.616,7 | 0.87 |
| Clay Pelloxerert I (120-150cm) | Clay loam | 0.513 | 7.8 | 0.18 | 35.266,7 | 0.95 |
| Clay  Pelloxerert II (0- 10cm) | Clay | 0.983 | 77 | 0.77 | 78.546,7 | 0.90 |
| Clay  Pelloxerert II (90- 100cm) | Clay | 0.843 | 8.3 | 0.30 | 35.656,7 | 1.02 |
| Clay loam Xerofluvent I (0-  10 cm) | Clay loam | 1.293 | 7.7 | 0.77 | 59.796,7 | 0.96 |
| Sandy loam Xerofluvent II (0- 10cm) | Sandy loam | 0.713 | 7.2 | 0.93 | 131.426,7 | 0.90 |
| Sandy loam Xerofluvent II (10-20cm) | Sandy loam | 0.373 | 6.9 | 0.78 | 382.426,7 | 0.97 |
| Sandy clay loam Xerofluvent III (0- 20cm) | Sandy clay loam | 2.733 | 6.3 | 3.08 | 112.976,7 | 0.88 |
| Loam Eutro- chrepts I (0-25 cm) | Loam | 1.863 | 6.5 | 1.43 | 77.036,7 | 0.90 |
| Loam Eutro- chrepts I (50-100 | Loam | 0.683 | 6.8 | 1.14 | 167.976,7 | 0.94 |

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| 2,4-D | | | | | | | |
| Soil name | Soil type | OC (%) | pH (CaCl2) | KF  (mL/g) | KFOC  (mL/g) | 1/n (-) | Evaluated on EU level  Reference |
| cm) |  |  |  |  |  |  |  |
| Loam Haploxeralf (0-10cm) | Loam | 2.413 | 6.5 | 1.64 | 68.116,7 | 0.93 |
| Clay loam Hap- loxeralf (10-40 cm) | Clay loam | 0.473 | 6.5 | 0.43 | 91.516,7 | 0.96 |
| Silty loam Hap- loxeralf (70-100 cm) | Silty loam | 0.283 | 6.5 | 0.41 | 147.256,7 | 0.82 |
| Silty loam Eutro- chrepts II (0-25 cm) | Silty loam | 2.523 | 7.8 | 2.20 | 87.396,7 | 0.92 |
| Clay loam Eutro- chrepts II (50-85 cm) | Clay loam | 0.493 | 7.7 | 0.68 | 139.566,7 | 0.96 |
| soil no. 205 | - | - | - | 2.23 | 116.857 | 0.95 |
| Silt loam (Illinois) | Silt loam | 2.23 | 5.9 | -4 | 41 | 0.896 | Yes,  McCoy, K.M. (1988) |
| **Silt loam (Cali- fornia)1** | **Silt Loam** | **0.22** | **7.5** | **-**4 | **31** | **0.632** |
| Loam (North Da- kota) | Loam | 3.08 | 6.8 | -4 | 35 | 0.930 |
| Clay (Mississippi) | Clay | 1.26 | 7 | -4 | 74 | 0.795 |
| Median (n=42) | | | | | 58.6 | - |  |
| Arithmetic mean (n=42) | | | | | - | 0.87 |  |
| pH-dependency: | | | | | No | | |

1 Soil excluded (in bold) from selection of modelling input parameters since 1/n is out of acceptable range (0.7-1.1)

2 FAO classification

3 Calculated; %OC = %OM / 1.724

4 Not given in study report

5 No soil property data given in study report

6 Corrected KFOC values given in Hermosin (1991) originally divided KOM by 1.724 instead of multiplying

7 Calculated; KFOC = KFOM × 1.724

**Table 8.5-2: Summary of soil adsorption/desorption for 2,4-DCP**

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| 2,4-DCP | | | | | | | |
| Soil Name | Soil Type | OC (%) | pH (-) | KF  (mL/g) | KFOC  (mL/g) | 1/n (-) | Evaluated on EU level  Reference |
| Clay loam (M800) | Clay loam | 1.3 | 7.1 | 10 | 765 | 0.85 | Yes,  Yoder, R.N. (2011) |
| Loamy sand (M801) | Loamy sand | 1.1 | 5.2 | 4 | 405 | 0.80 |
| Loam (M802) | Loam | 2.5 | 5.0 | 16 | 655 | 0.94 |
| Silt loam (M803) | Silt loam | 3.6 | 5.9 | 25 | 690 | 0.94 |
| Sandy loam (M804) | Sandy loam | 1.4 | 7.5 | 3 | 244 | 0.88 |
| Silt loam (M816) | Silt loam | 0.9 | 5.9 | 5 | 574 | 0.83 |
| Clay loam (M822) | Clay loam | 4.4 | 7.2 | 11 | 250 | 0.93 |
| Sand (Plain- field)1 | Sand |  |  |  | 368 | 0.906 | Yes, Fathulla, R (1996b) |
| Silty clay loam (Arizona)1 | Silty clay loam |  |  |  | 374 | 0.739 |
| Arithmetic mean (n=9) 1 | | | | | - | 0.868 |  |
| Geomean mean (n=9) 1 | | | | | 444 | - |  |
| pH-dependency: | | | | | No | | |

1 Two additional soils were given the EFSA Conclusion (2014;12(9):3812, revised 21 March 2017). These studies are considered complementary (RAR Addendum (2014), Vol. 3, Annex B.8), and the arithmetic mean of KFOC = 512 L/kg and 1/n = 0.88 was used in modelling to remain consistent with the previous EU agreed endpoints (EFSA Journal 2014; 12(9):3812, revised 21 March 2017, page 54 of 81).

**Table 8.5-3: Summary of soil adsorption/desorption for 2,4-DCA**

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| 2,4-DCA | | | | | | | |
| Soil Name | Soil Type | OC (%) | pH (CaCl2) | KF  (mL/g) | KFOC  (mL/g) | 1/n (-) | Evaluated on EU level  Reference |
| Clay loam (M800) | Clay loam | 1.3 | 7.1 | 18 | 1386 | 0.85 | Yes, |

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| 2,4-DCA | | | | | | | |
| Soil Name | Soil Type | OC (%) | pH (CaCl2) | KF  (mL/g) | KFOC  (mL/g) | 1/n (-) | Evaluated on EU level  Reference |
| Loamy sand (M801) | Loamy sand | 1.1 | 5.2 | 18 | 1630 | 0.93 | Yoder, R.N. (2011) |
| Loam (M802) | Loam | 2.5 | 5.0 | 21 | 841 | 0.93 |
| Silt loam (M803) | Silt loam | 3.6 | 5.9 | 27 | 746 | 0.93 |
| Sandy loam (M804) | Sandy loam | 1.4 | 7.5 | 12 | 836 | 0.95 |
| Silt loam (M816) | Silt loam | 0.9 | 5.9 | 10 | 1137 | 0.92 |
| Clay loam (M822) | Clay loam | 4.4 | 7.2 | 27 | 622 | 0.92 |
| Sand (Plainfield) 1 | Sand | 0.46 | 5.6 | - | 436 | 0.955 | Yes, Fathulla, R (1996c), |
| Sandy loam (Cali- fornia) 1 | Sandy loam | 0.58 | 6.7 | - | 667 | 0.978 |
| Silty clay loam (Arizona) 1 | Silty clay loam | 0.87 | 7.9 | - | 616 | 0.809 |
| Arithmetic mean (n=9) 1 | | | | | - | 0.917 |  |
| Geomean mean (n=9) 1 | | | | | 827 | - |  |
| pH-dependency: | | | | | No | | |

1 Three additional soils were given the EFSA Conclusion (2014;12(9):3812, revised 21 March 2017). These studies are considered complementary (RAR Addendum (2014), Vol. 3, Annex B.8), and the arithmetic mean of KFOC = 1028 L/kg and 1/n = 0.92 was used in modelling to remain consistent with the previous EU agreed endpoints (EFSA Journal 2014; 12(9):3812, revised 21 March 2017, page 55 of 81).

The adsorption of 4-CP was investigated in a new study (Swales, 2015b) which had not previously been evaluated at an EU level. Results for 4-CP are shown in [Table 8.5-4.](#_bookmark14) A summary of the study is given in Appendix 2.3.

**Table 8.5-4: Summary of soil adsorption/desorption for 4-CP**

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| 4-CP | | | | | | | |
| Soil Name | Soil Type | OC (%) | pH (CaCl2) | KF  (mL/g) | KFOC  (mL/g) | 1/n (-) | Evaluated on EU level  Reference |
| Empingham | Clay loam | 3.6 | 7.6 | 5.82 | 162 | 0.7564 | No,  Swales, S.E.; (2015b) |
| Warsop | Loamy sand | 0.7 | 4.1 | 1.78 | 254 | 0.7888 |

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| 4-CP | | | | | | | |
| Soil Name | Soil Type | OC (%) | pH (CaCl2) | KF  (mL/g) | KFOC  (mL/g) | 1/n (-) | Evaluated on EU level  Reference |
| Kenslow | Loam | 3.8 | 5.5 | 7.07 | 186 | 0.8481 |  |
| Brierlow | Silt loam | 2.4 | 6.1 | 3.72 | 155 | 0.7581 |
| LAD-SCL-PF | Clay/clay loam | 0.9 | 8.1 | 1.4 | 155 | 0.8108 |
| Arithmetic mean (n=5) | | | | | 182 | 0.792 |  |
| pH-dependency: | | | | | No | | |

The adsorption of 1,2,4-benzenetriol was investigated in a new study (Swales, 2015c) which had not previously been evaluated at an EU level. A summary of the study is given in Appendix 2.4. How- ever, the results of the preliminary tests (solubility, adsorption to containers and stability) indicated that the 1,2,4-benzenetriol was not stable in aqueous media. Therefore, adsorption characteristic of 1,2,4-benzenetriol could not be determined as it is not sufficiently stable to perform the test by ana- lysing both aqueous and soil phases. In addition, 1,2,4-benzenetriol cannot be perceived to be an en- vironmental hazard in aqueous solution due to the rapid hydrolysis

## Column leaching (KCP 9.1.2.1)

Column leaching studies were not required for 2,4-D during the EU review since reliable adsorption coefficient values are available from the adsorption/desorption studies. No additional studies have been performed.

## Lysimeter studies (KCP 9.1.2.2)

A lysimeter study with 2,4-D was previously 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.

## Field leaching studies (KCP 9.1.2.3)

Field leaching studies were not required for 2,4-D during the EU review since reliable adsorption co- efficient values are available from the adsorption/desorption studies. No additional studies have been performed.

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

The fate and behaviour of 2,4-D and the metabolites 2,4-DCP in water and sediment systems are pre- sented in the corresponding document of the EU review dossiers of 2,4-D (EFSA Conclusion (2014;12(9):3812, revised 21 March 2017)).

Studies showed that 2,4-D is stable to hydrolysis at 50°C in the range of pH 4-9. According to the available studies, aqueous photolysis of 2,4-D, under normal environmental conditions, will usually take place at a slower rate than the biological degradation in water. However, in an aqueous photoly- sis study, presented in the dossier submitted for the first approval, a major photolysis metabolite, 1,2,4-benzenetriol (max. 31.7% AR at the end of the study), was identified. Since it is not possible to completely exclude the formation of this metabolite in the environment it should be considered in the aquatic exposure and risk assessment.

The endpoints are summarized in [Table 8.6-1](#_bookmark19) to [Table 8.6-2.](#_bookmark20)

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

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| 2,4-D Distribution (max. | | water 100 % after 0 days, and max sediment 24.7 % after 7 days.) | | | | | | | |
| Water/sediment system | pH water/ sed. | Temp  ℃ | DegT50  / DegT90 whole syst.  (d) | Kinetic, Fit | DissT50  / DissT90 water  (d) | Kinetic, Fit | DissT50  / DissT90 sed.  (d) | Kinetic, Fit | Evaluated on EU level y/n/ Reference |
| Pond system | 6.5/6.4 | 20 | 18/60 | SFO | 12.6/ | SFO | 9.8/32.6 | SFO | Yes, |
| (loamy sand) |  |  |  |  | 41.9 |  |  |  | Laughlin, L.A. |
|  |  |  |  |  |  |  |  |  | (2011) |
| Pond system (silt loam) | 8.3/7.8 | 20 | 6.4/21.1 | SFO | 4.7/1  5.7 | SFO | - | - |
| Pond system  (silty clayloam) | 6.9/7.8 | 25 | 291 (52)/96.3 | SFO | - | SFO | - | - | Yes,  Concha, N (1993) |
| Geometric mean (n=3) | | | 18.16/49.6 | - | 7.7 | - | 9.8 | - | |

1 DT50 normalised to 20 ℃ = 52d

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

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| 2,4-DCP Distribution (max. water 2.6 % after 26 days, and max. | | | | | | sediment | 31.8 % after | 13 days.) | |
| Water/sediment system | pH water/ sed. | Temp  ℃ | DegT50  / DegT90 whole syst.  (d) | Kinetic, Fit | DissT50  / DissT90 water  (d) | Kinetic, Fit | DissT50 / DissT90 sed.  (d) | Kinetic, Fit | Evaluated on EU level y/n/ Reference |
| Pond system (loamy sand) | 6.5/6.4 | 20 | 1000 1,2 | SFO | - | - | 197.2/654.7 | SFO | Yes, Laughlin,  L.A. (2011) |
| Pond system (silt loam) | 8.3/7.8 | 20 | 10.8 3 | SFO | - | - | 11/36.3 | FOMC |
| Geometric mean (n=3) | | | 103.9 | - | - | - | 46.6 | - | |

1 No acceptable fit could be derived

2 Default value

3 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-DCP | Max. in water/sediment 32.1% | Yes,  EFSA Conclusion (EFSA Journal 2014; 12(9):3812,  revised 21 March 2017) |

|  |  |  |
| --- | --- | --- |
| 2,4-DCA | Max. in water/sediment 5.3% | Yes,  EFSA Conclusion (EFSA Journal 2014; 12(9):3812,  revised 21 March 2017) |
| 4-CP | Max. in water/sediment 6.9% | Lewis, C.J. (2011) |
| 1,2,4-benzene- triol | Max. in water/sediment 31.7% | EFSA Conclusion (EFSA Journal 2014; 12(9):3812,  revised 21 March 2017 |

## Predicted Environmental Concentrations in soil (PECSOIL) (KCP 9.1.3)

|  |
| --- |
| **Review Comments:**  The PECsoil calculations for 2,4-D and its metabolites: 2,4-DCP, 2,4-DCA, 4-CP were provided by the Applicant and are considered acceptable. The EU agreed endpoints were used for PECsoil calculations with exception of 2,4-D soil DT50 of 66.6 days and 4-CP the soil DT50 of 0.69 days. Those values are considered acceptable.  The PECsoil reported below can be used for the risk assessment of the non-target organisms. Please refer to Section B9. |

## Justification for new endpoints

The soil PEC values for 2,4-D and its soil metabolites 2,4-DCP, 2,4-DCA, 4-CP have been calculated using the maximum DT50 values established in either the EU review (EFSA Journal 2014; 12(9):3812, revised 21 March 2017) or new studies provided in the Appendix of this document.

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

**Table 8.7-1: Input parameters related to application for PECsoil calculations**

|  |  |
| --- | --- |
| Use No. | 1 |
| Crop | Spring cereals |
| Application rate (g a.s./ha) | 750 g a.s./ha |
| Number of applications/interval | 1/- |
| Crop interception (%)1 | 0 |
| Depth of soil layer (relevant for plateau concentra- tion) (cm) | 5 |

1 FOCUS groundwater interception values (FOCUS, 2021[1](#_bookmark25))

The Predicted Environmental Concentrations in soil for 2,4-D were calculated using the methods described in ‘Soil persistence models and EU registration’ – the final report of the soil modelling work group of FOCUS (February, 1997) and the following equation:

A[g/ha]  (1 – F)

Where:

A = Application rate

PEC (mg/kg) =

100 × d [cm]  ρ [g/cm3]

F = Fraction intercepted by crop

d = Depth of field soil layer (5 cm)

ρ = Dry bulk density (1.5 g/cm3)

1 FOCUS, 2021, Generic Guidance for Tier 1 FOCUS Ground Water Assessments Version 2.3, June 2021.

The calculation assumes an even distribution to a depth of 5 cm with a soil bulk density of 1.5 g/cm3. The FOCUS groundwater interception values (FOCUS, 2021[1](#_bookmark24)) were used where appropriate along with the maximum laboratory DT50 values established in the EU review.

The PEC at specific times (t) after the final application is given by:

PEC(mg/kg) = Initial PECS after last application × e-kt

Where:

k = first order degradation/dissipation rate constant (ln(2)/half-life)

The maximum (‘moving window’) time weighted average (TWA) PEC values are found by calculating a set of TWA PEC over a time window that is moved along the time axis. The average PEC within a day is calculated by:

Average PEC over a day (mg/kg) =

Actual PEC at start of day × (1-e-k) k

The TWA over the moving window is calculated from the simple numerical average of these daily values.

**Table 8.7-2: Input parameter for active substance(s) for PECsoil calculation**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Compound | Molecular weight (g/mol) | Max. occurrence (%) | DT50  (days) | Value in accord- ance with EU end- point y/n/  Reference |
| 2,4-D | 221 | - | 66.6 (SFO nor- malised worst- case, laboratory study)1 | Yes,  Cohen, S.P. (1991a) |

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

**Table 8.7-3: PECsoil for 2,4-D on spring cereals (1 x 750 g a.s./ha)**

|  |  |  |  |
| --- | --- | --- | --- |
| PECsoil (mg/kg) | | Spring cereals | |
| Single application | |
| Actual | TWA |
| Initial | | 1.000 | - |
| Short term | 24h | 0.990 | 0.995 |
| 2d | 0.979 | 0.990 |
| 4d | 0.959 | 0.979 |

|  |  |  |  |
| --- | --- | --- | --- |
| Long term | 7d | 0.930 | 0.964 |
| 14d | 0.864 | 0.931 |
| 21d | 0.804 | 0.898 |
| 28d | 0.747 | 0.867 |
| 48d | 0.607 | 0.787 |
| 100d | 0.353 | 0.621 |
| Plateau concentration (5cm) after year 2 | | - | - |
| PECaccumulation  (PECactual +PECsoil plateau) | | - | - |

As the DT90 of 2,4-D in soil is <365 days, an accumulation in soil calculation was not required

**PECsoil of metabolites**

Predicted Environmental Concentrations in soil for the metabolites 2,4-DCP, 2,4-DCA and 4-CP were obtained using pseudo application rates using correction factors according to the following equations:

Ametabolite (g/ha) = Aparent × Where:

maximum metabolite observed (%)

100 × molar correction factor

Aparent = Total application rate of the parent, adjusted for crop interception (g a.s./ha) Ametabolite = Equivalent application rate of the metabolite (g a.s./ha)

Molar correction factor =

molecular weight of metabolite (g/mol) molecular weight of parent (g/mol)

**Table 8.7-4: Input parameter for 2,4-D metabolites for PECsoil calculation**

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Compound | Molecular weight (g/mol) | Molar  correction fraction [-] | Max.  occurrence (%) | Worst-case non- normalised persistence soil DT50  (days) | Pseudo application rate (g a.s./ha) | Value in accordance with EU endpoint y/n/  Reference |
| 2,4-DCP | 163 | 0.738 | 8.7 | 14.0 | 48.15 | Y |
| 2,4-DCA | 177 | 0.801 | 15 | 15.4 | 90.11 | Y,  Liu, D.  (2011) |
| 4-CP1 | 128.6 | 0.582 | 33 | 0.69 | 144.05 | N, Swales, S.E.;  Crabtree, G.A. |

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
|  |  |  |  |  |  | (2015a) |

1 Note that anaerobic conditions leading to the formation of 4-CP in soil are not expected when used according to the intended GAP, however it is included in the risk assessment for the avoidance of any doubt.

**Table 8.7-5: PECsoil for 2,4-DCP on spring cereals (1 x 750 g a.s./ha)**

|  |  |  |  |
| --- | --- | --- | --- |
| PECsoil (mg/kg) | | Spring cereals | |
| Single application | |
| Actual | TWA |
| Initial | | 0.0642 | - |
| Short term | 24h | 0.0611 | 0.0626 |
| 2d | 0.0581 | 0.0611 |
| 4d | 0.0527 | 0.0582 |
| Long term | 7d | 0.0454 | 0.0543 |
| 14d | 0.0321 | 0.0463 |
| 21d | 0.0227 | 0.0399 |
| 28d | 0.0161 | 0.0347 |
| 48d | 0.0060 | 0.0245 |
| 100d | 0.0005 | 0.0129 |
| Plateau concentration (5cm) | | - | - |
| PECaccumulation  (PECact +PECsoil plateau) | | - | - |

**Table 8.7-6: PECsoil for 2,4-DCA on spring cereals (1 x 750 g a.s./ha)**

|  |  |  |  |
| --- | --- | --- | --- |
| PECsoil (mg/kg) | | Spring cereals | |
| Single application | |
| Actual | TWA |
| Initial | | 0.120 | - |
| Short term | 24h | 0.115 | 0.117 |
| 2d | 0.110 | 0.115 |
| 4d | 0.100 | 0.110 |
| Long term | 7d | 0.088 | 0.103 |
| 14d | 0.064 | 0.089 |
| 21d | 0.047 | 0.078 |
| 28d | 0.034 | 0.068 |
| 48d | 0.014 | 0.049 |
| 100d | 0.001 | 0.026 |
| Plateau concentration (5cm) | | - | - |
| PECaccumulation  (PECact +PECsoil plateau) | | - | - |

**Table 8.7-7: PECsoil for 4-CP on spring cereals (1 x 750 g a.s./ha)**

|  |  |  |  |
| --- | --- | --- | --- |
| PECsoil (mg/kg) | | Spring cereals | |
| Single application | |
| Actual | TWA |
| Initial | | 0.192 | - |
| Short term | 24h | 0.070 | 0.121 |
| 2d | 0.026 | 0.083 |
| 4d | 0.003 | 0.047 |
| Long term | 7d | 0.000 | 0.027 |
| 14d | 0.000 | 0.014 |
| 21d | 0.000 | 0.009 |
| 28d | 0.000 | 0.007 |
| 48d | 0.000 | 0.004 |
| 100d | 0.000 | 0.002 |
| Plateau concentration (5cm) | | - | - |
| PECaccumulation  (PECact +PECsoil plateau) | | - | - |

## Predicted Environmental Concentrations in groundwater (PECGW) (KCP 9.2.4)

|  |
| --- |
| **Review Comments:**  The PECGW calculations for 2,4-D and its metabolites 2,4-DCP, 2,4-DCA and 4-CP were provided by the applicant and are considered acceptable.  The EU agreed endpoints, derived from the datasets presented in the EFSA Journal 2014; 12(9):3812, revised 21 March 2017, were used, with exceptions of the 2,4-D the KFOC of 58.6 mL/g and soil DT50 of 4.14 days and 4-CP mean DT50 of 0.22 days. Those values were accepted in other XXXX products e.g. Tricera.  The results of FOCUS groundwater calculation for 2,4-D and its metabolites 2,4-DCP, 2,4-DCA and 4-CP indicated that PECGW values do not exceed the regulatory trigger of 0.1 µg/L at 1 m depth in any of the scenarios. |

## Justification for new endpoints

The PEC of 2,4-D and its metabolites 2,4-DCP, 2,4-DCA and 4-CP in ground water (PECGW) have been assessed with either the EU agreed endpoints (EFSA Journal 2014; 12(9):3812, revised 21 March 2017) or new studies provided in the Appendix.

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

The following groundwater modelling report on 2,4-D and the soil metabolites 2,4-DCP, 2,4-DCA and 4-CP has not previously been reviewed and is provided in support of this assessment.

|  |  |
| --- | --- |
| Report: | CP 9.2.4.1/01, Verity, C. (2022) |
| Title: | A modelling assessment of 2,4-D and its metabolites applied to spring cereals in groundwater in the central zone |
| Document No.: | Report No. 0572580-GW2 |
| Guidelines: | FOCUS (2021)1  EC (2018)[2](#_bookmark30) |
| GLP: | Not applicable |

The representative uses of the 2,4-D 95 SP formulation are summarised in [Table 8.8-1.](#_bookmark29)

**Table 8.8-1: Input parameters related to application for PECGW calculations**

|  |  |
| --- | --- |
| Use No. | 1 |
| Crop | Spring cereals |
| Application rate (g a.s./ha) | 1 x 750 g a.s./ha |
| Number of applications/interval (d) | 1 / - |
| Crop interception (%) | 0%1 |
| Frequency of application | Annual |
| Models used for calculation | FOCUS PEARL v5.5.5, FOCUS PELMO v6.6.4 |

1 Crop interception (%) derived from Generic Guidance for Tier 1 FOCUS Ground Water Assessments v2.3 (2021[1](#_bookmark24))

Simulations were performed to cover the application regime mentioned above using all appropriate FOCUS scenarios in PEARL (version 5.5.5) and PELMO (version 6.6.4). According to Central Zone guidance (EC 2018) only relevant scenarios to the central zone are reported herein. The application timing in the simulations was set using absolute timings (Klein, 2019 ,AppDate 3.06) and are pre- sented in [Table 8.8-2.](#_bookmark31)

2 EC (2018) Working Document of the Central Zone in the Authorisation of Plant Protection Products – Section 8 – Environmental Fate and Behaviour. Version 1 rev. June 2018.

**Table 8.8-2: Application dates used for groundwater risk assessment**

|  |  |
| --- | --- |
| Scenario | Actual application date (absolute) |
| Spring cereals 1 x 750 g a.s./ha BBCH 15-25 | |
| Châteaudun (C) | 20-March (79) |
| Hamburg (H) | 08-April (98) |
| Kremsmünster (K) | 08-April (98) |
| Okehampton (N) | 07-April (97) |
| Porto (O) | 20-March (79) |

Values in parentheses are Julian Days

## 8.8.2.1 2,4-D and its metabolites

The input parameters used in the modelling for 2,4-D and its metabolites 2,4-DCP, 2,4-DCA, 4-CP are summarised in [Table 8.8-3](#_bookmark33) and [Table 8.8-4.](#_bookmark34) Endpoints were taken from the EFSA Conclusion (EFSA Journal 2014; 12(9):3812, revised 21 March 2017), RAR Addendum (2014), Vol. 3, Annex

B.8 and new metabolite (4-chlorophenol) studies.

In the EFSA conclusion, a data gap was identified regarding the anaerobic metabolite 4-CP. More information was needed to assess the exposure and risk to the different environmental compartments. In order to address the data gap new studies on soil degradation were performed for 2,4-D and anaer- obic metabolite 4-CP as well as soil adsorption/desorption studies for 4-CP (Swales & Crabtree, 2015a and 2015b). These studies have not previously been reviewed at an EU level. Summaries of these study reports are included in Appendix 2.

Anaerobic conditions would not be expected to occur during or shortly after the application of 2,4-D to spring cereals according to the recommended GAP, therefore it is not necessary to consider the an- aerobic metabolite 4-CP in surface water and sediment. Nevertheless, for the avoidance of any doubt, a risk assessment for 4-CP has been included here. The inputs parameters for 4-CP are shown in [Ta-](#_bookmark34) [ble 8.8-4.](#_bookmark34)

**Table 8.8-3: Input parameters related to active substance 2,4-D PECgw calculations**

|  |  |  |
| --- | --- | --- |
| Parameter | Value | Remarks |
| **Physico-chemical** | | |
| Molecular weight (g/mol) | 221 | EFSA Conclusion (EFSA Journal 2014; 12(9):3812, revised 21 March 2017, page  24 of 81). |
| Water solubility at 20°C (mg/L) | 24300 | EFSA Conclusion (EFSA Journal 2014; 12(9):3812, revised 21 March 2017, page  25 of 81) 1 |
| Vapour pressure at 20°C (Pa) | 9.9 x 10-6 | EFSA Conclusion (EFSA Journal 2014; 12(9):3812, revised 21 March 2017, page  51 of 81) 2 |
| Molar enthalpy of vaporization (kJ/mol) | 95 | FOCUS recommendation |
| Diffusion coefficient in water (m²/d) | 4.3 x 10-5 (20°C) (PEARL) |
| Diffusion coefficient in gas (m²/d) | 0.43 (20°C) |
| **Degradation in soil** | | |
| DT50 soil (d) | 4.14 | Re-normalized SFO lab DT50; Q10 = 2.58 20°C, pF2. (Cohen. S.P. (1991); Liu, D. (2011)).3 |
| Temperature correction function  Reference temperature (°C) PELMO: Q10 (-)  PEARL: (kJ/mol) | 20  2.58  65.4 | FOCUS recommendation |
| Moisture correction function  PEARL/PELMO: moisture exponent (-) | pF 2  0.7 |
| **Sorption to soil** | | |
| KFOC (mL/g) | 58.6 | EFSA Conclusion (EFSA Journal 2014; 12(9):3812, revised 21 March 2017, page  51 of 81)  Median (n = 42) 4 |
| KFOM (mL/g) | 34.0 | Calculated KFoc / 1.724 |
| Freundlich exponent 1/n (-) | 0.87 | EFSA Conclusion (EFSA Journal 2014; 12(9):3812, revised 21 March 2017, page  51 of 81)  Arithmetic mean (n = 42) d |

|  |  |  |
| --- | --- | --- |
| Parameter | Value | Remarks |
| **Crop/management related parameters** | | |
| Crop uptake factor (-) | 0.0 | Default |
| Washoff Factor (1/m) (PEARL) | 0.0001 | Default |
| Foliar DT50 (d) | 10 | Default |

1 Note that the value presented in the EU review (EFSA conclusion (2014) 12(9):3812, revised 21 March 2017) was incorrectly reported as occurring at 25°C.

2 Note that the value presented in the EU review (EFSA conclusion (2014) 12(9):3812, revised 21 March 2017) was incorrectly reported. A comment was added on page 51 that for further calculations the actual measured value for 2,4-D of 9.9x10-6 Pa at 20℃ is to be used.

3 Recalculated geometric mean DT50 after moisture normalization of the Mississippi silt loam (20°C/pF2). See detailed discussion in section [8.3.1](#_bookmark4) for more detail.

4 Incorrect value presented in the original EFSA Conclusion (2014;12(9):3812); KFOC and 1/n was incorrectly reported for 7 soils. Endpoints are based on corrected data derived from RAR Addendum (2014, Vol. 3, An- nex B) and in the revised EFSA Conclusion (revised 21 March 2017).

**Table 8.8-4: Input parameters related to active substance 2,4-D metabolites PECgw calcula- tions**

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Parameter | 2,4-DCP | | 2,4-DCA | | 4-CP | |
| Value | Remarks | Value | Remarks | Value | Remarks |
| Molecular | 163 | EFSA Conclusion | 177 | EFSA Conclusion | 128.6 | Euro Chlor |
| weight (g/mol) |  | (EFSA Journal |  | (EFSA Journal |  | (2002): Euro |
|  |  | 2014; 12(9):3812, |  | 2014; 12(9):3812, |  | Chlor Risk As- |
|  |  | revised 21 March |  | revised 21 March |  | sessment for the |
|  |  | 2017, page 54 of |  | 2017, page 55 of |  | Marine Environ- |
|  |  | 81) |  | 81) |  | ment. |
|  |  |  |  |  |  | OSPARCOM Re- |
|  |  |  |  |  |  | gion – North Sea. |
|  |  |  |  |  |  | Monochlorophe- |
|  |  |  |  |  |  | nols. February |
|  |  |  |  |  |  | 2002.[3](#_bookmark35) |
| Water solubility | 4870 |  | 96.3 |  | 27100 | Euro Chlor |
| at 20°C (mg/L) |  |  |  |  |  | (2002): Euro |
|  |  |  |  |  |  | Chlor Risk As- |
|  |  |  |  |  |  | sessment for the |
|  |  |  |  |  |  | Marine Environ- |
|  |  |  |  |  |  | ment. |
|  |  |  |  |  |  | OSPARCOM Re- |
|  |  |  |  |  |  | gion – North Sea. |
|  |  |  |  |  |  | Monochlorophe- |
|  |  |  |  |  |  | nols. February |
|  |  |  |  |  |  | 2002.3 |
| Vapour pressure at 20°C (Pa) | 0 | Default value of parent (FOCUS, 2014) | 0 | Default value of parent (FOCUS, 2014) | 0 | Default value of parent (FOCUS, 2014) |

3 Euro Chlor (2002): [https://www.eurochlor.org/wp-content/uploads/2019/04/8-11-4-14\_marine\_ra\_monochlo-](https://www.eurochlor.org/wp-content/uploads/2019/04/8-11-4-14_marine_ra_monochlorophenols.pdf) [rophenols.pdf](https://www.eurochlor.org/wp-content/uploads/2019/04/8-11-4-14_marine_ra_monochlorophenols.pdf) (accessed September 2022).

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Parameter | 2,4-DCP | | 2,4-DCA | | 4-CP | |
| Value | Remarks | Value | Remarks | Value | Remarks |
| KFOC (mL/g) | 512 | EFSA Conclusion | 1028 | EFSA Conclusion | 182 | Calculated based |
|  |  | (EFSA Journal |  | (EFSA Journal |  | on Swales, S.E. |
|  |  | 2014; 12(9):3812, |  | 2014; 12(9):3812, |  | (2015b) |
|  |  | revised 21 March |  | revised 21 March |  | (geometric mean |
|  |  | 2017, page 54 of |  | 2017, page 55 of |  | n =5) |
|  |  | 81); arithmetic |  | 81); arithmetic |  |  |
|  |  | mean (n = 7) |  | mean (n = 7) |  |  |
| KFOM (mL/g) | 297 | Calculated KFoc / 1.724 | 596 | Calculated KFoc / 1.724 | 105 | Calculated KFoc / 1.724 |
| 1/n | 0.88 | EFSA Conclusion (EFSA Journal 2014; 12(9):3812,  revised 21 March  2017, page 57 of | 0.92 | EFSA Conclusion (EFSA Journal 2014; 12(9):3812,  revised 21 March  2017, page 57 of | 0.792 | Calculated based on Swales, S.E. (2015b); (arith- metic mean n =5) |
|  |  | 81) |  | 81) |  |  |
|  |  | (arithmetic mean n |  | (arithmetic mean n |  |  |
|  |  | = 7) |  | = 7) |  |  |
| DT50 soil @ 20°C & pF2  (days) | 7.0 | EFSA Conclusion (EFSA Journal 2014; 12(9):3812,  revised 21 March  2017, page 55 of | 10.4 | EFSA Conclusion (EFSA Journal 2014; 12(9):3812,  revised 21 March  2017, page 55 of | 0.22 | Calculated based on Swales, S.E. (2015ba); (geo- metric mean n =4) |
|  |  | 81) |  | 81) |  |  |
|  |  | (geomean, lab, |  | (geomean, lab, |  |  |
|  |  | normalised, n = 3) |  | normalised, n = 3) |  |  |
| Plant uptake fac- tor | 0 | Default value | 0 | Default value | 0 | Default value |
| Formation frac- | 1.0 | EFSA Conclusion | 1.0 | EFSA Conclusion | 1.0 | EFSA Conclusion |
| tion |  | (EFSA Journal |  | (EFSA Journal |  | (EFSA Journal |
|  |  | 2014; 12(9):3812, |  | 2014; 12(9):3812, |  | 2014; 12(9):3812, |
|  |  | revised 21 March |  | revised 21 March |  | revised 21 March |
|  |  | 2017) – represents |  | 2017) – represents |  | 2017) – repre- |
|  |  | worst case |  | worst case |  | sents worst case |
| Transformation Rate | N/A | Formation fraction of 1.0. None to sink. | N/A | Formation fraction of 1.0. None to sink. | N/A | Formation frac- tion of 1.0. None to sink. |
| Washoff Factor (1/m) (PEARL) | 0.0001 | Default | 0.0001 | Default | 0.0001 | Default |
| Foliar DT50 (d) | 10 | Default | 10 | Default | 10 | 0.0001 |

The PECGW (80th percentile annual average leachate concentration at 1 m soil depth) as modelled us- ing FOCUS PEARL (version 5.5.5) and PELMO (version 6.6.4), for 2,4-D and its metabolites for an annual application rate to the crops in the proposed GAP are presented in [Table 8.8-5](#_bookmark36) 5 and [Ta-](#_bookmark37)

[ble 8.8-6.](#_bookmark37) Modelling with FOCUS MACRO (version 5.5.4) was not performed as PECGW of all sub- stances in all modelled scenarios were <0.001 µg/L/.

**Table 8.8-5: PECgw for 2,4-D and metabolites on spring cereals (with FOCUS PEARL 5.5.5)**

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Crop | Scenario | 80th Percentile PECgw at 1 m Soil Depth (g/L) | | | |
| 2,4-D | 2,4-DCP | 2,4-DCA | 4-CP |
| Spring ce- | Châteaudun | <0.001 | <0.001 | <0.001 | <0.001 |
| reals |  |  |  |  |  |
| Hamburg | <0.001 | <0.001 | <0.001 | <0.001 |
| 1 x 750 g |
| a.s./ha |
| Kremsmünster | <0.001 | <0.001 | <0.001 | <0.001 |
| BBCH |
| 15-25 | Okehampton | <0.001 | <0.001 | <0.001 | <0.001 |
|
|  | Porto | <0.001 | <0.001 | <0.001 | <0.001 |

**Table 8.8-6: PECgw for 2,4-D and metabolites on spring cereals (with FOCUS PELMO 6.6.4)**

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Crop | Scenario | 80th Percentile PECgw at 1 m Soil Depth (g/L) | | | |
| 2,4-D | 2,4-DCP | 2,4-DCA | 4-CP |
| Spring ce- | Châteaudun | <0.001 | <0.001 | <0.001 | <0.001 |
| reals |  |  |  |  |  |
| Hamburg | <0.001 | <0.001 | <0.001 | <0.001 |
| 1 x 750 g |
| a.s./ha |
| Kremsmünster | <0.001 | <0.001 | <0.001 | <0.001 |
| BBCH |
| 15-25 | Okehampton | <0.001 | <0.001 | <0.001 | <0.001 |
|
|  | Porto | <0.001 | <0.001 | <0.001 | <0.001 |

Simulations of the leaching behaviour of 2,4-D and its soil metabolites 2,4-DCP, 2,4-DCA and 4-CP were conducted with the FOCUS PEARL (version 5.5.5) and FOCUS PELMO (version 6.6.4) groundwater models and relevant scenarios. The simulations were based on application of the plant protection product containing 2,4-D as an active substance.

The predicted 80th percentile average annual concentrations for 2,4-D following application to spring cereals were lower than the 0.1 µg/L regulatory threshold in groundwater at 1 m depth for all sce- nario combinations.

The PECGW values for metabolites 2,4-DCA, 2,4-DCP and 4-CP following annual application 2,4-D to crops were also lower than the 0.1 µg/L regulatory threshold in groundwater at 1 m depth for all the available scenario combinations.

These results demonstrate that 2,4-D 95 SP formulation can be used safely as proposed without the risk of 2,4-D and its metabolites 2,4-DCA, 2,4-DCP and 4-CP exceeding acceptable levels in ground- water.

## Predicted Environmental Concentrations in surface water (PECSW) (KCP 9.2.5)

|  |
| --- |
| **Review Comments:**  The PECSW calculations for 2,4-D and its metabolites 2,4-DCP, 2,4-DCA and 4-CP were provided by the Applicant and are considered acceptable.  The EU agreed endpoints, derived from the datasets presented in the EFSA Journal 2014; 12(9):3812, revised 21 March 2017, were used, with exceptions of the 2,4-D soil DT50 of 4.14 days and 4-CP mean DT50 of 0.22 days. Those values were accepted in other XXXX products e.g. Tricera.  Additional calculations for substitute crop were required, as for all crops the appropriate for Poland scenarios must be included (for surface water: D3, D4, R1). Thus, the Applicant was requested to perform calculation for oilseed rape spring at BBCH 09 in order to present the necessary R1 scenario.  The PECsw reported below can be used for the risk assessment for aquatic organisms. Please refer to section 9. |

## Justification for new endpoints

The PEC of 2,4-D and its metabolites 2,4-DCP, 2,4-DCA and 4-CP in both surface water and sedi- ment (PECSW and PECSED) have been assessed with either the EU agreed endpoints (EFSA Journal 2014; 12(9):3812, revised 21 March 2017) or new studies provided in the Appendix.

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

The 2,4-D 95 SP formulation use on spring cereals is included in the GAP for this product authorisa- tion application. This use has been evaluated in a new modelling assessment. The following surface water modelling report on 2,4-D and the soil metabolites 2,4-DCP, 2,4-DCA, 4-CP and 1,2,4-ben- zenetriol has not previously been reviewed and is provided in support of this assessment.

|  |  |
| --- | --- |
| **Report:** | ~~CP 9.2.4.1/01, Verity, C.; Lee, R (2022)~~ |
| **Title:** | ~~A modelling assessment of 2,4-D and its metabolites applied to spring cereals in surface water in the central zone~~ |
| **Document No.:** | ~~Report No. 0572580-SW3~~ |
| **Guidelines:** | ~~FOCUS (2001) FOCUS (2015)~~ |
| **GLP:** | ~~Not applicable~~ |

|  |  |
| --- | --- |
| **Report:** | CP 9.2.5/01, Verity, C.; Lee, R (2023) |
| **Title:** | A modelling assessment of 2,4-D and its metabolites applied to spring cereals in surface water in the central zone |
| **Document No.:** | Report No. 0572580-SW4 |
| **Guidelines:** | FOCUS (2001)[4](#_bookmark41)  FOCUS (2015)[5](#_bookmark42) |
| **GLP:** | Not applicable |

The potential for 2,4-D and its metabolites (2,4-DCP, 2,4-DCA, 4-CP and 1,2,4-benzenetriol) to reach surface water and sediment was examined following application made in accordance with the supported uses in the GAP. Simulations were based on field application to spring cereals using the FOCUS suite of surface water models.

In order to present the necessary R1 scenarios, oilseed rape spring was modelled at Step 3 as a surro- gate crop for spring cereals. As an earlier growth stage is used (BBCH 09), the interception and ap- plication timing is adequate to cover the application to spring cereals.

The application of 2,4-D to spring cereals based on the GAP has been summarised in [Table 8.9-1.](#_bookmark43)

4 FOCUS (2001). FOCUS surface water scenarios in the EU evaluation process under 91/414/EEC. Report of the FOCUS working group on surface water scenarios. EC document reference SANCO/4802/2001-rev.2, 245pp

5 FOCUS (2015). Generic Guidance for FOCUS surface water Scenarios. Version 1.4. May 2015.

**Table 8.9-1: Supported uses of 2,4-D modelled for this report**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Crop | Application rate (g a.s./ha) | Number of ap- plications | Interval between applications | BBCH growth stage at application |
| Spring cereals | 750 | 1 | - | 15-25 |

Unless stated otherwise, all input parameters were taken from the EFSA Conclusion (2014;12(9):3812, revised 21 March 2017).

In the EFSA conclusion (EFSA Journal 2014; 12(9):3812, revised 21 March 2017) a data gap was identified regarding the anaerobic metabolite 4-chlorophenol (4-CP) and photolysis metabolite 1,2,4- benzenetriol. More information was needed to assess the exposure and risk to the different environ- mental compartments for each metabolite. In order to address the data gap new studies on soil degra- dation were performed for 2,4-D and anaerobic metabolite 4-CP as well as soil adsorption/desorption studies for 4-CP (Swales & Crabtree, 2015a and 2015b). These studies have not previously been re- viewed at an EU level. Summaries of these study reports are included in Appendix 2.

Anaerobic conditions would not be expected to occur during or shortly after the application of 2,4-D to spring cereals according to the recommended GAP, therefore it is not necessary to consider the PEC of the anaerobic metabolite 4-CP. Nevertheless, for the avoidance of any doubt, a risk assess- ment for 4-CP in surface water and sediment has been included here. Values for metabolite 4-CP have been taken from new studies (Swales & Crabtree, 2015a and 2015b) which have not previously been re- viewed at an EU level. The inputs parameters for 4-CP are shown in [Table 8.8-4.](#_bookmark34)

It was not possible to determine input parameters for aquatic photolysis metabolite 1,2,4-benzenetriol (Swales & Crabtree, 2015c), therefore, PECSW for the metabolite 1,2,4-benzenetriol were calculated based on the maximum PECSW of the parent taking into account the molar mass ratio and the maxi- mum occurrence of the metabolite in surface water. Similarly, PECSED for the metabolite 1,2,4-ben- zenetriol was also calculated based on the maximum PECSED of the parent.

Where:

### PEC

SW,ini,metabolite

PECSW,ini,parent

### = 100 \*P

max,SW

\*fmol

PECSW,ini,parent = max. PECSW, parent [μg/L]

Pmax,SW = maximum occurrence metabolite in surface water (31.7%; EFSA Conclusion (2014;12(9):3812, re- vised 21 March 2017) [%]

fmol = molecular correction factor (molecular mass metabolite (126.1 g/mol) / molecular mass parent (221 g/mol)) [-]

The input parameters used in the modelling for 2,4-D are summarised in [Table 8.9-2,](#_bookmark44) and the input parameters used for the metabolites of 2,4-D are summarised in [Table 8.9-3.](#_bookmark45)

**Table 8.9-2: Input parameters used in the surface water modelling for 2,4-D**

|  |  |  |
| --- | --- | --- |
| Parameter | Value | Remarks |
| **Physico-chemical** | | |
| Molecular weight (g/mol) | 221 | EFSA Conclusion (EFSA Journal 2014; 12(9):3812, revised 21 March 2017, page 24  of 81) |
| Water solubility at 20℃ (mg/L) | 24300 | EFSA Conclusion (2014;12(9):3812, revised 21 March 2017, page 24 of 81) 1 |
| Vapour pressure at 20℃ (Pa) | 9.9x10-6 | EFSA Conclusion (EFSA Journal 2014; 12(9):3812, revised 21 March 2017, page 51  of 81) 2 |
| **Degradation in soil** | | |
| DT50 soil (d) | 4.14 | Re-normalized SFO lab DT50; Q10 = 2.58 20°C, pF2. (Cohen. S.P. (1991); Liu, D. (2011)).3 |
| Temperature correction function |  | FOCUS recommendation |
| Reference temperature (°C) | 20 |  |
| MACRO: (K-1) | 0.095 |  |
| PRZM: Q10 (-) | 2.58 |  |
| Moisture correction function Reference moisture (-)  PRZM/MACRO: moisture exponent (-) | pF 2  0.49 |  |
| **Sorption to soil** | | |
| KFOC (mL/g) | 58.6 | EFSA Conclusion (EFSA Journal 2014; 12(9):3812, revised 21 March 2017, page 51  of 81)  Median (n = 42) 4 |
| KFOM (mL/g) | 34.0 | Calculated KFOC / 1.724 |
| Freundlich exponent 1/n (-) | 0.87 | EFSA Conclusion (EFSA Journal 2014; 12(9):3812, revised 21 March 2017, page 51  of 81)  Median (n = 42) 4 |
| **Degradation in aquatic systems** | | |
| DT50 whole system (d) (Step 1) | 18.16 | EFSA Conclusion (EFSA Journal 2014; 12(9):3812, revised 21 March 2017, page 24 of 81) – value given “*for future calculations*”) |
| DT50 water (d) (Step 2) | 18.16 | EFSA Conclusion (EFSA Journal 2014; 12(9):3812, revised 21 March 2017, page 24 of 81) – value given “*for future calculations*”) |
| DT50 sediment (d) (Step 2/3) | 18.16 / 1,000 | EFSA Conclusion (EFSA Journal 2014; 12(9):3812, revised 21 March 2017, page 24 of 81) – value given “*for future calculations*” for Step 2 and the FOCUS default for Step 3 |
| DT50 crop (d) | 10 | FOCUS recommendation |
| Temperature correction function |  |
| Reference temperature (°C) | 20 |
| TOXSWA: activation energy (J/mol) | 65400 |

|  |  |  |  |
| --- | --- | --- | --- |
| Parameter | | Value | Remarks |
| Crop uptake factor (-) | | 0.0 | EFSA conclusion (2014) |
| Wash off coefficient |  |  | FOCUS recommendation |
| PRZM: | (cm-1) | 0.5 |  |
| MACRO: | (mm-1) | 0.05 |  |

1 Note that the value presented in the EU review (EFSA conclusion (2014) 12(9):3812, revised 21 March 2017) was incorrectly reported as occurring at 25°C.

2 Note that the value presented in the EU review (EFSA conclusion (2014) 12(9):3812, revised 21 March 2017) was incorrectly reported. A comment was added on page 51 that for further calculations the actual measured value for 2,4-D of 9.9x10-6 Pa at 20℃ is to be used.

3 Recalculated geometric mean DT50 after moisture normalization of the Mississippi silt loam (20°C/pF2). See detailed discussion in section [8.3.1](#_bookmark4) for more detail.

4 Incorrect value presented in the EFSA Conclusion (2014;12(9):3812, revised 21 March 2017). KFOC and 1/n was incorrectly reported for 7 soils. Endpoints are based on corrected data derived from RAR Addendum (2014, Vol. 3, Annex B) and in the revised EFSA Conclusion (revised 21 March 2017).

**Table 8.9-3: Input parameters used in the surface water modelling for metabolites**

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Parameter | 2,4-DCP | | 2,4-DCA | | 4-CP | | 1,2,4-benzenetriol | |
| Value | Remarks | Value | Remarks | Value | Remarks | Value | Remarks |
| Molecular | 163 | EFSA Conclusion | 177 | EFSA Conclusion | 128.6 | Euro Chlor (2002): Euro | 126.1 | Calculated from |
| weight (g/mol) |  | (EFSA Journal 2014; |  | (EFSA Journal 2014; |  | Chlor Risk Assessment |  | EPISuite V4.1.1 |
|  |  | 12(9):3812, revised 21 |  | 12(9):3812, revised 21 |  | for the Marine Environ- |  |  |
| Water solubil- ity at 20℃ (mg/L) | 4870 | 96.3 | 27100 | - | No data available |
| March 2017, page 54 of | March 2017, page 55 of | ment. OSPARCOM Re- |
| 81) | 81) | gion – North Sea. Mono- |
|  |  | chlorophenols. February |
|  |  | 2002.[6](#_bookmark46) |
| KFOC (mL/g) | 512 | EFSA Conclusion (EFSA Journal 2014;  12(9):3812, revised 21  March 2017, page 54 of 81); arithmetic mean (n  = 7) | 1028 | EFSA Conclusion (EFSA Journal 2014;  12(9):3812, revised 21  March 2017, page 55 of 81); arithmetic mean (n  = 7) | 182 | Calculated based on Swales, S.E. (2015b) (geometric mean n =5) | - | No data available. |
| KFOM (mL/g) | 297 | Calculated KFOC / 1.724 | 596 | Calculated KFOC / 1.724 | 106 | Calculated KFOC / 1.724 | - | No data available. |
| DT50 soil @ | 7.0 | EFSA Conclusion | 10.4 | EFSA Conclusion | 0.22 | Calculated based on | - | No data available. |
| 20°C & pF2 |  | (EFSA Journal 2014; |  | (EFSA Journal 2014; |  | Swales, S.E. (2015a) |  |  |
| (days) |  | 12(9):3812, revised 21  March 2017, page 54 of |  | 12(9):3812, revised 21  March 2017, page 55 of |  | (geometric mean n =5) |  |  |
|  |  | 81) |  | 81) |  |  |  |  |
|  |  | (geomean, lab, n = 3) |  | (geomean, lab, normal- |  |  |  |  |
|  |  |  |  | ised, n = 3) |  |  |  |  |
| Max % ob- | 8.7 | EFSA Conclusion | 15.0 | EFSA Conclusion | 331 | EFSA Conclusion | - | No data available. |
| served in soil |  | (EFSA Journal 2014; |  | (EFSA Journal 2014; |  | (EFSA Journal 2014; |  |  |
|  |  | 12(9):3812, revised 21 |  | 12(9):3812, revised 21 |  | 12(9):3812, revised 21 |  |  |
|  |  | March 2017, page 54 of |  | March 2017, page 55 of |  | March 2017, page 41 of |  |  |
|  |  | 81) |  | 81) |  | 81) |  |  |

6 Euro Chlor (2002): <https://www.eurochlor.org/wp-content/uploads/2019/04/8-11-4-14_marine_ra_monochlorophenols.pdf>(accessed September 2022).

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Parameter | 2,4-DCP | | 2,4-DCA | | 4-CP | | 1,2,4-benzenetriol | |
| Value | Remarks | Value | Remarks | Value | Remarks | Value | Remarks |
| DT50 water (d) | 103.9 | EFSA conclusion | 1000 | FOCUS default value | 1000 | FOCUS default value | - | No data available. |
|  |  | (EFSA Journal 2014; |  | (worst case) |  | (worst case) |  |  |
| DT50 sediment (d) | 103.9 | 1000 | 1000 | - |
| 12(9):3812, revised 21 |  |  |  |
| March 2017, page 54 of |  |  |  |
| DT50 total sys- tem (d) | 103.9 | 81) (geomean n =2) | 1000 |  | 1000 |  | - |  |
|
| Max % ob- | 32.1 | EFSA Conclusion | 5.3 | EFSA Conclusion | 6.9 | RAR Addendum (2014), | 31.7 | EFSA Conclusion |
| served in wa- |  | (EFSA Journal 2014; |  | (EFSA Journal 2014; |  | Lewis, C.J. (2011) |  | (EFSA Journal 2014; |
| ter/sediment |  | 12(9):3812, revised 21 |  | 12(9):3812, revised 21 |  |  |  | 12(9):3812, revised 21 |
|  |  | March 2017, page 54 of |  | March 2017, page 55 of |  |  |  | March 2017, page 49 of |
|  |  | 81) |  | 81) |  |  |  | 81) |

1 Note that anaerobic conditions leading to the formation of 4-CP in soil are not expected when used according to the intended GAP, however the formation in the anaerobic study is included here for the avoidance of any doubt..

At Steps 1 and 2, season of application and crop interception were estimated based on the BBCH growth stages. The region of use, season of application and crop interception values used are presented in [Ta-](#_bookmark47) [ble 8.9-4.](#_bookmark47)

**Table 8.9-4: Model parameters used in FOCUS Steps 1 and 2 surface water modelling**

|  |  |  |  |
| --- | --- | --- | --- |
| Crop | Zone (Step 2) | Season | Interception |
| Spring cereals | North Europe | Mar-May | Minimal crop cover |
| Jun-Sep |
| South Europe | Mar-May |
| Jun-Sep |

Only parent was carried forward to Step 3. For all uses at Step 3, the linear foliar application method was selected (CAM 2) with the default incorporation depth of 4 cm.

In accordance with FOCUS recommendations, irrigation was applied as set internally within the FOCUS Step 3 scenarios. An application window must be specified from which the Pesticide Application Timer (PAT), internal to the model, determines actual application dates which were set generically for all sce- narios. Application window dates are presented in [Table 8.9-6](#_bookmark48) and [Table 8.9-7.](#_bookmark49) The dates were selected with the tool App Date v3.06 (Klein, 2019) based on BBCH growth stages given in the recommended GAP.

In order to present the necessary R1 pond and R1 stream scenarios, oilseed rape spring was modelled at Step 3 as a surrogate crop for spring cereals. As an earlier growth stage is used (BBCH 09), the intercep- tion and application timing is adequate to cover the application to spring cereals.

**Table 8.9-5: Model parameters used in FOCUS surface water modelling**

|  |  |  |
| --- | --- | --- |
| Plant protection product | Parameter | |
| Use No. | 1 | 21 |
| Crop | Spring cereals | Oilseed rape, spring |
| Application rate (kg a.s./ha) | 0.750 | 0.750 |
| Number of applications | 1 | 1 |
| Application method | Foliar spray | Foliar spray |
| CAM (Chemical application method) | CAM 2 | CAM 2 |
| Soil depth (cm) | 4 | 4 |
| Models used for calculation | FOCUS SWASH v5.3, FOCUS PRZM v4.3.1, FOCUS MACRO v5.5.4, FOCUS TOXWA v5.5.3 | |

1 Modelled at Step 3 only, as a surrogate crop for spring cereals, in order to present the R1 scenarios.

**Table 8.9-6: Application windows for spring cereals – FOCUS Step 3**

|  |  |  |
| --- | --- | --- |
| Scenario details | FOCUS default dates | |
| Scenario | Start | End |
| Spring cereals (FOCUS spring cereals), 1 x 750 g a.s./ BBCH 15-25 | | |
| D1 | 11-May (131) | 10-Jun (161) |
| D3 | 08-Apr (98) | 08-May (128) |
| D4 | 02-May (122) | 01-Jun (152) |
| D5 | 22-Mar (81) | 21-Apr (111) |
| R4 | 22-Mar (81) | 21-Apr (111) |

Values in parentheses are Julian Days

|  |  |  |  |
| --- | --- | --- | --- |
| **Table 8.9-7: Application window for oilseed rape, spring – FOCUS Step 3** | | |  |
| Scenario details | FOCUS default dates | | |
| Scenario | Start | End | |
| Oilseed rape, spring (FOCUS oilseed rape, spring), 1 x 750 g as/ BBCH 09 | | | |
| R1 | 10-April (100) | 10-May (130) | |

Values in parentheses are Julian Days

The maximum PECSW and PECSED for 2,4-D and its metabolites at FOCUS Steps 1 and 2, as calculated by the FOCUS surface water models, are given in [Table 8.9-8](#_bookmark50) and [Table 8.9-9.](#_bookmark51)

**Table 8.9-8: Maximum PECSW and PECSED for 2,4-D and its metabolites application to spring cere- als (1 x 750 g a.s./ha, BBCH 15) – FOCUS Step 1**

|  |  |  |  |
| --- | --- | --- | --- |
| Crop / Application | Substance | Max PECSW (µg/L) | Max PECSED (µg/kg) |
| Spring cereals 1 x 750 g a.s/ha  BBCH 15 | 2,4-D | 238.78 | 135.883 |
| 2,4-DCP | 46.342 | 232.325 |
| 2,4-DCA | 17.438 | 177.401 |
| 4-CP | 46.987 | 85.358 |
| 1,2,4-benzenetriol1 | 43.190 | 24.578 |

1 Calculated based on parent

**Table 8.9-9: Maximum PECSW and PECSED for 2,4-D and its metabolites following application to spring cereals (1 x 750 g a.s./ha, BBCH 15) – FOCUS Step 2**

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Crop / Application | Substance | Region | Season | Max PECSW  (µg/L) | Max PECSED  (µg/kg) |
| Spring cereals  1 x 750 g a.s/ha,  BBCH 15 | 2,4-D | NEU | Mar-May | 29.366 | 16.487 |
| Jun-Sep | 29.366 | 16.487 |
| SEU | Mar-May | **53.104** | **30.020** |
| Jun-Sep | 41.235 | 23.182 |

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Crop / Application | Substance | Region | Season | Max PECSW  (µg/L) | Max PECSED  (µg/kg) |
|  | 2,4-DCP | NEU | Mar-May | 5.977 | 29.646 |
| Jun-Sep | 5.977 | 29.646 |
| SEU | Mar-May | **10.861** | **54.487** |
| Jun-Sep | 8.419 | 42.067 |
| 2,4-DCA | NEU | Mar-May | 2.552 | 25.911 |
| Jun-Sep | 2.552 | 25.911 |
| SEU | Mar-May | **4.951** | **50.557** |
| Jun-Sep | 3.751 | 38.234 |
| 4-CP | NEU | Mar-May | 1.065 | 1.908 |
| Jun-Sep | 1.065 | 1.908 |
| SEU | Mar-May | **1.892** | **3.412** |
| Jun-Sep | 1.478 | 2.660 |
| 1,2,4-benzenetriol1 | NEU | Mar-May | 5.312 | 2.982 |
| Jun-Sep | 5.312 | 2.982 |
| SEU | Mar-May | **9.605** | **5.430** |
| Jun-Sep | 7.458 | 4.193 |

Worst-case shown in bold

1 Calculated based on parent

Maximum PECSW and PECSED values for 2,4-D, based on FOCUS Step 3 simulations, are presented in [Table 8.9-10](#_bookmark52) and [Table 8.9-11.](#_bookmark53)

**Table 8.9-10: Maximum PECSW and PECSED for 2,4-D following application to spring cereals (1 x 750 g a.s./ha, BBCH 15) – FOCUS Step 3**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Scenario | Waterbody | Max. PECSW (µg/L) | Main route of entry | Max. PECSED  (µg/kg) |
| D1 | Ditch | 4.867 | Spray drift | 1.685 |
| D1 | Stream | 3.882 | Spray drift | 0.345 |
| D3 | Ditch | 4.749 | Spray drift | 0.870 |
| D4 | Pond | 0.164 | Spray drift | 0.176 |
| D4 | Stream | 3.888 | Spray drift | 0.192 |
| D5 | Pond | 0.164 | Spray drift | 0.201 |
| D5 | Stream | 3.776 | Spray drift | 0.089 |

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| R4 | Stream | 3.128 | Spray drift | 0.255 |

**Table 8.9-11: Maximum PECSW and PECSED for 2,4-D following application to oilseed rape, spring (1 x 750 g a.s./ha, BBCH 09) – FOCUS Step 3**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Scenario | Waterbody | Max. PECSW (µg/L) | Main route of entry | Max. PECSED  (µg/kg) |
| R1 | Pond | 0.164 | Spray drift | 0.224 |
| R1 | Stream | 3.131 | Spray drift | 0.261 |

The maximum PECSW values for the parent and metabolites at Step 2 were 53.104 µg/L for 2,4-D, 10.861 µg/L for 2,4-DCP, 4.951 µg/L for 2,4-DCA, 1.892 µg/L for 4-CP, and 9.605 µg/L for 1,2,4-ben- zenetriol for spring cereals. Parent was taken forward to Step 3 which reached a maximum of 4.867 µg/L in the D1 Ditch for spring cereals.

**PECSW/SED of formulation**

As formulation components other than the active ingredient are assumed to dissipate rapidly in the environment following application, the main route of potential surface water exposure to the 2,4-D SP 95 formulation will be via spray drift. Surface water contamination via spray drift was considered using the FOCUS drift calculator within SWASH v5.3.

The maximum PECSW values after application to spring cereals are summarised in [Table 8.9-12.](#_bookmark54)

**Table 8.9-12: PECSW for 2,4-D 95 SP on spring cereals**

|  |  |  |  |
| --- | --- | --- | --- |
| Active substance/ preparation | Maximum use rate (g formulation/ha)1 | Waterbody | Max PECSW (μg/L) |
| 1 application (90th percentile drift) field crops | | | |
| 2,4-D / 2,4-D 95 SP | 932.8 | Ditch | 5.9929 |
| Pond | 0.2043 |
| Stream | 5.3372 |

1 Formulation components other than the active ingredient are assumed to dissipate rapidly in the environment, therefore only one application is considered.

2 Includes a 20% input from upstream catchment

Time-dependent PECSW values, PECSW values from drainage and run-off and PECSED values are not ap- propriate for the formulation since it is considered to separate into its constituent components by transport and dissipation processes in the environment.

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

|  |
| --- |
| **Review Comments:**  The data on atmospheric degradation and behaviour in air for 2,4-D provided by the Applicant are considered acceptable. The justification for non-assessment via volatilization is accepted. Exposure of adjacent surface waters and terrestrial ecosystems by 2,4-D due to volatilization with subsequent deposition is not expected. |

**Table 8.10-1: Summary of atmospheric degradation and behaviour**

|  |  |
| --- | --- |
| Compound | 2,4-D |
| Direct photolysis in air | Not studied – no data requested |
| Quantum yield of direct phototransformation | No data |
| Photochemical oxidative degradation in air | DT50 (h): 1.6 days (assuming 1.5x106 OH radicals cm3) |
| Volatilisation | Vapour pressure (Pa): 9.9 × 10-6 Pa  Henry's Law Constant (Pa m3/mol): 1.3 × 10-5 |

The vapour pressure at 20 °C of the active substance 2,4-D is < 10-5 Pa. Hence the 2,4-D is regarded as non-volatile. Therefore, exposure of adjacent surface waters and terrestrial ecosystems by 2,4-D due to volatilization does not need to be considered.

# 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 | Owner |
| CP | Crabtree, G.A | 2015 | [14C] 2,4-D: Aerobic Soil Metabolism and | N | 2,4-D TF |
| 9.1.1.1/01 |  |  | 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 |  |  |
|  |  |  | **XXXX Report No. 90019368 (full)** |  |  |
|  |  |  | **XXXX Report No. 9019368A (summary)** |  |  |
|  |  |  | GLP: Yes |  |  |
|  |  |  | Unpublished |  |  |
| CP | Swales, S.E., | 2015a | 4-Chlorophenol: Aerobic Soil Degradation in Three EU | N | 2,4-D TF |
| 9.1.1.1/02 | Crabtree, G.A. |  | 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 |  |  |
|  |  |  | **XXXX Report No. 90019369 (full)** |  |  |
|  |  |  | **XXXX Report No. 9019369A (summary)** |  |  |
|  |  |  | GLP: Yes |  |  |
|  |  |  | Unpublished |  |  |

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| 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 | Owner |
| CP | Swales, S.E., | 2015b | 4-Chlorophenol: Adsorption in Four EU Soils and one | N | 2,4-D TF |
| 9.1.2/01 | Crabtree, G.A |  | US Soil |  |  |
|  |  |  | Smithers Viscient (ESG) Ltd, UK |  |  |
|  |  |  | Report No. 3200920, 28 August 2015 |  |  |
|  |  |  | Dow AgroSciences No. 141221 |  |  |
|  |  |  | PCTR No. 10001705-004-70601-0001 |  |  |
|  |  |  | **XXXX Report No. 90019370 (full)** |  |  |
|  |  |  | **XXXX Report No. 9019370A (summary)** |  |  |
|  |  |  | GLP: Yes |  |  |
|  |  |  | Unpublished |  |  |
| ~~CP~~ | ~~Swales, S.E.,~~ | ~~2015c~~ | ~~1,2,4-Benzenetriol: Adsorption in Four EU Soils and~~ | ~~N~~ | ~~2,4-D TF~~ |
| ~~9.1.2/02~~ | ~~Crabtree, G.A~~ |  | ~~One US Soil~~ |  |  |
|  |  |  | ~~Smithers Viscient (ESG) Ltd, UK~~ |  |  |
|  |  |  | ~~Report No. 3200921, 28 August 2015~~ |  |  |
|  |  |  | ~~Dow AgroSciences No. 141224~~ |  |  |
|  |  |  | ~~PCTR No. 10001705-004-70601-0002~~ |  |  |
|  |  |  | **~~XXXX Report No. 90019371 (full)~~** |  |  |
|  |  |  | **~~XXXX Report No. 9019371A (summary)~~** |  |  |
|  |  |  | ~~GLP: Yes~~ |  |  |
|  |  |  | ~~Unpublished~~ |  |  |

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| 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 | Owner |
| CP | Verity, C. | 2022a | A Modelling Assessment of 2,4-D and its Metabolites Applied to Spring Cereals in Groundwater in the | N | ADAMA |
| 9.2.4.1/01 |  |  | Central Zone. |  |  |
|  |  |  | ERM, Harrogate, UK |  |  |
|  |  |  | Report No. 0572580-GW2 |  |  |
|  |  |  | Not GLP |  |  |
|  |  |  | Unpublished |  |  |
| CP | Verity, C., Lee, R. | 2023 | A Modelling Assessment of 2,4-D and its Metabolites Applied to Spring Cereals in Surface Water in the | N | ADAMA |
| 9.2.5/01 |  |  | Central Zone. |  |  |
|  |  |  | ERM, Harrogate, UK |  |  |
|  |  |  | Report No. 0572580-SW4 |  |  |
|  |  |  | Not GLP |  |  |
|  |  |  | Unpublished |  |  |

**List of data submitted or referred to by the applicant and relied on, but already evaluated at EU peer review**

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| 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 | Owner |
| KCP 9.1.1 | Cohen, S.P | 1991a | Aerobic Soil Metabolism Study of 2,4-D. Study Number: CHMR, 6503A. | N | 2,4-D TF |
| KCP 9.1.1 | Liu, D. | 2011 | Soil Degradation of 2,4-D under Aerobic Condition. Study Number not stated. | N | 2,4-D TF |
| KCP 9.1.2 | Barrusio, E. | 1991 | Soil Type and Herbicides Adsorption; Intern. J. Environ. Anal. Chem. 46, 117-128. | N | 2,4-D TF |
| KCP 9.1.2 | Burgener, A. | 1993 | 2,4-D (in Form of DMA Salt); Mobility and degradation in Soil in Outdoor Lysimeters. Study Number: 272586 | N | 2,4-D TF |
| KCP 9.1.2 | Cohen, S.P | 1991b | Mobility of Unaged 2,4-Dichlorophenoxyacetic Acid Using Batch Equilibrium Technique. Study Number: CHMR, 6224A. | N | 2,4-D TF |
| KCP 9.1.2 | Euro Chlor | 2002 | Euro Chlor Risk Assessment for the Marine Environment. OSPARCOM Region – North Sea. Monochlorophenols. February 2002. [https://www.eurochlor.org/wp-content/uploads/2019/04/8-11-4-](https://www.eurochlor.org/wp-content/uploads/2019/04/8-11-4-14_marine_ra_monochlorophenols.pdf) [14\_marine\_ra\_monochlorophenols.pdf](https://www.eurochlor.org/wp-content/uploads/2019/04/8-11-4-14_marine_ra_monochlorophenols.pdf) (accessed September 2022). | N | 2,4-D TF |
| KCP 9.1.2 | Fathulla, R. | 1996a | The adsorption and desorption of 14C-2,4-D on representative agricultural soils. Study Number: CHW 6397-166. | N | 2,4-D TF |
| KCP 9.1.2 | Fathulla, R. | 1996b | The adsorption and desorption of 14C-2,4-DCP on representative agricultural soils. Study Number: CHW 6397-168. | N | 2,4-D TF |
| KCP 9.1.2 | Fathulla, R. | 1996c | The adsorption and desorption of 14C-2,4-DCA on representative agricultural soils. Study Number: CHW 6397-168. | N | 2,4-D TF |
| KCP 9.1.2 | Hermosin, M.C. | 1991 | Soil Adsorption of 2,4-D as Affected by the Clay Mineralogy. Tox. and Envir. Chem. 31-32, 69-77, 1991. | N | 2,4-D TF |

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| KCP 9.1.2 | Lewis C.J. | 2011 | [14C]-2,4-D: Degradation in Water-Sediment Systems under Anaerobic Conditions. Study Number: 8245065. | N | 2,4-D TF |
| KCP 9.1.2 | McCoy, K.M., | 1988 | Soil adsorption properties of 2,4-D, 2-ethylhexyl ester and butyl ester of 2,4-D. Study Number: GH-C 1993. | N | 2,4-D TF |
| KCP 9.1.2 | Swoboda, T. | 2006 | 2,4-D Acid Adsorption – Desorption in Soil. Study Number: G/61/03. | N | 2,4-D TF |
| KCP 9.1.2 | Yoder, R.N. | 2011 | Batch equilibrium adsorption/desorption of 2,4-D and adsorption of its aerobic soil metabolites. Study Number: 110601. | N | 2,4-D TF |

The following tables are to be completed by MS

**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 | Owner |
| CP  9.1.2/02 | 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  **XXXX Report No. 90019371 (full)**  **XXXXX Report No. 9019371A (summary)**  GLP: Yes  Unpublished | N | 2,4-D TF |

**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 | Owner |
|  |  |  |  |  |  |

# Appendix 2 Detailed evaluation of the new Annex II studies

In order to address the data gaps identified during the peer review (2,4-D; EFSA Journal 2014; 12(9): 3812), additional studies on soil degradation were performed for 2,4-D and anaerobic metabolite 4- chlorophenol (4 CP) as well as soil adsorption/desorption studies for 4-CP and aquatic photolysis me- tabolite 1,2,4-benzenetriol. Summaries of these studies are presented below.

## A 2.1 Aerobic degradation of 2,4-D in soil

Comments of zRMS:

The study was evaluated and agreed by the zRMS (NL) during the zonal evaluation of XXXX formulation AG-D2-600 SL finalised in September 2017.

|  |  |
| --- | --- |
| Reference: | CP 9.1.1.1/01 Crabtree, G.A. (2015) |
| Report | [14C] 2,4-D: Aerobic Soil Metabolism and Transformation in Acidic Soils |
| Document No: | 3200898  Dow AgroSciences No. 141222 |
| Guideline(s): | * 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 accepta- ble to use this soil. |
| GLP: | Yes |
| Acceptability: | 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.s./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 con- ducted 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 per- formed 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 (mi- nor) 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.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Soil type** | **2,4-D** | | **2,4-DCP** | |
| **DT50 [days]** | **DT90 [days]** | **DT50 [days]** | **DT90 [days]** |
| Warsop | 4.8 | 15.8 | 0.45 | 1.5 |
| Kenslow Wood | 4.4 | 14.7 | 0.64 | 2.1 |

**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: 99.5%

Description (physical state): Not applicable

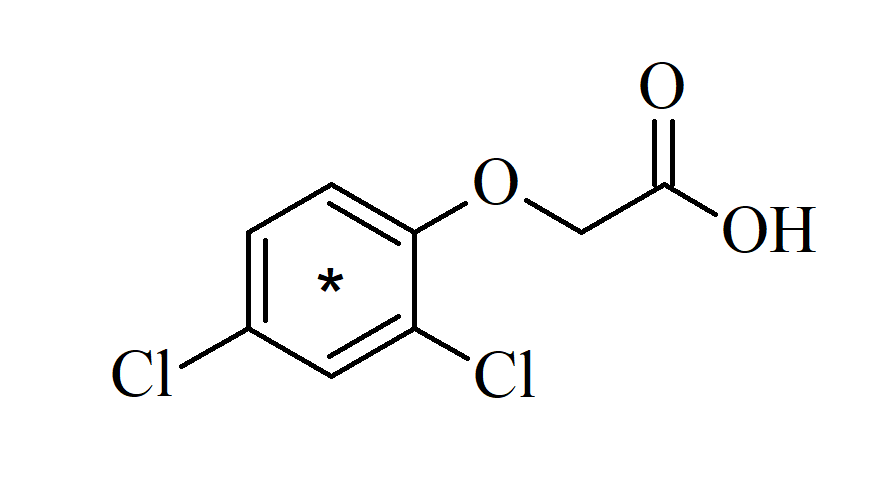
Lot/batch no.: Morris/1710

CAS no.: Not applicable

SMILES string: Not applicable

Radiolabelled test item #1

Name: 2,4-D-Ph-UL-[14C]

Test item (chemical/other name): (2,4-dichlorophenoxy)acetic acid-Ph-UL-14C 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 A2.1-2: 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 collec- tion 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 A2.1-3: 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/cm3] | 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.

|  |  |  |
| --- | --- | --- |
| **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 concentra- tions | mg a.s./kg soil | 0.50 |
| g a.s./ha | 0.1 |
| Control conditions, if used | |  |
| Number of repli- cates | Controls, if used | 6/soil |
| Treatments | None |
| Test apparatus (Type/material/volume) | | Glass vessels (250 mL volume, 6 cm diameter), flow-through system |
| Traps for CO2 and organic volatiles, if any | | Two sodium hydroxide traps |
| If no traps were used, is the system closed/open | | Not applicable |
| Identity and concentration of co-solvent | | Acetonitrile (<0.05%) |
| Test item applica- tion | 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 popula- tion of control soil | | 286.5 µg C/g (Warsop); 557.5 µg C/g (Kenslow Wood); |
| Final microbial biomass/microbial popula- tion of control soil | | 127.6 µg C/g (Warsop); 571.6 µg C/g (Kenslow Wood); |
| Initial microbial biomass/microbial popula- tion of treated soil, if provided | | Not measured in treated soil |
| Final microbial biomass/microbial popula- tion 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 |

#### Definitive Study Experimental Conditions Table A2.1-4: Experimental parameters

#### 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.

#### Sampling

#### Table A2.1-5: 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 CO2 and vola- tile 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 tripli- cate (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 sam- pling 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 inter- val (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 com- bined 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 NaOH (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 sys- tem 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).

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 Environ- mental Fate Studies. In order to estimate DT50 and DT90 values, two different kinetic models were fit- ted 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 discussions Route of Degradation** Test conditions

Aerobic conditions were maintained throughout the study. Soil biomass was determined at study ini- tiation and termination. In Warsop soil the final microbial 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 A2.1-6: Biotransformation of 2,4-D, expressed as percentage of the applied radio- activity, 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, Ave = average

**Table A2.1-7: 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, Ave = average

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 in- creased 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 sam- pling 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 bar- ium 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

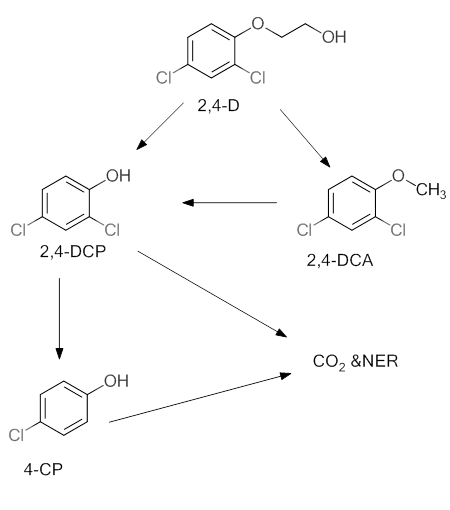
The decline of 2,4-D was followed by an increase in the formation of three metabolites, (which were known) during the course of the study. These included the major metabolite 2,4-DCP and minor me- tabolites 2,4-DCA and 4-CP (each <5% AR).

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 separa- tion 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 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 2.1-1: Aerobic biotransformation pathway of 2,4-D in acidic soil**

**Table A2.1-8: Chemical names and CAS numbers for the transformation products of test item**

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| **Code name** | **CAS num- ber** | **CAS and/or IUPAC chemical name(s)** | **Chemical formula** | **Molecular weight** | **SMILES**  **string** | **Maximum**  **% formed** |
| 2,4-DCP | 120-83-2 | 2,4-Dichlorophenol | C6H4Cl2O | 163.0 | Clc1cc(Cl)c( O)cc1 | 14.8 |
| 2,4- DCA | 553-82-2 | 2,4- Dichloroanisole | C7H6Cl2O | 177.03 | COc1ccc(cc 1Cl)Cl | 2.9 |
| 4-CP | 106-48-9 | 4-Chlorophenol | C6H5ClO | 128.56 | C1cc(ccc1O) Cl | 1.1 |

#### Rate of Degradation

Degradation rate

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

**Table A2.1-9: Degradation rate of 2,4-D**

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| **Test item** | **Soil type** | **DT50**  **[days]** | **DT90**  **[days]** | **Model used** | **χ2 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

#### Rate of Degradation at 10°C

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

#### 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 A2.1-10: Degradation rate of metabolites formed**

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| **Test item** | **Soil type** | **DT50**  **[days]** | **DT90**  **[days]** | **Model used** | **Formation fraction** | **χ2 er- ror %** | **Parameters** |
| 2,4-DCP | Warsop | 0.45 | 1.5 | SFO | 0.9 | 16.0 | visual fit good; t-test prob <0.05; confi-  dence intervals >0 |
| 2,4-DCP | Kenslow Wood | 0.64 | 2.1 | SFO | 1 | 19.0 | visual fit good; t-test prob <0.05; confi-  dence 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. Charac- terisation 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 in- corporated into soil.

## A 2.2 Aerobic degradation of 4-CP in soil

Comments of zRMS:

The study was evaluated and agreed by the zRMS (PL) during the zonal evaluation of XXXX formulation Camaro 306 SE (AG-FD1-306 SE) finalised in March 2017.

*Worst case soil DT50 of 4-chlorophenol was determined to be 0.69 days (16.6 hours) and mean DT50 was 0.22 days.*

|  |  |
| --- | --- |
| Reference: | CP 9.1.1.1/02 Swales, S.E. & Crabtree, G.A. (2015b) |
| Report | 4-Chlorophenol: Aerobic Soil Degradation in Three EU Soils and One US Soil |
| Document No: | 3200919  Dow AgroSciences No. 141220 |
| Guideline(s): | * OECD 307    OSCPP 835.4100, OPPTS 835.4100 |
| Deviations: | No |
| GLP: | Yes |
| Acceptability: | Yes |

**Study summary**

The rate of degradation of 4-chlorophenol was studied in three EU soils and one US soil under aero- bic 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.s./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 fur- ther sampling occasions for Brierlow, Speyer 5M and Warsop soils and seven further sampling occa- sions 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-chlo- rophenol 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 condi- tions.

|  |  |  |
| --- | --- | --- |
| **Soil type** | **4-Chlorophenol** | |
| **DT50 [hours]** | **DT90 [hours]** |
| Brierlow | 1.9 | 6.4 |
| Speyer 5M | 3.2 | 10.7 |
| Warsop | 16.6 | 55.0 |
| LAD-SCL-PF | 7.4 | 24.5 |

**Materials and methods**

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

#### Soil Characteristics

**Table A2.2-1: Description of soil collection and storage**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Description** | **Brierlow** | **Speyer 5M** | **Warsop** | **LAD-SCL-PF** |
| Geographic location | Brierlow, Derby- shire, UK | In der Speyerer Hohl, Nr 977, Mechtersheim, Rheineland-Pfalz, Germany | Warsop, Notting- hamshire, 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 A2.2-2: 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 ca- pacity | 73.6 | 39.8 | 20.4 | 60.3 |
| Bulk density [g/cm3] | 0.9 | 1.3 | 1.1 | 1.0 |
| Soil taxonomic classifi- cation | 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.

|  |  |  |
| --- | --- | --- |
| **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 concentra- tions | mg a.s./kg soil | 1.0 |
| g a.s./ha | 750 |
| Control conditions, if used | |  |
| Number of repli- cates | Controls, if used | 6/soil |
| Treatments | None |
| Test apparatus (Type/material/volume) | | Glass vessels (500 mL volume), adapted lids to allow continu- ous air exchange |
| Traps for CO2 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 applica- tion | 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 popula- tion 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 popula- tion 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 popula- tion of treated soil, if provided | | Not measured in treated soil |
| Final microbial biomass/microbial popula- tion 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 |

#### Definitive Study Experimental Conditions Table A2.2-3: Experimental parameters

#### Aerobic Conditions

Each test vessel had a perforated lid allowing continuous air exchange.

#### Supplementary Experiments

None

#### Sampling

#### Table A2.2-3: 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 CO2 and vola- tile 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 (us- ing 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 L), 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 concentra- tion. Validation included consideration of the following criteria; linearity, specificity, precision, re- covery, 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 sam- ple 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 Environ- mental Fate Studies. In order to estimate DT50 and DT90 values, two different kinetic models were fit- ted 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 discussions**

#### Recovery of 4-Chlorophenol

Test conditions

Soil biomass was determined at study initiation and termination. In Brierlow soil, the final biomass declined from 792 µg C/g to 512.7 µg/g, over the course of the study. In Speyer 5M soil, the final bi- omass 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), pre- cision 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 interfer- ences, the specificity of the method was demonstrated.

**Table A2.2-4: 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 A2.2-5: 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 A2.2-6: 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 A2.2-7: 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

#### 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 A2.2-8: Degradation rate of 4-chlorophenol**

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| **Test item** | **Soil type** | **DT50**  **[hours]** | **DT90**  **[hours]** | **Model used** | **χ2 er- ror %** | **Parameters** |
| 4-CP | Brierlow | 1.93 | 6.40 | SFO | 3.15 | visual fit good;  t-test prob <0.05; confi- dence intervals >0 |
| 4-CP | Speyer 5M | 3.21 | 10.7 | SFO | 4.26 | visual fit good;  t-test prob <0.05; confi- dence intervals >0 |
| 4-CP | Warsop | 16.6 | 55.0 | SFO | 4.34 | visual fit good;  t-test prob <0.05; confi- dence intervals >0 |
| 4-CP | LAD-SCL-PF | 7.38 | 24.5 | SFO | 4.85 | visual fit good;  t-test prob <0.05; confi- dence intervals >0 |

#### Supplementary Experiment - Results

None

#### Rate of Degradation at 10°C

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

#### 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 2.3 Mobility of Plant Protection Product in soil: 4-chlorophenol

Comments of zRMS:

The study was evaluated and agreed by the zRMS (PL) during the zonal evaluation of XXXX formulation Camaro 306 SE (AG-FD1-306 SE) finalised in March 2017.

*Kfoc values for 4-chlorophenol in 5 soils were in range 155-254 L/kg.*

|  |  |
| --- | --- |
| Reference: | CP 9.1.2/021 Swales, S.E. & Crabtree, G.A. (2015b) |
| Report | 4-Chlorophenol: Adsorption in Four EU Soils and One US Soil |
| Document No, | 3200920  Dow AgroSciences No. 141221; PCTR No. 10001705-004-70601-0001 |
| Guideline(s): | OECD 106  OSCPP 835.1230, OPPTS 835.1230 |
| Deviations: | None |
| GLP: | Yes |
| Acceptability: | 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, War- sop 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 (Emp- ingham 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 us- ing a validated method (SMV 3200920-03V). Due to the instability of 4-chlorophenol over the dura- tion 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 (KFOC) 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 KFOC), 4-Chlorophenol can be classified as having ‘medium mobility’ in all five soils.

4-Chlorophenol

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Soil** | **Adsorption** | | | |
| **KF** | **KFOC** | **1/n** | **r2** |
| 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 |

KF - Freundlich adsorption coefficient

Koc - Coefficient adsorption per organic carbon (KF x 100/% organic carbon) 1/n -Slope of Freundlich adsorption isotherm

r2 - Correlation coefficient of Freundlich equation

**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 A2.3-1: Description of soil collection and storage**

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Description** | **Empingham** | **Warsop** | **Kenslow** | **Brierlow** | **LAD-SCL-PF** |
| Geographic location | Empingham, Rutland, UK | Warsop, Not- tingham, UK | Kenslow, Mid- dleton, Derby- shire, UK | Brierlow, Der- byshire, 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 A2.3-2: 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/cm3] | 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 equi- librium, 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 g/mL. Adsorption of the test mate- rial to test vessels was assessed at a concentration of 0.5 g/mL. The soil:solution ratio and equilib- rium time tests were conducted in duplicate with 4-chlorophenol at a concentration of 1.0 g/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 A2.3-3: 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 CaCl2 | | | | |
| Control used (with salt solution only) (Yes/No) | | Yes | Yes | Yes | Yes | Yes |
| Test material concentrations  (mg/L) | Nominal appli- cation | 0.5, 1.0, 5.0. 10.0 and 50.0 mg/L | | | | |
| Analytically measured con- centrations | 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 solu- tion, if provided | | NA | NA | NA | NA | NA |
| No. of replica- tions | 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 superna- tant | | 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 sepa- ration of soil and solution | Supernatant decanted | | | | |

Tier 3 samples were sterilised by gamma irradiation prior to sample treatment to minimize degrada- tion 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 in- termediate 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 quantifi- cation (0.05 mg/L), at an intermediate concentration (2.0 mg/L) and at the highest expected concen- tration (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 L), 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 sam- ple concentrations.

Detection limits (LOD, LOQ) for the parent compound

|  |  |  |
| --- | --- | --- |
| **Matrix** | **LOD [µg/mL]** | **LOQ [µg/mL]** |
| CaCl2 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 discussions**

#### 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 g/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, Brier- low and LAD-SCL-PF soils.

For the determination of equilibrium time, recovery of 4 chlorophenol was >70% at sampling inter- vals 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 re- sult, an equilibrium time could not be obtained. A 3 hour equilibrium time was selected for the defin- itive 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 suit- able.

The values obtained for calcium chloride were generally higher, than those obtained for soil with in- dividual 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 A2.3-4: Recovery of 4-chlorophenol, expressed as percentage of the applied amount, in soil after adsorption**

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Soil** | **Rep** | **% Adsorb** | **% soil** | **%** | **%** |
| **Solution** | **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 |
| 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 | 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 | 5.6 | NA | 77.6 |

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Soil** | **Rep** | **% Adsorb** | **% soil** | **%** | **%** |
| **Solution** | **Extract** | **NER** | **Total** |
| Warsop | | | | | |
| 50 µg/mL | 1 | 79 | 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 | 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 | NA | 91.8 |
| 0.5 µg/mL | 1 | 60.7 | 25 | 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 |
| Brierlow | | | | | |
| 50 µg/mL | 1 | 57.3 | 32.1 | NA | 89.4 |
| 50 µg/mL | 2 | 71 | 28.5 | NA | 99.5 |
| 10 µg/mL | 1 | 63.4 | 37.8 | NA | 101.2 |
| 10 µg/mL | 2 | 63 | 36.4 | NA | 99.4 |
| 5 µg/mL | 1 | 54.6 | 30 | 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 |
| 0.5 µg/mL | 1 | 41.4 | 27.2 | NA | 68.6 |
| 0.5 µg/mL | 2 | 42.5 | 26.7 | NA | 69.2 |

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Soil** | **Rep** | **% Adsorb** | **% soil** | **%** | **%** |
| **Solution** | **Extract** | **NER** | **Total** |
| LAD-SCL-PF | | | | | |
| 50 µg/mL | 1 | 219 | 17.6 | NA | 89.7 |
| 50 µg/mL | 2 | 210 | 16.9 | NA | 89.7 |
| 10 µg/mL | 1 | 43 | 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 | 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 A2.3-5: Concentration of 4-chlorophenol, in the solid and liquid phases at the end of ad- sorption equilibration period**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Conc**  **[μg/mL]** | **Rep** | **Sorbed** | **In soln** | **%** |
| **[μg/g]** | **[μg/mL]** | **Sorbed** |
| Empingham | | | | |
| 50 | 1 | 120.896 | 44.3 | 9.9 |
| 50 | 2 | 99.603 | 46.3 | 8.2 |
| 10 | 1 | 26.6446 | 8.66 | 11.2 |
| 10 | 2 | 28.2332 | 8.63 | 11.9 |
| 5 | 1 | 23.6164 | 3.97 | 19.9 |
| 5 | 2 | 13.6645 | 4.37 | 11.2 |
| 1 | 1 | 5.0844 | 0.795 | 20.5 |
| 1 | 2 | 3.8431 | 0.838 | 15.9 |
| 0.5 | 1 | 3.1141 | 0.382 | 24.9 |
| 0.5 | 2 | 3.1121 | 0.383 | 24.6 |

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Conc**  **[μg/mL]** | **Rep** | **Sorbed** | **In soln** | **%** |
| **[μg/g]** | **[μg/mL]** | **Sorbed** |
| Warsop | | | | |
| 50 | 1 | 32.7642 | 44.1 | 13 |
| 50 | 2 | 39.395 | 42.9 | 15.7 |
| 10 | 1 | 8.3501 | 7.96 | 17.7 |
| 10 | 2 | 8.1954 | 8.19 | 17 |
| 5 | 1 | 5.9879 | 3.77 | 24.5 |
| 5 | 2 | 5.5162 | 3.83 | 22.8 |
| 1 | 1 | 1.2201 | 0.751 | 24.9 |
| 1 | 2 | 1.2692 | 0.74 | 25.8 |
| 0.5 | 1 | 0.833 | 0.343 | 33.1 |
| 0.5 | 2 | 0.8286 | 0.346 | 32.6 |
| Kenslow | | | | |
| 50 | 1 | 100.6343 | 46.2 | 8.1 |
| 50 | 2 | 335.164 | 37 | 26.9 |
| 10 | 1 | 29.4568 | 8.52 | 12.4 |
| 10 | 2 | 37.8578 | 8.34 | 15.7 |
| 5 | 1 | 24.7924 | 4 | 20 |
| 5 | 2 | 25.5246 | 3.96 | 20.8 |
| 1 | 1 | 7.2832 | 0.717 | 29.8 |
| 1 | 2 | 6.9435 | 0.719 | 28.2 |
| 0.5 | 1 | 2.6327 | 0.405 | 20.9 |
| 0.5 | 2 | 2.5721 | 0.402 | 20.4 |
| Brierlow | | | | |
| 50 | 1 | 87.3638 | 32.8 | 34.9 |
| 50 | 2 | 50.0399 | 40.4 | 20 |
| 10 | 1 | 12.677 | 7.19 | 26.3 |
| 10 | 2 | 13.152 | 7.15 | 27 |
| 5 | 1 | 9.3808 | 3.09 | 38 |
| 5 | 2 | 8.9349 | 3.08 | 36.9 |
| 1 | 1 | 2.3419 | 0.512 | 47.8 |
| 1 | 2 | 2.2655 | 0.529 | 46.3 |
| 0.5 | 1 | 1.3304 | 0.24 | 52.8 |
| 0.5 | 2 | 1.3108 | 0.244 | 51.9 |

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Conc**  **[μg/mL]** | **Rep** | **Sorbed** | **In soln** | **%** |
| **[μg/g]** | **[μg/mL]** | **Sorbed** |
| LAD-SCL-PF | | | | |
| 50 | 1 | 38.0424 | 42.2 | 15.4 |
| 50 | 2 | 40.3624 | 41.8 | 16.3 |
| 10 | 1 | 4.4465 | 8.87 | 9.2 |
| 10 | 2 | 4.2468 | 8.92 | 8.7 |
| 5 | 1 | 5.3487 | 3.87 | 21.7 |
| 5 | 2 | 5.1798 | 3.86 | 21.3 |
| 1 | 1 | 1.1566 | 0.746 | 23.8 |
| 1 | 2 | 1.2337 | 0.746 | 25.1 |
| 0.5 | 1 | 0.72 | 0.362 | 28.6 |
| 0.5 | 2 | 0.5797 | 0.389 | 23.1 |

**Table A2.3-6: Adsorption constants of 4-chlorophenol, in the soils**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Soil** | **Adsorption** | | | |
| **KF** | **KFOC** | **1/n** | **r2** |
| 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 |

KF - Freundlich adsorption coefficient

KFOC - Coefficient adsorption per organic carbon (KF 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).

Kd values were 4.76, 1.49, 6.46, 3.32 and 1.23 in Empingham, Warsop, Kenslow, Brierlow and LAD- SCL-PF soils, respectiely.

Koc 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 Kd or KFOC.

**Conclusion**

Freundlich coefficients KFOC 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 KFOC), 4-chlorophenol can be classified as having ‘medium mobility’ in all five soils.

## A 2.4 Mobility of Plant Protection Product in soil: 1,2,4-Benzenetriol

Comments of zRMS:

Study not evaluated.

|  |  |
| --- | --- |
| Reference: | CP 9.1.2/02 Swales, S.E. & Crabtree, G.A. (2015c) |
| Report | 1,2,4-Benzenetriol: Adsorption in Four EU Soils and One US Soil |
| Document No: | 3200921  Dow AgroSciences No. 141224; PCTR No. 10001705-004-70601-0002 |
| Guideline(s): | * OECD 106    OSCPP 835.1230, OPPTS 835.1230 |
| Deviations: | None |
| GLP: | Yes |
| Acceptability: | 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-ben- zenetriol 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 DT50> 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.

**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: c1cc(c(cc1O)O)O

#### Methods

#### Soil Characteristics

No soils were used as it was determined during the preliminary tests that 1,2,4-benzenetriol was hy- drolytically 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 con- centration 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 concen- tration). The samples were mixed and aliquots (100 µL) removed for analysis (pre-shake). The re- maining 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-benzene- triol 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, fur- ther 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 an- alysed 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 con- ducted.

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 sam- ple 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 Discussions**

#### 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 con- centration of 500 µg/mL (the highest proposed concentration of a treatment solution). Duplicate solu- tions (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 cal- cium 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 con- ducted in the absence of soil using plastic and Teflon® test vessels containing 0.01M calcium chlo- ride 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 Tef- lon® 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 A2.4-1: 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 acetoni- trile (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 (ace- tonitrile), 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 Solu- tion

Samples, treated with 1,2,4-benzenetriol (0.1 µg/mL) with stock solution 1 (acetonitrile), were ana- lysed immediately after application and after 3 hours.

#### Table A2.4-2: Concentrations of 1,2,4-benzenetriol in comparison of stability between sterile and non-sterile conditions

|  |  |  |  |
| --- | --- | --- | --- |
| **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 ac- etonitrile 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 solu- tion 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 recov- ery results are shown below.

**Table A2.4-3: 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 |

|  |  |  |  |
| --- | --- | --- | --- |
| **Sampling interval [min]** | **Concentration [µg]** | **% Recovery** | **Mean Recovery** |
| 1440 | 0.0380 | 38.0 | 38.5 |
| 1440 | 0.0389 | 38.9 |

Inconclusive results; see next table for repeated experimental results.

**Table A2.4-4: 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 insuffi- cient mixing rather than poor analytical recoveries

**Table A2.4-5: 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 |

|  |  |  |  |
| --- | --- | --- | --- |
| **Sampling interval [min]** | **Concentration [µg]** | **% recovery** | **Mean Recovery** |
| 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 A2.4-6: 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 recover- ies 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 pro- cess 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-benzene- triol 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 sta- ble to perform the test, even by analysing both aqueous and soil phases. In addition, 1,2,4-benzene- triol cannot be perceived to be an environmental hazard in aqueous solution due to its instability, par- ticularly 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 3 Additional information provided by the applicant (e.g. detailed model- ling data)**

## A 3.1 Predicted Environmental Concentrations in groundwater (PECGW) (KCP 9.2.4.1)

|  |  |
| --- | --- |
| Report: | CP 9.2.4.1/01, Verity, C. (2022) |
| Title: | A modelling assessment of 2,4-D and its metabolites applied to spring cereals in groundwater in the central zone |
| Document No.: | Report No. 0572580-GW2 |
| Guidelines: | FOCUS (2021)1  EC (2018)[7](#_bookmark64) |
| GLP: | Not applicable |

**Materials and methods**

The purpose of this report was to address the use of formulation 2,4-D 95 SP applied as a foliar spray to spring cereal. Simulations of the leaching behaviour of 2,4-D and its soil metabolites 2,4-DCP,

2,4-DCA and 4-CP were conducted with the relevant FOCUS groundwater scenarios in the FOCUS PEARL (version 5.5.5) and FOCUS PELMO (version 6.6.4) groundwater models.

The modelling simulations were carried out in accordance with the FOCUS groundwater scenarios workgroup guidelines (FOCUS, 2000, 2021) and EFSA (2004).

The input parameters used in the modelling for 2,4-D are summarised in Table A3.1-1 and the input parameters for the metabolites 2,4-DCP, 2,4-DCA, 4-CP are summarised in Table A3.1-2. Endpoints were taken from the EFSA Conclusion (EFSA Journal 2014; 12(9):3812, revised 21 March 2017), RAR Addendum (2014), Vol. 3, Annex B.8 and new metabolite (4-chlorophenol) studies.

In the EFSA conclusion, a data gap was identified regarding the anaerobic metabolite 4-CP. More information was needed to assess the exposure and risk to the different environmental compartments. In order to address the data gap new studies on soil degradation were performed for 2,4-D and anaer- obic metabolite 4-CP as well as soil adsorption/desorption studies for 4-CP (Swales & Crabtree, 2015a and 2015b). These studies have not previously been reviewed at an EU level.

Based on the recommended GAP, anaerobic conditions would not be expected to occur during or shortly after the application of 2,4-D to spring cereals, therefore assessing the anaerobic metabolite 4- CP in surface water and sediment is not considered necessary. Nevertheless, for the avoidance of any doubt, a risk assessment for 4-CP has been included here to demonstrate acceptable uses.

7 EC (2018) Working Document of the Central Zone in the Authorisation of Plant Protection Products – Section 8 – Environmental Fate and Behaviour. Version 1 rev. June 2018.

**Table A3.1-1: Input parameters used in the groundwater modelling for 2,4-D**

|  |  |  |
| --- | --- | --- |
| Parameter | Value | Remarks |
| **Physico-chemical** | | |
| Molecular weight (g/mol) | 221 | EFSA Conclusion (EFSA Journal 2014; 12(9):3812, revised 21 March 2017, page  24 of 81). |
| Water solubility at 20°C (mg/L) | 24300 | EFSA Conclusion (EFSA Journal 2014; 12(9):3812, revised 21 March 2017, page  24 of 81) 1 |
| Vapour pressure at 20°C (Pa) | 9.9 x 10-6 | EFSA Conclusion (EFSA Journal 2014; 12(9):3812, revised 21 March 2017, page  51 of 81) 2 |
| Molar enthalpy of vaporization (kJ/mol) | 95 | FOCUS recommendation |
| Diffusion coefficient in water (m²/d) | 4.3 x 10-5 (20°C) (PEARL) |
| Diffusion coefficient in gas (m²/d) | 0.43 (20°C) |
| **Degradation in soil** | | |
| DT50 soil (d) | 4.14 | Re-normalized SFO lab DT50; Q10 = 2.58 20°C, pF2. (Cohen. S.P. (1991); Liu, D. (2011)).3 |
| Temperature correction function  Reference temperature (°C) PELMO: Q10 (-)  PEARL: (kJ/mol) | 20  2.58  65.4 | FOCUS recommendation |
| Moisture correction function  PEARL/PELMO: moisture exponent (-) | pF 2  0.7 |
| **Sorption to soil** | | |
| KFOC (mL/g) | 58.6 | EFSA Conclusion (EFSA Journal 2014; 12(9):3812, revised 21 March 2017, page  51 of 81)  Median (n = 42) 4 |
| KFOM (mL/g) | 34.0 | Calculated KFoc / 1.724 |
| Freundlich exponent 1/n (-) | 0.87 | EFSA Conclusion (EFSA Journal 2014; 12(9):3812, revised 21 March 2017, page  51 of 81)  Arithmetic mean (n = 42) d |

|  |  |  |
| --- | --- | --- |
| Parameter | Value | Remarks |
| **Crop/management related parameters** | | |
| Crop uptake factor (-) | 0.0 | Default |
| Washoff Factor (1/m) (PEARL) | 0.0001 | Default |
| Foliar DT50 (d) | 10 | Default |

1 Note that the value presented in the EU review was incorrectly reported as occurring at 25°C.

2 Note that the value presented in the EU review was incorrectly reported. A comment was added on page 51 that for further calculations the actual measured value for 2,4-D of 9.9x10-6 Pa at 20℃ is to be used.

3 Recalculated geometric mean DT50 after moisture normalization of the Mississippi silt loam (20°C/pF2). See detailed discussion in section [8.3.1](#_bookmark4) for more detail.

4 Incorrect value presented in the original EFSA Conclusion (2014;12(9):3812); KFOC and 1/n was incorrectly reported for 7 soils. Endpoints are based on corrected data derived from RAR Addendum (2014, Vol. 3, An- nex B) and in the revised EFSA conclusion (revised 21 March 2017).

**Table A3.1-2: Input parameters used in the groundwater modelling for 2,4-D metabolites**

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Parameter | 2,4-DCP | | 2,4-DCA | | 4-CP | |
| Value | Remarks | Value | Remarks | Value | Remarks |
| Molecular | 163 | EFSA Conclusion | 177 | EFSA Conclusion | 128.6 | Euro Chlor |
| weight (g/mol) |  | (EFSA Journal |  | (EFSA Journal |  | (2002): Euro |
|  |  | 2014; 12(9):3812, |  | 2014; 12(9):3812, |  | Chlor Risk As- |
|  |  | revised 21 March |  | revised 21 March |  | sessment for the |
|  |  | 2017, page 54 of |  | 2017, page 55 of |  | Marine Environ- |
|  |  | 81) |  | 81) |  | ment. |
|  |  |  |  |  |  | OSPARCOM Re- |
|  |  |  |  |  |  | gion – North Sea. |
|  |  |  |  |  |  | Monochlorophe- |
|  |  |  |  |  |  | nols. February |
|  |  |  |  |  |  | 2002. |
| Water solubility | 4870 |  | 96.3 |  | 27100 | Euro Chlor |
| at 20°C (mg/L) |  |  |  |  |  | (2002): Euro |
|  |  |  |  |  |  | Chlor Risk As- |
|  |  |  |  |  |  | sessment for the |
|  |  |  |  |  |  | Marine Environ- |
|  |  |  |  |  |  | ment. |
|  |  |  |  |  |  | OSPARCOM Re- |
|  |  |  |  |  |  | gion – North Sea. |
|  |  |  |  |  |  | Monochlorophe- |
|  |  |  |  |  |  | nols. February |
|  |  |  |  |  |  | 2002. |
| Vapour pressure at 20°C (Pa) | 0 | Default value of parent (FOCUS, 2014) | 0 | Default value of parent (FOCUS, 2014) | 0 | Default value of parent (FOCUS, 2014) |
| KFOC (mL/g) a) | 512 | EFSA Conclusion | 1028 | EFSA Conclusion | 182 | Calculated based |
|  |  | (EFSA Journal |  | (EFSA Journal |  | on Swales, S.E. |
|  |  | 2014; 12(9):3812, |  | 2014; 12(9):3812, |  | (2015b) |
|  |  | revised 21 March |  | revised 21 March |  | (geometric mean |
|  |  | 2017, page 54 of |  | 2017, page 55 of |  | n =5) |
|  |  | 81); arithmetic |  | 81); arithmetic |  |  |
|  |  | mean (n = 7) |  | mean (n = 7) |  |  |
| KFOM (mL/g) | 297 | Calculated KFoc / 1.724 | 596 | Calculated KFoc / 1.724 | 105 | Calculated KFoc / 1.724 |
| 1/n | 0.88 | EFSA Conclusion (EFSA Journal 2014; 12(9):3812,  revised 21 March  2017, page 57 of | 0.92 | EFSA Conclusion (EFSA Journal 2014; 12(9):3812,  revised 21 March  2017, page 57 of | 0.792 | Calculated based on Swales, S.E. (2015b); (arith- metic mean n =5) |
|  |  | 81) |  | 81) |  |  |
|  |  | (arithmetic mean n |  | (arithmetic mean n |  |  |
|  |  | = 7) |  | = 7) |  |  |
| DT50 soil @ 20°C & pF2  (days) | 7.0 | EFSA Conclusion (EFSA Journal 2014; 12(9):3812,  revised 21 March  2017, page 55 of | 10.4 | EFSA Conclusion (EFSA Journal 2014; 12(9):3812,  revised 21 March  2017, page 55 of | 0.22 | Calculated based on Swales, S.E. (2015ba); (geo- metric mean n =4) |
|  |  | 81) |  | 81) |  |  |
|  |  | (geomean, lab, |  | (geomean, lab, |  |  |
|  |  | normalised, n = 3) |  | normalised, n = 3) |  |  |

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Parameter | 2,4-DCP | | 2,4-DCA | | 4-CP | |
| Value | Remarks | Value | Remarks | Value | Remarks |
| Plant uptake fac- tor | 0 | Default value | 0 | Default value | 0 | Default value |
| Formation frac- | 1.0 | EFSA Conclusion | 1.0 | EFSA Conclusion | 1.0 | EFSA Conclusion |
| tion |  | (EFSA Journal |  | (EFSA Journal |  | (EFSA Journal |
|  |  | 2014; 12(9):3812, |  | 2014; 12(9):3812, |  | 2014; 12(9):3812, |
|  |  | revised 21 March |  | revised 21 March |  | revised 21 March |
|  |  | 2017) – represents |  | 2017) – represents |  | 2017) – repre- |
|  |  | worst case |  | worst case |  | sents worst case |
| Transformation Rate | N/A | Formation fraction of 1.0. None to sink. | N/A | Formation fraction of 1.0. None to sink. | N/A | Formation frac- tion of 1.0. None to sink. |
| Washoff Factor (1/m) (PEARL) | 0.0001 | Default | 0.0001 | Default | 0.0001 | Default |
| Foliar DT50 (d) | 10 | Default | 10 | Default | 10 | 0.0001 |

The application of 2,4-D applied as a foliar spray to spring cereals, based on the GAP have been summarised in Table A3.1-3.

**Table A3.1-3: Summary of the application rate and use patterns of 2,4-D to be simulated**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Crop | Application rate (g a.s./ha) | BBCH growth stage | Crop intercep- tion. (%) | Effective application rate  (g a.s./ha) |
| Spring cereals | 1 x 750 | 15-25 | 0 | 1 x 750 |

Simulations were performed to cover the application regime mentioned above using all appropriate FOCUS scenarios in FOCUS PEARL (version 5.5.5) and FOCUS PELMO (version 6.6.4). Accord- ing to central zone guidance (EC 2018) only relevant scenarios to the central zone are reported herein. The application timing in the simulations was set using absolute timings (Klein, 2019, AppDate 3.06) and are presented in Table A3.1-4.

**Table A3.1-4: Actual application dates simulated for modelling with FOCUS PEARL and PELMO**

|  |  |
| --- | --- |
| Scenario | Actual application date (absolute) |
| Spring cereals 1 x 750 g a.s./ha | |
| Châteaudun (C) | 20-March (79) |
| Hamburg (H) | 08-April (98) |
| Kremsmünster (K) | 08-April (98) |
| Okehampton (N) | 07-April (97) |
| Porto (O) | 20-March (79) |

Values in parentheses are Julian Days

**Results and discussions**

The PECGW (80th percentile annual average leachate concentration at 1 m soil depth) as modelled

using FOCUS PEARL (version 5.5.5) and FOCUS PELMO (version 6.6.4), for 2,4-D and its metabo- lites for an annual application rate to the crops in the proposed GAP are presented in Table A3.1-5 and Table A3.1-6. Modelling with FOCUS MACRO (version 5.5.4) was not performed as PECGW of all substances in all modelled scenarios were <0.001 µg/L/.

**Table A3.1-5: PECGW following annual application of 2,4-D in accordance with the GAP, using the FO- CUS PEARL 5.5.5 model**

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Crop | Scenario | 80th Percentile PECGW at 1 m Soil Depth (g/L) | | | |
| 2,4-D | 2,4-DCP | 2,4-DCA | 4-CP |
| Spring | Châteaudun (C) | <0.001 | <0.001 | <0.001 | <0.001 |
| cereals |  |  |  |  |  |
| Hamburg (H) | <0.001 | <0.001 | <0.001 | <0.001 |
| 1 x 750 |
| Kremsmünster (K) | <0.001 | <0.001 | <0.001 | <0.001 |
| g a.s./ha |
| BBCH |
| 15-25 | Okehampton (N) | <0.001 | <0.001 | <0.001 | <0.001 |
|
|  | Porto (O) | <0.001 | <0.001 | <0.001 | <0.001 |

**Table A3.1-6: PECGW following annual application of 2,4-D in accordance with the GAP, using the FO- CUS PELMO 6.6.4 model**

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Crop | Scenario | 80th Percentile PECGW at 1 m Soil Depth | | (g/L) | |
| 2,4-D | 2,4-DCP | 2,4-DCA | 4-CP |
| Spring | Châteaudun | <0.001 | <0.001 | <0.001 | <0.001 |
| cere- | (C) |  |  |  |  |
| als |  |  |  |  |  |
| Hamburg (H) | <0.001 | <0.001 | <0.001 | <0.001 |
| 1 x |
| Kremsmünster (K) | <0.001 | <0.001 | <0.001 | <0.001 |
| 750 g |
| a.s./ha |
| BBCH | Okehampton (N) | <0.001 | <0.001 | <0.001 | <0.001 |
| 15-25 |
|  | Porto (O) | <0.001 | <0.001 | <0.001 | <0.001 |

**Conclusion**

Simulations of the leaching behaviour of 2,4-D and its soil metabolites 2,4-DCP, 2,4-DCA and 4-CP were conducted with the FOCUS PEARL (version 5.5.5) and FOCUS PELMO (version 6.6.4) groundwater models and relevant scenarios. The simulations were based on application of the plant protection product containing 2,4-D as an active substance.

The predicted 80th percentile average annual concentrations for 2,4-D following application to spring cereals were lower than the 0.1 µg/L regulatory threshold in groundwater at 1 m depth for all sce- nario combinations.

The PECGW values for metabolites 2,4-DCA, 2,4-DCP and 4-CP following annual application 2,4-D to crops were also lower than the 0.1 µg/L regulatory threshold in groundwater at 1 m depth for all the available scenario combinations.

These results demonstrate that 2,4-D 95 SP formulation can be used safely as proposed without the risk of 2,4-D and its metabolites 2,4-DCA, 2,4-DCP and 4-CP exceeding acceptable levels in ground- water.

## A 3.2 Predicted Environmental Concentrations in surface water (PECsw) (KCP 9.2.4.1)

|  |  |
| --- | --- |
| **Report:** | ~~CP 9.2.4.1/01, Verity, C, Lee, R. (2022)~~ |
| **Title:** | ~~A modelling assessment of 2,4-D and its metabolites applied to spring cereals in surface water in the central zone~~ |
| **Document No.:** | ~~Report No. 0572580-SW3~~ |
| **Guidelines:** | ~~FOCUS (2001) FOCUS (2015)~~ |
| **GLP:** | ~~Not applicable~~ |

|  |  |
| --- | --- |
| **Report:** | CP 9.2.5/01, Verity, C, Lee, R. (2023) |
| **Title:** | A modelling assessment of 2,4-D and its metabolites applied to spring cereals in surface water in the central zone |
| **Document No.:** | Report No. 0572580-SW4 |
| **Guidelines:** | FOCUS (2001)[8](#_bookmark66)  FOCUS (2015)[9](#_bookmark67) |
| **GLP:** | Not applicable |

## Materials and methods

The purpose of this report was to address the use of 2,4-D 95 SP formulation applied as a foliar spray to spring cereals in the central zone. The potential for 2,4-D and its metabolites (2,4-DCP, 2,4-DCA, 4-CP and 1,2,4-benzenetriol) to reach surface water and sediment was examined following applica- tion made in accordance with the supported uses in the GAP. Simulations were based on field appli- cation to spring cereals using the FOCUS suite of surface water models.

PECSW and PECSED values for spring cereals were refined from the values generated at Steps 1-2 for 2,4-D using FOCUS Step 3 surface water scenarios with the FOCUS suite of surface water models (MACRO version 5.5.4, PRZM version 4.3.1, SPIN version 2.2 and TOXSWA version 5.5.3) in the SWASH version 5.3 shell were used.

In order to present the necessary R1 scenarios, oilseed rape spring was modelled at Step 3 as a surro- gate crop for spring cereals. As an earlier growth stage is used (BBCH 09), the interception and ap- plication timing is adequate to cover the application to spring cereals.

The input parameters used in the modelling for 2,4-D are summarised in Table A3.2-1, and the input parameters used for the metabolites of 2,4-D are summarised in Table A3.2-2. Unless stated other- wise, all input parameters were taken from the EFSA Conclusion (2014;12(9):3812, revised 21 March 2017). Values for metabolite 4-CP have been taken from new studies (Swales & Crabtree, 2015a and 2015b) which have not previously been reviewed at an EU level. It was not possible to determine input parameters for aquatic photolysis metabolite 1,2,4-benzenetriol (Swales & Crabtree, 2015c), there- fore, default and parent values were used for the PECSW and PECSED assessment.

Based on the recommended GAP, anaerobic conditions would not be expected to arise during or shortly after the application of 2,4-D to spring cereals. Therefore, assessing the anaerobic metabolite 4-CP in surface water and sediment is not considered necessary. Nevertheless, for the avoidance of any doubt, a

8 FOCUS (2001). FOCUS surface water scenarios in the EU evaluation process under 91/414/EEC. Report of the FOCUS working group on surface water scenarios. EC document reference SANCO/4802/2001-rev.2, 245pp

9 FOCUS (2015). Generic Guidance for FOCUS surface water Scenarios. Version 1.4. May 2015.

risk assessment has been included for 4-CP to demonstrate acceptable uses.

**Table A3.2-1: Input parameters used in the surface water modelling for 2,4-D**

|  |  |  |
| --- | --- | --- |
| Parameter | Value | Remarks |
| **Physico-chemical** | | |
| Molecular weight (g/mol) | 221 | EFSA Conclusion (EFSA Journal 2014; 12(9):3812, revised 21 March 2017, page 24  of 81) |
| Water solubility at 20℃ (mg/L) | 24300 | EFSA Conclusion (2014;12(9):3812, revised 21 March 2017, page 24 of 81) 1 |
| Vapour pressure at 20℃ (Pa) | 9.9x10-6 | EFSA Conclusion (EFSA Journal 2014; 12(9):3812, revised 21 March 2017, page 51  of 81) 2 |
| **Degradation in soil** | | |
| DT50 soil (d) | 4.14 | Re-normalized SFO lab DT50; Q10 = 2.58 20°C, pF2. (Cohen. S.P. (1991); Liu, D. (2011)).3 |
| Temperature correction function  Reference temperature (°C) MACRO: (K-1)  PRZM: Q10 (-) | 20  0.095  2.58 | FOCUS recommendation |
| Moisture correction function Reference moisture (-)  PRZM/MACRO: moisture exponent (-) | pF 2  0.49 |
| **Sorption to soil** | | |
| KFOC (mL/g) | 58.6 | EFSA Conclusion (EFSA Journal 2014; 12(9):3812, revised 21 March 2017, page 51  of 81)  Median (n = 42) 4 |
| KFOM (mL/g) | 34.0 | Calculated KFOC / 1.724 |
| Freundlich exponent 1/n (-) | 0.87 | EFSA Conclusion (EFSA Journal 2014; 12(9):3812, revised 21 March 2017, page 51  of 81)  Median (n = 42) 4c |
| **Degradation in aquatic systems** | | |
| DT50 whole system (d) (Step 1) | 18.16 | EFSA Conclusion (EFSA Journal 2014; 12(9):3812, revised 21 March 2017, page 24 of 81) – value given “*for future calculations*”) |
| DT50 water (d) (Step 2) | 18.16 | EFSA Conclusion (EFSA Journal 2014; 12(9):3812, revised 21 March 2017, page 24 of 81) – value given “*for future calculations*”) |
| DT50 sediment (d) (Step 2/3) | 18.16 / 1,000 | EFSA Conclusion (EFSA Journal 2014; 12(9):3812, revised 21 March 2017, page 24 of 81) – value given “*for future calculations*” for Step 2 and the FOCUS default for Step 3 |
| DT50 crop (d) | 10 | FOCUS recommendation |
| Temperature correction function |  |

|  |  |  |  |
| --- | --- | --- | --- |
| Parameter | | Value | Remarks |
| Reference temperature | (°C) | 20 |  |
| TOXSWA: activation energy (J/mol) | | 65400 |
| Crop uptake factor (-) | | 0.0 | EFSA conclusion (2014) |
| Wash off coefficient | |  | FOCUS recommendation |
| PRZM: | (cm-1) | 0.5 |  |
| MACRO: | (mm-1) | 0.05 |  |

1 Note that the value presented in the EU review was incorrectly reported as occurring at 25°C.

2 Note that the value presented in the EU review was incorrectly reported. A comment was added on page 51 that for further calculations the actual measured value for 2,4-D of 9.9x10-6 Pa at 20℃ is to be used.

3 Recalculated geometric mean DT50 after moisture normalization of the Mississippi silt loam (20°C/pF2). See detailed discussion in section [8.3.1](#_bookmark4) for more detail.

4 Incorrect value presented in the original EFSA Conclusion (2014;12(9):3812); KFOC and 1/n was incorrectly reported for 7 soils. Endpoints are based on corrected data derived from RAR Addendum (2014, Vol. 3, An- nex B) and in the revised EFSA conclusion (revised 21 March 2017).

**Table A3.2-2: Input parameters used in the surface water modelling for metabolites**

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Parameter | 2,4-DCP | | 2,4-DCA | | 4-CP | | 1,2,4-benzenetriol | |
| Value | Remarks | Value | Remarks | Value | Remarks | Value | Remarks |
| Molecular | 163 | EFSA Conclusion | 177 | EFSA Conclusion | 128.6 | Euro Chlor (2002): Euro | 126.1 | Calculated from |
| weight (g/mol) |  | (EFSA Journal 2014; |  | (EFSA Journal 2014; |  | Chlor Risk Assessment |  | EPISuite V4.1.1 |
|  |  | 12(9):3812, revised 21 |  | 12(9):3812, revised 21 |  | for the Marine Environ- |  |  |
| Water solubil- ity at 20℃ (mg/L) | 4870 | 96.3 | 27100 | - | No data available |
| March 2017, page 54 of | March 2017, page 55 of | ment. OSPARCOM Re- |
| 81) | 81) | gion – North Sea. Mono- |
|  |  | chlorophenols. February |
|  |  | 2002. |
| KFOC (mL/g) | 512 | EFSA Conclusion (EFSA Journal 2014;  12(9):3812, revised 21  March 2017, page 54 of 81); arithmetic mean (n  = 7) | 1028 | EFSA Conclusion (EFSA Journal 2014;  12(9):3812, revised 21  March 2017, page 55 of 81); arithmetic mean (n  = 7) | 182 | Calculated based on Swales, S.E. (2015b) (geometric mean n =5) | - | No data available. |
| KFOM (mL/g) | 297 | Calculated KFOC / 1.724 | 596 | Calculated KFOC / 1.724 | 106 | Calculated KFOC / 1.724 | - | No data available. |
| DT50 soil @ | 7.0 | EFSA Conclusion | 10.4 | EFSA Conclusion | 0.22 | Calculated based on | - | No data available. |
| 20°C & pF2 |  | (EFSA Journal 2014; |  | (EFSA Journal 2014; |  | Swales, S.E. (2015a) |  |  |
| (days) |  | 12(9):3812, revised 21  March 2017, page 54 of |  | 12(9):3812, revised 21  March 2017, page 55 of |  | (geometric mean n =5) |  |  |
|  |  | 81) |  | 81) |  |  |  |  |
|  |  | (geomean, lab, n = 3) |  | (geomean, lab, normal- |  |  |  |  |
|  |  |  |  | ised, n = 3) |  |  |  |  |
| Max % ob- | 8.7 | EFSA Conclusion | 15.0 | EFSA Conclusion | 33 | EFSA Conclusion | - | No data available. |
| served in soil |  | (EFSA Journal 2014; |  | (EFSA Journal 2014; |  | (EFSA Journal 2014; |  |  |
|  |  | 12(9):3812, revised 21 |  | 12(9):3812, revised 21 |  | 12(9):3812, revised 21 |  |  |
|  |  | March 2017, page 54 of |  | March 2017, page 55 of |  | March 2017, page 41 of |  |  |
|  |  | 81) |  | 81) |  | 81) |  |  |

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Parameter | 2,4-DCP | | 2,4-DCA | | 4-CP | | 1,2,4-benzenetriol | |
| Value | Remarks | Value | Remarks | Value | Remarks | Value | Remarks |
| DT50 water (d) | 103.9 | EFSA conclusion | 1000 | FOCUS default value | 1000 | FOCUS default value | - | No data available. |
|  |  | (EFSA Journal 2014; |  | (worst case) |  | (worst case) |  |  |
| DT50 sediment (d) | 103.9 | 1000 | 1000 | - |
| 12(9):3812, revised 21 |  |  |  |
| March 2017, page 54 of |  |  |  |
| DT50 total sys- tem (d) | 103.9 | 81) (geomean n =2) | 1000 |  | 1000 |  | - |  |
|
| Max % ob- | 32.1 | EFSA Conclusion | 5.3 | EFSA Conclusion | 6.9 | RAR Addendum (2014), | 31.7 | EFSA Conclusion |
| served in wa- |  | (EFSA Journal 2014; |  | (EFSA Journal 2014; |  | Lewis, C.J. (2011) |  | (EFSA Journal 2014; |
| ter/sediment |  | 12(9):3812, revised 21 |  | 12(9):3812, revised 21 |  |  |  | 12(9):3812, revised 21 |
|  |  | March 2017, page 54 of |  | March 2017, page 55 of |  |  |  | March 2017, page 49 of |
|  |  | 81) |  | 81) |  |  |  | 81) |

The application of 2,4-D to spring cereals based on the GAP has been summarised in Table A3.2-3.

**Table A3.2-3: Supported uses of 2,4-D modelled for this report**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Crop | Application rate (g a.s./ha) | Number of ap- plications | Interval between applications | BBCH growth stage at application |
| Spring cereals | 750 | 1 | - | 15-25 |

At Steps 1 and 2, season of application and crop interception were estimated based on the BBCH growth stages. The region of use, season of application and crop interception values used are pre- sented in Table A3.2-4.

**Table A3.2-4: Model parameters used in FOCUS Steps 1 and 2 surface water modelling**

|  |  |  |  |
| --- | --- | --- | --- |
| Crop | Zone (Step 2) | Season | Interception |
| Spring cereals | North Europe | Mar-May | Minimal crop cover |
| Jun-Sep |
| South Europe | Mar-May |
| Jun-Sep |

Only parent was carried forwards to Step 3. For all uses at Step 3, the linear foliar application method was selected (CAM 2) with the default incorporation depth of 4 cm.

In accordance with FOCUS recommendations, irrigation was applied as set internally within the FO- CUS Step 3 scenarios. An application window must be specified from which the Pesticide Applica- tion Timer (PAT), internal to the model, determines actual application dates which were set generi- cally for all scenarios. Application window dates are presented in Table A3.2-5 and Table 3.2-6. The dates were selected with the tool AppDate v3.06 (Klein, 2019) based on BBCH growth stages given in the recommended GAP.

**Table A3.2-5: Application windows for spring cereals – FOCUS Step 3**

|  |  |  |
| --- | --- | --- |
| Scenario details | FOCUS default dates | |
| Scenario | Start | End |
| Spring cereals (FOCUS spring cereals), 1 x 750 g a.s./ BBCH 15-25 | | |
| D1 | 11-May (131) | 10-Jun (161) |
| D3 | 08-Apr (98) | 08-May (128) |
| D4 | 02-May (122) | 01-Jun (152) |
| D5 | 22-Mar (81) | 21-Apr (111) |
| R4 | 22-Mar (81) | 21-Apr (111) |

Values in parentheses are Julian Days

**Table A3.2-6: Application window for oilseed rape, spring – FOCUS Step 3**

|  |  |  |
| --- | --- | --- |
| Scenario details | FOCUS default dates | |
| Scenario | Start | End |
| Oilseed rape, spring (FOCUS oilseed rape, spring), 1 x 750 g as/ BBCH 09 | | |
| R1 | 10-April (100) | 10-May (130) |

Values in parentheses are Julian Days

**Results and discussions**

The maximum PECSW and PECSED for 2,4-D and its metabolites at FOCUS Steps 1 and 2, as calcu- lated by the FOCUS surface water models, are given in Table A3.2-6 and Table A3.2-7.

**Table A3.2-6: Maximum PECSW and PECSED for 2,4-D and its metabolites application to spring cereals (1 x 750 g a.s./ha, BBCH 15) – FOCUS Step 1**

|  |  |  |  |
| --- | --- | --- | --- |
| Crop / Application | Substance | Max PECSW (µg/L) | Max PECSED  (µg/kg) |
| Spring cereals 1 x 750 g a.s/ha  BBCH 15 | 2,4-D | 238.78 | 135.883 |
| 2,4-DCP | 46.342 | 232.325 |
| 2,4-DCA | 17.438 | 177.401 |
| 4-CP | 46.987 | 85.358 |
| 1,2,4-benzenetriol1 | 43.190 | 24.578 |

1 Calculated based on parent

**Table A3.2-7: Maximum PECSW and PECSED for 2,4-D and its metabolites following application to spring cereals (1 x 750 g a.s./ha, BBCH 15) – FOCUS Step 2**

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Crop / Application | Substance | Region | Season | Max PECSW  (µg/L) | Max PECSED  (µg/kg) |
| Spring cereals  1 x 750 g a.s/ha,  BBCH 15 | 2,4-D | NEU | Mar-May | 29.366 | 16.487 |
| Jun-Sep | 29.366 | 16.487 |
| SEU | Mar-May | **53.104** | **30.020** |
| Jun-Sep | 41.235 | 23.182 |
| 2,4-DCP | NEU | Mar-May | 5.977 | 29.646 |
| Jun-Sep | 5.977 | 29.646 |
| SEU | Mar-May | **10.861** | **54.487** |
| Jun-Sep | 8.419 | 42.067 |
| 2,4-DCA | NEU | Mar-May | 2.552 | 25.911 |
| Jun-Sep | 2.552 | 25.911 |
| SEU | Mar-May | **4.951** | **50.557** |
| Jun-Sep | 3.751 | 38.234 |
| 4-CP | NEU | Mar-May | 1.065 | 1.908 |
| Jun-Sep | 1.065 | 1.908 |

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
|  |  | SEU | Mar-May | **1.892** | **3.412** |
| Jun-Sep | 1.478 | 2.660 |
| 1,2,4-benzenetriol1 | NEU | Mar-May | 5.312 | 2.982 |
| Jun-Sep | 5.312 | 2.982 |
| SEU | Mar-May | **9.605** | **5.430** |
| Jun-Sep | 7.458 | 4.193 |

Worst-case shown in bold

1 Calculated based on parent

Maximum PECSW and PECSED values for 2,4-D, based on FOCUS Step 3 simulations, are presented in Table A3.2-7 and Table A3.2-8.

**Table A3.2-7: Maximum PECSW and PECSED for 2,4-D following application to spring cereals (1 x 750 g a.s./ha, BBCH 15) – FOCUS Step 3**

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Scenario | Waterbody | Max. PECsw (µg/L) | Main route of entry | 21 d TWA  (µg/L) | Max. PECsed (µg/kg) |
| D1 | Ditch | 4.867 | Spray drift | 0.735 | 1.685 |
| D1 | Stream | 3.882 | Spray drift | 0.072 | 0.345 |
| D3 | Ditch | 4.749 | Spray drift | 0.219 | 0.870 |
| D4 | Pond | 0.164 | Spray drift | 0.123 | 0.176 |
| D4 | Stream | 3.888 | Spray drift | 0.017 | 0.192 |
| D5 | Pond | 0.164 | Spray drift | 0.132 | 0.201 |
| D5 | Stream | 3.776 | Spray drift | 0.007 | 0.089 |
| R4 | Stream | 3.128 | Spray drift | 0.027 | 0.255 |

**Table A3.2-8: Maximum PECSW and PECSED for 2,4-D following application to oilseed rape, spring (1 x 750 g a.s./ha, BBCH 09) – FOCUS Step 3**

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Scenario | Waterbody | Max. PECSW  (µg/L) | Main route of entry | 21 d TWA  (µg/L) | Max. PECSED  (µg/kg) |
| R1 | Pond | 0.164 | Spray drift | 0.127 | 0.224 |
| R1 | Stream | 3.131 | Spray drift | 0.028 | 0.261 |

**Conclusion**

The purpose of this report was to address the use of formulation 2,4-D 95 SP applied as a foliar spray to spring cereal. The potential for 2,4-D and its metabolites 2,4-DCP, 2,4-DCA, 4-CP and 1,2,4-benzenetriol to reach surface water and sediment was examined following application made in accordance with the sup- ported uses of 2,4-D 95 SP formulation in the central zone. Simulations were based on field application to spring cereals using the FOCUS suite of surface water models.

The maximum PECSW values for the parent and metabolites at Step 2 were 53.104 µg/L for 2,4-D, 10.861 µg/L for 2,4-DCP, 4.951 µg/L for 2,4-DCA, 1.892 µg/L for 4-CP, and 9.605 µg/L for 1,2,4-ben- zenetriol. Parent was taken forwards to Step 3 which reached a maximum of 4.867 µg/L.